

EFFECT OF CHITOSAN ON PROPERTIES OF PAPER FOR PACKAGING

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The effect of chitosan additives on the mechanical and hydrophobic properties, and air permeability of paper sheets was investigated. As chitosan additives, molecular chitosan and nanochitosan were used. Molecular chitosan was obtained by dissolving chitosan in 1% acetic acid. Nanochitosan was obtained using a thermocatalytic destruction method. It has been established that chitosan additives improve the mechanical properties of paper sheets (tensile strength in dry and wet states, burst strength). In the case of molecular chitosan, tensile index in dry and wet states increases with increasing chitosan dosage till 2.5-3.0% and then remains constant. It can be explained by the fact that chitosan forms ionic bonds and polyelectrolyte complexes with hemicelluloses and cellulose. At the dosage of 2.5-3.0%, all possible ionic bonds are already formed and further chitosan can form only hydrogen bonds by amino groups with cellulose. In the case of micro-nanochitosan, micro-nanoparticles fill also the submicroscopic voids in the porous structure of paper and create additional bonds. Chitosan additives also improve the hydrophobic properties (decrease of water adsorption, and increase of wetting time) and air permeability of paper sheets.

Keywords: chitosan, micro-nanochitosan, tensile index, burst index, water adsorption, wetting time, air permeability

INTRODUCTION

Chitosan is a natural, biodegradable and non-toxic polymer, which is produced by deacetylation of chitin. Chitin is a structural element in the exoskeleton of crustaceans (such as crabs and shrimps), insects, some fungi and water-plants. A common method for the production of chitosan is the deacetylation of chitin using sodium hydroxide. Chitosan is a linear polysaccharide, composed of randomly distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine. Its molecular structure is similar to that of cellulose, but, in chitosan, C-2 hydroxyl groups are replaced by acetamido groups. Chitosan has high reactivity, stability to radiation, sorption ability, selectiveness, biocompatibility with living tissues and biodegradability. It is also bioinert, and has bacteriostatic properties, good adhesion, coagulation ability and immunostimulating

activity. Owing to these properties, chitosan can be used for different applications: in medicine, pharmacology, perfumery and cosmetics, in the food industry, the agriculture, the textile industry, for purification of water and in other fields.¹⁻⁸ In medicine and pharmacology, chitosan is used as a diluent or a filler, as a film former, as an antibacterial agent, an anti-cancer agent, an anticoagulant, an antifungal; it has fat blocking properties and antioxidant activity. In perfumery and cosmetics, chitosan is used for production of moistening creams, lotions, emulgators, and products for skin, hair and oral care. In the food industry, chitosan is applied as a viscosity regulator, a stabilizer, for dietary food, to reduce cholesterol. In agriculture, it is used primarily as a natural seed and fruit treatment and plant growth enhancer, and to protect plants against fungal infections and pests. In the textile industry,

chitosan, especially microcrystalline one, among other materials, is used as an impregnation agent for fabrics and knitted fabrics, a binding agent for non-wovens, and an auxiliary preparation for flame retardant textiles. It improves the textiles' mechanical properties, dyeability and electroconductivity, and affects the bacteriostatic and antimicrobial behaviour.

Chitosan is also widely used in the paper industry for improving the papermaking process and paper properties. Indeed, the molecular structure of chitosan is similar to that of cellulose, which promotes the creation of strong bonding.⁷ To improve the paper properties, chitosan is added in paper furnish,⁹⁻¹⁴ or chitosan and its derivative coatings are used.¹⁵⁻²⁸ In both cases, chitosan mainly improves the strength of paper sheets. It has been shown that addition of chitosan and its derivatives leads to improvement in the strength properties of unaged and aged paper sheets.¹⁰ Values of breaking length, obtained with the addition of chitosan and its derivatives into the pulp suspension are higher than those obtained by dipping paper in chitosan and its derivatives solutions, whereas the opposite trend is observed for the tear factor. More generally, it was shown that, by using chitosan in paper production, the mechanical properties were improved. Chitosan and its derivatives also improve the electrical, printing, barrier and antibacterial properties of paper.

