

Hydrophobic Films and Their Efficiency against Moisture Transfer. 1. Influence of the Film Preparation Technique

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The barrier properties of two hydrophobic materials, oil and wax paraffins, were studied as a function of the characteristics of the technique employed to prepare hydrophobic films with a constant content of paraffin. Three cellulose derivatives with different polarity and porosity were used as supports to prepare films by several techniques: emulsion, emulsion plus coating (methylcellulose), and dipping (porous filter paper and nonporous cellophane). Results show that the ability of the hydrophobic substances to retard moisture transfer depends on the homogeneity of its final repartition in the matrix and/or on the surface. The least efficient films to retard the movement of water correspond to the highly heterogeneous systems (emulsion and dipped filter paper) independent of the nature of the substance as seen by scanning electron microscopy. The most efficient difference, a 100-fold in water vapor permeability, is obtained in the cellophane films with homogeneous repartition of paraffin wax independent of thickness and relative humidity. This behavior is in contrast to that of the paraffin oil.

INTRODUCTION

Protection of foods and increased conservation can be achieved by using edible or nonedible films to limit vapor or water transfer and to allow selective gas transfer. This applies especially to water vapor migration, which can induce some deteriorations: if the water vapor pressure differential at the food surface is higher than the relative humidity of its surroundings, the dehydration causes a loss of organoleptic characteristics; in the opposite case, the action of the exchange of moisture from environment to food may create favorable conditions for the growth of microorganisms and also give rise to a loss of texture (Labuza and Contreras-Medellín, 1981; Labuza, 1982).

To limit moisture migration, substances that are able to prevent the transfer of water vapor molecules must be used. Several studies have shown that some edible films containing hydrophobic substances can limit water vapor transfer (Lovegren and Feuge, 1954; Landman et al., 1960; Kester and Fennema, 1986; Biquet and Labuza, 1988; Greener and Fennema, 1989; Guilbert and Biquet, 1989). The most efficient are paraffin wax and beeswax (Schultz et al., 1949; Kamper and Fennema, 1984a; Kester and Fennema, 1989a). In contrast to some polysaccharides, proteins, and synthetic materials, these hydrophobic substances form thicker and more brittle films; consequently, they must be associated with film-forming agents such as proteins (Torres et al., 1985) or cellulose derivatives (Kamper and Fennema, 1985; Kester and Fennema, 1989b; Hagenmaier and Shaw, 1990) to improve the mechanical properties of the film.

Several types of interactions between hydrophobic substances and film-forming agents can occur to form a film: chemical reaction (Bull and Breese, 1967), dispersion of hydrophobic substances corresponding to the emulsion technique (Kamper and Fennema, 1984a,b), coating over an emulsified support (Kester and Fennema, 1989b), or adsorption over a more or less porous support (Martín-Polo and Voilley, 1990; Kester, 1988; Torres et al., 1985).

Differences in efficiency against moisture transfer have been noted between films obtained by several preparation techniques. Comparisons made by Schultz et al. (1949) have shown that the most efficient hydrophobic substances

are fatty acids and waxes (paraffin, jojoba, or beeswax) coated over LM-pectin support, as opposed to the films obtained by their dispersion with the support before casting.

Contrary to these results, Kamper and Fennema (1984a) have observed a greater capacity to retard the movement of water in films prepared according to the emulsion technique. In this case, hydrophobic substances such as a blend of fatty acids (stearic and palmitic acid) using hydroxypropyl methylcellulose as a film-forming agent were used.

In this study the films used were composed of a hydrophobic substance, either paraffin wax or oil, and a polar support. Three cellulose derivatives were used as supports depending on the technique of preparation of the hydrophobic film. A soluble derivative like methylcellulose was used in emulsion and in emulsion plus coating techniques. Filter paper (porous support) and cellophane (nonporous support) were employed in the dipping technique to evaluate the effect of the surface heterogeneity.

The aims of this work are to study the influence of the technique used in the preparation of hydrophobic films on their efficiency against moisture and to determine factors that influence their barrier properties. For dipped films the influence of thickness and the water vapor pressure differential across the film were also studied.

