Resistance of Lipid Films to Oxygen Transmission

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Various lipids, mounted on a polar filter paper matrix, were evaluated as barriers to O_2 transmission. Among those lipids tested, stearyl alcohol was most resistant to oxygen transmission, the most likely reason being its ability to crystallize as compactly overlapping platelets with their planes normal to the direction of O_2 diffusion. Tristearin, beeswax, and acetylated monoglycerides were, respectively, 39, 43 and 61% less resistant to O_2 transmission than the fatty alcohol. Activation energies of O_2 transport were 7.0, 7.5, 15.0 and 27.5 kcal/mole, respectively, for stearyl alcohol, tristearin, beeswax, and acetylated monoglycerides. Stearic acid was substantially less resistant to O_2 flux than the above four lipids. In addition, the fatty acid was unique among the lipids tested in its temperature dependence, i.e., resistance to O_2 transmission increased with elevation of temperature yielding a negative activation energy of −17.2 kcal/mole. This was attributed to the presence of small interplatelet channels in the stearic acid film, which presumably act as the principal route for gas transport. Hexatriacontane displayed poor O_2 barrier properties compared to the other lipids, a consequence of relatively large pores in the alkane film.

Lipid coatings have historically been used to enrobe confectionery products, fresh fruits, and fresh vegetables to retard moisture exchange (gain or loss) with the surrounding environment. Lipids are also utilized, in conjunction with high-molecular weight polymers, for microencapsulation of food materials that are sensitive to changes in moisture content (1, 2). The oxygen-barrier characteristics of lipid materials are also of considerable importance when lipid-based films are used to encapsulate food components that are susceptible to oxidation. Furthermore, thin lipid coatings, when applied to the surface of fresh fruits and vegetables, will limit O_2 influx and retard desiccation. These coatings can suppress the rate of aerobic respiration, and, if this is done to an appropriate degree, post-harvest storage life can be extended (3).

Blank (4-6) studied the influence of the chemical nature of lipids on O_2 transport through compressed lipid monolayers which had been formed on a water surface. The monolayers most resistant to O_2 transmission were formed from saturated, straight-chain, fatty acids, fatty alcohols, and esters containing 16 carbons or more. Increased oxygen permeability was observed as the degree of unsaturation or branching of the hydrocarbon chain was increased, or chain length was decreased. These results are attributable to a reduction in van der Waals' interactions between adjacent acyl chains, resulting in greater chain mobility and molecular expansion at the air/water interface (7,8), both effects facilitating gas transport across lipid monolayers.

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Successful employment of lipids in protective, edible films is hindered by a lack of fundamental knowledge concerning the relationship of lipid solid-state structure to gas and vapor barrier properties. Hence, the objective of this investigation was to evaluate the resistance of various lipids to O_2 transport and to assess the dependence of their barrier properties on solid-state morphological characteristics, as revealed by scanning electron microscopy.

MATERIALS AND METHODS

Tristearin, stearyl alcohol, and stearic acid, were obtained from Sigma Chemical Company, St. Louis, MO. The hexatriacontane and white beeswax were obtained from Aldrich Chemical Company, Milwaukee, WI, and acetylated monoglycerides (Myvacet 5-07; distilled acetylated monoglycerides from hydrogenated cottonseed oil, 48.5%-51.5% acetylation) from Eastman Chemical Products, Kingsport, TN. Purities of these substances, as indicated by the suppliers, are listed in Table 1.

Film fabrication. Lipid films were formed on Whatman No. 50 (W50) filter paper (9,10). A filler paper support was needed to assist in the formation of lipid films that were acceptably free of structural defects and to enable these films to be handled without breakage. Uncoated W50 filter displayed very low resistance to O_2 transmission. Other supporting matrices considered were glass-fiber filters, mixed-cellulose ester filters, and ethylcellulose films. These were rejected either because of inadequate strength (making it difficult to apply a continuous and uniform lipid coating) or because they displayed inconsistent rates of O_2 transmission. A consistent value for O_2 transmission through the supporting matrix was, of course, a prerequisite for accurate interpretation of transmission rates through lipid-coated matrices.

The use of hydrophilic W50 filter paper as the support for lipids in this study approximates the formulation necessary in many lipid-based, edible films, i.e., lipids often are used in combination with a polar hydrocolloid (11-14). Inclusion of a high-molecular weight polymer in the film formulation is required to achieve adequate film-forming properties and to yield lipid-based films with appropriate durability and integrity (15).

Lipid application to W50 filters was accomplished by immersing a 9 cm-diameter filter paper disc in molten lipid (100°C) until saturation was achieved, suspending the lipid-saturated filter paper in a vertical position and allowing it to drain overnight at 100°C, and then cooling it to room temperature (25°C). The immersion-draining procedure resulted in approximately 3 mg of lipid per 1 cm^2 of filter area. An additional 1 mg lipid/cm^2 was applied as a surface coating. This was done by affixing the lipid-saturated filter paper flush on the surface of a glass plate and then applying 0.5 ml of molten lipid (100°C) in a thin line adjacent

TABLE 1

Properties of Lipid Materials Studied for Resistance to O_2 Transmission.

Lipid	Reported purity (%)[a]	Reported melting point or range (°C)	Reported iodine value	Measured X-ray short spacings[b] (A)	Polymorphic form	Crystal system (subcell)
Tristearin	90	54.9[d]	0	4.13(vs)	∝	Hexagonal
Stearyl alcohol	99	57.9[d]	0	3.65(s),4.12(vs),4.32(m)	β′	Common orthorhombic
Stearic acid	90	69.6[d]	0	3.70(s),4.13(vs),4.34(m),4.67(w)	C	Common orthorhombic
Hexatriacontane	98	76.2[d]	0	3.73(s),4.12(vs)	β′	Common orthorhombic
Acetylated monoglyceride[c]		41-46[e]	5[e]	4.10(vs)	∝	Hexagonal
Beeswax (white)	commercial	62-64[f]	8-11[f]	3.73(s),4.14(vs)	—	Common orthorhombic

[a]Supplier designation.
[b]Intensity scale: vs=very strong, s=strong, m=medium, w=weak.
[c]Distilled acetylated monoglycerides from hydrogenated cottonseed oil, 48.5-51.5% acetylation.
[d]Ref. 49.
[e]Ref. 17.
[f]Ref. 54.

to the filter disc. The molten lipid was immediately spread uniformly over the surface with a preheated (150°C) thin layer chromatography spreader to yield a finished lipid-W50 composite film. Total lipid content per unit film area, as determined by weighing filter discs before and after lipid application, was 4.0 ± 0.2 mg/cm² ($\bar{X}$ ± SD). Approximately 75% of the total lipid was embedded within the filter paper matrix and 25% was on the surface. Thickness of lipid-W50 films was 0.11-0.12 mm.

