Water Barrier Properties of Zein-Oleic Acid Films

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ABSTRACT

Free-standing films were prepared from zein formulations containing 30, 40, 50, 60, 70, and 80% oleic acid (OA). Zein/OA formulations were also used as coating films for rodent diet bars. Water vapor permeability (WVP) of films and moisture loss rate (MLR) of coated rodent diet bars were measured at 4 and 25°C. Temperature affected the water barrier properties of films and coatings. At 4°C, WVP of films decreased with OA concentration while it increased at 25°C. WVP behavior was attributed to oleic acid phase changes due to temperature. At 4°C, OA is a crystalline solid that limits water diffusion through the films. At 25°C, liquid OA increased the system free volume and allowed for water diffusion. The effect was more pronounced the higher the OA concentration in films. Differential scanning calorimetry (DSC) of zein/OA films showed endothermic peaks at 12–18°C, confirming the melting of OA in that temperature range. MLR of coated rodent diet bars was also affected by temperature and OA concentration in coating formulations. In this case, formulations containing 40, 50, and 60% OA were better moisture barriers than coatings with higher OA content at both 4 and 25°C. Moisture losses were reduced at 4°C due to OA solidification.

Interest in edible films and coatings is largely due to their potential to control moisture migration in or out of foods for improved quality and extended shelf life (Krochta 2002). Lipid-based coatings, including oils, fats, and waxes have been used as moisture barriers because of their hydrophobic nature (Morillon et al 2002). However, they present limitations in many applications due to poor mechanical properties including low ductility and malleability. Protein-based films have a broader spectrum of mechanical properties but their utilization is limited by their hydrophilic character. In some cases, proteins have been combined with lipids seeking to take advantage of both materials. A thorough review of the preparation and properties of protein-based edible films and coatings can be found in Gennadios (2002).

Zein, a good film former, is considered markedly hydrophobic among proteins. Moisture barrier properties of zein films have been studied by several researchers (Aydt et al 1991; Park et al 1994; Herald et al 1996; Parris and Coffin 1997; Parris et al 1997; Lai and Padua 1998; Wang and Padua 2004). Reported literature values of water vapor permeability (WVP) for free-standing zein films plasticized by glycerol, polyethylene glycol, lactic acid, triethylene glycol, sorbitol, and polypropylene glycol have ranges of 29.4 g·mm/m^2·d·kPa for glycerol-polypropylene glycol-zein at 1:3:9.3 (Parris and Coffin 1997) and 102.8 g·mm/m^2·d·kPa for lactic acid-triethylene glycol-sorbitol-zein at 2:2:1:12 (Herald et al 1996). WVP of unplasticized zein films is 14.7 g·mm/m^2·d·kPa (Parris and Coffin 1997). Zein films plasticized with oleic acid measured at 1.04–3.70 g·mm/m^2·d·kPa (Wang and Padua 2004). In general, the incorporation of hydrophobic plasticizers yields films with lower water absorption rates (Lawton 2004). Santosa and Padua (1999) reported that increasing concentrations of oleic acid in zein film formulations decreased water absorption rate of films. The objective of this work was to investigate the effect of OA concentration on the WVP of zein/OA free-standing films and on moisture loss rate (MLR) of rodent diet bars coated with zein/OA formulations. The effect of temperature on WVP of films and MLR was also investigated.

MATERIALS AND METHODS

Materials used included regular grade zein (F4000, protein content 88.7%, Freeman Industries, Tuckahoe, NY); oleic acid (cis-9-octadecenoic acid, C18:1, 90%, Aldrich Chemical Co., Milwaukee, WI); distilled mono-glycerides (DMG-130, Archer Daniels Midland Co., Decatur, IL); technical grade ethanol (Midwest Grain Products, Pekin, IL); reagent grade anhydrous calcium sulfate, calcium nitrate (Fisher Scientific, Fair Lawn, NJ); rodent diet (Harlan Teklad 22/5 rodent diet [W], Harlan Industries, Madison, WI).

To prepare zein/OA films, 50 g of zein and OA at ratios (w/w) of 7:3, 6:4, 5:5, 4:6, 3:7, and 2:8 (30, 40, 50, 60, 70, and 80% OA, respectively) were added to 125 mL of 95% ethanol. DMG-130 (2 g/50 g zein + OA) was used to enhance OA dispersion. Mixtures were stirred at 60°C for 10 min and poured onto nonstick Mylar films. Free-standing films were peeled off after drying at ambient conditions for 24 hr. Film thickness was measured with an AMES dial gauge with 0.01-mm precision. The average of 15 measurements was used in WVP calculations.