MATERIALS AND METHODS

Materials. Two hydrophobic substances were used: paraffin wax, mp 48 °C (Merck), and paraffin oil, density 0.88 g L⁻¹ (Merck). These substances were tested with three supports: methylcellulose, cellophane 300P, and filter paper. Their characteristics are as follows: methylcellulose (Methocel A15 LV Premium, Dow Chemical Co.) with a methoxyl content of 27-31.5%; cellophane 300P (Courtaulds Films), regenerated non-coated cellulose having a surface density of 30 g m⁻²; and filter paper W-111 (Whatman), medium-speed paper having an ash content of 0.06%.

In the emulsion technique polyethylene glycol 400 (Merck) was introduced as a plastifier.

Methods. Film Preparation Techniques. (a) *Dipping.* Disks of cellophane or filter paper (diameter 3.5 cm) were dipped for 30 s in molten paraffin wax at 95 °C or in paraffin oil at room

Table I. Emulsified Film Composition

4.25 g of methylcellulose	25 mL of distilled water
4.25 g of paraffin wax or paraffin oil	50 mL of absolute ethanol (99.8% purity)
1.3 mL of PEG (400)	

temperature and then drained for 1 min. Dipped W-111 filter paper was heated at 70 °C for 18 h to remove excess paraffin. This operation ensures a constant quantity of paraffin wax per unit area equal to $45 \pm 6 \text{ g m}^{-2}$. Prior to dipping, W-111 filter paper and cellophane disks were dehydrated over P_2O_5 to ensure constant disk weight. The thicknesses of dipped films were $190 \pm 10 \text{ }\mu\text{m}$ for W-111 and $80 \pm 10 \text{ }\mu\text{m}$ for cellophane.

(b) *Emulsion*. The composition of the films was derived from the work of Kester and Fennema (1989a). The proportions of materials we have used are shown in Table I. The methylcellulose was dissolved at 75 °C in a mixture of water and absolute ethanol (1:2). The hydrophobic material (paraffin wax or oil) was added under magnetic stirring to form an emulsion. The emulsion was applied onto glass plates with a thin-layer chromatography spreader (thickness fixed to 1 mm), both preheated at 100 °C. The coated plates were dried for 24 h at room temperature. After drying, the thicknesses of the film were $130 \pm 20 \text{ }\mu\text{m}$ for paraffin oil and $200 \pm 20 \text{ }\mu\text{m}$ for paraffin wax.

(c) *Emulsion and Coating*. The emulsified plus coated film is made in two steps. First, methylcellulose and paraffin wax (1:0.025 w/w) are emulsified in a mixture of water and absolute ethanol as previously described. This emulsion is spread onto glass plates and dried at room temperature. Second, the glass plates covered with the emulsified film and the spreader are preheated at 70 °C before they are coated with molten paraffin wax at 95 °C. Plates were then allowed to cool at room temperature. The thickness of the final film was $140 \pm 20 \text{ }\mu\text{m}$.

(d) *Storage Conditions*. Before the water vapor transmission rate (WVTR) of the films was tested, they were stored for 24 h either at ambient conditions or in desiccators containing a saturated salt solution of potassium chloride with a relative humidity (RH) of 84.3%.

Characterization of the Films. (a) *Contact Angle Measurement*. To estimate the hydrophobicity of the prepared films and supports, the advance contact angle between distilled water and test material surface was measured at 20 °C with the aid of a microscope equipped with a goniometric eyepiece (LG 40; Kruss GmbH). Each angle value reported is the mean of four measurements.

(b) *Thickness*. For each type of film except dipped cellophane in paraffin oil, thickness was measured with a micrometer (0.01 mm) at five different places for several films. Means and standard deviations of thickness were then calculated. The thickness of the dipped film of cellophane into paraffin oil was calculated by using the expression

$$e_f = (m/dA) + e_s \quad (1)$$

where e_f is the thickness of the film (cellophane plus paraffin oil) (m), m is the weight of paraffin oil on cellophane (g), d is the density of paraffin oil (g m^{-3}), A is the area (m^2), and e_s is the thickness of the cellophane (m).

