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Alginate and Chitosan as a Functional Barrier for Paper-Based Packaging Materials

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Abstract: Paper-based food packaging materials are widely used, renewable, and biodegradable. Because of its porous structure, paper has poor or no barrier performance against grease, water vapor, water, and volatile organic compounds. Moreover, recycled paperboard can be a source of organic residuals that are able to migrate into packed food. Two different types of paperboard produced from primary and secondary cellulosic fibers were coated using renewable materials, such as alginate and chitosan, and comprehensive barrier measurements showed multifunctional barrier properties of these two biomaterials. Both paper substrates were successfully coated using a draw-down coater, and the measured air permeability of the coated samples was $0 \text{ mL} \cdot \text{min}^{-1}$. Grease resistance was improved, while it was possible to reduce water vapor transmission, the migration of mineral oil saturated hydrocarbons and mineral oil aromatic hydrocarbons (MOSH/MOAH), and the permeation of volatile compounds for both paper substrates when compared with uncoated substrates. Wettability and water absorptiveness of chitosan- and alginate-coated papers were found to be substrate-dependent properties, and could be significantly affected by bio-based coatings. In summary, industrially produced paperboard was upgraded by coating it with the naturally biodegradable biopolymers, alginate and chitosan, thus achieving extraordinary barrier performance for various applications within the packaging industry.

Keywords: barrier coating; paper-based food packaging material; chitosan; alginate; water vapor transmission rate; MOSH/MOAH migration; permeation; grease barrier; water absorptiveness; HPLC–GC coupled with a flame ionization detector (FID)

1. Introduction

Food packaging materials based on cellulosic fibers must keep their functionality under permanently changing conditions in the surrounding environment, such as temperature, storage time, or moisture, which are major influences on the shelf-life and quality of the packed food [1–3]. Paper-based packaging assures the strength and stability of the packaging, but due to its porous structure, paper lacks most of the important barrier functions needed nowadays. Furthermore, paperboard produced from so-called recycled or secondary cellulosic fibers can contain residues of mineral oils, better known as mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH), which represent a serious source of contaminants for packed food products. The sources of mineral oil residues in secondary fibers are ubiquitous, including mineral-oil-based printing inks in particular [4–8]. In order to control and prevent the permeation

or migration of water vapor, mineral oils, grease, or liquids, paper must be further upgraded by a suitable barrier coating, in order to ensure the required packaging function. Therefore, the surface of paper-based packaging materials is treated either by extrusion, using thermoplastic petroleum-based polymers, or by dispersion coating, using synthetic water-based polymer dispersions [9–11]. In recent years, significant research efforts in academia, as well as in industry, focused on the replacement of oil-based polymer materials in the surface treatment of paperboard. Driving forces for these developments are not necessarily only coming from the producers, but also from the consumers [2]. Bio-based materials applied on paper could provide interesting barrier functionalities while still maintaining the environmentally friendly characteristics of the packaging material. The challenge with paper-based packaging materials is that, for different products, different barrier properties are needed. Multiple layers of barrier materials are sometimes the solution chosen in practice [3,12,13].

Our investigation focused on sodium alginate and chitosan, and their application as barrier materials for paper intended to be used as primary or secondary food-packaging materials. Alginate is a polysaccharide naturally present in brown algae, and is usually available as salts of sodium and calcium. Alginates and its derivatives are already used in large amounts in the food industry as additives, and therefore, are also considered to be safe for their use as functional barriers for food-contact materials. Various water-soluble alginate formulations are available on the market, which can be applied with conventional coating equipment used in the paper and packaging industries [14–16]. Chitosan is an abundant, natural polysaccharide derived from chitin, a substance in the exoskeletons of crustaceans and insects. Economically interesting quantities are already produced from fishing industry waste, mainly during the processing of crabs and shrimps [17–21].

Our work investigated the coatability and barrier properties of these two water-soluble biopolymers, chitosan and alginate, from renewable resources. Both were applied under the same conditions onto two different paper grades, with the aim of evaluating their potential for reducing the migration and permeation of mineral oil components (MOSH/MOAH) [11], aromatic components, and water vapor. Furthermore, the coating layer's quality was analyzed via scanning electron microscopy, and its resistance toward grease, water absorption, and air permeability was determined. Similar studies with chitosan and alginate were reported in the literature for some of above-stated barrier functions [22–30]. The novel aspect of this work involves the systematic comparison and quantitative study of the barrier properties of alginate and chitosan, and their interaction with two different industrially produced paper substrates. In particular, the effect of these two bio-based barrier materials against the migration of mineral oil fractions (MOSH and MOAH) contained in paper, measured and quantified with HPLC–GC coupled with a flame ionization detector (FID), is yet to be reported.

2. Materials and Methods

2.1. Coating Materials

Powdered chitosan used in the preparation of the coating solution was kindly supplied by BioLog Heppe GmbH (Landsberg, Germany). This industrially produced chitosan with a degree of deacetylation 88%–95% was made from the carapace skin of crustaceans. According to the product specifications, the chitosan powder consisted of particles with a diameter ≤ 200 μm , and an ash content $< 1\%$ (w/w). The dynamic viscosity of a 1% (w/w) chitosan aqueous solution dissolved in 1% (w/w) acetic acid at pH 4 and 20 °C was 20 mPa·s. Acetic acid (100%, Rotipuran) used for adjustment of the pH of dissolved chitosan in water was purchased from Carl Roth GmbH+ Co. KG (Karlsruhe, Germany). Sodium alginate (viscosity 15–25 mPa·s 1% (w/w) in water at 25 °C) was purchased from Sigma-Aldrich (Saint Louis, MO, USA).

2.2. Preparation of Aqueous Coating Solutions

A chitosan coating solution with a solid content of 4% (*w/w*) was prepared by dissolving it in heated deionized water (70 °C), adding the chitosan powder in small amounts and stirring for 6 h at 400 rpm. Subsequently, acetic acid was added in small portions in order to achieve a pH of 4, measured constantly by a portable pH meter (inoLab pH 7110, WTW, Weilheim, Germany). This chitosan aqueous solution was stirred and heated for 4 h at 70 °C until a yellow solution was obtained and no visible particles were observed.

