Packaging-Related Properties of Alkyd-Coated, Wax-Coated, and Buffered Chitosan and Whey Protein Films

M. Gällstedt,[1] M. S. Hedenqvist[2]

[1]*Packforsk, The Institute for Packaging and Logistics AB, Box 9, SE-164 93 Kista, Sweden*
[2]*Royal Institute of Technology, Department of Fiber and Polymer Technology, SE-100 44 Stockholm, Sweden*

ABSTRACT: Packaging-related properties of coated films of chitosan–acetic acid salt and whey protein concentrate (WPC) were studied. Chitosan (84.7% degree of deacetylation) and WPC (65–67% protein) were solution cast to films. These films are potential oxygen barriers for use in packaging. Coatings of wax or alkyds were used to enhance the water-barrier properties. The packaging-related properties of chitosan films treated in a buffering solution, with a pH of 7.8, were also investigated. The coated films were characterized with respect to Cobb absorbency, overall migration to water, water vapor transmission rate, and oxygen permeability. The creasability and bending toughness were determined. The wax was a more efficient barrier to liquid water and 90–95% relative humidity than the alkyd. However, the alkyd-coated material had superior packaging-converting properties. The alkyd-coated WPC and chitosan–salt films were readily folded through 180° without any visible cracks or delamination. The overall migration from the alkyd-coated materials was below the safety limit, provided the coat weight was higher than 7.5 mg/cm^2 on WPC and 2.1 mg/cm^2 on chitosan–salt. The barrier properties of chitosan film under moist conditions were improved by the buffer treatment. However, the buffering also resulted in shrinkage of the film. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 60–67, 2004

Key words: proteins; polysaccharides; coatings; barrier; films

INTRODUCTION

The possibility of using polymer films based on residual products from the food industry in a packaging context is appealing from an environmental point of view and commercially challenging. Interesting examples of raw materials are chitin and whey protein, byproducts from the fish and dairy industries. Replacing synthetic polymers with renewable polymers provides an efficient use of our natural resources.

Chitosan is a derivative of chitin, which is the second most abundant natural polymer after cellulose. Chitin occurs as the load-bearing component in, for example, shells of exoskeleton fishes, fungi, insects, krill, and zooplankton.[1–5] Chitosan has a wide range of applications such as a component in cosmetics,[3,6–8] pharmaceutics,[3,5,6,9–13] and dietary foods.[5,9] It is also used in glues in sore plasters and other skin applications; in hair-care products[7,8]; as resorbable sutures[14]; blood thickeners; contact lenses; membranes for blood dialysis; gene technology, given its ability to abstract DNA[5,15]; as a clarifier of orange juices[5]; as an additive in animal feed; for water purification[3,5,6,9,12–18]; in adhesives, photo film applications; and in different kinds of fiber treatments.[6,14,19–21] The antibacterial and fungicidal properties[3,5,22] of chitosan make it attractive to mix in soil to avoid attacks from, for example, nematodes on the roots of seeds and to apply to fruits to prevent fungi.[3,23] Several studies have shown that chitosan in combination with cellulose in paperboards[24] enhances the mechanical strength,[12,20] increases the dyability,[6,12,20] and has antielectrostatic effects on cloths.[5]

Whey proteins are among the most studied proteins today. They are used, for instance, as additives in pharmaceuticals, as nutrition agents, and in human and animal foods.[25,26] The four main whey proteins are β-lactoglobulin (∼ 50 wt %), α-lactalbumin (∼ 20 wt %), bovine serum albumin (∼ 10 wt %), and immunoglobulins (∼ 10 wt %).[26–28] Because β-lactoglobulin is the main protein in whey, it also dominates its properties.[25,29]

The protein concentration in the solution casting of whey protein films is important for the final quality. Too high a concentration of whey protein leads to premature gelation during the heat denaturation, and this complicates the film casting and yields inhomogeneous films.[25] On the other hand, as we have observed, too low a concentration of protein results in inferior film-forming properties, most certainly because of the low content of intermolecular hydrogen and disulfide bonds.

