1. Reasons for coating plastics

- To improve resistance to
  - U.V., solvents, abrasion, T,
- To obtain optical properties
  - gloss, colour and shade
  - Special effect (e.g. metallic)
  - Multi-coloured decoration
- To improve surface quality
  - To fill pits, voids, porosity, touch up damaged areas
- To modify electrical properties
2. Why are polymers difficult to coat?

- Chemical inertness / solvent sensitivity
- Presence contaminants: antioxidants, plasticizers, antistatics, mould release agents
- Temperature sensitivity
- Low surface tension/energy means poor adhesion thus weak ability to interact with surrounding medium

main problem
more pronounced with waterborne paints

3. Painting of plastics

- good coating adhesion = good wetting + interaction
- wetting is related to relative $\gamma_l$ and $\gamma_s$ - measured by $T_{water}$

A LIQUID WETTING A SOLID SURFACE

<table>
<thead>
<tr>
<th>Wetting</th>
<th>poor wetting</th>
<th>intermediate angle</th>
<th>good wetting</th>
<th>complete wetting</th>
</tr>
</thead>
<tbody>
<tr>
<td>$180^\circ$</td>
<td>$&gt;135^\circ$</td>
<td>$90^\circ$</td>
<td>$&lt;45^\circ$</td>
<td>$0^\circ$</td>
</tr>
</tbody>
</table>

- creating functional groups to react with the paint
4. Surface treatments

- Change chemical composition to promote coating adhesion (presence of surface functional groups or hetero-atoms)
- Modify the crystalline morphology and surface topography
- Remove contaminants and weak boundary layers
- To render plastics conducting for electrostatic spraying
- To create a new surface, but the bulk properties of the material must be preserved delaminating risks.
- Each method (dry or wet) permits to bring one or more types of modifications to a surface
  \[ \Rightarrow \text{new properties (roughness, oxidation, wetting)} \]

A. Acid etching

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Treatment</th>
<th>( \perp ) (MPa) 2-K PUR</th>
<th>IR spectroscopy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Conc. ( \text{H}_2\text{SO}_4 )</td>
<td>60 min/70°C</td>
<td>2.3</td>
<td>1030, 1150 -SO(_3)H</td>
</tr>
<tr>
<td>( \text{K}_2\text{Cr}_2\text{O}_7 ) 7g</td>
<td>60 min/70°C</td>
<td>7.2</td>
<td>1720, 3500 C=O, -C-O-H</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 ) 150g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) 12g</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Efficiency proportional to:
  - duration of the treatment
  - chemical nature of substrate
- Smooth hydrophobic surface © rough hydrophilic surface by dissolution of amorphous region and oxidation
- Large-scale use of chromic acid is undesirable \( \text{N} \)
SEM of non-treated PP (homopolymer)

SEM of PP (homopolymer) after acid etching (2h/80°C)
SEM of a copolymer PP/PE after acid etching (2h/80°C)

B. Treatment with solvents

- Immersion in trichloroethylene (80°C / 60 sec : Homo PP)
- Roughness but no oxidation
- Environmental consideration:
  An aqueous system would be preferable to one employing organic, particularly chlorinated, solvents
C. Treatment of fluorinated polymers

- PTFE, FEP, PCTFE: strong chemical resistance, very low surface tension

  ⇒ very aggressive methods
- Treatment with Na in liquid NH₃, metallic Na or ….

<table>
<thead>
<tr>
<th>Solution</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>1 L</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>128 g</td>
</tr>
<tr>
<td>Na</td>
<td>23 g</td>
</tr>
</tbody>
</table>

  1’ up to 10’

- Very dangerous mixture because reacts violently with water
- C-F + Na ⇒ -C-OH + C=O + C=C + NaF
- FEP: T_{water} = 109 ° 52
D. Adhesion promoters

- Creation of a layer at the interface between coating and substrate: chemical structure of the primer is intermediate between those of the coating and of the substrate
- Chemical groups are moving toward coating or substrate according to their affinity: binding (diffusion)
- Always in diluted solutions: thin layers (2-3 µm)

- Before: solventborne chlorinated polyolefins
- Now: chlorinated polyolefins, *emulsified in water*
- Now also: waterborne N-CPO (non-chlorinated polyolefin)

- Priming of automotive bumpers
E. Flame treatment

- Surface is exposed to an oxidising flame: 1100–3200°C
- Parameters affecting surface treatment:
  - Air to gas ratio (excess of air): is the most critical variable
  - Distance: influence on T° and on oxido/reodox property flame
  - Uniformity with which flame will contact the area to be treated
  - Contact time < 1 sec: speed of processing: 20 m/min
  - Heat of combustion (amount of heat delivered by the burner)
  - Burner has to match the shape of the part to be treated

- Oxidation ⇒ C=O (infrared spectroscopy)
- Depth 40 to 90Å
- Hot air gun: 500 to 600°C; improved safety

- Applications: Massive pieces; bumpers (car industry)

SEM of a copolymer PP/PE after flame treatment
F. Corona Discharge Treatment (CDT)

- To improve bondability and printability of polyolefin films.
- Occurs in the gap between 2 electrodes distant of a few mm: one at 20kV and 10 to 20 kHz; the other is earthed.
- Active (air, O₂) or inert (N₂, Ar, He) gases in the gap are ionised.

