

EFFECT OF MOLECULAR CHITOSAN ON RECOVERED PAPER PROPERTIES DESCRIBED BY A MATHEMATIC MODEL

LAURA ANDZE,^{***} JURIS ZOLDNERS,^{*} LINDA ROZENBERGA,^{***} INESE SABLE,^{*} MARITE SKUTE,^{*} MARIANNA LAKA,^{*} LINDA VECBISKENA,^{*} MARTINS ANDZS^{*} and ANDRIS ACTINS^{**}

^{*}*Latvian State Institute of Wood Chemistry, 27, Dzerbenes Str., LV-1006 Riga, Latvia*

^{**}*Department of Physical Chemistry, University of Latvia, 1, Jelgavas Str., LV-1004, Riga, Latvia*

^{***}*P2i, 127, Olympic Avenue, Milton Park, Abingdon, Oxfordshire, UK*

✉ *Corresponding author: Laura Andze, laura.andze@gmail.com*

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In this work, the effect of three different molecular chitosans on the properties of paper obtained from recovered paper has been studied and experimental data have been explained by mathematical modelling. The physical-mechanical properties, such as dry and wet strength, as well as water sorption of paper, have been analysed. The results showed that the molecular chitosan additive improved the tensile index of dry paper by approximately 15-25%, the wet strength – up to 9 times. The optimum quantity of chitosan was determined to be 2.5% of the fiber weight, which agrees with the fibre sorption capacity of chitosan, calculated by the function of the mathematical model for sorption. A higher amount of the chitosan additive no longer significantly improves the properties of a fibre sheet.

Keywords: chitosan, recovered paper, tensile index, wet strength, water sorption, mathematic model

INTRODUCTION

Every year, several hundred million tons of paper are produced.¹ One of the industries increasingly using paper as a packaging material is the food industry. Paper packaging materials include paper with aluminium and polymer coatings, paper bags, cardboard boxes, packaging made from moulded paper fibres, paper cups and plates *etc.*²⁻⁴ Cellulose and wood pulp based materials are environmentally friendly, but the additives intended to improve paper properties are the main source of pollution in waste paper.⁵ Paper additives are used to help the paper production process or to improve the final properties of products. The use of paper additives was introduced in the very first years of paper manufacturing. Nowadays, the additives used for improving paper properties and paper coatings are most often produced from fossil raw materials. A great number of wet strength agents are formulated based on carcinogenic formaldehyde-releasing or organochlorine polymers, causing environmental pollution and harmful effects on health.

Paper additives

Starch and its derivatives (cationic, anionic, hydroxyalkyl starch and starch esters) and cellulose derivatives are the most commonly bio-based additives used to improve the mechanical strength of paper under dry conditions.^{6,7} Other natural compounds, such as hemicelluloses⁸ (galactomannan and xyloglucan) and natural resins,⁹ have been studied as additives to improve the mechanical properties of paper. These types of additives have given equally good results as those achieved with starch additives, but at higher costs because they are more expensive and more difficult to obtain.^{10,11} However, starch and cellulose derivatives cannot provide other paper properties that are requested for specific applications. The main limitation of starch/cellulose derivatives consists in their sensitivity to water and microbial attack. The wet strength can be improved by synthetic polymers as wet end or coating additives,²⁻¹⁴ such as the polyethylene-imide, polyamine-polyamide-epoxy or polyamine-polyamide-epichlorohydrin resins, and polyamine-polyamide-polyurethane copolymer resin.^{11,14-16} These additives and coatings make recycling or composting such packaging materials difficult.⁵

Chitosan

Chitosan is a linear polysaccharide composed of connected β -(1-4)-D-glucosamine and N-acetyl-

