Chitosan as a coating additive in paper and paperboard

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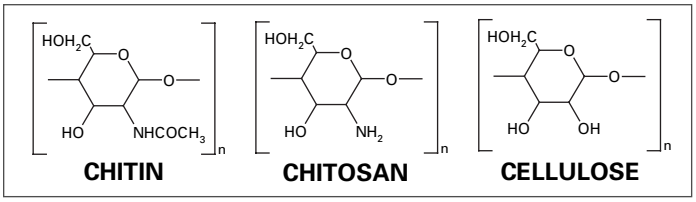
ABSTRACT: Chitosan can be used as precoating, before extrusion coating, to give better adhesion and improve barrier properties. A chitosan from natural polysaccharide was studied as a potential additive in paper coating. Four chitosan solutions were made with concentrations of 0.1%, 0.25%, 0.5%, and 0.75% by weight of total dry coating weight. Bending strength was improved significantly, but tear index and tensile index were improved only slightly. Water absorption was slightly reduced. This preliminary study indicates that chitosan has good adhesion onto cellulose and could be used as an environmentally friendly coating material. Future studies will concentrate on the aroma and oxygen barrier properties of chitosan.

Application: Coating paper with chitosan, an abundant material, improves its bending stiffness and MD tensile strength.

Chitin is the second most abundant polymer in nature after cellulose [1]. It can be extracted from shells of crustaceans and insects, from the cell walls of micro-organisms, and from the tissues of some fungi. Processed from chitin, chitosan is composed of glucosamine and *N*-acetylglucosamine, which are constituents of mammalian tissues [2].

The main objective of our work was to show that chitosan has potential as a biodegradable, nontoxic, environmentally safe material for coatings for packaging products. A secondary objective was to prove that this material can be applied on the industrial scale by showing that the coating process is easy to perform. To study this potential use of chitosan, we characterized the mechanical, optical, and barrier properties of the coated paper sheets.



1. Chitin, chitosan, and cellulose formulas.

BACKGROUND

Chitosan can be considered a cellulose derivative since the only difference is the group attached to the C2 atom. In this position, cellulose has a hydroxyl group, whereas chitosan has an amino group or an acetoamido group. **Figure 1** shows the chemical structures for chitin, chitosan, and cellulose.

The ratio of acetamido groups to amino groups in the chain is important and is called the "degree of deacetylation." When deacetylation exceeds 50%, the term "chitosan" is used. Chemically, chitosan is classified as a polycationic polysaccharide [3]. It is quite easy to make membranes out of chitosan by dissolving them in an aqueous solution of organic acid, like acetic acid, and evaporating the solvent. The strength of the solution depends on the acid used, or more precisely on its pKa value (defined as the negative logorithm of the acid dissociation constant Ka) and the concentration of the chitosan in the solution. Generally, chitosan dissolves when the pH of the solution decreases below 6.5, as the amino groups protonize.

When solutions are made with different amounts of chitosan, it is beneficial to use the equivalent amounts of acid and chitosan. That way, the effect of the acid remains constant. Any residual acid can be washed away with 1*M* NaOH, and the residual NaOH can be washed away with distilled water. A pH meter can be used to control the removal of residual alkali and produce flexible, transparent, homogeneous films. Because of chitosan's chemical nature, the films are completely biodegradable and nontoxic. They also degrade down to oligosaccharides without producing any harmful toxic substances. This feature would be beneficial in hospital textiles and in the food packaging industry.

Chitosan is abundant, and no special equipment is required to apply its film onto paper or paperboard. Processing units utilized for applying surface sizing and pigmented coatings can be used for chitosan coatings. The physical properties of chitosan can be changed through simple chemical methods without the need for extensive syntheses. This simplicity is an advantage when different applications are being developed. Because chitosan is currently extracted from seafood as a side product, there is abundant raw material available. Furthermore, the possibility of producing chitosan from fungi could make chitosan even more available.

