Adhesion in Extrusion Coating & Laminating - the Importance of Machine Variables

Bruce Foster
Mica Corporation
Outline

• Identify key factors that affect adhesion

• Examine Machine Variables that affect these factors
The Extrusion Coating System:

- **Primary Substrate** (paper, film, foil, fabric, etc)
  - **Surface modifier** (corona, flame, chemical primer)
  - **Extrudate** (LDPE, copolymer, ionomer = adhesive)
  - **Secondary substrate** (if extrusion lamination)

- **Primary Substrate** (paper, film, foil, fabric, etc)
- **Extrudate** (LDPE, copolymer, ionomer = adhesive)
- **Secondary substrate** (if extrusion lamination)
- **Surface modifier** (corona, flame, chemical primer)
Two Key Components for Adhesion

1. **Intimate contact** between adhesive & substrate, which permits:

2. **Chemical bonding** between adhesive & substrate
Factors Influencing Intimate Contact

- Adhesive Thickness (thicker = more easily deformed, longer solidification time)
- Adhesive mobility/ deformability (viscosity, modulus, solidification temp., wet-out)
- Substrate morphology (rough surface = less intimate contact)
- Substrate wettability (poor wetting = less intimate contact)
Machine Factors That Can Improve Intimate Contact

- Extrudate thickness
- Nip conditions (pressure & length)
- Melt temperature
Factors Influencing Chemical Bonding

- Degree of intimate contact
- Substrate surface chemistry
- Adhesive surface chemistry
- Migratory chemicals (in adhesive or substrate)
- Environmental stresses
Machine Factors That Can Improve Chemical Bonding

- Substrate treatment conditions (corona or flame power level, or primer application variables)
- Choice of extrudate type
- Extrudate thickness
- Air-gap distance
- Melt temperature of extrudate
- Extruder back-pressure
- Ozone assist
Intimate contact + Chemical bonding = Durable Adhesion
Now, Examine Each Machine
Factor in More Detail...
Machine Factors That Can Improve Intimate Contact

1. Extrudate thickness
2. Nip conditions (pressure & length)
3. Melt temperature
Extrudate Thickness

Single most important variable in achieving good adhesion*

*Thicker is almost always better

*(Assumption: Other extrusion conditions are in “normal” ranges)
Fig. 1 - Typical Adhesion Response to Coating Thickness

Ref. 1 - Foster, Bruce; Baker, Mike, Effect of Extrusion Parameters on Adhesion of Polyester – A Line Study, 2001 TAPPI Polymers, Laminations, Coatings Conference Proceedings, TAPPI PRESS, Atlanta, paper 17-2
Why Thickness is Important

- Transfer of thermal mass to insure intimate contact
- Thermal mass aids in surface oxidation of the extrudate
- Thicker = more compressible, important for non-smooth substrates
Why Thickness is Important

Objective: Transfer thermal energy from die to nip
Fig. 2 - Transfer of Thermal Energy

Time in Nip, msec = \( \frac{60 \times \text{Nip length, mm}}{\text{Line speed, mpm}} \)
Transfer of Thermal Energy

Solidification Model Gives Insight...

1-dimensional unsteady-state heat conduction equation:

Model predicts solidification of polymer in the nip

Fig. 3 – Modeling Polymer Solidification
Time vs. Thickness

2 - Assumed Solidification Temperatures (Ts):

- Ts = 80°C
- Ts = 100°C
Fig. 4 – Solidification Time vs. Melt Temperature
Fig. 5 – Solidification Time vs. Chill Roll Temperature
Machine Factors That Can Improve Intimate Contact

1. Extrudate thickness

2. Nip conditions (pressure & length)

3. Melt temperature
Fig. 6 – Nip Conditions

Nip Roll

Nip impression (deformation of rubber)

Time in Nip, msec = \[
\frac{60 \times \text{Nip length, mm}}{\text{Line speed, mpm}}
\]
Effect of Nip Length & Line Speed

Fig. 7

Nip Impression, mm:
- 20
- 10
- 5

Line Speed, mpm

Nip Time, msec
Fig. 3
Solidification Time vs. Thickness

2 - Assumed Solidification Temperatures (Ts):

