

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
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Master's Degree Program in Chemical and Process Engineering

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GELATIN AS AN ADDITIVE IN BIO-BASED BARRIER FILMS

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ABSTRACT

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Gelatin as an additive in bio-based barrier films

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The main objective of the present study was to verify the approach on starch-gelatin blending for the paperboard coating formulations with enhanced barrier and mechanical properties. Based on that, another objective was to find out, how the approach will function with wood-based polysaccharides (CMC, EHEC and HPC) by analyzing their barrier properties and convertibility. The last objective was to find out, if pigments can be used in the composition of polysaccharide-protein blends without causing any negative effect on stated properties.

The whole process chain of the barrier coating development was studied in the research. The methodology applied included pilot-scale coating and converting trials for the evaluation of mechanical properties of obtained coatings, namely their exposure to cracking with the loss of barrier properties.

The results obtained indicated that the combination of starch with gelatin, in fact, improves the grease barrier properties and flexibility of starch-based coatings, thereby confirming the offered approach. The similar results were obtained for CMC, exhibited elevated barrier properties and surface coverage, proving that the approach also functions with wood-based polysaccharides. The introduction of equal amounts of talc gave various effects at different gelatin dosages on barrier properties of wood-based polysaccharides. Mainly, the elevation of grease barrier properties was observed. The convertibility of talc-filled coatings was not sufficient.

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Anastasia Annushko

LIST OF ABBREVIATIONS

BC	Bacterial cellulose
CMC	Carboxymethyl cellulose
cP	Centipoise
DSC	Dry solids content [%]
EAB	Elongation at a break [%]
EHEC	Ethylhydroxyethyl cellulose
EM	Elastic modulus [Pa]
HPC	Hydroxypropyl cellulose
HPMC	Hydroxypropylmethyl cellulose
HPS	Hydroxypropylated starch
MC	Methyl cellulose
OGR	Oil and grease resistance [min]
OTR	Oxygen transmission rate $[(\text{cm}^3 \mu\text{m})/(\text{m}^2 \text{ day kPa})]$
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
RH	Relative humidity [%]
RPM	Rotations per minute
SEM	Scanning Electron Microscopy
SPC	Soy Protein Concentrate
SPI	Soy Protein Isolate
T_g	Glass-transition temperature [$^{\circ}\text{C}$]
TS	Tensile strength $[\text{N}/\text{m}^2]$
WG	Wheat Gluten
WPI	Whey Protein Isolate
WR	Water retention [%]
WVTR	Water vapour transmission rate $[\text{g}/(\text{m s Pa})]$

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1 INTRODUCTION

Recently, great attention has been paid to the research and development in the sphere of natural polymers usage. The interest towards bio-based materials is tending to rise with time due to several reasons. First, random and uncontrolled use of conventional synthetic plastics led to its enormous accumulation into the environment causing, in turn, a huge number of related ecological problems and side effects. The second reason establishes current situation with finite oil resources, currently the main raw material for oil-based plastics. /1/

Nowadays, a number of conventional plastics (PE, PP, PET, etc.) is used in the food packaging industry due to their high barrier properties to ambient, enhanced performance and quite reasonable price. However, these materials do not decompose in the nature, so negative environmental impact can occur further. Another widely used group of chemicals for providing high barrier performance, namely grease repellency, of paper and paperboard materials are fluorochemicals, which can be harmful for human health and environment due to their toxicity. /2/

Thus, it is clear from the evidence, that there is a strong need in other safe and environmentally friendly materials and coatings for providing paper and paperboard barrier properties. Therefore, latest studies show the possibility of natural polymers application for these purposes. /3/

Starch is one of the most prevalent natural biopolymers, having a great potential for utilization in the sphere of sustainable packaging materials production as a substitute for conventional plastics. Starch-based films and coatings offer a range of advantages, such as decomposability, recyclability and elevated oxygen barrier properties. However, excessive moisture sensitiveness and inferior mechanical properties, inherent to many bio-based polymers, limit the application of starch-based coatings in the packaging production, determining their challenging behavior during converting operations. Therefore, it is clear from the evidence, that there is a need for tailoring the initial properties of starch-based coatings in order to

overcome these problems and extend the scope of their application in the sphere of packaging materials production. /4/ /5/ /6/

The approach of bio-based polymers blending, extensively studied in recent times, is intended to overcome biopolymer-related challenges. In this way, one of such approaches /2/ claims, that proteins (gelatin) can be successfully used to enhance the barrier (grease resistance) and mechanical properties of starch-based coatings. High coat weight of starch is usually required to provide adequate grease barrier properties, resulting in stiff and brittle end product exposed to cracking and loss of barrier properties. Meanwhile, pure protein coatings become often sticky in humid and hot conditions. The authors of the patent /2/ claim that the combination of starch and gelatin functions well as a grease barrier at a relatively low coat weight, without making the end product excessively brittle and stiff.

Based on that, one of the main targets of the present research was to prove the approach /2/ proposed, namely, to find out if gelatin addition is able to adjust the barrier and mechanical properties of starch-based paperboard coatings in fact. Another aim was to observe the applicability of this approach to wood-based polysaccharides, such as carboxymethyl cellulose (CMC), ethylhydroxyethyl cellulose (EHEC) and hydroxypropyl cellulose (HPC), and to investigate the effect of pigment addition to these blends.

The whole process chain of the barrier coating development was studied in the research. The methodology applied included pilot-scale coating and converting trials for the evaluation of mechanical properties of obtained coatings, namely their exposure to cracking with the loss of barrier properties.

2 STARCH AS A NATURAL POLYSACCHARIDE

Starch is one of the most important carbohydrates, being widely spread in nature. The availability of starch is a second to the cellulose. It is renewable and biodegradable natural polymer, produced by different parts of plants as a store of sun energy. Moreover, starch is a very attractive biopolymer, used in many industrial applications, such as food, paper and adhesives production processes. /7/

2.1 Characteristics of chemical structure and properties of starch

Starch macromolecule consists of a large number of glucose units, joined together by α -d-1, 4-glycosidic bonds, sensitive to pH conditions, with molecular formula $(C_6H_{10}O_5)_n$. The general structural formula of starch macromolecule is presented in the Figure 1. /8/ /9/

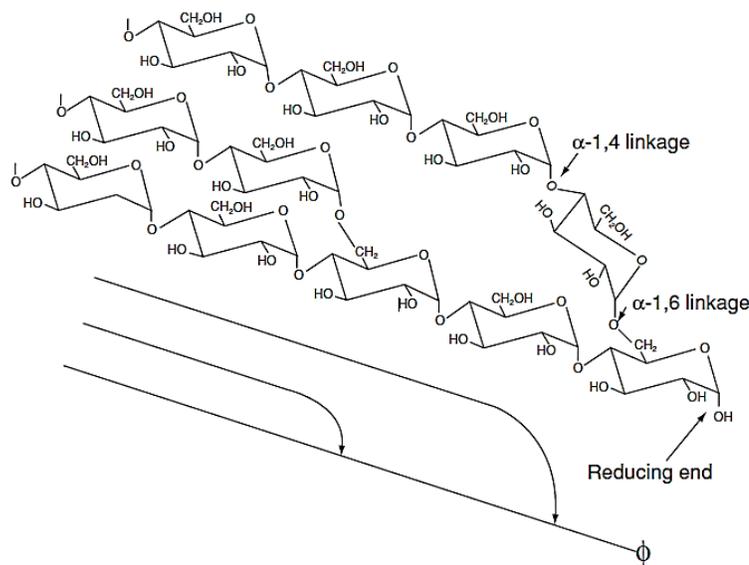


Figure 1: Starch macromolecular structure. /9/

There are two main anhydroglucose polymers constituting starch composition: amylose (20-25%) and amylopectin (75-80%), the content of which is dependent on starch origin. Amylose is a linear α - D-(1, 4)-glucan with molecular weight of 0.2–2 million. Meanwhile, amylopectin represents highly branched α - D-(1, 4)-glucan, linked by α -1, 6-bonds at the branching, with molecular weight of 100–400 million. Amylose structure is presented in Figure 1 in the form of linear parts of starch macromolecule. Amylose macromolecular chains are coiled and connected with lipids in the starch of plant cells. Amylopectin structure is a branched structure of starch macromolecule (Figure 1), the number of glucose units in amylopectin branches can reach twenty in average. Amylopectin macromolecules are also coiled, moreover, short branches of side chains form double helices. /8/ /10/ /9/ /11/

However, the real spatial structure of amylopectin is not completely clear yet. There are some models, in which attempts to explain branched amylopectin structure with its ability to form crystalline regions are made. One of such models is Robin – Mercier model (Figure 2). As it is clear from the Figure 2, in this model location of amorphous and crystalline regions are considered. Amorphous regions are formed of amylopectin chain branching, meanwhile linear parallel packed fragments of amylopectin macromolecules form more dense packed structure - crystalline regions, containing less water molecules. The Figure 3 shows how the total starch structure is formed by regular packing of amylose and amylopectin double helices, including complex linking with lipid molecules. Amylose – lipid complexes also form V – structures in the starch. The way of starch structure formation is determined by biological information, starch modification, and other technological conditions. /9/ /12/ /13/

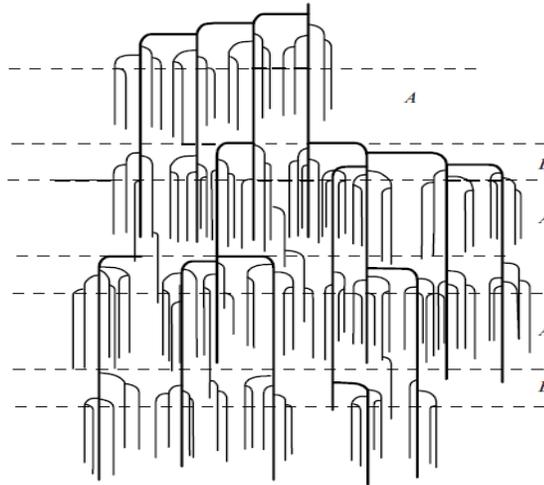


Figure 2: Model of amylopectin structure: A – crystalline regions, B – amorphous regions. /13/

Native starch crystallinity degree depends on starch origin and varies in a range of 15-45%. It was revealed that crystalline structures of starch differ depending on the part of a plant, from which it was extracted. Therefore, in a particular starch one of the following crystalline modifications (Figure 2) – A, B or C (combination of A and B) can dominate. /12/

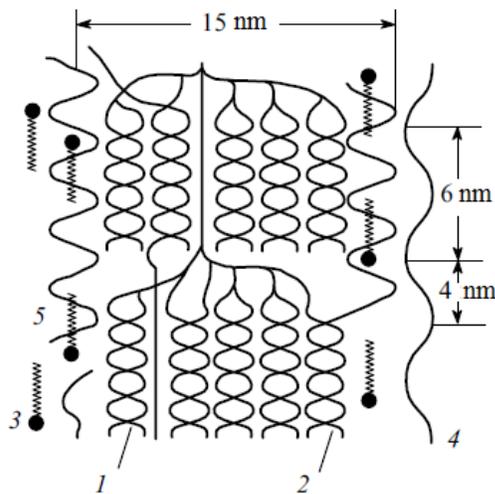


Figure 3: Native starch structure: 1 – amylopectin helices, 2 – hybrid helices of amylopectin, 3 – free lipids, 4 – free amylose, 5 – amylose V – structures. /14/

Due to the ability of branched amylopectin chains to form helical structure, native starch exists in the form of discrete microscopic granules with the size of 2–100 μm , which are bounded

together by hydrogen bonds. These granules have layered structure, each layer is formed by radially oriented microcrystalline micells, in which amylose and amylopectin molecule fragments constitute crystallites. /11/ /14/ /15/

Natural starch is highly hydrophilic polymer, which can contain up to 30–40% of bounded water. There are some differences in water interactions between A- and B – crystalline modifications of starch (Figure 4). Starch structure of B – type modification binds and also eliminates water molecules more easily. Meanwhile, water in A – type crystallite forms layered structure, strongly bounded with amylose double helixes. Therefore, A – type modification is less sensitive to changes in relative humidity of the atmosphere than B – type. /8/

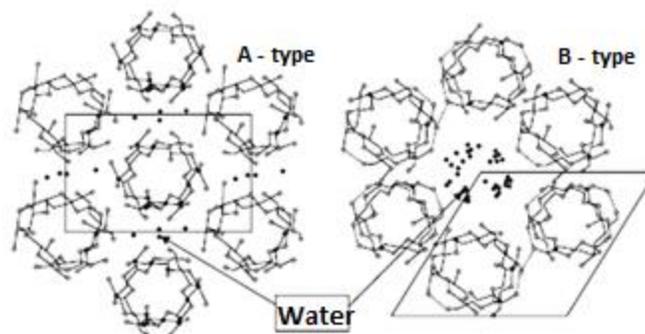


Figure 4: Structure of water – amylose crystalline modifications (A and B) complexes. /8/

2.1.1 Starch gelatinization process

In its initial state starch is an odorless and tasteless white powder, insoluble in alcohols and cold water due to strong hydrogen bonds, holding the starch chains together. However, starch becomes soluble in water at elevated temperatures and the destruction of semi-crystalline starch structure occurs. Starch granules begin to swell and dehisce, and the lowest polymeric fractions of amylose, in turn, come out of the granules. Therefore, the viscosity increases due to this new network structure created. The process of such physical starch modification is

called gelatinization. The temperature of gelatinization starting point is usually dependent on the original source of starch (Table 1). /1/ /10/ /16/ /5/

2.1.2 Starch retrogradation process

When cooling down and during storage starch dispersion undergoes aging, which leads to the semi-crystalline structure reconstruction due to the interactions between amylose and amylopectin fractions, accompanied by forcing out water molecules. This process is called retrogradation (recrystallization). The retrogradation ability of starch is dependent, in some degree, on the starch macromolecular chains organization in the semi-crystalline structure of native starch granules, which affects further the total extent of starch granules swelling during the process of gelatinization. It should be mentioned, that the temperature range of starch retrogradation is usually slightly lower than that of its gelatinization, which can be explained by new deteriorated crystalline structure of amylopectin chains obtained during the recrystallization process. Thus, aged starches contain higher percentage of amorphous fractions. Both gelatinization and retrogradation processes play significant role in industrial starch processing due to their influence on changes in semi-crystalline starch structure. /1/ /10/ /16/ /5/

2.1.3 Thermoplasticity of starch

The glass transition temperature (T_g) of dry native starch powder cannot be determined directly, since it exceeds the decomposition temperature. Due to this, native starch is a non – thermoplastic polymer, requiring some physical or chemical modifications for further conventional polymer processing. However, for glass transition temperature evaluation plasticizing action of water can be used. Water molecules penetrate into the amorphous regions of starch structure, causing the destruction of hydrogen bonds between starch macromolecular chains and simultaneously formation of these bonds between water

(plasticizer) and starch molecules. Therefore, forces holding starch macromolecules are reducing together with the reduction of glass – transition temperature, and the starch obtained is already thermoplastic starch with more homogenous structure. This process of native starch structure elimination is also called destructurezation, which can be enhanced by application of appropriate amount of plasticizer (water), heat and shear stresses. Among other plasticizers used for native starches are glycerol, glycol, sorbitol, and polyethylene glycol. /3/ /8/ /14/ /5/

2.2 The use of starch in paper and paperboard surface coatings

Starch is widely used in many industries for numerous types of applications. For instance, the food industry extensively consumes starch as a food additive, imparting required viscosity, colour and consistency. Moreover, textile and papermaking industries also utilize starch in their manufacturing processes. /17/

Starch is an additive, commonly used in a range of papermaking processes from stock preparation to size presses, in order to achieve desired functional properties of paper and paperboard, such as dry and wet paper strength, retention, printing and other surface properties. The scale of starch utilization in papermaking industry is affected by the desired final properties of the product, processing technology, raw materials grade and other factors. /15, 16/ /18/ /19/

The use of starch in paper and paperboard surface sizing makes it possible to modify uneven structure of the paper surface and reduce the porosity. Therefore, the more even and uniform surface arrangement of the fibrous network can be obtained, resulting not only in strength and dimensional properties improvement, but also enhanced resistance to grease and gases. Thus, this ability of starch to create a thin continuous film on the paper and board surface allows its exploitation as a good barrier surface size in fiber-based packaging materials production. /20/

However, native starch is used very rarely in paper industry. It always needs to be modified chemically or physically. The modification route is mainly determined by the desired properties of the end product.

2.2.1 Starch-Based Biodegradable Films and Coatings

In recent times, the application of renewable biodegradable materials (which are also edible) in the packaging production industry has become the matter of the greatest interest. Bio-based edible films and coatings from natural polymers have a great advantageous potential of their application as barrier providing materials for paper and paperboard instead of conventional unsustainable synthetic plastics. Moreover, the physical and chemical properties of these bio-based materials can be effortlessly modified, which allows using them in a wide range of coating and film-forming applications. /21/ /22/

Paper and paperboard are the most essential sustainable packaging materials, providing exceptional mechanical properties and versatility. However, high moisture sensitivity and gas permeability hinder its application as a food packaging material, so the surface has to be modified by the coating layer application. The use of bio-based coating materials enables fully bio-based barrier packaging material, which can be easily repulped. /23/

Basically, there are three main groups of bio-based natural materials for packaging barrier films and coatings production can be identified: polysaccharides, proteins and lipids. Currently, the most part of these bio-based film-forming coatings for fiber-based packaging materials, including their barrier properties and performance, is under investigation. /21/ /22/

Starch is one of the biopolymers extensively considered to use in the packaging production as a substitute for petroleum-based indecomposable plastics. Because of starch abundance, film-forming properties, reasonable price, biodegradability, edibility and renewability, the potential of its utilization as a packaging material (especially for food products) is very high in our days. /21/

2.2.2 Barrier properties of starch-based films and coatings

Films and coatings are intended to enhance the barrier properties of packaging materials and to maintain, therefore, the quality and the shelf life of the product inside. Barrier properties of biopolymer-based coatings and films, applied in the packaging industry, are mainly quantified by water vapour transmission rate (WVTR), oxygen transmission rate (OTR) and carbon dioxide (CO₂) gas permeability, water and oil resistance. /22/ /24/

Starch-based freestanding films and coatings mostly find their application, where the high resistance to oxygen is required, since they act like very good oxygen barrier materials. Since the rate of the gas molecules permeability through the film (OTR) depends on the material porosity (free volume) which, in turn, is in inverse ratio with the crystallinity degree of the film structure, the gas resistance of amylose- and amylopectin-based starch films differs. Thus, more crystalline high-amylose starch films exhibit better oxygen resistance than amylopectin films. However, both amylopectin and amylose films in ambient conditions (20°C, 50-60% relative humidity (RH)) surpass even one of the commercially used oxygen barriers – synthetic ethylene vinyl alcohol copolymer (EVOH) (Table II) /25/. /26/

Table II: Oxygen permeability of starch-based and synthetic films /21/

Film type	Oxygen permeability, (cm ³ μm)/(m ² day kPa)	Relative humidity (RH), %
Starch-based		
Amylose – glycerol (in a ratio of 2.5:1)	7	50
Amylopectin – glycerol (in a ratio of 2.5:1)	14	50
Synthetic		
Ethylene vinyl alcohol (EVOH)	0.01 – 0.1	0
Ethylene vinyl alcohol (EVOH)	12	95

Starch films demonstrate poor resistance to carbon dioxide, as it can be explained by the theory of gases absorption and solubility in the film thickness. Polar CO₂ gas, having higher solubility in starch-based films than O₂, interacts with starch hydrogen bonds and weakens them, so carbon dioxide molecules can easily go through the film. /25/

Starch-based films and coatings are not outstandingly good barriers against water vapour due to their high moisture sensitivity, provided by the hydrophilic nature of these natural polymers. In general, the WVTR through the film or coating is determined by the capillary forces in the starch-based material, surface roughness, chemical properties and pores structure. Starch-based coatings usually increase the surface roughness of the coated material, making its surface more hydrophilic.

