ATMOSPHERIC PLASMA - THE NEW FUNCTIONAL TREATMENT FOR EXTRUSION COATING AND LAMINATION PROCESSES

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ABSTRACT

Electrostatic corona pretreatment has traditionally been a very cost-efficient treatment method to optimize adhesion levels during the extrusion coating and lamination process. While it is cost-effective, the residence times may be insufficient to permit penetration of the active species that effect change into the surfaces of web materials. Low-pressure plasmas have been used for many years to surface treat three-dimensional plastic objects and polymer films, therefore, the benefits of plasma treatment are well recognized: reduced degradation of surface morphology, higher treatment (dyne) levels, elimination of backside treatment, and extended life of treatment over time. However, the complexity, slow speed and high cost of these contained plasma systems make them impractical for all but the most esoteric applications. Now a system has been developed that allows plasmas to be sustained at atmospheric pressure in a way that permits the surface treatment of substrates to enhance adhesion strength and hot tack in the extrusion coating and lamination processes on a continuous web handling system similar to a corona treating system. The Atmospheric Plasma Treatment (APT) process allows treatment in a broad range of reactive chemistries and has been successfully tested on various films, foils, nonwovens and metals. Further, depending upon the dyne level required and type of material, line speeds in excess of 400 fpm are practical and up to 1,000 fpm have been achieved. Specialty applications requiring stringent surface morphology specifications, specific surface modification such as hydrophilicity, precise surface coating or tightly controlled electrical characteristics will find the APT system especially attractive and useful.

INTRODUCTION

Products made from polymers of various chemistries introduce an every-growing number of conveniences to our lives. Although polymers are common in every day living, the most commonly used group of polyolefins exhibit a significant problem. As shown in Table 1, the intrinsic surface energy of these materials is rather low, and processes like lamination, printing or coating present rather difficult challenges:

<table>
<thead>
<tr>
<th>Polymer Surface Tensions [dynes/cm²]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>31</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>32</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>33</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>27</td>
</tr>
<tr>
<td>Polytetrafluorethylene</td>
<td>19</td>
</tr>
</tbody>
</table>
A lamination or coating bond with a substrate is lower when one or both surfaces are non-polar. Modifying surface energy to introduce polar groups to make two materials more polar increases bond strength. This is a necessary objective, since performance demands on flexible packaging constructions continue to drive the need for new innovations and efficiencies within extrusion coating and laminating processes. Down-gauging, along with changes in melt temperatures to adjust surface oxidation levels (and the subsequently induced surface polarity) and increases in production speeds, are key process variables being adjusted to meet these market demands. These strategies, in turn, require a focus on adhesion promoting process treatments such as corona or ozone to re-optimize lamination and coating adhesion. It is well known, for instance, that when either corona or corona and ozone are used, adhesion levels can be improved as melt temperatures decrease. Pretreatment of the substrate with corona, and the extrudate with ozone, results in very good adhesion even at melt temperatures below 300°C. Use of higher polymer coating weights can also increase adhesion in the area of contact between substrates by carrying more heat to the substrate and maximizing what is nipped into the voids of the substrate material(s). This paper is a continuation of a study of the beneficial effects of atmospheric plasma treatment in promoting adhesion, with a current focus on application within extrusion coating and laminating processes.

BACKGROUND

The most important property in extrusion coating and laminating is adhesion of the polymer to the substrate(s). Without adequate adhesion, the coating can be easily removed from the substrate. Typically, adhesion for a nonpolar polymer such as Low Density Polyethylene (LDPE) is accomplished by a combination of oxidation of the extrudate and treatment of the substrate. The level of oxidation is a function of:

1. Melt Temperature
2. Line Speed
3. Air Gap
4. Coating Weight

Some combinations of these variables will yield acceptable adhesion, but also may produce undesirable effects such as increased taste and odor or poor heat seal strength.

The most common methods used for the treatment of web substrates with ionized gases are:

- Flame Treatment
- Corona Treatment
- Plasma Treatment in Vacuum
- Plasma Treatment in Air

All of these methods are similar in that the gas at the surface of the substrates is ionized, either with the help of an electric field, or with a chemical reaction. For a differentiation of the different method one has to look at the method of ionization as well as the electron density and the electron temperature generated by the different methods.

Flame Treatment is used to promote adhesion in some extrusion processes and is generated by aiming a combustion flame, typically a propane or butane flame, onto the substrate surface. The electron density, and hence the ionization rate, in a flame is at the lower end of plasmas used for surface treatment.

