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Barrier and surface properties of chitosan-coated greaseproof paper

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Abstract

Greaseproof papers with different air permeances were coated with chitosan, both on a bench scale and on a pilot scale to study the conditions necessary to obtain a packaging material with good barrier properties towards oxygen, nitrogen, carbon dioxide and air. In addition, barrier properties against grease and water were measured. The results showed that an oxygen permeability in the same range as that of poly(ethylene terephthalate) was obtained at coat weights exceeding 5 g/m^2. The oxygen permeability was not substantially affected by temperature changes, provided that the air permeance of the base paper was low. Carbon dioxide and nitrogen permeabilities were low enough to be measurable only at a coat weight exceeding 5 g/m^2 and only on the two base papers with the lowest air permeance. The mechanical properties were characterized by tensile strength and fracture strain. The tensile strength was not affected by the coat weight, whereas the fracture strain was highest for coat weights exceeding 5 g/m^2. High grease resistance values were also obtained at this coat weight, whereas the water resistance deteriorated slightly due to the hygroscopic character of the chitosan. However, a coat weight as high as 5 g/m^2 could only be achieved on a bench scale. On a pilot scale, the maximum coat weight was 0.2 g/m^2 because the solids content of the coating solution used was limited to 1.0 wt% due to the high molecular weight of the chitosan used and the resultant high viscosity of the polymer solution. The coating on a pilot scale was performed using the metered size press technique.

Keywords: Greaseproof papers; Air permeance; Coatings; Chitosan; Oxygen–barrier properties

1. Introduction

A low gas permeability is a crucial requirement for many food packaging materials and a low oxygen transmission rate is one of the main requirements (Paine & Paine, 1992). Other important gases to which food packaging should be impermeable are carbon dioxide and nitrogen. To meet this demand, paper-based packaging materials are laminated with aluminium or extrusion-coated with synthetic oxygen–barrier polymers. However, the lamination and extrusion processes are performed off-line and they are therefore less cost-effective than in-line processes. Barrier coatings based on chitosan offer benefits because these polymers can be applied to the paper in-line as an aqueous solution using conventional coating techniques. In addition, the use of recoverable oxygen–barrier coatings instead of laminates with aluminium or synthetic polymers may yield environmental benefits (Lang, 1995).

Chitosan is a polymer based on a renewable material, which exhibits excellent oxygen–barrier properties due to its high crystallinity and the hydrogen bonds between the molecular chains (Gällstedt, 2001; Kittur, Kumar, & Tharanathan, 1998). Moreover, it exhibits a good barrier against grease (Kittur et al., 1998) and good antibacterial and fungicidal properties (Luyen & Rossbach, 1992; Outtara, Simard, Piette, Bégin, & Holley, 2000; Shahidi, Arachchi, & Jeon, 1999).

Chitosan also possesses good mechanical properties, as has been shown in the work of Arvanitoyannis, Kalichevsky, Blanshard, and Psomiadou (1994) and

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Arvanitoyannis, Nakayama, and Aiba (1998). These researchers studied the mechanical properties of films composed of chitosan/gelatine and chitosan/poly(vinyl alcohol) (PVA) and found that the tensile strength was increased when the fraction of chitosan in the film was increased. Chitosan has also been tested as a wet end additive in paper board and the mechanical properties of the product were reported to be improved (Laleg & Pikulik, 1991). The chitosan retention was also reported to be good, due to the different charges of the chitosan and cellulose, the former being cationic and the latter being anionic. This charge difference can also be expected to yield good adhesion between a chitosan coating and a cellulose-based substrate.

These properties make chitosan an attractive polymer for the barrier coating of cellulose-based materials for food packaging purposes. Chitosan definitely has a promising potential, but many questions and problems still have to be solved before it can be commercially used as a replacement for aluminium and synthetic polymers. These questions concern the demands on the chitosan coating and the cellulose substrate as well as on the coating process.

One of the most frequently used processes for applying an aqueous coating to a paper substrate is the Metering Sized Press (MSP) (Klass, 2002), which consists of two rolls (transfer rolls), on each side of the paper, in contact with each other onto which a pre-metered amount of the coating is dosed, usually with a smooth or wire-wounded rod. The coating is transferred to the paper in the nip between the two transfer rolls, and the two sides of the paper can be simultaneously coated. With a starch solution at 5–18% solids, a dry coat weight of 0.7–4.0 g/m^2 can be obtained (Klass, 2002). A higher coat weight can be obtained using curtain coating (Schweizer, 2002) which is a coating technique in which the paper industry has begun to show a considerable interest.

