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Novel Packaging Paper Made From Blend Fillers of Chitosan and Rice Starch

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Abstract: *In our research, paper sheets with a blend fillers of chitosan and rice starch have been made. The novelty of this paper is the use of blend mixture, different concentrations of chitosan and rice starch in paper production. This led to positive effect on the barrier, mechanical and printing properties. The goal of our research was to improve paper properties and to make a paper sheets, which will be suitable as packaging paper. To evaluate the effect of the bio based fillers, the smoothness, air permeability, grease resistance, moisture, water absorptiveness, tensile properties, surface and printing quality were determined. The research showed that the water absorptiveness and the resistance toward capillary rise improved at 7.5% blend mixture of chitosan and rice starch. Grease resistance at papers with fillers improved up to 88%. Furthermore, smoothness and air permeability improved at papers with chitosan and rice starch. As expected, the fillers affected the surface, fibres were bonded, fewer and smaller pores were detected. 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, are more flexible, easy to print and maintain the colour quality. Therefore, preparing paper using 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*

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I. Introduction

In the packaging industry, plastic materials are still widely used. Newer packaging materials, with which producers reduce the environmental pollution, are based on bio polymers. Thus, these polymers are biodegradable, nontoxic and environmentally friendly, as well are possessing sufficient barrier properties which could be used in this industry market [1-3].

In recent years, the materials 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.

Additives in papermaking should be compatible with the cellulose, meaning it should strongly interact with the cellulosic substrates [4]. The use of fillers in packaging and paper industry usually provides cost and energy savings, but there can occur many problems. The problems are associated with the negative effects of filler loading, causing unstable paper strength, sizing, difficulties with retention and tendencies of filler, which can cause abrasion or dusting [5]. On the other hand, they can improve tensile, barrier and optical properties, printability and general appearance. Natural polymers can be used as fillers in order to enhance bonding capacities with pulp fibres and to improve many properties, important for packaging paper (oxygen, grease, antimicrobial properties etc.). They should also be biodegradable, clean and nontoxic. Such needs are met by rice starch and chitosan. Starch has been found highly effective as filler, as it was described by researchers [6-9]. Controlled conditions of the preparation of the starch, improved tensile and optical properties of paper and printability as well [7]. Dias et al. analyzed and prepared films based on rice starch and rice flour and proved to be useful in packaging field [10]. Romani et al. made a research about active and sustainable materials from rice starch, protein and essential oil for food packaging [11]. Rice starch was in previous research mostly used as coating additive, as binder or as film for packaging materials. Blends and composites to gels and complex networks from biopolymers was carefully described and presented by Thomas et al. [12]. As seen from the previous published papers, rice starch was mostly used as additional component in films forming blends with other biopolymers, but rarely as filler in the paper [13-16].

Still, the use of starch in paper should be careful, since in higher amounts, the elasticity can decrease and cannot be used in packaging applications. In general, starch is sensitive to water and to have an efficient filler, other polysaccharides should be included into the pulp mixture.

Chitosan, which is a linear copolymer of β-(1,4)-2-acetoamido-2-deoxy-D-glucopyranose unites 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 [17]. The presence of $–NH_2$ group transforms into a polycation in a dilute acidic solution. Therefore, the cationic character causes stronger adsorption by electrostatic interactions to the paper pulp, which has an anionic character [18]. Chitosan interacts in combination with cellulose, which causes improved tensile properties and promotes good printability of paperboard [19]. Blends of different cellulose and chitosan in papermaking processes have been studied and presented earlier [20-25]. Laleg and Pikulik presented that chitosan additives increased the strength of wet paper towels, disposable diapers, and grocery bags [20]. Li et al. studied 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 [21]. 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 [22]. Nada et al. found that the chitosan, cyanoethyl and carboxymethyl chitosan enhanced the strength properties of aged and un-aged paper sheets [23]. Fernandes et al. studied the distribution of chitosan onto the paper sheets, using a fluorescent derivative [24]. Their results have proven that chitosan and its modifications could be used as probe to understand the deposition of chitosan onto the paper.

The aim of our research was to improve the mechanical (tensile strength, elongation, tear resistance etc.) and barrier properties (moisture, grease, air permeability) and also printing properties of paper sheets, 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. There was not noticed research about the printing quality of such paper. The purpose of our research was to investigate different ratios of blends, as improving the barrier components with fillers into the papermaking process.

Our research was focused on the effect of bio polymers as fillers and to investigate the possibility of producing such paper sheets. 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.

