Enhancing the Bonding of Dissimilar Materials with Plasma

Andy Stecher
Plasmatreat North America
**Key Take-Aways**

- Materials’ joining in manufacturing of lightweight, often dissimilar substrates present technical challenges.

- Surface conditioning prior to bonding dissimilar materials enables better adhesion.

- Plasma cleans surfaces by removing surface contaminants and activates surface chemistries - eliminating primers.

- Plasma stabilizes manufacturing bonding processes.

- Plasma coatings modify surfaces to provide corrosion protection, and improves or inhibits adhesion.
About Plasmatreat

- Subsidiaries and distribution partners worldwide in 34 countries

Germany
Steinhagen
Birkenfeld

China
Shanghai
Guangdong - Dongguan

Japan
Tokyo
Osaka

USA & Canada
Elgin
Belmont
Ancaster

Singapore

Great Britain
London

France
Paris

Spain
Barcelona

Italy
Venice

Turkey
Istanbul
About Plasmatreat

• PlasmaTreat™ North America Inc. is part of PlasmaTreat® Worldwide operating in 34 countries with 15 subsidiaries and over 200 employees.

• North America with three locations: Toronto, Ontario; San Francisco, CA and Chicago, IL.

• Breakthrough Openair™ plasma technology introduced to industry in 1995, patented worldwide in 1998 - more than 100 international patents

• Over 6,000 Systems with more than 20,000 Plasma Jets in Service.

• Automotive, Aerospace, Medical, Electronics, and other high-performance applications.
Outline

1. Industry Trends and Motivation
2. Surface Conditioning and Adhesion
3. Plasma Composition and Generation
4. Surface Cleanliness and Activation
5. Process Measurement
6. PlamaPlus® Coating
7. Important Results
1. Industry Trends and Motivation
2. Surface Conditioning and Adhesion
3. Plasma Composition and Generation
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5. Process Measurement
6. PlamaPlus® Coating
7. Important Results
Industry Trends & Motivation

Top Challenges to Achieve Fuel Efficiency / Emission Standards

- Reducing vehicle weight: 46%
- Drive train: 30%
- Battery technology: 30%
- Repackaging of the vehicle: 23%
- Assembling the car: 11%
- Production of individual parts: 11%
- Control system technology: 11%
- Utilizing new materials: 11%
- Servicing the vehicle: 10%
- Other: 5%

Source: Aberdeen Group, August 2013
Weight reduction involves substituting lightweight materials such as aluminum, alloys, composites and plastics for steel.
“Without the use of bonding technology, modern lightweight designs would hardly be feasible – especially when it comes to bonding dissimilar and/or new materials.”

Dr. Andreas Gross, Fraunhofer IFAM
### Industry Trends & Motivation

#### Materials Joining Challenges

**Overall Rank**

<table>
<thead>
<tr>
<th>Challenge</th>
<th>Rank by Sector</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Increased use of new materials and material combinations</td>
<td>Automotive 4</td>
</tr>
<tr>
<td>2. Qualifying new processes and procedures</td>
<td>Oil &amp; Gas 2</td>
</tr>
<tr>
<td>3. Maturing and successfully transitioning technologies from R&amp;D to production</td>
<td>Defense 1</td>
</tr>
<tr>
<td>4. Keeping staff current on the latest materials joining processes and methods</td>
<td>Aerospace 4</td>
</tr>
<tr>
<td>5. Shortage of engineers and designers with materials joining expertise</td>
<td>Heavy Mfg. 2</td>
</tr>
<tr>
<td>7. Competition from low labor-cost countries</td>
<td></td>
</tr>
<tr>
<td>8. Cost to introduce new processes, procedures or product designs</td>
<td></td>
</tr>
<tr>
<td>9. First-time quality expectations are increasing</td>
<td></td>
</tr>
<tr>
<td>10. Shortage of skilled welders and other skilled trades</td>
<td></td>
</tr>
</tbody>
</table>