In this study, greaseproof papers with different air permeances (AP) were coated with chitosan on both a bench scale and a pilot scale to study the conditions required to obtain a packaging material with a good gas barrier. Greaseproof paper was chosen as a substrate for the coating because it is a dense and well-bonded paper on which the coating can be expected to form a homogeneous surface. Base paper structure is of great importance for the homogeneity and the barrier properties of the applied coating (Schuman, Wikström, & Rigdahl, 2004). The results showed that a good oxygen–barrier as well as good grease resistance was achieved at coat weights exceeding 5 g/m^2. However, the nitrogen and carbon dioxide barrier properties seemed to be affected by the pore structure of the base paper even at such high coat weights. The water resistance was, however, slightly lower at a coat weight of 5 g/m^2. Coat weights of 5 g/m^2 could only be achieved on a bench scale. On a pilot scale, the maximum achievable coat weight was considerably less.

2. Experimental

2.1. Materials

Greaseproof papers with four different air permeance (AP) levels were used as base paper for the coatings. These papers were produced on PM3 at Nordic Paper AB, Säffle, Sweden, by varying the type of pulp used and the freeness level of the fibre furnish. Two pulps were used, a bleached sulphite produced on site and a bleached sulphate, Robur Flash TCF, from Rottneros AB, Vallvik, Sweden. The composition of the base papers and their AP-values are found in Table 1.

The chitosan grade used had a degree of deacetylation of 85% and a relative molecular mass of 400,000 g mol^{-1}, received as platelets with a dry solids content of 92% from Fluka, Sigma–Aldrich Sweden AB, Stockholm, Sweden. The chemical structure of chitosan is shown in Fig. 1.

Glacial acetic acid puriss 98% from Labassco AB, Partille, Sweden, was used in the bench-scale trials to protonize the chitosan amine group and make the chitosan soluble in water. In the trial on a pilot scale, glacial acetic acid of a 98% technical grade from Univar AB, Malmö, Sweden, was used.

The chitosan solution used in the bench-scale trials was prepared by dissolving 3.0 g of chitosan in 250 g water and 3.0 g acetic acid. The solution was mixed for 1 h before use. The chitosan solution used in the pilot trials was prepared by dissolving 1.5 kg of chitosan in 150 kg water and 1.5 kg acetic acid under continuous stirring. The viscosity of the solution was measured using a conventional controlled-shear-stress rheometer, Paar Physica, MCR 300, Graz, Austria. Viscosity measurements were performed with a concentric cylinder geometry at 25 °C. The viscosity of the prepared chitosan solution was 449 mPa s at a shear rate of 129 s^{-1}.

2.2. Methods

The base papers were coated with an aqueous chitosan solution having a concentration of approximately 1 wt%

Table 1
Composition of base papers used for coating trials

Paper no	Pulp composition	Beating	Air permeance (nm/Pa s)
1	100% sulphite	High	1.5
2	100% sulphite	Low	3.1
3	100% sulphate	High	200
4	100% sulphate	Low	660

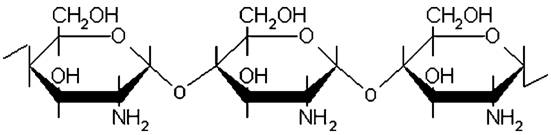

Fig. 1. Chemical structure of chitosan.

both on a bench scale and on a pilot scale. The bench-scale coatings were performed using a rod coater for sheets, K101 Control Coater, RK Print Coat Instruments Ltd, Herts, UK. Six coat weights within the range from 1.2 to 5.2 g/m^2 were applied, where the coat weight was varied by varying the diameter of the wire on the rod. The sheets were coated on one side and were dried under ambient conditions.

The pilot-coated material was produced at BTG-UMV Coating Systems, Säffle, Sweden. The technique used was TWIN-HSM gravure. In this technique, the chitosan solution was applied to the transfer roll with the help of an engraved roll. The specifications of the engraved roll used were 43 lines/cm and 39.5 cm^3/m^2. Two coat weights were applied; 0.1 and 0.2 g/m^2. To achieve the higher coat weight, the paper was coated twice. The machine speed was 200 m/min and the speed of the gravure roll was 190 m/min. The dryer section of the pilot coater consisted of one infrared dryer and three air-dryers.

