Chapter 11

Performance of High-Barrier Resins with Platelet-Type Fillers

Effects of Platelet Orientation

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The use of platelet-type fillers, preferably fine particle size mica, in ethylene vinyl alcohol (EVOH) copolymers increases oxygen barrier performance approximately threefold. The benefit is ascribed to the increased diffusion path length (tortuous path) produced by the overlapping platelets. Typical polymer processing operations used in packaging lead to the preferred orientation with the platelets aligned parallel to the surfaces. An exception was found in a blow molded bottle test where nonparallel alignment gave minimum barrier improvement. This result is explained by the mismatched die swell between the structural and barrier layers of the multilayer parison. Changes in polymer rheology or the type of machine reduced or eliminated the problem and gave the expected barrier performance.

Plastics continue to expand into food packaging applications traditionally served by metal and glass containers. The oxygen barrier properties of the plastic food container is frequently a major consideration affecting its suitability for a specific application. Polymers used in packaging films and containers can be classified by their relative permeation to oxygen. Of the many classes of polymers used in packaging, only three can be designated as high barrier materials, i.e., those having an oxygen permeation value of less than 1 cm^3-mil/100 in^2-day-atm (Table I).

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Table I. Melt Processible High Barrier Resins

Resin	Oxygen Permeation Value*	
	Dry, 25°C	80% RH, 25°C
EVOH - 30 mole % E	.01	.11
EVOH - 44 mole % E	.09	.24
PVDC - high barrier extrudable	.15	.15
AN - copolymer (BAREX)	.8	.8

*cm^3 O_2-mil/100 in^2-day-atm

Among the high barrier resins, the ethylene vinyl alcohol (EVOH) copolymers are showing the most rapid growth. Familiar containers relying on EVOH oxygen barrier are the squeezable ketchup bottle and the single serving, shelf-stable and microwaveable entree container.

Introductory guides to the selection and use of fillers (1,2) generally start by classifying fillers according to shape classes such as spheres, cubes, blocks, flakes and fibers. The first three classes have shape or aspect ratios close to 1 and, therefore, cannot display orientation in polymer systems. Only flakes (or platelets) and fibers (needles) with significant aspect ratios can show orientation.

The most common reasons for adding fillers, especially high aspect ratio fillers, to polymers is to improve physical properties such as increased modulus (stiffness) or reduced creep.

In addition to this major use to improve mechanical properties, high aspect ratio flake-type fillers have been added to polymers for a variety of other purposes. They include improved thermal stability (3), high voltage resistance (4), electrical conductivity, radiation shielding (5) and optical and aesthetic effects (6).

High aspect ratio flakes or platelets have also been previously used to improve the gas barrier properties of low and medium barrier polymers (7,8).

The diffusion of small molecules in a polymer film can be described by Fick's first law of diffusion

$$J = -Ddc/dx \qquad (1)$$

which simply states that the flux of a gas permeating the film at a constant concentration or pressure differential will be inversely proportional to the distance the diffusing gas must travel. The addition of platelet fillers distributed in the polymer film can greatly increase this diffusion distance by creating a tortuous path for the diffusing species. A recent paper by Cussler, et al., (9) uses the more picturesque term "wiggle length" to describe segments of this pathway.

Several attempts have been made in the literature to model this system of platelets dispersed in a polymer film in order to predict the relative reduction in flux in a platelet filled system, J_o/J_n, where J_o is the flux measured with an unfilled film and J_n is the flux measured with the platelet-filled film.

An early model proposed by Prager (10) assumed random orientation of fillers of various shapes. His predictions showed that while platelets would give a greater improvement than cylinders or spheres, the relative improvement with a 20 volume % loading of randomly oriented platelets would yield only about a 40% reduction in permeability. This would be a J_o/J_n of 1.67.