#### Technology Needs

**Overall Rank**

<table>
<thead>
<tr>
<th>Technology Need</th>
<th>Rank by Sector</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Joining of high-performance materials</td>
<td>Automotive 1</td>
</tr>
<tr>
<td>2. Educating designers and engineers on joining alternatives</td>
<td>Defense 1</td>
</tr>
<tr>
<td>3. Arc welding advancements (productivity, quality, etc.)</td>
<td>Aerospace 1</td>
</tr>
<tr>
<td>4. Dissimilar materials joining methods</td>
<td>Heavy Mfg. 1</td>
</tr>
<tr>
<td>5. Online access to materials joining expertise and data</td>
<td>Adv. Energy 1</td>
</tr>
<tr>
<td>6. More sensitive, accurate and reliable non-destructive evaluation (NDE)</td>
<td></td>
</tr>
<tr>
<td>7. High-productivity thick section welding processes</td>
<td></td>
</tr>
<tr>
<td>8. Improved (faster, better, cheaper) welder training methods</td>
<td></td>
</tr>
<tr>
<td>9. Validation strategy for new processes</td>
<td></td>
</tr>
<tr>
<td>10. Resistance welding advancements (quality, reliability, etc.)</td>
<td></td>
</tr>
<tr>
<td>11. Additive manufacturing technologies</td>
<td></td>
</tr>
</tbody>
</table>

*Source: EWI 2010*
Industry Trends & Motivation

- Adhesion to combinations of difficult substrates
- Unequal thermal expansion coefficients
- Galvanic reactions between dissimilar metals
- How to uniformly distribute mechanical stresses
- Paintability of mixed assemblies

Source: Mix and Match for Lightweight Autos, Manufacturing Engineering, September 2014
Industry Trends & Motivation

Steel is easy

To Clean  To Bond To  To Paint
## Industry Trends & Motivation

Compared with metals, plastics have low surface energy

<table>
<thead>
<tr>
<th>Metals/Other Materials</th>
<th>High Surface Energy Plastics</th>
<th>Low Surface Energy Plastics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium: 850</td>
<td>ABS: 42</td>
<td>Acetal: 36</td>
</tr>
<tr>
<td>Copper: 1100</td>
<td>Acrylic: 38</td>
<td>EVA: 33</td>
</tr>
<tr>
<td>Glass: 250-50</td>
<td>Kapton: 50</td>
<td>PE (Polyethylene): 31</td>
</tr>
<tr>
<td>Lead: 450</td>
<td>Noryl resin: 38</td>
<td>PP (Polypropylene): 29</td>
</tr>
<tr>
<td>Stainless steel: 700-1100</td>
<td>Nylon: 46</td>
<td>Polystyrene: 36</td>
</tr>
<tr>
<td>Tin: 500</td>
<td>Phenolic: 46</td>
<td>PTFE: 18</td>
</tr>
<tr>
<td>Zinc: 750</td>
<td>Polycarbonate: 42</td>
<td>PVA: 37</td>
</tr>
<tr>
<td></td>
<td>Rigid PVC: 39</td>
<td>PVF: 28</td>
</tr>
</tbody>
</table>

*Surface energy in mJ/m²*

Source: Permabond® Engineering Adhesives
The Six Challenges of Lightweighting

1) Dealing with adhesion to lighter weight substrates

Substrates such as plastics can have significantly different surface and mechanical properties that must be accommodated in new, lighter weight designs. (see our webinar on LSE Plastic Bonding here). Lower surface energy plastics such as polypropylene can give very useful weight savings but are trickier to bond but 3M can help - our range of LSE bonding adhesives such as 3M 360 PSA adhesive or 3M DP8005/DP8010 can bond to polyolefins (often without the need for surface pre-treatment). When changing from steel to aluminium in light duty trailers; from aluminium to engineering plastic in small appliances, or from engineering plastic to polyethylene or propylene (PE/PP), 3M has a wide range of adhesives and tapes specially formulated to meet these challenges.
1. Industry Trends and Motivation
2. Surface Conditioning and Adhesion
3. Plasma Composition and Generation
4. Surface Cleanliness and Activation
5. Process Measurement
6. PlamaPlus® Coating
7. Important Results
According to Sherwin-Williams, 80% of coating failures can be tied to inadequate surface preparation.

Surface Conditioning & Adhesion

Covalent Bonding

Any contamination that comes between the ink, coating or adhesive and the substrate surface will weaken the bonding forces.

Mechanical

Mechanical Interlocking
Surface Conditioning & Adhesion

- **Weldon (2009):** Surface preparation is a critical factor in obtaining good adhesion. **Soils and other contaminants inhibit adhesion through both chemical and physical pathways.** By reducing the influence of intermolecular forces between the surface and the applied material, or by blocking sites that provide an opportunity for physical anchoring.

