PVDC –
New Developments, New Opportunities

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Introduction

The information in this presentation will provide basic background information on the use of PVDC resins and coatings in packaging applications. It will also give data on new grades of PVDC resins and latex, which can lead to the development of new packaging films by flexible packaging converters and film manufacturers.

Background

Polyvinylidene chloride (PVDC) resins and coatings have been a part of the flexible packaging world for more than 50 years, with a unique combination of functional characteristics that has found numerous applications. It is available in a variety forms:

- Aqueous dispersions, or latex, for coating on a number of different film and paper substrates,
- Extrudable powders, for monolayer or multilayer films and sheet, and
- Soluble powders, for solvent-based coatings on films.

According to 2004 estimates\(^1\), approximately 160,000 metric tons of PVDC are used annually around the world in extruded, coextruded, coated and laminated structures.

In a study of high barrier packaging films released in late 2005\(^2\), PVDC was reported to be the leading barrier polymer in high performance packaging films. For example, in dry food packaging, PVDC-coated BOPP films hold a 53% share of barrier films used to package dry foods. Also, the forecasted growth for PVDC-coated PET films is a healthy 9% per year, driven primarily by new applications including lidstock for prepared foods, retort applications, and clear, stand-up pouches.

The unique combination of properties offered by PVDC include:

- Protection from moisture loss or gain
- Protection against oxidation of ingredients
- Protection from aroma and flavor loss or pickup
- Prevention of oil and grease permeation
- Good seal integrity, using heat seals, high-frequency seals or ultrasonic seals
- Excellent transparency and gloss
- Good antifog properties
- Excellent printing characteristics
- Good scratch and abrasion resistance

PVDC also complies with the requirements for direct food and pharmaceutical contact of regulatory agencies around the world.

When it comes to barrier properties, PVDC is different from most other barrier polymers, providing excellent barrier to both oxygen and water vapor while most other barrier polymers offer just one or the other. The gas barrier properties are unaffected by relative humidity, so the performance can be relied on through a wide range of packaging and environmental conditions.

All PVDC products on the market are actually copolymers of vinylidene chloride (VDC) and other comonomers. The relative amount of VDC in the copolymer dictates some key properties. With more VDC, the barrier properties are generally better; with less VDC, flexibility usually improves. However, the amount and type of comonomer(s), as well as other additives and processing technology used, will influence other properties such as sealing, surface properties, transparency, gloss, coefficient of friction, etc.

**New PVDC Developments**

Even though PVDC has been around for so many years, new grades of PVDC latex and resins have been introduced in recent years that offer improved barrier vs. standard grades that have been used traditionally. Reductions in both oxygen and water vapor transmission rates are allowing flexible packaging converters the ability to offer higher barrier, lighter-weight, and/or less costly packaging solutions.

**PVDC Latex for Pharmaceutical Blister Packaging**

For example, a new grade of PVDC latex was introduced this year for use in pharmaceutical blister packaging. PVDC coatings have been used in this application since the late 60s, with duplex (PVDC/PVC) and triplex (PVDC/PE/PVC) structures being the most common ones used. In fact, estimates show that approximately 67% of the barrier blister packaging market uses these PVDC-coated films. Typical coating weights used include 40, 60, 90 and 120 g/m², with the water vapor transmission rate (WVTR) for a typical 120 g/m² PVDC-coated PVC film being around 0.16 g/m²·d at 40°C and 75% R.H.
The target of this development was a PVDC latex that would provide twice the water vapor barrier of the standard grades used for pharmaceutical blister packaging, while maintaining the machining properties necessary for the end use. R&D tests as part of this work included evaluations of the various polymers used in pharmaceutical packaging, comparisons of WVTR test methods, and WVTR tests on both flat and thermoformed films.

From these studies, several key observations were made:

1. With proper machine setup, the forming properties of most polymers used for pharmaceutical blister packaging behave very similarly.

2. Likewise, the WVTR properties of these same polymers show very similar differences between flat and thermoformed films.

