A Model to Predict the Ability of a Flexible Package to Contain Materials.

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Abstract: Testing the ability of a flexible multi-layer package to hold or "contain" a material is cumbersome and subjective. This model qualitatively predicts the outcome based on the rate the contained material permeates the sealant and the ability of the contained material to disrupt the adhesive bond. Key factors which affect permeation and bond disruption are discussed as well as the role of the sealant and the robustness of the adhesive or primer.

Introduction: When food or other materials are stored in flexible packages they have a shelf life. When specifying a shelf life one must not only consider the rate food degrading gasses such as oxygen and water vapor pass through the package, but also how the contained material affects the integrity of the package over time. Some contained materials can dramatically affect the integrity of the package by swelling the sealant or by penetrating the sealant to disrupt the bond.

A common way to test the ability of a package to "contain" a material is to:

- Make a package.
- Fill it with the material.
- Put the filled package in a warm oven and then test the integrity of the package over several weeks or months by pulling apart the package and inspecting it.

This procedure is cumbersome, subjective, and gives little insight into why the package failed.

The Model:

The basis of this model is the assumption that to be destructive, a contained material must first pass through sealant layer (permeation) AND must degrade the bond of sealant to substrate.

Expressed as an equation: The probability of package failure = permeability (of the contained material through the sealant) X adhesive bond disruption (by the contained material).

There are other failure modes. For example, the material can swell the sealant so much that it puts stress on the package and the inter-layer bonds through differential expansion. For this paper, we will ignore this and other failure mechanisms.

Figure 1 shows the concept graphically. The horizontal axis represents the rate of permeation of the contained material through the sealant and the vertical axis is the ability of a contained material to disrupt the bond of the adhesive or primer.

If the horizontal and vertical axes are in the "low" quadrant (upper left), the probability that the material package will hold its integrity is good because the sealant acts as a barrier to bond disruption by the material. Even if some material penetrates the sealant, the bond, by definition of this quadrant, is largely unaffected. The lower right quadrant is the worst case. The contained material readily migrates to the adhesive interface and readily disrupts the bond. The other quadrants are intermediated situations but to improve the containment in these two quadrants, the packaging solution may be different.

Factors that affect the permeation of a material through a sealant:

The permeation of a liquid through a polymer is governed by the equation $P = D \times S$ where P is the permeation rate, D is the diffusivity and S is the solubility of the contained material in the sealant [1]. The diffusivity as the rate of transport of the material through the sealant and the solubility is the concentration of the material in the sealant. If the contained material is not very soluble in the sealant (low S), but it travels through at a fast rate (high D), then the amount of material available to disrupt the adhesive bond may be just as high as a material that is very soluble (high S) but diffuses slowly (low D).

Two of the many factors that affect diffusivity is the size of the molecule, as measured by molecular weight, and the temperature. Figure 2 shows the huge differences in permeation when the molecular weight of the material and temperature are varied. The Y axis is a log scale. At 20°C - about room temperature - note that materials with a molecular weight of about 1500 Daltons take a year for most of the material to migrate through the sealant. This is a longer than the shelf life of many packages. However, if the molecular weight is cut by only a third to 500 Daltons, the contained material can migrate through the sealant in only 1 hour! By the same token, the 1500 Dalton molecular weight material can migrate through in only 80 hours (or 3 days) if the temperature is raised from 20°C (68°F) to 50°C (122°F).

The crystallinity and glass transition temperature of the sealant significantly affects permeation of the contained material. This is because the crystallites act as cross-links which lower the free volume of the sealant (lowers D) and by lowering solubility (S) of the contained material in the sealant. For example, a typical contained material will migrate through highly crystalline polypropylene 44 times slower than through moderately crystalline polyethylene.

Finally the composition of the contained material and the sealant can affect permeation through the sealant. A material that has a polarity similar to that of the sealant is more likely to swell (be soluble in) the sealant. Non-polar oils such as mineral oil are much more likely to swell non-polar polyolefins than polar polyethylene terephthalate (PET).

Figure 3 shows the swelling we measured of several sealant polymers in various liquids. One can see the following trends:

- The polarity match between the sealant and contained material is important.