Corona Treatment systems are also typical adhesion promoters in extrusion, with ionization created by applying a high frequency high voltage to an arrangement of two opposing electrodes, of which at least one is insulated with a dielectric. This creates streamer like discharges, which ionize the discharge gap. Although the technology has been long-established, it still bears some major drawbacks. The streamer-like discharge is highly non-uniform and it has been shown that once a streamer hits the polymer surface, it leaves a local discharge which in return attracts the next streamer to the exact same spot. The result is a localized treatment. The maximum achievable treatment level therefore is an average of the treated areas and untreated areas. A second disadvantage of Corona Treatment is the
high voltage required to initiate the discharge. The voltage can be high enough to create a discharge on the backside of fast moving webs, resulting in treatment of the backside as well, an effect not wanted in most cases.

With Plasma Treatment in vacuum, the low pressure levels in vacuum coating chambers allow the generation of uniform plasma, usable for highly effective treatment of polymer surfaces. The technology is widely used for web coating application and for the treatment of 3D objects like automotive bumpers. The uniformity of the plasma allows for high treatment levels.

The high functionality of a uniform plasma discharge in vacuum has driven many efforts to establish a uniform glow discharge at atmospheric pressure, making this technology applicable to extrusion processes at atmospheric pressure. Recently, Enercon Industries and Sigma Technologies International have developed a line source which can produce an Atmospheric Plasma Treatment (APT) stable glow discharge. The differences to a Corona Treatment system are as follows:

1. Injection of Plasma Gas directly into the discharge gap.

   In order to achieve a stable glow discharge free of streamers it is required to use noble gases, whose high metastable phases allow the steady glow discharge. In order to reduce the consumption of these gases to a minimum the gas is injected directly into the discharge gap. Doing it this way also allows the injection of other treatment gases, which get highly ionized in the discharge and allow users to address the specific chemistry of the treated polymer.

2. Creation of a stable, homogeneous and uniform glow discharge.

   Unlike Corona, where the discharge occurs in streamers, the APT creates a uniform glow in the discharge gap. This allows for uniform treatment on the substrate surface, thus a higher treatment level of the surface is achievable.

3. Lower Voltage.

   The voltage required to initiate the gas discharge is greatly reduced compared to Corona Treatment Systems. This prevents backside treatment, one of the major drawbacks of corona.

**EXPERIMENTAL DESIGN**

The objective of the experimental design was to determine differences in the peel adhesion strength of LDPE film which was untreated, treated with corona discharge, and treated with the APT process.

**Materials**


**Equipment**

- Enercon Covered Roll corona treating system w/ metal electrodes
- Enercon/Sigma APT lab station
- Thwing-Albert Model 225-1 Friction Peel Tester with sled and peel clamp

The LDPE film was pre-treated under the following conditions:

**Table 2: Variables in Experimental Design**

<table>
<thead>
<tr>
<th>Substrate Treatment</th>
<th>Corona Treatment</th>
<th>APT Treatment</th>
<th>No Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Line Speed</strong></td>
<td>50 fpm</td>
<td>50 fpm</td>
<td>n/a</td>
</tr>
</tbody>
</table>
The peel adhesion test was measured in accordance with ASTM test method D3330A and utilized a 180 degree peel fixture with 3M 800 acetate film acrylic adhesive tape.

RESULTS

The peel adhesion tests took place from within thirty minutes to seventeen days of the pretreatment protocol to determine peel adhesion strength and longevity. Longevity of treatment and average peel adhesion statistics are summarized in Figure 1 and Figure 2, respectively.

Figure 1. Longevity of Treatment of LDPE in Dynes/cm over 17 day period

Figure 2. Average Peel Adhesion of LDPE in lbs./in over 17 day period
CONCLUSION

The data indicates that the surface functionalization capability of APT treatment can significantly improve the surface tension and adhesion of LDPE film compared to standard corona treatment. Moreover, the specific chemistries utilized with APT treatment in this trial protocol provided a significant increase in treatment longevity, with LDPE retaining over 44% more surface adhesion strength over comparable periods of time compared to corona discharge.

The application of the APT process on extrusion coating and laminating lines to increase the bond between substrates for liquid, flexible and paperboard packaging structures appears to offer promising process advantages. Post-treatment on these lines using APT systems would also appear to offer unique and longer-term surface functionalizations for downstream converting operations compared to corona treatment.

REFERENCES
Atmospheric Plasma -
The New Functional Treatment for Extrusion Coating & Laminating Processes

presented by:
Dave Markgraf
Senior Vice President
Enercon Industries
### Surface Activation

Q: Why activate a material surface?
A: Intrinsic surface energy of most surfaces very low

<table>
<thead>
<tr>
<th>Treat Material</th>
<th>Untreated Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (PP)</td>
<td>29</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>31</td>
</tr>
<tr>
<td>Teflon®</td>
<td>18</td>
</tr>
<tr>
<td>EVA</td>
<td>33</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>36</td>
</tr>
<tr>
<td>Polytetrafluorethylene (PTFE)</td>
<td>19</td>
</tr>
</tbody>
</table>
Atmospheric Plasma Treatment (APT) – What is it?

