Food Packaging Performance and Environmental Impact of Polysaccharide-Coated Papers

Mirela Roman,[a] Petronela Nechita,[b,]* Aida Mihaela Vasile,[c] and Maria Violeta Guiman [d]

The food packaging characteristics and environmental impact of paper coated with polysaccharide dispersions were analyzed. Colloidal dispersions of xylan and xylan derivatives, as well as their combinations with chitosan and nanocrystalline cellulose, were applied in thin layers on both sides of the paper surface (5 g/m²). The barrier properties to water, water vapor, gases, oil/grease, and the antimicrobial properties of the coated paper were evaluated. Generally, polysaccharide coatings improved the barrier and antimicrobial features of coated papers compared to uncoated paper. Significant improvements were obtained by combining xylan derivatives and chitosan, where the contact angle of the coated paper reached 92.8° and achieved 100% inhibition of *Bacillus sp.* Furthermore, food simulant tests indicated that all tested polysaccharide combinations are suitable for use in food packaging, especially for fatty products. After 28 and 42 days of soil degradation, all samples of xylan and xylan/xylan derivatives/chitosan/nanocellulose coatings reached similar degradation levels (70 to 80% and 14 to 16 mg CO_2 production).

DOI: 10.15376/biores.19.4.6994-7018

Keywords: Xylan hemicellulose; Food packaging paper; Coated paper; Antimicrobial; Biodegradation; Chitosan; Polysaccharides

Contact information: a: Doctoral School of Fundamental and Engineering Sciences, Dunărea de Jos University of Galați, Brăila 817112, Romania; b: Department of Environmental, Applied Engineering and Agriculture, Faculty of Engineering and Agronomy, Dunărea de Jos University of Galați, Brăila 817112, Romania; c: Department of Food Science, Food Engineering, Biotechnologies and Aquaculture, Faculty of Food Science and Engineering, Dunărea de Jos University of Galați, Romania; d: Faculty of Mechanical Engineering, "Transilvania" University of Brasov, 500024 Brasov, Romania;
** Corresponding author: petronela.nechita@ugal.ro*

INTRODUCTION

There is a global focus on exploring biodegradable materials for packaging purposes (Mitrano *et al.* 2021). Utilizing plant biomass as a source for packaging materials production is an appealing option. These materials have the potential to be biodegradable, renewable, abundant, and cost-effective, as they can be derived from agricultural residues or lignocellulosic biomass (Imre *et al.* 2019; Macedo *et al.* 2022).

Paper is inherently biodegradable, making it an eco-friendly option for packaging. However, its hygroscopicity and porosity pose significant challenges in food packaging, as they can lead to food contamination through the exchange of gases and liquids with the environment. To address these issues, it is crucial to use biodegradable materials for paper coatings. Polysaccharides, which are chemically compatible with paper, can offer the advantages of being less hygroscopic than paper and derived from renewable resources. The polysaccharides have garnered significant attention in recent decades within the food packaging industry. This interest is due to their advantages and substantial potential for creating environmentally friendly products. Studies have demonstrated that some polysaccharides can exhibit excellent barrier properties against moisture, gas, thermal, and grease when applied under optimal manufacturing conditions and concentrations. To meet the demands of environmentally friendly food packaging, it is important to enhance their physical and chemical properties. Improving aspects such as hydrophobicity, flexibility, and mechanical strength is vital for extending the industrial-scale application of polysaccharides in the food packaging sector. The diversity in their categories and sources leads to different monosaccharide compositions and glycosidic linkages in polysaccharides, resulting in unique biological activities and functional characteristics. For example, chitosan's antibacterial properties are attributed to the presence of amino groups (Liu *et al.* 2001), while the antioxidant properties of sodium alginate are mainly due to its sulfate groups. These structural variations make polysaccharides highly versatile in their applications and functionalities (Jiao *et al.* 2011; Raposo *et al.* 2015).

The abundant active hydroxyl groups present in polysaccharides facilitate prompt and diverse chemical modifications. These modifications can tailor the properties of polysaccharides, enhancing their functionality for specific applications. By modifying these hydroxyl groups, the characteristics such as solubility, thermal stability, mechanical strength, barrier to gases, water and oil, as well as bioactivity, can be improved, thereby expanding the potential uses of polysaccharides in various industries, including pharmaceuticals, food packaging, and biotechnology.

When used in food packaging applications, the polysaccharides can be utilized as edible films or as dense coating layers on the surface of paper. This is achieved through the intertwining or chemical binding of polysaccharide molecular chains with paper fibers. These films and dense coating layers, along with the functional groups present on the polysaccharides, effectively impede the penetration of oxygen, water, or oil. This barrier property enhances the protective and functional capabilities of the paper, making it suitable for various industrial applications, such as packaging and preservation.

Common examples of polysaccharides include cellulose, hemicellulose, pectin, starch, chitosan, and sodium alginate. Hemicellulose is the second most abundant class of polysaccharide in nature and is made up of pentose and hexose monomers; these contribute multiple hydroxyl groups that give it a strong affinity for water (Farhat *et al.* 2018; Melati *et al.* 2019; Zhao *et al.* 2020). The structure of hemicellulose is heterogeneous, consisting of various molecules that differ among plant species and even within the same individual's tissues (Braga and Poletto 2020; Felipuci *et al.* 2021).

In the majority of biomass resources, xylan is the most abundant type of hemicellulose. As raw material with high added value, xylan has been utilized in various products and it is abundant in residual biomass produced by agricultural activities, food processing, sugar, alcohol, and the pulp and paper industry (Alves *et al.* 2020).

As with many other polysaccharides, the high number of free hydroxyl groups in xylan hemicelluloses makes them sensitive to humidity, resulting in low barrier resistance in moist conditions. However, this characteristic is advantageous for chemical functionalization through a variety of reactions that make use of the hydrophobic groups attached to the hemicellulose chains. Such modifications result in xylan derivatives with improved barrier properties. Notable chemical reactions used for modifying xylan hemicellulose include esterification (*e.g.*, acetylation) and etherification (*e.g.*, carboxymethylation or alkoxylation). Additional strategies to enhance the functional properties of xylan hemicelluloses involve the use of plasticizers, modification with long-chain anhydrides, or combining them with other biopolymers (Roman *et al.* 2023).

Results reported in the authors' previous study (Nechita *et al.* 2021) on the performance of xylan hemicellulose coatings for food packaging papers indicate that, due to its high hydrophilic character, there were no significant improvements in the barrier properties of the coated papers. To improve the hydrophobic features of xylan hemicellulose, in this study two xylan derivatives were synthetized by acetylation with acetic anhydride and reaction of alkyl ketene dimers, and their performances in coatings for food packaging papers were evaluated.

Chitosan is a unique natural cationic polysaccharide that is biodegradable, biocompatible, and non-toxic. It is obtained by deacetylation of natural chitin. Furthermore, chitosan has various beneficial properties, such as antibacterial and good film-forming capacity (Ifuku *et al.* 2013; Tang *et al.* 2020). It has been used in a broad range of applications, such as packaging, textile, fruits coating, and tissue engineering (Roy *et al.* 2020; Tanpichai *et al.* 2020; Du *et al.* 2021). The abundant hydroxyl and amino groups in chitosan enable it to form strong hydrogen bonds with the hydroxyl groups present in cellulose. This interaction has been leveraged to enhance the water resistance and mechanical properties of paper when chitosan is used in coatings for paper surface (Tanpichai *et al.* 2020; Du *et al.* 2021).

Other studies have reported that by the utilization of chitosan and its derivatives in paper coating, improved antimicrobial properties as well as barriers against oxygen, water vapors, oils, and grease are obtained (Hampichavant *et al.* 2005; Bordenave *et al.* 2010; Solier *et al.* 2022).

Nanocellulose offers several advantages when applied to paper (Lengowski *et al.* 2019, 2020, 2023). The use of nanocellulose, particularly NFC, in paper products can be regarded as potentially advantageous due to its chemical compatibility, maintenance of biodegradability, and safety for human health. This makes it a promising material for enhancing the performance and sustainability of paper-based products. When applied as a coating on paper, NFC can enhance the paper's barrier properties, such as its permeability to air, gas, oil, and grease, and improves its thermal and mechanical properties, making it a more suitable material for food packaging (Fujisawa *et al.* 2011; Hubbe *et al.* 2017; Lengowski *et al.* 2023a). There are many studies that reported high performance for oxygen barrier and water vapor transmission performance, strength properties, and the susceptibility of nanocellulose-based films and coatings to the presence of humidity or moisture (Plackett *et al.* 2010; Chinga-Carrasco and Syverud 2012; Rodionova *et al.* 2012b; Shimizu *et al*. 2016).

The combination of polysaccharides can yield synergistic properties, resulting in packaging materials with enhanced functional characteristics. In this context, there is reported research regarding the utilization of xylan hemicellulose to reduce the swelling capacity and water absorption of nanocellulose films, that confirm that their combination with other polysaccharides are beneficial to improve the properties of packaging materials (Chonnipa *et al.* 2021).

Furthermore, films prepared using a combination of xylan and chitosan in various proportions exhibited enhanced mechanical strength and improved water and oxygen barrier properties compared to films made solely of chitosan (Cheng *et al.* 2024). Additionally, these films exhibited superior antimicrobial activity against *E. coli* and *S. aureus* bacteria (Schnell *et al.* 2017; Solier *et al.* 2022).

This research study evaluated the food packaging performance and environmental behavior of coated papers and homogeneous films created by combining xylan derivatives, chitosan with a molecular weight of 234,000 Da, and nanocrystalline cellulose. The xylan derivatives were synthesized in the laboratory, and colloidal dispersions with a mass ratio of 50:50 of xylan-NCC and xylan-chitosan, and respectively, 50:50 of xylan derivatives – NCC and xylan derivatives – chitosan, were prepared. These dispersions were used as single-layer coatings for packaging paper and to produce homogeneous films using the casting method.

Studies were conducted on the solubility of homogeneous films in food simulants. The functional properties of the coated papers were analyzing, including their barriers to water, water vapor, oil, and grease, their resistance to microbial attack, as well biodegradation rate through soil burial and CO_2 production quantification.

EXPERIMENTAL

Materials

Xylan hemicellulose (Xy), obtained from beech wood was purchased from Carl Roth Germany as powder. It was coloured light beige to brown with a molecular weight of 20.000 g/mol and loss on drying ≤ 10.0%.

Hydrophobized xylan that had been reacted with alkylketene dimer (XyAKD) and acetylated xylan (XyAc) were synthetized in the laboratory.

Chitosan (Ch), a white to beige powder and glacial acetic acid (≥99.85%) were supplied by Sigma-Aldrich (Taufkirchen, Germany). For improved film-forming properties, chitosan with medium molecular-weight (234,000 Da) and 88% degree of deacetylation was used in the experiments.

Nanocrystalline cellulose (NCC) purchased from Nanografi Nanotechnology Germany, as aqueous suspension of 6 wt% of 1 to 45 µm particles.

Commercial packaging paper from unbleached pulp, 50 g/m^2, was used as base paper for different coatings.