X-ray diffraction. Lipids were scraped off W50 filter supports for analysis by x-ray diffraction. Nickel-filtered copper K_α radiation (λ=1.5418 A) was generated by a Norelco x-ray powder diffractometer (Phillips Electronic Instruments, Mt. Vernon, NY). An accelerating voltage of 40 kv and a current of 30 mamp were used. A diffracted angle range of 15-28 °2θ was scanned at a rate of 1 °2θ/min.

Scanning electron microscopy (SEM). Uncoated W50 filter paper and the lipid surface of lipid-W50 composite films were examined by SEM utilizing a JEOL JSM-35C electron microscope. The samples to be examined were mounted onto aluminum stubs and coated with gold-palladium alloy (15 nm), using a Balzers Union SCD 030 sputter coater. The samples were observed using an accelerating voltage of 10 kv and with the electron beam directed either normal to the surface or at a 45° angle.

Measurement of O_2 transmission rate. An Oxtran Model 100 Oxygen Permeability Tester (Modern Controls, Inc., Minneapolis, MN) was utilized to measure O_2 transmission rates (O_2TR) through W50 filters and lipid-W50 films according to method D3985 of the American Society for Testing and Materials (16). Units of O_2TR are g $O_2 \cdot m^{-2} \cdot sec^{-1}$. The Oxtran instrument was calibrated using a polyester film (Standard Reference Material #1470) obtained from the National Bureau of Standards (Washington, D.C.). Lipid-W50 films were inserted into the Oxtran diffusion cell with the lipid surface exposed to oxygen; either pure O_2, air (20.95% O_2) or a 1% O_2 — 99% N_2 mixture depending on the barrier properties of the film.

The area of the film exposed to O_2 was controlled by means of stainless steel masks with openings of various sizes. The area exposed to O_2 was smaller for films that were highly permeable than it was for films that were slightly permeable. O_2TR was determined at 25, 30, 35, and 40°C, all at 0% relative humidity. At least four replicates of each film type were evaluated for O_2TR.

At temperatures above 25°C, all lipids were examined by x-ray diffraction both before and after determination of O_2Tr to confirm the absence of polymorphic transitions at the new temperature. Tristearin and acetylated monoglyceride were not evaluated at 40°C because a polymorphic transition was observed in the former, and the latter was too close to its melting range of 41-46°C (17).

Calculation of resistance to O_2 transmission. To compare the O_2 barrier properties of the different lipids, we chose to express O_2 transport in terms of resistance. Resistances of uncoated W50 and lipid-W50 films to O_2 transmission were calculated from the following equation:

$$r(O_2) = [\Delta c/O_2TR] = sec \cdot m^{-1} \quad [2]$$

where Δc is the driving force for gas transport expressed in terms of a concentration gradient across the film (g $O_2 \cdot m^{-3}$), O_2TR is the steady-state gas transmission rate (g $O_2 \cdot m^{-2} \cdot sec^{-1}$), and $r(O_2)$ is the film resistance in units of $sec \cdot m^{-1}$. The above equation defining resistance is simply a rearranged form of the general equation characterizing all molecular transport processes, i.e., the rate of transfer is equal to the driving force divided by the resistance (18). This equation is often used in the literature to express gas and vapor-barrier properties of lipid monolayers (6, 19-22), cuticular membranes of plant tissue (23-27), and wax coatings applied to fresh fruit (28).

The relationship of $r(O_2)$ to the diffusion constant (D) and solubility coefficient (S) of O_2 in the film can be evaluated from Fick's first law equation (29). This equation states that gas flux is proportional to D and the gas concentration gradient in the direction of flow:

$$O_2TR = -D(dc/dx)$$

Under conditions of steady-state gas flux, integration of Fick's equation, and application of Henry's solubility law—which states that concentration is the product of solubility and pressure (29)—yields the following equation:

$$O_2TR = D \bullet S\,(\Delta p/\Delta x)$$

where Δp is the O_2 partial pressure differential across the film and Δx is film thickness. O_2TR is directly proportional to D and S, hence from the equation defining resistance, $r(O_2)$ is inversely related to the same parameters.

The Student's t-distribution was used to compute 99% confidence intervals for $r(O_2)$, and to evaluate the statistical significance ($P \leqslant 0.05$) between calculated activation energies for O_2 transport (30).

RESULTS AND DISCUSSION

The properties of the six lipid materials studied are presented in Table 1. Tristearin, stearyl alcohol, stearic acid, and hexatriacontane were chosen to represent the triacylglycerol, fatty alcohol, fatty acid, and alkane classes of lipid molecules, respectively. An alkane with 36 carbons was selected instead of the 18-carbon homologue (octadecane, mp=28°C) because its melting point is similar to those of the other three lipid types. In the solid-state, tristearin, stearyl alcohol, and stearic acid all exist in structures with 36-carbon chain lengths. Tristearin crystallizes in a double chain-length modified tuning fork, or chair conformation, with fatty acids in positions #1 and #3 pointing opposite to the fatty acid chain in position #2 (31). Both stearyl alcohol and stearic acid form hydrogen-bonded dimers in the crystalline state. Existence as dimers is, in fact, the reason why the 18-carbon fatty alcohol and acid have much higher melting points than that of octadecane.

