Comparison of Atmospheric Plasma and Corona Treatments in Promoting Seal Strength

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Discussion Agenda

- Study Objective
- Extrusion Coating Optimization
- Corona Discharge & Adhesion Promotion
- APPD Technology & Adhesion Promotion
- Impact of Key Surface Treatment Parameters
- Experimental Design
- Experimental Results
- Supporting Comments
- Conclusions
Examine how the use of atmospheric plasma surface treatment technology compares to the use of corona discharge as pretreatments in promoting seal strength of extrusion-coated flexible packaging structures, specifically involving oriented polypropylene (OPP) and OPET.
Consumer Packaging & Surface Preparation

Extrusion
- Film extrusion (cast, blown, performance layers)
- Extrusion coating (polyolefin to paper, films, foils)

Lamination
- Wet Lamination (typical for paper + foil)
- Dry Lamination (heat, pressure)

Printing
- Solvent-based (Gravure, Offset, Flexographic)
- Water-based (Flexographic, Gravure)
- Radiation-cured (UV/EB – Flexographic, Gravure)
- Digital (typically solvent-based)

Coating
- Water-based (Flexographic, Gravure, Smooth Roll)

Converting
- Slitting/rewinding
- Forming
- Filling
- Sealing
Optimizing the Extrusion Coating Process

Process Variables in Extrusion Coating

- Polymer Melt Temperature
- Resin Flow (Melt Index)
- Die Position
- Air Gap
- Extrudate Pretreatment (ozone)
- Substrate Pretreatment (corona, flame, plasma)
- Substrate Pre-Heating
- Substrate Type
- Substrate Surface
- Coating Speed
- Coating Thickness
- Nip Pressure
- Chill Roll Temperature
Corona Discharge Technology

Bare Roll
- Advantages
  - No roll covering to fail
  - Ceramic electrodes
  - Treats conductive / non-conductive materials
  - All converting applications
- Disadvantages
  - Roll oxidation requires cleaning
  - Requires large volumes of makeup air, as air is needed to cool the electrodes.

Covered Roll
- Advantages
  - Wide range of roll coverings, metal electrode
  - Designed to treat non-conductive materials
  - Easy to adjust treat width, and lane treating with segmented electrodes
- Disadvantages
  - Organic roll coverings can have short life
  - Cannot treat conductive materials

Dual Dielectric
- Advantages
  - Ceramic roll covering, ceramic electrode
  - Treats conductive / non-conductive materials
  - Higher treat levels
  - Even distribution of discharge
  - Increased roll surface capacitance.
  - Nearly eliminates wrinkling, pinholes, backside treat
- Disadvantages
  - None
How Corona Treatment Promotes Adhesion

- Corona energy breaks molecular bonds on surface of a substrate
- Open molecular chains bond with free oxygen radicals forming additional polar groups on the substrate surface.
- Polar groups have strong affinity to polar inks, coatings and adhesives; therefore improving wettability and the potential for better adhesion.
Atmospheric Plasma Technology

Highly Functionalizing:
- Homogeneous, diffuse atmospheric plasma discharge for high energy density (Wmin/m²) surface treatment.
- Capable of near oxygen-free atmospheres to establish high area density (nm²) surface functionalities.

Durability:
- Robust station design for low-high speed treatment of polymer films, foils, wovens, nonwovens, paperboard.
- Suitable for clean room environments.

Versatility:
- In-line, continuous surface modification of a wide range of roll-to-roll material surface orientations, including conductive/ non-conductive, porous/ nonporous, and one/two sides.
- Temperature-controllable electrode/roll design.
- Designed for use with a wide range of noble and reactive gases.
- Electronically-controlled gas flow and ppm concentration calibration.

Surface Modification Effects:
- Surface chemistry change initiated by non-thermal activation of particles via collisions.
- Etches, functionalizes and cleans/sterilizes wide range of substrate surfaces.
- Promotes free radical surface reactions.
- No ozone destruction required.
How Plasma Treatment Promotes Adhesion

Glow Discharge Plasma Source
(Discharge composed of molecules, atoms, ions)

Exhaust Stream
Volatilized, vaporized contaminants, water vapor, CO, CO2, unreacted process gases

Exhaust Stream
Volatilized, vaporized contaminants, water vapor, CO, CO2, unreacted process gases

Polymer Film
Clean surface w/ dangling bonds

Film Processing Direction
Impact of Treatment Gap and Frequency

1mm gap, high frequency
4mm gap, high frequency
8mm gap, high frequency
1mm gap, low frequency
4mm gap, low frequency
8mm gap, low frequency
Experimental

- Formed extrusion-coated specimens

- Polymer materials used in this study included OPP, OPET, DuPont Bynel®, and LDPE.

- Base film substrates were OPP and OPET, and polymer resin extrudates were LDPE and Bynel®.

- OPP film contained an antioxidant additive to prevent polymer degradation during pelletizing and downstream polymer processing.

- OPET film did not contain antioxidant additives, and had high dimensional stability.
Experimental

- **Bynel® resin - Series 2200** (modified ethylene acrylate)

- **Contains a temperature-stable ester**, which makes it functional in high temperature extrusions.

- **Physical properties typical of polyethylene/acrylate copolymer resins** with similar density and melt flow rate values.

- **Layer ratio for this trial was 0.73 mils Bynel® -- 0.17 mils LDPE.**
Corona and Plasma Treatment

- Conducted at the DuPont Technical Service & Development facility in Wilmington, Delaware, USA.