For the films made by dipping the cellophane support, a complementary study of the influence of the thickness on WVTR was carried out. Different thicknesses were obtained by varying the temperature to melt the paraffin wax or by dilution of the paraffin oil with hexane (care was taken to ensure complete evaporation of hexane before the water vapor transmission measurements were made).

(c) *Surface density* is expressed as grams of hydrophobic material per square meter of film (g m^{-2}) and was fixed to $45 \pm 6 \text{ g m}^{-2}$ for all types of film. For the dipping technique, the surface density is obtained by weighing the cellophane or W-111 paper filter disks before and after the application of the hydrophobic substance. For the emulsion technique, it is calculated by the difference between the surface density of the emulsified film and the prepared methylcellulose support. For the emulsified plus coated films, the surface density is calculated by difference with respect to the support.

(d) *Scanning Electron Microscopy (SEM)*. Surface morphology, hydrophobic substance distribution, and thickness were evaluated with a JEOL JSM-35CF (JEOL Ltd., Tokyo) scanning electron microscope. Pieces of film of 5 mm^2 were mounted on copper stubs, fixed with double-sided tape, and then coated with gold. The samples were observed using an accelerating voltage of 15 kV with the electron beam directed either parallel to the surface or at a 45° angle.

(e) *Measurement of Water Vapor Transmission Rate*. Efficiency of the films was tested by measuring the WVTR. It was determined gravimetrically at 25 °C according to the AFNOR (1974) procedure (NF H00-030). A disk of film was placed in a glass cell containing a saturated solution of potassium acetate (Merck, 22.6% RH) (Martín-Polo and Voilley, 1990). The cell was placed in a desiccator maintained at 84.3% RH with a saturated solution of potassium chloride. The emulsified and emulsified plus coated films were placed in the cell so that the side which was in contact with air when still on the glass plate was orientated to the highest RH compartment.

From the measured WVTR (eq 2) the corresponding permeability is calculated (eq 3) as

$$\text{WVTR} = \Delta w / \Delta t A \text{ (g m}^{-2} \text{ s}^{-1}) \quad (2)$$

$$\text{WVP} = (\text{WVTR})l / (p_1 - p_2) \text{ (g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}) \quad (3)$$

where $\Delta w / \Delta t$ is the amount of moisture gain per unit time of transfer (g s^{-1}), l is the film thickness (m), A is the area exposed to moisture transfer (m^2), p_1 and p_2 are the vapor pressures of water on either side of the film, $(p_1 - p_2)$ is the driving force (Pa), and P is the film permeability ($\text{g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$).

This equation is derived from Fick and Henry's laws for vapor or gas diffusion through the film. These laws are obeyed when there is no interaction between water vapor and the film (Crank, 1975).

Each type of film preparation technique is done in three replicates and two disks are tested each time. The cells are weighed daily for 3 days. Results given are the mean of at least six values. The steady state was obtained for all films after 48 h.

The influence of the water vapor pressure differential on the barrier properties was studied for cellophane dipped films for both hydrophobic substances. The external relative humidity was kept constant at 84.3%. Two other internal relative humidities, 43.8 and 57.7%, obtained from saturated salt solutions of potassium carbonate and sodium bromide, respectively, were used.

(f) *Statistical Analysis*. For each type of film, data were subjected to analysis of variance according to the method of Steel and Torrie (1980). Differences among means were tested for statistical significance at the $p < 0.05$ level according to the t -Student-Newmans-Keuls test.

RESULTS AND DISCUSSION

Paraffin wax and oil were chosen because of their chemical composition and structure. They are composed of alkanes of different chain lengths. The major components in paraffin oil are $\text{C}_{16}\text{H}_{34}$ and $\text{C}_{14}\text{H}_{28}$. The most abundant compounds, however, in paraffin wax are $\text{C}_{26}\text{H}_{54}$ and $\text{C}_{40}\text{H}_{82}$ (Lawrence et al., 1982; Lawrence and Iyengar, 1983). These differences in composition induce two physical states: solid and liquid. Paraffin oil and wax are hydrophobic substances like lipids normally used to prepare edible films. Highly hydrophobic substances were chosen to minimize possible interactions with water.