II. Materials And Methods

2.1 Materials

The softwood pulp was delivered by SCA, Sweden and is bleached sulphate kraft cellulose from pine and spruce trees. The properties include; breaking length of 3300m, acc. ISO 1924/2, Tensile index of 26 N.m/g acc. ISO 1924-2, Burst index of 1.5 kPa m^2/g acc. ISO 2758, Tear index of 18.8 mN.m^2 /g acc. EN 21974 and 80% brightness acc. ISO 3088.

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

Chitosan, with the molecular weight lower than 20 kDa and deacetylation degree higher than 85%, was purchased from Sigma Aldrich (Austria). Acetic acid (99%) was purchased from Sigma Aldrich (Austria). 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 $cP_{(0,5\%,25^oC)}$ and Conductivity 66,6 $\mu S_{(0,5\%)}$.

2.2 Methods

2.2.1. Preparation of the pulp

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

2.2.2. 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 5% and 7.5% of the solution. The solution was mixed for 10 min at 85°C and then cooled to room temperature.

Rice starch was also prepared separately by dissolving rice starch in distilled water. It was mixed until it gelatinised (85°C for 10 min) and also cooled to room temperature. The chitosan-rice starch solution was prepared by mixing the same amount of rice starch and chitosan solution (5% or 7.5%).

The procedure of mixing pulp and other additives was as followed: firstly 23,5g 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% of 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)

2.2.3 Preparation of paper sheets

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

2.2.4 Printing

Printing was proceeded on inkjet printer HP Office jet Pro at ambient conditions (T=22±2°C; RH=45±3%) by a drop-on-demand mode with replaceable cartridges. All samples were printed with this technique.

2.2.5 Characterisation of the samples

Turbidity, dewatering

After preparation of each pulp mixture, the turbidity and dewatering time has been measured. For determination of turbidity, TB1 Turbidimeter (TB1 – VELP SCIENTIFICA) was used, acc. ISO 7027, which was equipped with integrated pH meter and temperature recorder.

The dewatering time was determined by Shopper Riegler apparatus (Germany). The measuring conditions are the same as for determination of beating degree in Shopper Riegler, according ISO 5267-1/AC: 2004, but the central vertical out-pipe is closed. The concentration is 0.2% (2g o.d.f in 1000ml water). The apparatus provides the possibility of measuring the dewatering ratio of different pulp and paper suspensions by measuring the time (in seconds) for obtaining from 200,300, 400… to 700 ml filtrate. In the current experiment the dewatering time was measured for 700ml filtrate.

Grammage, density, specific surface, thickness

It was necessary to determine 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 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 form 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 ISO 287 by measuring weight loss after the 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 (100ml) of water was in contact with the paper for 60 seconds and weight differences were compared. For each paper, five sample tests were made.

The capillary rice of paper samples was determined with 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 minutes 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 T-507, which was presented from Park et al. [25]. Smaller stained areas per hour on paper indicated greater grease resistance.

Tensile properties (tensile strength and elongation at break), bursting strength, bending and tear resistance

Tensile strength and elongation at break of papers were determined on a tensile testing machine Instron 6022. The samples were analysed in the standard atmosphere at 23 °C of temperature and 50% of relative humidity. The cross speed head was 0.15 mm/s. Paper stripes of 18 cm in length and 1.5 cm in width were used and a minimum of ten probes for each sample was tested. During the sample stretching, several load and elongation data per second were recorded until the break of a sample occurred. After the measurement and determination of tensile strength, the tensile index was calculated. The tensile index is tensile strength divided by grammage, the unit being Nm/g [26].

For packaging papers, bursting strength is very important. Depending on the grammage of paper, it was determined according to the standard method EN ISO 13938/2. It was measured as the maximum hydrostatic pressure required to rupture the sample paper. The pressure applied through a rubber diaphragm with a 30.5 mm diameter was constantly increasing. For each paper, ten samples were tested.

Furthermore, tear strength was determined according to the standard ISO 1974-9290, where four samples of each paper were tested with the Elmendorf method. Tear resistance was determined in mN, as the force required to tear a sample after a cut was already started. All samples were tested at 23 °C and 50% RH. When tear resistance is normalised with respect to grammage, then the tear index can be calculated and the unit is mNm^2/g [27].

Bending resistance was measured according to standard TAPPI T511, with specimen preload 1000g, where 175 bending/minute has been proceeded.

Tear resistance is the force, required to tear the sample after a cut was already made. The test was performed with an Elmendorf tester and proceeded as described in standard ISO 1974:2012. For each paper sheet, two parallels were measured. When tear resistance is normalized with respect to grammage, then the tear index can be calculated and the unit is mNm^2/g [28].