<table>
<thead>
<tr>
<th>Table 1: WVTR of various films before and after thermoforming</th>
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<tbody>
<tr>
<td><strong>Film</strong></td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>PVC, 250 μm</td>
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<tr>
<td>COC, 190 μm</td>
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<tr>
<td>COC, 240 μm</td>
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<tr>
<td>COC, 300 μm</td>
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<tr>
<td>PCTFE (15 μm)/PVC</td>
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<tr>
<td>PCTFE (51 μm)/PVC</td>
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<tr>
<td>PVDC Duplex, 40 g/m²</td>
</tr>
<tr>
<td>New PVDC Triplex, 90 g/m²</td>
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<tr>
<td>New PVDC Triplex, 120 g/m²</td>
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</tbody>
</table>

3. There is good correlation between WVTR measurements made using the USP 671 weight-gain test traditionally used in the pharmaceutical industry, and permeation tests on formed films done according to ASTM F 1249 (Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor).
Table 2: Comparison of WVTR results obtained by different test methods

<table>
<thead>
<tr>
<th>Material</th>
<th>ASTM F 1249 [g/cavity/d]</th>
<th>USP 671 [g/cavity/d]</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC, 250 μm</td>
<td>0.00454</td>
<td>0.00400</td>
<td>12%</td>
</tr>
<tr>
<td>COC, 190 μm</td>
<td>0.00050</td>
<td>0.00048</td>
<td>4</td>
</tr>
<tr>
<td>COC, 240 μm</td>
<td>0.00045</td>
<td>0.00039</td>
<td>13</td>
</tr>
<tr>
<td>COC, 300 μm</td>
<td>0.00029</td>
<td>0.00033</td>
<td>15</td>
</tr>
<tr>
<td>PCTFE, 15 μm/PVC</td>
<td>0.00048</td>
<td>0.00060</td>
<td>20</td>
</tr>
<tr>
<td>PCTFE, 51 μm/PVC</td>
<td>0.00010</td>
<td>0.00010</td>
<td>0</td>
</tr>
<tr>
<td>PVDC Duplex, 40 g/m²</td>
<td>0.00083</td>
<td>0.00081</td>
<td>3</td>
</tr>
<tr>
<td>New PVDC Triplex, 90 g/m²</td>
<td>0.00019</td>
<td>0.00020</td>
<td>4</td>
</tr>
<tr>
<td>New PVDC Triplex, 120 g/m²</td>
<td>0.00010</td>
<td>0.00010</td>
<td>0</td>
</tr>
</tbody>
</table>

The new DIOFAN® Super B PVDC latex now being introduced achieved all of the key targets. WVTR values for 120 g/m² duplex and triplex structures are consistently around 0.08 g/m²·d, which is half that of structures made with traditional PVDC grades used for pharmaceutical packaging. Excellent oxygen barrier is also achieved, with typical OTR values for a 120 g/m² structure at 0.1 cm³/m²·d·bar. Films made with the new grade can also be thermoformed and sealed at the same machine speeds as those made with standard grades. These new PVDC-coated films will give pharmaceutical manufacturers the protection they need for their products when they are stored, handled or shipped in some of the most aggressive, tropical environments.

Improved PVDC Extrusion Resins

New IXAN® PVDC resins for coextruded films have also been developed that offer significant improvements over standard PVDC resins used in packaging for many years. These resins are made using proprietary new polymerization and formulation technologies, cutting oxygen transmission rates by more than half.

For example, simple, 3-layer, cast EVA/PVDC/EVA films were produced using both a traditional vinylidene chloride/methyl acrylate (VDC/MA) copolymer resin formulated for extrusion processing, as well as the new VDC/MA resin, also formulated for extrusion processing. The oxygen transmission rate (OTR) of the film made with the traditional resin was ~13 cm³·10 μm/m²·d·b @ 23°C & 85% R.H., while the OTR of the film made with the new VDC/MA resin was ~5.3 cm³·10 μm/m²·d·b, an improvement of nearly 60%. This same new resin was also used to make a 5-layer, blown LDPE/EVA/PVDC/EVA/LDPE shrink film, and an OTR of just 3.5 cm³·10 μm/m²·d·b @ 23°C & 85% R.H. was achieved.
These resins are now giving manufacturers new possibilities for better, more cost-effective performance in their extruded film products. Samples are currently being evaluated by a number of film and sheet converters.

**Recycling of Multilayer Structures Containing PVDC**

Finally, new technology has been developed and demonstrated that can allow the recycling of film structures containing PVDC and other polymers. The process involves selective dissolution of the materials involved, followed by separation and cleaning, allowing the PVDC and other polymers to be separated into relatively pure recycle streams. The technology has been shown to be feasible for several different mixed polymer structures, including

- PVC/PVDC
- PVC/PE/PVDC
- PE/EVA/PVDC/EVA/PE, and
- PET/PVDC.