Results for different storage conditions (84.3% RH or ambient conditions) were not significantly different under tested conditions for any type of film or support.

Influence of the Thickness of Dipped Films. Results show that WVTR and water vapor permeability of dipped cellophane film support depend on the nature of the hydrophobic substance and on the film thickness (Figure 1). For the paraffin wax, the variation of the

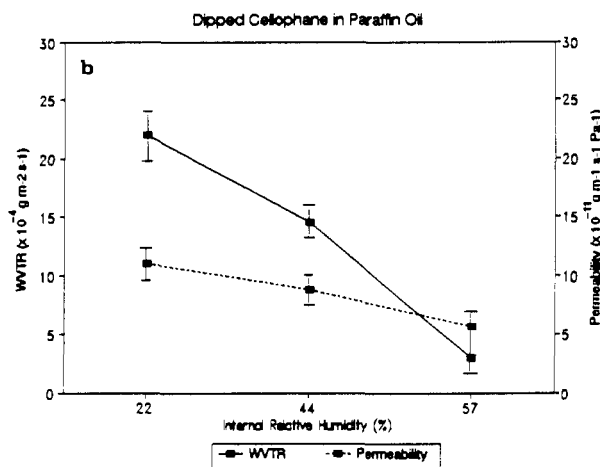
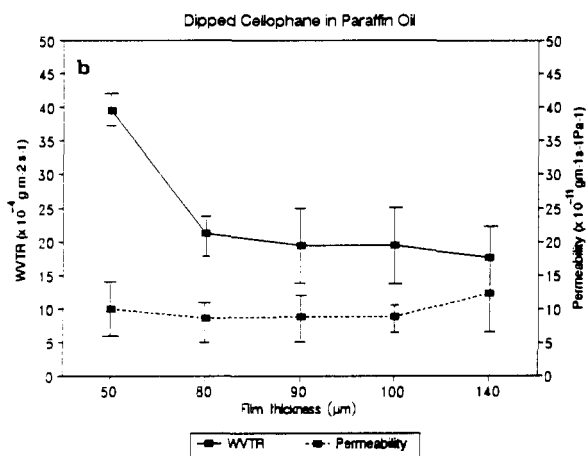
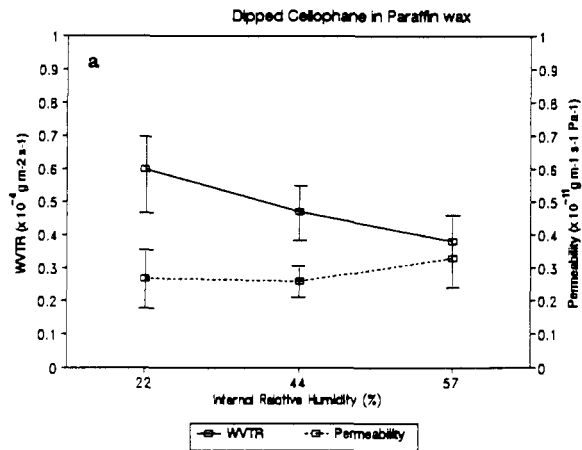
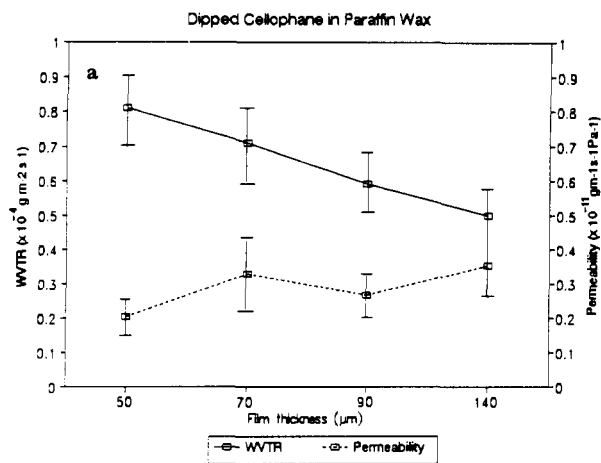


Figure 1. Influence of thickness on the WVTR and permeability of dipped cellophane in paraffin oil (b) and wax (a) (25 °C and 22–84% RH).