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 at the magnification 1000×.

Printing quality

a) Colour values and gloss

The colour of sample papers was determined with a CIE colorimeter X-rite. The CIE Lab scale was used to determine the L*, a* and b* colour values. The plate was used as a standard (L* = 92.82, a* = –1.24, b* = 0.5). For each sample, ten measurements were made at different locations on the surface. Before the colour measurements, the samples were conditioned at 60% RH and 27 ± 2 °C for 72 h.

Gloss was determined as the specularly and diffusely reflected light component determination against the known standard and was measured at 60° angle. The measurements and determination were conducted by using the standard ISO 8254 method and ten measurements on each sample has been made.

b) Abrasion resistance

The abrasion resistance of all samples-printed papers were made on rub tester Labthink (China), according to TAPPI T830 standard. The test was proceeded on dry samples and two of each paper samples were tested. The procedure was carried out on dual stations with arc movement. In our research two stroke (Rubbing Times) were determined: 25 and 50 cycles, at rubbing speed 106cpm and rub pressure 8.9N. For determination of print abrasion, optical density was measured before and after rubbing.

III. Result And Discussions

3.1 Pulp suspension analysis

After preparation of each pulp suspension, the turbidity (T_{NTU}) and dewatering time ($T_{700,s}$) has been measured. Usually, the dewatering ability gives us indirect information about the flocculation ability of the paper suspension. Not all of the examined bio-based combinations have positive effect over the accelerate drainage of the paper suspensions (Table 1). Best results are obtained in the presence of 7.5% chitosan, followed by the combination of 5% chitosan and starch. In sample 5% CH, the presence only of 5% chitosan probably is not enough to compensate the negative charge of the pulp fibers so that the resulting flocks to be uniform and stable. The effectiveness of 7.5% chitosan and starch, over the dewatering of the suspensions is higher than that in sample 5% CH (only 5% chitosan), which means that the system is overloaded and the flocculation and dewatering have no homogenous character.

Regarding the turbidity of the white waters the results are similar to those for the dewatering ability, but here all the examined combinations have positive effect compared to the sample with only pulp. Best results are obtained for sample with 7.5% of chitosan, which means that the white waters are clarified and the

flocculation has its optimal conditions. Higher turbidity of sample, which is only pulp and retention additive, probably is due to the large molecular weight of the modified polyacrylamide and for this combinations of softwood and hardwood pulp the retention additive should be with lower molecular weight, so that the obtained flocks to be smaller.

	P	PR	5% CH	5% CHR	7.5% CH	7.5 CHR
$T_{700,s}$	6.37	11.16	7.51	6.09	5.56	6.60
T_{NTU}	18.50	21.60	16.20	15.60	13.90	16.10

Table 1 Dewatering time ($T_{700,s}$) and turbidity (T_{NTU}) of all pulp mixtures

Before the testing process, paper sheets were conditioned at temperature of 23°C ±1°C and relative humidity 50% ± 5%, for 24 hours.

3.2 Basic paper properties (grammage, density, specific surface, thickness)

To evaluate the influence and effect of bio based components onto paper, it was essential to establish and make 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 fibres, dimensions of the fibres and addition of the fillers have influence on thickness of the paper. This plays an important role at end usage, especially at printing papers.

As expected, the thickness of the samples had mostly the same values (Table 2). Paper with only pulp, combination of softwood and hardwood fibres with no additives, had the lowest thickness (0.0084 mm). With addition of the retention additive and fillers, the thickness at all other paper sheets increased respectively.
The changes were also detected at specific surface and density, where sample P, with only pulp and no additives, had the highest density, compared to other tested papers.

	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 Basic properties (grammage, thickness, specific surface and density) of all paper samples

3.3 Barrier properties

It is known that paper has 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 Figure 1, the decrease of moisture was noticed at samples with the retention additive and fillers. With increasing amount of fillers, the moisture decreased.

