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Surface Treatment of Fibre-Based Materials Using Biopolymers

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Abstract

Fibre based packaging materials such as paper and board are widely used, environmentally friendly, recyclable and biodegradable. In order to utilize paper and board as primary or secondary packaging it is frequently treated with barrier and strength additives in order to fulfil its functions. Today additives used in the surface treatment of packaging papers for functionality improvement are predominantly petroleum-based non-renewable polymers. While starch and other plant derived polysaccharides have been applied in the paper industry since decades, other natural and renewable materials such as lignosulfonate, kraft lignin, nanocelluloses, chitosan and alginate are currently in the focus of research and have the potential to substitute synthetic polymers used for surface or internal treatments of paper based packaging materials.

In the first part of this work, two technical lignins were successfully isolated, purified and applied in the surface sizing of recycled packaging papers. The benefits of lignin application in surface sizing are improved mechanical (tensile strength, bending stiffness, burst strength and SCT) and surface properties, which are comparable to the conventional starch-based surface sizing formulations. Technical lignins contribute both to the development of strength and the improvement of the water resistance of the treated papers. Depending on the planned application of the packaging material, lignin formulation properties can be adjusted by blending with enzymatic starch. Furthermore, the concept of applying lignin in surface sizing could result in a successful bio-refinery oriented application where lignin as a coproduct of the pulp mill, which is presently mainly used for energy production, could be directly utilized as a material for the improvement of paper properties needed for final packaging applications.

In the second part of this work, alginate and chitosan were successfully applied as functional barriers for food packaging materials. These materials showed excellent performance when the formation of grease and mineral oil barriers as well as the reduction of gas transmission are required. The materials behave differently depending on the substrate quality and film formation is not always necessary in order to achieve good barrier properties. The application of chitosan shows multifunctional effects on the paper properties, since besides surface functionalization and barrier capacities it also contributes to the development of mechanical strength. Overall, this work provides a feasible technical approach to apply natural biopolymers

to improve the technological properties of packaging papers. The application technology and the materials used in this work are commercially available and upscaling of the results from these scientific investigations to industrial practice should be possible, but will of course also depend on economical conditions.

Kurzfassung

Papierbasierte Verpackungsmaterialien sind weitverbreitet, umweltfreundlich, rezyklierbar und biologisch abbaubar. Um Papier als Primär- oder Sekundärverpackungsmaterial zu verwenden, wird es in der Praxis mit chemischen Additiven zur Verbesserung der Barriereeigenschaften oder zur Erhöhung der Trocken- und Nassfestigkeit behandelt. Heutzutage werden in der Papierherstellung überwiegend synthetische Polymere als chemische Additive verwendet, die häufig Erdöl als Ausgangsstoff haben. Während Stärke und andere technische Polysaccharide seit Jahrzehnten in der Papierindustrie eingesetzt werden, stehen derzeit andere Biopolymere wie Lignosulfonate, Kraftlignine, Nanocellulosen, Chitosane und Alginate im Fokus der Forschung, da sie das Potenzial haben, die synthetischen Polymere künftig zu ersetzen.

Im ersten Teil dieser Arbeit wurden zwei technische Lignine erfolgreich isoliert, aufgereinigt und als Oberflächenleimungspräparation auf Verpackungspapieren aus rezyklierten Fasern aufgetragen. Die Vorteile bei der Anwendung vom Lignin in der Oberflächenleimung sind verbesserte mechanische Eigenschaften (Zugfestigkeit, Biegesteifigkeit, Berstdruck und SCT) sowie Oberflächeneigenschaften, die mit den auf Stärke basierenden Formulierungen vergleichbar sind. Technische Lignine tragen somit sowohl zur Festigkeitsentwicklung, als auch zur Verbesserung der Wasserresistenz der behandelten Papiere bei. Je nach zukünftiger Anwendung des Verpackungsmaterials können die Eigenschaften der ligninbasierten Formulierungen z.B. durch Mischen mit enzymatischer Stärke modifiziert werden. Derzeit wird Lignin als Nebenprodukt der Zellstofferzeugung hauptsächlich zur Energiegewinnung verbrannt. Die potenzielle Anwendung von Lignin als Oberflächenleimungsmittel in der Papierherstellung stellt eine weitere mögliche Anwendung in Richtung der Bestrebungen der Industrie hin zu einer Bioraffinerie dar, da hier ein Nebenprodukt aus dem Zellstoffwerk wieder direkt in die Papierproduktion einfließt.

Im zweiten Teil dieser Arbeit wurden Alginate und Chitosane erfolgreich als funktionelle Barrieren für Lebensmittelverpackungsmaterialien eingesetzt. Diese Materialien zeigten eine hervorragende Barrierewirkung in Hinsicht auf Fette und Mineralöle, sowie hinsichtlich Reduktion des Gastransports durch das Papier. Dabei sind die Eigenschaften auch stark von der Substratqualität abhängig, wobei eine Filmbildung an der Papieroberfläche nicht immer notwendig ist, um gute Barriereeigenschaften zu erzielen. Chitosan wirkt multifunktionell auf

die Papiereigenschaften, da es neben der Verbesserung der Barriereeigenschaften auch die mechanischen Eigenschaften positiv beeinflusst.

Insgesamt bietet diese Arbeit einen praktikablen technischen Ansatz zum Einsatz von weiteren Biopolymeren, um die technologischen Eigenschaften von Verpackungspapieren zu verbessern. Die angewandten Streichverfahren, sowie die verwendeten Materialien, sind kommerziell verfügbar, was die industrielle Umsetzbarkeit dieser wissenschaftlichen Ergebnisse realistisch erscheinen lässt, sofern die wirtschaftlichen und gesellschaftlichen Rahmenbedingungen passen.

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List of Peer-Reviewed Publications

(I) **Kopacic, S**.; Ortner, A.; Gübitz, G.; Kraschitzer, T.; Leitner, J.; Bauer, W. Technical Lignins and Their Utilization in the Surface Sizing of Paperboard. *Ind. Eng. Chem. Res.* **2018**, *57*, 6284-6291, doi:10.1021/acs.iecr.8b00974

(II) **Kopacic, S**.; Walzl, A.; Hirn, U.; Zankel, A.; Kniely, R.; Leitner, E.; Bauer, W. Application of Industrially Produced Chitosan in the Surface Treatment of Fibre-Based Material: Effect of Drying Method and Number of Coating Layers on Mechanical and Barrier Properties. *Polymers* **2018**, *10*, 1232, doi:10.3390/polym10111232.

(III) **Kopacic, S.;** Walzl, A.; Zankel, A.; Leitner, E.; Bauer, W. Alginate and Chitosan as a Functional Barrier for Paper-Based Packaging Materials. *Coatings* **2018**, *8*, 235, doi: 10.3390/coatings8070235.

Table of Content

1. Introduction

1.1.1 Objectives and motivation

Packaging materials produced from cellulosic fibres are light, versatile, environmental friendly and cost-efficient materials with a good ability to physically protect and preserve the packed goods. Surface treatment of the fibre-based materials intended to be used as a packaging papers is one of the most important processes in the paper based packaging industry, as this treatment with appropriate coating or sizing formulations is the most important surface modification step regarding improvement and adjustment of paper functionalities and final properties demanded by end users [1-3]. The paper surface is generally treated directly in the paper or coating machine during the paper manufacturing process with an aqueous suspensions or dispersions or subsequent treatments are carried out in an off-line process, often using thermoplastic polymers in an extrusion process [4-6]. During paper production, packaging papers are mass or surface sized and this process is designed to improve water resistance, increase surface and paper strength properties and to modify paper surface chemistry. In the case of coated papers this process is often carried out as a pre-treatment step. The term coating in the paper industry refers mainly to so-called pigment coatings, where standard coating formulations composed of pigments, binders, co-binders and other additives are applied and printing relevant properties such as surface porosity, gloss, smoothness, brightness and opacity are improved [7]. Papers intended to serve as packaging materials must be coated with appropriate barrier formulations in order to meet food, cosmetic or drug packaging requirements [8, 9]. Over the past decades, surface sizing and coating of paper and paperboard to enhance barrier and strength properties has been performed using coatings containing mainly synthetic polymers, but the current trend in paper coating is to replace these with sustainable natural materials [10-13]. The aqueous barrier coatings are normally applied to the paper surface using well-known application processes for surface sizing or pigment coating of paperboard such as a filmpress or more recently a curtain coater [14-18].

As the demand for packaging materials is strongly correlated to the increase of global populations and e-commerce the demand for packaging should follow these trends and increase by at least 4 % per year in the coming decades [19, 20]. Demand for petroleum-based plastics in Europe is round 50 million tons per year and around 40 % of the plastics are converted into coatings, strength additives or plastic packaging [21]. Plastic packaging consumption results in extensive pollution of our environment and new solutions for environmental friendly packaging materials are urgently needed. Thus the policy makers, producers and consumers are desperately looking for a new generation of renewable materials which could be produced in Europe and utilized as a strength or barrier additive [22, 23]. In this work, the focus lies on biopolymers and their application as functional barrier and strength additives for paper intended to be used as primary or secondary food packaging materials. As a result of a comprehensive literature study and the practical work performed, an approach of combining the use of commercially available bio-based materials such as technical lignins, chitosan and alginate with conventional coating technologies such as film press has been evaluated. The main targets of the investigation concern the study and optimization of the coatability of the developed barrier formulations as well as the assessment of the contribution natural material can make to the development of barrier and mechanical properties.

This approach should encourage the application of biopolymers as barrier and strength additives for paper based packaging material. In the first part of this work, technical lignins were successfully extracted from the black liquor of a kraft and sulphite pulping process and applied in surface sizing formulation for brown packaging papers (**Paper I**). The prime target was to prove the coatability and to evaluate the effects of surface sizing formulations containing ligninsulfonate and kraft lignins, applied pure or in mixtures with starch onto packaging papers, on the mechanical strength properties and on the wetting behaviour

The second part of this work deals with the application of chitosan and alginate in barrier coating, where also different substrates were coated and the influence of the interaction barrier material – raw paper was quantified by measurements of barrier properties against gas, grease and aromas (**Paper II**). A further important aspect was the evaluation, whether the bio-based materials are able to hinder the migration of mineral oil fractions (MOSH/MOAH) originating from recycled fibres.

The third part includes the study of barrier and strength properties of paper coated with industrial produced chitosan. Process relevant parameters such as the influence of drying and coat weight on the development of the barrier and strength properties were evaluated (**Paper III**).

1.1.2 Food packaging and materials

Irrespective of packaging material, food packages must fulfil primary and secondary functions in order to qualify to serve for food packaging. They should protect the packed food from spoilage and physical damage as well as increasing the shelf life, thus avoiding food waste. Depending on the packaged good, the requirements regarding level and type of protection may vary, as the food ingredients (e.g. lipids, proteins or carbohydrates) interact or react differently with the surrounding (gaseous) environment. For food packaging applications, many factors regarding the compliance with existing national or international legislation must be considered for food contact materials. They have to ensure proper hygienic protection, to avoid loss of nutritional value and to rule out contact to any toxicological or harmful compounds [24-27]. These primary packaging functions are mostly related to technological aspects, thus they depend on packaging material selection and also material processing. Secondary packaging functions, which today are of the same importance as the primary functions, include functional design, appropriate communication and marketing possibilities, recyclability and sustainability. By appropriate design of packaging and by information of both content and packaging material, the producers influence food waste, shelf life, tampering with the packed goods and the whole packaging value chain in a very positive way [28].

In Europe, around 40 % of food packaging materials is produced from paper and paperboard, which are well known as renewable and biodegradable materials [29]. Due to the heterogeneous structure of paper, even when using virgin cellulosic fibres and extensive refining, it is not possible to reach the same material strength and tightness as with the more uniform thermoplastic synthetic materials. By contrast with engineered plastics having a consistent, homogeneous and uniform structure, paper is porous, heterogeneous and usually has a bulk material density of less than 0.8 g/cm³, which is not sufficient to prevent gas permeation into the package (see **Figure 1**) [30].

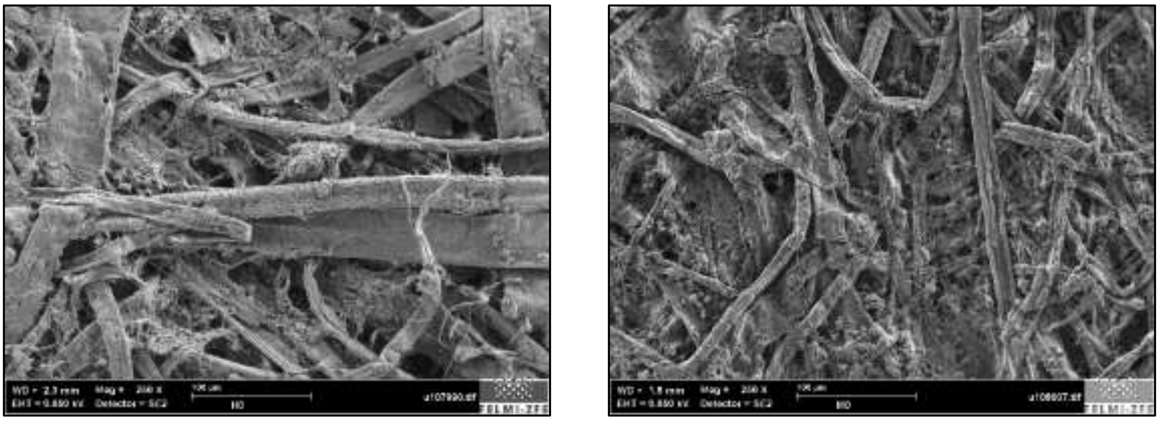

(a) (b)

Figure 1. SEM image of the uncoated raw packaging paper produced from (a) secondary and (b) primary fibres indicating the heterogenic paper structure with visible pores and voids.

Still, food-packaging materials based on cellulosic fibres must exhibit protection against physical, biochemical, microbiological and organoleptic changes, in order to be accepted by the converters and consumers and therefore it is often used in material combinations with thermoplastics. Paper based food-packaging materials should able to sustain and maintain a high protection level for packed food even for long-term storage and frequent interaction with the surrounding environment. Given the permanently changing conditions in the environment regarding temperature, time, moisture, light, gases and pressure, which have an enormous influence on the shelf-life of food and its quality, the development of a fully bio-based packaging material is very challenging [31-35]. Apart from good resistance against the external factors stated above, the required strength properties must also be ensured as insufficient strength leads to mechanical damage mostly occurring during transport, which often leads to spoilage and waste of the food [36]. By sizing and barrier coating of the paper, most of above mentioned factors, which cause food waste and reduce the shelf life, could be controlled and prevented.

The only way to control the atmosphere inside a paper or board packaging is by coating the surface with an appropriate barrier. For most packed foods, moisture and oxygen content in the packaging are crucial parameters. Through water vapour and gas permeation, alteration of the atmosphere inside the package is induced. At increasing the moisture, the growth of microorganisms is stimulated, resulting in food spoilage and higher food waste. Secondly, increased moisture can reduce the quality of dry food such as loss of crispness [37-39]. A low oxygen transmission trough packaging material is an important property for packaging applications. Oxygen is able to facilitate irreversible oxidation reactions in packed food, which reduces the shelf life. Some of the unwanted reactions upon uncontrolled oxygen transmission can lead to development of side products which mediate undesired off-flavours, colour changes, rancidity or the loss of nutritional values. Especially unsaturated lipids in foods can oxidise in presence of oxygen leading to changes of the packed food as described above [40, 41].

The challenge for paper based packaging material is that different barrier properties must be considered for different products [42]. A multiple-layer barrier is the solution in some cases, and is already used in practice, however this approach is not always technologically and economically feasible [43, 44]. Synthetic petroleum based polymers such as ethyl vinyl alcohol (EVOH), polyethylene terephthalate (PET), low or high-density polyethylene (LDPE/HDPE) accompanied mostly with aluminium are frequently used in surface treatment of fibre based packaging materials. These polymers are thermoplastic, non-sustainable and non-renewable materials and an extrusion coater as an additional manufacturing process step is needed in order to treat paper or board surface [45-46]. Recently, these multi-component blends of synthetic polymers with other materials have become a subject of greater attention and the application of synthetic polymer dispersions for functional paper coating has already to some extent replaced the conventional methods of surface treatment such as lamination or extrusion [47,48].

On the other hand, environmental concerns together with the issues of increasing oil-prices and unstable political situations in oil producing countries have forced the development of new bio-based environmentally friendly and recyclable materials. Over the long term, these developments should contribute positively to overall growth and expansion of the European circular bio-economy [49-51].

Intensive research in the academic and private sector has focused on the replacement of oil-based polymeric materials for surface treatment of fibre-based materials. The driving forces behind this development are not necessarily the producers alone but pressure also comes from the consumer side [52-54]. Due to changing habits and increased demand for environmentally and consumer appealing product packaging, the companies are changing their profiles and marketing strategies in order to meet requirements demanded by the end consumers. Preferences and behaviour of the consumers are the most important factors that must be considered prior to development and bringing the packed product onto the market [55].

Nevertheless, the material developers and researchers are facing major challenges in finding new materials or new applications for existing natural materials that are competitive to the already well-established synthetic materials. Unfortunately, much of the scientific work carried out in past decades has remained in the laboratory and never reached pilot or industrial scale. An enormous optimization potential in terms of economic and material specific properties thus still exists for the application of novel bio-based materials in the field of paper and packaging [56-58]. This thesis is one small step towards the above-mentioned general targets concerning the replacement of plastic materials by a more extensive utilization of natural alternatives.

2. Experimental – Materials and Methods

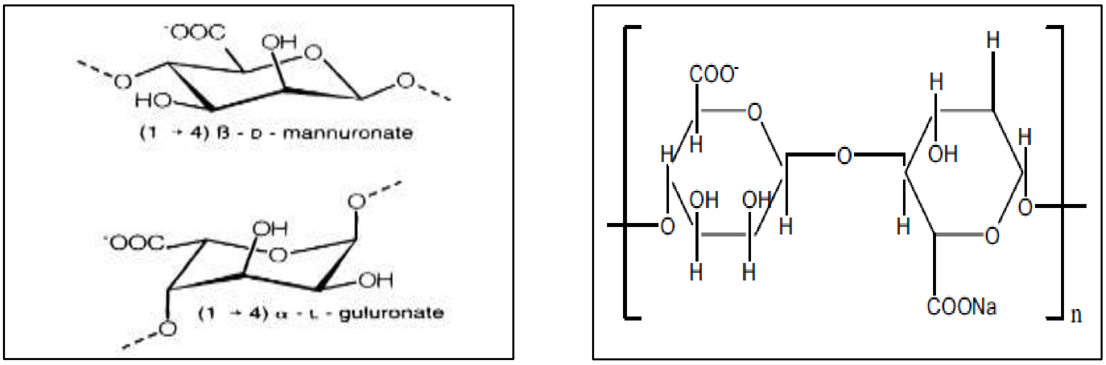
2.1 Materials

2.1.2 Natural materials

Several research studies in recent years investigated the use of bio-based materials for cellulose fibre based food packaging. From a technological point of view, the advantage of bio-based materials such as cellulosic materials or derivatives, polysaccharides and proteins are their ability to form stable films with low permeability and higher density compared to conventional synthetic polymers [59-66]. The films made from suitable natural materials manifest crystalline or semi-crystalline structures, which lead to low permeation of most gaseous substances, and make them very interesting for replacing fossil-based barrier polymers [67-72]. Secondly, due to chemical or physical interaction with cellulosic fibres, they can also contribute to material strength properties, elasticity and increase of the desired impermeability [70-74]. In this work, water-soluble natural materials such as alginate, chitosan, lignosulfonate and kraft lignin are evaluated regarding their potential use in barrier coating and surface sizing of paper and board.

2.1.3 Alginate (Paper II)

Alginate is a naturally occurring anionic biopolymer and is obtained by alkali extraction from brown algae. Due its high availability in nature, it has been extensively studied for many applications in recent decades [75-76]. It is considered to be non-toxic and safe to be used for technical or medical applications. Alginate can be defined as a linear heteropolysaccharide of D-mannuronic and L-guluronic acid and belongs to the group of natural polysaccharides (see **Figure 2a**.). These two monomeric units are stereochemically different and alginate extracted from different seaweed species typically shows differences when it comes to the ratio or contents of these two components [77-78]. Alginate as a linear block biopolymer consist of the two above-mentioned monomeric units, which are joined by 1.4 linkages. The mannuronic (M) and guluronic (G) acids ratio (M/G) depends on the raw material source and might vary between 0.43 and 2.26 [79-81]. The alginates, which are commercially available, are normally extracted using sodium hydroxide solution. After the extraction process, the filtrates are usually treated with sodium carbonate and calcium chloride in order to ensure the precipitation of the respective alginate salts (see **Figure 2b)**. The advantage of monovalent alginate salts such as sodium alginate for dispersion coatings is their water solubility. On the other hand bivalent alginate salts (Ca- Alginate) are not necessarily water-soluble and manifest tendency to form a gels due to inter- and intramolecular chelation phenomena [82,83].



(a) (b)

Figure 2. Chemical structures of buildings segments-mannuronic and guluronic acid in chair conformation (a) and commercially available water-soluble sodium alginate unit drawn in the Haworth projection (b) [84, 85].

Alginates and derivatives are used in large quantities today in the food industry as additives and are therefore safe for use in the packaging field as a functional barrier additive intended to be in direct contact with the packed food. Depending on their application, thickness and chemical composition, alginate films might well be able to provide the good gas, fat and grease barriers that are required by the food packaging industry [86, 87]. The physical and chemical data of the alginate used for the barrier coating trials are presented in the “Materials and Methods” section of **Paper II**. The preparation of sodium alginate coating solution was conducted by dissolving the sodium alginate powder in deionized water at neutral pH value. In order to accelerate the solubilisation process, the solution was heated for 6 hours at 75 °C. After 6 hours, dissolution was completed resulting in an homogenous aqueous solution. Prior coating, the measurements of the solid contents using the moisture analyser (HR73 Mettler Toledo) as well as viscosities with Brookfield II+, at 23 °C and 50 rpm were performed as presented in details in the “Materials and Methods” section of **Paper II**.

2.1.4 Chitosan (Paper II and III)

Chitosan is derived from chitin, which is the second most abundant polysaccharide after cellulose. Chitosan is at the present time obtained predominately from fishing industry waste. From a mechanical perspective, it is a light but highly resistant building material found in the exoskeletons of crustaceans and insects. Economically interesting quantities are currently being extracted from the shells produced during the processing of crabs and shrimps [88, 89]. By simply cleaving the N-acetyl groups, chitin is modified to form chitosan, which as a cationic polysaccharide, has a number of interesting properties, which open up a broad range of applications (see **Figure 3**.).

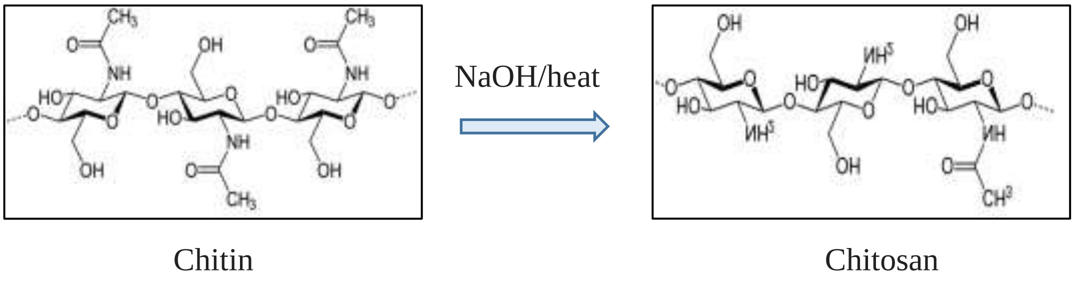


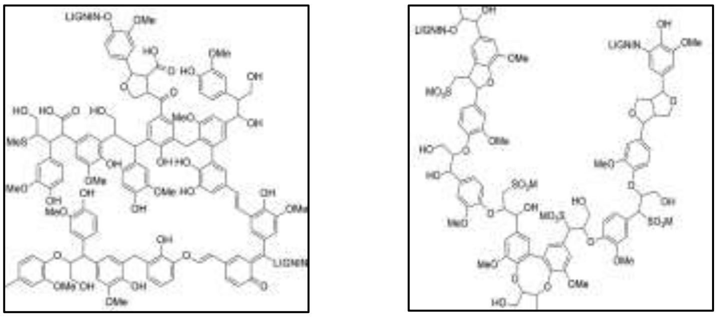
Figure 3. Most common industrially used chemical transformation of water insoluble chitin into potentially water-soluble chitosan. The process is based on cleaving the N-acetyl group by alkali and heat treatment. [90].

Chitosan is a good alternative for the total or partial replacement of synthetic polymers due to its production from a renewable resource, its biodegradability and capacity to form resistant, elastic and flexible films [91]. By means of different raw materials and process parameters, chitosan properties can be adjusted and differ significantly when it comes to degree of deacetylation, the molar mass and the ash content. This possible variation of the product parameters results in the need to select the optimal product for the particular application [92, 93]. Chitosan films also provide efficient oxygen barriers, however they are poor water barriers, which can be improved by incorporation of a hydrophobic compound, forming an emulsified film [94-97]. Commercial grades of chitosan used either for medical or technical purposes have a degree of deacetylation of 70–90%. Industrially produced chitosan forms a highly viscous, shear-thinning solution that can be coated on various substrates or cast into transparent, freestanding films. The films are transparent, flexible and semi-crystalline, thus giving low oxygen permeability. Due to its cationic character, chitosan can bind strongly to the anionic cellulose fibers leading to an improvement of overall paper strength. Chitosan also exhibits natural antibacterial and fungicidal properties, thus making it attractive for use in the coating of paper and paperboard for food or medical applications. [98-103]. The chitosan (technical grade) used in this work is supplied by the Biolog Heppe GmbH (Germany) and its chemical and physical properties are summarized in the “Materials, Equipment and Methods” section of **Paper III**. The formulation was prepared by dissolving the chitosan powder in acidified water (pH≥4, pure acetic acid, Rotipuran). Depending on the desired solid content, intense stirring is required and the solubilisation process took in some cases more than 8 hours as presented in details in the “Materials and Methods” sections in both **Paper II** und **Paper III**. The rheological characterisation of chitosan at low, medium und high shear rate was performed using the rotational rheometer (Paar Physica MCR 301) and is fully described in the “Materials, Equipment and Methods” section of **Paper III**.

2.1.5 Technical lignins (Paper I)

Technical lignins such as kraft lignin and lignosulfonate, which are the predominant co-products of the pulping industry, have a high potential for use as value added products in various technical fields. The pulping industry produces more than 130 million tons of lignin worldwide, which is mostly used as fuel for energy generation and for the recovery of pulping chemicals. Less than 10 % is used for the creation of value added products [104]. Kraft lignin and lignosulfonate are the best known technical lignins. Due to their chemical, physical properties as well as the high quantities produced they are probably the most interesting biopolymers for scientific investigation as well as technological applications within the paper and packaging industry. Especially lignosulfonates have already found applications in agriculture, in cosmetics and the construction industry. Lignin is one of the few biopolymer containing hydrophilic and hydrophobic functional groups and thus might potentially replace synthetic sizing additives used in the surface treatment of the fiber-based packaging materials [105, 106].

In principle, the chemical structure of lignin (see **Figure 4**) with the presence of the different aromatic and alcoholic compounds is a good prerequisite for using it as an additive in a surface sizing as it can enhance strength and hydrophobicity of the cellulosic fibres. The structure of lignin has been investigated intensively in recent years, but the heterogeneity of the chemical structure of technical lignins and their recalcitrance still present a challenge regarding their further utilization and modification. Molecular weight distribution, which is one of the crucial parameters for technical lignin applications, differs from wood to wood species and also depends on the type and process conditions of the industrial pulping process [107-108].

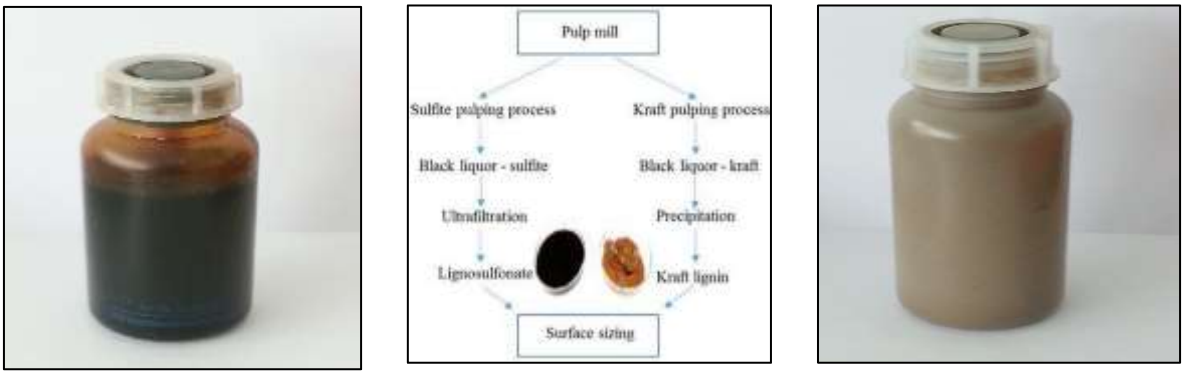


(a) (b)

Figure 4. Proposed chemical structures of kraft lignin (a) and lignosulfonate (b) [109].