The properties of the coated papers were investigated without any calendering. The papers were stored at 23 °C and 50% relative humidity (RH) for 3–20 days before testing.

Free chitosan films were prepared for the determination of the glass transition temperature (T_g) by casting chitosan solution into petri dishes. The films were allowed to dry for two days at 23 °C and 50% RH. The thickness of the films was 100 μm.

2.3. Testing

The coated material was tested with respect to air permeance, oxygen transmission rate, carbon dioxide permeability, nitrogen permeability, water absorbency, grease resistance, tensile strength and surface texture. In addition, the glass transition temperature (T_g) was measured on pure chitosan film.

The air permeance tests were performed using an Air Permeance Tester SE168 low range from Lorentzen & Wettre AB, Stockholm, Sweden, in accordance with SCAN P-26:78. Papers which were outside the measurement range were tested using a Bendtsen Tester 114 from Lorentzen & Wettre AB, Stockholm, Sweden, in accordance with SCAN P-60:87. The results are reported as the average of five measurements.

The oxygen transmission rate (OTR) tests were performed with a Mocon Ox-Tran Twin apparatus, Modern Controls Inc., Minneapolis, USA, in accordance with ASTM D 3985-95 and the test conditions were 23 °C and 0% relative humidity (RH). The sample area was 5 cm^2 and the partial pressure of the oxygen was 1 atm. The OTR was normalized with respect to the oxygen pressure and material thickness to yield the oxygen permeability (OP). The results are reported as the average of two measurements. The carbon dioxide and nitrogen transmission rates were performed with a Mocon Permatran C-200, Modern Controls Inc., Minneapolis, USA, at 23 °C and 0% RH. The transmission rates were normalized in the same way as the OTR to obtain the permeabilities. The reported results for carbon dioxide permeability are the average of four measurements and for nitrogen permeability as the average of two measurements. The thickness value used in the calculation of the gas permeability was the thickness of the coated papers. The thickness of all the studied materials was determined using a Thickness Tester Type 21 from Lorentzen & Wettre AB, Stockholm, Sweden, in accordance with SCAN-P 7:96. The thickness was determined at five positions on each sample.

In the water absorbency tests, the apparatus used was a Cobb Sizing Tester from Lorentzen & Wettre AB, Stockholm, Sweden. The Cobb$_{60}$ value was determined in accordance with ISO 535. The results are reported as the value from a single measurement.

The grease resistance was measured in accordance with Tappi T-454, the turpentine oil being applied on the coated side. The results are reported as the average of five measurements.

The tensile strength and elongation in the machine direction of the papers were measured using a tensile strength tester LRX Type No TG 420 from Lloyd Instruments Ltd, Royston, UK, with a load cell of 500 N. The tests were performed in accordance with ISO 1924-2 and the test conditions were 23 °C and 50% RH. The clamp separation was 100 mm and the strain rate was 100 mm/min. The reported results are the average of five measurements.

The surface texture of the papers was studied by scanning electron microscopy (SEM), using a JSM-820 Scanning Electron Microscope from JEOL, Tokyo, Japan.

The glass transition temperatures (T_g) of the chitosan films were determined at 1.0 Hz with a temperature increase of 4.2 °C/min using a DMA/SDTA861^e, Mettler Toledo Inc., Schwerzenbach, Switzerland.

3. Results

3.1. Air permeance

The air permeance (AP) is listed in Table 2 for the four base papers coated on a bench scale. AP = 0.001 nm/Pa s is the lower detection limit for the method used and we define this as being the value at which the coating had sealed the

Table 2
Air permeance at different coat weights for papers (1–4) coated in the bench-scale coater

Coat weight (g/m^2)	Air permeance (nm/Pa s)			
	Paper 1	Paper 2	Paper 3	Paper 4
0	1.5	3.1	200	660
1.2	0.16	0.57	27	30
1.4	0.40	0.077	11	30
1.9	0.052	0.063	1.2	22
2.4	<0.001	<0.001	1.1	23
3.9	<0.001	<0.001	0.046	1.0
5.2	<0.001	<0.001	<0.001	<0.001

surface pores in the base paper. This value thus gives the coat weight, W_c, at which the pores in the base papers are sealed and a continuous chitosan film is beginning to develop. It is evident in Table 2 that W_c increased with increasing AP of the base paper.

