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Fat resistance properties of chitosan-based paper packaging for food applications

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Abstract

The objective of this study was to potentially replace fluorocarbon-treatment of paper-based materials by chitosan coating to produce oil barrier packaging. With this work, the nature of interactions existing between fatty acids, chosen as model lipids (such as oleic acid, largely present in the food field), and chitosan was particularly investigated. The influence of the fatty acid content and the effect of pH were studied. The ability of chitosan to interact with lipid was shown to be pH sensitive. In acidic conditions, the polycationic chitosan exhibited a stabilization of the fatty acid emulsion, which was attributed to its capacity to bind with anionic lipid molecules, as suggested by the sudden change in residual free oleic acid concentration with a slight shift in pH. Since calcium adsorption from foodstuff is known to decrease the nutritional value of the product and since chitosan exhibits chelating properties, interaction between chitosan and calcium was concurrently investigated. Whatever the pH used, adsorption of Ca^{2+} ions by chitosan was found to be minor.

The fat barrier properties of paper and chitosan-coated paper were also compared in application tests. It was concluded that chitosan coating could be used as fat barrier but treatment cost remained high compared with fluorinated resins. In an attempt to decrease both treatment cost and fat transfer, other natural molecules such as cellulose ethers and alginates were included with chitosan, in the coating formulations. Alginates were found to give the best results.

Keywords: Fat barrier paper; Lipid–chitosan interactions; Biocoated paper; Chitosan; Fatty acid

1. Introduction

The storage of high fat content foodstuffs such as dry pet food requires packaging films with oil barrier properties. According to Lange, Pelletier, and Wyser (2002), dry pet foods are generally packed in paper-based materials and the packaging requires a good resistance against staining through fat migration from the product. In general, staining is more of an aesthetic than a product quality problem but this issue still has to be addressed. The staining mechanism for pet food packaging is complex and the transportation and storage conditions, such as temperature and humidity, have a major influence on staining behaviour. Lange et al. (2002) mentioned that two basic staining mechanisms could be identified from a paper-based dry pet food packaging: a dynamic staining during transport and a static staining during storage. The high contact pressures would influence the dynamic staining during vibration. The static staining was found to be more chemical in nature, with the aggressiveness of the pet food overcoming the chemical resistance of the treatment. When pet foods are packed under paper materials, fat resistance is generally achieved either by coating the paper or paperboard with a polyethylene layer or by treating the material with fluorocarbon chemicals (Lange et al., 2002). The polyethylene coating works by providing a physical barrier against fat penetration and is therefore sensitive to defects (pinholes) and mechanical abuse. The more commonly used fluorocarbon chemical treatment inhibits the wetting of the fibres by reducing the surface energy of the sheet but does not necessarily stop the fat from penetrating the paper. Lange et al. (2002) suggested that the fluorocarbon chemical treatment is less sensitive to

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mechanical stress and protects against staining. However, fluorinated resins present disadvantages, due indirectly to their negative impact on the environment and their high price. Consequently, there are only a limited number of companies producing fluorocarbon-treatment chemicals. The market leader (3M with Scotchban) decided in 2000, to stop its production for environmental reasons. Therefore, it will be soon necessary to replace these resins by molecules of natural origin, able to limit fat penetration.

Chitosan, a polysaccharide notably derived from crustacean chitin, is of particular interest in the food packaging area. Both chitin and chitosan biopolymers are composed of glucosamine and *N*-acetylated glucosamine (2-acetylamino-2-deoxy-D-glucopyranose) units linked by (β 1→4) glycoside bonds. Chitin is extensively acetylated, while chitosan corresponds to a deacetylated form (Koide, 1998). In addition, chitin and chitosan are biodegradable, bioresorbable and chitosan exhibits bioactive properties either in its polymeric or oligomeric form (Begin & Van Calsteren, 1996; Coma, Deschamps, & Martial-Gros, 2003; Coma et al., 2002; Fang, Li, & Shih, 1994; Siragusa & Dickson, 1992; Tsai, Wu, & Su, 2000). Due to its positive charge on the amino group in acidic conditions, chitosan binds to negatively charged molecules such as fats and lipids (Jumaa & Müller, 1999; Muzzarelli, Frega, Miliani, Muzzarelli, & CartolariTorres, 2000; Shu & Zhu, 2002a–c; Shu, Zhu, & Song, 2001). Muzzarelli (1996) mentioned that the formation of corresponding salts from chitosan and fatty acid is mainly ionic in nature and that a soluble form of chitosan would be able to interfere with intraluminal lipid absorption through the interaction with micelle formation or emulsification of lipids in the enteric phase. Other studies revealed that oral chitosan could increase the amount of fat eliminated in the stool (Ormrod, Holmes, & Miller, 1998).