Water vapor permeability (WVP) of zein films was measured according to ASTM E 96-95 desiccant method (ASTM 1995). Test cells, covered and sealed by test films, were placed in sorbostats maintained at 51% rh by a saturated solution of calcium nitrate. Anhydrous calcium sulfate was used to maintain 0% rh inside the test cells. The sorbostat was stored at 25 ± 2°C. Water vapor permeability was calculated asWVP = (WVT/$S[R_1 - R_2]$) × L, where WVT = G/tA. WVT is water vapor transmission, G is the weight change of the test cell, t is the time during which G occurred, and A is the test area. G/t was obtained from the slope of the linear portion of the plot of G vs. t. S is saturation of vapor pressure at test temperature (3.17 × 10 Pa at 25°C), R_1 is rh in the test sorbostat expressed as a fraction, R_2 is rh inside the test cell expressed as a fraction, and L is film thickness. Typically, G/t was measured after 12 hr of the start of the experiment. The testing area for WVT trials was 28.27 cm^2.

WVP of zein films was also determined at refrigeration temperature. The setup for WVP measurements was placed in a chamber at 4 ± 1°C. The saturation vapor pressure at 4°C is 0.85 × 10^3 Pa; R_1 was measured at 69% with a monitor (model 007, Decagon Devices, Pullman, WA); and R_2 was assumed to be 0%.

Rodent diet bars of elliptical cross-section measuring 15 × 10 mm were cut into pieces 1 cm in length. Diet pieces were preconditioned at 25 ± 2°C and 97% rh for one week, which brought the moisture content to 24.5%. Sample diet pieces were dip-coated in warm zein/OA solutions for 5 sec and allowed to dry in air at room conditions for 1 min. The process was repeated three times. Coated products were kept in aluminum pans for 1 hr at room conditions to evaporate the alcohol and water in the coating formulation. Rodent diet bars were coated by the same process with a formulation consisting of 70% stearic acid and 30% zein, which was obtained by dissolving 35 g of stearic acid in 125 mL of warm 95% ethanol containing 15 g of zein and 2 g of emulsifier.

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To determine moisture loss rate (MLR) of coated rodent diet, coated products were weighed initially (w_o) and placed into desiccators containing saturated calcium nitrate solution. Desiccators were kept at 25 ± 2°C or at 4 ± 1°C. Coated samples were periodically weighed (w_t). A plot of w_t/w_o over time was recorded to evaluate the MLR of coated samples.

Moisture content was determined gravimetrically. Samples were weighed and dried in an oven at 103°C for 1 hr, cooled down in a desiccator, and weighed again. The procedure was repeated until the change in calculated moisture was <0.2%.

DSC scans were taken for films containing 30, 40, 50, 60, 70, and 80% OA. Measurements were made in a differential scanning calorimeter (model 2920, TA Instruments, New Castle, DE) operated in the standard mode. Before analysis, samples in aluminum pans (0.033–0.035 g) were placed in a desiccator containing anhydrous calcium sulfate for two weeks or longer to remove moisture. Samples were scanned from –30 to 50°C at a rate of 10°C/min. A refrigeration system was used to cool the chamber.

RESULTS AND DISCUSSION

Preliminary experiments indicated that up to four parts of oleic acid could be incorporated per part of zein (80% OA) and still form free-standing films by solution casting. Such films were homogeneous and could be easily peeled off from casting surfaces indicating good compatibility between zein and oleic acid. Formulations containing higher OA/zein ratios were too weak to be lifted off as films. Protein content of films as measured by Leco protein/nitrogen determinations (FP-528, Leco Corp., St. Joseph, MI) was very close to the nominal value in every case, indicating that OA losses during film preparation were negligible. Film thickness measured were 0.12–0.19 mm.