- Ts = 80°C
- Ts = 100°C
Guidelines for Nip Length & Pressure

- **Softer Polymers** (e.g.: LDPE, EVA, EMA)
  - Longer impression, lower pressure (softer nip roll)

- **Harder Polymers** (e.g.: HDPE, PP, PET)
  - Shorter impression, higher pressure (harder nip roll)
Machine Factors That Can Improve Intimate Contact

1. Extrudate thickness
2. Nip conditions (pressure & length)
3. Melt temperature
Melt Temperature (T) & Intimate Contact

\[ T \rightarrow \text{Lower Viscosity} \quad \ldots\ldots\text{Yes!} \]

\[ T \rightarrow \text{Improve intimate contact?} \quad \ldots\ldots\text{No!} \]

Well...... maybe..........
Fig. 4 – Solidification Time vs. Melt Temperature
Melt Temperature (T) & Intimate Contact

↑ T → More surface oxidation

↑ Surface oxidation → Better wetting of substrate
Machine Factors That Can Improve Intimate Contact

1. Extrudate thickness
2. Nip conditions (pressure & length)
3. Melt temperature
Intimate contact + Chemical bonding = Durable Adhesion
Machine Factors That Can Improve Chemical Bonding

- Substrate treatment conditions (corona or flame power level, or primer application variables)
- Choice of extrudate type
- Extrudate thickness
- Air-gap distance
- Melt temperature of extrudate
- Extruder back-pressure
- Ozone assist
Substrate Treatment

- Treatment adds reactive sites to substrate
- Consult the supplier for PROPER treatment levels for your substrates
- Avoid over-treatment
Substrate Treatment

Substrate (as received)

Substrate (after proper treatment)

Corona, flame, plasma, priming

Reactive sites

Substrate (as received)
Avoid Over-Treatment!

Substrate fracture

Substrate (as received)

Excess Corona, flame, plasma, priming

Substrate fracture

Substrate (after over-treatment)

Reactive sites

Substrate (as received)
Corona Treatment of Films

Use Proper Watt-Density

Watt-Density = Power / area / time

Metric Units: W/m²/minute

\[ \frac{\text{KW setting} \times 1000}{\text{Line Speed (m/min) \times width (m)}} \]

Example: Treater is 3.0kW, line speed is 130mpm, and the treater width is 1400mm (1.4m), then the watt-density is:

\[
\frac{(3.0 \times 1000)}{(130 \times 1.4)} = 16.5 \text{ W/m}^2/\text{min}
\]

Important: You must determine optimum watt-density for each film and each set of running conditions. Some starting suggestions:

- BOPP films: 30 – 40 WD
- OPET films: 15 – 20 WD
- BON films: 5 – 15 WD
Other Treatment Methods

- Flame – proper air/gas ratio & manifold position
- Chemical priming – primer choice, proper amount & complete drying
- Plasma – ask the experts!
Machine Factors That Can Improve Chemical Bonding

- Substrate treatment conditions (corona or flame power level, or primer application variables)
- Choice of extrudate type
- Extrudate thickness
- Air-gap distance
- Melt temperature of extrudate
- Extruder back-pressure
- Ozone assist
Choice of Extrudate
(General “Rules of Thumb”)

• LDPE – for paper, primed plastics & primed foils
• Acid copolymers – for metal substrates & primed films
• Ionomers – for metal & primed substrates
• Acrylate copolymers – for PP & PET films, & primed surfaces
Machine Factors That Can Improve Chemical Bonding

- Substrate treatment conditions (corona or flame power level, or primer application variables)
- Choice of extrudate type
- Extrudate thickness
- Air-gap distance
- Melt temperature of extrudate
- Extruder back-pressure
- Ozone assist
Thickness, Air-Gap, Melt Temp

Extrudate

Substrate >>>

Air gap

Nip

Chill Roll
4 – References:

Ref. 3 - W.J. Ristey and R.N. Schroff; The Degradation and Surface Oxidation of Polyethylene During the Extrusion Coating Process, 1978 TAPPI Paper Synthetics Proceedings, TAPPI PRESS, Atlanta, p.267

Ref. 4 - V. Antonov and A.M. Soutar; Foil Adhesion With Copolymers: Time in the Air Gap, 1991 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p.553

