Impact of Biodegradable Chitosan-Based Coating on Barrier Properties of Papers

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Received January 14, 2014; Accepted April 02, 2014

ABSTRACT: Aroma and oxygen-barrier properties of chitosan-coated papers were measured in order to evaluate the potential of these materials as biodegradable materials for food packaging. Firstly, two chitosans (Chi-244 and Chi-652) were studied according to their ultimate biodegradability. Chi-652 showed the best final biodegradation rate and was then used for subsequent tests in association with papers. Then, oxygen-barrier and aroma-barrier properties of papers, Chi-652 films and Chi-652-coated papers were investigated. The Chi-652 films exhibited oxygen-barrier at low relative humidity and aroma-barrier comparable to synthetic materials already used in the packaged food industry. Both papers exhibited poor barrier properties toward oxygen and aromas. Although chitosan-coated papers showed promising results in regard to the aroma-barrier performance of papers, it did not improve their oxygen-barrier properties, probably because of the impact of the coating process on the tri-dimensional structure of the papers.

KEYWORDS: Chitosan, coated paper, oxygen transfer, biodegradability, aroma transfer

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1 INTRODUCTION

Food packaging has been under several strong constraints over the past decades. More than ever, it must participate in enhancing food preservation and food safety [1] without raising environmental concerns [2], i.e., it should preferentially be made from sustainable resources.

Effective protection of food products is indeed of essential importance for maintaining food quality during storage. Packaging-driven food safety approaches with inherently antimicrobial packaging materials, with simple contact between antimicrobial matrix and food surface, with controlled delivery of antimicrobial substances or with controlled atmosphere within the packaging, are just a few of the well-recognized techniques [3]. The use of sustainable resources has been explored through the use of natural polymers, the incorporation of these natural polymers into composite materials with synthetic materials or the use of fermentation-produced polymers in order to avoid the use of non-sustainable oil-based polymeric materials [4–6]. In this perspective, paper and chitosan have been tested in order to meet preservation, safety and environmental requirements of food packaging [7–10].

In general, paper shows only very low barrier properties, including toward organic compounds. Therefore, it is a common approach to improve the barrier properties of papers by coating a thin layer of a material that provides good intrinsic barrier properties. Chitosan, a linear cationic polymer of D-glucosamine made from the deacetylation of chitin, an essential component of crustacean exoskeleton and a waste of the shrimp-fishing industry, has recognized film-forming, barrier and antimicrobial properties that makes it suitable for sustainable and antimicrobial food-packaging applications [11–14]. Chitosan-based materials have successfully shown their antimicrobial efficacy against several pathogenic

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DOI: 10.7569/JRM.2014.634105

foodborne bacteria [7, 15]. However, as the vast majority of polysaccharides, chitosan is highly hydrophilic and several efforts have also been conducted in order to enhance chitosan physicochemical properties, its sensitivity toward moisture and liquid water and to adapt its use to high-moisture environments or high water-activity food systems [8, 16–20]. Other studies focused on improving mechanical properties of chitosan-based materials to make them able to compete with usual synthetic materials used in food packaging [14, 21, 22]. Nevertheless, beside these studies, only little data are available on the properties of chitosan-based materials regarding other essential requirements that food packaging materials must meet, namely aroma barrier properties or oxygen barrier properties. Indeed, aroma loss or oxidation caused by oxygen absorption are detrimental to food organoleptic properties [23, 24]. Individual aroma and odor compounds can either be absorbed by or permeate through the packaging materials, resulting in a loss of aroma intensity or an unbalanced flavor profile (“flavor scalping”). In addition to the preservation of the aroma of the packaged product, flavor and odor barriers prevent undesired external flavor and odors from reaching and contaminating the product.

Moreover, sustainability is among the top reasons for using biopolymers in food packaging, but very few studies actually paid attention to the biodegradability of the packaging materials prepared from chitosan [25, 26].

So, this study aims at understanding how chitosan can improve oxygen and aroma barrier properties of paper-based materials, while maintaining their biodegradability. In other words, the main objective of this work was to investigate if chitosan could have potential as a biodegradable, nontoxic and environmentally safe material for food packaging applications in combination with paper.

In more detail, the real ultimate aerobic biodegradability of some chitosans was evaluated in order to select a biodegradable polysaccharide-based coating potentially interesting to improve the barrier properties of paper-based matrix without decreasing the inherent biodegradability of paper. Then, oxygen and aroma barrier properties of chitosan-based materials were investigated. The permeation of volatile organic compounds through chitosan-coated paper samples and a pure chitosan film, as well as the solubility of these compounds in the respective materials, were comparatively measured. This was achieved by a method established previously [27, 28] measuring the permeation of a set of model organic compounds commonly occurring as odor/aroma in foods or being used as odor/aroma in non-food products. These model compounds span a large range of octanol/water partition coefficients (LogP), volatility and molecular weight, and therefore serve in evaluating the aroma barrier properties of packaging materials.

2 EXPERIMENTAL

2.1 Chemicals and Standards

All chemicals and standards were analytical grade (> 99% pure) and purchased either from VWR International (Fontenay-sous-Bois, France; Darmstadt, Germany) or Sigma-Aldrich (Lyon, France; Munich, Germany). Gases were Alphagaz 2 grade and bought from Air Liquide (Paris, France).

2.2 Materials

Commercial grade chitosans were used in this study (France Chitine, Marseille, France): Chi-244 (flakes, deacetylation degree higher than 95%, Mw = 400 kDa) and Chi-652 (powder, deacetylation degree higher than 85%, Mw = 165 kDa).

Papers were provided by Ahlstrom (Ascoflex 40, non-calendered, one side coated with calcium carbonate, grammage 40 g.m^{-2}, 48 µm thick, Grenoble, France) and Stora Enso (Performa Nature 320, non-calendered, one side coated with calcium carbonate, grammage 320 g.m^{-2}, 344 µm thick, Helsinki, Finland), where grammage is the weight per unit area of the papers.

