Permeation properties of moisture sensitive barrier materials under end use conditions

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ABSTRACT: Standard methods for permeation tests do not measure the increased effectiveness to oxygen permeation at low relative humidity of today's high barrier materials. Studies of gas permeation at refrigerator and freezer conditions of new amorphous blends show barrier properties comparable to amorphous nylon alone. Film structures containing optimized blends should therefore maintain modified atmospheres of nitrogen and carbon dioxide under meat case conditions more economically. This presentation also examines barrier behavior of ethylene vinyl alcohol copolymers in monolayer and coextruded film structures.

KEYWORDS: Barriers, carbon dioxide, end use, EVOH polymers, humidity, moisture barriers, nylon, oxygen, penetration, permeability, polyamides, standards, temperature.

Product development, marketing, and packaging play key roles in the success of a new food product. A food processor must meet consumer demands for innovative products in a relatively short time. Consumers want the best value for their money and rate this aspect higher than resealability, convenience, recyclability, and tamper proof evidence.[1] Developing suitable packaging should therefore lead to a value added system—one which saves money and retains product integrity.

An informed decision regarding the efficacy of a package will consider the barrier properties. Barrier testing of such a packaging system is only valid under end use conditions. Often barrier testing with oxygen and carbon dioxide permeation are involved.

A very important consideration in the design of a barrier packaging material using a coextruded structure is the correct placement of the barrier layers. This can significantly increase the shelf life of a food product.

Permeation studies under refrigerator and freezer conditions of 0–5°C with greater than 95% RH indicate that an amorphous nylon blend can outperform current systems. Nylon and polyvinylidene chloride (PVDC) coextruded film structures containing an optimized ratio of these components should maintain modified atmosphere packaging (MAP) under freezer conditions more economically than previously expected. This has a direct impact on packaging for the meat and cheese markets.

Extremely careful examination of ethylene vinyl alcohol (EVOH) copolymers indicates minimum oxygen permeation at 50% RH compared to values previously reported for 0% RH conditions. A dry snack food or a hot fill container with this EVOH barrier should therefore exhibit enhanced shelf life performance not previously anticipated during normal distribution and storage of these foods.

This paper will review the barrier behavior of an amorphous nylon and an EVOH in monolayer and coextruded films. It will show that the benefits of using the amorphous nylon blend for refrigerator and freezer conditions and of using the EVOH for shelf stable foods add value to food product packaging.

Testing conditions

Barrier testing at the expected storage conditions of a food product help to predict the anticipated shelf life more accu-

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[1]Ashton, R., Packaging, 36(7): 32(1991).

I. Testing conditions for food

Food	Storage & testing conditions	Processing	Shelf life, years
Soups, low acid, vegetables	Shelf, 30°C 80% RH	Retort 121°C Sterilization Some aseptic	2+
High acid, condiments, deserts	Shelf, 30°C 80% RH	Hot fill 85°C Pasteurization	0.5–2
Juices, sports drinks	Shelf, 30°C 80% RH	Hot fill 80°C Aseptic	1–2
Juices, beverages	Refrigerator, 0–5°C, 95% RH	Aseptic Cold fill	0.1–0.5
Meat, cheese, entrees	Refrigerator and freezer, -15–0°C, 95% RH	Cold fill	0.1–0.5

II. Amorphous nylon and nylon 6 blends

Sample	Amorphous nylon, %	Nylon 6, %
A	100	0
B	80	20
C	50	50
D	30	70
E	20	80
F	0	100

III. Oxygen permeation values for nylon blends, cc–mil/100 in.²/day–atm

Sample	Relative Humidity, % 0	50	80	100
A	3.8	1.7	1.7	1.8
B	3.9	2.0	2.3	4.3
C	3.9	2.0	3.2	7.5
D	3.9	2.0	3.5	11.0
E	3.9	2.2	4.4	14.0
F	4.0	2.5	6.5	15.0

rately. The particular storage conditions of any food product will determine the actual testing conditions. **Table I** provides examples of testing conditions for various food types.

A shelf stability standard of 30°C at 80% RH is realistic, if the product experiences warehouse storage or transportation in unrefrigerated trucks. A symmetrical coextruded structure containing a wet food product, i.e., 100% RH on the inside and 50% RH on the outside, reaches a steady state equilibrium of 80% RH. A refrigerated food product experiences 0–5°C at 95% RH for symmetrical or asymmetrical coextruded structures. Freezer conditions are generally –10°C at 95% RH.