Ref. 5 - B.A. Morris & N. Suzuki; The Case Against Oxidation as a Primary Factor for Bonding Acid Copolymers to Aluminum Foil, 2000 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta

Ref. 6 – B. Foster; Effect of Extrusion Coating Parameters on Activation of a Primed Film, 2002 TAPPI PLACE Proceedings, TAPPI PRESS, Atlanta Paper 14-2.
Ristey & Schroff - 1978

- Studied Effects of:
  - Air-Gap
  - Melt Temperature
  - Thickness

- On These Properties:
  - Molecular Weight Changes
  - Surface Oxidation
Ristey & Schroff - 1978

• Most Significant Conclusion:

25mm ↑air-gap = 5.5°C ↑melt temp

For LDPE surface oxidation between 321 – 338°C
4 – References:

Ref. 3 - W.J. *Ristey* and R.N. *Schroff*; The Degradation and Surface Oxidation of Polyethylene During the Extrusion Coating Process, 1978 TAPPI Paper Synthetics Proceedings, TAPPI PRESS, Atlanta, p.267

Ref. 4 - V. *Antonov* and A.M. *Soutar*; Foil Adhesion With Copolymers: Time in the Air Gap, 1991 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p.553

Ref. 5 - B.A. *Morris* & N. *Suzuki*; The Case Against Oxidation as a Primary Factor for Bonding Acid Copolymers to Aluminum Foil, 2000 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta

Ref. 6 – B. *Foster*; Effect of Extrusion Coating Parameters on Activation of a Primed Film, 2002 TAPPI PLACE Proceedings, TAPPI PRESS, Atlanta Paper 14-2.
Antonov & Soutar - 1991

Introduced the concept of:

**Time In the Air-Gap (TIAG)**

Simplifying Assumption: Extrudate Speed = Line Speed

Then, \( \text{TIAG (msec)} \approx \frac{\text{Air-Gap (mm)} \times 60}{\text{Line Speed (mpm)}} \)
Antonov & Soutar - 1991

• Most Significant Conclusion:

Air-gap time of ca. 80 – 120 msec

To allow oxidation of EAA & thereby get good adhesion to aluminium foil

Subsequently found to be a good “rule of thumb” for LDPE resins
Time In the Air-Gap

Has been & continues to be a useful tool for troubleshooting adhesion problems in extrusion coating & laminating processes

But....
4 – References:

Ref. 3 - W.J. *Ristey* and R.N. *Schroff*; The Degradation and Surface Oxidation of Polyethylene During the Extrusion Coating Process, 1978 TAPPI Paper Synthetics Proceedings, TAPPI PRESS, Atlanta, p.267

Ref. 4 - V. *Antonov* and A.M. *Soutar*; Foil Adhesion With Copolymers: Time in the Air Gap, 1991 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p.553

Ref. 5 - B.A. *Morris* & N. *Suzuki*; The Case Against Oxidation as a Primary Factor for Bonding Acid Copolymers to Aluminum Foil, 2000 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta

Ref. 6 – B. *Foster*; Effect of Extrusion Coating Parameters on Activation of a Primed Film, 2002 TAPPI PLACE Proceedings, TAPPI PRESS, Atlanta Paper 14-2.
Most significant conclusion:

Oxidation is *not* the mechanism for EAA* adhesion to aluminium foil, but

Time in the air-gap *does* influence the adhesion

* For Nucrel grades of 9% & 12% acid
Another conclusion:

For LDPE & low-acid EAA copolymers,

Oxidation *is* a key mechanism for adhesion.
4 – References:

Ref. 3 - W.J. Ristey and R.N. Schroff; The Degradation and Surface Oxidation of Polyethylene During the Extrusion Coating Process, 1978 TAPPI Paper Synthetics Proceedings, TAPPI PRESS, Atlanta, p.267

Ref. 4 - V. Antonov and A.M. Soutar; Foil Adhesion With Copolymers: Time in the Air Gap, 1991 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p.553

Ref. 5 - B.A. Morris & N. Suzuki; The Case Against Oxidation as a Primary Factor for Bonding Acid Copolymers to Aluminum Foil, 2000 TAPPI Polymers, Laminations, and Coatings Conference Proceedings, TAPPI PRESS, Atlanta