A sodium-alginate coating solution with a solid content of 4% (*w/w*) was prepared by dissolving sodium-alginate powder in deionized water at a neutral pH. The sodium-alginate powder was added to water in portions, stirred at 400 rpm, and the aqueous solution was heated for 6 h at 75 °C. After this time, sodium alginate was completely dissolved, resulting in a homogenous coating solution. Due to the heating and evaporation of water, the solid contents of both coating solutions slightly increased. Therefore, the solid content was remeasured using a moisture analyzer (HR73, Mettler Toledo, Columbus, OH, USA), and adjusted to 4% (*w/w*) with deionized water. Finally, the coating solutions with the adjusted and desired solid contents were cooled to room temperature. The viscosities (Brookfield II+, at 50 rpm, *n* = 3) of 4% (*w/w*) chitosan and 4% (*w/w*) alginate coating solutions, measured at room temperature, were 2911 mPa·s ± 57 and 1448 mPa·s ± 20, respectively.

2.3. Paper-Substrate Characterization

Two different commercial paper grades were used in the coating trials. The first was a paper (PF) made from 100% primary-fiber furnish (mixture of hardwood and softwood), mass-sized using 100% active liquid alkenyl succinic anhydride (ASA), and surface-sized using starch and a calender machine. The second substrate was a paperboard (SF) made from 100% secondary or recycled fibers with no surface treatment. Prior to coating, the basic properties of the substrates were measured, and are summarized in Table 1 (*n* = 15).

Table 1. Basic characterization of substrates used for barrier coating (*n* = 15).

Substrate	Furnish	Grammage (g·m ⁻²)	Thickness (μm)	Sheet Density (g·cm ⁻³)	Bendtsen Roughness (mL·min ⁻¹)
Primary fiber (PF) uncoated	100% Primary fiber	72.0 ± 0.5	96.0 ± 1.2	0.760 ± 0.01	150 ± 26
Secondary fiber (SF) uncoated	100% Secondary fiber	129.0 ± 0.6	197.0 ± 2.6	0.660 ± 0.01	1271 ± 211

2.4. Standardized Physical Paper Properties and Barrier Measurements

Prior to the measurements, the raw (uncoated) paper substrates and paper samples coated with the alginate and chitosan formulations were conditioned for 48 hours at 23 ± 1 °C and 50 ± 3% relative humidity (RH) [31]. Measurements for grammage, thickness, density, roughness, air permeability, water-vapor transmission rate, water absorptiveness, contact angle, and grease resistance were performed according to the standardized methods listed in Table 2.

2.5. Coating Trial with Laboratory Draw-Down Coater

A coating trial was performed using a laboratory draw-down coater from RK Printcoat Instruments Ltd. (Litlington, UK). A target coat weight of 6 g·m⁻² (single-sided application), with a standard deviation of less than 10%, was achieved by applying two layers of barrier-coating solution. The coater speed was 4 m·min⁻¹, and the wet-film thickness for the first and second coating layers, defined by the wire-wounded rod used, was 40 μm for both coating solutions. Drying of the coated paper samples was performed with hot air at 150 °C for 60 s.

Table 2. Paper properties and standard methods used for the testing of uncoated and coated samples.

Property	Method	Standard
Grammage	Weighing	ISO 536 [32]
Thickness	Lehmann thickness tester	ISO 534 [33]
Density	Calculation	ISO 534 [33]
Air permeability	Bendtsen	ISO 5636-3 [34]
Bendtsen roughness	Bendtsen	ISO 8791-2 [35]
Contact angle	Fibrodat 1100	T 558 [36]
Grease resistance	KIT Test	T 559 [37]
Cobb	Frank-PTI Cobb tester	ISO 535 [38]
Water-vapor transmission rate	Gravimetric determination	T 448 om-09 [39]

2.6. Surface Evaluation of Uncoated and Coated Paper Substrates

The surface topography of uncoated raw paper, and chitosan- and alginate-coated paper was investigated using low-voltage scanning electron microscopy (LVSEM, Everhart-Thornley detector for the detection of secondary electrons; Zeiss Sigma 300, Oberkochen, Germany) [40]. The samples were cut (1 cm × 1 cm), then attached to SEM stubs using a double-sided conductive carbon tape, and imaging (magnification 500×) was performed at an acceleration voltage of 0.65 kV.