There have also been models based on very regular arrays of the platelets distributed in a film matrix. An early model proposed by Barrer (11,12) modeled the system as a uniform dispersion of a lattice of rectangular parallelepipeds. Using this model, Murthy (13) calculated that a large reduction in permeation could be achieved with a platelet filler volume of 20%. A sample calculation from data in the latter paper predicted that 20 volume % of a platelet filler having a long dimension of 5 microns and a thickness of 0.1 micron would yield 144 layers of platelets in a 50 micron membrane. There would be a spacing of .32 micron between layers of platelets with a 1.0 micron separation between the rectangular platelets in a layer. The calculated ratio of the diffusion coefficient of the filled composite to that of the matrix is 0.04. This represents a J_o/J_n of 25.

A recent paper by Cussler, et al., (9) using a regular array model also predicted quite high barrier improvements. Their equation (Equation 2) predicted that aspect ratio and volume fraction of filler would be the major variables. They incorporated a universal correction designated, μ, as a geometric factor to correct for the reality that available platelet fillers were not shaped like uniform rectangular parallelepipeds of uniform size and shape.

$$J_o/J_n = 1 + \mu\alpha^2(\phi^2/(1-\phi)) \qquad (2)$$

Substituting values in the Cussler equation, which we will show later to be in a practical range, of 12 volume % loading (ϕ) of a filler having an aspect ratio of 23 (α) and assuming an ideal geometric factor of 1 would predict a relative barrier improvement, J_o/J_n of 10.

There are very few reports in the literature documenting the improvement in gas barrier properties that can be achieved using commercially available platelet-type fillers in melt processed polymer films and none showing the improvement in that class of polymers previously identified as high barrier polymers.

Some of the best data on a practical system is that of Murthy, et al., (13) based on blends of talc in polyethylene and nylon films. Their data demonstrated relative barrier improvements (J_o/J_n) of 1.8-1.9 using filler loadings in a practical range of about 12 volume %.

EXPERIMENTAL

There are basically only three types of platelet-type fillers which can be considered for use in thin barrier films. These are aluminum flake, mica and talc (Table II). Other types of platelets, such as glass, stainless steel or brass flakes and certain aluminum silicate minerals, such as kaolin clay, are either too large in particle size or have too low an aspect ratio to be useful. With these three preferred fillers, comparable particle size products can be obtained by selection of appropriate grinding and size classification techniques. The 7 micron average platelet diameter is a good median particle size for blending into polymers designed for extrusion into thin films and layers in coextrusions.

Table II. Representative Platelet-Type Fillers

Type Supplier Grade	Al Flake Reynolds Metal Co. 40XD	Mica Franklin Mineral #3 MICROMESH	Talc Pfizer MP 12-50
Screen Analysis	99.5% <325	100% <400	100% <400
Average Part Diameter μm (D)	7	7	7
Platelet Thickness μm (T)	0.2	0.3	1
Aspect Ratio D/T	35/1	23/1	7/1
Density, g/cc	2.7	2.77-2.88	2.7-2.9
Price, $/lb	4.00	.30	.06
Price/EVOH Volume Equivalent	9.00	.70	.14

Table II shows that there are major differences in aspect ratio and cost between these three fillers. The relative costs of the barrier enhancing platelets and the matrix resin are a major consideration for the practical viability of this approach. The bottom row of this table shows the price of filler on a volume basis assuming it is displacing an equivalent volume of EVOH resin. A price of $2.40/lb was assumed for the EVOH resin.

During initial studies, blends of several types of ethylene vinyl alcohol copolymers were made with all three types of platelet fillers, aluminum flake, mica and talc. Blend loadings were from 9 to 33 wt % filler. Thin films, 1 to 2 mils in thickness, were melt pressed from these composites and used to measure oxygen and water permeation rates.

Subsequent larger scale evaluations were made using both pilot and commercial scale polymer processing equipment. These included both single and multiple layer cast and blown film lines for flexible structures. Rigid containers with mica-filled EVOH were made by both melt and solid phase pressure forming of multilayer sheet and by coextrusion blow molding. Most of the rigid container testing was done on bottles made on a Bekum five-layer coextrusion blow molding machine using a one-liter Boston round bottle mold.