In the pilot-scale coating trial, the coat weights obtained were much lower. The highest obtained coat weight was 0.2 g/m^2. The AP decreased after coating, as shown in Fig. 2, but 0.2 g/m^2 was apparently too low a coat weight to seal the pores in the base papers, because the AP values were higher than 0.001 nm/Pa s.

Figs. 3a and b show scanning electron microscope (SEM) images of the surface of the base paper and of the same paper coated on a bench scale. These pictures show that the coating had covered the fibres at that coat weight and that the coating had formed a continuous film over the fibres.

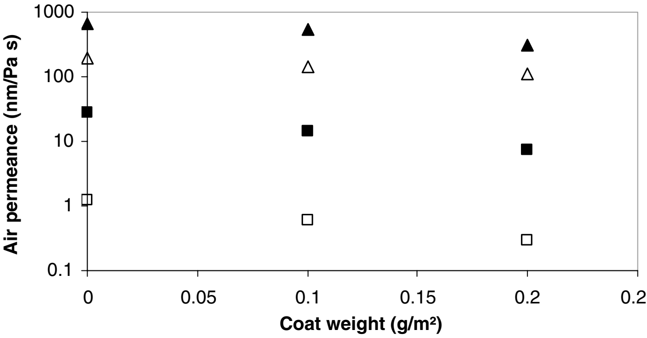

Fig. 2. Air permeance (logarithmic scale) as a function of coat weight for papers coated in the pilot-scale coating plant: paper no 1 (□), paper no 2 (■), paper no 3 (△) and paper no 4 (▲).The average pooled standard deviation of air permeance was 10.8%.

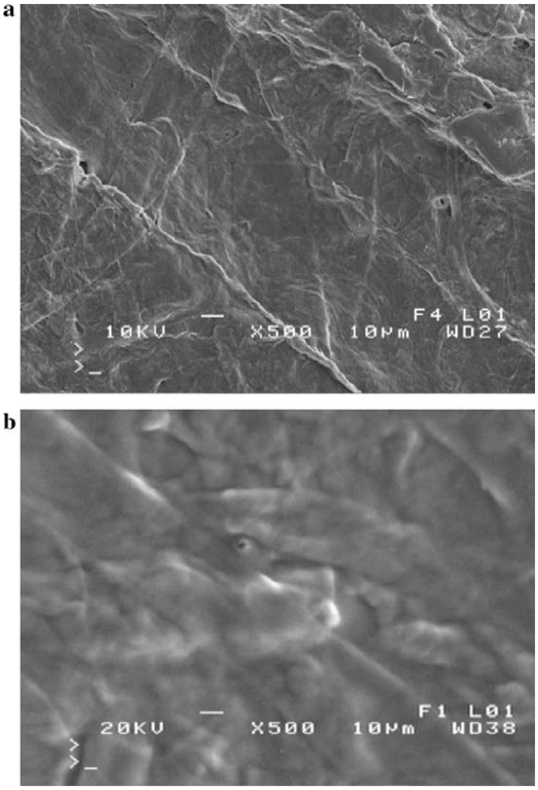

Fig. 3. (a) SEM-image of uncoated base paper no 1. (b) SEM-image of base paper no 1 coated with chitosan with a coat weight 5.2 m^2.

3.2. Oxygen permeability

Oxygen permeability (OP) values low enough to be measurable were obtained only for the bench-scale coated material at coat weights exceeding W_c. In the case of the pilot-scale coated papers, the coat weight was too low to give an oxygen–barrier. The upper limit of the oxygen permeability tester used was 20,000 cm^3/(m^2 atm day). The thickness used in the calculation of the OP was the total thickness of the coated material, i.e., coating + base paper. This thickness was determined largely by the thickness of the base paper and was 85 μm for all the coated papers independent of coat weight. The thickness of the chitosan film at coat weights of 2.4 and 5.2 g/m^2, assuming no penetration and a density of 1.5 g/cm^3 for the chitosan, was estimated to be 1.6 and 3.5 μm, respectively.

In Fig. 4, the OP is plotted versus the air permeance (AP) of the base papers for two coat weights exceeding W_c. Evidently the AP of the base paper did not affect the OP-value of the coated paper.

