Improving the performance of UV cure coatings & adhesives on plastic substrates

Adhesives & Sealants Council 2017

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Outline of my remarks

• Motivation for the use of UV Cure materials
• Why UV materials have adhesion problems
• A coating innovation: UV powder coating
• What is plasma? How does it work?
• The UV powder coating solution
• UV cure adhesives examples
The advantages of UV Curing

- High Speed
- Low Heat
- Hard, durable, water-clear finish
- Environmentally friendly technology
Typical UV coated products
Overview of the UV curing process

- Oligomers
- Monomers
- Photoinitiators

Substrate

- Ultraviolet Radiation

Substrate

UV energy hits the photoinitiators which become excited, passing energy along to the other components. This stimulates a bonding process between molecules.

Excited components are called free radicals. Free radicals keep the reaction going.

- Oligomers
- Monomers
- Rupted Photoinitiators

When all of the components are used up, you are left with a cured or polymerized film.
UV vs. thermal chemistry comparison

(UV = Highly Cross-linked)  Conventional Coating

<table>
<thead>
<tr>
<th>Property</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight per Double Bond</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Faster Cure Speed</td>
<td>Faster</td>
<td>Slower</td>
</tr>
<tr>
<td>Lower Flexibility</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Higher Tensile Strength</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Higher Shrinkage</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Higher Chemical Resistance</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Worse Adhesion</td>
<td>worse</td>
<td>Better</td>
</tr>
</tbody>
</table>
The desired outcome is easy

Crosshatch tape testing

Strong cohesive and adhesive forces needed in bonding
Getting UV materials to stick is not easy.

Adhesion is often hard to control (Substrate, Ambient Condition, Contamination).

Sometimes requires some kind of reformulation to the chemistry, change of substrate, or more commonly surface treatment.

However there are adhesion issues.
Example: Powder Coating

- **E**conomy
- **E**xcellence of Finish
- **E**nergy Efficiency
- **E**asy to Apply
- **E**nvironmentally Friendly
Powder coated products
Thermoset Powder Thermal Profile

Temperature

Melt & Flow

Cure

Build

Hold

375 °F

15-60 Minutes

Time
## Typical Powder Thermal Profile

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Standard Cure</th>
<th>Low Temp. Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>20’ @ 350°F</td>
<td>25’ @ 235°F</td>
</tr>
<tr>
<td>Epoxy Polyester</td>
<td>20’ @ 375°F</td>
<td>25’ @ 250°F</td>
</tr>
<tr>
<td>Polyester</td>
<td>20’ @ 375°F</td>
<td>25’ @ 275°F</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>20’ @ 390°F</td>
<td>25’ @ 295°F</td>
</tr>
<tr>
<td>Acrylic</td>
<td>25’ @ 350°F</td>
<td>30’ @ 250°F</td>
</tr>
<tr>
<td>Silicone</td>
<td>25’ @ 420°C</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Problem: Plastic Deflection Temp.

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Deflection Temperature at 0.46 MPa (°C)</th>
<th>Deflection Temperature at 1.8 MPa (°C)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>98</td>
<td>88</td>
<td>-</td>
</tr>
<tr>
<td>ABS + 30% Glass Fiber</td>
<td>150</td>
<td>145</td>
<td>-</td>
</tr>
<tr>
<td>Acetal Copolymer</td>
<td>160</td>
<td>110</td>
<td>200</td>
</tr>
<tr>
<td>Acetal Copolymer + 30% Glass Fiber</td>
<td>200</td>
<td>190</td>
<td>200</td>
</tr>
<tr>
<td>Acrylic</td>
<td>95</td>
<td>85</td>
<td>130</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>160</td>
<td>60</td>
<td>220</td>
</tr>
<tr>
<td>Nylon 6 + 30% Glass Fiber</td>
<td>220</td>
<td>200</td>
<td>220</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>140</td>
<td>130</td>
<td>-</td>
</tr>
<tr>
<td>Polyethylene, HDPE</td>
<td>85</td>
<td>60</td>
<td>130</td>
</tr>
<tr>
<td>Polyethylene Terephthalate (PET)</td>
<td>70</td>
<td>65</td>
<td>250</td>
</tr>
<tr>
<td>PET + 30% Glass Fiber</td>
<td>250</td>
<td>230</td>
<td>250</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>100</td>
<td>70</td>
<td>160</td>
</tr>
<tr>
<td>Polypropylene + 30% Glass Fiber</td>
<td>170</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>95</td>
<td>85</td>
<td>-</td>
</tr>
</tbody>
</table>
Possible Thermal Solutions

