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Investigation on the barrier and antibacterial properties of packaging papers with blend fillers of chitosan and rice starch

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Bio-based materials or biomaterials fall under the broad category of bio-products or bio-based products which includes materials, chemicals and energy derived from renewable biological resources. Paper and cellulose fibers are the first materials in this list. Therefore, the usage of bio-based additives in paper production would have an increased application in the future years. In the present experiment, packaging paper with blend fillers of chitosan and rice starch were made with blended mixtures of different concentrations of chitosan and rice starch. Investigations were made in order to evaluate the effect on the barrier and antibacterial properties of the obtained paper samples. The goal of our research was to improve paper properties and to make paper sheets, which will be suitable as packaging paper. To evaluate the effect of the bio based fillers, air permeability, grease resistance, moisture, water absorptiveness and antibacterial activity were determined. The research showed that the barrier properties of the obtained packaging paper towards air, water and grease improved but the used chitosan mixtures had no antibacterial activity against *Escherichia coli* K12. The results showed that blend fillers of chitosan and rice starch are effective paper fillers in the preparation of cellulose mixtures for bio based papers. Therefore, preparing paper using a combination of chitosan and rice starch blend fillers is an improved and convenient procedure to enhance many properties of such papers.

Keywords: chitosan, rice starch, pulp, paper additives, bio polymers, modified paper

INTRODUCTION

Paper is one of the main materials used for food packaging that provides preservation and protection for the final product till reaching the consumer without compromising the quality. There are many types of paper for food packaging such as sulfite paper, kraft paper, grease-free paper, paperboards and laminated paper among others. Improving barrier properties of paper for food packaging is essential since the presence of oxygen or water vapor is a key factor that limits shelf life of foodstuffs. The reason for that is the effect of oxidation on taste, color and odor. Moreover, presence of oxygen facilitates the growth of microorganisms and insects. Therefore, removal of oxygen and increasing barrier properties of the packaging material has been the main target for food packaging researchers [1]. Protection of foodstuffs largely depends on the barrier properties of the packaging material that can be enhanced by several ways.

Latest tendencies show that packaging materials, with which producers reduce environmental pollution, are based on bio polymers and increase their consumption due to their biodegradable, nontoxic and environmentally friendly nature, as well sufficient barrier properties. [2-4]. According to the Pro Carton "Consumer attitude survey" - a major independent study of 7000 European consumers in seven countries, 90% of the responding shoppers in all surveyed countries said, they'd like information about the environmentally-friendliness of packaging and four out of five consumers (81%) said that, given the choice, they would choose paper/carton board packaging over plastic [5]. The research also reveals that Europeans have a good working understanding of different packaging forms, highlighted by the fact that 52% of all Europeans believe paper/cardboard to be the most environmentally-friendly packaging – a result broadly echoed across each country. Glass came in second with 32% of the Europe-wide vote. Some 9% of Europeans believe plastic is the most environmentally-friendly form of packaging, whereas only 5 % chose tin so it still appears that there’s an education job to be done [5]. The primary packaging function is to protect its content, but in the last years, the technical performance, promotion of the product, costs and other characteristics have been inferior to recyclability. In recent years, the materials

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used in the packaging of goods, such as fruit, vegetables, bakery products or flowers, have improved in developing recyclable packaging from waste or abundant materials.

As far as packaging materials containing paper are considered, such as paper-polyethylene terephthalate (PET) and paper-aluminium laminates, the quality of the commodity paper is decisive for the microbiological quality of the final product, since paper usually contains a certain microbial load that is not completely eliminated during the production process. Compared to other materials such as metals, glass or plastics, rather low temperature treatment is applied to those laminates [6]. Therefore, from practical point of view an important focus should be set on the prevention of microbiological activity to ensure sufficient barrier and antibacterial packaging paper properties.

Bio-based polymers are polymers which can be directly extracted from biomass (polysaccharides, proteins and lipids), polymers which are synthesized from bio-derived monomers (polylactic acid – PLA or other polyesters) or polymers which are produced directly by microorganisms (polyhydroxyalkanoates – PHA, bacterial cellulose, xanthan, pullulan and curdlan). They can be used alone or in combination. Bio based polymers are usually coated on papers and cardboards, applied with different coating techniques (solution coating, surface sizing, curtain coating or compression molding) [7-9].