Nylon blends

The amorphous nylon in this study contains hexamethylenediamine, isophthalic acid, and terephthalic acid. There were six blends as shown in **Table II.**

The oxygen permeation values (OPV) of this amorphous nylon improve as relative humidity increases. This unique phenomenon is most likely due to water molecules filling the free volume in the microvoids, since the polymer is mainly hydrogen bonded.

There are other beneficial properties for this amorphous nylon in addition to the improvement in oxygen barrier. Amorphous nylon exhibits a 20% improved extruder output compared to nylon 6 or nylon 66. Improved deep draw thermoforming is also possible because of the excellent melt strength of the amorphous nylon. Another benefit is UV protection from the fluorescent lamps which are commonly found in a supermarket meat display to make meat more visually appealing to the consumer.[2]

A blend of the amorphous nylon with nylon 6 retains the properties of amorphous nylon while reducing the cost of the package. In addition, the blend gains the mechanical properties of nylon 6.

Amorphous nylon blends exhibit a minimum OPV at 50% RH. Previous data had placed the minimum at 80% for amorphous nylon and nylon 6 blends. This new minimum arose during testing after extended drying of the test blends. The refrigerated conditions of 0–5°C at 95–100% RH had an improvement in oxygen barrier of more than five times that of the 30°C values as shown in **Fig. 1.** The data also indicate that at 30°C the blend containing 30% amorphous nylon is sufficient, since no significant gain in OPV occurs with increased amounts of amorphous nylon. **Table III** shows the oxygen permeation values of monolayer blown film at 30°C.

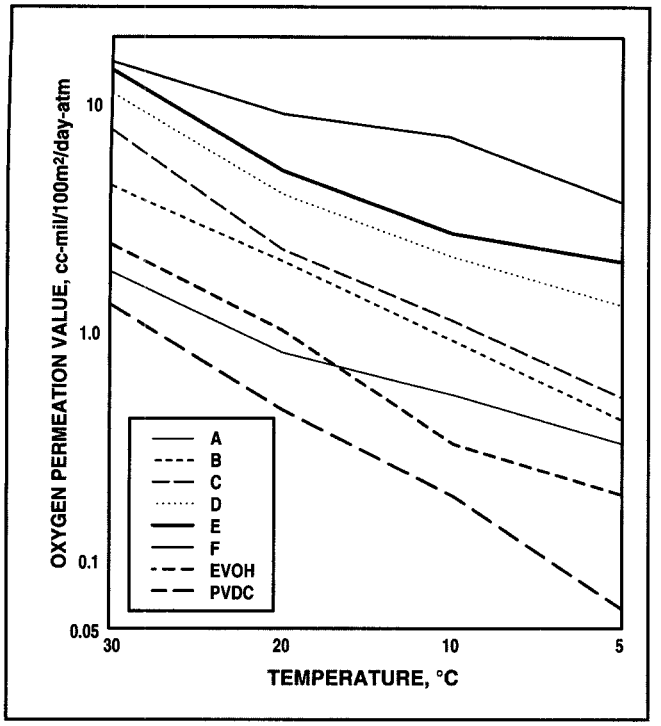
The carbon dioxide permeation values show a ten–fold improvement for amorphous nylon over nylon 6 indicated in **Fig. 2.** Carbon dioxide barrier information is useful for evaluating potential use in MAP.

Coextruded amorphous nylon barrier properties

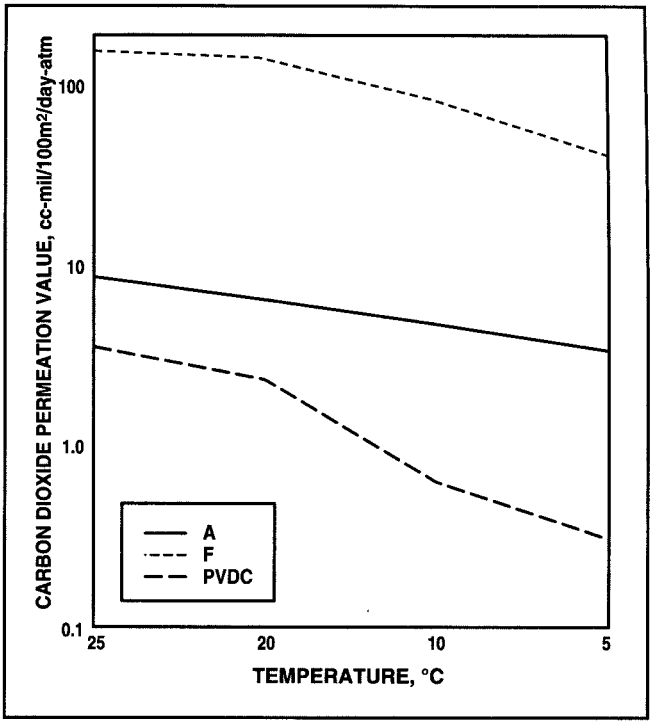
We conducted a trial simulating a typical meat or cheese package to determine the time necessary for the film samples to reach equilibrium and to measure the OPV at steady state conditions. The composition of the samples consisted of a five-layer, commercially blown, coextruded film. The layers were low–density polyethylene (LDPE)/tie layer/blend of amorphous nylon and

[4]Broussard, R. A., personal communication.

