PVdC – Past and Current Barrier Material

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Topics

- Brief history of Polyvinylidene dichloride (PVdC)
- A little chemistry
- PVdC properties
- Barrier terms and considerations
- Barrier comparisons
- Factors influencing PVdC barrier
- Selection and uses
- Handling, application and drying
- Summary
Vinylidene Dichloride

- French chemist, Regnault in the 1830’s.
- No further interest was shown until the 1929.
- German chemist, H. Staudinger for synthetic rubber.
- Dow Chemical scientists created VC Plastics.
- 1940 this line was trade named as Saran®.
- Solid resins were used from 1942 through 1970.
- Water based latex of this material, as well as solvent based solutions.
- Barrier properties of paper and films by coatings, in addition to extrusion or lamination.
Vinylidene Chloride (VDC) monomer, \( \text{CCl}_2\text{CH}_2 \)
- Sweet odour
- Clear liquid
- B.P. 31.7° C
- Fairly Toxic to liver and kidneys in some animals
- \( \text{LD}_{50} \) in rats is 1500mg/kg
Chemistry

- VDC will self polymerize.
- Hard, brittle polymer.
- MP = 198 - 205°C.
- Decomposes at 210°C.
- Not useful as coating or barrier material.
Chemistry

- VDC copolymerized with other monomers.
- Could use vinyl chloride, various acrylic and acrylate and nitrile.
- VDC content still high, typically 70 to 90 %.
- Results in 35 to 45 % crystallinity.
- Crystallinity determines ultimate barrier properties.
Polyvinylidene dichloride (PVDC) can be used in many forms:

- Solid powder for melt extrusion.
- Solid powder for solvent solutions.
- Water based latex through emulsion or suspension process.
- Water and solvent base coatings used for barrier enhancement of substrates.
Chemistry

Water base coatings also contain
- emulsifiers,
- surface tension control,
- pH modification,
- anti-foam,
- sometimes plasticizer.
Chemistry

Solvent base coatings contain
- Very aggressive solvents
- Solvents selected based on crystallinity of resin/powder
- Additives for slip, abrasion
- Sometimes plasticizer.
Properties

The main advantage of PVdC is the resistance to permeation of gases and liquids.

- Oxygen permeabilities at 23° C range from 0.04 to 1 cc.-mil/100 in²-day-atm,

- Water transmission rates of 0.05 to 0.5 g.-mil/100 in²-day at 37° C and 90 % relative humidity.

- Carbon dioxide permeabilities range from 0.1 to 2.4 cc.

- n-hexane is 0.0001 to 0.001 g.-mil/100 in²-day.
Properties

- Backbone has symmetrical regions.
- Creating crystalline regions.
- Still considered a thermoplastic.
- Crystallinity can be lessened or destroyed when temperatures approach the melt point.
- As the polymer cools, the barrier returns.
- Crystallinity forms in 10 to 15 days at RT.
- As little as one to two hours at 100°C.
- Dried film density high: 23 - 27 lb./R per mil. 37 – 43 gsm/ 0.0254 mm.
Barrier Comparisons

- An understanding of terms.
- **Barrier** = resist absorption, diffusion, desorption or evaporation of gases or moisture through it.
- Permeability is the measured behaviour when measuring the ability of liquids, gases or moisture to penetrate through a material.
- **Permeability** = \((\text{Quantity of Material}) \times \text{Thickness} \times \text{Time} \times \text{Area} \times \text{Partial Pressure Drop}\)

Permeabilities are commonly reported in barrier units.
Barrier Considerations

Barrier can be considered additive for multiple layers,

\[ \frac{1}{P_t} = \frac{1}{P_1} + \frac{1}{P_2} + \ldots + \frac{1}{P_n} \]

Where \( P_t = \) total permeability of the structure
\( P_1 = \) permeability of first layer
\( P_2 = \) permeability of second layer
\( P_n = \) permeability of \( n \) layer of multilayer structure

but

Some materials are Fickian in permeation response = linear.