Because dry and pure whey protein films are rather brittle, plasticizers have to be added. The most commonly used plasticizers in whey protein films are polyfunctional alcohols, such as polyethylene glycol,[29] glycerol,[29–34] and sorbitol.[25,29,30,35] Glycerol normally yields a higher gas permeability than sorbitol at a comparable concentration because of the higher plasticization efficiency.[35]

Several previous studies have been performed on different packaging-related properties of whey protein isolate (WPI) films.[25,29–36] Whey protein concentrate (WPC) has a lower concentration of proteins and a higher concentration of lactose and fats than that of WPI. Fewer purification steps lead to a lower price for WPC than for WPI. The packaging market is very cost sensitive and thus WPC (65–67% proteins) was used in this study. WPC is obtained from liquid whey by ultrafiltration and spray drying.[28]

Because of the high content of hydrogen bonds in chitosan and whey protein films these materials are very good gas barriers under dry conditions but they are also rather sensitive to polar matter such as water. To use these materials in contact with polar liquids and gases, they have to be protected by a hydrophobic coating. We showed in a previous work that it is possible to expose chitosan–salt and WPC films to liquid water when they are coated with a nitrocellulose lacquer,[36] although there were some difficulties with this coating, which is brittle and shows somewhat poor adhesion to the substrate.

In the present investigation, films of chitosan–acetic acid salt and WPC were coated with an alkyd lacquer and beeswax, and their properties were compared with those of the nitrocellulose-coated materials reported earlier.[36] The reason for testing the alkyd lacquer was that it has better mechanical and substrate adhesion properties than the nitrocellulose lacquer and the reason for using beeswax is its hydrophobicity and that it has a lower water vapor transmission rate than that of poly(ethylene terephthalate),[30,32] for example. To enhance the humidity resistance, films of chitosan–salt were treated in a basic buffer solution to remove acetic acid residues.

EXPERIMENTAL

Materials

Whey protein concentrate films

Ultrafiltered and spray-dried cheese WPC powder was kindly supplied by MD Foods AB (Sweden). It was free from sodium nitrate and contained 65–67 wt % proteins (50 wt % β-lactoglobulin and 15 wt % α-lactalbumin), 5–6 wt % fat, 3.5 wt % ash, and 17–20 wt % lactose. Glycerol (purity 99%) was obtained from VWR International AB (Sweden) and the deionized water was prepared in a Miele Aqua Purificator G7749

(VWR International GmbH, Germany). The films were produced by stirring 100 g deionized water, 6 g glycerol, and 12 g of WPC powder in a glass cup for 20 min. The solution was thereafter heated to 65°C for 20 min, and 300-μm-thick films were obtained by pouring the solution into petri dishes and subsequently allowing the solution to dry for 2 days at 23°C and 50% relative humidity (RH). The petri dishes were coated with a release agent layer of polytetrafluoroethylene supported by aluminum foil (Bytac Type AF-21; Norton Performance Plastics Corp., Wayne, NJ). The thickness of the WPC films was not allowed to deviate by more than 10% from 300 μm.

Chitosan–acetic acid salt films

Chitosan [2-amino-2-deoxy-(1-4)-β-D-glucopuranan; molar mass $(M_r) \approx 400,000$, degree of deacetylation 84.7%] was received as platelets from Fluka/Sigma-Aldrich Sweden AB (Sweden). Chitosan (1.17 wt %) was dissolved in 1.17 wt % acetic acid and 97.66 wt % deionized water. Acetic acid (glacial, PA, 99.8%; Acros Organics, Morris Plains, NJ) was used to protonize the amino groups. The solution was stirred for 20 min with a magnetic stirrer in a 600-mL glass cup, and then mixed in a Waring commercial blender (Waring Products, New Hartford, CT) at the highest speed for 4 min. The solution was vacuum degassed for 2 h to remove air bubbles trapped during mixing. The chitosan solution was subsequently poured into Bytac-coated petri dishes and allowed to dry for 2 days at 23°C and 50% RH. The thickness of the chitosan–salt films was not allowed to deviate by more than 10% from 40 μm. The final WPC and chitosan film thicknesses were a direct consequence of the casting formulations and procedures, and thus were not selected in advance.

