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Packaging-related mechanical and barrier properties of pulp–fiber–chitosan sheets

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Abstract

In order to investigate ways of incorporating an oxygen- or air-barrier component, in this case chitosan or chitosan-acetic acid salt (chitosan salt), at an early stage in the paper-making process, sheets of chitosan and pulp fiber were produced in a hand sheet mould or solution cast in petri dishes. Some sheets were buffered in an alkaline solution, in order to reduce the moisture sensitivity. The sheets were characterized with respect to air permeance, oxygen permeability, fracture stress and strain, young's modulus and moisture content. The addition of the chitosan solution to the pulp slurry led to a substantial loss of fiber and chitosan through the wire screen and consequently a low grammage and high sheet porosity and air permeance. Forming a wet pulp fiber sheet before introducing the chitosan solution increased the grammage and the amount of remaining chitosan, the latter revealed by infrared spectroscopy. In addition, pressing the sheets before drying reduced the porosity and the air permeance. Air mixing, included in conventional laboratory sheet making, yielded a more heterogeneous sheet and inferior mechanical and barrier properties. In general, the paper sheets prepared in the hand sheet mould became weaker, softer and less ductile with increasing content of chitosan. Only solution casting in petri dishes resulted in good barrier properties. Scanning electron microscopy showed that holes were absent in this case. In addition, optical microscopy and infrared spectroscopy revealed that the chitosan-salt formed a continuous phase and that it was uniformly distributed in the sheet. Interestingly, the problem of shrinkage when chitosan salt sheets are buffered for improved high-moisture gas-barrier properties, was reduced significantly by the restraining action of the pulp fibers.

Keywords: Pulp fiber; Chitosan; Blends; Mechanical properties; Barrier properties; Moulding; Casting

1. Introduction

An increase in the environmental awareness of the customer has resulted in a demand that synthetic packaging polymers be replaced with renewable and biodegradable materials. Several different renewable materials have been studied for packaging applications, but only a few are on the market today. The most common renewable packaging materials are cellulose-based, including corrugated board, paperboard and paper. These have, however, usually poor gas- and moisture-barrier properties. Chitosan-acetic acid salt films have excellent gas-barrier properties, and are interesting oxygen-barrier materials in dry conditions.

Chitin, the original source of chitosan, is the load-bearing component in the shells of exoskeleton fishes and in the cell walls of molds, fungus, insects, krill, zooplankton, etc. (Jeuniaux, Voss-Foucart, & Bussers, 1989, Poulicek, Voss-Foucart, & Jeuniaux, 1986). After purification and derivatization, chitosan can be solved in water at pH$<$6.2 and solution-cast to films (Chenite, Buschman, Wang, Chaput, & Kandani, 2001).

Chitosan has not only good gas-barrier properties but also other interesting properties, indicated by the many potential applications. It can be used as a clarifying agent in juices and as an additive to animal feed (Knorr, 1991; Luyen & Rossbach, 1992; McCurdy, 1992; Weiner, 1992). Since it has anti-bacterial and fungicidal properties, it is suitable to mix into soil in order to protect roots of seed from nematodes and fruits from fungi (Luyen & Rossbach,

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1992; Outtara, Simard, Piette, Bégin & Holley, 2000; Sandford, 1989). Chitosan coatings on paper, paperboard and cellophane have been considered for anti-microbial or medical purposes (Domszy, Moore, & Roberts, 1985; Ho et al., 2003; Hosokawa & Nishiyama, 1988; Krasavtsev, Maslova, Degtyareva, Bykova, & Noudga, 2002).

Other applications include the treatment of glass-boards to increase their wettability and as an additive in adhesives, in photographic films and in various kinds of fiber treatment (Allan, Carroll, Hirabayashi, Muvundamina, & Winterown, 1989; Laleg & Pikulik, 1991; Lower, 1985; Struszczyk, Wawro, & Niekraszewicz, 1992; Wei & Hudson, 1992). Chitosan in combination with cellulose increases the mechanical strength of paperboard, has anti-electrostatic effects on cloth and promotes the dyability of paperboard (Allan et al., 1989; Luyen & Rossbach, 1992; Makino & Hirata, 1997; Struszczyk & Kivekäs, 1990). The printability of paper increases with the addition of chitosan due to the fact that the paper surface becomes smoother (Thomson, 1985). A similar effect has also been observed for chitosan-coated cotton fibers, where the chitosan also increases the adsorption capacity of the fiber, a useful property in medical drug supply (Liu, Nishi, Tokura, & Sakairi, 2001). Chitosan has been blended with micro-crystalline cellulose to obtain coatings and gels for medical textiles and for waste water treatment (Riedel & Taeger, 1999). Chitosan can also be used as a sorbant for lead cations from recycled wool-based nonwovens (Radetic, Jocic, Jovancic, Thomas, & Petrovic, 2003). Domszy et al. (Domszy et al., 1985) observed that the rate of adsorption of chitosan onto cotton fibers increased with decreasing chitosan molar mass.