- Polar water does not swell these relatively non-polar sealants.
- Slightly polar alcohol and vinegar swell the non-polar PE or PP very little but do swell the slightly polar poly(ethylene acrylic acid) and ionomer.
- Non-polar oils swell all of these sealants, but EAA, being more polar than PE, swells less.

- Crystallinity is very important:
  - PP is the most crystalline sealant tested and swells the least in just about every material.

Factors that affect bond disruption by contained materials.

Several factors can affect the bond strength of an adhesive or primer to a substrate or sealant.

The factors include:

- Chemical bond disruption where the contained material is present in or near the adhesive in high concentration and competes with the adhesive for bonding sites. This is shown in Figure 4 where acetic acid displaces the acrylic acid of poly(ethylene acrylic acid) at its bonding site with an aluminum surface.
- The contained material can degrade the adhesive. Figure 5 shows that alcohol can transesterify a polyester polyurethane. This can lower the molecular weight of the polyurethane adhesive and thus lower its strength.
- Physical bond disruption can lower the cohesive strength of the adhesive or primer. Figure 6 shows a conceptualized plot of the modulus of an adhesive when it is diluted in solvent. If the contained material is soluble in the adhesive it will plasticize. The stiffness and strength of the adhesive is then lowered to such an extent that the bonds may fail under stress.

For this study we evaluated the effect of numerous materials on the bond strength of a PE/primer/aluminum foil structure. Various primers were tested. The structure was soaked in the material for four days and then the peel force was measured. Only a representative sample of the data is shown here in Figure 7. Primer A holds up well in non-polar materials but is susceptible to attack by acidic or slightly polar materials. The bonds in primer B are generally superior to primer A. Primer B was designed to have particularly robust bonds to the aluminum and polyethylene and is not very soluble in most materials.

Figure 8 shows the results of our study graphically. Please note that these results apply only for the primers tested. Other adhesives or primers may behave differently. These primers should easily contain material that do not readily pass through the sealant and do not disrupt the bonding of the adhesive (upper left). Examples include dry foods and water. If the contained material readily passes through the sealant but is not aggressive towards the adhesive (upper right quadrant), like non-polar oils, containment should be good – but the sealant may swell. Material that are aggressive to the adhesive bonding (lower left quadrant) like acetic acid or alcohol/water mixtures may require good barrier sealants like polypropylene or co-polyester for the package to last a long time. Materials that are aggressive to the adhesive cannot be expected to last long in packages that use permeable sealants (lower right). With the primers tested here, very aggressive materials that readily pass through polyethylene (lower right quadrant) are very difficult to contain. In order to contain this material either a good barrier sealant and a robust primer must be used.

Conclusions:

The probability of package failure = permeability (of the contained material through the sealant) X adhesive bond disruption (by the contained material).

Proper selection of sealant and adhesive can maximize the integrity of the package over time.

References:

W.J. Koros, Permeation Processes in Barriers and Membranes: Complementary Differences.”, TAPPI PLACE Conference (2002).

Figure 1: The Containment Model.