Polysaccharides mostly used are chitosan, starches (rice, wheat, maize, corn and potato), cellulose and alginates. They are nontoxic, widely used and available in the market also as waste materials. With high gas, aroma and grease barriers, such coatings have great potential in packaging materials. Because of their hydrophilic nature, polysaccharides exhibit poor water vapour barrier [7-9].

However, additives to paper packaging, such as polysaccharides enhance mechanical strength and barrier properties of the final product. Moreover, polysaccharides such as chitin and starch are belonging to green chemicals and characterized by their availability, renewability and biodegradability [1].

Chitosan, which is a linear copolymer of β-(1,4)-2-acetoamido-2-deoxy-D-glucopyranose units and β-(1,4)-2-amino-2-deoxy-D-glucopyranose units, is one of the most widespread natural polysaccharide. It exhibits excellent oxygen-barrier properties due to its highly crystallinity and hydrogen bonds between molecular chains [10]. The $-NH_2$ group present transforms into a polycation in dilute acidic solution. Therefore, the cationic character causes stronger adsorption by electrostatic interactions to the paper pulp, which has an anionic character [11]. Chitosan interacts in combination with cellulose, which causes improved tensile properties and promotes good printability of paperboard [12]. Blends of different cellulose and chitosan in papermaking processes have been studied and presented earlier [13-19]. Laleg and Pikulik reported that chitosan additives increased the strength of wet paper towels, disposable diapers, and grocery bags [13]. Li *et al.* found that chitosan was absorbed onto the surface of the cellulosic fibres, which was caused due to cationic amino groups and electrostatic interactions between the chitosan and cellulose pulp [14]. Chitosan in combination with polyvinyl alcohol and starch was studied by Mucha and Miskiewicz. They determined strong ionic interactions between the fillers and increase of the paper tensile properties [15]. Nada *et al.* found that chitosan, cyanoethyl and carboxymethyl chitosan enhanced the strength properties of aged and un-aged paper sheets [16]. Fernandes *et al*. studied the distribution of chitosan onto the paper sheets, using a fluorescent derivative [17]. Their results have proven that chitosan and its modifications could be used as a probe to understand the deposition of chitosan onto the paper.

Numerous researchers published investigations on the antibacterial properties of coated paper with bio-based polymers like starch [20], chitosan [21, 22], E-poly-L-lysine in combination with carboxymethyl cellulose [23] and others.

Few studies are currently available on the application potential of chitosan derivatives in papermaking. Nevertheless, several papers demonstrate the efficiency of chitosan derivatives as process and functional additives. Although scarce, the experimental data available on this subject provide promising results, which validate the versatility and multifunctionality of chitosan derivatives as papermaking additives [19].

The aim of our research was to make paper sheets, which will be suitable as packaging paper and to improve its properties by using two different bio polymers as fillers (chitosan and rice starch). The literature shows no record of previous research done on the blend of rice starch and chitosan as paper fillers. The purpose of our research was to investigate different ratios of blends to evaluate the barrier - air permeability, grease resistance, moisture, water absorptiveness and antibacterial activity of the obtained paper. The chemistry of the preparation process of these paper sheets is fully environmentally friendly and paper is characterized with improved properties, compared to the classic type of papers.

EXPERIMENTAL

Materials

The used softwood pulp was bleached sulfate kraft cellulose from pine and spruce trees, delivered by SCA, Sweden with: breaking length of 3300 m, acc. to ISO 1924/2; tensile index of 26 N.m/g acc. to ISO 1924-2; burst index of 1.5 kPa m^2/g acc. to ISO 2758; tear index of 18.8 mN.m^2 /g acc. to EN 21974 and 80% brightness acc. to ISO 3088.

The used hardwood pulp was bleached hardwood kraft pulp from beech trees, delivered by Svilosa AD, Bulgaria. The kraft pulp is placed on the market under the registered trade mark SVILOCELL®. The properties include; breaking length of 1900 m, acc. to ISO 1924/2, tensile index of 18 N.m/g acc. to ISO 1924-2, burst index of 0.75 kPa m^2/g acc. to ISO 2758, tear index of 2.3 mN.m^2 /g acc. to EN 21974 and 80% brightness acc. to ISO 3088.

Both chitosan and acetic acid (99%) were purchased from Sigma Aldrich (Austria). The chitosan is with molecular weight lower than 20 kDa and deacetylation degree higher than 85%.