In our work, we investigated the use of two types of purified technical lignins (kraft lignin and lignosulfonate) in the surface sizing formulations for packaging papers with the target to better understand the influence of the physico-chemical properties of technical lignins on the development of paper strength properties and the surface and bulk hydrophobicity. Surface sizing solutions containing different mass ratios of the two technical lignins and starch were prepared and applied on an industrially produced substrate (100 % recycled paper) using a laboratory film press. The detailed surface sizing trials and the formulations used are presented in the Table 1. of **Paper I**.

The trials concentrated on the partial or total substitution of enzymatically modified starch and synthetic surface sizing agent (Perglutin) by technical lignins. Since lignosulfonate and kraft lignin represent poly-dispersed systems with a wide range of molecular distributions an approach was developed to purify, extract and concentrate these two materials (see **Figure 5**.). Kraft lignin was precipitated using a pilot precipitation plant at acidic condition (sulphuric acid) and filtrated prior to application. The experimental procedure with the corresponding measurements are demonstrated in the Figure 2. of **Paper I.** The purification of the lignosulfonate was performed using ultrafiltration. Ultrafiltration of lignosulfonates is a convenient purification process, which offers a high purity lignosulfonate fraction [110,111]. By using different membranes with varying cut off sizes (from 5 kDa to 150 kDa) large amount of low molecular weight lignosulfonate could be separated. For the surface sizing application, the fraction with the largest molecular weight was used.

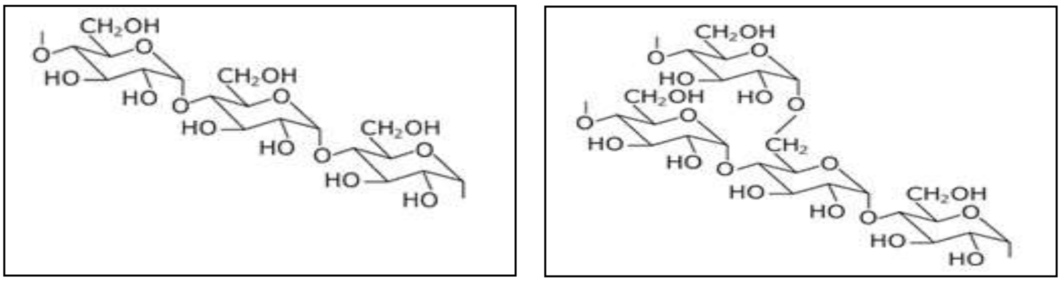


Lignosulfonate Extraction and purification process Kraft lignin

Figure 5. Simplified process flow for lignosulfonate and kraft lignin extraction and purification from black liquor for the application in surface sizing (see **Paper I**).

2.1.6 Starch (Paper I)

A technical grade of enzymatically converted starch is used in this work in order to evaluate its contributions to surface sizing and compare it to the technical lignins. Starch is a naturally abundant polymer consisting of the two components amylose and amylopectin (see **Figure 6**). Amylose has been described as a linear molecule consisting of glucose units linked together by 1.4 glucosidic bonds. Amylopectin is a highly branched molecule and branches are bound to the main chain by 1.6 glucosidic bonds [112].



(a) (b)

Figure 6. Chemical structure of two starch building units: (a) amylose and (b) amylopectin [113].

Depending on the sources of the starch, the percentage of amylase and amylopectin can vary and therefore the material-specific parameters such as the crystallinity of starch also vary. Native starch shows semi-crystallinity, which is formed when linear amylase and the linear parts of amylopectin are oriented parallel to each other. Hydrogen bonds are facilitated through parallel orientation of these two starch building units [114]. In the formation of the crystalline phase not only the structure but also the amorphous phase of amylase plays an important role. Amylase has a significant amorphous phase portion compared to amylopectin, and this has a great influence on the crystallinity. Amylopectin is thus mainly responsible for the crystalline order in the native starch granules. Both amylase and amylopectin play a significance role in the homogeneous film formation [115]. Higher mobility of linear amylose fractions in starch is responsible for film flexibility and bonding ability of the film when it comes into contact with a substrate such as paper or board. Starch is a hydrophilic material and might provide good barrier against fat and grease and also a moderate barrier against water vapour. Water retention and water vapour permeability of films comprised of starch can be influenced by adding a plasticizer, which enables faster mobility of linear amylase fraction and the forming of greater crystallinity regions [116]. The starch used in this work, an enzymatically treated native corn starch, was supplied with a solid content of 25 % (w/w) by an Austrian Paper mill. Starch based surface sizing formulations are used as references for the trials with technical lignins and full description of their preparation and application is presented in the "Experimental" section of **Paper I**.

2.1.7 Paper substrates (Paper I, II and III)

The substrates (raw papers) used for the coating trials are three industrially produced paper grades which are shown in the **Table 1**.

Table 1: Basic properties of papers (substrate) used for the surface sizing and barrier coating.

Substrate	Furnish	Thickness [µm]	Grammage [g/m²]	Process	Publication
Untreated Fluting	100 % Secondary fibers	172.0 ± 5.0	117.0 ± 0.8	Surface sizing	**Paper I**
Wood-free-uncoated paper	100 % Primary fibers	96.0 ± 1.2	72.0 ± 0.5	Barrier coating	**Paper II and III**
Untreated testliner	100 % Secondary fibers	197.0 ± 2.6	129.0 ± 0.6	Barrier coating	**Paper II**

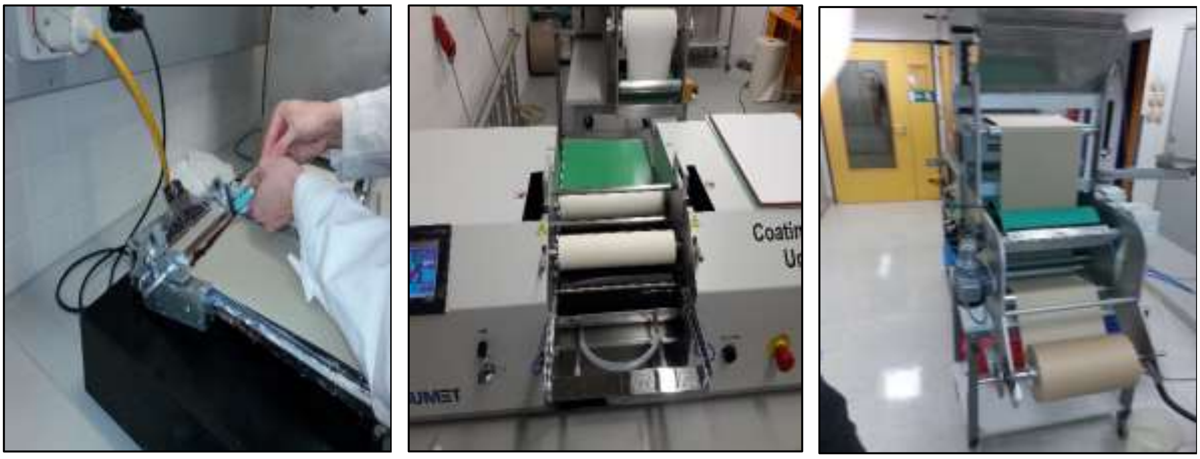
Full description of the substrates used for surface sizing trials is given in Table 2 and Table 3 of **Paper I**. Details and physical properties of the substrates used in the barrier coating trials are presented in Table 1. of **Paper II**.

2.2 Methods

2.2.1 Surface treatment of fibre-based material (Paper I, II and III)

Three different methods for surface treatment of packaging papers were used in this work. For initial proof of concept trials, a drawdown coater (RK Printcoat Instruments Ltd.) was used for both, sizing and barrier coating of the packaging papers. Using the drawdown coater coating pick-up weight could be easily adjusted and the papers were treated on either the top or bottom side. After the application of the materials onto the paper surface, drying was carried out using a hot air dryer at temperatures between 100-150 °C which were adjusted according to coat weight, solids content and other parameter (see **Figure 7a**).

Sized paper or barrier properties of the materials depend on many parameters such as coat weight, drying regime, rheology of the formulations, penetration of the materials into the base paper and film formation, which are difficult to adjust on a drawdown coater. Therefore, another two lab application methods were also used and evaluated regarding their capacity to show a possible correlation of end product properties with process parameters that correspond to the industrial experience. A Sumet coater (Coating unit CU 5 - film press) was predominantly utilized for functional barrier coating of papers produced from either primary or secondary fibres (see **Figure 7b**). The process parameter such as speed and wet film thickness can be adjusted in a reliable and repeatable way and therefore industrial conditions can be simulated quite well in the laboratory allowing a faster scale-up of the processes. A further advantage of the Sumet coater is, that different drying regimes such as infrared (IR), hot air (HA) or simultaneously drying regime with both infra-red and hot air (IR+HA) can be applied. The effect of these drying regimes on barrier properties of chitosan-coated paper were studied and presented together with the measured mechanical properties in **Paper III**. A reel-to-reel laboratory film press (Dow® coating machine at the coating laboratory of Norske Skog, Bruck, Austria), which enables two-sided application of sizing or coating formulations, was used for the sizing trials with technical lignins (see **Figure 7c**). This machine operates at higher coating speeds (max. 20 m/min) and is typically considered as the last trial stage before going to an industrial pilot machine or directly to a paper or coating machine. In this case, the drying method for the surface sizing with lignin were both, infra-red and hot air drying.



(a) (b) (c)

Figure 7. Laboratory draw-down coater (a), Sumet coater (b) and laboratory film press (Dow) (c) used in the sizing and barrier coating trials.

2.2.2 Free-standing films and foils (Paper II)

In order to assess the specific film formation properties, physical properties and to estimate the potential of the material to be used as a barrier material, freestanding films were produced in the laboratory. This was the case for both alginate and chitosan, where the materials were dissolved in water and cast by pouring the aqueous solution in Petri dishes (Polystyrene, 145 mm x 20 mm with vents from Greiner Bio-One Hungary Kft, Hungary) (see **Figure 8ab**). The same type of raw materials described in section "Materials and Methods" of **Paper II** were used for casting of freestanding films. The solid contents of the aqueous chitosan and alginate solutions were 1 % (w/w). The alginate solution was prepared by dissolving alginate powder in distilled water at neutral pH, which was stirred at 400 rpm and heated at 60 °C for 4 hours. A chitosan solution for free-standings films with solid content of 1 % (w/w) was prepared by dissolving chitosan powder in heated acidified water ($pH \geq 4$) 60 °C and stirring for 4 hours at 400 rpm. The acidic pH of the water was reached by adding small portion of acetic acid (pure, technical grade from Rotipuran) prior to the dissolution process. After solubilisation of the material, the homogeneous solution was cooled to room temperature and subsequently poured into Petri dishes. Freestanding films were dried for 3 days at ambient temperature (23 °C).


(a) (b)

Figure 8. Freestanding film of chitosan (a) and alginate (b) produced using casting method.

2.2.3 Specific film density

As the density of the material is a key property regarding its barrier properties and permeability, the specific film density of free-standing films presented in **Figure 8** was determined experimentally using a “flotation” method at 23 °C. In accordance with the method (flotation) presented in literature tetrachloroethylene (C_2Cl_4, >99 % anhydrous, Thermo Fischer (Kandel) GmbH) with a density of 1.62 g/cm³ and n-heptane (C_7H_{16}, ≥99%, Rotipuran-Roth) with a density of 0.680 g/cm³ were used for the density measurements [117]. The film was cut in small pieces (1.5 x 1.5cm²), immersed in 10 ml n-heptane and the beaker with heptane and film was placed on an analytical balance. The burette (50 mL) was taken and filled with the tetrachloroethylene, which was added drop wise to the beaker containing the immersed film. Addition of the tetrachloroethylene occurred until the film started to float in the n-heptane/tetrachloroethylenes solution. Subsequently the amount of the tetrachloroethylene was recorded by both weight and volume, which was used for calculation of specific film density (g/cm³) according to **Equation 1** [118].

$$\textbf{Film Density}\ (\frac{\mathrm{g}}{\mathrm{cm}^3}) = \frac{(\mathbf{V}\mathrm{h} * \boldsymbol{\rho}\mathrm{h} + \mathbf{V}\mathrm{t} * \boldsymbol{\rho}\mathrm{t})}{\mathbf{V}\mathrm{h} + \mathbf{V}\mathrm{t}} \qquad \textbf{(1)}$$

- $\mathbf{V}\mathrm{h}$ – Volume of heptane in cm^3
- $\boldsymbol{\rho}\mathrm{h}$ – Density of heptane in $\frac{\mathrm{g}}{\mathrm{cm}^3}$
- $\mathbf{V}\mathrm{t}$ – Volume of tetrachloroethylen in cm^3
- $\boldsymbol{\rho}\mathrm{t}$ – Density of tetrachloroethylen in $\frac{\mathrm{g}}{\mathrm{cm}^3}$

2.2.4 Surface properties of treated papers (Paper I, II and III)

After the barrier coating or sizing trials the treated paper surface was visualized using scanning electron microscopy (SEM) in order to evaluate paper surface texture, the quality of the coating and the presence of pores and voids. In the case of surface sizing, the samples were analysed using the TM3030 Tabletop Microscope from HITACHI (SEM) as described in the "Experimental Section" of **Paper I**. The surface evaluation of barrier-coated papers was performed by low-voltage scanning electron microscopy (LVSEM, Everhart-Thornley detector for the detection of secondary electrons; Zeiss Sigma 300, as briefly described in "Material and Methods" section of **Paper II** and **III**. The quantification of the barrier layer thickness of the coatings was conducted using a rotary microtome coupled with a light microscope following a method developed at the Institute of Paper, Pulp and Fibre Technology at Graz University of Technology (**Figure 9**) [119,120].


(a) (b)

Figure 9. Microtome coupled with a light microscope for investigation of the paper cross section and exemplary cross section image of coated paper.

Combining the informations obtained from the cross section and surface evaluation enabled us to obtain a clear picture regarding surface closure, effectiveness and quality of surface treatment and the existence of pores and voids in the coatings. This approach was also used to establish the relation between the layer thickness and barrier properties.

2.2.5 Mechanical properties (Paper I and III)

The characterization of the papers sized with lignin or coated with bio-based barrier materials was performed in accordance with the standards and method given in the **Table 2**. The most important strength properties of packaging papers such as tensile strength, burst strength, short-span compression, bending stiffness and tensile energy absorption were assessed for the sized or coated paper. All measurements were performed in a climate room at the defined temperature of 23 °C and 50 % relative humidity in accordance with the standard EN ISO 187.

Table 2: Paper property, method and device and standards used for the physical characterization of the treated and untreated paper samples.

Paper property	Method and device	Standard
Grammage	balance	EN ISO 536
Thickness	LDAL 03 thickness tester	EN ISO 534
Density	calculation	EN ISO 534
Tensile strength	L&W tensile tester	EN ISO 1924-2
Tensile energy absorption	Zwick Z010	EN ISO 535
Burst strength	L&W burst strength tester	EN ISO 2758 and 2759
SCT (short span compression)	Zwick Z010 tester	T 826
Bending stiffness	Messmer/Büchel	ISO 2493-1

2.2.6 Gas permeability (Paper II, III and unpublished work)

Permeation and transmission of water vapour through packaging materials must be controlled in order to avoid the growth of microorganisms in packed food and loss of food quality. Pre-selection of suitable materials and consideration of the properties of food such as water loss or water uptake is required. The water vapour transmission rate (WVTR) is defined as the amount of water vapour that is transmitted through a unit area in a unit time under specified conditions. WVRT is a reliable measurement for packaging materials and is standardized according to ASTM, ISO, DIN and TAPPI [121,122]. Water vapour permeation mainly takes place in the amorphous region of the coated barrier films and of course at those parts of the film where pinholes, voids and cracks are noticeable. It can be noted from the literature that WVRT values of barrier-coated paperboard are increasing exponentially with the decreasing barrier film thickness [123]. Permeability of the gas is defined as a product of solubility in the barrier film and diffusion through the film. The proposed mechanisms for gas permeation (CO2, O2 or H2O) are given in **Figure 10**. A model for an ideal film without pinholes considers four main processes in gas permeation and these are: sorption-condensation, solubilization, diffusion and desorption of the gas molecules. The driving force for permeation is of course, the concentration gradient equivalent to the gas pressure of the gas molecule [124].

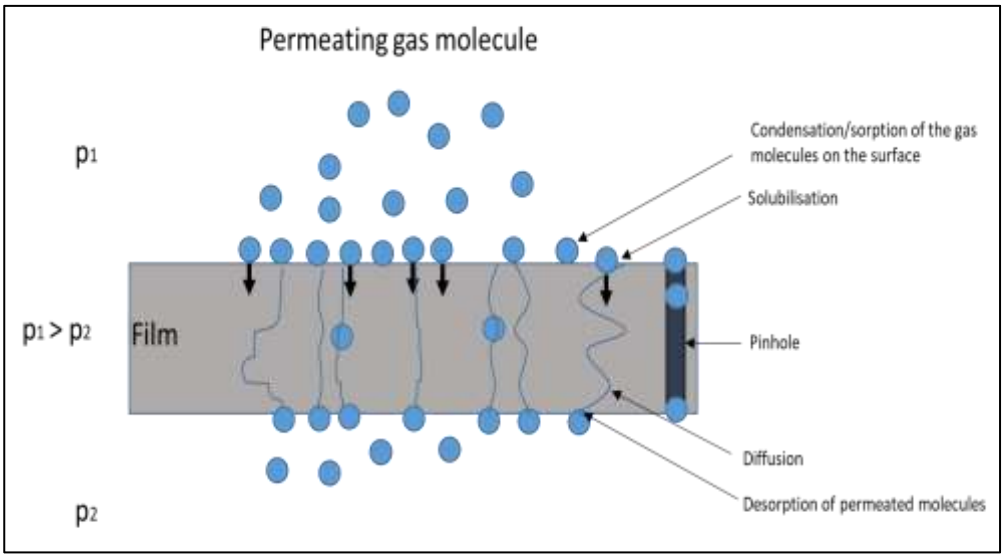
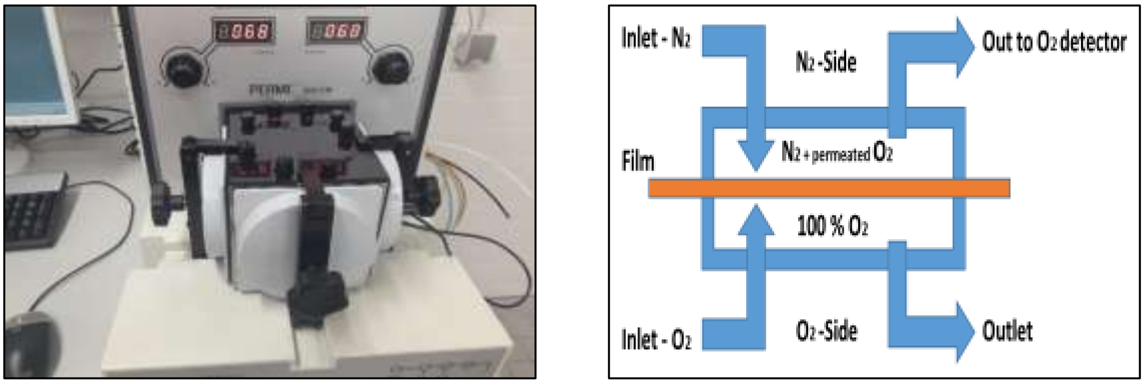


Figure 10. Schematic illustration of gas permeation through a barrier film with a pinhole [125].

Most synthetic and natural polymers are able to absorb some quantities of gas such as oxygen or water vapour depending on their surface chemistries and structures. Although oxygen permeability through polymer materials has been very well described, the measurement of oxygen transmission in practice is a difficult and tedious procedure requiring considerable practice and extensive knowledge of the measured barrier materials. The amount of oxygen in cubic centimetres that is transmitted per sample area in 24 hours is the standard quantification method. It is commonly quantified and given as the OTR (oxygen transmission rate) value (cm^3/m^2*day). Oxygen transmission measurement must be performed under controlled conditions such as pressure, relative humidly and temperature in dependence of the barrier material. Oxygen transmission varies with the temperature and relative humidity and also in dependence of a hydrophilic character of the barrier materials It increases exponentially with increased relative humidity [126-128]. The oxygen transmission of the films and papers in the work has been measured using a Labthink® Perme OX2/230 oxygen transmission rate test system in accordance with the ASTM D3985 standard (see **Figure 11**).



(a) (b)

Figure 11. Labthink® Perme OX2/230 used for measurement of oxygen transmission rates (a) and schematic principle of the oxygen transmission through the film taking place in the measuring chamber.

2.2.7 Grease resistance (Paper II and III)

As the chemical structure of the biopolymers showed potential to serve as a good grease and oil barrier, oil and grease resistance testing has also been carried out for the coated papers. Oil and grease resistant papers are usually produced using fluorochemicals, which are applied in surface treatment. The grease, fat and oil resistance of coated paper and board can be tested by different standardized methods. Well-established methods are TAPPI 454 and TAPPI 507, which use dyed testing substances such as vegetable or synthetic oils. A widely used and very popular method in the paper packaging industry is the KIT-test (TAPPI 559 cm-12), which is a very realistic method for the assessment of grease resistance. In this work grease, resistance was assessed using the KIT test with freshly prepared KIT solutions based on Castrol oil, n-hexane and toluene (see detailed description in "Materials and Methods" sections of **Paper II** and **III**). All of the methods are based on optical observation and require highly skilled personnel to be carried out satisfactorily [129-131].

2.2.8 Water resistance and surface hydrophobicity (Paper I, II and III)

Absorption of water by a paper surface is generally measured by means of the so-called Cobb test in accordance with the EN ISO 535. Depending on the intended application it can be evaluated after 30 s, 60 s or even 1800 seconds. It is defined as the amount of water absorbed over a standardized test area and given as gram of water absorbed per square meter of paper. The measurement has to be performed under controlled climatic conditions (23 °C and 50 % relative humidity) at atmospheric pressure. In addition to water uptake measurements, the wettability of the surface was analyzed by measuring the time dependent contact angle for 10, 30 or 60 seconds using deionized water using a FibroDat 1129 device as presented in the "Experimental" sections of **Paper I** and **II**.

2.2.9 Migration and permeation of organic compounds (Paper II)

One of the most important criteria for food packaging material produced from secondary fibers is to be free from potentially harmful organic compounds such as MOSH and MOAH, which might come as residues from the printing inks in recycled fibres [132]. In this work, the migration of mineral oils and barrier capacities of the alginate and chitosan coatings toward successful prevention of the organic volatile compounds to permeate through or migrate from the paper was measured. To assess the functional bio-based barriers state of the art analytical methods developed by the Institute of Analytical and Food Chemistry (ACFC) of Graz University of Technology were applied, which are based on gas and liquid chromatography coupled with flame ionization detection [133]. The analysis was performed using Tenax as a food simulant, which is able to adsorb the mineral oil fractions MOSH and MOAH. After adsorption of the organic residues, they were extracted, separated chromatographically and quantified by internal standards. Furthermore, the permeation was studied using a specially designed cell for one or two sided permeation of volatile active compounds (Migracell), thus also testing the potential of the barrier materials to serve as an aroma barrier (see **Figure 12**) [134].

(a) (b)

Figure 12. Permeation cell used for evaluation of barrier capacities against organic volatile compounds (a). Online chromatography (HPLC-GC-FID) measurement system used for separation and quantification of organic volatile compounds (b) [135].

3. Results and discussion

3.1 Technical lignins

3.1.1 Pre-treatment of technical lignins prior surface sizing: Isolation, purification and solubilisation in water (Paper I)

The starting materials provided by the industrial partners for the technical lignin trials were black liquor samples from the intermediate stage of the evaporation unit in an industrial pulping process. Lignin in its native form is a macromolecule and has a complex and variable structure, which is susceptible to structural modifications and degradation, which can be influenced by the chemicals and conditions of the pulping process. Depending on the cooking time and the process conditions, the degradation might be higher or lower. In black liquor, inorganic salts, various impurities as well as residues of cellulosic fibres can also be present and have to be removed prior to lignin sizing. Lignosulfonates are water soluble due to sulphuric groups and after ultrafiltration and concertation to the desired solids content, they can be used directly in surface sizing formulations [105-110]. The precipitated kraft lignins, however, have to be further treated in order to make them soluble in water. Due to its water insolubility at acidic pH value, kraft lignin can be easily precipitated using sulphuric acid and thus be successfully separated from the black liquor. As the precipitated lignin takes a solid form and cannot be dissolved at neutral or slightly alkaline conditions, it must be re-alkalized and solubilized in water using e.g.sodium hydroxide. In this work, the hysteresis of the kraft lignin solubility was utilized and the solubilization of the kraft lignin was improved under slightly alkaline conditions suitable for surface sizing of packaging paper using a film press [136]. The illustration in the **Figure 13** demonstrates the applied process for achieving improved kraft lignin water solubility. The kraft lignin in its H-form (protonated) is alkalized at a pH greater than 11. At this alkaline pH value, the kraft lignin is transformed into its water soluble Na-form. Subsequently the pH value again was reduced to a slightly alkaline region and kept constant prior to surface sizing.

Figure 13. Pre-treatment of precipitated Kraft lignin and adjustment of the pH value prior surface sizing using the film press.

3.1.2 Technical lignins as total or partial replacement for starch and synthetic surface sizing agents in surface sizing formulations (Paper I)

Isolated and purified lignins were used in varying proportions from 0 to 100% in mixtures with enzymatically converted starch in surface sizing formulation of packaging paper (see **Table 3**). The starch formulation containing the synthetic surface sizing agent Perglutin and the 100% starch formulation served as references for the lignin based formulations. The function of the starch is to improve the surface and bulk strength of the treated paper, but also is used to reduce dusting during production [137]. Perglutin is a synthetic sizing additive, acts as a hydrophobic agent and solely affects the water resistance and wettability of the paper [138]. The trial was designed with the target to evaluate the effect of technical lignins on paper strength, water absorption and wettability. On this basis the surface sizing trials with pure starch and pure lignin as well as starch with Perglutin and mixtures of the starch, kraft lignin and lignosulfate were prepared and tested. Regarding coatability and miscibility of the formulation components technical lignins had a similar performance as starch. Thus from a technological perspective, the application technology used for starch (film press) can also be used for the the technical lignins.

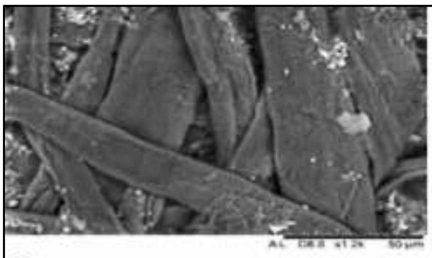
Table 3. Starch and lignin based surface sizing formulations with measured solid content, pH, and viscosity used for assessment of the lignin contributions to both hydrophobicity and paper strength.

Formulation number	Surface sizing formulation	Weight percentage [%]	Solid content [%]	pH value	BF- viscosity 100 rpm [mPa.s]
1	Starch	100	17.6	7.1	57.2
2	Starch + Perglutin	97 + 3	17.6	4.3	52.4
3	Lignosulfonate	100	12.4	9.6	20.0
4	Lignosulfonate + Starch	50 + 50	12.4	9.3	23.8
5	Kraft lignin	100	17.5	8.8	33.2
6	Kraft lignin + Starch	50 + 50	17.3	9.0	43.0

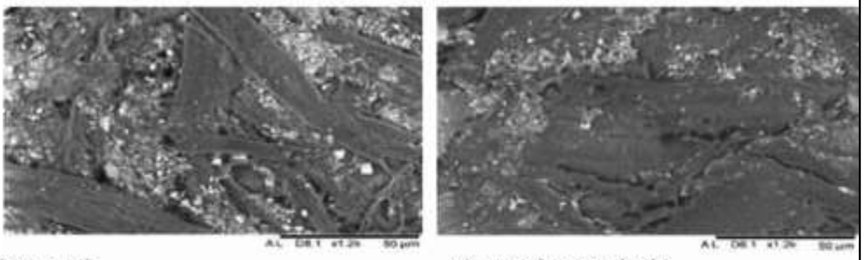
The desired pick-up weight in the coating trials was 6 g/m². In order to reach desired pick-up weight several factors such as substrate roughness, absorptiveness, solid content, viscosity and temperature of the formulation must be tested prior to surface treatment. Taking into account all those parameters, pre-trials were performed and, depending on the results, the basic parameters of the formulations were adjusted. The results of the pre-trials indicated that for lignosulfonate based formulations lower solid contents were needed to achieve 6 g/cm² compared to other surface sizing formulations (see **Table 3**). The detailed description of the surface sizing parameters and the surface sizing apparatus is presented in the "Experimental" section of **Paper I**.