2.7. Migration Experiments

In this study, migration experiments were performed according to EU-Regulation No. 10/2011 [41]. As a food simulant, Tenax[®], a poly (2,6-diphenyl-p-phenylene oxide) (Tenax[®] TA (refined), 60–80 mesh; SUPELCO, Bellefonte, PA, USA), was used for the simulation of dry foods such as rice, cereals, cocoa, coffee, and spices. The standard test conditions for long-term storage of these products for above and below six months at room temperature should be 60 °C for 10 days, but can be adapted using the Arrhenius equation. This was done, with conditions tested and set as 80 °C for two days. The Tenax[®] was applied in an amount of 4 g·dm⁻². The experiments were performed in triplicate in migration cells (MigraCell[®]; FABES Forschungs-GmbH, Munich, Germany) with a tested surface area of 0.32 dm². The cell was assembled according to the manufacturer's instructions, with the coated side facing the Tenax[®], and placed in an oven for two days at 80 °C. Afterward, the Tenax[®] was drained into a glass vial with a screw cap, and 25 µL of an internal standard mix was added. The internal standard for migration experiments consisted of dodecane-d₂₆ (C₁₂D₂₆; EURISO-TOP SAS, Saint-Aubin, France), nonadecane-d₄₀ (C₁₉D₄₀; 98%; Cambridge Isotope Laboratories, Inc.; Tewksbury, MA, USA), benzophenone-d₁₀ (C₁₃D₁₀O; 99 at.%; Sigma-Aldrich Co., St. Louis, MO, USA), and bis(2-ethylhexyl)phthalate-d₄ and di-n-butyl phthalate-d₄ (both "analytical standard", purchased from Sigma-Aldrich Co., St. Louis, MO, USA). All were used at a concentration of 200 mg·L⁻¹ in acetone (ROTISOLV[®] ≥99.9%, UV/IR-Grade; Carl Roth GmbH + Co. KG, Karlsruhe, Germany). The Tenax[®] was extracted three times with 10 mL of n-hexane (Picograde[®] for residue analysis; LGC Promochem GmbH; Wesel, Germany) and three minutes of vortexing. The extracts were combined through a folded filter in a 50-mL evaporation vial, and the solvent was evaporated to 0.5 mL in an automatic solvent evaporator (TurboVap[®] II; Biotage, Uppsala, Sweden). The extracts were then transferred into 1.5-mL glass vials with screw caps; the evaporation vials were rinsed with 0.5 mL of hexane, and this solvent added to the 1.5-mL vials. The extracts were stored in a refrigerator, and only a small amount was filled into a 1.5-mL glass vial with a micro insert and screw cap for measurements. The extracts were measured on a gas chromatograph with a flame ionization detector (GC-FID) to determine the overall migration. The separation was done using a Hewlett Packard 6890 Series GC System equipped with an Optima delta-6 capillary column (7.5 m × 100 µm × 0.10 µm, Macherey-Nagel, Germany). The oven was programmed to 60 °C (hold 1 min), then raised at 15 °C·min⁻¹ to 300 °C (3 min). The carrier gas used was hydrogen with a linear velocity of 48 cm·s⁻¹. Aliquots of one microliter were injected with a split of 1:20. The injection-port temperature and

detector temperature were set to 280 and 320 °C, respectively. Data evaluation was done using the “GC ChemStation” software, version B.04.03 (Agilent Technologies, Santa Clara, CA, USA).

For the analysis of MOSH and MOAH, online-coupled HPLC–GC–FID was used as described in [7,8]. Prior to analysis, a MOSH/MOAH internal standard mix was added in a concentration of 1.5–6 µg·mL⁻¹. The standard purchased by Restek Corporation (Bellefonte, PA, USA) contained the following substances in 1-mL ampoules in toluene: n-undecane (300 µg·mL⁻¹), n-tridecane (150 µg·mL⁻¹), bicyclohexyl (300 µg·mL⁻¹), cholestane (5- α -cholestane; 600 µg·mL⁻¹), 1-methylnaphthalene (300 µg·mL⁻¹), 2-methylnaphthalene (300 µg·mL⁻¹), n-pentylbenzene (300 µg·mL⁻¹), perylene (600 µg·mL⁻¹), and 1,3,5-tri-tert-butylbenzene (300 µg·mL⁻¹). For the calculation of retention indices and the determination of cutting fractions in HPLC–GC–FID, a “C₇–C₄₀ saturated alkane standard” from SUPELCO (Bellefonte, PA, USA) was used. The concentration of the alkanes was 1000 µg·mL⁻¹ in hexane, and was diluted to 1 µg·mL⁻¹ with hexane prior to analysis.

The HPLC used was a Shimadzu LC-20AD (Shimadzu Corporation, Kyoto, Japan) equipped with an Allure Silica 5 µm column (250 mm × 2.1 mm). A gradient elution was used, starting with 100% n-hexane (flow 0.3 mL·min⁻¹), before being raised to 35% CH₂Cl₂ within 2 min (hold for 4.20 min). The column was then backflushed at 6.30 min with 100% CH₂Cl₂ (flow 0.5 mL·min⁻¹; hold for 9 min), and reconditioned to 100% n-hexane (flow 0.5 mL·min⁻¹; hold for 10 min). The flow was subsequently decreased to 0.3 mL·min⁻¹ until the next injection. The UV-detector was equipped with a D₂-lamp set at 230 nm and a cell temperature of 40 °C. The GC was a Shimadzu GC 2010 dual-FID (Shimadzu Corporation, Kyoto, Japan), equipped with two guard columns, Restek MXT Siltek (10 m × 0.53 mm inner diameter (id)), and two analytical columns Restek MTX[®]-1 (15 m × 0.25 mm id × 0.1 µm d_f). The carrier gas used was hydrogen with an analysis pressure of 150 kPa, and an evaporation pressure of 87 kPa for MOSH and 85 kPa for MOAH. The oven was programmed to 60 °C (hold 6 min), and raised at 20 °C·min⁻¹ to 100 °C (0 min) followed by 35 °C·min⁻¹ to 370 °C (9.29 min). The LC–GC interface was controlled by a Chronect-LC–GC by Axel-Semrau (Sprockhövel, Germany); data evaluation was done using the LabSolutions software version 5.92. According to a proposed method published by the German Bundesinstitut für Risikobewertung (BfR), quantification was done by integration of the hump for various molecular weight regions. They propose the ranges of C₁₆–C₂₅ and C₂₅–C₃₅ for food-contact materials for dry non-fatty food and storage at room temperature [5].

2.8. Permeation Experiments

The used migration cell allowed a one-sided migration experiment (as described in Section 2.7), and a two-sided application for simultaneously testing the migration and permeation. When performing a two-sided test in the migration cell, three changes of the experimental set-up were made. Firstly, a piece of cellulose was placed at the bottom of the cell where the modeling substances for the permeation were spiked. Secondly, the metal plate in the middle of the cell was removed. Therefore, thirdly, the colorless silicone ring had to be replaced by a FEP (Fluorinated ethylene propylene)-coated red ring to prevent the contamination of the Tenax[®] with siloxanes. As modeling substances, deuterated n-alkanes of various chain lengths were chosen because they best simulated a possible migration of mineral oil hydrocarbons through the sample (C₁₄D₃₀, C₂₀D₄₂, and C₂₄D₅₀, 98%-at.%D, purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA); C₁₆D₃₄, 99%-at.%D, purchased from abcr GmbH (Karlsruhe, Germany); and C₂₈D₅₈ 98%-at.%D, purchased from C/D/N/ Isotopes, Inc. (Pointe-Clair, QC, Canada)). The deuterated substances were used to prevent the interference of permeation and migration tests, because these n-alkanes were also present in the tested paper samples. To simulate aromatic permeability, a set of four aromatic compounds were selected (DL-Menthol, ≥95%; Eugenol, ReagentPlus[®], 99%; Vanillin, ≥97%; and Acetovanillone, ≥98%; purchased from Sigma-Aldrich Co. (St. Louis, MO, USA)). One hundred microliters of a stock solution in acetone containing each of the mentioned substances in a concentration of 100 mg·L⁻¹ were spiked into the bottom of the cell. The test conditions, extraction, and analysis stayed the same as described above.

