Saran PVDC Barrier Concepts for Demanding Coextrusion and Lamination Applications

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ABSTRACT

Copolymers of polyvinylidene chloride (PVDC), are-well known for their use in demanding barrier packaging applications to minimize the permeation of oxygen, water vapor, and odors. New die designs incorporating Dow’s patented early encapsulation technology (US Patent 6,685,872, International Publication Number WO 02/06047, US Patent 4,643,927), coupled with temperature isolation technology from Brampton Engineering and Macro Engineering, have eliminated degradation problems existing in the typical spiral mandrel dies used in the blown film process. These new die designs, coupled with new Saran* resin offerings; enable PVDC resins to be processed on large multilayer blown film dies. Multilayer films incorporating PVDC resins with higher temperature polymers such as Nylon, PP, and LLDPE in the skins are now possible.

The advantage of coextruded multilayer films incorporating PVDC in the offering, in a one step process, is the combination of outstanding barrier performances, resistance to in-use conditions such as humidity and flexes cracking, and specific physical properties given by the skin polymers. It represents the possibility to increase product shelf life or down gauge the barrier material as well as reducing processing steps compared to laminated composite products.

INTRODUCTION & BODY OF TEXT

Copolymers of polyvinylidene chloride (PVDC), are-well known for their use in demanding barrier packaging applications to minimize the permeation of oxygen, water vapor, and odors. In this respect, PVDC is often used as a coating on non barrier films. In order to obtain the desired level of barrier, several passes of coating are necessary. Coating PVDC is a complex process which requires expertise and attention so that the coated PVDC layer is consistent and resists the packaging process. It is as well a costly operation when more than one pass coating is needed.

In the 1960’s, Dow developed feed block coextrusion technology. This allowed PVDC resins to be combined with other polymer materials to produce a multilayer film or sheet. For example, a five-layer coextruded film can be produced that has two polyethylene skin layers that are each about 40 to 45 percent of the total film thickness. The center of the film is a PVDC polymer layer that is about 10% of the total film thickness. The PVDC copolymer is attached to the skin layers with tie layers, typically consisting of ethylene vinyl acetate (EVA) copolymer. The resulting film has the advantage to combine the physical properties of the polyethylene layers and the barrier properties of the PVDC layer, all in one processing step.

Feed block coextrusion technology is not applicable to blown film processes. For blown film, spiral mandrel dies are commonly used. Spiral mandrel blown dies are effective for many polymers but cannot easily be used with thermally sensitive materials, such as PVDC, due to long flow paths and large surface areas that can lead to polymer degradation.

The most significant recent development of PVDC resin extrusion technology is in the design of large multi-layer blown film dies coupled with new resin offerings for blown coextruded films. New die designs incorporating early encapsulation technology, coupled with temperature isolation technology from Brampton Engineering and Macro Engineering were developed. With an encapsulation die, the PVDC polymer is encapsulated as it exits the extruder, to minimize the contact with the metal surfaces in the die. If the molten PVDC polymer contacts the metal surfaces, it tends to stick, resulting in long residence times, thermal degradation, and the formation of carbon. Dow patented a crossover mandrel technology (US Patent 6,685,872, International Publication Number WO 02/06047, US Patent 4,643,927), coupled with new channel geometry to deliver a uniform barrier layer around the circumference of the die. On the other hand, the thermal isolation die thermally isolates the molten PVDC polymer from the high temperature skin layers, which minimizes the potential for thermal degradation.
These new dies are the enabling technologies to allow PVDC polymers to be processed with acceptable yields in large (>10") commercial blown film coextrusion equipment. It also allows versatile structures such as coextrusion with high temperature skin materials like Nylon. As a result, it opens up many new market opportunities for PVDC resins. These die technologies are commercially available today at Macro Engineering and Brampton Engineering, and they can be used equally well with both PVDC and EVOH resins. Several converters in various parts of the world have installed blown coextrusion film equipment designed for PVDC resins.

Simultaneously to these advancements in processing technologies, Dow introduced new PVDC resins with improved properties. When comparing multilayer PVDC coextruded film specifications to competitive products such as composites of metallized film, PVDC coated film or EVOH laminated structures, PVDC will show similar or slightly lower performances. Typically these data are generated on flat film, in laboratory conditions, e.g. 23 DegC and 50% humidity, and one can question how much they correlate to in-use conditions. For example, during its shelf life, a package will be exposed to ambient humidity (in refrigerators, shipping environments, or retort conditions) and to flexing during filling, transport and storage. Film performances should be looked at in tests done in conditions representative of in-use.