At present, papers and boards are often used for packing of various objects and products. Therefore, it is important to obtain papers with properties suitable for this application, such as high strength in dry and wet states, low water absorption, and improved barrier properties.

The aim of this work was thus to investigate the effect of chitosan on the properties of paper and also the difference of behaviours between molecular and micro-nanochitosan. For this purpose, mechanical (tensile strength in dry and wet states, burst strength) and wettability (contact angle, wetting time and water absorption) properties, as well as air permeability, of the paper handsheets treated with chitosan were investigated.

EXPERIMENTAL

Furnish consisting of ECF bleached Kraft pulp from spruce (70%) and TCF bleached Kraft pulp from birch (30%) (Södra Cell AB) was used. Chitosan ("Bioprogress", Moscow region, Russia), obtained from exoskeletons of crustaceans, with a deacetylation

degree of 79% and a molecular weight of 310 kDa, was used for preparing chitosan solution in acetic acid and micro-nanochitosan gels.

Chitosan solutions (molecular chitosan) were prepared by dissolving chitosan in an aqueous solution of 1% acetic acid.

Chitosan micro-nanoparticles were obtained using a thermocatalytic destruction method developed at the Laboratory of Cellulose of the Latvian State Institute of Wood Chemistry.²⁹⁻³⁰ According to this method, chitosan was dissolved in a 0.7% hydrochloric acid solution and thermally treated at 102-106 °C during 5-6 h till it reached its dry state. Then, the resulting depolymerized chitosan was diluted in distilled water, precipitated at pH~9 with NaOH, filtered and washed out from hydroxide. As a result, gels containing chitosan micro-nanoparticles were obtained. By the laser distribution method, using a Zeta Nanosizer ZS 90 (Malvern Instruments Ltd, UK), it was established that most of the particles had a length of 400-500 nm.

Pulp was soaked in tap water for 4 h using a filter and disintegrated with a Lhomargy disintegrator for 10 min at 3000 rpm/min at a concentration of 2% (w/w). Pulp quantity was calculated to produce 10 paper sheets with a basis weight of 75 g/m² together with additives by decreasing the amount of added pulp. The dosage of molecular chitosan was of 1-7.5% and that of micro-nanochitosan of 2.5-20 (w/w, o.d.). For each dosage, the required amount of macromolecular chitosan was dissolved in 100 mL of a 1% acetic solution, but the micro-nanochitosan gel was mixed in 100 mL water by ultrasonification and added to the fibre suspension (2-2.2 L of suspension at 2%) under stirring with a Lhomargy device for 1 min at 3000 rpm/min. The addition of the chitosan solution was made without changing the pH of the fibre suspension, but, because of the acidic character of the added solution, the pH dropped from 7.2 to 6.7. The fibre suspension was then diluted to 0.2% (weight of fibre/weight of suspension) by tap water (pH changed to 7.0) and allowed to rest for 10 min, so that chitosan could adsorb onto pulp fibres. Paper sheets were made on a "Rapid Koethen" sheet former (Germany) (ISO 5269/2-1980 (E)). Drying was performed at 92 °C under vacuum.

Paper sheets were conditioned for 24 h at 23 °C and 50% relative humidity (RH) before testing.

Determination of paper sheet tensile index, [N m/g] (ISO 5269- 1:1979), and burst index, [kPa m²/g] (ISO 2758:1983), was carried out on a tensile tester "Frank-PTI" (Germany) under standard conditions (RH of 50%, temperature of 23 °C). The determination of the tensile index in the wet state was based on TAPPI Standard T 220 om-87, using a tensile tester "Frank-PTI" (Germany). Paper strips were immersed in deionized water. The contact time of the paper samples with water was of 2 min. Then, excess water was removed by placing a sample between two paper filters without pressure for 2 s. At least 9 parallel strips of

each sample for each parameter were tested, and all the data presented are the average values of these tests.