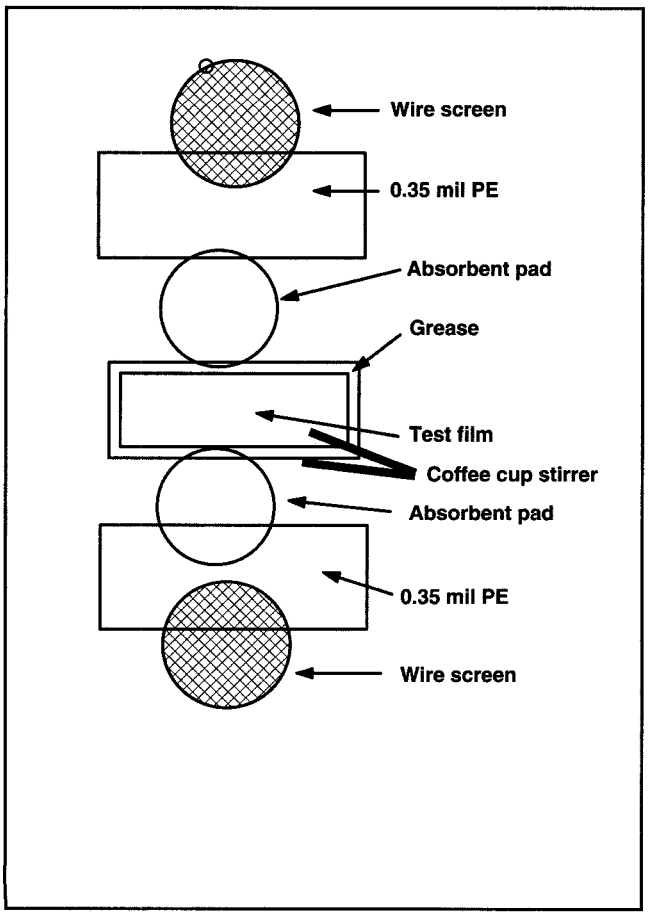
1. Effect of temperature on oxygen permeation value at 100% RH



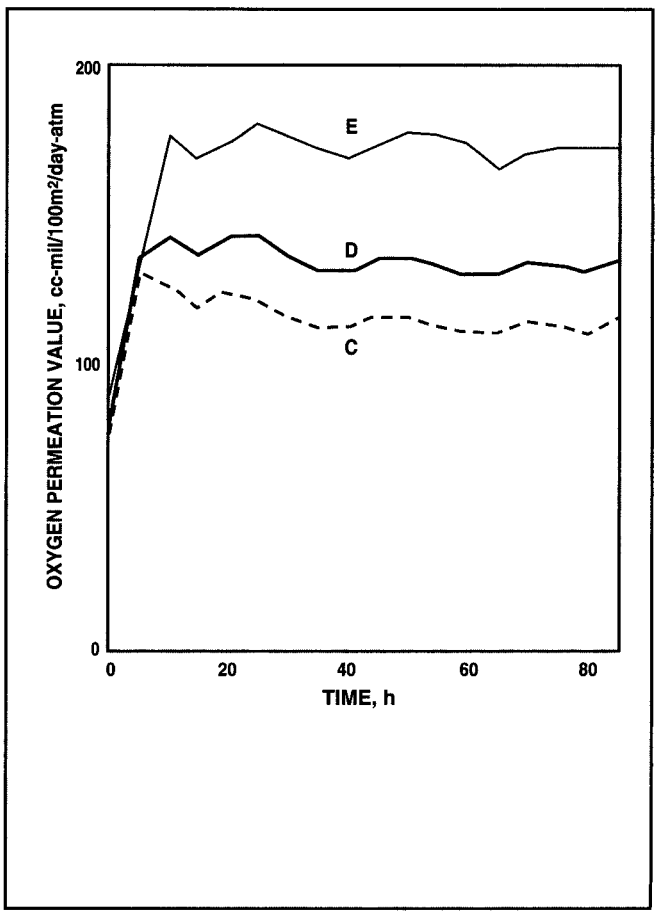
2. Effect of temperature on carbon dioxide permeation value at 100% RH