3.1.3 Effects of technical lignins on paper surface (Paper I)

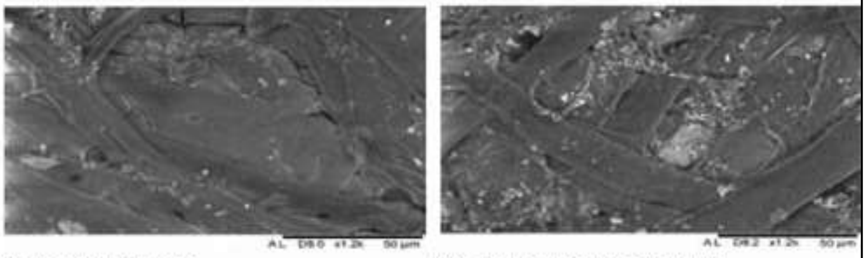
The raw paper was surface sized in a laboratory film press with the formulations given in **Table 3** on both sides and total pick-up weight was 6 g/m² for each sample. From the SEM images, (see **Figure 14**) it is evident, that both types of technical lignins as well as starch based formulations were able to fill the surface voids and pores of the paper. In general, all applied surface sizing formulations covered the paper surface well and filled the pores and voids which are clearly visible when compared to raw (unsized) paper. Some indication for film formation on the surface is visible for pure lignosulfonate and kraft lignin, where the fibers seem to be almost completely covered with the surface-sizing formulations. Although the viscosity of the lignins is lower compared to starch, retention of the lignin on the surface appears to be better compared to that of starch based formulations.



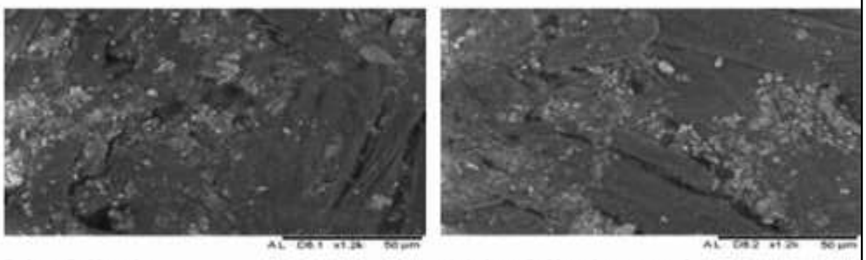
(a) raw paper



(b) starch c) starch+perglutin



(d) lignosulfonate (e) lignosulfonate+starch



(f) kraft lignin (g) kraft lignin+starch

Figure 14. SEM images of raw paper and surface-sized papers.

Due to the good coverage of the substrate, the air permeability decreased for all surface sized papers which is in correlation with the SEM images of the raw and sized papers (see **Figure 15**).

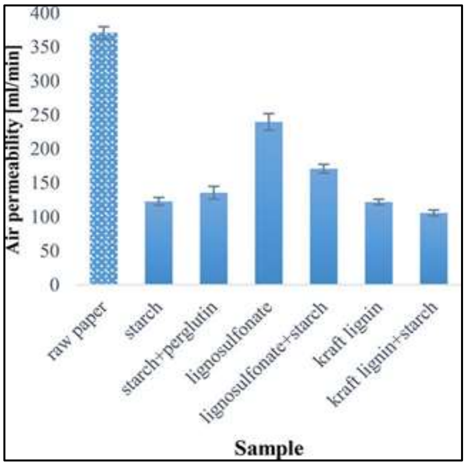
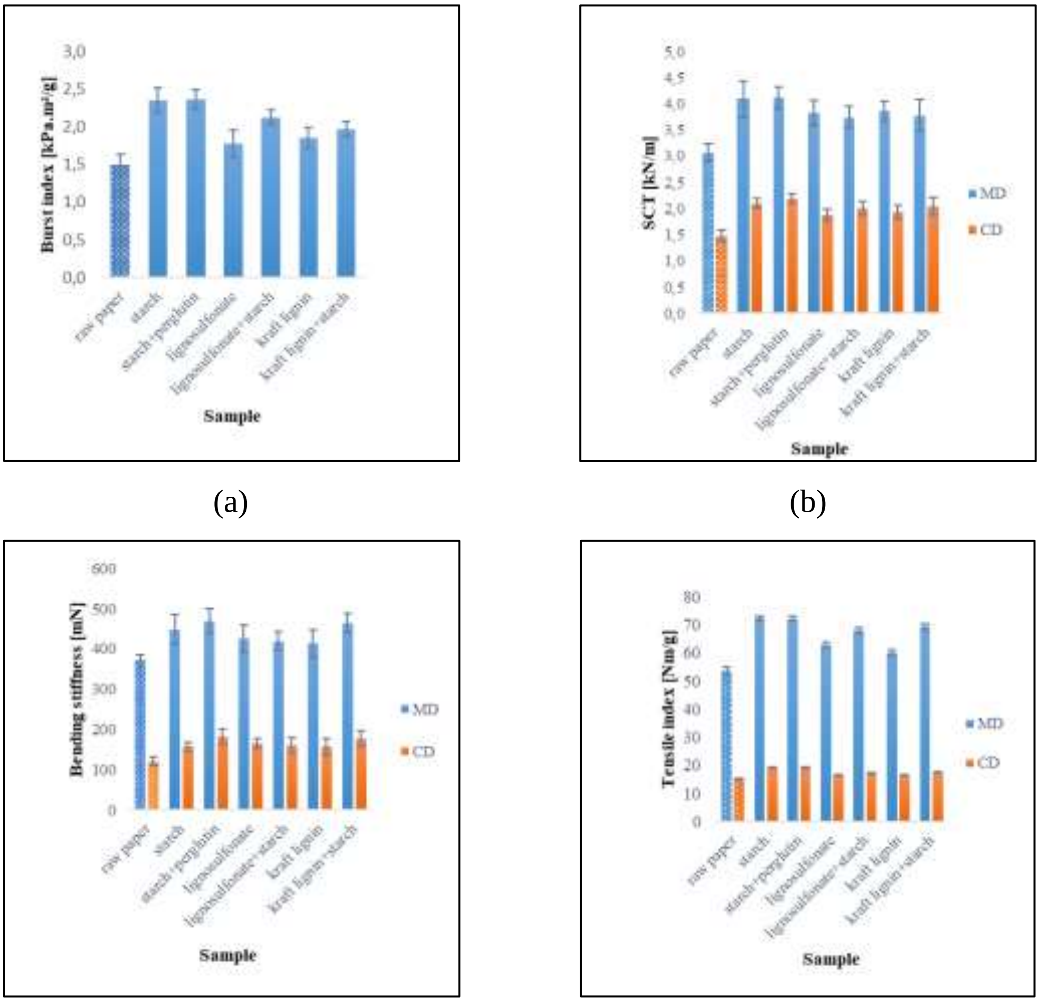


Figure 15. Air permeability of the raw paper and papers treated with the starch and lignin based surface sizing formulations.

The lowest air permeability values were achieved with the kraft lignin and starch based formulations and this correlates well with the measured molecular weights, as the kraft lignin (Mw=3193g/mol) had an average molecular weight 5 times lower than that of lignosulfonates (Mw=16830 g/mol) (see **Figure 15**). A more detailed discussion of the surface analysis as well as correspondence to average molecular weights of lignin is presented in the "Results and Discussion" section of **Paper I**.

3.1.4 Effects of technical lignins in surface sizing formulations on mechanical properties (Paper I)

An ideal surface sizing formulation should reduce the wettability and water absorption of the treated raw paper and contribute to the development of strength. In industrial practice, surface sizing starches are mixed with a synthetic surface sizing agent and this mixture should ensure both surface hydrophobicity plus good strength properties. The mechanical properties of the unsized and sized paper were quantified by determination of the burst and tensile indices, SCT and bending stiffness (see **Figure 16**). It is noticeable that the paper sized with starch shows the expected good mechanical properties. When it comes to comparison of lignin and starch based formulations, starch sized paper manifest slightly higher values of SCT, bending stiffness and tensile index. Nevertheless, the measured mechanical properties indicate that both technical lignins are able to contribute to mechanical properties and significantly improve paper strength in comparison to unsized raw paper. (see **Figure 16**)



(a) (b)

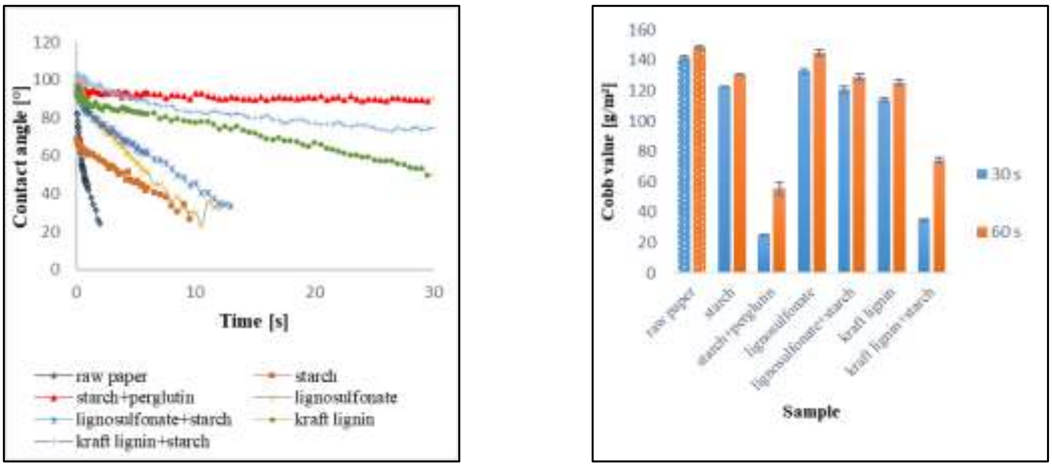
(c) (d)

Figure 16: Mechanical properties of the raw paper and paper sized with technical lignins and starch based formulations: (a) Burst index; (b) SCT; (c) bending stiffness; (d) tensile index.

An increase of at least 10 % in strength values is achieved by applying both starch or lignin based formulations compared to raw paper, which should be sufficient for the most of applications where recycled paperboard is utilized as a packaging material. (for more details see **Paper I**)

3.1.5 Effects of technical lignins on water uptake and wettability (Paper I)

The contact angle measurements indicated that the paper surface was hydrophobized using the technical lignins compared to the 100% starch formulation, with the best performance for the formulations containing kraft lignin (see **Figure 17a**). The performance of the starch+perglutin formulation (reference) has not been reached, however improvements compared to the unsized raw paper and to paper sized with 100% starch were achieved. In this context, it is interesting to note that the 50/50 blend of kraft lignin and starch changed the surface chemistry dramatically and showed higher contact angles than the pure kraft lignin formulation as well as the best performance when it comes to the reduction of water uptake (see **Figure 16b**). A similar performance – but on a lower level of contact angles – was observed for the lignosulfonates indicating a synergistic effect of technical lignins and starch.



(a) (b)

Figure 17. Contact angles (a) and Cobb values (30s and 60s) (b) of unsized and surface-sized papers measured with deionized water.

The contact angles and water absorption values correlate for some materials and this can be clearly seen for the starch+perglutin formulation. Nevertheless, this correlation is not always straightforward as can be seen from **Figure 17ab** especially for the pure starch formulation in comparison to the formulations containing technical lignins. For a material such as paper in particular, both measurements are required in order to see the effects of the surface sizing formulation on the substrate properties. (see “Results and Discussion” of **Paper I**)

3.1.6 Achieved surface sizing effects of technical lignins (Paper I)

Since technical lignins can contribute to both the development of the surface hydrophobicity and better strength properties, they might be considered as potentially interesting materials for an at least partial replacement of starch and conventional synthetic surface sizing agents. Lignin possesses both hydrophilic and hydrophobic properties and has a different interaction with the cellulosic fibers compared to starch or conventional surface sizing agents. Depending on the final application requirements, the water absorption might be optimized to a level of Cobb 60s < 50 g/m² and further improvement could be achieved by adjustment of the substrate properties and additional optimization of the formulation properties, which is currently evaluated.

3.2 Barrier materials

3.2.1 Application of chitosan and alginate and their interaction with the substrate (Paper II)

Chitosan and alginate are both hydrophilic biopolymers and water soluble at standard conditions. The hydrophilicity of the alginate film can be influenced and improved in the direction of achieving higher water resistance depending on the quantities of ammnuronic and guluronic acids and their ratios [139]. The solubility of chitosan depends largely on the pH value, the solubilisation conditions (e.g. temperature, time or shear rate) and the specific material properties such as crystallinity, molecular weight and deacetylation [140-142]. Good water solubility is an essential requirement for the application of these biopolymers in functional barrier coatings for packaging papers using a film or a size press. Both materials have a shear thinning rheological behaviour, which is required regarding coatability using the above mentioned applications processes [143, 144]. Both materials exhibit a high viscosity described in the “Materials and Methods” sections of **Paper II** and **III**. Due to this high viscosity and tendency to form a gel at solid contents > 10 % (w/w) the maximal solid content for both materials used in this work is 4 to 5 % (w/w). Chitosan and alginate were both dissolved in aqueous solvent systems, under conditions found in the literature and described in detail in **Paper II**. The solutions of these materials were applied on two different base paper grades made of primary fibres (PF) and secondary fibres (SF) respectively (see **Table 1**). Due to the low achievable solid contents of 5 % (w/w), two coating layers were needed to reach the target coat weight of 6 g/m². For the characterization of barrier properties, only samples with a coat weight of 6.0 ± 0.3 g/m² were selected for characterisation. (see **Table 4**).

Table 4. Thickness, density, grammage and coat weights of chitosan and alginate coated papers made of primary (PF) and secondary (SF) fibres.

Sample	Thickness [µm]	Density [g/cm³]	Grammage [g/m²]	Coat weight [g/m²]
PF uncoated	96.0 ±1.2	0.760 ± 0.01	72.0 ± 0.5	0
SF uncoated	197.0 ± 2.6	0.660 ± 0.01	129.0 ±0.6	0
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

A noticeable increase in the density of the coated samples compared to the uncoated samples indicated the creation of a denser paper-barrier material composite network, which is beneficial for barrier properties. The air permeability of all samples dropped to 0 ml/min after coating partially due to the density increase and serves as an indication of the creation of an impermeable coating layer (see **Figure 18**).

3.2.2 Film formation properties, tightness of chitosan and alginate films and their effects on grease resistance (Paper II and unpublished work)

Air permeability may correlate with the grease resistance of the coated packaging material [145] and for this reason it was plotted against grease resistance (KIT number), in order to assess the possible relation between these two measurements (see **Figure 18**). According to our investigation, the KIT value improved with chitosan and alginate coating for both substrates, however does not necessarily correlate well with the air permeability. The reason is different surface chemistry of the coated papers, which is despite closure of the paper surface crucial for the grease resistance.

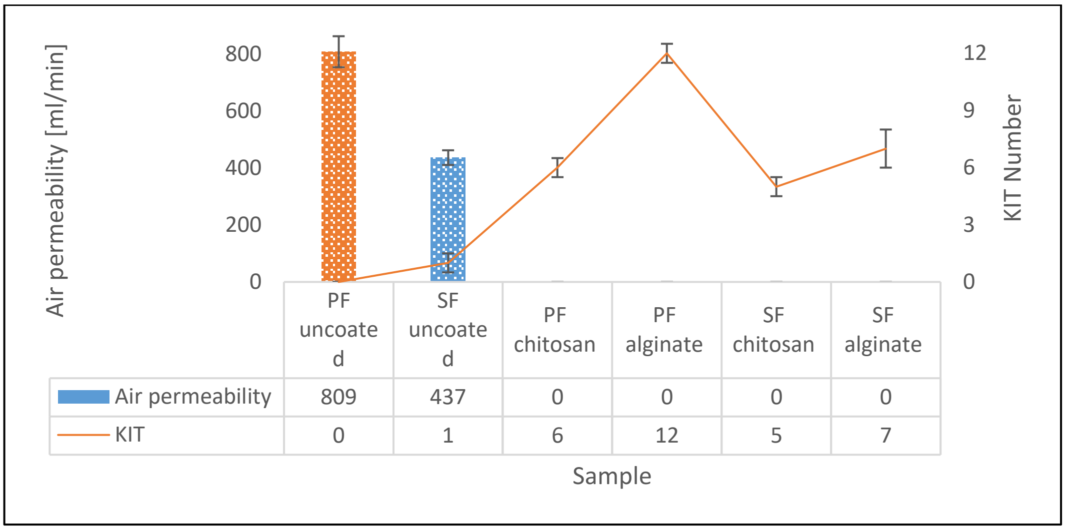
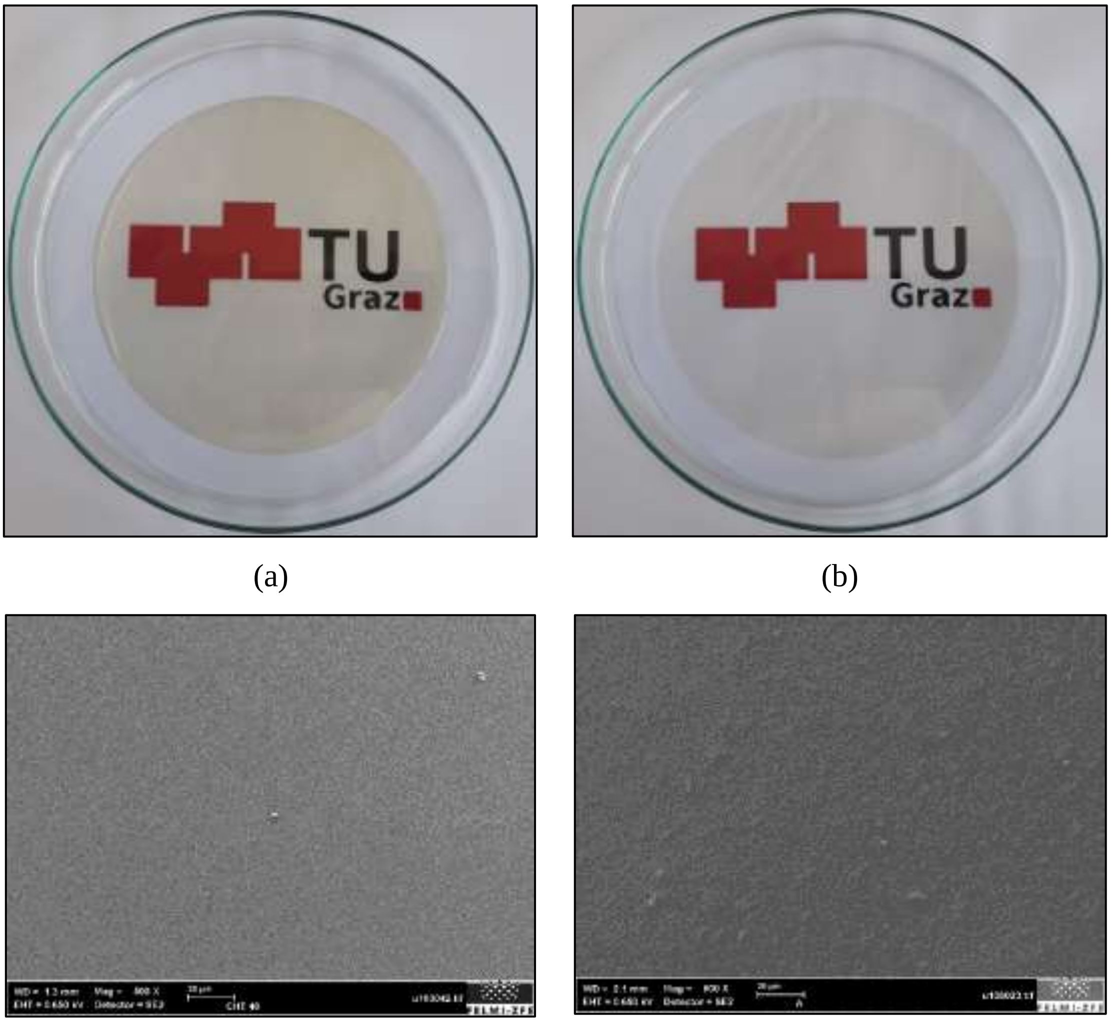


Figure 18. Air-permeability and grease-resistance values (KIT test) for uncoated and coated primary-fiber (PF) and secondary-fiber (SF) paper.

In order to assess the potential of the biopolymers for barrier coating applications prior to paper coating trials, free standing films made from pure alginate and chitosan were casted and tested regarding their physical properties such as density or gas permeability (see **Figure 18ab**). The results were compared to the results obtained in the paper coating trials. Both biopolymers showed excellent film forming properties resulting in homogeneous films. According to density measurements performed using the free-standing films and the flotation method described in chapter 2.x?, the alginate film had a specific density of 1.59 g/cm^3 and the chitosan film of 1.47 g/m^2, which is higher than most of the conventional barrier materials such as PET (1.38 g/m^2), LDPE (0.92 g/cm^3), HDPE (0.94 g/cm^3) or EVOH (1.20 g/cm^3) [146-148].

The surface of the film was evaluated using SEM and showed to be homogenous without pores (see **Figure 18cd**). Furthermore the measured oxygen transmission rate of the cast chitosan and alginate films with a thickness of 30 µm were 49.6 ± 3.8 and 9.85 ± 3.4 cm^3/m^2*24 h respectively. An oxygen transmission rate below 100 cm^3/m^2*24h is considered to be a sufficient barrier for food packaging and both films with thicknesses of 30 µm and OTR < 100 cm^3/m^2*24h can therefore be considered as good to excellent oxygen barriers [149,150].



(a) (b)

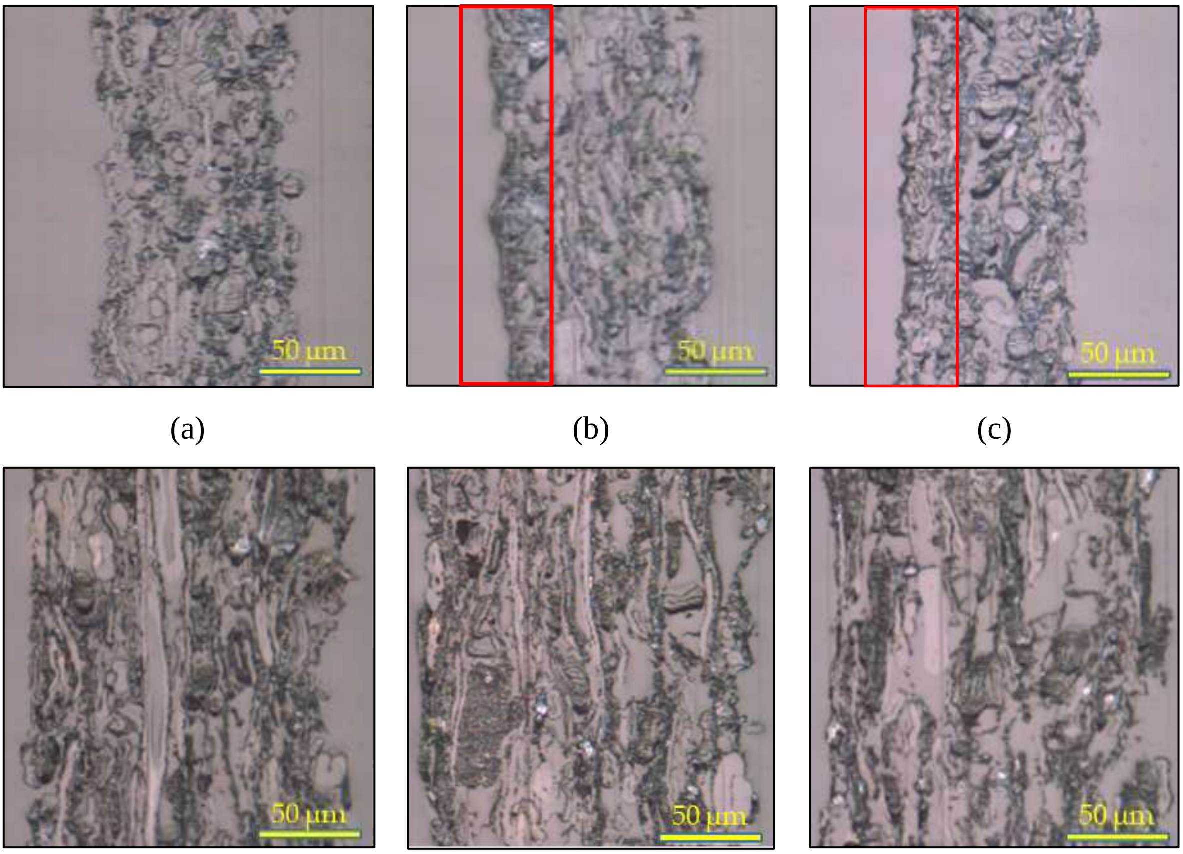
(c) (d)

Figure 18. Free-standing chitosan (a) and alginate (b) films produced in the laboratory under standard conditions using the casting method and used for measurement of film density and oxygen transmission.

3.2.3 Barrier layer formation and interaction of barrier coatings with the base paper substrates (Paper II and unpublished work)

As the thickness of the barrier correlates to both the barrier performance and the package costs, it was crucial to examine the paper cross sections and to evaluate the barrier film layer thickness as well. In addition to this, it was also important to see, whether the formation of a biopolymer film on the paper surface is a prerequisite for good barrier performance, when different base paper grades are used.

The cross sections of the alginate and chitosan coated papers showed clear film formation when the PF base paper was used (see **Figure 19a-c**). The reason for this was, that this base paper was mass sized using a synthetic sizing agent (ASA). The Bendtsen roughness of the PF base paper was 150 ± 26 ml/min and thus more than eight times lower compared to the SF base paper (1271 ± 211 ml/min). In the cross sections the SF base paper showed to be fully impregnated and a clear film layer could not be detected in this optical microscopy based method (see **Figure 19d-f**).

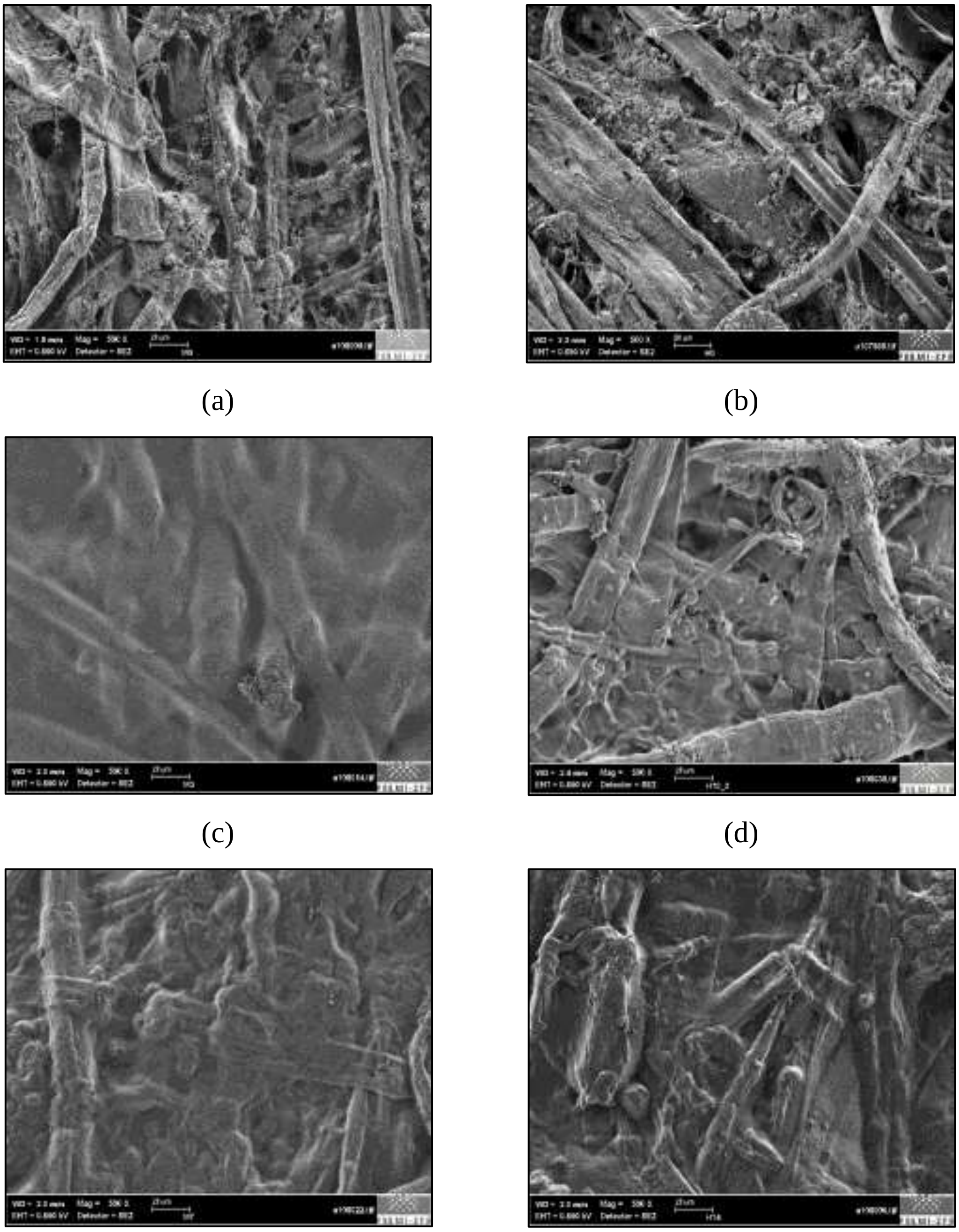


(a) (b) (c)

(d) (e) (f)

Figures 19. Cross-sections of the uncoated and coated paper with visible coatings layers (red frame): (a) primary fibres-uncoated; (b) primary fibres-chitosan; (c) primary fibres-alginate; (d) secondary fibres-uncoated; (e) secondary fibres-chitosan; (f) secondary fibres-alginate.

