Designing barrier film structures

J. Perdikoulias and W. Wybenga

Blown film coextrusion allows us to combine two films with different properties, giving a single film with improved gas transmission and resistance to oxygen permeability.

Approximately 50% of the food in third world countries spoils for lack of proper packaging (*1*). The importance of developing cost-effective packaging in the food packaging industry is one reason high-barrier flexible packaging is such a rapidly growing area of polymer processing. Technological advances in both machinery and resin design have made blown film coextrusion a viable way to create many different structures. The greatest advantage of coextrusion comes from the ability to combine the important properties of each material into one structure.

A multilayer barrier structure generally consists of a relatively expensive barrier resin coextruded between layers of a less expensive structural resin. In most cases, the barrier resin restricts the transmission of oxygen into the package to prevent the food from spoiling. The structural resin is usually a polyolefin and is primarily used to add strength to the package and protect the barrier layer. For many polymers, the barrier properties diminish in the presence of moisture. Polyolefins are generally good moisture barriers and have this additional function in protecting the barrier layer from moisture. In cases in which the barrier resin does not adhere to the structural resin, an additional adhesive layer is employed. The choice of materials for the structural layers depends on the package requirements and may be different on either side of the package. In addition to protecting the food from oxygen, the package must also move properly through the packaging equipment for efficient production.

The ability to produce a multitude of structures now makes it more difficult to decide which structure or combination of materials will be the most economical. Here, we will bring together information from various sources and discuss some important aspects of designing barrier packaging, to help make this decision easier. To provide a common starting point, we will first review the basic theory of gas transmission. The terms associated with this field will be defined, and some examples of the type of calculations that must be performed will also be presented.

Perdikoulias is process engineer and Wybenga is president, Brampton Engineering Inc., Brampton, Ontario, Canada L6T 3V1

Gas transmission

The rate at which a substance will pass through a film is a function of many parameters. Since the detailed theory can be found in almost any mass transfer text book (*2*), we will will not elaborate in this area. For our purposes, it is sufficient to say that the governing equation is:

$$N_A = D_A [(C_{A1} - C_{A2})/z] \quad (1)$$

The term N_A, often called the "flux," is the rate of diffusion of a Substance A through a solid. It is the amount of gas passing through a unit area of polymer surface in a unit amount of time. D_A is the diffusivity of that substance through the solid, and C_{A1} and C_{A2} are the concentrations of the gas at each side of the solid of width z. The equilibrium solubility of the gas on the surface of the solid is directly related to the partial pressure, so Eq. 1 becomes:

$$N_A = D_A S_A [(P_{A1} - P_{A2})/z] \quad (2)$$

The term S_A is the solubility coefficient, and P_{A1} and P_{A2} are the partial pressures of the substance on either side of the solid. The common practice is to combine the diffusivity and the solubility into one material parameter called the "permeability," P_A, and is defined as:

$$P_A = D_A S_A \quad (3)$$

Equation 2 then becomes:

$$N_A = P_A [(P_{A1} - P_{A2})/z] \quad (4)$$

Equation 4 implies that the flux (or the rate of gas transmission) can be reduced by increasing the thickness z or choosing a substance with a low permeability. The partial pressure gradient is commonly an uncontrollable parameter that depends on the environment.

Permeability data are determined under steady state conditions, but the diffusivity and the solubility coefficient determine how much time it will take to reach steady state. This topic has been discussed by DeLassus (*3, 4*), who describes several methods of obtaining these data. Salame (*5, 6*) also points out the importance of distinguishing between solubility, diffusivity, and permeability. The diffusivity indicates the rate at which the gas can pass through the solid. The solubility will determine how much

of the gas will be absorbed into the solid. If the emphasis is on preventing oxygen from entering the package, then the amount of oxygen absorbed into the outer surface is of no concern. It is the rate at which the oxygen migrates through the package (diffusivity) that is important. However, if a certain flavor or aroma has to be contained in the product, the solubility may also be important. The solubility will determine how much flavor or aroma will be absorbed into the package walls. This amount can be significant enough to severely affect the quality of the packaged product. A low permeability coefficient will keep the substance in the package but not necessarily in the product being packaged.