Contact angle [°] was measured in compliance with TAPPI standard method T558, using a dynamic contact angle analyser system OCA (Germany). The contact angle between a droplet of water and the sample surface was measured as a function of time. The volume of the droplet was 5 µL, and the contact angle was measured at a time interval of 20 ms. At least three strips of each sample were used, and all the data presented are the average of these tests.

Wetting time [s] was determined by using ultrasonic equipment from Müttek (Penetration Dynamic Analyser, PDA). The principle is based on the modifications of the intensity of ultrasonic waves passing through the tested paper, this modification depending on the interaction between paper and water. For this purpose, a sample of paper was placed in a sample holder, which was immersed in water. Ultrasonic waves were propagated through the sample, and the detector registered the ultrasonic intensity change as a function of time. Wetting time corresponds to the time needed for water to come into close contact with the paper surface.

Water adsorption [g/m²], based on TAPPI standard method T 441 om-98, was tested by a modified Cobb tester. A metal ring with a test area of 10 cm² and 10 mL of deionized water were used. Water was removed after 45 s and a blotting paper was put on the paper side in prior contact with water at 60 s exactly. The results were reported as an average of 5 measurements per each sample.

Air permeability (SCAN-P 60-87) tests were performed using a Bendtsen tester (Lorentzen & Wettre). The results were reported as an average of fifteen measurements.

RESULTS AND DISCUSSION

The obtained results showed that the retention of the added chitosan was of about 80-90%, if the pH of the fibre suspension was more than 6.9, and of 20-30%, if the pH was less than 6.2. In this study, only the results for which the fibre suspension pH exceeded 6.9 are presented.

The standard deviation of the obtained indices is shown in the figures.

Effect of chitosan additives on the mechanical properties of paper sheets

One of the most important paper properties for food packaging is tensile strength. Figure 1 shows how the tensile and burst indices in the dry state depend on the dosage of molecular chitosan and micro-nanochitosan. It can be seen that the tensile index increases when increasing the dosage of molecular chitosan till 2.5-3% and then remains constant. At a dosage of molecular chitosan of

2.5%, the tensile index increases by 15%. It can be explained by the fact that positively charged amino-groups of the added chitosan may form ionic bonds and polyelectrolyte complexes with pulp components, such as hemicelluloses, which contain negatively charged carboxyl groups.³¹ At a dosage of 2.5-3%, all possible ionic bonds are probably already formed and further additions imply that chitosan can be linked with cellulose only by hydrogen bonds or Van der Waals interactions. In the case of micro-nanochitosan, it also forms ionic and hydrogen bonds and polyelectrolyte complexes with cellulose and hemicelluloses. In addition, micro-nanoparticles may fill the submicroscopic voids of the porous paper structure during the sheet forming stage and may then create additional bonds during the drying stage. In this case, the tensile index gradually increases with increasing chitosan dosage. At a chitosan dosage of 20%, the tensile index of paper increases by 29%. The effect of the molecular and micro-nanochitosan dosage on the burst index is similar, although, after molecular chitosan dosage reaches 2.5%, the burst index continues to increase, but more slowly. However, other authors have found that molecular chitosan significantly improves the bending strength, tearing strength, Young's modulus, and elongation at break, while the tensile strength increases slightly.^{11,19,21,22} It is worth noting that, for all the results presented in this work, the mentioned dosages of chitosan correspond to the added amount and not to the retained quantity.

