Resistance of Lipid Films to Water Vapor Transmission

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Various lipids, mounted on a polar filter paper support, were evaluated as barriers to the transmission of water vapor. Beeswax was most resistant to moisture transmission followed by stearyl alcohol, acetylated monoglycerides, tristearin, and stearic acid in order of decreasing resistance. Resistance of beeswax to the transmission of water vapor is similar to that of polyethylene terephthlate and polyvinyl chloride. Temperature dependence of resistance to water vapor transport was influenced markedly by the polar-supporting matrix. This was attributed to the moisture sorption characteristics of the support, a finding that has relevance to edible, lipid-based films that contain hydrophilic polymers for structural integrity.

Considerable research has been conducted on moisture-resistant, edible films and coatings for foods (1,2). Some of these studies have dealt with limiting moisture exchange between the food and the surrounding atmosphere (3-5), while others have focused on the more difficult problem of retarding intercomponent water transport in heterogeneous food products (2, 6-12). In addition to macro-scale films, microencapsulation is practiced to protect susceptible food ingredients from moisture uptake (13).

Since the principal function of an edible film or coating is to impede moisture transfer, lipids are generally used in the film because of their hydrorepellency. Studies with artificial bilayer membranes and compressed monolayers have elucidated the influence of lipid molecular structure on the transport of liquid water or water vapor across lipid films. In general, the rate of water transfer increases as the lipid hydrocarbon chain length is decreased and the degree of unsaturation or branching of acyl chains is increased (14-18). This occurs because lateral packing of acyl chains is less efficient, causing a reduction in van der Waals' interactions and an increase in hydrocarbon chain mobility (19-21). These molecular effects accelerate water transport by elevating the effective H_2O diffusion constant and by increasing the solubility of water in the lipid membrane.

Considerable literature exists pertaining to liquid water and water vapor barrier properties of relatively thick (compared to mono- and bilayer) lipid films and coatings (4-8, 22-29). Several of these studies have confirmed that the water barrier properties of thick lipid films are influenced by hydrocarbon chain length and degree of unsaturation in a qualitatively similar fashion to that exhibited by lipid mono- and bilayers. Furthermore, moisture resistance of thick lipid films is influenced by the relative polarity of the lipid molecule. Highly nonpolar lipids, such as paraffin wax, are generally the most effective barriers. More hydrophilic lipids tend to be less resistant to the passage of water. This is caused by sorption of migrating water molecules to polar groups of the lipid, thereby facilitating water transport (23).

The objective of this investigation was to evaluate the resistance of various lipids to the transmission of water vapor as influenced by temperature and by hydrophilicity of the supporting matrix. Differences in water vapor transmission properties of the lipids are discussed in relation to lipid polarity and solid-state surface morphology.

MATERIALS AND METHODS

Lipids evaluated for resistance to O_2 flux in a previous study (30) were investigated for moisture-resistance. These were tristearin (90% pure), stearyl alcohol (99% pure) and stearic acid (90% pure) from Sigma Chemical Company, St. Louis, MO; hexatriacontune (98% pure) and white beeswax (commercial grade) from Aldrich Chemical Company, Milwaukee, WI and acetylated monoglycerides (acetyl MG; Myvacet 5-07 distilled acetylated monoglycerides from hydrogenated cottonseed oil, 48.5%-51.5% acetylation, melting range 41-46C) from Eastman Chemical Products, Kingsport, TN.

Film fabrication. Lipid-coated filter paper (Whatman No. 50; W50) was prepared according to the method described in detail previously (30). Briefly, this involved immersion of a W50 filter paper disk in molten lipid (100C), drainage at 100C and then cooling it at room temperature. This procedure added approximately 3 mg lipid/cm^2 of filter. An additional 1 mg/cm^2 was applied as a surface layer by spreading molten lipid uniformly over the surface with a preheated thin-layer chromatography (TLC) spreader. Total lipid content per unit of film area, determined by weighing filter disks before and after lipid application, was 4.0 ± 0.2 mg/cm^2 ($\overline{X} \pm SD$). Approximately 75% of the total lipid was embedded within the filter paper matrix and 25% was on the surface. The thickness of the completed film (hereafter referred to as the lipid-W50 film) was 0.11-0.12 mm.

Hydrophilic W50 filter paper was used as the supporting matrix in films because it has minimal resistance to moisture vapor transmission and because a supporting matrix is needed to prepare moderately thick films of lipids that are free from major structural defects. Furthermore, lipid-containing edible films often contain polar hydrocolloids (1, 2, 8-12, 31) to achieve adquate film-forming properties and to yield finished films with appropriate durability and integrity.

To investigate the influence of polarity of the supporting matrix on water vapor transport through lipids, polytetrafluoroethylene (PTFE, pore diameter 10 μm) membrane filters obtained from Millipore Corporation (Bedford, MA) were also tested as a support for acetyl MG. Lipid was applied to the hydropobic PTFE in a manner similar to that used for the hydrophilic W50 filters. The only change in procedure was that the drainage time following immersion in the lipid was limited to 2 min at 100C and the TLC spreader used for forming the lipid surface layer was preheated at 50C. The amount of lipid

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per unit area of film was 4.2 and 5.6 mg/cm^2 for determination of water vapor and O_2 flux, respectively.

