Water Vapor and Oxygen Permeability of Wax Films

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The water vapor (WVP) and oxygen (O_2P) permeabilities of beeswax (BW), candelilla wax (CnW), carnauba wax (CrW) and microcrystalline wax (MW), formed as free-standing films, were determined. CnW and CrW both had small values for O_2P (0.29 and 0.26 $g{\cdot}m^{-1}{\cdot}sec^{-1}{\cdot}Pa^{-1} \times 10^{-14}$, respectively), which are less than half the value for high-density polyethylene and about a decade greater than the value for polyethylene terephthalate. O_2P values for BW and MW were about 6–9× greater than those of CnW and CrW. WVP of CnW was 0.18 $g{\cdot}m^{-1}{\cdot}sec^{-1}{\cdot}Pa^{-1} \times 10^{-12}$, which is about one-half the value for CrW and MW and about one-third the value for BW. The WVP of CnW was somewhat less than that of polypropylene and somewhat greater than that of high-density polyethylene. Differences in permeabilities among the wax films are attributed mainly to differences in chemical composition and crystal type as determined by X-ray diffraction.

KEY WORDS: Beeswax, candelilla, carnauba, crystallinity, films, microcrystalline, oxygen, permeability, water vapor, wax.

Aside from being a major source of calories in typical diets, lipids, in the form of food coatings, have been used to add gloss to confectionery products, to retard respiration of fruits and vegetables, and to lessen moisture loss from foods to the environment. Recently, many investigators have taken advantage of the hydrophobic nature of lipids and combined them with hydrocolloids, for structural support, to form edible films that are excellent barriers to moisture migration (1–7). These edible films can function internally as moisture barriers between food components of differing water activity, a_w, or externally between the food and its environment.

On a smaller scale, lipids can also function effectively for encapsulating meat processing aids, flavoring agents and spices, minerals, leavening agents, sodium chloride, sweeteners and vitamins (8,9). Suitable lipids for this purpose include waxes, hydrogenated fats and oils, fatty acids and the high-melting fraction of butterfat (9,10). In recent studies on the barrier properties of lipids to water vapor and oxygen, the lipid film was cast on, or embedded in, an inert supporting matrix to provide mechanical support (1,5,11–15). This approach was chosen because of the difficulty in preparing and handling films of pure lipids. However, data obtained in this manner are likely to be somewhat inaccurate because of the possible influence of the supporting material. The method used in the present study allows the barrier properties of wax films to be determined without a supporting matrix.

The four waxes chosen for this study were beeswax, candelilla, carnauba and microcrystalline wax. They were chosen because they are potentially useful as edible films, they differ considerably in chemical composition and physical characteristics, and accurate information on their permeabilities to oxygen and water vapor is lacking.

Beeswax, according to Tolluch (16), consists of 71% wax esters, 15% hydrocarbons, 8% fatty acids and 6% unidentified substances. Findley and Brown (17) reported higher concentrations of hydrocarbons and fatty acids, 23 and 12%, respectively, and an ester concentration of 65%. Both yellow and white beeswax are currently approved for use in selected food products at defined limits of 0.065% for chewing gum, 0.005% for confections and frostings, 0.04% for hard candies, 0.1% for soft candy and 0.02% or less for all other food categories (18,19; 21CFR 184.1973).

Refined candelilla wax consists of about 57% hydrocarbons and 29% wax esters, with the remainder consisting mainly of fatty alcohols and fatty acids (17). Candelilla wax possesses a relatively small amount of volatile esters, 6%, relative to other natural waxes (20). This wax has generally-recognized-as-safe (GRAS) status, with no limitations on use levels, other than current good manufacturing practice, for surface finishes, chewing gums and hard candies (19; 21CFR 184.1976).

Carnauba wax consists of 82% wax esters (40% aliphatic, 13.2% ω-hydroxy and 28.8% cinnamic aliphatic diesters), 11% fatty alcohols, 5.5% fatty acids, 1% hydrocarbon and 0.5% moisture and inorganic substances (21,22). This wax has GRAS status with no limitations on usage levels, other than current good manufacturing practice, for surface finishes, baking products, chewing gum, confections and frostings, fresh fruits and fruit juices, soft candy, processed fruits and fruit juices, gravies and sauces (19; 21CFR 184.1978).

Microcrystalline wax is composed entirely of hydrocarbons, mainly C_{41}–C_{50}, some of which are branched-chain and others aromatic (21). This wax has only a few legal uses in food, namely, as a masticatory substance in chewing gum base, as a protective coating on raw fruits and vegetables, and as a defoaming agent (19; 21CFR 172.887).