Analytical purity chemical reagents as ethylic alcohol and acetic acid were used for food simulants preparation.

Homogenous films were obtained according to the scheme presented in Fig. 1 and the composition from Table 1.

Obtaining of Xylan Derivatives

Hydrophobized xylan (XyAKD) was obtained by esterification reaction of native xylan with long chain anhydrides as alkyl ketene dimers (AKD) at 20 °C and 24 h while using a magnetic stirrer at 1500 rpm (Nechita *et al.* 2022).

Acetylated xylan (XyAc) with degree of substitution of 0.48 was obtained by esterification reaction of native xylan with acetic anhydride at 50 °C for 1 h and molar ratio of acetic anhydride to functional hydroxyl groups in the structural unit of xylan about 8:1 (Roman *et al.* 2023).

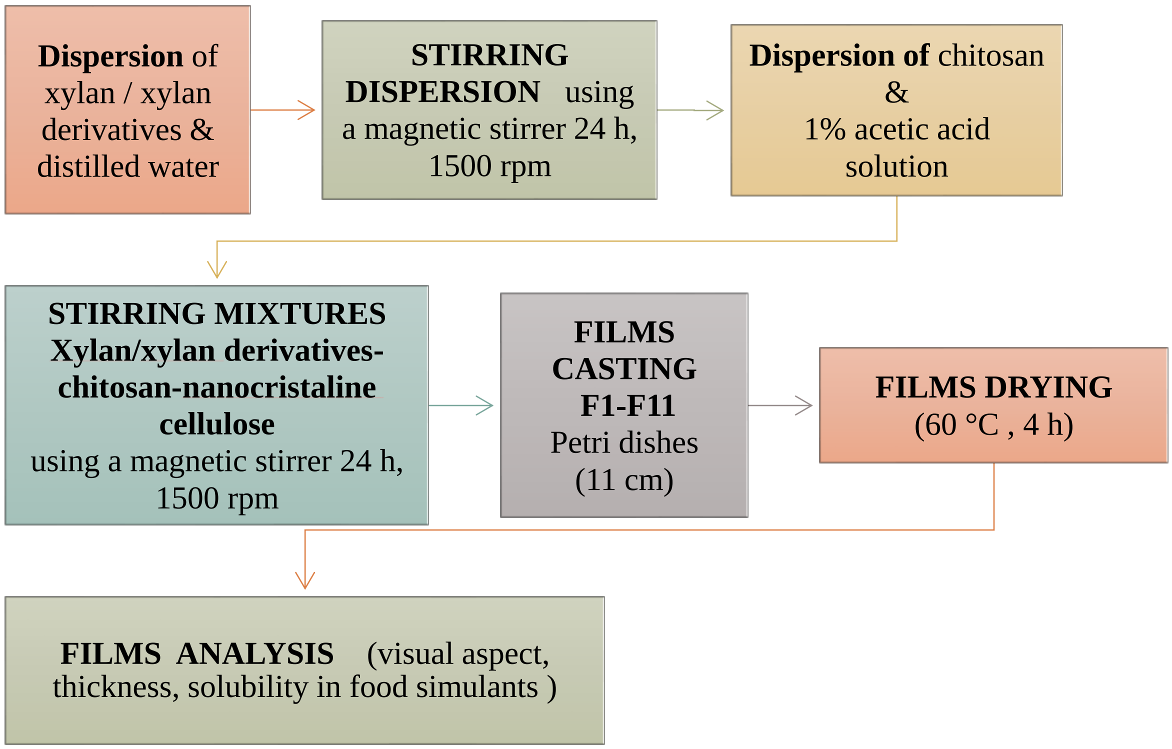

Fig. 1. The stages of homogenous films obtaining

Table 1. The Codification and Composition of Homogenous Films

Sample Codes	Coating Formula (%)				
	Native Xylan (Xy)	Hydrophobised Xylan (XyAKD)	Acetylated Xylan (XyAc)	Chitosan (Ch)	Nanocrystalline Cellulose (NCC)
F1	100	-	-	-	-
F2	-	100	-	-	-
F3	-	-	100	-	-
F4	-	-	-	-	100
F5	50	-	-	-	50
F6	-	50	-	-	50
F7	-	-	50	-	50
F8	-	-	-	100	-
F9	50	-	-	50	-
F10	-	50	-	50	-
F11	-	-	50	50	-

Preparation of Xylan/Xylan Derivatives/Chitosan/Nanocrystalline Cellulose Colloidal Dispersions

A dispersion of 2.5 g/L chitosan (Ch) in a 1% acetic acid solution was mechanically stirred at 950 rpm for 2 h. Dispersions of xylan and acetylated xylan (2.5% in distilled water) were obtained under magnetic stirring at 1500 rpm for 24 h.

Colloidal dispersions of xylan/xylan derivatives (Xy/XyAKD/XyAc), chitosan (Ch), and nanocrystalline cellulose (NCC) were prepared by the dropwise addition of the xylan/xylan derivatives solution to the chitosan/NCC dispersion at a rate of approximately 60 mL/h under magnetic stirring. After the complete addition of the chitosan/NCC, the mixture of colloidal dispersions was magnetically stirred for 24 h. To ensure adequate electrostatic interaction between xylan, xylan derivatives, chitosan, and NCC, the pH of the dispersions was adjusted to 4.5 to 5.0 prior to mixing, as all biopolymers are partially ionized under these conditions. Colloidal dispersions with a (Xy/XyAKD/XyAc)/Ch/NCC mass ratio of 50:50 were prepared and used as coatings for paper.

Obtaining of Polysaccharides Films

Homogeneous films were prepared following the stages presented in Fig. 1. The biopolymer mixtures, with the ratios presented in Table 1, were obtained by adding xylan/xylan derivative dispersions to chitosan and NCC solutions. The mixture was kept under magnetic stirring at 1500 rpm for 24 h. The resulting mixture was divided into samples of approximately 1 g dry material, cast into Petri dishes with an 11 cm diameter, and dried at 60 °C for 4 h.

Preparation of Polysaccharides Coated Papers

(Xy/XyAKD/XyAc)/Ch/NCC colloidal dispersions were applied on paper surface as homogenous coatings in a single layer of 5 g/m^2 on both sides of paper.

An automatic film applicator (TQC SHEEN type, TQC B.V., Netherlands) was used for coating. In this system, the aqueous coating dispersion is applied in front of a rod of 6 mm diameter. The automatic rotation of the rod over the paper substrate in longitudinal direction at 100 mbar and 125 mm/s ensures a well-defined amount of coating dispersion is applied. The thickness of the coating layer is controlled by the diameter of the rod.

A total of 20 samples of coated papers, each measuring 20 × 25 cm, were obtained. These samples were tested for their functional properties. Uncoated paper (base paper) was used as references (Table 2).

Table 2. The Codification and Composition of Polysaccharides Coated Papers

Sample Codification	Coating Formula (%)				
	Native Xylan (Xy)	Hydrophobised Xylan (XyAKD)	Acetylated Xylan (XyAc)	Chitosan (Ch)	Nanocrystalline Cellulose (NCC)
P1	100	-	-	-	-
P2	-	100	-	-	-
P3	-	-	100	-	-
P4	-	-	-	-	100
P5	50	-	-	-	50
P6	-	50	-	-	50
P7	-	-	50	-	50
P8	-	-	-	100	-
P9	50	-	-	50	-
P10	-	50	-	50	-
P11	-	-	50	50	-

Homogenous Film Analysis

The aspect of films as integrity, homogeneity, the presence of microcracks, flexibility or resistance to handling were evaluated by visual inspection.

Thickness, was measured using an INSIZE IP65 electronic micrometer, in a range of 0 to 25mm/+0,0001mm accuracy.

Solubility in food simulants, %, was determined according to a method stated by López De Dicastillo *et al.* 2011). The films, cut into strips of 2 cm x 2 cm, were totally immersed for 24 h at 25 °C in (30 mL) food simulants prepared according to Simoneau, 2009 and Directive 85/572/EEC (Table 3). After that, the strips were oven dried at 40 °C for 24 h. The solubility of the film was calculated as the percentage weight of the film that dissolved in the simulant after 24 h.

Surface Morphology

The effect of polysaccharides coating layers on the surface morphology of coated papers was investigated using a scanning electron microscope (SEM) FEI QUANTA 200 operating at an acceleration voltage of 20 kV. Prior to this, the paper samples were mounted on aluminum stub through the conductive carbon adhesive tape and sputtered with a thin gold layer, using an SPI Sputter Coater Module equipment (SPI Supplies, West Chester, PA 19380-4512, USA). The materials were evaluated at 1000x magnifications and a representative number of pictures were taken.

Table 3. Food Type and Food Simulants

Food Type	Aqueous Foods (pH>4.5)	Acidic Foods (pH ≤ 4.5)	Alcoholic Foods	Milky Foods	Fatty Foods
Food simulant	Distilled water	3% (v/v) acetic acid in water	10% (v/v) ethanol in water	50% (v/v) ethanol in water	95% (v/v) ethanol in water
Abbreviation	Simulant A	Simulant B	Simulant C	Simulant D1	Simulant D2

Wettability

A contact angle meter (Ossila Contact Angle goniometer) equipped with a high-resolution CCD camera was used to measure the wettability of the coated and uncoated paper samples, according to TAPPI T-458 cm-04 (2004). Using a micro syringe, a single droplet of 1 μL distilled water was dropped on the surface paper sample, and the contact angle between the droplet and the tangent of the liquid surface was measured every 5 s of water-substrate contact. Five replicates were determined for each sample.

The water absorption capacity of paper, measured as the Cobb60 index, was determined according to the standard method described in ISO 535 (2014). This method measures the amount of water absorbed by the paper over a 60-second period, providing essential data for evaluating the paper's suitability for applications where water resistance is a critical property.

Oil and Grease Resistance

The oil absorption capacity of paper, measured as the Unger-Cobb600 index, is determined following the TAPPI T 441 om-09 (2009) standard. This index measures the amount of oil absorbed by a paper sample over a specified period. The paper sample came into contact with a given amount of rapeseed oil for 600 s and weight differences were compared.

Grease resistance was tested according to the TAPPI T 559 cm-12 (2012) standard methodology to determine the KIT rating of paper samples. KIT solutions numbered 1 to 12 are prepared as mixtures with varying contents of castor oil, n-heptane, and toluene. Each solution corresponds to a specific KIT number, with higher numbers indicating more challenging conditions for grease resistance. Each paper sample is placed on a clean and flat surface with the test side facing up. A drop of a specific kit solution is released onto the surface of the paper sample. The solution is left on the paper surface for 15 seconds. After the 15-second period, any excess solution is removed from the paper surface. The back of the paper sample is inspected for any signs of staining. If no stain appears on the back, the paper sample is considered resistant to that specific kit solution. The highest KIT number of the solution that does not cause a stain on the back of the paper sample is recorded as the grease resistance value (KIT rating) for that sample.