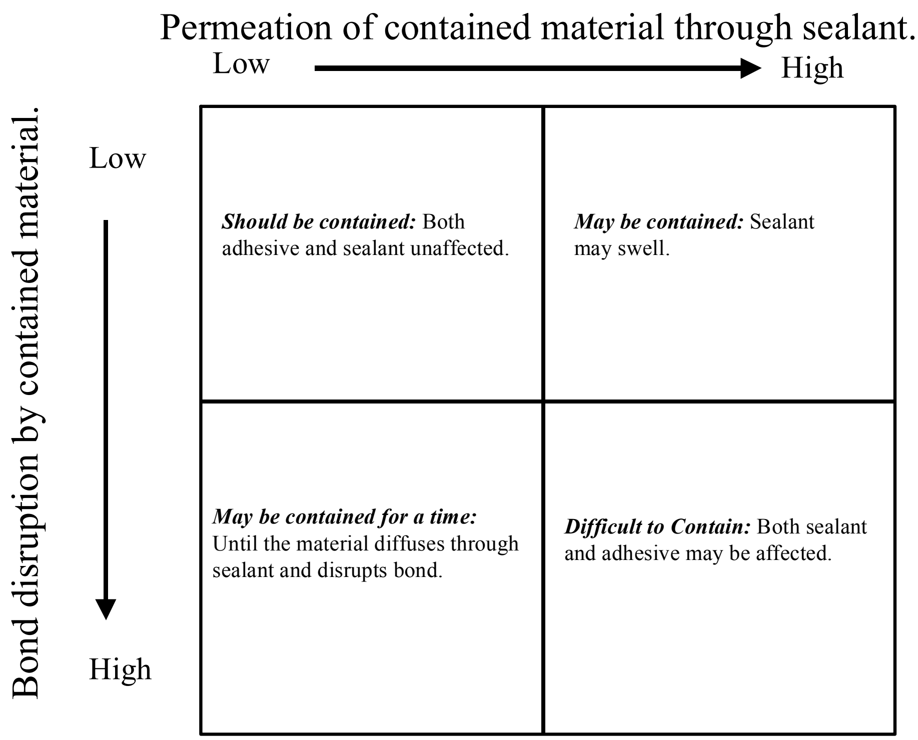


Figure 2: Diffusion Affected by Molecular Weight and Temperature.

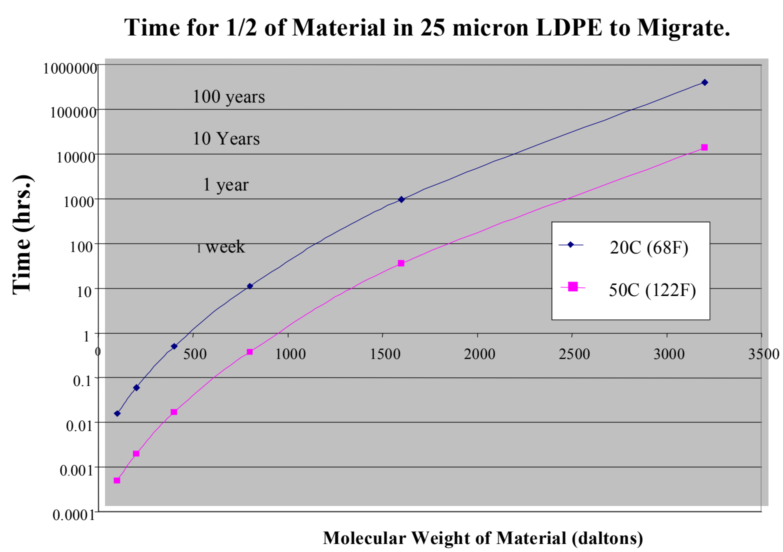


Figure 3: Swelling (%) of Sealants in Various Materials.

Contained Material	***LDPE***	***EAA***	***Ionomer***	***PP copolymer***
Water	0	-0.9	-3.1	0
IPA	2.1	19.1	13.0	2.9
Vinegar	0	1.0	0.7	0
Tabasco	1.0	0.7	2.0	0.6
Mineral oil	8.4	5.0	8.3	3.8
Motor oil	10.5	6.5	10.9	3.0
Skin-So-Soft	15.3	14.7	21.0	9.5
Dioctyl sebecate	4.8	4.8	4.8	4.8

Figure 4: Bond Disruption by Competition for Bonding Sites.

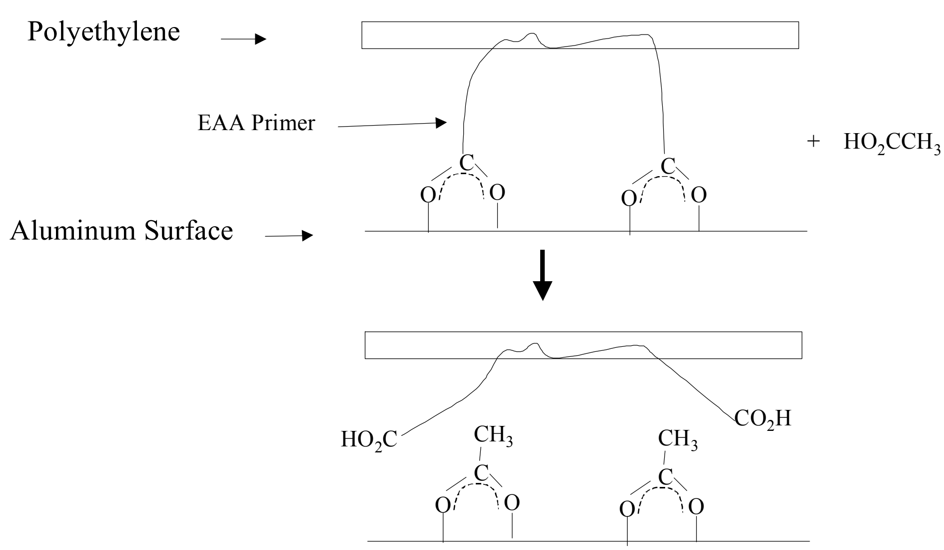


Figure 5: Bond Disruption by Chemical Reaction with Adhesive.