WVTR with the film thickness is almost linear ($r^2 = 0.9295$), with constant water vapor permeability.

For paraffin oil, we observed an increase in WVTR with decreasing film thickness below 80 μm . From this value up to 140 μm the WVTR and water vapor permeability remained almost constant. This probably means that for thin films discontinuities in the paraffin oil layer may occur and moisture transfer occurs through the cellophane.

The uniformity of the film thickness is of some importance because other properties in turn depend on it, especially the water vapor permeability as pointed out by Hagenmaier et al. (1990).

From the sorption diffusion model of permeation described by Fick and Henry's laws (Crank, 1975), the WVTR varies as a reciprocal of film thickness; indeed, the water vapor permeability remains constant. The dipped cellophane films show a WVTR that is nearly constant with thickness variation between 80 and 140 μm . For both oil and paraffin wax permeability increases slightly with thickness. Usually coated films like waxed paper and moisture proof cellophane show this kind of behavior (Cairns et al., 1974).

Influence of the Water Vapor Pressure Differential across Dipped Films. For both paraffin wax and oil the WVTR decreases when the internal RH increases, but for paraffin oil it is nearly linear. The water permeabilities of the films calculated from eq 2 describe the same behavior. Both curves are shown in Figure 2.

Similar results were obtained by Kamper and Fennema (1984b) with an emulsified film of paraffin or stearic acid

Figure 2. (a, b) WVTR and permeability of coated and non-coated cellophane under three different internal relative humidities at 25 °C. (External RH equal to 84.3%.)

when internal RH was kept constant to 0%. WVTR was highest when the water vapor pressure differential was maximum, as normally expected.

As proposed by Kamper and Fennema (1984a), differences in permeability between liquid and solid can be explained in terms of the solubility of water vapor and/or the molecular organization of the lipid film. In our case this effect is probably due to a lack of barrier efficiency of the liquid material originating in its molecular organization compared to that of the solid one and not due to the sorption behavior (Martín-Polo et al., 1992).

(a) *Effect of Added Hydrophobic Substance.* The water vapor transmission curves as a function of time for the different techniques and hydrophobic substances are all straight lines ($r^2 = 0.9998$). The highest transmission rate is observed for W-111 and the smallest for dipped cellophane in paraffin wax.

For all tested films when a hydrophobic substance like paraffin oil or wax is added, a significant decrease in WVTR is observed. Its magnitude depends on the technique and support. For each technique the paraffin oil decreases 1.3 times the WVTR of the support and for the paraffin wax from 1.4 to 62 times.

The effectiveness of the emulsified and dipped filter paper containing the hydrophobic substance inside the matrix can be compared to that of the support by the expression

$$\text{Eff} = [(\text{WVTR}_s - \text{WVTR}_f) / \text{WVTR}_s] \times 100 \quad (4)$$

where Eff is the effectiveness to retard the moisture

Table II. Characteristics of Films Prepared by the Emulsion and Emulsion plus Coating Techniques and the Methylcellulose Support (22.6–84.3% RH at 25 °C)^a