The objectives of this study were to determine the water vapor and oxygen permeabilities of these four waxes in pure form and to correlate their barrier properties with: (i) their thermal properties as determined by differential scanning calorimetry, (ii) their crystalline packing order as indicated by X-ray diffraction and (iii) their surface morphologies as determined by scanning electron microscopy.

EXPERIMENTAL PROCEDURES

Film fabrication: pure film. Four waxes were studied: beeswax (Australian White Beeswax, National Wax, Skokie, IL), candelilla (pure refined, Strahl and Pitsch, Inc., West Babylon, NY), carnauba (#1a Yellow, Pure refined, Strahl and Pitsch, Inc.) and microcrystalline (Paxwax 305, National Wax). Wax films were formed by casting molten wax on a dried film of methylcellulose (MC) (Methocel, A15LV, Dow Chemical Co., Midland, MI) and then dissolving away the MC film. The MC film was prepared from a 3% (wt/vol) aqueous solution of MC. Forty-five mL of solution was poured onto a level glass plate that had been previously cleaned with acetone. A plastic frame (17.5 cm × 17.5 cm) was used to confine the solution to 306 cm^2. The film was dried overnight at ambient conditions.

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A thin-layer chroamtography spreader (heated to 150°C) was used to spread molten wax over the supporting MC film. Approximately 2 mL of molten wax (heated to 100°C) were pipetted onto the leading edge of the film-covered glass plate. The spreader was then drawn across the MC film, depositing a wax film of the desired thickness. The plate was then rotated 90°, and a second layer was applied in the same manner.

The wax-MC film was then removed from the plate and immersed in warm tap water (30–35°C) to dissolve the hydrocolloid. The resulting wax film was carefully rinsed to remove any residue of MC, blotted dry with towels and more completely dried overnight under vacuum at room temperature. Wax films were then stored in a desiccator until tested.

Differential scanning calorimetry (DSC). The melting temperatures of the waxes were determined by DSC (Perkin Elmer DSC-7; Norwalk, CT). Liquid N_2 was used as the cooling medium, and indium was used as a calibration standard. Molten wax samples (5–10 mg) were used as a calibration standard. Molten wax samples (5–10 mg) were accurately weighed into aluminum pans, hermetically sealed and placed in the DSC. To ensure consistency between all samples, waxes were first heated to 100°C, at a rate of 200°C/min, held for 2 min and then cooled (20°C/min) to 25°C and held for 5 min prior to testing. Melting transitions were obtained by heating the samples from 25°C (15°C for microcrystalline wax) to 85–100°C at a rate of 8°C/min. Three samples of each wax were tested, and each type of sample was analyzed three times. Melting points and enthalpies of melting, ΔH_t, were calculated from the means of the three trials for each wax sample.

Scanning electron microscopy (SEM). Surface morphologies of wax films were examined with a Model S-570 Hitachi Scanning Electron Microscope (Hitachi, Ltd., Tokyo, Japan). Samples were mounted on aluminum stubs and coated with 100 Å gold. An accelerating voltage of 10 Kv was used to examine the samples, with the electron beam directed at a 45° angle to the sample surface.

X-ray diffraction (XRD). Samples of wax films were mounted on glass slides with double-sided cellophane tape. Copper-K_α radiation ($\lambda = 1.5418$ Å) was generated by a Scintag/USA PAD-V Diffractometer (Scintag, Inc., Santa Clara, CA). Samples were observed at an accelerating voltage of 45 Kv and a current of 40 ma. A diffracted angle range of 15–28°2Θ was scanned at a rate of 1°2Θ/min.

To determine if rate of cooling had any effect on the crystalline properties of waxes, wax at 100°C was either rapidly cooled (cast as thin films as described earlier) or poured into aluminum molds (36 mm × 36 mm × 1 mm). Wax in mold was then slowly cooled by placing samples in an oven at 100°C, turning off the oven and allowing it to cool. These samples cooled at a rate of about 0.4°C/min.

At least two samples of each wax film, cooled by each method, were examined by XRD.

Oxygen permeability (O_2P). O_2P of the wax films was determined with an Ox-tran 100 (Modern Controls, Inc., Minneapolis, MN). The carrier gas was 1% H_2/99% N_2, and the test gases were oxygen and air (20.95% O_2).

Calibration factors were determined at 25, 30, 35 and 40°C with a standard polyester film (Standard Reference Material #1470; National Bureau of Standards, Washington, D.C.). A stainless-steel plate was used to decrease the area available for O_2 transmission from 100 cm^2 to 0.7 cm^2.