Chitosan films and chitosan coated papers were prepared as described previously [8]. Briefly, 5 mL of a solution of 2% w/w chitosan in 1% w/w aqueous solution of acetic acid were coated evenly and at constant speed on the aforementioned papers with a K101 Control Coater instrument equipped with a 120 µm blade (Erichsen, Rueil-Malmaison, France) on 210 × 297 mm sheets of test papers, leading to a deposit of 0.1 g dry chitosan per sheet (1.6 g.m^{-2} on Ahlstrom paper, 0.005 g.m^{-2} on Stora Enso paper). Materials tested in this study and their characteristics are listed in Table 1; they consist of chitosan films, papers and papers coated with chitosan.

2.3 Biodegradability and Rate of Biodegradation of Chitosans

This evaluation was carried out according to the norms issued by the British Standards Institution [29]. It consists of the titration of CO_2 released from the oxidation by bacteria of the tested sample’s organic carbon in aqueous media, at 23°C.

The absolute percentage of biodegradation (%B) is given by the following formula:

$$\%B = CO_{2-released} \times {}^{100}\!\big/_{CO_{2-theoretical}} \tag{1}$$

where $CO_{2\text{-}released}$ is the actual amount of CO_2 titrated during the test, and $CO_{2\text{-}theoretical}$ is the theoretical amount

Table 1 Grammage (weight per unit area), thickness and coating density of tested materials. Values are Mean ± Confidence Interval ($n > 3$; $p < 0.05$).

Material	Grammage ($g.m^{-2}$)	Thickness (μm)	Coating density ($g.\ m^{-2}$)	Oxygen Transmission Rate ($cm^3.m^{-2}.d^{-1}$)	Oxygen Permeability ($cm^3.\ \mu m.m^{-2}.\ d^{-1}$)	Absolute final biodegradation	Relative final biodegradation[b]
Chi-244 film	–	19 ± 1	–	–	–	11 ± 9 %	12 ± 11 %
Chi-652 film	–	20 ± 2	–	30 ± 7	600 ± 200	73 ± 4 %	81 ± 10 %
Ahlstrom paper	40	48 ± 1	0	> 40,000[a]	$> 1.9\times10^6$	–	–
Ahlstrom paper coated with Chi-652	41.6	56 ± 1	1.6	> 40,000[a]	$> 2.2\times10^6$	–	–
StoraEnso paper	320	344 ± 1	0	> 40,000[a]	$> 13.8\times10^6$	–	–
StoraEnso paper coated with Chi-652	321.6	402 ± 2	1.6	> 40,000[a]	$> 16.1\times10^6$	–	–

[a] Readings were above instrument's maximum transfer rate reading value (> 40,000 $cm^3.m^{-2}.d^{-1}$).

[b] Calculated on the basis on Avicel absolute final degradation: 91 ± 7%.

of CO_2 released if the totality of the total organic carbon of the sample had been biodegraded.

$CO_{2\text{-released}}$ is measured as follows: Pressured air flows sequentially through CO_2 traps and the reactor containing the test sample. There, it carries CO_2 released from the biodegradation of the test sample to CO_2 traps containing potassium hydroxide; they react quantitatively to form potassium carbonate, which is then titrated with hydrochloric acid.

$CO_{2\text{-theoretical}}$ is calculated as follows: Elemental analysis is carried out on the original test sample (measurement of total carbon) and on the mineral residues left after ignition of the test sample at 575°C (measurement of mineral carbon). Total organic carbon is the difference between these two values. $CO_{2\text{-theoretical}}$ is the amount of CO_2 derived from the amount of total organic carbon contained in test samples.

In a reactor containing water inoculated with bacteria derived from the supernatant of a water treatment plant, 0.6 g of the test sample is placed at 23°C. $CO_{2\text{-released}}$ is measured at regular time intervals over 2–3 months until it reaches a plateau. The baseline measurement, consisting of ambient CO_2 in the air, is subtracted from the readings.

Chi-244 flakes and Chi-652 powder were run in duplicate. In parallel, two blanks and two reference samples are run. The reference samples are Avicel microcrystalline cellulose containing 42% organic carbon. In this study both Chi-244 and Chi-652 were tested for their biodegradability and rate of biodegradation.

In addition to the absolute percentage of biodegradation (*%B*) achieved by each tested material, a relative percentage of biodegradation (*rel%B*) was calculated on the basis of the Avicel's percentage of biodegradation: $rel\%B_{tested\ material} = \%B_{tested\ material}\ /\ \%B_{reference}$.

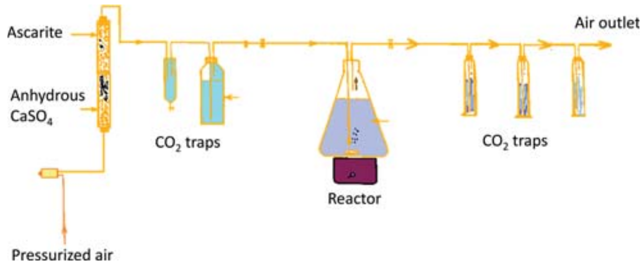

Figure 1 Experimental setup for materials biodegradation evaluation.

The experimental set up is shown in Figure 1.

2.4 Oxygen Barrier Properties

Oxygen barrier properties were measured according to the norm ASTM D3985 [30] with an Oxygen Permeation Analyzer 8000 (Systech Instruments, Nanterre, France). Oxygen transmission rates were determined at 23°C and 0% relative humidity.

The samples were evaluated in triplicate in permeation test cells with a permeation area of 50 cm^2. In the lower cell chamber N_2 was circulating at 20 $cm^3.min^{-1}$, and O_2 was circulating at 10 $cm^3\ .min^{-1}$ in the upper chamber cell. The O_2 permeating through the test material was transported by the nitrogen stream to a calibrated coulometric detector. A blank test was run with a metal plate as test material.

Oxygen transmission rate (OTR) of Chi-652 films and Chi-652 coated papers were then measured cm^3.m^{-2}.d^{-1} and oxygen permeability was calculated as OTR x thickness of the material and expressed in cm^3.µm.m^{-2}.d^{-1}.

2.5 Aroma Barrier Properties

Aroma barrier properties were measured according to the method described in earlier works [27, 28].