Nevertheless, starch-based films exhibit good resistance to oil and grease at low and normal RH /4/. /21/ /27/ The term “oil resistance” can be referred to the lack of affinity for fats of any of origin that are usually liquid or liquefiable at room temperatures. Meanwhile “grease resistance” can be defined as resistance to any type of fats, which are semisolid or solid at room temperatures. /28/

The major factor, limiting the use of starch-based coatings as excellent barrier materials, is that revealed high oxygen barrier properties are strongly dependent on the starch-based material moisture content, as for many other polar bio-based polymers (e.g., carbohydrates) /22/. Thus, the starch films containing 15% of water and less are recognized to have low oxygen permeability, whilst increased water content (more than 20%) makes starch films highly oxygen permeable /25/.

2.2.3 Mechanical properties of starch-based films and coatings

Mechanical properties are crucially important when considering the barrier films and coatings as an integral part of packaging material, since they have to satisfy the requirements of material durability and maintain the product integrity and quality during the whole life cycle of the package. /4/ One of the most important processes in packaging production, where high enough mechanical properties are required, is folding. Thus, the coating layer has to stay undamaged and resist the cracking, which can occur due to the high mechanical pressure during the folding and converting operations. Therefore, the flexibility of the coating layer is very essential. /29/

As to concern the physical structure and mechanical properties of starch-based biopolymers, they mostly influenced by the ratio of crystalline and amorphous phase, determining the glass-transition temperature of the polymer. At normal temperature (which is below the T_g of starch biopolymer) and ambient conditions, starch-based materials demonstrate excessive brittleness and rigidity due to quite low starch molecular chains mobility in the amorphous regions. The minor in quantity crystalline phase of starch is represented as an association of small crystallites, acting like an association of separate interacting particles, providing the starch-based material structure reinforcement in the form of increased strength properties and stiffness. Therefore, highly crystalline more flexible amylose-based starches take precedence over amylopectin-based starches when comparing their mechanical properties, including elongation and tensile strength. /25/ /30/ /31/

There are several variables affecting the glass-transition temperature of semi-crystalline starch biopolymer as a key factor, determining the mechanical properties and performance of the polymer: amylose and amylopectin proportion, moisture (or plasticizer) content in the polymer and external conditions (relative humidity). Thus, the mechanical properties of the starch-based polymers can be adjusted through the altering of these variables. /30/

Plasticizers are widely used for plastics performance and operational characteristics enhancement (flexibility, extensibility). Plasticizing agents act like special low-molecular

additives, penetrating in the spaces between polymer macromolecular chains, pulling them out of each other, therefore, increasing the amount of free volume in the system, and as a result, the mobility and flexibility of macromolecules. There are also special chemicals used for starch biopolymer plasticizing. The most spread among them are glycerol, sorbitol and other polyols. Water also acts like a plasticizer in relation to starch. /21/ /30/ /32/

The amount of the added plasticizer is usually dependent on desired resulting properties of the polymer and the type of plasticizer used itself. The content of plasticizing chemicals in starch-based films and coatings can alter significantly: from 15 to 60% on dry basis /25/. There is also anti-plasticizing effect can occur in the cases of too low plasticizer content, what can be caused by the creation of tough interactions (hydrogen bonds) between starch macromolecules and plasticizer. Therefore, there are critical values of particular plasticizer content exist. For instance, for sorbitol the limit value is 27%, meanwhile glycerol gives anti-plasticizing effect at concentrations lower than 15% /25/. Another problem, conjugated with the use of plasticizer, is that permanent plasticizing effect sometimes cannot be reached because of its dependency on the climate conditions.

It also has been stated /33/, that the use of plasticizer in starch-based films affects not only mechanical, but also barrier properties. Thus, both water vapour and oxygen transmission rates (WVTR and OTR) of sorbitol and glycerol plasticized rice starch films increased in direct ratio with plasticizer concentration. Moreover, plasticizer can soften and dilute the film structure, resulting in poorer water resistance properties and hindering the formation of moisture barrier coatings. /34/

It is clear from the evidence, that there is a need for further and more sophisticated understanding of starch-based material and plasticizer interactions in order to reach the targeted equilibrium of mechanical and barrier properties of such materials. It is crucially important to maintain desired mechanical properties of the packaging material with minimal influence (namely, negative influence) on its barrier properties. Thus, there is the continuous interest in the field of tailoring the properties of starch-based and many other natural polymers, aiming to reach the most appropriate for particular use set of characteristics, by choosing the

proper type and amount of plasticizer or any other additives and using different modification routes. /4/

3 NATURAL FILM-FORMING MATERIALS

3.1 Film-forming natural polymers

Film or coating layer formation requires presence in the film structural model at least one component, which is able to create “supporting matrix” /6/ and hold together all the other components. In general, natural hydrocolloids (carbohydrates and proteins) and their derivatives have been recognized as the most promising natural film-forming materials, providing three-dimensional cohesive structures. Hydrocolloid materials represent a group of hydrophilic polymers, containing a large number of hydroxyl groups /35/. Carbohydrate and protein films are usually utilized as good barriers against gases, aroma and grease at low RH. Their main drawback is high sensitiveness to water. /36/ Lipids are also used in the composition of biopolymer-based films and coatings. From one hand, lipid compounds are capable for forming excellent moisture barriers, from another hand, their film-forming ability is not outstandingly good due to non-polymeric origin /36/. The main natural film-forming biopolymers are presented on the Figure 5.

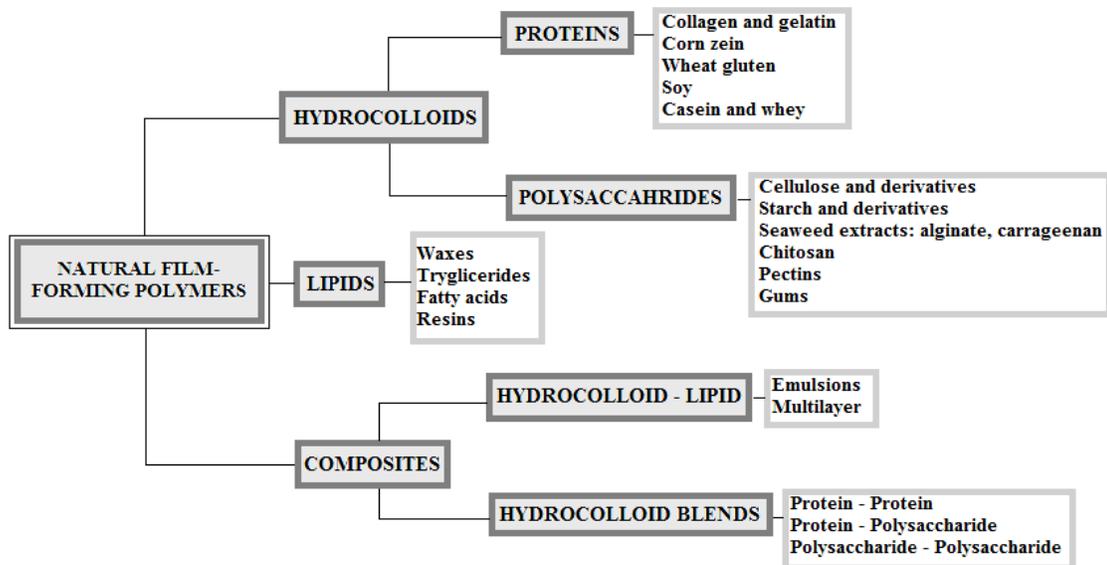


Figure 5: The main natural film-forming biopolymers for barrier films and coatings. /36/

Natural film-forming polymers can be used as itself, or in the combinations (composites) (Figure 5). There are also a set of additives used in the composition of biopolymer materials with a view to enhance processability and functionality of the resulting film or coating (Table III). Plasticizers are intended to improve mechanical properties of the biopolymer dispersion, whereas surfactants (emulsifiers) are used for the affinity intensification between matrix-forming and dispersed phases of the film-forming solutions /37/. Functional additives comprise various antioxidants, antimicrobial agents and other improving agents. /36/ /38/

Table III: Additives used in the formulation of biopolymer-based films and coatings. /36/

Additives	Materials
Technological (enhance cohesion, adhesion, stability)	
Plasticizers	Glycerol, sorbitol, propylene glycol, polyethylene glycol, sucrose, water
Surfactants	Lecithins, Tweens®, Spans®
Functional	Antimicrobials, antioxidants, texture enhancers, colors

3.2 Protein-based film – forming materials

3.2.1 Protein chemical structure

Films and coatings can be prepared from both animal- and plant-derived proteins /36/ /39/. Basically, proteins are represented as heteropolymers, composed of different amino acid monomer units, linked by peptide bonds in the head-to-tail organization. Protein macromolecules (polypeptide chains) are able to form three-dimensional structures /40/.

There is a great number of possible amino acid sequences (primary structures /40/) and macromolecular configurations, leading, therefore, to high chemical reactivity potential of

proteins. The Figure 6 presents the schematic illustration of the universal amino acid structural formula. /36/ /40/

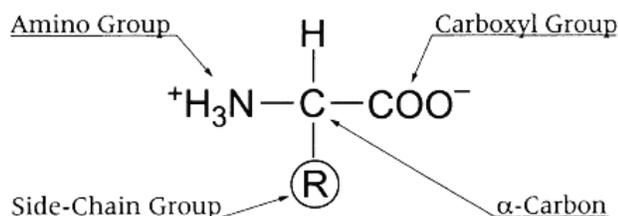


Figure 6: Schematic representation of the general formula of an amino acid. /40/

Proteins are composed of 20 amino acids – building blocks of protein chain. Typical amino acid contain a carbon atom with attached amino ($-\text{NH}_3$), carboxyl (COO^-) and a side-chain ($-\text{R}$) groups. The side-chain group chemical structure and character (which can be acidic or basic, hydrophilic or hydrophobic) vary in different amino acids, therefore, affecting the most important properties (including also film-forming ability) of compiled protein macromolecules: ionic charge, hydrophobicity and reaction capacity. The ionic charge of amino acids, due to the presence of both basic and acidic functional groups, depends on the pH, which is positive at low and negative at high pH values. There are also non-polar types of amino acids exist (valine, phenylalanine, methionine, etc.), where side-chain radical is represented as aliphatic hydrocarbon group, aromatic ring or sulfur-containing group. These amino acids are hydrophobic and less soluble in water, comparing to polar amino acids (serine, threonine, etc.), where R- groups are able to form hydrogen bonds with water molecules. /40/

3.2.2 Protein barrier properties and performance

Basically, the protein film-forming properties are determined by original properties of proteins and external factors. The protein inherent properties include amino acid composition, polarity,

charge, molecular size and shape. The external factors, affecting the properties of protein as a film-forming material comprise ionic strength, temperature, pH, RH, pressure and shear stresses during the processing. /40/

Proteins are recognized as a good film-forming materials, providing improved barrier properties, namely, excellent oxygen and carbon dioxide, and lipid resistance. The oxygen resistance may be associated with numerous internal hydrogen bonding in the proteins polypeptide chains /41/. Meanwhile, the water barrier properties are poor mainly for a range of hydrophilic (polar) proteins. Barrier properties of protein-based films and coatings may be enhanced by increasing the intermolecular cohesion of protein macromolecules (cross-linking), which is thought to result in better water-vapour resistance and mechanical characteristics. /42/

In general, protein films and coatings exhibit brittleness and perspective to cracking. Therefore, different plasticizing agents, such as sorbitol, polyethylene glycol, etc., are used to enhance flexibility and overall performance of protein films and coatings produced. The creation of natural polymer blends and composites with proteins represents also one of the most important possible ways to alter the barrier and mechanical properties of protein-based materials.

3.2.3 Plant – origin proteins

Cereal grains, legumes, tubers and pulses are referred to the group of plants with high protein contents /39/. The film-forming ability of these proteins has been investigated more or less precise.

Wheat gluten

Wheat gluten (WG) is a group of water-soluble proteins, which are formed by globular protein molecules, obtained as a by-product of wheat starch production. The films produced from WG exhibit enhanced selectivity to gases permeability, transparency, mechanical strength and homogeneity. There are several research works devoted to investigation of film-forming and barrier properties of WG-based materials (/43/, /44/). /36/ /45/

Corn zein

Zein implies a group of alcohol-soluble proteins, derived from corn endosperm /36/. Due to the presence of non-polar amino acids, zein is hydrophobic natural protein, which largely affects the barrier properties of zein-based materials. The films and coatings produced from zein protein are distinguished by their gloss, toughness, and greaseproofness. The commercial use of film-forming zein protein primarily includes production of medical tablet coatings. However, the potential of zein application in biodegradable packaging composition also has been recognized already /46/. /39/

Soy protein

Soybeans contain much more protein than cereal grains. The most part of the soybeans protein is soluble in neutral salt solutions. Soy protein isolate (SPI) is a type of soy protein, containing more than 90 % protein and having excellent film-forming ability. The films and coatings produced from SPI are good barriers against oxygen and oil, however, poor mechanical properties and water sensitivity hinder their usage as barrier materials. Nevertheless, the modification of barrier and mechanical properties of SPI films and coatings still captures the attention /47/ /48/ /49/. /36/

3.2.4 Animal – origin proteins

Milk proteins

Casein (80% of the milk proteins) and whey protein are two components comprising milk proteins. Casein tends to form films with improved flexibility due to its ability to create hydrogen bonds widely. Films produced from casein are very attractive for their utilization as a packaging material due to remarkable transparency, absence of flavor and good mechanical properties. Casein protein is also utilized as an emulsifying agent. Whey protein is defined as a protein, remaining in the milk after casein coagulation at pH of 4.6 and 20°C. Whey protein isolate (WPI), a form of whey with higher protein content, is used for water insoluble edible films and coatings production, having good mechanical properties, oxygen and oil resistance. /36/ /39/

Collagen and gelatin

Collagen is a fibrous insoluble stromal protein (a type of meat proteins), being a part of animal connective tissue, skin, bones and tendons. Collagen is recognized to be one of the most widely used film-forming proteins for edible films (mostly sausage casings). Collagen is a hydrophilic protein and it owes its hydrophilicity to the high content of amino acids with basic, acidic and hydroxylated residues. Films obtained from collagen exhibit outstanding mechanical properties (strength and extensibility), and beneficial oxygen barrier properties (at low RH). /36/ /39/ /42/

Gelatin is a product of collagen hydrolysis, composed of 19 amino acids /50/ (with high content of glycine, prolyne and hydroxyprolyne amino acids) /51/. There is also a combination of unfolded hydrophilic polypeptide chains that may be found in the gelatin chemical structure. Gelatin aqueous solutions with the concentration higher than 0.5% tend to form thermoreversible gels when cooling under the temperature of approximately 40°C (gelation

process). The gelation process implies the formation of ordered structures caused by the renaturation of gelatin polypeptide chains to collagen-like structures with triple helices. /51/ /52/ The properties of the gel obtained depend on pH, gelatin molecular weight, temperature and concentration /41/.

The use of gelatin includes primarily applications in pharmaceutical and food industries in the form of medicine coating and thickening agent respectively. /39/ Meanwhile, the exploitation of gelatin in barrier films and coatings for food packaging applications has invited increased attention of many researches recently due to its low cost and excellent film-forming ability /53/.

Gelatin films are recognized to be very clear, flexible, strong, impermeable to oxygen and resistant to moisture and oil, what makes them in a combination with increased mechanical properties good barrier materials. Moreover, gelatin is also used in the form of thin edible coating on the food surface (e.g. meat) to reduce oxygen and oil transmission, and therefore, extend the product shelf-life. However, hydrophilic nature of gelatin limits its resistance to water vapour. /42/ /51/

Gelatin is not only thermally unstable, but also very sensitive to bacteria, being an excellent substratum for their growth. This bacterial contamination reduces such important processing properties of gelatin as required gel strength and viscosity. The bacterial infection of gelatin-based films and coatings for food packaging production is also unacceptable due to strict sanitary requirements for food packaging materials. Therefore, either special antimicrobial agents or preservatives addition to gelatin-based materials is required. /52/

3.3 Non-starch polysaccharide – based film - forming materials

The uses of starch as the most common natural film-forming polysaccharide, its chemical structure and inherent properties, more or less similar to these of other naturally occurring polysaccharides, have already been described previously.

Basically, non-starch polysaccharides may be obtained from a wide range of natural sources, including cellulose and its derivatives, seaweed extracts, conjunctive tissue of crustaceans (chitosan) and other sources, such as plant and microbial gums. In general, the polysaccharide macromolecule is usually composed of a limited variety of monomer units, unlike protein chains, built from a wide range of existing amino acids. However, the molecular weight of polysaccharides is considerably larger than that of proteins. /36/ /54/

The polysaccharide films as itself or in a combination with other film-forming materials provide hardness, thickening effect (imparting required viscosity level) and adhesiveness /35/. Moreover, polysaccharide-based films and coatings reveal moderate gas permeability properties due to the conformation of the polysaccharide macromolecules, what makes them excellent materials for modified atmospheres creation. Nevertheless, there is a still problem related to polysaccharides hydrophilicity, diminishing their water vapour barrier properties.

4 WOOD-BASED POLYSACCHARIDES

Cellulose is a natural linear high-molecular weight polymer, composed of D-glucose monomer units, linked by β -D-1,4 glycosidic bonds. Cellulose is widely spread in nature, being a constituent part of all land plant cell walls. It is highly crystalline and insoluble in water biopolymer due to its regular chemical structure and presence of strong hydrogen bonding between macromolecules. The films (regenerate films) may be produced from pure cellulose by its dissolution in particular solvents (e.g. mixture of sodium hydroxide and carbon disulfide) with further regeneration (recasting in sulfuric acid) in the form of continuous web (cellophane). /54/

Cellulose derivatives are obtained through chemical modification of cellulose, namely, through the partial substitution of hydroxyl groups. The most widely produced commercial cellulose derivatives include ionic cellulose ether carboxymethyl cellulose (CMC) and nonionic cellulose ethers, such as methyl cellulose (MC), hydroxypropyl cellulose (HPC) and hydroxypropylmethyl cellulose (HPMC). Cellulose derivatives, as other hydrocolloids, tend to form thermo-reversible gels. Films and coatings, based on cellulose derivatives, exhibit absence of odor and taste, flexibility, transparency, fine barrier properties against oil and grease and moderate OTR. Despite the fact, the wide utilization of these materials is limited by their high costs, associated with difficulties in the derivatization process of highly crystalline cellulose structure. /36/ /54/

4.1 Carboxymethyl cellulose

CMC is a water-soluble anionic linear cellulose-derived polysaccharide, having high molecular weight. It is widely utilized industrial biopolymer, finding its application as a functional additive in flocculation, detergents, textiles and papers, food and medicines to provide appropriated texture, moisture control and to enhance product stability and quality. /55/

The wide range of CMC applications can be mainly attributed to its non-toxic and non-allergic nature, versatile viscosity and reasonable cost. As a natural hydrogel, CMC exhibit elevated water content and biodegradability.

Due to its high molecular weight CMC can be successfully used as natural film-forming material, providing good mechanical and barrier properties. A great number of hydroxyl and carboxylic groups provoke binding of water and increase moisture sorption of CMC-based materials.