Chitosan films are sensitive to water, like many synthetic oxygen-barrier polymers. Chitosan-acetic acid salt films are soluble in water unless they are buffered in an alkaline solution, but the buffering operation leads to substantial film shrinkage (Gällstedt & Hedenqvist, 2004). However, in the presence of the pulp fibers, the shrinkage is expected to be less. If chitosan was mixed with pulp fibers, it might be possible to enhance the gas-barrier properties, or decrease the air permeance, of paper sheets. Using a chitosan solution, it might be possible to introduce the barrier component early in the papermaking process and thus eliminate additional lamination steps with an oxygen- or air-barrier material.

Blends of different kinds of derivatized cellulose and chitosan have been studied earlier. Nakamura et al. (Nakamura, Kinoshita, Hatakeyama, & Hatakeyama, 1998) observed that the absorption of water by carboxymethylated cellulose and chitosan was reduced when these were mixed, an effect attributed to strong polymer–polymer interactions. Hosokawa et al. (Hosokawa, Nishiyama, Yoshihara, & Kubo, 1990) found that films made of chitosan blended with homogenized cellulose had good oxygen-barrier properties. However, they used ozone-oxidized cellulose which requires an additional production step and glycerol as plasticizer which increases the oxygen permeability and decreases the mechanical strength.

Several studies have been performed using chitosan as a wet-end additive in papermaking systems to increase the wet strength (Laleg & Pikulik, 1991). Chitosan additives have also been found to increase the strength of wet towels, grocery bags and disposable diapers, and to increase the efficiency of the wood fiber beating process (Thomson, 1985). Li, Du, and Xu (2004) found that the chitosan was almost completely adsorbed onto the surfaces of the cellulosic fibers, and that this adsorption increased with increasing amount of cationic amino groups, due to the electrostatic interactions between the chitosan and the anionic cellulose pulp. Mucha and Miskiewicz (2000) observed that chitosan, in blends with poly(vinyl alcohol) and gelatinized starch as a filler for paper, increased the paper strength due to the strong ionic interactions.

However, fundamental studies of the adsorption phenomena and the interactions between paper components in relation to the development of the properties of the paper sheets are still lacking (Li et al., 2004). The purpose of the present study is not to investigate the mechanisms of the chitosan–cellulose interactions, but to investigate different ways of inserting the barrier component at an early stage into the papermaking process. The purpose is also to explore possible synergistic effects of mixing pulp fibers and chitosan in terms of the barrier properties of the sheet and the buffering-induced shrinkage. The papermaking processes was simulated here either by using a laboratory paper machine or by solution-casting sheets in petri dishes.

2. Experimental

2.1. Materials

2.1.1. Chitosan solution

Chitosan (with a degree of deacetylation of 84.7%), 2-amino-2-deoxy-(1-4)-β-D-glucopuranan, with a viscosity of 200 mPas in 1% acetic acid, and with a molar mass of $M_r \approx 400{,}000$, was received as platelets from Fluka, Sigma-Aldrich Sweden AB. Chitosan (1.17 wt%) was dissolved in 1.17 wt% acetic acid and 97.66 wt% deionized water. Acetic acid (Glacial, PA, 99.8%) supplied by Acros Organics, USA, was used in order to protonize the amino groups. The solution was stirred for 20 min with a magnetic stirrer in a 600 ml glass cup, and then mixed in a Waring Commercial Blendor at the highest speed for 4 min. The solution was vacuum degassed for 2 h in order to remove trapped air bubbles introduced during mixing. The solution was combined in several ways with the pulp fiber suspension as described in Methods 1–5.

2.1.2. Preparation of laboratory sheet

The laboratory sheets were produced in accordance with SCAN-CM 26:99, with a final grammage of 60 g/m^2, using a laboratory paper machine supplied by OY Lorentzen & Wettre AB, Finland, and a Sheet Press from Lorentzen & Wettre AB, Sweden. First, 13.6 dm^3 of water was added to the hand sheet mould. 411 g pulp fiber suspension, with a dry content of 3.54 g/dm^3, a water retention value of 1.49 g/g and a Shopper–Riegler value of 29, was then poured into the hand sheet mould. A softwood kraft pulp bleached with oxygen, chlorine dioxide and hydrogen peroxide was used. The pulp fiber suspension was mixed for 10 s at 2 atm air pressure, supplied through eight air channels with diameters of 8 mm. The white water was, after a further 10 s, emptied through the wire screen, with a mesh number of 120, to yield a square sheet with a side dimension of 16.5 cm. The sheet was covered with a blotting paper and a pressure of 1 kPa was applied for 20 s to remove excess water. The sheet was thereafter removed from the wire screen, covered with a blotting paper and a metal plate and pressed at 400 kPa for 5 min to remove further excess water. Finally, the sheet was dried at 23 °C and 50% relative humidity (RH). The laboratory sheet was used as a reference and was compared with sheets made of a mixture of the pulp fiber suspension and the chitosan solution as described in *Methods 1–5* below.

