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Barrier and Antimicrobial Properties of Coatings Based on Xylan Derivatives and Chitosan for Food Packaging Papers

Mirela Roman (Iana-Roman) [1], Petronela Nechita [2,*], Mihaela-Aida Vasile [3] and Alina-Mihaela Cantaragiu Ceoromila [4]

[1] Doctoral School of Fundamental and Engineering Sciences, Dunărea de Jos University of Galați, 817112 Brăila, Romania; mirela.roman@ugal.ro
[2] Department of Environmental, Applied Engineering and Agriculture, Faculty of Engineering and Agronomy, Dunărea de Jos University of Galați, 817112 Brăila, Romania
[3] Department of Food Science, Food Engineering, Biotechnologies and Aquaculture, Faculty of Food Science and Engineering, Dunărea de Jos University of Galați, 800201 Galați, Romania; aida.vasile@ugal.ro
[4] Cross-Border Faculty, Dunarea de Jos University of Galati, 800201 Galați, Romania; alina.cantaragiu@ugal.ro
* Correspondence: petronela.nechita@ugal.ro; Tel.: +40-744-704928

Abstract: This paper analyzes the potential of coatings based on xylan derivatives and chitosan to provide barrier properties and antimicrobial protection for paper food packaging and also to substitute the synthetic materials currently used in the food packaging industry. Colloidal dispersions of xylan derivatives (hydrophobized xylan with alkyl ketene dimers—XyAKD—and acetylated xylan—XyAc) and a chitosan biopolymer (Ch) were applied as coatings in single and two successive layers on a paper substrate using a laboratory automatic film applicator. The assessment of the water and fatty compound barrier properties of coated paper samples showed differences in effectiveness among xylan derivatives and their combination with chitosan. Generally, xylan derivative coatings improved the barrier and antimicrobial features of coated papers compared with native xylan. However, important improvements were obtained by adding to the coating formula a chitosan biopolymer. Thus, the best barrier properties for water, water vapors, oils and greases were obtained for paper coated with the acetylated xylan and chitosan formula in a single layer, where values of 30 g/m^2.day for the water vapor transmission rate (WVTR), a 92.8° contact angle (CA) and a KIT rating of 8 were achieved. All coated paper samples exhibited the total inhibition of *Bacillus* sp. both after 24 and 48 h. Based on the obtained results in this study, one can conclude that the area of application of xylan hemicelluloses could be extended. Their utilization in appropriate chemical structures and combinations as coatings for paper can be a sustainable alternative for the food packaging industry.

Keywords: hemicellulose; xylan derivatives; chitosan; coatings; paper; food packaging; barrier properties; antimicrobial properties

Citation: Roman, M.; Nechita, P.; Vasile, M.-A.; Cantaragiu Ceoromila, A.-M. Barrier and Antimicrobial Properties of Coatings Based on Xylan Derivatives and Chitosan for Food Packaging Papers. *Coatings* **2023**, *13*, 1761. https://doi.org/10.3390/coatings13101761

Academic Editor: Fátima Poças

Received: 6 September 2023
Revised: 29 September 2023
Accepted: 3 October 2023
Published: 12 October 2023

1. Introduction

Food packaging materials are an important part of the packaging industry. Nowadays, due to environmental issues, and considering that food industry waste is an important source of pollution, the production of biodegradable food packaging is of great interest. In this context, existing food packaging solutions need to be redesigned in a more sustainable way [1,2]. Generally, packaging materials are designed to protect products from external environmental factors during storage and transport. To meet the environmental needs, paper and board materials are promising candidates for food packaging, based on their high biodegradability, flexibility and good mechanical properties compared with plastic packaging. However, due to their porous structure and the hydrophilic nature of cellulose fibers, when they are used as food packaging, paper and boards encounter several critical aspects regarding their barrier properties (i.e., gas permeability, water and water vapors). The current solutions to address these barrier properties are based on coating with synthetic

polymers [3] or lamination with plastic [4], glass [5] and metal foils. These solutions use non-renewable and non-biodegradable materials, which carry major environmental risks and increased recycling costs. There is a need for researchers and packaging producers to develop new bio-based alternative materials to replace the existing petroleum-based ones in the packaging industry [6,7].

In recent decades, biopolymers originating from renewable resources have gained the attention of researchers in the packaging industry due to their numerous advantages and large potential to develop environmentally friendly products [8,9]. There are many studies that report the excellent barrier properties (moisture, gas, thermal and grease) of biopolymers when they are applied in packaging under optimal manufacturing conditions and concentrations. However, to meet the requirements of environmentally friendly food packaging, improving their physical and chemical properties, such as hydrophobicity, flexibility and mechanical properties, plays an important role in the food packaging field to extend the industrial-scale application of these materials [10].

Nowadays, the most studied biopolymers for food contact packaging are starch-based materials used alone or in combination with synthetic biodegradable biopolymers and polylactic acid (PLA). For food contact packaging, PLA is the most studied biopolymer, but, due to hydrolysis and chain scission, it degrades during processing [11].

Among the biopolymers used in food packaging, polysaccharides originating from plants, marine biomass, bacteria or fungi such as starch, cellulose, hemicelluloses, chitosan, alginates, etc., have the potential to be used as coatings for paper/boards, edible coatings and films. In addition, they are considered an adequate matrix to embed bioactive compounds to obtain bioactive and sensor materials in active and intelligent packaging [12].

Hemicelluloses are heterogeneous polysaccharides, the second class after cellulose, which exist in almost all plant cell walls. Although it is known that hemicelluloses exhibit good barrier properties towards aromas or oxygen and have a film-forming ability, these types of polysaccharides are still limited in their industrial applications. There are a large number of publications that refer to hemicellulose films or coatings for foods, but very few of them are concerned with coatings for paper- and cardboard-based substrates or for industrial application.

Xylan is the most abundant hemicellulose, found mainly in hardwood and annual plants. In packaging, xylans have been used as additives to improve the strength and biodegradability of plastic packaging, but they are insufficiently explored as coatings for packaging papers. Due to their low molecular weight, high glass transition temperature and poor film-forming capacity, xylans have not been successful in packaging applications, resulting in brittle films with low mechanical strength and sensitivity to moisture [13,14].

As with many other polysaccharides, due to the high number of free hydroxyl groups in their chemical structure, xylan hemicelluloses are sensitive to humidity and display low barrier resistance in moist conditions. However, this is beneficial for chemical functionalization using a variety of chemical reactions when hydrophobic groups are attached to hemicellulose chains. In this way, xylan derivatives with improved barrier properties are obtained. Esterification (i.e., acetylation) and etherification (i.e., carboxymethylation or alkoxylation) are some reported reactions for the chemical modification of xylan hemicelluloses [15]. Other proposed solutions to improve the functional properties of xylan hemicelluloses use plasticizers, long-chain anhydride modification [16] or a combination of them with other biopolymers [17–19].

Chitosan is a unique natural cationic polysaccharide that is biodegradable, biocompatible, non-toxic and obtained through the deacetylation of natural chitin. Based on its film-forming ability and antimicrobial properties, chitosan has strong potential for use in food packaging. For example, chitosan was investigated as an antimicrobial active polymer for edible/biodegradable coatings on fruit/vegetables [20,21].

Numerous research studies have reported the utilization of chitosan and its derivatives in paper coating to impart active antimicrobial characteristics and create barriers against oxygen, water vapors, oils and grease [19,22,23]. In these applications, chitosan can be

employed as an aqueous solution or emulsion, using various coating methods or press sizes to be applied to the paper's surface.