The methods described were used to test the barrier efficiency of the two uncoated papers, and the papers coated with alginate and chitosan.

3. Results and Discussion

3.1. Physical Characterization of Coated Samples

The substrates made out of primary fibers (PF) and coated with chitosan or alginate were labeled as PF chitosan or PF alginate, respectively. For the secondary-fiber (SF) substrates, this principle resulted in the sample descriptions, SF chitosan and SF alginate. The average values of thickness, density, grammage, and coat weight, with their corresponding standard deviations are shown in Table 3.

Table 3. Thickness, density, grammage, and pick-up values of alginate- and chitosan-coated primary-fiber (PF) and secondary-fiber (SF) samples ($n = 15$).

Sample	Thickness (μm)	Density ($\text{g}\cdot\text{cm}^{-3}$)	Grammage ($\text{g}\cdot\text{m}^{-2}$)	Pick-Up ($\text{g}\cdot\text{m}^{-2}$)
PF chitosan	98.0 ± 1.0	0.780 ± 0.01	78.0 ± 0.7	6.0 ± 0.2
PF alginate	98.0 ± 1.4	0.800 ± 0.01	78.1 ± 0.6	6.1 ± 0.2
SF chitosan	199.0 ± 2.4	0.670 ± 0.01	135.1 ± 0.5	6.1 ± 0.2
SF alginate	198.0 ± 3.1	0.680 ± 0.01	135.0 ± 0.9	6.0 ± 0.3

3.2. Surface Evaluation, Film Formation, and Coating Quality

The topography of the coated and uncoated samples was assessed based on SEM images. The conventional technologies for the barrier coating of paper, such as extrusion or lamination, are based on the application of a specific polymer, and the formation of a distinct film is indispensable. Depending on the substrate and its specific physical properties, the amount of barrier coating sometimes exceeded $20 \text{ g}\cdot\text{m}^{-2}$ or $30 \text{ g}\cdot\text{m}^{-2}$, in order to ensure good barrier efficiency [9]. In this respect, it was of interest whether bio-based coating materials must form a film on top of the paper surface in order to perform well as a barrier.

The SEM images of the uncoated raw substrates, SF and PF, showed the expected clear difference between the two different paper grades (Figure 1). Voids, and different sizes and alignments of fibers and pores between the fibers were visible, and the measured values for roughness and density (see Table 1) confirmed the difference in the structure of substrates produced from primary and secondary furnishes (Figure 1a,b).

Due to these differences between the paper substrates, it is obvious that chitosan and alginate interacted differently with the substrates, as illustrated by the SEM images. The PF substrate coated with chitosan had a completely covered surface, with no voids or pores visible, and a significant amount of the chitosan was also visible on the single fibers. In contrast, the SF chitosan sample showed that the fibers were not completely covered, and the coating appeared to have impregnated the material so that no clearly visible film was formed. A similar behavior was observed for the alginate coatings. Alginate also formed a film on the PF paper's surface, and covered the paper's surface completely, while it impregnated the SF paper. This can be explained by the higher roughness of the SF paper, resulting in impregnation rather than a full coverage of the paper's surface.