Measurement of water vapor transmission rate (WVTR). A Permatran W1A Water Vapor Transmission Rate Tester (Modern Controls, Inc., Minneapolis, MN) was used to measure WVTR (g $H_2O^{-2}\cdot sec^{-1}$) through uncoated and lipid-coated filters according to method F372 of the American Society for Testing and Materials (32). Prior to determining WVTR, all films were equilibated at 25C in a conditioning chamber (Modern Controls, Inc.) that maintained a 100% relative humidity (RH) gradient across the film. Lipid-coated filters were placed in the conditioning chamber and Permatran diffusion cell with the lipid surface exposed to an atmosphere maintained at 100% RH with distilled H_2O. The other side of the film was continuously purged with dry air. The Permatran instrument was calibrated with a standard polyester film supplied by Modern Controls, Inc.

According to the relative barrier properties of each film type, the area of film exposed to water vapor was varied by using stainless steel masks with openings of different sizes. WVTR was determined at 25, 30, 35, and 40C for most films. Following an increase in temperature, sufficient time (ca 5-10 hr) was allowed to ensure a stable, equilibrium WVTR. At least five replicates of each film type were evaluated, except for the acetyl MG-PTFE film which was tested in triplicate.

All lipids were evaluated by x-ray diffraction (short-spacing region) before and after determination of WVTR at temperatures above 25C to confirm the absence of polymorphic transitions during the determination (30).Tristearin was not evaluated for WVTR at 40C because partial transformation to a new polymorphic form could not be avoided. Acetyl MG was not evaluated at 40C because this temperature was too close to its melting point range (41-46C).

Measurement of O_2 transmission rate (O_2TR). An Oxtran Model 100 Oxygen Permeability Tester (Modern Controls, Inc., Minneapolis, MN) was used to measure O_2TR (g $O_2\cdot m^{-2}\cdot sec^{-1}$) through uncoated PTFE and acetyl MG-PTFE composite films according to the procedure described by Kester and Fennema (30). O_2TR was determined in triplicate at 25, 30, and 35C and at 0% RH.

Calculation of resistance to water vapor and O_2 transmission. Resistance of uncoated and lipid-coated films to vapor and gas transmission was calculated from the following equation: $r = \Delta c/J = sec\cdot m^{-1}$ where r is the film's resistance to vapor [$r(H_2O)$] or gas [$r(O_2)$] transmission in sec·m^{-1}, Δc is the driving force for vapor or gas transport expressed in terms of a concentration gradient across the film is (g·m^{-3}) and J is the steady-state flux of water vapor (WVTR) or oxygen (O_2TR) in units of g·m^{-2}·sec^{-1}. The water vapor concentration gradient across the film is equal to the density of pure water vapor at saturation over water. Densities of pure water vapor at 25, 30, 35 and 40C were obtained from Weast (33).

The above equation for resistance has been cited numerous times in the literature for evaluating gas or vapor barrier properties of lipid monolayers (14, 34). plant cuticular membranes (35-37) and wax coatings on fresh fruits (38). It is simply a rearranged form of the general equation which characterizes all molecular transport processes, i.e., the rate of transfer is equal to the driving force divided by the resistance (39).

The steady-state rate of vapor or gas transport (J) through a film is related to the diffusion constant (D) and solubility coefficient (S) of the permeant in the film according to the integrated form of Fick's first law equation (40): $J = D\cdot S\ (\Delta P/\Delta X)$ where Δp is the gas partial pressure differential across the film and Δx is film thickness.

Diffusion of simple gases (e.g., O_2, N_2, CO_2) through a film generally obeys Fick's law, i.e., J is directly proportional to Δp and D is constant. However, in the case of water vapor diffusing through a polar film matrix, J will increase as Δp is moved up in the vapor pressure spectrum. This occurs because the sorption isotherms for hydrophilic polymers are sigmoidal, causing S to increase significantly as vapor pressure rises. The greater amount of sorbed water plasticizes the film causing D to increase. Hence, Fick's law is not strictly obeyed and D is not a constant for water vapor migration through hydrophilic film matrices. Therefore, when moisture-barrier properties of lipid-W50 films were evaluated, the resistance obtained was regarded as an "effective" resistance [eff $r(H_2O)$], which is correct under the given environmental conditions (i.e., % RH, temperature). For the same reason, temperature dependence of resistance to vapor transport should be expressed as an "apparent " activation energy (E_{app}).

The Student's t-distribution was used to compute 95% confidence intervals for eff $r(H_2O)$ and $r(O_2)$ and to evaluate the statistical significance ($P < 0.05$) between apparent activation energies for H_2O transport (41).

Scanning electron microscopy (SEM). Uncoated and lipid-coated filters were examined by SEM as described by Kester and Fennema (30).

RESULTS AND DISCUSSION

Tristrearin, stearyl alcohol, stearic acid and hexatriacontane were chosen for this study as representative of the triacylglycerol, fatty alcohol, fatty acid and alkane classes of lipid molecules. The 36 carbon alkane was chosen for study, rather than the 18 carbon homologue, because its melting point is close to those of the other three lipids. Acetyl MG and beeswax were evaluated because of the long standing interest in these lipid materials as edible moisture-barriers.

