Permeability of Amylose Film to Moisture Vapor, Selected Organic Vapors, and the Common Gases

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Amylose, the linear starch fraction, has been reported as a raw material useful for preparation of self-supporting films (*4*, *14*, *22*). Exploitation of such a use is, of course, dependent on the economical production of amylose. Most common starches contain approximately 1/4 amylose and 3/4 amylopectin, the branched fraction (*10*). In the past few years the breeding of a hybrid corn containing 50 to 80% amylose (*5*, *13*, *23*) in the starch has renewed interest in the potentialities of amylose as a raw material for such industrial uses as films and fibers. A large proportion of all types of commercially produced films now are used for packaging, such as wrapping, liners, and bags. The value of amylose films in such applications is dependent, in part, on their permeability characteristics, for which data have been obtained in the present studies.

The most important permeability factors in packaging foods and drugs are water vapor and gas permeabilities. Successful packaging of any food product must take one or both of these factors into account—for example, respiration of fresh fruits and vegetables necessitates some permeability to carbon dioxide (*15*). Food products containing fat, such as roasted ground coffee and dried whole milk, are susceptible to spoilage by oxygen (*19*). In some instances another permeability characteristic assumes importance and must be taken into consideration in packaging foodstuffs. Permeability of films to organic vapors falls in this category. This factor is of interest because of its relation to possible losses or retention of flavor and odor constituents of packaged materials.

Studies carried out in work on amylose films include determinations of water vapor transmission at various relative humidity gradients; measurements of permeability to vapors of selected organic acids, alcohols, ketones, aldehydes, and esters; and determination of permeability to nitrogen, oxygen, air, carbon dioxide, ammonia, and sulfur dioxide.

EXPERIMENTAL MATERIALS

Test Films. Both lacquered and untreated (*22*) amylose films were used for permeability measurements. Data on amylose films were compared with results obtained on the following commercial films:

1. Nonplasticized, nonmoistureproofed, non-heat-sealing cellophane (Du Pont PUT-0, No. 300).
2. Plasticized, moistureproofed and semimoistureproofed, heat-sealing cellophane (Sylvania MS-1 and DS-2, No. 300, respectively).
3. Visqueen (polyethylene) Visking Corp.

Coating Composition. For coating amylose film the lacquers consisted of: a film former, nitrocellulose; a moistureproofing agent, paraffin wax; an ester gum for blending; and a plasticizer to give flexibility to the coated film. A mixture of organic solvents was used to maintain these solids in solution. A typical composition (*3*) in which total solids were 10 grams in 90 grams of solvent mixture, was as follows:

Solid Constituents	% Based on Total Weight of Solids
Hercules nitrocellulose (Type R.S. 1/2 second or SS 1/2 second)	35 or 52
Ester gum (acid No. 5-9, m.p. 95°-105°C.)	52 or 35
Tricresyl phosphate or dibutyl phthalate	10
Paraffin wax (m.p. 56°-8° C.)	3

Solvents	% Based on Total Volume of Solvents
Ethyl acetate	62
Toluene	27
Ethyl alcohol	9
Butyl acetate	2

Test Gases and Liquids. All gases used, except air, were purchased in commercial cylinders. The purities quoted by the manufacturers varied from 99 to 100%. Organic liquids for the vapor permeability measurements either conformed to ACS specifications or were redistilled before use.

APPARATUS AND METHODS

Coating Procedure. Lacquered films were prepared by immersing the films in a mixture of the desired composition and drawing them through a metal slit set at 0.0045-cm. opening to remove the excess solution and leave a uniform residual coating. Films were then dried at 70° C. for 2 hours in an oven through which air was circulated at a slow rate. A flexible, nontacky, odorless, and durable coating was obtained which did not peel or rub off. Portions of the coated films selected for testing had no blushing spots or greasiness and were uniform in appearance. The coating of moistureproofed amylose films was approximately 0.00075 mm. thick (total both sides), but was not always uniformly applied, as indicated by results of water vapor permeability tests.