Figure 2 shows the impact of the dosage of molecular and micro-nanochitosan on the tensile index of paper sheets in the wet state. In this case, the effect of molecular chitosan on wet strength is more pronounced than that of micro-nanochitosan. When adding molecular chitosan (from 0 to 2.5%), the wet tensile index increases linearly from about 3 N m/g to 12.2 N m/g, which corresponds to an increase of 281% (see Fig. 2). Under the same conditions, micro-nanochitosan leads to an increase of 62% of the wet tensile index. This can be also explained by the formation of ionic bonds and polyelectrolyte complexes with hemicelluloses in the pulp, which are more stable in water than the bonds existing in untreated paper. Indeed, chitosan can form hydrogen bonds not only via OH-groups, but also via amino-groups. These bonds are stronger and are retained in water medium. The strength of hydrogen bonds in cellulose is thus of 21 kJ/mol, which is close to the strength of hydrogen bonds

in water (18 kJ/mol). In comparison, the strength of hydrogen bonds between the amino group and OH-group is of 29 kJ/mol, which is stronger than hydrogen bonds with water.³² It should be noticed that the measured wet strength may be

overestimated because of the short contact time between paper and water, as already mentioned. The improvement of the wet strength of paper using molecular chitosan was also observed by other authors.²⁴

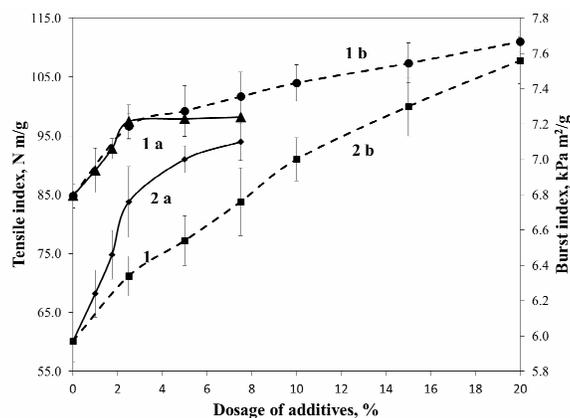


Figure 1: Tensile index in a dry state (1a, 1b) and burst index (2a, 2b) of paper sheets versus the additive dosage of molecular chitosan (a) and micro-nanochitosan (b)

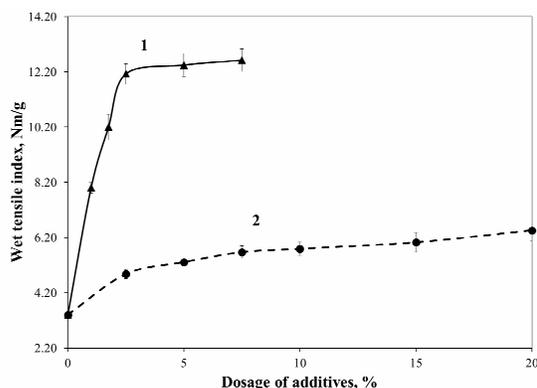


Figure 2: Wet tensile index of paper sheets versus the additive dosage of molecular chitosan (1) and micro-nanochitosan (2)

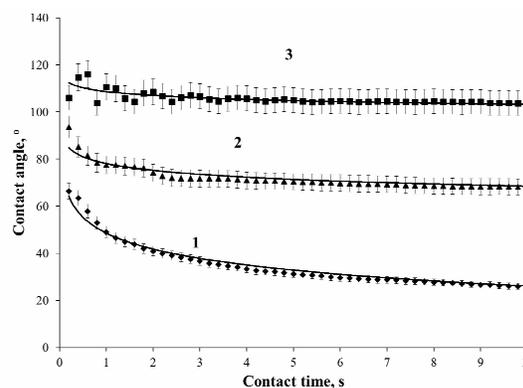


Figure 3: Evolution in time of contact angle between the water droplet and paper surface for paper sheets without additives (1) and with 7.5% micro-nanochitosan (2) and 2.5% molecular chitosan (3)

Effect of chitosan on wettability and air permeability of paper sheets

Wettability and water absorption properties are important for food packaging. For improving these properties, coatings and additives from fossil raw materials are usually applied. However, they hinder the recycling of paper and are not biodegradable. Therefore, it is important to improve the water stability of paper using natural polymers.