When the chitosan coating had formed a continuous film, at a coat weight of 5.2 g/m^2, it was evident that the barrier properties of the composite were determined by the coating layer. At a coat weight of 2.4 g/m^2, only the two base papers with the lowest AP-values yielded measurable OP-values, and for these the OP-value was slightly lower for the base paper with the lowest AP. Even at a coat weight of 5.2 g/m^2 the most open base paper (paper 4) also gave OP-values above the measurable range.

The OP for the coated papers with a coat weight of 5.2 g/m^2 was also measured at 37 °C and 0% RH. Paper 2, with an air permeance of 3.1 nm/Pa s for the base paper, had an OP of 1.6 cm^3 mm/(m^2 24 h atm), which is of the same magnitude as the values obtained at 23 °C and 0% RH. The base papers with the highest air permeances (paper 3 and paper 4) when coated gave OP-values above

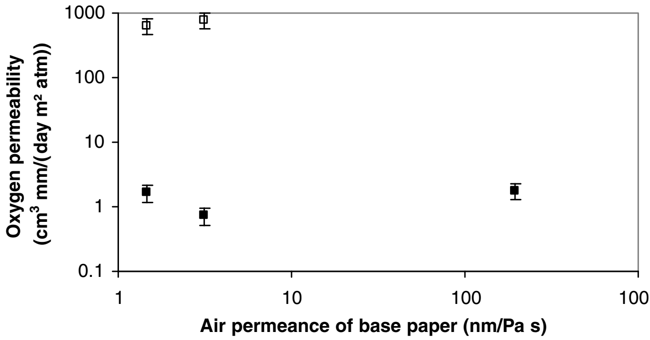

Fig. 4. Oxygen permeability (23 °C, 0% relative humidity) at two different coat weights, 2.4 g/m^2 (□) and 5.2 g/m^2 (■), as a function of the air permeance of the base paper. Error bars denote standard deviations.

the measurable range. The coated paper 1 was not measured at 37 °C and 0% RH. Gas diffusion and permeability, including oxygen permeability were measured at different temperatures by Arvanitoyannis et al. (1994) and were found to increase with increasing temperature.

3.3. Carbon dioxide and nitrogen permeability

Permeability values in the measurable range for carbon dioxide were obtained only for papers 1 and 2 at the highest coat weight, 5.2 g/m^2. These values are shown in Table 3. For nitrogen permeability, only paper 1 gave values within the measurable range. The carbon dioxide and nitrogen permeabilities for the other papers exceeded the measurable range, i.e., were above 40,000 cm^3/(m^2 atm day) equal to 3400 cm^3 mm/(m^2 atm day) for coated papers with a thickness of 85 μm.

3.4. Glass transition temperature

In Fig. 5, the loss tensile modulus for chitosan, E″, measured on a cast film with a thickness of 100 μm using the DMA-technique is plotted against the temperature. The glass transition temperature (T_g) for the chitosan was in the range of 125–130 °C. This value agrees with values reported by other researchers, e.g., Kittur, Harish Prashanth, Udaya Sankar, and Tharanathan (2002) and Dong, Ruan, Wang, Zhao, and Bi (2004).

Table 3
Carbon dioxide and nitrogen permeability values for the papers at a coat weight of 5.2 g/m^2

Permeability (cm^3 mm/m^2 24 h 0.1 MPa)	Paper 1	Paper 2	Paper 3	Paper 4
CO_2	71	85	Out of range	Out of range
N_2	490	Out of range	Out of range	Out of range

The thickness of the coated papers were 85 μm.

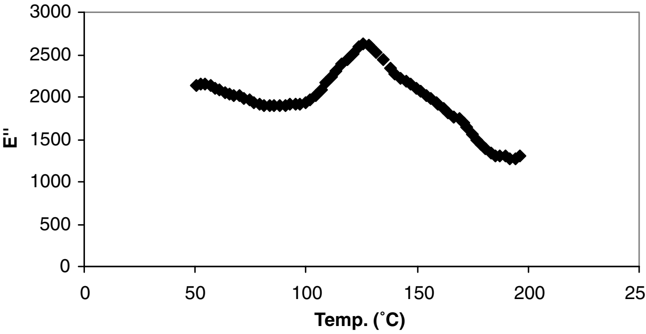

Fig. 5. Loss tensile modulus, E″ of free chitosan films as a function of temperature.

