Basic Principles of Thin Film Barrier Coatings

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Key Words: Permeation barrier coatings; Oxygen permeation; Surface treatment; Vapor permeation

ABSTRACT

There is hardly any application used in Thin Films Technology, with as widespread use as the Barrier Coating on Packaging Films. But despite this fact, there is – still – not a comprehensive understanding as to why and how Barrier Coatings actually work. In fact even the biggest producers of barrier coated materials seem to struggle when it comes to explanations why certain coatings and procedures work or fail. It has become apparent though, that sometimes even the most fundamental aspects of the function of barrier coatings are not understood. This report will try to put together some of the basic principles of Thin Film Barrier Coatings. In addition it will point to some of the aspects of the function of barrier coatings, which require more attention in the scientific field.

THE DIFFUSE WORLD OF BARRIERS AND WHY GASES PASS THROUGH SOLIDS

Now, what exactly is a barrier or barrier coating? In the simplest terms it is a membrane that creates a partition between two areas, for example keeping certain materials – gases, liquids or solids – on one side of a separation preventing it from reaching the other side. Packaging films function in a similar manner: they contain a packaged produce and lock out environmental impact to the degree desired. Unfortunately there is no such thing as total separation in the world of physics, and for understanding why we need to look at the effect of diffusion.

Diffusion is the movement of matter through a medium driven by the kinetic motions of atoms and molecules. Directional diffusion – that is the preferred flux of matter in a specific direction – is caused by nature's strive for equilibrium and occurs in the opposite direction to the gradient of concentration of the particular species.

The rate of diffusion *(j)* of matter *(i)* is described by Fick's 1st law, which states:

$$j_i = D_{ij} \frac{dc_i}{dx} \tag{1}$$

where D_{ij} is the diffusion coefficient of the matter i in a medium j, and $\frac{dc_i}{dx}$ describes the concentration gradient in the diffusion direction. Values of D_{ij} are typically in the order of $10^{-1}\ \frac{cm^2}{s}$.

Diffusion in gases is quite well understood and the diffusion coefficient for most gases within gases can be calculated using gas kinetic theories as shown in Equation 2:

$$D_{ij} = 0.002662 \frac{\sqrt{T^3}}{p\sigma_{ij}^2 \sqrt{M_{ij}}\,\Omega_D} \tag{2}$$

where σ_{ij} represents the gas kinetic parameters of the Lennard Jones length [Å] and Ω_D the diffusion collision integral, which is a correction factor for the interaction between the gas molecules. M_{ij} is the reduced molar mass which recognizes the molar distribution of the gas mixture. The derivation of these gas kinetic parameters can be found in Equation 1.

The diffusion of gases in solids however is not as simple to calculate. This is dependent on many more factors such as the degree of crystallinity, porosity, chemical interaction with the gas atoms, polarity of the gas etc.

Diffusion of gases, such as oxygen, through totally crystalline materials is typically very slow due to the very constricted interstitial spaces of the lattice. The diffusion mechanism, when no chemical reaction takes place, is considered to occur by a "random walk" of atoms or molecules through the interstices of the lattice. In this case, the diffusivity is given by

$$D = \gamma \bar{\lambda}^2 \Gamma \tag{3}$$

where γ is a geometric factor, $\bar{\lambda}^2$ is the average of the squares of the jump distances and Γ is the jump frequency. For gas diffusion in single crystals, lattice defects and to a lesser extent crystallographic orientation often control the diffusivity. For partially crystalline solids diffusion is largely dictated by the amorphous content as migration through the amorphous phase occurs considerably faster than through the crystalline lattice. This is also the case for the grain boundaries, which act as short circuit pathways for diffusion. It should be noted that if the solid is porous then a number of additional mechanisms exist for the flow of gases through the structure; these include viscous flow where the gas migrates unhindered through a pore of diameter around 100 nm, Knudsen flow which involves the occasional collision between the diffusing gas and the pore wall (pore diameter between around 4 nm and 100 nm), and surface diffusion (involves the gas migrating along the pore wall). The extent to which each mechanism contributes to the overall gas flow depends on the size of the permeating molecule (or atom) and the number and size of each class of pore present in the solid. The diffusion coefficient of these solids is considerably lower than those for the cases previously outlined.

The diffusion behavior of water vapor in solids differs significantly to that of oxygen, due to its reactive nature and bi-polar structure. A non-interactive model based on a Fickian mechanism of molecular water vapor diffusion in silicon oxide has been proposed but to date has not been supported by experimental evidence. The data suggest that the migration of water vapor through some solids involves attractive interaction and/or reaction. In some cases, hydrolysis has been shown to be a partial pathway in a non-Fickian mechanism of water diffusion through oxides.

Generally the diffusion coefficient of gases in solids is many orders lower than in gas. The diffusion coefficient for Oxygen (O_2), which is considered to be non-reactive, in air is about $0.15 \frac{cm^2}{s}$ and in Polyester, depending upon crystallinity, it is in the region of $10^{-9} \frac{cm^2}{s}$. Typical barrier materials like metal oxides or aluminum however have a diffusion coefficient for oxygen several magnitudes lower than this, for example silicon oxide has a reported value of $10^{-13} \frac{cm^2}{s}$. Oxygen diffusion in aluminum is a special case, since oxygen chemically reacts with aluminum forming aluminum oxide, which in turn alters the diffusion properties of the solid. In the absence of defect space within the matrix, diffusivities as low as $10^{-18} \frac{cm^2}{s}$ have been measured for water vapor migration through silicon oxide at standard temperature and pressure.