Quite often, packaging requires barrier properties. Water repellency and water vapor barrier properties are the main barrier features, but barrier properties against odor are also needed. Extrusion coating with LDPE is most often used to give sufficient water vapor barrier. Permeation of molecules through a film or coating is controlled by diffusion. Diffusion and layer thickness are related inversely, as Eq. 1 shows [4]:

$$J_s = D(c_0 - c_1)/t \qquad (1)$$

where

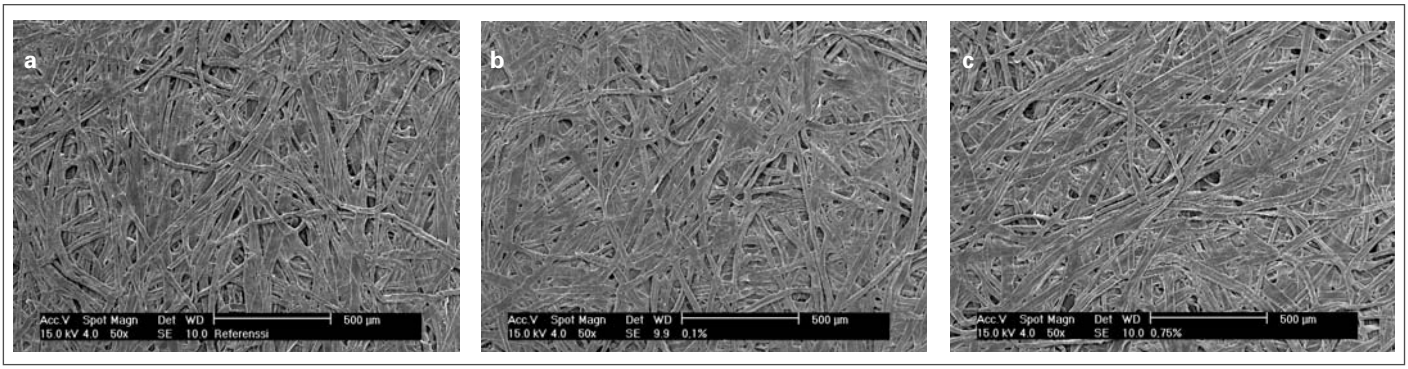
J_s = diffusion flow
c_0, c_1 = concentration of permeating molecules on the layer's surfaces
t = layer thickness.

For multilayer structures, Eq. 2 can be written [5, 6]:

$$\frac{t}{P_c} = \frac{t_1}{P_1} + \frac{t_2}{P_2} + \frac{t_3}{P_3} + \ldots + \frac{t_n}{P_n} \qquad (2)$$

where

P_n = coefficient of permeability of layer n
t_n = layer thickness of layer n.



2. SEM images of reference paper and chitosan-coated samples (50x). (a: reference paper. b: 0.1 wt% chitosan. c: 0.75 wt% chitosan).

3. SEM images of reference paper and chitosan-coated samples (1000x). (a: reference paper. b: 0.1 wt% chitosan. c: 0.75 wt% chitosan).

	Coating wt., g/m²	
Conc., wt%	BS	TS
0.10	1.83	1.46
0.25	1.92	1.54
0.50	2.06	1.63
0.75	2.46	1.90

BS=bottom side. TS=top side.

I. Chitosan concentrations and coating weights.

According to Despond *et al.*, the water absorption and water vapor transmission rate of chitosan film is high because of its polar nature [7]. In other words, it attracts water molecules as a result of hydrogen bonding. Also, Yu *et al.* have reported that chitosan films resist water poorly [8]. However, chitosan could be used as a precoating, before extrusion coating, to impart to functional properties other than water vapor barrier properties, such as better adhesion to extrusion coating or a better barrier against odors and oxygen in food packaging.

MATERIALS AND METHODS

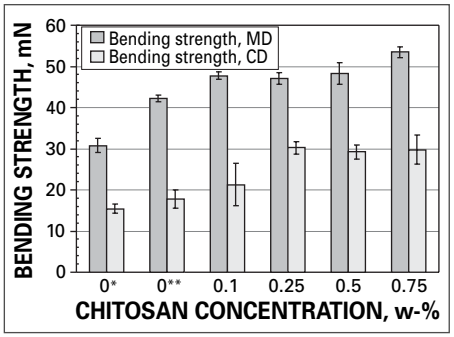
In our experiments, we used microcrystalline chitosan with the deacetylation degree of 73% and molecular weight of 240 kg/kmol. The chitosan was of technical grade, extracted from crab shells and purchased from Valioravinto Ltd., Pietarsaari, Finland. The organic acid was acetic acid (Merck 99%).