Hydrocarbon chain packing and surface morphologies, as revealed by electron microscopy, of the six lipid materials have been reported by Kester and Fennema (30). Tristearin and acetyl MG solidified in their lowest-melting, least-stable, α-polymorphic states with hexagonal packing of acyl chains. Stearyl alcohol, stearic acid and hexatriacontane crystallized in their most stable polymorphic forms with hydrocarbon chains packed in a common orthorhombic orientation. Beeswax also solidified with acyl chains arranged in an orthorhombic manner.

Resistance to water vapor transmission. The effective resistance [eff $r(H_2O)$] at 25C of each film type is listed in Table 1. Uncoated W50 displayed a low eff $r(H_2O)$ of 0.45 X 10^3 sec·m^{-1}. The porous nature of the W50 support, as well as its hydrophilic character, accounts for its low resistance to water vapor migration. Comparison of the eff r(H_2O) of uncoated W50 to the corresponding values for lipid-W50 composite films (Table 1), reveals that the W50 support accounts for 0.2 to 11% of the total resistance to water vapor flux, depending on the lipid coating.

Stearic acid was the least resistant of the lipid-W50 films. Limited moisture-barrier properties have been reported for long-chain fatty acids by several investigators (4, 5, 22, 24, 27, 29). Fox (23) stated that polar groups in a lipid film sorb water vapor, thereby assisting moisture migration through the film. SEM micrographs of these films showed an extensive array of crystal platelets with apparent channels or void regions between adjacent platelets (30). It seems likely that these channels contribute to a low eff r(H_2O) by providing relatively low-resistance pathways for vapor movement.

Tristearin films were approximately 46% more resistant to H_2O transport than the fatty acid, yielding an eff r(H_2O) of 5.88 X 10^3 sec·m^{-1} at 25C. However, this is lower than the resistances of all other lipid films, which differs from the comparative O_2-barrier properties of these films as reported previously (30). Tristearin was second only to stearyl alcohol in resistance to O_2 transport. Obviously, data on resistance to O_2 transmission is not reliable for predicting transport behavior of water vapor. This has also been noted for synthetic polymer films (42). The reason for this is that the solubility of the easily condesable water vapor in the barrier film is generally greater and more dependent on hydrophilic properties of the barrier than is the case with difficult-to-condense or noncondensable gases (43, 44). Hence, the sorption property of the film matrix tends to be more dominant in governing the net flux of water vapor through the film. The relatively low eff r(H_2O) of tristearin is perhaps attributable, in part, to the significant interaction of water vapor with the carbonyl groups of the triacylglycerol. The fact that fluid triacylglycerols can be induced to form ordered monolayers on the surface of water is indicative that these molecules do interact with water to a significant degree (45).

Hexatriacontane-W50 films displayed an eff r(H_2O) of 7.69 x 10^3 sec·m^{-1}, 30% larger than tristearin and 90% greater than stearic acid. This was somewhat surprising because of previously reported electron micoscopic evidence indicating that pores existed in the hexatriacontane films that were used and that these pores accounted for very poor O_2 barrier properties compared to those of other lipids tested (30). However, this result again highlights the importance of sorption properties on resistance to water vapor migration. Straight-chain, saturated hydrocarbons are extremely nonpolar: interaction with water will be negligible. This probably accounts for the higher eff r(H_2O) of hexatriacontane compared to the triacylglycerol and fatty acid, despite the presence of pores in the alkane film. Many studies have, in fact, shown that alkanes or paraffin wax are the most water-resistant lipid materials when cast in a continuous layer (8, 22, 24-27, 29). If the hexatriacontane film could have been cast without pores, its moisture-resistance probably would have been greater than that of the other lipid materials tested.

Acetyl MG-W50 films were the next most resistant among those films tested yielding an eff r(H_2O) of 9.65 x 10^3 sec·m^{-1}. This result is somewhat perplexing because the melting point of this heterogeneous lipid material is relatively low (41-46C). Thus, acyl chain fluidity at 25C is presumably greater than that of tristrearin, which should result in greater moisture sorption and a larger effective diffusion constant for water vapor; hence, lower resistance to water migration. A possible explanation for this apparent anomaly may lie with the physical structure of the acetyl MG film as observed with electron microscopy (30). These films have a relatively smooth surface without any well defined morphological characteristics. This perhaps results in few low resistance routes for vapor transport, such as might exist along the interfacial boundaries of crystals or platelets projecting from the surface.

Stearyl alcohol was very effective at blocking water vapor transfer. The fatty alcohol was approximately 5 and 7-fold more resistant, respectively, than were the triacylglycerol and fatty acid films. The polar hydroxyl group of stearyl alcohol presumably interacts to a certain extent with migrating water molecules, but probably less than either the carboxyl group of stearic acid or the carbonyl groups of tristearin. Furthermore, electron micrographs of this film showed an extensively layered morphology wih numerous relatively large crystalline platelets of about 1 μm thickness projecting out from the bulk lipid (30). According to Fox (23), when lipids crystallize as platelets, and these platelets are oriented approximately normal to the direction of vapor flow, resistance to vapor flow is usually great. Thus, it seems likely that the layered structure of stearyl alcohol platelets contributed, in part, to the high eff r(H_2O).