- Use a higher temperature plastic
- Use a lower temperature powder
- Use UV curing
The UV Powder Coating Process

1. **Powder Application**
2. **Apply Heat to Melt Powder**
3. **Powder Flow/Leveling**
4. **Exposure to UV for Polymerization**
UV Powder Temperature Profile

Temperature

Melt/Flow Stage

Exposure to UV

Time
UV Powder Coatings

A highly desirable technology:

- Excellent Surface Properties
- Low Heat/High Speed Processing
- No Waste
- Heat Sensitive Substrates

Thermoset UV Cure

400°F
200°F
A Flashback…

In 1998 Baldor Electric Motor began UV powder coating pre-assembled electric motors.
The Needs for Surface Preparation

- **STATIC REMOVAL**: Static attracts dust and similar contaminants which interfere with surface processes.

- **CLEANING**: All surfaces, no matter how clean they seem, have *surface contaminants* that interfere with bonding and coating applications.

- **ACTIVATION**: Advanced engineering polymers tend to be chemically inert – with few or no *functional groups* on which to bond.

- **PASSIVATION**: Metals are prone to oxidation and require treatment to retard the oxidation process.
## Plastics with Low Surface Energy

### Table 1. Plastic Surface Energy vs. Energy Required for Adhesion

<table>
<thead>
<tr>
<th>Surface Energy of Common Plastics:</th>
<th>Approximate Surface Energy Needed for adhesion with:</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE &lt; 20 mN/m</td>
<td>Waterborne Coatings 50-56</td>
</tr>
<tr>
<td>PP 30</td>
<td>Solvent Coatings 46-52</td>
</tr>
<tr>
<td>PE 32</td>
<td>UV Coatings 54-60</td>
</tr>
<tr>
<td>PS 34</td>
<td></td>
</tr>
<tr>
<td>PC 34</td>
<td></td>
</tr>
<tr>
<td>ABS 34</td>
<td></td>
</tr>
<tr>
<td>PUR 34</td>
<td></td>
</tr>
</tbody>
</table>

Note: Water Surface Energy 72 mN/m (dyne)
The Challenges of Solvents

Solvents
(Routes of Exposure: Absorption, Ingestion, Injection, Inhalation)

Properties
- Dissolving Power
  - Viscosity
  - Evaporation rates
  - Color
  - Odor
  - Toxicity
  - Flammability
  - Environmental Impact

Molecular Forces
- Van der Waals Forces
- Dispersion Forces
- Polar Forces
- Hydrogen Bonding Forces

Affects on Human Health
Factors
- Dose
- Potency
- Route of Exposure

Symptoms
Including but not limited to:
- Damage to the nervous system, reproductive system, respiratory system, liver, and kidneys
- Could lead to cancer, dermatitis, and death

Courtesy Texas A&M University
Plasma Surface Treatment

- **What is plasma?**
  - How is plasma generated and applied

- **Functions of plasma treatment**
  - Cleaning of glass, plastics, metals, ceramics
  - Activation of Plastics (Polyolefins, etc) and Hybrids (GFRP)
  - Functionalization of ceran and galvanized steel
Naturally Occurring Plasmas

Low Pressure (vacuum)  Atmospheric Pressure
Man-made Plasma

Photo: Safe, Cost-Effective, Environmentally Friendly Man-Made Plasma
The Plasma Treatment Process

- Substrate
- Inner Electrode
- Ring Electrode (SS casing)
- Discharge Chamber
- Plasma Beam
- Ionization Gas
- Inner Electrode
- High voltage Current
- Ring Electrode (SS casing)

Image of plasma treatment process.
Plasma Surface Treatment

Surface Contamination
- Organic layers (Additives, waxes, grease.....)
Polymer
- UV varnish
- OPP, PE, PET, Acetate.....

Cleaning effect

Attack surface contamination
Plasma Surface Treatment

Cleaning effect

Remove surface contamination

Surface contamination

Polymer Substrate
OPP, PE, PET, Acetate, UV varnish
Plasma Surface Treatment

Form functional sites

Carbonyl Groups

Hydroxyl Groups

Polymer Substrate
OPP, PE, PET, Acetate....