After steady-state gas flux was attained at the lowest temperature of measurement, the temperature of the test cell was increased to the next higher temperature. The rate of oxygen transmission (O_2TR) was determined at 25, 30, 35 and 40°C, all at 0% relative humidity (RH). O_2P was calculated and expressed as g $O_2 \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$. Unless otherwise noted, at least four replicates of each wax were tested.

Water vapor permeability (WVP). The water vapor transmission (WVT) rate of wax films was determined with a Permatran W1-A instrument (Modern Controls, Inc.). Samples were tested at a 100-0% RH gradient and an airflow of 10 mL/min across the 0% RH side of the film. The Permatran was calibrated with mylar film 0.13 mm (5 mil) thick. Stainless-steel masks were used to decrease the transmission area to 20 cm^2. Beeswax films were equilibrated in the Permatran Conditioning Rack-1 (100-0% RH; Modern Instruments, Inc.) prior to testing, whereas the other wax films were equilibrated overnight in the Permatran-W1A test cell. The latter was done because the higher air flow in the conditioning rack damaged some of the films.

Rates of equilibrium WVT were determined at 25, 30, 35 and 40°C. WVP was calculated and expressed as $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$. At least four replicates were tested for each wax.

Activation energy. The activation energy for permeation, E_p, was obtained from the slope of a plot of log permeability *vs.* K^{-1}. Unless otherwise noted, E_p values reported for water vapor and oxygen permeation of waxes are means of four replicates.

Film thickness. A micrometer was used to measure film thickness, and reported values are means of five measurements.

Wax films used for the O_2P measurements were 0.04–0.05 mm (1.6–1.8 mil) thick, whereas wax films for the WVP measurements were 0.09–0.11 mm (3.5–4.5 mil), except for beeswax which was 0.04–0.05 mm (1.6–1.8 mil). Films for WVP measurements were generally thicker than those for O_2P measurements because WVP measurements required exposure of a larger film area (with correspondingly greater strength) than was required for the O_2P studies. Except for beeswax, wax films thinner than 0.09 mm (3.5 mil) often exhibited mechanical failure when tested in the Permatran.

RESULTS AND DISCUSSION

Melting properties of waxes. Melting curves—DSC—for the four waxes studied are shown in Figure 1. Terminal melting points (m.p.) and ΔH_t for the four waxes are shown in Table 1. The DSC curves and the values for m.p. and ΔH_t are similar to those reported by Flaherty (23) and Craig *et al.* (24).

Besides the major m.p. values listed in Table 1, all waxes underwent other solid-solid (s-s) transitions (Fig. 1). Beeswax had an s-s transition at 52°C and candelilla wax at 59°C. Carnauba wax exhibited two s-s transitions, one at 57°C and the other at 75°C. A possible s-s transition may have occurred in microcrystalline wax at 57°C, but this was difficult to ascertain because of the broad melting range of this wax.

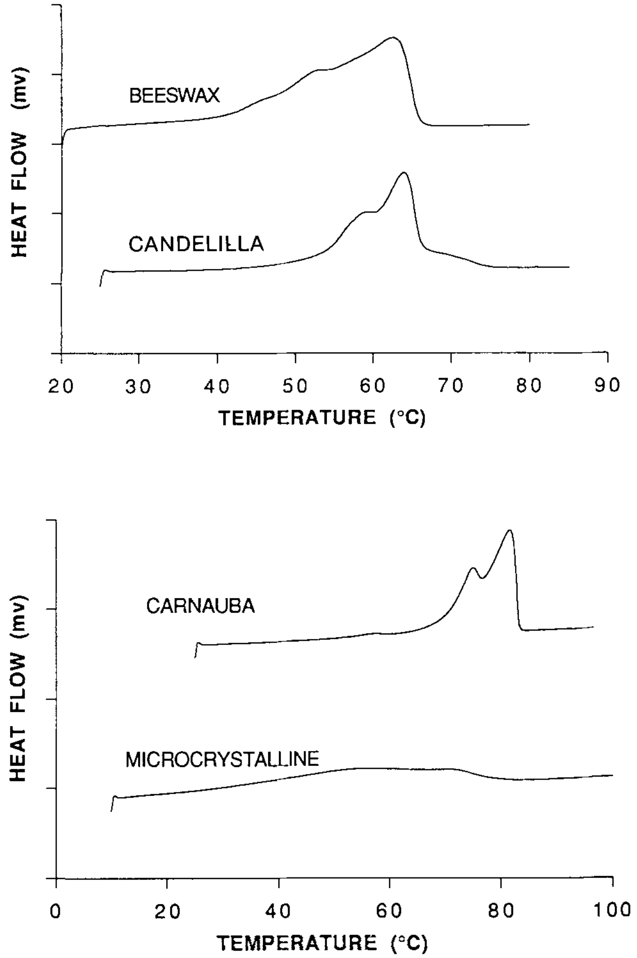

FIG. 1. Melting curves of waxes. Samples were 5–15 mg, the rate of heating was 8°C/min.