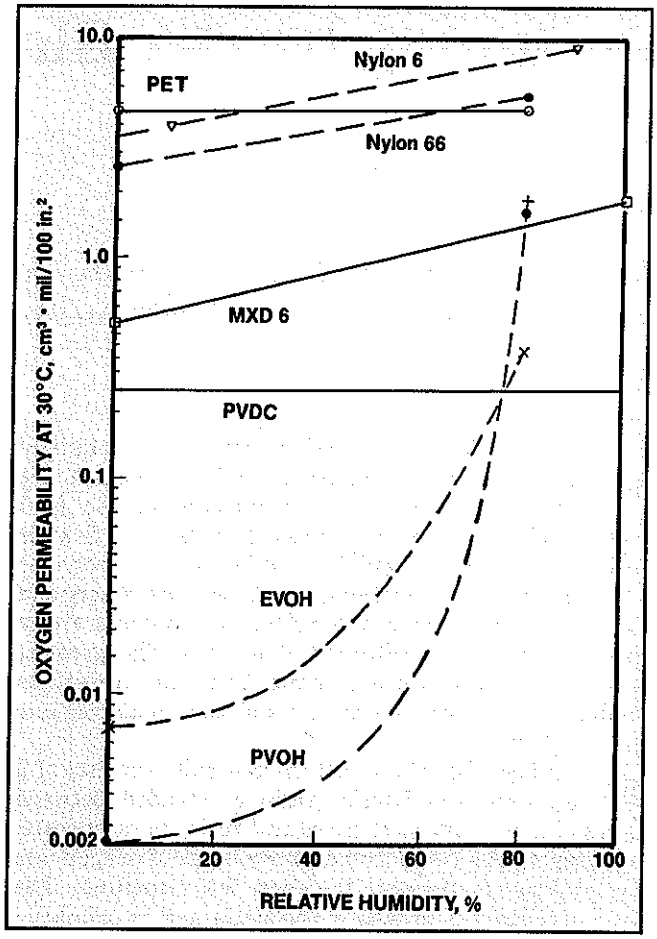
What impels the mass transfer of the gas, whether oxygen, carbon dioxide, or water vapor, is the difference in concentration of the gas on either side of the film. This difference is usually expressed as a partial pressure difference in units of pressure. The partial pressure is the pressure that a gas would exert if all other gasses were removed from the system. At or near sea level, the atmospheric pressure is about 14.7 psi, or 1 atmosphere. Air consists of approximately 21% oxygen and 79% nitrogen. This means that the partial pressure of oxygen in air, at or near sea level is 3.1 psi, or 0.21 atm. Nitrogen makes up the remaining 11.6 psi, or 0.79 atm. If the oxygen in the atmosphere is being restrained from entering an oxygen-free package, then the impelling force would be 3.1 psi, or 0.21 atm of oxygen (i.e., the fraction of oxygen in the air). If the package already contained the equivalent of 0.21 atm of oxygen, then there would be no impelling force, and no mass transfer would occur. A package that remains exposed to the atmosphere indefinitely will eventually absorb the equivalent of 0.21 atm of oxygen.

For moisture vapor transmission, the impelling force is usually expressed in terms of the difference in relative humidity between the two sides of the film. Permeability data should always include a unit of pressure or a statement giving the partial pressure difference at which the test was performed. Often, the permeability coefficients for water vapor transmission do not contain the units for the impelling force, in which case the relative humidity on each side of the film sample must be reported. The ASTM E96 is a common method used to determine the water vapor transmission of polymers.

For some polymers, exposure to moisture has a strong effect on the barrier properties. **Figure 1** shows the effect of relative humidity on oxygen permeability for some common barrier polymers. Temperature may also play an important role in deciding what barrier polymer is best suited to a package. **Figure 2** shows the effect of temperature on the oxygen permeability of some polymers. The permeability data required will depend on the application and the environment that the package is exposed to. Using data obtained under dry conditions to construct a package that will be exposed to high levels of humidity is likely to result in severe losses arising from inadequate product protection. Placing the oxygen barrier layer between moisture barrier layers does not mean that the center layer will remain dry. Inevitably, an equilibrium will result with the barrier layer containing some degree of moisture.

The Eval Company of America has produced a technical bulletin (No. 110) (*7*) on gas transmission through polymers

1. The effect of humidity on O_2 permeability (24 h at 1 atm) of some polymers (PET = polyethylene terephthalate. MDX 6 = polymetaxylylenediamine. PVDC = polyvinylidene chloride. EVOH = ethylene vinyl alcohol. PVOH = polyvinyl alcohol.)