D-glucosamine molecules.¹⁷ These molecules are similar to the cellulose molecules, with the exception of the second carbon atom, where there is an amino group instead of the hydroxyl group.¹⁸ Research on the use of chitosan in paper production is developing fast due to the new and cheaper separation methods and related industrial developments.^{6,19-22} In recent studies, more attention has been given to the use of chitosan derivatives to improve paper properties,^{12,19,23,24} or its use in coatings of the paper surface as an agent improving barrier properties.²⁵⁻³⁰ Chitosan is a polyelectrolyte with active hydroxyl and amino groups that may participate in various reactions. It is capable of forming complex compounds with the ions of transition metals and polyelectrolyte complexes with negatively charged molecules.^{31,32} The pKa value of chitosan is ~6.5, which means that chitosan protonates in an acidic environment (pH below 6.5), easily binds to negatively charged molecules, ions and compounds.³³ Chitosan is a non-toxic, bio-adhesive natural polymer that is capable of decomposing in the environment, presenting antibacterial, antifungal, antitumoral activity and biocompatibility both in tissue and bones.^{32,34} Chitosan is widely used in the medicine and food industry, as well as in agriculture, in order to treat seeds with the aim to facilitate growing. One of the oldest applications of chitosan is in water treatment, since it is able to bind colloidal particles, making easier their separation afterwards.³⁵ Since the amino group of chitosan can form an ionic bond with the carboxyl groups existing in cellulose, it was investigated as an agent for improving the paper wet strength. The amino groups in chitosan can form hydrogen bonds with the hydroxyl group of cellulose on the same principle as the amino group of the epoxy resin. The hydrogen bonds between the nitrogen of the amino group and the hydrogen of the hydroxyl group give paper an extra strength.³⁶ Chitosan fulfils the main requirements of a paper additive: it easily dissolves in aqueous solutions of organic acids, and can be straightforwardly used in paper production; it is compatible with the cellulose surface and can form hydrogen bonds; it has a sufficiently high molecular weight to form inter-fibre bonds; it possesses film-forming properties; it contains an amino group that can build strong bonds with cellulosic fibres; its linear structure is spatially similar to that of the cellulose, providing better mutual binding; it is non-toxic, biodegradable; it does not cause issues in the paper recycling process.³⁷

Research aim

The aim of the present research is to develop a paper material with improved physical-mechanical properties and describe the effect of molecular chitosan on paper properties by a mathematical model.

EXPERIMENTAL

Materials

Paper recovered for recycling, representing used newspapers, magazines, carton boxes and office papers, was received from producers of egg boxes SIA V.L.T. in Valmiera, Latvia. Three different chitosan types with the polymerisation degree between $2 \cdot 10^5$ and $3.5 \cdot 10^5$ were used as the additives to obtain handsheets from recycled fibres. The characterization of chitosan is summarized in Table 1. 1% chitosan solutions (molecular chitosan) were prepared by dissolving chitosan in an aqueous solution of 1% acetic acid.

Table 1
Characterization of chitosan samples

Sample symbol	Chem	An	Tech
Producer	Bioprogress, Russia	Sigma Aldrich, Germany	G.T.C. Union Group Ltd., China
Purity	Chemically pure	Analytically pure	Technically pure
Degree of deacetylation	79%	>90%	>70%
Polymerisation degree	$3 \cdot 10^5$ - $3.5 \cdot 10^5$	$2 \cdot 10^5$ - $3 \cdot 10^5$	$2 \cdot 10^5$ - $2.5 \cdot 10^5$

Preparation of paper handsheets

An amount of paper recovered for recycling necessary to obtain 10 handsheets of 75 g m^{-2} was disintegrated according to the ISO 5263 standard in a disintegrator (Frank-PTI, Austria), as 1% fibre-water suspension. A chitosan solution of 1% concentration was added to the fibre suspension, with varying weight ratios (dry chitosan weight relative to an absolutely dry fibrous mass, expressed as percentage, w/w, %) was added to the fibre suspension. The suspension was mixed with chitosan by stirring at 3500 rpm for 1 minute in order to prepare the paper stock. Then, the obtained paper stock of pH 5.5 was diluted with filtered tap water up to ten litres (pH increased to 7-7.5): paper samples (handsheets) were prepared on a laboratory paper machine (RapidKöthen, PT, Austria) by using 1 L of paper stock suspension for each sheet, corresponding to a grammage of 75 g m^{-2} (according with ISO 5269/2-1980 standard) and to an average thickness of 0.06-0.07 mm. The wet sheets were dried on the same paper machine, under vacuum, at $92 \text{ }^\circ\text{C}$ for 10 minutes. Before testing, the paper samples were conditioned for 24 h, at $23 \text{ }^\circ\text{C}$ and 50% relative humidity (RH), according to TAPPI T 220 standard.

