Electron Beam Crosslinking of Polyolefin Films for Various Packaging Applications

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Radtech Europe 2017
October 17 – 19 2017
Prague, Czech Republic
Agenda

• EB Crosslinking History

• EB Crosslinking Chemistry of Polyolefins

• Market Applications in Packaging

• Status of Low voltage EB Equipment

• Conclusions
History

Developments:

- Charlesby reported "Radiation processing of Polyethylene (PE)" in 1952.
- Radiation of Elastomers/polybutadienes/natural rubber Firestone early 1970’s
- The Raychem Co. in the United States put the radiation cross-link to practical use first in sixties.
  - Electrical Cable & Heat Shrinkage Tube
EB X-Linking Not New

- Radial tire:

- Wire and Cable & Shrink Tubes
EB Crosslinking of Polyethylene For Shrink Bags

Courtesy: USP 3,022,543
Baird et al. 1962
# Effect of Irradiation on Properties of Oriented Polyethylene

<table>
<thead>
<tr>
<th></th>
<th>Irradiated</th>
<th>Not Irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Specific Gravity</strong></td>
<td>0.916</td>
<td>0.916</td>
</tr>
<tr>
<td>gm/cc</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tensile Strength psi</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At 22 C</td>
<td>8000-16000</td>
<td>1500-3000</td>
</tr>
<tr>
<td>At 93 C</td>
<td>1500-3000</td>
<td>100-200</td>
</tr>
<tr>
<td><strong>% Elongation</strong></td>
<td>100-200</td>
<td>600</td>
</tr>
<tr>
<td><strong>Heat Seal range C</strong></td>
<td>150-300</td>
<td>110-150</td>
</tr>
<tr>
<td><strong>% Shrinkage 98 C</strong></td>
<td>80</td>
<td>60</td>
</tr>
</tbody>
</table>

Courtesy: USP 3,022,543 Baird et al 1962
EB X-Linking Applications

- Shrink Films For Meats/Poultry: Largest for EB Crosslinking Applications
EB Chemistry of Crosslinking of Polyolefins, Polyethylene in Particular
Reaction - Generation of Radicals -

- Electron (from electron beam) collides with the atomic nucleus and the electron in the material.
- These electrons cuts each bonds (C-H, C-C etc), then the radicals generate.
Reaction -Basic Reaction-

- Basic Reaction (PE)
  Generation of radicals
  -CH₂-CH₂-CH₂- \rightarrow \text{CH₂-CH₂-CH⁻} + H⁻
  -CH₂-CH₂-CH₂- \rightarrow \text{CH₂-CH₂} + \text{CH₂-}
  Termination reaction and Movement of radicals
  H⁻ + H⁻ \rightarrow H₂, \text{-CH₂-CH₂} + \text{CH₂-} \rightarrow \text{-CH₂-CH₂-CH₂-}
  \text{-CH₂-CH₂-CH⁻} + H⁻ \rightarrow \text{-CH₂-CH₂-CH₂-}
  \text{-CH-CH-CH₂-} \rightarrow \text{-CH=CH-CH₂-}
  \text{-CH₂-CH₂-CH⁻} + H₂ \rightarrow \text{-CH₂-CH₂-CH₂-} + H⁻
  \text{-CH₂-CH₂-CH₂-} + H⁻ \rightarrow \text{-CH₂-CH⁻CH₂-} + H₂
The cross-linking reaction generates a small amount of H₂ gas that is safely removed with web handling equipment.

- The cross-linking reaction produces small amounts of hydrogen as a byproduct
- The hydrogen migrates to the film surfaces, and forms a bubble within the tube
- ESI can suggest a vendor to provide a re-wind/un-wind system that safely removes the gasses from the tube after cross-linking
Cross-link - Properties

• **Molecular Weight**
  Increases

• **Heat proof**
  Example : PE(commercial grade) 90 degree C
  PE(EB radiated type) 200 degree C

• **Resistance of solvent**
  Example : PE(commercial grade) dissolves by Xylene
  PE(EB radiated type) doesn’t dissolve
Market Applications For EB Crosslinking

• High Barrier Shrink Bag Films

• Vacuum Skin Pack Films (VSP)

• Display Shrink Films
High Barrier Shrink Film Bags
Meats, Poultry, Sausage Casings
High Barrier Shrink Film Bags Double Bubble Process Using 3-Layers
Structure of High Barrier Shrink Film Bags

Structure: Total wall thickness about 65 Microns.