The most effective barrier to water vapor flux, by a large margin, was the beeswax-W50 film. Beeswax has been shown to be an excellent moisture-barrier in previous studies (8, 11, 12, 27, 28). The effectiveness of beeswax as a moisture barrier is likely related to both its physical structure and chemical composition. Electron micrographs showed a relatively smooth surface morphology without apparent crystalline structure (11, 30). However, x-ray diffraction confirmed that beeswax is at least partially crystalline in nature and that hydrocarbon chains are packed in an orthorhombic orientation (30). As previously postulated for acetyl MG, the lack of well-defined morphological features on the surface may contribute to a high resistance by minimizing crystal boundaries that otherwise might serve as low resistance pathways for vapor migration.

Probably the major reason that beeswax is such an effective moisture barrier is that it consists of a blend of lipid molecules with desirable nonpolar properties. Beeswax is comprised of 71% esters of long-chain fatty alcohols and acids, 15% long chain hydrocarbons, 8% free fatty acids, and 6% unidentified components (46). The hydrocarbon group is, of course, very nonpolar. Even though a polar group is present in the wax esters, the carboxyl residue of the component fatty acid, it is buried within the molecule and is effectively masked by long hydrocarbon chains, thereby contributing little hydrophilicity (45, 47). Negligible interaction of these molecules with water is substantiated by the fact that esters of long chain fatty alcohols and acids do not spread on the surface of water (45).

TABLE 1

Effective resistance of uncoated Whatman 50 filter paper (W50) and various lipid-W50 composite films to H_2O transmission (25C).

Film[a]	eff $r(H_2O)$[b] (sec·m^{-1})
W50	0.45 (0.42, 0.49) x 10^3
Tristearin - W50	5.88 (5.20, 6.75) x 10^3
Stearyl alcohol - W50	29.7 (27.5, 32.5) x 10^3
Stearic acid - W50	4.02 (3.58, 4.57) x 10^3
Hexatriacontane - W50	7.69 (6.85, 8.77) x 10^3
Acetyl MG - W50	9.65 (8.80, 10.7) x 10^3
Beeswax - W50	213 (174, 276) x 10^3

[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 five replicates; 95% confidence interval limits are in parentheses.

TABLE 2

Resistance of synthetic packaging films to H_2O transmission (25C).

Film[a]	eff $r(H_2O)$[b] (sec·m^{-1})
Polyvinylidene chloride	6,500 x 10^3
Polypropylene	694 x 10^3
Low-density polyethylene	325 x 10^3
Polyethylene terephthalate	237 x 10^3
Polyvinyl chloride	196 x 10^3
Nylon 6	43 x 10^3
Polystyrene	25 x 10^3
Ethylcellulose	2.3 x 10^3

[a] Thickness of films was 0.025 mm (1 mil).

[b] Water vapor permeability data used to calculate $r(H_2O)$ are from Troller and Christian (53), except for nylon 6, polystyrene and ethylcellulose which are from Myers et al. (54).

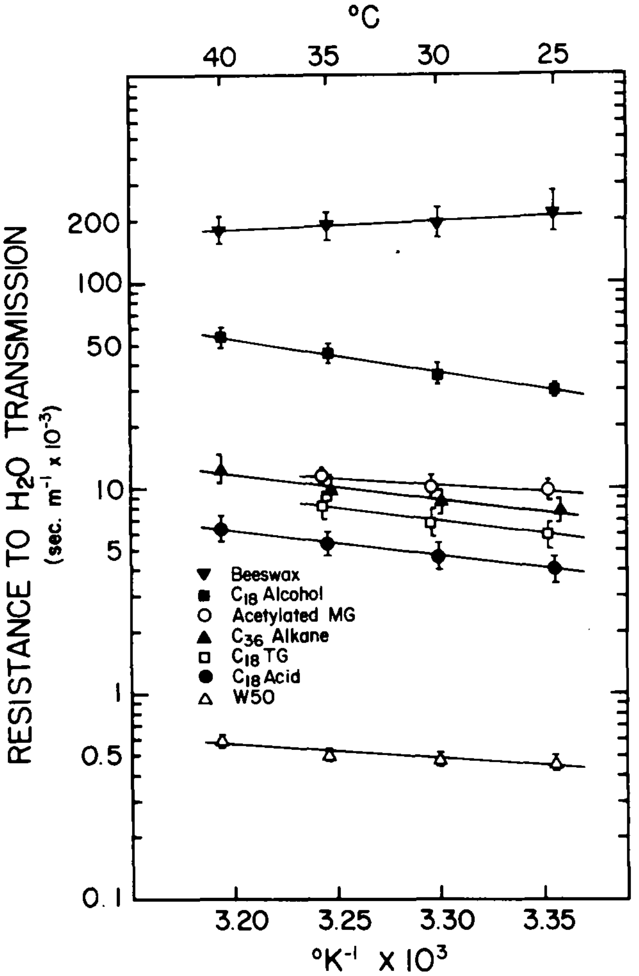


FIG. 1. Temperature dependence of the effective resistance to water vapor transmission [eff $r(H_2O)$] for uncoated Whatman 50 filter paper (△, W50) and the following lipid-W50 composite films: beeswax (▼), stearyl alcohol (■), acetyl MG (○), hexatriacontane (▲), tristearin (□) and stearic acid (●). Numerals on ordinate have been reduced by a factor of x 100^3. Amount of lipid per unit area of film was 4.0 ± 0.2 mg/cm^2 ($\bar{X}$ ± SD). Each datum point is the mean of at least five replicates. Vertical bars represent 95% confidence intervals. Least-squares regression lines are drawn through each set of data. See Table 3 for regression equations and correlation coefficients.

