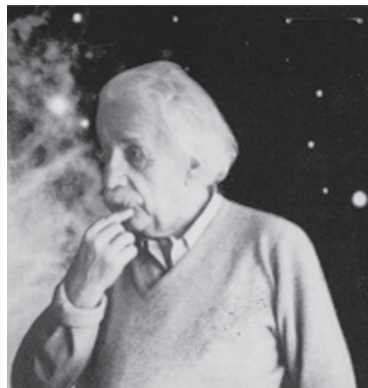


WHITE PAPER

Combining Barrier Technology with Other
Important Properties in Flexible Electronics

Background

In the early 1900s, when J.J. Thomson¹ was involved with Cambridge University's Cavendish Labs, this was a popular dinner toast, "To the electron: may it never be of any use to anybody!" In 1926, Albert Einstein wrote the following oft-cited quote referring to quantum theory, „Jedenfalls bin ich überzeugt, daß der [Herrgott] nicht würfelt.“ (Anyhow, I am convinced that God does not play dice.)



Even if we allow that the Cavendish toast may have been tongue in cheek, it's likely that these two brilliant men did not foresee, at this early stage, the extent that their own work would revolutionize human society: For at least fifty years, the semiconductor and photovoltaic (PV) industries have harnessed quantum effects and manipulated electrons to produce technologies that once would have been considered miraculous. This includes all conventional electronics as well as flexible and printed electronics: Devices such as touch-sensitive screens, flexible

and printed circuits, bistable displays and solid state lighting were barely imaginable not so long ago. Today, another revolution is occurring in these industries: New discoveries coax even more materials to do our sub-atomic bidding.

Nevertheless challenges remain: The properties that enable OLEDs, phosphors, and organic PV materials to work often make these materials susceptible to degradation by reaction with water or oxygen or both. For example, a bistable e-reader display may contain moisture-sensitive printed flexible TFTs and a layer of electronic ink requiring the maintenance of a specific range of moisture. An OLED lighting structure may have a cathode layer susceptible to corrosion. Some types of reactions are easily reversible; other types are permanent. Technologies such as OLED and OPV, whose degradation reactions are not easily reversible, need higher levels of protection than have historically been available in transparent flexible form.

This paper will describe the predominant options for protecting electronically and photonically active materials, with a primary focus on flexible barrier technologies.

Comparisons of Commercial Barrier Types

Table 1 shows commercially available barrier technologies. Glass is included as a reference even though it is not generally thought of as flexible². There are a few other technologies with ultra-barrier performance not shown in the table because they are still in pre-commercial status. These include ceramic barriers with nano-particle filled pinholes.

¹J.J. Thomson, the British scientist credited with the discovery of the electron, was Cavendish Professor of Experimental Physics at Cambridge from 1884 to 1918 and was awarded the 1906 Nobel Prize in physics.

²Corning is developing a very promising flexible glass capable of roll-to-roll processing, but it is not yet commercial.