UV varnish

Stable wetting
Plasma Surface Treatment

Topological Modification (AFM Study of PET [1 \( \mu m \)])

Courtesy: Fraunhofer Institute for Processing Technology and Materials Research
Plasma Surface Treatment

Atmospheric Pressure Plasma Process - Activation

PP: untreated (surface free energy: 27.0 mN/m)  PP: Openair™ Plasma treated (surface free energy: up to 72 mN/m)
Surface Energy of Polypropylene
After Plasma Treatment

Plasma Surface Treatment

- 60-80
- 40-60
- 20-40
- 0-20

Speed [m/min]

Gap [mm]

mN/m
Plasma flexibility

Flexibility for many applications

A wide selection of standard and custom jets adapt to a wide range of part shapes and sizes.
Atmospheric plasma generators are easy to install and integrate with simple connections.
UV Powder / Plasma Process

Powder Coating on Automotive Plastic!

- Plasma Cleaning & Activation
- Conductive Agent
- Powder Application
- Heat (IR or Convection)
- UV Cure
Objective: To compare adhesion results of several powder coated plastics when untreated and treated with plasma.

Powder Coating: PCRG 002-36-113 UV Curable powder

Substrates:
- PT Natural (proprietary formulation)
- Nylon
- Polypropylene
- ABS
- PC/ABS
Plasma results

Source: Powder Coating Research Group
Plasma results

Source: Powder Coating Research Group
Plasma results

Source: Powder Coating Research Group
Plasma results

Source: Powder Coating Research Group
Plasma results

Source: Powder Coating Research Group
Plasma results

Source: Powder Coating Research Group
### Plasma results summary

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Rating without Openair® Plasma</th>
<th>Rating with Openair® Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT Natural</td>
<td>0B</td>
<td>4B</td>
</tr>
<tr>
<td>Nylon</td>
<td>0B</td>
<td>0B</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0B</td>
<td>3B</td>
</tr>
<tr>
<td>ABS</td>
<td>0B</td>
<td>4B</td>
</tr>
<tr>
<td>PC/ABS</td>
<td>4B</td>
<td>4B</td>
</tr>
</tbody>
</table>

Cross Hatch Test Criteria: ASTM D3359 02 “0B – 5B)
The environmental benefits of atmospheric plasma are a good fit for UV technology

• Elimination of high VOC content primers or adhesive promoters – replace these with environmentally safe plasma

• Low power consumption

• No ozone generation

• No pollutants
Plasma results on adhesives

- Not only an increase in bond performance

(Source: Kegel & Schmid 1999)
Without Plasma  With Plasma

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

Plasma results on adhesives

(Source: Kegel & Schmid 1999)
Plasma results on adhesives

Plasma results on adhesives

2-part epoxy system:
Curing: 175° F, 2 hours
UV cure: shear strength

PBT/PET Blend Substrate

Compression shear strength (MPa)

Initial value

2 w 85°C/85% humidity

2 w 40°C/100% humidity

Degreased
Atmospheric plasma
Polyamide with Cationic Bonding

CATIONIC BONDING PROCESS

Compression shear strength [MPa]

- **KB554**
  - Initial value cleaned
  - Initial value APP
  - 14 d 40 °C / 95 % cleaned
  - 14 d 40 °C / 95 % APP

- **45952**
  - Initial value cleaned
  - Initial value APP
  - 14 d 40 °C / 95 % cleaned
  - 14 d 40 °C / 95 % APP
Polyamide free-radical curing

Compression shear strength [MPa]

- **4494**
  - Initial value cleaned
  - Initial value APP
  - 14 d 40 °C / 95 % cleaned
  - 14 d 40 °C / 95 % APP

- **AD494**
  - Initial value cleaned
  - Initial value APP
  - 14 d 40 °C / 95 % cleaned
  - 14 d 40 °C / 95 % APP
Summary of take-aways

• UV offers attractive benefits to manufacturer (e.g., low heat, fast cure, tough surfaces)

• However, UV also presents greater challenges to adhesion due to the highly crosslinked chemistry

• Plasma has been shown to improve UV coating adhesion even on UV powder coatings

• Plasma improves UV adhesive bond performance.
THANK YOU FOR YOUR ATTENTION!

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