- Outer Layer = 48 microns (18% EVA + LDPE)
- Middle Layer = 7 microns (PVDC) O₂ Barrier (7 – 9 cc/m² / 24 Hrs)
- Inner Layer = 8 microns (18% EVA + LDPE)
Performance requirements for shrink bags/tubes used in meat, poultry and sausage packaging

- Very high shrink ratios are preferred in shrink bag/tubes used for meat, poultry and sausage wrappings in order to
  - Maintain aesthetics
  - Maintain the shape of “cooked-in” meats during processing
- The high shrink ratios are achieved by introducing high mechanical stresses into the film through the “Double Bubble” process
- High Temperature resistance of the outer layers is required to allow broader heat seal range and higher temperature to obtain higher seal strengths.
Improving shelf stability for shrink tube often involves a trade-off of stability vs. performance.

- The high stored stresses needed to achieve good shrink ratios can cause problems in handling, filling and sealing operations.
- “Cold-shrink” – a premature shrinking of the film prior to use.
- Sealing issues - shrinking and curling during sealing operations.
EB Cross-linking Benefits.

- EB cross-linking adds stability to the film in the expanded state
  - Prevents cold shrink during storage
- The stabilized film is not prone to curling and shrinking as a result of heat-sealing temperatures
- Allows higher heat sealing temperatures therefore faster filling and sealing operations. Better Seal strength
  - Outer Cross-linked layer avoids Burn Through
EB Conditions: 70-125 kV, 50-80 kGy
Both Sides Same EB Unit

- The tube structure is designed to cross-link the outer skin without affecting the interior sealing layer
  - The outer skin has a higher melting point than the sealing layer
  - Allows high heat sealing temperatures therefore faster filling and sealing operations
- The outer skin has improved the physical and chemical properties
  - Puncture resistance
  - Fat resistance

Cross-linked outer skin
- Higher melt temp. allows contact with hotter sealing bar
- Puncture resistance
- Fat resistance
- High Gloss

Uncross-linked sealing Layer
- Lower melt temp. melts faster when higher temp is applied to skin
Typical EB Conditions for this Application

125-70 kV, 50-80 kGy Double Pass

Typical Non-Drum EB System
200 kV Unit for High Barrier Shrink Film Bags
Typical Dose 50-80 kGy

- EB Treatment After the First Bubble In-line with Extruder.
- Typical Wall Thickness about 550 GSM
- Bi-Lateral Treatment To X-link outer about 150 GSM.
- Typical non drum EB system
EB Cross-linking Benefits

• Higher Shrink ratios. Memory affect

• Temperature Resistance to the Outer Layers

• Some Mechanical Property Improvements
200 kV EB Unit for some high barrier shrink Bag applications
Vacuum Skin Packaging (VSP)

The Vacuum Skin Packaging (VSP) process uses a tray and special films that gently surround the product and seal over the entire surface of the pack like a second skin, preserving shape, texture and product integrity for a premium retail presentation.

Appealing shelf presentation
- Reduced packaging size and volume takes up less shelf space, cheaper to transport
- Reduced purge, increased shelf life lowers food waste, improves stock management
- Shelf life increased to 2-6 weeks vs MAP trays (6-10 days)
Typical Structure of VSP Film

Structure: Typical 80 – 150 microns (5 layers)

Outside
Surlyn Ionomer Provides Puncture, and other properties

Tie Layer
EVOH 44% Provides O_2 Barrier < 10 cc/m^2/24 hrs

Tie Layer

Inside Sealant layer (LDPE/EVA)
Advantage of EB Curing

- Provides Temperature Resistance to the outer layers > 200 C.
- High Seal Temperature required to provide high seal strengths to avoid leakage
- Low Voltage operation allows inside layers to seal at lower temperature allowing good seal
- Provides Stability to the film during sealing operation
- Some mechanical property improvements
Barrier VSP Films From DuPont

- Nine-layer films produced on a Macro blown film line at DuPont’s Technical Center in Wilmington DE
- Films are 125 microns thick with the basic structure:

(outside) PE-Elvax®-2Bulk Layers-Bynel®-Eval E-Bynel®-Bulk Layers-Appeel® (seal side),

Where:

- Bulk Layers are either Surlyn® ionomers or Elvax® ethylene vinyl acetate.
  - Surlyn® is DuPont’s tradename for its ethylene acid ionomer resins used in food packaging and industrial applications. Its sealability, formability, abrasion resistance and toughness provide a desirable combination of properties for food packaging applications.
  - Elvax® is DuPont’s tradename for ethylene vinyl acetate. EVA is widely used in food packaging as sealing and bulking resins.
- Bynel® is DuPont’s tradename for its extrudable adhesive resins and is used here to bond the bulk layer to ethylene vinyl alcohol.
- Appeel® is DuPont’s tradename for its peelable sealant resins, and is used here to allow for easy peelability of the VSP film from the tray by the consumer.