Buffered chitosan films

Chitosan–salt films were treated in a basic buffer solution to eliminate residues of acetic acid and to eliminate protonization of the amino groups on exposure to water. The films were washed in deionized water after the buffer treatment. The buffer was a pH 7.8 solution consisting of 0.1M Na$_2$HPO$_4$·H$_2$O and 0.1M Na$_2$HPO$_7$·7H$_2$O. The salts were supplied by VWR International AB (Sweden).

Alkyd coating

The alkyd coating (LS H74-101) consisted of a solution of alkyd (58.26 wt %), nitrocellulose (13.50 wt %), n-butyl acetate (5.08 wt %), a resin of carbamide (8.5 wt %), and melamine (8.5 wt %). The dry content of the carbamide–formaldehyde resin was 91% and the dry content of the melamine-formaldehyde resin was

95%. The curing agent (DV309) was ethanol-borne and based on p-toluene sulfonic acid and sulfuric acid. The coating system was designed to suit the present study by the supplier Becker-Acroma AB (Sweden).

The alkyd was based on phthalic acid, penta erytriol, and fatty acids with an excess of hydroxyl groups. The alkyds were crosslinked by etherification and reetherification on the methylene of the melamine–formaldehyde and of the carbamide–formaldehyde resin, when adding the p-toluene sulfonic acid. The cellulose-nitrate contributes to fast drying, resulting in shorter time to loss of tackiness. The functional groups in the resin bridges were previously described by Blank.[37] The drying time of this system was about 10 h at 25°C, although it could be shortened by increasing the temperature.

The coating was prepared by mixing 85 wt % alkyd solution with 15 wt % curing agent solution in a glass container. The alkyd lacquer was coated onto the chitosan–salt and WPC films using an Erichsen Applicator Model 360 99227 (Erichsen GmbH and Co. KG, Germany), having four different slit sizes: 30, 60, 90, and 120 μm. The alkyd solution was poured into the applicator that was subsequently drawn over the films at a rate of 10 cm/s. The final coating thickness after drying was determined by measuring the thickness of the alkyd lacquer on poly(ethylene terephthalate) (PET) films.

Wax coating

The wax, Tenax Wax, contained beeswax, paraffin, and gum damar, with a melting point of 55–60°C. It was supplied by SS White Manufacturing Ltd. (UK). The specific wax was chosen because of its relatively high ductility at room temperature. Melted wax, at a temperature of 70°C, was applied onto the films by pouring it into a preheated applicator (heated in an oven to 105°C), which was subsequently drawn over the films.

Methods

Preconditioning was performed at 50% RH and 23°C for all samples and tests.

Bending test

Coated films were folded through 180° and bent through 90° over a sharp edge and then studied under a transmission light microscope from SpectraTech (Shelton, CT), for detecting fractures and for delamination.

Crease test

The creasing device consisted of a metallic wheel, with a diameter of 15 mm, having a blunt edge, 1.7 mm wide and 1.5 mm deep. The crease was obtained by applying pressure manually to the creaser while it was rolled once over the specimen. Two replicates of each sample were tested.

Stiffness test

PET films were coated with the alkyd lacquer to different thicknesses corresponding to dry alkyd coat weights of 2.65, 1.76, 1.39, and 0.63 mg/cm^2, respectively. PET was used as a substrate because it had a good combination of stiffness and reproducible properties. A rectangular specimen, 38 × 50 mm, was fixed horizontally in a clamp so that about 5 mm was outside the clamp just in front of a blunt edge. The force needed to bend the specimen to an angle of 7.5° was measured in a stiffness tester (AB Lorentzen and Wettres, Sweden), according to SCAN-P 29/95.[38] The test was performed at 50% RH and 23°C. The stiffness index (S_i, Nm^6/kg^3) was obtained from the force (F) and the mass per unit area ($w = $ kg/m^2) of the specimens: $S_i = F/w^3$. The specimens were bent so that the alkyd was in both convex and concave mode to compare the resistance to bending in both compression and extension. Four replicates of each sample were tested.