Tristearin solidified from the melt in its lowest-melting, least-stable alpha (α) polymorphic form. This crystalline state was determined from the single, strong x-ray diffraction short-spacing at 4.13 A (Table 1). In this form, the fatty acid hydrocarbon chains are vertically oriented with respect to the end group planes, and molecular packing is in accord with the hexagonal system (32). The acyl chains possess a certain degree of molecular freedom, which has been described by Larsson (33) as torsional oscillation.

The x-ray short-spacing patterns of stearyl alcohol, stearic acid, and hexatriacontane (Table 1) match previously published patterns for their most stable polymorphic states (34–36). In each case, the hydrocarbon chains are tilted with respect to the methyl end-group planes, and the lateral chain packing is of the common orthorhombic type.

The two additional lipids investigated were distilled acetylated monoglyceride (acetyl MG) and white beeswax. Acetyl MG has been studied extensively for use as an edible coating (37–39). This material solidified in the lowest-melting α polymorphic state with hexagonal chain packing (Table 1). The α form of acetyl MG is unusually stable and possesses a high degree of flexibility.

Solidified beeswax displayed a pair of strong diffraction spacings at 3.73 and 4.14 A (Table 1), indicative of an orthorhombic cross-sectional arrangement of hydrocarbon chains.

Scanning electron microscopy. Structural morphology of the surfaces of uncoated W50 and lipid-W50 films were examined with SEM. Micrographs of the various films are shown in Figure 1 A-H. Uncoated W50 has a porous structure in which individual fibers and relatively large pores are evident (Fig. 1A).

The tristearin-W50 film has a dimpled surface (Fig. 1B). Similar surface appearances have been observed in this laboratory for other triacylglycerols, including tripalmitin and fully-hydrogenated vegetable oils. Examination at higher magnification confirmed that the indentations do not extend down to the underlying W50 support. Small discrete crystals are evident on the surface of the tristearin-W50 film. The number and size of protruding surface crystals increased with the time of storage spent at room temperature. Similar behavior was observed with tripalmitin and fully-hydrogenated vegetable oils when they were solidified in the lowest-melting, least-stable, α polymorphic form. We assume the projecting surface crystals are indicative of an incipient polymorphic transition to a higher-melting, more stable crystalline form. Pertinent to this assumption, is the observation of several investigators that chocolate bloom, caused by crystalline transformation of cocoa butter from the desired polymorphic form V to the more stable form VI, is associated with the appearance of fat crystals protruding from the surface (40–43).

The stearyl alcohol film (Fig. 1C) has a morphology characterized by layers of crystalline platelets, 1 μm or less in thickness, extending out of the bulk lipid. The layered surface structure is very evident at higher magnification (Fig. 1D). Platelet crystal growth is commonly observed for straight-chain lipids, such as fatty alcohols, fatty acids, and alkanes. In the solid-state, hydrocarbon chains of these molecular species are aligned with each other and arranged in sheets with strong van der Waals' interactions between laterally adjacent chains. At the methyl end-group planes the sheets of molecules are held together by much weaker end-group interactions, which tend to retard crystal growth in the direction of the chain axes (44, 45).

The platelet morphology of stearic acid is clearly evident in Fig. 1E. Although both stearyl alcohol and stearic acid give rise to crystalline platelets, obvious morphological differences exist between them. The stearic acid surface, in contrast to that of the fatty alcohol, is characterized by channels or void regions of varying sizes between the platelets. It is impossible to know how far these channels extend through the film, however, even if they do not traverse the entire film they reduce the effective thickness of the barrier layer.

Pores exist in the lipid surface of the hexatriacontane-W50 film (Fig. 1F). These pores, having diameters of approximately 10–20 μm, extend through the entire thickness of the lipid surface layer, exposing fibers of the underlying W50 filter support. Formation of the pores probably results from the extreme hydrophobicity of the 36-carbon alkane, making