The current study was thus conducted to investigate the possibility of producing biopolymer-coated paper to give an effective fat barrier to pet food-packaging applications. Chitosan being a biopolymer with fat adsorption properties and having good film-forming capacities, a positively charged chitosan-coated paper (bi-layer matrix) was prepared and the resulting food fat barrier studied. The fat resistance was first evaluated from fatty acid–chitosan interactions experiments. Because of the chelating properties of chitosan, chitosan-paper bi-layer matrix could have a disadvantage because of calcium adsorption from the foodstuff and could lead to a decrease of the nutritional value of the product. Chang and Lin (2000) suggested that chitosan might interact with Ca^{2+} and a potential complex could be formed. The adsorption of calcium by chitosan was thus evaluated via atomic absorption experiments. Finally, the effect of chitosan coating was evaluated from stain resistance essays related to static staining. In order to decrease both treatment cost and fat transfer, other natural molecules such as cellulose ethers and alginates were associated with chitosan in coating formulations.

2. Materials and methods

2.1. Materials

Compounds. Chitosan 241 (technical grade, deacetylation degree more than 90%, low viscosity, ash < 1%) and Kraft paper (Silvana 1, 70 g/m^2, characterized by a Kit test < 1) were provided by France Chitine (Marseille, France) and Papeteries de Gascogne (Mimizan, France), respectively. Carboxymethyl cellulose (Blanose 7L2C, substitution degree range 0.65–0.90, purity 98% minimum, moisture 8% maximum), Hydroxypropylmethyl cellulose (Culminal 50, purity 98% minimum) and Hydroxypropyl cellulose (Klucel, purity 98% minimum) were provided by Hercules (France) and Alginates (Scogin XL, low viscosity,, Scogin LV, low–medium viscosity) by FMC Biopolymer (Norway). Oleic (purity 95%), stearic (purity 95%), and margaric acid (purity 98%) were supplied by SIGMA Chemical (USA).

2.2. Methods

Statistical treatment. All experiments were replicated at least three times. Treatment means were separated using the Student's *t*-test at 95% probability ($p < 0.05$).

FTIR analysis. ATR (Attenuated Total Reflectance) infrared spectra were recorded by a Nicolet 210 apparatus, in the 500–4000 cm^{-1} zone, using 200 scans, at a resolution of 4 cm^{-1}. No specific preparation was required for film infrared analysis.

2.2.1. Chitosan–fatty acid sorption experiments

The capacity of chitosan to interact with fatty acids was studied as a function of pH, using a 0.5% chitosan solution (w/v), in 1% aqueous acetic acid (w/w). The chitosan solution was dispersed in 0.1–1.5% (w/v) fatty acid aqueous emulsions and the resulting mixture was magnetically stirred (500 rpm) for 0.5–18 h. The desired proportion of chitosan was added to stearic acid–water emulsion at 80 °C (stearic acid melting point = 72 °C) and to oleic acid–water emulsion at ambient temperature. The pH of the resulting solution was adjusted to the selected value using sodium hydroxide (0.1 N) or HCl (0.1 N). Each emulsion batch was prepared in triplicate. The amount of chitosan 'bound' to the fatty acid was estimated from the residual free fatty acid, recovered by the extraction process. The extraction was carried out after different contact times. Preliminary experiments showed that diethyl ether extraction caused an interfacial emulsion to form, which was difficult to break without affecting the ionic configuration of the chitosan. Hexane extractions were therefore preferred due to a weaker interfacial emulsion, which was easily broken after 30 min. The hexane extraction was replicated three times and, before esterification of free fatty acid, an internal standard (myristic acid $C_{17:0}$) was added to the organic phase. Free fatty acids were converted to methyl esters using the diazomethane