Water Vapor Permeability. Two types of aluminum cups (*16*) were used. One was 5.4 cm. deep and the other 1.9 cm., and both had an inside diameter of 6.3 cm. The wax sealing the test film to the cup was a mixture of equal parts of crude beeswax and gum rosin. For defining the test area (0.0035 sq. meter) and effecting the wax seal, a template was used (*1*).

Desiccators (top inside diameter of 25 cm.) served as the test chambers. A fan operated inside the desiccator at 1200 to 1400 r.p.m. was used for circulation. The fan blades were approximately 3.6 cm. above the test films. For the same determination like values were obtained in the various desiccators using the two types of cups.

Constant relative humidity was maintained in the test chamber and in the cup by use of inorganic salts and their saturated solutions. The desiccant was 8-mesh anhydrous calcium chloride, 1% RH (*9*). Saturated solutions of magnesium nitrate, 53% RH (*20*), ammonium sulfate, 81% RH (*8*), and calcium chloride, 29% RH (*12*) were used. The desiccant in the cup was placed about 0.14 cm. from the film. This distance was increased to about 1 cm. when humidity conditions were reversed and water or a saturated salt solution was used in the cup. This change prevented direct contact of water with the film during handling.

Water vapor permeability measurements were made in a constant temperature room (25° ± 1° C.). After assembly, the cups were weighed and placed in a desiccator. The cups were removed at intervals and weighed. Each experiment extended from 1 to 2 days. This assured equilibration of cups in the test chambers and a constant rate of transmission of water vapor for test films. A removable aluminum disk covered the test films during weighings.

Organic Vapor Permeability. The experimental procedure for determining permeability of films to organic vapors was essentially that of Simril and Hershberger (*17*). A Thwing Albert Vapometer cup was used with the test area of film specimens at 0.0032 sq. meter.

Cups were placed during the determination in a controlled temperature oven (35° ± 0.5° C.), through which air dried by bubbling through concentrated sulfuric acid and preheated at 35° C. was constantly circulated at a flow rate of 200 liters per hour.

Cups were filled with 50.0 ml. of the test liquid, loosely assembled, and placed in the test chamber. After 2 hours the cups were removed, the screws tightened in place, and the cups weighed, and then replaced. Additional weighings were made at appropriate time intervals. Experiments were carried on for 24 hours and calculations were made on the weight loss of the last 17-hour period when the rate had become constant. Earlier work showed little or no difference in the rate of loss on extending the test periods 48 and 72 hours.

Gas Permeability. The apparatus for determining gas permeability of the films was developed from specifications of Todd (*21*). It consisted of a metal cylindrical chamber of two parts (10- and 669-ml. volume), which faced against the test film and were bolted together. In order to assure gas-tight seals on the rubber gaskets between the metal and film surfaces a commercial sealer was used—a synthetic rubber-base compound that cured on admixture with an accelerator. Effective test area of film was the inside diameter (8.23 cm.) of the chamber.

Experiments were carried out according to Todd's "dry procedure" but at 25° C. The test period depended on how permeable the gas was to the film, varying from 3 minutes for an extremely high rate to 2 days for a very low permeability. Readings were made at regular intervals to determine if rate of transmission was uniform.

RELIABILITY OF RESULTS

An average number of trials of each permeability test was 6 for water vapor, 11 for organic vapor, and 3 for gas transmission. At best, permeability studies of sheet material are noted for their low order of precision and accuracy (*1*, *2*). Results obtained by any one procedure on several specimens from the same sample sometimes differed as much as 10% from their average—in a few cases more. Therefore, two significant figures were sufficient to characterize the samples. Average trends of permeability measurements were definite and are useful both for indicating the order of magnitude and for comparative purposes.

VARIATIONS IN EXPERIMENTAL PROCEDURE

Effect of Air Circulation. Schultz, Miers, Owens, and Maclay (*16*) report that water vapor permeability of their films was reduced 18% when air circulation was decreased on the higher humidity side of the film. In the runs reported here no significant difference was observed between results obtained at 1100 and 2400 r.p.m. In some organic vapor tests a fan was operated inside the oven at approximately 1500 r.p.m. to promote further circulation about the cups. The order of magnitude and the reproducibility of results were not changed by this modification. However, effect of circulation is demonstrated by differing water vapor permeability values (compare columns 7 and 8 with 9 and 10 in Table II) obtained when positions of water and desiccant were reversed. The increased permeation of water through the film when the atmosphere outside the cup was humid is attributed to the improved circulation of moist air, which caused more water molecules to encounter the film surface.