2.1.3. Method 1

The chitosan solution was blended with the pulp fiber suspension, at a dry content of 3.54 g/dm^3, to yield chitosan concentrations of 0, 2, 10, 20, 25 and 33 wt%. The total weight of the pulp fiber suspension and chitosan mixture was always 411 g. The procedure was then as described in *Preparation of laboratory sheet*.

2.1.4. Method 2

13.6 dm^3 water was poured into the hand sheet mould and 411 g of the pulp fiber suspension, with a dry content of 3.54 g/dm^3, was then poured into the hand sheet mould. The suspension was thereafter emptied through the wire screen until 5 cm (=1.36 dm^3) remained and a wet sheet had formed on the wire screen. In the next step the chitosan solution was added to yield chitosan solution concentrations of 0, 2, 10, 20, 25 and 33 wt%. The suspension was left for 30 s, and the white water was thereafter poured through the wire screen. The procedure thereafter was as described in *Preparation of laboratory sheet*. The preparation was carried out with and without pressure to remove excess water.

2.1.5. Method 3

1.36 dm^3 (=5 cm water) was poured into the hand sheet mould and 411 g of the pulp fiber suspension, with a dry content of 3.54 g/dm^3, was then added. The chitosan solution was then added to yield chitosan solution concentrations of 0, 2, 10, 20, 25 and 33 wt%. The suspension was thereafter left for 30 s and then mixed for 10 s at 2 atm air pressure in order to ensure proper mixing of the pulp fibers and chitosan solution. The suspension was thereafter poured through the wire screen. The procedure then was as described in *Preparation of laboratory sheet*. The preparation was carried out with and without pressure to remove excess water.

2.1.6. Method 4

Chitosan solution was blended with pulp suspension, with a dry content of 35.4 g/dm^3, to give chitosan solution concentrations of 50, 80, 90, 95 and 99 wt%. The total weight of the pulp fiber and chitosan mixture was always 41.1 g. The difference between this method and Method 3 was that the pulp fiber suspension here was more concentrated and thus contained less water. The blend was poured into the hand sheet mould that contained 1.36 dm^3 (=5 cm) water. The procedure thereafter was as described in *Preparation of laboratory sheet*. The preparation was carried out with and without pressure to remove excess water.

2.1.7. Method 5

The chitosan solution was blended with the pulp fiber suspension, with a dry content of 35.4 g/dm^3, to yield chitosan solution concentrations of 50, 80, 90, 95 and 99 wt%. The total weight of the pulp fiber–chitosan mixture was always 41.1 g. Subsequently the chitosan–pulp fiber suspension was poured into Bytac-coated petri dishes and dried for 2 days at 23 °C and 50% RH. The thickness of the sheets was not allowed to deviate by more than 10% from 40 μm.

2.1.8. Buffer treatment and shrinkage analysis

Samples produced by Method 5 were treated in an alkaline buffer solution in order to eliminate residues of acetic acid and thereby to eliminate protonization of the amino groups. The sheets were rinsed in deionized water after the buffer treatment. The buffer was a pH 7.8 solution consisting of 0.1 M $Na_2HPO_4 \cdot H_2O$ and 0.1 M $Na_2HPO_7 \cdot 7H_2O$. The salts were supplied by Merck Eurolab. The shrinkage was measured as the area decrease on five replicates.

2.2. Measurements

2.2.1. Dry substance of the pulp fiber suspension

The dry substance of the pulp fiber suspension was measured in accordance with SCAN-C17:64. Five replicates of each sample were used.

2.2.2. Surface weight

The grammage was determined at 23 °C and 50% RH in accordance with SCAN-P 6:75, using a Sartorius MC1 Analytic AC 210S. Five replicates of each sample were used.

2.2.3. Thickness

The thickness of the sheets were measured in accordance with SCAN-P 7:96, at 23 °C and 50% RH, with a precision micrometer under a static pressure of 100 kPa. The thickness was determined at five positions on each sheet, using a thickness tester from Lorentzen & Wettre AB, Sweden. Five replicates of each sample were used.