The combination of anionic xylan with cationic chitosan offers an interesting, fully bio-based alternative. Under controlled pH conditions, a strong ionic interaction between oppositely charged polyelectrolytes can be expected, which could provide additional advantages in terms of the film's properties [14,24].

Films prepared by combining xylan and chitosan in different proportions have demonstrated enhanced mechanical strength and improved water and oxygen barrier properties compared with those composed solely of chitosan. Additionally, enhanced antimicrobial activity was reported when these films were tested against *E. coli* and *S. aureus* bacteria [14,19].

The objective of this research study was to evaluate the barrier and antimicrobial performance of colloidal dispersions based on xylan derivatives (hydrophobized xylan with alkyl ketene dimers—XyAKD—and acetylated xylan—XyAc) and a chitosan biopolymer (Ch) when used as coatings for food packaging papers. The xylan derivatives were synthetized in the laboratory, and colloidal dispersions with two mass ratios (50/50 and 75/25) of xylan derivatives to chitosan were prepared. These dispersions were used as coatings, applied in single and double layers on packaging paper. To evaluate their performance in food packaging, the coated paper samples were analyzed for their barrier properties towards water, water vapors, oil and grease, as well as for air permeability and antibacterial/antifungal properties.

2. Materials and Methods

2.1. Materials

Xylan hemicellulose (Xy), obtained from beech wood, was purchased from Carl Roth (Karlsruhe, Germany), as a light beige to brown powder with a molecular mass of (132)n and a loss on drying of ≤10.0%.

Chitosan (448877), in the form of a white to beige powder, was purchased from Sigma-Aldrich (Taufkirchen, Germany). For improved film-forming properties, a medium-molecular-weight chitosan with a molecular weight of 234,000 Da and an 88% deacetylation degree was used for the experiments.

Alkyl ketene dimer (AKD), as commercial product AquapelTM 210D, was purchased from Solenis Technologies (Sobernheim, Germany). It was a milky white liquid, odorless, with total solids of 16.2% and viscosity of 4 cPs/t = 25 °C.

The other reagents, such as acetic anhydride, acetic acid and ethylic alcohol, were of analytic purity and were purchased from Sigma-Aldrich (Taufkirchen, Germany).

Commercial packaging paper made from unbleached pulp, with a weight of 50 g/m^2, was sourced from Ceprohart SA (Brăila, Romania), and was used as the base paper for coating.

2.2. Methods

- Obtaining xylan derivatives

Hydrophobized xylan (XyAKD) was obtained by the reaction of native xylan (Xy) with long-chain anhydrides such as alkyl ketene dimers (AKD), resulting in the formation of β-keto ester compounds with hydroxyl groups of xylan (Figure 1). For the dispersion, 25 g/L of xylan was mixed with a 2.5% solution of AKD and the mixture was magnetically stirred at 1500 rpm at 20 °C for 24 h [25]. The resulting dispersion was used for paper coating.

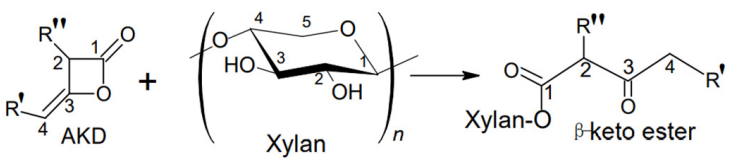

Figure 1. Reaction of xylan hemicellulose with AKD. Note that **R′** and **R″** are typically in the range of C4–C16 ($C_{14}H_{29}$).

Acetylated xylan (XyAc) with a degree of substitution of approximately 0.48 was obtained through the esterification of native xylan with acetic anhydride at 50 °C for 1 h, using an 8:1 molar ratio of acetic anhydride to functional hydroxyl groups in the structural unit of xylan (Figure 2). The acetylated xylan was precipitated using ethanol and dried for 24 h at 40 °C.

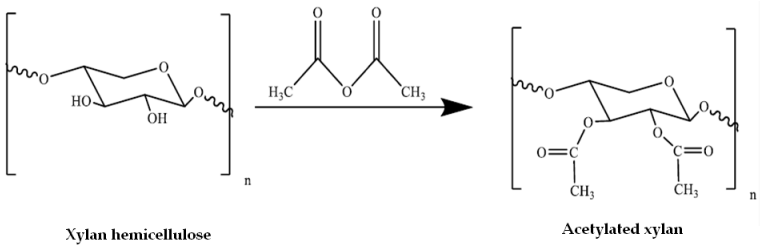

Figure 2. Reaction of xylan with acetic anhydride.

- Preparation of xylan/xylan derivatives/chitosan 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. The dispersions of xylan and acetylated xylan (2.5% in distilled water) were obtained under magnetic stirring at 1500 rpm for 24 h.

The colloidal dispersions of (Xy/XyAKD/XyAc) and chitosan (Ch) were prepared by the dropwise addition of the xylan/xylan derivative solution to the chitosan solution at a rate of approximately 60 mL/h, while under magnetic stirring. After the complete addition of chitosan, the colloidal dispersions were stirred magnetically for 24 h [14,24].

To ensure adequate electrostatic interaction between xylan and chitosan, the pH of the dispersions was adjusted to 4.5–5.0 before mixing, as both biopolymers are partially ionized under these conditions. Colloidal dispersions with two (Xy/XyAKD/XyAc)/Ch mass ratios (50:50 and 75:25) were prepared and used as coatings for paper.

- Coating of papers

(Xy/XyAKD/XyAc)/Ch colloidal dispersions were applied on the paper surface in two series: homogenous coatings, in a single layer, and as composite coatings in two successive layers. The total weight of the coating layers on both sides of the paper was approximately 5 g/m^2. For the coating process, an automatic film applicator of the TQC SHEEN type (TQC B.V.Molenbaam, The Netherlands) was used. In this system, the aqueous coating dispersion is applied in front of the wire rod, and, by the automatic rotation of the rod over the 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 (Figure 3).

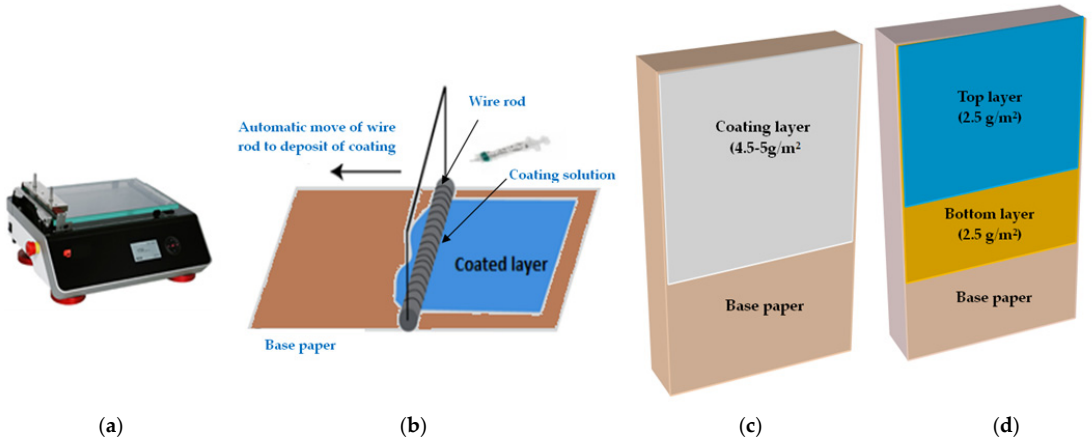

Figure 3. Representation of laboratory coating papers: (**a**) automatic coating applicator; (**b**) details of the coating deposition on the paper surface; (**c**) homogeneous coating in single layer; (**d**) composite coatings in two successive layers.