These results from the paper cross section analysis are in accordance with the observations from the SEM analysis, where the PF base paper coated with chitosan appears fully covered and film formation is clearly observed (see **Figure 20a-f**).



(a) (b)

(c) (d)

(e) (f)

Figure 20. Scanning electron microscopy (SEM) images of uncoated and coated paper substrates at 500× magnification: (a) primary-fibre (PF) uncoated paper; (b) secondary-fibre (SF) uncoated paper; (c) chitosan-coated PF paper; (d) chitosan-coated SF paper; (e) alginate-coated PF paper; (f) alginate-coated SF paper.

For the alginate coated PF base paper, some film formation is also visible but not to the same extent as for the chitosan-coated paper produced from primary fibres. The reason for this observation is most likely the viscosity of these two materials. At the same solid content and a temperature of 23 °C, the Brookfield 50 viscosity of the chitosan (2911 mPa.s ± 57) is at least 50 % higher compared to alginate (1448 mPa.s ± 20) (see “Materials and Methods” section of

Paper II). Therefore, the retention of chitosan on the paper surface is higher compared to that of alginate under the same coating conditions as less penetration into the base paper occurs.

In the SEM images of the coated SF papers, no clear and measurable film formation was observed which correlates to the results obtained from the paper cross sections using light microscopy. The fibres are covered, voids and pores well filled, but the material penetrates rapidly into the paper structure and as a result, film formation on the paper surface is less pronounced.

The penetration into the base paper was calculated using a method described by Guillaume et al. [60]. The calculation of the penetration **(i)** and a maximum film layer thickness **(ii)** is based on the film layer thickness measured from the cross sections using the light microscopy method **(iii)**, the measured specific film density ρ **(iv)** and the applied coat weight (CW) **(v).** An exemplary calculation for the penetration of chitosan into PF base paper is demonstrated here*:*

(i) $\text{Penetration} = 100 * \left[1 - \left(\frac{3.47\mu\text{m}}{4.09\mu\text{m}}\right)\right] = 15.1\ \%$

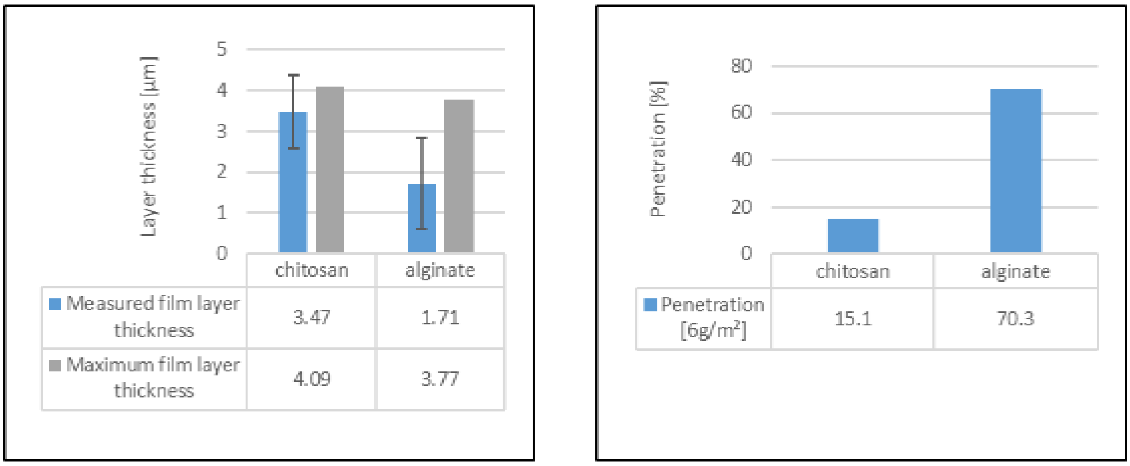
(ii) $\text{Maximum film layer thickness} = \frac{\text{CW}[\frac{\text{kg}}{\text{m}^2}]}{\rho\ [\frac{\text{kg}}{\text{m}^3}]} = 4.09\ \mu\text{m}$

(iii) $\text{Measured film layer thickness} = 3.47\ \mu\text{m}$

(iv) $\text{Film density } (\rho)\ = 1470\,\frac{\text{kg}}{\text{m}^3}$

(v) $\text{Coat weight (CW)} = 6.0\,\frac{\text{g}}{\text{m}^2}$

The thicknesses of the alginate and chitosan layer on the paper surface were measured using a method described in the literature [119-120] and compared to, the maximum film layer thickness, which was calculated by dividing the coat weight by the specific film density (see **Figure 21a**) [60]. The calculated results for the penetration of the alginate (70%) and chitosan (15%) agree well with the observations from the SEM images (see **Figure 21b.**).

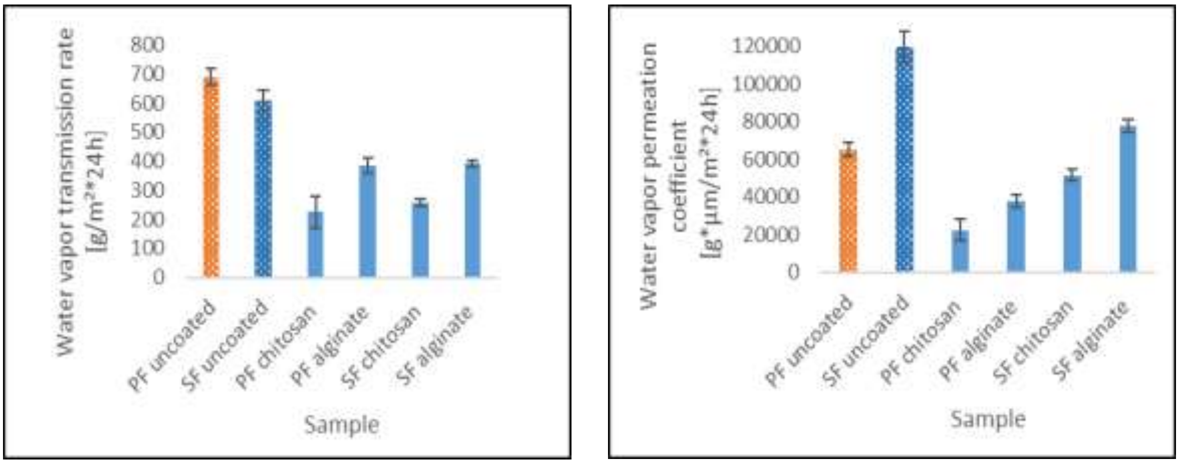


(a) (b)

Figure 21. Experimentally determined (blue) and theoretically calculated (grey) maximum film-layer thickness (a) and penetrations of chitosan and alginate into the PF base paper (b).

3.2.4 Effects of chitosan and alginate on wettability, water vapour transmission and water absorption (Paper II)

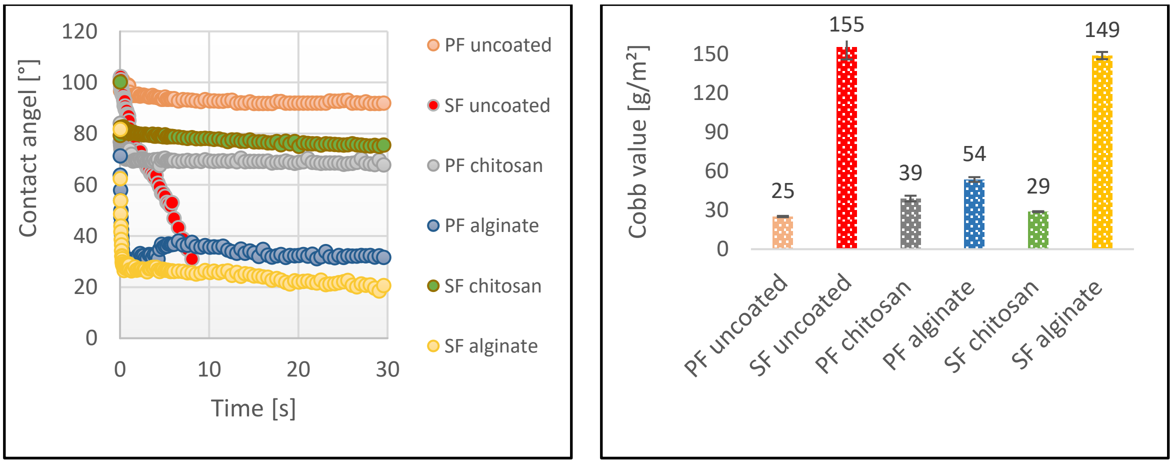
Both biopolymers were able to reduce the water vapour transmission significantly (see **Figure 22**). Due to good film formation properties and the ability to impregnate the paper the gas transport through the coated paper is reduced compared to raw paper. In this context chitosan performed better than alginate as it is reported that chitosan can have a slightly hydrophobic character under appropriate conditions such as a pH higher than 7 [140-142, 144]. Considering the lack of film formation for the coatings on the SF base papers and the reduced water vapour transmission rate, a logical conclusion could be that film formation on the paper surface is not required and even for a paper impregnated with the biopolymers a barrier against water vapour can be achieved.



(a) (b)

Figure 22. Water-vapour transmission rates (a) and water-vapour permeation coefficients (b) for uncoated and coated paper samples made from primary (PF) and secondary fibres (SF).

According to the wettability measurements (contact angle), coating with alginate and chitosan changed the surface chemistry for both the PF and SF substrates (**see Figure 23a**). The uncoated PF base paper was already quite hydrophobic due to mass sizing with ASA, whereas the uncoated SF base paper was unsized and quite hydrophilic. After coating the biopolymers became the dominant factor regarding wettability, leading to the effect that the PF paper became slightly more hydrophilic after coating with chitosan and significantly more hydrophilic for the alginate. For the SF base paper the coated paper surface became significantly more hydrophobic after coating with chitosan while the effect of the alginate was far less pronounced.



(a) (b)

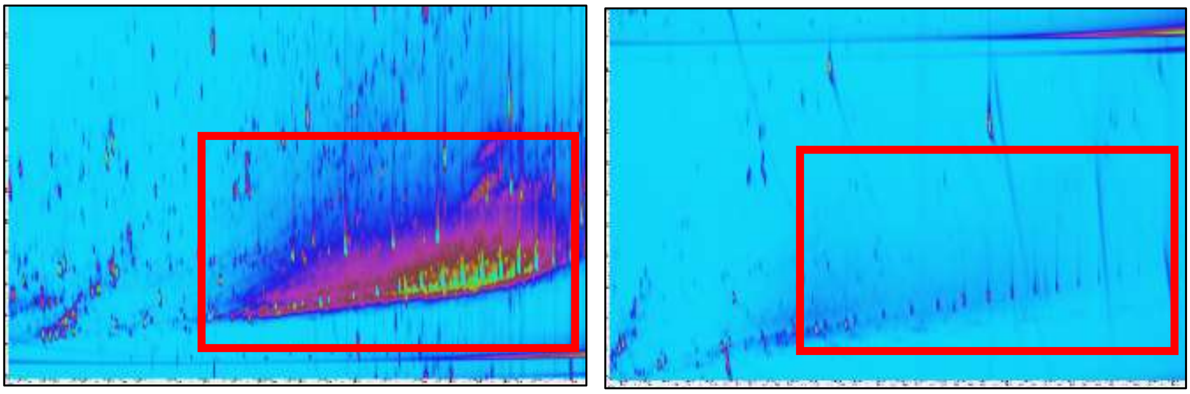
Figure 23. Wettability (a) and water resistance-Cobb (b) of uncoated and with alginate and chitosan coated secondary and primary fibres.

Chitosan is as weak base and depending on degree of deacetylation (DD) it can be dissolved in water between pH 4 (DD > 85%) and pH 9 (DD ≤ 40%). Thus, at high degrees of acetylation it can exhibit an “hydrophobic” character and become insoluble in water at neutral pH value. As the chitosan solution used for coating trials is acidic and the secondary fibers of SF substrate are untreated and fully available to positively charged chitosan, an intense interaction can take a place between the fibres and chitosan. Furthermore, after application of chitosan onto secondary fibres, pH might be shifted to the alkaline region at which chitosan shows a more hydrophobic character (see “Results and Discussion” section of **Paper II**). This finding is in accordance with the literature and it is confirmed by the experimental results of water absorption tests (Cobb 60 seconds in **Figure 23b**) [151,152]. The Cobb values of the primary fibres coated with alginate and chitosan decreased and with secondary fibres coated with chitosan, the Cobb was significantly improved and reduced from 155 to 29 g/m².

3.2.5 Effects of chitosan and alginates on migration and permeation of organic volatile compounds (Paper II)

As chitosan and alginate both have high densities and are relatively hydrophilic rather than hydrophobic in character, the sorption and solubility of the volatile organic compounds in the chitosan and alginate layers is limited. Secondly, both polymeric materials are able to impregnate the paper and to close the surface without visible pinholes. Thus the permeation process of organic compounds in accordance with the general model shown in **Figure 8** is reduced.

This was experimentally confirmed by analysing the migration of mineral oil fractions (mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH)) at the Institute of Analytical Chemistry and Food Chemistry at Graz University of Technology. By coating the SF base paper with alginate the overall migration was successfully reduced by 84% and by coating with chitosan by 71% compared to the uncoated SF paper (for details see **Paper II**). Again, it can be seen from the MOSH and MOAH migration studies, that film formation does not seem to be required and impregnation of the base paper with the biopolymer (in this case the alginate) is sufficient to improve the barrier properties. Thus by impregnation of the SF-substrate with the two biopolymers, the migration of the saturated and aromatic hydrocarbons could be reduced to an acceptable level (see **Figure 24a-b**).



(a) (b)

Figure 24. Chromatogram representing the uncoated SF base paper (a) and SF base paper coated with alginate (b). The framed region in figure (a) indicates the MOSH and MOAH fractions, which is hardly visible after coating with alginate, thus that alginate acts as a barrier against the volatile fractions of the mineral oils [133].

Furthermore, the permeation of odour active compounds can be reduced by up to 50 % with both materials depending on the volatility and quantity of carbon atoms in each odour active compound. A general trend was observed that compounds with a lower number of carbons permeate as expected faster and in a greater amounts than those with a carbon number >14 (see “Results and discussion” section of **Paper II**).

3.2.6 Effect of drying regime on barrier and mechanical properties of chitosan coated paper (Paper III)

The barrier coating process of fibre-based material usually consists of three steps: applying a surplus of the coating formulations to the substrate, metering the coating (wet-film thickness) and drying the coating. The aim of drying is to remove the excess water and to immobilize the coating layer on the substrate surface. Drying plays a crucial role regarding the dewatering of coating formulations and the film formation [153]. As chitosan showed a positive influence on the barrier properties in the draw down coater trials, it was necessary to upscale the trials using a Sumet coater and to study the influence of drying and coat weight on coated paper properties. The trial with industrially produced chitosan was designed with the aim of determining, whether chitosan can sustain the different drying regimes, which are used in the paper based packaging industry (see **Table 4**.). Drying plays an important role in functionalization of the paper surface and it must be considered in particular in the context of linking the material functionality and the process relevant parameters. A coating layer is usually successfully dried, when the material is dry to the touch, with the result that smooth running occurs and no sticking to parts of the coating machine takes place.

Table 4. Design of the coating trial with defined wet layer thickness and number of layers, drying regimes and coat weights. Trials 1, 2 and 3 were coated with one layer of chitosan and trials 4, 5 and 6 with two chitosan layers.

Trial	Wet Layer Thickness [µm]	Number of Layers	Drying Regime	Drying Time [s]	Dry Coat Weights [g/m³]
1	60	1	IR + Hot air	4+120	3 g/m^2
2	60	1	IR	4	
3	60	1	Hot air	120	
4	60	2	IR + Hot air	4+120	6 g/m^2
5	60	2	IR	4	
6	60	2	Hot air	120	

In practice, there are many ways to remove the excess water from the coating formulation. In the case of coated papers contactless drying methods have to be used., In industry, IR-dryers or hot air dryers are used to dry coated paper. Depending on the machine design and final application, different types of dryer units or combinations of these units are possible. Excessive or incorrect use of drying units can lead to the creation of the pinholes or degradation of the coating material, resulting in the loss of its final function. Thus, drying plays an important role regarding the application of natural barrier materials such as chitosan.

Figure 25. Drying section of the Sumet coater with 3xIR and hot air emitters.

The drying methods used in the coating industry have been tested for coatings containing synthetic polymeric chemicals, such as e.g. styrene-butadiene or styrene-acrylate latices in pigment coatings. The influence of different drying methods on the functionalities of barrier biopolymers still have to be further studied and if necessary optimized. Some studies have reported that drying might have some influence on the barrier or strength properties of biomaterials, but these studies have mostly been performed with free standing films, where the films were dried at different temperatures and the barrier or the mechanical properties were subsequently evaluated [154-156].

3.2.7 Impact of drying methods and number of chitosan coating layers on paper surface (Paper III)

The drying energy input for the three applied drying methods infrared (IR), hot air (HA) and simultaneous drying of infrared and hot air (IR+HA) are different. Thus, the retention of chitosan on the paper surface varies and is strongly dependent on the drying time. From the SEM images it can be seen that one layer of chitosan is not sufficient to fully cover the paper surface irrespective of the drying methods used (see **Figure 26a, b, d, f**). With two layers of chitosan, film formation has taken place and the paper surface is fully covered (see **Figure 26c, e, g**).

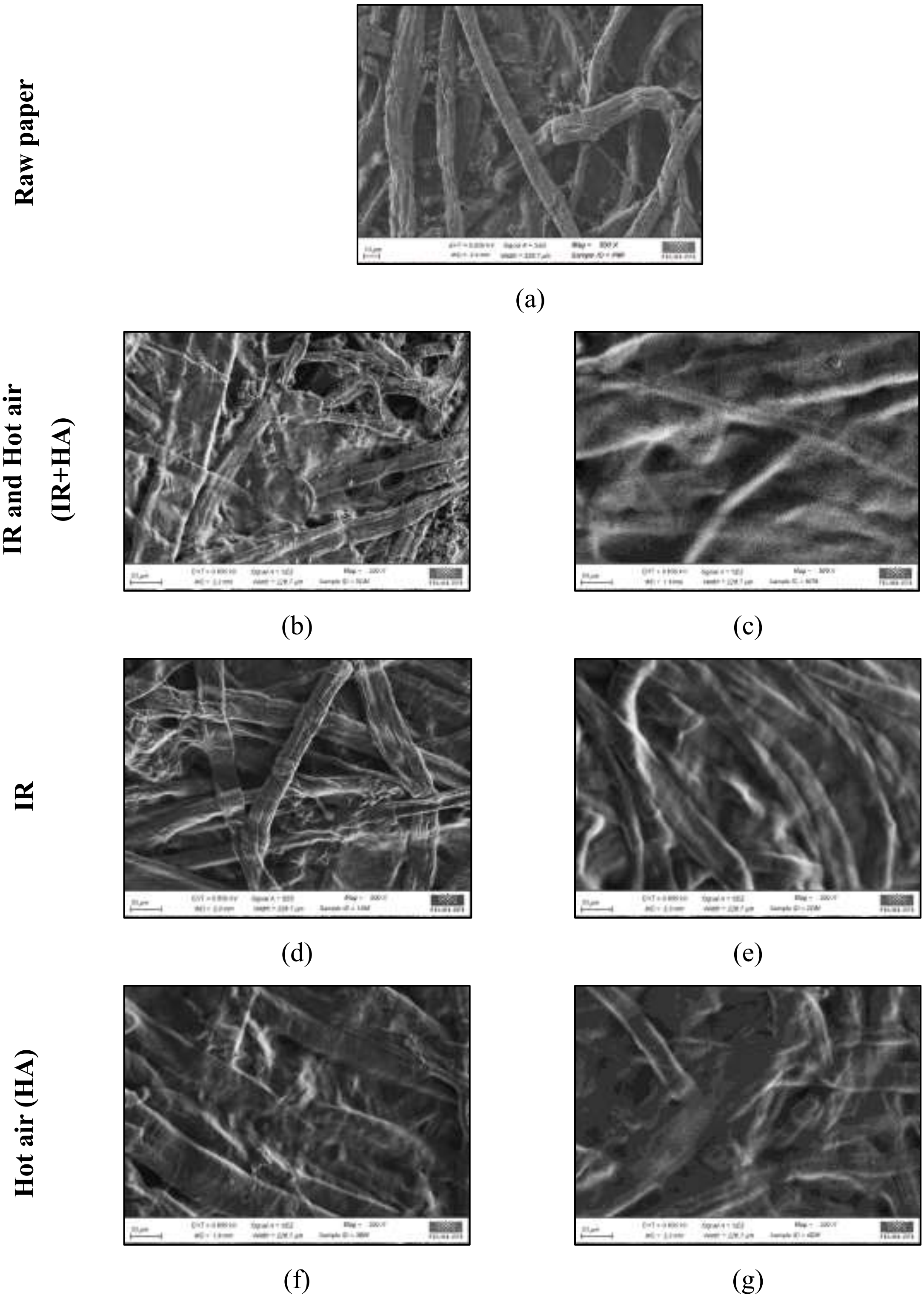
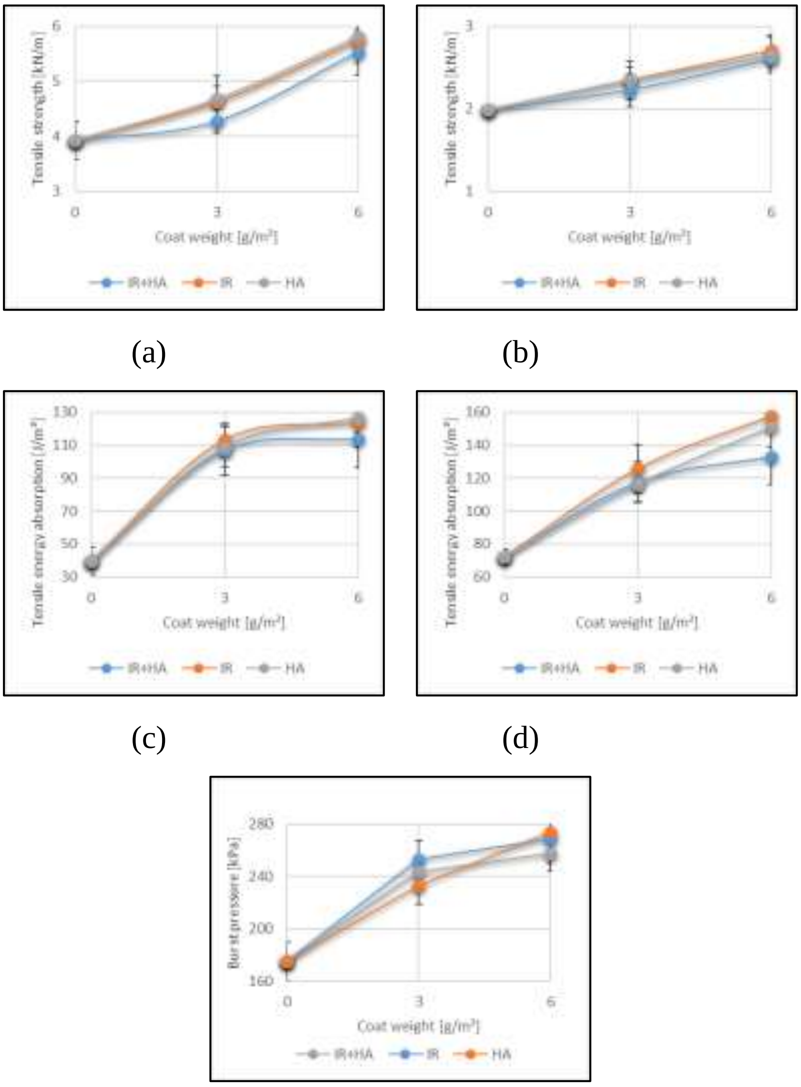


Figure 26. SEM images of uncoated raw paper and chitosan-coated samples dried using various methods: (a) Raw paper; (b) IR + Hot air (1 layer); (c) IR+Hot air (2 layers); (d) IR (1 layer); (e) IR (2 layers); (f) Hot air (1 layer); (g) Hot air (2 layers).

Given these observations, the investigation of the mechanical properties in paper coated with one and two chitosan layers was a matter of interest. Penetration of applied strength enhancing materials into the paper structure is required for the mechanical strength of the paper, in order to create larger bonding areas or more bonds between fibers. Enhanced penetration is thus a requirement for achieving improved paper strength. On the other hand, film formation is not always necessary, but it is certainly beneficial for the barrier properties (see **Paper II**).

3.2.8 Effects of drying and coated chitosan layers on mechanical properties of the paper (Paper III)

Due to intense interaction of cationic chitosan and anionic fibres the formation of new bonds results in an improvement of the tensile strength, tensile energy absorption and burst pressure. These are among the most important strength properties for packaging papers and the strength was increased already by at least 10 % by the use of only one chitosan layer (see **Figure 27a-e**.).



(a) (b)

(c) (d)

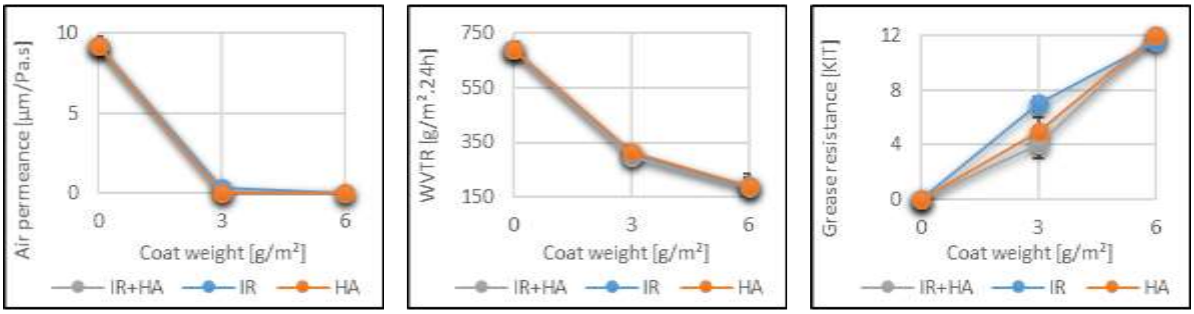
(e)

Figure 27. Mechanical properties of uncoated and chitosan coated paper dried with IR, HA, and IR+HA: Tensile strength in MD (a) and CD (b); Tensile energy absorption in MD (a) and CD (b); burst strength (e).

According to statistical analysis (ANOVA) there are no significant differences between the three drying regimes, meaning that irrespective of the drying method chitosan can contribute positively to the development of strength properties. This trend is also observed for two layers of chitosan, where the increase is greater compared to that for one single chitosan layer as the amount of chitosan in relation to the paper mass was increased from 4 to 8%. While the topography of the sample varies as a result of the different drying methods, there is no statistically significant impact on the mechanical properties.