A Mocon (Modern Controls, Inc.) instrument modified for accurate humidity control was used to measure the oxygen permeation value (OPV) on film structures. These were generally measured at 30°C and 80% relative humidity and are reported as cm^3 O_2/100 in^2-day-atm.

The barrier performance of rigid containers was measured on both a second modified MOCON instrument and by a head space technique in which nitrogen purged and sealed containers were stored in an oxygen environment for periods of time. Containers were generally measured at 23°C with 100% relative humidity (RH) inside and either 50 or 75 RH outside. Container oxygen transmission rates (OTR) are expressed as $cm^3 O_2$/container-day-atm.

Platelet sizes, distribution and orientation of the EVOH blends in the film and container structures were examined by SEM. Samples were prepared by cryogenically fracturing the coextruded structures and the using an oxygen plasma etch on the exposed cross section to erode away some of the polymer. This exposed the edges of the fractured mica platelets, giving micrographs with good contrast and clearly defined platelet orientation.

RESULTS ON SINGLE LAYER FILMS

Figure 1 shows the oxygen permeation values for a series of blends of aluminum, mica and talc in an EVOH resin containing 44 mole % ethylene. The relative effectiveness of the three fillers are proportional to their aspect ratios as predicted by theory. Aluminum flake was the most effective, but the high cost and the hazard of handling dry aluminum flake rule out the commercial usefulness of such blends. Mica was clearly superior to talc as would be anticipated on the basis of the aspect ratio data.

Balancing relative costs and effectiveness favored mica as the preferred platelet-type filler for enhancing the barrier of EVOH resins.

Larger scale testing confirmed the earlier scouting tests. Additional permeability data obtained with cast films made with a 30 mole % ethylene EVOH blended with various levels of mica are shown in Figure 2. A loading of 23.1 wt % mica was selected as a good compromise for obtaining low permeability while maintaining good polymer processing characteristics. At this loading, barrier testing on single layer films showed an improvement in the J_o/J_n ratio of 3 to 5 times that of unfilled resin. Thicker films tended to show the higher level of improvement.

The initial samples submitted for customers' evaluations were simply labeled SELAR OH plus mica. This name stuck and the products are generally referred to as SELAR OH Plus. Two grades are currently being offered as commercial products (Table III). At a mica loading of 23%, the melt flow of the blend is reduced to approximately one-half that of the unfilled resin.

Table III. SELAR OH Plus Grade Summary

Grade Description	EVOH Melt Flow*	EVOH % E	Mica Wt %	Blend Melt Flow*
SELAR OH 3002P3	3	30	23.1	1.5
SELAR OH 4408P3	16	44	23.1	8.0

*g/10 min, 2160 g, 210°C

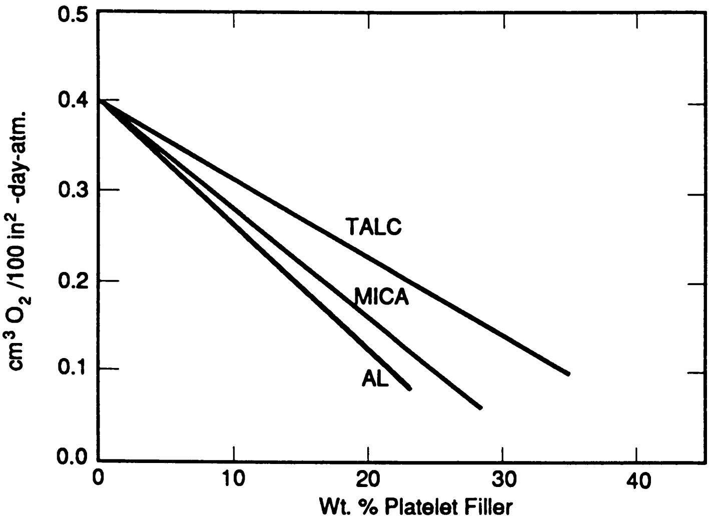

Figure 1. Effect of Platelet-Type Fillers on the Oxygen Permeability of EVOH Resins.