3.5. Water absorbency

The water absorbency expressed as Cobb$_{60}$-values of the base papers varied widely between 25 and 50 g/m^2. The highest Cobb$_{60}$-values were obtained on the base paper with highest AP-value, paper 4.

The chitosan coating reduced the Cobb$_{60}$-values for the base papers having high Cobb-values, but had little effect on the papers having low Cobb$_{60}$-values, Table 4. The results show that the chitosan coating did not provide any extra barrier against water absorption.

3.6. Grease resistance

The grease resistance improved when the coat weight was increased, and the air permeance decreased, as shown in Fig. 6. At air permeance values lower than 0.1 (nm/Pa s) all papers exhibited the same high grease resistance value.

3.7. Tensile strength and fracture strain

The tensile strength was measured both on the base papers and on the coated papers. No significant statistical difference in tensile strength between base paper and coated paper was observed. The tensile strength was not affected by the chitosan coating, as shown in Fig. 7. Only the papers coated on bench scale were tested.

Table 4
Cobb values at different coat weights for papers coated in the bench-scale coater

Coat weight (g/m^2)	Cobb$_{60}$ (g/m^2)			
	Paper 1	Paper 2	Paper 3	Paper 4
0	25.2	27.0	51.5	48.6
1.2	25.8	27.5	24.4	23.1
1.4	21.1	23.7	18.4	21.7
1.9	25.6	30.3	23.5	25.7
2.4	29.0	29.4	22.7	24.8
3.9	37.9	29.1	23.1	27.3
5.2	30.9	30.8	24.9	33.9

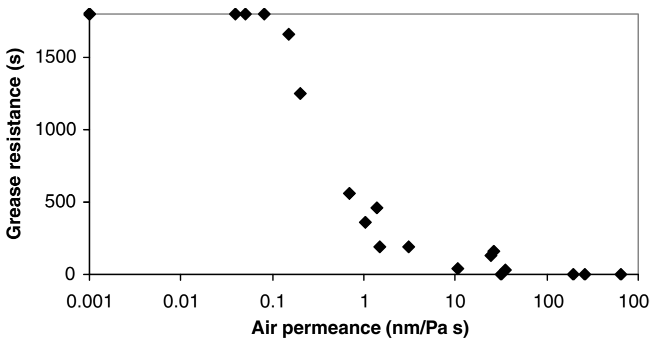

Fig. 6. Grease resistance according to Tappi T-454 as a function of air permeance for papers coated in the bench-scale coater. Results for all four base papers are included in the figure. The maximum grease resistance value in this test is 1800 s. The average standard deviation was 15.4%.

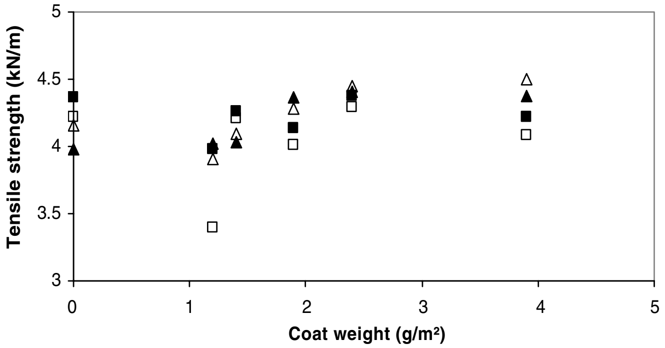

Fig. 7. Tensile strength as a function of coat weight for papers coated in the bench-scale coater: paper 1 (□), paper 2 (■), paper 3 (△) and paper 4 (▲). The average pooled standard deviation of tensile strength was 5.4%.

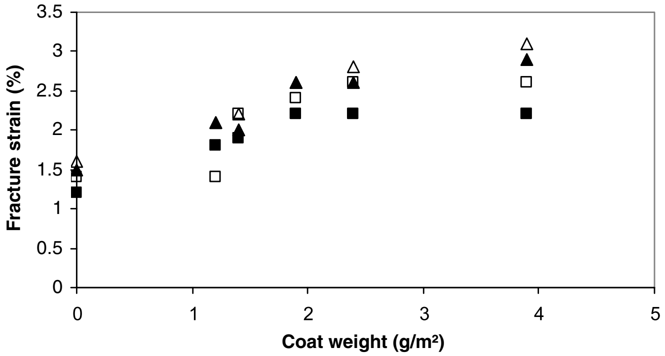

Fig. 8. Fracture strain as a function of coat weight for papers coated in the bench-scale coater: paper 1 (□), paper 2 (■), paper 3 (△) and paper 4 (▲). The average pooled standard deviation of elongation was 10.9%.