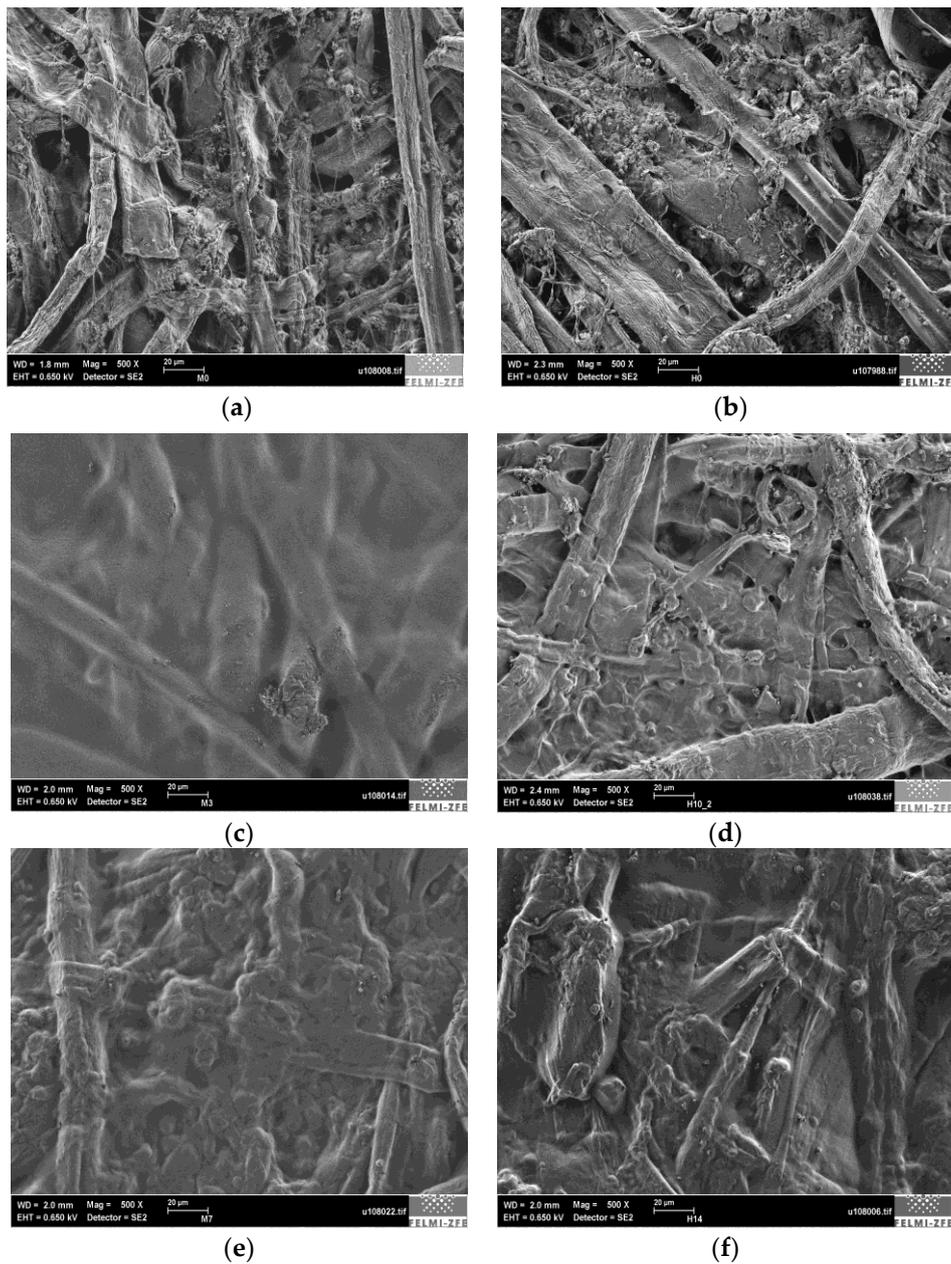


Figure 1. Scanning electron microscopy (SEM) images of uncoated and coated paper substrates at 500 \times magnification: (a) primary-fiber (PF) uncoated paper; (b) secondary-fiber (SF) uncoated paper; (c) chitosan-coated PF paper; (d) chitosan-coated SF paper; (e) alginate-coated PF paper; (f) alginate-coated SF paper.

3.3. Air Permeability and Grease Resistance (KIT Test)

Air permeability is a purely physical measurement, and gives the volume of ambient air able to pass through voids or pinholes through a paper substrate during a defined time period (one minute). The air permeability of the uncoated samples, SF and PF, was 809 mL \cdot min $^{-1}$ and 437 mL \cdot min $^{-1}$, respectively (Figure 2).

After coating with alginate and chitosan, the measured air-permeability values for all samples were 0 mL \cdot min $^{-1}$. Low air permeability also indicates that no pinholes or voids are present in the coated paper.

The KIT test is a common method for the evaluation of fat and grease resistance of paper. The method is primarily designed to evaluate fluorochemical-based coatings for grease barriers, but was successfully applied to bio-based barrier coatings as well [42]. KIT solutions are numbered from 1 to 12, with higher numbers indicating higher grease resistance, and vice versa. The grease resistance of a coated packaging material depends on its surface chemistry (hydrophilic or hydrophobic character), the barrier quality, density, present pores and voids, as well as thickness of the substrate and barrier. KIT solutions are organic, non-polar compounds (castor oil, toluene, and n-heptane) with low density ($<1 \text{ g}\cdot\text{cm}^{-3}$), able to penetrate easily through the porous structure of uncoated paperboard. In order to build a good barrier against grease, assessed with the KIT method, the barrier should, therefore, be hydrophilic rather than hydrophobic [43]. Alginate and chitosan manifest hydrophilic characteristics, and are able to close the voids and pores of the paper surface, thus meeting the initial criteria for a good grease barrier. Alginate applied on SF paper improved grease resistance to a medium level (KIT Number: 7.0 ± 1), which could already be of interest for some applications in the packaging industry. The PF substrate coated with alginate reached the maximum KIT number of 12.0 ± 0.5 , and thus, is classified as an excellent barrier material against grease. Contrary to alginate, where the performance on SF and PF paper was significantly different, the chitosan barrier gave rather similar KIT values on both papers (6.0 ± 0.5 on PF, and 5.0 ± 0.5 on SF substrate). Although chitosan fully covered the fibers and closed the surface of the PF substrate, it did not reach such high KIT numbers when compared with alginate. The reason for this could be the distinctive hydrophilicity of the alginate, which is of course higher than that of chitosan, which may also have hydrophobic characteristics [44].

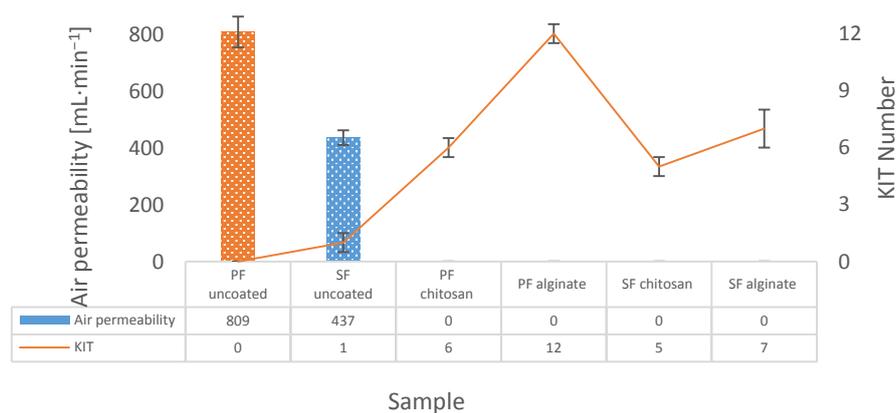


Figure 2. Air-permeability ($n = 15$) and grease-resistance values (KIT test, $n = 9$) for uncoated and coated primary-fiber (PF) and secondary-fiber (SF) paper.