2.2.4. Tensile properties

Test pieces were cut out from each sheet and measured in accordance with SCAN-P 38:80 at 23 °C and 50% RH. The fracture strain, fracture stress and Young's modulus were determined using a Zwick Z010 instrument, from Zwick GmbH & Co, Germany, controlled by a testXpert 7.1 computer program. Ten replicates from each sample were used.

2.2.5. Air permeance

The air permeance was measured using the Gurley method in accordance with SCAN-P 53:84 at 23 °C and 50% RH. The L & W Air Permeance Tester Type 12 from Lorentzen & Wettre AB, Sweden, was used. The values were normalized with respect to the grammage. Ten replicates from each sample were used.

2.2.6. Moisture content

The loss of volatile mass was measured as described in ASTM D 644-94. The test pieces were weighed and then stored for 24 h at 105 °C in a Nûve FN400 oven, supplied by LabRum Klimat AB, Sweden. The specimens were subsequently cooled in desiccators at 0% RH and 23 °C and then weighed to determine the loss of volatile mass. Five replicates from each sample were used.

2.2.7. Oxygen permeability

The oxygen transmission rate was determined in accordance with ASTM D 3985-95, at 23 °C and 0% RH, using a Mocon Ox-Tran 2/20, from Modern Controls Inc., MN, USA. The test pieces were mounted in isolated diffusion cells and subsequently purged with nitrogen gas (2% hydrogen) in order to measure the background oxygen leakage of the instrument. Each specimen was tightly sandwiched between two aluminum foils so that an area of 50 cm^2 was exposed for the measurements. One side of the sample was exposed to flowing oxygen (99.95%) at atmospheric pressure. The oxygen transmission rate was normalized with respect to the oxygen pressure and the film thickness to yield the oxygen permeability. Two replicates from each sample were used.

2.2.8. Optical transmission microscopy

The chitosan-salt blended pulp fiber sheets were examined in a Leitz Ortholux II POL-BK, equipped with a camera, Leica DC300. The microscope was controlled by a Leica IM50 v1.20 computer program. The equipments was supplied by Leica Microsystems AG, Germany.

2.2.9. Infra-red (IR) spectroscopy

The content (mol%) of chitosan in the final composites were estimated from reflection-IR spectra obtained by a Perkin–Elmer 2000 FTIR-spectrophotometer, from Perkin–Elmer Inc., USA, equipped with a Golden Gate accessory from Graseby Specac Ltd, UK. The chitosan content was estimated by first normalising the sample and pure pulp fiber spectrum with respect to the C–O–C– vibration at approximately 1030 cm^{-1} (Pawlak and Mucha, 2003) and then subtracting the former from the latter. It was here assumed that the intensity of the C–O–C peak was independent of the composition of chitosan and pulp fiber. The difference in the interval 1750 and 1510 cm^{-1} was associated with the chitosan left in the sheet. This difference corresponded primarily to the NH bend (~1550 cm^{-1}) and the NH$_2$ amino group vibration (~1590 cm^{-1}) and consequently with the content of chitosan (Pawlak and Mucha, 2003). In order to obtain the amount of chitosan in the film, the difference in the interval 1750 and 1510 cm^{-1} was normalised with the difference between a pure chitosan film and the pure pulp fiber film. The range in IR vibrations analysed correspond to a depth of sheet penetration of 3–4 μm (refractive index of chitosan = 1.5 (Jiang, Su, Caracci, Bunning, Cooper and Adams, 1996; Hedenqvist, Krook, & Gedde, 2002)).

3. Results and discussion

In Method 1, the wire screen trapped the pulp fibers but some of the dissolved chitosan which was not adsorbed onto the pulp fibers, was lost in the white water passing through the wire screen. This led to a decreasing grammage with increasing chitosan solution concentration (Fig. 1), which is also the reason to why the estimated content of remaining chitosan in the films did not increase with increasing content of the chitosan solution (Table 1). Holes appeared in the sheets due to the flocculating effect of chitosan on the pulp fibers (Laleg & Pikulik, 1991). The amount and size of the

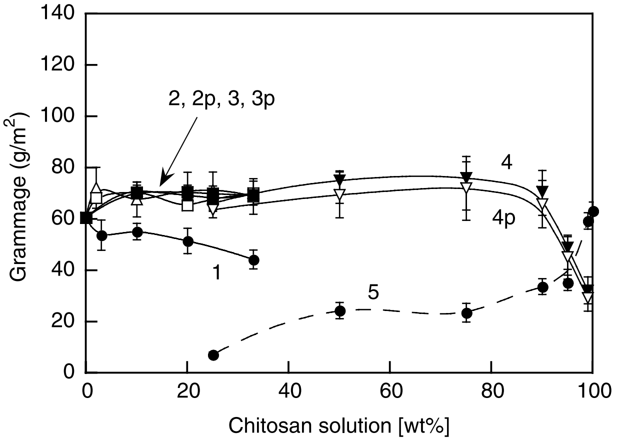

Fig. 1. Grammage as a function of chitosan solution content in the pulp fiber suspension, for sheets produced by Method 1 (○), Method 2 (2p, △), Method 2 without the pressure step (2, ▲), Method 3 (3p, ❍), Method 3 without pressure (3, ■), Method 4 (4p, ▽), Method 4 without pressure (4, ▼), and Method 5 (●). The error bars represent a confidence range of 90%.