The fracture strain increased with increasing coat weight of chitosan, as shown in Fig. 8.

4. Discussion

The oxygen permeability (OP) measurements at 23 °C and 0% relative humidity (RH) showed that chitosan can be used as a coating on greaseproof paper to obtain a material with oxygen–barrier properties, provided the coating seals the pores in the base paper and forms a continuous and homogeneous film. This condition was fulfilled at a coat weight of 5.2 g/m^2 for the three densest base papers and at a coat weight of 2.4 g/m^2 for the two densest base papers. On the most open base paper (AP 660 nm/Pa s) no oxygen–barrier was obtained at any of the studied coat weights. However, coat weights as high as 2.4 g/m^2 could only be obtained by bench-scale coating. On the pilot-coated material, the coat weight achieved was only 0.1 g/m^2 and at that coat weight none of the coated papers provided any oxygen–barrier.

At a coat weight of 5.2 g/m^2, the measured OP-values (0.7–1.8 cm^3 mm/(m^2 atm day)) are of the same magnitude as that reported for PETP (poly(ethylene terephthalate)) (Andrew, 1995). For comparison it can be mentioned that Gällstedt, Törnqvist, and Hedenqvist (2001) have reported OP-values of 0.01–2 cm^3 mm/(day m^2 atm) at 90–95% relative humidity (RH) for chitosan films coated with nitrocellulose lacquer, and that Kittur et al. (1998) have reported an OP-value of 0.16×10^{-5} cm^3 mm/(day m^2 atm) at 65% RH and 27 °C for pure chitosan films. However, OP-values for chitosan-coated papers cannot be directly compared with values for free chitosan films, since the thickness by which the transmission rate is normalized, is determined both by the thickness of the base paper and the thickness of the chitosan coating. The chitosan coating, which controls the OP, is thin in comparison with the base paper.

Measurements of OP at a higher temperature, 37 °C and 0% RH, showed values similar to or slightly higher than those obtained at 23 °C and 0% RH for the coated sulphite base paper. The influence of the base paper seemed to increase with increasing temperature. It has earlier been reported that OP-values increase with increasing temperature (Arvanitoyannis et al., 1994). The small changes in OP-values between the two temperatures for the coated sulphite papers in this study can probably be explained by the fact that both the temperatures were far from the T_g of chitosan, which was in the range of 125–130 °C. The glass transition temperature indicates the temperature at which the molecule chains in the polymer pass from a lower degree of flexibility to higher degree of flexibility. The flexibility of the molecule chains governs gas diffusion and this increases with increasing temperature (Pauly, 1989).

Measurable permeability values for carbon dioxide and nitrogen were obtained only at a coat weight of 5.2 g/m^2 on the densest base paper. The values of carbon dioxide and nitrogen permeability of the coated papers, 71 and 490 cm^3 mm/(m^2 atm day), respectively, were higher than those reported for films of poly(ethylene terephthalate) (PETP) or EVOH, which are in the range of 0.001–10 cm^3 mm/(m^2 atm day) (Plastics Design Library, 1995). PETP and EVOH are polymers which are considered to provide an excellent barrier against these gases. The permeability of a polymer coating such as chitosan is governed by the product $S \times D$, where S denotes the solubility and D the diffusion coefficient. D is governed by the size of the penetrating gas molecule. The total bond length of the gases (picometres) used in the study were: oxygen 121, carbon dioxide 232 and nitrogen 110 (Lide, 1999). The smaller the molecule the higher is the penetrating rate and the higher is the value of D. A comparison of the molecule size and the measured permeability suggests (a) that the nitrogen had a higher permeability than carbon dioxide due to its smaller molecule size and (b) that nitrogen and carbon dioxide had a higher permeability than oxygen due to their greater solubility in chitosan (Makino & Hirata, 1997).

The AP of the coated material had a great influence on the grease resistance. The base paper affects the grease resistance up to the coat weight, W_c, at which the air permeance of the material is below the measurable range. This coat weight is not the same for all the base papers, but increases with increasing AP of the base paper. All papers exhibited excellent grease resistance at coat weights exceeding 5 g/m^2. At lower coat weights, only the coated papers with the lowest air permeance of the base paper exhibited excellent grease resistance.