4.2 Ethylhydroxyethyl cellulose

Ethylhydroxyethyl cellulose (EHEC) is a water-soluble nonionic cellulose ether, widely exploited in a range of industrial applications. EHEC is recognized to have advantageous functional properties, such as thickening, dispersing, stabilizing and water retaining. There was a great interest towards applying this chemical in paper and paperboard coating formulations due to listed properties. However, EHEC differs from other wood-based polysaccharides. The characteristic feature of this cellulose derivative is that it tends to exhibit a cloud point, meaning a decrease of solubility at elevated temperatures. /56/

4.3 Hydroxypropyl cellulose

HPC is a water-soluble nonionic cellulose ether with a diverse combination of properties. It exhibits thickening and stabilizing properties, inherent to other cellulose polymers, at the same time being able to make solutions both with water and polar organic solvents. But the main feature of this cellulose derivative is its thermoplastic nature (unlike other cellulose polymers), so it can be extruded and create flexible heat-sealable films and coatings. /57/

5 NATURAL POLYMER BLENDS FOR BARRIER FILMS AND COATINGS

In general, starch as many other biopolymers in the form of film or a coating layer tends to exhibit reduced values of its processability and performance. The polymer can be characterized by its limited stability due to hydrophilic nature, retrogradation changes in the structure caused by aging and lowered mechanical properties due to excessive brittleness and rigidity of the starch biopolymers itself. /5/

The use of plasticizer (polyols), intended to modify the polymer structure and provide enhanced operational characteristics of starch, sometimes is limited due to some adverse aspects, including possible anti-plasticizing effect, challenges with permanent plasticizing achievement and direct influence on barrier properties of the polymer (resistance to moisture and gases) /33/ /34/. Hence, it is evident, that there is a demand for a totally new solution, which can overcome this challenge and bring to a commercialized level the production of bio-based materials.

One of the most promising and sustainable ways to modify the structure and obtain desired properties of the starch biopolymer is to blend it with other natural film-forming polymers. Blending of different natural polymers in order to obtain new materials for barrier films and coatings allows combination of advantageous properties of each component, depending on the targeted features of the product. Moreover, it gives possibility to develop fully bio-based biodegradable materials. /5/ /6/

5.1 Natural composites

Composite biopolymer films represent a material based on a compatible mixture of several film-forming natural polymers, where one of the components provides a structural supporting matrix for others. In general, the main purpose of such biopolymer combinations consists in a

development of new bio-based materials with a new advantageous range of combined properties. Therefore, the initial characteristics of biopolymer affect largely the properties of the final film or coating produced /38/. Moreover, polymers mixed have to be compatible to each other /5/.

Natural biopolymer composites are produced in the form of homogeneous mixtures (blends), multilayered structures and fiber-reinforced composites (Figure 7) in the way, similar to conventional polymer films, in order to optimize and mix the most advantageous properties of each component /38/. Many natural polymers may be reinforced with cellulose fibers or fillers to enhance their mechanical properties. The filler-reinforced biopolymers, for instance, tend to exhibit the creation of particular structures, capable for material improved performance and properties. /56/ Multilayer films, produced by laminating of several biopolymer films, are intended to provide better barrier properties of the material (mostly moisture resistance). However, such composites are often exposed to the problem of delamination, accompanied by inferior mechanical properties, compared to blended composites. /36/ /58/

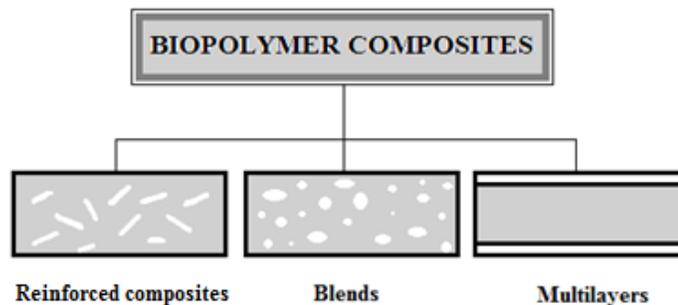


Figure 7: Types of biopolymer composite materials. /5/

Biopolymer blending is quite simple and low-cost technique, using the conventional equipment and processing technology. This methodology shows the great potential of overcoming a range of challenges, related to the natural polymers processing, such as moisture sensitivity, excessive brittleness and difficulties in handling. /58/

5.2 Biopolymer blends

A great variety of existing biopolymers offers limitless possibilities for the modification of their properties by blending. Biopolymer blending is the easiest way to create new materials with desirable properties. Moreover, the adjustment of these properties is possible by simple modification of the blend composition. /58/ Biopolymer blending presents many advantageous possibilities, such as material properties altering (modification of the Tg range, barrier and mechanical properties, rates of material degradation, etc.) and production costs reduction. /59/

Since the most part of biopolymers are not fully miscible, the new structure created usually tends to be heterogeneous. There are several factors, determining the properties of these heterogeneous blends: inherent properties of each component, blend composition, structure and interactions between the components. It is possible to state, that the most important factor is interactions taking place, as they designate the character of mixture compatibility and the blend structure. In addition, biopolymer blends are likely to develop sometimes much more stronger interactions between their components, compared to conventional synthetic plastics. This can be explained by the fact that biopolymers contain a great number of polar groups, stimulating formation of strong dipole-dipole interactions. /59/

5.3 Polysaccharide – protein blends and composites

Proteins and polysaccharides are the most common natural film-forming polymers /58/. Some representatives of these two groups of biopolymers, their film-forming ability and other properties, owing to which they can be used as barrier films and coatings, have already been described in Chapters 2 and 3. The cross-linking of polysaccharides and proteins by means of producing biopolymer blends is one of the promising routes to enhance the functional and barrier properties of hydrocolloid films. /54/

5.3.1 Starch – protein blends

There are several research works available in the area of starch – protein blending with a view of barrier and functional properties modification. The preparation of thermoplastic starch – corn zein blends, plasticized with glycerol, is able to decrease the hydrophilic character of starch-based compositions in inverse ratio to zein content /60/. Zein, containing a great number of nonpolar amino acid groups, decreased moderately the water uptake of the blend produced; however, no influence of zein addition in the type of starch crystallinity was discovered. Additionally, the processing of the starch blends containing zein was reported to be more facilitated due to appropriate viscosity level.

Edible glycerol-plasticized films, prepared from blend of cassava starch and soy protein concentrate (SPC) were analyzed on their appearance, mechanical, barrier (namely, WVTR) and solubility properties /61/. Thus, the addition of SPC influenced on the colour of the films produced, which was observed to vary from light to dark with increasing content of SPC. The mechanical properties of the cassava starch films, quantified by their tensile strength (TS), were reported to increase linearly with SPC addition due to the creation of denser starch-protein three-dimensional structures, leading to improved strength properties. The increase in elastic modulus (EM) and elongation at the break (EAB) of initially brittle starch-based films was also observed with increased proportion of SPC added, attributed to the possible decrease of cassava starch crystallinity degree. The solubility properties (an indicator of material water resistance) and WVTR of starch-based films decreased with higher SPC content in the blend, providing strong intermolecular starch-protein interactions.

The combinations of corn starch with other different proteins (casein, gelatin, albumin) and their mechanical and permeability properties have been studied previously in order to determine the possibility of their application as barrier materials /62/. It was reported, that the films produced from thermally blended starch-protein mixture exhibit elevated opacity, clearness and thickness uniformity, saying about blend constituents compatibility. Starch-based films produced with casein addition have shown the best mechanical properties, namely,

the maximum EAB and TS. The same tendency was observed for permeability properties, where starch films, containing casein exhibited reduced WVTR and water absorption. Moreover, the attention is paid to the fact, that starch-casein blends were produced by intensive mixing and elevated temperatures, which probably caused “crosslinking effect” /62/, changing the hydrophilic character of the blended components to hydrophobic properties of the resulting blend. Another assumption accounting for high water vapour resistance of obtained blends consists in potential creation of crystalline phase (insoluble in water), produced by starch and protein amorphous phases incorporation.

There is also some information available on developing edible films and coatings by blending starch and gelatin. One of the sources /63/ evaluated the possibility of using hydroxypropylated corn starch-gelatin blends, plasticized with polyethylene glycol, for capsule materials. At first, it was revealed, that the transparency of solutions increases linearly with the gelatin content. The addition of polyethylene glycol also provided an increase in transparency level of obtained solutions, what indicates the compatibilizing action of polyethylene glycol, providing better compatibility of starch-gelatin blends. Concerning mechanical properties of produced films, elevated gelatin content provoked a slight increase in TS and EAB. In general, it was noticed that films containing higher starch proportion in relation to gelatin tended to be more brittle and rigid. The analysis of water contact angles of films with different starch-gelatin ratio showed that all films produced with gelatin addition have almost the same values of water contact angle, whereas pure starch films exhibit a sharp decrease in measured parameter. The results point out that gelatin acts like a continuous phase, covering separate apportioned phases of more hydrophilic starch in the blends.

5.3.2 Carboxymethyl cellulose – protein blends

CMC is one of the main water-soluble cellulose derivatives, widely used as an additive in food, pharmaceutical and textile industries as an additive, improving a range of processing properties of the product. The food grade CMC was considered to enhance the properties of SPI films and coatings by means of blending /64/. Several blended solutions with varying CMC/SPI ratio were prepared and tested on their mechanical and water solubility properties. The results obtained recount that all films containing CMC exhibited higher TS and EAB than those made of pure SPI. This rise in mechanical properties was attributed to the long-chain molecular structure of CMC providing a great number of hydroxyl groups, taking part in creation of strong CMC-SPI interactions of different character (hydrogen, dipole-dipole bonding). It was also reported that the water sensitivity of all blends decreased with increasing CMC content.

The physical and mechanical properties of CMC-gelatin films were studied /65/. The authors claim that the higher CMC proportion in the blend resulted in more aggregated structures of gelatin in the films, providing an EM increase.

5.3.3 Bacterial cellulose – protein nanocomposites

Nanocomposite is a composite material, obtained by the combination of several (two or more) components, one of which provides a continuous phase for others, representing intermittent nano-sized dimensional phases (not more than 100 nm size) /66/. BC nanostructure, composed of nanofibrils network provides an opportunity for various types of nano-reinforced composites creation with the view of obtaining new properties.

Gelatin was proposed to be used in a combination with BC in order to overcome its compressibility as a restraining factor for different biomedical applications /67/. It was reported, that the dipping of BC films into the gelatin dispersion resulted in the “double-

network hydrogel” /67/ formation, conjoining superior TS of BC and gelatin compressive resistance. The new structure created has shown that gelatin addition did not bring any significant changes to BC crystalline phases, remaining its initial layered dense structure. However, it was suggested, that gelatin could penetrate inside the BC structure, occupying cellulose-free spaces. The compressive modulus of the BC-gelatin composite material increased outstandingly, and 200 times exceeded that of pure BC films. Moreover, the material even was able to recover after applying the 30% deformation strain, which was not observed for BC alone. In conclusion, it was proposed, that the degree of mechanical properties modification, obtained by BC-gelatin combination is determined mostly by the crosslinking degree between these two components and by the ratio of initial BC network to obtained double network.

Therefore, the approach of polysaccharide-protein blending gives very interesting results, expressed in actual improvement of the resulting blend properties. The fact, in turn, tends to attract more and more attention to the developing of films and coatings obtained from different blends of these natural polymers.

5.4 Biopolymer-pigment blends

Barrier coating formulations are often filled with pigments, such as clay, silica and talc, with the view of improving the runnability of the coating process, optical properties of the end product and reduction of production costs. Therefore, pigment introduction to biopolymer films and coatings is one of the ways to control the properties of these materials. /21/

Addition of pigments is able to enhance the rheological and textural properties of the biopolymer-based matrix. Moreover, it can reinforce a biopolymer by increasing the strength and density of the material. Besides that, improvement of barrier properties is also can be reached with pigment addition. Biopolymer-pigment composites exhibit elevated gas and vapour barrier properties.

Barrier and mechanical properties of biopolymer-pigment blends can be influenced by the size, shape and dosage of the pigment. In this way, it was reported that barrier properties of such systems are often dependent on the aspect ratio of the pigment particles, and the highest aspect ratios can give significant improvement of gas barrier properties. /21/

It was stated, that coatings filled with grounded calcium carbonate usually tend to exhibit elevated grease barrier properties, compared to unfilled. However, the negative effect of pigment introduction on flexibility of these coatings was observed, providing cracking of coat layer during converting operations. /68/

6 COATING OF BIO-BASED POLYMERS

The use of biopolymers for biodegradable films and edible coatings in packaging applications tends to rise continuously, since these polymers are able to provide a range of barrier properties, comparable to conventional plastics. However, exploitation of many biopolymers in the sphere of paper and paperboard barrier coatings formulation is limited. /21/ The fact can be referred to the challenging behavior of biopolymers during processing (low dry solids content and rheology problems), unreasonable cost and restricted availability. Despite that, starch, as widely occurring natural polysaccharide, is one of the commercially used biopolymers in paper and paperboard barrier coatings.

Basically, coating techniques that can be exploited for bio-based barrier dispersions application to the paper and paperboard are similar to that applied for the conventional surface sizes. These techniques include blade, film press, size press, rod and air-knife coating. Recently, spray-, curtain extrusion and spot/pattern coating have also received attention. /21/

The application of the biopolymer-based dispersions in the conventional coating techniques is often limited by their problematic rheological behavior and sensitiveness to the temperature and pH changes. Thus, the viscosity of hydrocolloid solutions is greatly dependent on their concentrations. Higher concentrations of biopolymer dispersions tend to result in sharp increase of viscosity values due to elevated entanglement of macromolecular chains. Rheological behavior of biopolymers is also greatly affected by the temperature, because of different thermal sensitiveness of intermolecular interactions. Finally, the rheological properties of bio-based dispersions are dependent on the presence of other biopolymers, comprising the bio-based blend. /69/

Among other procedures during coating, where biopolymers tend to exhibit their challenging properties is drying. Generally, drying is an essential part of the coat layer formation on the paper or paperboard surface, since it determines the quality and the final properties of the coated material. In the case of biopolymer-based barrier coatings the drying conditions consideration becomes much more essential.

It was reported, that drying conditions, namely air temperature and RH, can have an effect on barrier and mechanical properties of protein films /70/. Fast water evaporation during the drying procedure changes the conformation of the protein chains, therefore, affecting the type and amount of interactions between these chains (S-S bonds, ionic and hydrogen bonds). These interactions, in turn, determine the new structure of the material and its final properties.

One of the studies revealed the dependency of permeability and mechanical properties of methyl cellulose films on the drying conditions /71/. The radical changes in water vapour and oxygen permeability of dried films were explained by elevated crystallinity degree obtained during drying. It was also concluded, that drying at lower rates and higher RH can lead to better barrier and mechanical performance.

7 CONVERTIBILITY OF BIO-BASED COATINGS

Convertibility is a key property for coated paper and paperboard, determining the ability of the material to be easily folded without causing any cracks of the coat layer, and therefore, losses of barrier properties. Cracking of barrier coating can occur during the folding and creasing operations due to high compressive or tensile strength, depending on the position of the coat layer with respect to the folding direction /72/.

There are several studies available, describing the dependence of the coat layer convertibility on its composition. It was revealed, that partial replacement of latex with starch in kaolin- and ground calcium carbonate-based coating dispersions has led to the increase of the cracked area, however, the scale of the crack was smaller in the second case respectively /73/. By comparison of the bio-based paperboard laminates, it was observed, that nitrocellulose-whey protein layered coating exhibited better performance during creasing operations than nitrocellulose-chitosan paperboard laminate /74/.

The introduction of inorganic pigments (fillers) to the bio-based coating dispersions can greatly affect the convertibility of coatings obtained. It was reported, that coatings, filled with pigments tend to exhibit reduced flexibility /68/, leading to poor performance of the coated paperboard during the folding operations, and therefore, barrier properties reduction. A great number of small cracks created, which mostly occur for platy pigment particles, says about loss of barrier properties.

It should be also mentioned, that convertibility of biopolymer-coated paperboard is influenced by the ambient conditions, such as temperature and RH, since these parameters largely affect the mechanical properties of moisture-sensitive biopolymers /36/.

8 TARGETS OF RESEARCH

The main target of the research was to prove, whether the approach on starch-gelatin blending /2/ with a view of biopolymer properties modification works or not. Based on that, another target of the experimental part was to find out, how this approach functions with other polysaccharides (wood-based polysaccharides) by analyzing the barrier properties and convertibility of coatings, based on these blends. The last objective was to study if pigments can be used in the composition of biopolymer blends without causing any losses of their barrier properties and convertibility.

9 MATERIALS AND METHODS

9.1 Reference paperboard

In the experimental part, two types of reference paperboard as a baseboard for surface sizing were used. The materials were Stora Enso's Trayforma Natura solid bleached sulfate A4 paperboard sheets for food trays thermo formation with the grammages of 290 and 350 g/m². /74/ /75/ The basic characteristics of the base paperboard materials, presented in the Table IV, were measured in the laboratory.

Table IV: Reference paperboard.

Trade name	Grammage, g/m ²	Thickness, μm	Air permeance, ml/min
Trayforma Natura	275	377	384
	340.7	440	184

9.2 Biopolymers

The main materials used in the experimental part for the polysaccharide-protein blending approach verification were modified hydroxypropylated starch (HPS) Solcoat P55 for paperboard barrier surface sizing and food grade protein Meira Gelatin. Other polysaccharides used were cellulose derivatives: CMC (Finnfix 4000G, CP Kelco), ethylhydroxyethyl cellulose (EHEC) (Bermocoll EBS41, Akzo Nobel) and HPC water-soluble cellulose ether (Klucel J). The CMC grades exploited in the work were Finnfix 4000G in the preliminary tests and Finnfix 30 in the main test series. The pigment used for the investigation of its effect on biopolymer blends barrier properties was talc (Finntalc c15b, mondo Minerals).

9.3 Coating dispersion preparation

The chemicals used needed to be dispersed in water in order to obtain solutions ready for further trials. HPS was prepared by dispersing dry starch granules in purified cold water (30%) and warming then on a self-organized water bath until it started to boil. The continuous manual stirring was maintained during the process in order to prevent starch granules agglomeration. The duration of cooking was approximately 25-30 min. After cooking the starch dispersion was diluted with water for obtaining desired dry solids content (DSC) equal to 16%.

Gelatin solution (5%) was also prepared by cooking on water bath at constant mixing until it was completely dispersed. Gelatin solutions were prepared each time immediately before blending and coating trials in order to prevent it from gel formation and possible microbial contamination.

The preparation of CMC, EHEC and HPC aqueous solutions has been carried out using the laboratory DT Mixer by adding of small portions of dry powders to the bucket filled with purified water and mixing continuously during approximately 25 min. In the case of EHEC preparation the water used was preheated first (approximately 60 - 70°C). The mixing strategy was also important. The speed of the impeller was elevated considerably at the end of the mixing in order to provide total dispersion of used chemicals. The obtained solutions used in the experimental part and their target values of dry solids content were CMC (3%), CMC (5%), EHEC (3%) and HPC (10%). However, due to high air saturation of dispersions during mixing the real values of dry solids content were determined after the preparation.

The blending of gelatin and other polysaccharide dispersions (and pigment addition) was made with a laboratory mixer just after the preparation of gelatin solution in dosages, specified in the experimental plan.

9.4 Coating dispersion analyses

The measurements of the coating dispersion properties are intended to provide better understanding of the coating process and required information for the process optimization /76/. The quality parameters of the coating dispersion directly affect the runnability of the coating process in general and the performance of the obtained coated product.

In this research, the analyzed coating dispersion parameters were DSC, pH, temperature, viscosity and water retention (WR).

9.4.1 *Dry solids content*

DSC is an important parameter in coating dispersion analyzing, since it determines the content of the major solid components, capable for creation of coating layer structure. This parameter has a direct effect on the resulting coat weight, determining also process runnability and energy consumption during drying.

DSC in percent (w/w %) was determined by quick method of drying a small portion of dispersion (approximately 0.3 g) in the laboratory moisture analyzer Precisa HA 300.