Analysis of paper samples

Mechanical strength

The tensile strength of the paper samples was measured in both dry and wet conditions, using a Tensile tester F81838 (Frank, Germany) according to the standard DIN EN ISO 1924-2.

Cobb test

Measurements of water absorption were carried out according to the T 441 om-98 method (TAPPI standard), using a Cobb measuring device (Lorentzen & Wettre, Sweden). The area of the sample in contact with water was 100 cm^2 , the volume of deionized water was 100 mL ($18 \text{ }^\circ\text{C}$), and the testing time was 60 s.

RESULTS AND DISCUSSION

All the respective data are presented as the added chitosan amount (% of total fibre mass) and not the retained quantity.

The presented results with regard to mechanical properties are the calculated average values of 5 fibre sheets. In order to measure the tensile strength in dry and wet conditions and calculate water absorbency, 3 measurements for each handsheet were made. All the results obtained in the study were summarized in graphs and tables, and the statistical evaluation of the obtained results was carried out.

Mathematical modelling of tensile index and water sorption

When processing the data, it was observed that the results could be described with the exponential equation “-e-x” using 3 parameters. Equation 1 describes the graph:

$$y = B - (B - S)e^{Kx} \quad (1)$$

where S – the initial value; B – the end value; K – constant of the function.

EXCEL Data Solver was used to optimise the parameters of the functions and obtain the lowest standard deviation of the function Sn. To determine whether it is reasonable to describe the results by the exponential equation, the weighted average standard deviation value of two linear functions was calculated and compared with the value of the standard deviation of the exponential function. A comparison of standard deviations can be seen in Table 2. The values of the standard deviations of the calculated functions (exponential and two linear functions) are very similar, but in Figure 1, it can be seen that the equation of the exponential function does not visually accurately describe the experimental results on the dependence of paper properties on the amount of added chitosan. The highest deviation is noted at the point where the addition of chitosan no longer significantly affects the changes of paper properties. For this reason, the use of the exponential function is not justified.

When searching for an appropriate mathematical model, the most suitable one was decided to be based on the chemical sorption of chitosan on the surface of fibres. The sorption equation of Langmuir contains selected parameters, which makes it possible to describe the results of this study with one function.

Table 2

Comparison of standard deviations of different mathematical functions used to describe experimental data

Parameter to be measured	Chitosan type and pH of fibre suspension	Sn exp	Sn lin	Sn ads
Dry tensile index, Nm g ⁻¹	Chem, pH 4.5	0.5	0.5	0.3
	Chem, pH 7.5	0.8	0.7	0.6
	An, pH 7.5	0.8	0.8	0.8
	Tech, pH 7.5	0.9	0.8	0.6
Wet tensile index, Nm g ⁻¹	Chem, pH 4.5	0.4	0.3	0.3
	Chem, pH 7.5	1.0	1.0	0.5
	An, pH 7.5	1.1	1.1	0.3
Cobb 60 index, g m ⁻²	Tech, pH 7.5	1.1	1.0	0.5
	Chem, pH 4.5	3	3	1.0
	Chem, pH 7.5	5	4	4
	An, pH 7.5	9	9	0.2
	Tech, pH 7.5	3	3	3

Sn exp – standard deviation of exponential function; Sn lin – average standard deviation of two linear functions; Sn ads – standard deviation of adsorption mathematic model function