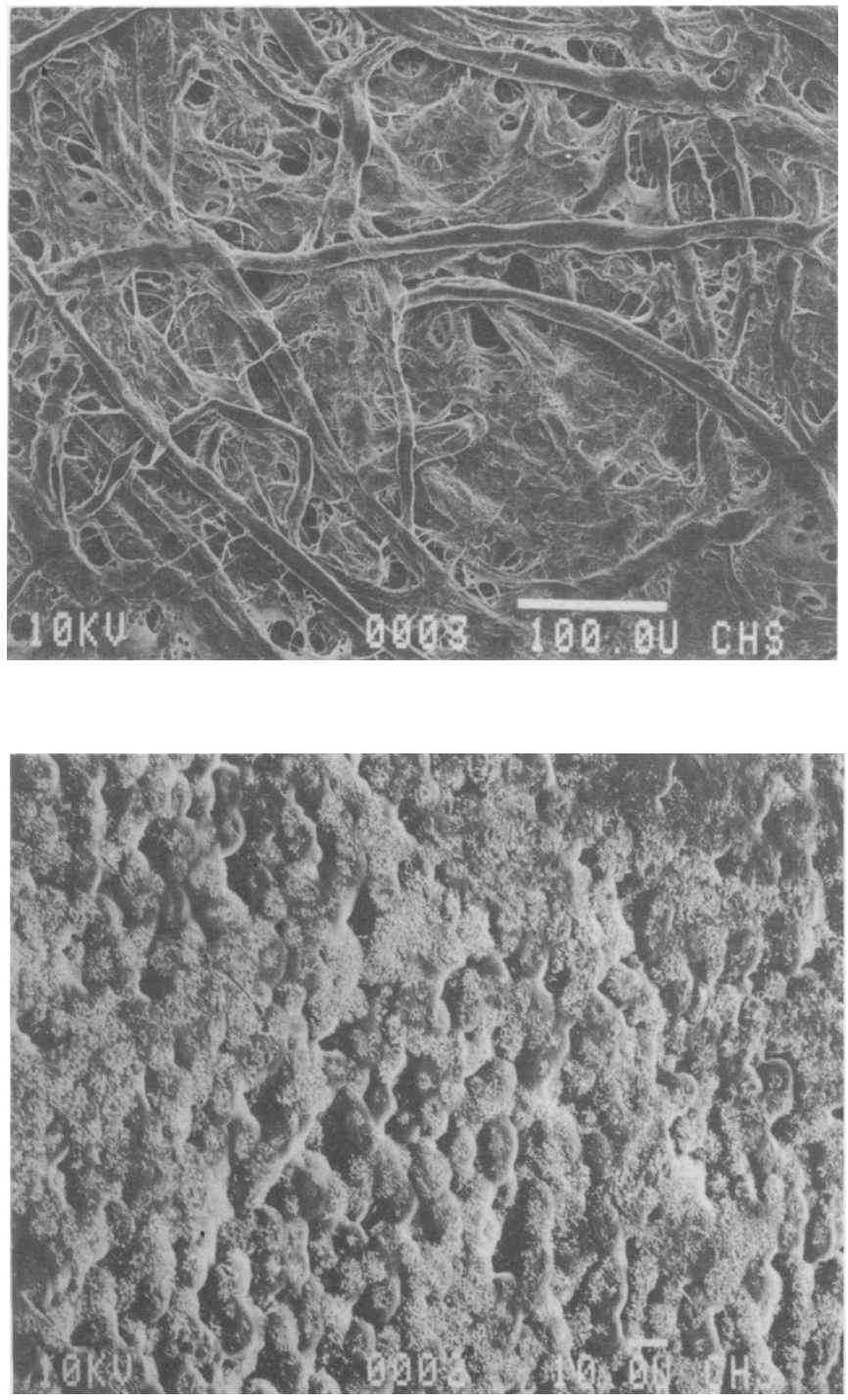

FIG. 1A & B (Continued).

it difficult to form a continuous layer on a polar surface.

The acetyl MG-W50 film has a relatively smooth surface without any well-defined morphological characteristics (Fig. 1G). Individual crystals are not evident at this magnification. Assuming that the outgrowth of crystals on the surface, as was observed with α-tristearin (Fig. 1B), is caused by incipient polymorphic transformation, the appearance of the acetyl MG surface is consistent with the fact that heterogeneous acetoglycerides are quite stable in the α form (37).

The surface appearance of beeswax-W50 films (Fig. 1H) is much like that of the acetyl MG films—

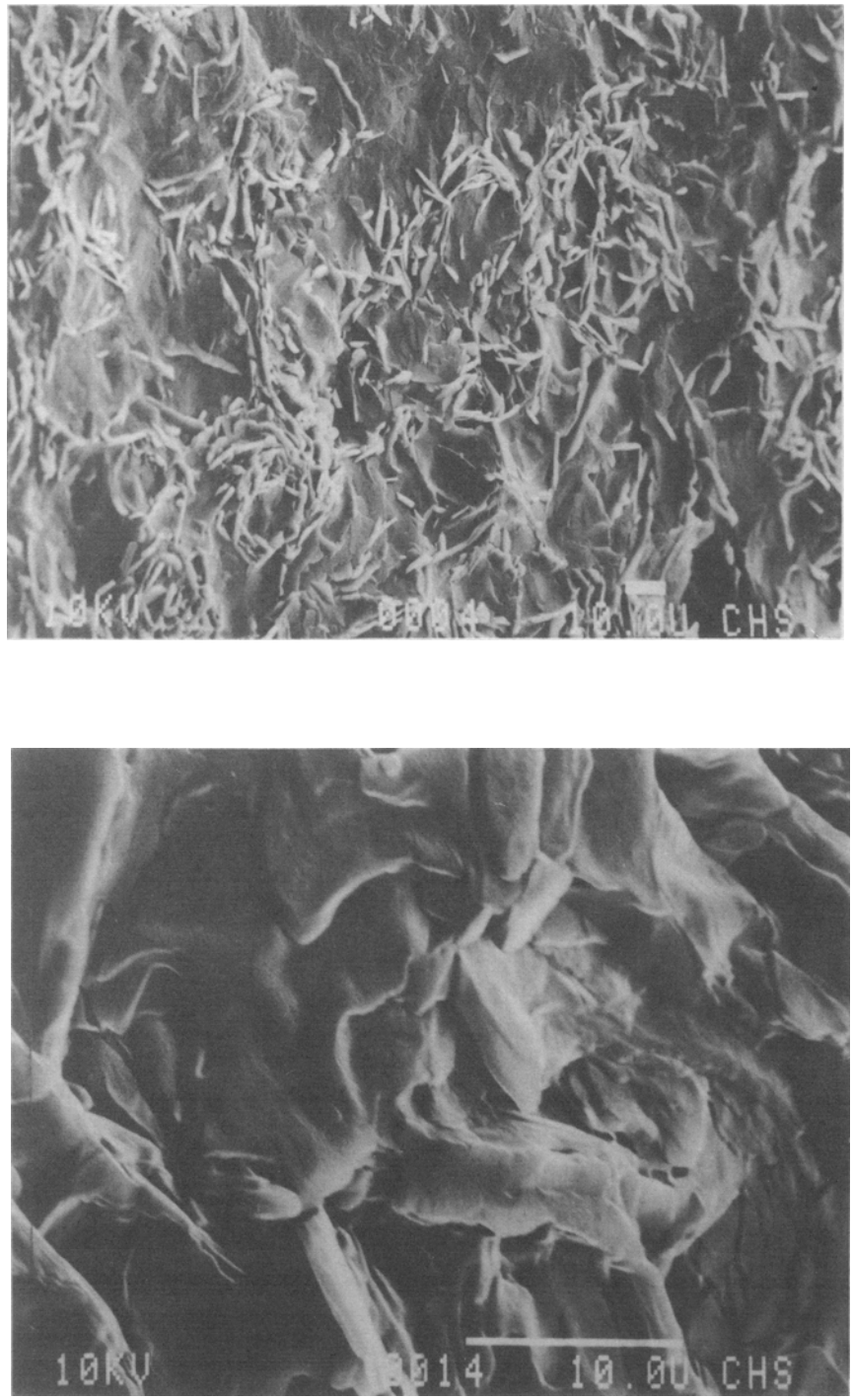

FIG. 1C & D (Continued).

relatively smooth and devoid of distinctive morphological features.