The comparison of the eff $r(H_2O)$ of lipid-W50 films (Table 1) to their respective $r(O_2)$ values (30) reveals that their resistance to water vapor is much lower than their resistance to oxygen. This agrees with previous studies concerning gas and vapor permeability of acetoglyceride (26, 48) and synthetic polymer films—a behavior attributable to water being more soluble than oxygen in the lipid film (43, 44). In the case of lipid-W50 films, the difference in oxygen versus water vapor flux is magnified because the hydrophilic support interacts with water vapor but not O_2.

Listed in Table 2 are $r(H_2O)$ values for eight synthetic polymer films. These values were calculated from water vapor permeability data in the literature. The most effective lipid barrier, beeswax-W50, was about as resistant to moisture transport as polyethylene terephthalate and polyvinyl cholride. The stearyl alcohol-W50 film had an eff $r(H_2O)$ intermediate between nylon 6 and polystyrene. Although these comparisons are useful to conceptualize the relative barrier properties of the lipid-W50 film, one should not place too much emphasis on the absolute resistance values. This is because a polysaccharide or protein film-former (e.g., cellulose ether, zein), when used as a structural matrix in a lipid-based, edible film, is likely to somewhat alter the resistance of the lipid component to the transmission of water vapor as compared to that obtained using the W50 matrix.

Temperature dependence of eff $r(H_2O)$. Temperature effects on the resistance of lipid films to the transmission of vapor or gas can be meaningfully depicted by means of Arrhenius plots (30) and these are shown in Figure 1 for the various films tested. Equations for the linear plots, correlation coefficients and apparent activation energies (E_{app}) for the transport of water vapor are presented in Table 3. It is quite obvious that the temperature dependence of water vapor migration through lipid-W50 films is very different from that previously reported for O_2transport (30). While the majority of lipid films displayed positive slopes for O_2 transport, the slopes of

TABLE 3

Regression equations and activation energies relating to the temperature dependence of the effective resistance to water vapor transmission [eff r(H_2O)] of uncoated Whatman 50 filter paper (W50) and various lipid-W50 composite films[a]

Film	Regression constant (a)	Regression coefficient (b)	Correlation coefficient (r)	Activation energy[b] (E_{app})
W50	4.87	-663.85	-0.9543	-2.9 ± 0.9^{A}
Tristearin W50	8.09	-1288.10	-0.9905	5.9 ± 0.5^{B}
Stearyl alcohol-W50	9.92	-1624.35	-0.9982	-7.4 ± 0.8^{C}
Stearic acid-W50	7.69	-1218.16	-0.9978	-5.6 ± 0.2^{B}
Hexatriacontane-W50	8.01	-1234.20	-0.9818	-5.7 ± 0.8^{B}
Acetyl MG-W50	6.19	-659.40	-0.9153	-3.0 ± 0.5^{A}
Beeswax-W50	3.76	464.45	0.9592	2.3 ± 1.2^{D}

[a] Regression equation is Log [eff r(H_2O)] = b(1/T) + a; amount of lipid per unit area of lipid W50 films was 4.0 ± 0.2 mg/cm^2 ($\bar{X}$ ± SD); regression lines for each film are plotted in Figure 1.

[b] Units of E_{app} are kcal/mole; data are means ± SD; values with different superscript letters are significantly different ($P < 0.05$).

regression lines for water vapor transmission are negative for most of the films, thus yielding negative E_{app} values. The only lipid film which displayed a positive slope was beeswax-W50, for which an E_{app} of 2.3 ± 1.2 kcal/mole was obtained. The fact that uncoated W50 displayed a negative slope suggests that the sorption behavior of the polar support affects the temperature dependence of water vapor transmission.