9.4.2 *Determination of pH*

The pH value has an effect on the stability of prepared coating dispersions. Moreover, it determines the behavior and the main properties of the bio-based polymers, capable for their film-forming ability and reactivity, such as ionic charge, hydrophobicity or hydrophilicity and reaction capacity.

During the experimental process, the pH values of the prepared coating dispersions and blends were analyzed by pH bench meter Mettler Toledo EL20. Each sample was measured twice. An average value of two measurements was taken as a result, and the variation from average was calculated. The temperature values were fixed each time, since pH is dependent on temperature changes.

9.4.3 Viscosity

Viscosity implies the resistance of fluids against deformation by shearing force /77/. It is one of the main parameters, characterizing rheological behavior of dispersions, and therefore, determining the runnability of the coating process. The problem of high viscosity is inherent to many bio-based polymer dispersions due to their high molecular weights, resulting in challenging rheological behavior.

Viscosity measurements were carried out by using Brookfield DV-II+ Viscometer with rotating spindle as a measurement tool. The device measures the viscosity by driving the spindle immersed in the tested dispersion at fixed rates through the calibrated spring (Figure 8). The viscosity value is obtained by the measurement of the spring deflection with the rotary transducer, caused by the viscous drag of the fluid against spindle. The viscosity unit is centipoise (cP), the measurement range is affected by the basic parameters of the spindle: rotational speed, size and shape. /78/

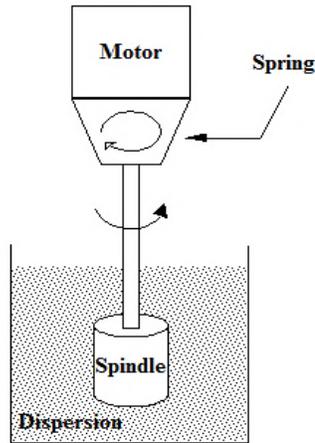


Figure 8: Brookfield-type viscometer working principle. /79/

During the viscosity measurements, the spindle №5 was chosen as a measurement tool. The spindle rotational speed in rotations per minute (RPM) was adjusted to each tested dispersion, depending on the viscosity, but was 100 RPM in most cases.

Temperature is one of the most important parameters, affecting the rheological properties of fluids. The Brookfield Viscometer provides simultaneous fixing of the temperature by inbuilt temperature probe. The viscosity and temperature values were measured twice for each dispersion sample with an average value and variation calculation.

9.4.4 Water retention

The water retention capacity of the coating dispersions is an essential parameter, determining the interactions between the base material (paper or paperboard) and the continuous water phase of the dispersion. /80/ The dewatering speed of the coating dispersion during the coating layer consolidation affects the quality of the final coat surface.

There are direct and indirect techniques for the water retention of coating colors determination exist. Direct ones imply evaluation of the amount of water from the coating color penetrated

into the base material under the applied pressure. The indirect techniques evaluate other parameters, affecting the penetration of the liquid phase into the base materials, such as conductivity and coating color viscosity. /76/

In the frame of the coating dispersion analyses, the water retention was measured by the direct gravimetric method with the ÅA – GWR IV Water Retention Meter (Figure 9).

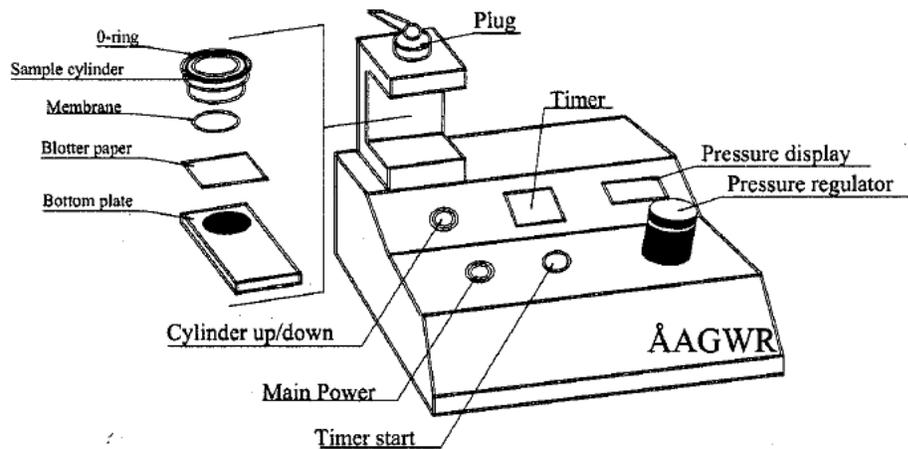


Figure 9: The water retention meter. /81/

The sample cylinder is filled with a portion of the tested dispersion (10 ml). The dispersion is separated from the pre-weighted blotting paper (base paperboard) by the non-hygroscopic polycarbonate membrane. The external pressure (1.5 bar) is applied to the system during the specified period of time (1.5 min). After this period, the blotting paper with absorbed water is weighted and the amount of water is calculated by the subtraction of the dry blotting paper weight. The result in percent (%) was calculated using the Equation 1:

$$WR = 100 - \left[\frac{W_2 - W_1}{V} \times 100 \right], \quad (1)$$

where: WR water retention, %;
 W₁ weight of the dry base paper, g;
 W₂ weight of the base paper after the test, g;
 V amount of the dispersion sample, 10 ml.

The results were reported as an average of two parallel water retention measurements.

9.5 Coating techniques

9.5.1 Rod coating

Rod coating technique implies the coating process in which the metering is performed using metering rods. This type of coating allows to obtain uniform surface coverage. /76/

In the preliminary coating trials, the small-scale manual laboratory rod coater (Venema Rod Coater, supplied from Lorentzen & Wettre) with profiled rod was used. A small portion of the coating dispersion was applied to the paperboard surface with the syringe along the rod, positioned above, close to one of the edges of the paperboard sheet. Then the paperboard sheet was pulled manually, when the rod provided the spreading and simultaneous metering of the coating dispersion.

The rod wire coils diameter (namely, the depth of grooves between coils) determines the amount of the coating dispersion that will stay on the coated surface after it has moved along the paperboard sheet, and therefore, it affects the resulting coating thickness. The schematic illustration of the rod metering device is presented on the Figure 10.

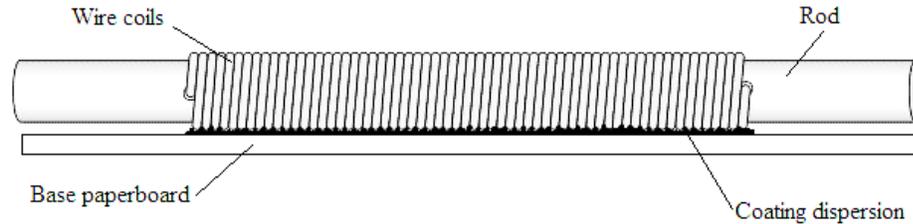


Figure 10: Metering rod.

The choice of the rod wire diameter depends on the viscosity of dispersions used in the coating trials. Therefore, the calibration process was carried out in order to determine the most appropriate rod type. The coatings produced by 0.4 and 0.6 rod wire diameters were compared. The 0.4 rod was chosen, since it provided better runnability of the process and paperboard surface coverage.

Coated paperboard samples were dried in an oven (at temperature of approximately 45°C) for 20 min.

9.5.2 Blade coating

The blade coating technique implies the application of the excess amount of the coating dispersion to the paperboard surface, followed by the metering with the blade. The blade coating allows to obtain elevated surface smoothness due to the blade geometry. /76/

In the main test series the coating trials were performed on a pilot-scale DT Laboratory Coater, which can be modified to operate in three coating units: blade, film and size press. The DT Laboratory Coater allows to coat sheets as well as the web.

During the coating on a DT Laboratory Coater, the film of the coating color is formed on the rotating applicator roll, immersed in the coating dispersion, and simultaneously applied on the large backing roll with the paper or paperboard web on it. The flexible metering blade

removes the excess of the coating dispersion and forms smooth coated surface. The schematic representation of the blade coating unit is given in the Figure 11.

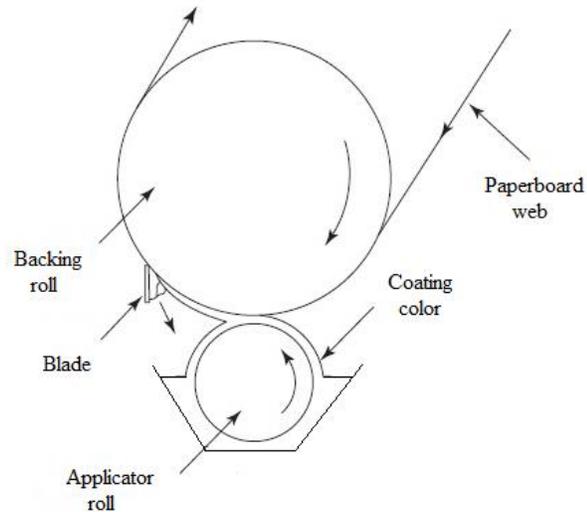


Figure 11: Blade coater. /82/

The coating process was carried out by using A4 reference paperboard sheets, which were positioned on the backing roll by attaching with the tape, as it shown on the Figure 12. In this case the backing roll made only one rotation, during which the coating color was applied to the paperboard sheet and metered with the blade.



Figure 12: The DT Laboratory Coater in paperboard sheets coating mode.

The main parameters, adjusted during the coating process in order to maintain optimal thickness of the wet coat were blade angle and pressure, varied depending on the viscosity of the coating dispersions. The less viscous dispersions required lower blade pressure values (approximately 0.5 – 0.7 bar), whereas more viscous ones required elevation of the blade pressure even above 1 bar. However, various blade angle adjustments at fixed pressure values also had different effects on the runnability of the coating process.

After that, coated paperboard samples were dried with the separate infrared heater. The duration of drying varied depending on the coat DSC and the coat weight of the samples (18-30 seconds). It should be mentioned, that the drying was performed stepwise (several periods of 6 seconds) in order to prevent paperboard ignition.

Prepared coated paperboard samples were conditioned prior the further measurements in the constant climate room at 23°C and 50% RH.

9.6 Converting trials

One of the main targets of the present research was to observe the behavior of the coated paperboard samples during the converting operations in order to determine the changes in mechanical properties of used bio-based polymer blends. Convertibility is one of the key properties of the coated packaging materials, since the coating layer has to resist all the stresses occurring while converting operations without cracking and loss of barrier properties.

LUT Metal Technology provided the assistance and support in converting trials performed on the pilot-scale converting equipment. The total scope of the work consisted of several steps, including conditioning of samples, creasing and pressing into food trays, which are described further.

9.6.1 Conditioning of samples

Before converting trials all samples were conditioned in the constant climate chamber at 22°C and 78% RH until the optimal moisture content of coated paperboard equal to approximately 9% was reached. This moisture content value is required by the press forming process in order to provide sufficient behavior of the paperboard during converting and prevent possible breakages as such, presented in the Figure 13. /83/

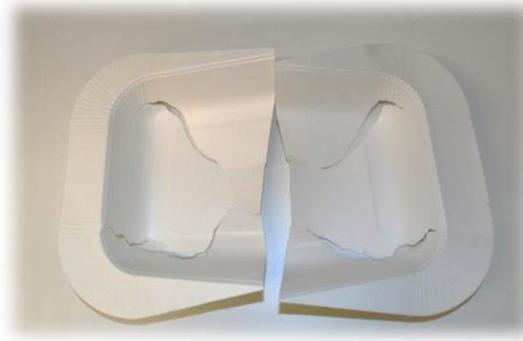


Figure 13: The breakage occurred during the tray pressing due to low moisture content of the paperboard

9.6.2 Creasing and pressing into food trays

After being conditioned, two samples of the same test point were attached together with the paper tape along their machine direction fiber orientation. This attachment of the sheets was done in order to match the dimensions of the creasing tool, which exceeded the size of one A4 sheet. After that, the sample was ready for converting operations. First, the creasing and die cutting were performed in order to obtain creased paperboard blanks, used in press forming process (Figure 14). Sufficient creasing facilitates and determines the quality of converting operations.

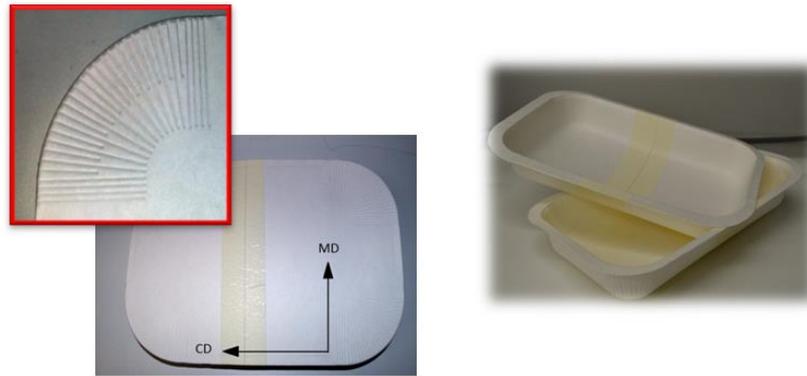


Figure 14: Creased paperboard blank (left). Ready paperboard food tray (right).

Creased paperboard blanks were fed then to the forming section of the converting machine for pressing into food trays (Figure 14). The layout of the pressing process is illustrated in the Figure 15. First, creased paperboard blank is positioned between moulding tools (1) (upper – male tool, lower – female tool). Then, the blank is tightened with the female mould by the rim tool (2). After that, the male tool presses blank into the female tool (3) and stays there for a while (4) (approximately 0.5 – 1 seconds), when the coating softens and the creases in corners of the tray are sealed together. Meanwhile, the rim tool (5) flattens the flanges of the tray. Finally, the tray is removed and a new blank can be fed into the press (6). The final rigidity of the tray is achieved when it cools down.

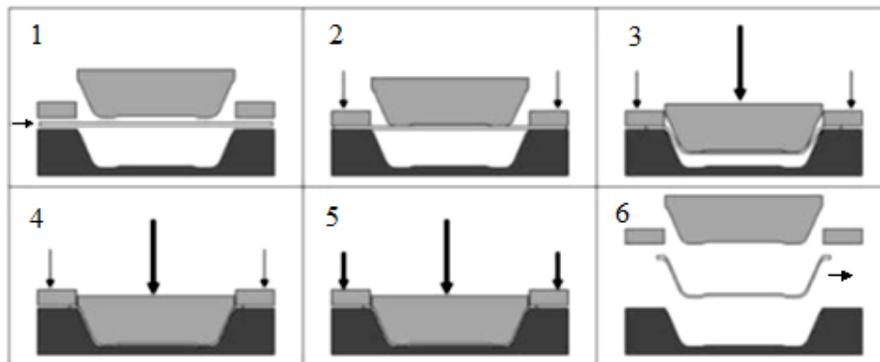


Figure 15: Trays pressing process layout. /84/

The main parameters, maintained during the pressing are listed in the Table V.

Table V: Parameters of the pressing process.

Temperature of Male Mould, °C	Pressing Speed, mm/s	Pressing Dwell Time, ms
20	130	1000
Temperature of Female Mould, °C	Pressing Force, kN	Rim Holding Force, kN
145	135	1.16

Two samples were produced for each coating test point: one creased paperboard blank and one pressed tray. Both creased and pressed areas were analyzed by the grease resistance determination tests in order to evaluate the effect of converting operations on the bio-based coatings integrity. The details of the grease resistance determination method are described in Chapter 9.7.3.

9.7 Testing of coated paperboard

9.7.1 General properties

The coated paperboard samples were tested, first, on several general properties, such as basis weight (g/m^2), coat weight (g/m^2), thickness (caliper) (μm), density (kg/m^3) and bulk (m^3/kg), since these are important parameters, determining the paperboard properties /85/. The basic properties of coated paperboard were determined on the preliminary trimmed with the cutting device samples (141×141 mm) according to the following standards:

- ISO 536, Paper and board – Determination of grammage;
- SCAN-P 7:75, Paper and board – Thickness and apparent density.

The coat weight of prepared samples was determined by the subtraction of the weight of trimmed uncoated reference paperboard sample from the weight of the coated one.

9.7.2 Air permeability and roughness

Air permeability is one of the important parameters, characterizing the material resistance to gases passage (one of the most important barrier properties of packaging materials). However, air permeability measurement concedes to the OTR determination in relation to gas barrier properties analysis, but there is still a linkage between these two parameters. Roughness determination of the coated surface is also essential, since it can affect to some extent both printability and barrier properties of the material.

The air permeability and roughness (ml/min) were measured on the trimmed paperboard samples by using Bendtsen tester (Lorentzen & Wettre) according to the following standards:

- SCAN-P 60:87, Bendtsen air permeability;
- SCAN-P 21:67, Bendtsen roughness.

The air permeability was measured on a Bendtsen tester as a volume of the air, which passes through the area of 10 cm² of the tested sample under the pressure (1.47 kPa). The roughness of the paperboard was determined as an amount of the air, escaped between the measuring ring and the material surface.

The results for both air permeability and surface roughness were reported as an average of eight parallel measurements for each test point, calculated by the tester.

9.7.3 Grease permeability

All prepared samples of coated paperboard produced during the coating trials for each test point (uncreased, creased and pressed into food trays) were tested on their grease resistance according to the ISO/DIS 16532-1 standard (Paper and board – Determination of grease resistance – Part 1: Grease permeability method). The method is based on measurement of the period of time, when grease penetrates through the testing material under a weight at elevated

temperature of 60°C. The used testing grease was red-dyed palm kernel oil. The tested samples were 50×50 mm in size.

Four parallel measurements of the grease resistance time were done for each uncreased paperboard test point: three measurements from coated side and one from uncoated (the grease penetration from uncoated side was fast, almost the same as for the base paperboard). The grease resistance of creased areas of paperboard blanks was measured separately for creases, located in machine and cross-direction fiber orientation of the paperboard (two parallel measurements for each orientation). Converted food trays were tested in their corners (two measurements), where the coating layer was supposed to be sealed during the pressing (Figure 16). The testing of trays was performed in an oven at temperature of 60°C



Figure 16: Position of the converted paperboard food trays during the grease permeability tests.

9.7.4 Microscopic imaging

The scanning electron microscopy (SEM) was performed for some coated paperboard samples in order to evaluate the structure and surface coverage of the coating layer. The images were obtained with JEOLJSM-5800 scanning microscope using secondary SEI-detector (secondary electrons) at acceleration voltage of 15 kV. Before imaging, all samples were coated with gold in Edwards Scancoat 6 sputter-coater.

Some of the converted and unconverted samples were tested after the grease resistance test with Olympus SZX9 Microscope in order to investigate the character of the grease penetration into the tested material.

9.8 Experimental plan

The total scope of the experimental part was performed in two steps. First, the small-scale preliminary tests were organized, basically, in order to reach one of the main targets of the research – to prove the approach on starch-gelatin blending /2/ and to study, how this approach will function with other polysaccharides (wood-based polysaccharides). The first matter of the interest in the preliminary tests was mainly to study the applicability and functionality of chosen polysaccharides in relation to the approach stated (namely, to observe the changes in barrier properties when gelatin was added).

The pilot test series, including more sophisticated layout, pilot-scale equipment and methods of the research, implied the investigation of the whole process chain of coating colors development, from dispersion preparation and analysis to testing of converted and unconverted coated paperboard samples. These tests, organized according to the results obtained during the preliminary tests, were aimed to reach also other targets of the research: to analyze the convertibility of obtain coatings and to study the pigment addition to these coatings. Moreover, some changes in the range of exploited materials were done at this stage. All the materials and methods used in both preliminary and main tests are listed in the Table VI.

Table VI: Materials and methods with division on preliminary and main test series.