Oxygen barrier properties. The resistances of each film type to O_2 transmission [$r(O_2)$] at 25°C are listed in Table 2. Uncoated W50 had a very low $r(O_2)$ of 1.1 $\times$ 10^3 sec•m^{-1}. This was the desired and expected result.

The least resistant of the lipid-W50 films was hexatriacontane. This is undoubtedly attributable to the relatively large pores present in the lipid surface layer of the alkane film (Fig. 1F). Gas flux through films possessing pores, cracks, or other defects is generally orders of magnitude greater than that through intact films (46). Even though hexatriacontane films were substantially less resistant than the other lipids, $r(O_2)$ of the alkane film is still 300-fold greater than that of

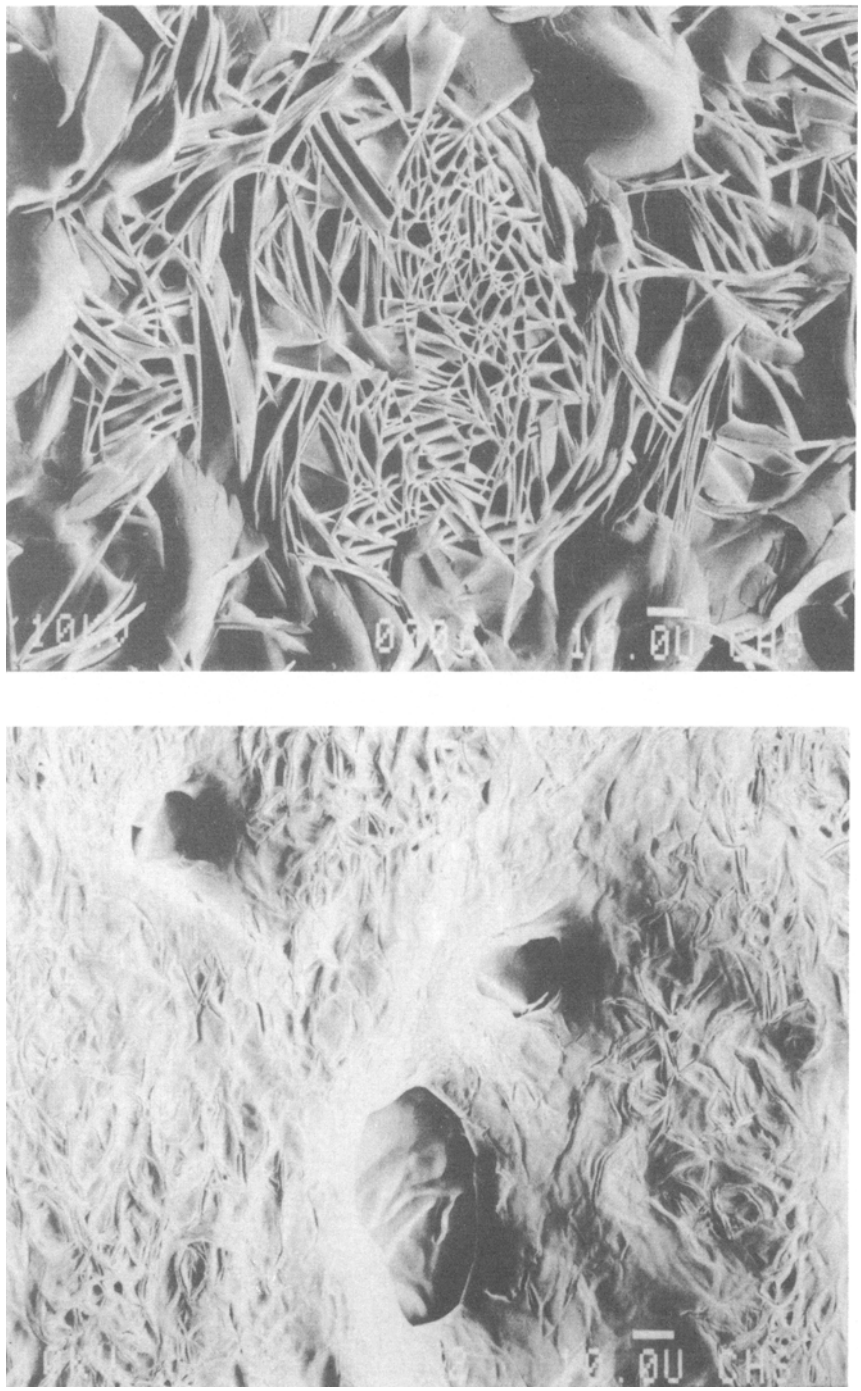

FIG. 1E & F (Continued).

uncoated W50. Thus, the lipid provides virtually 100% of the total resistance to O_2 flux of the lipid-W50 model system. Our inability to form a flawless layer of highly-hydrophobic hexatriacontane on a hydrophilic matrix suggests that film-matrix interactions may have an important influence on the barrier performance of fabricated edible films.

