

Permeability of Coatings Made with Emulsified Polyethylene Wax

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Emulsions of polyethylene wax (oxidized polyethylene) were coated onto highly permeable film. Gas permeability of the dried coating was determined from measurements of permeance and coating thickness. With oleic acid and morpholine used as emulsifiers, water vapor permeability of a high-density polyethylene wax coating was 1.7-3.2 g mil/(m² day mmHg) depending on the relative humidity gradient. For the same coating the respective O₂ and CO₂ permeabilities of the coating at 30 °C were 34 000 and 135 000 mL (STP) mil/(m² day atm). In general, coatings made from polyethylene wax have values of O₂ and CO₂ permeability that are high compared to those of most other polymers.

Polyethylene wax, also called oxidized polyethylene (OPE) or hydrocarbon wax, is permitted in the United States as a protective coating for fresh avocados, bananas, beets, coconuts, eggplant, garlic, grapefruit, lemons, limes, mango, muskmelons, onions, oranges, papaya, peas (in pods), pineapple, plantain, pumpkin, rutabaga, squash (acorn), sweet potatoes, tangerines, turnips, watermelon, Brazil nuts, chestnuts, filberts, hazelnuts, pecans, and walnuts (all nuts in shells) (CFR, 1990). The polyethylene wax so approved is produced by the mild air oxidation of polyethylene; it has a number-average molecular weight of at least 1200 and contains a maximum of 5% by weight total oxygen.

Polyethylene wax is said to have the advantage of allowing the coated fruit to respire, thus avoiding the flavor changes that occur with less permeable coatings (Davis and Hofmann, 1973; Ben-Yehoshua, 1967). A number of polyethylene wax based coatings have been developed (Eastman Chemical Products, 1986; Fischer et al., 1981; Gassner et al., 1967; Hall, 1981; Kaplan, 1986; Wildgruber, 1982). Such coatings have been used with mixed success (Ben-Yehoshua, 1969; Cohen et al., 1990; Cuquerella et al., 1981; Davis and Harding, 1960; Davis and Hofmann, 1960; Durand et al., 1984; El-Latief and Abd-El-Wagab, 1975; Lakshminarayana et al., 1974; Siade and Petraza, 1977). However, the polyethylene wax coatings used by these workers often included carnauba wax and other polymers; thus, the results of the fruit storage tests are not always attributable to any one ingredient.

Measurements to date of gas permeability of polyethylene wax are limited to studies with methane (Xu et al., 1987). The present study focuses on permeability to O₂, CO₂, and water vapor, all of direct importance for fruit coatings. Permeability to water vapor is directly related to water loss of stored fruit. Permeability to O₂ and CO₂ governs the relationship between respiration and internal gas concentration. Of some importance also is permeability to other gases, especially ethylene.

A piece of coated fruit might be likened to one sealed inside a plastic film, an area of current research (Leshuk and Saltveit, 1990) that makes use of permeability data of the plastic films. Similarly, for selection or formulation of fruit coatings it is important to have the relevant permeability data, which is the contribution of this study.

MATERIALS AND METHODS

Microemulsions of oxidized polyethylene were received from three suppliers. Epolene E-10 and Epolene E-20 emulsions (E10 and E20) were from Eastman Chemical Products, Inc., King-

sport, TN. Duramul 869 and Duramul 831 emulsions (D869 and D831) came from Astor Wax Corp., Doraville, GA. Finally, A-C 629 and A-C 316 emulsions (AC629 and AC316) were supplied by Allied Corp., Morristown, NJ. Table I summarizes some of the properties of these emulsions, which are but six of many such waxes available and cannot be construed to be similar to other polyethylene waxes from the same suppliers.

To prepare the coating, the microemulsion was brushed onto a polymer film and dried (Hagenmaier and Shaw, 1991a). Coatings of 0.3-0.8-mil thickness resulted, with the thinner coatings more suitable for the emulsions made from high-density polyethylene. The polymer films used were linear, low-density polyethylene for O₂ and CO₂ and cellulose acetate for water vapor permeance. The thickness of the coating was taken as the average of (a) that measured to the nearest micrometer with a micrometer caliper and (b) the thickness calculated from coating density and weight. To prepare uncoated films, the liquid coating was spread on the film and then rinsed off before it dried.