Effect of Area of Film Exposed. In a few experiments the exposed area of the test film was restricted to one tenth of the full aperture by the use of aluminum disks. The permeability rates of water vapor per unit area of surface increased 42% above those obtained when the normal area of the film was exposed. The salt in the cup was not in direct contact with the film surface. Narrowing the aperture of the test area, therefore, made available a larger surface area of desiccant per unit area of film tested, which probably improved equilibrium conditions at the surface of the desiccant and caused the increased rates. Previous workers (*16*) also observed similar phenomena. They found a restricted test area (one tenth of full aperture) increased their results by 12 to 25%. The higher values are not reported in Table II, as the larger test area was chosen for measurements [recommended in ASTM procedure E 96-53T (*1*)].

Effect of Film Thickness. Laboratory batch-cast amylose film was not as uniform as commercial cellophane; therefore, the effect of thickness was examined. Table I shows that film thickness of amylose affected permeabilities of both vapors and gases. Although in some cases differences were within limits of reproducibility, the trend appears definite. Transmission rates on a weight or volume basis, as expected, decreased with increasing film thickness. However, variability may also be noted in the permeability constants which supposedly correct for film thickness. Such variation indicates the limitations in use of this constant, which are reported consistently because of its use by others in the field.

Table I. Relation of Film Thickness of Amylose to Permeability to Vapors and Gases

	Film Thickness, Mm.	Grams/Sq. M./24 Hours	$P^a \times 10^{13}$
Methanol vapor (0% RH)	0.028	510	25
	0.032	410	23
	0.038	330	22
1-Butanol vapor (0% RH)	0.026	13.0	4.0
	0.029	9.4	3.2
	0.030	7.1	2.5
Water vapor (50% RH)	0.027	240	330
	0.028	230	340
	0.029	210	320
Water vapor (100% RH)	0.015	1700	680
	0.019	1500	790
	0.020	1500	800
Carbon dioxide (0% RH)	0.016	240^b	26^c
	0.027	220^b	40^c

[a] P (permeability constant) moles/sq.cm. area/cm. thickness/sec./cm. Hg vapor pressure difference.
[b] Ml./sq.m./24 hours.
[c] $P \times 10^{17}$.

EXPRESSION OF RESULTS

Such factors as thickness, the relative size of area of film exposed, temperature, pressure difference across the film, and the speed at which test vapors or gases circulated affect

Table II. Permeability of Films to Water Vapor at 25° C

		Relative Humidity Difference							
		1 to 53%		29 to 81%		1 to 100%		1 to 100%[a]	
Test Film	Film Thickness Mm.	Grams /sq. m./ 24 hours	$P^b \times 10^{13}$	Grams /sq. m./ 24 hours	$P^b \times 10^{13}$	Grams /sq. m./ 24 hours	$P^b \times 10^{13}$	Grams /sq. m./ 24 hours	$P^b \times 10^{13}$
Amylose, untreated	0.026 to 0.032	230	340	1100	1500	3100	2700	1500[c]	760
Amylose, semi-moisture-proofed treatment	0.030 to 0.035	18	28	...	...	100	65	...	...
Amylose, moisture-proofed treatment	0.020 to 0.035	3.4	4.8	...	...	38	31	...	...
PUT-O, No. 300, cellophane, untreated	0.022	110	125	880	1000	2500	1500	1400	850
DS-2, No. 300, cellophane, semi-moisture-proofed treatment	0.027	25	34	43	61	98	84	110	84
MS-1, No. 300, cellophane, moisture-proofed treatment	0.027	5.7	8.2	16	23	62	46	51	37
Visqueen, polyethylene, untreated	0.040	3.0	6.8	...	...	21	21	...	...