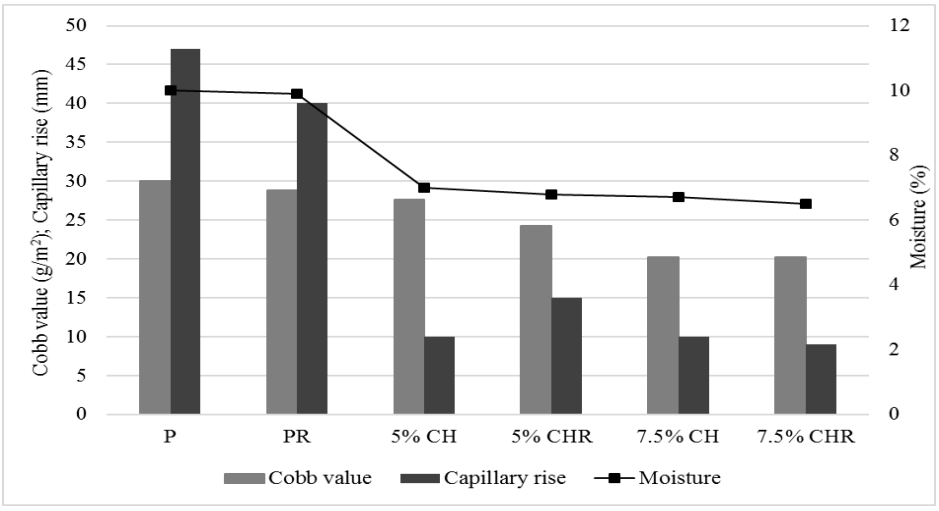


Fig. 1. Water barrier properties (moisture, $Cobb_{60}$ value, capillary rise) for all tested samples.

Ability of fluids to penetrate the structure of paper is highly significant property to the use of packaging paper. Resistance towards the penetration of water was measured by $Cobb_{60}$values, as explained in ISO 535. From the obtained results, the addition of chitosan-rice starch decreased water absorptiveness i.e. $Cobb_{60}$value, as seen in Figure 1. The higher, the concentration of the filler content was, higher resistance towards water penetration has been detected. At paper, where 7.5 % of chitosan and rice starch was used, the water absorptiveness decreased for 33%, compared to paper with only pulp. At samples, where 5% of fillers was used, 8% (5% CH) and 19% (5% CHR) decrease was detected. It is known that chitosan has

It was also proven that retention additive had an influence on paper structure and properties.

The same trend was detected at capillary rise (Figure 1). With addition of chitosan and rice starch, the resistant towards water capillarity increased. With higher concentration of used bio polymer components, capillary rise decreased. The most significant change was detected at sample, where 7.5 % of chitosan and rice starch was used. The decrease was from 80% (7.5% CHR) to 68% (5% CHR). Chitosan is insoluble in water and on the other hand 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 highly porous material, composed of a felted layer of fibres and the additives could cause the variation of many properties. One 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 mentioned polymers.

Smoothness was better at samples with chitosan and rice starch. When the amount of bio polymers increased, the smoothness improved as well. As expected and seen in Figure 2, the air permeability was the worse at paper, where only pulp was included. With 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 paper with 7.5% CHR, where only 1186 mml/min was measured.

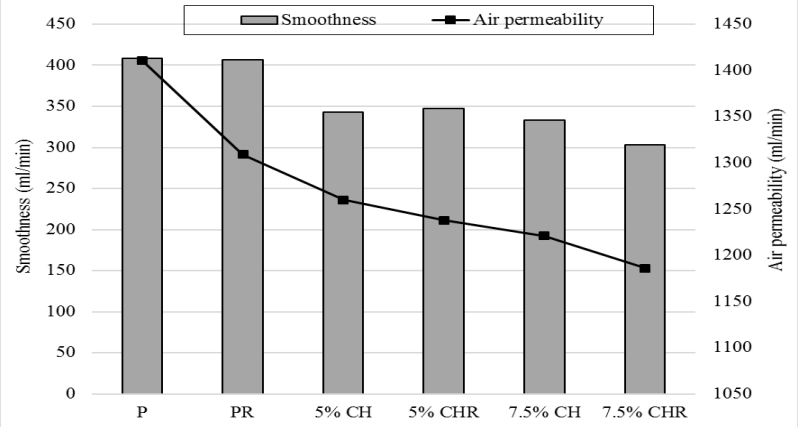


Fig. 2. Smoothness and air permeability of all sample papers.

Grease barrier properties of analysed papers were affected by the fillers and additives in paper samples.

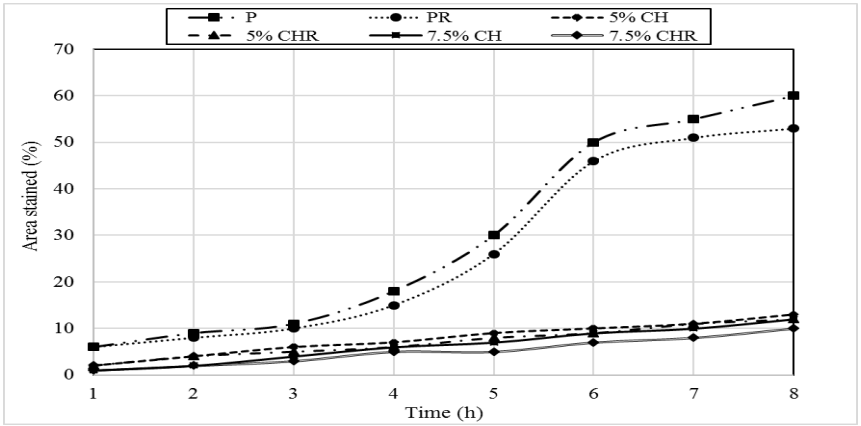


Fig. 3. Grease permeation of sample papers.