Rice starch was obtained from Farmalabor Srl (Italy) and had 14% of moisture content, 1% of proteins and 0.6% of ashes. Modified cationic polyacrylamide was delivered by Kemira, Finland and is with molecular weight of 11.10^6 g/mol, charge density of 1.05 meq/g, viscosity (Brookfield) 700 cP$_{(0.5\%,25°C)}$ and conductivity 66.6 µS$_{(0.5\%)}$.

Methods

Preparation of the pulp. Two types of kraft pulp - softwood and hardwood - were used in our experiment, which were refined by a laboratory Jokro mill method with six refining units, acc. to ISO 5264-3:21979. The refining concentration in each unit was 6% (16 g o.d.f in 267 ml of water). The two celluloses were separately refined. The Schopper Riegler value (ISO 5267-1/AC:2004) of the softwood pulp was 20 ºSR and of the hardwood pulp 42ºSR. After mixing the pulps the Schopper Riegler value of the suspension was 29 ºSR.

Preparation of pulp suspensions. Paper suspensions were prepared using 6 combinations of pulp suspensions, bio polymers (chitosan and rice starch) and retention additive. Pulp suspension was prepared with 50% of softwood (pine and spruce) and 50% of hardwood (beech). Chitosan solution was prepared by dissolving chitosan in acetic acid in order to prepare a 5% and a 7.5% solution. The solution was mixed for 10 min at 85°C and then cooled to room temperature. Rice starch was also separately prepared by dissolving rice starch in distilled water. It was mixed until it gelatinized (85°C for 10 min), then was cooled to room temperature. The chitosan-rice starch solution was prepared by mixing the same amounts of rice starch and chitosan solution (5% or 7.5%). The procedure of mixing pulp and other additives was as follows: firstly 23.5 g o.d.f. were stirred in tap water (2000 ml), then the chitosan and rice starch were added. The mixing proceeded and after that the retention additive was added. The preparation was followed with mixtures:

1) Only pulp (P);
2) Pulp and 0.05% retention additive (PR);
3) Pulp, 5% chitosan, 0.05% retention additive (5% CH);
4) Pulp, 5% rice starch and chitosan, 0.05% retention additive (5% CHR);
5) Pulp, 7.5% chitosan, 0.05% retention additive (7.5% CH);
6) Pulp, 7.5% of rice starch and chitosan, 0.05% retention additive (7.5% CHR).

Preparation of paper sheets. The papermaking process was simulated by using a laboratory paper-sheet machine. All samples were prepared on a paper laboratory machine (Rapid-Kothen, Germany) acc. to ISO 5269-2:2005, with a grammage of 80 g/m^2, with drying conditions of - 90°C and duration of 7 min.

Characterisation of the samples

Grammage, density, specific surface, thickness. It was necessary to determine the grammage of all samples. Grammage was determined in accordance with the ISO 536 standard, 10 samples of each paper were cut into size 10 × 10 cm and weighed. The thickness of the samples was measured with a precision digital micrometre Mitutoyo Corporation, Japan, to the nearest 0.0001 µm at 10 random locations on each paper. Density and specific surface volume were calculated from grammage and thickness, as described in the standard method ISO 534.

Moisture, water absorptiveness (Cobb value), determination of capillary rise (Klemm method). Moisture content was determined according to ISO 287 by measuring weight loss after drying in a laboratory oven at 105 ± 1 °C until constant weight. Five samples of each paper were tested and the results were expressed in percentage. Water absorptiveness was determined with the Cobb value, as described in the standard method ISO 535, where a given amount (100 ml) of water was in contact with the paper for 60 sec and weight differences were compared. For each paper, five sample tests were made. The capillary rise of the paper samples was determined by the Klemm method, as described in

ISO 8787. Two samples of each paper were tested and the results were expressed in mm, as height of water uptake after 10 min in distilled water.

Smoothness, air permeability and grease resistance. Smoothness and air permeability were determined according to standard TAPPI T460 and ISO 8791-2. Grease resistance of all sample paper sheets was determined using a modified TAPPI test -507, which was presented by Park *et al.* [24]. Smaller stained areas per hour on paper indicated greater grease resistance.

Surface (SEM). The SEM micrographs of paper surfaces were taken with a scanning electron microscope (JSM-6060 LV). The instrument operated at 10 kV and magnification 1000×.