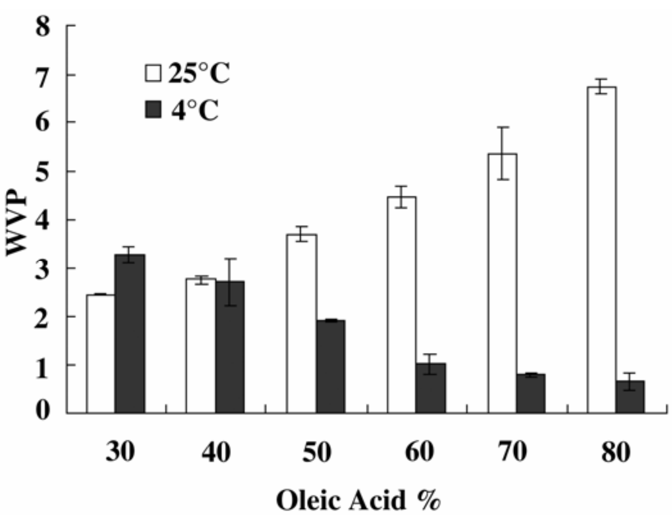

Fig. 1. Water vapor permeability (WVP) of zein/oleic acid (OA) films at 4 and 25°C.

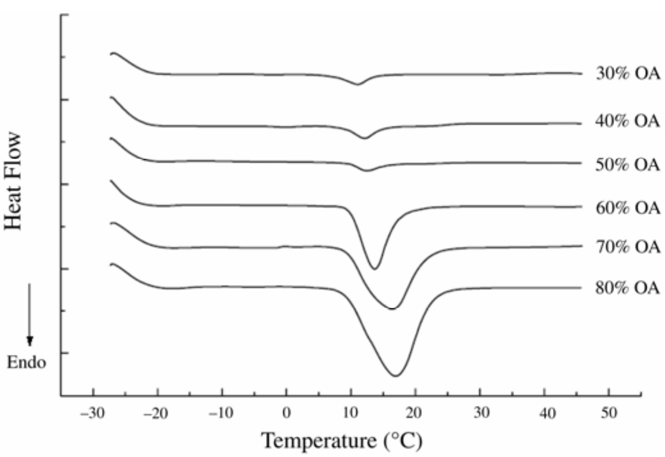

Fig. 2. Differential scanning calorimetry (DSC) thermograms of zein/oleic acid (OA) films.

WVP

WVP determinations for zein films at 25 and 4°C are presented in Fig. 1. At 4°C, WVP of films decreased continuously with oleic acid concentration. This trend was expected in view of the hydrophobic character of oleic acid. Increasing mass fraction of a hydrophobic compound in the formulation decreases water affinity of films resulting in lower WVP. However, at 25°C, WVP of films increased with OA concentration as seen in Fig. 1. The effect of temperature on WVP behavior was explained in terms of oleic acid phase changes. DSC thermograms of zein/OA films in Fig. 2 show endothermic peaks between 12 and 18°C, which were attributed to melting of OA. Accordingly, OA was a crystalline solid at 4°C and a melt at 25°C.

Gas permeability is affected by diffusion which tends to be slower in crystalline solids than in liquids. CH groups are reported to have lower volume and more dense molecular packing in crystalline than in liquid phases (Perron and Ollivon 1992). Oleic acid may have assumed a dense packing structure in films kept at low temperature, preventing water vapor permeability. Also, the solubility of water is lower in solid than in liquid lipids (Kamper and Fennema 1984; Callegarin et al 1997) leading to a lower solubility at 4°C.

Films containing 30% OA, however, showed a higher WVP at 4°C than at 25°C. This was believed due to the relatively high amount of zein (70%) in the formulation that adsorbed a higher amount of water at the higher rh prevalent at 4°C. Kester and Fennema (1989a) reported an increase in moisture transfer rate as temperature decreased when studying the moisture barrier efficiency of fats as a function of temperature. They explained that higher moisture sorption resulted from the filter paper used as a mechanical support. Those authors (Kester and Fennema 1989b) also showed a V-shaped curve of moisture permeability over temperature, in which WVP decreased as temperature decreased from 40 to 15°C but increased at 4°C. They explained this behavior in terms of structural changes due to phase transitions, formation of defects such as holes or cracks because of temperature dilatation, or by a greater moisture sorption at low temperatures.

DSC thermograms in Fig. 2 also show that OA melting peak areas are larger for samples containing 60–80% OA than for samples with 30–50% OA. Differences in peak area suggested that OA content of films affected their structure. It appeared that in samples with low OA content, OA was mostly bound to zein with only a small fraction present as free phase. In samples with high OA content, a larger fraction was present as free OA. At 25°C, free-phase OA was liquid, which increased the system free volume leading to higher diffusion coefficients and higher WVP of films.