Table 1
Content of chitosan in the papersheets

Method[a]	Pressure[b]	Content (%)[c]	Spot content (%)[d]
1–9.5	Yes	3 ± 0.1	10
1–33	Yes	4 ± 0.5	
2–10	No	14 ± 0.1	
2–34	No	7 ± 4	17
2–34	Yes	20 ± 3	58
3–10	No	11 ± 0.5	
3–10	Yes	10 ± 0.6	
4–80	No	9 ± 2	19

Molar content of chitosan relative to 100% chitosan.

[a] Method of preparation and the mass content (%) of the chitosan solution in the pulp–chitosan mixture.

[b] With or without pressure as decribed in the experimental section.

[c] Taken as the average of at least one measurement from each side of the sheet.

[d] Chitosan content in chitosan-rich spots observed in some of the films.

pores and holes increased with increasing content of the chitosan solution, and as observed by IR spectroscopy some of these were filled with chitosan (the spots in Table 1). The loss of chitosan, and consequently the loss in grammage, was less when a wet sheet was prepared prior to adding the chitosan solution (compare Method 1 and 2, Fig. 1). The reason for the difference in grammage between Methods 1–3 was also that the total amount of material in the hand sheet mould in Methods 2 and 3 increased continuously with increasing amount of chitosan solution. The amount of residual chitosan was also larger in the Methods 2 and 3 sheets (Table 1). A smaller volume of water was used in the hand sheet mould in Methods 2–4 (1.36 dm^3 instead of 13.6 dm^3) to increase the concentration of chitosan in the suspension. Here the white water passed slowly through the wire screen until the first wet sheet was formed, and then more rapidly through holes that were larger but fewer than in Method 1 (Fig. 2). The time for the white water to pass through the wire screen in Method 2 was shorter (110 s) than for Method 1 (120 s), and the surface of the Method 2 sheets was less smooth. The unevenness could probably have been reduced by using a wire screen with a higher mesh number, but that would have dramatically increased the retention time for the white water. Slow dewatering and long retention times are undesirable in commercial processes. Here, for comparative reasons, all the sheets were produced with the same wire screen.

The white water retention time for the highest chitosan concentration (Method 4) was 610 s, i.e. 480 s longer than for the laboratory sheet. The high amount of chitosan decreased the bridging effect of chitosan, since all possible sites on the fiber surface available to chitosan were occupied (Li et al., 2004). This resulted in fiber-to-fiber repulsion and anti-agglomeration effects that, in turn, decreased the grammage and yielded a surface with a larger amount of pores and holes (Fig. 2). Consequently, the amount of residual chitosan in the Method 4 sheets was small, considering the high concentration of chitosan solution used (Table 1). The holes that were filled with chitosan solution during sheet formation, as observed by IR spectroscopy (spots, Table 1), were reduced in number and size in the subsequent pressure operation. Thus, if this pressure operation was omitted, less chitosan solution was lost and the grammage became higher (cf. curves 4 and 4p in Fig. 1). The sheets, however, then became more porous and this resulted in a higher air permeance (cf. curves 4 and 4p in Fig. 3). The greater degree of fiber agglomeration associated with the air mixing (Method 3) yielded more holes and pores, and consequently a higher air permeance after pressing than in Method 2 (cf. curves 3p and 2p in Fig. 3). Fig. 3 shows that the pressure operation always reduced the air permeance as a result of the reduced amount of holes and pores. In addition, it seemed as if the pressure operation increased the amount of chitosan in the spot-free part of the Method 2 sheets, but that it did not have an effect on the chitosan content in Method 3 sheets (Table 1).

The air-mixing (Method 3) also affected the mechanical properties. The higher fiber agglomeration and greater hole formation, due to electrostatic attractions between the pulp fibers and the chitosan during air mixing (Mucha & Miskiewicz, 2000), decreased the fracture stress and, for the unpressed sheets, also the fracture strain (compare Methods 2 and 3 in Figs. 4 and 5).

When the air mixing was omitted and the sheet was formed in two steps, as in Method 2, it appeared that the chitosan acted as a glue and a homogeniser rather than an agglomerating agent. These mechanisms were not further exploited but they can be found elsewhere (Li et al., 2004).