Knowing the diffusion coefficients of our "enemy" gases through our packaging material still does not really tell us how much gas actually penetrates the package and reaches the product. Knowing the permeation would provide us with this information. If we substitute Henry's law [Eq. 2], which describes the solubility S of gas in solid materials (c_x and p_x are the concentration and the pressure respectively),

$$c_x = S \cdot p_x \tag{4}$$

into [Eq. 1] we yield the molar flux

$$j_i = \frac{D_{ij} \cdot S \cdot (p_1 - p_2)}{d} = \frac{P_m^*}{d} \cdot \Delta p \tag{5}$$

were $\mathbf{P_m^*} = D\ S$ is the **molar Permeability of the film** normalized to a unit thickness. Dividing $\mathbf{P_m^*}$ by the film thickness t delivers the **Permeation P**:

$$P = \frac{P_m^* \cdot M}{\rho \cdot d} \left[\frac{cm^3}{m^2\, day\ atm}\right] \tag{6}$$

Typical values of oxygen permeation through polymer packaging materials are listed in Table 1, and one can see that indeed a significant amount of oxygen reaches the contents of the package.

Table 1: Permeation Values of Basic Polymers

Polymer	**Permeability** $\left[\frac{cm^3 O_2}{m\,d\ atm}\right]$	**Permeation** $\left[\frac{cm^3 O_2}{m^2\ d\ atm}\right]$	**Film Thickness [μm]**
LD-PE	$3.61e^{-1}$	60000	60
HD-PE	$6.70e^{-3}$	100	60
PP	$1.51e^{-1}$	2500	60
PET	$1.20e^{-3}$	100	12

FLUX THROUGH THE PLASTIC DESPITE THE PRESENCE OF A BARRIER!

So one can see that our typical shopping bag material is rather a sieve (especially if the bag is made from LD-PE)! Our "fresh" potato chips would go stale within a day, and snack food would be no fun any more. Fortunately industry has shown us ways in which to place barriers in the way of oxygen and water, and the most common form used is the application of a thin coating of metal or oxide, which as we have seen above has much lower diffusion coefficients than the polymer materials. Below is a list of such barrier constructions (see Table 2).

Surprisingly the barrier values listed in Table 2 are actually a lot worse, than one would expect from the diffusion values of oxygen or water in these coating materials (see above!). Is there a chance, that the diffusion coefficients are actually off, or is the world, once again, not as perfect as we think? Let's have a look at the different possibilities.

Table 2: Oxygen and water vapor barrier performance of different barrier materials (Reference [15], unless stated otherwise)

Barrier Material	Thickness of Substrate or Coating	Oxygen Transmission [ccm/m²/day/atm]	Water Vapor Transmission [g/m²/day/atm]	Deposition Process	Film Composition	Source
PET/Blank	12.00 µm	100	64.64			
PVDC	24.00 µm	8	0.3			[2]
EVOH	24.00 µm	0.16 - 1.86 *	N/A			[2]
m-OPA	15.00 µm	30				
Aluminized PET^{+} (single)	~ 30 nm	0.31 - 1.55	0.31 - 1.55	Evaporation	Al	[3,4]
Aluminized PET^{++} (double)	~ 30 nm each	0.03	N/A	Evaporation	Al	[3,4]
Aluminum on PE	7 µm Al	0.001	N/A	Laminated	Al	
SiO_x on PET	10 - 80 nm	0.35 - 10**	0.46 - 1.24	Evaporation	SiOx	[5–8]
SiO_x on PET	10 - 80 nm	0.08 - 1.55	0.5 - 5.0	PECVD	SiOx	[9–11]
Al_2O_3 on PET	20 nm	1.5	5.0	Reactive Evaporation	Al_2O_3	[12,23]
Al_2O_3/SiO_x on PET	50 nm	2.0 - 3.0	1.0	Evaporation	Al_2O_3/SiO_x	[12,13]
Diamond-like Carbon on PET	20 nm	2	1.50	PECVD	Diamond	[14]

*depending on relative humidity and ethylene content
**depending on used process

$^{+}$: Al 30 nm / PET 12 µm
$^{++}$: Al 30 nm / PET 12 µm / AL 30 nm

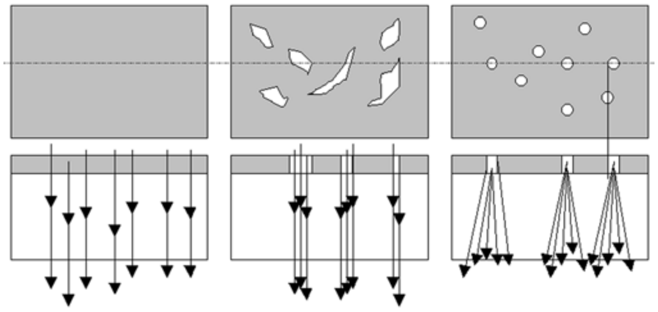
RIGHT THROUGH THE BARRIER OR WHY DOES THE FOOD GO BAD IN THE BAG

To calculate the success of our barrier coating a factor is introduced at this point, which we will call the **B**arrier **I**mprovement **F**actor, or BIF, which is defined by the expression:

$$\mathrm{BIF} = \frac{P_{\mathrm{Substrate}}}{P_{(\mathrm{Substrate+Barrier})}} \tag{7}$$

and describes the improvement in barrier property achieved by applying a specific barrier layer. The impact, which the substrate's properties (thickness and permeability) as well as the barrier's properties (defect ratio and permeation) have on the BIF, can be shown using different models (Figure 1). None of the models shown below is valid alone but they supplement each other. Furthermore, they don't cover all aspects of permeation through thin defective or defect free layers, but they do give some insight into what needs to be achieved in order to obtain a barrier improvement of the film structure. The three models covered here are the

- Electric Analogy Model
- Coverage Model
- Pinhole Model



Electric Analogy Coverage Model Pinhole Model

Figure 1: Schematic of Permeation Models.