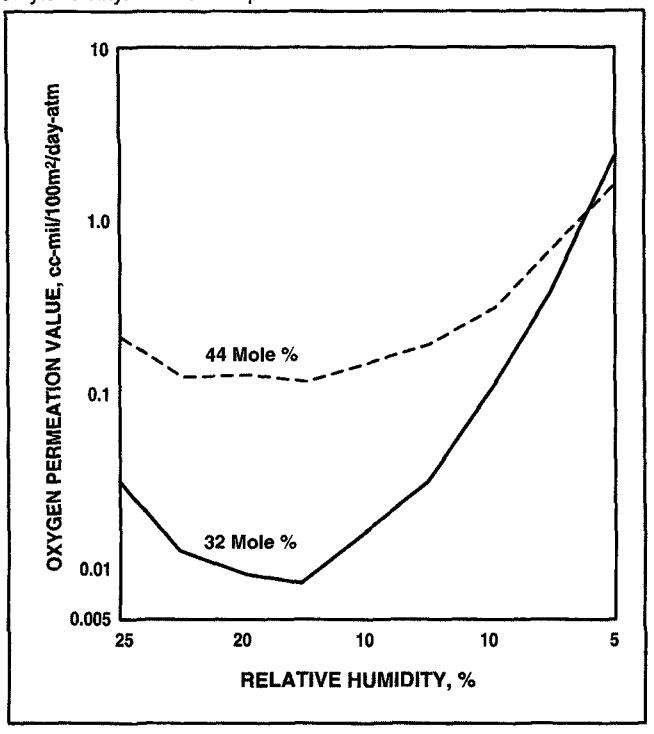
3. Dry sandwich simulating meat packaging



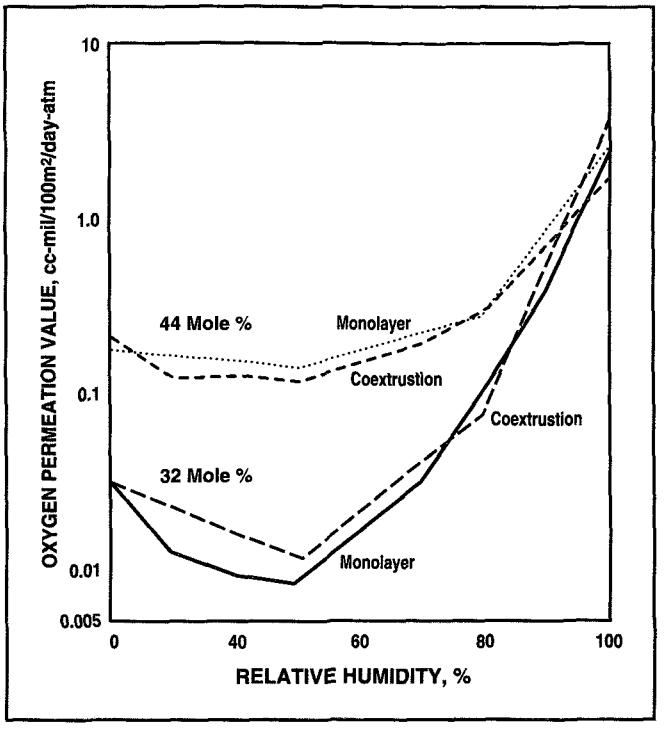
4. Oxygen transmission rate as a function of time at 30°C



5. Effect of humidity at 30°C on oxygen permeation values for ethylene vinyl alcohol samples



6. Effect of relative humidity at 30°C on oxygen permeation values for monolayer and coextrusion



IV. Oxygen permeation values for coextruded films, cc–mil/100 in.²/day–atm

Sample	Thickness, mils	5°C, 0% RH	5°C, 100% RH	30°C, 0% RH	30°C, 100% RH
1	1.2–1.3	1.0	0.47	2.7	8.8
2	0.9–1.1	1.1	0.65	3.3	10.0
3	1.2–1.3	1.1	0.75	3.7	11.0

V. Oxygen permeation values for coextruded ethylene vinyl alcohol samples, cc–mil/100 in.²/day–atm

Mole % ethylene	5°C, 0% RH	5°C, 100% RH	30°C, 0% RH	30°C, 100% RH
32	0.016	0.48	0.032	3.9
44	0.057	0.41	0.175	2.7

nylon 6/tie layer/ethylene vinyl acetate (EVA) copolymer containing 7.5% vinyl acetate.