The coated papers provided no barrier against water absorption. Once the base papers were coated it was obvious that the chitosan coating was the limiting factor affecting the water barrier properties of the coated material. The water sorption in the base papers increased with increasing air permeance, as is evident in Table 4. This suggests that the pore sorption increased when the AP increased. However, not only the pores in paper but also the fibres themselves take up water. The Cobb-values of 25 g/m^2 for the base papers with the lowest AP-values suggest that the up take in those papers was predominately controlled by fibre sorption. When these papers were coated, the Cobb-value increased to approximately 30 g/m^2 at the highest coat weight. This increase in the Cobb-value shows that the water sorption by the chitosan coating was higher than for the cellulose fibres in the base papers. For the base papers with higher AP-values, which had Cobb-values in the 40–50 g/m^2 range, the Cobb-value decreased to approximately 30 g/m^2 at the highest coat weight, i.e., the same as that for the base papers with the lowest AP-values. The decrease in Cobb-value is probably due to a clogging by the coating of the pores in the base paper, which reduced the pore sorption. This reduction was greater than the uptake of water by the chitosan coating.

Chitosan is reported to exhibit good tensile strength and fracture strain (Arvanitoyannis et al., 1998). This was not, however, reflected in the coated paper studied in this paper. The tensile strength remained unaffected by the chitosan coating, probably because the coat weights were low in comparison with the grammage of the base papers. Thus, the tensile strength of the coated paper was controlled by the tensile strength of the base paper. The increase in fracture strain observed is probably caused by a stress relaxation in the base paper during the coating process when the base paper was exposed to the water in the coating colour. Our results are in agreement with those of Kuusipalo, Kaunisto, Laine, and Kellomäki (2005), who used chitosan as a pre-coating before extrusion coating.

In the metered size press technique used in the pilot-scale coating trial, the coating was applied to the transfer roll using an engraved roll. This technique is reported to give higher coat weights than rod or roll application (Salt et al., 2002), which is the most frequently used application technique in metered size press coating. Using starch solutions of 5–18% concentration, a coat weight of 0.7–4.0 g/m^2 can be obtained (Klass, 2002).

Application with an engraved roll is volumetric, i.e., with a given roll the same volume is always applied, independent of the concentration of the polymer solution. A comparison of our coat weight, 0.1 g/m^2 at a concentration of 1%, with Klass's 0.7 g/m^2 at a concentration of 5% shows that the wet coat weight was roughly the same in our and Klass's experiments.

This shows that a coat weight greater than 0.1 g/m^2 cannot be achieved using a chitosan solution of 1.0 wt% in coating with the metered size press. The concentration of the solution must be considerably increased if a satisfactory coat weight is to be obtained. This can be achieved by using chitosan of lower molecular weight. A lower molecular weight and higher degree of deacetylation decrease the viscosity of the chitosan solution (Tsaih, Chen, & Lin, 1995). An alternative coating technique which yields higher coat weights may also be needed. Curtain coating may offer that possibility (Schweizer, 2002).

5. Conclusions

The results show that:

- Greaseproof paper can be upgraded to give low oxygen as well as low nitrogen and low carbon dioxide permeability through coating with chitosan, provided the base paper is dense and provided the coating forms a continuous film on the paper. The latter requires a high coat weight. An oxygen–barrier was obtained already at a coat weight of 2.4 g/m^2 while a barrier against nitrogen and carbon dioxide required a coat weight of 5.2 g/m^2.
- The grease resistance was excellent within the coat weight range of 2.4–5.2 g/m^2.
- Chitosan coating does not provide any barrier against water and its water sorption was found to be greater that the fibre sorption in the base paper.
- The coating did not affect the tensile strength of the coated paper. The fracture strain was, however, slightly increased.
- With the chitosan grade used, a coat weight of only 0.1 g/m^2 could be achieved using the metered size press coating technique, although this technique can yield high coat weights in this type of application. The low coat weight was due to the low solids content of only 1.0 wt% in the coating solution. Concentrated solutions with solids content in the range of 20% are necessary to give a sufficiently high coat weight. This requires a chitosan product of lower molecular mass. A coating technique which gives higher coat weights may also be necessary.

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