Oxygen permeance was measured with an Ox-tran 100 oxygen permeability tester. This unit was calibrated at 0% relative humidity with Standard Reference Material 1470 from the National Bureau of Standards. Samples of film were tested for permeability according to ASTM D-3985-81 (ASTM, 1981) except that relative humidity conditions of other than 0% were employed. To accomplish this, film samples were held overnight at the desired relative humidity. During the test, the air and carrier gas were passed at 10 cm³/min through bubblers maintained at the appropriate wet bulb temperature and thence into the cell maintained at 30 °C. All permeance values were measured under steady-state conditions.

Carbon dioxide permeance was measured in similar fashion with a sample cell made in our laboratory and using a Hewlett-Packard Model 5890A gas chromatogram as a detector. The effluent from the sample cell was connected in-line to a two-position loop injector. The column was a 30 m × 0.53 mm GSQ fused silica capillary type (J&W Scientific, Folsom CA). The temperatures of the column and the thermal conductivity detector were 40 and 120 °C, respectively. The He carrier gas flow rate through the column was 4.8 mL/min. Peak areas were calculated using a Hewlett-Packard 3345A integrator and calibrated with standard mixtures of CO₂ in nitrogen.

Water vapor permeance of coated films was measured with the Permatran-W1A water vapor permeability tester according to ASTM F-1249-89 (ASTM, 1989). A standard calibration curve was made with aluminum foil and three reference films whose WVTR had been determined gravimetrically. Samples of film were conditioned for 2 h at the relative humidity conditions used for the test.

O₂ and CO₂ permeability are expressed in units of mL (STP) mil/(m² day atm), the ASTM-recommended metric units (ASTM, 1984). One mil equals 0.001 in. For water vapor the units of permeability are g mil/(m² day mmHg). The permeance of coatings was calculated as

Table I. Properties of the Polyethylene Wax Samples

emulsion	wax		wax emulsion	
	identity	density	% ts ^a	ingredients, % of solids
E10	E-10	0.94	30	75% OPE, 13% oleic acid, 11% morpholine
E20	E-20	0.96	30	same as E10
AC629	Lot 6N6291I	0.93	30	78% OPE, 19% Igepal CO-710, ^b 1.9% KOH, and 0.8% Na ₂ S ₂ O ₅
AC316	Lot 5N69512	0.98	30	78% OPE, 19% Igepal CO-630, ^b 1.7% KOH, and 0.8% Na ₂ S ₂ O ₅
D869	Vestowax 2733	0.93	30	OPE, oleic acid, KOH, and NH ₃ , amounts unknown
D831	Vestowax 1535	0.96	28	same as D869

^a Total solids. ^b Igepal CO-710 and CO-630 (CAS 9016-45-9) are nonionic surfactants.

$$1/P_c = 1/P_{cf} - 1/P_s \quad (1)$$

where P_c , P_{cf} , and P_s are permeances of coating, coated film, and support film, respectively. Permeability was calculated as permeance \times thickness.

The water vapor permeance data are the means of three trials; O₂ and CO₂ permeances are based on six trials. For each trial a different piece of film was used. The confidence ranges correspond to 95% probability.

In calculating the water vapor permeability of the coatings, it was necessary to take into consideration the variable water vapor permeability of the cellulose acetate used as a support film. The water vapor permeance was 20.2–22.5 g/(m² day mmHg) for the cellulose acetate when the relative humidity was 75% on the coated side; 20.2 g/(m² day mmHg) with 32% relative humidity on the coated side; and 28.4–32.4 g/(m² day mmHg) for samples having 75% relative humidity on the uncoated side of the film.

RESULTS AND DISCUSSION

Water Vapor Permeability. For coatings AC629 and AC316 the permeability was over 5 times as high when the coated side was at 75% rather than 0% relative humidity (Table II). The permeability of the other samples was somewhat less dependent on relative humidity. Some change in permeability is expected at different values of humidity, simply because the coatings are water-based. At relative humidity near 100% the coatings were microemulsions. During the drying process, as the humidity was reduced, the coatings became tacky, and by the time the relative humidity fell to 50% (typical drying conditions) the coatings were dry to the touch. Their physical form and thus their properties are influenced by relative humidity. Using a different water-based coating, Kamper and Fennema (1984) also found that water vapor permeability was considerably higher as humidity was increased, which they attributed to increased hydration of the film components.