Water absorbency by the Cobb method

The water absorbency was determined as described in SCAN-P 12/64.[39] The apparatus used consisted of a rubber-mat baseboard and a 5-cm-high metal cylinder with an inner area of 100.0 cm^2. The tester was provided with a clamping device to fasten the cylinder on the baseboard. After the initial weight of the film was measured, the film sample was placed on top of the mat and a leakproof seal was formed when the cylinder was clamped into position. Subsequently, 100 mL of distilled water was poured into the cylinder. When determining Cobb$_{60}$, the absorption time was 60 s. The water was poured out after 45 s and after an additional 15 s the test piece was removed from the instrument and the adsorbed water was removed by pressing the film between blotting papers under a brass roller. Finally, the film was weighed and the Cobb value X (the water absorbency in g/m^2) was calculated as $X = 100(m_f - m_i)$, where m_f and m_i are the weights (in g/dm^2) of the test piece before and after exposure to water, respectively. A few additional tests, according to Cobb$_{24 h}$, were performed. Cobb$_{24 h}$ is similar to Cobb$_{60}$, but the test pieces were exposed to water for 24 h. Two replicates of each sample were tested.

Water vapor transmission rate

The water vapor transmission rate (WVTR) was measured on four replicates of each sample using a Mocon

Permatran-W Twin (Minneapolis, MN), at 23°C and 100% RH, as described in ASTM F 1249-90.[40] The specimens, with specific coat weights ranging between 0.63 and 7.94 mg/cm^2, were tightly sandwiched between two pieces of aluminum foil providing a 5-cm^2 active area for the WVTR measurements. They were mounted in isolated diffusion cells with deionized water and conditioned for 18 h in a conditioning rack for the Permatran-W Twin. The water vapor transmission through each sample was measured for a maximum of 6 h after the conditioning. The WVTR was normalized with respect to the total film thickness (i.e., coating plus substrate). The SD of the method was ±9.9%, calculated from results obtained from 12 round-robin tests.

Oxygen permeability

The oxygen transmission rate was determined at 23°C and 90–95% RH, using a Mocon Ox-Tran Twin apparatus, according to ASTM D 3985-95.[41] The specimens, with coat weights ranging between 0.63 and 7.94 mg/cm^2, were mounted in isolated diffusion cells and subsequently purged with nitrogen gas (2% hydrogen) to measure the background oxygen leakage of the instrument. Each sample was tightly sandwiched between two pieces of aluminum foil providing a 5-cm^2 active area for the measurements. One side of the sample was exposed to flowing oxygen (99.95%) at atmospheric pressure after the background measurements. The flow rate through the specimen was measured for a maximum period of 6 h after it had been conditioned for 18 h. The oxygen transmission rate was normalized with respect to the oxygen pressure and the film thickness to yield the oxygen permeability (OP). The SD of the method was ±10.9%, calculated from results obtained from 11 round-robin tests. Four specimens of each film material were analyzed.

Overall migration

The measurement was performed according to EN 1186-5,[42] a test method for overall migration into aqueous food simulants. Cell type B was used. Films were inserted in migration cells and exposed to deionized water for 10 days. The volume inside the cell was 100 mL, and the exposed film area was 1.13 dm^2. Flasks were dried in an oven at 105°C for 1 h and subsequently placed in a desiccator, at 0% RH, for 1 h. The flasks were intermittently weighed using an AT261 Delta Range balance from Mettler Toledo (Sweden), until the difference between two consecutive weighings differed by less than 0.5 mg. After 10 days, 50 mL water from each migration cell was poured into each flask except for a reference flask. The water in each flask was allowed to evaporate using a Büchi Rotavapor R-124 (Büchi Labortechnik AG, Switzerland), with

a Millipore vacuum pump XF54 (Millipore, Milford, MA) and a Büchi Waterbath B-480.

