Nano-Engineered Additives for Active Coatings

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Content approved for public release (JUN 2007)
Development of self-segregating additives for polymer systems

Underlying Concepts

Model Systems

Implementation

Approved for Public Release (JUN 2007)
Changing threats dictate new approaches to asset protection

Reduce Asset Susceptibility to Non-Conventional Attacks

VS.

C. albicans
Staph
E. coli
Critical performance characteristics

• Topcoats are complex multirole formulated systems
  – Camouflage
  – Corrosion protection
  – Low sorption
  – Materials limitations
  – Cost effective
• Approaches for surface modification
  – Plasma treatment
  – Self-assembly
  – Additive incorporation
Self-Directing Materials

Asymmetric response desired to maximize additive impact

Self-segregating materials address several issues

- Decreased additive requirement
- Minimizes mass transport issues
- Minimizes diffusion limitations
- Minimal impact on base coating
Hyperbranched polymers provide readily available scaffolds for the preparation of polymer additives.

Desired characteristics
- Low chain entanglements
- High solubility
- Large number of reactive sites
Surface transport was demonstrated for polyoxometalates, mild oxidation catalysts.

- HBP-POM complex demonstrates migration, ~10 fold increase in surface concentration

<table>
<thead>
<tr>
<th>Polymer</th>
<th>90° TOA- Atomic Comp.</th>
<th>30° TOA- Atomic Comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>F</td>
</tr>
<tr>
<td>POM + TPU</td>
<td>79.32</td>
<td>-</td>
</tr>
<tr>
<td>TPU + HBP 6-H⁺</td>
<td>64.28</td>
<td>13.52</td>
</tr>
<tr>
<td>I</td>
<td>61.61</td>
<td>10.31</td>
</tr>
<tr>
<td>II</td>
<td>61.65</td>
<td>14.51</td>
</tr>
<tr>
<td>III</td>
<td>62.11</td>
<td>16.56</td>
</tr>
<tr>
<td>IV</td>
<td>63.33</td>
<td>11.39</td>
</tr>
<tr>
<td>V</td>
<td>63.80</td>
<td>12.03</td>
</tr>
<tr>
<td>VI</td>
<td>63.61</td>
<td>13.49</td>
</tr>
</tbody>
</table>

Soluble complex when protonated

H₅PV₂Mo₁₀O₄₀
Visualization of depth profile was accomplished with RBS, confirming enhancement of base polymer POM + TPUPOM-HBP + TPU. RBS results correlate with XPS results, showing ~11 fold increase in surface concentration of metal catalyst sites.
Alternate Surface Materials

- Silver is good candidate
  - Forms bonds readily; S-Ag or N-Ag good covalent, ligand interactions
  - Known antimicrobial activity
  - Available as nanoparticle (NP), ion, or inorganic-supported particles
- Heavy element allows use of XPS or RBS

YahooNews, 08/19/2005

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Sharp band of Ag enrichment indicates efficient surface migration

- Limited Oleylamine transport
- PEI-HBP-AgNP yields thick layer, tapering conc. profile; ca. 2% Ag by RBS
- PE-HBP-AgNP yields sharp layer, ~2nm in depth, large depletion zone, RBS indicates ca 10% Ag in thin slice
- Ag layer thinner than resolution of instrument

**Graph:**

- TPU + Oleylamine-NP
- TPU + PEI-NP (N-Ag)
- TPU + PE-NP (S-Ag)

**Diagram:**

- Thiol detected
- Silver signal only
Ag uptake at surface scales with strength of Ag-X bond formed, delivery by Ag-protein complex.

- Rinsing removes 99+% of Ag
- Ag-protein complex delivery
- Note intensity of RBS signal correlates to bond strength: Ag-S > Ag-N > physisorption
- Trend reverses in hexane delivery solvent
Expanded palette of functional groups/active sites are being investigated, shortfall from commercial sources