Stearic acid-W50 was 130-fold more resistant to O_2 transfer than the alkane. This suggests that the channels or void regions between platelets (Fig. 1E) do not traverse the entire depth of the fatty acid surface layer. Another possibility is that the channels may be sufficiently small and tortuous to offer substantial resistance to the flow of gases (18). Either explanation could account for the markedly greater $r(O_2)$ of the

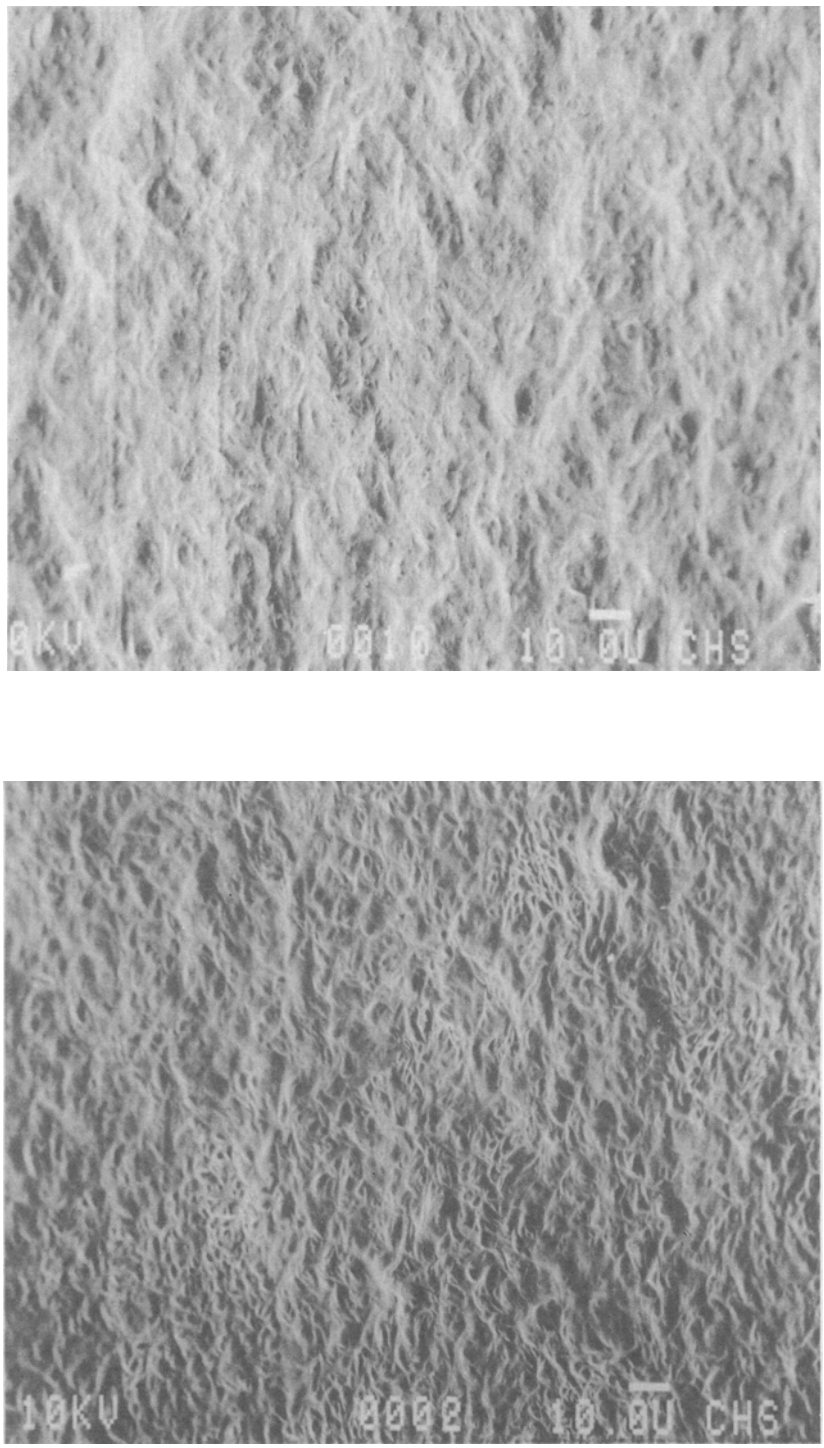

FIG. 1. Electron micrographs of uncoated Whatman 50 filter paper (W50) and various lipid-W50 films as viewed from the lipid side. Amount of lipid per unit area of filter paper was 4.0 ± 0.2 mg/cm^2 ($\bar{X}$ ± SD). Micrograph A was taken with the electron beam directed normal to the film surface; all others were taken at a 45° angle. The white bar is 100 μm in length in micrograph A and 10 μm in length in the remaining micrographs. A is uncoated W50 filter paper; B is tristearin-W50; C, D are stearyl alcohol-W50; E is stearic acid-W50; F is hexatriacontane-W50; G is acetylated monoglyceride-W50; and H is beeswax-W50.

fatty acid as compared to that of hexatriacontane.

The remaining lipid materials (acetyl MG, beeswax, tristearin, stearyl alcohol) did not possess, as determined by SEM, any obvious pores or other low-resistance routes for O_2 flux. Hence, the $r(O_2)$ values at 25°C were approximately 25, 38, 40, and 66-fold larger, respectively, than that of stearic acid (Table 2).

In the absence of pores, cracks, or other defects in the lipid layer, O_2 will migrate by molecular diffusion as driven by a concentration gradient (47). Resistance to O_2 transport is inversely related to D and S, the diffusion constant and solubility coefficient for O_2 in the film. Of the four lipid materials which displayed relatively high $r(O_2)$ values, acetyl MG has the lowest melting point (41-46°C) and consists of a blend of solid and fluid components at room temperature. It is likely that this results in significantly greater O_2 solubility compared to lipids which possess greater solid contents at room temperature. In addition, the greater mobility of the fluid hydrocarbon chains would also result in a larger O_2 diffusion constant. Both factors probably account for acetyl MG having a lower $r(O_2$ (111×10^7 sec•m^{-1}) than beeswax, tristearin, and stearyl alcohol. Lovegren and Feuge (39) studied gas permeability through acetylated monostearin films. Converting their data on O_2 permeability to $r(O_2)$ yields a value of 108×10^7 sec•m^{-1} at 22°C, a result very close to our value of 111×10^7 sec•m^{-1}.