3.2.9 Effects of drying and number of chitosan layers on air permeability, water vapour transmission rate and grease resistance (Paper III)

Chitosan can effectively close the paper surface and reduce the air permeance of the substrate. Impregnation of the paper took a place even with only one layer of chitosan with resulting air permeance reduced from 9.2 µm/Pa.s (uncoated paper) to at least 0.11 µm/Pa.s (one layer dried with HA) (see **Figure 28a**). Two of the most important barrier properties, water vapour transmission rate and grease resistance were both improved in dependence of chitosan amount applied onto the paper surface (see **Figure 28bc**). The diffusion process of the water vapour was impaired as result of the closed surface and the lack of pores and voids and already by coating the substrate with one layer of chitosan, the water vapour transmission rate was reduced by at least 50 %. While the ANOVA analysis did not show a statistically significant influence of drying regime on WVTR, it indicated that the grease resistance of single coated paper expressed as KIT value is influenced positively when the coated paper was dried only with IR.(for more details regarding ANOVA see “Results and Discussion” section of **Paper III**).

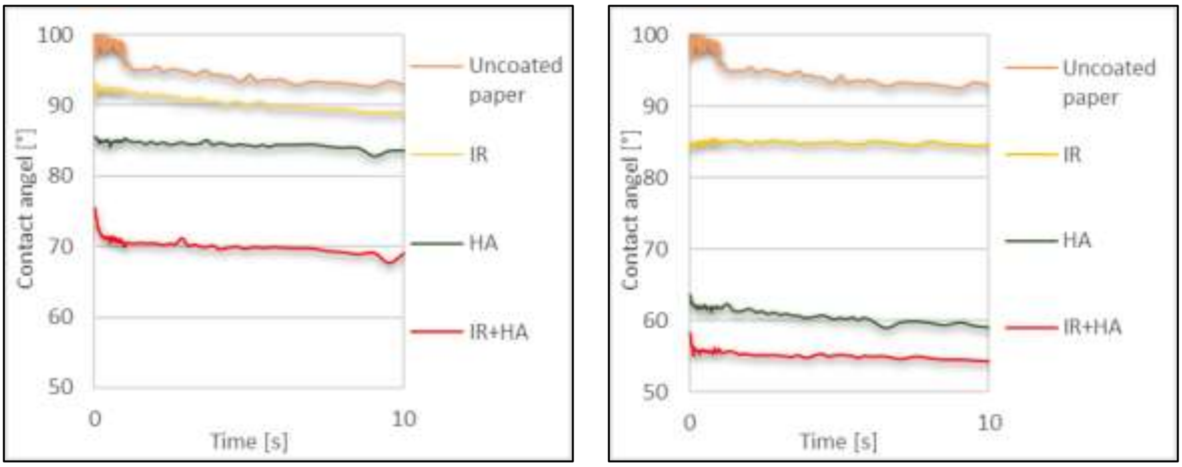


(a) (b) (c)

Figure 28. Air permeance (a), water vapour transmission rate (b) and grease resistance of the raw paper, single and double chitosan coated papers dried with the IR+HA, IR and HA.

3.2.10 Effects of drying and number of chitosan layers on wettability and water uptake (Paper III)

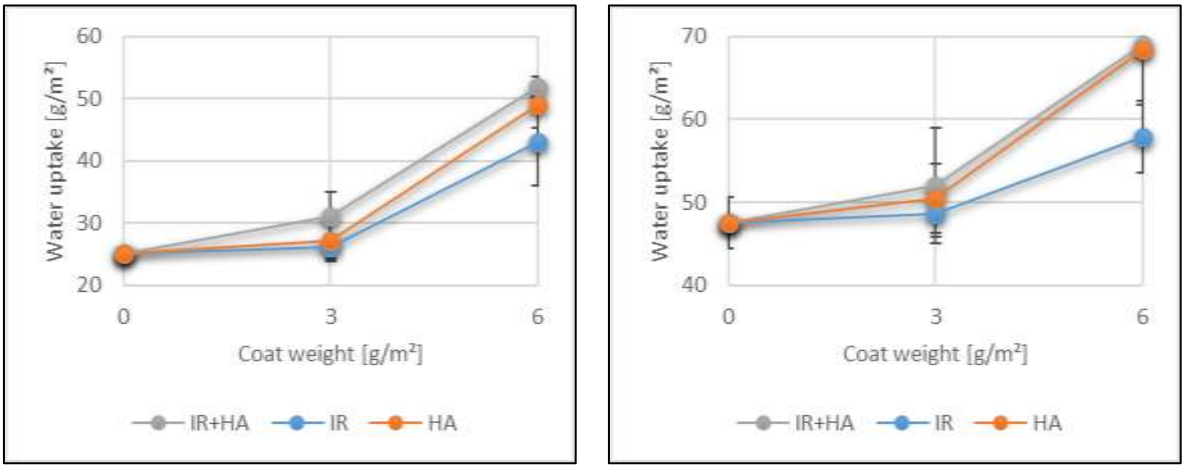
As the surface of the chitosan-coated samples is modified by applying chitosan and different drying methods, the surface wettability was changed dramatically. The uncoated paper surface is as consequence of mass sizing hydrophobic and shows higher contact angles compared to chitosan-coated paper (see **Figure 29ab**). With one layer of chitosan the contact angle decreases and an impact of the type of drying in accordance with the SEM surface images can be observed. A moderate drying regime and shorter drying time (e.g. IR drying) leads to greater penetration and lower retention of the chitosan. As a consequence the surface with fibres which are already hydrophobic due to mass sizing and not fully covered by the applied chitosan appears to be more hydrophobic compared to the samples where the chitosan was retained on the surface (e.g. HA). The contact angle difference of IR dried samples to the uncoated paper is lower compared to IR+HA drying which led to faster layer immobilization, higher chitosan retention on the paper surface and results in the hydrophilization of the paper surface. This effect is naturally more pronounce with two chitosan layers, as the second layer of chitosan forms visible films and creates a more hydrophilic surface.



(a) (b)

Figure 29. Contact angles of uncoated paper and chitosan coated paper with one layer (a) and two layers (b), indicating a hydrophilization of the paper surface and drop of contact angles for all chitosan-coated samples depending on coat weight and drying method.

The same trend is observed with Cobb measurements for 60 and 1800 seconds respectively (see **Figure 30ab**). Due to the partial chitosan retention or penetration, not only the surface is hydrophilized but the bulk paper structure as well. This leads to higher water uptake by the paper and agrees well with the results found in the literature [145].



(a) (b)

Figure 29. Water uptake (Cobb 60s and 1800s) of uncoated paper and chitosan coated paper with one layer (a) and two layers (b), indicating a higher uptake of water due to the hydrophilization of the paper structure.

From the contact angle and Cobb measurements it can be concluded that the different drying regimes might be used as a tool for surface functionalization in terms of hydrophilization or hydrophobization for chitosan coated industrially produced paper. By combining the different drying regimes and adjustment of drying time and intensity, desired surface properties of the chitosan-coated paper might be achieved by affecting the retention or penetration of this barrier material.

4. Concluding remarks and future perspectives

The need for sustainable and renewable packaging materials is increasing and in the future these will play a key role in the design and implementation of an environmentally and economically sustainable circular system. Although less than 5 % of the total crude oil worldwide is used for thermoplastic packaging, coating and strength additives, it nevertheless represents a serious impact on the environment as these products are non-degradable and will remain unchanged and a burden to nature for hundreds of years. The shortfall in the utilization of natural materials for packaging is clearly apparent in the fact that 50 million tons of oil annually is converted into plastics in Europe and 40 % of this is for packaging applications [21]. The natural materials used in this work represent effective alternatives to the synthetic ones in use in either sizing or barrier coating formulations. A further advantage of the chosen additives is that they are all based on non-food, renewable bioresources and therefore their industrial use does not compete with the need to feed the growing world population. The current trend in Europe is the conversion of non-food biomass, co-products and residues into useful products. The wood based, agricultural and fishing industries are already functioning as biorefineries and are transforming more and more bioresources, co-products and residues into valuable additives used in the packaging but also in the pharmaceutical, textile and automotive industries.

This work presents the potential application of three different biobased materials and their utilization in sizing and coating formulations for fiber based packaging materials. Using spent liquor and appropriate extraction, purification and application technologies the utilization of the synthetic sizing additives currently used by many manufacturers can be reduced. By using a co-product from the pulping process, especially integrated packaging paper producers would also be less dependent on starch which is produced from food crops such as corn or potatoes and frequently shows highly volatile price changes. Lignin is one of the few natural materials with hydrophilic and hydrophobic functional groups, which can be used as a basis for further developments regarding sizing efficiency. In this work a technologically feasible separation method for kraft lignin and lignosulfate from spent black liquor is presented and the isolated technical lignins could readily be applied using existing surface sizing processes.

Moreover, the application of alginate and chitosan as functional barrier materials against water vapour, aroma, migration of mineral oil fractions, grease and fats have been tested. As these two materials show high density and low permeation of gaseous substances, they present a high potential in functional barrier coating of paper or paperboard used either for food or other packaging requirements. The thus produced paper and board grades could also be recycled and help to further increase the use of recycled fibres, where already today more than 70 % of the cellulosic fibers in Europe are recycled at least six times and reused in packaging, printing, hygienic or special grade papers [157].

When used in primary packaging applications, recycled fibers can however also present a risk in the form of migration of mineral oil hydrocarbons coming from printing ink and therefore have to be coated with a functional barrier. Current solutions on the market offer multi-layer coating to prevent migration of the MOSH and MOAH fractions. Alginate and chitosan have proved their effectiveness and high barrier capacities in reducing the migration of mineral oil fractions. Considering that, these barrier materials represent less than 10 % of overall packaging paper weight, they perform very well as strength and barrier additives.

Chitosan and alginate layers with a thickness of less than 5 µm already provide good barrier capacities for mineral oil, grease and aroma compounds. The casted chitosan and alginate films with a thickness of 30 µm additionally exhibit acceptable oxygen transmission rates which are comparable with well-known synthetic barrier coatings chemicals such as LDPE (Oxygen permeability (OP) ≥ 50-100 $cm^3.mm/m^2.day.atm$), PP (OP ≥ 50-100 $cm^3.mm/m^2.day.atm$), PET (OP ≥ 1-5 $cm^3.mm/m^2.day.atm$) and PVC (OP ≥ 2-8 $cm^3.mm/m^2.day.atm$) [158]. However, when these two biopolymers are applied on raw uncoated paper a layer thickness of more than 5 µm is be needed to lower oxygen transmission rate values to a level required for food packaging applications. It has also been shown that impregnation of the base paper with the natural barrier materials is not only a possibility to increase paper barrier properties, but it can also enhance the strength properties of the materials. A further benefit of applying aqueous chitosan, alginate or lignin suspensions/dispersions is that either no or very low additional investments are needed, when these materials are used in the existing processes currently operational in the paper industry. The logistic and production costs might also be reduced, as an additional converting step in an extrusion unit might be avoided depending on required barrier properties.

Apart of many advantages of bio-based materials clearly demonstrated in this work, there are also many critical points, which have to be addressed in future research. Taking into account the practical experience gained after three years of working in the coating field as well as inputs from the scientific and industrial community, two fundamental approaches could be considered in future studies. In the first approach, which focusses on the scientific fundamentals, questions regarding the interaction of cellulosic fibres with bio-based barrier materials on the fibre level should be addressed by investigating the influence of these materials on fundamental properties of cellulosic fibres such as swelling, bonding, fibre strength, surface charge or reactivity. Based on these findings, in a next step of this fundamental approach, laboratory made paper sheets from different pulp fibre qualities should be treated with the bio-based polymers of interest. Based on these data, industrially manufactured paper could be optimized regarding fibre quality and refining, and subsequently utilized in coating or sizing using natural materials. It is well known that paper as a natural and heterogenic material has a complex structure and significant variations are found depending on pulp quality or process parameters in the paper and pulp mill.

The second important approach would be to perform simulation and modelling of transport phenomena trough the barrier materials. Especially for novel bio-based composite materials such as alginates, chitosans or nanocelluloses other factors might come into play compared to the synthetic barrier materials already studied for decades.

Based on these fundamental studies, the application of materials and feasibility of the up-scaling to industrial scale should be in focus, which obviously requires the cooperation of scientists, paper and coatings producers. Regarding converting, it would be interesting to design and convert the coated paper into packages and test those packages under real environmental conditions.

From both technological and economical point of view, it would also be of interest to study in detail the influence of coat weights of bio-based materials and do evaluate the effect of pre-treatments of paper such as pigmenting or surface sizing, as this might be beneficial for the overall barrier properties. According to literature and practical knowledge, novel barrier materials such as alginate and chitosan were usually applied to papers in the laboratory using rod coating or film press application and it would be necessary to also test rather novel application technologies in paper industry such as single or multi-layer curtain coating, which could be interesting technologies considering the challenging rheology of these materials.

Possible issues regarding application of technical lignins, such as solubilisation, type/demand of chemicals needed for dissolution and possible odour development for lignin coated papers, which were already evaluated on lab scale, would be best approached by moving to the next step, which means upscaling of current lab-scale technology to industrial practice, which is already envisaged in one of our projects in the field.

The steps to be taken in the future will require dedication not only from the scientific community but also from the private sector and from policy makers to bundle the forces and support the technological implementation of future-oriented bio-based technologies.

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Appendix

List of Conference and Paper Contributions

1. **Samir Kopacic** und Wolfgang Bauer (2016). *Application of Technical Lignins for Surface Sizing of Packaging Papers*, PhD Summer School, Uppsala, Sweden
2. **Samir Kopacic**, Wolfgang Bauer, Andreas Ortner, Georg Gübitz, Klaus Eibinger, Thomas Kraschitzer & Heribert Winter (2016). *Technical lignins in surface sizing applications for packaging papers*. Workshop on Insights and Strategies towards a Bio-based Economy, Montevideo, Uruguay.
3. **Samir Kopacic**, Andreas Ortner, Thomas Kraschitzer, Klaus Eibinger, Heribert Winter, Georg Gübitz, Wolfgang Bauer (2017). *Technical Lignins for Surface Sizing*, ACS San Francisco, USA
4. **Samir Kopacic**, Andreas Ortner, Georg Gübitz, Wolfgang Bauer (2017). *The use of Technical Lignins in the Development of Surface Sizing Formulations for Packaging Papers*, 43th International Meeting of Slovenian Papermakers, Bled, Slovenia
5. Andreas Ortner, Karin Hofer, Gibson S. Nyanhongo, Heribert Winter, Kai Mahler, **Samir Kopacic**, Georg Gübitz, Wolfgang Bauer (2017), *Development and Performance of Enzymatically Modified Lignosulfonates as Coating Binders*, ACS San Francisco, USA
6. **Samir Kopacic**, Wolfgang Fischer, Wolfgang Bauer (2017), *Biopolymers Barrier Coatings for Paper- based Food Packaging Materials,* 4. International Meeting on Material & Bioproducts Interaction, Porto, Portugal
7. Andrea Walzl, **Samir Kopacic**, Erich Leitner, Wolfgang Bauer (2018), *Characterization of Functional Barriers for Food Contact Materials* , XIX Euro Analysis, Stockholm, Sweden
8. **Samir Kopacic**, Andrea Walzl, Armin Zankel, Erich Leitner and Wolfgang Bauer (2018). *Barrier Coating using Biopolymers*, Minisymposium Verfahrenstechnik, Linz, Austria
9. **Samir Kopacic**, Andrea Walzl, Armin Zankel, Erich Leitner and Wolfgang Bauer

(2018). *Barrier Coating of Paperboard using Technical Biobased Materials,* Paper & Biorefinery, Graz, Austria

10. **Samir Kopacic**, Andrea Walzl, Armin Zankel, Rudolf Kniely, Erich Leitner and Wolfgang Bauer (2018). *Functional Barrier Coating of Paper,* 45th International Meeting of Slovenian Papermakers, Bled, Slovenia
11. **Samir Kopacic** (2018). *Functional Barrier Coating and Surface Sizing using Renewable Natural Materials,,* Paper & Beyond, Brussels, Belgium
12. Andrea Walzl, **Samir Kopacic**, Wolfgang Bauer and Erich Leitner (2018). Characterization of Natural Polymers as Functional Barriers for Cellulose Based Pack aging Materials, *Journal Food Additives and Contaminants,* **submitted.**

Publications

(I) **Kopacic, S**.; Ortner, A.; Gübitz, G.; Kraschitzer, T.; Leitner, J.; Bauer, W. Technical Lignins and Their Utilization in the Surface Sizing of Paperboard. *Ind. Eng. Chem. Res.* **2018**, *57*, 6284-6291, doi:10.1021/acs.iecr.8b00974

(II) **Kopacic, S**.; Walzl, A.; Hirn, U.; Zankel, A.; Kniely, R.; Leitner, E.; Bauer, W. Application of Industrially Produced Chitosan in the Surface Treatment of Fibre-Based Material: Effect of Drying Method and Number of Coating Layers on Mechanical and Barrier Properties. *Polymers* **2018**, *10*, 1232, doi:10.3390/polym10.111232.

(III) **Kopacic, S.;** Walzl, A.; Zankel, A.; Leitner, E.; Bauer, W. Alginate and Chitosan as a Functional Barrier for Paper-Based Packaging Materials. *Coatings* **2018**, *8*, 235, doi:10.3390/coatings8070235.

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Technical Lignins and Their Utilization in the Surface Sizing of Paperboard. *Ind. Eng. Chem. Res.* **2018**, *57*, 6284-6291, doi:10.1021/acs.iecr.8b00974.

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Technical Lignins and Their Utilization in the Surface Sizing of Paperboard

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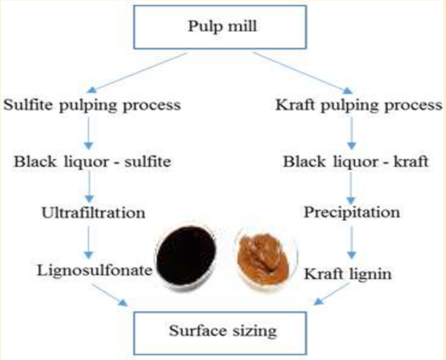
ABSTRACT: Technical lignins, which are the coproducts of the pulping industry, have a high potential for use in surface sizing of paperboard. We investigated the use of kraft lignin and lignosulfonate in surface sizing of paperboard with the target of understanding the influence of lignins on the development of strength and hydrophobicity. Prior to surface sizing, the lignins are purified by ultrafiltration and precipitation respectively. Strength properties and hydrophobicity of lignin-sized paperboard were measured and compared with references as well as with unsized paper. An increase in the strength properties of lignin-sized samples was observed, which was in the same range as references and at least 10% higher compared to unsized paperboard. Moreover, air permeability, hydrophobicity, and water absorptiveness were affected, and depending on the lignin art, an improvement was achieved. These results encourage partial or total substitution of conventional surface-sizing chemicals by technical lignins.



■ INTRODUCTION

The importance of using renewable materials for packaging such as paperboard and coproducts like lignin from the pulp and paper industry has now become crucial for the further development and growth of the sector and also for the sustainable exploitation of natural resources. Due to the high recyclability of paper-based products, utilization of recycled cellulosic fibers in paper-producing countries has already reached a high level.[1,2] However, producing the fiber-based packaging materials out of so-called recycled secondary fibers requires the input of additional resources, in order to achieve the common strength and surface properties dictated by the end consumers. Consequently, application of petroleum-based chemicals for improvement of materials properties for packaging application could impact sustainability of renewable and environmentally friendly material such as paperboard in a negative way. One of the possible approaches to achieve better strength is to treat paperboard surface with either pure modified industrial starch or mixtures out of starch and synthetic polymeric sizing agent in order to improve both strength and surface properties such as hydrophobicity.[3−5] The synthetic surface-sizing agent improves the hydrophobicity, thus enabling the naturally hydrophilic paperboard to be more water resistant, and usually does not influence paperboard strength properties. Different grades of starch such as enzymatic, oxidized, and cationic starch are already well-known for improving paper strength.[6−8,31] Currently, paper mills around the world treat paper surfaces with above-mentioned surface-sizing materials. However, they must be purchased externally, making paperboard producers more dependent on the constantly changing prices of starch or synthetic surface-sizing agents like a perglutin as used in this work. On the other hand, coproduct from pulp mill as a black liquor is a source of technical lignin, and for many decades this has been regularly combusted for the generation of process energy instead of being reused as a replacement for surface-sizing chemicals. From both technological and economical points of view, partial or total substitution of surface-sizing chemicals by coproducts such as technical lignins gained from black liquor could have very positive impact on the entire pulp and paper industry. Lignin is the third most abundant biopolymer after cellulose and hemicellulose. In the plants, lignin is commonly associated with cellulosic and hemicellulosic structures, and harsh process conditions are usually needed to remove or dissolve lignin. Traditionally lignin extraction is achieved using a pulping process under high-pressure, high-temperature, and thus high-energy consumption. These conditions are harmful for the lignin polymeric structure, and extensive degradation results. The advantage of lignin is in the

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varied chemical functional groups, which result from the cleaving of the lignin native structure into fragments. Lignin could thus be used as an intermediate for diverse chemical reactions or extracted and purified and then used for, e.g., the coating and sizing of fiber-based materials. Solubility plays a crucial role when the water-based formulation of lignin is targeted. Among other factors, the solubility of native lignin is influenced largely by the proportion of its functional groups, which are both aromatic and aliphatic.[15−19,29]

In recent decades, many attempts have been made to explore how different types of lignin can contribute to both hydrophobicity and development of paper strength. Different sources of technical lignin, purified or even as a black liquor, have been applied and studied for surface treatment of paperboard. Theoretically and practically, it has been proved that depending on the basic lignin properties and application, lignin may contribute to both better hydrophobicity and development of material strength.[9,10] Several researchers have already reported on lignin−cellulose interaction and the possible mechanisms of how lignin can interact with the cellulose. It has be shown that lignin can improve the strength properties of the bleached fiber and thus also the strength of fiber-based packaging materials.[10−14,30]

One of the most challenging tasks currently is to separate, purify, and concentrate lignin for use in value-added products. In this work, two different technical lignins were used: kraft lignin obtained from the industrial kraft process and lignosulfonate obtained from the industrial sulfite pulping process. The method for purification of black liquors from these two pulping processes is in the first case precipitation with sulfuric acid and in the second case ultrafiltration. The advantage of raw lignosulfonate compared to raw kraft lignin is water solubility under neutral, acidic, and alkaline conditions. Lignosulfonate is sulfonated after the pulping process, and due to sulfonate groups on the aliphatic side, water solubility is not an issue.[32] On the other hand, the selective removal of lignin cannot be achieved with either the sulfite or the kraft pulping process. Further purification must be performed in order to remove nonlignin compounds such as carbohydrates and inorganics by either selective precipitation or ultrafiltration. .[20−24] After the precipitation process dry kraft lignin is not soluble in water, and solubility must be accomplished under alkaline conditions. It has been reported that there is a hysteresis of lignin solubility in aqueous solution. If the kraft lignin is transferred from a protonated H-form into a deprotonated Na-form with sodium hydroxide, it can gain polyelectrolytic behavior and remain stable at a neutral or alkaline pH value. This approach was used in the present work, and as a result the kraft lignin solubility under alkaline conditions was improved, allowing surface-sizing application at a pH range used in industrial surface sizing of paper.[11]

The focus of this work is on the purification of spent black liquors from two Austrian pulp mills using the kraft and sulfite process respectively in order to allow the application of the technical lignins obtained in surface sizing of industrially produced packaging paper. Separating lignin from black liquors has the objective of reducing heterogeneity and concentrating the lignin with higher molecular weights. A very important part of our investigation was to prepare suitable references and compare them with both kraft lignin and lignosulfonate sized samples. In our case, surface-sizing materials used as references are industrially produced enzymatic starch and perglutin, both well-known on the market and used for industrial surface sizing of paperboard. Taking into account input from local paper mills, we have prepared two surface-sizing formulations out of 100% (w/w) enzymatic starch as well as mixture made of 97% (w/w) enzymatic starch and 3% (w/w) perglutin. Additionally, we have prepared surface-sizing formulations from pure kraft lignin or lignosulfonate and mixtures consisting of 50% (w/w) enzymatic starch and 50% (w/w) lignin, with the aim to see if the lignin can be used as a complementary additive to starch or it can solely reach desired paperboard properties after surface sizing. Comprehensive assessment of technical lignin in contribution of both strength and surface properties and their potential in substitution of conventional surface-sizing chemicals was evaluated.

EXPERIMENTAL SECTION

Materials. The substrate for the surface-sizing trials was a standard corrugated medium supplied by a paper mill. The grammage of the corrugated medium was 117 g/m^2, and the thickness was 172 μm. The specific volume and density were 1.47 cm^3/g and 0.67 g/cm^3. The substrate was produced out of 100% recycled fibers and was not treated with starch or any other conventional surface-sizing agent. Enzymatically treated corn starch (ES) was received from a paper mill in Austria. ES with a solid content of 25% (w/w) was applied at a temperature of 70 °C. Perglutin is a cationic synthetic sizing agent produced by Kurita and kindly supplied by the paper mill supplying the substrate. It has an acidic pH value and original solid content of 45% (w/w). Figure 1 depicts the principal process steps to obtain the technical lignins used in surface sizing from the black liquors.

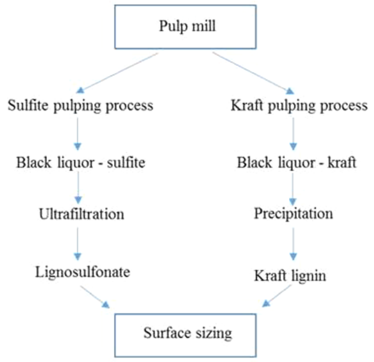

Figure 1. Flowchart: kraft lignin and lignosulfonate production and purification.

Precipitation. Kraft lignin was precipitated using a pilot precipitation plant. Precipitation was performed using 50% (w/w) sulfuric acid to a pH of 2.5 followed by thickening on a filter press to a final solid content of 45% (w/w). In this process several washing steps are carried out in order to reduce the inorganics content expressed as ash content, which was 1% for the precipitated kraft lignin.

Ultrafiltration. Lignosulfonate from spent sulfite liquor with a total dry substance (TDS) of 30% was prefiltered with a 5 μm paper filter to remove solid particles, ash, and fibrous material. Salts and smaller lignin fractions were subsequently removed with a Memcell ultratiltration lab unit from Osmo Membrane Systems using a 150 kDa membrane by repeatedly adding distilled water (around 10 times) until the permeate was colorless. The retentate had a final concentration of 7% TDS.

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Ind. Eng. Chem. Res. 2018, 57, 6284−6291

Therefore, the retentate had to be adjusted by evaporation to a TDS of 12.5% used for the experiments.

Pretreatment of Kraft Lignin. Kraft lignin obtained after precipitation has a solid content of 45% (w/w) and cannot be used in surface sizing at neutral pH value because of its insolubility in water. The solubility at a solid content of 17.5 % (w/w) of the kraft lignin must be ensured at pH 8−9 in order to apply it onto the paperboard surface in the sizing process. Unmodified kraft lignin in its native form contains functional groups such as hydroxyl (aromatic and aliphatic), methoxyl, carbonyl, and carboxyl groups. Among many other factors, solubility is also affected by proportions of main functional groups, and because of ionization of hydroxyl and carboxyl functional groups under alkaline conditions, lignin can reach a relatively high degree of solubility.[16] Improvement of precipitated kraft lignin solubility in water was performed by applying principles reported in the literature.[11] Precipitated kraft lignin was first alkalized using 20% (w/w) sodium hydroxide and stirred with a laboratory mixer at rate of 500 rpm for 2 h. After transferring the kraft lignin from its H-form into Na-form, kraft lignin solution reached pH of 11.5 and was completely deprotonated in water. The color of the lignin solution changed from brown to black, and no particle or agglomerate formation could be optically observed. Once the kraft lignin was dissolved in water, the pH value had to be lowered to pH 8 or 9 by adding sulfuric acid. In addition to optical observation, monitoring of the suspension stability was performed by measuring of zeta potential using Stabino particle charge mapping analyzer. The zeta potential measured was above − 60 mV at pH 11.5, and at least −30 mV at pH 8−9 indicating a stable kraft lignin suspension[25] (see Figure 2)

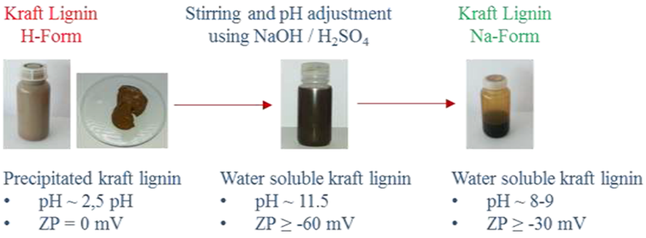


Figure 2. Pretreatment of precipitated kraft lignin and adjusting of the pH value.