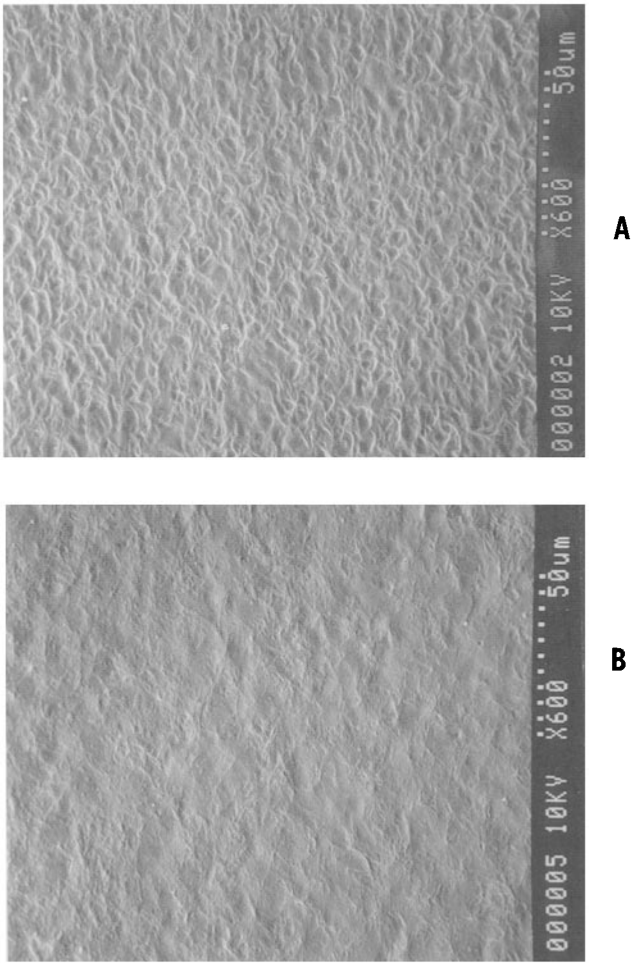

FIG. 2. Scanning electron microscopy micrographs of (A) beeswax and (B) candelilla wax. Micrographs were taken at a 45° angle to the film surface. Distance between first and last white dot is 50 μm.

TABLE 1

Terminal Melting Points and Enthalpies of Melting for Waxes

Wax	Melting point (°C)[a]	ΔH_t (J/g)[b]
Beeswax	62.0 ± 0.1	158 ± 5
Candelilla	64.0 ± 0.1	144 ± 3
Carnauba	81.7 ± 0.3	196 ± 4
Microcrystalline	71.7 ± 0.7	145 ± 1

[a] Terminal melting point is the temperature at which the last of the solid phase melts. Means of three trials ± 95% confidence interval. [b] Enthalpy of melting (ΔH_t). Means of three trials ± 95% confidence interval.

Microscopic appearance of waxes. SEM micrographs of the surface of the wax films are shown in Figures 2 and 3.

The surface appearance of beeswax (Fig. 2A) is consistent with that reported by other investigators (1,14). Penetrating imperfections on the beeswax film surface were not evident. Candelilla wax (Fig. 2B) had a surface appearance intermediate between that of beeswax and microcrystalline wax (Fig. 3B), and penetrating imperfections were not evident.

Carnauba wax (Fig. 3A) had a somewhat "hilly" appearance with some small pores that disrupted the otherwise smooth contours. It is unlikely, however, that these pores penetrated the entire thickness of the wax film because this film possessed excellent barrier properties to water vapor and oxygen. Microcrystalline wax had a fine-textured appearance with no evidence of imperfections (Fig. 3B).

XRD properties of waxes. XRD scans of the four wax films are shown in Figure 4. All wax films displayed peaks at 21.5-21.6 and 23.8-23.9°2Θ, corresponding to d spacings of 4.13-4.14 Å and 3.72-3.73 Å, respectively. Thus, all waxes were partially crystalline, and the d spacings of 3.7-3.8 Å and 4.1-4.2 Å are characteristic of orthorhombic subcell packing in lipids (25,26). The peaks at 3.73 Å and 4.13 Å are known to represent short spacings, indicating side-by-side orientation of hydrocarbon chains. Long spacings, indicative of end-to-end packing, were not found in any of the waxes used in this study.