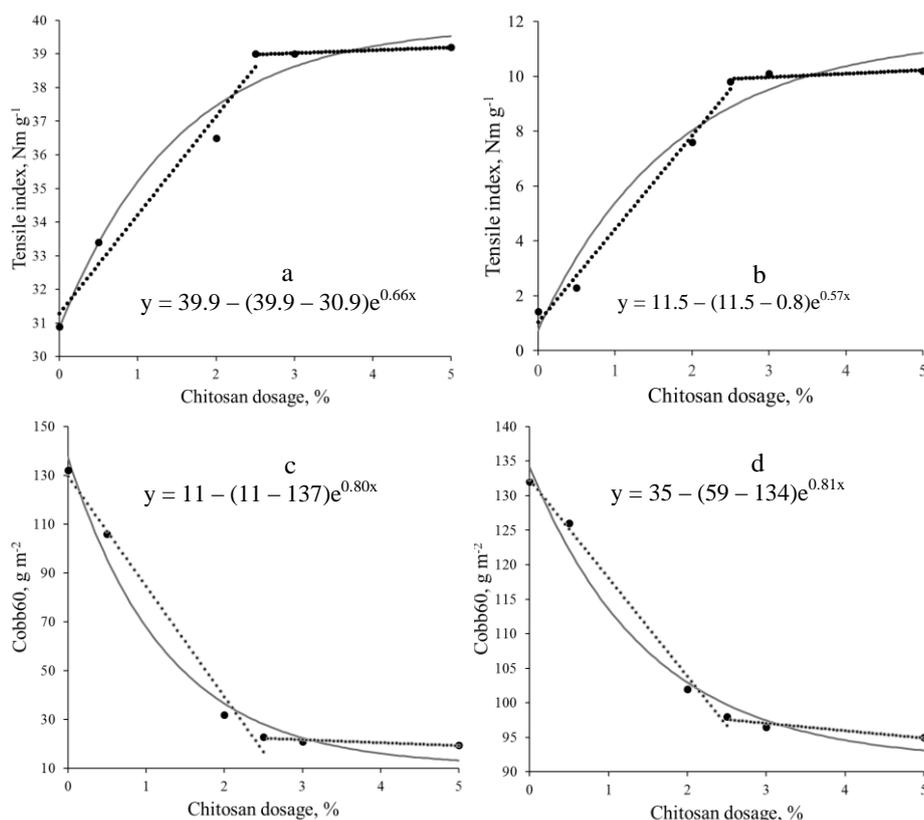


Figure 1: Examples of exponential functions and two linear functions for describing experimental data: a) dry tensile index Chem, pH 7.5; b) wet tensile index Tech, pH 7.5; c) Cobb 60 An, pH 7.5; d) Cobb 60 Chem, pH 4.5

The retention of chitosan in fibres depends not only on the sorption of chitosan on cellulose fibres, but also on its ability to create a film between the fibres of cellulose. A chitosan film develops due to the formation of hydrogen bonds between the molecules of chitosan; these bonds are the same as the hydrogen bonds between the molecules and the fibres of cellulose. For this reason, the formation of films does not significantly improve the properties of fibre sheets, especially in a wet condition. Changes in the properties of fibre sheets are ensured by the ability of chitosan to form strong chemical bonds with the fibres of cellulose. The preparation of handsheets was carried out in water medium,

where cellulose is a suspension of fibres and the added chitosan is a solution. It can be assumed that there is sorption of chitosan from the solution to the surface of fibres. The sorption of solution on a surface of solid substances is described by the Langmuir model (Eq. 2):

$$a = \frac{a_{oo}KC}{1+KC} \quad (2)$$

where a – the sorbed amount of chitosan, %; a_{oo} – the maximal sorption capacity, %; K – sorption constant; C – steady-state concentration of chitosan, $g L^{-1}$.

The balance equation of sorption is as follows:

$$a * m + V * C = x * m \quad (3)$$

where a – the sorbed amount, %; m – mass of paper pulp, g ; C – steady-state concentration of chitosan, $g L^{-1}$; V – volume of the reaction, L ; x – the weight ratio % of the added chitosan to pulp.

For further calculations, the parameter P or ΔP is used, which describes the measured property difference between B – the end value, and S – the initial value. Visual description of parameter P is shown in Figure 2. $P = [N / m * g]$ in the case of tensile index and $P = [g / m^2]$ in the case of water absorption. The sorbed amount a and the maximal sorption capacity a_{oo} can be described as:

$$a = \frac{P}{\alpha} \quad (4)$$

where a – the sorbed amount, %; P – parameter of measured property, N/m^*g or g/m^2 ; α – constant of equation transformation, N/m^*g or g/m^2 .