Research stage	Materials	Methods			
		Coating dispersion analyses	Coating technique	Converting trials	Testing of coated paperboard
Preliminary tests	<ul style="list-style-type: none"> - Reference base paperboard, 290 g/m² - Gelatin - Hydroxypropylated starch (HPS) - Carboxymethyl cellulose (CMC) - Ethylhydroxyethyl cellulose (EHEC) 	No	Rod coating (Venema)	No	Yes
Pilot tests	<ul style="list-style-type: none"> - Reference base paperboard, 350 g/m² - Gelatin - HPS - CMC - Hydroxypropyl cellulose (HPC) - Talc 	Yes	Blade coating (DT Coater)	Yes	Yes

9.8.1 Preliminary tests

Together with the HPS, two cellulose derivatives, such as CMC and EHEC were involved in the preliminary tests. The test point matrix, implying addition of 10, 20 and 30% gelatin dosage is presented in Appendix I (Table I).

It is important to mention, that gelatin was introduced into the blend as an additive, therefore, 100 parts of the main polysaccharide was taken for each test point (the main polysaccharide was not substituted by gelatin).

9.8.2 Pilot tests

The test point matrix for the pilot tests is presented in the Appendix I (Table I). Some chemicals were moved to the main tests from the preliminary tests, however some were eliminated. In addition, the baseboard used in the preliminary tests was replaced with a product having higher basis weight. The addition of the pigment (talc) is considered at this stage. The more explanations about these changes in the experimental plan will be given in Chapter 10, describing the results obtained.

It should be mentioned, that in this case the pigment (talc) substituted the main polysaccharide. The gelatin was added to the polysaccharide-talc blend (comprising together 100 parts) as an additive.

10 RESULTS AND DISCUSSION

10.1 Preliminary tests

In this chapter the main results obtained during the preliminary tests, performed with the laboratory rod coater, will be presented. The general properties of the coated paperboard samples, produced from various blends of chosen polysaccharides with gelatin according to the experimental plan for preliminary tests, are presented in Appendix II (Tables 1-3) in comparison with the reference base paperboard.

10.1.1 Hydroxypropylated starch-gelatin blends

The coat weights of starch-based coatings (Appendix I, Table I), obtained for samples of different starch-gelatin ratio, varied slightly. However, these changes, probably, can be attributed mainly to the variations of the basis weight of the reference base paperboard. These coat weight values can be treated as approximations.

All the samples, coated with dispersions containing gelatin (except HPS:gelatin, 100:30) exhibited insignificant increase in the thickness values, compared to those, coated with pure HPS dispersion. The thickness variations can be explained by the differences in the structures of coatings occurred due to different film-forming properties of obtained dispersions or characteristics of the drying strategy [61]. Both these factors could affect the formed structure of the coat layer. Density and bulk values, in turn, also varied slightly due to diverse thicknesses.

The surface microstructure of the HPS-gelatin coatings was studied using SEM (Figure 17).

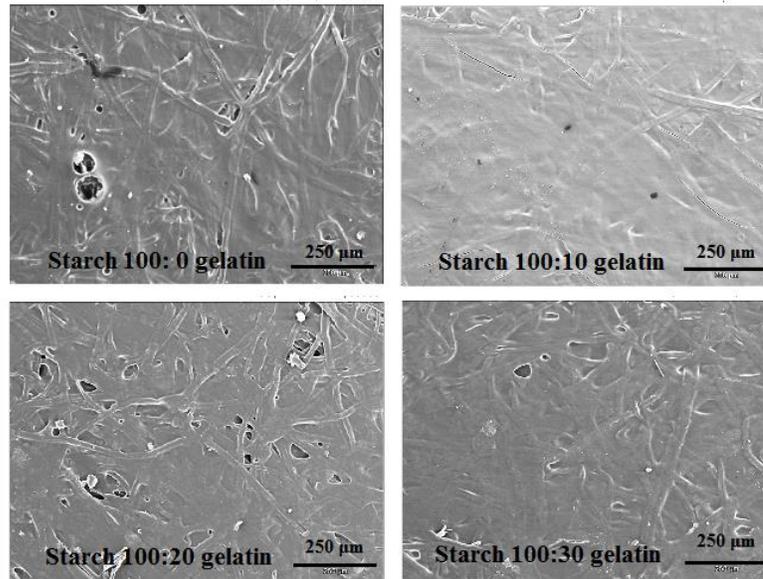


Figure 17: SEM images of surface microstructure obtained by coatings of various HPS-gelatin ratios (120x magnification, accelerating voltage: 15 kV).

By analyzing the surface structure of pure HPS coatings (Figure 17, Starch 100:0 gelatin), some blistering effect can be observed. However, this effect disappeared in coatings, containing different amounts of gelatin. The surface coverage and smoothness also increased with gelatin addition to the HPS coating dispersion. The best surface coverage of the base paperboard was reached by the dispersion containing 10% of gelatin. It should be mentioned, that the coat weight (the highest value was observed for HPS-based dispersion containing 10% of gelatin) also had an effect on improved surface smoothness in this case.

The analyses of barrier properties of HPS-gelatin blends included Bendtsen air permeability (ml/min) and grease permeability (min) tests. The charts illustrating dependences of these measurements on gelatin addition are illustrated in Figures 18 and 19 respectively. The coat weight variations between different samples are also reflected on the charts.

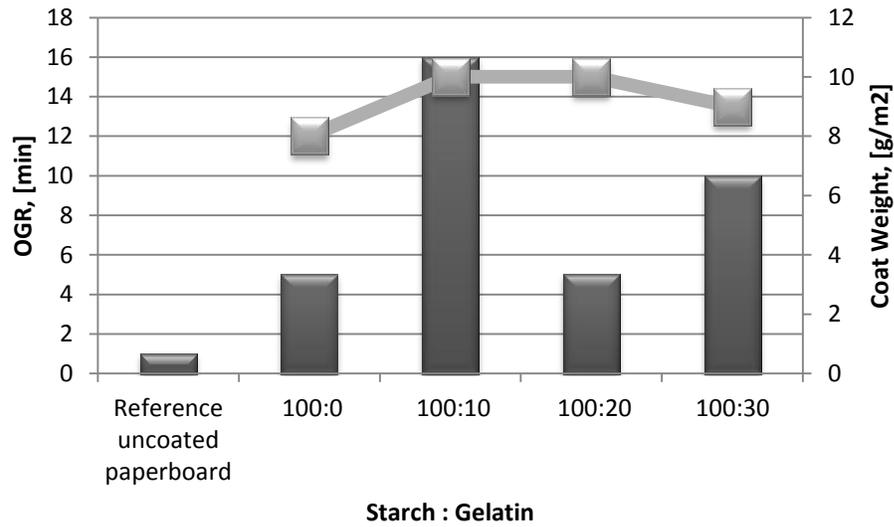


Figure 18: Grease permeability time (bars) of coatings produced from blends of different starch-gelatin ratios with coat weight variation (the curve) between samples.

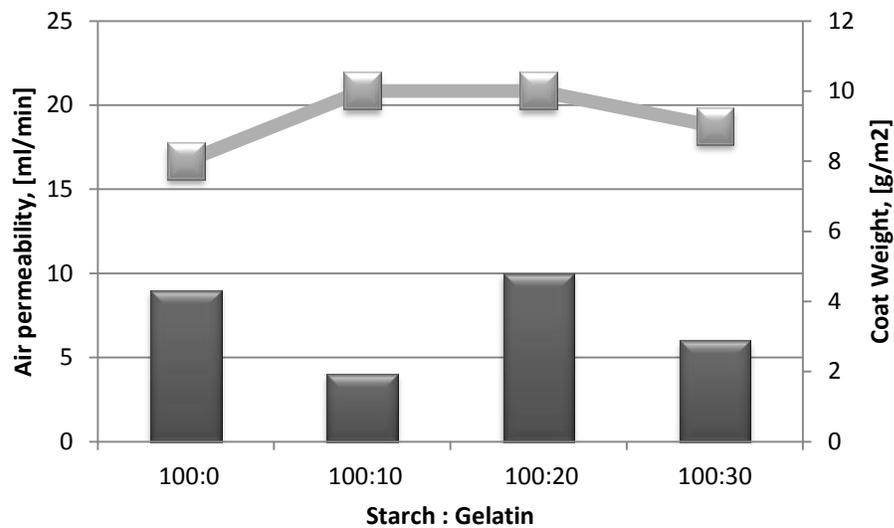


Figure 19: Air permeability (bars) of coatings produced from blends of different starch-gelatin ratios with coat weight variation (the curve) between samples.

As it is clear from the Figure 18, the grease resistance increased significantly for the starch-based coating with 10% gelatin addition, compared to pure starch. It becomes more evident in

comparison with not so sharp elevation of grease resistance between uncoated reference paperboard and coated with pure starch paperboard samples. Air permeability values of samples in most cases (except HPS:gelatin, 100:20) decreased with gelatin addition. The fact can be attributed to that proteins are usually considered as more effective gas-barriers, creating together with the starch more packed cross-linked structures with reduced pore volume /62/ /86/.

10.1.2 Carboxymethyl cellulose-gelatin blends

Despite of the quite low coat weight obtained for the CMC-based coatings (CMC grade was 4000G) with the rod coating technique (Appendix I, Table II), the effect of gelatin addition on improved surface coverage of coatings produced from CMC-gelatin dispersions still can be observed (Figure 20), especially in the case of 20% gelatin dosage.

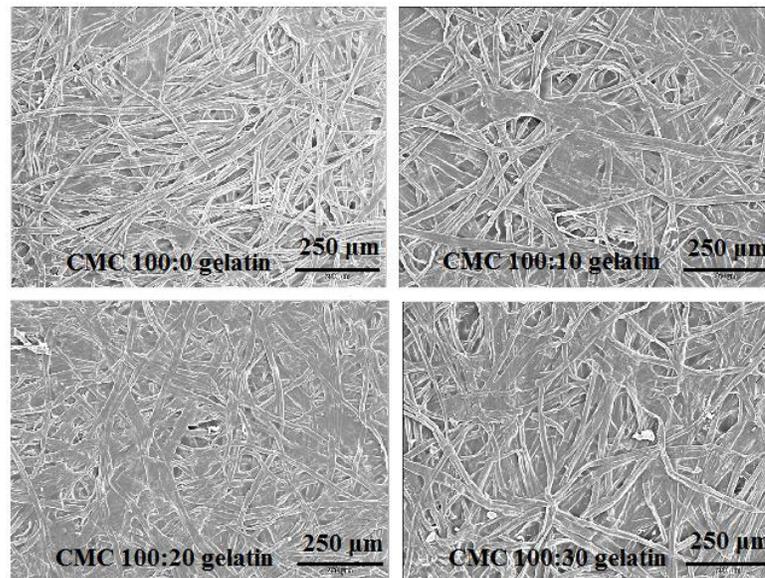


Figure 20: SEM images of surface microstructure obtained by coatings of various CMC-gelatin ratios (120x magnification:, accelerating voltage: 15 kV).

The tendency of gradual grease permeability time elevation with increasing gelatin content is evident from the chart, presented on the Figure 21. The highest value of the grease resistance was obtained with 20% gelatin proportion as well as the best surface coverage. However, in this case the grease resistance improvement was slightly dependent on the coat weight increase.

There was also decrease in air permeability observed with increasing gelatin content in CMC-gelatin blends (Figure 22). The 20% gelatin proportion was recognized again as sufficient in elevation of barrier properties of CMC-based coatings.

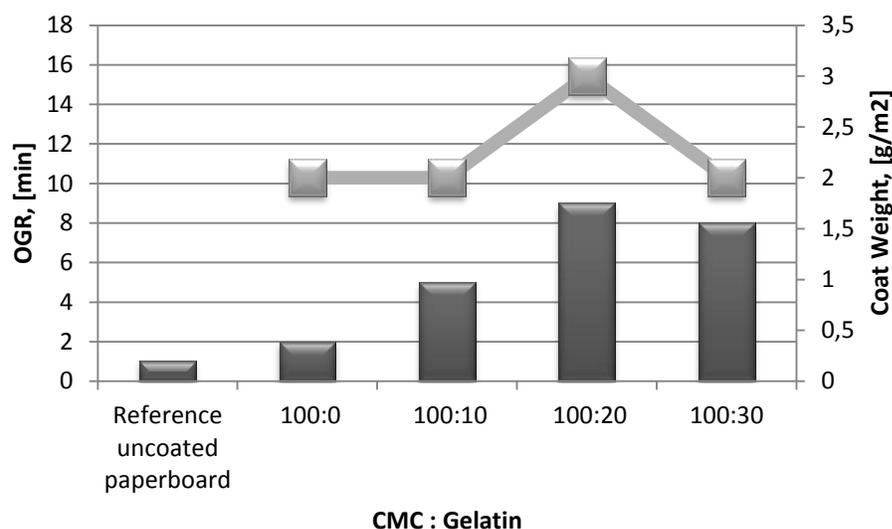


Figure 21: Grease permeability time (bars) of coatings produced from blends of different CMC-gelatin ratios with coat weight variation (the curve) between samples.

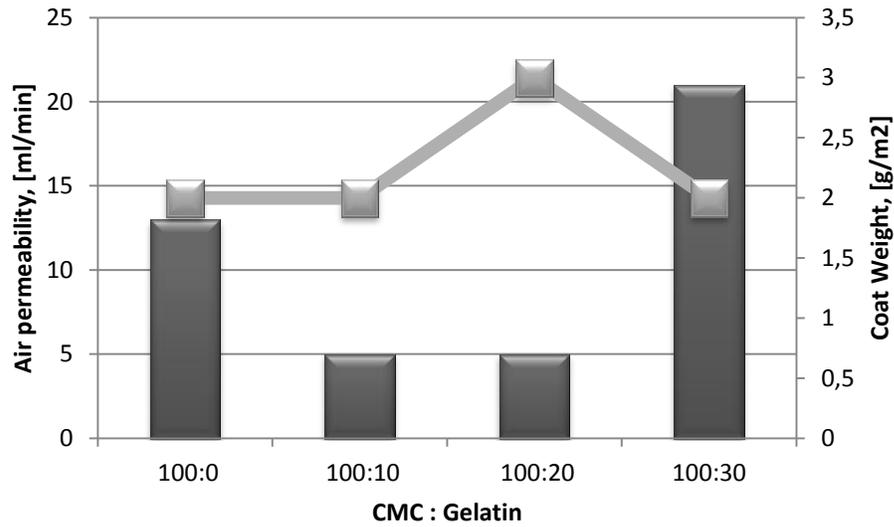


Figure 22: Air permeability (bars) of coatings produced from blends of different CMC-gelatin ratios with coat weight variation (the curve) between samples.

10.1.3 Ethylhydroxyethyl cellulose-gelatin blends

The surface coverage of the coatings produced from EHEC-gelatin blends was very poor at different gelatin dosages (Figure 23). Probably, this can be attributed to the extremely low coat weights obtained for the EHEC-based coatings (Appendix I, Table II), caused by challenging behavior of this biopolymer due to its high viscosity (41000cP, 20 RPM shear rate, 10°C) at quite low DSC (3%) during coating trials with the rod coater. However, approximately the same coat weight values (even lower) were obtained for CMC-based coatings (described previously), exhibited improved surface coverage and barrier properties with gelatin addition.

Therefore, no improvements in the grease resistance were revealed both for pure EHEC and EHEC-gelatin coatings (Figure 24). However, the slight decrease of air permeability was observed for coatings produced from blends with increased gelatin content (Figure 25). The best results were obtained with 30% gelatin dosage. However, the air permeability values in this case are comparable to that of reference base paperboard.

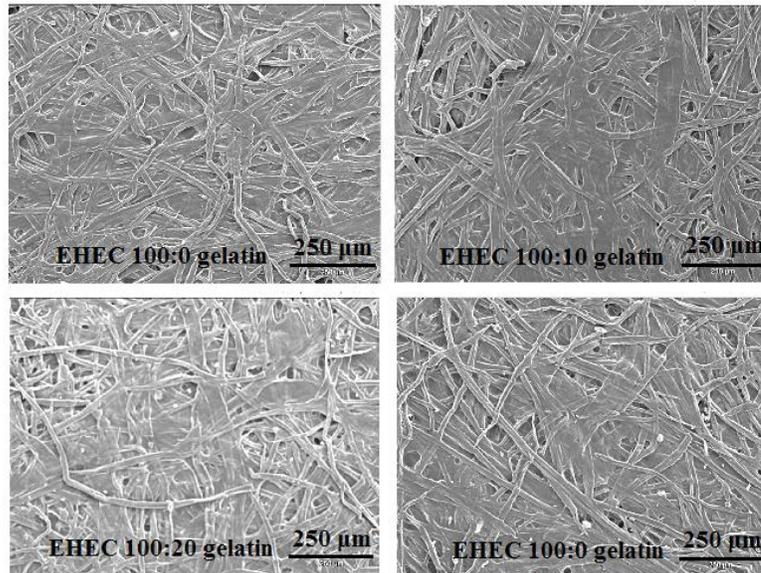


Figure 23: SEM images of surface microstructure obtained by coatings of various EHEC-gelatin ratios (120x magnification, accelerating voltage: 15 kV).

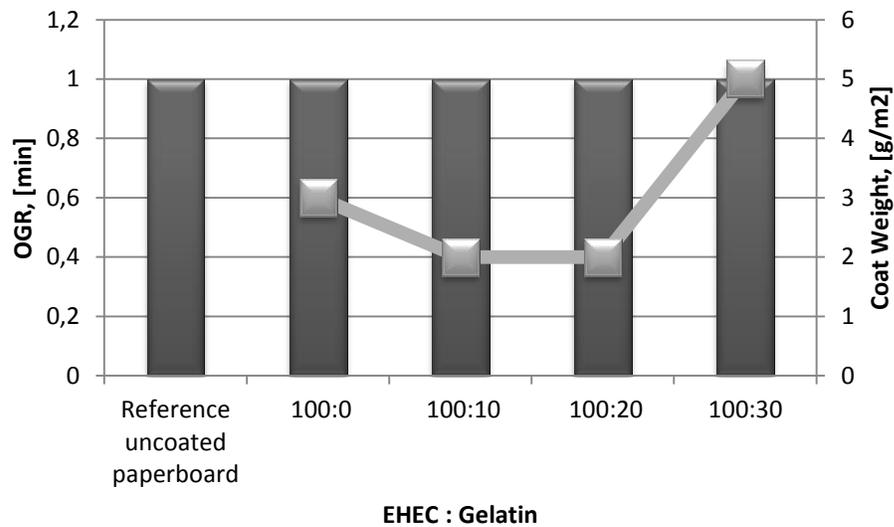


Figure 24: Grease permeability time (bars) of coatings produced from blends of different EHEC-gelatin ratios with coat weight variation (the curve) between samples.

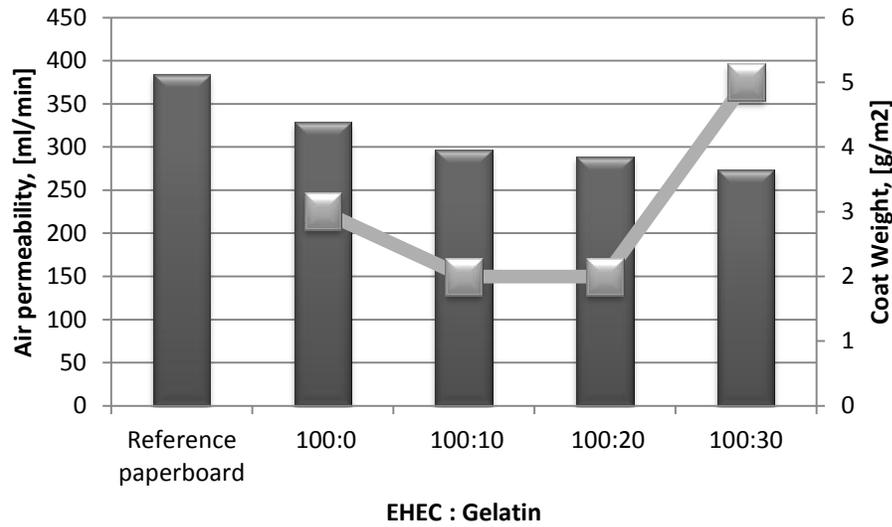


Figure 25: Air permeability (bars) of coatings produced from blends of different CMC-gelatin ratios with coat weight variation (the curve) between samples.