Kreger (27) found d spacings of 4.01 Å (intensity very strong) and 3.53 Å (intensity strong) for carnauba wax. The discrepancies in short spacings may have arisen because Kreger used natural wax samples, whereas the

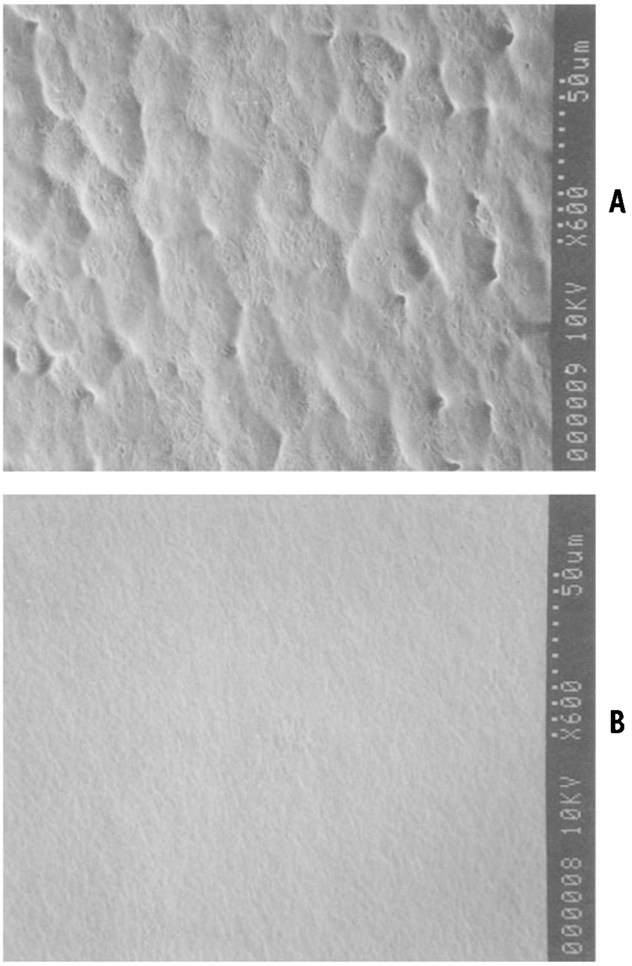

FIG. 3. Scanning electron microscopy micrographs of (A) carnauba wax and (B) microcrystalline wax. Micrographs were taken at a 45° angle to the film surface. Distance between the first and last white dot is 50 μm.

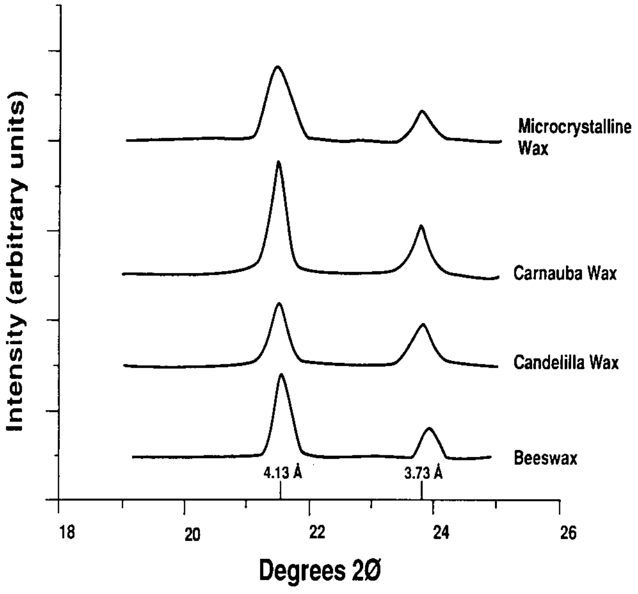

FIG. 4. X-ray diffraction patterns of waxes formed as films.

samples used here were commercially processed. Processing may have altered the crystalline properties of the natural wax.

Carnauba and candelilla waxes have previously been described as amorphous (21,28); however, substantiating data were not provided.

XRD scans of the four waxes were examined, and differences in relative intensity ratios (RI) of the peaks were observed. RIs were examined because several investigators have used these values to assess alterations in crystalline structure of waxes and fibers (26,29,30). RIs of XRD peaks (3.73 Å/4.13 Å) for waxes rapidly cooled as films, and for those slowly cooled in molds are reported in Table 2. To provide a standard of comparison, a sample of paraffin wax, known to crystallize in the orthorhombic crystal system, was examined by XRD. Its RI was 0.63, and this is consistent with the value reported by Edwards (26). Kreger (27) reported that the crystalline spacings of candelilla wax and paraffin wax are similar.