method as described by Schlenk and Gellerman (1960) and the products analysed by gas chromatography (Fisons GC 8000 Series, equipped with a flame ionization detector). A capillary DB WAX column (30 m, 0.32 mm i.d. and 0.25 μm film thickness) grafted with a polyethylene glycol stationary phase was used. Helium was the carrier gas (60 kPa). Split conditions were used with a ratio of 80. The experiment was replicated three times and data were treated using the Student's *t*-test ($p > 0.05$). The percentage of residual free fatty acid was calculated as follows:

$$\text{Residual fatty acid (\%)} = \frac{\text{residual fatty acid determined by CPG}}{\text{initial fatty acid}} \times 100$$

In the case of stearic acid, suspended particles were observed in the emulsion, which could not be solubilized by hexane in our experimental conditions. In order to determine the nature of these suspended particles, emulsion was centrifuged (4000 rpm, Jouan BR4) at 20 °C for 5 min and the residue was analysed by FTIR using KBr tablets.

The variation in residual oleic acid after contact with chitosan was studied as a function of pH, in the pH range 2–8. Experiments were conducted on oleic acid–chitosan emulsion (0.5–0.5%, w/v).

2.2.2. Chitosan–calcium sorption experiments

The ability of chitosan to retain calcium ions was studied as a function of pH, in a beaker, by stirring, 25 ml of a standard 75 mg/l $CaCl_2$ solution with 100 mg chitosan, for 1 h. Preliminary kinetics experiments, performed at pH 2 and 5, showed that maximum chitosan calcium adsorption was attained within the first hour. The supernatant solution was then filtered on cellulose ester Millipore membranes, with 0.45 μm pores. These membranes were selected after preliminary experiments confirming that calcium did not bind to the membrane. The amount of initial and residual calcium was determined by atomic absorption spectroscopy with an Instrumentation Laboratory spectrometer (IL 151). The amount of calcium fixed was evaluated by difference between the initial and final concentrations of Ca^{2+} in solution. The pH of the suspension was automatically monitored and maintained constant by small additions of a 0.01 M NaOH solution: this was devised to anticipate any cation exchange mechanism between Ca^{2+} and chitosan $-NH_3^+$ groups. The pH range studied was 2–5.7, domain in which no calcium precipitation (in the form of calcium hydroxide) occurs.

2.2.3. Biopolymer-paper bi-layers elaboration

Chitosan-based film-forming solutions (0.75–1.5%, w/v) were obtained by dispersing chitosan in a 1% aqueous acetic acid solution, as described previously (Coma et al., 2002). The solution was filtered on 5.3 and then 0.65 μm membranes (Millipore) and degassed under reduced pressure.

2.2.3.1. Chitosan-paper materials from coating table.

The paper was coated with the film-forming solution detailed above, on a coating table (K101 Control Coater Erichsen) at ambient temperature, using a 120 μm blade, then dried at 70 °C for 1 h. The double-layered materials were subsequently conditioned at 23 °C and 50% relative humidity, for 5 days, before measurements.

2.2.3.2. Chitosan-paper materials from a size-press.

Coating was carried out with a size-press (Laboratory Foulard model horizontal). The coating speed was fixed at 2 m/min and the pressure between the cylinders, at 32.5 kg/cm^2. Other natural molecules were associated with chitosan: cellulose ethers and alginates. For coating systems based on a mixture of biomolecules, carboxymethyl cellulose and alginates were dispersed, at different content, directly in the chitosan–acetic acid solutions. For bi-layer coating systems, the additional natural molecules were dispersed in distilled water and only the first chitosan layer was coated.