Electrical Analogy Model

The electrical analogy model assumes, that permeation through different layers is like electrical current passing through a series of resistors (Figure 2).

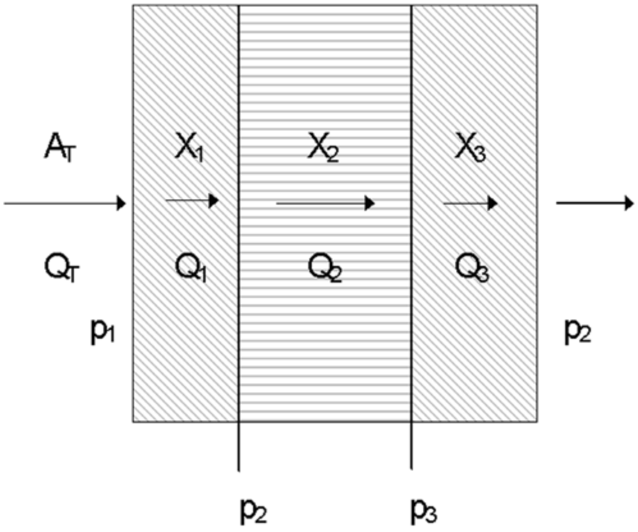


Figure 2: Electric Analogy Model.

The gas volume Q_T permeating through an area $A_T=A_1=A_2=A_3$ of a multilayer structure with the total thickness $d_T = d_1 + d_2 + d_3$ is constant in each layer, so that

$$Q_T = Q_1 = Q_2 = Q_3 \tag{8}$$

Substituting in [Eq. 5] leads to

$$Q = \frac{P^*}{d} \cdot A \cdot (\Delta p) \tag{9}$$

or

$$\begin{aligned} Q_T &= \frac{P_T^*}{d_T} \cdot A_T \cdot (p_1 - p_4) = \frac{P_1^*}{d_1} \cdot A_1 \cdot (p_1 - p_2) \\ &\frac{P_2^*}{d_2} \cdot A_2 \cdot (p_2 - p_3) = \frac{P_3^*}{d_3} \cdot A_3 \cdot (p_3 - p_4) \end{aligned} \tag{10}$$

Rearranging eq. [Eq. 10] and with *$(p_1-p_4)=(p_1-p_2)+(p_2-p_3)+(p_3-p_4)$ yields*

$$\frac{Q_T d_T}{A_T P_T^*} = \frac{Q_T}{A_T}\left[\frac{d_1}{P_1^*} + \frac{d_2}{P_2^*} + \frac{d_3}{P_3^*}\right] \tag{11}$$

therefore

$$\frac{d_T}{P_T^*} = \frac{d_1}{P_1^*} + \frac{d_2}{P_2^*} + \frac{d_3}{P_3^*} \quad \text{or} \quad \frac{1}{P_T} = \frac{1}{P_1} + \frac{1}{P_2} + \frac{1}{P_3} \tag{12}$$

Since the diffusion through a multilayer structure can be calculated like resistors in series (when $\mathbf{\frac{1}{P}}$ reflects the resistance of the particular layer) this model is called the "Electrical Analogy Model" and is commonly referred to as the ideal laminate. Assuming the thin film barrier layer is free of defects the BIF than can be expressed by

$$\mathrm{BIF} = 1 + \frac{P_{\mathrm{Substrate}}}{P_{\mathrm{Barrier}}} \tag{13}$$

and therefore

$$\mathrm{BIF} = 1 + \frac{P^*_{\mathrm{Substrate}}}{d_{\mathrm{Substrate}} P_{\mathrm{Barrier}}} \tag{14}$$

Coverage Model

If the thin film barrier material can be considered to have a perfect barrier that is it is impermeable, then any permeation through the barrier layer must take place through defects. The Coverage Model assumes that the permeation is directly proportional to the defect area ratio (Θ) exposing the area fraction of the uncovered polymer. It is furthermore assumed that the diffusion through the substrate polymer is unidirectional or totally attributed to the bare polymer surface. Thus, the permeation P through the structure is

$$\mathrm{P} = \Theta \frac{P^*_{\mathrm{Subsrate}}}{d_{Substrate}} \tag{15}$$

[Eq. 15] in [Eq. 5] shows, that the BIF for a polymer is independent of the thickness *d* and inverse proportional to the defect area ratio:

$$\mathrm{BIF} = \frac{1}{\Theta} \tag{16}$$

Although the unidirectional diffusion seems to be unlikely, the coverage model is valid for the extreme cases that either the thickness of the substrate is very small (thus the spreading can be neglected) or the coverage is very small [$(1 - \Theta) << 1$]. The Metallized Pinhole Model, outlined below, highlights the restricted application of the coverage model in an analytical way.

Metallized Pinhole Model (Pinhole Model)

The unidirectional diffusion assumed in the coverage model is an idealization that does not match reality. It is more realistic to assume that the gas diffusing through a hole will spread out in all directions in the polymer. In 1958 Prins and Hermans [16] proposed a model for the gas diffusion through pinholes in metallized polymers.