- **Schuman and Thames (2005):** A variety of important coating properties such as hardness, scratch resistance, chip resistance and gloss are affected by the underlying surface’s cleanliness, hardness, smoothness and chemical bonding to the coating.
Davis (1993): Contamination “is one of the most insidious factors affecting adhesive bond performance”
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Surface Conditioning & Adhesion

Plasma: Cleans Activates Coats

Prior to: Printing Decorating Bonding

On: Plastics Glass Metal Ceramic
Plasma Composition & Generation

Diagram showing the transition from solid, liquid, gas, to plasma through energy input.
Adding energy to oxygen breaks apart the O\textsubscript{2} molecules, and then the oxygen atoms themselves, to produce a number of reactive species:
Plasma Composition & Generation

Cleaning Effect

Remove surface contamination
Plasma Composition & Generation

- Generator
- Transformer
- Plasma Jet
Plasma Composition & Generation

OPENAIR® Plasma Jet

- High voltage
- Current
- Ionization Gas
- Cathode
- Discharge Chamber
- Plasma Beam
- Substrate
Plasma Composition & Generation

OPENAIR® Plasma Jet

RD 2004
Plasma Composition & Generation
Plasma Composition & Generation

Aurora LC
Openair® plasma is routinely used for 3-dimensional, contoured surfaces using fixed automation or 6-axis electronic robots.
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Surface Cleanliness and Activation

External Surface Contamination

- Oil
- Dust
- Contamination
- Grease
- Finger-prints

Internal Surface Contamination

- Anti-oxidants
- Cross-linkers
- Slip Agents, Waxes
- Pigments
- Fillers
- UV Modifiers
- Contamination
- Fillers
- UV Modifiers
- Slip Agents, Waxes
- Cross-linkers
- Anti-oxidants
Surface Cleanliness and Activation

Surface Modification Options

Mechanical
- Scuff
- Sand
- Blast

Wet Chemical
- Cleaner
- Solvent
- Primer

Physical
- Flame
- Corona
- Plasma
Surface Cleanliness and Activation

Organic solvents used to dissolve contaminants are well known to pose some significant health, safety and environmental risks.
Surface Cleanliness and Activation

Surface Modification Options

Mechanical:
- Scuff
- Sand Blast

Wet Chemical:
- Cleaner
- Solvent Primer

Physical:
- Flame
- Corona
- Plasma
# Surface Cleanliness and Activation

## Surface Modification

**Comparison of Treatment Technologies**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Flame</th>
<th>Corona</th>
<th>Openair™ Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attainable Surface Energy</td>
<td>Typically 50 dynes</td>
<td>Typically 50 to 55 dynes</td>
<td>Typically beyond 72 dynes (wets out with water)</td>
</tr>
<tr>
<td>Treatment Speed</td>
<td>Up to 200 ft/min</td>
<td>Up to 50 ft/min</td>
<td>Up to 150 ft/min</td>
</tr>
<tr>
<td>Penetration into Grooves or Small Cavities</td>
<td>Good</td>
<td>Poor</td>
<td>Excellent</td>
</tr>
<tr>
<td>Thermal Distortion</td>
<td>Very High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Sensitivity to Humidity</td>
<td>None</td>
<td>High</td>
<td>None</td>
</tr>
<tr>
<td>Explosion or Fire Risk</td>
<td>High</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Treatment of Metal Parts</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Ozone Emissions</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Voltage on Surface</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Operating Cost</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>ISO/QS Compliant</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Homogenous Treatment</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Safety</td>
<td>Poor - fire/explosion danger</td>
<td>Poor - shock hazard potential</td>
<td>Excellent - very safe</td>
</tr>
</tbody>
</table>
Surface Cleanliness and Activation

Differences in coefficients of thermal expansion constrain the use of high temperatures for many applications where expansion causes dimensional tolerance issues or mechanical stresses/thermal shock.