Size Exclusion Chromatography (SEC). The molecular weights obtained were determined by a LC (SEC) system equipped with a quaternary/binary pump, an autosampler 1260 series from Agilent Technologies (Palo Alto, CA), DAD (diode array detector), and an RI (refractive index) detector system (Agilent Technologies 1260 Infinity), specially equipped with a MALLS HELEOS DAWN II detector from Wyatt Technologies (Dernbach, Germany). The SEC column system consists of a precolumn PL aquagel-OH MIXED Guard (PL1149-1840, 8 μm, 7, 5 × 50 mm, Agilent, Palo Alto, CA) and a separation column PL aquagel-OH MIXED H (PL1549-5800, 4.6 × 250 mm, 8 μm, Agilent, Palo Alto, CA) with a mass range from 6 to 10 000 kDa. The lignin samples were diluted with the mobile phase (50 mM $NaNO_3$, 3 mM NaN_3) to a concentration of 1 mg/mL before loading 100 μL onto the column. The system was operated with a total runtime of 90 min. The Agilent Software Openlab Chemstation CDS, as also ASTRA 7 software from Wyatt technologies, was used for data acquisition and data analysis. BSA served as a standard for the normalization, band broadening, and alignment of the MALLS detector.

Formulation Preparation. In total six different surface-sizing formulations based on kraft lignin, starch, lignosulfonate, and perglutin were prepared for the size press trials (see Table 1). Pure starch and the starch + perglutin mixture are considered as references, and both were prepared with a solid content of 17.5% (w/w). Kraft lignin with the solid content of 17.5% (w/w) was applied in pure form and as a mixture with enzymatic modified starch in a ratio of 50:50 (w/w). Lignosulfonate with a solid content of 12.5% (w/w) was also once applied in pure form and as a mixture with enzymatic modified starch in ratio 50:50 (w/w). The pH values of the references are purely material specific, and adjustments of these were not undertaken. The performance of the references should yield the desired surface-sizing effect at the given pH values and also in use on an industrial scale, as stated many times in the literature and also known from practical experience. By doing this, the aim was to achieve a real comparison between lignin-sized samples and references made out of starch and starch + perglutin.

Table 1. Surface Sizing Formulations with Measured Solid Content, pH, and Viscosity (Brookfield).

formulation number	surface sizing formulation	weight percentage (%)	final solid content (%)	final pH value	BF viscosity 100 rpm (mPa s)
1	starch	100% (w/w)	17.6	7.1	57.2
2	starch + perglutin	97% + 3% (w/w)	17.6	4.3	52.4
3	lignosulfonate	100% (w/w)	12.4	9.6	20.0
4	lignosulfonate + starch	50% + 50% (w/w)	12.4	9.3	23.8
5	kraft lignin	100% (w/w)	17.5	8.8	33.2
6	kraft lignin + starch	50% + 50% (w/w)	17.3	9.0	43.0

Surface Sizing. The corrugated medium was delivered in roll form and was sized at standard conditions in the coating lab of the Norske Skog mill in Austria. The pilot-coating machine (DOW) used in the trial was a size press. The desired pickup of surface-sizing formulation was 6 g/m^2, and for this reason the optimal solid content and viscosity of surface-sizing formulation were evaluated and optimized prior to the adjustment of operating parameters. Once the targeted application 6 g/m^2 of the surface-sizing formulation was reached, the operating parameters were adjusted and kept constant for all surface-sizing formulations. The velocity was 15 m/min, the temperature of the drying section 220 °C, nip pressure 0.9 bar, and rod pressure 1 bar. The temperature of paper web measured at the rewinding unit was 70 °C. Both sides of substrate were sized under the same conditions.

Pickup [g/m^2] on substrate was calculated according to the following equation (eq 1):

$$\text{pickup (g/m}^2) = \text{grammage of sized paper (g/m}^2) - \text{grammage of raw paper (g/m}^2) \quad (1)$$

Basic physical properties such as thickness and density of the raw paper and surface-sized papers with applied surface-sizing formulation are summarized in the Table 2.

Table 2. Basic Properties of Paper Samples Sized with Starch, Starch + Perglutin, Lignosulfonate, Kraft Lignin, and Mixtures Prepared from Lignins and Starch

sample	thickness (μm)	density (g/m^3)	grammage (g/m^2)	amount of surface-sizing formulation (g/m^2)
raw paper[a]	172 ± 5	0.68 ± 0.02	117 ± 0.8	
starch	181 ± 4	0.68 ± 0.02	123 ± 0.8	
starch + perglutin	180 ± 3	0.68 ± 0.01	123 ± 0.5	
lignosulfonate	180 ± 6	0.67 ± 0.02	122 ± 0.6	6 ± 0.8
lignosulfonate + starch	180 ± 5	0.69 ± 0.02	124 ± 0.6	
kraft lignin	174 ± 5	0.70 ± 0.02	123 ± 0.7	
kraft lignin + starch	176 ± 5	0.69 ± 0.02	122 ± 0.6	

[a] Raw paper is without surface sizing.

Characterization of Raw and Surface-Sized Paper. Raw paper and paper samples sized with the above-described formulations were conditioned for 48 h at 23 ± 1 °C and 50% ± 3% RH. All measurements were performed according to the standardized methods listed in Table 3.

Table 3. Property and Methods Used for Characterization of Raw Paper, Sized Paper, and Surface-Sizing Formulations

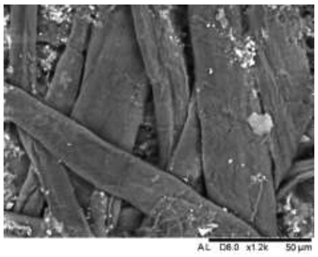
property	method and device	standard
grammage	weighting	EN ISO 536
thickness	LDAL 03	EN ISO 534
density	calculation	EN ISO 534
air permeability	Bendtsen	ISO 5636-3
contact angle	Fibrodat 1100	T 558
tensile index	L&W tensile tester	EN ISO 1924-2
Cobb	PTI Cobb tester	EN ISO 535
ash content	muffle furnace	DIN 54370
burst index	L&W burst strength tester	EN ISO 2758 and 2759
SCT short span compression	UPM zwick	T 826
bending stiffness	Messmer/Büchel	ISO 2493-1
solid content	HR73 halogen moisture analyzer	–

Scanning Electron Microscope (SEM). Scanning electron microscopy (SEM, TM3030 Tabletop Microscope, HITACHI, Japan) was used for observing the surface. The sample (1 × 1 cm) was placed with a double-sided carbon tape on the sample holder, and the images were captured at 15 kV.

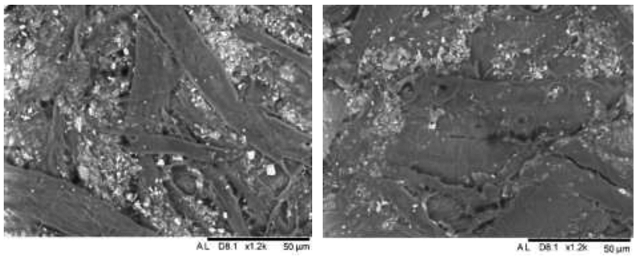
■ RESULTS AND DISCUSSION

Average Molecular Weight of Lignins. The average molecular weights of lignosulfonate and kraft lignin were measured via SEC. Lignosulfonate had an average molecular weight of 16 830 g/mol, which was around 5 times higher than of kraft lignin, which was 3193 g/mol.

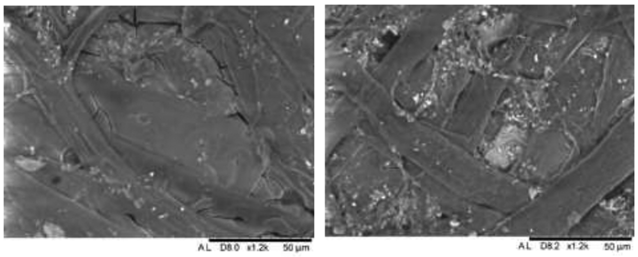
Surface Analysis. Surface analysis performed with a scanning electron microscope shows clear differences between sized and raw paper (see Figure 3). Primarily, the pores and voids of raw paper samples are clearly visible and could be linked to higher air permeability, lower water resistance, and lower contact angle. For sized samples, film formation is visible, and the voids between fibers are filled. Noticeable film formation is observed for lignosulfonate, where even some cracks can be seen, most probably as results of extensive drying. Kraft lignin and also lignosulfonate are able to form stable films on the paper surface, and the coverage of the paper is comparable with the starch and starch + perglutin samples. Kraft lignin and starch + perglutin sized samples are very similar with respect to coverage. Hence the higher water resistance is measured for those two samples. Presumably due to its lower average molecular weight, kraft lignin generally fills all the voids and pores completely and in addition also covers the fibers.



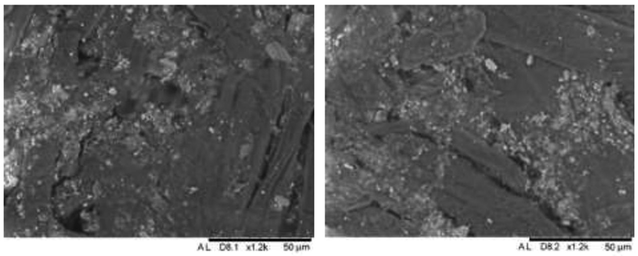
(a) raw paper



(b) starch c) starch+perglutin



(d) lignosulfonate (e) lignosulfonate+starch



(f) kraft lignin (g) kraft lignin+starch

Figure 3. SEM images of raw paper and surface-sized papers.

Air Permeability. Air permeability is expressed as the volume of air which is able to pass through the sample per minute. Lower air permeability was measured for all sized samples compared to raw paper (see Figure 4). Kraft lignin and kraft lignin + starch formulations have comparable air permeability values to starch and starch + perglutin sized papers. In contrast the lignosulfonate and lignosulfonate + starch, air permeability values are slightly higher but still significantly lower compared to raw paper. Due to application of sizing formulation, the paper pores are being closed, and it

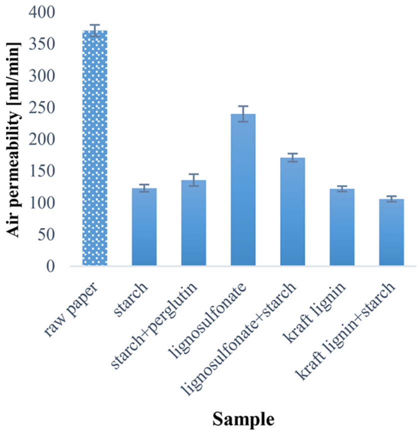


Figure 4. Air permeability of raw paper, starch, lignosulfonate, and kraft lignin surface-sized paper.

comes to a densification of the paper surface. The lowest air permeability was achieved with the kraft lignin + starch formulation followed by pure kraft lignin and starch formulations. According to SEC analysis, kraft lignin has the smallest Mw and therefore the penetration into paper as also the filling of the voids between fibers and closing of pores were accomplished more effectively in comparison with the lignosulfonate formulation, which has much higher Mw. According to SEM analysis both lignins show good film formation properties, but some cracks are observed when the samples are sized with the lignosulfonate-based formulations. The air permeability is thus higher for lignosulfonate-treated samples compared to kraft lignin based formulations.

Effect on Mechanical Properties. In addition to having good surface properties, packaging materials must also comply to demanding mechanical properties specifications to ensure good convertibility. During the transport and storage of packed goods, packaging is subjected to compression loading. Specific mechanical properties must be well defined in order to predict whether a paper grade can withstand the loads and stresses involved. The most important mechanical properties such as compressive and tensile strength, bending stiffness, and bursting index were measured and evaluated.

Short Span Compressive Test (SCT) and Bending Stiffness. .[26] Together with the bending stiffness, SCT values are among the most important physical properties for surface-sized corrugated board. Pickup weight of 6 g/m^2 is a significant amount of lignin applied to the paper surface. Consequently, the bonding between fibers increases, and due to this, the strength properties of paper board are affected.[10] The SCT of starch-sized paper is slightly higher than that of lignin-sized papers. Nevertheless lignosulfonate and kraft lignin have an SCT around 20% higher than that of raw paper. The mixtures, kraft lignin + starch and lignosulfonate + starch, show no significant differences to a formulation based on pure lignins (see Figure 5). The measured bending stiffness for both the MD and CD of all sized papers is at least 10% higher than that of raw paper. The highest values are obtained with the kraft lignin + starch formulation and starch + perglutin followed by starch, lignosulfonate, lignosulfonate + starch, and the kraft lignin formulation. While the bending stiffness of starch-sized paper is slightly higher compared to lignosulfonate and kraft lignin sized paper, both technical lignins still contribute significantly to achievement of higher bending stiffness (see Figure 6).

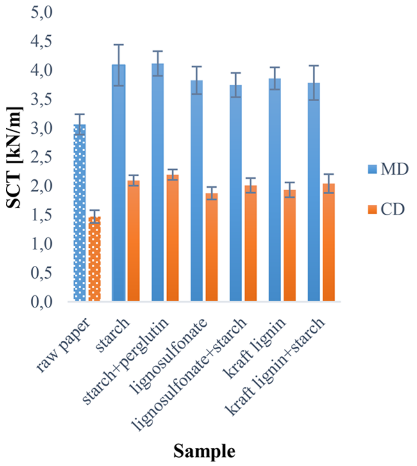


Figure 5. Short span compressive tests (SCT) for raw and surface-sized surface paper. The orange bar indicates the cross direction (CD) and the blue bar the machine direction (MD).

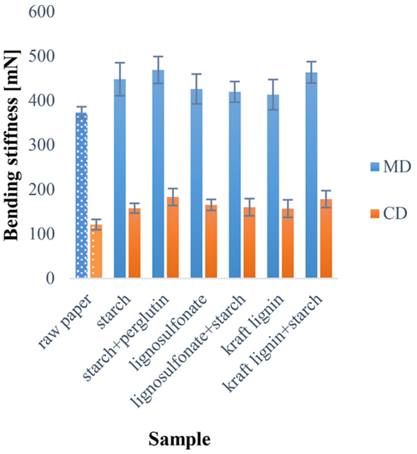


Figure 6. Bending stiffness of raw and surface-sized paper. The orange bar indicates the cross direction (CD), and the blue bar indicates the machine direction (MD).

Tensile (TI) and Burst Index (BI). As already, reported lignin can have a positive impact on the tensile or burst strength of the paperboard.[10] Tensile and burst indexes are obtained by dividing of measured tensile and burst strength respectively by paperboard grammage. By considering the deviation of paperboard grammage due to pickup weight, the burst and tensile index represent real surface-sizing material contributions to development of paper strength. An increase of the tensile index is observed for all surface-sized papers. References made from pure starch and a mixture of starch and pergluten reached the highest values, while kraft lignin and lignosulfonate formulations have a tensile strength at least 10% higher than that of raw paper (see Figure 7). Formulations made of 50% starch and 50% kraft lignin or lignosulfonate also exhibit higher values compared to pure lignins formulations, meaning that partial substitution of the starch by lignin could be beneficial for some specific packaging applications. The burst index of the raw paper is significantly lower compared to the surface-sized samples. Formulations prepared from pure kraft lignin and lignosulfonate increased the burst index by at least 15% compared to raw paper. The two starch and starch + perglutin reference formulations have at least 20% higher burst indexes compared to lignosulfonate and kraft lignin and at least 10%

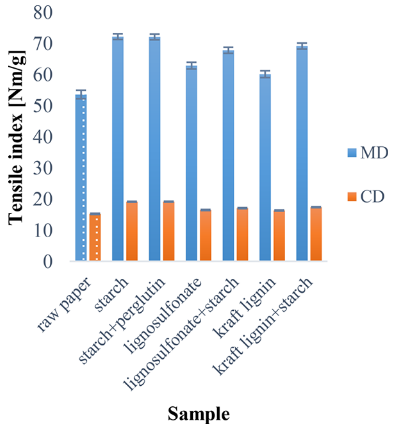


Figure 7. Tensile index of raw and surface-sized paper. The orange bar indicates the cross direction (CD), and the blue bar indicates the machine direction (MD).

compared to lignin + starch mixtures. Hence, starch contributes most to the development of bursting strength (see Figure 8).

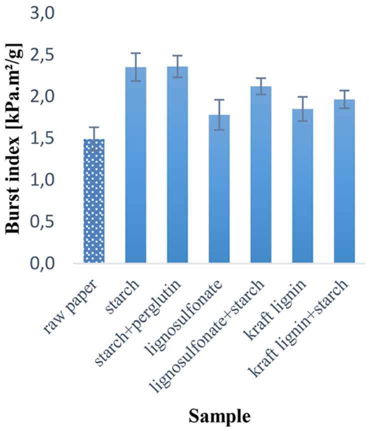


Figure 8. Comparison of the bursting index for raw paper and surface-sized paper.

From mechanical measurements TI, BI, and SCT, a similar trend is observed: pure starch and starch accompanied with perglutin exhibit the highest values, followed by lignins mixed with starch and pure kraft lignin or lignosulfonate.

Effect on Paper Hydrophobicity. *Water Absorptiveness.* The Cobb value is a good indicator for assessing the water absorptiveness of paper.[27] The water resistance of the raw paper is very low as it absorbs more than 141 g of water per m^2 of paper in 30 s and more than 148 g/m^2 in 60 s. Paper is considered to be a hydrophilic material, and consequently depending on grammage and furnish it can absorb large amounts of water. Application of starch lowers the water absorption by at least 15%. With starch and perglutin as reference, Cobb values of 24 and 55 g/m^2 for 30 and 60 s were achieved. Kraft lignin surface-sized sample has Cobb values of around 114 and 125 g/m^2 at 30 and 60 s, which is around 15% lower than lignosulfonate-sized samples. The kraft lignin and starch formulation shows Cobb values comparable to that of starch + perglutin.The lignosulfonate formulation can decrease the hydrophilicity of the paper, but not significantly as can be seen from Figure 9.

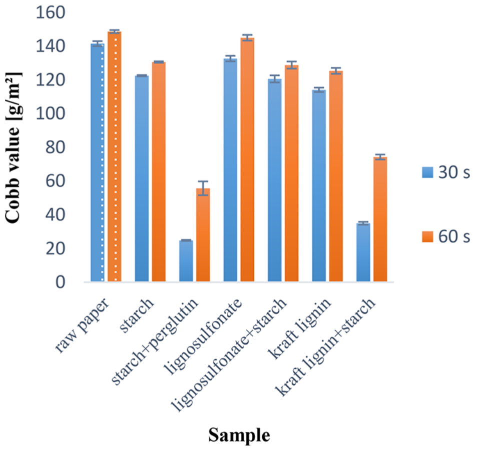


Figure 9. Cobb values of raw and surface-sized papers. The orange beam indicates the Cobb value measured for 60 s, and the blue beam indicates the Cobb measured for 30 s.

Contact Angle. The contact angle measured with deionized water is an additional measurement performed with raw and surface-sized papers to evaluate an improvement in paper surface hydrophobicity. In some cases the contact angle and the Cobb value correlate, and a clear correlation is observed for starch + perglutin and kraft lignin formulations.[28] The highest contact angle is the indicator for the highest hydrophobicity and highest water resistance of the sample. A stable contact angle of 30 s duration was measured for both for starch + perglutin and kraft lignin + starch. It has already been reported that kraft lignin as a hydrophobic material can improve hydrophobicity of the paper surface. The contact angles for raw paper and surface sizing with starch were the lowest and decreased rapidly within several seconds indicating spreading and penetration of the water drop into the paper substrate. The contact angle results for the lignosulfonate and lignosulfonate + starch sized samples show higher initial contact angles which also decrease rapidly indicating a lower paper surface hydrophobicity (see Figure 10).

■ CONCLUSION

Technical lignins—kraft lignin and lignosulfonate—were successfully isolated, purified, and utilized in surface sizing of corrugated paperboard material. The surface-sizing trials using these technical lignins showed that an improvement of both the

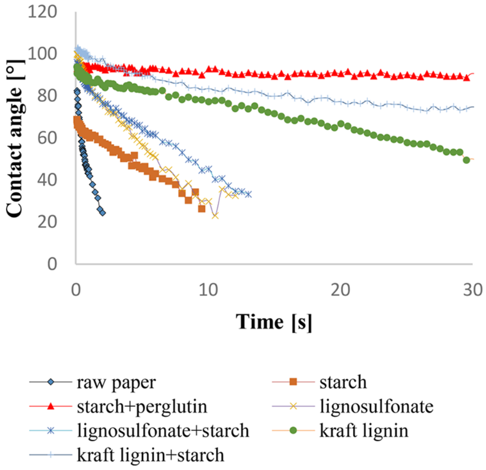


Figure 10. Contact angles of raw and surface-sized papers measured with deionized water for a duration of 30 s.

strength and the hydrophobic properties of paper can be realized. Paper sized with starch shows the expected good physical properties and a high degree of hydrophilicity. A combination of starch with a synthetic surface-sizing agent such as perglutin shows a positive effect on both strength and water resistance. In accordance with the measured values for tensile index, SCT, burst index, and bending stiffness, technical lignins show the potential to allow a complete substitution possibility for modified starch, while synthetic surface-sizing agents such as perglutin could be partially substituted. Pretreated water-soluble kraft lignin in particular manifested good film formation, development of strength properties, and improvement of hydrophobicity in the evaluations based on contact angle and Cobb measurements. Lignosulfonate in surface-sizing formulation yields improved strength properties compared to raw paper, while water resistance is not significantly improved. Both technical lignins are able to form stable and homogeneous films on the paper surface, illustrated in this case with SEM images. Pores and voids between fibers are filled by lignin resulting in a slightly higher density and lower air permeability. The surface-sizing effect is present and measurable for kraft lignin and lignosulfonate sized paper.

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Notes

The authors declare no competing financial interest.

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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 $\leq$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 ($g \cdot m^{-2}$)	Thickness (µm)	Sheet Density ($g \cdot cm^{-3}$)	Bendtsen Roughness ($mL \cdot min^{-1}$)
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 $g \cdot m^{-2}$ (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 $m \cdot min^{-1}$, 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 $g\cdot dm^{-2}$. The experiments were performed in triplicate in migration cells (MigraCell®; FABES Forschungs-GmbH, Munich, Germany) with a tested surface area of 0.32 dm^2. 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-d_{26} ($C_{12}D_{26}$; EURISO-TOP SAS, Saint-Aubin, France), nonadecane-d_{40} ($C_{19}D_{40}$; 98%; Cambridge Isotope Laboratories, Inc.; Tewksbury, MA, USA), benzophenone-d_{10} ($C_{13}D_{10}O$; 99 at.%; Sigma-Aldrich Co., St. Louis, MO, USA), and bis(2-ethylhexyl)phthalate-d_4 and di-n-butyl phthalate-d_4 (both "analytical standard", purchased from Sigma-Aldrich Co., St. Louis, MO, USA). All were used at a concentration of 200 $mg\cdot L^{-1}$ 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 $°C\cdot min^{-1}$ to 300 °C (3 min). The carrier gas used was hydrogen with a linear velocity of 48 $cm\cdot s^{-1}$. 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 $\mu g \cdot mL^{-1}$. The standard purchased by Restek Corporation (Bellefonte, PA, USA) contained the following substances in 1-mL ampoules in toluene: n-undecane (300 $\mu g \cdot mL^{-1}$), n-tridecane (150 $\mu g \cdot mL^{-1}$), bicyclohexyl (300 $\mu g \cdot mL^{-1}$), cholestane (5-α-cholestane; 600 $\mu g \cdot mL^{-1}$), 1-methylnaphthalene (300 $\mu g \cdot mL^{-1}$), 2-methylnaphthalene (300 $\mu g \cdot mL^{-1}$), n-pentylbenzene (300 $\mu g \cdot mL^{-1}$), perylene (600 $\mu g \cdot mL^{-1}$), and 1,3,5-tri-tert-butylbenzene (300 $\mu g \cdot mL^{-1}$). For the calculation of retention indices and the determination of cutting fractions in HPLC–GC–FID, a "C_7–C_{40} saturated alkane standard" from SUPELCO (Bellefonte, PA, USA) was used. The concentration of the alkanes was 1000 $\mu g \cdot mL^{-1}$ in hexane, and was diluted to 1 $\mu g \cdot mL^{-1}$ 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 $mL \cdot min^{-1}$), before being raised to 35% CH_2Cl_2 within 2 min (hold for 4.20 min). The column was then backflushed at 6.30 min with 100% CH_2Cl_2 (flow 0.5 $mL \cdot min^{-1}$; hold for 9 min), and reconditioned to 100% n-hexane (flow 0.5 $mL \cdot min^{-1}$; hold for 10 min). The flow was subsequently decreased to 0.3 $mL \cdot min^{-1}$ until the next injection. The UV-detector was equipped with a D_2-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 $°C \cdot min^{-1}$ to 100 °C (0 min) followed by 35 $°C \cdot min^{-1}$ 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 C_{16}–C_{25} and C_{25}–C_{35} 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 ($C_{14}D_{30}$, $C_{20}D_{42}$, and $C_{24}D_{50}$, 98%-at.%D, purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA); $C_{16}D_{34}$, 99%-at.%D, purchased from abcr GmbH (Karlsruhe, Germany); and $C_{28}D_{58}$ 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 $mg \cdot L^{-1}$ 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).

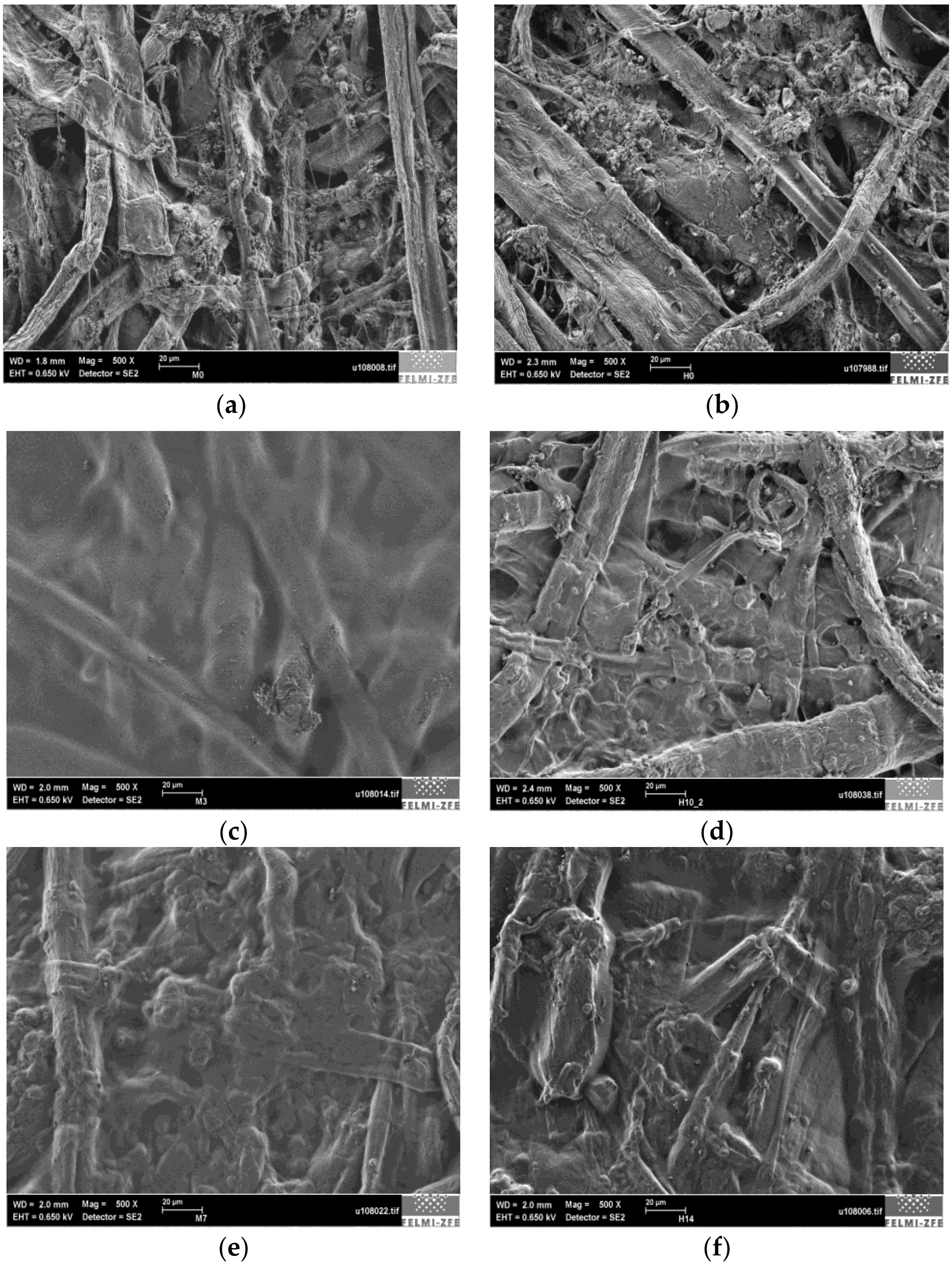
Sample	Thickness (µm)	Density ($g{\cdot}cm^{-3}$)	Grammage ($g{\cdot}m^{-2}$)	Pick-Up ($g{\cdot}m^{-2}$)
PF chitosan	98.0 ± 1.0	0.780 ± 0.01	78.0 ± 0.7	6.0 ± 0.2
PF alginate	98.0 ± 1.4	0.800 ± 0.01	78.1 ± 0.6	6.1 ± 0.2
SF chitosan	199.0 ± 2.4	0.670 ± 0.01	135.1 ± 0.5	6.1 ± 0.2
SF alginate	198.0 ± 3.1	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 $g{\cdot}m^{-2}$ or 30 $g{\cdot}m^{-2}$, 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.



