The Flame Treatment of Injection Moulded Polypropylene: New Insights on an Established Process

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Flame Treatment Used for Many Years
X-ray photoelectron spectroscopy showed that a normal flame treatment level of oxidation in low-density polyethylene, 0.02% of the antioxidant butyl-p-cresol did not reduce the degree of oxidation or the level of ad to the extrusion of low-density polyethylene. It is estimated that the is between 40 and 90 Å which is much less than for a moderate chrom or with extrusion. There were no significant changes in the XP-spectra of flame treated samples after 12 months.
Effect of flame treatment on formulated polyvinylchloride surface: A study using ARXPS

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ABSTRACT

Industrial PVC samples have been flame treated in order to improve their surface properties for adhesion. Using a novel procedure to avoid X-ray damage, as-received and treated PVC were analysed by angle resolved X-ray photoelectron spectroscopy (ARXPS) to assess the effect of the flame treatment. An increase of wettability was obtained and tested using dye inks showing that the flame treatment has an effect on the surface. In terms of chemistry, it was found that a reduction of the covalent chlorine to chloride is observed while a decrease of carbon and increase of oxygen concentrations are the other main effects. ARXPS shows that the chloride species appear to segregate to deeper layers than the immediate surface intimating that the difference in wettability may have been obtained by eliminating already pre-existent surface contamination.
Automotive Flame Treatment

The Surface Analysis Laboratory

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Outline of Presentation

• Flame Treatment
• Industrial Examples
• Methods and Materials
• XPS Surface Composition as Function of Treatment Parameters and Sample Type
• Valence Band Studies
• Treatment Layer Thickness
• ToF-SIMS: Oxygen Functionalisation
• ToF-SIMS: Additives
• Conclusions
Flame treatment

- Increases the surface energy
- Ablative cleaning
- Improved adhesion

Active region

Main reaction zone

The Aerogen Company (2013)
Industrial Examples of Flame Treatment
## Polypropylene

### Designation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Filled with carbon Black</td>
<td></td>
</tr>
<tr>
<td>A homopolymer with no additional filler</td>
<td>A</td>
</tr>
<tr>
<td>A homopolymer with 40% talc</td>
<td>B</td>
</tr>
<tr>
<td>A copolymer with 20% talc</td>
<td>C</td>
</tr>
<tr>
<td>A polymer with 20% long glass fibre</td>
<td>D</td>
</tr>
</tbody>
</table>

**NB** Plus unknown processing aids

---

1 dyn cm\(^{-1}\) = 1 mN m\(^{-1}\)

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<table>
<thead>
<tr>
<th>DESIGNATION</th>
<th>POLYMER DESCRIPTION</th>
<th>TYPICAL USE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A:</td>
<td>Super high impact polypropylene copolymer</td>
<td>Bumpers</td>
</tr>
<tr>
<td>Sample B:</td>
<td>40 % talc-filled polypropylene homopolymer</td>
<td>Under the hood (fan shrouds)</td>
</tr>
<tr>
<td>Sample C:</td>
<td>20 % talc-filled polypropylene homopolymer</td>
<td>Under the hood (fan shrouds)</td>
</tr>
<tr>
<td>Sample D:</td>
<td>20 % long glass filled polypropylene copolymer</td>
<td>Various (e.g. instrument panel carriers)</td>
</tr>
</tbody>
</table>
Flame Treatment Conditions

- Equivalence ratio = 0.93
  (stoichiometric amounts =1, so slightly oxygen rich)
- Natural gas and filtered compressed air mixed in a venturi 5 m upstream of burner
- Burner PP gap = 100 mm (18 – 200 mm range)
- Conveyor speed = 1 ms⁻¹
- Dwell time in flame = 0.02 s
- Multiple passes; 90 s recovery allowed between passes
- PP injection moulded plaques 3 mm thick
- Dyne pens immediately after flaming then wrapped in Al foil
Instrumentation Used
XPS/Cluster Profiling

X-ray photoelectron spectroscopy performed using the Thermo Scientific K-Alpha system

- Monochromated X-ray source
- Fully automated acquisition

**MAGCIS** (monatomic and gas cluster ion source) used to produce craters

- Ar Cluster size up to 2000 atoms
- Ion energy = 2 - 8 keV

Monatomic Ar ion beam
Parameters Investigated

Parameters
• Burner to substrate distance
• Equivalence ratio $= \phi$
• Dwell time

\[
\phi = \frac{m_{\text{fuel}}/m_{\text{oxidiser}}}{(m_{\text{fuel}}/m_{\text{oxidiser}})_{\text{stoich}}}
\]

Effects
• Depth of treatment
• Ablation of surface material
• Ageing
• Chemical changes
• Topography changes
• Surface energy changes
Example XPS Spectra

XPS spectra for Sample A untreated (lower) and treated (upper).
## Surface Composition vs Contact Angle

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Surface Composition</th>
<th>Water Contact Angle (°)</th>
<th>Dyne Ink (mN m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic %</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>Oxygen</td>
<td>Sulphur</td>
</tr>
<tr>
<td>A</td>
<td>100.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>96.8</td>
<td>2.9</td>
<td>0.3</td>
</tr>
<tr>
<td>C</td>
<td>98.5</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>D</td>
<td>100.0</td>
<td>0</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Influence of Dwell Time