When submitting packaging materials to the Gelbo Flex test, with number of cycles ranging from 5 to 100, one can observe that PVDC coated materials and metallized films and foil laminates have their oxygen or water vapor transmission increased by 10x to 50x after only 5 flex cycles. This higher transmission barrier data is representative of the true performance the packaging is offering in in-use conditions, and should correlate closer to actual shelf life performance. The advantage of the PVDC resin in a multilayer coextruded structure is that it will resist these flex cycles and maintain its barrier properties longer, extending the shelf life of the packaging.
Using PVDC coextruded multilayer films as an alternative opens the possibility to increase the shelf life of the final product or to down-gauge the film structure for cost savings. A further advantage of PVDC copolymers versus other barrier polymers is that the oxygen barrier properties are not affected by relative humidity. Some polymers such as EVOH resins, can offer outstanding oxygen barrier property at low humidity, but see their barrier transmission performance increase by 2x to 4x when relative humidity of 80% and above are reached. On the contrary, the outstanding oxygen barrier property of PVDC coextruded blown film, unchanged in any humidity conditions, will allow package designers to develop clear barrier packages with improved shelf stability.

One example of an opportunity is retort packaging. PVDC blown coextruded films are an excellent option to replace foils or metallized films when a microwaveable or transparent package is desired together with resistance to flex cracking and to moisture. A new tie layer technology, under development, allows combining polypropylene as a skin layer and PVDC polymer in a multilayer film that can withstand the retort process. Such a film will provide, in one step, the combination of sealability, oxygen and aroma barrier even in high humidity conditions and resistance to pin holing with a transparent solution.

Other applications for PVDC blown coextruded films include dry mixes, snacks, cereals and heavy-duty shipping sacks where high moisture and aroma barrier is required. PVDC blown coextruded films are an excellent option to replace PVDC coated films, foils or metallized films and Nylon in order to save on process cost as well as improving flex cracking resistance.

More generally PVDC coextruded blown multilayer films, including one thin multipurpose barrier layer, opens opportunity for versatile design:

- Increased freedom to use other polymers to improve package properties (toughness, hot tack, sealing…)
- All properties in one film reduces multiple lamination and/or coating steps
- Lower modulus films
- Down gauging of the barrier material if more shelf life is not needed
CONCLUSIONS

Although PVDC resins were first commercialized in 1939, they have undergone many changes. Improvements to the resin and formulation have resulted in less thermal degradation. Improvements to the fabrication techniques have opened up new application areas. PVDC coextruded multilayer films can be effective when demanding end use packaging conditions are experienced, as well as when cost effective solutions are needed.

New potential application areas, such as extrusion coating and blow molding, may be developed in the near future to provide even more opportunities. As a result, PVDC resins remain a premier barrier packaging material over 60 years after their original introduction and the use of PVDC resins is expected to continue to grow for many years to come.

ACKNOWLEDGEMENTS

Steve Jenkins, The Dow Chemical Company
Mike Mounts, The Dow Chemical Company

References


3. US Patent 6,685,872

4. International Publication Number WO 02/06047

5. US Patent 4,643,927

* Trademark of The Dow Chemical Company
Discussion Topics

- PVDC new extrusion technology
  - Early encapsulation
  - Temperature isolation
  - New PVDC resin technology

- Increased multilayer design capability with PVDC coex films
  - One thin, transparent layer gives superior barrier to oxygen, moisture and aroma
  - Oxygen barrier is unaffected by humidity or moisture
  - Best extrusion moisture barrier (WVTR) resin

- Barrier film specifications vs. true package performance
  - Do high barrier film specifications correlate to long shelf life?
  - Understanding of in-use package barrier lead to new designs
  - Longer shelf life, lower cost, or clear packages

High Barrier PVDC Resins

- Oxygen Vapor Permeability
  - (g/25.4 microns/m2 day) at 75% RH

- Moisture Vapor Permeability
  - (g/25.4 microns/m2 day) at 38° C and 50% RH
**High Barrier PVDC Resins**

**What is PVDC?**
- High barrier to oxygen, moisture and aromas
- **Coated** on substrate → high barrier packaging

**Can PVDC be Coextruded in Blown Line?**
- In **one step process** → a blown multilayer high barrier PVDC film

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**Process Technology Advancements**

**Most Significant Recent Developments!**
- Coextrusion of multi-layer PVDC film
  + Possible to process PVDC on large blown film dies
    - Macro Engineering
    - Brampton Engineering
  + Easier processing PVDC resins

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**Process Technology Advancements**

**Early Encapsulation & Temperature Isolation Technologies**


- Early encapsulation eliminates PVDC contact with metal
  » Less die cleaning!
- Temperature isolation
  » Higher temperature skin and tie layer possible
    e.g. nylon skin resins
  » Minimize degradation
Pre-encapsulation Die

Overlap Barrier

Path 1
Path 2

PVDC O2 Barrier = 1.24 cc-mil/m²-day-atm
LDPE O2 Barrier = 6510 cc-mil/100in²-day-atm
Ratio = 5250