Table 1: Comparison of Barrier Types

Barrier type	WVTR ³ g/m ² /day	O ₂ TR ³ cm ³ /m ² /day	Strengths	Weaknesses
Polymer — O ₂ — H ₂ O	10 ⁺¹ –10 ⁺² 10 ⁻¹	10 ⁻¹ –10 ⁰ 5x10 ⁺¹	<ul style="list-style-type: none"> • Excellent clarity • Flexible, may be creased without damage • Excellent toughness • High fatigue resistance 	<ul style="list-style-type: none"> • High performance H₂O & O₂ barriers not usually found in a single polymer • Expensive • WVTR can change abruptly⁴
Ceramic-coated polymer	10 ⁰ –10 ⁻²	3x10 ⁻¹	<ul style="list-style-type: none"> • Good clarity • Somewhat flexible because of thin deposition 	<ul style="list-style-type: none"> • Brittle in tension • Fair fatigue resistance • Must not be creased
Multilayer ceramic-coated polymer	10 ⁻³ –10 ⁻⁶ (depends on layer count)	10 ⁻¹ –10 ⁻⁴ (depends on layer count)	<ul style="list-style-type: none"> • Good clarity • Somewhat flexible because of thin deposition 	<ul style="list-style-type: none"> • Brittle in tension • Lower fatigue resistance • Must not be creased or wrinkled • High cost for more than two barrier layers
Metal foil < 25 μm thick	< 10 ⁻¹	< 3x10 ⁻¹	<ul style="list-style-type: none"> • Economical • Somewhat flexible • May be able to double as a grounding plane or EMI/RF Shield 	<ul style="list-style-type: none"> • Opaque • Must not be creased or wrinkled • Prone to wrinkles or tears unless supported by polymer laminate • Pinholes may cause spot defects in non-reversible reaction products
Metal foil ≥ 25 μm thick	zero	zero	<ul style="list-style-type: none"> • Zero gas transmission at ≥ 25 μm thickness • Somewhat flexible • May be able to double as a grounding plane or EMI/RF Shield 	<ul style="list-style-type: none"> • Opaque • Must not be creased or wrinkled • Prone to wrinkles or tears unless supported by polymer laminate
Glass (for reference purposes)	zero	zero	<ul style="list-style-type: none"> • Zero gas transmission • Transparent • Scratch resistant 	<ul style="list-style-type: none"> • Not (yet) processable roll-to-roll

Metal Foils and Ceramic Layers — Pinhole-Dependent Barrier Performance

Whereas polymeric barriers have actual WVTRs that decrease in proportion to their thickness of the polymer, the behavior of metal foils and ceramics is different. Table 1 splits metal foils into two categories: thinner than or thicker than 25 microns. Aluminum foils thicker than 25 μm have essentially zero oxygen and water vapor transmission—like glass at any usable thickness. Foils thinner than 25 microns tend to have occasional pinholes. It is these pinholes which prevent thin foils from being perfect barriers. Their WVTRs are proportional to the pinhole area which is not linearly dependent on thickness. Figure 1 illustrates this concept.

The ceramic barrier layers coated on polymers also have occasional pinholes and other microscopic defects. As is the case with metal foils, these defects prevent the ceramic coatings from being perfect barriers. Unlike metal foils, however, there is no viable option to thicken a single ceramic layer to eliminate pinholes: It is both too costly and the thicker ceramic layers are no longer flexible.

Because of this, barriers have been produced with additional thin layers of ceramic material separated by flexible layers, usually polymeric. How much does this help to reduce permeation? More than one might expect!

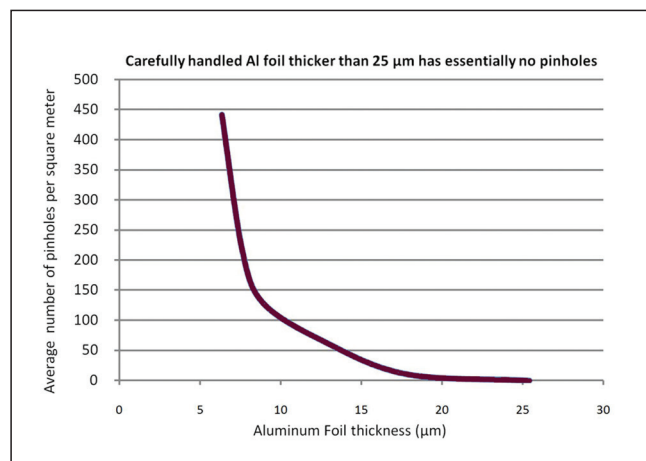


Figure 1: Pinhole Distribution in Aluminum Foil

³See glossary

⁴Water vapor transmission in polymers is a function of diffusion and solubility. If the polymer reaches solubility saturation, for example in the case of extreme environmental exposure which could occur in an accelerated test, the transmission rate can increase noticeably.

Factors Affecting Permeation

The amount of gas flow is a function of the inherent properties of the material, the cross sectional area, the distance the gas must travel, the timeframe, and the concentration driving force. Equation 1 illustrates this.