2.2.4. Assessment of fat barrier properties of bi-layered materials

Kit test procedure. The grease resistance was evaluated according to the standard method Tappi T559 pm-96. Paper samples were tested with a series of solutions with different Kit numbers (1–12), which contained specific proportions of three reagents: castor oil, toluene and *n*-heptane. Oil number 1 is the least aggressive oil, i.e. with the highest surface energy and oil number 12 is the most aggressive oil, i.e. with the lowest surface energy. The various liquids are dropped onto the paper surface from a predetermined height. After 15 s, oils are removed with tissue. The highest numbered liquid that remained on the surface of the paper sample, without causing staining, was reported as the Kit value for the paper. A paper with a Kit test 12 indicates the most fat resistant surface. Different chitosan film-forming solutions were tested, from 1 to 3%, in 1% (v/v) aqueous acetic acid solution. The solutions viscosities were measured with a DV II+ Brookfield Viscometer, at room temperature and with spindle 3/speed 50 rpm (0.2–0.6 Pa s) or spindle 6/speed 50 rpm (4.8 Pa s), depending on the viscosity interval.

3. Results and discussion

3.1. Chitosan–fatty acid interaction

Stearic ($C_{18:0}$) and oleic ($C_{18:1}$) acids, the major fatty acids in olive oil, were selected as models in order to characterize the nature of interaction between fatty acid and chitosan. The first experiments were conducted using oleic acid at pH 5, acidic conditions frequently found in food products. At this pH, the positively charged chitosan ammonium group (pK_a $NH_3^+/NH_2 \sim 6.5$) could interact with the negatively charged carboxylate function of oleic acid (pK_a $COOH/COO^- \sim 4.8$). A chitosan film-forming

solution was then added to the stirred lipid–water emulsion for a definite time, before extraction and gas chromatography quantification of remaining free fatty acid.

3.1.1. Preliminary experiments

The extraction and quantification methods were first validated on 0.5% (w/v) oleic acid–water emulsions (without chitosan) and on film-forming solution with HPMC instead of chitosan (identical molar ratio of polysaccharide). Chitosan was replaced by HPMC, a polysaccharide without cationic groups, to determine the influence of a non-cationic polysaccharide on the lipid recovering and to validate the extraction/quantification techniques. Five experiments, for each emulsion, were conducted in parallel. From oleic acid–water emulsions, only $70 \pm 5\%$ of the fatty acid introduced was titrated by gas chromatography, after extraction and methylation procedures. From oleic acid–HPMC–water emulsions, $72 \pm 4\%$ of the oleic acid was analysed. Therefore, after extraction and chromatography analysis, about 30% of the fatty acid could not be titrated. Fatty acid associated to chitosan will thus always be over-estimated and the method can only be used as a comparative tool.

Chitosan was then added and the influence of contact time on the free fatty acid was determined. No differences in residual oleic acid was observed after 2 h of chitosan–lipid contact. As a result, a 2 h contact time was selected, prior to lipid extraction and analysis.

After 30 min contact between chitosan and oleic acid, the emulsion (Fig. 1) always turned white, suggesting a potential interaction between these compounds. When the same experiment was carried out with hydroxypropylmethyl cellulose (HPMC, free of cationic groups) instead of chitosan, the emulsion remained colourless (data not shown). However, white emulsion indicated that a good dispersion (thin and homogeneous emulsion) was achieved and that there is still no miscibility between phases. The white aspect could also be due to a latex formed from a dispersion in a highly viscous continuous phase. As a result, the structure of the emulsion could be explained by potential

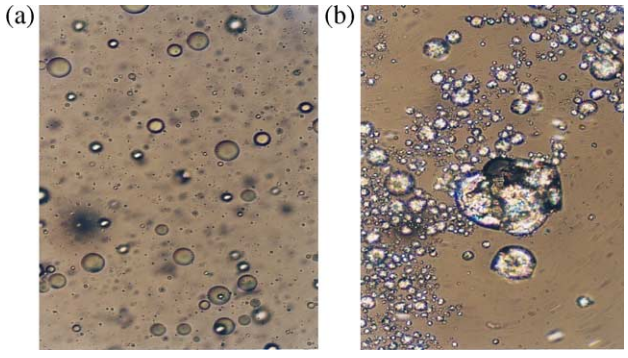

Fig. 1. Photomicrographs of emulsions with (a) 0.5% chitosan–0.1% oleic acid; (b) 0.5% chitosan–1.5% stearic acid. Magnification ×20 (Olympus BH-20).