nature of the film	thickness, $\times 10^6$ m		contact angle, deg	WVTR, $\times 10^4$ g m ⁻² s ⁻¹	permeability, $\times 10^{11}$ g m ⁻¹ s ⁻¹ Pa ⁻¹	
	micrometer	SEM			micrometer	SEM
support						
methylcellulose (MC)	70 \pm 10	not measured	28 \pm 1	29.48 \pm 4.36 ^A	10.81 \pm 1.57 ^{A,1}	
emulsion						
MC + paraffin oil	130 \pm 20	99 \pm 10	51 \pm 2	18.20 \pm 1.96 ^B	12.04 \pm 2.24 ^B	9.11 \pm 0.98 ¹
MC + paraffin wax	200 \pm 20	89 \pm 8	62 \pm 3	21.23 \pm 4.34 ^B	17.33 \pm 1.30 ^B	9.55 \pm 1.95 ¹
emulsion + coating with paraffin wax	140 \pm 20	82 \pm 9	102 \pm 3	0.57 \pm 0.38 ^C	0.41 \pm 0.31 ^C	0.23 \pm 0.15 ²

^a Reported data are $\bar{X} \pm$ SD for at least three trials. Mean values having the same superscript are not significantly different ($p < 0.05$). Statistical analysis are made independently for WVTR and permeability.

Table III. Characteristics of Films Prepared by the Dipping Technique for Each Type of Support (22.6–84.3% RH at 25 °C)^a

nature of the film	thickness, $\times 10^6$ m	contact angle, deg	WVTR, $\times 10^4$ g m ⁻² s ⁻¹	permeability, $\times 10^{11}$ g m ⁻¹ s ⁻¹ Pa ⁻¹
porous support				
filter paper (W-111)	180 \pm 10	(absorption)	38.63 \pm 4.00 ^A	35.13 \pm 3.64 ¹
dipped filter paper				
W-111 + paraffin oil	190 \pm 10	71 \pm 5	28.20 \pm 4.91 ^B	26.51 \pm 4.60 ²
W-111 + paraffin wax	190 \pm 10	116 \pm 2	29.48 \pm 3.13 ^B	28.96 \pm 2.48 ²
nonporous support				
cellophane (C)	30 \pm 10	8 \pm 1	37.40 \pm 2.40 ^A	5.67 \pm 0.36 ¹
dipped cellophane				
C + paraffin oil	80 \pm 10 ^b	not measured	22.02 \pm 2.68 ^B	9.29 \pm 1.65 ²
C + paraffin wax	90 \pm 10	104 \pm 3	0.60 \pm 0.09 ^C	0.27 \pm 0.04 ³

^a Reported data are $\bar{X} \pm$ SD for at least three trials. Mean values having the same superscript are not significantly different ($p < 0.05$). Statistical analysis are made independently for WVTR and permeability for each type of support. ^b Thickness calculated by eq 1.

transfer (%). Subscript s denotes the support and subscript f the hydrophobic film. The WVTR values are expressed in g m⁻² s⁻¹. Effectiveness of the emulsified and dipped filter paper films is similar, ranging from 25 to 38%.

For coated emulsified plus coated and dipped films the permeability of the coating layer can be evaluated by the equation

$$\frac{l_t}{P_t} = \frac{l_1}{P_1} + \frac{l_2}{P_2} \quad (5)$$

where l is the thickness (m), P is the permeability (g m⁻¹ s⁻¹ Pa⁻¹), the subscript t denotes the coated films, and subscripts 1 and 2 denote, respectively, the support and the coating layer.

The calculated permeabilities (from eq 5) for paraffin wax in the emulsified plus coated and in the dipped cellophane films are 0.18×10^{-11} and 0.06×10^{-11} g m⁻¹ s⁻¹ Pa⁻¹, respectively. This difference means that the paraffin wax is more efficient over a nonporous support than over an emulsified one. The calculated permeability of the paraffin oil in dipped cellophane is 15.1×10^{-11} g m⁻¹ s⁻¹ Pa⁻¹, showing that the liquid hydrophobic material is about 100 times less efficient than the solid material.

Results of measured WVTR, permeabilities, and contact angles are regrouped in Tables II and III for each type of support. The highest WVTR and permeabilities correspond to the smallest contact angle value, as expected for the polar supports (methylcellulose and cellophane).