In the first hour at all samples with fillers, lower percent of stained area was detected, compared to paper with only pulp and retention additive (Figure 3). Chitosan has great grease barrier properties, compared to rice starch. The results of grease migration at papers with fillers is also due to open surface (pores) between the paper fibres, where grease could permeate through the paper [29]. We could avoid and increase grease resistance with higher amount of fillers or as paper coatings. There is also important factor of beating degree of the pulp, where highly beaten papers have smaller pores [30]. Our grease permeability analyse has shown that fillers and additive filled and reduced pore sizes, which was also proven with scanning electron microscope analysis. After 5 hour of the test, the grease migration increased at all samples, the major detection was at samples P and PR, where it increased from 6 to 30% of stained area. As expected, slight increase was at papers with fillers, from approx. 2 to 9% (sample 5% CH). After 8 hours the same trend as before, was detected at all tested samples. As predicted, the analysis has shown that at the paper with no fillers, more stained areas were detected.

3.4 Mechanical properties (tensile strength and elongation, bursting strength, bending and tear resistance)

Chitosan used as coating or filler has some great mechanical properties. From the previous researches it has been reported to be used as a wet end additive in paperboard, to improve mechanical properties such as bending strength [31]. On the other hand, it could be used as crosslinking agent between paper and fibres. Therefore, the increase in the paper strength could be detected. Fibres and papers are stringed by hydrogen bonds, which affects the distance between fibres crosslinking [32]. Rice starch has limitations in the use to improve mechanical properties, because it decreases elongation at break. To increase paper strength and to use biopolymers at the same time, additives, fillers or coatings should be used, such as polysaccharides, proteins etc.

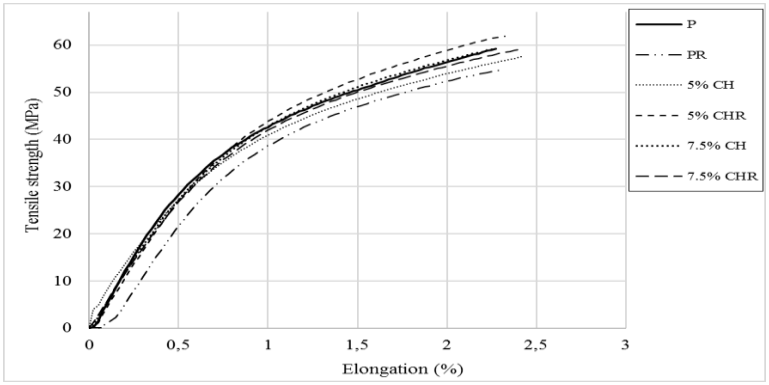


Fig. 4. Tensile properties – tensile strength and elongation for all samples, tested at 23°C and 50% RH

The effect of chitosan and rice starch separately and in the blends, on tensile strength and elongation on paper sheets, is shown in Figure 4. The tensile strength indicated the ability of paper to resist tension and elongation and it indicates the flexibility, which are both depending on the strength of fibres and bond between them, fibre length and surface area. The difference in tensile strength among papers is mainly due to the difference in the fillers and its concentrations. As expected, the tensile strength and elongation is the highest at paper where only chitosan was used. Paper with blends of fillers achieved lower tensile strength but still high elongations, compare to paper sheets where only chitosan was added.