Source: Permabond® Engineering Adhesives
Surface Cleanliness and Activation

- Dry
- No thermal impact
- Touchless
- Avoids penetrating or impacting the bulk matrix
- No Waste
Plasma from oxygen (present in air) react with organic materials to form harmless carbon dioxide and water:

\[
\text{Organic Contaminants} \xrightarrow{\text{O}_2 \text{ plasma}} \text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{HO}_2\text{C} \xrightarrow{\text{O}_2 \text{ plasma}} \text{CO}_2 + \text{H}_2\text{O}
\]
Surface Cleanliness and Activation

Before Plasma Cleaning

After Plasma Cleaning

Baseline Carbon Level

Source: Shun’ko & Belkin, 2007
Surface Cleanliness and Activation

<table>
<thead>
<tr>
<th>Element</th>
<th>After Detergent/Solvent-cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>27%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>42%</td>
</tr>
<tr>
<td>Carbon</td>
<td>31%</td>
</tr>
</tbody>
</table>

XPS spectra

Courtesy, BTR Labs
Surface Cleanliness and Activation

XPS spectra

<table>
<thead>
<tr>
<th>Element</th>
<th>Detergent/Solvent-based</th>
<th>Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>27%</td>
<td>43%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>42%</td>
<td>55%</td>
</tr>
<tr>
<td>Carbon</td>
<td>31%</td>
<td>2.5%</td>
</tr>
</tbody>
</table>

Courtesy, BTR Labs
Surface Cleanliness and Activation

- Waxes
- Thicker film oils
- Denser Contamination
- Inorganic Contamination
Surface Cleanliness and Activation

- Waxes
- Thicker film oils
- Denser Contamination
- Inorganic Contamination

Openair® Plasma + Compressed Process Gas
Surface Cleanliness and Activation

- Waxes
- Thicker film oils
- Denser Contamination
- Inorganic Contamination

→ Openair® Plasma/Laser
Surface treatment using Plasma and Laser Hybrid Technology is unprecedented. A new global patent for surface cleaning.
Surface Cleanliness and Activation

**Activation Effect**

- **Carbonyl Groups**
- **Hydroxyl Groups**
Surface Cleanliness and Activation

Atmospheric Pressure Plasma Process - Activation

Activation results in the formation of Oxygen functional groups (e.g. Carbonyl, Hydroxyl) as well as Nitrogen functional groups (e.g. Nitrate).

PP: untreated
(surface free energy: 27.0 mN/m)

PP: Openair\textsuperscript{tm} Plasma treated
(surface free energy: up to 72 mN/m)

Courtesy: Fraunhofer Institute for Processing Technology and Materials Research
Surface Cleanliness and Activation

Atomic Force Microscopy Study on PET 1µm
Surface roughness decreased, actual surface area increased by 30%

UNTREATED

PLASMA TREATED
1. Industry Trends and Motivation
2. Surface Conditioning and Adhesion
3. Plasma Composition and Generation
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5. Process Measurement
6. PlamaPlus® Coating
7. Important Results
Contaminated and low energy surfaces cause water to bead up and do not wet out.
Handheld easy-to-operate yet accurate and reliable contact angle measurement uses a self contained reference fluid.
Process Measurement

An OSEE Surface Cleanliness Measurement System
The Photo Electric Effect:
Optically Stimulated Electron Emission (OSEE)
Process Measurement

An OSEE Surface Cleanliness Measurement System

Before Cleaning  After Cleaning
1. Industry Trends and Motivation
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6. PlamaPlus® Coating
7. Important Results
PlasmaPlus® Coating Process

- As substitution for primers on metals
- Long-term durable bonding
- Corrosion inhibiting
- Environmentally friendly because no solvents are used and no drying is required
- Recyclable because if their marginal layer thickness
PlasmaPlus® Coating Process

Adhesion promoting layers for hybrid materials (thermoplastic-metal or rubber-metal)

- Coating of steel, stainless steel, zinc-plated steel, titanium, aluminum and electro-deposition.
- Good success with PA6, PBT and TPU
- No primer necessary
1. Surface cleaning (organic materials)
PlasmaPlus® Coating Process

1. Surface cleaning (organic materials)

2. Coating with silicon-organic compounds
PlasmaPlus® Coating Process

1. Surface cleaning (organic materials)

2. Coating with silicon-organic compounds

3. Activation to improve bonding
Depth profile of a silicon-organic adhesion promoter coating on aluminum (Auger Electron Spectroscopy)

Uniform, Approx. 130nm thick Carbon-poor (<5 %) inorganic coating
PlasmaPlus<sup>®</sup> Coating of a windscreen for primer-free bonding (FORD Motor Company)

**Properties:**
- Silicon-organic and organic coatings with functional groups
- Hydrophilic or hydrophobic properties
- Layer-densities between 20 and 700 nm
- Deposition rates up to approx. 1µm/sec
- Substrates: metals, polymers, ceramics, glass