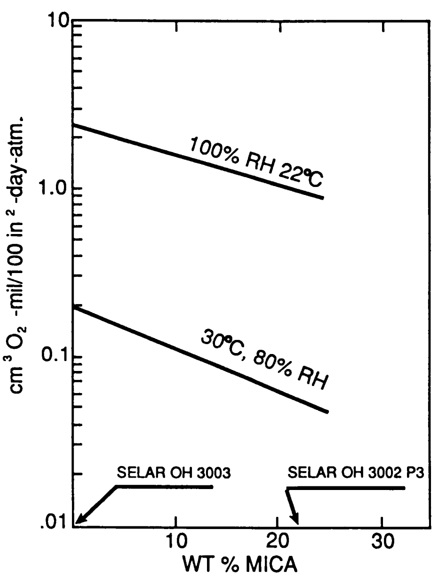

Figure 2. Barrier Enhancement of SELAR OH Resin With Mica Filler.

As inferred from the prior discussion of models, in order to obtain maximum benefit with a high aspect ratio flake filler, it is necessary for the flakes or platelets to be aligned with their major plane parallel to the surface of the film or sheet. Fortunately, most polymer processing operations for both flexible and rigid packaging favor this preferred orientation. Flow patterns in the melt during the extrusion or coextrusion of film or sheet align the platelets parallel to the surfaces. Further improvement in the desired orientation is achieved when there is biaxial stretching of the melt following extrusion such as occurs with blown film or thermoforming operations. Figure 3, which shows the SEM of a typical cross section of a SELAR OH Plus barrier layer, illustrates this parallel alignment.

RESULTS ON COEXTRUDED STRUCTURES

Ethylene vinyl alcohol barrier resins are never used as single layer films in packaging but rather are utilized in coextruded structures combined with less expensive structural polymers.

FILMS. Table IV shows data on a five-layer flexible film structure made with mica-filled EVOH, an unfilled-EVOH control and a blend of the two. Approximately a three-fold improvement was measured on the multilayer film structure in good agreement with the previous monolayer data.

Table IV. Oxygen Permeation of Coex Films Containing SELAR OH Resins

Barrier Layer Resin	Barrier Layer Thickness Mil	Oxygen Permeation Value,* 30°C, 75% RH
SELAR OH 3003	0.3	0.109
SELAR OH Blend 50% 3003 50% 3004P3	0.3	0.063
SELAR OH 3004P3	0.3	0.037

Structure is LDPE/BYNEL E208/SELAR OH/E208/MDPE
Total thickness = 2.2 mil
*cm^3-mil/100 in^2-day-atm

THERMOFORMED CONTAINERS. Table V shows data on a melt-formed, rigid container. This container, together with its unfilled EVOH control, was subjected to a simulated retort cycle at 121°C. The mica-filled container in this example showed an improvement of 2.5 times that of the control.