A total of 20 samples, each measuring 20 cm × 25 cm, were obtained for each series of coated papers, and they were tested regarding their functional properties. Uncoated paper (base paper) and coated paper with xylan and chitosan only were used as references (Table 1).

Table 1. Codification and composition of xylan/chitosan coatings.

Sample Codification	Xylan, %	AKD Hydrophobized Xylan, %	Acetylated Xylan, %	Chitosan, %
P0 (base paper)	-	-	-	-
Homogenous coatings—single layer—5 g/m^2				
P1	100	-	-	-
P2	-	100	-	-
P3	-	-	100	-
P4	75	-	-	25
P5	-	75	-	25
P6	-	-	75	25
P7	50	-	-	50
P8	-	50	-	50
P9	-	-	50	50
P10	-	-	-	100
Composite coatings—2 layers—5 g/m^2				
P11	100 (bottom layer)	-	-	100 (top layer)
P12	-	100 (bottom layer)	-	100 (top layer)
P13	-	-	100 (bottom layer)	100 (top layer)

- Structural analysis of xylan derivatives by FT-IR

The structural characteristics, highlighting the presence of specific chemical groups in the modified xylan samples, were analyzed using a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with an attenuated total reflection (ATR) accessory and a diamond crystal plate, in transmission mode. The spectrometer was placed in a temperature-controlled laboratory (21 ± 2 °C). Infrared spectra were measured in the spectral range 4000–400 cm^{-1} at 2 cm^{-1} spectral resolution and with 32 background/sample scans using the OMNIC software (Thermo Fisher Scientific Inc., Waltham, MA, USA). The background spectrum was collected by taking air as a reference before each measurement, and the diamond crystal plate was cleaned with alcohol.

- Surface morphology by SEM

The microstructure of the coated paper surfaces was investigated using the scanning electron microscopy technique with the Quanta 200 system (FEI). SEM images (100 µm and 10 µm scale bars) were captured at 20 kV as an accelerating voltage using the secondary electron signal in low-vacuum conditions. All paper samples were fixed to carbon doubled-sided tape by attachment onto metal support stubs. Subsequently, they were coated with a thin metallic layer for better conductivity, using sputtering equipment (SPI Supplies, West Chester, NY, USA). The surface structure of the tested materials was evaluated at 1000× magnification. A representative number of pictures were taken and analyzed.

- Barrier properties

Air permeability [s] was analyzed according to standard ISO 5636-5 (2013). A determined air volume was passed through the paper sample with a given area and the time for air passage was recorded [26].

The water vapor transmission rate (WVTR) [g/m^2.day] was determined as described in the standard method ISO 2528 (2018). Dishes containing $CaCl_2$ as a desiccant and sealed with the paper samples to be tested were placed in a controlled atmosphere (23 °C and 50% RH) for 4 days. Every 24 h, the dishes were weighed and the WVTR was determined by measuring the weight increase [27].

The static water contact angle [○] was measured following standard T-458 cm-04 (2004) by the static sessile drop method. An Ossila Contact Angle Goniometer equipped with a digital camera for image recording and the OCA v.4.13.0 software for results processing were utilized. Paper samples were fixed with clamps on the test table of the goniometer and water droplets of 5 µL were deposited on the surface using a micro syringe. The contact angle value was recorded after 5 s of water–paper substrate contact [28].

The water absorption capacity, expressed as the Cobb60 index in [g/m^2], was evaluated according to the standard method described in SR ISO 535 (2014). In this method, a specific quantity of water was brought into contact with the paper sample for 60 s, and the weight differences were then compared [29].

The oil absorption capacity (Unger–Cobb600 index) [g/m^2] was measured following the standard method Tappi T 441 om-09 (2009). In this method, the paper sample came into contact with a given amount of rapeseed oil for 600 s and the weight differences were then compared [30].

The grease resistance, evaluated in terms of the KIT rating, followed the methodology outlined in standard T-559 cm-12 (2012). KIT solutions (KIT no. 1-12) were prepared as mixtures with varying content of castor oil, n-heptane and toluene. Each paper sample was placed on a clean and flat surface with the test side facing up and a drop of a specific kit solution was released onto the surface. After 15 s, the excess solution was removed and the presence or absence of a stain on the back of the paper sample was verified. The solution with the highest KIT number that remained on the surface of the sample without causing stains on the back was adopted as the fat repellence value [31].

- Antimicrobial properties

The antimicrobial properties of coated papers were tested against Gram-positive bacteria, *Bacillus* sp., and two strains of fungi, *Aspergillus niger* and *Penicillium* sp., from the MIUG Collection of the BioAliment Research Platform—Dunărea de Jos University of Galaţi [32].

The antibacterial activity of the coated papers was assessed using a modified and adapted method derived from the SR EN ISO 846/2000 standard [33]. Following this method, the paper samples coated with xylan derivatives and chitosan, previously sterilized by UV for 15 min, were positioned on the surface of the culture medium (Plate Count Agar, Merck Millipore, Darmstadt, Germany). The inoculation of coated paper samples was performed by spraying them with a 1 µL bacterial suspension (18 h aged). The samples were then incubated in a thermostat, at 37 °C, and analyzed after 24 and 48 h. The antibacterial effect was evaluated as the inhibition percentage of the coated surface, which was correlated with the degree of bacterial culture development on/around the paper samples.

To evaluate the antifungal activity of the coated paper samples, fungal suspensions of approximately 10^7 ufc/mL were cultivated on the culture medium (Rose Bengal, Merck, Darmstadt, Germany). Two methods were applied: Method A involved pulverizing paper samples with a conidia suspension and placing them on the culture medium, while Method B included flooding the nutrient medium surface with a conidia suspension and placing the paper samples on the medium surface. For both methods, the samples were incubated in a thermostat at 25 °C and 85% RH for 21 days. The degree of fungal growth was evaluated after 3, 7, 14 and 21 days as the percentage of the paper surface covered with fungi.

3. Results and Discussion

3.1. Structural Analyses by FT-IR

Xylan derivatives were obtained through esterification using alkyl ketene dimer and acetic anhydride and the resulting samples were characterized using FT-IR. The typical IR spectra are presented in Figure 4 compared with the IR spectrum of native xylan. It is observed that important modifications appear in the range between 800 and 1790 cm^{-1} and between 2800 and 3500 cm^{-1}. The absorption peaks between 3300 and 3400 cm^{-1} can be attributed to the stretching vibrations of the OH groups from xylan hemicellulose, while the peak at 2890 cm^{-1} corresponds to the C-H vibrations of CH_2CH_3 groups. Peaks

at 820 and 1790 cm^{-1} arise from β-glucosidic bonds between sugar units (896 cm^{-1}) and the band between 1000 and 1200 cm^{-1} belongs to C=O stretching. In the case of acetylated xylan, shown in Figure 4b, the acetylation process is evident from the presence of –C=O ester bands at 1750 cm^{-1}, –C–CH_3 at 1375 cm^{-1} and a –C–O– stretching band at 1244 cm^{-1}. The absence of peaks at 1840–1760 cm^{-1} suggests that there is no unreacted acetic anhydride [34].