Ref. 6 – B. Foster; Effect of Extrusion Coating Parameters on Activation of a Primed Film, 2002 TAPPI PLACE Proceedings, TAPPI PRESS, Atlanta Paper 14-2.
## Experiment Set #1 – Feb ‘02

**Experimental Design - Modified Box-Benkin (center and edge-centers)**

**Variables:** Melt temp, Acid#, Coat Wt, Offset

**Fixed Line-Speed @26mpm (85fpm) & Air-Gap at 44mm (100msec)**

<table>
<thead>
<tr>
<th>Point #</th>
<th>Melt Temp deg C (deg F)</th>
<th>Acid #</th>
<th>Coat Wt gsm (#/rm)</th>
<th>Offset (0, -0.5)</th>
<th>Adhesion (g/25mm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>271 (520)</td>
<td>0</td>
<td>20 (12)</td>
<td>0 &amp; -0.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>271 (520)</td>
<td>3</td>
<td>10 (6)</td>
<td>-0.5</td>
<td>FT @300</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>271 (520)</td>
<td>3</td>
<td>30 (18)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>271 (520)</td>
<td>9</td>
<td>20 (12)</td>
<td>0</td>
<td>FT @2000</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>293 (560)</td>
<td>0</td>
<td>10 (6)</td>
<td>0 &amp; -0.5</td>
<td>FT @300</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>293 (560)</td>
<td>0</td>
<td>30 (18)</td>
<td>0 &amp; -0.5</td>
<td>FT @900</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>293 (560)</td>
<td>3</td>
<td>20 (12)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>293 (560)</td>
<td>9</td>
<td>10 (6)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>293 (560)</td>
<td>9</td>
<td>30 (18)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>315 (600)</td>
<td>0</td>
<td>20 (12)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>315 (600)</td>
<td>3</td>
<td>10 (6)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>315 (600)</td>
<td>3</td>
<td>30 (18)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>315 (600)</td>
<td>9</td>
<td>20 (12)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

- Degraded melt
- Max T= 302 (575)
- not tested
Experiment Set#2 – May ‘02

Following are designed to vary air-gap distance & TIAG, all with LDPE only:
(and the primed stock is now 4 months old!)

<table>
<thead>
<tr>
<th>Pt. #</th>
<th>Melt Temp deg C (F)</th>
<th>Line Speed mpm(fpm)</th>
<th>Coat Wt gsm (#/rm)</th>
<th>Air-Gap mm (inch)</th>
<th>Air Gap, msec</th>
<th>Adhesion (g/25mm)</th>
<th>Failure Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>293 (560)</td>
<td>15 (50)</td>
<td>10 (6)</td>
<td>25 (1.0)</td>
<td>100</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>293 (560)</td>
<td>26 (85)</td>
<td>10 (6)</td>
<td>44 (1.7)</td>
<td>103</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>293 (560)</td>
<td>15 (50)</td>
<td>10 (6)</td>
<td>89 (3.5)</td>
<td>350</td>
<td>300</td>
<td>FT</td>
</tr>
<tr>
<td>4</td>
<td>293 (560)</td>
<td>15 (50)</td>
<td>20 (12)</td>
<td>25 (1.0)</td>
<td>100</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>293 (560)</td>
<td>26 (85)</td>
<td>20 (12)</td>
<td>44 (1.7)</td>
<td>103</td>
<td>500</td>
<td>FT</td>
</tr>
<tr>
<td>6</td>
<td>293 (560)</td>
<td>26 (85)</td>
<td>20 (12)</td>
<td>64 (2.5)</td>
<td>147</td>
<td>500</td>
<td>FT</td>
</tr>
<tr>
<td>7</td>
<td>293 (560)</td>
<td>26 (85)</td>
<td>20 (12)</td>
<td>89 (3.5)</td>
<td>206</td>
<td>500</td>
<td>FT</td>
</tr>
<tr>
<td>8</td>
<td>293 (560)</td>
<td>15 (50)</td>
<td>20 (12)</td>
<td>89 (3.5)</td>
<td>350</td>
<td>500</td>
<td>FT</td>
</tr>
<tr>
<td>9</td>
<td>282 (540)</td>
<td>15 (50)</td>
<td>10 (6)</td>
<td>25 (1.0)</td>
<td>100</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>282 (540)</td>
<td>26 (85)</td>
<td>10 (6)</td>
<td>44 (1.7)</td>
<td>100</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>282 (540)</td>
<td>26 (85)</td>
<td>10 (6)</td>
<td>89 (3.5)</td>
<td>206</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>282 (540)</td>
<td>15 (50)</td>
<td>10 (6)</td>
<td>89 (3.5)</td>
<td>350</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>282 (540)</td>
<td>15 (50)</td>
<td>20 (12)</td>
<td>25 (1.0)</td>
<td>100</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>282 (540)</td>
<td>26 (85)</td>
<td>20 (12)</td>
<td>44 (1.7)</td>
<td>100</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>282 (540)</td>
<td>26 (85)</td>
<td>20 (12)</td>
<td>89 (3.5)</td>
<td>206</td>
<td>500</td>
<td>FT</td>
</tr>
<tr>
<td>16</td>
<td>282 (540)</td>
<td>15 (50)</td>
<td>20 (12)</td>
<td>89 (3.5)</td>
<td>350</td>
<td>500</td>
<td>FT</td>
</tr>
<tr>
<td>17</td>
<td>282 (540)</td>
<td>26 (85)</td>
<td>30 (18)</td>
<td>44 (1.7)</td>
<td>100</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>
Oxidation -vs- Air Gap Time