The $r(O_2)$ values of tristearin and beeswax-W50 films were 174 and 164 $\times 10^7$ sec•m^{-1}, respectively, and did not differ significantly ($P \leq 0.05$). Stearyl alcohol films were the most resistant to O_2 transport, having a $r(O_2)$ of 286×10^7 sec•m^{-1} at 25°C. The heterogeneous composition of beeswax may account for its $r(O_2)$ being smaller than that of the fatty alcohol. Beeswax contains approximately 4% unsaturated hydrocarbons (48) and, as previously discussed, fluid acyl chains tend to accelerate gas flux through lipids.

Several possible reasons can be offered to explain why tristearin is less resistant to the passage of oxygen than stearyl alcohol. First, the hydrocarbon chains of the α polymorph of tristearin are packed in a hexagonal orientation, which is molecularly less dense than the orthorhombic lateral packing of stearyl alcohol. The mean cross-sectional surface area per hydrocarbon chain in the hexagonal packing mode is 20 A^2, compared to 18.8 A^2 in the orthorhombic lattice (49). A second factor, which is probably related to the first point, is that hexagonally-packed polymethylene chains possess greater mobility than chains packed in an orthorhombic orientation (33, 36). Gas permeability through synthetic polymer films markedly increases as the mobility of chain segments increases (50). A third reason relates to morphological differences between tristearin and stearyl alcohol (Fig. 1B, C, D). According to Fox (51), large, closely-packed plate crystals oriented perpendicularly to the direction of gas or vapor flow have excellent barrier properties. The layered morphology of stearyl alcohol (Fig. 1D) appears to correspond more closely to this arrangement than does the structure of tristearin.

The three factors just mentioned would alter $r(O_2)$ by changing the effective O_2 diffusion constant. Although the relative contribution of each factor is unknown, permeability studies with the different polymorphic forms of triacylglycerol films suggest that differences in packing density and molecular mobility between the hexagonal and orthorhomic orientations are of relatively minor importance (52). Thus, it appears that a properly layered morphology with platelets that compactly overlay one another is the predominant factor accounting for the high $r(O_2)$ of stearyl alcohol films.

TABLE 2

Resistance of uncoated Whatman 50 filter paper (W50) and various lipid-W50 composite films to O_2 transmission at 25°C.

Film[a]	$r(O_2)$[b] (sec•m^{-1})
W50	0.00011 (.00010, .00012) $\times 10^7$
Tristearin-W50	174 (153, 201) $\times 10^7$
Stearyl alcohol-W50	286 (265, 312) $\times 10^7$
Stearic acid-W50	4.31 (3.91, 4.81) $\times 10^7$
Hexatriacontane-W50	0.0332 (.0233, .0581) $\times 10^7$
Acetyl MG-W50	111 (105, 118) $\times 10^7$
Beeswax-W50	164 (150, 182) $\times 10^7$

[a]Amount of lipid per unit area of lipid-W50 films was 4.0 ± 0.2 mg/cm^2 ($\bar{X}$ ± SD).

[b]Data are means of at least four replicates, except uncoated W50 which was tested in triplicate; 95% confidence interval limits are in parentheses.

Comparison of the O_2 barrier characteristics of lipid-W50 model films with those of synthetic packaging films (Table 3) reveals that the beeswax, tristearin, and stearyl alcohol films are more resistant to O_2 flux than all of the synthetic materials except polyvinylidene chloride. Acetyl MG has a resistance approximately equal to that of polyethylene terephthalate, while resistance of the stearic acid-W50 film is similar to that of high-density polyethylene.

The extremely good O_2 barrier characteristics of stearyl alcohol and, to a lesser extent, tristearin, beeswax, and acetyl MG, suggest that these lipids would be useful wall materials for micro- or macroencapsulation of food components for the purpose of retarding oxidation.

Temperature dependence of $r(O_2)$. The influence of temperature on resistance to gas or vapor transfer across lipid films usually conforms to the Arrhenius relationship (5, 19, 21). An Arrhenius plot of the logarithm of $r(O_2)$ against the reciprocal of absolute temperature will normally yield a straight line with the slope being proportional to the activation energy (Fig. 2). Table 4 lists the equations [$\log r(O_2) = b(1/T) + a$], correlation coefficients and calculated activation energies for each regression line plotted in Fig. 2.

Uncoated W50 and hexatriacontane-W50 exhibited little temperature dependence. This is a consequence of the pores present in both films (Fig. 1A, F). Transmission of gases through films possessing pores, cracks, or other low resistance routes for gas migration occurs principally by a convective process and the rate of gas transport through such films is often relatively insensitive to temperature (46, 53).

The four lipid-W50 films with the best O_2 barrier characteristics displayed Arrhenius plots with positive slopes and positive activation energies (Fig. 2,

TABLE 3

Resistance of synthetic packaging films to O_2 transmission at 25°C.

Film[a]	$r(O_2)$[b] (sec•m^{-1})
Polyvinylidene chloride	$1{,}030 \times 10^7$
Polyethylene terephthalate	103×10^7
Nylon 6	86.4×10^7
High-density polyethylene	4.3×10^7
Polyvinyl chloride	2.9×10^7
Polypropylene	2.2×10^7
Low-density polyethylene	0.95×10^7

[a]Film thickness 0.025 mm (1 mil).

[b]Oxygen permeability data used to calculate $r(O_2)$ values are from Troller and Christian (55), except for Nylon-6 and high-density polyethylene which are from Karel (46).

Table 4). Lebovits (47) reported that activation energies (E) for most permeation processes are generally between 5 to 16 kcal/mole. Most synthetic polymer films display E values for O_2 transport within this range (46). Activation energies for O_2 transfer through stearyl alcohol, tristearin, and beeswax-W50 films are within this range. However, the acetyl MG-W50 film displayed an unusually large temperature dependence (E=27.5 ± 1.5 kcal/mole). This is probably attributable to the relatively low melting point range and heterogeneous composition of the acetoglyceride. As temperature is elevated, the proportion of lipid components in the fluid state increases markedly, causing a rapid decrease in resistance to O_2 transport. Lovegren and Feuge (39) measured O_2 permeability through acetyl MG films at 22, 26, and 30°C. They did not compute an activation energy of transport; however, calculations using their data yields an E value of approximately 24 kcal/mole, which is very similar to our result.