Antibacterial activity. The potential antibacterial activity of the obtained paper materials against *Escherichia coli* K12 was evaluated on the basis of the inhibition-zone size. The cultures were grown, sub-cultured and maintained in Luria-Bertani (LB) medium and stored at 4 ºC. For the experiment a single colony of each organism was inoculated into 50 ml of LB broth and incubated overnight (24 h) at 37 ºC for *E. coli* K12 under shaking at 200 rpm. 100 µL of the bacterial suspension with concentration of 1×10^6 CFU mL^{-1} were seeded in agar plates with solid LB medium by the pour plate technique. After 10 min, 10 mg of pressed test materials were placed on the plates. Inhibition zones were measured after incubation overnight at 37 ºC for *E. coli* K12. The formation of a clear zone (restricted bacterial growth) around the tested paper samples is an indication of antibacterial activity for the obtained materials.

RESULTS AND DISCUSSION

Basic properties

To evaluate the effect of bio based components onto the barrier and antibacterial properties of the paper, it was essential to obtain paper samples with the same grammage. Therefore, the paper sheets were prepared with the grammage 80 g/m^2. The beating degree of a pulp, hardwood fibers, dimensions of the fibers and addition of the fillers have influence on the thickness of the paper. As expected, the thickness of the samples had mostly the same values (Table 1). Paper with only pulp, combination of softwood and hardwood fibers with no additives, had the lowest thickness (0.0084 mm). With addition of the retention additive and fillers, the thickness of all other paper sheets increased.

Changes were also detected for specific surface and density, where sample P, with only pulp and no additives, had the highest density, compared to other tested papers.

Barrier properties

It is known that paper has a certain grade of moisture, which depends on relative humidity, types of used pulp, degree of refining and types of used coatings. For packaging materials, it is very important to have excellent barrier properties. Among moisture, absorption ability and capillary rise, which are presenting water barriers, are also gas and grease barriers important for this kind of paper.

As expected and seen in Table 2, the decrease of moisture was noticed for samples with the retention additive and fillers. With increasing amount of fillers, the moisture decreased.

Table 1. Basic properties of all paper samples

	Samples					
	P	PR	5% CH	5% CHR	7.5% CH	7.5% CHR
Grammage, g/m^2	80	80	80	80	80	80
Thickness, mm	0.084	0.095	0.091	0.090	0.095	0.096
Specific surface, m^3/g	0.0011	0.0012	0.0011	0.0011	0.0012	0.0012
Density, g/m^3	952.38	842.11	879.12	888.89	842.11	833.33

Table 2. Water barrier properties of all tested samples

	Samples					
	P	PR	5% CH	5% CHR	7.5% CH	7.5% CHR
Cobb value, g/m^2	30,04	28,82	27,63	24,21	20,27	20,24
Moisture, %	10	9,9	7	6,8	6,7	6,50
Capillary rise, mm	47	40	10	15	10	9

Ability of fluids to penetrate the structure of paper is a highly significant property to the use of packaging paper. Resistance towards the penetration of water was measured by Cobb$_{60}$ values acc. to ISO 535. From the obtained results it is seen that the addition of chitosan-rice starch decreased water absorptiveness, i.e. Cobb$_{60}$value (Table 2). The higher the filler content, the higher resistance towards water penetration was detected. For the paper with 7.5 % of chitosan and rice starch, the water absorptiveness decreased by 33%, compared to paper with only pulp. For samples, where 5% of fillers were used, 8% (5% CH) and grease barrier properties were affected by the fillers and additives in paper samples. In the first hour, for all samples with fillers, lower percent of stained area was detected, compared to paper with only pulp and retention additive (Figure 1). Chitosan has a high grease barrier ability, compared to rice starch. The grease migration for papers with fillers is also due to open surface (pores) between the paper fibers, where grease could permeate through the paper [25]. There is also an important factor of beating degree of the pulp, where highly beaten papers have smaller pores [26]. Our grease permeability analyses showed that fillers and additive filled and reduced pore sizes, which was also proven with scanning electron microscope analysis. It is visible from the graph (Fig. 1) that chitosan and rice starch samples have no significant grease permeation, which proves that such type of bio-based fillers are suitable for packing of products (food or technical details) for long lasting periods.

19% (5% CHR) decrease was detected. It was also proven that retention additive had an influence on paper structure and properties. The same trend was detected for capillary rise. With addition of chitosan and rice starch, the resistance towards water capillarity increased. With higher concentration of bio polymer components, the capillary rise decreased. The most significant change was detected for the sample with 7.5 % of chitosan and rice starch. The decrease was from 80% (7.5% CHR) to 68% (5% CHR). Chitosan is insoluble in water while rice starch has a hydrophilic nature. Therefore, the sample, where only chitosan was used, achieved higher values, but still much lower than paper sheet, where only pulp and pulp with retention additive was used.