Barrier to Air and Water Vapours

The air permeability of paper, determined using the Gurley method (ISO 5636-5:2013), involves measuring the time it takes for a specified volume of air to pass through a paper sample of a given area. This method provides a reliable way to quantify the air permeance of paper and board, which is essential for applications where breathability or barrier properties are important.

The water vapor transmission rate (WVTR) of paper samples, determined according to the ISO 2528:2018 standard, uses the gravimetric (dish) method to measure the rate at which water vapor passes through the paper. By using a controlled atmosphere and desiccant-filled dishes, this method accurately quantifies the rate at which water vapor permeates the paper over a set period, providing essential data for evaluating the paper's barrier properties against moisture.

Before testing, all of the samples were kept for 24 to 48 h in conditioned atmosphere at 23 °C and 50% RH, according to methodology presented in ISO 187:2022. All tests were performed in triplicate, and for each tests the average values and standard deviations (SD) were calculated.

Antimicrobial Properties

To evaluate the antimicrobial effect of chitosan the papers coated with xylan derivatives and chitosan were tested against Gram positive bacteria, *Bacillus sp.* from MIUG collection of BioAliment research Platform – Dunărea de Jos University of Galaţi.

The antibacterial activity of the coated papers was tested using a modified and adapted method of the ISO 846 (2000) standard. According to this method, the paper samples coated with xylan derivatives and chitosan, previously 15 min UV sterilized were placed onto culture medium surface (Plate Count Agar, Merck Germany). The inoculation of coated paper samples was realized by spraying with 1 µL of bacterial suspension (18 h aged). The samples were incubated in a thermostat, at 37 °C and analyzed after 24 and 48 h. The inhibition percentage of bacterial growth on and around the coated paper samples serves as a quantifiable indicator of the antimicrobial properties imparted by the chitosan coating. The level of bacterial growth was evaluated after 24 h and 48 h of incubation at 37 °C.

Biodegradation Capacity

The soil burial degradation test was done to examine the biodegradability of coated samples according to ASTM D5988 (2012). The biodegradation rate was obtained from measurements of weight losses (%) and CO_2 production (mg) after 7, 14, 28 and 42 days of soil burial of coated paper samples.

The dried paper samples were cut to the dimensions 100 mm × 100 mm, put into clean textile bag, and were buried in the soil to a depth of 5 cm from the surface for 7, 28, 42 days. Prior soil burial, the initial mass of each sample was weighed. After the specified time period, bags with samples were removed from the soil, rinsed with water and dried. The samples were weighed again and weight losses were calculated.

$$\text{Weight loss (\%)} = (W_0 - W_t) \times 100 \quad (1)$$

where W_t is the paper sample weight after t days of soil burial (g) and W_0 is the paper sample weight before burial (g).

To measure CO_2 production during the biodegradation of paper samples in soil, the assay was performed using hermetic containers. The CO_2 evolved over time was monitored by titrating the amount of KOH that reacts with CO_2.The containers (1 L volume) were filled with 200 g of soil with 50 to 70% humidity and samples of 3 × 3 cm^2 (0.5 to 1 g) were buried approximately 2 cm from the surface. A container with soil and no paper sample was used as a control for further calculations. Inside of each container a beaker with 50 mL of distilled water and a beaker with 20 mL of 0.5 KOH 0.5N of were placed. The containers were sealed to ensure the air tight seal and introduced in a dark place for 7, 14, 21, and 28 days. After each incubation period, titration the content of beaker with 20 mL KOH 0.5 N with HCl 0.5 N (mL) using phenolphthalein was performed. The CO_2 evolved was calculated using the following equation,

$$\text{mg of } CO_2 = 50 \times (V_{tC} - V_{tPi}) \times 0.044 \times f_{\text{HCl}} \quad (2)$$

where V_{tc} represents the volume of titrant (HCl) spent on the control, V_{tPi} is the volume of titrant (HCl) spent on the sample, 50 is the conversion factor equivalent to μmol of CO_2, 0.044 is the conversion factor of μmol of CO_2 to mg of CO_2, and f_{HCl} is the titrant (HCl) correction factor.

Following the biodegradation period, the presence and activity of microorganisms in the soil were analyzed to further understand the biodegradation process of the polysaccharide-coated papers. This involved isolating and counting the colony-forming units (CFUs) of microorganisms from the soil. Soil samples containing microorganisms were suspended in distilled water and the suspension was autoclaved with 0.85% NaCl to prepare it for microbial inoculation. The microbial suspension was used to inoculate Petri plates containing Potato Dextrose Agar (PDA) medium. Two sets of plates were prepared: with antibiotics: to promote the growth of filamentous fungi and without antibiotics: to facilitate the counting of single-celled microorganisms. After incubation in thermostatic chamber at 25 to 30 °C, for 3 days, the CFUs were counted on both sets of plates.

RESULTS AND DISCUSSION

Homogenous Films Characteristics

Due to its insufficient chain length and poor solubility, native xylan hemicellulose faces challenges in forming stable, flexible films. This results in brittle films with low mechanical stability. To address these issues, besides the utilization of plasticizers such as sorbitol, xylitol, glycerol, and propylene glycol to improve film properties, compounding xylan with other biopolymers can further enhance the film features. These solutions help to improve the flexibility and durability of the films by reducing the intermolecular forces between the xylan chains, thus enhancing their mobility and interaction. By visual evaluation of films based on xylan derivatives and their combination with chitosan, flexible and uniform structure were observed with thickness values in the range from 0.11 to 0.22 mm and without cracks compared with xylan derivatives and nanocrystalline cellulose films (Figs. 2, 3).

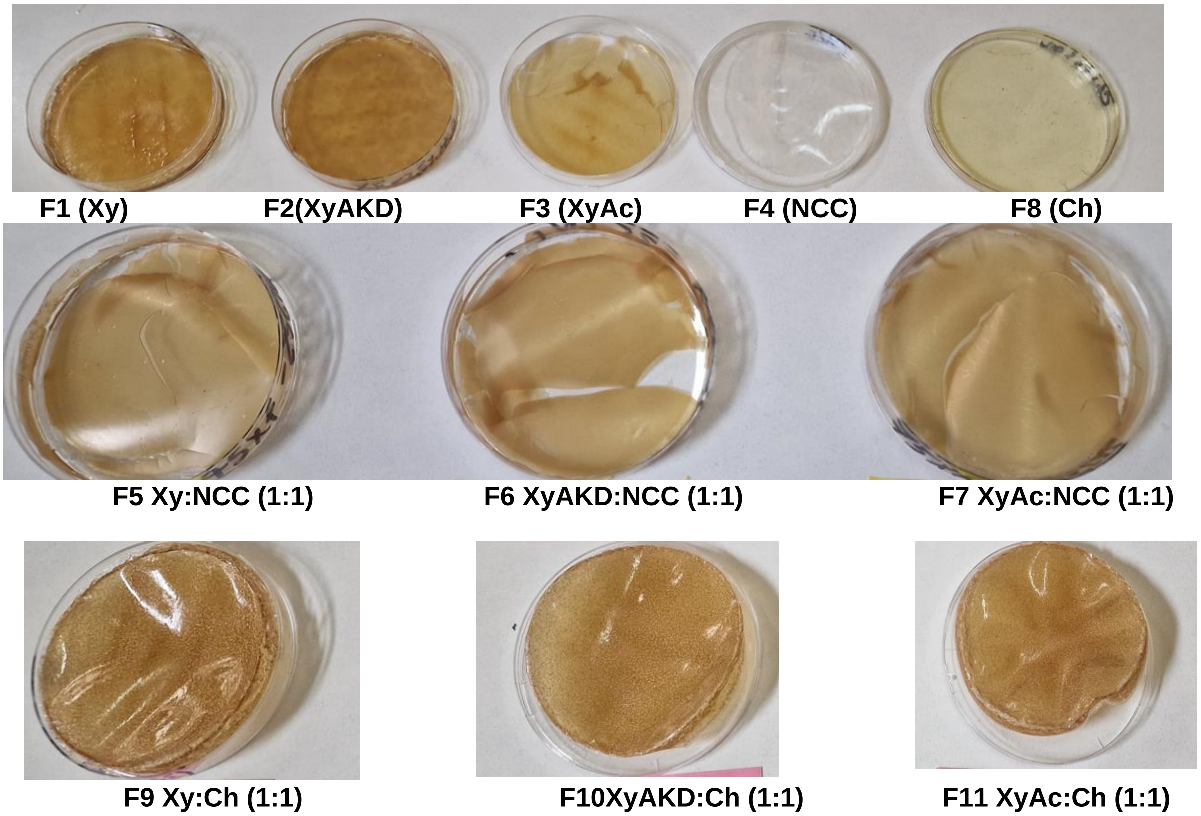

Fig. 2. The aspect of polysaccharides films

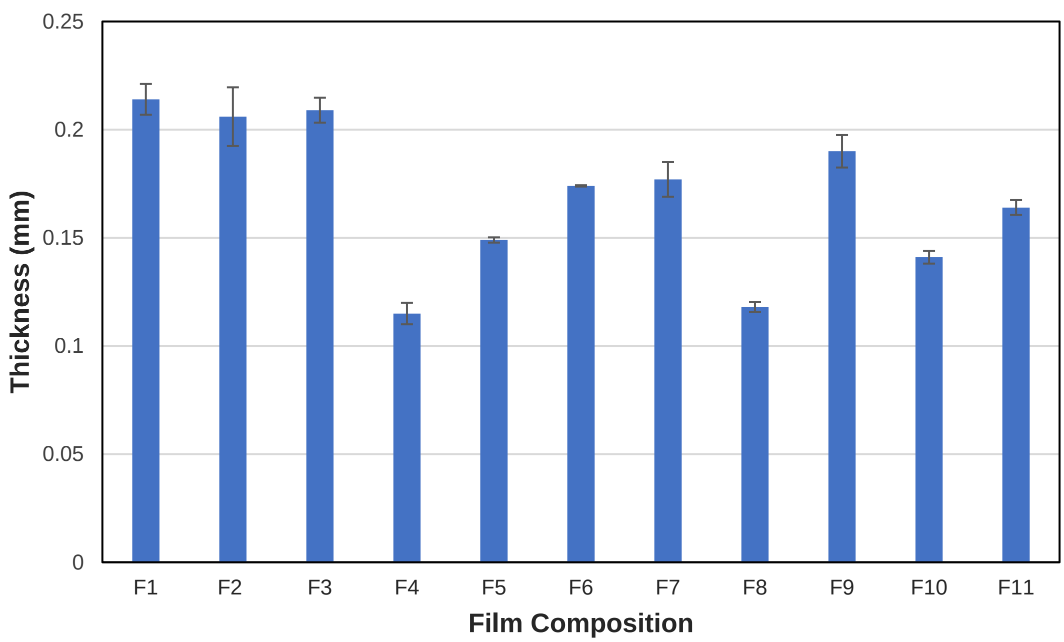

Fig. 3. The thickness of polysaccharides films

The food simulants solubility of xylan-based films is presented in Fig. 4. It was found that xylan and its derivatives, when combined with nanocrystalline cellulose (NCC), exhibited high solubility in both aqueous and alcoholic food environments. Conversely, films made from the hydrophobic xylan derivatives and chitosan showed lower solubility in these food simulants. Based on these findings, it can be inferred that all the tested polysaccharide combinations are suitable for use as packaging or coatings on paper packaging, particularly for fatty products (Fig. 4).