A cocktail containing the following aroma compounds was used: isoamyl actetate, D-limonene, cis-3-hexen-1-ol, linalyl acetate, menthol, citronellol and diphenyl oxide (Figure 2). A mixture of the seven model flavors (relative amounts, see Table 2) was dissolved in polyethylene glycol (PEG) 400 at a concentration of 5% (w/w) to yield model flavor feed pressures as given in Table 2. For permeation measurements, 20 g of the PEG 400 solutions were applied to the permeation test cell to establish constant feed pressures. Feed pressure determinations of test permeants, permeation measurements, gas chromatographic determination of permeants and data evaluation were carried out as described previously [19, 20, 27, 28].

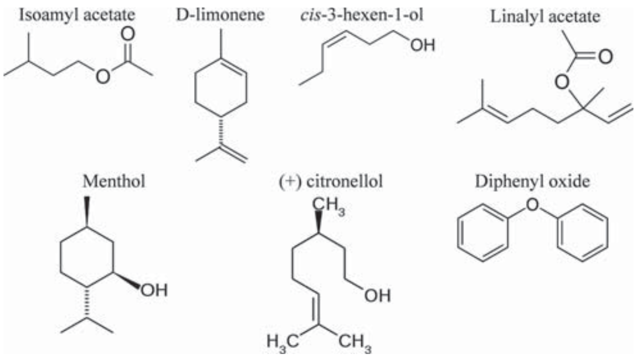

Figure 2 Aroma compounds used in assessment of aroma barrier properties.

The samples were evaluated in test cells with a permeation area of 78.5 cm^2 kept at approx. 23°C. A glass dish containing 20 g of the aroma cocktail (5% w/w in PEG-400) was placed in each lower cell chamber, serving as a release reservoir for the test permeants. The test samples were then placed above the dish with the chitosan-coated side facing the aroma cocktail.

A dry nitrogen stream (1 ml.min^{-1}) is circulated over the test samples through the upper cell chamber to transport the permeated substances to a solid phase extraction (SPE) column. The SPE column was changed at regular time intervals.

The aroma compounds were then eluted from the SPE column with 0.5 mL hexane twice and this extract was analyzed by gas chromatography with flame ionization detection (GC-FID). Then 2 µL of each extract were injected on a SE-10 capillary column (length: 30 m; inner diameter: 0.32 mm; coating thickness: 0.5 µm) with the following temperature program: 1 min isotherm at 60°C, heating rate of 10°C.min^{-1} up to 220°C, 8 min isotherm at 220°C. Quantification of the test substances was made by the external standard method.

Chi-652 film and Chi-652 coated papers were run in triplicate for 38–77 days until steady-state of permeation was reached.

Transmission rates of permeants were calculated and expressed in µg.m^{-2}.h^{-1}, and aroma permeability was calculated as transmission rate x thickness and expressed in µg. µm.m^{-2}. h^{-1}.

Breakthrough times of permeants across the materials were evaluated as the time at which steady-state of permeation was established.

Once steady-state was reached, the test samples were removed from the cells and extracted: 12 cm^2 of the test samples were extracted once with isooctane (72 h at 40°C) and once with ethanol (48 h at 40°C).

Table 2 Cocktail of seven model flavors used for permeation measurements.

Compound	Molecular weight (g.mol^{-1})	Log P[1]	Relative amount in mixture (w/w ratio)	Vapor pressure over 5 % solution in PEG 400 [$\times 10^{-6}$ bar]
Isoamyl acetate	130	2.12	0.05	2.9
Limonene	136	4.45	0.05	2.3
cis-3-Hexenol	100	1.61	1	3.0
Linalyl acetate	196	3.83	5	4.7
Menthol	156	3.20	10	3.9
Citronellol	156	3.38	10	1.1
Diphenyl oxide	170	4.21	10	1.0

[1] Octanol/water partition coefficient.

The extracts were also analyzed by GC-FID in order to determine the permeants relative solubilities in the test materials.

2.6 Data Analysis

The OTR and aroma transfer experiments were repeated three times. Biodegradation experiments were repeated two times. Data are mean values given with a Student's confidence interval at 95% probability ($p < 0.05$).

3 RESULTS AND DISCUSSION

Overall, chitosan- and paper-based materials developed in former studies [7, 8] have been tested according to their biodegradability in soil environment and their oxygen-barrier and aroma-barrier properties, in order to address the question of the applicability of such materials on real food packaging systems.

3.1 Biodegradability and Rate of Biodegradation of Chitosans

Total organic carbon (TOC) was measured as 39.2% w/w for Chi-244 and 39.3% w/w for Chi-652, on a dry-matter basis.

Figure 3 shows biodegradation of Avicel (reference), Chi-244 and Chi-652 films (average of two duplicates) over time. Avicel reference reached a final percentage of biodegradation of 91 ± 7%. Regarding Chi-244, the biodegradation rate was slow and plateaued after 25 days with a final relative biodegradation value of 12 ± 11%. Regarding Chi-652, the biodegradation rate was comparable to Avicel over the first 8 days, then slowed down and plateaued after 60 days with a final relative biodegradation value of 81 ± 10%. Results are reported in Table 1. Although biopolymers generally exhibit a wide range of final biodegradation values, this is consistent with values reported before in other studies [25, 26].

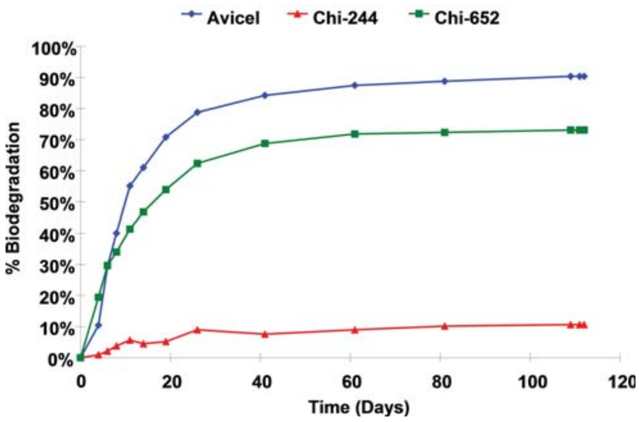

Figure 3 Absolute percentage of biodegradation of Avicel, Chi-244 and Chi-652 as a function of time.