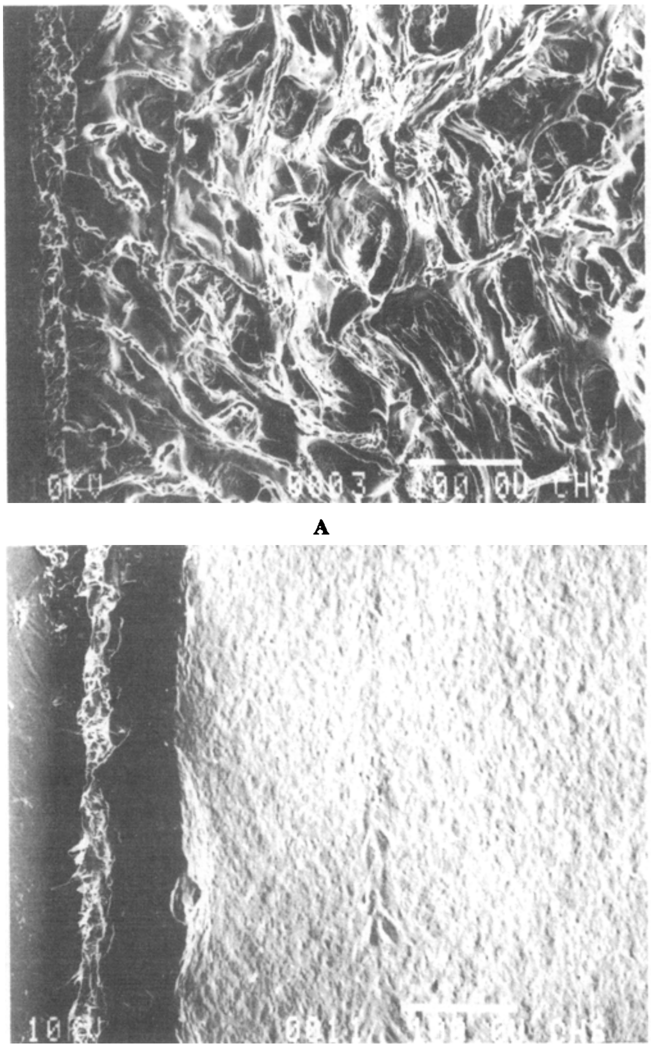
The energy of activation for the permeation of gases and vapors through films can be considered as the sum of two components (43, 44): $E = E_d + \Delta H_s$, where E_d is the activation energy of the diffusion process and ΔH_s is the heat of solution of the permeant in the film matrix. For simple gases, such as O_2, E_d is large and positive and ΔH_s is generally small and positive; thus, a positive E is obtained for the transport process. In the transmission of water vapor through polar film matrices, E_d is again positive; however, ΔH_s is negative (43, 44). As temperature is increased, the equilibrium amount of sorbed water at a given %RH is reduced: the water solubility coefficient decreases as temperature rises. Since sorbed water acts as a plasticizer, its decrease at elevated temperatures will tend to lessen the temperature-induced rise in the effective diffusion constant: the positive E_d is reduced in magnitude. The net effect for lipid W50 films is that the negative ΔH_s exceeds the positive E_d, resulting in a negative E_{app}. Similar increases in resistance (or decrease in permeability) with elevation in temperature have been reported for transmission of water vapor through polyvinyl alcohol (49) and cellulose ester films (50, 51).

Beeswax-W50 films displayed a positive E_{app} for water vapor transport, probably because of the heterogeneous lipid composition. Approximately 4% of the wax consists of *cis* unsaturated hydrocarbons (principally C_{31} and C_{33}) with relatively low melting points (46). As the temperature is raised, the increased fluidity of the olefinic components and other low-melting constituents would tend to greatly increase the effective diffusion constant of water vapor through the lipid. Thus for beeswax, the positive E_d exceeds the negative ΔH_s resulting in a positive E_{app}.

Although beeswax-W50 displayed a positive E_{app} for water vapor migration, the value is significantly smaller than that reported previously for a beeswax-coated, cellulose ether edible film (11). Assuming that neither type of film contained structural flaws sufficient to have a significant influence on their barrier properties—a reasonable assumption based on their microscopic appearance and their low permeability to water vapor—this difference in E_{app} must be an indirect consequence of different moisture sorption characteristics of the hydrophilic support components of the two films. The negative ΔH_s for beeswax-W50 films must be greater in magnitude than the corresponding value for the beeswax-cellulose ether edible film.

Lipids mounted on a polytetrafluoroethylene (PTFE) support. To test whether the negative slopes observed in Figure 1 resulted from the water sorption behavior of the polar support, acetyl MG was mounted on hydrophobic PTFE filters and evaluated for resistance to water vapor and oxygen transmission. Like W50, uncoated PTFE filters displayed low r(O_2) and r(H_2O) values: respectively, 10.8 X 10^3 and 0.37 X 10^3 sec·m^{-1} at 25C. However, PTFE filters are much thinner than W50 filters (compare Figures 2A and 3A), and the majority of the lipid was deposited as a thick layer on the surface (Figure 2B). In contrast, approximately 75% of the lipid was embedded within the interior of the W50 filter matrix; the remaining 25% was deposited as a surface layer (Figure 3B). Certainly, the differences in lipid distribution between the two model film systems could influence the absolute resistance to gas and vapor flux; however, our interest was not a comparison of absolute resistances, but rather of the temperature dependence of resistance (E_{app}).

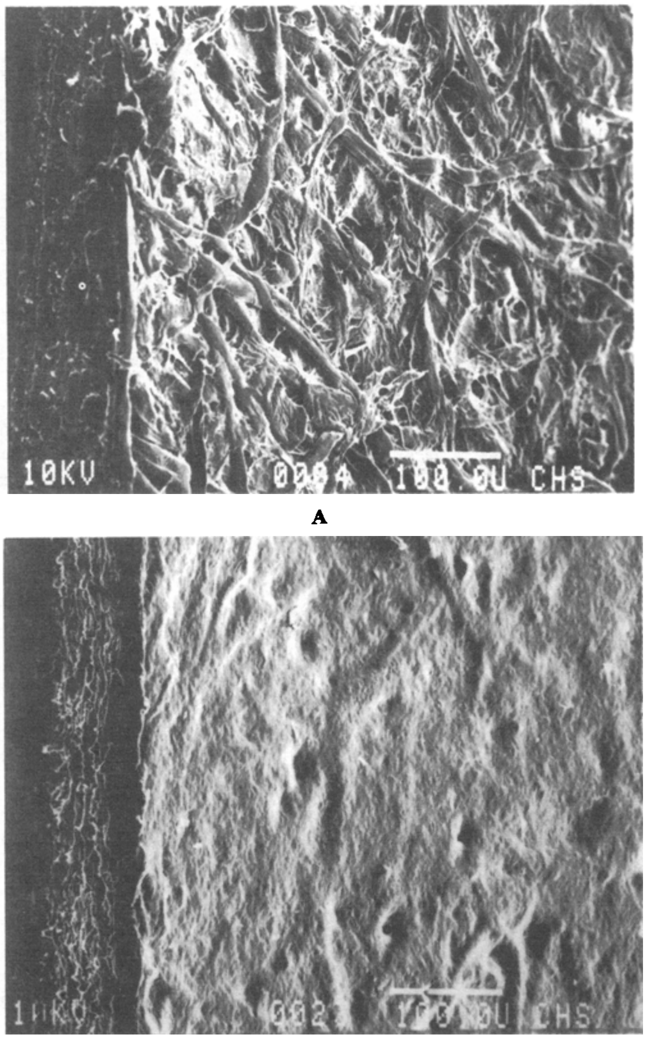
Shown in Figure 4 are Arrhenius plots indicating the temperature dependence of r(O_2) and eff r(H_2O) for acetyl MG-PFTE films. Linear regression data and calculated activation energies of transport are listed in Table 4. The activation energy of O_2 transport through acetyl MG-PTFE is 21.3 ± 1.0 kcal/mole. This is somewhat lower than the E measured for O_2 transmission through the acetyl MG-W50 film (27.5 ± 1.5 kcal/mole); however, both values are of approximately the same magnitude compared to the other lipid films tested.