1978 Data of Ristey & Schroff

\[
y = 9 \times 10^{-5}x^{1.7915} \\
R^2 = 0.9649
\]

\[
y = 0.0002x^{1.6735} \\
R^2 = 0.9107
\]

\[
y = 0.0001x^{1.9016} \\
R^2 = 0.965
\]

Carbon Absorbance

- 321 C (610 F)
- 329 C (625 F)
- 338 C (640 F)

Power (321 C (610 F))

Power (329 C (625 F))

Power (338 C (640 F))

Air Gap, msec
Foster -2002

• Most Significant Conclusion:

(For oxidation of LDPE in air gap):

– Air-gap time > thickness > melt temp
# Scale-Up Differences

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pilot-Line Conditions</th>
<th>“Typical” Production Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Line speed:</strong></td>
<td>26m/min (85ft/min)</td>
<td>100-400m/min (~300-1300ft/min)</td>
</tr>
<tr>
<td><strong>Air-gap:</strong></td>
<td>44mm (1.75 inches)</td>
<td>150-300mm (6-12 inches)</td>
</tr>
<tr>
<td><strong>Die shear rate:</strong></td>
<td>190sec(^{-1})</td>
<td>500-2500sec(^{-1})</td>
</tr>
</tbody>
</table>
Foster – 2002

Q – Is die shear rate an important factor?
Surface Oxidation -vs- Die Shear Rate

Die Shear Rate, 1/s

Carbonyl Absorbance

Recent Experiment – Jan ‘05
Q – Is die shear rate an important factor?

A – Maybe! More work needed...
Machine Factors That Can Improve Chemical Bonding

- Substrate treatment conditions (corona or flame power level, or primer application variables)
- Choice of extrudate type
- Extrudate thickness
- Air-gap distance
- Melt temperature of extrudate
- Extruder back-pressure
- Ozone assist
Extruder Back Pressure

Back Pressure:

- Creates more shear
- More polymer chain ends
- More oxidation
- More degradation! (possible heat-seal & bond aging problems)
Machine Factors That Can Improve Chemical Bonding

- Substrate treatment conditions (corona or flame power level, or primer application variables)
- Choice of extrudate type
- Extrudate thickness
- Air-gap distance
- Melt temperature of extrudate
- Extruder back-pressure
- Ozone assist
Ozone Assist:

- **Ozone**
- **Substrate >>>**
- **Air gap**
- **Chill Roll**
- **Nip**
- **die**

Diagram showing the process with labeled components.
Ozone Assist

- Aids surface oxidation
- Lower melt temps and/or thinner coat weights may be possible
- Many References available
Conclusions

- Many factors affect adhesion
- More research needed to better understand the oxidation / mechanical process in the air-gap.