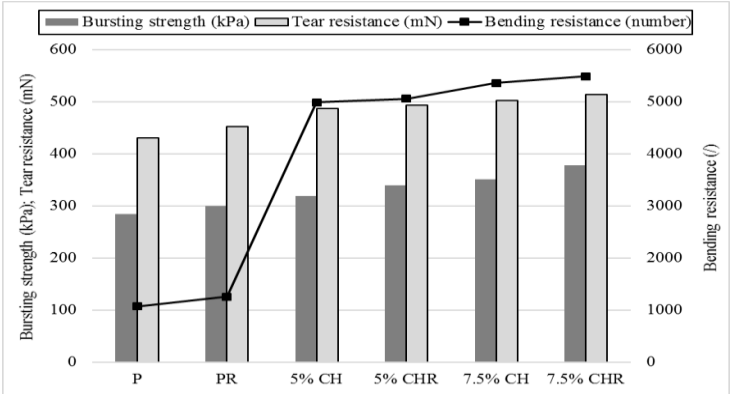


Fig.5. Bursting strength, bending and tear resistance for all paper samples

Figure 5 presents the effect of additive and fillers on the bursting strength, bending and tear resistance. Bursting strength is particularly important for paper bags, as it determines how much pressure paper can tolerate before it ruptures. It depends on the grammage of paper and can also be presented as bursting index, calculated from bursting strength and grammage. The investigation of burst strength has shown that results are much better after filling the paper with higher amount (7.5 % CHR) of chitosan and rice starch (378 kPa). Among filled paper sheets sample, which only had 5% of chitosan, the burst strength decreased the most (319 kPa). As expected, the worse bursting strength had paper with no additives and fillers (285 kPa).

The tear resistance determines the force applied during the tearing procedure. It indicates the behavior of paper and it is important in packaging papers, where the toughness and shock absorption are very important factors. The fact is that fillers and additives improve tear strength, as it tends to distribute the stress over the whole over long, cellulose fibres in the paper. The trend was the same, as at the bursting strength. The tear resistance is the highest at chitosan and rice starch paper (514 mN). The tear resistance increased with the amount of fillers. It was proven that chitosan and rice starch improved and bonded the fibres in the paper, which influenced on this paper property.

Bending resistance is a resistance offered to a bending force by rectangular sample. Measuring of bending resistance is important of papers which have low grammage, high flexibility, are used in many end use applications such as wrapping, printing, high speed mechanical handling etc. The results presented in Figure 6 show very good and major improvement of paper sheets with added fillers, especially at the 7.5% CHR sample, which achieved 5489 bendings before breaking down. Very low resistance to bending had samples with only pulp and retention additive (sample P-1070 bending's and sample PR-1260 bending's).

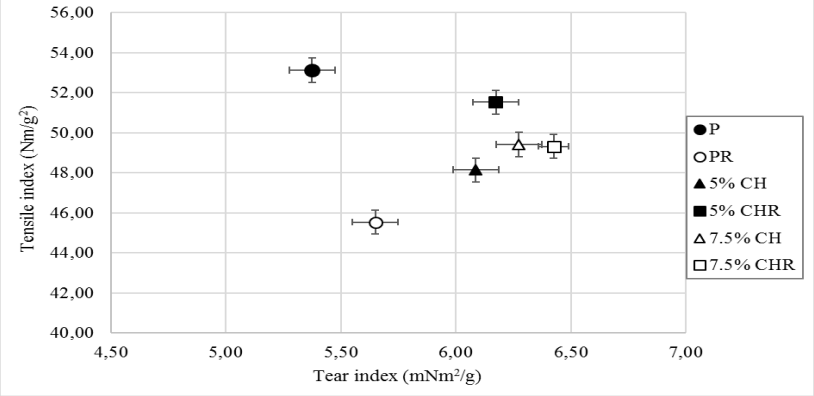
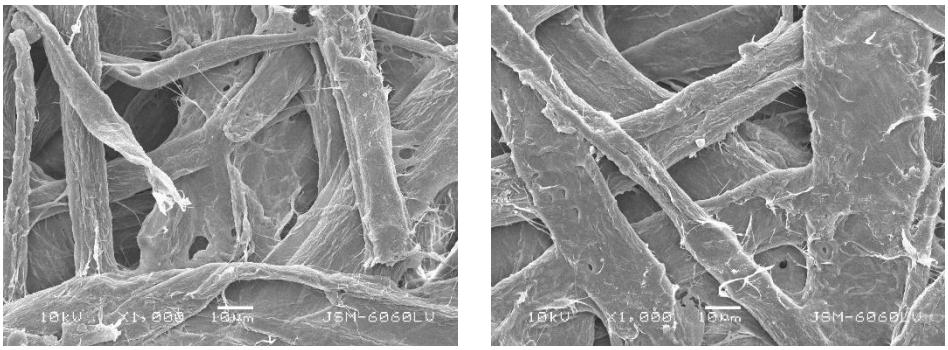


Fig. 6 Tensile and tear indices for all paper samples.