For the porous filter paper, the contact angle cannot be measured because water droplets are instantaneously absorbed. For the dipped filter paper films, even if the surface possesses a strong hydrophobicity, the WVTR and permeability values are high due to its porosity, but they do not limit moisture transfer as effectively as the dipped cellophane in paraffin wax.

(b) *Influence of Film Preparation Technique.* Results are discussed only for paraffin wax films. Four different preparations were made (three techniques and four

supports). The best efficiency in retarding vapor transfer is obtained with emulsified plus coated and dipped cellophane films (Tables II and III). This behavior can be explained by the repartition of the paraffin wax in a continuous layer, limiting moisture transfer, as seen from the scanning electron micrographs (Figures 3c and 4b).

In the other preparations paraffin wax disperses in the form of droplets in the emulsified film with methylcellulose or fills the pores of the dipped filter paper (Figures 3a,b and 4a).

The surface of emulsified films is clearly irregular (Figures 3b and 4a) with spherical masses that are obviously not well incorporated into the bulk of the film. This nonuniform surface might be responsible for the higher WVTR compared to the uniform distribution observed for the emulsified plus coated and for dipped cellophane film. Measurement of the film thickness with the micrometer is influenced by the roughness of the surface; it is nearly 2 times higher than the one obtained from SEM. The elevated spots on the films stop the micrometer and explain the high readings.

Moisture transfer preferentially occurs through non-crystalline areas free of paraffin wax or through unfilled filter paper pores as pointed out by Fox (1958). Using the thickness obtained by SEM, the water vapor permeabilities of the emulsified films are smaller than that of the support but they are not significantly different ($p < 0.05$).

Our results are in agreement with those of Schultz et al. (1949); their laminated film of LM-pectinate with paraffin wax was more efficient than the emulsified one (at 81–31% RH; 9 and 170 g m⁻² day⁻¹ for the coated film and the emulsified one, respectively).

Nevertheless, Kamper and Fennema (1984a) have shown that emulsified films are more efficient than laminated ones for a palmitic and stearic acid blend used as the hydrophobic substance. These fatty acids may give a homogeneous emulsion forming a film with a good repartition of fatty acid droplets compared to the fatty acids

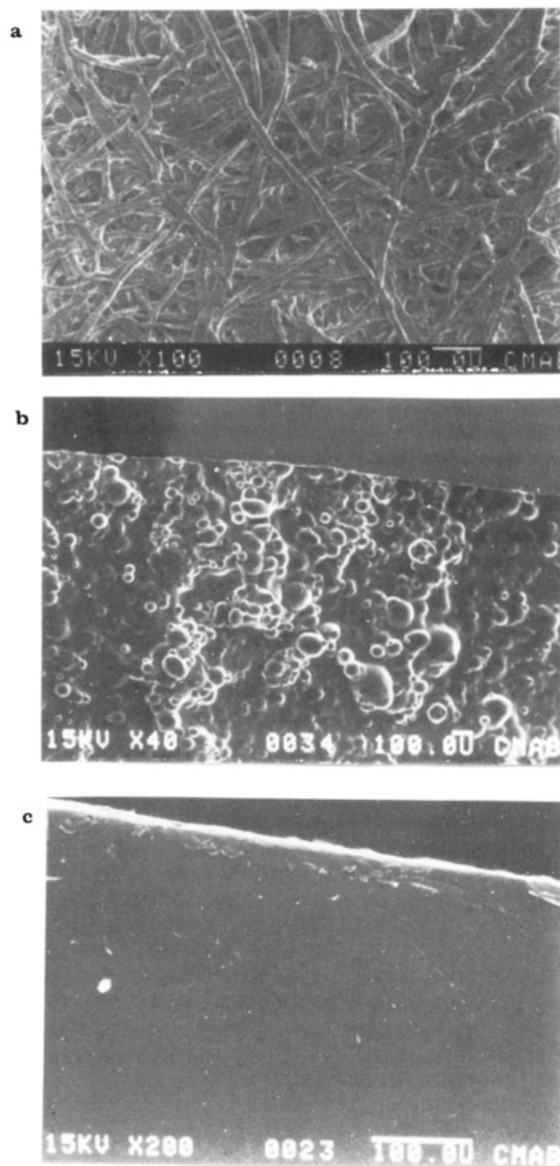


Figure 3. Electron micrographs of hydrophobic paraffin wax films surfaces: (a) dipped filter paper; (b) emulsified; (c) dipped cellophane. Electron beam is directed normal to the surface. White bars represent 100 μm .

in laminated films that solidify forming spangles which are less efficient in their case.