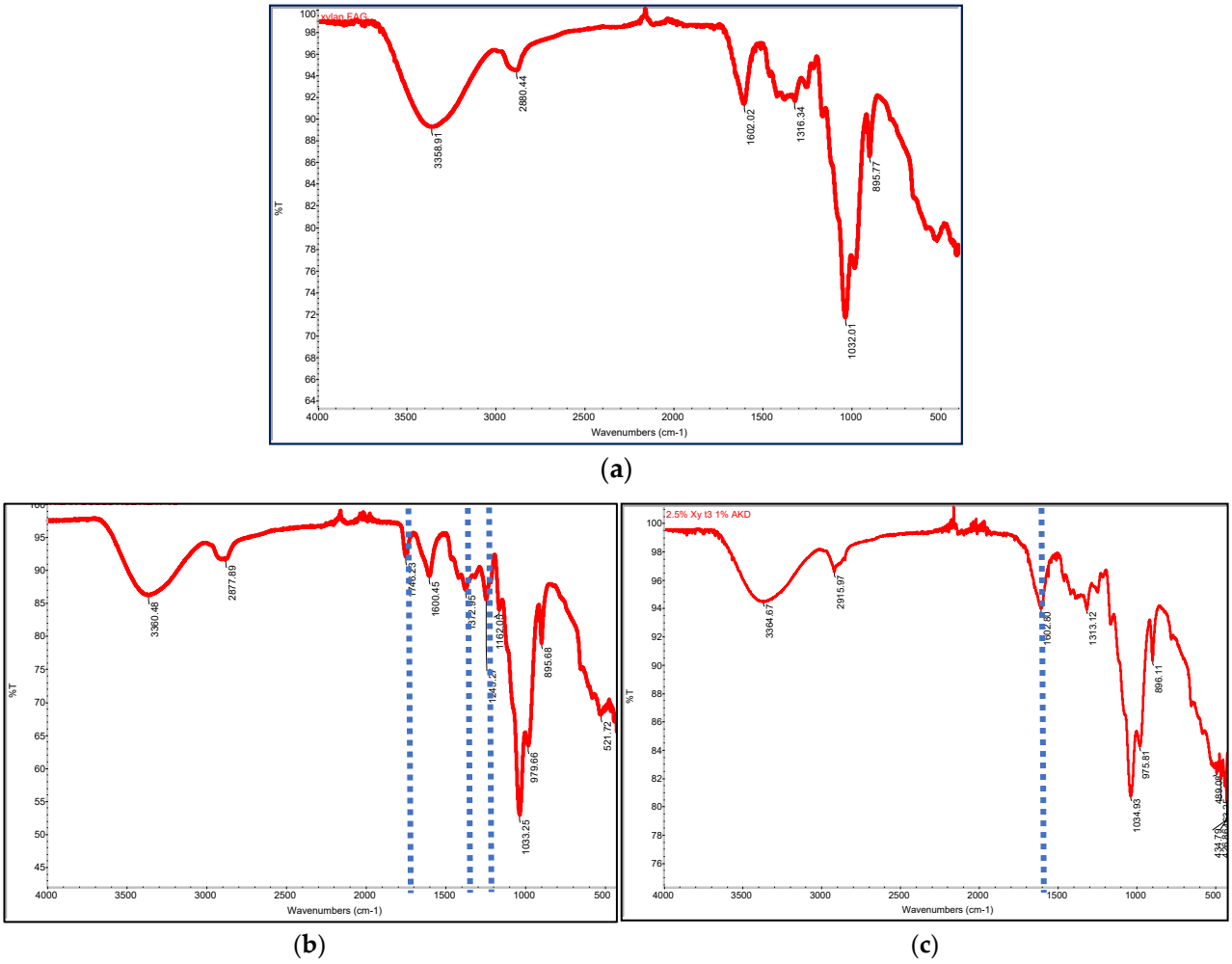

Figure 4. FT-IR spectra of (**a**) hardwood xylan; (**b**) acetylated xylan; (**c**) AKD hydrophobized xylan.

The vibration stretching characteristic of the absorption peaks of β-ketone esters and bonds formed between xylan hemicellulose and AKD appear in the range of 1600–1700 cm^{-1} (Figure 4c).

3.2. Surface Morphology of Coated Papers

The surface topography of the uncoated and coated samples was assessed based on the SEM images presented in Figure 5.

It is observed that the uncoated paper samples exhibit a porous structure with a large number of cavities between cellulose fibers. With the incorporation of coatings based on xylan/xylan derivatives and chitosan, the pores between the cellulose fibers decrease, resulting in a smooth, homogeneous and dense surface. The good film-forming capacity of the chitosan biopolymer is observed for both types of coated samples, whether in single or double layers. The paper samples coated with chitosan (P10) and xylan derivatives and chitosan (P7, P8, P9) in a single layer have a completely covered surface without visible voids or pores, in contrast to paper samples coated with xylan and its derivatives. In this

case, due to the poor film-forming ability of xylan, non-uniform surfaces of the coated papers with visible cracks are observed (P1, P2, P3).

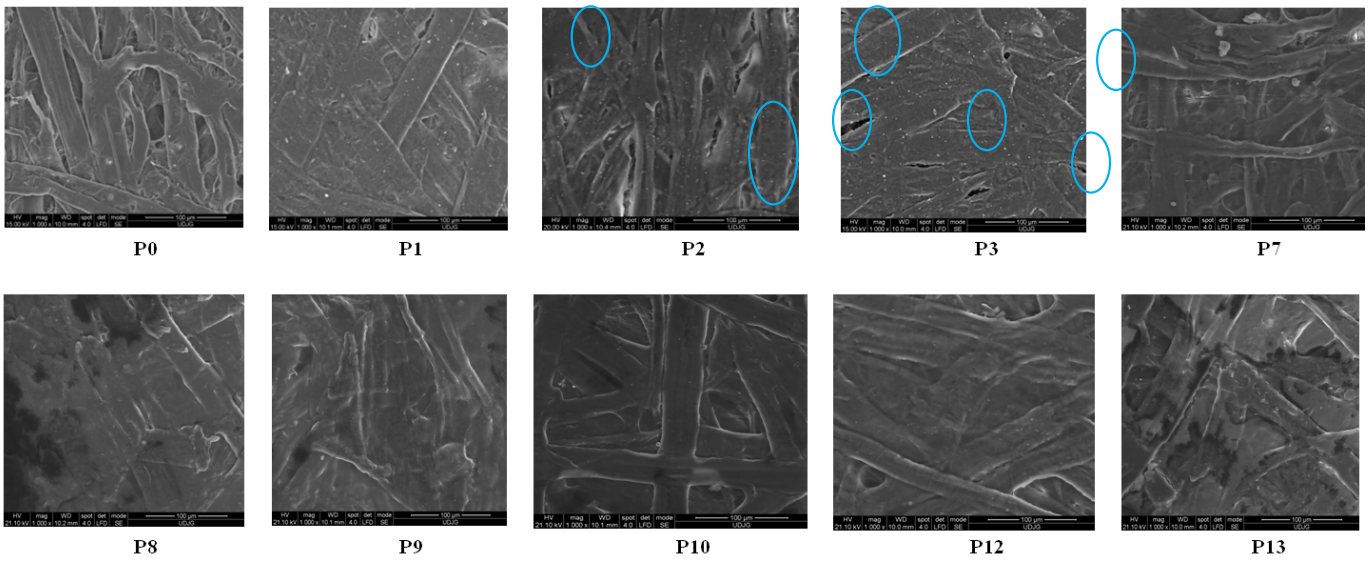

Figure 5. SEM images of paper samples coated in single and two successive layers based on xylan derivatives and chitosan. P0: base paper. Homogeneous coatings in single layer—P1: 100Xy; P2: 100XyAKD; P3: 100XyAc; P7: 50Xy50Ch; P8: 50XyAKD50Ch; P9: 50XyAc50Ch; P10: 100Ch. Composite coatings in two layers—P12: 100XyAKD + 100Ch; P13: 100XyAc + 100Ch. The blue circles highlight the non-uniformities and cracks in the coating layer structure.