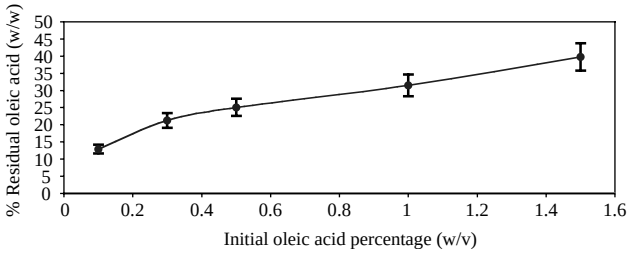

Fig. 2. Percentage of residual free oleic acid versus initial oleic acid content in aqueous emulsions containing 0.5% chitosan solution (w/v).

interactions between chitosan and lipid, that has to be verified by the following experiments, and/or by the emulsion structure (interfacial area and fat particle diameter distribution) It is believed that anionic lipid molecules interact electrostatically with cationic groups of glucosamine residues, leading to emulsion stability. With stearic acid, suspended particles were formed and results were not satisfactory. Difficulties, primarily due to its high melting point (72 °C), complicated the tests. An example of the type of emulsion obtained from the stearic acid is presented in the second part of Fig. 1.

3.1.2. Lipids/chitosan experiments

The ability of chitosan to retain fatty acids was first studied as a function of lipid concentration (i.e. chitosan/lipid molar ratio). Residual free stearic and oleic acids were plotted as a function of initial lipid concentration. Results from experiments conducted with oleic acid are illustrated in Fig. 2. As expected, the residual oleic acid increased with the initial acid content. From a 0.5% (w/v) oleic acid aqueous emulsion, 70% of the oleic acid were recovered without chitosan, as mentioned above, compared to 27% with 0.5% of chitosan (w/v), suggesting a significant interaction between both compounds. In the case of stearic acid, the results were randomly distributed. This latter emulsion contained suspended particles, which could not be solubilized by hexane in our experimental conditions. In order to determine the nature of these suspended particles, emulsion was centrifuged and the residue was analysed by FTIR using KBr tablets. The spectrum was compared with pure stearic acid spectrum (data not shown) but no differences could be observed between the two: peaks characteristic of fatty acid appeared, i.e. ν(OH) vibration between 2800 and 3300 cm^{-1} and carbonyl groups

Table 1
Effect of contact time on chitosan–oleic acid interaction

Contact time (h)	Residual free oleic acid (%)
0.5	23 ± 2
1	24 ± 4
2	14 ± 2
4	15 ± 3
18	13 ± 3

Percentages represent mean values from at least three experiments. Standard deviations were calculated using Student's t-test ($p < 0.05$).

Table 2
Influence of pH value on the percentage of residual free oleic acid

	pH value							
	2	4	5	5.5	6	6.5	7	8
Residual free-oleic acid (%)	50±4	35±3	27±5	9±2	6±2	25±3	62±8	71±4

Percentages represent mean values from at least three experiments. Standard deviations were calculated using Student's *t*-test ($p<0.05$).

vibration near 1740 cm^{-1}. No peak was observed in the area attributed to –NH of amino group of chitosan (1560 cm^{-1}), indicating that these particles are primarily of stearic acid. With oleic acid, no residual particles could be obtained after the centrifugation procedure, confirming the strong interaction between chitosan and fatty acid in that case, leading to a stabilization of the emulsion. Consequently, the procedure conducted to determine residual fatty acids could not be applied to stearic acid and the study was carried out with oleic acid–chitosan emulsion only (0.5–0.5%, w/v) (Table 1).