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

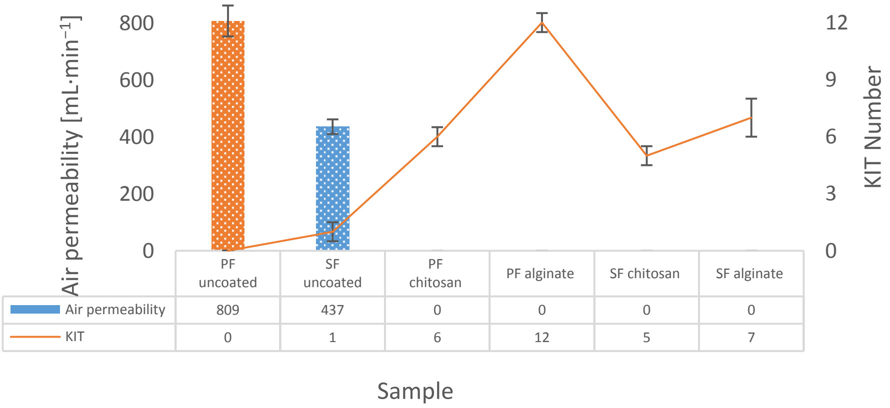
Figure 1. Scanning electron microscopy (SEM) images of uncoated and coated paper substrates at 500× magnification: (**a**) primary-fiber (PF) uncoated paper; (**b**) secondary-fiber (SF) uncoated paper; (**c**) chitosan-coated PF paper; (**d**) chitosan-coated SF paper; (**e**) alginate-coated PF paper; (**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·min^{-1} and 437 mL·min^{-1}, respectively (Figure 2).

After coating with alginate and chitosan, the measured air-permeability values for all samples were 0 mL·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 $g\cdot cm^{-3}$), 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].



	PF uncoated	SF uncoated	PF chitosan	PF alginate	SF chitosan	SF alginate
Air permeability	809	437	0	0	0	0
KIT	0	1	6	12	5	7

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 °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 $g\cdot m^{-2} \times 24$ h and 609 $g\cdot m^{-2} \times 24$ 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.

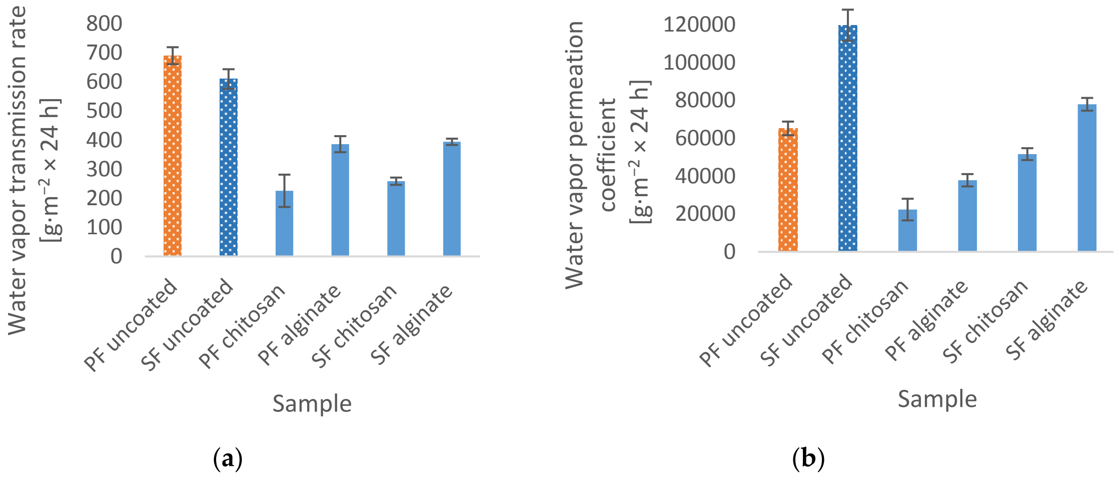


Figure 3. Water-vapor transmission rates (**a**) and water-vapor permeation coefficients (**b**) for uncoated and coated paper samples from primary fiber (PF) and secondary fiber (SF) (n = 6).

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 ~80° (chitosan) and ~35° (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.

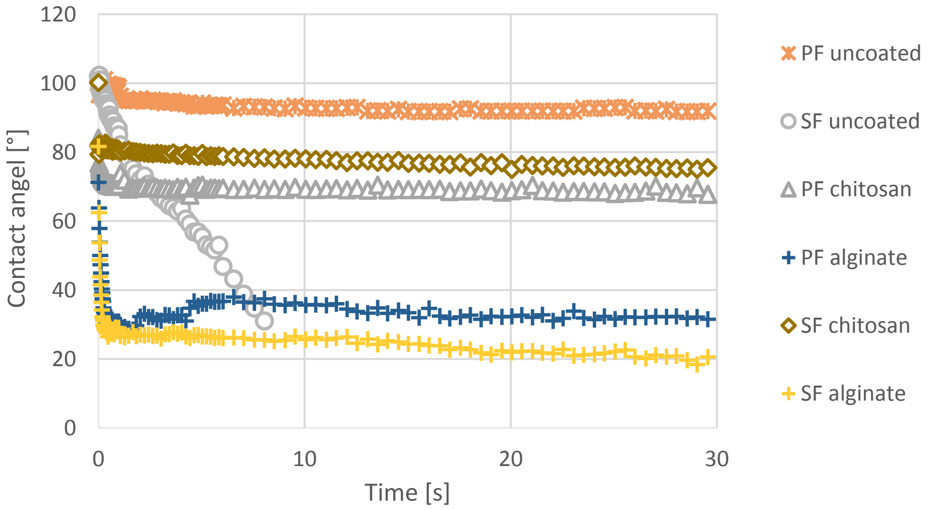


Figure 4. Contact angle of uncoated and coated samples measured with deionized water for 30 s (*n* = 6).

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

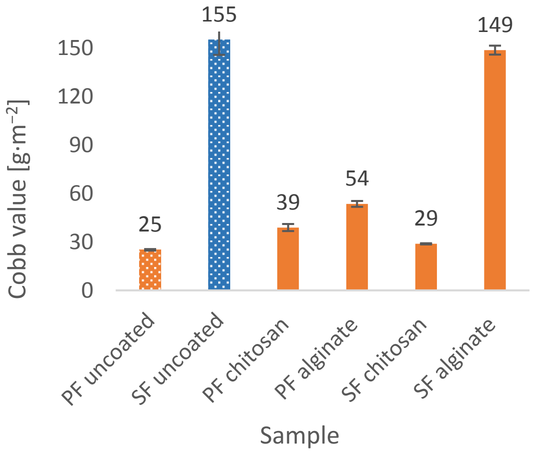


Figure 5. Cobb values for uncoated and coated samples measured for 60 s with deionized water (n = 6).

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% ± 0.1% of the observed migration was accounted for as mineral oil, which, in turn, consisted of 57.8% ± 0.1% MOSH and 6.02% ± 0.16% MOAH. Using the alginate coating, the overall migration could be reduced to 16.3% ± 1.0%, of which 7.9% ± 0.25% were mineral oil hydrocarbons (MOH), consisting of 5.49% ± 0.18% MOSH and 2.41% ± 0.42% MOAH. The chitosan coating reduced the overall migration to 29.5% ± 1.6%, which consisted of 9.16% ± 0.3% MOH, divided into 8.43% ± 0.2% MOSH and 0.73% ± 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 ± 0.10	57.80 ± 0.10	6.02 ± 0.16	36.2%
SF alginate	16.3 ± 1.0	7.90 ± 0.25	5.49 ± 0.18	2.41 ± 0.42	8.4%
SF chitosan	29.5 ± 1.6	9.16 ± 0.30	8.43 ± 0.20	0.73 ±0.34	20.3%

* Remnants consisted of substances with a retention time outside the range of C_{16}–C_{35}, 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 C_{24}, and not detectable beyond a chain length of C_{28}, 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-C_{16} and d-$C_{18.}$ An interesting observation was the behavior of the added aromatic active substances. Although all four compounds had a volatility and boiling points in the C_{12}–C_{16} 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-C_{14} to d-C_{20} were between 9.43 $\mu g \cdot dm^{-2}/day$ and 13.7 $\mu g \cdot dm^{-2}/day$ 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) ($\mu g \cdot dm^{-2}/day$; $n = 2$, data given individually).

$\frac{ug/dm^2}{d}$	**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 g·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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III

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polymers

Article

Application of Industrially Produced Chitosan in the Surface Treatment of Fibre-Based Material: Effect of Drying Method and Number of Coating Layers on Mechanical and Barrier Properties

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Abstract: Chitosan is a versatile biopolymer with many interesting functionalities. Its effects on the barrier and mechanical properties of single- or double-coated fibre-based packaging papers in dependence on the applied drying regime were successfully tested. Our investigations revealed chitosan to be a highly robust biopolymer, since the different drying regimes did not alter its contribution to the development of strength and barrier properties of the coated packaging papers. These properties showed a stronger influence of the applied coat weights than of the different drying regimes. The effect of chitosan coatings were quantified by measuring tensile strength (TS), burst strength (BS) and tensile energy absorption (TEA). These revealed that TS, BS and TEA of the coated papers increased significantly. Moreover, the chitosan-coated papers were less permeable against water vapor and air. High grease resistance was observed for double-coated papers, irrespective of the drying regimes. The coated paper surface showed a more hydrophilic character, resulting in lower contact angles and higher water absorption properties. In this study, industrially produced chitosan has been proven to be a renewable, robust biopolymer that can be utilized as an additive to increase strength and the barrier properties of fibre-based materials.

Keywords: industrially produced chitosan; surface treatment; fibre-based material; drying effects; multi-layering; barriers; mechanical properties

1. Introduction

Sustainable and renewable materials and products are constantly gaining importance in everyday life. The extensive utilization of bio-based materials is crucial for the further development of a circular bioeconomy to decrease our dependence on petroleum-based materials. Among the many well-known applications of fibre-based materials, packaging paper and board grades for food, pharmaceuticals and cosmetics are some of the most important in our daily life [1–6]. Unlike the homogeneous synthetic polymeric material, the building units of the paper network are cellulosic fibre that are heterogeneous by nature and creating a dense structure that lacks pores or voids without additives is almost impossible. The surface of fibre-based packaging materials is porous and must be treated either by applying petroleum-based polymers, biopolymers, or blends of polymeric and inorganic minerals [7–11]. Because of their innate structural properties, packaging papers and boards lack crucial barrier properties against the permeation of fat, oil, water vapor or other gases. For that reason, they have to be laminated or extrusion coated with petroleum-based polymers, which ultimately affects the sustainability, recyclability and biodegradability of the final, fibre-based packaging products [12–15]. The tensile properties of paper and board can be improved by blending cellulosic fibres with functional strength additives to increase the bonding area and strength between fibres, which leads to an increase in the overall packaging strength [16–20].

Packaging consumption is directly related to the growth of the global population and the increase in online commerce. The results of the current forecast for the global packaging market indicate a growth in consumption of at least 4% in 2018 to a market volume of almost 1 trillion USD. The demand for functional chemicals, such as strength additives and barrier coatings for packaging applications, that today still are mainly petroleum-based, has also increased since 2015 by at least 5% per year [21,22]. Possible alternatives for the substitution of non-renewable packaging materials are combinations of paper and board with renewable biopolymers, such as industrially produced chitosan. Its production has steadily increased along with growing application in the food, textile, pharmaceutical industries, and, more recently, in the packaging industry [23,24]. Chitosan is a biopolymer which is abundant in nature, fully biodegradable and renewable and has a high potential to be used in the surface treatment of paper and board to improve its structural, mechanical and barrier properties. Chitosan is derived from chitin, found in exoskeleton of insects or crustaceans. Under defined conditions regarding pH, degree of polymerization and deacetylation, chitosan has the character of a polyelectrolyte and becomes fully water-soluble [25–28].

The chitosan as a natural material is in focus of many researchers all over the world and several references citied in our work are dealing with chitosan barrier and strength properties investigations. However, previous investigations such as influence of drying on barrier and strength properties were mostly performed using casted freestanding films. Furthermore, the cellulosic fibre based substrates that have been used for coating are laboratory-produced paper sheets, which serve as a model for possible industrial applications [29–31]. The results of already published work represent valuable basis for further development and practical applications of chitosan in surface treatment of fibre based packaging material presented in our work.

The subject of our investigation was an experimental study of the barrier and mechanical properties of industrial grade chitosan coated onto paper surfaces. We investigated how chitosan coated onto paper is influenced by different drying regimes used in the paper coating industry (Infrared or hot air drying). Our experimental approach evaluated whether drying could potentially influence the development of strength properties and alter the surface and barrier properties. Additionally, we evaluated the impact of two different applied coat weights by single or double coating the paper on the barrier and mechanical properties. The coating technique applied in this work was a laboratory film press, which was designed to simulate the real industrial-coating environment accurately. For the thus coated papers grease resistance, water vapor transmission rate, air permeance, wettability (contact angle) and water absorption were determined. The coated surface was visualized using scanning electron microscopy (SEM) and the most important mechanical properties of packaging materials, such as the tensile strength, burst strength, tensile energy absorption were assessed. Our results indicate that chitosan has the potential to improve both the mechanical and barrier properties of fibre-based packaging material.

2. Materials, Equipment and Methods

2.1. Raw Materials and Characterization

Industrially produced chitosan (CAS: 9012-76-4, poly-[1,4]-β-D-glucosamine) was purchased from Biolog-Heppe GmbH (Landsberg, Germany). Chitosan was supplied as a solid powder (yellow particles). The most important, product-specific data received from the chitosan producer are summarized in Table 1. The applied chitosan has a medium molecular weight and viscosity, making it suitable for application using the film press method. The substrate used for surface treatment was an industrially produced base paper from an Austrian paper mill. The base paper consists of a mix of bleached hardwood and softwood chemical pulp. The paper was mass sized using alkyl ketene dimer (AKD) and the surface was untreated.

Table 1. Properties of industrially produced chitosan used for the preparation of the coating formulation [32].

Raw Material	Ash Content [%]	Molecular Weight [kDa]	Degree of Deacetylation [%]	Particle Diameter [μm]	Dynamic Viscosity * [mPa·s]
Chitin from crustaceans	≤1	115	90	≤200	135

* Viscosity of 1% chitosan (*w*/*w*) in 1% (*w*/*w*) acetic acid under standard conditions.

2.2. Coating Machine

The laboratory coater used for surface treatment of the fibre-based substrate was a film press Coating Unit CU 5 supplied by Sumet Messtechnik GmbH (Denklingen, Germany). The coater is equipped with an applicator roll (diameter of 95 mm and width of 300 mm) and, depending on the coating material and substrate, the contact force for rolls can be adjusted (0–1150 N at 8 bar). Between the application rod and substrate, the possible contact force ranges from 0 to 230 N at 8 bar. The coater was equipped with an air-drying system (max. 2000 W) and an infrared emitter (max. 3 × 1500 W). The coating speed was adjusted to 5 m/min for the performed trials 1–6 (Table 2). A drying time of 4 s (power output 100%) with infrared (IR) heating and 120 s (power output 100%) with hot air (HA) heating was used. During the simultaneous drying regime (IR + HA), drying was first conducted for four seconds with the IR emitter, followed by 120 s with the HA heater. Due to the shorter drying time and unequal energy input moisture content of dried samples is variable. The IR and HA dried samples might manifest higher amounts of moisture compared to intensive simultaneous drying method (IR + HA). For that reason, all samples dried with different drying methods were equally conditioned in climate chamber for 48 h at 23 °C and 50% RH prior characterization [33].

Table 2. Design of coating trial with defined layer thickness, number of layers, drying regimes and coat weights. Trials with one layer of chitosan are indicated by trial numbers 1, 2 and 3 (light blue) and trials with two chitosan layers are indicated by 4, 5 and 6 (light green).

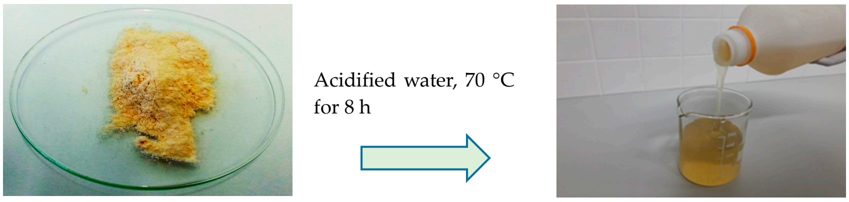
Trial	Wet Layer Thickness [μm]	Number of Layers	Drying Regime	Dry Coat Weights [g/m^3]
1	60	1	IR + Hot air	
2	60	1	IR	
3	60	1	Hot air	
4	60	2	IR + Hot air	
5	60	2	IR	
6	60	2	Hot air	

2.3. Design of Coating Trials

Table 2 lists the coating parameters which were altered in the six trials. The first three trials were performed with one layer of chitosan (see Table 2). The second layer was applied under the same conditions with a targeted coat weight of 3 g/m^2 for one layer and 6 g/m^2 for two layers. The top side of the paper was coated and all samples were one-side coated. The applied dry coat-weight was controlled for each coated sheet by weighing and only sheets that deviated less than 5% from the target coat-weight were accepted. The wet layer thickness was controlled by the use of a grooved rod and in both cases was 60 μm.

2.4. Preparation of Chitosan-Based Coating Solution

The desired solid content of the chitosan formulation used in coating trials was 5% (*w*/*w*). This concentration was achieved by dissolving the chitosan in hot water and adjusting the pH using acetic acid (pure, technical grade from Rotipuran) (see Figure 1). The distilled water was heated to 50 °C and stirred at 600 rpm for ten minutes. Subsequently, the chitosan powder was added in portions (1–2 g) to the heated water (held at 50 °C). After dispersion of the chitosan powder the temperature was increased to 70 °C. Small portions of acidic acids were added (0.5–1 mL) to improve and fully solubilize the chitosan, which occurs at a pH lower than 6 [34,35]. This solution was then stirred for 8 h at 70 °C, once the chitosan particles had fully dissolved. Deprotonated (referring to water-soluble chitosan) chitosan is positively charged and charge was monitored by measuring the zeta potential using a Stabino particle charge mapping analyser (Colloid and Particle Metrix GmbH, Inning am, Ammersee, Germany). The average zeta potential of the chitosan was +475.0 ± 45.3 mV, which indicated that the solution was stable.



Chitosan powder

(**a**)

Water-soluble chitosan coating solution

(**b**)

Figure 1. Chitosan powder in its native form (**a**) and chitosan fully dissolved in water, used for surface treatment of the fibre-based substrate (**b**).

2.5. Flow-Behaviour of Water-Soluble Chitosan Solution

The viscosity of the 5% (*w*/*w*) chitosan solution was measured using a rotational rheometer (Paar Physica MCR 301, Anton Paar, GmbH, Germany) at low, medium and high shear rates under standard conditions. In the Table 3 mean values and corresponding standard deviations of four-fold viscosity measurements for each shear rate are given (n = 4). The shear rates were chosen to represent the conditions in an industrial coating process regarding pumping, mixing and metering in a film press using a rod. Shear rates during pumping and mixing lie in the range of 0.1 to 1000 1/s, whereas in grooved rod metering shear rates of 50,000 1/s and higher are observed. The viscosity of the chitosan decreased at higher shear rates, meaning that the chitosan solution displayed shear-thinning flow behaviour. This is an important characteristic of a coating material intended to serve as a surface-treatment chemical in film press coating, as it is directly related to both the material coatability and to the runability of the coating machine [36–38].

Table 3. Viscosity of chitosan, shear rates, corresponding operation stages and units (n = 4).

Operation Stage	Operation Units	Shear Rate [1/s]	Viscosity [mPa·s]
1	Pumping	0.1	6760.1 ± 834.4
2	Mixing	1000	762.5 ± 44.6
3	Coating	50 000	59.5 ± 2.6

2.6. Determination of Dry Coat Weight; Basis Weight, Density and Thickness

The uncoated and chitosan-coated paper samples were conditioned according to the standard [33] in a climate room for 48 h at 50% relative humidity ±3% and 23 ± 1 °C. Conditioned samples were used for the assessment of basic physical properties, such as basis weight, thickness, density and dry coat weight as well as the evaluation of mechanical and barrier properties [39,40]. The basis weight of the uncoated raw paper was determined using an analytical balance (Sartorius BP 210D, Sartorius AG, Göttingen, Germany) and the thicknesses of the samples were measured with a Lehmann thickness tester. After determining the basis weight, the dry pick-up weight (equal to the dry coat weight) for coated samples was calculated using Equation (1), where the basis weight of the coated paper (cp) was subtracted from that of the uncoated paper (up).

$$\text{Dry coat weight}\left[\frac{\text{g}}{\text{m}^2}\right] = \text{Basis weight cp}\left[\frac{\text{g}}{\text{m}^2}\right] - \text{Basis weight up}\left[\frac{\text{g}}{\text{m}^2}\right] \tag{1}$$

2.7. Evaluation of Mechanical Properties

Important tensile properties for packaging materials, such as the tensile strength (TS) and tensile energy absorption (TEA), were measured using a universal tensile tester Zwick Z010 (Zwick, Ulm, Germany) and the data were analysed using the software testXpert V3.0. The measurements were performed for both the cross direction (CD) and machine direction (MD). The test speed (strain rate) of the Zwick tensile tester was the same for all samples (5 mm/min). Samples were cut into strips, each with a width of 15 mm and length of 15 cm. The clamp distance of the Zwick tensile tester at start position was 50 mm for all samples. The determination of the burst pressure was performed using an L & W bursting strength tester SE 180 [41]. The bursting strength of the samples is expressed as burst pressure. The clamp force and gauge pressure of the burst strength tester were 2900 N and 0.22 MPa, respectively.

2.8. Determination of Barrier Properties, Wettability and Water Absorption

The water vapor permeability, expressed as water vapor transmission rate (WVTR), was measured using a gravimetric method according to the standard at 23 °C and 50% RH [42]. The test area used was 50 cm^2 and the measurements were performed over 24 h. Silica gel was used as a desiccant (20 g of silica gel with indicator, Carl Roth GmbH, Karlsruhe, Germany), pre-dried at 160 °C for 24 h. The calculation of the water vapor transmission rate (g/m^2 24 h) was performed using Equation (2), where Δm represents mass gains in grams over the time period t, t is the time interval in hours and A is the sample test area exposed to desiccant.

$$WVTR = \frac{\Delta \text{m}}{\text{A} * \Delta \text{t}} \tag{2}$$

The grease resistance of the uncoated and coated samples was measured according to Tappi 559 paperboard [43]. This procedure is better known as the KIT test and represents the resistance of a material to penetration by oils and fats. Prior to testing the samples, fresh KIT testing solutions based on different mass ratios of hexane (analytical grade, Merck, Vienna, Austria), toluene (analytical grade, Carl Roth GmbH, Karlsruhe, Germany) and castor oil (pharmaceutical grade, Merck, Vienna, Austria) were prepared according to the standard. In total, twelve different solutions (1–12) were prepared and used for the assessment of grease resistance.

The air permeance of the coated samples was evaluated by measuring the air-flow rate according to the Bendtsen method [44]. The test area was 10 cm^2 and the applied testing pressure was 1.47 kPa. The air permeance (P) in µm/(Pa·s) was calculated by using the Equation (3) in accordance with the Bendtsen method: where q is the air flow rate in mL/min, A is the tested area of the sample (cm^2) and p is the testing pressure multiplied by factor k (k = 6).

$$P = \frac{\text{q}}{\text{k} * \text{A} * \text{p}} \tag{3}$$

The water absorption of the samples was measured using a Frank PTI Cobb tester [45]. The tested area of the samples was 100 cm^2. The water absorption of the uncoated and coated samples was measured using deionized water for 60 and 1800 s, respectively. The Cobb_{60s} and Cobb_{1800s} were given as the mass of water that was absorbed by sample (g/m^2) over the given period of time.

The surface wettability (Contact angle) of all samples were measured with deionized water using a Fibrodat 1100 device (Fibro System AB, Stockholm, Sweden) [46]. Samples were cut into strips (10 cm × 1.5 cm) and placed into the sample holder, then covered with double-sided tape. For each strip, 10 drops of water were placed on the strip and the contact angle was determined. The volume of the dosed water drop was 4 µL, which was kept constant for all samples.

2.9. Surface Analysis

The characterization of the surfaces was performed at low acceleration voltages of the electron beam (low voltage scanning electron microscopy, LVSEM, Technologies Inc., Salem, OR, USA) using the high resolution scanning electron microscope Zeiss Sigma 300 VP (Zeiss, Oberkochen, Germany) and the Everhart-Thornley Secondary Electron Detector (ETD, SE2 according to the databar of the micrographs, Oberkochen, Germany). All images were acquired at an acceleration voltage of 0.65 kV (i.e., the landing energy of the electrons is 0.65 keV) at small working distances with a magnification of 500× (horizontal image field width: 228.7 µm). Each of the samples was cut in squares measuring 1.5 cm × 1.5 cm. These squares were mounted on SEM stubs using a conductive double-faced adhesive carbon tape with no further preparation since LVSEM enables imaging of surfaces without coating [47].

2.10. Statistical Analysis

All data are given as mean values with the corresponding standard deviations. The number of replicates for each measurements is provided in the description of the figures and tables (n = number of replicates). An analysis of the experimental data was performed using the ANOVA function in Microsoft Excel with a confidence interval of $p < 0.05$. In order to establish the statistical differences between mean values, an analysis was performed using the Tukey-Kramer test with a confidence interval of $p < 0.05$.

3. Results and Discussion

3.1. Physical Characterization of Uncoated and Coated Samples

Table 4 shows the basis weight, bulk density, thickness and coat weights for all samples. The bulk density was calculated by division of the basis weight by thickness. As expected, the bulk density of the chitosan-coated samples increased compared to the uncoated paper with the double coated paper showing the highest densities. The dry coat weights were in the desired range of 3 and 6 g/m^2 with corresponding standard deviations of less than 5%.

Table 4. Basic characterization: thicknesses, basis weight, bulk densities, dry coat weights and number of chitosan layers of substrate and coated samples from trials 1–6 (n = 15).