- Films were tested as-produced or after e-beam treatment by ESI at 125kV 140 kGy using a drum system.
Barrier VSP Films Physical Properties

- Comparison of physical properties of films with e-beam treatment showed in general the following improvements over untreated film:
  - Higher tensile strength TD and MD
  - Improved puncture resistance
  - Higher impact strength
  - More robust film performance on vacuum skin equipment.

- Charts in the next couple of slides for tensile strength, impact and puncture.

- Ionomer grades in the charts are all commercial.
Tensile Strength of VSP Films with E-beam Treatment

PE/Elvax®/Bulk/Bynel®/Eval E/Bynel®/Bulk/Appeel®
125 microns

Tensile Strength, Kpsi

**Elvax®**  
Surlyn® 1  
Surlyn® 2  
Surlyn® 3  
Surlyn® 4  
Surlyn® 5

Bulk Layer Composition

- As-is MD
- E-beam MD
- As-is TD
- E-beam TD

* has Surlyn® sealant
Spencer Impact of VSP Films with E-beam Treatment

PE/Elvax®/Bulk/Bynel®/Eval E/Bynel®/Bulk/Appeel®
125 microns

Spenser Impact, g/mil

As-is  E-beam

**Elvax®  Surlyn® 1  Surlyn® 2  Surlyn® 3  Surlyn® 4  Surlyn® 5

Composition and Volume of Bulk Layers

* has Surlyn® sealant
Needle Instron Probe of VSP Films

PE-Elvax®-Bulk Layer-Bulk Layer-Bynel®-Eval E-Bynel®-Bulk Layer-Appeel®

125 microns

**Elvax®**
Surlyn® 1
Surlyn® 2
Surlyn® 3
Surlyn® 4
Surlyn® 5

- As-is IN to OUT
- E-beam IN to OUT
- As-is OUT to IN
- E-beam OUT to IN

Composition of Bulk Layers

* has Surlyn® sealant
Effect of E-beam on Defect Count of VSP Barrier Film
Reiser 15 mm Dome

P-Values, $\alpha=0.05$

- E-beam; Defects
- E-beam; No Defects
- As-is, Defects
- As-is, No Defects

Tray Count vs. Composition of Bulking Layers

Elvax®

Surlyn®1

Surlyn®2

Surlyn®3

Surlyn®4

Defects: looseness, poor conformance, film tear, film holes
Barrier VSP: Temperature Resistance on VSP Equipment

Barrier VSP Film treated with E-beam
175°C

Barrier VSP Film, untreated
150°C

Barrier VSP films that are e-beam treated have a wider window of operability on different VSP equipment.
VSP with Elvax® EVA Bulking Layer
Top with irradiated film. Bottom with no irradiation.
Reiser Repak RE20, 15mm dome
Typical EB Conditions for this Application

125 kV, 120-150 kGy Chill Drum Preferred
150 kV with Chilled Drum Optional
Non-Barrier Display Shrink Films For Packaging
Typical Structure of Display
Non-Barrier Shrink Film
Structure: Typical 12 – 19 microns (3 layers)

LLDPE / LLDPE / LLDPE

LLDPE Provides Better Shrink Ratios
Typical EB Conditions for this Application
125 kV, 25-30 kGy Chill Drum

FIGURE 2
DEPTH DOSE
8271 Chill Drum
01-DECEMBER-2015
125 kV EB Unit with Non-Drum Option
125 kV EB Unit with Drum Option
200 kV EB Unit with Non-Drum
Conclusions

• Low Voltage EB Equipment in the 80 – 200 kV range is used for various crosslinking applications mostly for packaging.

• Polyethylene, ionomers and EVA co-polymers are the substrates that crosslink with EB and provide the enhanced properties for these packaging applications.
Low Voltage EB Units For Crosslinking Applications

• High Barrier Shrink Film Bags
  – 80-125 kV, 40 – 80 kGy Bi-lateral EB treatment. After Second Bubble. Typical Offline Unit
  – 200 kV, 40 – 80 kGy Uni, Bi-lateral EB treatment. After First Bubble. In-line with Extruder
  – Most non-drum EB systems, few with drum
Low Voltage EB Units For Crosslinking Applications

• VSP
  – 125 kV, 120-150 kGy EB treatment. 150 kV with Drum as an option available.
  – Drum system recommended
  – Typical offline on a slitter

• Non Barrier Display Shrink Films
  – 125 kV, 25-30 kGy EB treatment
  – DRUM System mandatory
  – Typical Offline on a slitter
Low Voltage EB Units For Crosslinking Applications

- Nitrogen Not required for EB Crosslinking but recommended
- Ozone Exhaust Provided with EB Equipment
Acknowledgements

Thanks to Dr. I-Hwa Lee Research and Development Fellow at DuPont Packaging & Industrial Polymers Wilmington Delaware USA and her team for providing the films for VSP and doing the measurements.
Thank You

Any Questions