The flasks were subsequently dried at 105°C for 24 h and then placed in desiccators at 0% RH and weighed. This procedure was repeated until constant mass was attained. The reference flask was weighed together with the other flasks. The mass of migrated substance (M) was calculated in mg/dm^2: $M = 1000(m_a - m_b)/S$, where m_a is the residual mass after evaporation in grams, m_b is the difference between the mass of the reference flask before and after evaporation in grams, and S is the exposed area in dm^2. Four replicates of each sample were tested.

RESULTS AND DISCUSSION

The alkyd thickness decreased upon curing, and this resulted in average coating thicknesses of 5, 12, 14, and 21 μm (= coat weights of 0.63, 1.39, 1.76, and 2.65 mg/cm^2, respectively) for the corresponding applicator slit sizes of 30, 60, 90, and 120 μm. The average density of the dry alkyd was 1260 kg/m^3. Once the layer had dried, it was impossible to dissolve it in n-butyl acetate, a finding that verified that the coating was cured.

Mechanical properties

The alkyd-coated chitosan–salt and WPC films were flexible and the coating showed good adhesion to the substrates. In contrast to the nitrocellulose-coated films,[36] it was possible to bend the alkyd-coated films repeatedly through 180° without inducing cracks or delamination. The alkyd-coated films were also readily creasable. The creasing operation left a smooth striped pattern on the coated surface. At room temperature the wax coating fragmented and delaminated from the substrates upon bending through 90° and the wax was not creasable without the development of cracks and delamination. However, if the wax coating was heated to 35–40°C its properties changed dramatically and it was possible to bend it through 90° without causing any signs of cracks or delamination.

The alkyd-coated PET film appeared to be stiffer when bent with the coating on the convex side than on the concave side (i.e., the alkyd coating was softer in compression than in tension). This facilitates packaging converting operations (e.g., creasing and flexion), provided the coating is located on the concave surface of the packaging material. The stiffness of the alkyd coating was similar to that of the nitrocellulose lacquer[36] (Fig. 1). The decrease in stiffness index as a function of coating thickness may be attributable to a larger amount of plasticizing residual solvent in the thicker samples.
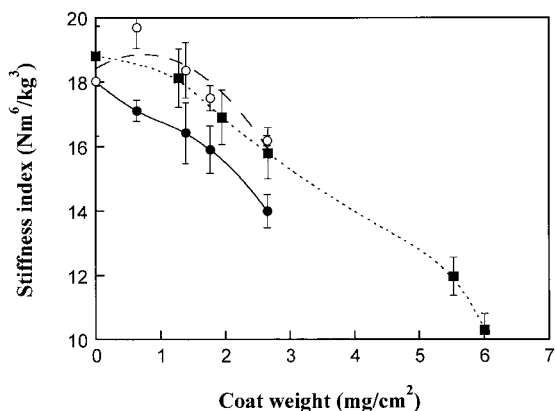
Figure 1 Stiffness index for PET-film as a function of alkyd coating thickness, in compression (●) and extension (○) obtained by bending the sample with the coating on the concave and on the convex surfaces, respectively. The alkyd data are compared with data for nitrocellulose-coated PET (■) from Gällstedt et al.[36] The values are given with confidence intervals of 95%.
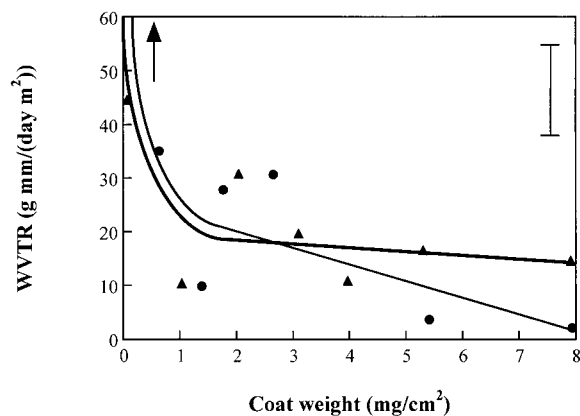