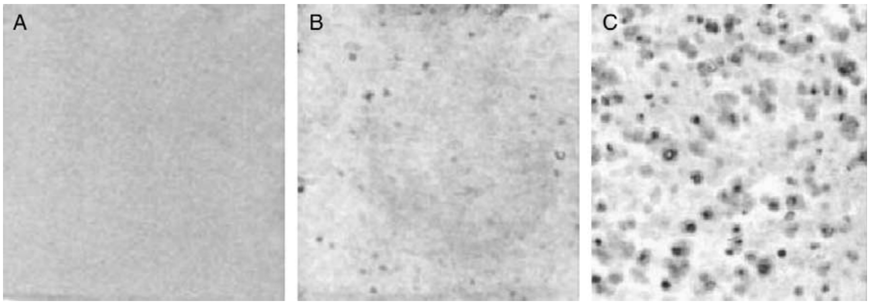

Fig. 2. Optical micrographs representing sheets produced according to (a) Method 1 (10 wt% chitosan solution), (b) Method 2 with 20 wt% chitosan solution and pressure (c) Method 4 with 90% chitosan solution and pressure. The sides of the micrographs correspond to 16.5 cm (A) and (B) and 8.25 cm (C).

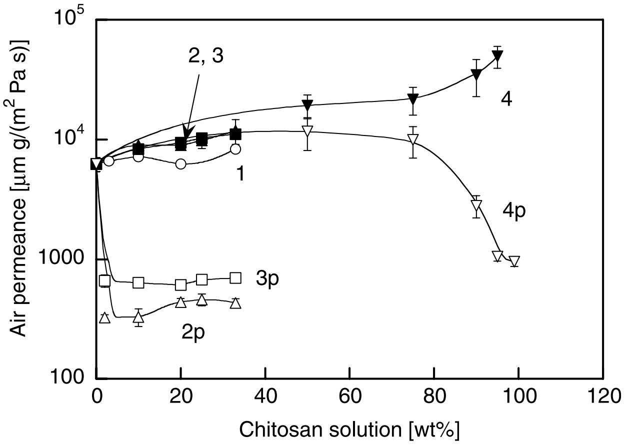

Fig. 3. Air permeance, normalized with respect to grammage, as a function of chitosan solution content in the pulp fiber suspension, for sheets produced by Method 1 (○), Method 2 (2p, △), Method 2 without the pressure step (2, ▲), Method 3 (3p, □), Method 3 without pressure (3, ■), Method 4 (4p, ▽) and Method 4 without pressure (4, ▼). The error bars represent a confidence range of 90%.

When the pressure in Methods 2–4 was omitted, the number of holes was higher. The larger holes resulted in an uneven and heterogeneous sheet, with a lower fracture stress (Fig. 4).

In the case of the suspensions with a larger content of chitosan solution (Method 4), the mechanical contribution from chitosan increased, as expected, with increasing chitosan concentration (Figs. 3–5). The chitosan-contribution was however, in accordance with the low residual chitosan left in the film (Table 1), modest considering the high chitosan solution concentrations used.

At high concentrations of chitosan solution, the solution-cast films had slightly better mechanical properties than the sheets produced in the laboratory paper machine (Figs. 3–5). However, at low concentrations, the opposite was observed and, in fact, the pure-solution-cast pulp fiber sheet was too fragile to be measured. The moisture content of the solution-cast sheets increased continuously with increasing chitosan content. It increased from 5.5% for the pure pulp fiber sheet to 12.7% for the pure chitosan-acetic acid salt sheet. A similar behavior was also observed for the sheets produced by Method 4. This suggested that the decreasing Young's modulus with increasing chitosan solution content might be due to the increasing concentration of plasticizing water (Fig. 6).

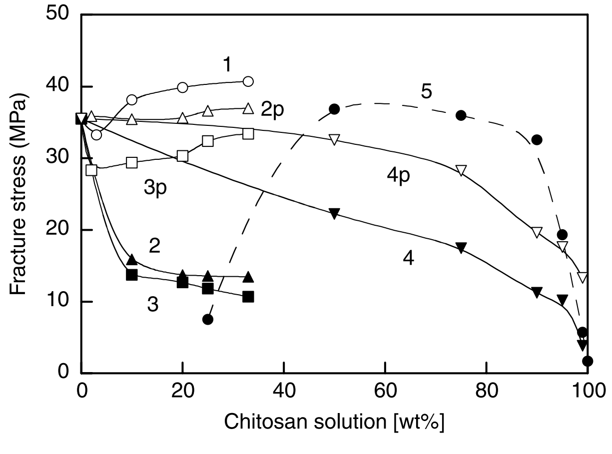

Fig. 4. Fracture stress as a function of chitosan solution content in the pulp fiber suspension of sheets produced by Method 1 (○), Method 2 (2p, △), Method 2 without the pressure step (2, ▲), Method 3 (3p, ○;), Method 3 without pressure (3, ■), Method 4 (4p, ▽), Method 4 without pressure (4, ▼), and Method 5 (●). The average 90% confidence range of all data was ±3.8.