For this model the following assumptions are made:

- no permeation through the thin film barrier material
- permeation is through the defects only
- all the defects are circular and can be described by their mean radius r_o and their number per unit area
- all defects are sufficiently far apart from each other to assume additivity

The defect area ratio is then defined by:

$$\Theta = \frac{r_0^2}{\Phi} \tag{17}$$

In a cylindrical coordinate system (see Figure 3), the steady state diffusion equation to solve is the following:

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} = 0 \tag{18}$$

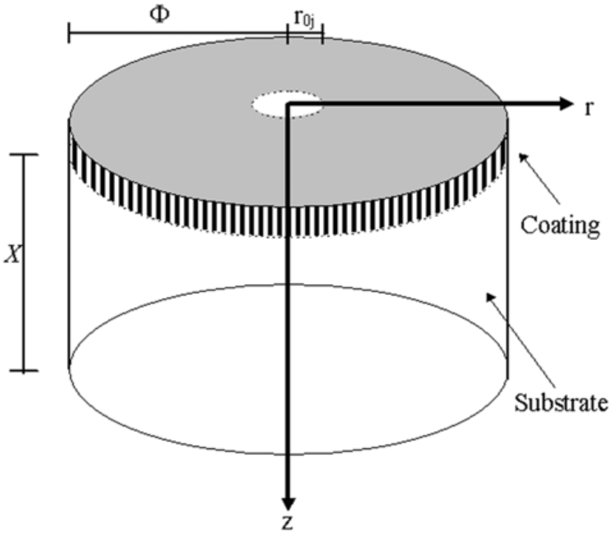


Figure 3: Pinhole Permeation Model.

Applying the following boundary conditions:

$c(r,0) = c_2\ , \quad r \le r_0$	Oxygen concentration at the surface, inside the pinhole is equal to the solubility of oxygen in the polymer at 1 atm
$\frac{\partial c}{\partial z}\big\rvert_{z=0} = 0\ , \quad r > r_0$	No permeation directly under the coating
$c(r, X) = c_1\ , \quad \forall\, r$	Zero oxygen on the opposite surface.

the following approximation for the oxygen flux has been found[1]

$$J = D \cdot \frac{(c_1 - c_2)}{d} \cdot \Theta \cdot (1 + 1.18\lambda) = D \cdot S \cdot \Theta \cdot (1 + 1.18\lambda) \tag{19}$$

when $\Theta << 1$ and $d > 0.3\ r_0$.. λ is the ratio between substrate thickness and pinhole diameter, thus:

$$\lambda = \frac{d}{r_0} \tag{20}$$

and hence [Eq. 19] is valid for l > 0.3. The Permeation P then is given by:

$$P = \frac{J}{\Delta p} = \frac{P^*_{\text{Substrate}}}{d} \cdot \Theta \cdot (1 + 1.18\lambda) \tag{21}$$

and the BIF is:

$$\text{BIF} = \frac{1}{\Theta(1 + 1.18\lambda)} \tag{22}$$

When the film thickness is small compared to the pinhole radius (λ << 1), [Eq. 22] goes over into the trivial solution

$$P = \frac{P^*_{\text{Substrate}}}{d} \cdot \Theta \quad \Rightarrow \quad \text{BIF} = \frac{1}{\Theta} \tag{23}$$

proving the validity of the coverage model for small substrate thickness.

It is interesting to also look at the inverse case, where only small islands of coating cover the surface (1 - Θ) << 1. In this case the boundary condition change to:

$c(r,0) = c_2\ , \quad r > r_0$	Oxygen concentration at the surface, outside the island is equal to the solubility of oxygen in the polymer at 1 atm
$\frac{\partial c}{\partial z}\big\rvert_{z=0} = 0\ , \quad r > r_0$	No permeation directly under the coating
$c(r, X) = c_1\ , \quad \forall\, r$	Zero oxygen on the opposite surface.

Here again for small substrate thickness there is the same trivial solution given in [Eq. 23]. It is interesting that the same result is obtained for λ >> 1, indicating that small amounts of coverage don't have an influence on the permeation at all.

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[1] The exact mathematical derivation can be found in [16]

Beu and Mercea [17] performed FEM analysis (see Figure 4) on metallized polymers, using the pinhole model. The solutions show that with increasing polymer thickness the gas concentrations at the outer radial boundaries (r=Φ) increases as well, causing higher diffusion over these boundaries. If the density of holes increases so the pinhole areas touch each other and the concentration gradient over the radial border becomes equal to zero and diffusion does not take place. At small thickness the radial diffusion becomes more and more neglectable.

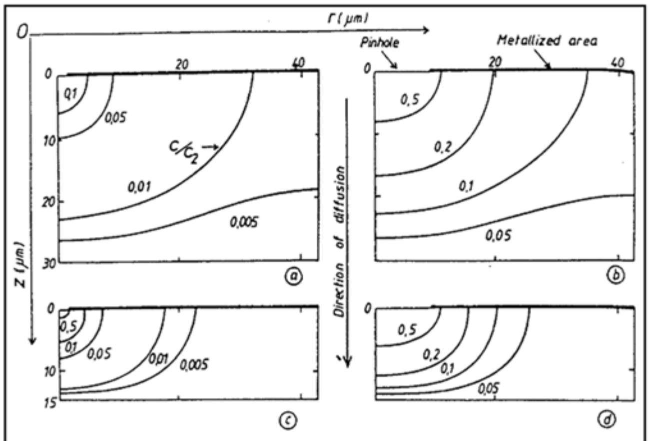

Fig. 2. Calculated normalized concentration profiles for:
a) l - 30 µm, r_o - 1 µm, b) l - 30 µm, r_o - 9 µm, c) l - 15 µm, r_o - 1 µm and d) l - 15 µm, r_o - 9 µm.