Figure 3 Water vapor transmission rate (WVTR) as a function of the coat weight for whey protein concentrate films coated with alkyd (●, thin line) and nitrocellulose[36] (▲, thick line). The arrow indicates that the WVTR value exceeds the measurable range of the equipment. The values are given with confidence intervals of 95%.

Water absorbency

The alkyd coating was less effective in protecting the chitosan–salt and WPC films from liquid water than the nitrocellulose coating presented in the previous study.[36] Figure 2 shows that the water absorbency increased with increasing alkyd coat weight. This was probably because of a larger amount of plasticizing residual solvent in the thicker samples. In the case of nitrocellulose, the coat weight had to be at least 1.4–1.7 mg/cm^2 (10–17 μm coat thickness) to provide proper protection to liquid water during the Cobb$_{60}$ test.[36] The wax-coated films (20–60 μm coat thickness)
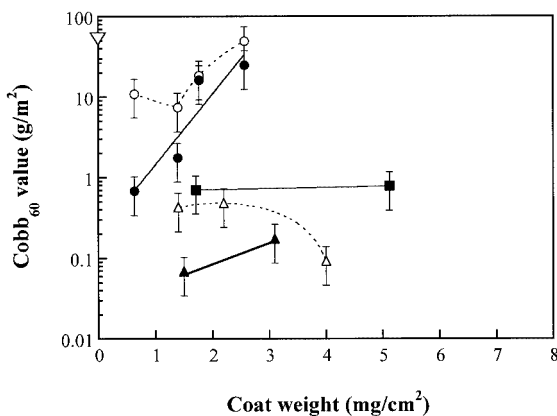

Figure 2 Absorbency according to Cobb$_{60}$ on a logarithmic scale as a function of coat weight for the whey protein concentrate film coated with alkyd (●), wax (■), and nitrocellulose (▲), and for the chitosan–salt film coated with alkyd (○) and nitrocellulose (△). The value for the uncoated buffered chitosan material is given by (▽). The nitrocellulose data are taken from Gällstedt et al.[36] The values are given with confidence intervals of 95%.

showed good resistance to liquid water during the Cobb$_{60}$ test, provided they were mechanically unaffected.[43] The Cobb$_{24 h}$ values revealed that neither the alkyd-coated nor the wax-coated films were resistant to liquid water. Small cracks in the wax, caused by the clamping, resulted in a time-dependent swelling of the substrate leading to further crack formation in the coating. Slow penetration of water through the alkyd layer resulted in expansion and further absorption of water into the substrate. The chitosan–salt film, as well as the WPC film, deteriorated completely when exposed to liquid water, but the buffered chitosan film sustained liquid water. The residues of acetic acid were removed by the buffering treatment, and this resulted in an insolubility in water because of the lack of protonization of the amino groups and thus no electrostatic repulsion. However, a disadvantage of the buffered chitosan is that the films shrank and became distorted during the buffering operation, problems that must be solved before the films could be used commercially.