While cellulose is not a bioactive polymer, chitosan films were shown to have antimicrobial properties [7]. Although this property is best achieved at acidic pH (to the cationic form of amino groups and dissolution in aqueous media), this phenomenon may have contributed to alter the microbial population of the test medium and decrease the microbial degradation of the two chitosans tested. The difference in degrees of deacetylation of Chi-244 and Chi-652 (> 95% and > 85%, respectively) could support this hypothesis, Chi-244 bearing more bioactive NH_3^+ moieties than Chi-652 in a close-to-neutral aqueous medium. Degree of deacetylation has already proven to impact biodegradation and to vary along the biodegradation process [31].

Moreover, our results show that Chi-652 (lower Mw and lower deacetylation degree) is more efficiently biodegraded than Chi-244 (higher Mw and higher deacetylation degree). This is consistent with other previous results [26] showing that chitosan biodegradation is inversely correlated with its deacetylation degree, as it relates to changes in chitosan crystalline structure, also a function of its deacetylation degree and molecular weight. Indeed, it has been shown that an increasing number of acetyl moieties in chitosan allows the disruption of order intermolecular structure, leading to a decrease in crystallinity, and reduced molecular weight improves chitosan water solubility [32–34].

Thus, these two factors combined could lead to a better physical accessibility of the polymer to be degraded by bacteria.

Nevertheless, from solely a legal standpoint [35], Chi-244 and Chi-652 cannot be considered as biodegradable, since a minimum value of 90% relative biodegradation must be achieved over a maximum of 6 months. At this point of the study, Chi-244 could not be considered as a good candidate for biodegradable packaging material. However, since Chi-652 was considered as a promising starting material, it was decided to proceed further with additional tests on Chi-652-based materials (films and coated papers).

3.2 Oxygen Barrier Properties

Oxygen barrier properties were measured on Chi-652 films and on papers coated with Chi-652. Results are shown in Table 1.

Chi-652 shows an OTR of 30 ± 7 $cm^3.m^{-2}.d^{-1}$, and both papers exhibit an OTR value higher than 40,000 $cm^3.m^{-2}.d^{-1}$. These values are consistent with those reported in other studies. Indeed, on the one hand, polysaccharides are known to be excellent O_2 barriers at low relative humidity [24], and our value for Chi-652 films also compares very well with those reported on chitosan (38–56 $cm^3.m^{-2}.d^{-1}$) [36]. On the other hand, while paper does not limit transfer to gases because of its inherent porosity [9, 37–39], it was proved that the coating of biopolymers onto papers was efficient in reducing O_2 transfer trough the material. However, the chitosan-coated papers we had prepared did not show the same trend, with OTR values higher than 40.000 $cm^3.m^{-2}.d^{-1}$. This can be explained by the observation reported in our previous work showing chitosan was not forming a continuous layer on top of the paper, but rather was penetrating into the paper core, impregnating and embedding the cellulose fibers as well as filling the inter-fiber pores [8]. By contrast, efficient barrier to oxygen transport has been achieved by Gallstedt and coworkers; a deposit of 19 g of chitosan per m^2 of paper was necessary to achieve acceptable O_2 barrier properties [22]. Nevertheless, although this latter approach is technically successful, it does not seem economically viable, considering the cost of chitosan. In our approach, the quantity of chitosan coated onto the papers (1.6 $g.m^{-2}$) remained at a level that: 1) would have minimal impact on the cost of the final material; 2) took into account technical limitations (solubility of chitosan and amount of water carried by the coating solution, resistance of paper to multiple coatings). Thus, our work shows that with common papers, satisfying oxygen barrier properties could not be achieved without significantly impacting the cost of the final material and without taking the risk of losing the paper's three-dimensional structure and integrity. So, chitosan by itself shows promising potential for oxygen barrier properties, but there are still technical hurdles to be overcome to transfer this potential to paper-based materials. Finally, it must be noted that oxygen transfer was measured at 0% RH, which makes these conclusions applicable to the packaging of dry foods. However, as shown in a previous study [8], these materials exhibit sensitivity to water. Thus, these conclusions drawn here may not be applicable to the packaging of perishable food with high water content or high water activity.

Then, similarly to oxygen transfer, the transfer of volatile aroma compounds through Chi-652 and Chi-652 coated papers was tested.

3.3 Aroma Barrier Properties

The transfer of aroma compounds through a given material depends on the aroma's physicochemical properties such as octanol/water partition coefficient, volatility and molecular weight on the one hand, and composition and matrix structure of the material on the other hand [40, 41]. In this study, we examined the permeation of seven model volatile food components through the abovementioned materials: isoamyl actetate, D-limonene, cis-3-hexen-1-ol, linalyl acetate, menthol, citronellol and diphenyl oxide. These seven model flavors cover a molecular weight range from 100 to 200 g/mol and represent chemical structures with a wide range of functional groups and partition coefficient (Figure 2). The selection of the model flavors, and thus permeation data obtained from this model cocktail, may be used for the prediction of the permeation behavior of other flavor compounds [28].

The permeation process of the flavor/odor compounds was characterized by permeation curves (Figures 4, 5 and 6) as well as calculated permeation

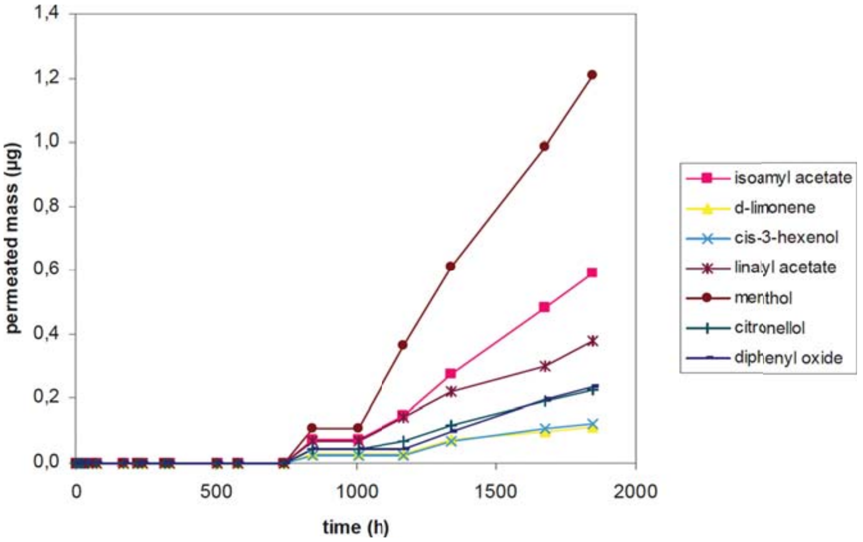

Figure 4 Aroma permeation curves of Chi-652 film.