All six of the polyethylene coatings had higher water vapor permeability than polyethylene film. [The permeability of low-density polyethylene film at 30 °C was determined to be 0.26–0.32 g mil/(m² day mmHg).] This explains why coating fruit with polyethylene wax is not as effective in preventing weight loss as wrapping it with polyethylene film (Ben-Yehoshua et al., 1979; Siade and Pedraza, 1977).

Activation Energy. The activation energies for oxygen and water vapor permeance were determined from measurement of permeability at 25, 30, 35 and 40 °C, using Arrhenius plots of ln (permeability) vs 1/ T . Results for coatings are shown in Table III. The average activation energy for oxygen is 4.7 kcal/mol, which means that

permeability increases approximately 30% per 10 °C rise in temperature. For low-density polyethylene film the activation energies for O₂ and water vapor permeability, respectively, were 9.0 \pm 0.5 and 2.6 \pm 0.1 kcal/mol. Thus, for O₂ permeability the coatings have lower activation energy than the less polar polyethylene film, although the opposite may have been expected on the basis of polarity (Rogers, 1985).

O₂ and CO₂. The O₂ and CO₂ permeance of coated and uncoated films showed only small differences except for samples AC316 and AC629 (Table IV). Because there is no significant difference ($P \leq 0.05$) between coated and uncoated for samples D869 and D831, permeability of these samples could not be calculated with eq 1. These same samples have the highest permeability of the coatings studied; the permeability to O₂ is not less than 120 000 mL (STP) mil/(m² day atm) and to CO₂ not less than 380 000 mL (STP) mil/(m² day atm) ($P \leq 0.05$). Film coated with samples E10, E20, AC629, and AC316 had permeance values significantly different from those of uncoated film ($P \leq 0.05$). The corresponding values of permeability, calculated from eq 1, are shown in Table V. For the same four samples, additional measurements of O₂ permeability at 34–75% relative humidity indicated there was no demonstrable dependence on relative humidity over this range. No conclusions can be made for relative humidities outside this range.

Density of the polyethylene is important. The higher density waxes (samples E20, AC316, and D831) had permeability 30–50% of the corresponding value for low-density polyethylene (Table V). The higher the density, the more crystalline the polymer structure, with the result that permeability is lower (Ashley, 1985).

The coatings containing ammonia or morpholine have higher O₂ and CO₂ permeability and also higher percentage of polyethylene (Tables I and V). The ammonia and morpholine keep the polyethylene dissolved and then evaporate after the coating dries. Thus, these have minimum effect on permeability of the dried coatings. By contrast, samples AC629 and AC316 contain nonvolatile surfactants that remain in the coating. Because these emulsifiers are polar, they tend to lower permeability of the coating (Ashley, 1985). Thus, use of a nonionic emulsifier partially defeats the purpose of using polyethylene wax. The work of Davis and Harding (1960) suggests that this reduction in permeability may be sufficient to alter the performance of a coating.

Adjuncts other than nonionic emulsifiers can also reduce permeability, which may explain why polyethylene-based coatings at times did not result in adequate respiration (Cohen et al., 1990; Cuquerella et al., 1981). For example, some polyethylene wax coatings contain shellac (Gassner et al., 1967; Cuquerella et al., 1981), which has much lower permeability than polyethylene wax (Hagenmaier and Shaw, 1991b).

There was a significant correlation, based on linear regression, between the permeabilities of O₂ and CO₂. For samples E10, E20, AC629, and AC316 the mean ratio was 0.21; the same ratio was 0.35 for low-density polyethylene film. Similar ratios apply to other polymers as well (Ashley, 1985; Rogers, 1985; Stannett, 1985) for O₂ permeability divided by CO₂ permeability.

As for other gases, the permeability of polyethylene wax to methane was reported to be 53 000–84 000 mL (STP) mil/(m² day atm) (Xu et al., 1987). Permeability to ethylene, not measured as part of this study, was found in separate work to be about half the value of CO₂ permeability for some commercial fruit waxes containing poly-

Table II. Water Vapor Permeability in g mil/(m² day mmHg) for Six Different Polyethylene Wax Coatings

film configuration	emulsion identity					
	E10	E20	D869	D831	AC629	AC316
75% RH ^b coated side	5.1 ± 0.8 ^a	3.2 ± 0.2	8.6 ± 0.7	10.4 ± 0.7	46 ± 4	65 ± 20
32% RH coated side	2.4 ± 0.3	1.7 ± 0.2	4.2 ± 0.2	4.3 ± 0.3	8.2 ± 0.3	10.7 ± 1.0
75% RH uncoated side	3.1 ± 0.4	2.4 ± 0.4	4.4 ± 0.9	4.3 ± 0.9	8.9 ± 1.8	10.7 ± 0.9

^a The 95% confidence range. ^b RH, relative humidity.