The ratio of nylon 6 to amorphous nylon varied during testing. Testing involved placing three replicates of these coextruded films measuring 4 in. on each side in a nitrogen glovebox overnight. The test sample configuration was in the form of a dry sandwich to simulate a typical meat package. There were two plastic coffee cup stirrers between 0.35 mil polyethylene (PE) and the sample as indicated in **Fig. 3.** When the oxygen in the nitrogen glovebox was below 0.5%, distilled water was directed to the top and bottom of the sample through the coffee cup stirrers. This method simulated a dry film sample in contact with a wet piece of meat on one side and refrigerator conditions on the other side (both at 95–100% RH).

These tests employed commercially available equipment for oxygen transmission rate measurement. After activation of the tester and examination for leakers, the unit ran until there was a steady-state equilibrium.

The results from these tests were intriguing. The samples at 30°C reached equilibrium in 10–15 h as shown in **Fig. 4.** This relatively short amount of time indicated an accurate prediction of shelf life. The samples at 5°C reached steady state after approximately 24–30 h. **Table IV** shows the values for oxygen permeation.

The preferred blends from an economical as well as processing and barrier property points of view are therefore in the range of 20-30% amorphous nylon and 80-70% nylon 6.

Ethylene vinyl alcohol

EVOH is rapidly becoming the resin of choice for coextruded plastic barrier containers due to its excellent protection against permeation by various flavors, oxygen, and carbon dioxide. There are several grades of EVOH polymers that comply with Food and Drug Administration regulations for direct food contact. There is, however, a concern about the decrease in the oxygen barrier at high relative humidity. Burying the EVOH in an asymmetrical or symmetrical structure can avoid this phenomenon. The barrier

layer of a symmetrical structure with a wet (100% RH) food product inside and 50% RH outside room conditions will reach approximately 75–80% RH at equilibrium. There is a preference for asymmetrical structures to protect the barrier layer from a wet food product because of the oxygen barrier testing performed on monolayers.

In addition to the superb oxygen barrier properties of EVOH, a much less advertised benefit is the excellent flavor and aroma barrier qualities. The high degree of crystallinity of EVOH aids the inhibition of flavor permeation and sorption. Furthermore, EVOH preserves the vitamin content of packaged products.

Ethylene vinyl alcohol monolayer oxygen properties

Figure 5 shows OPV vs. relative humidity data at 30°C for materials containing 32 and 44 mole percentage ethylene. Both permeation curves exhibit a minimum OPV at approximately 50% RH. Previous studies of EVOH indicated the optimum value at 0% RH. An explanation of this phenomenon is that water molecules fill the free volume similar to that of amorphous nylon until 50% RH occurs. The water then plasticizes the polymer breaking the hydrogen bonds.

The benchmark study comprised a two-month period. Five replicate blown-film samples dried in a desiccator for three weeks. In previous studies, it is possible that samples were not completely dry. An EVOH sample conditioned in room air reaches 50–70% RH. It will not dry completely when mounted on the testing equipment before an artificial equilibrium occurs. To ensure steady-state at each condition, samples remained on the equipment for 3–4 days after drying while incrementally increasing from 10 to 90% RH. Measurements for 100% RH values used the sandwich method similar to that shown in Fig. 3 without the coffee cup stirrers. All experiments used a commercial unit employing mass flow controllers of wet and dry gases to achieve the proper relative humidity.

The data measured here will help determine correct placement of the barrier layer for optimum shelf life of a food product. Placement of the EVOH layer closer to the outside environment will provide longer shelf life.

Ethylene vinyl alcohol coextruded oxygen barrier properties

Unfortunately, monolayer data for EVOH is not realistic. Tests for effectiveness should judge the oxygen barrier of commercially produced structures. In this case, testing involved a symmetrical structure of linear low-density polyethylene (LLDPE)/tie layer/EVOH/tie layer/LLDPE. **Figure 6** shows a good correlation between the monolayer and coextruded results. The coextruded film samples also exhibited a minimum OPV at 50% RH. **Table V** shows specific OPV for the coextruded samples.

At 95–100% RH, EVOH is a less effective oxygen barrier. It should therefore only have use as the food contact layer for organoleptic reasons in this range. EVOH is an excellent food contact layer, however, because of its earlier noted low tendency to absorb critical flavorants in food products.

Conclusion

The right decision for a new innovative package is only possible using the proper permeation data. Our results show that amorphous nylon and nylon 6 blends lead to an economical packaging structure for refrigerator and freezer foods. A combination of features makes this application of such a blend very sensible.

Contrary to previous publications, EVOH exhibits a minimum OPV at approximately 50% RH for monolayer and coextruded structures. This new finding will facilitate application of the proper placement of the barrier layer in a coextruded structure for shelf stable food products. ■

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