Equation 1:
$$\frac{Q}{T} = \frac{P \cdot A \cdot \Delta p}{X}$$
 where⁵ Q = flow
 T = time
 P = permeability constant for the barrier material
 A = cross sectional area of flow
 Δp = pressure difference
 X = distance of permeation

We will return to this equation shortly.

Determining the Effect of Multiple Layers in a Barrier Structure

The simplest case is multiple polymeric layers, or a single thin foil or ceramic layer with several polymeric layers. Let's say we have n layers with WVTRs w_1, w_2, \dots, w_n .

Equation 2:
$$W_{overall} = \frac{1}{\sum_{i=1}^n \frac{1}{w_i}}$$

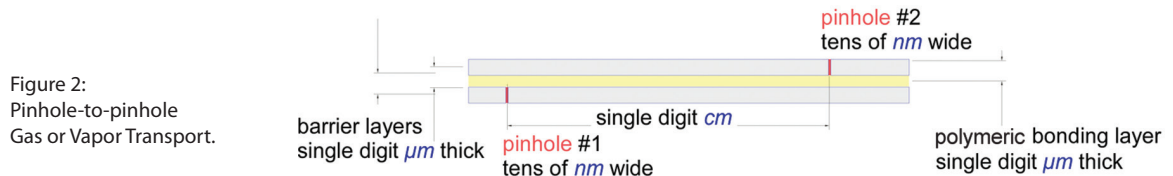
Layer 1	WVTR = w_1
Layer 2	= w_2
Layer 3	= w_3
...	...
Layer n	= w_n

The overall WVTR, w_{total} is related to the individual layers by equation 2:

One of the ramifications of this is that, if your structure consists of poor barriers and good barriers, you introduce very little error by ignoring the contributions of the poor barrier layers. (For large w_i , $\frac{1}{w_i}$ is small.) But the above relationship gets a little more complex if you have more than one layer whose WVTR is pinhole dependent. Here is why:

Because they are quite rare, the pinholes in one layer are extremely unlikely to coincide with those in the other layer and also tend to be relatively widely spaced. So, to pass through both layers of ceramic coating or both layers of thin metal foil, moisture vapor or oxygen must travel a great distance parallel to the barrier layers to get from a pinhole in one layer to the closest pinhole in the next layer.

Figure 2 shows the transmission from one pinhole to another in a typical double barrier structure.



With a very thin intermediate layer, the distances can be two to three orders of magnitude longer than the barrier thickness. Even with a comparatively poor barrier material comprising the intermediate layer, this can still produce a significant impediment to gas and vapor transmission. The more layers introduced in this way, the better the overall performance.

Here is equation 1 again:
$$\frac{Q}{T} = \frac{P \cdot A \cdot \Delta p}{X}$$

The intermediate layer may be two orders of magnitude higher in inherent transmission, represented by P , than the barrier layers, but the distance travelled by the vapor through the intermediate layer, represented by X , is centimeters compared to micrometers for the barrier layer—perhaps as much as four orders of magnitude difference. The higher transport distance more than compensates for the higher inherent transport rate, provided the thickness of that layer

is also kept low to minimize the cross-sectional area, *A*. This combination can reduce the apparent MVTR of that layer significantly. So, implemented correctly, this two-layer structure behaves like a three-layer structure with all three layers contributing significantly to the barrier performance.

Selecting an Appropriate Barrier Technology

Figure 3 plots two parameters:

1. Typical ranges of the requirements of various industries and device technologies
2. Typical ranges of the performance of various barrier technologies, including some specific examples indicated by these symbols:

These parameters are plotted against their water vapor and oxygen transmission values on a log-log scale.

The selection of the most appropriate barrier would appear to be merely a question of consulting data from Table 1 and Figure 3 and weighing the options. That would establish likely candidates for the barrier technology needed, but this is only part of the story.