Therefore, the polarity and the structure of the hydrophobic substance have an important effect on the efficiency of the emulsified films.

(c) *Influence of Support.* A support can be used to study the efficiency of hydrophobic substances against moisture transfer, and it allows the preparation of films with materials that are not film forming. The coated support can be also considered as a "food model covered with a protective material". Considering the structure of the support, it allows the study of the interactions like adhesion that may occur between the protective material (coating) and food.

The structure of the support influences the repartition of the hydrophobic substances, as described previously for paraffin wax. The same results are obtained for paraffin oil, with emulsified films and with the porous support filter paper: the moisture transfer is not greatly retarded.

At the same surface density, hydrophobic protective materials are not as efficient over a porous support as over

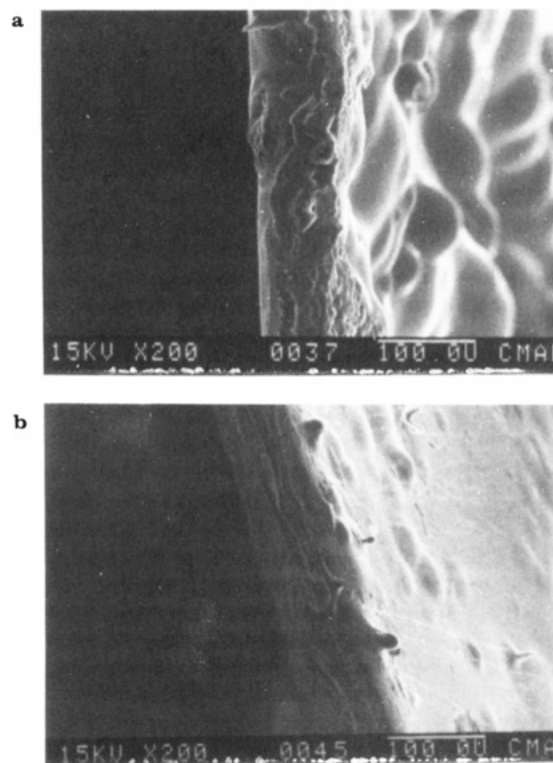


Figure 4. Electron micrographs of (a) emulsified and (b) emulsified plus coated paraffin wax with electron beam directed at 45° to the surface. White bars represent 100 μm .

a nonporous one; a paraffin wax continuous layer not imbibed in the support retards 100 times the moisture transfer (Figure 3a,c). The decrease of moisture transfer through dipped cellophane in paraffin oil is not as important as for paraffin wax. It seems that the fluidity is an important factor as pointed out by Kamper and Fenema (1984a). In the liquid phase the water-vapor transfer is more important than in the solid phase, as we have verified for the efficiency of dipped cellophane films.

In conclusion, some factors appear to be very important in the film preparation technique as they affect the efficiency against the water-vapor transfer.

(1) In the emulsion technique the high difference of polarity between support and hydrophobic substances used does not allow the formation of a stable emulsion. After drying, the nonhomogeneous repartition of substance cannot efficiently limit the water-vapor transfer as confirmed by SEM.

(2) In laminated or dipped cellophane films a continuous layer of a solid substance constitutes an efficient barrier against water-vapor transfer.

(3) The structure of the support would tend to modify the efficiency of the hydrophobic substance to retard moisture transfer. In porous filter paper, the paraffin oil or wax fills the pores, but the transfer occurs through the fibers free of the paraffins.

For practical application, interactions between film and food (normally porous) could induce a modification of the efficiency of the film-forming materials.

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