Four solutions were prepared. First we dispersed the chitosan powder in distilled water solutions (0.1, 0.25, 0.5, and 0.75 wt%) using magnetic stirring. While mixing the solution, we added equivalent amounts of acetic acid (0.1, 0.25, 0.5, and 0.75 wt%). Within 1 min, the solution became transparent. Mixing continued for approximately one hour. The solutions were stored in the refrigerator until coatings were prepared.

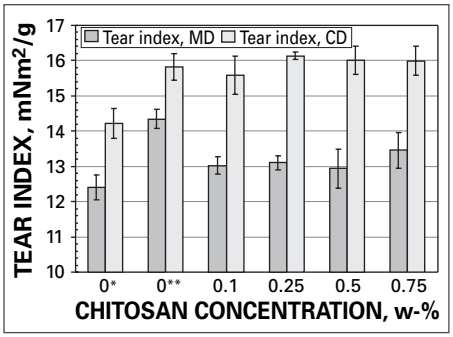
The base paper we used was a 90 g/m² UPM Swanwhite (UPM Kymmene) made of bleached chemical pulp and machine finished. Bendtsen roughness values were 350 mL and 250 mL per min (ISO 8791-2). The low-density polyethylene (LDPE) was an extrusion coating grade (CA7230, Borealis Polymers) having a melt index of 4.5 dg/min (190°C, 2.16 kg) and a density of 0.923 g/cm³. The polyethylene terephtalate (PET) was a blow molding grade (Lighter C98, Dow) with an intrinsic viscosity of 0.85 dl/g and a density of about 1.3 g/cm³. Melt temperatures in the extrusion coating process were 310°C (for LDPE) and 290°C (for PET).

The mechanical properties of paper sheets were tested by standard methods: SCAN P29 (bending resistance), SCAN P11 (tear index), and SCAN P67 (tensile index). Values for water absorption (Cobb 60) were determined according to SCAN P12. ISO brightness and opacity were measured with a color and brightness tester.

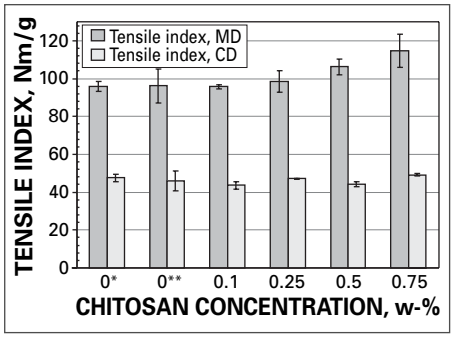
Chitosan solutions from concentrations of 0.1, 0.25, 0.5, and 0.75 wt% were applied with drawdown rods onto A4-size paper sheets. The coated sheets were dried in an oven at 160°C for 1 min. We used the Tampere University of Technology (TUT) coextrusion coating pilot line to coat LDPE and PET onto the chitosan sheets. The line consists of four extruders, a 5-layer feedblock, and a 700 mm wide die. The sheets were attached onto a web and then extrusion coated at the speed of 100 m/min. Some wrinkling and uneven extrusion coating thickness was observed as a result of this arrangement.



4. Effect of chitosan concentration on the bending resistance of the paper.



5. Effect of increasing chitosan content on tear index.



6. The effect of chitosan on tensile index.

The water vapor transmission rate (WVTR) was measured according to the SCAN P22:68 method at 25°C and 50% RH. We determined the pinhole density by spreading colored turpentine on the samples. After 10 min, the number of pinholes was measured from an area of 100 cm².

RESULTS AND DISCUSSION

Table I shows the coated chitosan concentrations and respective coating weights. Only the samples coated with chitosan on the top side were used in the barrier results. Unless otherwise specified, chitosan was coated on the bottom side of the sheets.