The results are according to literature (Tanpichai *et al.* 2022) and the research suggests that these polysaccharide-based films offer versatile and effective options for food packaging applications, especially for products with high oil and grease content.

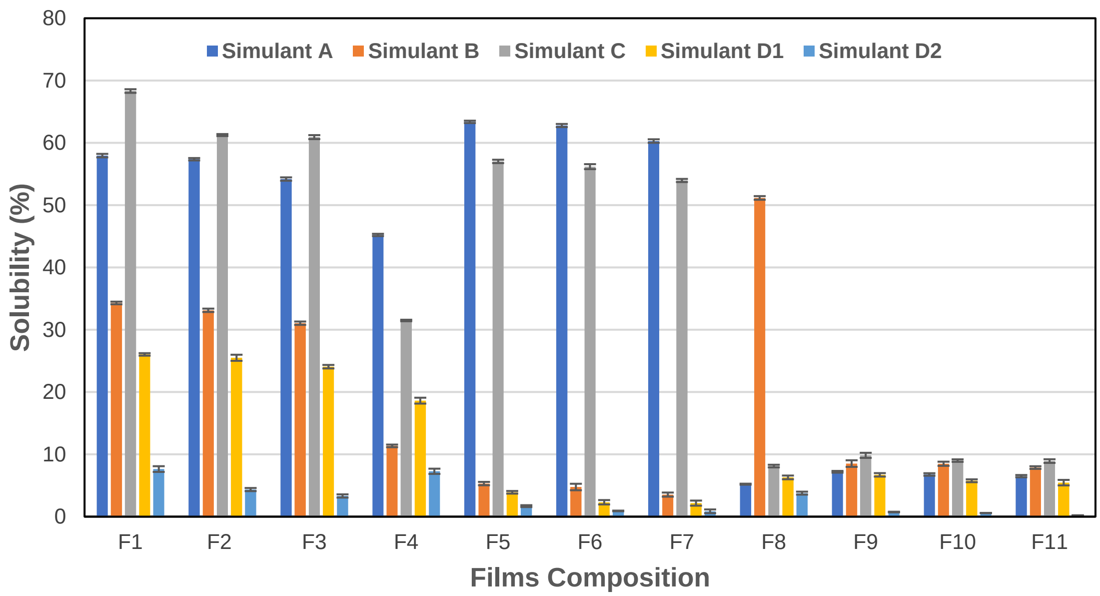

Fig. 4. The solubility of polysaccharides films in different food simulants

Surface Morphology

The surface morphology of polysaccharide-coated papers, as illustrated in Fig. 5, was found to vary according to the coating combination applied. The uncoated paper (P0) exhibited a porous structure of cellulose fibers with large amounts of cavities (Zhang *et al.* 2014). The incorporation of polysaccharide coatings, particularly those combining xylan derivatives with chitosan or NCC, significantly enhanced the surface morphology of paper by reducing porosity and creating a smooth, dense, and homogeneous surface. This was mainly attributed to the electrostatic bonding between the chitosan and xylan components and the superior film-forming capabilities of chitosan and NCC (Wang and Jing 2017; Feiz *et al.* 2021).

In addition, the use of nanocrystalline cellulose (NCC) in paper for food packaging offers several advantages due to its unique properties. With a larger surface area and nanometric dimensions, NCC can more effectively fill the empty spaces between fibers, resulting in a more homogeneous surface. This enhancement in surface quality is crucial for food packaging because it directly influences the barrier characteristics of the material (Spagnuolo *et al.* 2022; Lengowski *et al.* 2023b).

Improving surface quality by reducing empty spaces in paper represents a significant advancement in food packaging applications. Lower porosity in the packaging material enhances its barrier properties, making it more resistant to the passage of gases, moisture, and other substances. This improvement helps in maintaining the freshness and extending the shelf life of food products, thus offering better protection and preserving the quality of the packaged food (Wang *et al.* 2021).

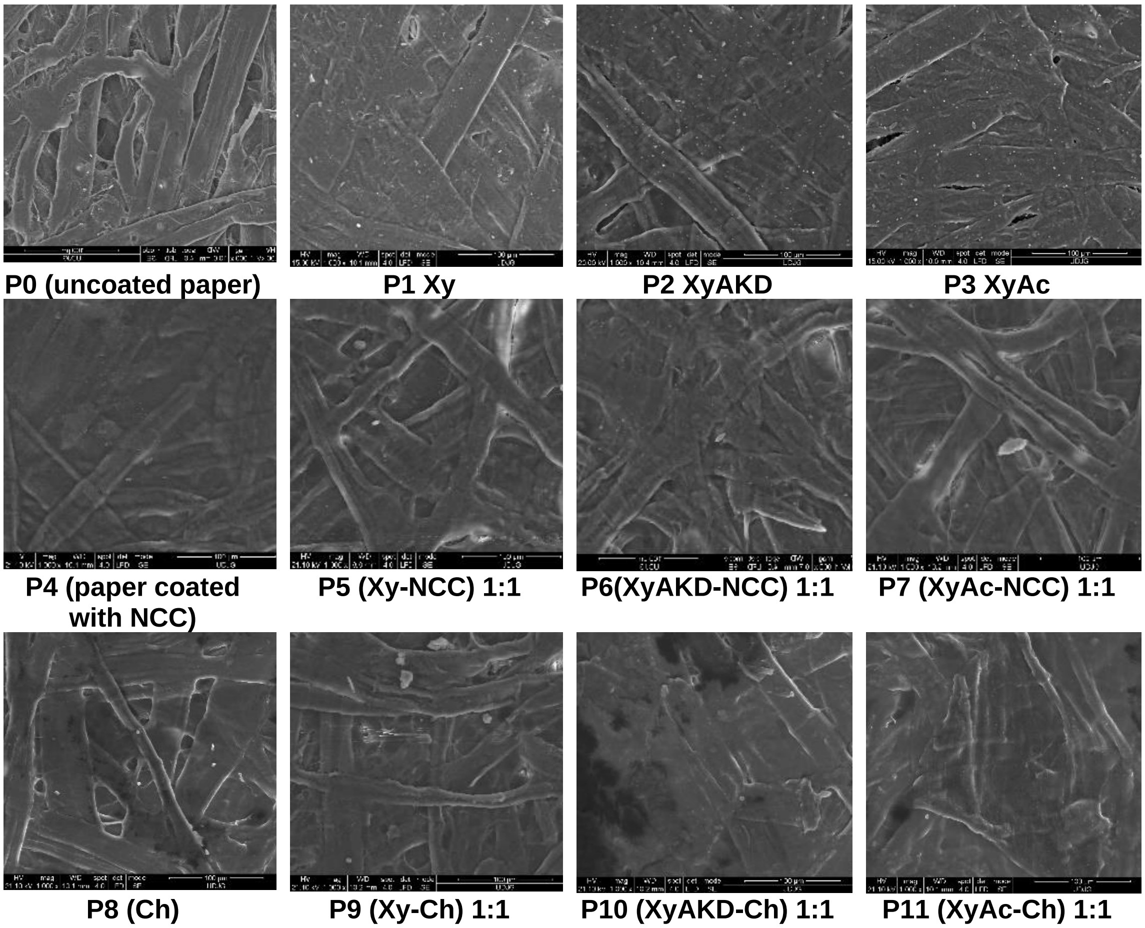

Fig. 5. Surface morphology of the polysaccharides coated papers

Wettability

The water contact angle test helps in understanding the wettability of the paper surface. A higher contact angle indicates a more hydrophobic surface, which is desirable in food packaging to prevent moisture penetration. Conversely, a lower contact angle suggests a hydrophilic surface, which might be less suitable for packaging applications where moisture resistance is required (Andze *et al.* 2017; Roman *et al.* 2023).

The water absorption test, conducted by immersing the samples in water for a specified duration, provides insight into how much water the paper can absorb. Lower water absorption indicates better barrier properties, enhancing the material's suitability for food packaging by reducing the risk of moisture-related degradation of the food product.

The results of contact angle tests are presented in Fig. 6. By including a coating layer on the paper surface, the contact angle increased to over 90° compared to uncoated paper, which had a contact angle of 63.8°. This increase is influenced by the type of polysaccharides used in the coating formula (Habibie *et al.* 2016). For instance, the contact angle of paper coated with xylan derivatives ranged between 74.2° and 82.7°, while combining xylan derivatives with chitosan led to even higher contact angles, ranging from 81.63° to 92.79°.

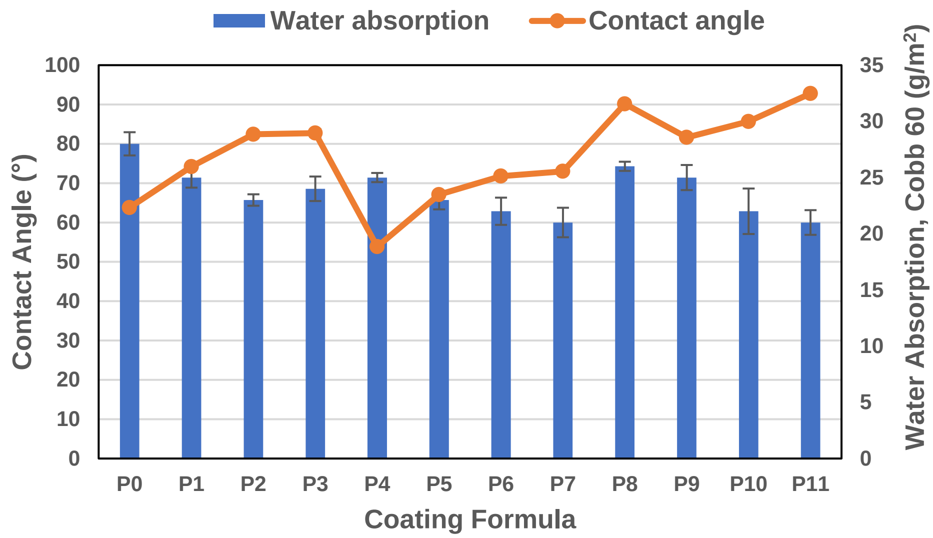

Fig. 6. Water barrier properties of polysaccharides coated papers

The chemical modification of xylan and its combination with other biopolymers provides an effective strategy to reduce the water affinity. In this study, xylan derivatives synthesized through esterification and combined with a chitosan biopolymer demonstrated enhanced water barrier properties. The coated samples exhibited contact angles ranging from 82.4° to 92.8°, which was significantly higher than the 74.2° contact angle of samples coated with native xylan (Stepan 2013; Egüésa *et al.* 2014).

For the paper samples coated with xylan derivatives and chitosan, the improvement was significantly greater, due to the supplementary effect of hydrophobic nature of chitosan when it is applied to cellulose fibers or integrated within the cellulose network. Additionally, chitosan filled the empty pores within the paper, reducing the number of freely available hydroxyl groups on the cellulose that can interact with water molecules. This reduction in available hydroxyl groups significantly enhanced the hydrophobic properties of the paper, as reflected in the higher contact angles (Ehman *et al*. 2022).