Equation 4 is placed in the balance equation of sorption $a * m + V * C = x * m$. Conversion 5 is made to express equilibrium concentration:

$$\frac{P}{\alpha} * m + V * C = x * m \quad (5)$$

$$V * C = xm - \frac{P}{\alpha} m$$

$$C = \frac{m}{V} \left(x - \frac{P}{\alpha} \right)$$

The equation of Langmuir $a = \frac{a_{oo}KC}{1+KC}$ can be described as $P = \frac{P_{oo}KC}{1+KC}$. For further calculations, the equation of Langmuir and the balance equation of sorption are combined in Equation 6:

$$P = \frac{P_{oo} \frac{Km}{V} \left(x - \frac{P}{\alpha} \right)}{1 + \frac{Km}{V} \left(x - \frac{P}{\alpha} \right)} \quad (6)$$

$$P = \frac{P_{oo} Km \left(x - \frac{P}{\alpha} \right)}{V + Km \left(x - \frac{P}{\alpha} \right)}$$

$$PV + Km x P - \frac{Km P^2}{\alpha} = P_{oo} x - \frac{P_{oo}}{\alpha}$$

$$\frac{P^2}{\alpha} + P_{oo} x - \frac{P_{oo}}{\alpha} P - x P - \frac{PV}{Km} = 0$$

$$P^2 + \alpha P_{oo} x - P_{oo} P - \alpha x P - \alpha \frac{PV}{Km} = 0$$

The resulting equation is derived after P :

$$P = \frac{P_{oo} + \alpha x + \frac{\alpha V}{Km} - \sqrt{\left(P_{oo} + \alpha x + \frac{\alpha V}{Km} \right)^2 - 4 \alpha x P_{oo}}}{2} \quad (7)$$

P_{oo} is replaced by $\alpha * a_{oo}$; and $\frac{V}{Km}$ can be described as r , since the mass of the cellulose and the volume of reaction do not change (equation constant) in all the experiments. Equation 8 is obtained:

$$y = S + \frac{\alpha a_{00} + \alpha x + \alpha r - \sqrt{(\alpha a_{00} + \alpha x + \alpha r)^2 - 4\alpha x a_{00}}}{2} \quad (8)$$

$$y = S + \alpha \frac{a_{00} + x + r - \sqrt{(a_{00} + x + r)^2 - 4\alpha x a_{00}}}{2}$$

The EXCEL Data Solver was used, in order to optimise parameters of the functions and obtain the lowest standard deviation of the function Sn: a_{00} – sorption capacity of fibres, %; r – constant of the function, containing the inverse quantity of the sorption constant $r = \frac{v}{km}$; α – constant of the function, $Nm\ g^{-1}$ or $g\ m^{-2}$; S – initial value, $x = 0$.

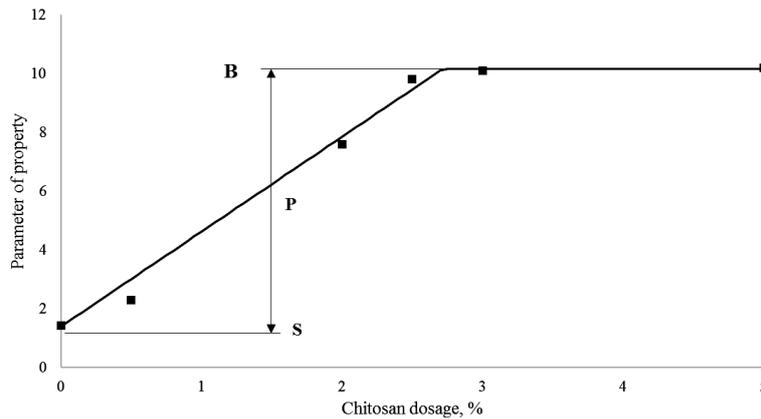


Figure 2: Visual description of parameter P

Table 3

Parameters of descriptive mathematic model function for the relationship between handsheet properties and chitosan dosage

Parameter to be measured	Chitosan type and pH of fibre suspension	α , $Nm\ g^{-1}$ or $g\ m^{-2}$	a_{00} , %	r	S
Dry tensile index, $Nm\ g^{-1}$	Chem, pH 4.5	2.20	2.92	0.01	31.10
	Chem, pH 7.5	2.90	2.66	0.0	31.30
	An, pH 7.5	3.00	2.67	0.00	31.60
	Tech, pH 7.5	2.70	2.87	0.00	31.15
Wet tensile index, $Nm\ g^{-1}$	Chem, pH 4.5	1.80	2.28	0.04	1.5
	Chem, pH 7.5	3.70	2.71	0.0	1.2
	An, pH 7.5	5.50	2.23	0.01	1.2
	Tech, pH 7.5	3.40	2.68	0.0	1.0
Cobb 60 index, $g\ m^{-2}$	Chem, pH 4.5	-15.8	2.35	0.017	133
	Chem, pH 7.5	-34.6	2.53	0.005	128
	An, pH 7.5	-53.2	2.13	0.016	132
	Tech, pH 7.5	-30.3	2.17	0.019	129

a_{00} – sorption capacity of fibres, %; r – constant of the function, containing the inverse quantity of the sorption constant $r = \frac{v}{km}$; α – constant of the function, $Nm\ g^{-1}$ or $g\ m^{-2}$; S – initial value