Among the waxes cast as films (rapidly cooled), candelilla wax had the largest RI, 0.65, which is almost identical to that for paraffin, mentioned above. For all waxes except candelilla, the RIs of slowly cooled samples were larger than those of rapidly cooled samples.

These differences in RI may relate to whether or not hexagonal crystals are present. Wax samples exhibiting a single peak, corresponding to short spacings of 4.12–4.20 Å, are known to contain hexagonal crystals (25). Thus, if hexagonal crystals were present in a sample containing orthorhombic crystals, the 4.14 Å peak would be enlarged, and the RI value would be smaller (26). Slow cooling, with the exception of candelilla wax, would appear to favor an increase in orthorhombic crystals.

O_2P: wax films. The O_2P at 25°C, and activation energies for permeation of oxygen through the wax films, are listed in Table 3. Carnauba and candelilla waxes had the smallest permeabilities. The O_2P for beeswax and microcrystalline waxes were about 6–9 times greater than those of candelilla and carnauba waxes. Carnauba and candelilla waxes also displayed lower activation energies than the other two waxes.

Kester and Fennema (13) reported an oxygen permeance of 6.10×10^{-10} m•s^{-1} for beeswax embedded in Whatman-50 filters (calculated from resistance data). This is significantly less than the value of 2.7×10^{-8} m•s^{-1}

TABLE 2

X-ray Diffraction Properties of Waxes

	Relative intensities (3.74Å/4.13Å)[a]	
Wax	Film (cooled rapidly)[b]	Molded (cooled slowly)[c]
Beeswax	0.34	0.58
Candelilla	0.65	0.36
Carnauba	0.41	0.53
Microcrystalline	0.37	0.45

[a] d-Spacing (Å).
[b] Standard film. Wax solidified almost immediately upon application to the hydrocolloid film.
[c] Molded samples were made by pouring molten wax into aluminum molds (36 mm × 36 mm × 1 mm), placing them in oven at 100°C, turning off the oven and allowing cooling to occur. This resulted in a cooling rate of about 0.4°C/min.

TABLE 3

Oxygen Permeabilities (25°C) and Activation Energies for Permeation of Oxygen Through Wax Films

Wax[a]	Oxygen permeability[b] (g[m•s•Pa]$^{-1}$ × 10^{-14})	Activation energy[b] (kJ•mol^{-1})
Beeswax	1.54 ± 0.08	48 ± 3
Candelilla	0.29 ± 0.05	40 ± 3
Carnauba	0.26 ± 0.07	30 ± 5
Microcrystalline	2.54 ± 0.31	51 ± 6

[a] Films were 0.04–0.05 mm (1.6–1.8 mil) thick.

[b] Values are means of four trials ± 95% confidence interval.

obtained for oxygen permeance through beeswax films (calculated from O_2P data in Table 3). This difference is likely traceable to properties of the Whatman-50 filter paper. When examined by SEM (data not shown), this filter paper consists of rather dense cellulose fibers. By soaking the filter paper in molten beeswax, intervening spaces are effectively filled (data not shown), leaving no obvious open channels. Because the cellulose fibers themselves may be better barriers to oxygen (based on the properties of cellophane; Table 4) than pure beeswax, it is reasonable that the intermingled combination of beeswax and Whatman-50 filter paper would resist migration of oxygen more effectively than beeswax alone.

O_2P values for carnauba, candelilla and microcrystalline waxes were not found in the literature.

Differences in the O_2P of the waxes can be attributed to several factors. In particular, these waxes differed in chemical composition and crystalline habit, and these attributes probably had an important influence on their oxygen barrier properties. It is apparent, however, that neither chemical composition, through its effect on melting point, nor RI, as it reflects crystal habit, is a reliable predictor of permeability of the films to oxygen.

Microcrystalline wax contains some distillate oil, causing this wax to have a less rigid structure than any of the other waxes. Because fluid lipids are more permeable to gasses than are solid lipids (13,31), this may explain, in part, the greater permeability of microcrystalline wax to oxygen.