3.4. Water-Vapor Transmission Rate (WVTR)

The water-vapor transmission rate is another important barrier property of packaging materials. Through the transmission of water vapor into a package, not only could the freshness of the packed food be affected, but the growth of microorganisms could also increase. In order to reduce and improve the water-vapor transmission rate (WVTR) of a fiber-based material, the coating barrier material should manifest resistance toward polar water vapor, and be able to close as many pores and voids as possible, preventing the interaction between the polar groups of cellulosic fibers and water vapor [45]. The WVTR was measured gravimetrically, and was expressed as an amount of water vapor in one gram able to pass through a material, usually within 24 h, in our study at $23 \text{ }^\circ\text{C}$ and 50% relative humidity. Raw untreated paper, as a hydrophilic and porous material, is known to be a poor barrier against water vapor. The WVTR values for uncoated PF and SF substrates were $690 \text{ g}\cdot\text{m}^{-2} \times 24 \text{ h}$ and $609 \text{ g}\cdot\text{m}^{-2} \times 24 \text{ h}$, respectively (Figure 3). The coated samples showed significantly improved WVTR values, with chitosan coated on SF paper showing approximately 60% lower values when compared with uncoated paper, and an even better performance on PF substrate. The behavior of the

alginate led to very similar WVTR values for both substrates, corresponding to a 35% reduction for alginate-coated SF and a 44% reduction for PF paper. Taking into account the different thicknesses of the samples, the water-vapor permeation coefficients (WVPCs) were calculated by multiplying the water-vapor transmission rate and the thickness of the sample (Figure 3). A significant reduction in the permeation coefficients was achieved with chitosan, where the WVPC values for both coated substrates were at least 50% lower than those of uncoated SF and PF paper. The same trend was observed and quantified for alginate-coated PF and SF samples (reductions of 35% and 42% for SF and PF, respectively). Both materials partially met the criteria stated above for the reduction in water-vapor transmission rate. After coating, the paper sheet was densified, and fibers were partially or totally covered with the coating material, resulting in the reduced interaction between cellulosic fibers and water vapor, and the reduced diffusion of water vapor. Thus, both materials, despite their hydrophilic characteristics, contributed to a reduction in water-vapor permeability.

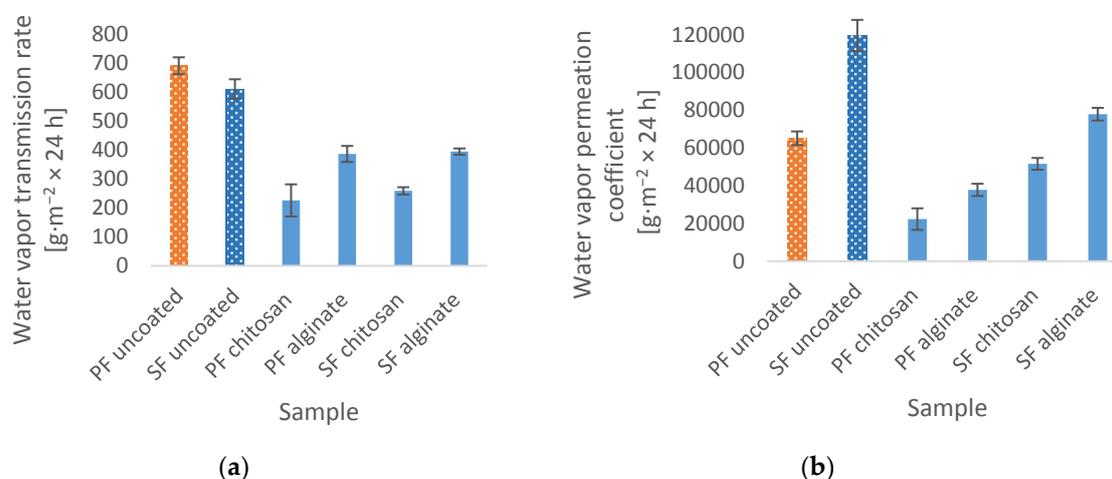


Figure 3. Water-vapor transmission rates (a) and water-vapor permeation coefficients (b) for uncoated and coated paper samples from primary fiber (PF) and secondary fiber (SF) ($n = 6$).

3.5. Wettability and Water Absorptiveness

The wettability of the uncoated and coated samples was assessed by a contact-angle (CA) measurement using deionized water (Figure 4). The water absorptiveness was characterized by performing Cobb measurements for 60 s, where the Cobb value was the amount of deionized water per area which could be absorbed by the substrate during the given period of time (Figure 5).

A contact angle below 90° is characteristic for hydrophilic surfaces. The uncoated PF substrate showed the highest CA, since this paper was already industrial-sized using ASA and starch. By applying chitosan and alginate onto the PF paper's surface, the initial contact angle decreased to $\sim 80^\circ$ (chitosan) and $\sim 35^\circ$ (alginate). On the other hand, the SF uncoated paper had very low CA, which was only measurable for eight seconds. The SF coated with chitosan exhibited a stable and higher CA (70° for 30 s) when compared with the uncoated SF paper. By coating the SF paper with alginate, the initial contact angle was lowered to 30° , but the time-dependent wettability was impacted, resulting in it being stable over the 30 s testing time.

Alginate-coated samples of both SF and PF were in a comparable range, when it came to surface hydrophobicity and water resistance.

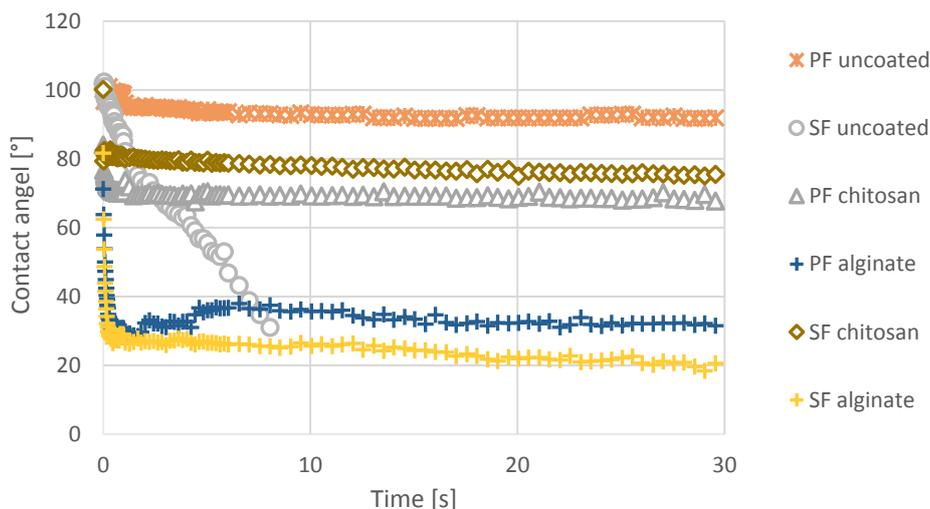


Figure 4. Contact angle of uncoated and coated samples measured with deionized water for 30 s ($n = 6$).