Figure 4: FEM Simulation for Diffusion through Pinholes.

Besides these limitations of the Pinhole Model it is interesting to have a look on the practicable outcome, i.e. what coverage actually is necessary for a specific polymer to even see the barrier effects from the coating. Figure 5 shows the influence of the pinhole diameter on the BIF with changing defect areas on a 12 µm PET substrate. In addition a curve for the Coverage Model is also drawn. It is seen that the smaller the hole diameter becomes the smaller the BIF will be at a given defect ratio. This is explainable through the larger number of holes required to get a certain defect ratio and by that again the better spreading of gas in the polymer. But once again, one has to obey the limitations of the model.

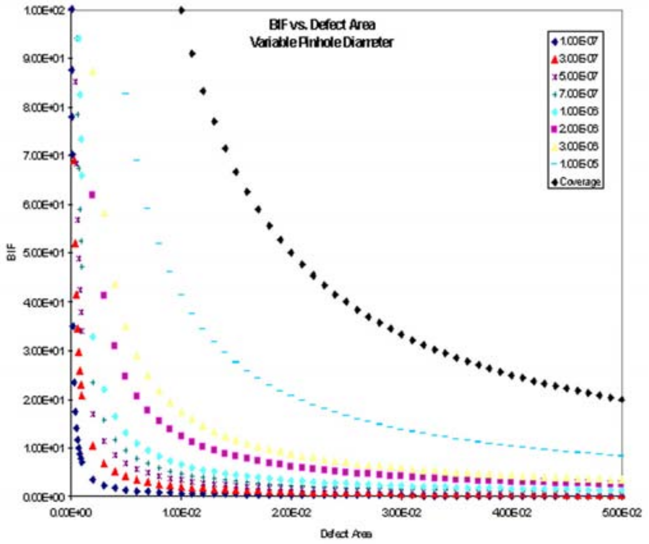

Figure 5: Influence of Pinhole Diameter and Coverage on the BIF for 12 µm Substrate.

Within the limitations of the model it appears that a coverage higher than 95% is necessary to begin to see some improvement on the barrier function of the system. This high value explains the humongous impact small pinhole defects in barrier coatings have on the overall performance of the barrier coating. If, in addition, the barrier material does allow permeation, as assumed in the Electrical Analogy Model, then the required coverage will increase even higher!

INTERFACE PHENOMENA

Although the equations of the Pinhole Model have been widely accepted and repeated [26], they do not represent the whole wisdom about barrier functions. In fact, there have been reports about interesting phenomena, which contradict parts of these equations. Examples of these disagreements are:

a. Metallization of Polymer Films with varying degrees of pre-treatment show different Barrier Properties, even though optical density and defect count appear to be the same.
b. Metallization of Polymer Films with Electron Beam Evaporation versus Resistive Evaporation or Free Span versus Supported Web yield different Barrier Properties, even though the material properties such as the optical density and defect density of the coating are the same.
c. Metallized Polymer Films laminated with either adhesive coatings or extrusion lamination show different Barrier Properties, to the extent that sometimes the barrier after lamination is higher than the barrier properties of the single layers would suggest.

In all three cases there is a relation to the surface of the substrate and the coating, which raises questions about the impact of the substrate before, during and after the coating. It is therefore the mating plane, or the interface, between substrate and coating, which has substantial impact on the barrier performance of the coating. It has to be mentioned though, that the physical and chemical effects taking place at the interface are far too complex to describe completely within the limited scope of this paper, so only the very basic aspects will be covered. Much more information can be found within the referenced literature. Some of the aspects described here have not been completely analyzed or examined and pledge goes out to further investigate these aspects in the near future to complete our understanding on how to make the perfect barrier.

Pre-Treatment: How the Surface prior to Coating Impacts the Outcome

In a quote attributed to the great physicist Linus Pauling, it was said: "God created Matter, but is was the Devil who created the surface!" There is a great deal of truth in this statement, as that in thin film technology the properties of the surface immediately before the deposition of any coating have tremendous impact on the properties of this coating. Coating polymer films presents a particular challenge; since the chemistry of polymers is so complex that even minor process modification can significantly alter the surface chemistry and topography of the substrate. For Barrier Coatings the goal must be to create a surface, which allows the formation of a perfect coating; the problem is, however, that most polymers have intrinsic physical and chemical properties that go contrary to the requirements.

Polymers like polypropylene, possibly the most common plastic film metallized for barrier applications, exhibit a surface energy as low as 32 dyne. Polypropylene is chemically rather inert, and as a homo-polymer is not metallizable. The saturated Carbon-Hydrogen chain does not give the aluminum or any other metal any locus to chemically connect with the surface. Metallization in such a case only happens based upon loose physical connection. For this reason most polymers are pre-treated in one-way or another. Treatment of polymer surfaces has been described in numerous publications [i.e. 18–22] and the most common methods are:

- Corona Treatment
- Flame Treatment
- Inline Plasma Treatment

All these methods expose the polymer surface to activated, ionized gases. Pretreatment causes three reactions on the polymer: Chain Scissioning, Cross Linking and Grafting. The latter is the most important, since it inserts reactive chemical groups onto the polymer. Typical is the oxidation of the polymer surface, which creates C=O, C-O-O-C, C-O-O-H or C-O-H goups on the surface.