A

B

FIG. 2. SEM micrographs of an uncoated polytetrafluoroethylene membrane filter (A) and an acetyl MG-PTFE film (B). Amount of lipid per unit area of film in B was 4.2 mg/cm^2. Micrographs were taken at a 45° angle to the film surface. The edge of each film is on the left. The lipid surface layer in micrograph B is marked with a black bracket. The white bars are 100 μm in length.



A

B

FIG. 3. SEM micrographs of uncoated Whatman 50 (W50) filter paper (A) and an acetyl MG-W50 film (B). Amount of lipid per unit area of film in B was 4.0 mg/cm^2. Micrographs were taken at a 45° angle to the film surface. The edge of each film is on the left. The lipid surface layer in micrograph B is marked with a black bracket. The white bars are 100 μm in length.

Of particular interest in the slope of the Arrhenius plot for water vapor transport through acetyl MG-PTFE (Figure 4). In contrast to the lipid-W50 model film, the slope is positive meaning that r(H_2O) decreases with an increase in temperature. The calculated activation energy is 4.6 ± 1.2 kcal/mole (Table 4), compared to -3.0 ± 0.5 kcal/mole for the acetyl MG-W50 film (Table 3). This confirms that when a hydrophilic structural polymer is embedded in a lipid film, the temperature dependence of water vapor transmission is very strongly influenced by the moisture sorption behavior of the polar component.

An interesting sidelight developed as a consequence of working with the hydrophobic PTFE filters. In addition to acetyl MG, stearyl alcohol and beeswax were also applied to PTFE in a similar manner. However, the barrier characteristics of these two lipid-PTFE films were extremely

TABLE 4

Regression equations and activation energies relating to the temperature dependence of resistance to oxygen transmission [r(o_2)] and effective resistance to water vapor transmission [eff r(H_2O)] of acetyl MG-PTFE films[a]

	Regression constant (a)	Regression coefficient (b)	Correlation coefficient (r)	Activation energy[d] (E)
r(O_2)[b]	-7.72	4657.77	0.9797	21.3 ± 1.0
eff r(H_2O)[c]	0.75	1021.67	0.9884	4.6 ± 1.2

[a] Regression equation is Log r = b(1/T) + a; regression lines are plotted in Figure 4.

[b] Amount of lipid per unit area of film was 5.6 mg/cm^2.

[c] Amount of lipid per unit are of film was 4.2 mg/cm^2.

[d] Units of E are kcal/mole; data are means ± SD.