Table III. Activation Energy for Water Vapor and Oxygen Permeability

emulsion	activation energy, kcal/mol	
	water vapor ^a	oxygen ^a
E10	3.7 ^b	5.7 ^c
E20	2.5	4.0
AC629	1.3	4.9
AC316	-0.4	4.0
D869	2.2	
D831	3.1	

^a The relative humidity was 0% on coating side, 75% on uncoated side. ^b O₂ permeability was measured at 50% relative humidity. ^c The least significant differences were 0.81 and 1.7 kcal/mol, respectively, for water vapor and oxygen permeability.

Table IV. O₂ and CO₂ Permeance^a at 30 °C, 50% Relative Humidity

identity	coating thickness, mil	oxygen ^b		carbon dioxide ^c	
		coated	uncoated	coated	uncoated
E10	0.8	12 660 ^d	14 820	38 360 ^d	42 500
E20	0.5	12 600 ^d	15 310	35 650 ^d	40 930
AC629	0.8	10 820 ^d	15 610	34 070 ^d	40 300
AC316	0.4	9 850 ^d	14 830	32 880 ^d	41 930
D869	0.7	15 680	16 430	43 360	43 540
D831	0.6	16 120	16 100	44 150	44 000

^a Units of permeance are mL (STP)/(m² day atm). ^b SD of mean is 380. ^c SD of mean is 1200. ^d Coated and uncoated differ significantly ($P \leq 0.05$).

Table V. O₂ and CO₂ Permeability^a at 30 °C, 50% Relative Humidity

identity	oxygen		carbon dioxide	
	mean	SE ^b	mean	SE ^b
E10	70 000	6400	450 000	160 000
E20	34 000	1300	135 000	11 000
AC629	30 000	1200	210 000	40 000
AC316	10 700	600	61 000	11 000

^a The units for permeability are mL (STP) mil/(m² day atm). ^b The standard error.

ethylene wax (Hagenmaier and Shaw, 1991b). It is beneficial for ethylene permeability of coatings to be high, thus permitting this gas to escape through the peel of coated fruit.

Although values of O₂ and CO₂ permeability were related, there was no such relationship between these and water vapor permeance. A similar lack of dependence has been noted for polymers in general (Ashley, 1985; Stannett, 1985).

Again, it is of interest to compare the coatings with polyethylene film. The O₂ and CO₂ permeabilities of sample E10 were 70 000 and 450 000 mL (STP)/(m² day atm), respectively (Table V). For linear low-density polyethylene, also at 30 °C, 50% relative humidity, the O₂ and CO₂ permeabilities were 15 000 ± 300 and 42 000 ± 4000 mL (STP)/(m² day atm), respectively. Thus, for both O₂ and CO₂ sample E10 has permeability several times higher than that polyethylene film, which is one of the more permeable packaging films (Ashley, 1985). Therefore, fruit coated with this coating can respire much better than seal-wrapped fruit.

Conclusion. Coatings made with polyethylene seem highly suited for fruit and vegetables stored under conditions that demand high respiration rate to avoid anaerobic metabolism. Consider an orange stored at 20 °C. The O₂ permeance of an uncoated orange is about 130 000 mL (STP)/(m² day atm) (Ben-Yehoshua et al., 1985). Assuming the pathway for O₂ exchange is by permeance rather than diffusion through open stomata, eq 1 applies. Now consider this same orange with a 0.1-mil coating having O₂ permeability of 50 000 mL (STP) mil/(m² day atm), typical for polyethylene (Tables III and V). The coating permeance (permeability/thickness) is 500 000 mL (STP)/(m² day atm). From eq 1 the permeance of the coated orange amounts to 103 000 mL (STP)/(m² day atm), 80% of the value for the uncoated orange. This model calculation shows how a polyethylene coating can permit high respiration rates in coated fruit.

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