[a] Water instead of desiccant placed in cup and anhydrous $CaCl_2$ in desiccator.
[b] P (permeability constant) moles/sq. cm. area/cm. thickness/sec./cm. Hg vapor pressure difference.
[c] Amylose film was 0.018 mm. thick in this case.

Table III. Permeability of Films to Organic Vapors at 35° C.[a]

	Amylose, Untreated				PUT-O, No. 300, Cellophane, Untreated[b]	
Organic Vapor	Vapor pressure 35° C., cm. Hg[c]	Film thickness, mm.	Grams /sq. m./ 24 hours	$P^d \times 10^{13}$	Grams /sq. m./ 24 hours	$P^d \times 10^{13}$
Methanol	20.4	0.030	470	25	1700	65
Ethanol	10.4	0.034	7.1	0.58	9.9	0.53
1-Propanol	3.74	0.031	5.4	0.86	9.3	1.1
1-Butanol	1.31	0.031	6.8	2.5	7.5	2.0
Acetic acid	2.67	0.037	2.1	0.56	3.7	0.59
Ethyl acetate	16.5	0.031	18	0.44	18	0.32
Acetone	34.6	0.026	23	0.34	32	0.41
Carbon tetrachloride	17.6	0.032	12	0.16	18	0.17
Benzene	14.8	0.026	24	0.63	26	0.57
Benzaldehyde	0.16[e]	0.038	3.1	8.0	2.8	4.1

[a] Dry test conditions.
[b] Film thickness for cellophane 0.022 mm.
[c] (7)
[d] P (permeability constant) moles/sq. cm. area/cm. thickness/sec./cm. Hg vapor pressure difference.
[e] (9), p. 223.

greatly the permeability of films. These are well established in the literature for all types of organic films. To facilitate a direct comparison for all films under various test conditions most workers express results in terms of a permeability constant (*6*, *11*, *16*). In the present investigation constant *P* is defined by the equation:

$$P = \frac{Ql}{at\,\Delta p}$$

where *Q* is the quantity of vapor or gas which permeates a film in time *t*, *a* is the area of film exposed, *l* is the film thickness, and Δp is the vapor pressure difference across the film. The units for this expression are like those cited by Simril and Hershberger (*17*, *18*)—that is, for a given temperature, *P* is expressed in number of moles of vapor or gas passing through 1 sq. cm. of film, having a thickness of 1 cm., per unit of time of 1 second, per 1-cm. (mercury) pressure difference, and is reported as $P \times 10^{13}$ for vapors and $P \times 10^{17}$ for gases. Permeability data are also reported in units recommended by ASTM procedure E 96-53T (*1*). The transmission rate is recorded in the tables as grams of vapor passing through 1 sq. meter of film in 24 hours (milliliters in the case of gases). Reporting values in this fashion gives an assessment of the quantity (weight or volume basis) of vapor or gas passing through an area of film in a given time. This aids a practical evaluation of permeabilities of amylose film in determining its usefulness as a packaging material.

RESULTS

Values for permeability to water vapor of amylose and the selected commercial films are shown in Table II. Both treated and untreated amylose film gave transmission rates of the same order of magnitude as similar films of cellophane. This is corroborated under various relative humidity differences. Permeability of test films is greater in moist regions than in drier atmospheres, as substantiated in Table II where equal vapor pressure differences, but different humidity levels, are shown in columns 3 and 4 compared with 5 and 6. However, permeability of amylose film to water vapor is reduced approximately 77 times by a supplementary moistureproofing coating. The values obtained (Table II) for coated amylose film are within the range found for polyethylene and moistureproofed cellophane. The favorable results with the one-coating composition tried, indicate that more extensive experimentation and varied moistureproofing compositions known to the trade could be applied with success.