Figures 2 and 3 illustrate the scanning electron micrographs (SEM) of the chitosan-coated samples. The reference sheets (*i.e.*, no chitosan) with coatings of 0.1 wt% and 0.75 wt% concentration were photographed at two magnifications (50X and 1000X). Chitosan coating did not form a uniform film on the paper surface. Instead, what happens is that the diluted solution penetrates the paper voids while chitosan simultaneously starts covering the fibers, since, theoretically, chitosan and cellulose have a chemical attraction by hydrogen bonding. In addition to that mechanism, according to the images, the chitosan probably strengthens bonding between fibers.

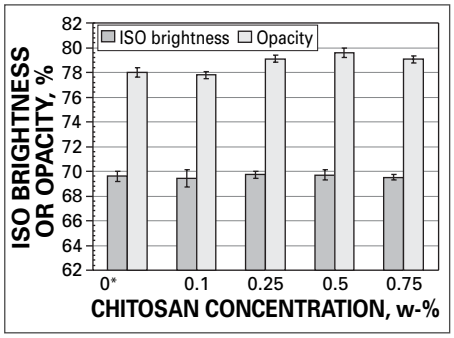
Mechanical properties

The effect of chitosan coating on the bending resistance of the paper is presented in **Fig. 4**. Chitosan coating improves bending strength, particularly above 0.1 wt% concentrations. In the machine direction, the increasing coating weight of chitosan does not show as pronounced a reinforcing effect as in the cross-machine direction. This outcome is partly attributable to the high initial bending resistance in the machine direction, where the resisting force comes from stiff lengthwise-oriented fibers. On the other hand, the reinforcing effect in the cross direction is substantial because the chitosan bonds fibers together.

The manual application of coating and nonsupported drying caused some degree of shrinking in A4 sheets, which might have limited our interpretation of the results. This effect can be seen in a water-coated sample, where the bending strength was improved, particularly in the machine direction. It could be that the bending strength is improved because free drying enlarges the bonding area between the fibers [9].

Figure 5 presents the influence of chitosan content on tear index. Tear strength was increased more in the cross direction than in the machine direction. On the other hand, the water-coated sample also had significant improvement, both in the machine and cross-machine directions. This improvement can also be explained by the unrestrained drying, which caused the bonding area to increase between fibers compared to the situation in which drying was restrained by tension in the machine direction and by contacts with the drying cylinders [8]. Therefore, the improvement in the MD tear index is partly attributable to shrinkage, caused by free drying, and partly due to the strengthening effect caused by chitosan from more bonding between fibers.

Figure 6 shows the influence of chitosan coating on tensile index. The pure water coating did not improve the tensile index at all. According to other sources [9, 10], free drying will lead to a decrease in tensile index. The CD tensile index of water-coated paper decreased, but the MD tensile index increased from the reference value—*i.e.*, the plain paper with restrained drying in a paper machine. An increase in the chitosan coating weight slightly improved the tensile index in the machine direction, while the values remained almost constant in the cross direction. The increased MD tensile index was most significant at the highest chitosan concentrations.



7. The effect of chitosan concentration on brightness and opacity.

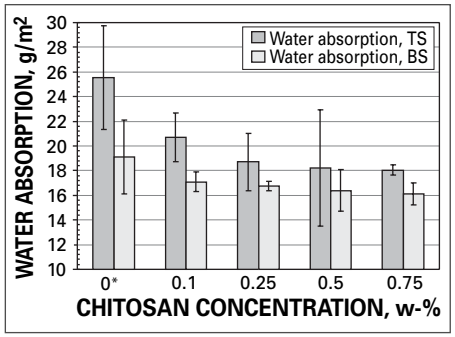
These tensile index results can be explained on the basis of fiber orientation. In the machine direction, chitosan connects cellulose fibers into bundles, which have much higher strength than individual fibers have. In the cross direction, the tensile index depends much more on the strength of the chitosan matrix, which leads to lower values.