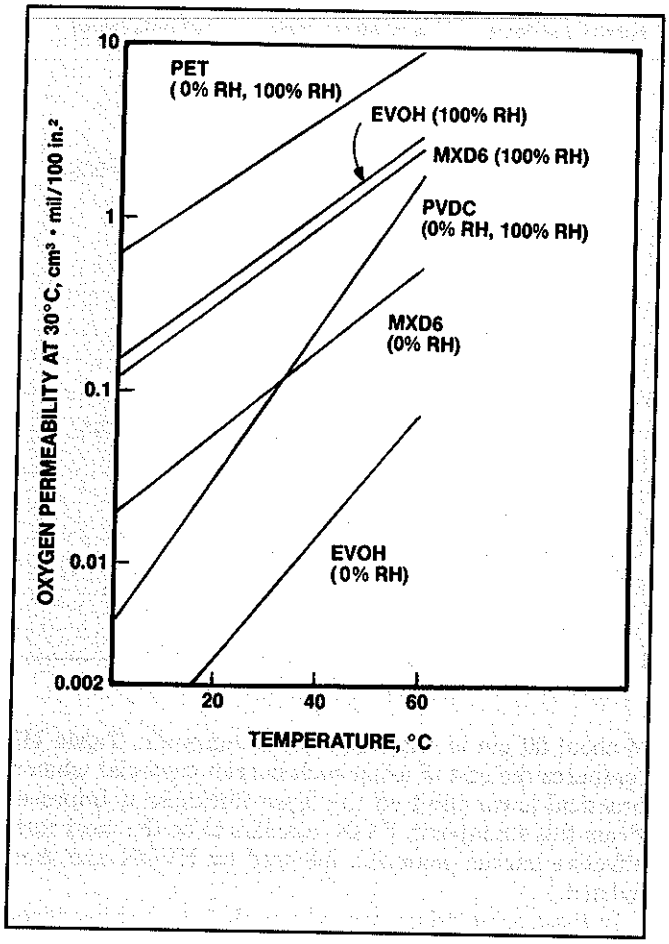


that outlines how the relative humidity of the barrier layer can be determined. Pike presented similar information at the 1986 TAPPI conference, where he compared the predicted and measured oxygen permeability of a LDPE/EVOH/LDPE film structure under different humidity conditions (*8*). These sources show how the choice of materials for the structures can control the equilibrium value of the relative humidity for the barrier layer.

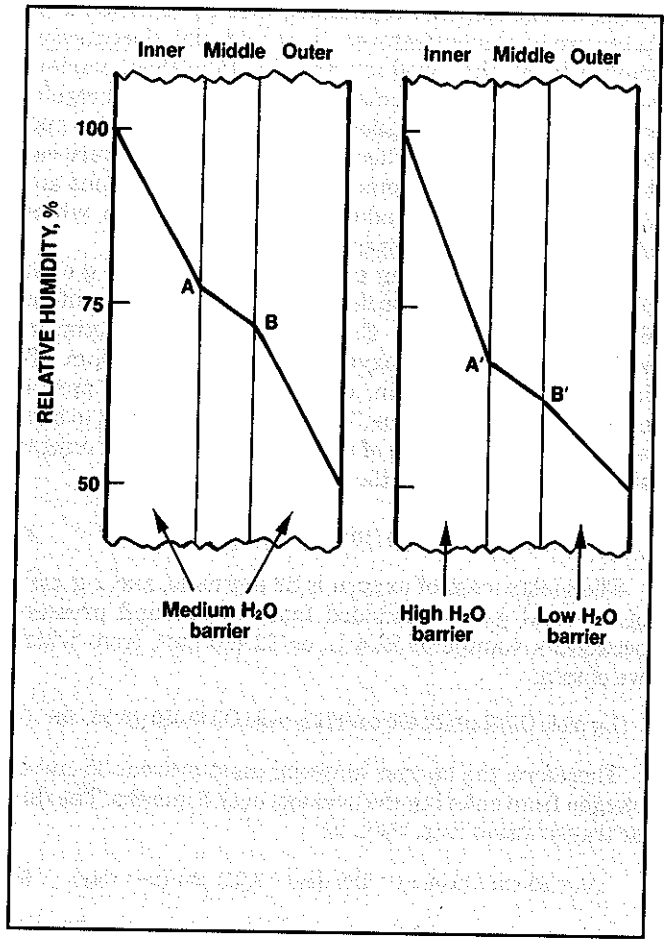
Consider the three-layer structure in **Fig. 3**, consisting of a barrier material between two identical polymers of equal thickness. The inside of the package is at 100% RH, and the outer surface is at 50% RH. The relative humidity gradient is represented by a line through the layer. The slope of the line in any layer represents the resistance of that layer to moisture diffusion. The higher the slope, the higher the resistance. When steady state has been reached, the average relative humidity of the barrier layer is the average value of Points A and B, or 75%.