If the interaction between chitosan and oleic acid is really electrostatic in nature, it should be sensitive to pH variations. Accordingly, the variation in free oleic acid after contact with chitosan, was studied as a function of pH, in the pH range 2–8. As expected, the maximum interaction occurred between pH 5.5 and 6 since only 9 and 6% of residual fatty acids were recovered at pH 5.5 and 6, respectively (Table 2). In this range of pH, a majority of chitosan amino groups is in the protonated form NH_3^+ (pK_a $NH_3^+/NH_2 \sim 6.5$), whereas a significant proportion of carboxylic functions is in the carboxylate form COO^- (pK_a $COOH/COO^- \sim 4.8$). Consequently, electrostatic interactions are optimum. The maximum of residual free fatty acid was obtained between pH 7 and 8, since about 60–70% of the oleic acid was recovered. Flocculates were always observed in that case, due to a re-precipitation of the dissolved chitosan. Above pH 8, the solution became colourless. The lipid–chitosan complex completely disappeared. At pH 8, all the amino groups being in the NH_2 form, no electrostatic interactions should take place and chitosan is not soluble any more, in this unprotonated form.

Between pH 2 and 5, a substantial amount of oleic acid was not recovered after contact with chitosan, although the fatty acid was not in the carboxylate form: at pH 4, only 35% of the oleic acid remained as free fatty acid in solution. Interaction between chitosan and fatty acids cannot be explained by pure electrostatic binding anymore and other types of processes have to be involved, such as the influence of the emulsion structure. Indeed, the number of bonds and interaction occurring between the two phase depends also on the interfacial area and surface tension.

3.2. Calcium–chitosan interaction

The ability of chitosan to adsorb Ca^{2+} ions was evaluated as a function of pH (Fig. 3). A batch process was used, in which chitosan was added to the stirred solution, filtered out and the solution analysed for residual calcium ion content. The quantity of calcium adsorbed at a given pH was deduced from the initial concentration. Fig. 3 shows that adsorption of Ca^{2+} by chitosan is rather poor since, whatever the pH may be, only 16% of Ca^{2+} was removed from the solution after contact with 4 g/l chitosan (0.07 mmol Ca^{2+}/g chitosan were adsorbed). Physical adsorption appears to be the mechanism involved since calcium–chitosan interaction is not pH dependent, i.e. no H^+ species of chitosan are displaced into the solution via exchange with Ca^{2+} cations.

3.3. Ability of bi-layers chitosan-coated paper as fat barrier

In the first part of the study, experiments showed a strong pH-dependent chitosan–oleic acid interaction, which could be made profitable in multi-layer material. The chitosan layer could act as a lipid trap coating to decrease fat transfer if the pH of the chitosan film-forming solution was adjusted to 5.5–6 prior to coating. To study the relationships between composition and fat barrier properties of the matrix, Kraft paper was coated with a chitosan film-forming solution, previously adjusted to pH 5, using two coating techniques: a laboratory size-press process and a coating table technique. The influence of chitosan content on fat barrier properties and cost was then evaluated. Moreover, various chitosan-biomolecules formulations were additionally tested.

3.3.1. Utilisation of chitosan alone

Results from chitosan-coated paper from size-press experiments are presented in Table 3. The Kit test numbers obtained are reported as a function of chitosan content. Addition of chitosan allowed an improvement of the fat barrier of Kraft paper, according to the Kit test values.

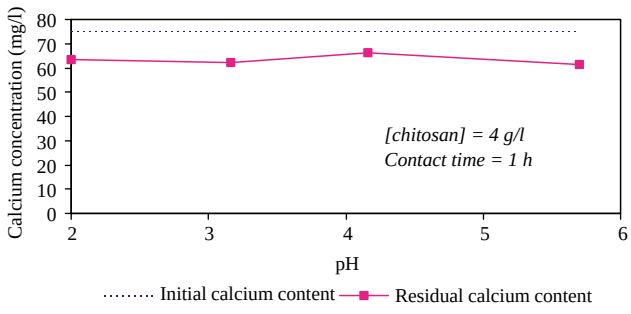

Fig. 3. Calcium–chitosan interaction as a function of pH.