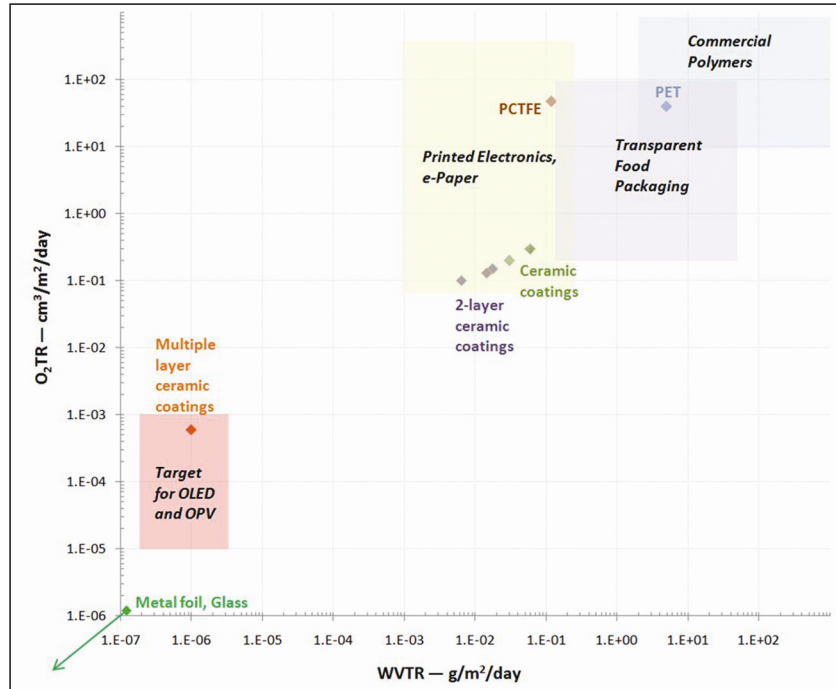


Figure 3: Barrier Types, Various Application Requirements, and Examples

Full Product Selection

The barrier, of course is not a stand-alone item. It must be integrated into the final device. That device may have other needs or wants such as:

- Anti-glare
- UV-resistance
- Scratch resistance (hardcoat)

It is possible to add such capabilities one by one. Doing so adds additional layers into the structure. Each additional layer requires another processing step and adds one or two material interfaces. Each interface affects the total light transmission as well as clarity and haze except in the unlikely event that the layers have matching refractive indices or a controlled sequence of refractive indices to maximize light transmission.

In addition, the manufacturing process may require:

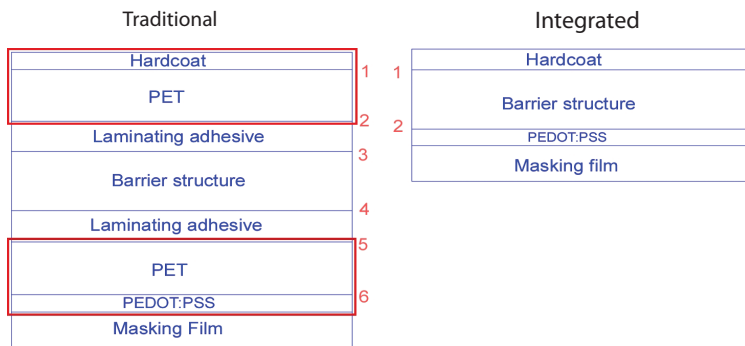
- Protective masking film on one or both sides
- Built-in heat seal or pressure-sensitive adhesive
- Clear conductive layer

We suggest that it would be better to combine as many of the requirements as possible into a simpler overall structure. This would drive down costs and, by minimizing material interfaces and total thickness, should improve light transmission properties.

Let’s look at an example of product feature integration as described above. The application is front encapsulation laminate for an e-reader. The laminate requires these characteristics:

- Criterion 1.** Transparent moisture barrier—selected by inspection of table 1 and figure 2, or similar data from other sources
- Criterion 2.** Protective front hardcoat—available on various films such as PET
- Criterion 3.** Clear conductive rear layer—available on various films such as PET
- Criterion 4.** Protective premask on rear—various sources

The traditional approach to this is an additive one. Let’s compare the traditional approach with an integrated one. We will use the same barrier structure and the same additional features in both approaches.



The integrated approach reduces the number of additional layer interfaces from six to two. (The outermost functional surfaces are unavoidable.) Of course a hybrid of these two extremes is also possible. For instance, if there was a minimum thickness requirement, one of the PET and laminating adhesive pairs could be included. This would still be only four interfaces instead of six.