- Like Corona, APT is the electrical ionization of a gas.

- The Plasma (glow) discharge creates a smooth, undifferentiated cloud of ionized gas with no visible electrical filaments.
Atmospheric Plasma Treatment (APT) – What is it?

- Unlike Corona, Plasma is created at much lower voltage levels.

- In both cases, the power level may be identical.
**Atmospheric Plasma Treatment (APT) – What is it?**

- **Example:**
  - Plasma will generally form in the 2 thru 5 kV Range. Corona generally requires about 8 to 20 kV. Yet, in both cases, the Watt Density may be the same.

\[
W_d = \frac{PS_w}{WW \times LS \times NST}
\]

**Where:**
- \(W_d\) = Watt Density (watts/m²/minute)
- \(PS\) = Power Supply (watts)
- \(WW\) = Web Width (meters)
- \(LS\) = Line Speed (m/minute)
- \(NST\) = Number of Sides Treated
Atmospheric Plasma Treatment (APT)

Major Advantages

- High Treatment Level
- Elimination of Backside Treatment
- Long-Lasting Surface Activation
- Elimination of Pin-Holing, Ozone
- “Cold Flame” with Controlled Chemistry
- Surface Morphology Unaffected
- Construction to Most Production Widths
Surface activation with plasma

Effects of plasma on surfaces

- Electron bombardment ➔ cross-linking
- Ion bombardment ➔ surface etching
- Excitation of plasma gas ➔ chemical reactions on the surface
- UV radiation ➔ similar to electron bombardment
# Surface activation with plasma

<table>
<thead>
<tr>
<th>Speed:</th>
<th>Speeds greater than 250 m/min. are being achieved.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Construction:</td>
<td>To most extrusion, lamination or production line widths.</td>
</tr>
<tr>
<td>Gas Statistics:</td>
<td>Consumption average is .013 liters/min. per mm of electrode.</td>
</tr>
<tr>
<td>Economies:</td>
<td>Low operational costs, with gas cost averaging US$14.00-$22.00/day.</td>
</tr>
<tr>
<td>Maintenance:</td>
<td>Only standard maintenance required.</td>
</tr>
<tr>
<td>Operational Mode:</td>
<td>Operates at atmospheric pressure without vacuum chambers.</td>
</tr>
</tbody>
</table>
Covered Roll Corona Discharge

Corona Discharge
With Only Air and PP Substrate in the Gap.
Atmospheric Plasma (Glow) Discharge

Plasma Discharge With Gas and LDPE Substrate in the Gap.
Surface activation with plasma

Polypropylene fiber prior to treatment

Polypropylene fiber after Atmospheric Plasma Treatment
Atmospheric Plasma System Positioning – Extrusion Coating/Laminating Line
APT Experimental Design

Objective
- Determine differences in peel adhesion strength of LDPE film which was untreated, treated with corona discharge, and treated with the APT process.

Materials

Equipment
- Enercon Covered Roll corona treating system w/ metal electrodes
- Enercon/Sigma APT lab station
- Thwing-Albert Model 225-1 Friction Peel Tester with sled and peel clamp
# APT Experimental Variables

<table>
<thead>
<tr>
<th>LDPE Treatment</th>
<th>Corona Treatment</th>
<th>APT Treatment</th>
<th>No Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Speed</td>
<td>50 fpm</td>
<td>50 fpm</td>
<td>n/a</td>
</tr>
<tr>
<td>Air Gap</td>
<td>.040</td>
<td>.040</td>
<td>n/a</td>
</tr>
<tr>
<td>Watt Density(w/ft²/min)</td>
<td>9</td>
<td>9</td>
<td>n/a</td>
</tr>
<tr>
<td>Pre-Trial Dyne</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Chemistry</td>
<td>n/a</td>
<td>He/C2H2</td>
<td>n/a</td>
</tr>
<tr>
<td>Initial Post-Trial Dyne</td>
<td>46</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>
Longevity of Treatment of LDPE in Dynes/cm

Longevity of Treatment

- Corona Treated
- APT Treated
- No Treatment

Days

Dynes/cm
Average Peel Adhesion (lbs./in.) vs. Position

![Graph showing average peel adhesion (lbs./in.) vs. position over 17 days for different treatments: Corona Treated, APT Treated, and No Treatment.](image)
Conclusions

- Surface functionalization can significantly improve the surface tension and adhesion capability of APT treatment of LDPE film compared to standard corona treatment.

- Specific chemistries utilized with APT treatment in this trial protocol provided a significant increase in treatment longevity, with LDPE retaining over 44% more surface adhesion strength over comparable periods of time compared to corona discharge.
Any questions?
Thank you for your interest in Atmospheric Plasma Treatment for the Extrusion Coating/Laminating Process.