According to Table 3, the maximum sorption capacity of the fibres ranges from 2.1 to 2.9%, which characterizes the chitosan and pulp ratio, the sorption on the fibre surface and the improvement of the papersheet properties. The average fibre sorption capacity is $2.62 \pm 0.12\%$ of chitosan relative to the pulp. Graphic images of the function (Figs. 4-6) show that the addition of more than 2.5-2.6% of chitosan to the pulp is not economically justifiable.

Effect of chitosan additives on the mechanical properties of paper

Figure 3 shows the effect of chitosan additives on the value of the tensile index in dry conditions. The increase of the tensile index by 30%, compared to the control sample, matches the increase of chitosan (0-2.5% of pulp), and agrees with the results of other authors.³⁹ In the above-mentioned

literature, the amount of 1% chitosan relative to the pulp mass was added to the handsheet, without considering a higher quantity. According to the data, the value of the tensile index depends on the dosage of the chitosan additive of 0-2.5% to the pulp, but a higher dosage of chitosan does not affect the increase of the tensile index, the results remaining the same as those for the virgin cellulose samples.^{40,41} This can be explained by the fact that, at the dosage of chitosan of 2.5%, the chitosan amino groups have formed the maximum possible chemical bonds – ionic bonds with the carboxyl groups of cellulose, and the hydrogen bonds with the hydroxyl groups of cellulose, and polyelectrolyte complex with hemicelluloses (found in cellulose in small amounts) and paper additives. Further addition of chitosan promotes only the formation of hydrogen bonds between the hydroxyl groups of chitosan and cellulose and the formation of the chitosan film between the fibres of cellulose, which does not contribute to improving the properties of the handsheets. Chitosan with the highest degree of deacetylation (90%) provides the highest increase in the value of the tensile index, as there are more free amino groups able to form chemical bonds with the fibres of cellulose. The studies of other authors imply that molecular chitosan improves Young's modulus, the bending and tearing strength, and elongation at break, but the tensile strength is improved slightly.^{9,12,13,42}

According to Figure 4, analytically pure chitosan (degree of deacetylation 90%) at pH 7.5 in the papermaking process improves the wet strength 9.3 times, and 7.3 times if technical grade chitosan (degree of deacetylation 70%) is used (the dosage of chitosan is 2.5% of pulp mass). The tensile index depends on the dosage of chitosan to pulp in a range from 0 to 2.5%. A higher amount of chitosan does not significantly affect the value of the tensile index in a wet condition. An improvement in the paper wet strength of the handsheets using molecular chitosan has been reported by other authors as well.¹⁵

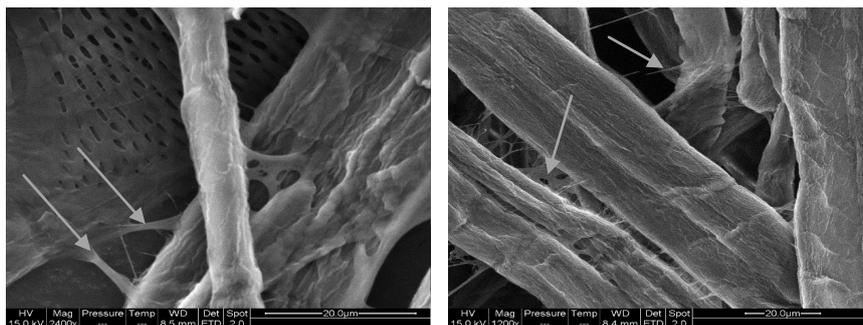


Figure 3: SEM images of cellulose fibers with adsorbed molecular chitosan at 3% chitosan dosage: a) 2400x; b) 1200x