Consider now a similar structure, in Fig. 3, that uses a material with a higher resistance to moisture diffusion on the inner layer and a lower resistance on the outer layer. In this structure, any moisture that manages to get to the barrier will diffuse through the outer layer faster than in the structure shown in Fig. 3. The equilibrium values of Points A and B will drop to Points A′ and B′,

2. The effect of temperature on O_2 permeability of some polymers (*14*)



3. Cross section of two film structures showing relative humidity profile



respectively. This drop will reduce the average relative humidity of the barrier layer (to below 75%). A similar effect can be had by placing a thicker layer of the structural material on the side exposed to the highest humidity and reducing the thickness of the layer exposed to the lower humidity.

The formula for determining the average relative humidity of the center layer in a three-layer structure is:

$$RH_c = + RH_i\,[(t_c/w_c) + (2t_o/w_o)]\,RH_o\,[(t_c/w_c) + (2t_i/w_i)]/\,[2(t_i/w_i) + (t_c/w_c) + (t_o/w_o)] \quad (5)$$

where

RH = the relative humidity

t = the thickness

w = the water vapor permeability

i = inside layer

c = center layer

o = outside layer.

The same formula can be used for a five-layer structure by neglecting the adhesive layers.

Discussing gas transmission under humid conditions, Pike cautions that "there are still no standard or official methods for this purpose" (*9*). Pike attributes this lack of development to the "extremely poor precision between laboratories when attempts have been made to collect data to support approval of methods." Some of the methods, however, provide satisfactory "within-laboratory" precision, and Pike discusses these. Because of this state of affairs, the safety margin built into the package design will have to be large enough to accommodate the poorest test results. The consequence will obviously be wasteful over-design, but until more precise test methods are developed, there is not much more that a package designer can do.

Package design

The design of a barrier structure must begin with a knowledge of the product that the structure is supposed to protect and what element the product is being protected from. Most barrier film is used to preserve food, usually by preventing oxygen from entering the package, which causes the food to spoil. The amount of moisture lost or gained is also an important factor when designing barrier packaging.

Table I contains some data on the degree of permeation

protection required by various foods. Although it is not precise, it will provide a starting point for the package designer. If the government has set certain standards that must be met, then those standards would be the target. If there is no imposed regulation, then the decision is up to the product manufacturer. By considering the expected shelf life of the product and its tolerance, various structures can be mathematically tested. Through careful marketing and distribution, the expected shelf life may be reduced to a point where a cost-efficient structure can be used. In any case, some preliminary calculations and considerations will make it easier to decide which structures should be pursued or neglected.

Consider the following example. Suppose 1000 g of an oil product are to be packaged with an expected life of 6 months (180 days). From Table I, the maximum estimated acceptable oxygen gain is 50–200 ppm. To include a safety margin, the lower value of 50 ppm is chosen as the target value. The package is assumed to have an exposed surface area of 600 cm^2. The amount of oxygen that is allowed to enter the package is:

$$(50/10^6)\,(10^3\ g) = 0.050\ g \qquad (6)$$

The molar mass of oxygen is 32 g/g mole, and 1 g mole of an ideal gas at standard temperature and pressure occupies a volume of 22.4 L, or 22,400 cm^3, from which we obtain:

$$(1\ g\text{-mole}\ O_2/32\ g)\,(22{,}400\ cm^3)/(1\ g\text{-mole}\ O_2)\,(0.050\ g) = 35\ cm^3 \qquad (7)$$