Table 3
Chitosan coating of Kraft paper (40 g/m^2; Kit test number <1), with the size-press technique

Product	Chitosan solution (%, w/w)	Viscosity 100 rpm (Pa s)	Active product level in/on paper (%, w/w)	Kit test	Treatment cost (€/paper ton)
Fluorinated resins			0.6	8–9	120
Chitosan	1	0.20	0.67±0.01	1–2	107
	1.5	0.6	0.82±0.01	5	131
	1.5	0.6	1.36±0.08	5–6	218
	3	4.8	2.21±0.08	10–11	357

Chitosan coating level (%, w/w paper) are mean values from at least three experiments. Standard deviations were calculated using Student's *t*-test ($p<0.05$). Kit test experiments were reproduced at least three times.

Table 4
Chitosan coating of Kraft paper (40 g/m^2; Kit test number <1), with the laboratory coating table technique

Product	Chitosan solution (%, w/w)	Viscosity 100 rpm (Pa s)	Chitosan coating level (%, w/w)	Kit test	Treatment cost (€/paper ton)
Chitosan	3	4.8	1.13±0.11	5	181
	3	4.8	5.41±0.12	10–11	840

Chitosan coating level (%, w/w paper) are mean values from at least three experiments followed by standard deviations. These later were calculated using Student's *t*-test ($p<0.05$).

Compared with fluorinated resins, a similar efficiency was obtained with chitosan, when a 2.2% coating level was used. This level engendered a substantial raise in cost treatment, which is not economically viable. In addition, the high viscosities of the initial 3% chitosan solutions could not be used in industrial size-press.

Coating experiments were carried out on a laboratory coating-table. Results are reported in Table 4 and show that chitosan-coated papers can be used as fat barrier packaging with chitosan coating level of 5.41%. However, treatment costs remain high compared with fluorinated resins.

3.3.2. Utilisation of chitosan-biomolecules formulations

In an attempt to reduce treatment cost, chitosan was associated with various natural polymers and molecules. Results in Table 5 show that incorporation of cellulose ether (CMC or HPC) in chitosan formulations did not improve the fat resistance. On the other hand, incorporation of sodium alginate considerably increased the fat barrier of coated papers and, at the same time, reduced the treatment cost (Table 5). Kit test numbers of 10 and 11 were obtained with a chitosan/sodium alginate bi-layer of 0.47%/1.83% coating levels, respectively. Alginates are generally used in sizing and/or coating paper to produce surface uniformity. According to alginate supplier specifications, alginate is resistant to solvents, oil and grease and exhibit interesting film-forming properties. Moreover, alginates could also act as a penetration controller when associated with pure starch. The chitosan/alginate mixture, after coating on paper, allowed a fat resistance with synergistic effect, taking into account the possible limitation of the chitosan penetration into the paper and the contribution to a smoother surface due to film-forming capacities of gums at low concentration. However, high Brookfield viscosities of the chitosan/alginate mixtures (2300 cP measured at 20 °C and 100 rpm) are limiting factors for industrial application with size-press, and only coating applications should be industrially considered.

Table 5
Chitosan–cellulose and chitosan–alginate coatings of Kraft paper (40 g/m^2; Kit test number <1), with the size-press technique

Product	Chitosan coating level (%, w/w)	Cellulose ether or alginate coating level (%, w/w)	Kit test	Treatment cost (€/paper ton)
Chitosan	0.55±0.05	–	1	
	0.67±0.05		1–2	
	0.82±0.01		5	
Chitosan+CMC mixture	0.67±0.09	0.67±0.09	<1	
Chitosan+HPC mixture	0.72±0.01	0.72±0.01	<1	
Alginate		1.67±0.13	3–4	
Chitosan+Alginate mixture	0.47±0.05	1.83±0.14	10–11	197

Chitosan and coating levels (%, w/w paper) are mean values from at least three experiments followed by the standard deviations. These latter were calculated using Student's *t*-test ($p<0.05$).

4. Conclusion

Coated chitosan on paper matrix could be a potential process to develop paper-based packaging materials to pet food applications, with fat barrier performances. Chitosan–alginate gum coated paper with Kit test numbers similar to the value obtained from fluorinated resins were obtained. The treatment cost remained higher than with fluorinated resins, but the use of natural molecules is a commercial argument, which can justify a cost difference. The high viscosities of film-forming solutions did not allow a size-press industrial application and further investigations are needed to explore the potential of chitosan oligomers as fat barrier coating.

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