For the paper samples coated with two successive layers (P12, P13) where the top layer is composed of chitosan, distinct surface topographies are achieved. In the case of paper samples coated with hydrophobized xylan in the bottom layer (P12), a smooth surface is obtained compared with the paper samples coated with acetylated xylan (P13). The latter, owing to its more hydrophilic properties, is absorbed readily by the cellulose fiber substrate, resulting in a less uniform surface. In comparison, the AKD hydrophobized xylan dispersion effectively fills the pores of the base paper, leading to a more uniform coated surface. These differences in the first layer of coated samples are evident in how the chitosan dispersion interacts differently in the top layer, as illustrated by the SEM images.

3.3. Barrier Properties

3.3.1. Air Permeability

As above mentioned, the air permeability is a physical characteristic that measures the time at which a certain volume of air passes through a paper substrate. Figure 6 presents the air permeability of coated paper samples in single and two successive layers.

When compared to uncoated and xylan derivative-coated papers, the paper samples coated with xylan derivatives and chitosan, both in single (P4–P9) and two successive layers (P11–P13), exhibited very low air permeability. This suggests a denser structure without pinholes and voids. The paper samples coated with hydrophobized xylan and chitosan coatings (P8) had the lowest air permeability as a result of the more hydrophobic nature of xylan and the good film-forming capacity of the chitosan biopolymer.

3.3.2. Water Vapor Transmission Rate (WVTR)

For food packaging materials, the water vapor transmission rate is another important barrier property. Through the transmission of water vapors into a package, the freshness of the packed food could be affected and also the growth of microorganisms is increased. The results of gravimetric measurements of the WVTR are presented in Figure 7.

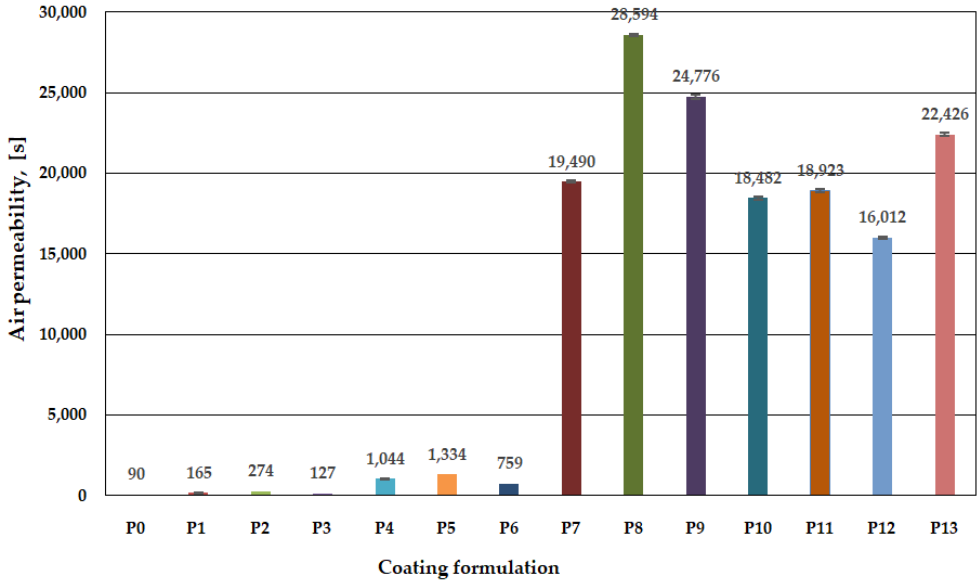

Figure 6. The air permeability of coated paper samples. P0: base paper. Homogeneous coatings in single layer—P1: 100Xy; P2: 100XyAKD; P3: 100XyAc; P4: 75Xy25Ch; P5: 75XyAKD25Ch; P6: 75XyAc25Ch; P7: 50Xy50Ch; P8: 50XyAKD50Ch; P9: 50XyAc50Ch; P10: 100Ch. Composite coatings in two layers—P11: 100Xy + 100Ch; P12: 100XyAKD + 100Ch; P13: 100XyAc + 100Ch.

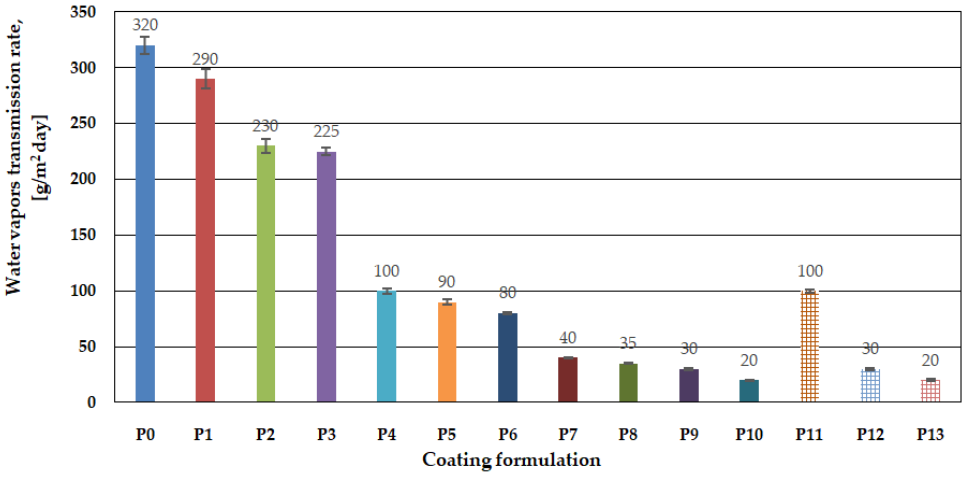

Figure 7. Water vapor transmission rates of coated paper samples. P0: base paper. Homogeneous coatings in single layer—P1: 100Xy; P2: 100XyAKD; P3: 100XyAc; P4: 75Xy25Ch; P5: 75XyAKD25Ch; P6: 75XyAc25Ch; P7: 50Xy50Ch; P8: 50XyAKD50Ch; P9: 50XyAc50Ch; P10: 100Ch. Composite coatings in two layers—P11: 100Xy + 100Ch; P12: 100XyAKD + 100Ch; P13: 100XyAc + 100Ch.

Overall, the coated paper samples demonstrated an improved WVTR when compared to uncoated paper. The improvements were influenced by the type of biopolymer used in the coating formula. A significant reduction in the permeation of water vapors in the paper substrate was achieved for samples coated with chitosan, whether in single or double layers. For single-layer coatings, the WVTR was approximately seven times lower for paper samples coated with composite coatings based on chitosan and xylan derivatives, compared to samples coated with xylan derivatives alone. In the case of two successive layers of coating, a substantial reduction in the WVTR was observed for paper samples coated with coatings based on acetylated xylan as the bottom layer and chitosan as the top layer. Coating partially or fully covers the cellulose fibers, resulting in the densification of the paper sheet and a reduction in the interaction between fibers and water vapors. This leads to a reduction in the diffusion of water vapors. Consequently, both types of biopolymers,

xylan derivatives and chitosan, despite their hydrophilic properties, contributed to the decrease in water vapor permeability.