Therefore, the barrier material must prevent 35 cm^3 of oxygen from entering the package over 6 months. The flux or transmission rate, then, is:

$$N_A = 35\ cm^3/(0.06\ m^2 \cdot 180\ day) = 3.241\ cm/(m^2 \cdot day) \qquad (8)$$

Let us assume that dry EVOH will be the barrier material and, from Salame (*6*), that the permeability is 0.017 (cm^3 · mil)/100 $in.^2$ per day at 1 atm. Converting to more appropriate units,

$$P_{EVOH} = 0.0067\ (cm^3 \cdot mm)/(m^2 \cdot 24\ h \cdot atm) \qquad (9)$$

Substituting what is known into Eq. 4, we obtain:

$$3.241\ cm^3/(m^2 \cdot day) = 0.0067\ (cm^3 \cdot mm)/(m^2 \cdot day \cdot atm)\,(0.21\text{–}0.0)\ atm/z \cdot mm \qquad (10)$$

Solving this equation for z, the required thickness is calculated to be 0.00043 mm. This calculation is made assuming that the reduction in the gradient pressure is negligible, as caused by the small amount of oxygen entering the package over its expected shelf life. The price of EVOH is about \$6102/m^3. Considering a layer thickness of 0.000043 cm, the barrier layer will cost approximately 0.262 cents/m^2.

This exercise was repeated for both PVDC and Nylon 6, and the results are reported in **Table II** (0% RH). EVOH appears to be the most cost-effective material, followed by PVDC and then nylon 6. A uniform EVOH layer thickness of 0.4 μm, however, is somewhat impractical. A more realistic value is a layer thickness of 8–10 μm. This is about 25 times the required protection and 25 times more cost. The PVDC appears to be a better candidate, but 2.5 μm is still a difficult layer thickness to control. A Nylon 6 layer of about 30 μm is relatively easy to maintain. **Table III** compares the cost of using each barrier material when a practical lower limit on the layer thickness is imposed. From this standpoint, PVDC appears to be the most cost-effective barrier material, followed by EVOH and then nylon 6.

I. Degree of permeation protection required (*13*)

Food or beverage	*Maximum estimated acceptable O_2 gain, ppm (mass basis)*	*Maximum acceptable H_2O gain or loss, % (mass basis)*
Canned milk, canned meats, canned fish, poultry	1–5	3% loss
Beer, ale, wine	1–5	3% loss 20% CO_2 (or SO_2) loss
Canned vegetables, soups, spaghetti, catsup, sauces	1–5	3% loss
Canned fruits	5–15	3% loss
Dried foods	5–15	1% gain
Fruit Juices, drinks	10–40	3% loss
Carbonated soft drinks	10–40	3% loss <15% CO_2 loss in 15 weeks
Oils, shortenings	50–200	10% gain
Salad dressings	50–200	10% gain
Jams, jellies, syrups, pickles, olives, vinegars	50–200	3% loss
Peanut butter	50–200	10% gain

In these calculations, we assume that the barrier layer is at 0% RH. This will not be the case because even if the inside of the package were void of moisture, the outside would most likely be exposed to the ambient relative humidity, which is rarely zero. The barrier layer would eventually reach an equilibrium value between the values on the inside and the outside of the package. For some polymers, this will mean that their barrier properties will be reduced, and a thicker layer of that polymer must be used to compensate.

Consider, for instance, that the environmental conditions are 65% RH and 27°C. [Oxygen permeability data are available from Foster (*13*).] These data are also compared in Table II. Note that the permeability of PVDC is different from its permeability at 0% RH, even though it is not supposed to be affected by moisture. The source for these data may be presenting data for a different grade of PVDC, or this difference may be due to the poor precision between laboratories, as previously mentioned. The required layer thickness has increased for each polymer, but EVOH is still theoretically cheaper. When a minimum layer thickness is imposed, as shown in Table IV, then PVDC is again found to be the most cost-effective, followed by EVOH and then nylon 6.