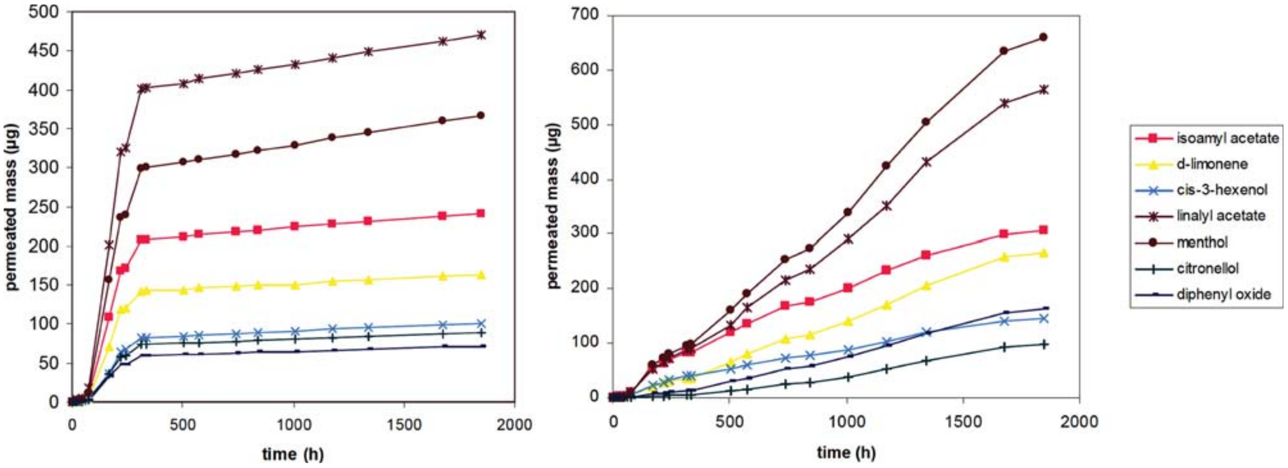

Figure 5 Aroma permeation curves of (left) Ahlstrom paper and (right) Chi-652 coated Ahlstrom paper.

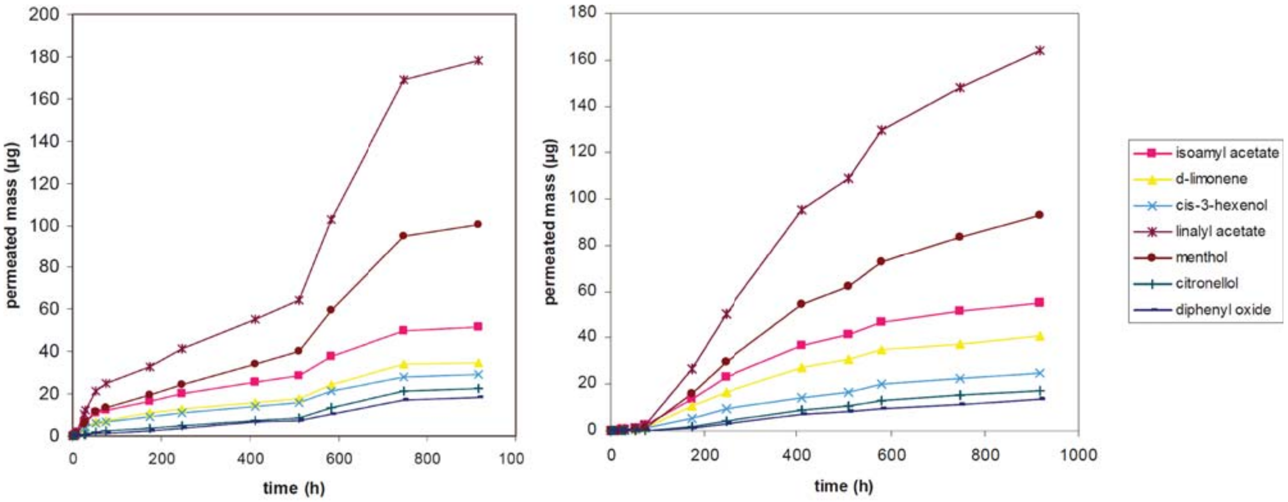

Figure 6 Aroma permeation curves of (left) Stora Enso paper and (right) Chi-652 coated Stora Enso paper.

rates (Table 3) and estimated breakthrough times (Table 4). As the permeation process is also dependent on the solubility of the test compounds in the sample material, their respective relative solubilities were also determined (Table 5).

Chi-652 films exhibited good aroma barrier properties consistent with values found for other films made of hydrophilic polymers [42]. Transmission rates and solubilities of test compounds were generally below detection limit (below 0.04 µg.m^{-2}.h^{-1} and 0.003 mg.g^{-1}, respectively). Moreover, a breakthrough of the respective test permeants was not detectable before approximately 1000 hours (42 days) of storage. Therefore the aroma barrier properties of the pure chitosan film are comparable to those established for conventional plastic materials like PET [27, 28]. This correlates well with a previous study showing low permeation of benzyl benzoate through cassava starch films, for example [43]. As suggested in former works, permeation properties of aroma compounds through edible and synthetic polymeric films are mainly dependent on their sorption, rather than on their diffusion itself [44, 45].

As permeation measurements were performed using vapor pressures simulating real food conditions, it can be concluded that the chitosan film has a high potential to be used in packaging applications

Table 3 Transmission rate (in µg. m^{-2}. h^{-1}) and permeability (in µg. µm.m^{-2}. h^{-1}) of test permeants through Chi-652 films, papers and papers coated with Chi-652.