10.1.4 Conclusions based on preliminary tests results

By analyzing the results obtained during the preliminary research, it is possible to make some conclusions and determine further direction for the main test series. The results of the preliminary tests revealed that the combination of HPS with gelatin really enhances the grease barrier properties of starch-based coatings. Therefore, the approach on starch-protein blending /2/ was proved. Moreover, 10% gelatin dosage was recognized to be the most reasonable, providing also improved surface coverage and smoothness of the coatings.

The similar results were obtained for CMC exploited in the preliminary tests as one of the most common cellulose derivatives. Thus, it was revealed, that offered approach /2/ also functions with wood-based polysaccharides, improving barrier properties and film-forming ability. However, CMC required higher gelatin dosage in order to obtain these improvements. In this way, the addition of 20 % gelatin allowed to reach elevated grease repellency and reduced air permeability of CMC-based coatings. In addition, the behavior CMC Finifix 4000G was quite challenging due to high viscosity.

The blending of EHEC with gelatin did not revealed any significant changes. The barrier properties and surface coverage were poor regardless of the gelatin addition. Based on these results, the following prospectives for the main tests were established:

- it is reasonable to increase the coat weight for wood-based polysaccharides (maintain approximately 10 g/m²);
- to replace insufficient EHEC used with another wood-based polysaccharide – HPC (to observe how the hydroxypropylation of this polysaccharide can affect its interactions with proteins);
- to take another CMC grade – Finnfix 30 with lower molecular weight, in order to lower viscosity without decreasing DSC;
- to take another base board grade – Trayforma Natura with higher basis weight (350 g/m²), in order to obtain better durability in pilot converting operations.

10.2 Pilot trials

In the pilot-scale trials, performed with the DT Laboratory Coater, three main bio-based polymers were exploited (HPS, CMC (Finnfix 30) and HPC) for blending with gelatin. The results of the whole process of the surface sizes development with these chemicals are presented further.

10.2.1 Dispersion analyses

All the coating dispersions, prepared according to the test point matrix for the pilot tests (Table VIII), were analyzed on viscosity and water retention, considering also pH and temperature values. It is worth to mention, that in pilot tests, the addition of the talc to blends with wood-based polysaccharides have been also considered. The values of water retention, viscosity, shear rates and temperatures, at which the measurements were performed, are presented in Appendix III.

The results of viscosity measurements (temperature and DSC varied in a small range) revealed the general tendency of viscosity reduction obtained for CMC and HPC coating dispersions with increasing gelatin content (Figures 26-27). In the case of HPS-based dispersions, the viscosity increased considerably at 15% gelatin dosage. However, it dropped sharply when 25% of gelatin was added (Figure 28).

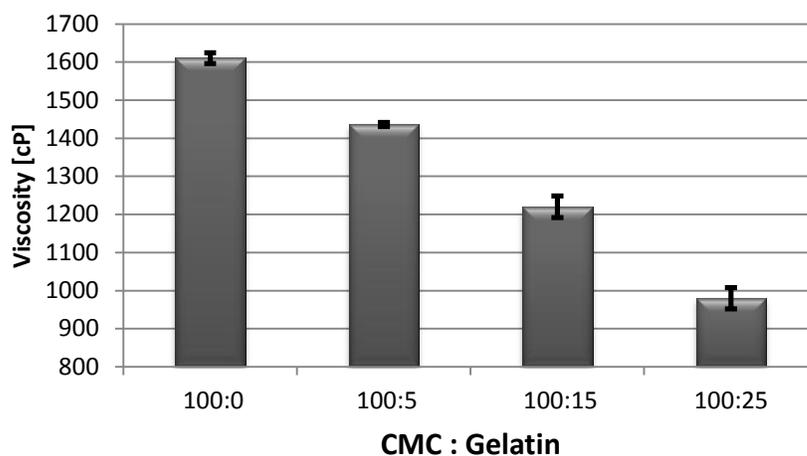


Figure 26: Viscosity of coating dispersions produced from blends of different CMC-gelatin ratios.

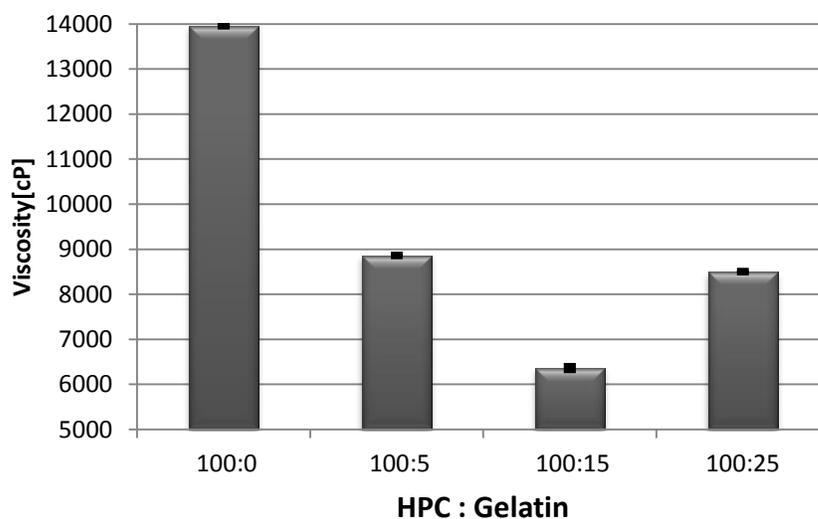


Figure 27: Viscosity of coating dispersions produced from blends of different HPC-gelatin ratios.

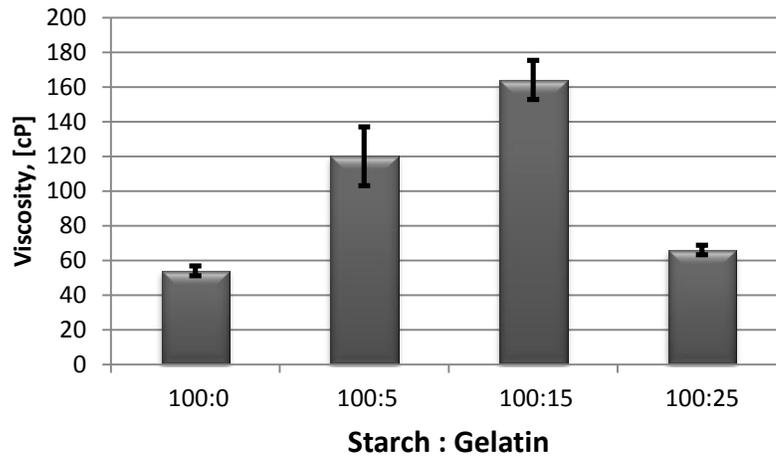


Figure 28: Viscosity of coating dispersions produced from blends of different starch-gelatin ratios.

This effect of viscosity reduction can be explained by the fact, that initial viscosity of gelatin dispersion was lower than that of CMC and HPC dispersions. The temperature variations also could affect the viscosity values. However, in the case of HPC-based blends, the tendency of viscosity reduction even with insignificant temperature decrease was observed. Moreover, the gelatin addition slightly increased DSC of prepared dispersions of cellulose derivatives, at the same time maintaining reduced viscosity values. Therefore, it is possible to conclude that gelatin addition is able to modify the rheology of cellulose derivatives.

The effect of talc addition on viscosity of obtained CMC-gelatin and HPS-gelatin blends also has been investigated at gelatin dosages of 5 and 25%. Figure 29 illustrates how talc addition affected viscosities of CMC-based dispersions containing 5 and 25% of gelatin.

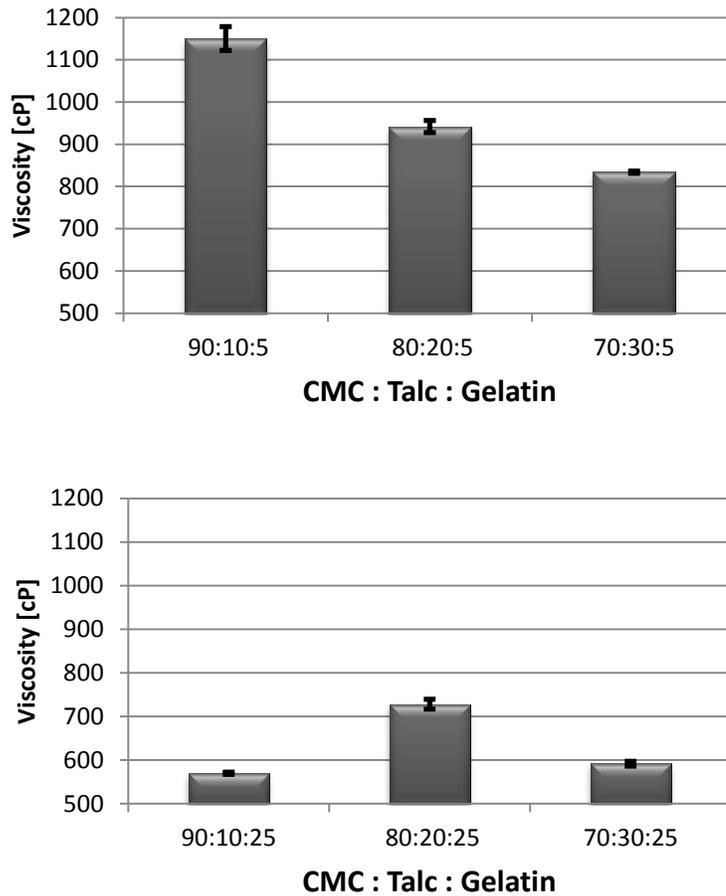


Figure 29: Viscosity of coating dispersions produced from CMC-gelatin blends containing 5% (upper) and 25 % (lower) of gelatin with different talc dosages.

The addition of 20% of talc gave absolutely different effect on CMC-based coating dispersions containing 5 and 25% of gelatin respectively, causing the viscosity reduction in the first case, and inverse effect in the second case. Probably, this effect can be attributed to that talc, substituted 20% of CMC, was able to form some kind of structures with gelatin, causing viscosity elevation. However, 30% talc addition gave sharp reduction of viscosity of CMC-gelatin blends with 25% gelatin dosage. The similar effect can be observed for HPC-based coating dispersions (Figure 30).

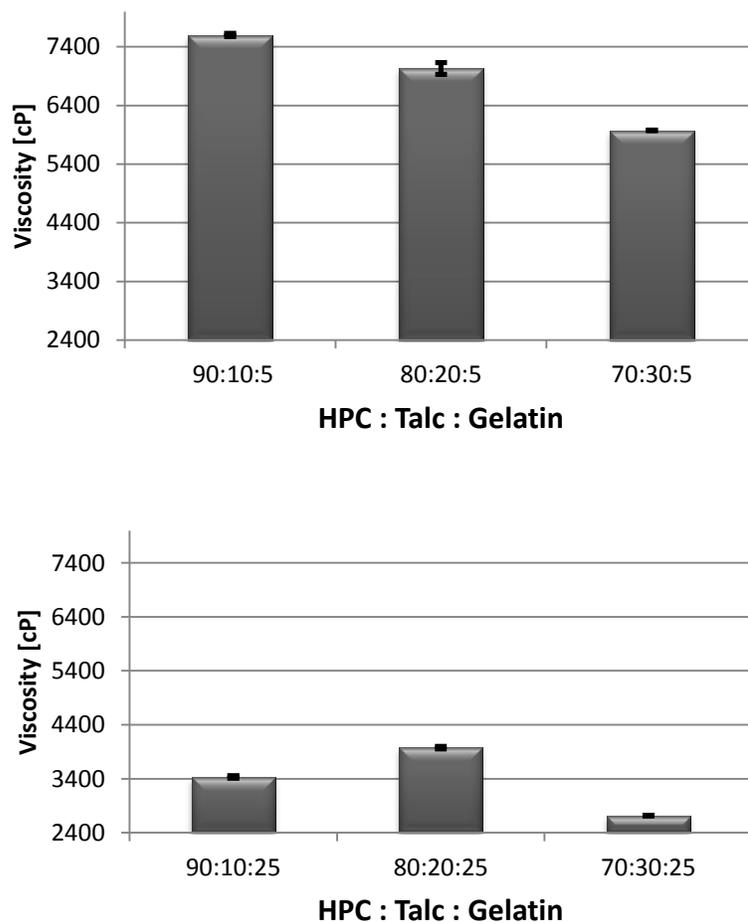


Figure 30: Viscosity of coating dispersions produced from HPC-gelatin blends containing 5% (upper) and 25% (lower) of gelatin with different talc dosages.

The water retention is an essential characteristic determining the speed of coating dispersion dewatering. It greatly affects both the runnability of the coating process and quality of the coat layer. For instance, if the water retention is low, the coating dispersion will be rapidly dewatered, which can cause excessive increase of DSC, leading metering problems and irregular coat surface /80/ The water retention values of obtained coating dispersions were analyzed as well. Positive effect of elevation of water retention values has been revealed for HPS-based coatings (Figure 31). Thus, addition of 15% of gelatin allowed to reach the best water retention capacity of produced HPS-gelatin blend. However, making reliable conclusions from these results is challenging due to large standard deviation in test point 100:5.

Gelatin acting like a continuous phase could improve the water holding capacity of hydrophilic starch granules by causing some changes in crystalline structure of starch, which usually tends to eliminate water molecules easily. /8/ /61/

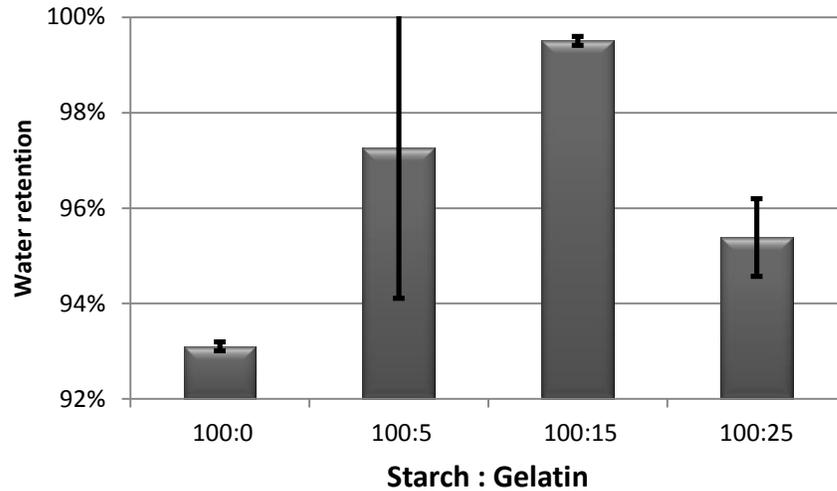


Figure 31: Water retention of coating dispersions produced from blends of different starch-gelatin ratios.

There were no significant changes revealed in water retention ability of CMC- and HPC-based coatings with regard to different gelatin dosages (Figures 32-33). However, in the case of HPC-gelatin blends minor decrease of water retention values with increasing gelatin content still can be observed (Figure 33).

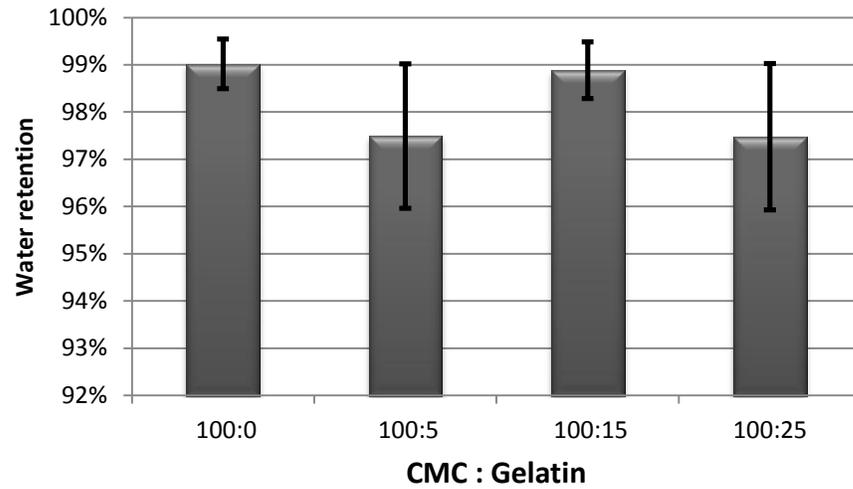


Figure 32: Water retention of coating dispersions produced from blends of different CMC-gelatin ratios.

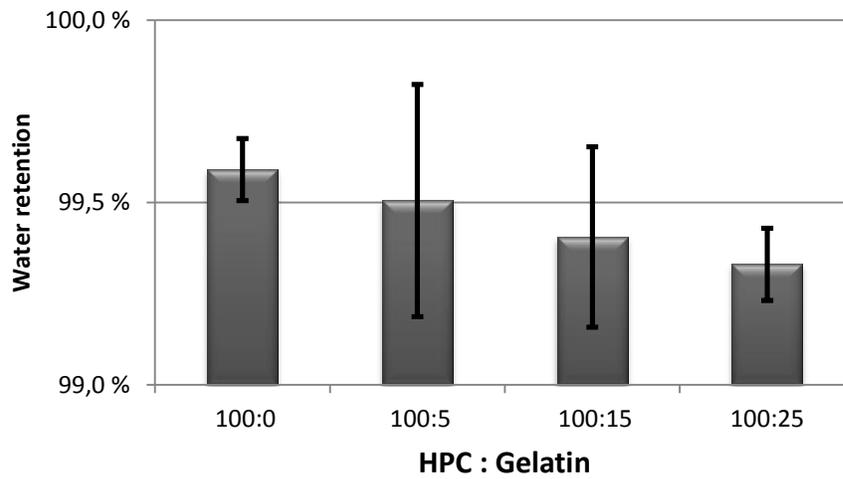


Figure 33: Water retention of coating dispersions produced from blends of different HPC-gelatin ratios.

Addition of talc also has brought some changes to the water retention values of CMC-gelatin and HPC-gelatin blends (Figure 34). In this way, negative effect of talc addition was observed for CMC-gelatin blends, containing 5% of gelatin. Meanwhile, addition of talc to the CMC-gelatin blend, containing 25 % of gelatin, led to the significant linear increase of water retention. However, standard deviation of some test points was so large that making reliable conclusions is difficult.