MLR of Coated Rodent Diet Bars

Rodent diet bars weighing 3.19–4.11 g were dip-coated with zein/OA formulations containing 30, 40, 50, 60, 70, and 80% OA. The average weight of zein/OA coatings was 0.430 ± 0.14 g. No correlation was found between coating formulation and coating weight. The rate of moisture loss of coated products was measured at 25 and 4°C. Results were plotted as w_t/w_o ratios over time. Results are shown in Figs. 3 and 4 for samples kept at 25 and 4°C, respectively.

Coated samples showed slower MLR upon desorption than uncoated samples. At 25°C (Fig. 3), samples containing 40, 50, and 60% OA showed similar MLR values (0.00094, 0.00095, and 0.00106 g/g/hr, respectively) while samples containing 70 and

80% OA showed faster MLR (0.00230 and 0.00353 g/g/hr, respectively). Moisture loss rate for uncoated samples was 0.00871 g/g/hr. MLR behavior was different from that of WVP of films, where WVP increased continuously with OA concentration. For samples with 30% OA, faster MLR (0.00129 g/g/hr) may be due to the high proportion of zein in the coating formulation, which because of its hydrophilic character facilitated water transport. Fast MLR of samples containing 70 and 80% OA may be attributed to the high proportion of OA in liquid phase that facilitated water diffusion.

MLR of the coated products was substantially reduced at 4°C (Fig. 4). Slow MLR was attributed to OA crystallization that prevented water diffusion through coatings. MLR values for coatings with 30, 40, 50, 60% OA were very close to each other (0.000075, 0.000066, 0.000062, and 0.000052 g/g/hr, respectively). MLR of coatings with 70 and 80% OA were slightly faster (0.000101 and 0.000106 g/g/hr, respectively), suggesting film structural differences with respect to the rest of the samples.

The initial moisture content of rodent diet bars after preconditioning at 97% rh was 24.5%. It was considered that the bars would still be viable for consumption at 18% moisture content, which corresponds to a w_t/w_o ratio of 0.92. Reaching a w_t/w_o ratio of 0.92 at 25°C took 28 hr for uncoated samples, 50, 110, and 190 hr for samples coated with 80, 70, and 30% OA formulations, respectively, and over 350 hr for samples coated with formulations containing 40, 50, and 60% OA (Fig. 3). At 4°C, the time required to reach a w_t/w_o ratio of 0.92 was extended to >500 hr for all coated samples.

Rodent diet bars were also coated with a formulation consisting of 70% stearic acid and 30% zein. Free-standing films could not be prepared from this formulation, thus WVP measurements were not possible to obtain. MLR data obtained at 25 and 4°C are shown in Fig. 5. MLR at room temperature (0.001564 g/g/hr) was slower than its 70% OA counterpart. Stearic acid is solid at room temperature, which decreased water diffusion. Figure 5 also shows that MLR at 4°C (0.000610 g/g/hr) was slower than at 25°C. For stearic acid coated samples, reaching a w_t/w_o ratio of 0.92 at 25°C took ≈200 hr. At 4°C it took 900 hr, a rate comparable to that of 70% OA samples at the same temperature. This observation indicates that moisture barrier properties of formulations containing stearic or oleic acid are comparable when both fatty acids are in the solid phase.

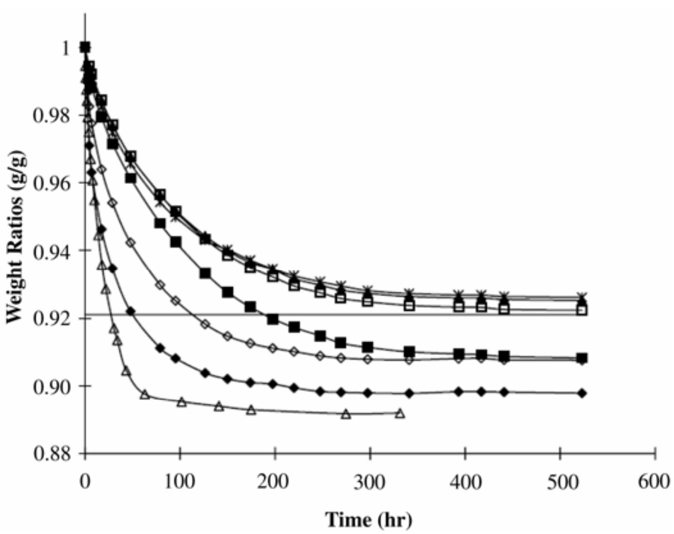

Fig. 3. Moisture loss rate of zein/oleic acid (OA) coated rodent diet bars at 25°C. 30% OA (■); 40% OA (□); 50% OA (▲); 60% OA (*); 70% OA (◇); 80% OA (◆); Uncoated (Δ). Horizontal line represents a w_t/w_o ratio of 0.92, the assumed end use point.