FLEXcon’s Flexible Electronics business team works with end users to custom design barrier products by incorporating additional features, like those listed above, into the barrier laminate. Often, a starting point for this is an initial selection from our standard FLEXguard™ product range. Figure 4 compares the physical, optical and barrier properties of these products.

Our FLEXguard™ range covers metal foil, ceramic and polymeric barrier categories. Each category has two levels of barrier performance with different price points.

Summary

We’ve seen that new functional materials for printed and flexible electronics present stability challenges. Barriers to moisture vapor and oxygen can help, if chosen appropriately. Additional requirements associated with surface protection, light management, transparent conductive layers and other items may be required and can be added one-by-one, or better yet, integrated into the overall design to minimize the number of interfaces and reduce total applied cost.

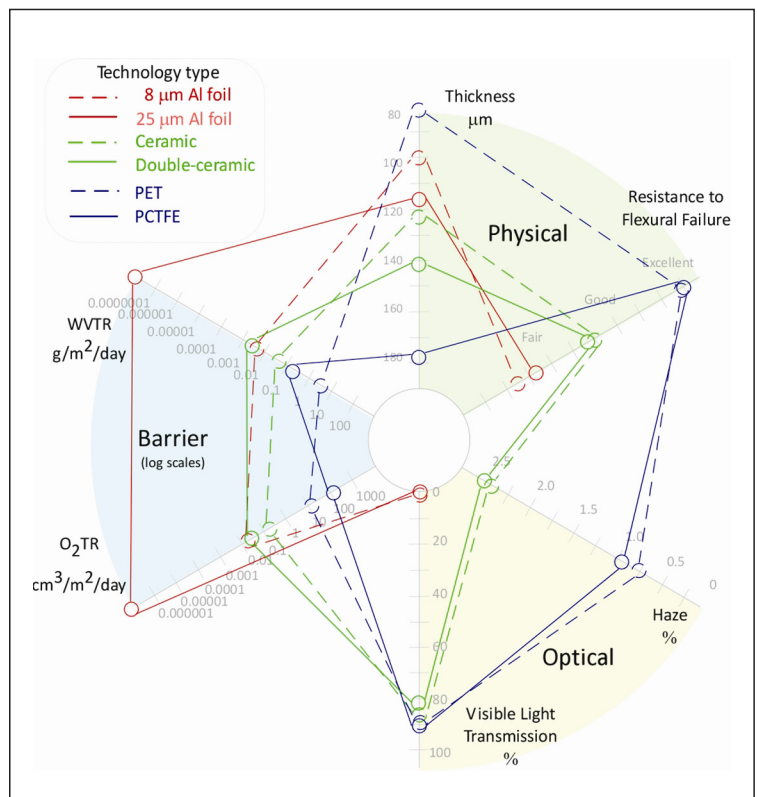


Figure 4: Physical Property Comparison of FLEXguard™ Standard Products



About the Author

Eric Barker joined FLEXcon in 2003. He is an Application Development Engineer with FLEXcon's Flexible Electronics division. Previously, over a 22 year span, Eric provided international technical support at Bayer Corporation (Polymers), was a Technology Principal at Monsanto Corporation (USA), and a Technical Service Specialist at Monsanto Australia. Eric earned his degree in chemical engineering from the University of New South Wales in Sydney Australia. He can be reached at (508) 885-8352 or ebarker@flexcon.com.

About FLEXcon

FLEXcon is an ISO 9001:2008 global manufacturer that coats, laminates and embosses films. We proactively strive to meet your performance, cost and delivery requirements with proven polymeric films and coatings for electronics applications. Our custom manufacturing capabilities provide you the opportunity to create a distinct competitive advantage. The company is headquartered in Spencer, Massachusetts, and has operations throughout North America and Europe, with distribution worldwide. For more information please call our Flexible Electronics Team at (508) 885-8413 or visit www.FLEXcon.com.