- \[ R^* + O_2 \rightarrow R-O_2^* \rightarrow R-O_2H \]

- Thickness: a few nm
- In semi-crystalline materials, only amorphous regions are affected

SEM of PP (homopolymer) after Corona treatment
ASTM D5175

?? Type of failure

adhesive

cohesive

SEM of PP (CDT treated) coated with Pergut after adhesion test
G. Cold Plasma

- Produced by electrical discharges in gases ⇒ partial or total ionization of the gas
- The low density of excited species balances the high T° of these species. Total energetic level is low ⇒ low overheating
- Excited species: atoms, molecules, ions, radicals, e^-, hν
- Thickness of treatment < 100 A° (< 0.01 µm)
- Reactors - a few cm^3 to several m^3
- Drawbacks - treatment under vacuum
- GHz: less deep vacuum ⇒ processing time
- Advantages - treatment in bulk, pipes, complex shapes
- no emission of solvents
- specific and controlled modification

1. Creating a hydrophilic surface
   - Use of “Oxidising gases”: O₂, Ar, N₂, CO₂, He, air, NH₃:
     - Free radicals are formed during the plasma discharge
     - Recombine among themselves (inter/intramolecular)
     - Recombine with O₂ during or after discharge (atmos p)
     - Oxidation of the surface even with Ar, He, NH₃!
       → with O₂: C-O, C=O, O-C=O
       → but with N₂: C-N (amine) and C=N (imine) but also oxidized functions

2. Creating a hydrophobic surface
   - Use of “passivating gases”: CF₄, SF₆ (allow to graft F atoms)
     - CF, CF₂, CF₃ are detected by XPS: surface energy

⇒ versatile method
## Plasma treatment of PP

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Θ&lt;sub&gt;water&lt;/sub&gt; (deg)</th>
<th>Adhesion (MPa)</th>
<th>Antiadhesion test (ng/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>97</td>
<td>0</td>
<td>1720</td>
</tr>
<tr>
<td>O₂</td>
<td>20</td>
<td>26.5</td>
<td>-</td>
</tr>
<tr>
<td>CF₄</td>
<td>130</td>
<td>-</td>
<td>48</td>
</tr>
</tbody>
</table>

SEM of PP after plasma treatment
SEM of PP (plasma treated), coated with PUR after adhesion test

ECOPO

- Research program in collaboration with FUNDP & UMH
- To degrease, activate & polymerize with cold plasma
- To increase protective properties (automotive & aeronautic)

Results

Degreasing: $T_{\text{water}}: 70 \rightarrow 0$ deg & $\% C: 18.3 \rightarrow 0$

Polymerization
H. Laser

✦ thermal effect
  - paint removal

✦ photochemical effect
  - activation of the surface

I. Other treatments

- Mechanical treatment
- Ion and electron-beam modification
- UV
- Plasma polymerisation
5. General comments

A) Treatment efficiency

<table>
<thead>
<tr>
<th></th>
<th>None</th>
<th>Plasma O₂</th>
<th>Corona</th>
<th>Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>87</td>
<td>22</td>
<td>35</td>
<td>60</td>
</tr>
<tr>
<td>PVC</td>
<td>90</td>
<td>35</td>
<td>35</td>
<td>79</td>
</tr>
<tr>
<td>Silicone</td>
<td>99</td>
<td>17</td>
<td>35</td>
<td>76</td>
</tr>
</tbody>
</table>

B) Change of wettability with time

<table>
<thead>
<tr>
<th></th>
<th>Flame</th>
<th>Plasma O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>t = 0 (non treated)</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>t = 1d</td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>t = 10d</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>t = 20d</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>t = 30d</td>
<td>65</td>
<td>50</td>
</tr>
</tbody>
</table>
C) Influence of storage conditions

<table>
<thead>
<tr>
<th>Plasma Fluorinated PMMA (θ_{water})</th>
<th>Dry</th>
<th>RH = 80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>t = 0</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>t = 2h</td>
<td>105</td>
<td>20 to 60</td>
</tr>
<tr>
<td>t = 24h</td>
<td>105</td>
<td>0 to 40</td>
</tr>
<tr>
<td>t = 7d</td>
<td>105</td>
<td>20</td>
</tr>
</tbody>
</table>

6. Conclusions

- It has been stressed that, after certain treatments and storage conditions, polymer surfaces reorient and restructure in response to their environment in order to minimise the interfacial free energy.

- Needless to say that each plastic paint application requires full test procedure of pre-treatment, primer/base and top coat system. Kind of plastic, moulding process, pre-treatment, base and top coat system, curing conditions and other parameters have strong influence on the final adhesion strength.
The end!

Questions?

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