The actual relative humidity of the barrier layer will depend on the relative humidity on each side of the package, as indicated in Eq. 6. For accurate calculations, correct data should be obtained from resin suppliers,

II. Relative cost comparison at 0% and 65% RH and 25°C

Polymer	Permeability,* $cm^3 \cdot mm/m^2$	Thickness required, mm	Resin cost, $/m^3	Layer cost, c/m²
		0% RH		
EVOH	0.0067	0.00043	6102	0.262
PVDC	0.0394	0.00255	4302	1.097
Nylon 6	0.4599	0.02980	3997	11.910
		65% RH		
EVOH	0.0197	0.00218	6102	0.781
PVDC	0.0591	0.00382	4302	1.640
Nylon 6	0.8274	0.05361	3997	21.430

*24 hours at 1 atm.

III. Relative cost comparison at 0% and 65% RH using practical layer thickness

Polymer	Minimum practical thickness, mm	Resin cost, $/m³	Layer cost, c/m²	Relative layer cost
		0% RH		
EVOH	0.010	6102	6.10	1.4
PVDC	0.010	4302	4.30	1.0
Nylon 6	0.030	3997	11.99	2.8
		65% RH		
EVOH	0.010	6102	6.10	1.4
PVDC	0.010	4302	4.30	1.0
Nylon 6	0.054	3997	21.6	5.0

literature, research institutes, or manufacturers of permeation measuring equipment.

Other factors to consider are availability and government regulations. Depending on the imposed tariffs or taxes in other countries or as rates change, the material costs may be different. Readers should substitute their own resin costs for a more accurate comparison. There are also additional costs that depend on the polymer being used. For instance, it was determined that PVDC was the most cost-efficient barrier polymer to use under humid conditions. However, this analysis did not factor in the special processing requirements of this polymer. There is the potential danger to the equipment arising from the corrosive nature of degraded PVDC. The capital cost of the equipment is higher because of the special metal alloys that need to be used. In addition, processing PVDC generally requires more frequent die cleaning, which means lost production time and higher labor costs. These factors can have a profound influence on the cost of the multilayer structure.

Having accounted for oxygen permeation, the designer must check the package for its resistance to other substances. Table I indicates the moisture loss or gain that is tolerated by various foods. In keeping with the oil pouch example, the acceptable amount of moisture gain is 10%. For the 1000-g package in our example, this amounts to preventing 100 of water vapor from entering the package. Since polyolefins are good water barriers with good mechanical properties and are relatively cheap, they are the most common choice for the outer layers of a multilayer structure. From Salame (*6*), a 25-μm (1 mil) LDPE layer would allow 100 g of water to permeate through in 550 days (100/0.18). Since the package is only being designed to last for 180 days (1/3 the time), the outer layers only require a combined thickness of 8 μm. A polyolefin layer thickness of 4 μm, other than being impractical, would not provide the mechanical properties required by the package. Since the designer knows that a combined outer layer thickness of 8 μm will be sufficient for moisture protection, emphasis can now be placed on obtaining the required mechanical properties.

If this exercise were performed with data from Foster (*13*), the results would be somewhat different. Foster's data for water vapor permeability were determined under what is commonly referred to as "tropical" conditions. Foster reposts the permeability of water through LDPE as over 8 times the value from Salame (*6*). This means that if the package was to be exposed to this "tropical" type of environment, the outer layers would require a combined layer thickness of 64 μm (8 μm × 8). The choice of barrier material will also affect the moisture permeability and can be included in the calculation through the use of a combined permeability (P_c). This calculation, analogous to determining the overall resistance of resistors in series, is (*10*):

$$1/P_c = (1/t)\sum_{i=1}^{n}(t_i/P_i) \qquad (11)$$

where

t = total thickness of the structure

t_i = thickness of individual layer

P_i = permeability of the individual layer.

This formula could also be used for oxygen calculations. However, when the permeability of the layers differs by a couple of orders of magnitude, only the contribution of the barrier layer is significant. This may not be the case

for other substances, and including the effect of all the layers may lead to significant cost savings. Whatever the case, the package designer, based on his knowledge of the environmental conditions that the package will be exposed to, must obtain the appropriate permeability data for the resins that he intends to use.

Some packaging requirements not only depend on the barrier properties of the resins but also on properties like grease resistance, sealability, chemical resistance, thermal stability, and mechanical properties. For example, for grease or oil applications, an ionomer will provide a better seal than a polyolefin or an EVA. PVDC has poor thermal stability. When it degrades, it forms corrosive by-products that can damage the equipment.