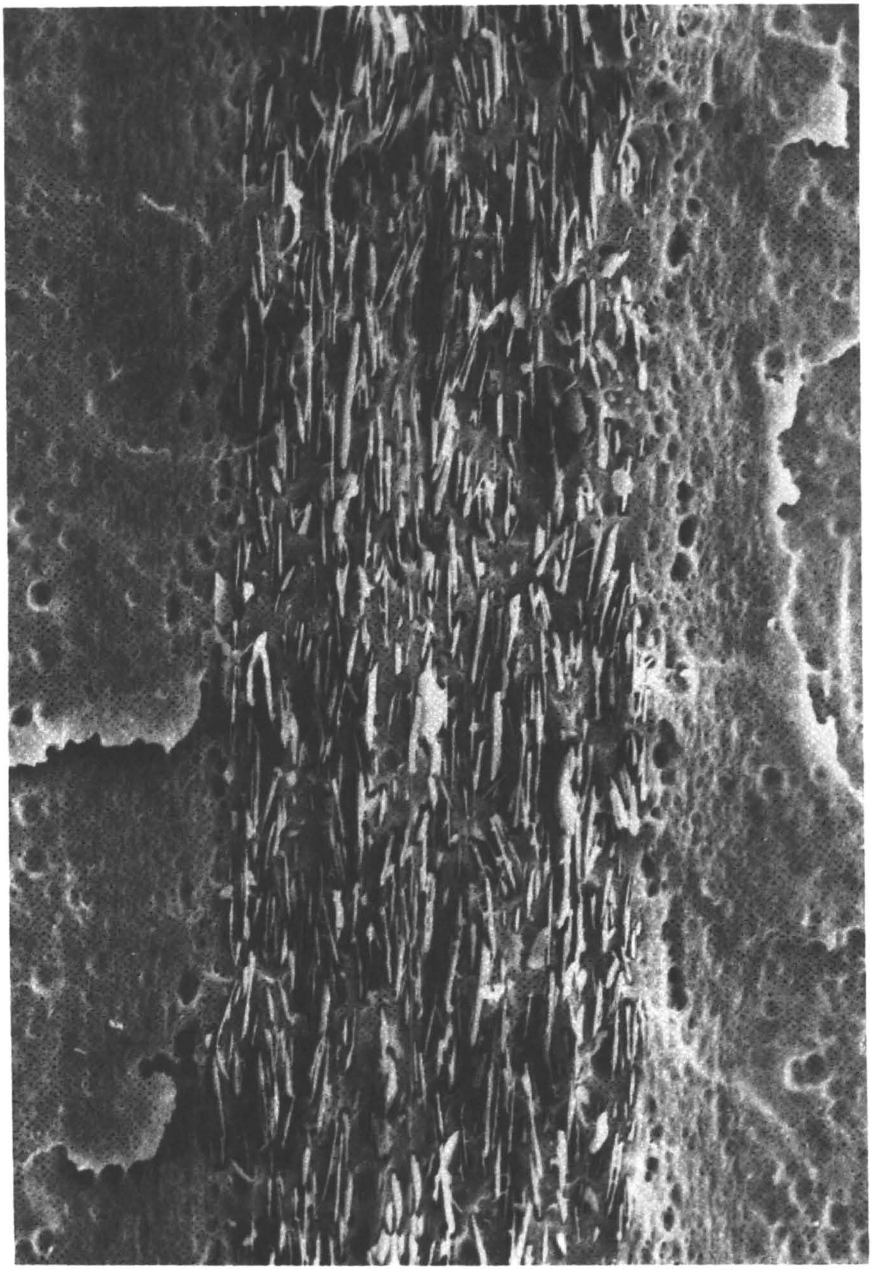

Figure 3. SEM Micrograph of Cross-Section of Coextruded Film Illustrating Mica Platelet Orientation in EVOH Barrier Layer.

Table V. Melt-Formed, Single-Serving Entree Cup

Barrier	cm^3 O_2/Container-Day-Atm
SELAR OH Plus Mica	.061
Unfilled EVOH Resin	.152

*Tested after simulated 121°C sterilization cycle

<u>BLOW-MOLDED CONTAINERS.</u> Initial evaluation of SELAR OH Plus in extruded blow molding containers was disappointing. Barrier improvements of only 30 to 40% were measured compared to the expected 300%. The resolution of this discrepancy provided some valuable insights into the role of platelet orientation in barrier improvement and the effects of die swell in multilayer extrusion blow molding.

The clue to the low barrier enhancement ratios came from SEM and TEM micrographs detailing platelet orientation in the sidewall barrier layer. When the sidewall barrier layer was cross sectioned in a vertical or extrusion direction, these photographs showed that the mica platelets were not aligned parallel to the bottle sidewalls. Instead the platelets showed a periodic alternating pattern similar to a classic sine wave, with most platelets aligned at a 45° angle to the surface (Figure 4). When sectioned in a "hoop" or cross extrusion direction, the exposed edges of the platelets appeared parallel to the surface. This platelet orientation would be estimated to give at best a 40% improvement. This value is based on the increased diffusion path length corresponding to the hypotenuse of a 45° right triangle.