According to the contact-angle measurements, the PF uncoated substrate appeared to be a hydrophobic material ($CA \geq 90^\circ$). The Cobb 60 s value for the PF uncoated substrate was $25 \text{ g}\cdot\text{m}^{-2}$. In contrast, the SF uncoated substrate reached saturation with water at 60 s, resulting in a higher water uptake (Cobb 60 s = $155 \text{ g}\cdot\text{m}^{-2}$), and complete water penetration.

Chitosan- and alginate-coated PF samples were able to absorb at least 50% more water for 60 s when compared with the PF uncoated substrate. Consequently, the PF coated with chitosan or alginate became more hydrophilic, which coped very well with the CA measurements for PF samples.

On the other hand, the chitosan coating enormously affected the water absorptiveness of the SF paper, where a reduction of at least 80% was achieved. The Cobb value obtained with alginate-coated SF paper ($149 \text{ g}\cdot\text{m}^{-2}$ for 60 s) was only slightly lower (<4%) when compared with uncoated SF paper, and no significant reduction was observed. SF paper is an unsized raw paper, which is considered to be very hydrophilic. By coating it with sodium alginate, which is also a hydrophilic material, the water uptake was not significantly reduced. On the other hand, the positively charged chitosan used for the coating of both substrates interacted very intensively with the negatively charged cellulosic fibers. The chitosan solution used for coating was only water-soluble in the presence of acetic acid at pH 4. Above this pH, chitosan was not water-soluble, and could be considered as “hydrophobic” [44]. Due to the fact that the SF paper was not treated with coating chemicals, and the fibers were fully available for positively charged chitosan, the interaction between the fibers and chitosan obviously took place. On that note, the pH could be shifted to the neutral or alkaline region, thus changing the paper’s water absorptiveness, and making chitosan-coated SF paper water-repellent. The PF paper, which was mass- and surface-sized, manifested a very low water uptake, and interacted differently with alginate and chitosan when compared with the SF coated samples. The Cobb values of the PF coated samples were higher when compared with the uncoated PF paper. According to these measurements, different trends could be observed for alginate- and chitosan-coated samples. Irrespective of the paper substrate, alginate caused a hydrophilization effect, while the influence of chitosan on water uptake depended strongly on the paper substrate and its composition.

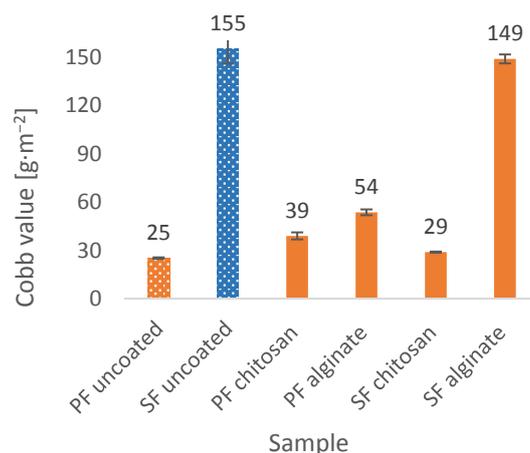


Figure 5. Cobb values for uncoated and coated samples measured for 60 s with deionized water ($n = 6$).

3.6. Migration Experiments

Since food-contact materials should not release any substances that cause unacceptable changes in the composition of the food, the overall migration needs to be kept as low as possible [41]. The two raw papers were of different qualities in this respect. A paper produced from secondary fiber is considered to be the worst case, especially in terms of contamination with mineral oil hydrocarbons, while a paper produced from clean primary fiber is preferable.

Table 4 shows the results of the migration tests performed in triplicate. Alginate and chitosan exhibited a good barrier performance for the SF paper. Setting the total migration of the uncoated SF paper to 100%, 63.8% \pm 0.1% of the observed migration was accounted for as mineral oil, which, in turn, consisted of 57.8% \pm 0.1% MOSH and 6.02% \pm 0.16% MOAH. Using the alginate coating, the overall migration could be reduced to 16.3% \pm 1.0%, of which 7.9% \pm 0.25% were mineral oil hydrocarbons (MOH), consisting of 5.49% \pm 0.18% MOSH and 2.41% \pm 0.42% MOAH. The chitosan coating reduced the overall migration to 29.5% \pm 1.6%, which consisted of 9.16% \pm 0.3% MOH, divided into 8.43% \pm 0.2% MOSH and 0.73% \pm 0.34% MOAH.

The migration of the PF sample was naturally low, and coatings to reduce migration were not actually necessary. As expected, the values of the samples coated with alginate and chitosan were below the detection limit, and are, therefore, not given in Table 4. Unlike other barrier properties, which depended on the quality of the coating layer, densification, pores, voids and surface chemistry, it seems that MOSH and MOAH migration primarily depended on the change in surface chemistry rather than the other factors mentioned in our work. An explanation for such a low migration could be the hydrophilic and polar characteristics of these two materials, resulting in a high resistance toward organic non-polar compounds. As such, alginate performed better than chitosan most probably due to its higher polarity and slightly higher densification of the paper.

Table 4. Overall migration of mineral oil hydrocarbons (MOH), mineral oil saturated hydrocarbons and mineral oil aromatic hydrocarbons (MOSH/MOAH), in uncoated and coated paper samples from primary fiber (PF) and secondary fiber (SF) (%), ($n = 3$).