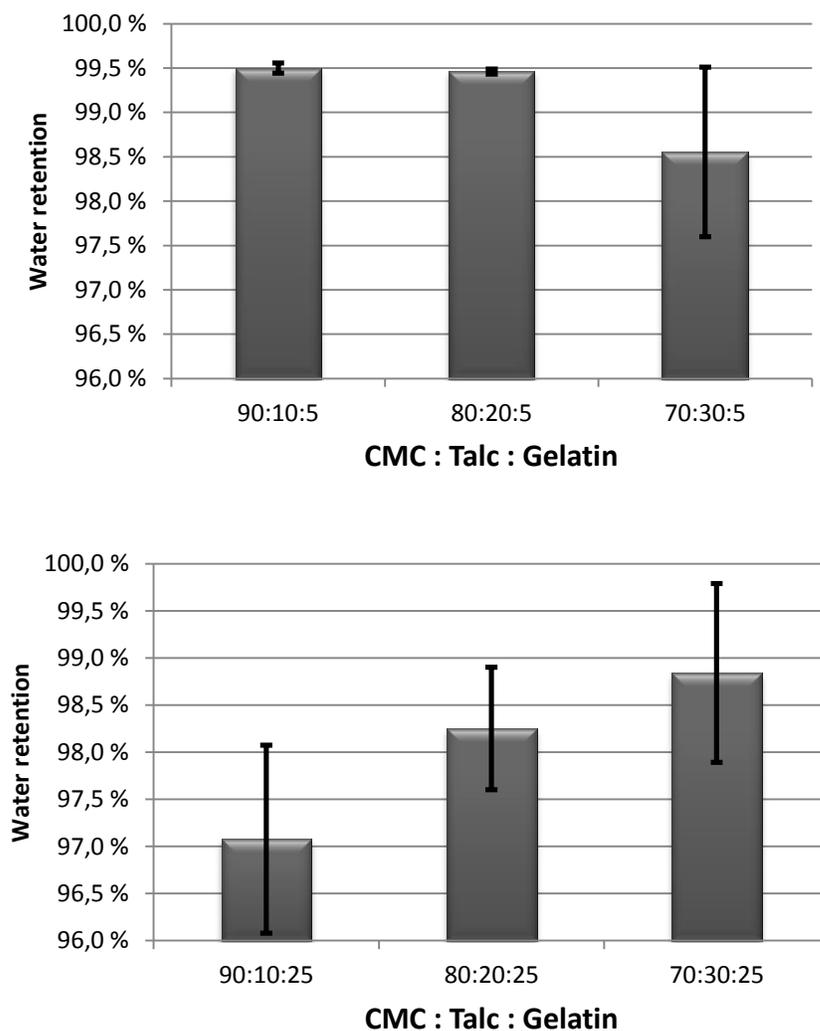


Figure 34: Water retention of coating dispersions produced from CMC-gelatin blends containing 5% (upper) and 25 % (lower) of gelatin with different talc dosages.

The tendency of water retention reduction was also revealed for HPC-gelatin blends, filled with talc (Figure 35). The different viscosities obtained for different dispersions can affect the variations of water retention values in fact.

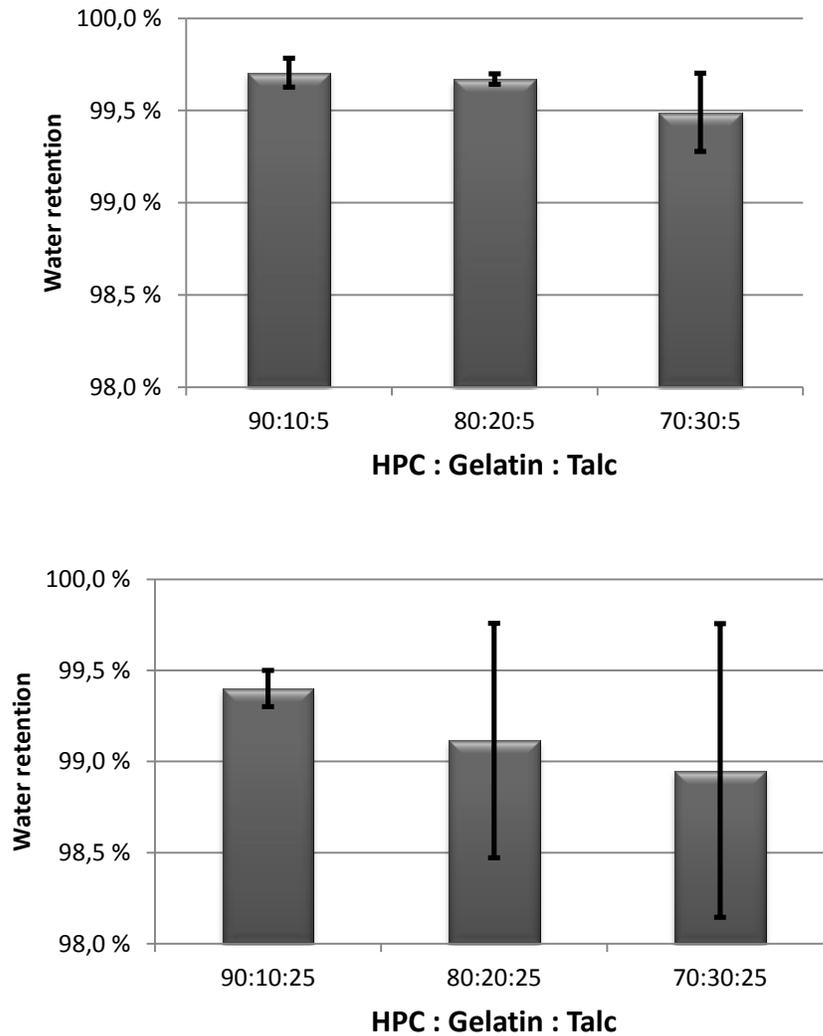


Figure 35: Water retention of coating dispersions produced from HPC-gelatin blends containing 5% (upper) and 25% (lower) of gelatin with different talc dosages.

10.2.2 Barrier properties

All prepared coated paperboard samples in the frame of pilot tests with DT Laboratory Coater were tested on their general properties first. The values obtained for HPS, CMC and HPC coatings produced from their blends with gelatin are presented in Appendix IV. Compared to the results of preliminary tests, where the tendency of slight thickness increase of coated samples was observed, thicknesses of the coated samples during the pilot tests decreased in some cases, accompanied, therefore, by the density elevation. This can be associated with the effect, obtained by another drying methodology applied at this stage (infra-red drying), influenced the creation of more packed structure of coat layers.

The grease barrier properties of coated samples were analyzed. The chart (Figure 36) illustrates the dependence of the grease resistance time of samples coated with HPS-gelatin blends on the gelatin dosage in dispersion. The coat weight variation between the samples is also reflected in the chart (a curve), since it is an essential parameter, having a direct influence on barrier properties of the coatings. However, the basis weight of the base paperboard could be varying considerably, so these values can be taken as approximations.

If it is assumed, that there were no base paperboard basis weight variations, it is evident from the chart (Figure 36), that grease repellency can be mainly attributed to the increase in gelatin dosage, but not the coat weight increase. Therefore, as it was already stated, the approach on starch-protein blending [2], in fact, helps to attain elevated grease resistance of starch-based coatings by reducing their porosity. The fact of porosity reduction was proven with the air permeability data obtained for HPS-based coatings containing different gelatin dosages (Appendix V, Table I).

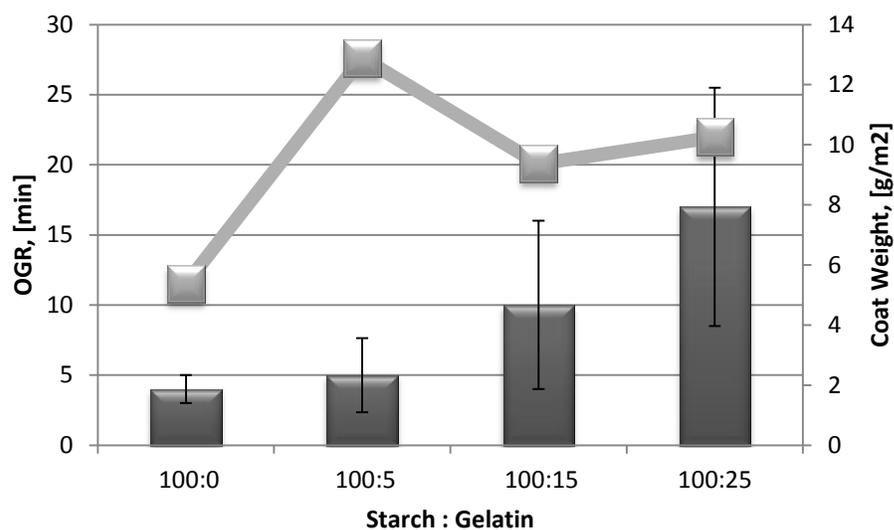


Figure 36: Grease permeability time (bars) of coatings produced from blends of different HPS-gelatin ratios with coat weight variation (the curve) between samples.

The addition of gelatin has also improved grease barrier properties of CMC-based coatings, regardless of the coat weight variations (Figure 37). The best results were obtained with approximately 10% gelatin dosage.

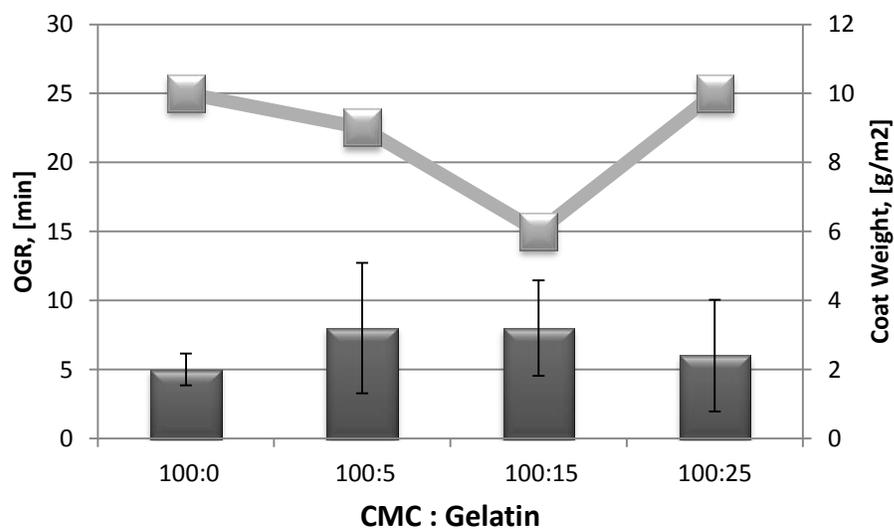


Figure 37: Grease permeability time (bars) of coatings produced from blends of different CMC-gelatin ratios with coat weight variation (the curve) between samples.

The enhanced barrier properties of CMC-gelatin blends can be referred to the new structures created during the film formation because of strong molecular interactions of gelatin with long-chain CMC macromolecules, containing the great number of hydroxyl groups, participating in these interactions /64/.

HPC was chosen as a wood-based polysaccharide for the pilot tests (instead of insufficient EHEC) in order to study the effect of gelatin addition on its barrier properties. The chart (Figure 38) reflects that this polysaccharide, along with CMC, also functions with gelatin, which linearly improved grease barrier properties of HPC-based coatings.

It was observed, that CMC-based coatings exhibited their grease resistance peak at lower gelatin dosages, than it required for HPS and HPC. Moreover, further increase of gelatin dosage up to 25% has led to the reduction of barrier properties. Probably, this can be explained in the way that hydroxypropylated grades of starch and cellulose (HPS and HPC respectively) were able to form much more interactions with gelatin molecules (therefore, higher gelatin dosages were needed), creating enhanced three-dimensional structures of the coatings, providing elevated barrier properties.

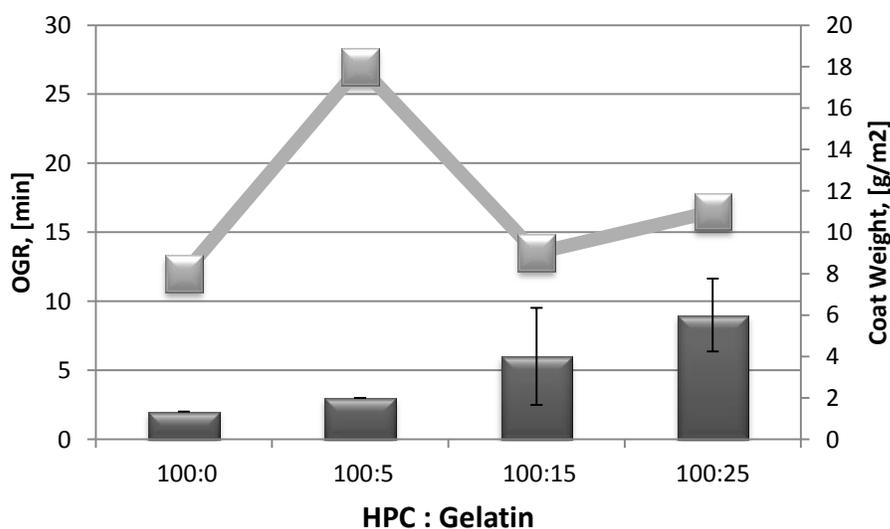


Figure 38: Grease permeability time (bars) of coatings produced from blends of different HPC-gelatin ratios with coat weight variation (the curve) between samples.

10.2.3 Effect of converting operations on barrier properties

The behavior of all prepared coated samples during the converting operations has been investigated during the pilot tests with the help of pilot-scale converting equipment. The coatings prepared from HPS, CMC and HPC blends with and without gelatin exhibited good formation during the converting process, and there were no great differences revealed in forming results between different coatings. The fact can be referred to that the coat layer, obtained by biopolymer dispersions was rather thin (compared to coating layers of synthetic polymers, which are mostly converted by using this type of equipment). Therefore, the base paperboard properties had the most effect on convertibility of prepared coated materials.

There were only two samples, which had a breakage during the forming process (HPC:gelatin 100:25 and 100:15). However, this problem was caused mainly by the insufficient moisture content of these samples (less than 9%, required by the forming process) /83/.

In order to analyze the effect of converting operations on the continuity and integrity of coatings produced from polysaccharide-gelatin blends (with the view of possible loss of barrier properties identification), all creased blanks and pressed food trays were analyzed on their grease barrier properties.

The gelatin addition to the HPS-based blends had a positive effect on the behavior of the coating layer during the creasing. The Figure 39 illustrates the creased samples (creases are oriented in cross-directional fiber orientation of the base paperboard) coated with pure HPS-based and containing 25% of gelatin coating dispersions after the grease permeability test. It is clear that the grease penetrated into the paperboard mainly in creased areas due to possible cracking of brittle starch coating. Meanwhile, 25% gelatin addition allowed to increase the flexibility of the coating layer and, therefore, prevent loss of barrier properties, so the amount of penetrated grease is less. The results obtained for CMC- and HPC- based coatings were not as evident as in the case of HPS- based coatings, however, slight improvements in the coating layers flexibility, preventing loss of barrier properties, were still investigated (Appendix V).



Figure 39: Microscopic images of creased samples coated with pure HPS (left) and containing 25% of gelatin (right) dispersions after OGR test (20x magnification, Olympus SZX9 Microscope)

Analyses of pressed areas of converted food trays revealed the same results for all coatings. The grease resistance time was equal to 1 min.

Generally, these behavior of HPS- based coatings can be attributed to that hydroxypropylated starches usually tend to have reduced interactions induced by hydrogen bonds between macromolecular chains leading to their improved flexibility and film-forming properties/84/ /88/. Addition of gelatin could provoke intensification of this effect.

It was reported also, that long-chain polysaccharide macromolecules are able to create cross-links with gelatin, resulting in their mechanical properties enhancement, which are determined by density and distribution of intermolecular interactions, dependent on the orientation of polymer macromolecules in this system. /89/

10.2.4 Effect of pigment introduction on barrier properties and convertibility

The effect of pigment addition to the bio-based polymer blends on the barrier properties and convertibility of obtained coatings has been considered. Paperboard samples coated with CMC- and HPC-gelatin blends filled with different talc dosages were tested on grease barrier properties before and after being converted.

The following tendency was observed for the CMC-gelatin blends. Addition of 10% of talc increased grease resistance of CMC-gelatin dispersions containing 5% of gelatin. However, further addition of talc (20%), accompanied by the coat weight increase, has led to the barrier properties reduction. In the case of CMC-gelatin coating dispersions with 25% of gelatin, grease resistance increased slightly with 20% talc addition and then dropped sharply when 30% of talc was introduced to the blend. These tendencies can be observed from the Figure 40.

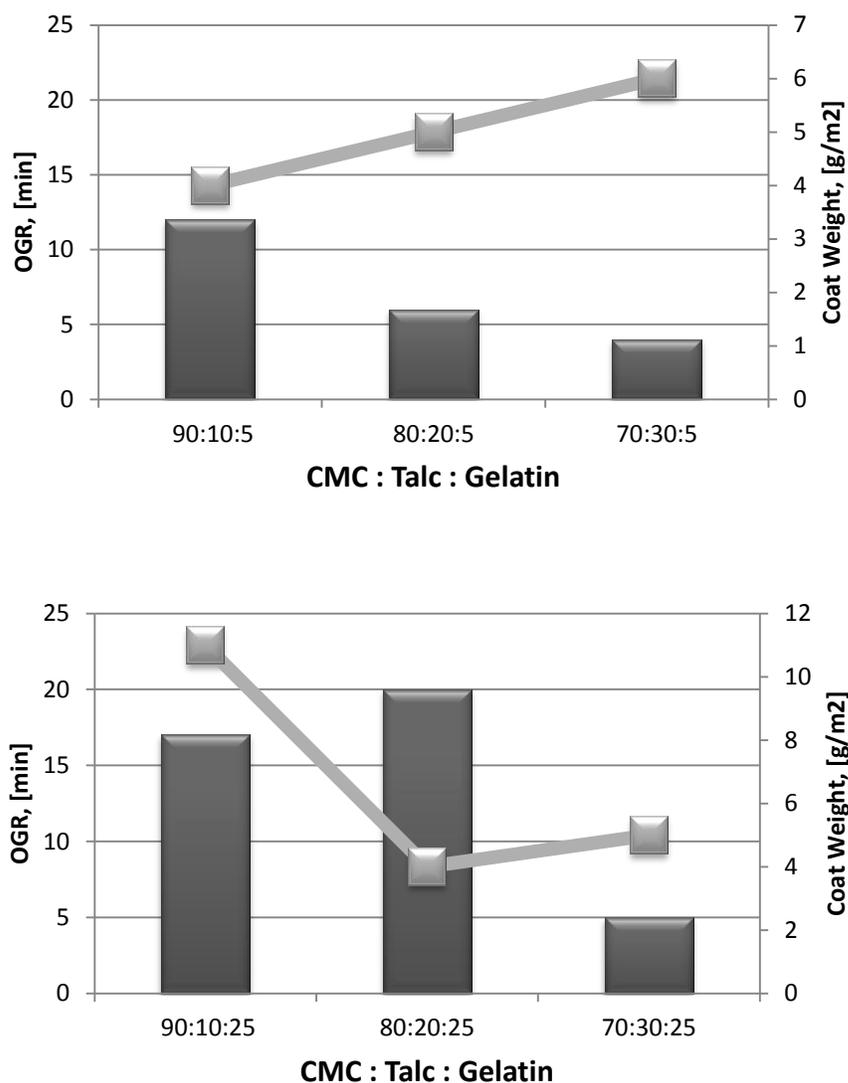


Figure 40: Grease permeability time (bars) of coatings produced from CMC-gelatin blends containing 5% (upper) and 25 % (lower) of gelatin with different talc dosages with coat weight variation (the curve) between samples.

The 20% talc dosage has brought absolutely different changes to the properties of blends (Figure 40). The fact can be referred to that this dosage was the most appropriate for creating reinforced structures with increased amount of gelatin (25%) in CMC-based dispersions. Meanwhile, the presence of 5% of gelatin in the CMC-based dispersion was not enough for that.

Despite of the evident effect of barrier properties elevation in this case, the convertibility of CMC-based coatings in fact has suffered a little with increasing talc content (Figure 41). It can be supposed that the coating layer, filled with talc has lost its elastic properties, and tented to create cracks, resulting to the loss of the coated paperboard barrier properties. The particle shape of talc also could have poor effect on convertibility (at the same time maintaining elevated barrier properties).