Figure 6 shows schematically how such a surface looks without and with treatment. The obvious advantage of pretreatment is that now the polymer exhibits a reactive surface with which the metal can react and form chemical bonds. Friedrichs et al. [24] analyzed plasma modified polymer surfaces after metallization and did find that the deposited metal indeed reacts with the activated surface creating metal-organic bonds. This is also shown through the higher adhesion between the metal layer and the polymer surface after treatment with oxygen, see Figure 7 The investigation was aimed at improvement of adhesion of metal layers on the polymer surface, so what is the impact on the barrier property?

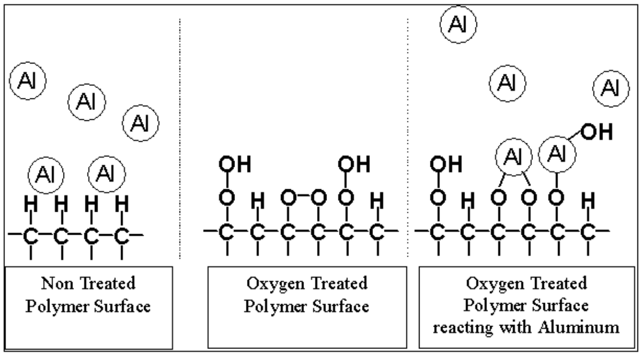

Figure 6: Non-Treated and Treated Polymer Surface at Metallization.

The deposited metal layer starts initially growing at condensation points, also known as nuclei. These sites are loci with surface energy high enough to allow the metal species arriving in the vapor cloud to discharge its energy and to connect with the surface. A treated surface however offers enough nucleation sites to start the condensation of the metal. The left half of Figure 8 depicts the nucleation phase of silver deposition on non-treated (outmost left) and treated (second from left) polymer surfaces. Obviously the treated surface (right half of Figure 8) shows a much higher density of nucleation points. During the coating process the metal layer grows into a dense structure at a lower thickness (outer right), while at the same average thickness the non-treated material still exhibits voids.

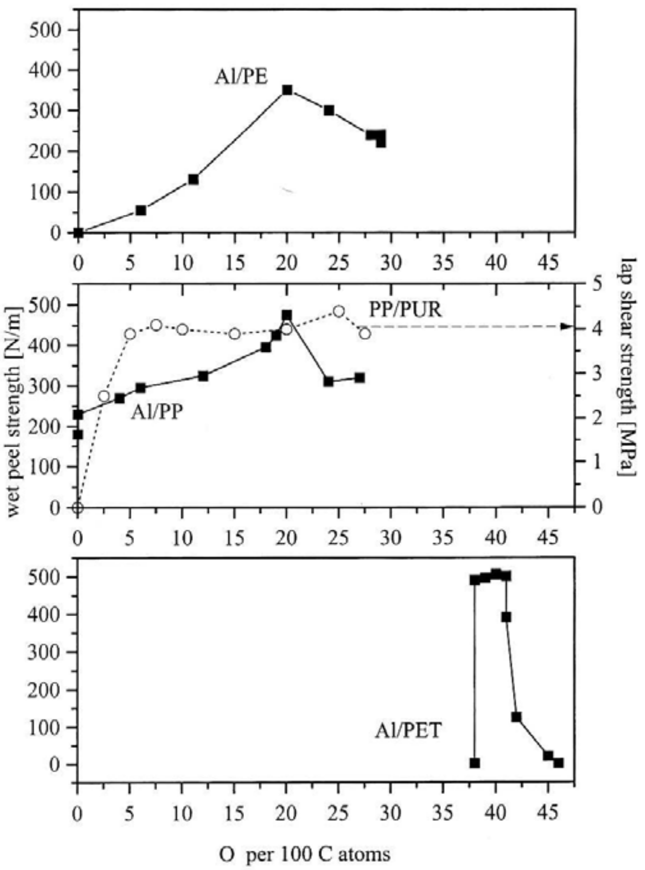

Figure 7: Correlation between O_2 Plasma Induced Oxygen uptake of PE, PP and PET surfaces as measured by XPS and peel strengths of Al-PE, Al-PP and Al-PET [23].

Figure 9 schematically depicts, why the higher nucleation density creates the better barrier. With low density there are voids left on the immediate surface, which allows gas permeating through a crack to have a relatively broad area where it can diffuse into the polymer surface. With high nucleation density a better surface coverage is achieved, gases permeating through cracks basically have only the narrow area between neighboring metal grains in which to diffuse into the polymer.

Another aspect of the surface that one has to be aware of is the surface morphology. A metallizable surface should be as smooth as possible, and that is for two reasons:

1. The higher the surface roughness the larger the effective surface area becomes. The effective surface area is the area exposed to the environment, and that means for rough surfaces gases have a larger area available to penetrate into the polymer.
2. With the exception of the Sputter and PA-CVD processes the coating processes are "line of sight" coating. This means that high surface roughness increases the probability of having non-coated areas, specifically in grooves and crevices.