On the other hand, no significant change in the water contact angle was observed for the paper coated with NCC combinations. This suggests that while NCC might improve other properties, such as mechanical strength or barrier properties against gases, its influence on the hydrophobicity of the paper is minimal (Abdul Khalil *et al.* 2012). The lack of significant change in the contact angle indicates that the NCC coating does not substantially alter the surface's interaction with water, maintaining a similar level of hydrophilicity as the uncoated paper

Paper samples coated with xylan and its derivatives exhibited a decrease in water absorptiveness by 15% to 18% compared to uncoated paper samples. A more significant reduction in water absorption, approximately 25%, was achieved for paper samples coated with xylan derivatives combined with chitosan and nanocrystalline cellulose (NCC). This indicates that the addition of xylan derivatives, especially when combined with chitosan and NCC, effectively reduced the water absorption properties of paper, enhancing its water resistance (Fig. 6).

Gases Barrier Properties

The barrier properties to gases of polysaccharides coated paper, as evaluated by analyzing the air permeability and water vapor transmission rate, are presented in Fig. 7. All coating combinations resulted in a reduction of the WVTR compared to uncoated paper. This indicates that the coatings improved the paper's resistance to water vapor transmission.

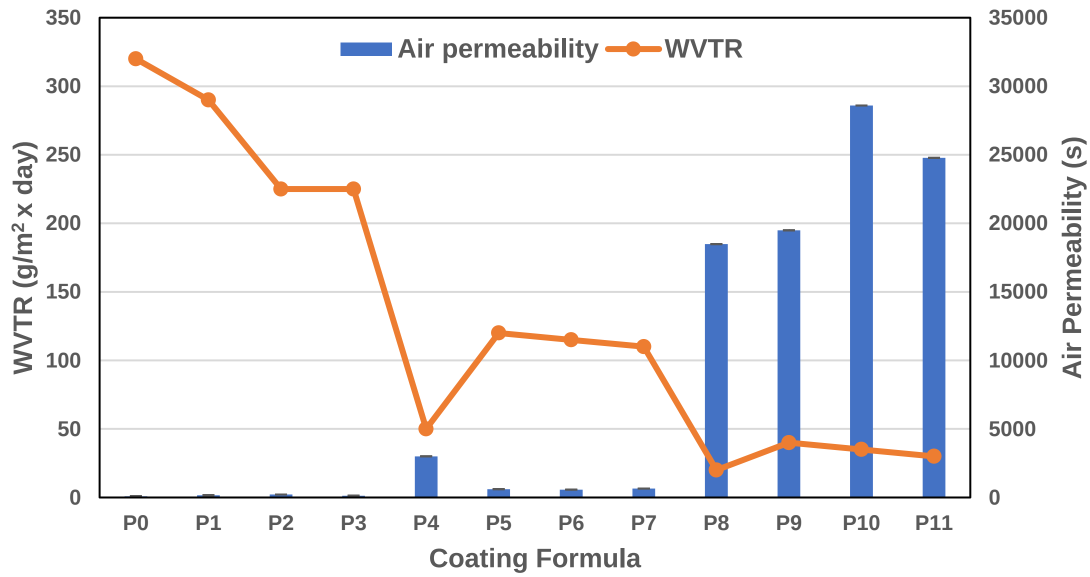

Fig. 7. The gases barrier properties of polysaccharides coated papers

The evolution of WVTR was found to be consistent with the changes in air permeability. This means that as the air permeability decreased, the WVTR also decreased, suggesting that the coatings effectively block the passage of gases and water vapor. Paper samples coated with a combination of xylan derivatives and chitosan showed the lowest air permeability and WVTR. This combination forms a denser structure without pinholes and voids, which was attributed to the excellent film-forming ability of chitosan.

When comparing coatings based on xylan or xylan derivatives alone with those that combine xylan/xylan derivatives and nanocrystalline cellulose (NCC), it has been observed that the combination with NCC results in better water vapor transmission rate (WVTR) and air permeability. This improvement is attributed to the synergistic effects between xylan/xylan derivatives and NCC, leading to a more compact and cohesive coating structure. The interaction between xylan/xylan derivatives and NCC creates a more compact and uniform coating matrix. This synergistic effect helps in filling the microvoids and cracks that might be present in xylan-based coatings alone, thus enhancing the overall barrier performance, as has been confirmed in other research (Aulin *et al.* 2010; Lavoine *et al.* 2012; Balan *et al.* 2015).

Oil Barrier Characteristics

In the context of food packaging, particularly for bakery products, fast food, and pet food storage, there is a high demand for materials that exhibit excellent resistance to grease and oil. This resistance is very important to prevent the migration and penetration of fats from the product into the packaging material, ensuring both the integrity of the packaging and the quality of the food. The detailed results, as shown in Fig. 8, highlight the effectiveness of different polysaccharide coatings in enhancing the grease and oil barrier properties of food packaging papers.

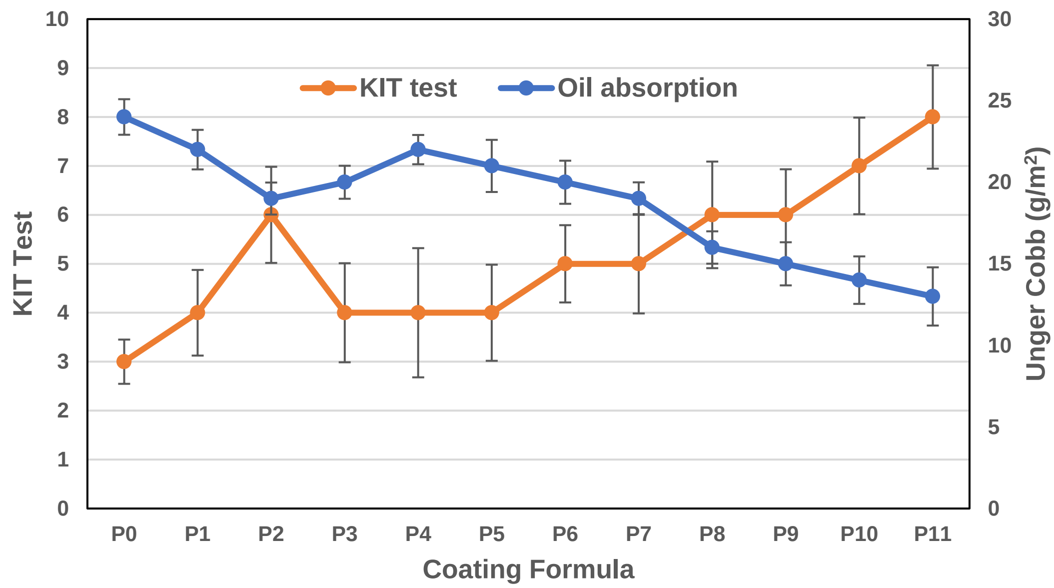

Fig. 8. Oil and grease barrier properties of polysaccharides coated papers

Xylan/xylan derivatives and their combinations with chitosan and nanocrystalline cellulose improved the grease and oil resistance of coated papers compared with uncoated paper. Therefore, the oil absorption and KIT rating of papers coated with xylan derivatives and NCC formula was about 21% lower and respectively two times higher compared with uncoated paper. The significantly improvements were obtained in case of paper coated with xylan derivatives and chitosan formula. In this case the KIT rating value was approximately three times higher compared to that of uncoated paper. For these samples, the oil absorption was 46% lower than that of uncoated paper.

The presence of cationic groups (NH_3^+) in the chemical structure of chitosan plays a crucial role in retaining fat and preventing its penetration into the substrate. This significantly enhances the oil and grease barrier properties (Pichavant *et al.* 2005). Both NCC and chitosan have excellent film-forming properties, contributing to their effectiveness as oil barriers. Their combination with xylan derivatives results in coatings that provide superior resistance to grease and oil penetration (Chen *et al.* 2023).

The obtained results demonstrate that polysaccharide-coated papers, particularly those using combinations of xylan derivatives with chitosan and NCC, can achieve grease and oil resistance properties similar to those of fluorochemical-coated papers. This finding is supported by existing literature and highlights the potential of these biopolymer-based coatings to serve as sustainable alternatives in food packaging (Kjellgren *et al.* 2005).

Antibacterial Properties

Bacillus sp. was selected to evaluate the antibacterial activity of the polysaccharides coated papers. Gram-positive bacteria, such as *Bacillus* sp., exhibit higher resistance to the bactericidal action especially of chitosan compared to Gram-negative bacteria. This characteristic makes them suitable for testing the efficacy of antibacterial coatings.

Bacillus subtilis is commonly used as a model organism in laboratory studies. It is often regarded as the Gram-positive counterpart to *Escherichia coli* (*E. coli*), which is a well-studied Gram-negative bacterium.

The results presented in Fig. 9 demonstrated that the xylan-/xylan derivative-/chitosan-coated papers exhibited significant antibacterial activity against *Bacillus sp.* The antibacterial properties of chitosan are attributed to its cationic nature, which allows it to interact with the negatively charged bacterial cell walls, leading to cell disruption and death. This effect was observed even with the increased resistance of Gram-positive bacteria. The results are well correlated with WVTR values, which for the samples P4, P8, P9, P10, and P11 were the lowest. This created a low moisture content, which was unfavorable for bacterial proliferation.

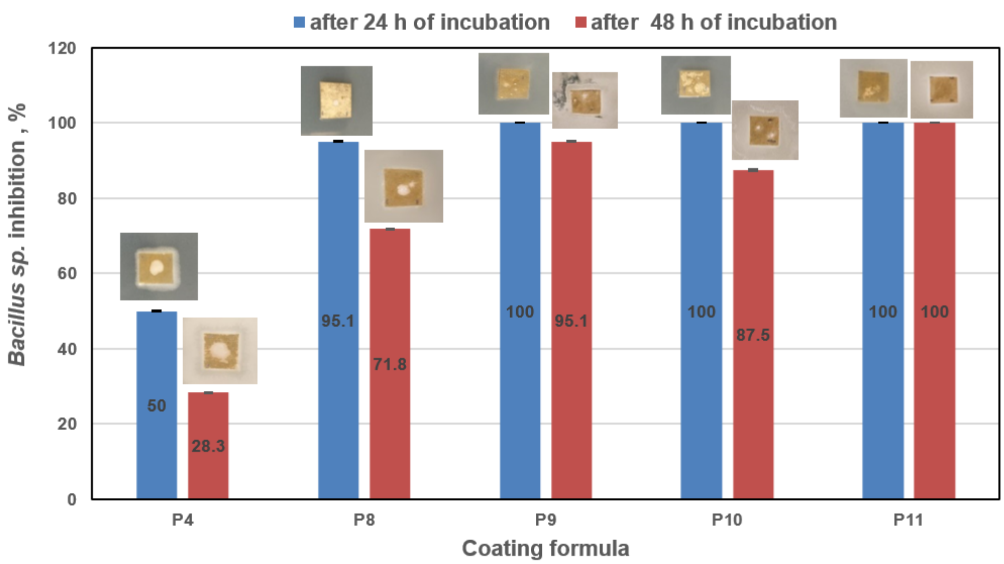

Fig. 9. The antibacterial activity of polysaccharides coated papers

Biodegradability capacity

The soil burial degradation test confirmed the biodegradability of the polysaccharide-coated papers. The combination of weight loss, CO_2 production, and visual inspection provided comprehensive evidence that the polysaccharides coated papers break down effectively in a soil environment. The results are presented in Figs. 10, 11, and 12.

