Flame Treatment of Polypropylene: A Study by Electron and Ion Spectroscopies

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*Aerogen
FLAME TREATMENT SPECIALIST

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Flame Treatment Used for Many Years
X-ray photoelectron spectroscopy studies of polymer surfaces

Part 3 Flame treatment of polyethylene

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X-ray photoelectron spectroscopy showed that a normal flame treatm
level of oxidation in low-density polyethylene, 0.02% of the antioxidants
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 c
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.

Flame surface modification of polypropylene film

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Abstract—Contact-angle measurements, the ASTM standard wetting test for polyolefin films, and X-ray
photoelectron spectroscopy (XPS or ESCA) were used to characterize flame-treated polypropylene
(PP) films. Two combustion models, STANJAN and PREMIX, were then used to determine the chemical
and physical properties of the flames used to treat the PP films. Both the flame equivalence ratio and
the position of the PP film in the flame are important variables in determining the extent of oxidation
and improvement in wettabiliy obtained by flame treating. The optimal equivalence ratio for the flame
treatment of PP is 0.93, while the optimal luminous flame-to-film distance is 0–2 mm. Modeling of
the combustion processes occurring in the flame provides evidence that the extent of treatment correlates
closely with the concentrations of H, O, and OH radicals present in the flame. The extent of surface
modification of the flame-treated PP does not appear to correlate with either the flame temperature or
the concentration of oxygen molecules. The mechanism of surface oxidation by flame treatment probably
involves polymer radical formation by O and OH, followed by rapid reaction of the polymer radicals
with O, OH, and O₂.

Keywords: Surface modification; polymer surfaces; flame; combustion; polypropylene.
Automotive Flame Treatment

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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
Flame treatment

Aerogen flame treatment automotive movie 28 05 12.mp4(360p_H264-AAC).mp4
Polypropylene

Automotive Grade PP

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Filled with carbon Black</td>
<td>A homopolymer with no additional filler</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

\[1 \text{ dyn cm}^{-1} = 1 \text{ mN m}^{-1}\]
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 18-200 mm (Optimum 100 mm)
- Conveyor speed = 1 ms\(^{-1}\) (double pass)
- 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

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Parameters Investigated

Parameters

- Burner to substrate distance
- Equivalence ratio $\equiv \Phi$
- 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).
As Received PP Samples
## Surface Composition vs Contact Angle

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Surface Composition</th>
<th>O/C ratio</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>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>Oxygen</td>
<td>Sulphur</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>100.0</td>
<td>0</td>
<td>0.00</td>
<td>98</td>
</tr>
<tr>
<td>B</td>
<td>96.8</td>
<td>2.9</td>
<td>0.3</td>
<td>104</td>
</tr>
<tr>
<td>C</td>
<td>98.5</td>
<td>1.1</td>
<td>0.4</td>
<td>103</td>
</tr>
<tr>
<td>D</td>
<td>100.0</td>
<td>0</td>
<td>0.00</td>
<td>99</td>
</tr>
</tbody>
</table>
Influence of Dwell Time
# 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>
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<tr>
<td>1</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</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</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>
</tbody>
</table>
Dwell Time
(Passes Through Flame)

• Increased by using more passes
1, 2 and 3 passes used (0.02, 0.04 and 0.06s respectively)

O/C Ratio

Contact Angle

- Sample A
- Sample B
- Sample C
- Sample D
Burner Gap

The Surface Analysis Laboratory

![Burner Gap Diagram]

- **Sample C** (diamond)
- **Sample D** (cross)
- **Sample A** (triangle)
- **Sample B** (square)

O/C ratio vs. Burner gap (mm)

Water contact angle (degrees) vs. Burner gap (mm)
Equivalence Ratio

The Surface Analysis Laboratory

Water Contact Angle (degrees)

Equivalence Ratio

- Sample A
- Sample C
- Sample B
- Sample D
Ageing Test

Water Contact angle (Degrees)

O/C Ratio

Sample C
Sample B
Sample A
Sample D
Valence Band

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

Briggs (1979)

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Mono XPS Valence Band
Depth of Treatment

- Angle Resolved XPS
- Mg-Al Source Comparison
- Depth profiling with cluster ions
Analysis on a K-Alpha using large cluster ions to etch (Ar$_{1000}$)
Depth calculation using estimate from Irganox reference.
ToF-SIMS Identification of Oxygenation

C₃H₅O

C₄H₉
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Mass / u

8 passes
6 passes
3 passes
2 passes
1 pass

Untreated

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Variation with Treatment

C_5H_9

C_4H_5O

C_3HO_2
### 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="image1.png" alt="Chemical structure" /></td>
<td>282, 310</td>
</tr>
<tr>
<td>Irganox™ 1010</td>
<td><img src="image2.png" alt="Chemical structure" /></td>
<td>57, 203, 219, 259</td>
</tr>
</tbody>
</table>
Ablation of Additives

**Ethylene Bis-steramide**

- $C_{18}H_{36}NO$
- $C_{20}H_{40}NO$

**Irganox™ 1010**

- $C_{15}H_{23}O$
- $C_{25}H_{38}O$

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Conclusions

• Increase of surface energy
• Level of treatment is most sensitive to equivalence ratio
• Depth of treatment ≈ 20nm
• Ablation of detected additives
• Reduction of the methyl pendant group.