3.3.3. Wettability and Water Absorptiveness

The hydrophobic and hydrophilic properties of materials are evaluated using the water contact angle method. Based on this parameter, a material is considered hydrophobic when its contact angle is greater than 90° and hydrophilic at lower values. The water contact angle (CA) was used to evaluate the surface wettability, and Cobb index measurements for 60 s were performed to determine the water absorption of the tested samples of coated papers. The results are plotted in the graphs in Figures 8 and 9. For the uncoated paper (P0), most of the water was immediately absorbed by the cellulose fibers, resulting in a lower CA value, approximately 63.8°. By applying xylan derivatives and chitosan in single or two successive layers onto the paper surface, the contact angle was increased as the chitosan content in the coatings was higher. For the paper samples coated with the acetylated xylan and chitosan dispersion in a single layer (P9), contact angle values greater than 90° were achieved (Figure 8). These results are in good agreement with those reported in other studies [35–38] and confirm that the acetylation of xylan contributes to reducing its water affinity.

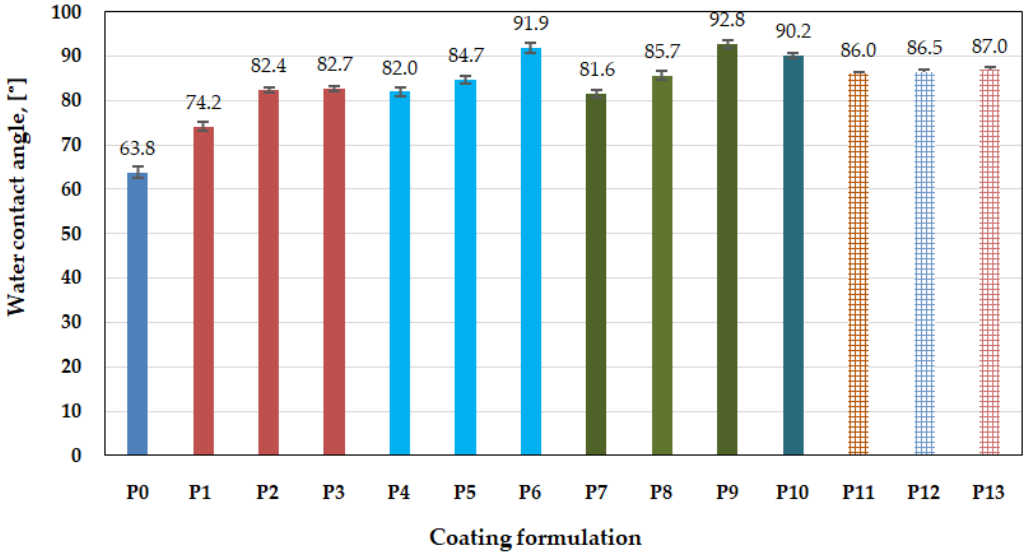

Figure 8. Contact angles of uncoated and coated samples measured with deionized water. P0: base paper. Homogeneous coatings in single layer—P1: 100Xy; P2: 100XyAKD; P3: 100XyAc; P4: 75Xy25Ch; P5: 75XyAKD25Ch; P6: 75XyAc25Ch; P7: 50Xy50Ch; P8: 50XyAKD50Ch; P9: 50XyAc50Ch; P10: 100Ch. Composite coatings in two layers—P11: 100Xy + 100Ch; P12: 100XyAKD + 100Ch; P13: 100XyAc + 100Ch.

The water absorption of coated paper samples with xylan derivatives and chitosan is in line with the CA measurements. When compared to uncoated paper, there was a decrease of approximately 15% in water absorptiveness for the paper samples coated with xylan and its derivatives. A larger reduction, approximately 25%, was achieved for the samples coated with xylan derivatives and chitosan in a single layer. When chitosan was applied in the top layer (P12 and P13 samples), the water absorptiveness registered the lowest value (Figure 9). This can be explained by the fact that the positively charged chitosan used for coating in the top layer interacted intensively with the xylan and xylan derivative substrates. The chitosan dispersion used for coating was water-soluble only in the presence of acetic acid, at a pH of approximately 4. At higher pH values, chitosan is less water-soluble and is considered hydrophobic in this case.

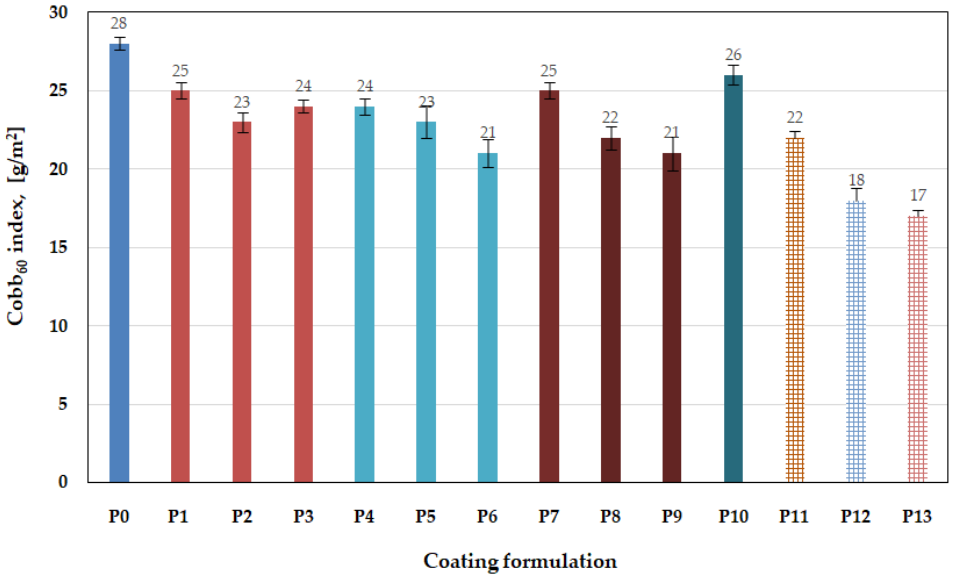

Figure 9. Water absorption of uncoated and coated samples measured for 60 s with deionized water. P0: base paper. Homogeneous coatings in single layer—P1: 100Xy; P2: 100XyAKD; P3: 100XyAc; P4: 75Xy25Ch; P5: 75XyAKD25Ch; P6: 75XyAc25Ch; P7: 50Xy50Ch; P8: 50XyAKD50Ch; P9: 50XyAc50Ch; P10: 100Ch. Composite coatings in two layers—P11: 100Xy + 100Ch; P12: 100XyAKD + 100Ch; P13: 100XyAc + 100Ch.

3.3.4. Grease and Oil Barrier

The barrier to oil and greases is a very important property of food packaging papers. Based on the results presented in Figure 10, it is noticeable that the high concentration of chitosan in the coating formula increased the KIT number and decreased the value of the Unger–Cobb index. This means an improvement in the permeability of the coated papers against oil and greases.