This unusual platelet orientation is believed to be caused by mismatched die swell in the different layers of the coextruded tube or parison used to form the bottle. The polypropylene (PP) used as the structural layer in these blow molding tests was a low melt flow grade recommended for blow molding applications. This resin normally gives a high degree of die swell which was readily observable as the parison exited the annular die under melt temperature and extrusion rate conditions optimized to make a bottle with uniform thickness sidewalls. Die swell at an annular die can be of two types, an increase in the diameter of tube versus that of the die opening and an increase in the thickness of the tube wall versus that of the die slit opening. It is the latter die swell phenomena that is responsible for the nonparallel mica platelet orientation. Filled polymers and especially platelet-filled polymers are well known to exhibit considerably lower die swell than unfilled resins. The individual layers in a multilayer extrusion must maintain their same individual percentage of the total structure throughout the melt flow pathway. Therefore, an internal EVOH layer must also increase in thickness as the structural PP layers undergo die swell exiting the die lips. Apparently in the case of a platelet-filled EVOH, this layer can become thicker only by folding back on itself, thus resulting in the sine wave pattern.

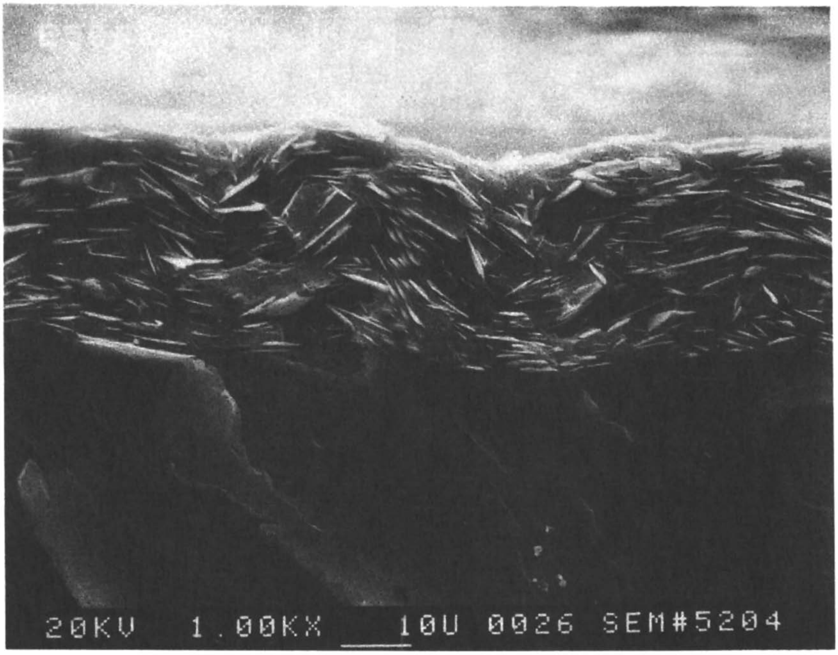

Figure 4. SEM Micrograph of Extrusion Direction Cross-Section of Coextruded Blow Molded Bottle Showing "Sine Wave" Pattern of Mica Platelets.

In a shuttle machine such as was used in this program, the multilayer tubular polymer melt is extruded downward with only gravity exerting a downward pull. When the tube is extruded to the proper length, it is transferred to a mold, the top cut off, the bottom is pinched shut and air pressure is introduced into the top. This expands the hot polymer tube into the shape of the finished bottle. Typically there is a three-fold or greater expansion in the hoop direction but practically none in the vertical or extrusion direction. This causes the axis of the mica platelets in the hoop direction (perpendicular to the extruder flow direction) to align parallel to the bottle surface. However, in the vertical or extruder direction, where no stretching takes place, the axes of the mica platelets retain the alternating tipped orientation or sine wave pattern developed in the swollen zone below the die lips.