Smoothness, air permeability and grease resistance

Paper is a highly porous material composed of a felted layer of fibers and the additives could cause variation of many properties. Some of the affected properties are for sure smoothness and air permeability. Chitosan and rice starch, included in the paper sheets, filled the pores and holes. The open surface of paper sheets decreased with increasing amount of the mentioned polymers.

Smoothness was better for samples with chitosan and rice starch. When the amount of bio polymers increased, the smoothness improved as well. As expected and seen from the results in Table 3, the air permeability was worse for paper with pulp included. With the addition of bio polymers and retention additive, the structure of the paper became more even and filled, therefore the properties improved. The best air permeability achieved was for the paper with 7.5% CHR, where only 1186 ml/min was measured.

Table 3. Smoothness and air permeability of all sample papers

	Samples					
	P	PR	5% CH	5% CHR	7.5% CH	7.5% CHR
Smoothness, ml/min	417	410	345	350	340	303
Air permeability, ml/min	1411	1309	1260	1238	1221	1186

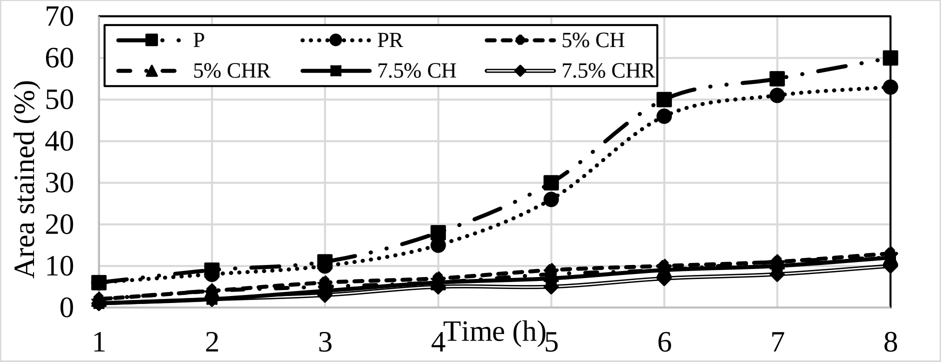
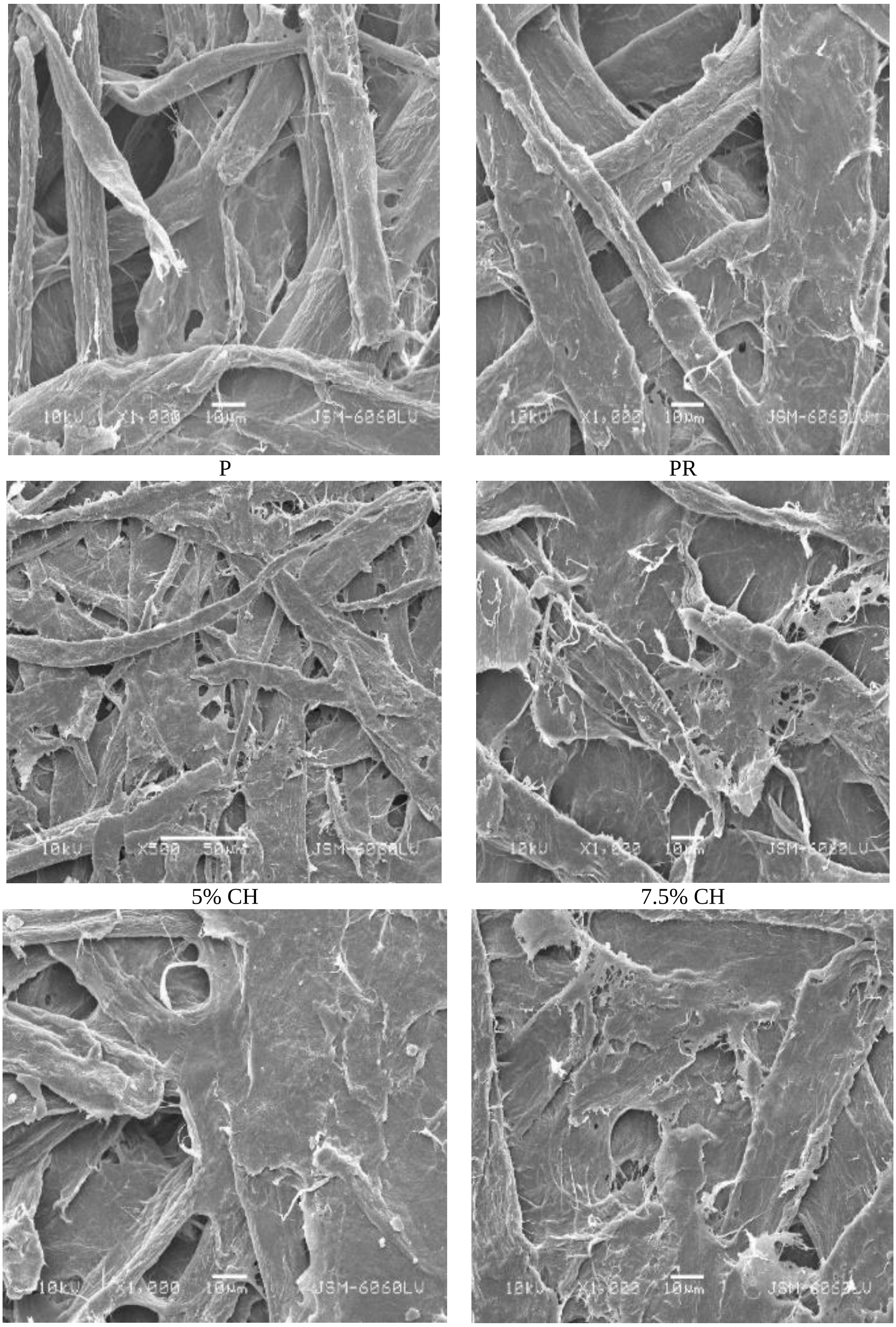