One of the more important wettability characteristics of paper is water contact angle. When a surface is hydrophobic, the contact angle

between a droplet of water and the surface is greater than 90°. A significant parameter for hydrophobicity is the time in which the contact angle remains above 90°. Figure 3 shows the change of the contact angle depending on time for paper sheets without additives, and with addition of micro-nanochitosan and molecular chitosan. The dosage of micro-nanochitosan and molecular chitosan was of 7.5% and 2.5%, respectively. It can be seen that chitosan increases the water contact angle because the hydrophobicity of paper sheets is increased. The contact angle is improved by molecular chitosan to a greater extent. Its value

remained above 100° for the testing period of time. After 10 s, the contact angle of paper sheets containing molecular and micro-nanochitosan was, respectively, ~ 4.4 times greater and ~ 2.8 times greater than the contact angle of paper sheets without additives. Nicu *et al.*²⁸ have established an increase of contact angle using alkyl-chitosan as paper coating materials. These coatings improved essentially the water barrier properties, which were positively influenced by the substitution degree and negatively by the alkyl chain length. The alkyl derivative with the shortest alkyl chain length and highest substitution degree led to the highest increase of contact angle (82.1%). In the same way, an increase in contact angle was observed by coating the paper with chitosan-palmitic acid emulsion or with a blend of chitosan and O,O'-dipalmitoylchitosan.²⁶

The wettability properties of paper sheets are also characterized by the wetting time. Figure 4 shows the dependence of wetting time, tested on ultrasonic equipment, on the dosage of additives for molecular chitosan and chitosan micro-nanoparticles. It can be seen that molecular chitosan increases the wetting time to a greater extent. In this case, wetting time essentially increases with increasing dosage of molecular chitosan till 2.5% and then changes less. In the case of micro-nanochitosan, wetting time increases with increasing chitosan dosage till 10%.

Figure 5 shows how the water adsorption (Cobb index) depends on the chitosan dosage.

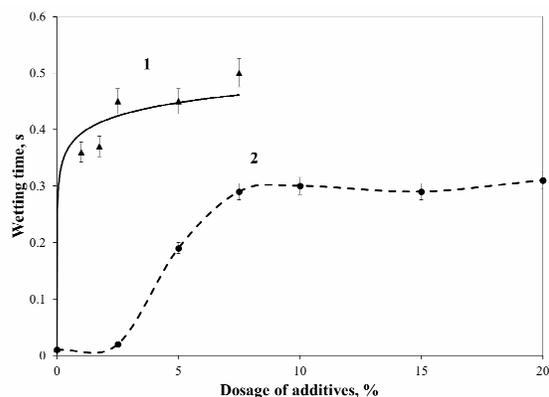


Figure 4: Wetting time of paper sheets versus the additive dosage of molecular chitosan (1) and micro-nanochitosan (2)

Under our experimental conditions, a molecular chitosan dosage of 2.5% induces a decrease of the water adsorption close to 25%. For further increasing chitosan dosage, water adsorption decreases insignificantly. With increasing chitosan micro-nanoparticle dosage, water adsorption decreases gradually. At a micro-nanochitosan dosage of 7.5%, Cobb water adsorption decreases approximately by 15%. A comparison of our results with those obtained by other investigators revealed that Reis *et al.*²³ also found that molecular chitosan decreases the Cobb index of paper. It was found that the application of a chitosan coating (3.5 g m^{-2} , wet basis) on Kraft paper sheets provides a significantly lower Cobb index (35%), as compared to uncoated Kraft paper. Kjellgren *et al.*¹⁶ have established that the effect of chitosan on the Cobb index depends on the air permeance of basic paper. At a low air permeance, chitosan coatings increase the Cobb index, while at a high air permeance, chitosan decreases the Cobb index. The authors explain it by the fact that, in the first case, the water sorption is predominantly controlled by fibre sorption and the sorption by chitosan coatings is higher than that for the cellulose fibres in the base paper. In the second case, the decrease in the Cobb value is probably due to the clogging of the pores in the paper by the coating, which reduces the pore sorption. It has been established²⁸ that, using alkyl-chitosan coatings with a short alkyl chain and a high substitution degree, they significantly decrease the paper Cobb index (82.6%).