Some materials are non-Fickian = permeation rates are nonlinear especially in the presence of water.
Barrier Comparisons

PVdC coatings and adhesives

- balance of properties
  - gas,
  - moisture vapor,
  - grease barrier,
  - heat sealability,
  - solvent resistance,
  - abrasion resistance,
  - flexibility,
  - gloss.
Barrier Comparisons

Other barrier materials

- impart good oxygen or moisture barrier.
- and/or good flavor/odor barrier.
- do not impart the wide balance of properties.
- many barrier materials are affected by the environment.
- temperature or humidity decreases the barrier properties.
- PVdC is not affected by these conditions.
<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>OTR Barrier (cc-mil/100 in²-day-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (ρ = 0.92)</td>
<td>−CH₂CH₂−</td>
<td>480</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>−CH₂−CH−CH₃</td>
<td>150</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>−CH₂CH−Cl</td>
<td>15</td>
</tr>
<tr>
<td>Poly(vinylidenechloride)</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Poly (acrylonitrile)</td>
<td>−CH₂CH−CN</td>
<td>0.04</td>
</tr>
</tbody>
</table>
**Barrier Comparisons – Table 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>OTR</th>
<th>WVTR</th>
<th>CO₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVdC</td>
<td>0.04</td>
<td>0.05</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>2.6</td>
<td>20</td>
<td>4.7</td>
<td>0.2</td>
</tr>
<tr>
<td>O Polyamide 6</td>
<td>1.2</td>
<td>10</td>
<td>6</td>
<td>0.7</td>
</tr>
<tr>
<td>PVdC – polyamide 6</td>
<td>0.2</td>
<td>0.2</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Metallized polyamide</td>
<td>0.05</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOPP</td>
<td>50</td>
<td>0.5</td>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>O PET</td>
<td>0.4</td>
<td>1.8</td>
<td>15</td>
<td>0.45</td>
</tr>
<tr>
<td>Metallized PET</td>
<td>0.08</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVdC-PET</td>
<td>0.4</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE</td>
<td>250</td>
<td>1</td>
<td>1000</td>
<td>180</td>
</tr>
<tr>
<td>HDPE</td>
<td>150</td>
<td>0.3</td>
<td>280</td>
<td>18</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>300</td>
<td>2</td>
<td>1000</td>
<td>40</td>
</tr>
</tbody>
</table>
## Barrier Comparisons – Table 1

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<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVOH 0 % RH</td>
<td>0.01</td>
<td>-</td>
<td>0.01 – 0.5</td>
<td>0.01 – 0.02</td>
</tr>
<tr>
<td>EVOH 100 % RH</td>
<td>0.65 – 1.15</td>
<td>1.4 – 8</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>PVC</td>
<td>4 – 5</td>
<td>8 – 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCTFE</td>
<td>7</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0.7</td>
<td>4.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>160</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48ga. PET-met / 1.2 mil HDPE (2.5 OD)</td>
<td>0.6</td>
<td>0.007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48ga. PET-met / 1.2 mil HDPE (1.8 OD)</td>
<td>0.96</td>
<td>0.014</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Real world adhesive laminations
OTR vs. WVTR of Various Polymers

Film thickness: 100 μm
Environment

OTR at O % RH (cc-mil/100 in2-day-atm)

Temperature C

EVOH

PVdC
Environment

OTR at 20 C (cc-mil/100 in^2-day-atm)

- EVOH
- PVdC

Relative Humidity

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
65
85
100
Factors Influencing Barrier

- Film formation.
- Substrate texture:
  - Plastic usually require one coat.
  - Paper requires 2 or more thin coats.
- Minimum coating will give maximum barrier.
- Grade of PVdC polymer.
- Coated substrate storage conditions.
Coating weight vs OTR Permeability

OTR (cc O2 /100 in. 2 / 24 hours)