Sample	Migration (%)	MOH (%)	MOSH (%)	MOAH (%)	Remnants* (%)
SF uncoated	100%	63.8 \pm 0.10	57.80 \pm 0.10	6.02 \pm 0.16	36.2%
SF alginate	16.3 \pm 1.0	7.90 \pm 0.25	5.49 \pm 0.18	2.41 \pm 0.42	8.4%
SF chitosan	29.5 \pm 1.6	9.16 \pm 0.30	8.43 \pm 0.20	0.73 \pm 0.34	20.3%

* Remnants consisted of substances with a retention time outside the range of C₁₆–C₃₅, and substances subtracted from the MOH (e.g., Diisopropylnaphthalene-DIPN).

3.7. Permeation Experiments

The use of deuterated n-alkanes allowed the performance of two-sided tests in the migration cells. This meant the determination of migration and permeation was possible in one experimental set-up without any interferences. This saved a lot of time and resources, and gave a quick and easy screening method for the barrier behavior of the natural polymers.

Gas-phase migration into dry food is limited by volatility. It was shown that it is relevant up to a chain length of C₂₄, and not detectable beyond a chain length of C₂₈, as substances with higher boiling points remain in the packaging material, and do not migrate [5]. According to the theory, the highest levels for permeation were found for d-C₁₆ and d-C₁₈. An interesting observation was the behavior of the added aromatic active substances. Although all four compounds had a volatility and boiling points in the C₁₂–C₁₆ range (Table 5), only menthol permeated through the papers (coated and uncoated). Apparently, the polar groups of the aromatic compounds interacted strongly with the polar groups of the paper.

Table 5. Boiling points of the aromatic compounds and n-alkanes in the same elution range.

Substance	Boiling Point (°C)
Menthol	212
C ₁₂	216.2
C ₁₄	253.5
Eugenol	254
Acetovanillon	265
Vanillin	285
C ₁₆	286.8

From the two tested biopolymers, the alginate-coated samples showed better barrier properties against permeation than the chitosan-coated samples, as shown in Table 6. Under the given test conditions, the permeation rates of d-C₁₄ to d-C₂₀ were between 9.43 $\mu\text{g}\cdot\text{dm}^{-2}/\text{day}$ and 13.7 $\mu\text{g}\cdot\text{dm}^{-2}/\text{day}$ for the uncoated recycled fiber, and was reduced with the chitosan coating by 37%–50%, and was reduced with the alginate coating by 18%–50%. We observed similar permeation rates of the deuterated n-alkanes through the uncoated SF and PF papers, but lower permeation rates for primary fiber after the coating process, especially for the alginate coating. An explanation might be the difference between the two papers in terms of the three-dimensional structures, as well as the chemistry of the fiber surfaces, and a higher pressure on the SF barriers, due to the high load of possible migrants [46].

Table 6. Comparison of the permeation rates of deuterated n-alkanes of various chain lengths, and menthol through coated and uncoated paper samples from primary fiber (PF) and secondary fiber (SF) ($\mu\text{g}\cdot\text{dm}^{-2}/\text{day}$; $n = 2$, data given individually).

$\frac{\mu\text{g}}{\text{dm}^2 \cdot \text{d}}$	d-C ₁₄		d-C ₁₆		d-C ₂₀		d-C ₂₄		Menthol	
SF uncoated	12.85	9.43	13.7	10.58	12.88	11.12	3.8	3.4	8.77	6.38
SF alginate	3.26	3.43	5.45	5.6	2.34	2.37	0.49	0.44	3.39	3.59
SF chitosan	4.8	4.8	6.85	7.63	4.88	6.24	0.72	0.89	1.99	2.19
PF uncoated	12.68	12.51	13.54	13.39	14.63	14.05	3.23	3.23	10.76	10.16
PF alginate	1.34	0.81	1.87	0.92	0.7	0.35	0.3	0.25	3.39	3.19
PF chitosan	5.14	4.46	6.85	5.76	5.46	3.9	0.65	0.53	5.18	4.98

4. Conclusions

Biomaterials, such as alginate and chitosan, are biopolymers with higher degrees of complexity when compared with conventional synthetic surface-treatment chemicals. Therefore, the interactions between these two materials and the substrate are variable, and could bring about a comparative advantage for paper-based packaging producers when compared with synthetic barrier materials. Applying those two bio-based materials could improve the barrier properties of paperboard for

food-packaging applications. Even with a pick-up weight of $6 \text{ g}\cdot\text{m}^{-2}$, the permeability, migration, and transmission were significantly reduced. Depending on the paper substrate, specific barrier properties were differently affected, and could be selectively optimized and adjusted for the consumer's needs, thus giving the packaging producers certain flexibility for some specific applications. One of the most interesting findings resulted from the combination of SEM imaging, and the tests of migration and permeation. It was shown that a continuous surface layer of the biopolymeric materials was not necessary to substantially improve the barrier properties. This is an interesting aspect not only for future research, but also for coating and packaging technologists in the industry. Irrespective of the use of substrates made from primary or secondary fibers, medium-to-high grease resistance was accomplished. The water-vapor transmission rate was reduced by at least 35%. The water resistance or absorptiveness was clearly substrate-dependent, and optimal values were conditioned through the further utilization of packaging materials. The overall migration of organic volatile compounds was successfully reduced by 70% and 84% upon coating the SF substrate with chitosan or alginate, respectively. Migration for the PF sample was naturally low, and coatings were not actually necessary to reduce migration. The permeation of deuterated n-alkanes through both papers was reduced by up to 50%.

Summarizing all results, alginate and chitosan showed excellent barrier behavior.

Author Contributions: S.K. designed and performed the coating experiments, physical measurements, and barrier characterization. A.W. performed the migration and permeation experiments for the samples, including the determination of MOH levels using HPLC–GC–FID. A.Z. performed the SEM experiments. S.K., A.W., E.L. and W.B. analyzed the data, and wrote the paper.

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