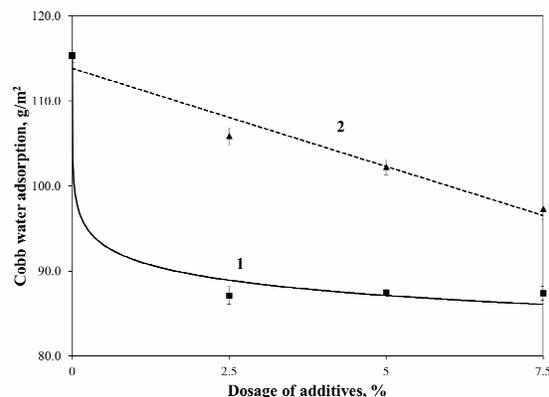


Figure 5: Cobb water adsorption of paper sheets versus the additive dosage of molecular chitosan (1) and micro-nanochitosan (2)

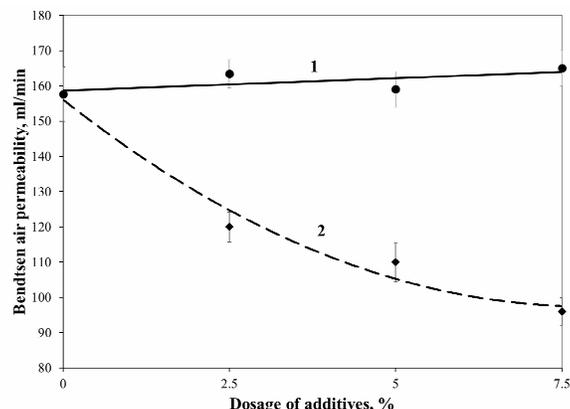


Figure 6: Air permeability of paper sheets versus the additive dosage of molecular chitosan (1) and micro-nanochitosan (2)

Another important property of paper sheets is air permeability. Figure 6 shows that chitosan micro-nanoparticles decrease the air permeability to a great extent. Micro-nanochitosan can accumulate onto the paper surface during sheet formation, and it modifies the smoothness and porosity at the surface. At the micro-nanochitosan dosage of 7.5%, air permeability decreases by 35%. In the case of molecular chitosan, air permeability of paper sheets practically does not change. However, other investigators have found that air permeability decreases by using molecular chitosan coatings.^{16,19,23} Air permeability decreases with increasing chitosan coating weight till reaching the weight at which the pores in the base paper are sealed and a continuous chitosan film begins to develop.

CONCLUSION

The effect of molecular chitosan and micro-nanochitosan on the mechanical, hydrophobic and barrier properties of paper sheets was investigated.

The obtained results showed that the retention of the added chitosan was of about 80-90%, if the pH of the fibre suspension was more than 6.9, and of 20-30%, if the pH was less than 6.2. In this study, only results for a fibre suspension pH exceeding 6.9 are presented.

Chitosan improves the mechanical properties of paper sheets. Micro-nanochitosan increases the tensile index in a dry state to a greater extent. This can be explained by the fact that micro-nanoparticles fill the submicroscopic voids of the porous paper structure and create additional bonds. In a wet state, the effect of molecular chitosan is greater.

Chitosan additives improve paper water retention and barrier properties (increase the contact angle between the water droplet and paper surface, increase the wetting time and decrease the water adsorption and air permeability).

Chitosan additives can be used for obtaining paper for packaging with improved properties – higher tensile and burst strength, higher hydrophobicity, and smaller water absorption and air permeability. For obtaining paper with higher strength properties and lower air permeability, it is better to use micro-nanochitosan additives.

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