**Possibilities:**
- Anticorrosion
- Adhesion promotion
- Release-coatings
- Non-Stick-coatings for tacky surfaces
- Optical coatings
- Protective coatings
1. Industry Trends and Motivation
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6. PlamaPlus® Coating
7. Important Results
## Important Results

<table>
<thead>
<tr>
<th>Material</th>
<th>Control MN/m²</th>
<th>Control psi</th>
<th>Plasma-Treated MN/m²</th>
<th>Plasma-Treated psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide (PMR®-15)</td>
<td>2.90</td>
<td>420</td>
<td>17.93</td>
<td>2600</td>
</tr>
<tr>
<td>Polyphenylene sulphide (Ryton® R-4)</td>
<td>2.00</td>
<td>290</td>
<td>9.38</td>
<td>1360</td>
</tr>
<tr>
<td>Polyether sulphone (Victrex® 4100G)</td>
<td>0.90</td>
<td>130</td>
<td>21.65</td>
<td>3140</td>
</tr>
<tr>
<td>Polyethylene / PTFE (Tefzel®)</td>
<td>----</td>
<td>Very Low</td>
<td>22.06</td>
<td>3200</td>
</tr>
<tr>
<td>HDPE</td>
<td>2.17</td>
<td>315</td>
<td>21.55</td>
<td>3125</td>
</tr>
<tr>
<td>LDPE</td>
<td>2.55</td>
<td>370</td>
<td>10.00</td>
<td>1450</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>2.55</td>
<td>370</td>
<td>21.24</td>
<td>3080</td>
</tr>
<tr>
<td>Polycarbonate (Lexan®)</td>
<td>2.83</td>
<td>410</td>
<td>6.40</td>
<td>928</td>
</tr>
<tr>
<td>Nylon®</td>
<td>5.86</td>
<td>850</td>
<td>27.58</td>
<td>4000</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3.93</td>
<td>570</td>
<td>27.58</td>
<td>4000</td>
</tr>
<tr>
<td>Mylar A®</td>
<td>3.65</td>
<td>530</td>
<td>11.45</td>
<td>1660</td>
</tr>
<tr>
<td>PVDF (Tedlar®)</td>
<td>1.93</td>
<td>280</td>
<td>8.96</td>
<td>1300</td>
</tr>
<tr>
<td>PTFE</td>
<td>0.52</td>
<td>75</td>
<td>5.17</td>
<td>750</td>
</tr>
</tbody>
</table>

## Test Results of Adhesive Bonded Joints

<table>
<thead>
<tr>
<th>Substrate Combination</th>
<th>Treatment</th>
<th>Joint Type</th>
<th>Bond Area (mm²)</th>
<th>Failure Mode</th>
<th>Joint Strength (Mpa)</th>
<th>Std. Dev. (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide + Titanium</td>
<td>Untreated</td>
<td>Overlap</td>
<td>312.5</td>
<td>Adhesive</td>
<td>0.23</td>
<td>0.10</td>
</tr>
<tr>
<td>Polyimide + Titanium</td>
<td>Atmospheric Plasma</td>
<td>Overlap</td>
<td>312.5</td>
<td>Cohesive</td>
<td>3.38</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Important Results

Aluminum EN6016, Thermal Cure Epoxy Adhesive

<table>
<thead>
<tr>
<th></th>
<th>before ageing</th>
<th>after 500 h salt spray test</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>AF</td>
<td>AF</td>
</tr>
<tr>
<td>plasma activation</td>
<td>AF</td>
<td>CF</td>
</tr>
<tr>
<td>plasma deposition</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lap Shear Strength [MPa]

error: ± 1 MPa
Important Results

Not only an Increase in Bond performance
But a Decrease in Variance

(Source: Kegel & Schmid 1999)
Peel test results from various pretreatments on aluminum. Urethane adhesive. Plasma treatment leads to cohesive failures. Plasma coated aluminum provides the bond line with greater protection through a 96 hour salt spray test.
Key Take-Aways

• Materials’ joining in manufacturing of lightweight, often dissimilar substrates present technical challenges.

• Surface conditioning prior to bonding dissimilar materials enables better adhesion.

• Plasma cleans surfaces by removing surface contaminants and activates surface chemistries - eliminating primers.

• Plasma stabilizes manufacturing bonding processes.

• Plasma coatings modify surfaces to provide corrosion protection, and improves or inhibits adhesion.
Thank You!
Time for Some Questions?

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