Fig. 1. Grease permeation of sample papers.

After 5 hours of the test, the grease migration increased for all samples, being the highest for the samples P and PR, where it increased from 6 to 30% of stained area. As expected, there was a slight increase for papers with fillers, from approx. 2 to 9% (sample 5% CH). After 8 hours, the same trend as before was detected for all tested samples. As predicted, the analysis showed that for the paper with no fillers, more stained areas were detected.



P

PR

5% CH

7.5% CH

5% CHR

7.5% CHR

Fig. 2. SEM micrographs of all samples taken at 1000× magnification and operating at 10 kV voltage.

Surface texture

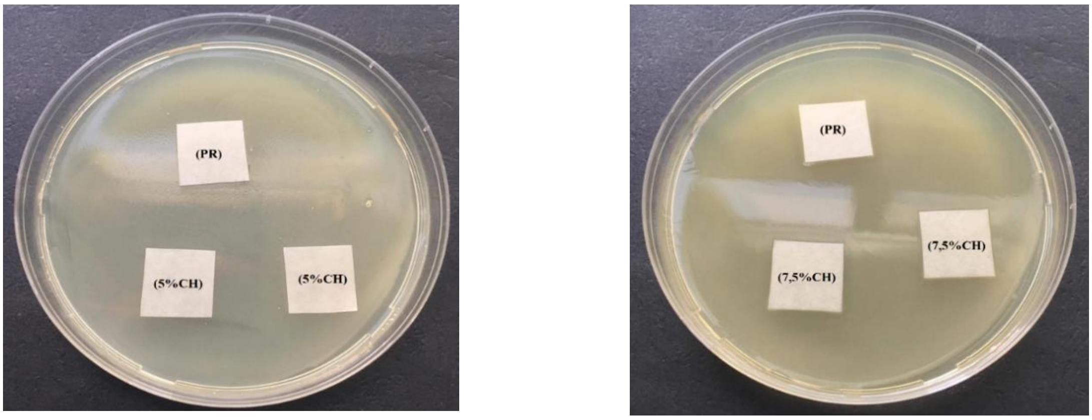
The distribution of chitosan and rice starch onto the paper sheets was evaluated by scanning electron microscopy (SEM).

The micrographs (Figure 2) show that the fillers covered the fibers and closed the pores and open areas in the base paper due to the increased fiber bonding and probable film-like covering process, which most likely occurs in the drying process of the paper samples where the drying temperature is above 95 °C and also increased due to the lower molecular weight of the used chitosan.