Glossary of Acronyms and Initialisms

FE: Flexible electronics

MVTR: Moisture vapor transmission rate; sometimes called WVTR: water vapor transmission rate, typically measured as grams of vapor transmitted per square meter per day at a standard temperature and relative humidity, frequently 38°–40°C and 90%–100% relative humidity

O₂TR: Oxygen transmission rate, typically measured as cubic centimeters of gas transmitted per square meter per day at 1 atmosphere pressure and room temperature (occasionally normalized to a specific thickness)

OLED: Organic light emitting diode

OPV: Organic photovoltaic

PCTFE: Poly(chloro-trifluoro-ethylene); aka Aclar¹ — a very good, very tough polymeric moisture barrier but a relatively poor oxygen barrier

PE: Printed electronics

PET: Poly(ethylene-terephthalate); "polyester", a commonly used plastic; in this context usually as a film

PV: Photovoltaic

TFT: Thin film transistor; can be printed. An array of TFTs can be used to control the images on a display.

WVTR: Water vapor transmission rate; sometimes called MVTR: moisture vapor transmission rate, typically measured as grams of vapor transmitted per square meter per day at a standard temperature and relative humidity, frequently 38°–40°C and 90%–100% relative humidity

¹Aclar is a registered trademark of Honeywell



Let's Talk Solutions

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Corporate Headquarters

1 FLEXcon Industrial Park
Spencer, MA 01562-2642 USA
Telephone (508) 885-8200
FAX (508) 885-8400
www.FLEXcon.com

Performance Products Business Team
Telephone (508) 885-8440
FAX (508) 885-8355

Product Branding Business Team
Telephone (508) 885-8370
FAX (508) 885-8399

Product Identification Business Team
Telephone (508) 885-8300
FAX (508) 885-8301

Flexible Electronics Business Team
Telephone (508) 885-8413
FAX (508) 885-1467

Manufacturing, Distribution & Sales Centers

Europe

FLEXcon Europe Ltd.
Whitworth Road
Southfield Industrial Estate
Glenrothes, Fife KY6 2TF
Scotland - UK
Telephone +44 1592 663 200
FAX +44 1592 663 201
europeinfo@FLEXcon.com

North America

FLEXcon Spencer, Massachusetts
1 FLEXcon Industrial Park
Spencer, MA 01562-2642
Telephone (508) 885-8200
FAX (508) 885-8400
FLEXexpress FAX: 1-800-428-4505

FLEXcon Columbus, Nebraska
2021 E. 23rd Street
Columbus, NE 68601
Telephone (402) 562-6131
FAX (402) 562-6054

Sales Offices

North America

FLEXcon Pennsylvania
Routes 1 & 202
The Weichert Building, Suite 260
P.O. Box 156
Chadds Ford, PA 19317
Telephone (610) 358-2571
FAX (610) 358-5946

FLEXcon Kansas
1305 South Fountain Drive
Olathe, KS 66061
Telephone (913) 768-8669
FAX (913) 894-5129
FLEXexpress FAX: 1-800-732-4329

Distribution & Sales Facilities

Asia-Pacific

FLEXcon Converting, Inc. Singapore
15 Changi South Street 2
CEVA Building, 3rd Floor
Singapore 486068
Telephone (508) 885-8223
FAX (508) 885-8355

Europe

FLEXcon Europe Ltd.
Flevolaan 3
1382 JX WEESP
P.O. Box 131
1380 AC WEESP
The Netherlands
Telephone +31 294 491 800
FAX +31 294 430 887
europeinfo@FLEXcon.com

Latin America, Africa and Middle East

FLEXcon International
Sales Office
1 FLEXcon Industrial Park
Spencer, MA 01562-2642
Telephone (508) 885-8223
FAX (508) 885-8355

North America

FLEXcon California
12840 Reservoir Street
Chino, CA 91710-2952
Telephone (909) 465-0408
FAX (909) 627-4136
FLEXexpress FAX: 1-800-446-4136

FLEXcon Ontario
1020 Lorimar Drive
Mississauga, Ontario L5S 1R8
Canada
Telephone (905) 795-5509
FAX (905) 795-8984
FLEXexpress FAX: 1-800-563-9143