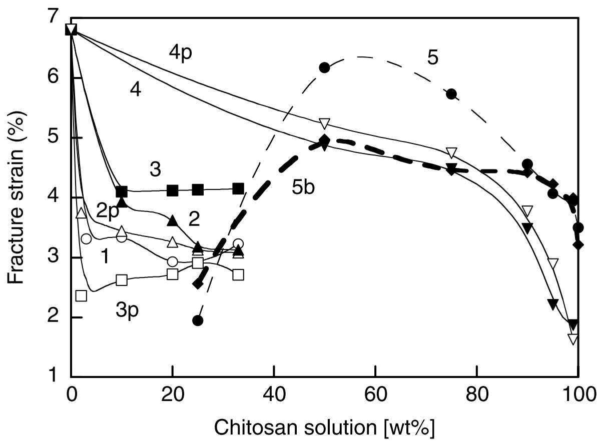

Fig. 5. Fracture strain as a function of chitosan solution content. Same notation as in Fig. 4 except that sheets produced according to Method 5 and also buffered are included (5b, ◆). The average 90% confidence range of all data was ±0.8.

A sufficiently continuous phase of chitosan-acetic acid salt, for oxygen-barrier applications, was achieved only in the solution-cast sheets and then only above a content of 25 wt% chitosan solution (Figs. 7 and 8). Fig. 8 shows that the OP of sheets above 90 wt% chitosan solution was excellent. This was consonant with the mechanical data, which also showed that the chitosan solution concentration had to be higher than 25 wt% to yield good mechanical properties. Although the air permeance was too low to be detected, the 25 wt% sheet had an oxygen permeability that was too high

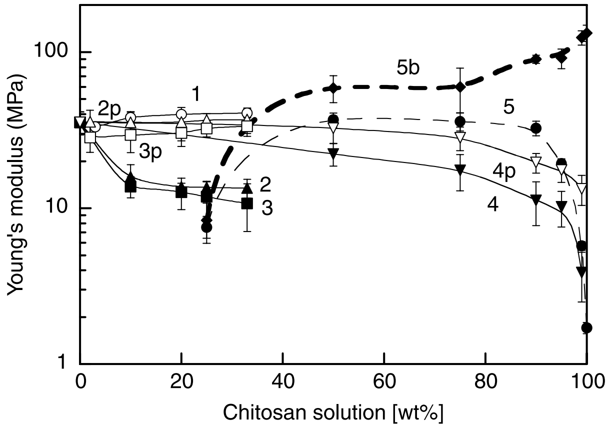

Fig. 6. Young's modulus as a function of chitosan solution content. Same notation as in Fig. 5. The error bars represent a confidence range of 90%.

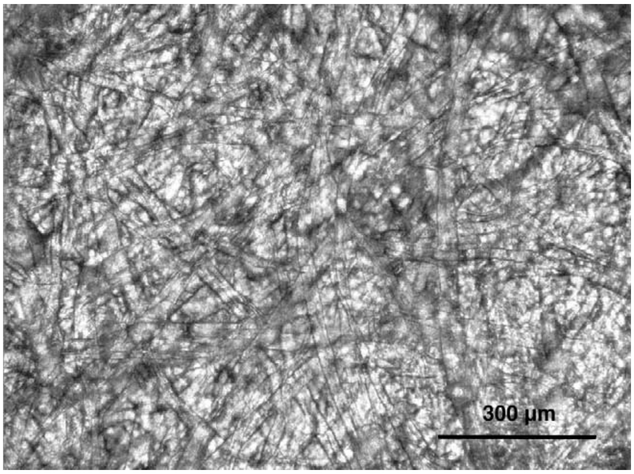

Fig. 7. Photomicrograph showing a sheet that has been solution-cast from a 50 wt% chitosan solution in a petri dish. The pulp fibers are observed as long stripes in the otherwise transparent chitosan-acetic acid salt matrix.

to be measured in the oxygen transmission rate test. This indicated that even though the chitosan, at this concentration, had an anti-agglomerating effect on the pulp fibers, it still could not penetrate and separate the pulp fibers. Since there is no loss of chitosan and fiber through a wire screen in solution-casting, the solid content of chitosan and pulp in the sheet was the same as in the solution. Extensive IR spectroscopy on a sheet, solution-cast from a 65 wt% chitosan solution concentration, with measurements at 10 positions on both sides revealed that chitosan and pulp fibers were always present and to approximately the same extent on both sides of the sheet. Thus the chitosan was homogeneously mixed with the pulp fibers and analysis of a great number of optical micrographs (Fig. 7) showed that chitosan wetted/covered the pulp fibers. However, pulp fibers were located occasionally also on the very surface of the cast films. That cannot be avoided unless the paper sheet is coated with chitosan in a subsequent separate step. Nevertheless the casting process seemed very promising for higher chitosan contents in that the sheet was made in one step.