Beeswax-W50 films also displayed a relatively strong temperature dependence (E=15.0 ± 0.7 kcal/mole), likely due to the heterogeneous composition of the wax. Although principally comprised of saturated lipids, beeswax does contain about 4% *cis*-unsaturated hydrocarbons (primarily C_{31} and C_{33}) which give the wax its plasticity (48). The enhanced fluidity of the olefinic constituents would accelerate O_2 transfer as temperature is increased,

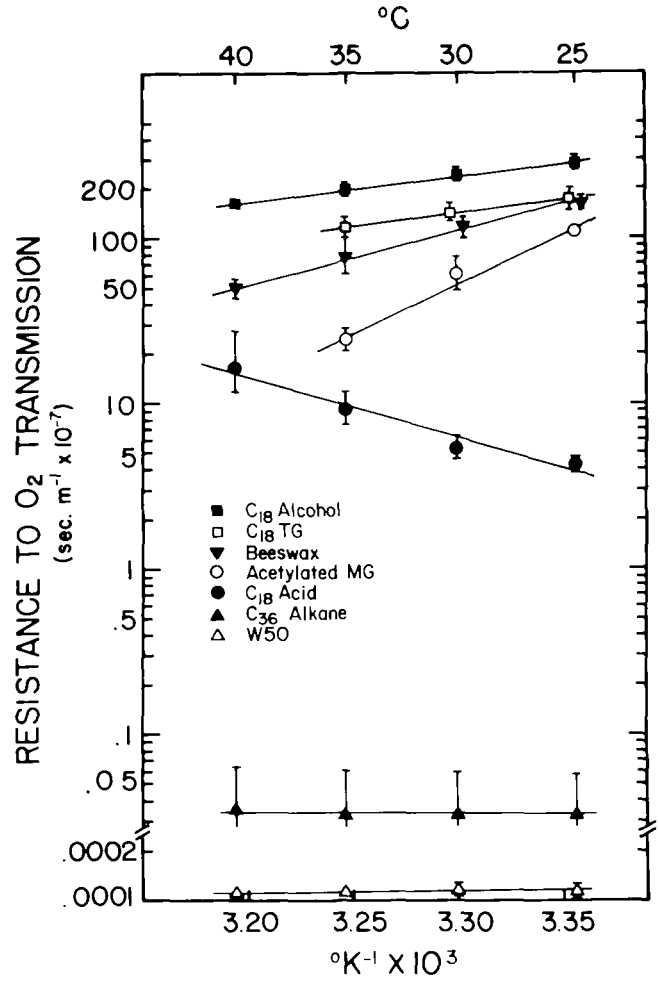

FIG. 2. Temperature dependence of the resistance to oxygen transmission $[r(O_2)]$ for uncoated Whatman 50 filter paper (Δ, W50) and the following lipid-W50 composite films: stearyl alcohol (■), tristearin (□), beeswax (▼), acetyl MG (○), stearic acid (●) and hexatriacontane (▲). All numerals on ordinate have been reduced by a factor of 1×10^7. Amount of lipid per unit area of film was 4.0 ± 0.2 mg/cm² (X ± SD). Each datum point is the average of at least four replicates, except W50 which was tested in triplicate. Vertical bars representing 95% confidence intervals are shown only when the interval exceeds the size of the symbol. Least-squares regression lines are drawn through each set of data. See Table 4 for regression equations and correlation coefficients.

TABLE 4

Regression equations and activation energies relating to the temperature dependence of resistance to oxygen transmission $[r(O_2)]$ for uncoated Whatman 50 filter paper (W50) and various lipid-W50 composite films[a]

	Regression Constant (a)	Regression Coefficient (b)	Correlation Coefficient (r)	Activation Energy[b] (E)
W50	2.77	86.29	0.8434	0.3 ± 0.3^A
Tristearin-W50	3.71	1648.80	0.9989	7.5 ± 0.5^B
Stearyl alcohol-W50	4.38	1513.17	0.9987	7.0 ± 0.3^B
Stearic acid-W50	20.03	−3706.92	−0.9795	-17.2 ± 3.1^C
Hexatriacontane-W50	6.00	−144.68	−0.7144	-0.7 ± 0.6^D
Acetyl MG-W50	−11.15	6023.92	0.9920	27.5 ± 1.5^E
Beeswax-W50	−1.79	3283.95	0.9971	15.0 ± 0.7^F

[a]Regression equation is Log $|r(O_2)|$=b (1/T)+a; amount of lipid per unit area of lipid-W50 films was 4.0 ± 0.2 mg/cm² ($\bar{X}$ ± SD); regression lines for each film are plotted in Fig. 2.

[b]Units of E are kcal/mole; data are means ± SD; E values with different superscript letters are significantly different (P≤0.05).

thereby contributing to a significant decrease in $r(O_2)$.

Tristearin and stearyl alcohol-W50 films displayed similar activation energies of 7.5 ± 0.5 and 7.0 ± 0.3 kcal/mole, respectively. These values are not significantly different ($P \leq 0.05$).

The stearic acid-W50 film exhibited a temperature dependence that was strikingly different from that of the other lipids. The Arrhenius plot for stearic acid-W50 has a negative slope, and, therefore, a negative activation energy of −17.2 ± 3.1 kcal/mole (Fig. 2, Table 4). This was repeated with a second set of stearic acid films and the same result was obtained. A possible explanation can be derived from the SEM micrographs of the stearic acid-W50 film (Fig. 1E), which show the presence of channels or void regions between platelet structures. Gas flow through a film containing fine pores, capillaries, or channels occurs principally through these regions. It is conceivable that an increase in temperature may cause crystalline expansion sufficient to close or lessen the size of these interplatelet channels, effectively decreasing the O_2 diffusion constant and causing $r(O_2)$ to increase with elevation in temperature.

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