CONCLUSIONS

Water barrier properties of zein formulated with oleic acid were investigated. Free-standing films were prepared from zein formulations containing 30–80% OA. OA concentration affected moisture barrier properties of films. At 25°C, WVP increased continuously with OA concentration. In spite of the hydrophobic character of oleic acid, high OA concentration did not reduce WVP, perhaps because OA in liquid phase increased the system free volume and allowed water diffusion through films. At 4°C, WVP decreased continuously with OA concentration due to OA crystallization that limited water diffusion. Zein/OA formulations were also used as coating films for rodent diet bars. At 25°C, moisture loss rate of diet bars was appreciably reduced by formulations containing 40, 50, and 60% OA with respect to uncoated samples. Higher OA concentration did not continue the trend perhaps because OA in liquid phase increased the system free volume and thus water diffusion. At 4°C moisture, loss rates were greatly reduced due to OA solidification.

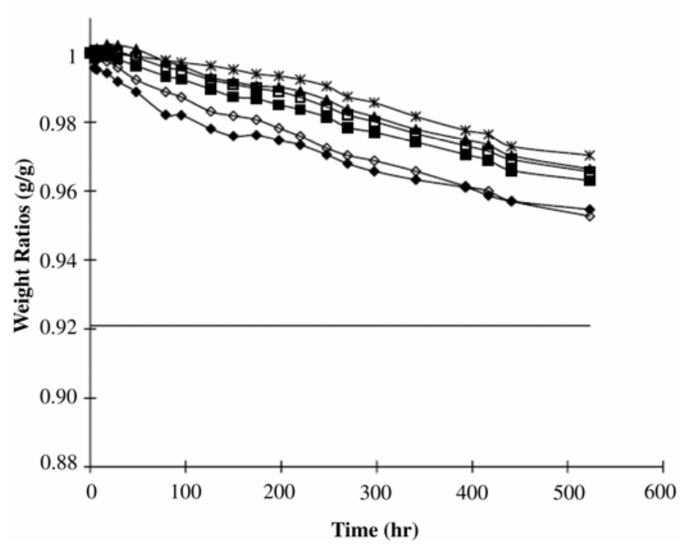

Fig. 4. Moisture loss rate of zein/oleic acid (OA) coated rodent diet bars at 4°C. 30% OA (■); 40% OA (□); 50% OA (▲); 60% OA (*); 70% OA (◇); 80% OA (◆). Horizontal line represents a w_t/w_o ratio of 0.92, the assumed end use point.

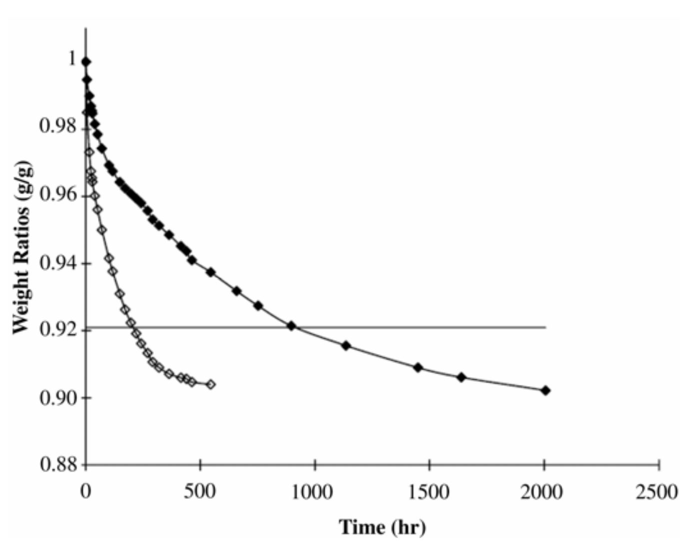

Fig. 5. Moisture loss rate of rodent diet bars coated with zein/stearic acid at 25°C (◇); 4°C (◆). Horizontal line represents a w_t/w_o ratio of 0.92, the assumed end use point.

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