	Material	Isoamyl actetate	Limonene	Cis-3-hexenol	Linalyl actetate	Menthol	Citronellol	Diphenyl oxide
Aroma transmission rates (µg. m^{-2}. h^{-1})	Chi-652 film	0.1	< 0.04	< 0.04	< 0.04	0.04	< 0.04	< 0.04
	Ahlstrom paper	2.5	1.7	1.3	5.5	5.4	1.2	1.0
	Ahlstrom paper coated with Chi-652	13.8	18.5	7.8	40.7	45.7	8.8	13
	StoraEnso paper	7.1	5.2	4.0	35.8	19	4.4	3.4
	StoraEnso paper coated with Chi-652	4.0	2.9	2.4	16.3	9.1	2.0	1.6
Aroma permeability (µg. µm.m^{-2}. h^{-1})	Chi-652 film	2	< 0.8	< 0.8	< 0.8	0.8	< 0.8	< 0.8
	Ahlstrom paper	120	82	62	264	259	58	48
	Ahlstrom paper coated with Chi-652	773	1036	437	2279	2259	493	728
	StoraEnso paper	2442	1789	1376	12315	6536	1514	1170
	StoraEnso paper coated with Chi-652	1608	1166	965	6553	3658	804	643

Table 4 Estimated breakthrough times (in h) of test permeants through Chi-652 films, papers and papers coated with Chi-652.

Material	Isoamyl actetate	Limonene	Cis-3-hexenol	Linalyl actetate	Menthol	Citronellol	Diphenyl oxide
Chi-652 film	1,000	1,100	1,100	1,000	1,000	1,000	1,100
Ahlstrom paper	25	48	48	19	25	75	75
Ahlstrom paper coated with Chi-652	25	75	75	48	75	169	169
StoraEnso paper	8	25	25	8	25	52	75
StoraEnso paper coated with Chi-652	52	75	172	75	172	172	172

Table 5 Relative solubilities (in mg.g^{-1}) of test permeants in Chi-652 films, papers and papers coated with Chi-652.

	Isoamyl actetate	Limonene	Cis-3-hexenol	Linalyl actetate	Menthol	Citronellol	Diphenyl oxide
Ahlstrom paper	< 0.003	< 0.003	0,028	0,103	0,120	0,183	0,200
Ahlstrom paper coated with Chi-652	< 0.003	< 0.003	0,019	0,055	0,063	0,089	0,099
StoraEnso paper	< 0.003	< 0.003	0,115	0,151	0,140	0,165	0,183
StoraEnso paper coated with Chi-652	< 0.003	< 0.003	0,115	0,152	0,132	0,146	0,166

demanding high barrier properties for aromas and flavorings. Possible examples could be food products with a shorter shelf-life and, due to the large dependency of chitosan's permeability to oxygen on relative humidity, most likely dry and fatty foods like potato snacks.

In order to evaluate the effect of chitosan coating on paper samples, the chitosan-coated paper samples were evaluated for their aroma barrier properties in comparison to the non-coated papers. Uncoated papers generally show poor aroma barrier properties due to their inherent porous structure. With the exception of menthol and linalyl acetate, transmission rates of the model flavor compounds obtained for the pure uncoated papers were comparable and ranged from 1.0–2.5 $\mu g.m^{-2}.h^{-1}$ for Ahlstrom and 3.4–5.2 $\mu g.m^{-2}.h^{-1}$ for Stora Enso paper, respectively (Table 3). Estimated breakthrough times for the test compounds ranged from 19–75 h and 8–75 h for Ahlstrom and Stora Enso papers, respectively (Table 4). Interestingly, menthol and linalyl acetate exhibited the highest transmission rate values (5.4–5.5 $\mu g.m^{-2}.h^{-1}$ for Ahlstrom, 19–35.8 $\mu g.m^{-2}.h^{-1}$ for Stora Enso) and the shortest breakthrough times for both paper samples.

Model flavor compounds also exhibited high solubilities in these uncoated papers, ranging from 0.028–0.200 and 0.115–0.183 $mg.g^{-1}$, for the Ahlstrom and the Stora Enso paper, respectively, except for isoamyl acetate and limonene, which were below the detection limit of 0.003 $mg.g^{-1}$ (Table 5).

The effect of chitosan coating on the Ahlstrom and Stora Enso papers led to opposite results. Both aroma transmission rates and permeabilities were increased by a factor of 6 to 15 by coating on Ahlstrom paper and decreased by a factor of 1.4–2.2 by coating on Stora Enso paper (Table 3). Breakthrough times were generally increased for both papers, but to very different extents: decrease by a factor as high as 3 by coating Ahlstrom paper, by a factor as high as 9.4 by coating Stora Enso paper (Table 4).

Overall, chitosan coating deteriorated the aroma barrier properties of Ahlstrom paper. Contrarily, chitosan coating led to an improvement of Stora Enso paper aroma barrier properties compared to the uncoated paper, as indicated by reduced permeation rates as well as by the shift of breakthrough times to up to seven days. However, breakthrough times were significantly shorter for chitosan-coated paper than for the pure chitosan film (approximately 2–7 days compared to more than 42 days). In both cases, the best improvements induced by coating were found for linalyl acetate and menthol. Accordingly, breakthrough times were significantly shorter for all chitosan-coated papers compared to Chi-652 film. Regarding solubility of the aroma compounds, isoamyl acetate and limonene remained below detection limit for the coated papers, and the solubility of the other compounds was generally reduced by chitosan coating onto paper, but once again to very different extents: −30 to −51% by coating on the Ahlstrom paper, +1 to −11% by coating on the Stora Enso paper (Table 5). The differences between partition coefficients of model aroma compounds may be an essential factor in trying to explain these observations: the compounds solubility decreases as their polarity decreases [46] and the consequence may be flavor scalping by selective transfer processed through the material [47].

The main effect induced by coating of chitosan on the permeation properties of papers may be its impact on the three-dimensional structure of papers. In a previous study, we have shown papers behave differently towards the chitosan-coating process: chitosan-coated Ahlstrom paper is homogeneously impregnated with chitosan and loses most of its three-dimensional structure due to wetting, while the three-dimensional structure of Stora Enso cellulose fibers is mostly preserved during penetration of chitosan due to greater thickness [8]. Using the same coating density of 1.6 $g.m^{-2}$ for the chitosan coating on both paper materials leads to different effects on the integrity of the paper materials, and it must be noted that the chitosan coating cannot be applied as a distinct dense coating layer on top of paper materials, as known from other plastic coating materials like, e.g., LDPE and PP. Rather, it penetrates the cellulose fiber structure.