TABLE 4

Oxygen Permeabilities of Edible and Nonedible Films

Film	Temperature (°C)	Oxygen permeability (g[m•s•Pa]$^{-1}$ × 10^{-14})
Candelilla wax[a]	25	0.29
Carnauba wax[a]	25	0.26
Beeswax[a]	25	1.54
Microcrystalline wax[a]	25	2.54
Starch (41)	24	21.7
Polyethylene, low-density (42)	25	4.56
Amylomaize (11)	25	2.45
Acetostearin (43)	26	2.25
Polyethylene, high-density (42)	25	0.76
Shellac (44)[b]	30	0.09–0.26
Polyethylene terephthalate (polyester) (43)	25	0.03
Saran (43)	25	0.005
Cellophane (11)	25	0.004

[a] Films from this study, Table 3.

[b] Shellac films were supported on a copolymer film of low-density polyethylene-vinyl acetate.

Similarly, beeswax contains a small amount of unsaturated hydrocarbons, and these hydrocarbons are responsible for its flexibility (16). This hydrocarbon fraction would tend to facilitate diffusion of oxygen through the film. In polymers, chain stiffness (corresponding to a lack of low-melting point components in lipids) is a prerequisite for good barrier properties (32).

Both candelilla and carnauba waxes are less pliable than either beeswax or microcrystalline wax. It is likely that the hardness (lack of low-melting point components) of these waxes enhances their resistance to gas transmission.

It is also interesting to compare the SEM (Figs. 2 and 3) and XRD patterns of the wax films (Fig. 4) to their barrier properties to oxygen. Microcrystalline wax, as the name suggests, contains microscopic-sized crystals. These small crystals (Fig. 3B) may present numerous intercrystalline paths for permeation of O_2 molecules. Microcrystalline wax also exhibited broader diffraction peaks, especially at 4.13 Å, than those of the other waxes. Broadening of a diffraction peak may result from irregular crystal sizes and lattice distortions (33), both of which could lead to numerous intercrystalline paths for permeation.

Permeability of lipids also may be influenced by whether they crystallize in the hexagonal system or in the denser orthorhombic system. The difference in molecular volume between the two crystal lattices is approximately 1.5 Å^3 per CH_2 group (34). Considering that many wax hydrocarbons are more than 30 carbons in length, this could be important. Because of their increased volume, the hexagonally-packed molecules possess more rotational freedom than those in an orthorhombic orientation (34). Thus waxes that crystallize in the orthorhombic system are much harder and less deformable than those that crystallize in the hexagonal system (26,28). Both characteristics would tend to decrease O_2P.

The influence of crystal structure on intracrystalline migration of gasses is of little interest because crystals are considered to be impermeable to gases (32).

An estimate of the crystalline content of waxes in this study, whether orthorhombic, or a mixture of orthorhombic and hexagonal, can be determined from the diffraction scans in Figure 4, and the derived RI values in Table 2. As RI values decrease from 0.65 (all crystals believed to be orthorhombic), increasing amounts of hexagonal crystals are believed to be present. Thus, crystals in films of candelilla wax (RI of 0.65) would be orthorhombic, and this is consistent with its excellent resistance to O_2P. The predominance of orthorhombic crystals in candelilla wax would not only result in denser packing of hydrocarbon chains than would be the case with hexagonal crystals, but would also decrease the prevalence of intercrystalline pathways that would probably result from the presence of two competing crystal systems. Both conditions would tend to reduce O_2P. The fact that candelilla wax had an RI value that was, by far, the largest of the group suggests that orthorhombic crystals were the predominant type present and that this physical attribute was a dominating determinant of this wax's low permeability to oxygen.

Films of beeswax and microcrystalline wax had the smallest RIs (0.37 and 0.34, respectively) of the waxes tested, and they were also the most permeable to oxygen. Again, this is consistent with the supposition that these waxes contained crystals in both the hexagonal and orthorhombic systems, a condition previously observed in waxes by Edwards (26).

Carnauba exhibited an RI value (Table 2) much smaller than that of candelilla and similar to those of beeswax and microcrystalline wax. On this basis, one might predict carnauba to exhibit a permeability to oxygen that was similar to those of beeswax and microcrystalline wax. Yet, its permeability to oxygen was excellent, almost identical to that of candelilla. Here, it would seem, the rigid nature (lack of molecular mobility), as reflected by its high terminal melting point and lack of a low-melting fraction (Fig. 1), had a dominating influence on permeability to oxygen.

The O_2Ps of the four test waxes and the permeabilities of other edible and nonedible films are listed in Table 4. The oxygen barrier properties of the edible waxes are superior to those of low-density polyethylene but inferior to those of polyethylene terephthalate, saran and cellophane.

WVP. The WVP of the wax films are listed in Table 5. Candelilla wax displayed the smallest WVP of the waxes tested. The low concentration of polar compounds and the large concentration of alkanes in this wax are likely responsible for its excellent water vapor barrier properties.