The grammage was at paper samples the same, but we could not determine the MD or CD direction. Therefore, the tensile and tear indexes have been calculated and are presented in Figure 6. As expected, the values of tensile and tear indices are higher at papers with chitosan and/or rice starch fillers. Both papers with only pulp and retention additive have lowest indices, but there is major difference between them. At paper, where only pulp (P) was used, the tensile index is much higher, compared to all paper samples (53.13 Nm/g^2). On the other hand, paper with pulp and retention additive (PR), achieved the lowest tensile index among all (45.53 Nm/g^2).

3.5 Surface texture

With scanning electron microscope (SEM) the evaluation of the distribution of chitosan and rice starch onto the paper sheets has been evaluated.



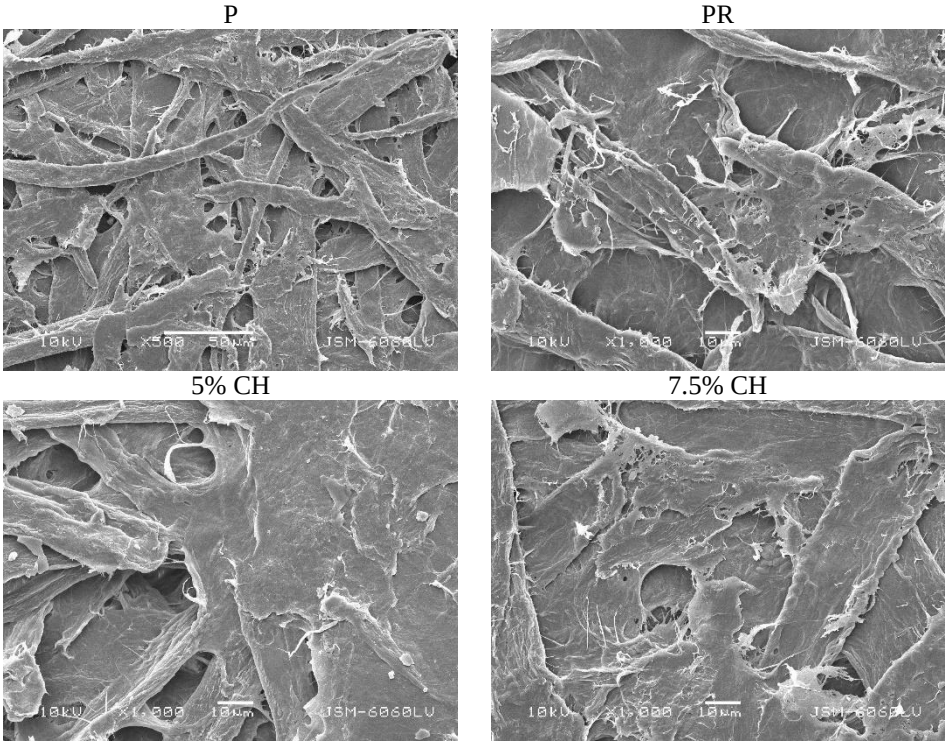


Fig.7. SEM micrographs of all samples taken at 1000x magnification and operating at 10kV voltage.

These micrographs (Figure 7) show that the fillers covered the fibres and closed the pores and open areas in the base paper. The surface of sample papers revealed a smoother and more even surface at paper with fillers (Figure 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 used fillers, but different concentrations, proved their effect, which is consistent with 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 fibre paper composition, many properties can worsen after and this can also influence the printing process (uneven print image and mottling).

3.6 Printing quality

At papers, colour is important for future finishing and printing procedures. It determines the quality of light reflected from by paper, as described by hue, saturation and darkness or lightness. Base paper determines the optical properties, where brightness should be as close as possible to the brightness of the sample paper. In the research, the used paper was not light white, it was a bit brown and the fillers with chitosan did not have such an effect as on white paper. Chitosan powder is naturally yellowish, but rice starch is white, hence the fillers onto paper did not make any greater changes on colour as it can be seen in Table 3. From the results of printed colours, the colour difference (ΔE) has been calculated.

	Colour values			ΔE	Gloss at 75°
Samples	L*	a*	b*	(/)	(/)
P	-0.601	2.80	1.29	/	4.2
PH	-0.603	2.81	0.90	0.39	4.4
5% CH	-0.606	2.84	2.56	1.27	5.6
5% CHR	-0.605	2.82	2.15	0.86	5.3
7.5% CH	-0.605	2.84	3.18	1.89	5.8
7.5% CHR	-0.605	2.82	2.84	1.55	5.6

Table 3 Colour values (L*a*b*), colour difference (ΔE) and gloss of all sample papers

The colour difference was calculated according to the sample, where only pulp (P) was included. As expected, the higher difference occurred at samples where chitosan and rice starch was added. At 5% of chitosan and rice starch, the colour difference was lower, compared to 5% of chitosan, due to addition of the rice starch. Chitosan, as yellow powder still has an effect on colour of the paper sheets, tor major, but it has been detected.