The different compositions of the coatings showed certain patterns in relation to the rate of biodegradability and CO_2 production. This could have been because the natural polysaccharides are highly compatible with the environment and made the sample degrade faster in the soil. Compared with uncoated paper, the CO_2 production was higher for all the paper samples coated with polysaccharides. This is related to the growing of microorganisms during the catabolic process of sugars. The growing microorganism may be due to of more enzymes that catalyze xylan hemicellulose, chitosan, or nanocellulose breakdown reactions, which degrade polysaccharides into oligosaccharides and monosaccharides, respectively (Carpinelli Macedo *et al.* 2022). At 28 days and 42 days of soil degradation, all the samples of xylan and xylan/chitosan/nanocellulose coatings reach similar degradation rate (70 to 80% and 14 to 16 mg CO_2 production, as is presented in Figs. 10 and 11.

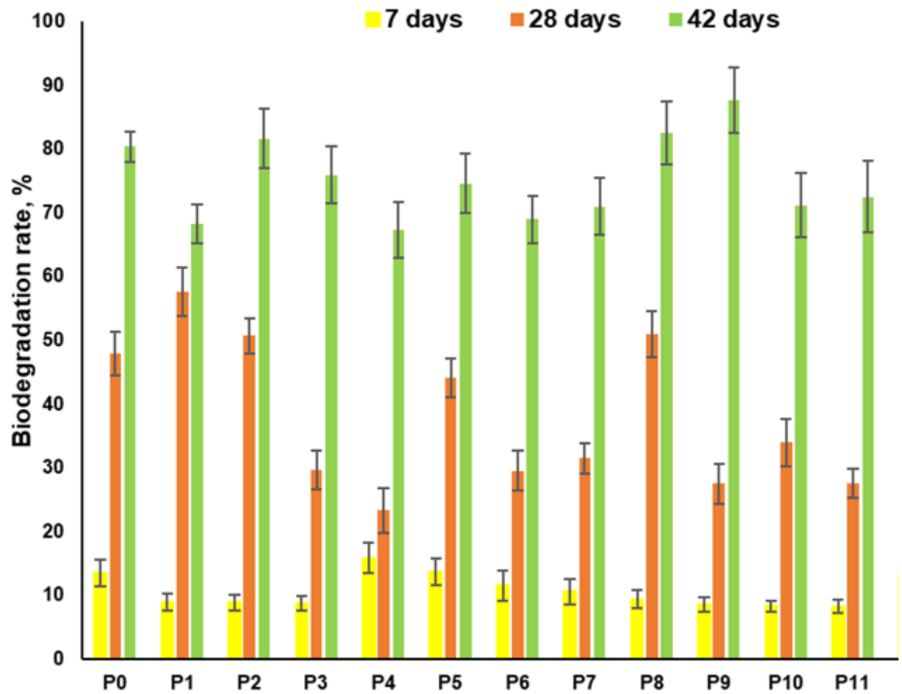

Fig. 10. Biodegradation rate of polysaccharides coated papers

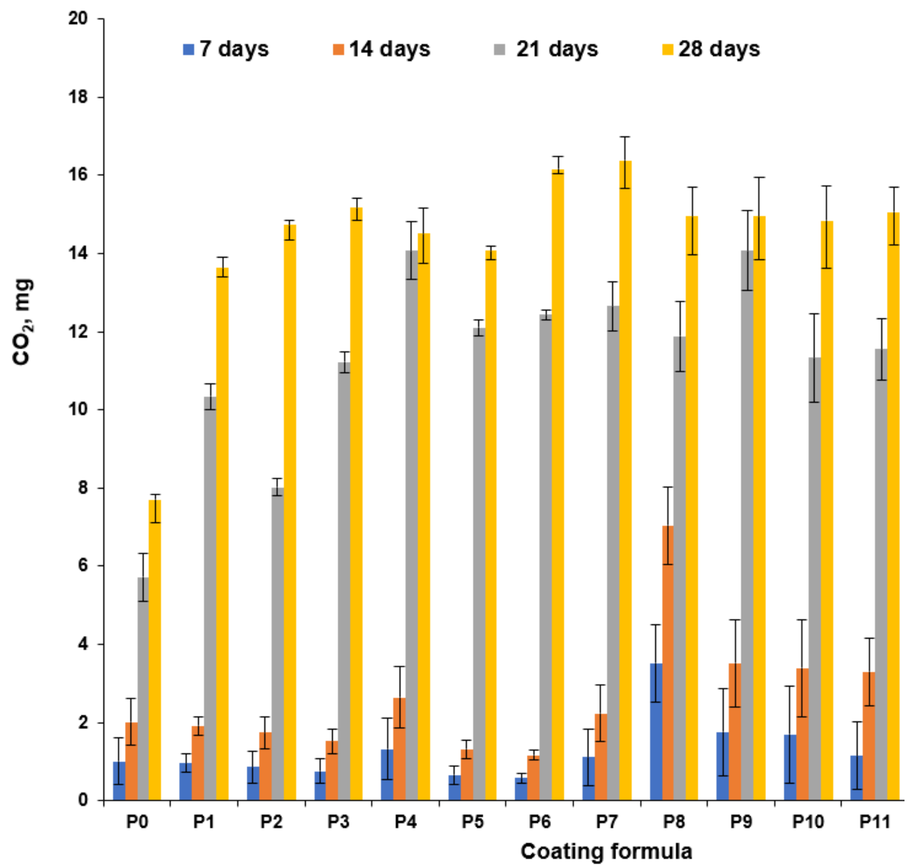

Fig. 11. CO_2 production from the biodegradation of polysaccharides coated papers

The presence of chitosan in paper coatings with combination of xylan/xylan derivatives reduces the crystallinity of thin coatings and facilitates the degradation during the first days of soil burial condition. The changes to the physical characteristics (color, shape, and size) of the samples during a soil burial degradation test can be seen in Fig. 12. All coated samples had broken into smaller pieces losing their physical integrity in correlation with the biodegradation rate and CO_2 production.

The microorganism's growth was evaluated in the soil before and after the biodegradation of polysaccharides coated papers. The influence of polysaccharides coatings on the microbiological growth is evidenced due to a higher number of colony-forming units (CFU) per gram of soil (Table 4) after the period in which coated paper samples were buried.

Table 4. Average Number of CFU/g Soil Before and After Biodegradation of Coated Papers

Sample	PDA Without Antibiotic (CFU/g soil)	PDA With Antibiotic (CFU/g soil)
Soil before biodegradation	3,07 x 105	2,11 x 104
Soil after biodegradation	5,43 x 105	1,1 x 105

During the post-biodegradation microbial analysis, distinct visual characteristics of filamentous fungal colonies were observed on the potato dextrose agar (PDA) plates. These observations help identify the types of fungi involved in the biodegradation process.

The predominant fungi showed rapid growth, displaying specific characteristics that suggest the presence of *Aspergillus fumigatus* and *Penicillium digitatum* (colonies were green in the center and white at the border). Due to the fact that the *P. digitatum* is a fungus that commonly develops in citrus fruits the chances of being *Aspergillus* are greater. Other small colonies with smooth margins colored in brown or other colored in white, cotton-like filamentous fungus, can be observed (Figs. 13 (a) and (b)).

The presence of these fungi, along with other identified species, supports the biodegradability of the coatings and highlights the active role of fungi in the degradation process.

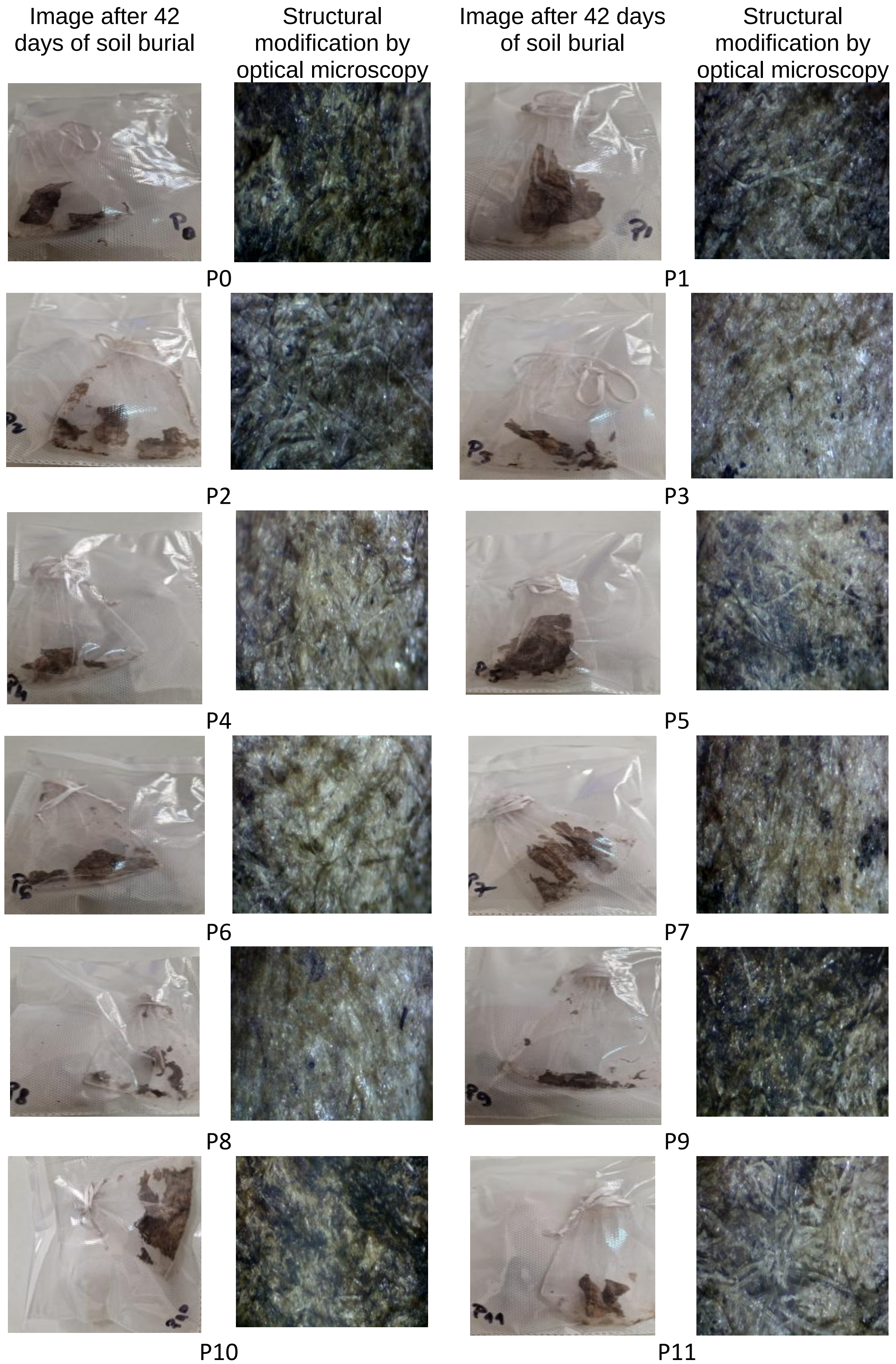

Fig. 12. Physical appearance of the polysaccharides coated papers after being buried in soil