Water vapor and oxygen barrier properties

The WVTR values for the alkyd-coated materials were similar to those of the nitrocellulose-coated materials[36,43] (see Figs. 3 and 4). It should be pointed out, however, that the WVTR was here determined after 24 h of exposure to 100% RH at 23°C, whereas the exposure time was 6–12 h at 37.8°C for the nitrocellulose-coated materials. This was because the WVTR for the nitrocellulose-coated materials reached a steady state in 6–12 h, whereas in the present case a complete leveling out of the WVTR was not observed even with 24-h exposure. The normalization of WVTR with re-
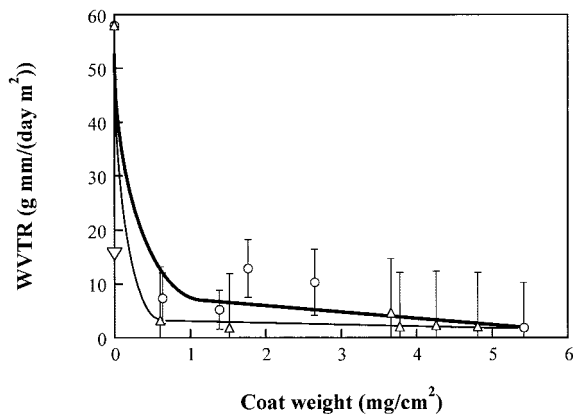
Figure 4 WVTR as a function of the coat weight for chitosan–salt film coated with alkyd (○) and nitrocellulose[36] (△). The value for the uncoated buffered chitosan material is given by (▽). The values are given with confidence intervals of 95%.
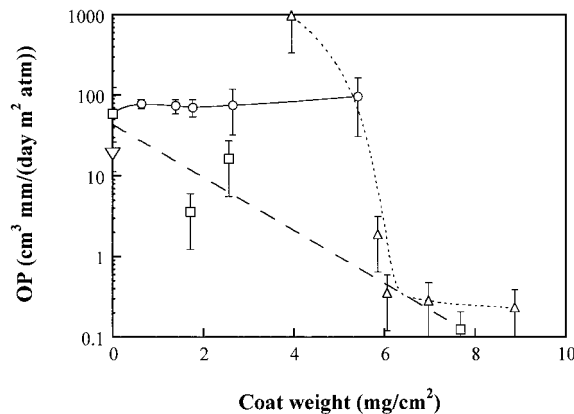

Figure 6 OP on a logarithmic scale as a function of coat weight on chitosan–salt film coated with alkyd (○), wax (□), and nitrocellulose[36] (△). The value for the uncoated buffered chitosan is indicated by (▽). The values are given with confidence intervals of 95%.

spect to thickness was based on the total thickness (i.e., substrate plus coating).

In the case of the OP, the alkyd-coated materials showed in general higher values than those of the corresponding nitrocellulose-coated materials[36] (Figs. 5 and 6). As in the case of WVTR, the OP value for the alkyd-coated materials did not reach a steady state within the 24-h exposure time. The wax-coated materials reached a steady state and the wax-coated chitosan–salt films had good oxygen barrier properties at 90–95% RH.

Overall migration

The results of the overall migration test (Fig. 7) indicate that the alkyd-coated chitosan–salt and WPC

films were unsuitable in direct food contact below coat weights of 2.1 and 7.5 mg/cm², respectively, corresponding to alkyd thicknesses of 21 and 63 μm.[43] Below these coat weights, the migration limit set by The Swedish National Food Administration[44] was exceeded. The migration values of the alkyd-coated specimens were of the same magnitude as those for the nitrocellulose-coated materials.[36] Species from the substrate probably migrated from the coated materials, given that the level of migration decreased with increasing coat weight.[43] The absorption of the alkyd into the WPC films was higher than that into the chitosan–salt films, and the WPC films showed much higher migration values than those of the chitosan–salt at comparable coat weights because of a less-effective
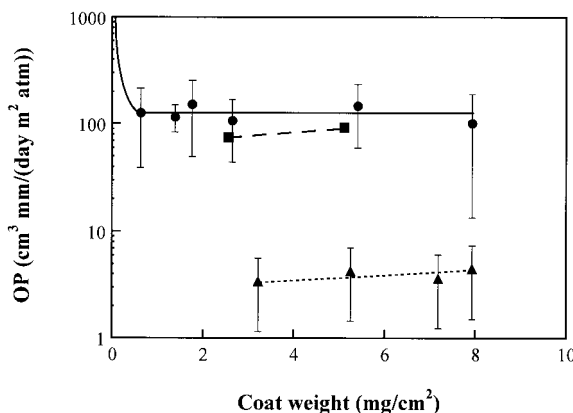