The same was at 7.5%, where the biggest colour difference was calculated at only chitosan (ΔE=1.89), but in combination with rice starch it was lower (1.55).

Colour is not one of the main properties for this packaging material and this kind of blend fillers does not have a substantial influence on the printing properties e.g. colours and therefore could be used in this field. Gloss is related to surface morphology and reached at the drying procedure. Due to the additives and fillers in the paper sheets, it is known that it also improves gloss values. The gloss of filled papers increased, even more at papers, where higher amount of fillers was used, especially at 7.5% of chitosan (by 5.8). Low gloss had papers where rice starch was added, but the difference is minor. This is consistent with the findings of previous research, reporting that fillers also improved surface smoothness, making the surface glossier after its use [33].

The abrasion resistance was used to evaluate the resistance of printed surfaces to rubbing abrasion. Failures or damages on paper are related to substrate-colour adhesion, paper additives, thickness and internal stress. It should be noted that there are several methods that can characterize other aspects of imaging materials degradation as result of frictional contact with various surfaces under different conditions. Therefore, the use of specific methods is depending on end-user applications, such as type of packaging materials and coatings, requirements for packaging paper barriers, etc. In our study TAPPI standard was used as standard method for determination of printing quality of rubbed sample papers.

In our research dry rub test and two stroke (Rubbing Times) were determined: 25 and 50 cycles, at rubbing speed 106cpm. As seen in Figure 9, the dry rub test showed that all paper samples, with bio polymers achieved better results (optical density) in comparison to paper only with pulp and retention additive.

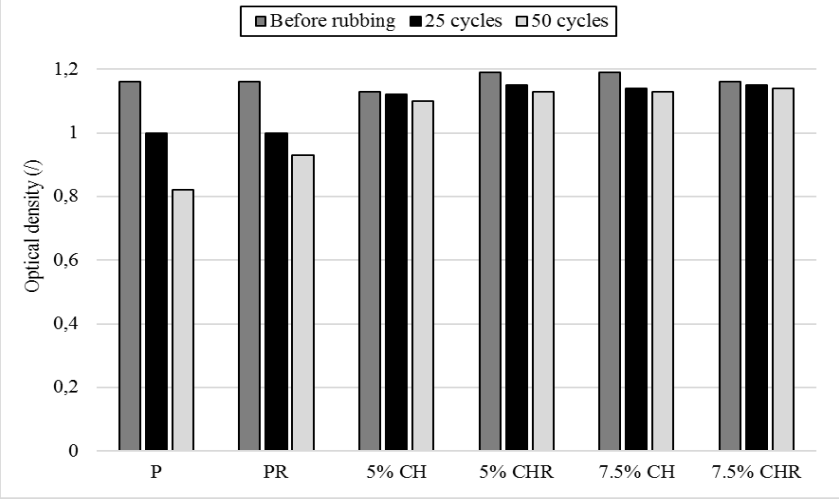


Fig. 8 Optical density of all paper samples before and after rubbing 25 and 50 cycles

After 25 cycles (Figure 8) papers, where chitosan and/or rice starch was included, achieved better quality, according to other papers. Before rubbing, the highest optical density (1.19) had papers with 5% chitosan and 7.5% of chitosan and rice starch. At paper, where the highest amount of fillers was used (7.5%) the smallest decrease after rubbing (25 and 50 cycles) of optical density was detected. Paper, where only chitosan was used, the optical density after rubbing, was almost the same as at paper with added rice starch. The highest the concentration of the fillers was, the most stable colour resistance was after rubbing 50 cycles. As expected, fillers increased colour stability, compared to paper sheet, where the fillers were not used. From this part is can be concluded that rice starch and chitosan had great influence on more stable and durable printing properties.

IV. Conclusion

Certain fillers in the paper can enable their functionality and the end usage of the paper. From previous and our research has been proven that the fillers can provide many benefits, such as improved tensile, printing, surface and many barrier properties.

The grease barrier properties, water absorptiveness, tensile properties and surface texture proved, that chitosan and rice starch positively affected the properties of paper sheets. For packaging paper, printing quality is among other properties important factor. The research has revealed that paper samples with bio based fillers improved abrasion resistance and at the same time, there was not major colour difference compared to the paper with no fillers. To further enhance the barrier properties of packaging paper, this kind of bio-based papers could be associated with additional additives and concentrations of polymers and additives presented in our study.

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