Optical properties

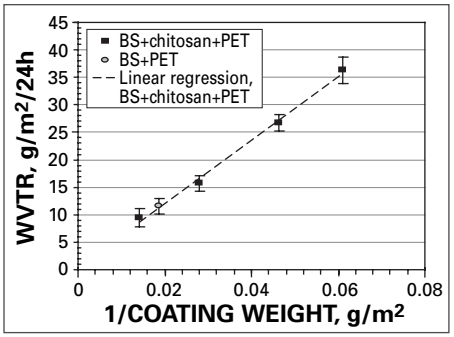
Chitosan coating had little influence on optical properties of the papers, as illustrated in **Fig. 7**. This outcome is probably due to the thin film and the rather transparent nature of chitosan. The chitosan coating also appears to increase paper opacity slightly as a result of an increase in light diffraction.

Barrier properties

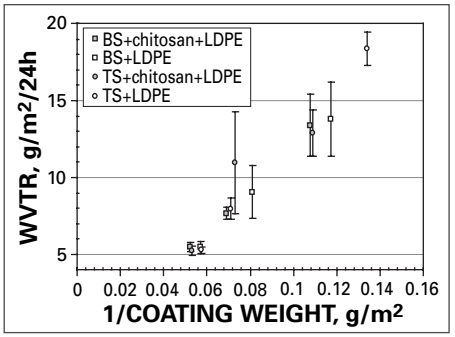
Figure 8 shows that water absorption fell as a function of chitosan concentration. The decrease in water absorption was greater in the top side of the coated sample than in the bottom side. Initially, the bottom side had a lower water



8. The effect of chitosan on water absorption. Chitosan was coated on the bottom side and the top side of the paper.



9. The effect of chitosan on water water vapor barrier as a function of reciprosal coating weight of PET (thickness), when the chitosan was coated on the bottom side of the paper. (The R^2 value of the linear regression trend line is 0.995.)



10. The effect of chitosan on water vapor barrier as a function of the reciprocal coating weight of LDPE, when the chitosan was on both sides of the paper.

Structure	Coating weight of LDPE, g/m²	Pinhole density, no./m²
TS+chitosan+LDPE	9.3	350
TS+chitosan+LDPE	14.5	350
TS+chitosan+LDPE	19.1	0
TS+LDPE	8.5	300
TS+LDPE	12.4	100
TS+LDPE	19.1	0
BS+chitosan+LDPE	9.2	550
BS+chitosan+LDPE	13.7	200
BS+chitosan+LDPE	18.9	0
BS+LDPE	7.5	n.a.
BS+LDPE	14.1	700
BS+LDPE	17.4	0

II. Pinhole densities of the LDPE extrusion-coated samples.

absorption value than the top side, probably because its surface was smoother as a result of a high concentration of fines on the wire side. The paper was made on a fourdrinier, and this difference in smoothness may have led to the minor influence that chitosan had on the bottom-side values. Above 0.1 wt% of chitosan concentration, the reduction in values was insignificant and was similar to both the top and the bottom sides of the coated samples.

Observing the SEM photographs (Figs. 2 and 3), we found that there is no uniform chitosan film. Therefore, it is difficult to make a complete analysis of the influence of chitosan. Nevertheless, the chitosan coating appears to slow down water absorption slightly when the absorption is being evaluated with the Cobb[60] method, even though it has been reported that chitosan coating has a poor resistance to water [7, 8].

Figure 9 presents the influence of chitosan coating, combined with PET extrusion coating, on water vapor barrier properties. As shown, the chitosan coating does not give any improvement in water vapor barrier. The WVTR values are inversely proportional to the PET coating thickness (R^2 value close to 1).

We also studied chitosan coating combined with LDPE extrusion coating. As shown in **Fig. 10**, we observed one outlying measured WVTR value, for the bottom side coated with chitosan and LDPE. This result is probably caused by nonuniform LDPE coating (possibly an excessive number of pinholes). However, as in PET coating, the chitosan coating did not improve the water vapor barrier.