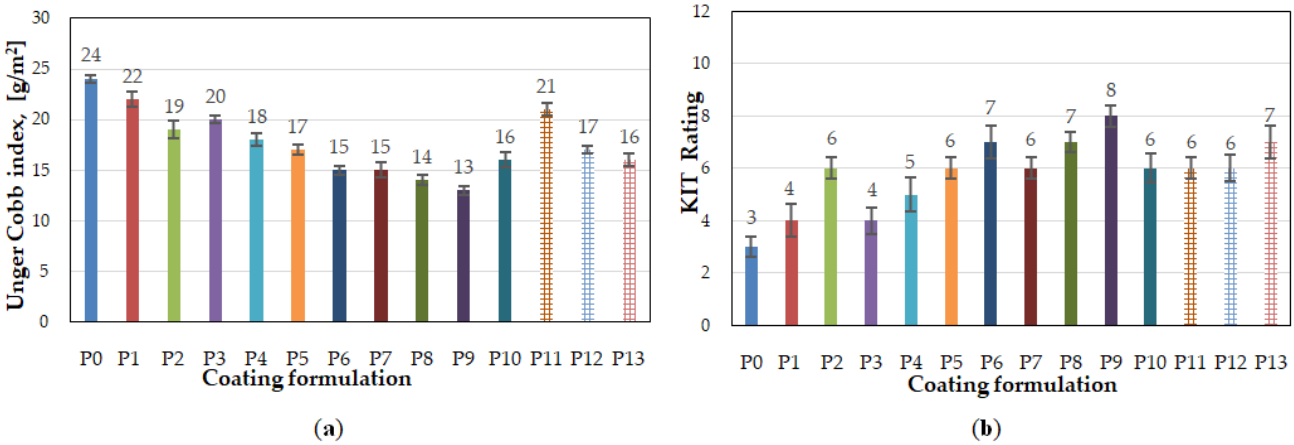

Figure 10. Oil and grease resistance of xylan/chitosan-coated papers. (**a**) Unger–Cobb index; (**b**) KIT rating. P0: base paper. Homogeneous coatings in single layer—P1: 100Xy; P2: 100XyAKD; P3: 100XyAc; P4: 75Xy25Ch; P5: 75XyAKD25Ch; P6: 75XyAc25Ch; P7: 50Xy50Ch; P8: 50XyAKD50Ch; P9: 50XyAc50Ch; P10: 100Ch. Composite coatings in two layers—P11: 100Xy + 100Ch; P12: 100XyAKD + 100Ch; P13: 100XyAc + 100Ch.

For the coated samples with a coating formula based on acetylated xylan and chitosan (50:50) in a single layer (P9), 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. In the case of layered coated papers, the best oil and grease

resistance was observed in the samples coated with acetylated xylan in the bottom layer and chitosan in the top layer (P13). The fat barrier property of chitosan is associated with the presence of cationic groups (NH^{3+}) in its structure, which interact electrostatically with the anionic groups of lipids. This contributes to the retaining of fat and prevents its penetration into the substrate [39]. The presence of two layers of coating contributes to the improvement of the fat barrier in coated samples. The acetylated xylan in the bottom layer fills the pores of the cellulosic matrix, and the chitosan applied on this surface forms a uniform film with better oil and grease resistance [40,41].

If it is considered that the KIT value for commercial greaseproof papers obtained with fluorochemicals typically falls within the range of 4–10 [42,43], the results obtained in this study are promising and indicate that the tested coated papers are suitable for food packaging. In addition, these coatings are based on renewable resources, biodegradable and highly recyclable.

3.4. Antimicrobial Properties

Bacillus sp. was used to evaluate the antibacterial activity of the xylan-/xylan derivative-/chitosan-coated papers. The selection of this type of bacterium was made considering the increased resistance of Gram-positive bacteria to the bactericidal action of chitosan, compared to Gram-negative ones [44]. In addition, for laboratory studies, *B. subtillis* has become widely adopted as a model organism, often considered as the Gram-positive equivalent of *E. coli*, an extensively studied Gram-negative bacterium.

Generally, the xylan derivative-coated papers showed a slight inhibitory effect, which meant that a reduced inhibition zone could be observed on the surface and its surroundings, as shown in Figure 11. The same result was also observed for uncoated paper samples. However, native xylan- and acetylated xylan-coated papers exhibited a better inhibitory effect. These results were in accordance with the WVTR values, which were lower for these coated samples, and with previously reported findings, which confirms that, in its native form, xylan hemicellulose exhibits slight antimicrobial effects against pathogenic bacteria [45,46].

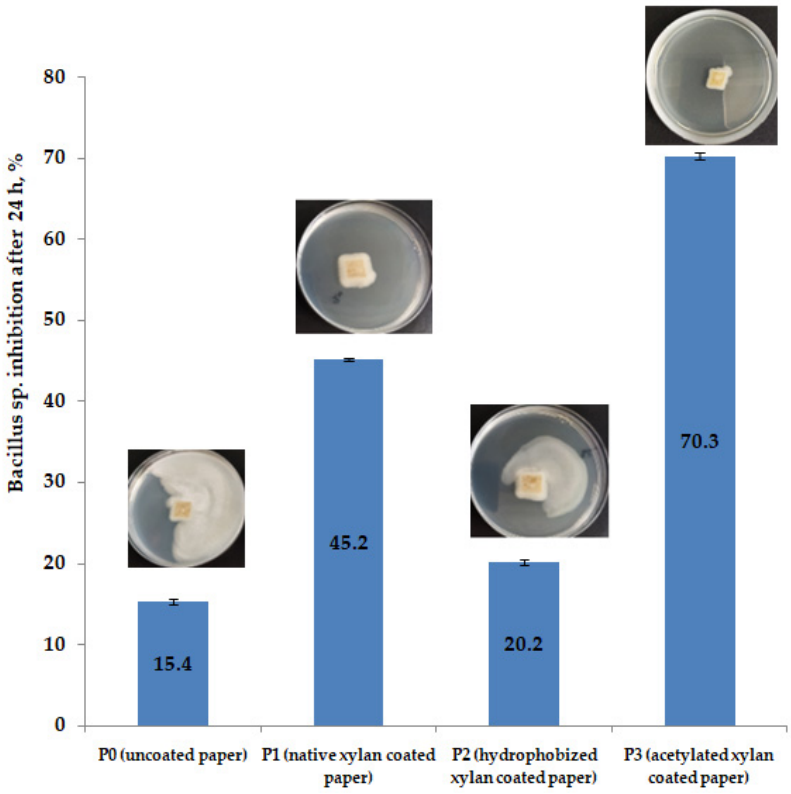

Figure 11. The antibacterial activity of xylan derivative-coated papers.

Xylan derivative-/chitosan-coated samples showed inhibition effects both as single- and double-layer coatings (Figure 12). The inhibition effect of chitosan coatings (P7, P8, P9, P10) results from the presence of amine groups in its chemical structure and its hydrophobic features, which create a dry environment that is not suitable for bacterial growth [47].

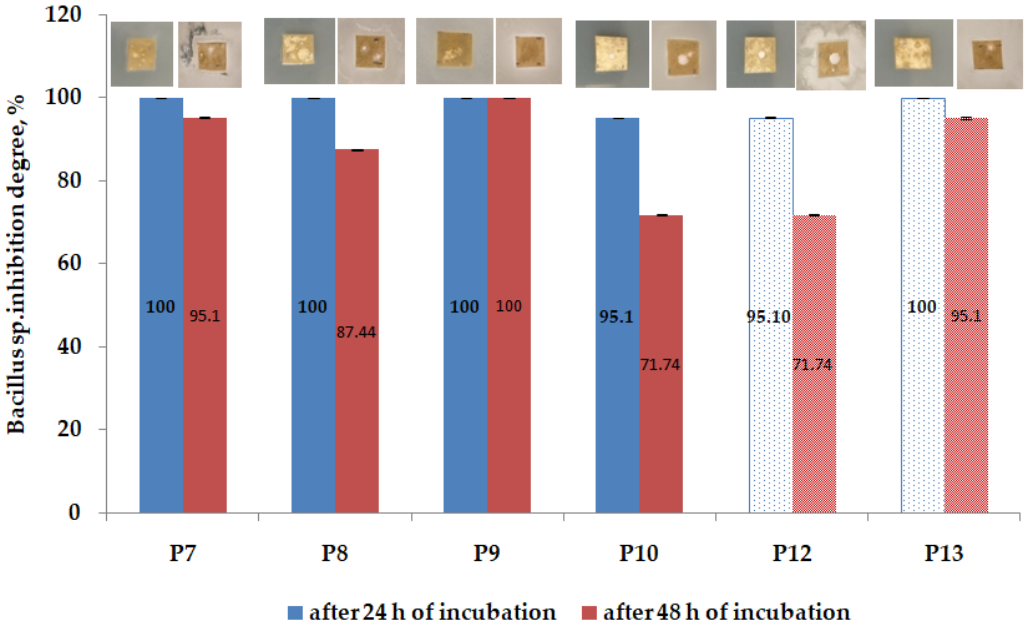

Figure 12. The antibacterial activity of xylan derivative-/chitosan-coated papers. Homogeneous coatings in single layer—P7: 50Xy50Ch; P8: 50XyAKD50Ch; P9: 50XyAc50Ch; P10: 100Ch. Composite coatings in two layers—P12: 100XyAKD + 100Ch; P13: 100XyAc + 100Ch.