Therefore, we can hypothesize that the low permeation of the model aroma compounds through chitosan, as well as the low solubility of those aroma compounds in the chitosan, result in improved barrier properties of Stora Enso paper. However, in paper-based materials, this effect is counterbalanced by the greater loss of structure and integrity in the case of Ahlstrom paper, leading to an increase in aroma permeability. The loss of structure for Ahlstrom paper may also explain the limited improvement in breakthrough time for coated Ahlstrom paper, in comparison to the coated Stora Enso paper.

Even though the good aroma barrier properties of the pure chitosan film compared to the coated papers are based predominantly on the greater thickness of the chitosan film as compared to the distribution of chitosan into the papers, the permeation process through the paper was not sufficiently inhibited by the coating in Stora Enso paper.

Our measurements indicate that the aroma/odor permeation through paper can in principle be decreased by coating with chitosan. However, in order to achieve sufficient aroma/odor barrier properties, an optimization of the chitosan coating should be addressed, finding a compromise between chitosan loading of the paper and loss of the paper's structure and integrity.

4 CONCLUSION

The barrier characteristics of chitosan on paper substrates were characterized by permeation rates, estimated breakthrough times and the relative solubility of the respective aroma compounds in the barrier materials. Although significant improvements still need to be achieved, chitosan-coated thick papers prepared in this study showed good potential for their application as food packaging materials. Indeed, although Chi-652 does not fall exactly into the category of biodegradable materials, it has good potential (especially if coated at low levels of deposit) and Chi-652 coating on paper allowed the improvement of the paper's barrier properties toward oxygen and aromas in dry environments, even though the values obtained cannot yet compete with the best synthetic materials. Nevertheless, the potential of the concept shown here could be overcome mainly by technological improvements. In order to achieve sufficient aroma/odor barrier properties, an optimization of the chitosan coating thickness as well as the used paper material must be addressed. This study showed that chitosan coating adds value to paper, especially if dry conditions were maintained around the biopolymer matrix.

DISCLAIMER

Nicolas Bordenave is an employee of PepsiCo Inc. The views expressed in this article are those of the authors and do not necessarily reflect the position or policy of PepsiCo, Inc.

REFERENCES

1. A.R. de Jong, H. Boumans, T. Slaghek, J. Van Veen, R. Rijk, and M. Van Zandvoort, Active and intelligent packaging for food: Is it the future? *Food Addit. Contam.* **22**, 975-979 (2005).
2. Anonymous, Environmental group tells store to stop buying grocery bags from Weyerhaeuser. *Recycled Paper News* **14**, 3-4 (2004).
3. P. Appendini and J.H. Hotchkiss, Review of antimicrobial food packaging. *Innov. Food Sci. Emerg. Technol.* **3**, 113-126 (2002).
4. O. López, M. García, and N.E. Zaritzky, Novel sources of edible films and coatings. *Stewart Postharvest Rev.* **6**, 1-8 (2010).
5. R.N. Tharanathan, Biodegradable films and composite coatings: Past, present and future. *Trends Food Sci. Technol*. **14**, 71-78 (2003).
6. A. Gandini, The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem*. **13**, 1061-1083 (2011).
7. N. Bordenave, S. Grelier, and V. Coma, Hydrophobization and antimicrobial activity of chitosan and paper-based packaging material. *Biomacromolecules* **11**, 88-96 (2010).
8. N. Bordenave, S. Grelier, F. Pichavant, and V. Coma, Water and moisture susceptibility of chitosan and paper-based materials: Structure-property relationships. *J. Agric. Food Chem.* **55**, 9479-9488 (2007).
9. M. Gällstedt, A. Brottmon, and M.S. Hedenqvist, Packaging-related properties of protein- and chitosan-coated paper. *Packag. Technol. Sci.* **18**, 161-170 (2005).
10. J. Vartiainen, R. Motion, H. Kulonen, M. Rättö, E. Skyttä, and R. Ahvenainen, Chitosan-coated paper: Effects of nisin and different acids on the antimicrobial activity. *J. Appl. Polym. Sci.* **94**, 986-993 (2004).
11. M. Aider, Chitosan application for active bio-based films production and potential in the food industry: Review. *LWT Food Sci. Technol.* **43**, 837-842 (2010).
12. P.K. Dutta, S. Tripathi, G.K. Mehrotra, and J. Dutta, Perspectives for chitosan based antimicrobial films in food applications. *Food Chem.* **114**, 1173-1182 (2009).
13. P. Fernandez-Saiz, M.J. Ocio, and J.M. Lagaron, The use of chitosan in antimicrobial films for food protection. *Perspect. Agric. Vet. Sci. Nutr. Nat. Resour.* **5**, 1-11 (2010).
14. P. Fernandez-Saiz, J.M. Lagarón, and M.J. Ocio, Optimization of the film-forming and storage conditions of chitosan as an antimicrobial agent. *J. Agric. Food Chem.* **57**, 3298-3307 (2009).
15. V. Coma, A. Martial-Gros, S. Garreau, A. Copinet, F. Salin, and A. Deschamps, Edible antimicrobial films based on chitosan matrix. *J. Food Sci.* **67**, 1162-1169 (2002).
16. S.K. Bajpai, N. Chand, and V. Chaurasia, Investigation of water vapor permeability and antimicrobial property of Zinc Oxide nanoparticles-loaded chitosan-based edible film. *J. Appl. Polym. Sci.* **115**, 674-683 (2010).
17. T. Bourtoom and M.S. Chinnan, Improvement of water barrier property of rice starch-chitosan composite film incorporated with lipids. *Food Sci. Technol. Int*. **15**, 149-158 (2009).
18. M. Pereda, G. Amica, and N.E. Marcovich, Development and characterization of edible chitosan/olive oil emulsion films. *Carbohydr. Polym.* **87**, 1318-1325 (2012).
19. M. Pereda, M.I. Aranguren, and N.E. Marcovich, Water vapor absorption and permeability of films based on chitosan and sodium caseinate. *J. Appl. Polym. Sci.* **111**, 2777-2784 (2009).
20. L. Sánchez-González, A. Chiralt, C. González-Martínez, and M. Cháfer, Effect of essential oils on properties of film forming emulsions and films based on hydroxypropylmethylcellulose and chitosan. *J. Food Engg.* **105**, 246-253 (2011).
21. N. Niamsa and Y. Baimark, Preparation and characterization of highly flexible chitosan films for use as food packaging. *Am. J. Food Technol.* **4**, 162-169 (2009).
22. K. Ziani, J. Oses, V. Coma, and J.I. Maté, Effect of the presence of glycerol and Tween 20 on the chemical and physical properties of films based on chitosan with