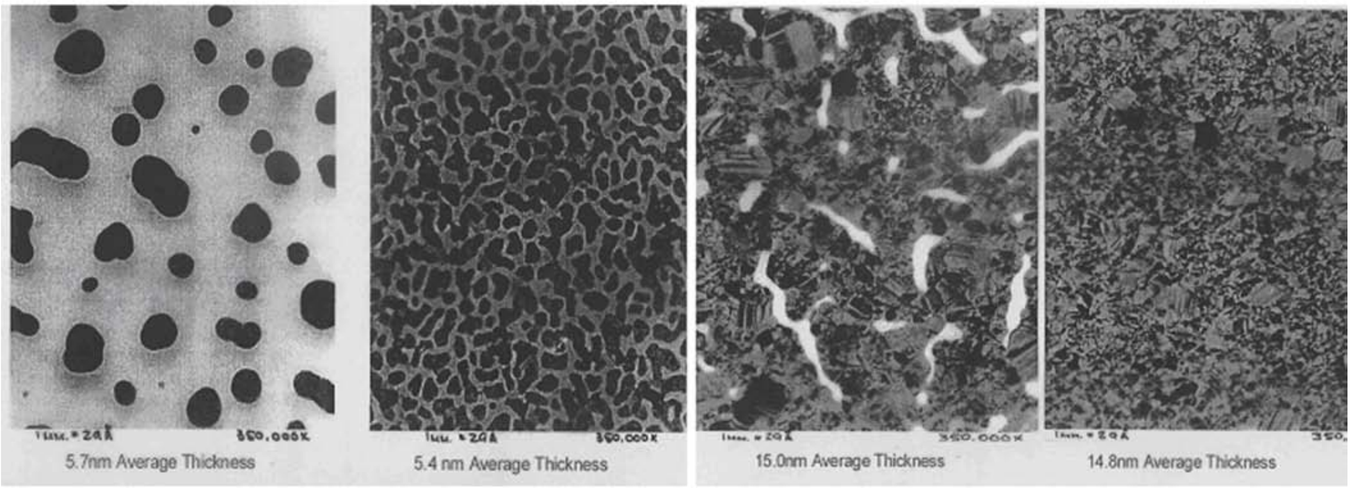

Figure 8: Nucleation and Layer Growth on Non-Treated and Treated Polymer Surfaces [25].

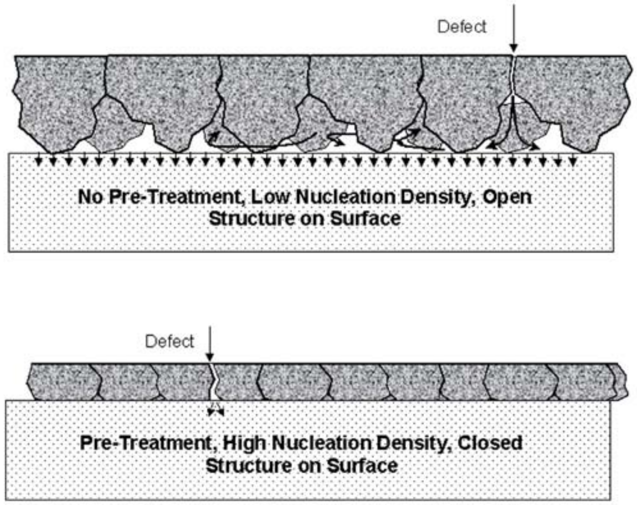

Figure 9: Impact of Nucleation Density on Barrier Property.

Mode of Operation: How the Different Coating Methods Affect the Coating

The coating techniques employed to put the barrier layer onto can have an impact on the barrier property of the final coating as well. Commonly used processes for the deposition of barrier metals or oxides are:

- Resistive Evaporation of Pure Metals
- Resistive Evaporation of Metals with Plasma Enhanced Oxidation
- Electron-Beam Evaporation of Metals and Oxides
- Sputter-Deposition of Metals and Oxides, Reactive and Non-Reactive
- Plasma Enhanced Chemical Vapor Deposition

Depending on the coating process used there are different sources of energy which work on the substrate surface:

- Radiation:
  - Heat Radiation from the Evaporator Boats or the Crucible
  - Electron Radiation from Reflected Electrons during E-Beam Evaporation
  - Electron-, Ion- and UV-Radation from Plasma during Sputtering or Plasma Enhanced Processes
- Heat of Condensation and Fusion as well as specific Heat from Material deposited (see Figure 10).
- Kinetic Energy of Material impacting the surface, specifically during sputtering.

The energy input into the web surface during metallizing a 50 nm layer of aluminum from Heat of Evaporation, Fusion and Cooling alone is about $1.70\frac{kJ}{m^2}$, which is about the same energy used for heavy Plasma Pre-Treatment. This heat does not include the heat transferred by radiation. It is therefore safe to expect that the coating process itself does have an impact on the substrate material. In another case it has been reported [23], that PET being coated in an E-Beam evaporator exhibited Oxygen transmission rates which were about ten times higher than the base material would allow. So what exactly can happen on the surface?

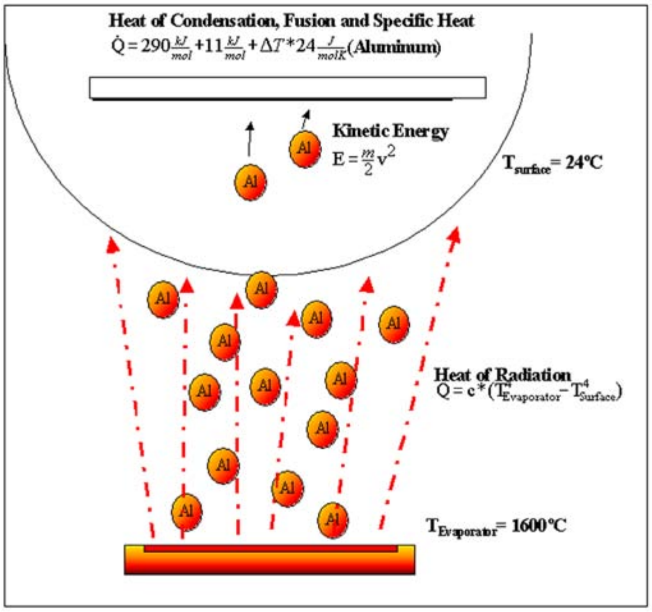

Figure 10: Sources of Heat impacting the Substrate Surface during the Deposition Process in Evaporative Coating.