Similarity of amylose film to cellophane is further emphasized by permeability values of the same order of magnitude obtained by use of various selected organic vapors (Table III). Methanol appears to be the single exception, it permeates amylose film considerably more slowly than cellophane. Table III perhaps illustrates the best instances of the manner in which the calculated permeability constant is useful in expressing results in a standardized comparative fashion. Thus, adequate cognizance for comparative purposes can be taken of such factors as the relatively high molecular weight of carbon tetrachloride and the low vapor pressure of benzaldehyde. On this basis permeability constants of the films to benzene, ethyl acetate, acetic acid, acetone, and carbon tetrachloride were low. Methanol permeated the films at a high rate; ethanol passed through much more slowly and at a rate comparable to that of compounds listed above; propanol, butanol, and benzaldehyde permeated faster than ethanol, increasing in the order named.

The permeability of untreated amylose and cellophane films to six gases is given in Table IV. Tested dry, both amylose and cellophane are very permeable to ammonia and sulfur dioxide, and considerably less so to carbon dioxide, and have extremely low permeabilities to nitrogen, oxygen, and air. The values for nitrogen, oxygen, and air should be construed chiefly as indicative of the order of magnitude, since they approach the limit of sensitivity of the apparatus and procedure employed. But here again as with water vapor and organic vapors, the similarity of values of gas permeabilities for both amylose and cellophane shows the likeness of physical characteristics of the two membranes.

Table IV. Permeability of Films to Various Gases at 25° C.[a]

	Amylose, Untreated			PUT-O, No. 300, Cellophane, Untreated[b]	
Gas	Film thickness, mm.	Ml./sq. m./ 24 hours	$P^c \times 10^{17}$	Ml./sq. m./ 24 hours	$P^c \times 10^{17}$
Air	0.020	±0	±0	8	1.2
Oxygen	0.020	±0	±0	27	4.0
Nitrogen	0.027	±0	±0	3	0.46
Carbon dioxide	0.016	240	26	450	58
Ammonia	0.016	100,000	11,000	23,000	3,400
Sulfur dioxide	0.016	71,000	7,800	22,000	3,400

[a] Dry test conditions.

[b] Film thickness for cellophane 0.022 mm.

[c] P (permeability constant) moles/sq. cm. area/cm. thickness/sec./cm. Hg pressure difference.

DISCUSSION

Mechanisms for passage of molecules of vapor or gas through films have been effectively summarized (*6, 11, 17, 18*). The mechanism that appears predominant in interpreting present data can be related to the absorption and solubility of vapors or gases by organic films. Molecules which are structurally similar to the film—that is, containing like functional, polar, or nonpolar groups—are more readily absorbed or dissolved by the organic polymer; they expedite a weakening or even disruption of the intra- and intermolecular secondary bonds of the film, and leave on the other side of the "weakened" film by evaporation. As a result the resistance to permeability of the film is lowered. For example, the active centers of hydroxyl groups of repeating anhydroglucose units present in amylose films show greater affinity to hydroxyl groups of water vapor than do films of an unlike structure, such as polyethylene. The effect of structural similarity on the passage of water vapor through amylose film is further exemplified by attainment of lower permeability rates when the film surfaces are coated with the structurally unlike composition wax (Table II).

Polar molecules such as ammonia and sulfur dioxide should be expected to dissolve more readily in a polar substance like amylose film. This is indicated by their higher permeabilities as compared with other test gases. Likewise, it should be predicted that under dry test conditions nonpolar gases like oxygen, nitrogen, and air would have the lower permeabilities values, as found (Table IV). However, on the basis of polarity, carbon dioxide appears to permeate the film at a much greater rate than other nonpolar gases. The same effect has been observed by other workers (*18*). They found that those gases which are most easily condensed (hydrogen sulfide and carbon dioxide) dissolve more readily in films than do the gases that are difficult to condense (hydrogen, oxygen, and nitrogen). The low permeability values found for nonpolar gases, oxygen, nitrogen, and air indicated that amylose is a structurally compact film free of existing submicroscopic holes, or the equivalent.

Generally speaking, the more polar alcohols permeated the films more rapidly than the less polar ketones, esters, and halogenated hydrocarbons. Perhaps a chemical combination to give acetals or some oxidation of the benzaldehyde were complicating factors accounting for the higher permeability shown by this compound. No explanation is at hand for the higher than expected permeation of benzene through the films.

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