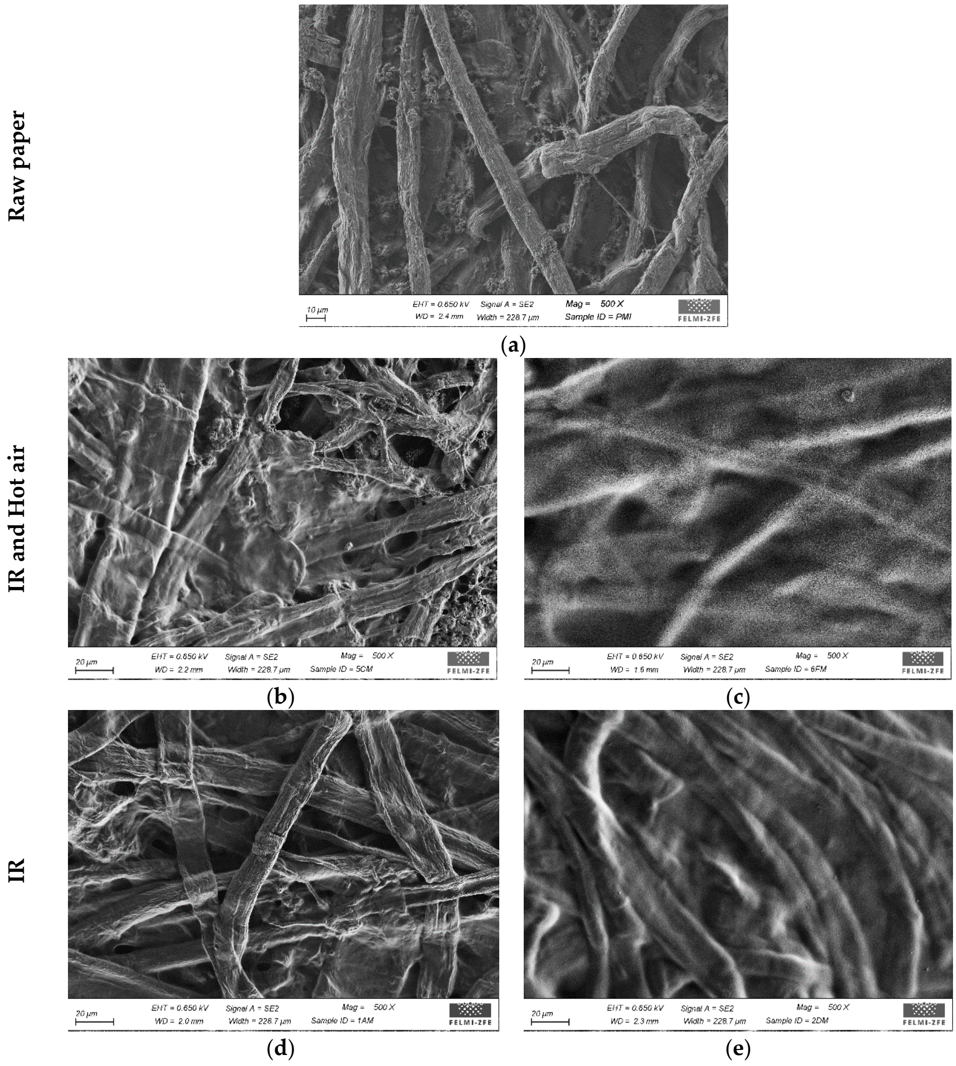
Specimen	No. of Chitosan Layers	Thickness (µm)	Basis Weight ($g{\cdot}m^{-2}$)	Bulk Density ($g{\cdot}cm^{-3}$)	Dry Coat Weight ($g{\cdot}m^{-2}$)
Substrate	-	95.8 ± 1.2	72.3 ± 0.5	0.75 ± 0.01	0
1 (IR + HA)	1	98.2 ± 1.0	75.4 ± 0.3	0.77 ± 0.01	3.1 ± 0.1
2 (IR)		98.0 ± 1.0	75.3 ± 0.4	0.77 ± 0.02	3.0 ± 0.1
3 (HA)		98.4 ± 1.1	75.4 ± 0.6	0.77 ± 0.01	3.1 ± 0.1
4 (IR + HA)	2	100.1 ± 1.3	78.3 ± 0.6	0.78 ± 0.01	6.0 ± 0.2
5 (IR)		99.9 ± 1.7	78.4 ± 0.7	0.78 ± 0.01	6.1 ± 0.2
6 (HA)		100.0 ± 1.4	78.4 ± 0.4	0.78 ± 0.02	6.1 ± 0.1

3.2. Effects of Drying and Chitosan Layers on Surface Topography

The coating layer quality was assessed using scanning electron microscopy (SEM). Conventional, water-based coating solutions, unlike those containing chitosan, usually have viscosities below

100 mPa·s. The lower viscosity of the coating solution promotes a higher degree of penetration into the substrate, which could be beneficial to the development of the material strength properties [37].

We used surface visualization to evaluate the differences between uncoated and coated samples and effects of the drying method on the formation of the chitosan layer on the paper surface. In the Figure 2, SEM images with magnifications of 500× are shown for the raw uncoated paper and coated paper samples. Surface of the uncoated raw paper with visible fibres and voids, seems to be very porous, thus enabling chitosan solution to penetrate easily into paper structure. In accordance with SEM images it can be optically seen that after coating of the raw paper, pores and fibres are partially or totally covered with chitosan. Samples coated with one layer show a poorer coating coverage compared to those coated with two layers of chitosan, where a homogenous layer without visible fibres or voids was observed. The differences between paper surface coated with one layer and dried with IR, HA and IR + HA are also observed and might depend on different drying time and drying energy input. We observed that the drying influenced the coverage of the fibres. It is noticeable that the HA and IR + HA drying methods allowed the layer to consolidate more rapidly due to higher drying energy input compared to 100% IR drying method, where the drying was conducted for shorter period of time (see Section 2.2). According to our results, it can be stated that two layers of chitosan are able to close the pores and covers the fibres surface, irrespective of drying method. When it comes to one layer of chitosan, shorter drying leads (IR) to worse surface coverage compared to longer drying (HA and IR + HA).

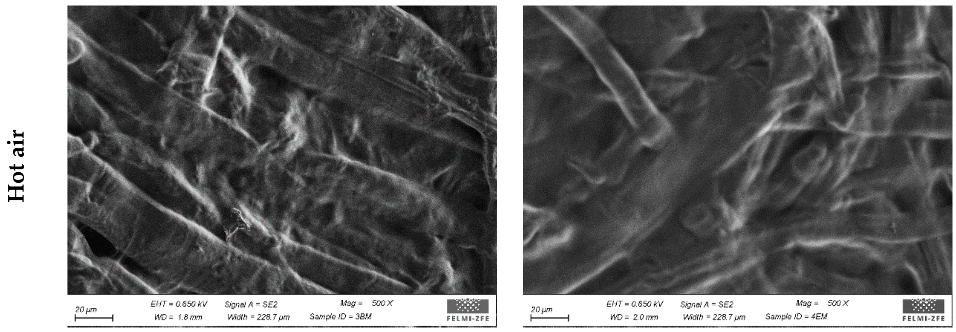


(**a**)

(**b**) (**c**)

(**d**) (**e**)

Figure 2. *Cont.*

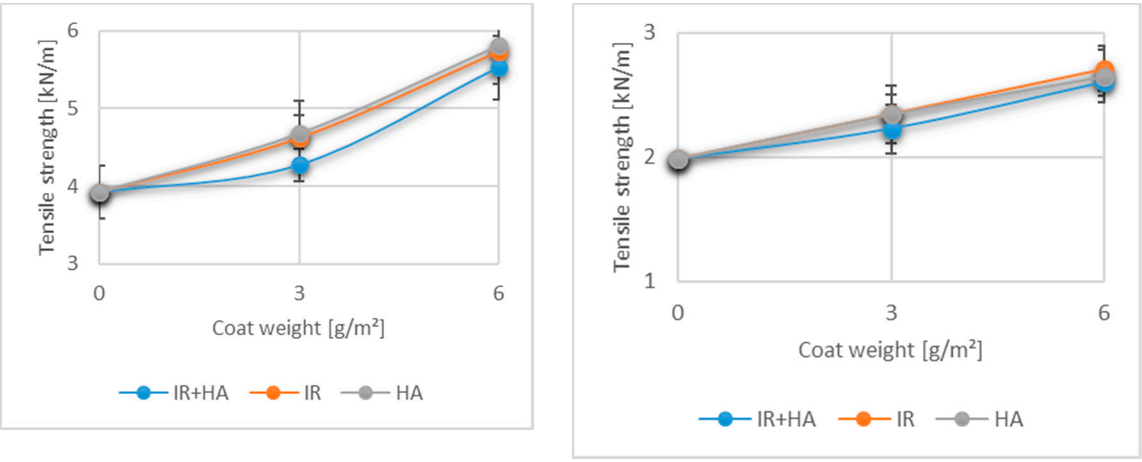


(**f**) (**g**)

Figure 2. Visualized surface (SEM) features of uncoated raw paper and chitosan-coated samples dried using various methods: (**a**) Raw paper; (**b**) IR + Hot air (1 layer); (**c**) IR + Hot air (2 layers); (**d**) IR (1 layer); (**e**) IR (2 layers); (**f**) Hot air (1 layer); (**g**) Hot air (2 layers).

3.3. Effects of Chitosan Coating and Drying Regime on Tensile Strength

The tensile properties of uncoated fibre-based materials are influenced predominately by the strength and length of individual fibres, bonding strength of fibre-fibre bonds and bonding area [48]. Tensile properties are one of the most important mechanical properties of paper-based packaging materials, due to their direct correlation to material failure during converting operations. Furthermore, they are also an indication of how paper will perform at different loads for some specific packaging application. In Figure 3 the mean values for tensile strength (n = 15) with corresponding standard deviations are given.



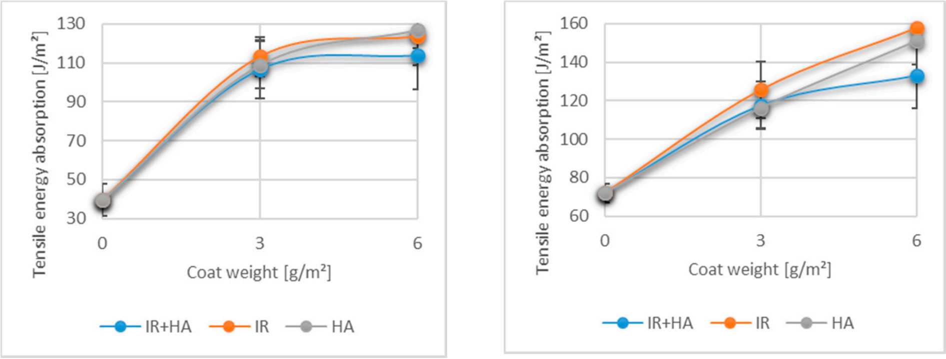
(**a**) (**b**)

Figure 3. Tensile strength (TS) of paper coated with 3 g/m^2 (1 layer) and 6 g/m^2 (2 layers) of chitosan: (**a**) TI for machine direction (MD); (**b**) TI for cross direction (CD). (n = 15).

For both measurements in MD and CD a noticeable increase in the paper tensile strength is observed for the papers coated with one and especially with two chitosan layers. The results of statistical analysis indicated no statistically significant effects of drying on the TS values obtained in both MD and CD for one or two layers ($p > 0.05$). These results agree well with research performed using chitosan films, which found no significant difference between different drying technologies [31]. Furthermore, obtained results are in alignment with published data reporting a positive influence of chitosan coatings on development of fibre-based material strength properties [49–51].

3.4. Effects of Chitosan and Drying on Tensile Energy Absorption

Tensile energy absorption (TEA) is a further significant property of packaging materials and is indicative for the energy taken up by the paper during fracture. It is defined as the total work consumed during tensile testing per unit area of the sample [52,53]. Figure 4 depicts the mean values and corresponding standard deviations for TEA (MD and CD) for one and two chitosan layers. It is evident that, even with one chitosan layer, the TEA in both CD and MD was improved by at least 60% compared to uncoated paper. With two layers of chitosan, an increase in the TEA of at least 85% compared to uncoated paper was observed.



(**a**) (**b**)

Figure 4. Tensile energy absorption (TEA) of paper coated with 3 g/m^2 (1 layer) and 6 g/m^2 (2 layers) of chitosan: (**a**) TEA for machine direction (MD); (**b**) TEA for cross direction (CD). (*n* = 15).

Although the values obtained with IR and HA drying were slightly higher than those obtained with HA + IR, again no statistically significant effects of the drying method were observed for the single or double chitosan coated samples ($p > 0.05$). According to the results of our analysis, chitosan generally has remarkable influence on the tensile energy absorption.

3.5. Effects of Chitosan and Drying on Burst Strength

Together with TI and TEA, bursting strength (see Figure 5) is a further important material property of packaging papers. Although the principle of measurement differs from TI and TEA, it can still be correlated with these values regarding the final application of paper-based packaging materials. Bursting strength is defined as the amount of hydrostatic pressure applied to circular sample area. It provides an indication of the resistance of the paper to rupturing and paper with a low burst strength cannot retain packed goods and tears easily [54]. The burst pressure of raw paper is 175.3 ± 15.0 kPa. By coating the paper with one layer of chitosan, the burst pressure can be enhanced by at least 25%. By adding two layers, the burst strength is improved still further, whereby an increase of 32% compared to that of uncoated paper was achieved.

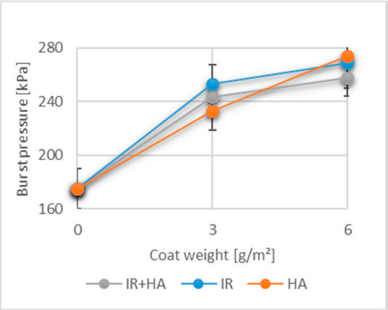


Figure 5. Burst pressure of uncoated paper and paper coated with 3 g/m^2 (1 layer) and 6 g/m^2 (2 layers) of chitosan. (*n* = 15).

The interaction between chitosan as a cationic biopolymer and cellulosic fibres seems to be intense, due to fact that the overall paper burst strength was improved. This improvement could be a result of new bonds created between chitosan and the fibres and a greater bonding area created between fibres. The development of the burst pressure follows the same trend that has already been seen with the tensile strength and tensile absorption energy. The mean values obtained from samples coated with one or two layers and then dried using either the IR, HA, or both methods, were not significantly different ($p > 0.05$) meaning that the increase in the burst strength was definitely affected by the higher coat weights and can potentially be improved greatly by using industrially produced chitosan.

3.6. Effects of Drying and Chitosan Layers on Air Permeance

The air permeance of uncoated and coated samples is shown in Figure 6. The air permeance of uncoated paper (9.2 ± 0.6 µm/Pa·s) was significantly higher than that of paper with one chitosan layer regardless of the drying method used. The air permeance values of the single coated samples dried using the IR (0.32 ± 0.01 µm/Pa·s), IR + HA (0.11 ± 0.05 µm/Pa·s) and HA (0.02 ± 0.01 µm/Pa·s) correlated with the observation from the SEM images. For all three drying techniques there was some penetration of the chitosan into the paper structure. This prevented full film formation, yet it resulted in a lower air flow. Statistical evaluation of the results, however, indicated, that the values were not significantly different. Two layers of chitosan, irrespective of the drying method used, reduced the airflow to 0 mL/min which indicates full film formation and surface closure. These results correlate well with the SEM images where a clear film formation was observed when two chitosan layers were applied to the paper making the sample impermeable to air.

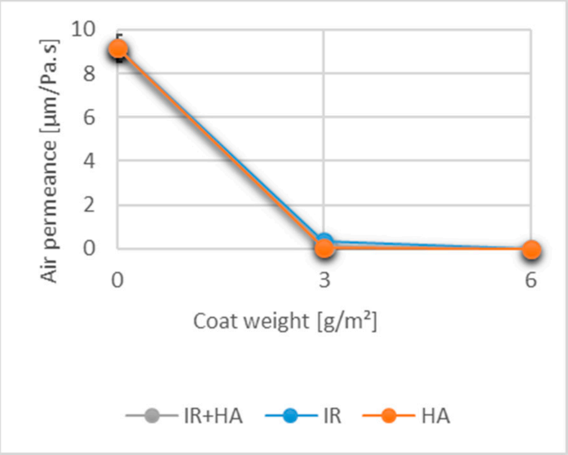


Figure 6. Air permeance for uncoated paper and coated substrates with one and two layers of chitosan. (n = 15).

3.7. Effects of Drying and Chitosan Layers on Greases Resistance

Grease (oil and fats) resistance is an important property of packaging materials. Depending on the future applications, coated material can come into direct contact with different types of oil and fat, which originate from different sources. The KIT test employed to measure the oil and fat resistance of our samples coated with one layer of chitosan gave the following results: 4.0 ± 1.0 (IR + HA), 5.0 ± 1.0 (HA) and 7.0 ± 0.5 (IR) (see Figure 7).

According to the results of the ANOVA analysis, the p-value was equal or greater 0.05, meaning that values are significantly different. Thus, the Tukey-Kramer test was performed to ascertain the differences between the use of the different drying methods. The fat resistance with IR drying was significantly different from that of IR + HA (one sided test), however, no significant difference was observed with HA drying.

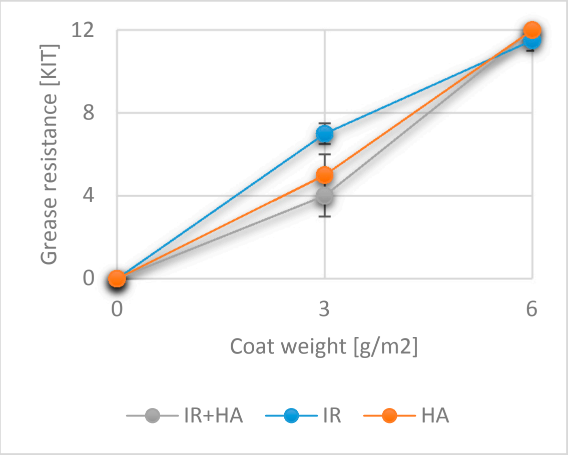


Figure 7. Grease resistance as measured with the KIT test for uncoated substrates and coated substrates with one and two layers of chitosan. (KIT, *n* = 6).

Irrespective of the drying method used, the KIT values for samples with two layers reached a maximum of twelve with a corresponding standard deviation of less than 5%. The behaviour of chitosan depends on the pH environment, level of de-acetylation, degree of polymerization and interactions with the substrate. It acts act as a hydrophilic agent which should be beneficial for grease resistance [38,55].

3.8. Effects of Drying and Chitosan Layers on the Water Vapor Transmission Rate

The water vapor transmission rate (WVTR) is one of the most frequently measured and important properties of food packaging materials. The controlled transmission of water vapor into packaging crucially affects the preservation of packed goods. Moisture can alter the quality of packaged goods by allowing the growth of microorganisms, increasing spoilage rates and shortening the product shelf life. Especially dry food and its quality features (e.g., crispness) are affected by uncontrolled water vapor transmission into packaging [3,4]. The average WVTR values measured for uncoated (689.7 ± 29.2 g/m^2 24 h) and coated paper are given in Figure 8. By adding one layer of chitosan, the WVTR was reduced by at least 50% for all drying methods. Adding two layers of chitosan prevented more than 70% of total water vapor transmission compared to the uncoated sample. For both single and double coated samples the effect of the drying regime showed no statistically significant influence.

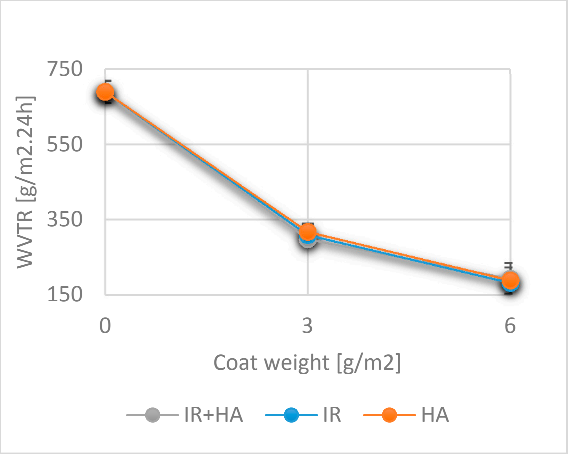
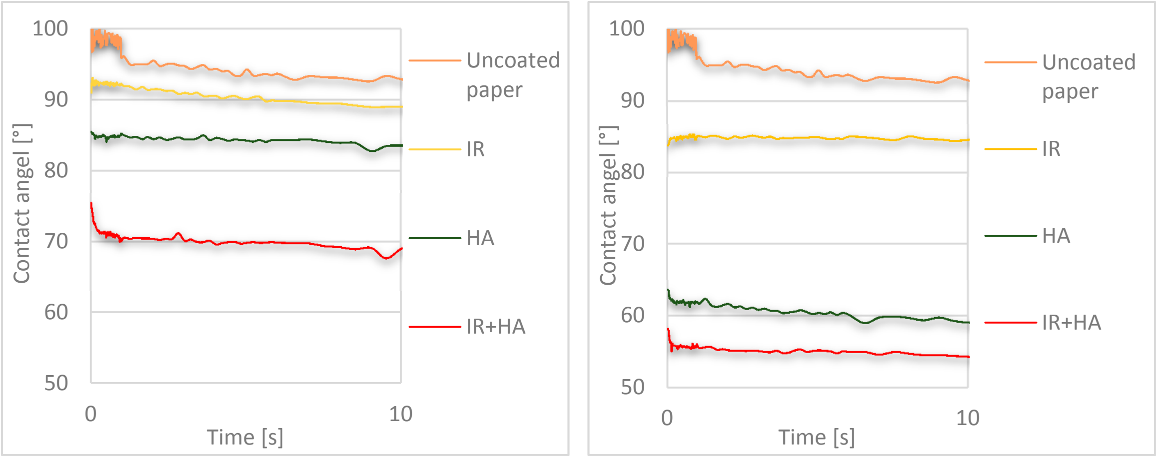


Figure 8. Water vapor transmission rates for uncoated paper and chitosan-coated paper. (*n* = 6).

These results lead us to the conclusion than chitosan, as a polymeric material, is able to impregnate the paper structure, close the pores, repress and reduce the transmission of water vapor. We believe that the largest part of the reduction in water vapor transmission is due to the closing of the pores as demonstrated by the air permeance measurements, Figure 6. However, unlike the air permeance water vapor transmission does not go down to zero at 6 g/m^2 coat weight. This can be attributed to the hydrophilic nature of the chitosan which enables water vapor diffusion through the closed paper surface. The results obtained are in accordance with those of previously reported investigations [31,56,57].

3.9. Effects of Drying and Chitosan Layers on Wettability and Water Absorption

The wettability of chitosan-coated and uncoated substrates was studied by measuring the contact angle over ten seconds using deionized water (Figure 9). Water absorption as a material bulk property was determined with Cobb measurements according to ISO 535 for 60 and 1800 s (Figure 10). The uncoated substrate, which was internally sized with an AKD size, had a higher contact angle (~90°) compared to the chitosan-coated samples. When adding one layer of the hydrophilic chitosan, the contact angle was reduced by nearly 5° with the IR, 10° with the HA and around 25° with the HA + IR drying methods. The lower influence for IR drying correlates well to the poorer coverage of the fibres by chitosan as observed in the SEM image (see Figure 2). As a result, the paper surface, which shows a high contact angle due to internal sizing with AKD, is more exposed to water compared to coated papers dried with the HA and IR + HA methods and the contact angle is more similar to the one of the uncoated paper. A similar observation was also made for samples with two chitosan layers, with the reduction in the contact angle being larger due to the higher coat weights. For IR drying the contact angle was reduced by up to 10°, using HA drying by 35–40° and for IR + HA by 40–45°. Based on these measurements, we can state that different drying methods have an effect on the wettability of single and double chitosan coated samples. However, the wettability definitely correlates with a higher amount of the hydrophilic chitosan coated onto the surface.

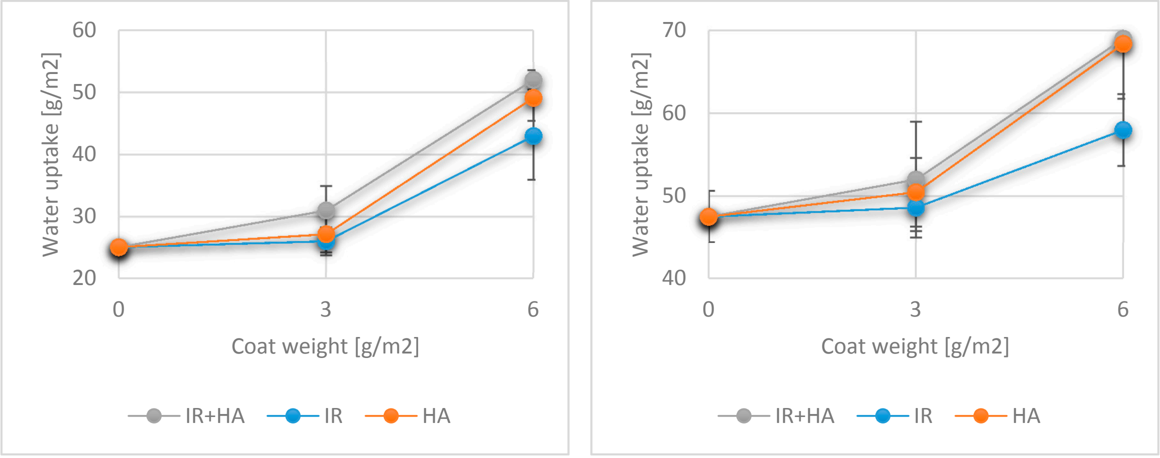


(**a**) (**b**)

Figure 9. Contact angle of uncoated samples and coated samples measured with deionized water for 10 s: (**a**) Cobb 60 s; (**b**) Cobb 1800 s. (*n* = 10).

The water absorption of materials is a time-dependent property and is measured as the capacity of the material to absorb water over a certain amount of time. The Cobb values of the uncoated substrate showed a higher uptake for 1800 s (47.5 ± 3.12 g/m^2) compared to the uptake for 60 s (25.09 ± 0.48 g/m^2). Water absorption over 60 s and 1800 s increased for samples coated with one layer of chitosan and further increased, when applying two chitosan layers. This correlation of higher amounts of chitosan coated onto the paper surface to the observed higher values for water absorption agrees with data found in the literature [58].

Comparison of the different drying regimes showed significantly different absorption values at 60 s and 1800 s for IR drying compared to the two other drying methods for both single and double coated papers. These results correlate well with the contact angle measurements, where IR drying also had a different effects on the surface wettability compared to other two drying methods.



(**a**) (**b**)

Figure 10. Cobb values for 60 s (**a**) and 1800 s (**b**) with uncoated samples and coated samples with one and two layers of chitosan. (*n* = 8).

According to the results of our investigations, a difference between the surface and bulk properties can be distinguished regarding the influence of chitosan application. The contact angle mostly depends on surface chemistry and presence of pores or voids and it was influenced by altering these parameters using chitosan as a coating material. Different drying methods seemed to affect the consolidation and retention of the chitosan layer on the paper surface, as seen in the SEM images and thus also the penetration of chitosan into the paper structure. For this reason, the wettability was also changed and the hydrophilicity of chitosan contributed to the measurement of lower contact angles and these contributions can be influenced by using different drying methods. On the other hand, bulk properties such as water absorption or grease resistance do not necessarily depend on the surface properties but rather on the material composition. In our case, one layer of 3 g/m^2 of chitosan seemed to be sufficient to impregnate the paper and to penetrate into the network structure, thus, changing the material composition. By adding two layers, this impregnation was followed by film formation, whereby both the bulk and surface composition were altered. This resulted in moderate changes in bulk properties such as water absorption, when one layer was added and a significant impact when two layers were added, independent of the drying method used.

4. Conclusions

Application of chitosan in surface treatment of fibre-based material improved the mechanical properties such as tensile strength, burst strength and tensile energy absorption. Voids and pores of the uncoated paper were partially covered with one layer of chitosan and fully covered with two layers, thus reducing the air or water vapor permeability. Air permeance can be reduced to 0 µm/Pa·s depending on the number of layers added. The water vapor transmission rate was also reduced compared to raw paper, however it due to the hydrophilic character of chitosan it does not go down to zero. The surface of coated paper was hydrophilized by chitosan addition as demonstrated by a lower water contact angle, the water absorption increased. Grease resistance of chitosan-coated paper is moderate with one coating layer (KIT = 4 to 7) and high with two layers (KIT = 12).

Based on the measurements and results of the statistical analyses, the barrier and mechanical properties of coated material are not significantly impacted by the use of the different drying methods.

While not significant in statistical tests the mechanical properties of IR + HA drying are worse in nearly every case and the surface hydrophilicity is higher, which indicates a systematic trend. We think that better surface retention of the chitosan due to higher energy input during IR + HA drying causes better film building with this drying method. These differences between the drying techniques could be a future approach to altering the surface functions of chitosan-coated paper.

According to our results it can be also stated that one layer of chitosan, is not sufficient to form the film onto paper surface. Therefore, for some specific application either substrate with smoother structure should be used or at least two chitosan layers must be applied in order to create clear homogenous film onto surface, irrespective of drying method used. The mass percentage of chitosan in the paper coated with 3 g/m^2 and 6 g/m^2 was around 4% and 8%, respectively, in terms of the paper basis weight. Considering that the mass percentage of conventional chemicals used as strength or barrier additives in paper-based packaging materials can exceed 10%, chitosan performed excellent as a strength and barrier additive [54]. With respect to the different drying methods, we conclude that chitosan performs well with infrared (IR), hot air (HA), or simultaneously drying (IR + HA) methods and, therefore, represents a potential functional coating material that can be used in an industrial production environment.

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