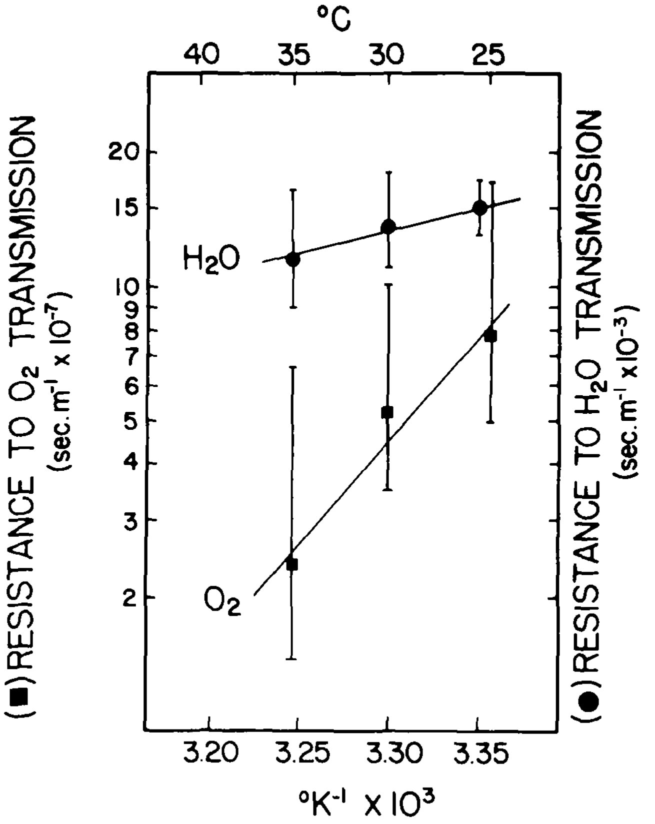
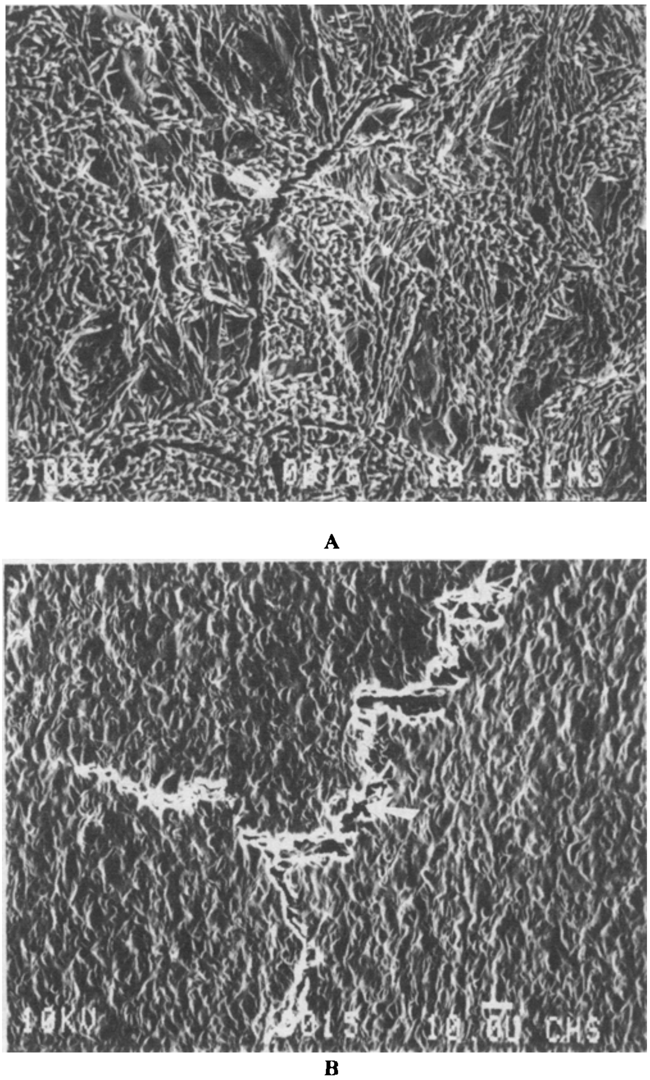


FIG. 4. Temperature dependence of the resistance to oxygen transmission (■) and the effective resistance to water vapor transmission (●) of acetyl MG-PTFE[a] films. Numerals on left ordinate have been reduced by a factor of 1×10^7 and on the right ordinate by a factor of 1×10^3. Amount of acetyl MG per unit area of film was 5.6 and 4.2 mg/cm^2 for oxygen and water vapor, respectively. Each datum point is a mean of three replicates. Vertical bars represent 95% confidence intervals for resistance. Least-squares regression lines are drawn through each set of data. See Table 4 for regression equations and correlation coefficients. [a]PTFE is polytetrafluoroethylene.



A

B

FIG. 5. SEM micrographs of stearyl alcohol-PTFE[a] (A) and beeswax-PTFE (B) films. Amount of lipid per unit area of film was 4.0 mg/cm^2. Micrographs were taken at a 45° angle to the film surface. The white bars are 10 μm in length. Cracks in the lipid films are identified with arrows.
[a]PTFE is polytetrafluoroethylene.

poor (data not shown). The reason for this is evident from the electron micrographs of the film surfaces, which showed the presence of cracks in the lipid layer (Figure 5). This phenomenon was never observed with the lipid-W50 films. A plausible explanation develops when one considers differences in lipid distribution between the two film types. In the lipid-PTFE system, a lipid was predominantly deposited in a separate layer on the surface of the support. On the other hand, in the lipid-W50 film system, approximately 75% of the total lipid was embedded in the filter matrix, and the remainder was on the surface. It seems likely that the fibers of the W50 matrix provided a stabilizing influence to prevent lipid fracture. This stabilization is missing when a lipid is deposited principally on the surface, as with the PTFE film. It is reasonable to suggest that acetyl MG can be successfully cast of PTFE without fracture of the lipid layer because of its excellent flexibility in the α-polymorphic state (52).

The observation that lipids display markedly different propensities to fracture when deposited on PTFE and W50 supports may be important when fabricating lipid-based edible films. The inclusion of high-molecular weight polymeric components into the lipid film may be desirable, not only for adequate film-forming properties, but also for purposes of structural cohesion and resistance to lipid fracture in the finished film. A pertinent observation is that fatty acids (C_{16}-C_{18}) are markedly more resistant to water vapor migration when incorporated into a cellulose ether film-forming solution prior to casting and drying of the film, than they are when coated on a preformed cellulose ether film (8). The probable explanation for this difference is that fracture of the lipid layer occurred in the latter film, whereas in the former film the fatty acid layer is intermixed sufficiently with the cellulose-ether polymer matrix to lessen lipid fracture.

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