- Corona discharge
  - Dual dielectric system, ceramic tube electrodes/ceramic-covered ground roll.

- Atmospheric pressure plasma discharge (APPD)
  - Similar dual dielectric system configuration
  - Higher RF discharge frequency
  - Process gas - 100% nitrogen gas, or mixture of 80% nitrogen and 20% Argon.

- 1.5mm treatment gap

- Power densities ranged 2.2 – 4.0 Wmin/ft² (23.7 – 43.0 Wmin/m²).
Extrusion Coating

- Single screw extruders with a screw length to diameter ratio of 28:1 and 24:1 (DuPont Technical Service & Development facility)

- Extrudate melt temperature at 610°F (321°C).

- Extrusion coating air gap (distance between die exit and chill roll) was 7.0 inches (17.8cm)

- Coat weight was 0.7 mils.

- Process speed was 500 fpm (152.4 meters/m)

- Time in Air Gap – 70 ms

- Line Speed – 152.4m/min (500f/min)
Adhesion Testing

- Peel test protocol –
  - Layers separated at the desired interface
  - Specimen placed into tensile tester for separation measurement.

- Peel strength –
  - Average load (force) per unit width of the bond line required to separate bonded materials where the angle of separation is 180 degrees (g/25.4mm).

- Mean peel strength among five trial specimens per condition represented the recorded data.
• **Use of APPD surface treatment on OPP promoted higher peel strengths than corona treatment for power densities greater than 2.2 Wmin/ft².**
• **Potential improvement in peel strength with the additional of argon**
• **None of these peels provided destructive peel tear.**
Results

Chart 2: OPET/LDPE 1 week Peel

- Initially indicates a “saturation/destruction” effect at, or before, the 2.2 Wmin/ft² power density.
- Destructive effect might also be assumed as the excessive formation of low molecular weight oxidized species will reduce peel adhesion.
- None of these peels provided destructive peel tear.
Results

- Peel strength following corona treatment of OPET increased with increasing applied power density.
- APPD treatment with N2 provided 50-60% improvement in peel strength over corona treatment in the 2.2 – 3.0 Wmin/ft² range, but 22% less peel strength at 4.0 Wmin/ft².
- Addition of argon underperformed corona and N2 plasma protocols.
- Peel/peel-tear” recorded for N2 APPD protocols (3.0, 4.0 Wmin/ft²), and 4.0 Wmin/ft² N2/argon APPD protocol.
Results

Stronger “peel-tear” results between OPP and Bynel® across all surface treatments, and generally at higher power density levels.

Highest incidence of structural “tear” (vs. peel-tear) occurred under the 3.0 Wmin/ft² nitrogen APPD protocol.

Suggests a possible adhesion optimization protocol under these trial conditions.
Results

Standard Deviation as a Percentage of Mean Peel Strength from Chart 4

<table>
<thead>
<tr>
<th></th>
<th>Peel-Tear</th>
<th>Tear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corona</td>
<td>32.9%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Nitrogen APPD</td>
<td>38.6%</td>
<td>45.5%</td>
</tr>
<tr>
<td>Nitrogen/Argon APPD</td>
<td>44.7%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

- High standard deviations indicate data points are spread out over a wider range of values.
- Sample size would need to increase in follow-up studies to reduce variability and increase significance.
Additional Comments

Time in the Air Gap (TIAG) = \(60 \times \text{air gap (mm)}\)
line speed (m/min)

- To obtain sufficient chemical bonding between an extrudate and non-porous film substrates, a level of oxidation of the substrate surface is necessary.

- Typically requires a high melt temperature as well as an appropriate air gap between the die and the chill roll nip.

- Common TIAG for polyethylene is between approximately 85-120 ms.

- Theorized that 70ms TIAG used restricted sufficient oxidation, reducing consistency of peel-tear results.

- Possible that high standard deviations were byproduct of this restricted oxidation, particularly with the OPP substrates.
Additional Comments

- One experimental protocol of a preliminary trial involved the use of a nitrogen/hydrogen APPD process gas mixture at 2.2Wmin/ft² with an OPP/ Bynel® structure

- Yielded a one-week bond strength of 847 g/25.4mm, and a one month mean peel strength of 1298 g/25.4mm.

- Indicates a other potential protocol candidate
Conclusions

- Insufficient TIAG oxidation may have increased variability in mean peel strength results within this study’s sample size.

- For OPP/LDPE structures, increasing power density generally increased mean peel strength for both corona and APPD-treatment specimens, with a nitrogen/argon APPD treatment providing the best result, but without creating specimen tear.

- Bond strength results for OPET/LDPE and OPET/Bynel® structures following corona and APPD treatments were divergent, where OPET bonding with LDPE decreased with increasing power density and OPET bonding with Bynel® generally increased with increasing power density.
Conclusions

• Further to the latter outcome, APPD treatments generated peel/peel-tear results, inferring that improved chemical bonding occurs when Bynel® interfaces with OPET which was pretreated by a nitrogen-based APPD.

• The most significant mean peel strength was achieved when tear occurred with the Bynel®/OPP specimen, where OPP was pretreated by a nitrogen-only APPD.

• A second study is necessary to optimize TIAG oxidation, as well as to validate the positive data-suggested influence of nitrogen (and nitrogen/hydrogen) APPDs on mean peel strength for extrusion coating structures involving OPET and OPP structures involving LDPE and Bynel® resins.
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