Figure 5 Oxygen permeability (OP) on a logarithmic scale as a function of coat weight on whey protein concentrate film coated with alkyd (●), wax (■), and nitrocellulose[36] (▲). The arrow indicates that the OP value exceeds the measurable range of the equipment. The values are given with confidence intervals of 95%.
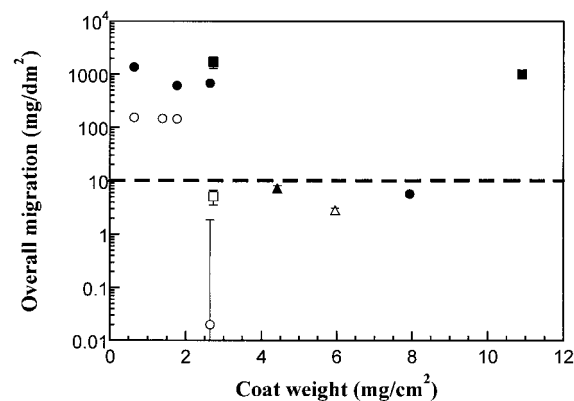

Figure 7 Overall migration to water on a logarithmic scale as a function of the coat weight for whey protein concentrate film coated with alkyd (●) and nitrocellulose[36] (▲) and wax (■), for chitosan–salt film coated with alkyd (○) and nitrocellulose[36] (△) and wax (□). The line at 10 mg/dm² is the upper tolerance limit set by The Swedish National Food Administration.[44] The values are given with confidence intervals of 95%.

coating. Degradation of the alkyd-coated WPC films was observed after 10 days by a distinct odor from the water inside the cell when it was poured out. Water from the migration cells with WPC films with alkyd coat weights below 7.5 mg/cm^2 was turbid, whereas water from the cells with the alkyd-coated chitosan–salt films was still transparent and odorless, even below 2.1 mg/cm^2 coat weight.[43] Because of the cracks in the wax, caused by the clamping, and the resulting time-dependent swelling of the WPC substrate, a high overall migration occurred. The migration value of a WPC film, with a wax coating of 10.91 mg/cm^2, was about 1000 mg/dm^2. The migration mass was most likely a substrate species, given that the wax-coated chitosan–salt films showed a migration of only 5.1 mg/dm^2 for a wax coat weight of 2.73 mg/cm^2. Migrated species of lactose, minerals, and glycerol from WPC, some of them having started to ferment, were probably responsible for the turbid appearance and distinct odor. In general, the migration mass of the chitosan–salt was lower. A difference ascribed to the substrate was also seen for the alkyd-coated films, even though the difference was smaller.

CONCLUSIONS

The alkyd-coated films exhibited, at least for applications in less-humid environments, interesting water vapor barrier properties, measured over a 24-h period. The alkyd coating has a better packaging-converting potential than the wax coating. Overall migration levels from the coated materials, except for the wax-coated whey protein concentrate (WPC) films, were below safety limits (10 mg/dm^2), provided the alkyd coat weights were higher than 7.5 mg/cm^2 ($\approx$63 μm, WPC) and 2.1 mg/cm^2 ($\approx$18 μm, chitosan–acetic acid salt). The wax-coated chitosan–salt film showed a migration value of 5.1 mg/dm^2 for the lowest coat weight, 2.73 mg/cm^2. The chitosan films that were treated in a basic buffer solution had much lower water vapor transmission rates than that of the untreated chitosan–salt film. However, the film shrinkage that occurred during buffering presented a problem that must be solved before further development. The alkyd-coated WPC and chitosan–salt films were readily folded through 180° without any visible cracks or delamination. The wax showed acceptable bending properties when folded at 35–40°C, but it was brittle at lower temperatures. The wax was a more efficient barrier to liquid water and 90–95% RH than the alkyd.

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