The choice of a barrier material may reduce the amount of structural material required to obtain certain mechanical properties and thus reduce the cost of the package. Also, the different natural affinities among some polymers to steel or aluminum will cause them to behave differently in bag making or packaging machinery. This effect can determine the maximum speed at which the process can run. These detailed type of considerations are more structure oriented and are therefore beyond our scope. More information can be found in the appropriate literature or can be obtained from resin suppliers. However, because of the rate at which new polymers are being developed, the required information may not be available. In this situation, the only alternative is trial and error.

Processing equipment

The equipment being used to produce the multilayer film is important. If existing equipment is going to be used to produce a new structure, one must ensure that the polymers being considered and their throughputs are compatible with the equipment design. The extruders must have sufficient power and appropriate screw designs for their respective polymers. The die flow passages and distribution systems must also be designed accordingly. If the new product structure is significantly different from what the system was originally designed for, unexpected problems will arise.

The equipment manufacturer, through the use of flow simulations, will be able to forewarn the processor of possible complications. The equipment manufacturer may suggest a procedure to follow for the test and what to do if a problem should arise. For example, the manufacturer may be concerned that the flow passages in a particular layer are not designed properly and may recommend that the layer be tested first.

Some materials form corrosive by-products when they degrade, which can damage the equipment. Special alloys need to be used for the flow passages of the potentially corrosive materials. The new polymer may process at a higher temperature and pressure than the die was originally designed for.

In an attempt to leave as many options open as possible, the processor will often provide the equipment manufacturer with a long list of structures that may be processed through the equipment. The nature of the coextrusion industry understandably makes it difficult to determine which structure will be the most profitable, but a "do-all" die is not the solution. To increase efficiency, the equipment should be designed for as few structures as possible. The more "all-purpose" the die is, the more the compromises that need to be made.

A multilayer die is basically designed with the emphasis placed on the most "difficult" material. Heat-sensitive materials, which require short residence times such as EVOH and PVDC, demand short passages with small cross-sectional areas so that the velocities remain relatively high. Polyolefins, on the other hand, are generally more viscous and more stable, allowing for the more open flow channels that are commonly used to keep the operating pressures low. A flow passage designed for a high-viscosity polyolefin will probably have too high a residence time for a heat-sensitive polymer. Conversely, processing a high-viscosity polyolefin through a flow passage designed for a heat-sensitive material will cause high back pressures and will restrict the output. A compromise will result in a die that will process the polyolefin at below its maximum output and will require more frequent cleaning when processing heat-sensitive materials.

Concluding remarks

Those involved in the multilayer packaging industry must be well informed about all of the factors that may affect the package. They need a working knowledge of mass transfer and of the relationships between permeability, diffusivity, and solubility. They need to understand how these relationships are affected by the environment.

The package designer should also be aware of the different processing requirements of each polymer in conjunction with the capabilities of the equipment. This knowledge will help the package designer communicate more efficiently with the resin producer and the equipment manufacturer, which will reduce the risk of package failure.□

Literature cited

1. Hinsken, H., Kunststoffe 77: 461(1987).
2. Treybal, R. E., Mass transfer operations, 3rd edn., McGraw-Hill Book Co., New York, 1980.
3. DeLassus, P. T., 1986 Polymer, Laminations and Coatings Conference, TAPPI PRESS, p. 333.
4. DeLassus, P. T., 1985 Polymer, Laminations and Coatings Conference, TAPPI PRESS, Atlanta, p. 445.
5. Salame, M., Plastics Packaging (July/August): 28(1988).
6. Salame, M., 1986 Polymer, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 363.
7. Eval Company of America, Gas barrier properties of EVAL R resins, Technical Bulletin No. 110.
8. Pike, L., 1986 Polymer, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 317.
9. Pike, L., Tappi J. 71(10): 163(1988).
10. Onasch, J. and Junk, P. B., Kunststoffe 77(7): 663.
11. Standard test methods for gas transmission rate of plastic film and sheeting, Designation D 1434, 1975 Annual Book of ASTM Standards, Part 35, p. 502.
12. Standard test methods for water vapor transmission of materials in sheet form, Designation E 96, 1975 Annual Book of ASTM Standards, Part 35, p. 918.
13. Foster, R. H., 1984 Polymer, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 437.
14. Louis, P. J., Latest food package developments in Japan, Europak '86, p. 207.

Received for review May 15, 1989.

Accepted July 5, 1989.