This recycling technology overcomes an historical belief that materials that have been combined with PVDC cannot be recycled. Since the process is based on the relative solubilities of the materials used, it must be designed specifically for each application. SolVin can provide support to interested parties to help evaluate the economics and feasibility of the process for a given end use.

**Conclusion**

SolVin announced earlier this year that they plan to build a second PVDC latex production plant to support continued growth in the use of PVDC coatings for both food and pharmaceutical packaging applications. With the polymer and application technology developments highlighted in this presentation, as well as new capacity for growth, PVDC is well positioned to continue to offer advanced solutions for flexible packaging needs for many years to come.

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3 Photo courtesy of Macro Engineering & Technology Inc.
PVDC

New Developments, New Opportunities

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SolVin – a division of
Solvay Advanced Polymers, L.L.C.
PVDC Background
PVDC Background

- PVDC has been part of flexible packaging for over 50 years
- Available in 3 different forms, for a variety of converting operations:
  - Aqueous dispersions (latex)
  - Extrudable powders
  - Soluble powders
Global PVDC Consumption by Application Process

Consumption 2004 = 160,000 Metric tons

- **Latex Coatings**: 18%
- **Solvent Coatings**: 9%
- **Extrusion resins**: 73%

PVDC remains the leading barrier polymer in high performance packaging films.

![PVDC's Position in the U.S. Barrier Packaging Market](image)

Value share polymer based barrier packaging films

- EVOH: 21%
- Nylon: 20%
- MET PP: 6%
- MET PET: 2%
- Other: 2%
- PVDC (Extrusion + Coating): 49%

PVDC’s Position in the U.S. Barrier Packaging Market

- Dry food applications*
  - PVDC-coated BOPP: market share ~53%
  - Forecasted growth of PVDC-coated PET films ~9% per year

- Future growth of PVDC-coated PET films
  - Lid stock for prepared foods, including retort applications
  - Barrier ply for clear stand up pouches

What is PVDC?

- **Steric hindrance**: $H_2O$ vapor barrier
- **Crystallinity**
- **Polarity**: $O_2$ barrier, HF sealability
- **Functionality**: Printability, adhesion
- **Low melt T**: Heat sealability
- **Low Tg**: Thermoforming, shrink, flexibility
- **Flame Resistance**: High LOI
- **Copolymer**: Tailor-made

Vinylidene chloride comonomer(s)
A Unique Combination of Properties

- **PVDC prevents:**
  - Moisture loss or gain
  - Oxidation of ingredients
  - Aroma and odor transfer
  - Oil and fat permeation

- **PVDC provides:**
  - Seal integrity (heat, HF, ultrasonic)
  - Consumer appeal
    - Transparency and gloss
    - Antimist
    - Printability
    - Scratch resistance
  - Regulatory compliance for direct pharmaceutical and food contact

K. Paisley – 2007 TAPPI PLACE Conference, St. Louis – 9/19/07
Barrier against Oxygen and Water vapor

Permeability of various polymers*

**Oxygen**
Dry: 23°C / 0% R.H.
cc • μm / m² • d • b

- LDPE: ca. 195,000
- HDPE: ca. 59,000
- OPP: ca. 49,000
- R-PVC: 2400 – 3200
- PA 6-6: 1600 – 2400
- PET: ca. 1600
- PAN: 100 – 320
- EVOH: 5 – 80
- Cellophane: 320 – 510
- PVOH (PVAL): 3 – 4

**Water vapor**
38°C / 90% R.H.
g • μm / m² • d

- LDPE: 300 – 500
- HDPE: ca. 150
- OPP: 100 – 200
- R-PVC: 590 – 910
- PA 6-6: 990 – 2010
- PET: ca. 790
- PAN: 1500 – 2010
- EVOH: 1500 – 3510
- Cellophane: ca. 98,500
- PVOH (PVAL): > 500,000

*Film thickness: 1 μm (= intrinsic permeability)
PVDC: Stable, Predictable Barrier at Humid Conditions

OTR at 20°C, cm³·µm/(m²·d·b)

- EVOH (29%mol. C₂H₄)
- EVOH (32%mol. C₂H₄)
- EVOH (44%mol. C₂H₄)
- N-MXD6 (bioriented film)
- N-MXD6 (cast film)

Relative Humidity

[Data Sources: SolVin, Datasheet Nippon-Goshei]
PVDC Latex Development
PVDC in Pharmaceutical Packaging

- 1962: Blister packaging of pharmaceuticals using rigid PVC films
- 1966: PVDC-coated PVC films for improved barrier

Most common structures:
- PVDC/PVC duplex
- PVDC/PE/PVC triplex

WVTR @ 120 g/m² = 0.16 g/m²·d at 40°C, 75% R.H.