Linear regression in Fig. 10 indicated the following R^2 values: 0.9993 (TS + chitosan + LDPE), 0.998 (TS + LDPE), 0.8146 (BS + chitosan + LDPE), and 0.9991 (BS + LDPE). Excluding the case of the bottom side coated with chitosan and LDPE, there is a good correlation between thickness values for WVTR and reciprocal LDPE. Furthermore, there is no significant difference for which side the coating was applied on, as far as it pertains to the water vapor barrier. The values seem to respond only to the LDPE thickness. This behavior was expected because the water absorption did not significantly improve when chitosan coating was applied. Typically, a coating that is a good barrier to water vapor gives Cobb values close to 1 g/m² when the treatment time is 3 min. In this study, the treatment time in the Cobb test was 1 min.

One additional test was carried out in which we measured the WVTR of both the plain paper and the chitosan-coated paper (bottom side). The thinnest LDPE coating was used in calculations, because it was clear that most of the barrier effect was imparted by the LDPE layer. The WVTR was 1218 g/m² per 24 h for the plain paper and 1166 g/m² for the chitosan-coated paper. These values demonstrate that the influence of the chitosan coating on water vapor barrier was negligible. These results were expected, based on a previous study [7]. However, the main reason for the high water vapor transmission rate was that cotasan did not form a film in the prepared samples.

Another issue that affects the barrier properties of a packaging material is pinhole density, which is characterized as the number of pinholes per unit area. **Table II** shows the pinhole densities of the LDPE extrusion-coated samples. Tested chitosan coatings did not provide a sufficient barrier to prevent pinholes in this test. The test liquid, turpentine, can penetrate through very small pinholes, so it correlates quite well with fat and grease permeation. Our results did not indicate that the pinholes would influence the water vapor barrier significantly. Chitosan slightly reduces the number of pinholes, when chitosan is coated on the bottom side. Samples coated with LDPE at the highest thickness did not show any pinholes.

Adhesion

Because chitosan was coated on A4 sheets and dried in an oven without restraint, the extrusion coating of sheets resulted in uneven coating weights and wrinkled sheets. The testing of adhesion was unreliable because of the free shrinkage of the sheets and the thickness variations of the coating. In further tests, chitosan will be coated and dried in a pilot line, where free shrinkage is

impeded and where it will be much easier to extrusion coat the chitosan-coated fiber web.

CONCLUSIONS

This preliminary study showed that chitosan coating adds value to paper. We found that certain mechanical properties of paper were enhanced as a function of chitosan pickup weight. Specifically, the bending resistance of the paper coated with citosan was substantially improved, while the MD tensile index also increased. However, more testing is needed to confirm these results, particularly when the chitosan coating is applied directly onto a paper web with an in-line coating unit. Furthermore, in future evaluations, thicker film coatings should be produced to create more uniform films and enable us to assess the influence of chitosan more reliably.

In water absorption values, some reduction as a function of chitosan coating content was observed. Improvement in the resistance to absorbing water was observed when the chitosan coating was applied to the top side of the paper. Chitosan coating did not improve the water vapor barrier. In future work, with regard to the barrier properties of chitosan coatings, thicker and more uniform layers should prove more interesting to study. Another interesting area to study is the adhesion between chitosan coating and common plastics, such as LDPE, polypropylene (PP), and polyethylene terephthalate (PET).

The barrier properties of chitosan coatings against odor and oxygen were not studied because the coatings probably would have been too thin and too nonuniform to give reasonable values in testing. The role of the coating in creating a barrier to oxygen and odor will be studied in future analyses. **TJ**

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INSIGHTS FROM THE AUTHORS

Our goal is to develop biodegradable polymer coatings for the paper and paperboard industry. We have studied other barrier dispersion coatings on paper, and chitosan is a promising new material in that area.

With natural polymers, controlled iteration of the process is always a challenge. This difficulty could be minimized with optimized process control and accurate documentation of results. Nevertheless, natural polymers can provide a functioning solution for various coating problems. It was surprisingly easy to implement and modify the coating process for chitosan.

For mills, the benefits are a general reduction in waste costs and a significant increase in producing environmentally friendlier products. For us, the next step is to make some pilot line runs with polymers, paying particular attention to the barrier against oxygen and aromas.

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