In previous studies, it was reported that chitosan showed a stronger antibacterial effect against Gram-positive bacteria than Gram-negative bacteria. This effect depends on the molecular weight and degree of deacetylation of chitosan as well. Generally, lower-molecular-weight chitosan possesses stronger antibacterial activity against Gram-negative bacteria compared to Gram-positive bacteria. In this study, medium-molecular-weight chitosan was used, which exhibited the expected antibacterial effect against Gram-positive bacteria [48–50].

It was observed that the papers coated with the acetylated xylan and chitosan formula (P9) exhibited total inhibition both after 24 h and 48 h. In this case, the acetylated xylan contributed to the improvement of the antimicrobial effect due to the reduction in water affinity by acetylation, as mentioned in recent studies.

For all samples coated with chitosan, the inhibition effect remained after 48 h as well. The inhibition effect of coated paper samples with xylan derivatives and chitosan formulas was also correlated with the WVTR values presented in Figure 6, which were lower than those of samples coated with xylan and xylan derivatives only. A lower rate of water vapor penetration into the coated paper substrate prevented bacterial growth.

Antifungal tests were performed by the pulverization and flooding method, using two strains of fungi, *Aspergillus niger* and *Penicillium* sp. The results are presented in Tables 2 and 3.

The results show that the xylan and xylan derivative-coated samples have no inhibitory effects against the growth of fungal strains. Only a slight inhibition effect is observed for acetylated xylan-coated papers using the strain flooding method after 3 days of incubation. The introduction of chitosan in the coating formula, both in single and two layers, led to the inhibition of fungal growth, which depended on the inoculation method (spraying or flooding). It is noticed that treating the paper with xylan derivatives in the bottom layer and chitosan in the top layer (P12 and P13) results in a stronger inhibition effect for both *Aspergillus* and *Penicillium* sp. strains compared to samples coated with a homogenous

formula in a single layer. The high antifungal effectiveness of these samples could be partly due to the more hydrophobic character of the coating layer, which creates a dry environment that is unfavorable for fungal development. This is also confirmed by the low WVTR values for these types of coated papers.

Table 2. Degree of fungal inhibition (%) for strain of *Aspergillus niger*.

Paper Sample	Percentage of Fungal Growth Inhibition(%)/Assessment Method							
	Spraying				Flooding			
	3 Days	7 Days	14 Days	21 Days	3 Days	7 Days	14 Days	21 Days
P0	1.00	0	0	0	0	0	0	0
P1	2.00	0	0	0	0	0	0	0
P2	0	0	0	0	0	0	0	0
P3	2.5	1.2	0	0	0	0	0	0
P7	65.00	0	0	0	95.00	55.00	39.00	0
P8	25.00	0	0	0	95.00	63.00	63.00	0
P9	21.12	0	0	0	95.00	40.00	23.00	0
P10	100.00	10.00	0	0	100.00	95.10	95.10	0
P12	50.00	0	0	0	100.00	90.00	90.00	0
P13	90.10	0	0	0	100.00	90.00	90.00	0

Table 3. Degree of fungal inhibition (%) for strain of *Penicillium* sp.

Paper Sample	Percentage of Fungal Growth Inhibition(%)/Assessment Method							
	Spraying				Flooding			
	3 Days	7 Days	14 Days	21 Days	3 Days	7 Days	14 Days	21 Days
P0	1.00	0	0	0	0	0	0	0
P1	0	0	0	0	2.4	1.2	0	0
P2	0	0	0	0	1.5	0	0	0
P3	0	0	0	0	3.4	2.6	1.7	0
P7	95.00	42.00	31.15	31.15	35.00	1.00	1.00	1.00

Table 3. *Cont.*

Paper Sample	Percentage of Fungal Growth Inhibition(%)/Assessment Method							
	Spraying				Flooding			
	3 Days	7 Days	14 Days	21 Days	3 Days	7 Days	14 Days	21 Days
P8	51.00	0	0	0	40.00	0	0	0
P9	65.12	0	0	0	30.00	1.00	1.00	1.00
P10	100.00	91.50	0	0	100.00	35.00	35.00	35.00
P12	100.00	100.00	100.00	100.00	95.00	35.00	35.00	35.00
P13	99.99	1.00	0	0	95.00	30.00	30.00	30.00

4. Conclusions

Based on its specific structure and functionalities, xylan hemicellulose could be considered a viable alternative to conventional synthetic polymers used for the surface treatment of paper and boards, but the high affinity for water restricts its use at large scale and in native form. The chemical modification of xylan or its combination with other biopolymers provides the means to overcome its limitations related to water affinity. The xylan derivatives synthesized through esterification and their combination with a chitosan biopolymer, as proposed in this paper, demonstrated characteristics suitable for the coating of food packaging paper. Generally, the paper samples coated with the xylan derivatives and chitosan formula, in single and two successive layers, exhibited improved barrier properties against water, water vapor and fatty compounds compared to uncoated and xylan coated paper. As a result, the WVTR of these paper samples was seven times lower than that of samples coated with xylan derivatives only, and the contact angle recorded values exceeding 90°. Due to its chemical structure, which is based on cationic groups (NH_3^+) that interact electrostatically with the anionic groups of lipids, chitosan enhances the fat and oil resistance of coated papers, achieving a KIT rating of 8 for homogenous coatings. Xylan derivative-/chitosan-coated samples exhibited inhibition effects on bacterial growth both as single- and double-layer coatings compared to samples coated with xylan/xylan derivatives only. Therefore, the papers coated with the acetylated xylan and chitosan formula (P9) showed complete inhibition of *Bacillus* sp. both after 24 and 48 h. Generally, the antimicrobial properties of coated papers are correlated with their water barrier properties; samples with reduced water and water vapor permeability exhibit the inhibition of bacterial growth. Regarding antifungal resistance, the composite-coated papers with chitosan in the top layer exhibited slight resistance against fungal attack by *Aspergilius niger* and *Penicillium* sp. strains.

Summarizing all the results, the xylan derivatives and chitosan coatings studied in this paper exhibited appropriate barrier properties similar to those of coatings based on synthetic polymers and fluorochemicals. They could provide sustainable alternatives to conventional materials used in food packaging applications.

Author Contributions: Conceptualization, P.N.; methodology, M.R., P.N., M.-A.V. and A.-M.C.C.; validation, P.N., M.R. and M.-A.V.; investigation, M.R., M.-A.V. and A.-M.C.C.; resources, P.N.; writing—original draft preparation, M.R. and M.-A.V.; writing—review and editing, M.R., P.N. and M.-A.V. visualization, P.N.; supervision, P.N. All authors have read and agreed to the published version of the manuscript.

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

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are provided in the paper.

Acknowledgments: The authors thank the Research Centre for Environmental and Agriculture "Lunca" within the Engineering and Agronomy Faculty in Braila, "Dunarea de Jos" University of Galati, Romania.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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