Of the four waxes tested, beeswax displayed the greatest permeability to water vapor. This is probably attributable to the larger concentration of fatty acids, fatty alcohols and esters in this wax than in the other three.

Even though microcrystalline wax contains a significant amount of distillate oil, its WVP is still less than that of beeswax. This is probably due to the absence of polar lipids.

Other WVP data for the waxes in Table 5 were not found in the literature. However, several investigators have reported that coatings made from these waxes possess good barrier properties to water vapor (2,35).

TABLE 5

Water Vapor Permeabilities (25°C) and Activation Energies for Permeation of Water Vapor Through Wax Films

Wax[a]	Water vapor permeability ($(g[m \cdot s \cdot Pa]^{-1} \times 10^{-13})$)	Activation energy[b] ($kJ \cdot mol^{-1}$)
Beeswax	5.81 ± 0.26	29 ± 3
Candelilla	1.76 ± 0.24	17 ± 6
Carnauba	3.30 ± 0.57	21 ± 4
Microcrystalline	3.38 ± 0.66	29 ± 7

[a] Films were 0.09–0.11 mm (3.5–4.5 mil) thick.

[b] Permeability and activation energy values are means of four replicates (except for the activation energies of candelilla and carnauba waxes which are means of three replicates) ± 95% confidence interval.

For the same reasons mentioned in the section on O_2P, it is likely that the crystalline order of these waxes, either hexagonal or orthorhombic, had an influence on their barrier properties to water vapor. However, these waxes, with the exception of microcrystalline wax, contained constituents that are sufficiently hydrophilic to interact with water vapor and thereby exert a significant influence on WVP of the films (36). This factor, which was not operative with respect to O_2P, along with the factor of film rigidity (lack of molecular mobility), appears to be more important than crystal habit.

Listed in Table 6 are the WVPs of waxes tested in this study, as well as values for other edible and nonedible films. WVPs of the four waxes studied here compare favorably with WVPs of many synthetic films that are commonly used for food packaging.

Temperature dependence of permeability. The temperature dependence of gas and vapor permeability through synthetic films has been studied for many years (37,38) and this relationship often conforms to the Arrhenius equation. Lipids also have been found to display this exponential relationship between temperature and permeability (13,14,39,40). Activation energies (E_p) for oxygen and water vapor permeation through various waxes

TABLE 6

Water Vapor Permeabilities of Edible and Nonedible Films

Film	Temperature (°C)	RH gradient (%)	Permeability ($(g[m \cdot s \cdot Pa]^{-1} \times 10^{-12})$)
Candelilla wax[a]	25	100-0	0.18
Carnauba wax[a]	25	100-0	0.33
Microcrystalline wax[a]	25	100-0	0.34
Beeswax[a]	25	100-0	0.58
Acetylated monoglycerides (45)	25	100-0	23.2–62.1
Chocolate (46)	20	81-0	12.3
Shellac (11)	30	100-0	4.63–6.61
Polyethylene terephthalate (polyester) (43)	37.8	95-0	0.6–1.1
Polypropylene (43)	37.8	95-0	0.2–0.3
Paraffin wax (45)	25	100-0	0.22
Polyethylene, high density (47)	37.8	91-0	0.11
Saran (43)	37.8	95-0	0.1–0.4

[a] Films from this study, Table 5. RH, relative humidity.

are listed in Tables 3 and 5, respectively. In all instances, regression equations for the slopes of log permeability *vs.* inverse temperature (°K) gave correlation coefficients (r) of at least 0.99. Tests were, of course, performed at temperatures below that at which major phase transitions would occur.

The E_p for oxygen through beeswax-Whatman-50 reported by Kester and Fennema (13), 62.7 kJ/mol, is greater than the value of 48 kJ/mol that was obtained for pure beeswax (Table 3). The presence of filter paper in the Kester–Fennema sample is the likely cause of this difference. Kester and Fennema (14) reported a smaller E_p (9.6 kJ/mol) for water vapor transmission through a beeswax-Whatman 50 filter than the value of 29 kJ/mol that was obtained here for pure beeswax. The polar filter paper exhibits a negative E_p when in contact with water vapor, thereby decreasing the overall E_p of the composite film (14).

The WVP and O_2P of beeswax and microcrystalline wax were more dependent on temperature than those of candelilla and carnauba waxes (Tables 3 and 5). The larger E_p values of beeswax and microcrystalline wax are likely attributable to the larger amount of low-melting components of these waxes (see Fig. 1). As temperature increases, the liquid fraction will increase to a greater degree in these waxes than in candelilla and carnauba waxes, and this, in turn, will favor increased gas transport.

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