- Ambient
- Aged*

LB. / R
<table>
<thead>
<tr>
<th>Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Typical Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum foil</td>
<td>Highest barrier – comparable to can or jar</td>
<td>Cost, opaque, can flex crack, pinholes</td>
<td>Multi layer pouches, retort containers, lidding</td>
</tr>
<tr>
<td>Metallized films</td>
<td>High durability- second to aluminum foil, good barrier properties</td>
<td>Opaque, cannot be thermoformed or shaped, can scratch during handling</td>
<td>Snacks and confectionery, coffee, light barrier and gas barrier containers</td>
</tr>
<tr>
<td>PVdC</td>
<td>Balance of oxygen and moisture barrier, transparent, flexible, retortable and heat sealable</td>
<td>Difficulty in application, limited extrusion temperatures, chlorine containing, disposal</td>
<td>Barrier packaging, bakery, chemically resistant applications</td>
</tr>
<tr>
<td>EVOH</td>
<td>Best non-metallic oxygen barrier when dry</td>
<td>Extruded only, poor moisture barrier, oxygen barrier drops when wet</td>
<td>Multi-layer extrusions, formed containers, meat and cheese</td>
</tr>
<tr>
<td>SiOx (silicon dioxide) and AlOx (aluminum oxide)</td>
<td>Transparent and environmentally friendly</td>
<td>Expensive, can crack or mar when handled, sometimes adhesion issues</td>
<td>Clear retort pouches, medical and pharmaceutical</td>
</tr>
<tr>
<td>Nylon</td>
<td>Multi purpose, formable, retortable, transparent, high puncture resistance</td>
<td>Lower oxygen barrier, some moisture sensitivity</td>
<td>Meat and cheese, cook in bag, retort containers</td>
</tr>
</tbody>
</table>
Selection

Select proper grade for intended use:
- What is final structure.
- What end properties are desired.
- Barrier adhesive bond strength.
- Heat seal bonds of coating.
- Coating/lamination equipment capabilities.
Uses

Paper - snack foods, cereal liners, dry cake mixes, and soft drink powders, ream wraps.

Films - snack foods, meat, cheese, and medical packaging.

Films made with PVdC coatings can result in lower environmental impact.

Helps meet the requirements of European Directive on Packaging and Packaging Waste.
Handling

- Water based, with a low pH (1.0 to 4.0).
- Corrosion and discoloration if allowed to contact ferrous or polyvalent metals.
- PVdC latices will freeze and become unusable.
- Solvent based PVdC have EHS issues.
- Latices contain surfactants that will cause foam when sheared or aggressively agitated.
Application

Different ways to apply PVdC to roll stock and sheet.

- Air knife,
- Mayer bar,
- Gravure,
- Reverse gravure,
- Smooth roll,

For 3-D objects, spray or dip coating.
Application

Paper – multiple thin coats to cover fibers and make continuous coat.

Films – single coat
  - may require in-line or out-of-line primer.
  - some latex are ‘primerless’.

Coatings weights applied depends on barrier required and function (adhesive, barrier, heat seal).

PVdC can be used as thin coat primer for other processes.
Drying

- PVdC easy to dry.
- 45 to 60 % solids in water.
- Much lower solids in solvent based versions – made by converter.
- Low film formation temperature.
- Sufficient temperature to coalesce particles.
- Air volume to remove volatile quickly.
- Radiant, frequency and conventional air impingement work well.
Inherent Non-flammability

- PVdC has high chlorine content.
- UL-94 rating of V-0 (self-extinguishing).
- LOI rating (Limiting Oxygen Index) of >70.
- Coating and impregnant for textiles, membranes and non woven materials to enhance or provide non flammable properties.
- Flame resistant wall coatings and paints.
Summary

• PVdC - a barrier material for decades.
• Best balance of barrier properties under a variety of use and test conditions.
• Still the preferred barrier material in many cases.
• Some market segments are continuing and actually growing.
• Converters make their own barrier combinations.
• Reduced lead time to meet orders and is an economical alternative.
• Application for flame retardancy.
• Three dimensional part coatings.
• Future use will continue in place of and in addition to alternate barrier technology.
References

1. “The History of Saran” – Dow Chemical Company Form No. 190-327-1084
4. W.J. Koros, “Permeation Processes in Barriers and Membranes” TAPPI PLACE 2002