Sample A
# Effect of Multiple Passes on Surface Properties

<table>
<thead>
<tr>
<th>Specimen</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>N</th>
<th>O/C ratio</th>
<th>Contact angle</th>
<th>Dyne ink level</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>98</td>
<td>30</td>
</tr>
<tr>
<td>1 pass</td>
<td>89.6</td>
<td>10.0</td>
<td>0.4</td>
<td>0.0</td>
<td>0.11</td>
<td>70</td>
<td>52</td>
</tr>
<tr>
<td>2 passes</td>
<td>89.3</td>
<td>10.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.12</td>
<td>66</td>
<td>56</td>
</tr>
<tr>
<td>3 passes</td>
<td>85.1</td>
<td>14.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.18</td>
<td>62</td>
<td>56</td>
</tr>
<tr>
<td>5 passes</td>
<td>83.9</td>
<td>16.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.19</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>7 passes</td>
<td>83.1</td>
<td>16.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.20</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Sample B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>96.8</td>
<td>2.9</td>
<td>0.3</td>
<td>0.0</td>
<td>0.03</td>
<td>104</td>
<td>&lt;30</td>
</tr>
<tr>
<td>1 pass</td>
<td>88.2</td>
<td>11.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.13</td>
<td>65</td>
<td>56</td>
</tr>
<tr>
<td>2 passes</td>
<td>82.4</td>
<td>14.8</td>
<td>1.2</td>
<td>0.8</td>
<td>0.18</td>
<td>68</td>
<td>52</td>
</tr>
<tr>
<td>3 passes</td>
<td>78.9</td>
<td>17.6</td>
<td>2.4</td>
<td>1.1</td>
<td>0.22</td>
<td>63</td>
<td>52</td>
</tr>
<tr>
<td><strong>Sample C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>98.5</td>
<td>1.1</td>
<td>0.4</td>
<td>0.0</td>
<td>0.01</td>
<td>103</td>
<td>&lt;30</td>
</tr>
<tr>
<td>1 pass</td>
<td>84.6</td>
<td>15.0</td>
<td>0.4</td>
<td>0.0</td>
<td>0.18</td>
<td>70</td>
<td>52</td>
</tr>
<tr>
<td>2 passes</td>
<td>90.9</td>
<td>7.4</td>
<td>1.7</td>
<td>0.0</td>
<td>0.08</td>
<td>72</td>
<td>52</td>
</tr>
<tr>
<td>3 passes</td>
<td>81.3</td>
<td>15.7</td>
<td>1.7</td>
<td>1.3</td>
<td>0.19</td>
<td>65</td>
<td>56</td>
</tr>
<tr>
<td><strong>Sample D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>99</td>
<td>32</td>
</tr>
<tr>
<td>1 pass</td>
<td>93.8</td>
<td>6.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.07</td>
<td>72</td>
<td>56</td>
</tr>
<tr>
<td>2 passes</td>
<td>91.6</td>
<td>8.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.09</td>
<td>73</td>
<td>56</td>
</tr>
<tr>
<td>3 passes</td>
<td>91.2</td>
<td>8.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.10</td>
<td>67</td>
<td>56</td>
</tr>
</tbody>
</table>
Ageing Test

Water Contact angle (Degrees)

O/C Ratio

Sample C
Sample B
Sample A
Sample D
Valence Band: Sample A

Valence band spectra for Sample A
untreated
treated with 1 pass
treated with 2 passes
treated with 3 passes

Briggs (1979)
Mono XPS Valence Band
Analysis on a Thermo Scientific K-Alpha using large cluster ions to etch (Ar_{1000}). Depth calculation using estimate from data of Cumpson et al (in press).
ToF-SIMS Identification of Oxygenation: Sample C

### Treated

### Untreated
8 passes
6 passes
3 passes
2 passes
1 pass
Untreated:
Sample A
## Additives: ToF-SIMS Spectra

<table>
<thead>
<tr>
<th>Additive</th>
<th>Chemical structure</th>
<th>Characteristic peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Bis-steramide</td>
<td><img src="ethylene_bis_steramide.png" alt="Chemical structure" /></td>
<td>282, 310</td>
</tr>
<tr>
<td>Irganox™ 1010</td>
<td><img src="irganox_1010.png" alt="Chemical structure" /></td>
<td>57, 203, 219, 259</td>
</tr>
</tbody>
</table>
Ablation of Additives: Sample A

**Ethylene Bis-steramide**

- Untreated
- Treated

**Irganox™ 1010**

- Untreated
- Treated
Conclusions

• Flame treatment can bring about three possible processes:
  - Removal of low molecular weight hydrocarbon
  - Removal of surface segregated processing aids etc
  - Oxygenation of PP

• Increase of surface energy

• Level of treatment is most sensitive to equivalence ratio

• Depth of treatment ≈ 15 nm

• Oxygenation of the methyl pendant group.