Once this unbalanced die swell mechanism was diagnosed, several solutions were suggested. One solution is to increase the die swell of the barrier resin. Since the degree of die swell is usually related to the molecular weight of the resin, a lower melt flow index (MI) EVOH resin blend with mica was evaluated. This was a 3 MI resin reduced to 1.5 MI after blending with mica. A 7 MI resin blend was used in the initial trials. Blow molded bottles made with this resin still showed the oscillating sine wave pattern of the mica platelets in extrusion direction cross sections. However, the average angle of the platelets was reduced to about 30°. Barrier testing of these bottles showed an improvement two times that of the unfilled control. This was definitely an improvement over the 30-40% previously observed.

A second solution is to reduce the die swell of the polypropylene layers. Known techniques to reduce die swell include using a lower molecular weight polymer, modifying the die configuration to extend the polymer compressed zone, adding slip agents or increasing the melt temperature. The latter was the simpliest test to run. Increasing the melt temperature of the polypropylene by 50°F gave an immediate and visible reduction in die swell. Extrusion direction cross sectioning of the sidewall showed only traces of the sine wave pattern with the average mica platelet reduced to an angle of about 15°. However, this set of bottles did not do well in barrier testing because of low bottle weight and large variability in sidewall thickness.

The third and most successful approach was accomplished on a wheel-type blow molding machine. Unlike the shuttle machine where only gravity acts on a downward extruded parison, a wheel machine draws or pulls the parison from the die. This allows extension in the extrusion direction and the opportunity to thin down the barrier layer and reorient the mica platelets.

A set of bottles made on a customer's wheel-type machine showed negligible disorientation of the mica platelets. Barrier results on these samples gave the expected three-fold improvement (Table VI). Summarizing these results on platelet orientation in blow molded bottles versus related barrier enhancement (J_o/J_n) (Table VII) shows that the same level of improvement is achieved as in other container processes when the platelets are aligned parallel to the container walls.

Table VI. Co-Ex Blow Molded Bottles*

Barrier	$cm^3 O_2$/Container-Day-Atm
SELAR OH Plus Mica	.0066
Unfilled EVOH Resin	.019

*Experimental bottle made with ketchup-style mold on wheel machine

Table VII. Effect of Platelet Orientation on Barrier Enhancement - Coextruded Blow Molded Bottles

Process Modification	Platelet Orientation to Plane of Wall	Barrier Enhancement J_o/J_n
Initial Test	45°	1.35
Low MI "OH Plus"	30°	1.9
Above Plus Reduced PP Die-Swell	15°	*
Wheel Machine	<5°	2.9

*Poor wall thickness control

While potential solutions for maximizing the barrier performance of SELAR OH Plus in blow molded bottles have been identified, the product has not found commercial acceptance in containers such as squeezable ketchup bottles. The mica imparts a slight yellow color to the resin which the consumer finds objectionable.

The major opportunities for this new barrier resin composite are in shallow solid phase pressure thermoformed containers and in melt phase thermoformed containers. These rigid containers are typically pigmented, thus eliminating the problem of the yellow tint (Table VIII).

Table VIII. SELAR OH Plus - Recommended Applications

Process	Suitability	Remarks
Coex Blow Molding	Barrier okay from wheel machine	Color may be unacceptable
Solid Phase Thermoforming	Okay on shallow draw containers	Barrier splits on deep draws
Melt Phase Thermoforming	Improved barrier demonstrated	Containers usually pigmented
Flexible Films	Improved barrier demonstrated	Poor flex crack color and transparency deficiencies

SUMMARY

1. A three-fold improvement in gas barrier has been demonstrated with a mica platelet filler in EVOH. This suggests that a value of about 0.3 would be appropriate as the geometric factor in the Cussler model using irregular flakes of nonuniform size typical of commercially available fillers.

2. Platelets must be aligned parallel to the surfaces of the film or membrane. The advantage of a tortuous path are rapidly lost when the platelets are tipped in the direction of gas permeation.

3. A phenomena of imbalanced die swell during coextrusion has been identified. This can produce thickening of the internal layer by a folding mechanism.

4. Practical packaging applications for platelet-filled high barrier resins have been identified.

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