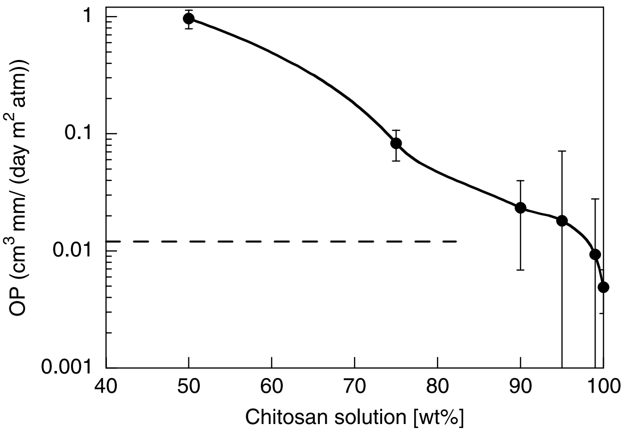

Fig. 8. Oxygen permeability (OP) as a function of weight percent chitosan solution in the pulp fiber suspension, for sheets produced by Method 5. The error bars represent a confidence range of 90%. The broken line corresponds approximately to the oxygen permeability at 0% RH for poly(ethylene-*co*-alcohol) (Guilbert, Cuq, & Gontard, 1997).

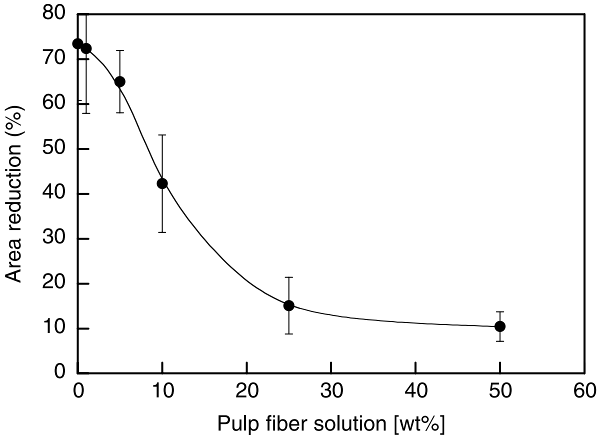

Fig. 9. Area reduction after buffer treatment of sheets produced by Method 5 as a function of pulp fiber content. The error bars represent a confidence range of 90%.

Solution-cast films of chitosan-acetic acid salt have in a previous report been treated with an alkaline buffer solution, with a pH of 7.8, followed by rinsing in water (Gällstedt & Hedenqvist, 2004). This was performed in order to remove residues of acetic acid and thus to decrease the water sensitivity. The repulsion between the amino groups protonized by residual acetic acid was absent, and this led to a lower moisture sensitivity (50% RH). This is shown in Fig. 5 as a higher Young's modulus for the buffered sheet than for the unbuffered sheet (Method 5). The buffer treatment resulted, as shown previously, in a shrinkage of the samples that could be a problem in several applications (Gällstedt & Hedenqvist, 2004). However, the chitosan matrix was here reinforced with the pulp fibers. This resulted in a decrease in the shrinkage, observed as a lower decrease in area, with decreasing concentration of the chitosan solution in the pulp fiber suspension (Fig. 9).

4. Conclusions

The incorporation of chitosan solution to the pulp slurry yielded sheets with a lower grammage due to loss of material through the wire screen. This could be reduced by forming a wet pulp fiber sheet before adding the chitosan solution. The heterogeneity and hole content in the sheets produced in the laboratory paper machine increased with increasing content of chitosan solution. Evidently the chitosan-acetic acid salt agglomerated with the pulp fibers. The sheet homogeneity increased during pressing after sheet formation. In general, considering the full chitosan solution concentration range, the stiffness, the fracture strain and the fracture stress decreased with increasing chitosan solution content. The most homogeneous sheets were obtained by solution-casting in petri dishes. At chitosan solution contents above 50 wt%, a sufficiently continuous chitosan-acetic acid salt phase was formed to yield a sheet with a low oxygen permeability. The shrinkage during the buffer treatment could be reduced effectively by the presence of pulp fibers. The buffered sheets also had the highest Young's modulus, possibly due to their low moisture content. Hence, a very interesting low moisture-sensitive high barrier chitosan sheet can be produced by the combined route of addition of pulp fibers and buffer treatment.

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