The impact of the deposition energy can actually change or alter the chemical and physical composition of the interface layer (see Figure 11). The alteration can create a layer with either much higher solubility for the specific gas or with lower solubility. Since the solubility becomes higher the lower the degree of crystallization in the polymer is, chances are, that the energy impact will degrade the crystalline structure, thus leading to a higher solubility in the interface layer. This off course leads to a faster radial diffusion under the pinholes, and with that the barrier value decreases.

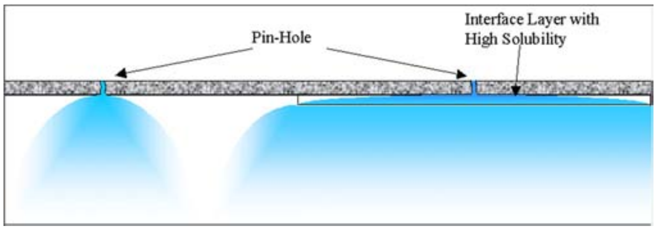

Figure 11: Change of Barrier Function through Degradation of Interface Layer

The higher kinetic energy of the depositing material can have a positive impact on the barrier property. Erlat et al. [27] indicate in their analysis of materials deposited by different processes, that Sputter Coating creates better Barrier Layers. They found that the higher kinetic energy in the deposited particles create a denser layer, reducing the number of micro and meso-defects, which contribute to the malfunction of the barrier coating. This thesis is also supported by the work of Schiller et al. [28].

Another important aspect, specifically in conjunction with plasma, plasma treatment and electron beam evaporation is the creation of surface charges. Especially with biased plasmas and the electron beam it is possible to create surface charges which exceed the breakdown voltage of the polymer. If this happens, a discharge through the polymer occurs and holes – sometimes microscopic in size – in the polymer results.

Barriers after Lamination

According to the Pinhole Theory the barrier properties of the barrier-coated film should increase by the same function as the single layer sheet:

$$J^{-1} = \left(D_1 \cdot S_1 \cdot \Theta \cdot (1 + 1.18\frac{d_1}{r_0}) \right)^{-1} + \left(D_2 \cdot S_2 \cdot \Theta \cdot (1 + 1.18\frac{d_2}{r_0}) \right)^{-1} \tag{24}$$

where Index 1 defines the properties of the base substrate and Index 2 the properties of the sheet laminated on top of the barrier layer. If the base substrate and laminate sheet are identical the diffusion through the laminate would therefore be cut in half (see Figure 12).

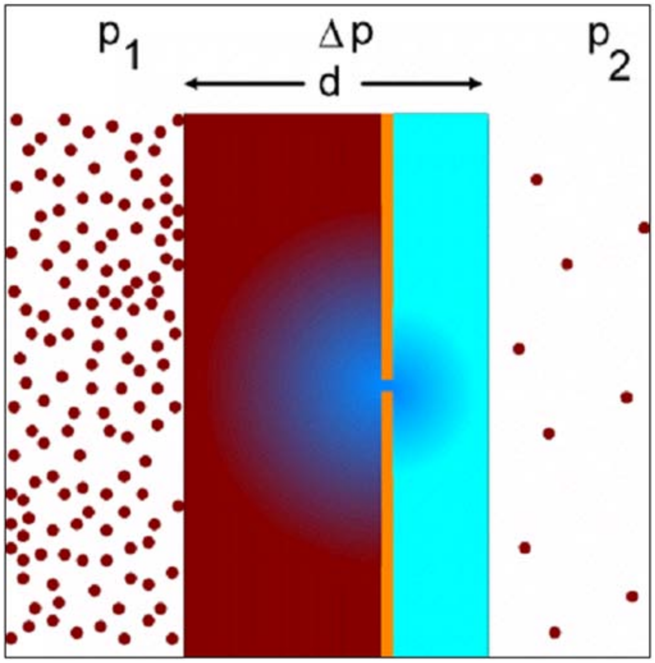

Figure 12: Diffusion through a laminated Barrier Construction [28].

Why, however, are the results varying? Sometimes the barrier property does not improve at all; in other cases the barrier again is better than the sum of the single layers would suggest. In the first case the answer can sometimes be straightforward: Handling damage caused by stretching, scratching, touching with dirty rollers in the converting equipment, can damage the thin barrier layer to a degree, that the initial barrier on the base substrate has decreased dramatically. In such cases the laminate does not improve the overall barrier, it rather recovers – sometimes barely – the damage inflicted on the base barrier layer.

In other cases however, surface chemistry can take effect again. Hot lamination or lamination with chemically very reactive adhesives can create metal-organic interfaces, which can positively impact on the overall barrier property. Research in this area has not progressed very far at this point, more investigation should be promoted in this area.

CONCLUSION

The function of a Barrier Coating is a very complex matter, witnessed by the enormous amounts of publications and the ongoing research in this area. The basic principles however, as described in this paper, should enable the converter to develop the required understanding of the impact of his procedures on the properties of his product. At the same time it is obvious, that there is still a big piece missing, specifically when it comes to the change in barrier behavior during subsequent converting procedures. For this, additional research, particularly in the area of the interface phenomena, is required and seems to have drawn the interest of several scientists working in this field.

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