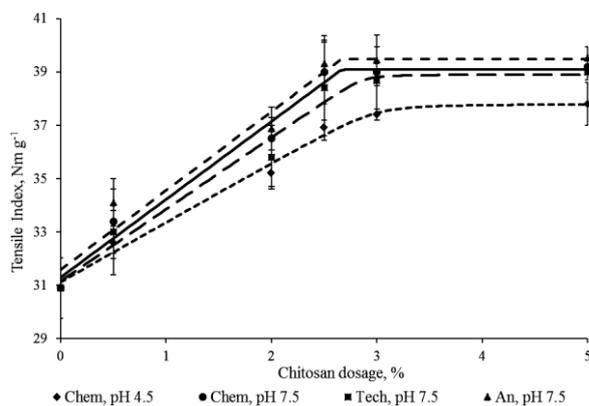


Figure 4: Dry tensile index *versus* chitosan dosage; points show experimental data, lines – the description of experimental data by mathematical modelling

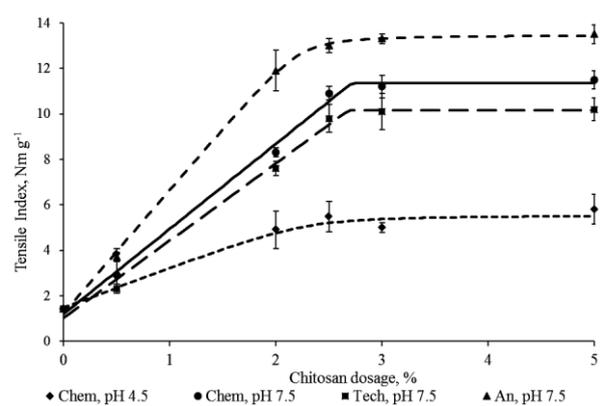


Figure 5: Wet tensile index *versus* chitosan dosage; points show experimental data, lines – the description of experimental data by mathematical modelling

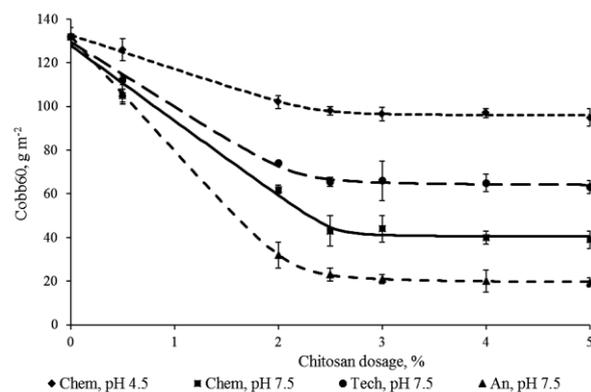


Figure 6: Water absorption capacity (Cobb₆₀ index) versus chitosan dosage; (points show experimental data, lines – the description of experimental data by mathematical modelling)

Effect of chitosan addition on water sorption of paper

The water sorption of the handsheets formed in a slightly alkaline environment depends on the dosage of chitosan added to the pulp in amounts of 0-2.5% (Fig. 5). A higher dosage of chitosan does not significantly affect the values of water sorption. The chitosan additive during the production of handsheets in a slightly alkaline environment decreases water sorption by 55-85%, depending on the type of chitosan. Chitosan with a higher degree of deacetylation decreases the water sorption of the handsheets better. In the studies of other authors, the evolution of water sorption as a function of the content of chitosan for coating the surface of paper has been evaluated.^{19,26,28} In the afore-mentioned literature, the water sorption value of the control sample was similar to that used in our study (~115 g m⁻²), and the addition of the chitosan coating decreased the water sorption to 90 g/m²;¹⁹ this value is lower than the results found in our research. It can be concluded that chitosan coating on paper surface affects the amount of water sorption less than the chitosan additive in the matrix of cellulose fibres.

CONCLUSION

The addition of molecular chitosan improves the wet strength of the paper 7-9 times and the mechanical strength by 20-30%, while decreasing the water sorption by 50%-80%.

The best mathematical model function was found to describe the experimental data on the effect of chitosan addition on paper properties.

The fibre sorption capacity of chitosan (~2.5%) was calculated using the mathematical model for sorption, and it corresponds to the experimentally observed optimal chitosan dosage on pulp.

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