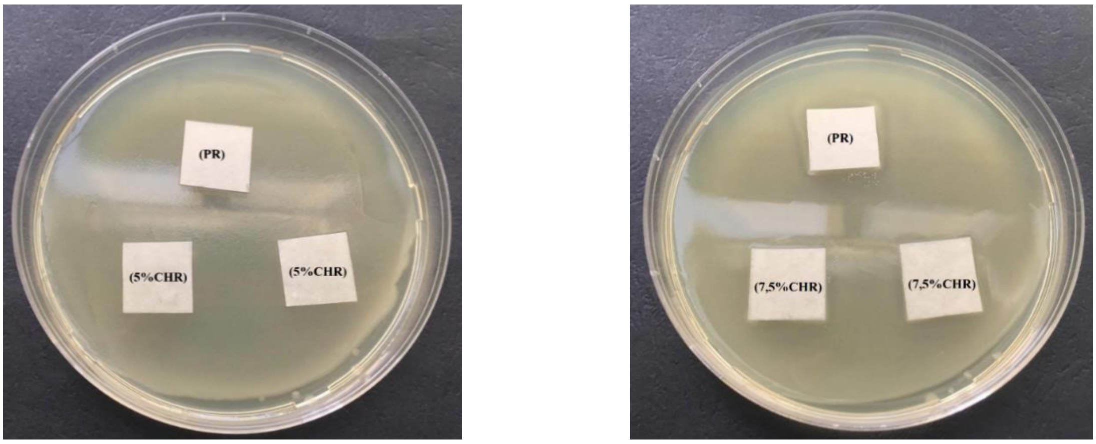
The surface of the sample papers was smoother and more even for paper with fillers (Figure 4) 7-5%CH, 5% CHR, 7.5% CH and 7.5% CHR), compared to the samples with no fillers (P and PR). A comparison between paper sheets with fillers of different concentrations proved their effect which is consistent with the improved mechanical, grease and water barrier properties. The absorption, thickness, moisture and roughness of the papers with fillers, have great influence on the properties of chemical structures, types of the fillers. If the fillers are uneven distributed in the fiber paper composition, many properties can worsen and this can influence not only the barrier but the printing properties.

Antibacterial activity

The antibacterial activity of the obtained paper samples was determined after a 24-hours stay in *Escherichia coli* K12 environment. Figure 3 presents the plate of *Escherichia coli* K12 for the obtained paper samples. As a zero probe paper samples with retention additive (PR) were used.



5% CH 7.5% CH



5% CHR 7.5% CHR

Fig. 3. Antibacterial activity of all samples against *Escherichia coli* K12

Chitosan has an inhibition effect due to the presence of amine group and its water-binding ability which cause a dry environment surrounding bacteria, not suitable for bacteria growth. A previous study reported that chitosan generally showed stronger antibacterial effects against Gram-positive bacteria than Gram-negative bacteria [21]. However, antibacterial activity also depends on the molecular weight and degree of deacetylation of chitosan. The molecular weight of chitosan used in this study is 20 kDa which is low. Chitosan of lower molecular weight possesses stronger antibacterial activity against Gram-negative bacteria. However, the filled packaging paper with chitosan and rice starch showed no inhibition zone, correspondingly, there is no antibacterial activity of the obtained packaging paper filled with chitosan and rice starch blends, probably due to the blocking of the amine groups by the OH-groups of cellulose in the paper suspension preparation process. This proved that chitosan and rice starch blends are efficient for water and grease resistance. In cases were antibacterial activity of packaging paper is needed, chitosan and rice starch blends could be used as a coating application solution.

CONCLUSION

The results showed that blend fillers of chitosan and rice starch are effective paper fillers in the preparation of pulp mixture for bio based papers. Such paper sheets have better moisture resistance. The research showed that the water absorptiveness and the resistance toward capillary rise improved for the 7.5% blend mixture of chitosan and rice starch. For paper, where 7.5 % of chitosan and rice starch were used, the water absorptiveness decreased by 33%, compared to paper with only pulp. Grease resistance of papers with fillers improved up to 88%. Furthermore, smoothness and air permeability improved for papers with chitosan and rice starch. Chitosan and rice starch blends provided water and grease resistance, but not antibacterial activity against *Escherichia coli* K12. Therefore, preparing paper using a combination of chitosan and rice starch blend fillers is an improved and convenient procedure to enhance many properties of such papers.

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