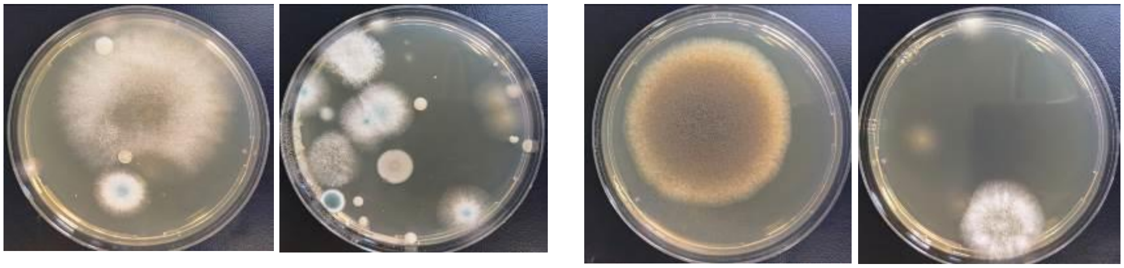

Fig. 13. Growth of soil microorganisms: (a) Colonies like as *Aspergillus fumigatus* (without antibiotic on PDA plate); (b) Cotton-like filamentous fungus (with antibiotic on PDA plate)

This method provides valuable insights into the environmental impact and decomposition rate of paper materials, which is essential for evaluating their suitability for sustainable and eco-friendly applications.

CONCLUSIONS

1. The study shows that, comparing with uncoated paper, the xylan/xylan derivatives hemicellulose-coated papers, especially when combined with nanocellulose or chitosan, offered significantly enhanced barrier properties against water, water vapor, oil, and grease. These biopolymer coatings were able to create a hydrophobic surface (contact angle 92.8°) that improved the moisture barrier and grease resistance (KIT rating 8), achieving performance levels similar to fluorochemical-treated papers.
2. The solubility tests in food simulants confirmed that polysaccharide coatings based on xylan derivatives, chitosan, and nanocellulose exhibited appropriate resistance to fatty, acidic, alcoholic, and aqueous environments. This makes them highly suitable for diverse food packaging applications, ensuring the protection and preservation of food products.
3. The combination of xylan derivatives and chitosan in paper coatings resulted in highly effective antibacterial properties, specifically against Gram-positive bacteria such as *Bacillus subtilis*. The total inhibition observed after 24 h of incubation, maintained even after 48 h. These findings underscore the potential of these coatings to serve as robust antimicrobial barriers in food packaging.
4. The presence of chitosan in xylan/xylan derivatives coatings effectively reduced the crystallinity, facilitating faster initial degradation under soil burial conditions. In addition, due the presence of (NH_3^+) groups, the chitosan can improve the C:N ratio, which is beneficial for biodegradation. Over 28 to 42 days, these coatings degraded at similar rates and promoted microbial activity, as indicated by consistent CO_2 production and increased CFU counts. This suggests that the coatings not only degrade but also promote microbial proliferation, likely by providing a nutrient source that supports microbial metabolism and growth.
5. This comprehensive analysis highlights the dual benefits of enhanced barrier properties and biodegradability in polysaccharide-coated papers, making them an excellent alternative for sustainable and effective food packaging solutions.

ACKNOWLEDGMENTS

This research was funded by the Ministry of Research, Innovation, and Digitization, CNCS—UEFISCDI, Romania, grant number PN-III-P4-PCE-2021-0714.

REFERENCES CITED

Abdul Khalil, H. P. S., Bhat, A. H., and IreanaYustra, A. F. (2012). "Green composites from sustainable cellulose nanofibrils: A review," *Carbohydrate Polymers* 87(2), 963-979. DOI: 10.1016/j.carbpol.2011.08.078

Alves, R. C., Melati, R. B., Casagrande, G. M. S., Contiero, J., Pagnocca, F. C., and Brienzo, M. (2020). "Sieving process selects sugarcane bagasse with lower recalcitrance to xylan solubilization," *J. Chem. Technol. Biotechnol.* 96(2), 327-334. DOI: 10.1002/jctb.6541

Andze, L., Laka, M., Filipova, I., Rozenberga, L., Grinfelds, U., Zoldners, J., Passas, R., and Mauret, E. (2017). "Effect of chitosan on properties of paper for packaging," *Cellul. Chem. Technol.* 51(12), 67-73.

ASTM D5988 (2012). "Standard test method for determining aerobic biodegradation of plastic materials in soil," ASTM International, West Conshohocken, PA, USA.

Aulin, C., Gallstedt, M., and Lindstrom, T. (2010). "Oxygen and oil barrier properties of microfibrillated cellulose films and coatings," *Cellulose* 17, 559-574.

Balan, T., Guezennec, C., Nicu, R., Ciolacu, F., and Bobu, E. (2015). "Improving barrier and strength properties of paper by multi-layer coating with bio-based additives," *Cellul. Chem. Technol.* 49(7-8), 607-615.

Bordenave, N., Grelier, S., and Coma, V. (2010). "Hydrophobization and antimicrobial activity of chitosan and paper-based packaging material," *Biomacromolecules* 11, 88-96.

Braga, R. S., and Poletto, M. (2020). "Preparation and characterization of hemicellulose films from sugarcane bagasse," *Materials.* DOI: 10.3390/ma13040941

Carpinelli Macedo, J. V., Manabu Abe, M., Bertolino Sanvezzo, P., Grillo, R., Branciforti, M. C., and Brienzo, M. (2022). "Xylan-starch-based bioplastic formulation and xylan influence on the physicochemical and biodegradability properties," *Polymer Bulletin* 80, 8067-8092.

Cheng, Z., Li, J., Su, M., Xiao, N., Zhong, L., Zhang, X., Chen, X., Chen, O., Liang, W., and Liu, M. (2024). "High-barrier oxidized cellulose nanofibril/chitosan coating for functional food packaging materials," ACS *Appl. Polym. Mater*. 6(5), 2877-2888. DOI: 10.1021/acsapm.3c03115

Chen, Q., Zhang, R., Su, Y., Zhao, T., Du, Q., and Liu, J. (2023). "Research status and prospects of bio-based materials for grease barrier coatings on paper food packaging," *PBM* 8(4), 44-54. DOI: 10.26599/PBM.2023.9260025

Chinga-Carrasco, G., and Syverud, K. (2012). "On the structure and oxygen transmission rate of biodegradable cellulose nanobarriers," *Nanoscale Res. Let.* 7, article no. 192. DOI: 10.1186/1556-276X-7-192

Csiszár, E., and Nagy, S. (2017). "A comparative study on cellulose nanocrystals extracted from bleached cotton and flax and used for casting films with glycerol and sorbitol plasticisers," *Carbohydrate Polymers* 174, 740-749. DOI:

10.1016/j.carbpol.2017.06.103

Directive 85/572/EEC, "The list of simulants to be used for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs," (85/572/EEC)

Du, H., Parit, M., Liu, K., Zhang, M., Jiang, Z., Huang, T.-S., Zhang, X., and Si, C. (2021). "Engineering cellulose nanopaper with water resistant, antibacterial, and improved barrier properties by impregnation of chitosan and the followed halogenation," *Carbohydr. Polym*. 270, 118372. DOI: 10.1016/j.carbpol.2021.118372

Farhat, W., Venditti, R., Ayoub, A., Prochazka, F., Fernandez-de-Alba, C., Mignard, N., Taha, M., and Becquart, F. (2018). "Towards thermoplastic hemicellulose: Chemistry and characteristics of poly-(ε-caprolactone) grafting onto hemicellulose backbones," *Mater. Des.* 153, 298-307. DOI: 10.1016/j.matdes.2018.05.013

Feiz, E., Mahyari, M., Ghaieni, H. R., and Tavangar, S. (2021). "Copper on chitosan-modified cellulose filter paper as an efficient dip catalyst for ATRP of MMA," *Sci. Rep.* 11(1), article 8257.

Felipuci, J. P., Schmatz, A. A., de Angelis, D. A., and Brienzo, M. (2021). "Biological pretreatment improved subsequent xylan chemical solubilization," *Biomass Conv Bioref*. DOI: 10. 1007/s13399- 021- 01506-w

Fujisawa, S., Okita, Y.,Fukuzumi, H., Saito, T., and Isogai, A. (2011). "Preparation and characterization of tempo-oxidized cellulose nanofibril films with free carboxyl groups," *Carbohydr. Polym.* 84(1), 579-583. DOI: 10.1016/j.carbpol.2010.12.029

Habibie, S., Hamzah, M., Anggaravidya, M., and Kalembang, E. (2016). "The effect of chitosan on physical and mechanical properties of paper," *J. Chem. Eng. Mater. Sci.* 7(1), 1-10. DOI: 10.5897/JCEMS2015.0235

Ham-Pichavant, F., Sèbe, G., Pardon, P., and Coma, V. (2005). "Fat resistance properties of chitosan-based paper packaging for food applications," *Carbohydr. Polym.* 61(3), 259-265. DOI: 10.1016/j.carbpol.2005.01.020

Hubbe, M. A., Ferrer, A., Tyagi, P., Yin, Y., Salas, C., Pal, L., and Rojas, O. J. (2017). "Nanocellulose in thin films, coatings, and plies for packaging applications: A review," *BioResources* 12(1), 2143-2233. DOI: 10.15376/biores.12.1.2143-2233

Ifuku, S., Ikuta, A., Egusa, M., Kaminaka, H., Izawa, H., Morimoto, M., and Saimoto, H. (2013). "Preparation of high-strength transparent chitosan film reinforced with surface-deacetylated chitin nanofibers," *Carbohydr. Polym.* 98(1), 1198-1202. DOI: 10.1016/j.carbpol.2013.07.033

Imre, B., Garcia, L., Puglia, D., and Vilaplana, F. (2019). "Reactive compatibilization of plant polysaccharides and biobased polymers: Review on current strategies, expectations and reality," *Carbohydr Polym* 209, 20-37. DOI: 10.1016/j.carbpol.2018. 12.082

ISO 2528 (2018). "Sheet materials — Determination of water vapour transmission rate (WVTR) — Gravimetric (dish) method," International Organization for Standardization, Geneva, Switzerland.

ISO 846 (2000). "Plastics — Evaluation of the action of microorganisms," International Organization for Standardization, Geneva, Switzerland.