Path 1 = 0.6 mils  Path 2 = 80 mm

Commercial Multilayer Blown Film Lines

• New line incorporates
  » correct die design for short residence time and distribution
  » materials of construction (high nickel alloys)
  » correct PVDC extruder barrel and screw design
  » early encapsulation and temperature isolation
  » processing of PVDC, EVOH and Nylon
**Film Structure Possibilities**

**Cast and Blown Multilayer Films**

- K-resin / EVA / Saran* / EVA / AFFINITY* POP
- NYLON 6,66 / Nylon tie / Saran / EVA / AFFINITY POP
- ELITE* EPE / DOWLEX* PE / EVA / Saran / EVA / ELITE PE
- PP sealant / tie layer / Saran / tie layer / PP
- HDPE / EVA / Saran / EVA / LDPE

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**New PVDC Coex Structure**

**How does it Compares with Composite Structures?**

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**High Barrier PVDC Resins**

<table>
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<th>Material</th>
<th>Oxygen Vapor Permeability (g/25.4 microns/24h day) at 75% RH</th>
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<tr>
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**Specification vs. Shelf Life**

**Film Specifications based on Flat Sheet Performance**

- WVTR<0.46 gm/m² or O2TR<1.0 cc/m²
  - Very thick PVDC layer structure

**HOWEVER**

*Does it correlate to in-use shelf life needs?*

- Impact of package flexing?
- What if thinner, lower cost structures matched shelf life?

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**High Barrier Possibilities**

**Translating End Use Demands into Film Specification**

- Determine product tolerance to:
  - Oxygen intake
  - Moisture loss or intake (e.g. retort conditions)
  - Flavor or aroma loss or intake
  - Flavor scalping

- Desired skin layer requirements and materials - Structural properties, sealing properties, etc.
- Understand the storage and use conditions

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**High Barrier Possibilities**

**Translating End Use Demands into Film Specification**

- What is actual barrier after filling, handling and shipment?
- If barrier is poorer after filling, handling and shipment
  - Can better economics be obtained with somewhat lower flat sheet barrier, but comparable or improved in-use barrier?
  - Can comparable in-use performance be obtained in a clear package?
Humidity at Barrier Layer

May 25th, 2005

Temp. = 1°C Outside
RH = 90%
Inside RH = 100%

Temp. = 4°C Outside
RH = 85%
Inside RH = 85%

Effect of Humidity on Oxygen Barrier

May 25th, 2005

Oxygen Permeability
(cc - mil/m² - day - atm)

PVDC Films a Transparent Alternative

PVDC Coextruded Films
are an Opportunity for a Cost Effective,
Clear Structure with Better In-Use
Shelf Life vs. Current Packages

- Cost effective alternative to PVDC coating
- Transparent alternative to metallized films/foil
Applications: High Oxygen Barrier

- **Retortability, Hot Fill**
  - Eliminate metal (metal detection)
  - Eliminate lamination steps
  - Potential for increased shelf life vs. EVOH
  - Aroma control
  - Microwavability
  - Clear pouches

Applications: High Moisture Barrier

- **Dry Mixes, Dry Sauces, Soups**
  - Eliminate processing steps, e.g.:
    - Film metallization
    - Lamination steps
  - Improved pinhole resistance
  - Eliminate metal (metal detection)
  - Transparent if needed

- **Cereals, Hot Cereals, Crackers**
  - Eliminate processing steps, e.g.:
    - Coating of PVDC
    - Lamination steps
  - Eliminate coating equipment capital
  - Aroma protection
  - Improved pinhole resistance vs. coating
PVDC Coex Films Add Functionality

**Opportunity:**

Versatile Multilayer Film Design

- Improved functionality of film structure
  - Only one thin layer of PVDC for Oxygen and aroma barrier in addition to strong WVTR
  - Increased freedom to use other polymers for improved package properties
  - One coextruded film -> Reduce multiple lamination steps

- Lower modulus films are possible
- Barrier layer can be asymmetrical towards food
  - Reduced scalping
- Excellent chemical resistance and formability
  - Spices, etc.
  - Deep draw applications
- Down gauged barrier layer if more shelf life is not needed

Conclusion

The Saran PVDC Coextruded Resin is there When you Need

1. High barrier performance in end use conditions
   - Excellent moisture barrier
   - Oxygen barrier in dry and humid conditions
   - Aroma protection
   - One thin, clear layer increase film design versatility
   - Retortability & hot fills, microwave ability
   - Metal free solution

2. Cost effectively
   - Elimination of lamination steps
   - Higher barrier performance allows down gauging
   - Elimination of several PVDC coating pass
Questions?

Thank You!

Living.
Improved daily.