different degree of deacetylation. *LWT Food Sci. Technol.* **41**, 2159-2165 (2008).
23. K. Marsh and B. Bugusu, Food packaging - Roles, materials, and environmental issues: Scientific status summary. *J. Food Sci.* **72**, R39-R55 (2007).
24. J.H. Han, *Innovations in Food Packaging*, pp., Academic Press, Boca Raton, FL, pp. 13–35 (2005).
25. I. Makarios-Laham and T.C. Lee, Biodegradability of chitin- and chitosan-containing films in soil environment. *J. Environ. Polym. Degrad.* **3**, 31-36 (1995).
26. J. Xu, S.P. McCarthy, R.A. Gross, and D.L. Kaplan, Chitosan film acylation and effects on biodegradability. *Macromolecules* **29**, 3436-3440 (1996).
27. R. Franz, Permeation of volatile organic compounds across polymer films—Part I: Development of a sensitive test method suitable for high-barrier packaging films at very low permeant vapour pressures. *Packag. Technol. Sci.* **6**, 91-102 (1993).
28. R. Franz, Permeation of flavour compounds across conventional as well as biodegradable polymer films, in *Foods and Packaging Materials - Chemical Interactions*, P. Ackermann, M. Jagerstad, and T. Ohlsson, (Eds.), pp. 45-50, Royal Society of Chemistry, Cambridge, UK (1995).
29. Packaging—Determination of the ultimate aerobic biodegradability of packaging materials in an aqueous medium—Method by analysis of evolved carbon dioxide, BS EN 14047 (2002).
30. ASTM International. ASTM D3985 - 05(2010)e1. Standard test method for oxygen gas transmission test method for oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor, in *ASTM Volume 15.10 Packaging; Flexible Barrier Packaging*, ASTM International, West Conshohocken, PA, (2010).
31. S. Bagheri-Khoulenjani, S.M. Taghizadeh, and H. Mirzadeh, An investigation on the short-term biodegradability of chitosan with various molecular weights and degrees of deacetylation. Carbohydr. Polym. **78**, 773-778 (2009).
32. I. Aranaz, M. Mengíbar, R. Harris, I. Paños, B. Miralles, N. Acosta, G. Galed, and Á. Heras, Functional characterization of chitin and chitosan. *Curr. Chem. Biol.* **3**, 203-230 (2009).
33. P.R. Rege and L.H. Block, Chitosan processing: Influence of process parameters during acidic and alkaline hydrolysis and effect of the processing sequence on the resultant chitosan's properties. *Carbohydr. Res.* **321**, 235-245 (1999).
34. G. Roberts, Chitosan production routes and their role in determining the structure and properties of the product, in *Advances in Chitin Science*, A. Domard, G.A.F. Roberts, and K.M. Varum (Eds.), pp. 22-31, Jacques Andre, Lyon, France (1998).
35. Packaging—Requirements for packaging recoverable through composting and biodegradation—Test scheme and evaluation criteria for the final acceptance of packaging, BS EN 13432 (2000).
36. P.C. Srinivasa, M.N. Ramesh, K.R. Kumar, and R.N. Tharanathan, Properties of chitosan films prepared under different drying conditions. *J. Food Eng.* **63**, 79-85 (2004).
37. J.H. Han and J.M. Krochta, Physical properties and oil absorption of whey-protein-coated paper. *J. Food Sci.* **66**, 294-299 (2001).
38. H. Kjellgren and G. Engström, Influence of base paper on the barrier properties of chitosan-coated papers. *Nordic Pulp Paper Res. J.* **21**, 685-689 (2006).
39. H. Kjellgren, M. Gällstedt, G. Engström, and L. Järnström, Barrier and surface properties of chitosan-coated greaseproof paper. *Carbohydr. Polym.* **65**, 453-460 (2006).
40. E. Habeych, A.J. van der Goot, and R. Boom, Prediction of permeation fluxes of small volatile components through starch-based films. *Carbohydr. Polym.* **68**, 528-536 (2007).
41. A.M. Seuvre, E. Philippe, S. Rochard, and A. Voilley, Retention of aroma compounds in food matrices of similar rheological behaviour and different compositions. *Food Chem.* **96**, 104-114 (2006).
42. M. Pau Balaguer, R. Gavara, and P. Hernández-Muñoz, Food aroma mass transport properties in renewable hydrophilic polymers. *Food Chem.* **130**, 814-820 (2012).
43. P. Boonsong, N. Laohakunjit, O. Kerdchoechuen, and P. Tusvil, Properties and permeability of aroma compounds in food through plasticized cassava films. *Int. Food Res. J.* **16**, 97-103 (2009).
44. J.A.Q. Gallo, F. Debeaufort, and A. Voilley, Interactions between aroma and edible films. 1. Permeability of methylcellulose and low-density polyethylene films to methyl ketones. *J. Agric. Food Chem.* **47**, 108-113 (1999).
45. J.A. Quezada-Gallo, F. Debeaufort, and A. Voilley. Mechanism of aroma transfer through edible and plastic packagings: Are they complementary to solve the problem of aroma transfer? *Food Packag. Testing Methods Appl.* **753**, 125-140 (2000).
46. P. Hernandez-Muñoz, R. Catalá, and R. Gavara, Food aroma partition between packaging materials and fatty food simulants. *Food Addit. Contam.* **18**, 673-682 (2001).
47. M.G. Sajilata, K. Savitha, R.S. Singhal, and V.R. Kanetkar, Scalping of flavors in packaged foods. *Comprehensive Rev. Food Sci. Food Safety* **6**, 17-35 (2007).