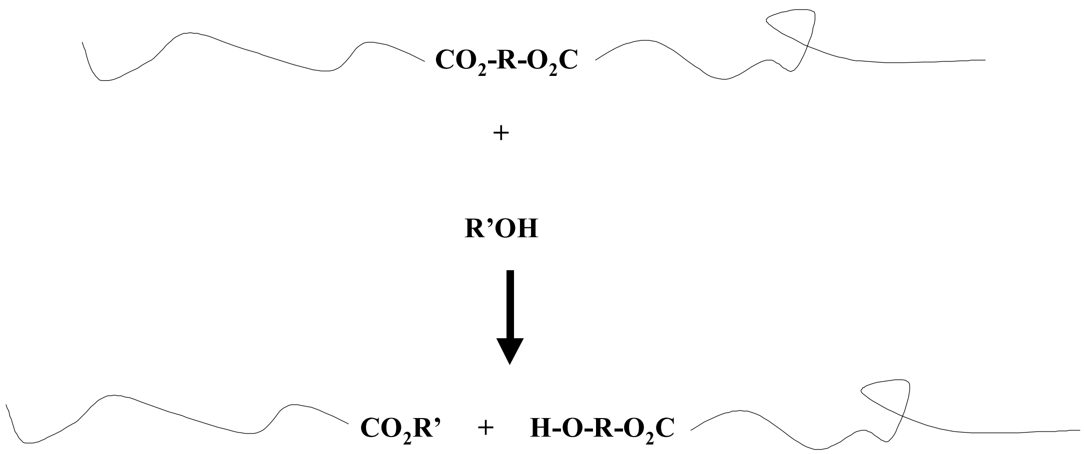
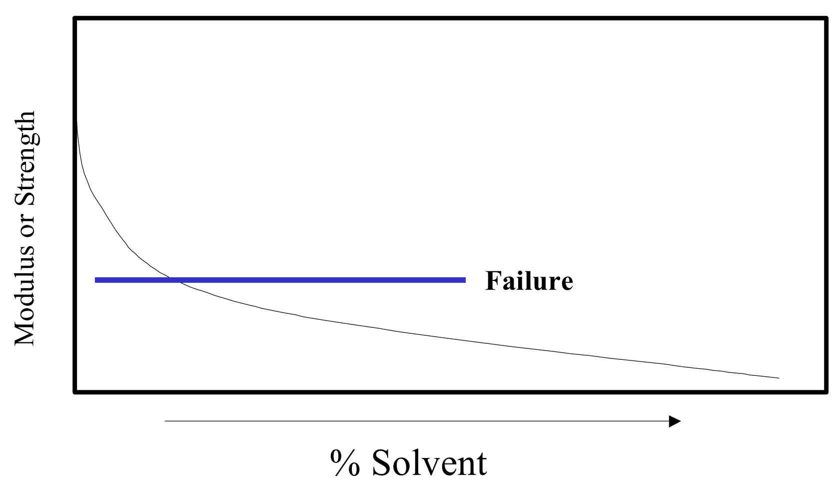


Figure 6: Physical Bond Disruption by Plasticization.



Small amounts of solvent can significantly weaken bond

Figure 7: Peel Force after Immersion in Material for 4 Days.

	Primer A Peak/Average (g/25mm)	Primer B Peak/Average (g/25mm)
None	835 Film tear	629 Film tear
Water	403/331	548 Film tear
Water/Ethanol 1:1	84/62	482/404
Soybean oil	1106 Film tear	593 Film tear
White Vinegar	32/18	300/240
Skin-So-Soft	739 Film tear	650/353
Hot sauce	265/180	465/362

Figure 8: Results of Testing.