ISO 535 (2014). "Determination of water absorptiveness," International Organization for Standardization, Geneva, Switzerland.

ISO 5636-5 (2013). "Paper and board — Determination of air permeance (medium range). Part 5: Gurley method," International Organization for Standardization, Geneva, Switzerland.

ISO 187:2022, “Paper, board and pulps — standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples,” International Organization for Standardization, Geneva, Switzerland.

Jiao, G., Yu, G., Zhang, J., and Ewart, H. S. (2011). “Chemical structures and bioactivities of sulfated polysaccharides from marine algae,” *Mar. Drugs* 9, 196-223.

Kjellgren, H., Gallstedt, M., Engstrom, G., and Jarnstrom L. (2006). “Barrier and surface properties of chitosan-coated greaseproof paper,” *Carbohydrate Polymers* 65(4), 453-460. DOI: 10.1016/j.carbpol.2006.02.005

Lavoine, N., Desloges, I., Dufresne, A., and Bras, J. (2012). “Microfibrillated cellulose—Its barrier properties and applications in cellulosic materials: A review,” *Carbohydrate Polymers* 90(2), 735-764. DOI: 10.1016/j.carbpol.2012.05.026

Lengowski, E. C., Bonfatti Júnior, E. A., Kumode, M. M. N., Carneiro, M. E., and Satyanarayana, K. G. (2019). “Nanocellulose in the paper making,” in: *Sustainable Polymer Composites and Nanocomposites*, Inamuddin, S. Thomas, R. K. Mishra, and A. M. Asiri, (eds.), Springer Nature, Cham, Switzerland, pp. 1027-1065.

Lengowski, E. C., Júnior, E. A. B., Simon, L., De Muñiz, G. I. B., De Andrade, A. S., Nisgoski, S., and Klock, U. (2020). “Different degree of fibrillation: Strategy to reduce permeability in nanocellulose-starch films,” *Cellulose* 27, 10855-10872.

Lengowski, E. C., Bonfatti Júnior, E. A., Coelho Simon, L., Bolzon de Muniz, G. I., Sulato de Andrade, A., Neves Leite, A., and Souza de Miranda Leite, E. L. (2023a). “Nanocellulose coating on kraft paper,” *Coatings* 13, article 1705. DOI: 10.3390/coatings13101705

Lengowski, E. C., Bonfatti Júnior, E. A., Muñiz, G. I. B., and Satyanarayana, K. G. (2023b). “Barrier properties of nanoparticle-based polymer composites,” in: *Synthetic and Natural Nanofillers in Polymer Composites*, N. M. Nurazzi, R. A. Ilays, S. M. Sapuan, and A. Khalina (eds.), Elsevier, Amsterdam, pp. 219-241.

Liu, X. F., Guan, Y. L., Yang, D. Z., Li, Z., and De Yao, K. (2001). “Antibacterial action of chitosan and carboxymethylated chitosan,” *J. Appl. Polym. Sci*. 79, 1324-1335.

Lopez de Dicastillo, C., Nerín, C., Alfaro Tena, P., and Catala, R. (2011). “Development of new antioxidant active packaging films based on ethylene vinyl alcohol copolymer (EVOH) and green tea extract,” *Journal of Agricultural and Food Chemistry* 59(14), 7832-7840. DOI: 10.1021/jf201246g

Macedo, J. V. C., Martins, J. R., Abe, M. M., Branciforti, M. C., and Brienzo, M. (2022). “Hemicellulose application for the production of bioplastics and biomaterials,” in: *Hemicellulose Biorefinery: A Sustainable Solution for Value Addition to Bio-based Products and Bioenergy. Clean Energy Production Technologies*, M. Brienzo (ed.), Springer, Singapore. DOI: 10.1007/978-981-16-3682-0_8

Mali, S., Grossmann, M. V. E., Garc, A. M. A., Martino, M. N., and Zaritzky, N. E. (2004). “Barrier, mechanical and optical properties of plasticized yam starch films,” *Carbohydr. Polym.* 56, 129-135. DOI: 10.1016/j.carbpol.2004.01.004

Melati, R. B., Shimizu, F. L., Oliveira, G., Pagnocca, F. C., Souza, W., Sant’anna, C., and Brienzo, M. (2019). “Key factors affecting the recalcitrance and conversion process of biomass,” *BioEnergy Res.* 12(1), 1-20. DOI: 10.1007/s12155-018-9941-0

Mitrano, D. M., Wick, P., and Nowack, B. (2021). “Placing nanoplastics in the context of global plastic pollution,” *Nat. Nanotechnol.* 16, 491-500. DOI: 10.1038/s41565-021-00888-2

Nechita, P., Mirela, R., and Ciolacu, F. (2021). “Xylan hemicellulose: A renewable material with potential properties for food packaging applications,” *Sustainability* 13,

article 13504.
Nechita, P., Roman, M., Cantaragiu Ceoromila, A., and Dediu Botezatu, A.V. (2022). "Improving barrier properties of xylan-coated food packaging papers with alkyl ketene dimer," *Sustainability* 14, article 16255.
Palasingha, C., Ströma, A., Amerb, H., and Nypelöa, T. (2021). "Oxidized xylan additive for nanocellulose films– A swelling modifier," *International Journal of Biological Macromolecules* 180, 753-759. DOI: 10.1016/j.ijbiomac.2021.03.062
Plackett, D., Anturi, H., Hedenqvist, M., Ankerfors, M., Gallstedt, M., Lindstrom, T., and Siro, I. (2010). "Physical properties and morphology of films prepared from microfibrillated cellulose and microfibrillated cellulose in combination with amylopectin," *J. Appl. Polymer Sci.* 117(6), 3601-3609. DOI: 10.1002/app.32254
Raposo, M. F. D. J., Morais, A. M. M. B., and Morais, R. (2015). "Marine polysaccharides from algae with potential biomedical applications," *Mar. Drugs* 13(5), 2967-3028. DOI: 10.3390/md13052967
Rodionova, G., Saito, T., Lenes, M., Eriksen, O., Gregersen, O., Fukuzumi, H., and Isogai, A. (2012b). "Mechanical and oxygen barrier properties of films prepared from fibrillated dispersions of TEMPO-oxidized Norway spruce and eucalyptus pulps," *Cellulose* 19(3), 705-711. DOI: 10.1007/s10570-012-9664-x
Roman, M., Nechita, P., Vasile, M.-A., and Cantaragiu Ceoromila, A.-M. (2023). "Barrier and antimicrobial properties of coatings based on xylan derivatives and chitosan for food packaging papers," *Coatings* 13, article 1761. DOI: 10.3390/coatings13101761
Roy, S., Van Hai, L., Kim, H.C., Zhai, L., and Kim, J. (2020). "Preparation and characterization of synthetic melanin-like nanoparticles reinforced chitosan nanocomposite films," *Carbohydr. Polym.* 231, article no. 115729. DOI: 10.1016/j.carbpol.2019.115729
Schnell, C., Galva´n, M., Peresin, M., Inalbon, M., Vartiainen, J., Zanuttini, M., and Mocchiutti, P. (2017). "Films from xylan/chitosan complexes: preparation and characterization," *Cellulose* 24, 4393-4403.
Shimizu, M., Saito, T., and Isogai, A. (2016). "Water-resistant and high oxygen-barrier nanocellulose films with interfibrillar cross-linkages formed through multivalent metal ions," *J. Membrane Sci.* 500, 1-7. DOI: 10.1016/j.memsci.2015.11.002
Simoneau, C. (2009). "Guidelines on testing conditions for articles in contact with foodstuffs," *JRC Scientific and Technical Reports.*
Solier, Z. N., Schnell, C. N., Galván, M. V., Mocchiutti, P., Zanuttini, M. A., and Inalbon, M. C. (2022). "Fast preparation of flexible wet-resistant and biodegradable films from a stable suspension of xylan/chitosan polyelectrolyte complexes," *Journal of Polymers and the Environment* 30, 114-124.
Spagnuolo, L., D'Orsi, R., and Operamolla, A. (2022). "Nanocellulose for paper and textile coating: The importance of surface chemistry," *ChemPlusChem* 87(8), article e202200204. DOI: 10.1002/cplu.202200204
Stepan, A. M. (2013). *Bioplastics from Biomass—Acetylation of Xylans with Green Chemistry*, Ph.D. Thesis, Chalmers University of Technology, Gothenburg, Sweden, 2013.
Tang, R. H., Li, M., Liu, L. N., Zhang, S. F., Alam, N., You, M., Ni, Y. H., and Li, Z. D. (2020). "Chitosan- modified nitrocellulose membrane for paper-based point-of-care testing," *Cellulose* 27 (7) 3835-3846.
Tanpichai, S., Witayakran, S., Wootthikanokkhan, J., Srimarut, Y., Woraprayote, W., and

Malila, Y. (2020). “Mechanical and antibacterial properties of the chitosan coated cellulose paper for packaging applications: effects of molecular weight types and concentrations of chitosan,” *Int. J. Biol. Macromol.* 155, 1510-1519.

Tanpichai, S., Srimarut, Y., Woraprayote, W., and Malila, Y. (2022). “Chitosan coating for the preparation of multilayer coated paper for food-contact packaging: Wettability, mechanical properties, and overall migration,” *International Journal of Biological Macromolecules* 213, 534-545

TAPPI T 441 om-09 (2009). “Water absorptiveness of sized (non-bibulous) paper, paperboard, and corrugated fiberboard (Unger Cobb test),” TAPPI Press, Atlanta, GA, USA.

TAPPI T-458 cm-04 (2004). “Surface wettability of paper (angle of contact method),” TAPPI Press, Atlanta, GA, USA.

TAPPI T-559 cm-12 (2012). “Grease resistance test for paper and paperboard. KIT test,” TAPPI Press, Atlanta, GA, USA.

Wang, S., and Jing, Y. (2017). “Study on the barrier properties of glycerol to chitosan coating layer,” *Mater. Lett.* 209, 345-348. DOI: 10.1016/j.matlet.2017.08.040

Wang, W., Gu, F., Deng, Z., Zhu, Y., Zhu, J., Guo, T.; Song, J., and Xiao, H. (2021). “Multilayer surface construction for enhancing barrier properties of cellulose-based packaging,” *Carbohydr. Polym.* 255, article 117431. DOI: 10.1016/j.carbpol.2020.117431

Zhang, W., Xiao, H., and Qian, L. (2014). “Enhanced water vapour barrier and grease resistance of paper bilayer-coated with chitosan and beeswax,” *Carbohydr. Polym.* 101, 401-406. DOI: 10.1016/j.carbpol.2013.09.097

Zhao, Y., Sun, H., Yang, B., and Weng, Y. (2020). “Hemicellulose-based film: Potential green films for food packaging,” *Polymers* 12, 1775. DOI: 10.3390/polym12081775

Article submitted: July 3, 2024; Peer review completed: July 18, 2024; Revisions accepted: July 29, 2024; Published: August 1, 2024.
DOI: 10.15376/biores.19.4.6994-7018