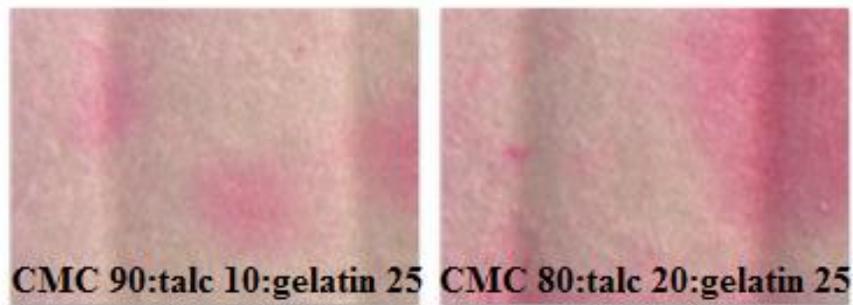


Figure 41: Microscopic images of creased samples coated with pure HPS (left) and containing 25% of gelatin (right) dispersions after OGR test (20x magnification, Olympus SZX9 Microscope)

The charts illustrating the effect of filler addition on barrier properties of HPC-based coatings with different gelatin content are presented on the Figure 42.

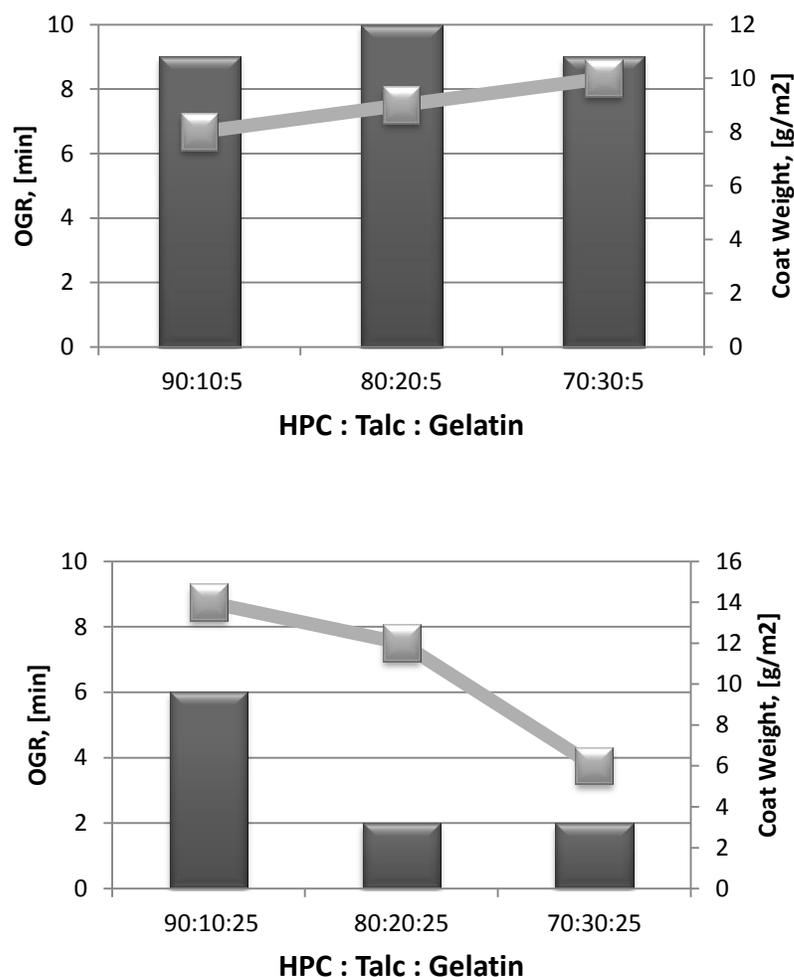


Figure 42: Grease permeability time (bars) of coatings produced from HPC-gelatin blends containing 5% (upper) and 25% (lower) of gelatin with different talc dosages with coat weight variation (the curve) between samples.

In the case of 20% of talc introduction to the HPC-gelatin blends, the opposite effect can be observed. This dosage increased considerably the grease resistance of coatings produced from HPC-based dispersion containing 5% of gelatin, meanwhile, the same addition of talc resulted in poor grease resistance of coatings produced from the same dispersions containing 25% of gelatin. It is also worth to mention, that grease resistance was slightly dependent on the obtained coat weights. No significant negative changes in convertibility of produced HPC-based coatings were revealed between different samples.

11 CONCLUSIONS

The total scope of the experimental part was performed in two steps. First, the small-scale preliminary tests were organized, basically, in order to reach one of the main targets of the research – to prove the approach on starch-gelatin blending /2/ and to study, how this approach will function with cellulose derivatives (CMC, EHEC and HPC).

The pilot test series, including more sophisticated layout, pilot-scale equipment and methods of the research, implied the investigation of the whole process chain of coating colors development, from dispersion preparation and analysis to testing of converted and unconverted coated paperboard samples. These tests, organized according to the results obtained during the preliminary tests, were aimed to reach also other targets of the research: to analyze the convertibility of obtained coatings and to study the pigment introduction to these blends and also its effect on barrier properties and convertibility.

The results of the preliminary tests indicated that the combination of HPS with gelatin, in fact, improves the grease barrier properties of HPS-based coatings, thereby confirming the offered approach. In addition to that, similar results were obtained for CMC, exhibited elevated barrier properties and surface coverage. Thus, it was proved, that the approach also functions with wood-based polysaccharides (cellulose derivatives), requiring, however, higher dosages of gelatin than HPS.

Analyses of coating dispersions in the pilot tests revealed general tendency of viscosity reduction for CMC- and HPC-based dispersions with increasing gelatin content. The inverse effect was observed for the HPS-based blends with gelatin. However, gelatin addition increased the water retention values of HPS coating dispersions, which was not observed for CMC and HPC. The effect of talc introduction on viscosity and water retention of wood-based polysaccharides varied considerably with respect to the gelatin content.

Analyses of barrier properties in the pilot tests once again proved the enhancement of the grease barrier properties of HPS, together with CMC and HPC, with increasing gelatin addition, regardless of the coat weights obtained. The convertibility of HPS-based coatings has

also been considerably improved by gelatin, which elevated flexibility and prevented loss of barrier properties of produced coatings. The results obtained for CMC- and HPC- based coatings were not as evident as in the case of HPS.

The introduction of talc to the composition of prepared blends had an effect on the barrier properties of coatings produced from these blends. It was revealed that barrier properties become more dependent on the gelatin dosages (differently for CMC and HPC) with the same amount of talc added. A generous amount of talc introduced resulted in poor barrier properties for all blends. It can be concluded, that gelatin still does not function with dual-component systems, containing specific inorganic pigment, most likely interacting only with biopolymer components.

The convertibility of coatings produced from CMC-gelatin blends has suffered with increasing talc content, saying about poor elasticity of the coating layer, filled with talc, leading to the loss of barrier properties due to cracking. No significant negative changes in convertibility of HPC-based coatings filled with talc were revealed.

The present study revealed, that gelatin as an additive, in fact, enhances not only barrier properties of starch, but also cellulose derivatives, providing at the same time improved surface coverage of coat layers. In addition, convertibility and post-converting barrier properties were observed to be improved with gelatin introduction. The use of gelatin in dual-component biopolymer-pigment systems did not show any beneficial improvements.

The approach on biopolymer blending can be a promising alternative intended to resolve a wide range of biopolymer-related problems, limiting the scope of their application in barrier films and coatings. Gelatin as functional additive can be successfully utilized in biopolymer blends formulation.

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LIST OF APPENDICES

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Test point matrices for preliminary and pilot tests

Table I: Test point matrix for the preliminary tests.

Test point	Composition of blends (parts added)			
	HPS	CMC	EHEC	Gelatin
Reference base paperboard	-	-	-	-
1	100	-	-	-
2	100	-	-	10
3	100	-	-	20
4	100	-	-	30
5	-	100	-	-
6	-	100	-	10
7	-	100	-	20
8	-	100	-	30
9	-	-	100	-
10	-	-	100	10
11	-	-	100	20
12	-	-	100	30

APPENDIX I (2/2)

Table II: Test point matrix for the pilot tests.

Test point	Composition of blends (parts added)				
	HPS	CMC	HPC	Gelatin	Talc
Reference base paperboard	-	-	-	-	-
1	100	-	-	-	-
2	100	-	-	5	-
3	100	-	-	15	-
4	100	-	-	25	-
5	-	100	-	-	-
6	-	100	-	5	-
7	-	100	-	15	-
8	-	100	-	25	-
9	-	-	100	-	-
10	-	-	100	5	-
11	-	-	100	15	-
12	-	-	100	25	-
13	-	-	-	100	-
14	-	90	-	5	10
15	-	80	-	5	20
16	-	70	-	5	30
17	-	90	-	25	10
18	-	80	-	25	20
19	-	70	-	25	30
20	-	-	90	5	10
21	-	-	80	5	20
22	-	-	70	5	30
23	-	-	90	25	10
24	-	-	80	25	20
25	-	-	70	25	30

APPENDIX II (1/2)

General properties of coated samples obtained in preliminary tests

Table I: General properties of the paperboard coated with HPS-gelatin blends.

Blend composition, HPS:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	275	-	377	729	0,00137
100:0	283	8	390	726	0,00138
100:10	285	10	400	713	0,00140
100:20	285	10	392	727	0,00138
100:30	284	9	388	732	0,00137

Table II: General properties of the paperboard coated with CMC-gelatin blends.

Blend composition, CMC:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	275	-	377	729	0,00137
100:0	277	2	379	731	0,00137
100:10	277	2	386	718	0,00139
100:20	278	3	380	732	0,00137
100:30	277	2	386	718	0,00139

APPENDIX II (2/2)

Table III: General properties of the paperboard coated with EHEC-gelatin blends.

Blend composition, EHEC:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	275	-	377	729	0,00137
100:0	278	3	381	730	0,00137
100:10	277	2	388	714	0,00140
100:20	277	2	385	719	0,00139
100:30	280	5	386	725	0,00138

APPENDIX III (1/3)

Analyses of coating dispersions

Table I: Properties of HPS-based coating dispersions with various gelatin dosages.

Blend composition, HPS:gelatin, parts	t°C	pH	Viscosity		Water retention, %	DSC, %
			cP	Shear rate, RPM		
100:0	33,5	5,87	54±3	100	93,11±0,09	16,50
100:5	23,5	5,67	120±17	100	97,26 ±3,15	13,93
100:15	20,1	5,48	164±11	100	99,51 ±0,09	11,92
100:25	25,7	5,45	66±3	100	95,39 ±0,81	12,40

Table II: Properties of CMC-based coating dispersions with various gelatin dosages.

Blend composition, CMC:gelatin, parts	t°C	pH	Viscosity		Water retention, %	DSC, %
			cP	Shear rate, RPM		
100:0	21,7	6,49	1610±14	20	99,02±0,52	3,30
100:5	17,5	6,08	1436±6	20	97,49 ±1,53	4,54
100:15	24,2	6,35	1220±28	10	98,89 ±0,60	4,35
100:25	24,3	6,13	980±28	10	97,48 ±1,55	5,39

Table III: Properties of CMC-based coating dispersions with various gelatin dosages.

Blend composition, HPC:gelatin, parts	t°C	pH	Viscosity		Water retention, %	DSC, %
			cP	Shear rate, RPM		
100:0	26,6	7	13960±28	20	99,02±0,52	8,95
100:5	19,5	5,67	8860±28	10	97,49 ±1,53	9,40
100:15	24,3	5,55	6360±57	5	98,89 ±0,60	9,29
100:25	21,2	5,52	8500±28	10	97,48 ±1,55	8,74

APPENDIX III (2/3)

Table IV: Properties of coating dispersions produced from CMC-gelatin blends with different talc dosages (5% gelatin dosage).

Blend composition, CMC:talc:gelatin, parts	t°C	pH	Viscosity		Water retention, %	DSC, %
			cP	Shear rate, RPM		
90:10:5	25,2	6,60	1150±14	20	99,50±0,06	5,20
80:20:5	26,9	6,61	942±3	20	99,46 ±0,03	6,21
70:30:5	25,0	7,34	834±3	20	98,56 ±0,95	7,00

Table V: Properties of coating dispersions produced from CMC-gelatin blends with different talc dosages (25% gelatin dosage).

Blend composition, CMC:talc:gelatin, parts	t°C	pH	Viscosity		Water retention, %	DSC, %
			cP	Shear rate, RPM		
90:10:25	24,6	6,24	570±3	100	97,08±1,00	5,35
80:20:25	23,8	6,21	728±11	100	98,25 ±0,65	5,86
70:30:25	26,0	6,72	592±6	100	98,56 ±0,95	10,06

Table VI: Properties of coating dispersions produced from HPC-gelatin blends with different talc dosages (5% gelatin dosage).

Blend composition, HPC:talc:gelatin, parts	t°C	pH	Viscosity		Water retention, %	DSC, %
			cP	Shear rate, RPM		
90:10:5	23,8	6,74	7600±28	50	99,71±0,08	10,30
80:20:5	23,8	6,92	7030±99	50	99,67 ±0,03	10,55
70:30:5	23,0	7,35	5972±6	50	99,49 ±0,21	12,79

APPENDIX III (3/3)

Table VII: Properties of coating dispersions produced from HPC-gelatin blends with different talc dosages (25% gelatin dosage).

Blend composition, HPC:talc:gelatin, parts	t°C	pH	Viscosity		Water retention, %	DSC, %
			cP	Shear rate, RPM		
90:10:25	22,9	5,72	3432±23	50	99,40±0,10	9,40 %
80:20:25	23,5	6,14	3976±23	50	99,12 ±0,64	8,64 %
70:30:25	27,6	5,97	2716±6	50	98,95 ±0,81	10,59 %

APPENDIX IV (1/3)

General properties of coated samples obtained in pilot tests

Table I: General properties of the paperboard coated with HPS-gelatin blends.

Blend composition, HPS:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	340	-	440	774	0,00129
100:0	346	5	435	795	0,00126
100:5	354	13	439	806	0,00124
100:15	350	9	435	805	0,00124
100:25	351	10	435	807	0,00124

Table II: General properties of the paperboard coated with CMC-gelatin blends.

Blend composition, CMC:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	340	-	440	774	0,00129
100:0	350	10	448	782	0,00128
100:5	349	9	443	788	0,00127
100:15	347	6	443	784	0,00128
100:25	351	10	438	801	0,00125

Table III: General properties of the paperboard coated with HPC-gelatin blends.

Blend composition, HPC:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	340	-	440	774	0,00129
100:0	349	8	453	770	0,00130
100:5	359	18	452	795	0,00126
100:15	349	9	442	790	0,00127
100:25	352	11	445	791	0,00126

APPENDIX IV (2/3)

Table IV: General properties of the paperboard coated with CMC-gelatin blends with different talc dosages (5% gelatin dosage).

Blend composition, CMC:talc:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	340	-	440	774	0,00129
90:10:5	344	4	438	786	0,00127
80:20:5	346	5	436	793	0,00126
70:30:5	346	6	450	788	0,00127

Table V: General properties of the paperboard coated with CMC-gelatin blends with different talc dosages (25% gelatin dosage).

Blend composition, CMC:talc:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	340	-	440	774	0,00129
90:10:25	352	11	437	805	0,00124
80:20:25	345	4	438	788	0,00127
70:30:25	345	5	440	784	0,00128

Table VI: General properties of the paperboard coated with HPC-gelatin blends with different talc dosages (5% gelatin dosage).

Blend composition, HPC:talc:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	340	-	440	774	0,00129
90:10:5	349	9	448	780	0,00128
80:20:5	351	10	446	788	0,00127
70:30:5	349	9	453	771	0,00130

APPENDIX IV (3/3)

Table VII: General properties of the paperboard coated with HPC-gelatin blends with different talc dosages (25% gelatin dosage).

Blend composition, HPC:talc:gelatin, parts	Basis weight, g/m ²	Coat weight, g/m ²	Thickness, μm	Density, kg/m ³	Bulk, m ³ /kg
Reference paperboard	340	-	440	774	0,00129
90:10:25	355	14	448	792	0,00126
80:20:25	353	12	440	802	0,00125
70:30:25	347	6	434	798	0,00125

APPENDIX V (1/3)

Barrier and surface properties of coated samples obtained in pilot tests

Table I: Barrier and surface properties of the paperboard coated with HPS-gelatin blends.

Blend composition, HPS:gelatin, parts	Roughness, ml/min	Air permeability, ml/min	OGR, min	
			Uncreased areas	Creased in CD areas*
Reference paperboard	1141±257	184±53	1	1
100:0	1536±368	15±2	4±1	1±0
100:5	1148±232	14±3	5±3	2±1
100:15	1670±288	13±3	10±6	2±1
100:25	1351±182	11±1	17±9	3±1

* - creases oriented in cross-directional fiber orientation of the base paperboard

Table II: Barrier and surface properties of the paperboard coated with CMC-gelatin blends.

Blend composition, CMC:gelatin, parts	Roughness, ml/min	Air permeability, ml/min	OGR, min	
			Uncreased areas	Creased in CD areas
Reference paperboard	1141±257	184±53	1	1
100:0	2051±246	14±2	5±1	19±1
100:5	2169±344	16±1	8±5	2±1
100:15	2181±298	16±2	8±3	2±1
100:25	1853±317	13±2	6±4	3±1

Table III: Barrier and surface properties of the paperboard coated with HPC-gelatin blends.

Blend composition, HPC:gelatin, parts	Roughness, ml/min	Air permeability, ml/min	OGR, min	
			Uncreased areas	Creased in CD areas
Reference paperboard	1141±257	184±53	1	1
100:0	1344±178	17±1	2±0	1±0
100:5	1409±211	14±3	3±0	2±1
100:15	1506±217	15±2	6±4	2±0
100:25	1450±212	14±1	9±3	1±0

APPENDIX V (2/3)

Table IV: Barrier and surface properties of the paperboard coated with CMC-gelatin blends with different talc dosages (5% gelatin dosage).

Blend composition, CMC:talc:gelatin, parts	Roughness, ml/min	Air permeability, ml/min	OGR, min	
			Uncreased areas	Creased in CD areas
Reference paperboard	1141±257	184±53	1	1
90:10:5	1657±211	13±1	12±11	5±5
80:20:5	914±218	11±1	6±2	16±13
70:30:5	1133±245	13±2	4±1	11±6

Table V: Barrier and surface properties of the paperboard coated with CMC-gelatin blends with different talc dosages (25% gelatin dosage).

Blend composition, CMC:talc:gelatin, parts	Roughness, ml/min	Air permeability, ml/min	OGR, min	
			Uncreased areas	Creased in CD areas
Reference paperboard	1141±257	184±53	1	1
90:10:25	1407±360	13±2	17±11	12±7
80:20:25	1536±349	13±2	20±15	22±6
70:30:25	1145±398	14±1	5±1	1710

Table VI: Barrier and surface properties of the paperboard coated with HPC-gelatin blends with different talc dosages (5% gelatin dosage).

Blend composition, HPC:talc:gelatin, parts	Roughness, ml/min	Air permeability, ml/min	OGR, min	
			Uncreased areas	Creased in CD areas
Reference paperboard	1141±257	184±53	1	1
90:10:5	784±210	15±1	8±3	7±2
80:20:5	838±247	13±1	9±6	7±5
70:30:5	1036±264	14±2	10±10	17±11

APPENDIX V (3/3)

Table VII: Barrier and surface properties of the paperboard coated with HPC-gelatin blends with different talc dosages (25% gelatin dosage).

Blend composition, HPC:talc:gelatin, parts	Roughness, ml/min	Air permeability, ml/min	OGR, min	
			Uncreased areas	Creased in CD areas
Reference paperboard	1141±257	184±53	1	1
90:10:25	1615±326	14±1	6±2	5±1
80:20:25	1088±209	13±3	2±1	2±0
70:30:25	1147±328	15±2	2±1	3±0