Specific weight of a PVDC film: ~1.65 kg/dm³
New PVDC Latex for Pharmaceutical Packaging

Development goals:

- WVTR ½ that of standard grades
- Maintain required machining properties

Evaluations included:

- Comparisons of polymers used in pharmaceutical packaging
- WVTR test method comparisons
- WVTR measurements of flat vs. thermoformed films
1. Forming properties of most polymers used for pharmaceutical blister packaging are very similar.
2. Very similar differences between the WVTRs of flat and thermoformed films.

<table>
<thead>
<tr>
<th>Film</th>
<th>ASTM F 1249, 40°C, 75% RH</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Flat, g/m²•d</td>
</tr>
<tr>
<td>PVC, 250 μm</td>
<td>4</td>
</tr>
<tr>
<td>COC, 190 μm</td>
<td>0.30</td>
</tr>
<tr>
<td>COC, 240 μm</td>
<td>0.25</td>
</tr>
<tr>
<td>COC, 300 μm</td>
<td>0.20</td>
</tr>
<tr>
<td>PCTFE, 15 μm</td>
<td>0.31</td>
</tr>
<tr>
<td>PCTFE, 51 μm</td>
<td>0.09</td>
</tr>
<tr>
<td>Std. PVDC Duplex, 40 g/m²</td>
<td>0.69</td>
</tr>
<tr>
<td>New PVDC Triplex, 90 g/m²</td>
<td>0.14</td>
</tr>
<tr>
<td>New PVDC Triplex, 120 g/m²</td>
<td>0.09</td>
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*Draw ratio of thermoforming tool = 2.3
3. Good correlation between USP 671 (weight gain) and ASTM F 1249 (IR) WVTR methods

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<tr>
<th>Film</th>
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<td>0.00010</td>
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<td>0</td>
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</table>
Testing of formed blisters using ASTM F 1249

- Film thermoformed on blister packaging machine
- Sealed with Al foil lidstock
- Foil cut away in blister area
- Sample placed on instrument and WVTR measurement made according to standard procedure
WVTR Comparison: USP 671 vs. ASTM F 1249

- PVC 250 µm /PVDC 40g/m²
- PVC 250 µm /PVDC 90g/m²
- PP 30 µm /COC 190 µm /PP 30 µm
- PVC 250 µm /New PVDC 90g/m²
- PVC 250 µm /PCTFE 51 µm

WVTR [mg/cavity•d]

- ASTM F 1249 IR measurement @ 38°C/90% RH
- USP 671 weight gain test @ 40°C/75% RH
New PVDC Latex for Pharmaceutical Packaging

- New DIOFAN® Super B PVDC latex meets the project’s development goals
  - WVTR @ 120 g/m² of 0.08 is ½ that of standard grades
  - OTR @ 120 g/m² of 0.1 cm³/m²·d·bar
  - Thermoforms and seals at same speeds
- Became commercially available in early 2007
- Some films have been introduced, others in development
Outline

PVDC Extrusion Resin Development
New PVDC Extrusion Resin Development

- New vinylidene chloride/methyl acrylate (VDC/MA) resins
- Made using proprietary polymerization and formulation technology
- Oxygen transmission rate (OTR) less than half that of conventional VDC/MA resins
New PVDC Extrusion Resin Development

- 3-layer cast films made with conventional and new VDC/MA resins
- OTR results (cm³·10 μm/m²·d·b @ 23°C, 85% RH):
  - With conventional resin: 13
  - With new resin: 5.3
New PVDC Extrusion Resin Development

- 5-layer, blown shrink film
- OTR of 3.5 cm³·10 μm/m²·d·b @ 23°C, 85% RH
Outline

- PVDC Background
- PVDC Latex Development
- PVDC Extrusion Resin Development
- Recycling Technology Development
Originally developed to recover and separate polymers from mixed-polymer waste containing PVC
Trials have shown that the technology will work for:

- PVC / PVDC
- PVC / PE / PVDC
- PE / EVA / PVDC / EVA / PE
- PET / PVDC

Process is based on relative solubilities of the polymers

- Must be designed for each application

Assistance is available for evaluating feasibility and economics
PVDC: Well-Positioned for the Future of Packaging

- New, improved products
- New application developments
- New production capacity
Thank You

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Please remember to turn in your evaluation sheet...