- AgNP are a nice model system, but cost and long-term stability remain question marks
- Commercial options for antimicrobials and chemical decon groups are low probability solutions
  - Silver zeolites– leaching, sorption
  - Small molecule biocides– leaching, porosity
  - $M_xO_y$ nanoparticles for chemical decon (Al, Mg, Zn, Cu)– deactivation
  - $TiO_2$ particles– long term coating stability, light driven
- ARL developing library of mixed end-group additives with specific functionality
  - Quaternary ammonium salts (in conjunction with TSI, Inc.)
  - Biguanides (in conjunction with TSI, Inc.)
  - Alkanolamines
  - N-halamines, hydantoins

\[
\begin{align*}
\text{Quaternary ammonium salts:} & \quad \text{Biguanides:} \\
\begin{array}{c}
R_1^+ \quad \text{Br} \\
\text{H}_2\text{N} \quad \text{N} \quad \text{NH}_2 \\
\text{\text{NH}} \quad \text{N} \quad \text{NH} \\
\text{R} \quad \text{H} \quad \text{N} \\
\end{array} & \quad \\
\begin{array}{c}
R_1^+ \\
\text{H} \\
\text{O} \\
\text{N} \\
\text{O} \\
\end{array} & \\
\text{Cl} & \quad \\
\text{Cl} \quad \\
\end{align*}
\]
Antimicrobial activity in TPU was assayed using an array of techniques to show efficacy.

- ASTM E2180 test for hydrophobic surfaces challenged with *E. coli*, *S. aureus*, *C. albicans*, *P. aeruginosa*
- AATCC Method 100, adapted for hydrophobic surfaces challenged with *S. aureus*, *K. pneumoniae*
- Kirby-Bauer test for leaching of additives challenged with *E. coli* and *S. aureus*

<table>
<thead>
<tr>
<th>HBP</th>
<th>% Reduction <em>C. albicans</em></th>
<th>% Reduction <em>E. coli</em></th>
<th>% Reduction <em>MRSA</em></th>
<th>% Reduction <em>S. aureus</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI/Q</td>
<td>99.9999</td>
<td>99.99</td>
<td>52.51</td>
<td>99.9999</td>
</tr>
<tr>
<td>PE/Q</td>
<td>99.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI/B</td>
<td>65.99</td>
<td>99.93</td>
<td>99.9999 (2 wt%)</td>
<td>99.9999</td>
</tr>
<tr>
<td>PE</td>
<td>94.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI</td>
<td>21.80</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Increased efficacy at elevated additive levels
- Reasonable activity in TPU proxy system

- ASTM E2180 test w/ 1% additive in TPU, 24 h exposure
Transitioning technology to coating systems presents new technical barriers, performance characteristics, requirements

Additive reacts during cure, potential for anchoring additive at surface, may also influence cure kinetics and migration efficiency

Surface characteristics of coatings are of paramount importance

**Equations:**

- Solvent Evaporation: $r = \alpha C_S$
- Pigment Settling: $r = \beta \rho_p$
- HBP surface-segregation
- Pigment Settling
- R’OH
- R-NH$_2$
- N=C=O
- R
- R’OH
- H$_2$O

**Diagram:**

- Substrate
- Pigment
- HBP surface-segregation
- Solvent Evaporation
- Pigment Settling
- R’OH
- R-NH$_2$
- N=C=O
- R
- R’OH
- H$_2$O
XPS provides most direct method to ascertain surface composition of additive, monitoring fluorine.

**PUrth**  \( \text{PE-HBP + PUrth} \)

**Bulk concentration** of fluorine \(~0.3\%\), observed ca. 7\% at surface of coating.
Candidate HBP scaffolds evaluated in a range of coating systems demonstrate migration, ca. 20 – 30 fold increase

<table>
<thead>
<tr>
<th>Coating</th>
<th>HBP</th>
<th>F 1s</th>
<th>N 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurea</td>
<td>None</td>
<td>0.0</td>
<td>5.22</td>
</tr>
<tr>
<td>Polyurea</td>
<td>PEI-F-Alk</td>
<td>2.01</td>
<td>7.36</td>
</tr>
<tr>
<td>Epoxy</td>
<td>None</td>
<td>0.0</td>
<td>3.15</td>
</tr>
<tr>
<td>Epoxy</td>
<td>PE-F-Alk</td>
<td>7.18</td>
<td>3.16</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>None</td>
<td>0.0</td>
<td>4.62</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PE-F-Alk</td>
<td>9.62</td>
<td>5.80</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PEI-Alk</td>
<td>0.0</td>
<td>5.64</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PEI-F-Alk</td>
<td>0.62</td>
<td>5.14</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PEI-F-Alk-Quat</td>
<td>0.32</td>
<td>5.58</td>
</tr>
</tbody>
</table>

- Most HBP segregated to surface of coatings using PEI and PE-based additives:
  - Coating/PE bulk Fluoro conc. = 0.3 mol%
  - Coating/PEI bulk Fluoro conc. ~ 0.07 mol%
Acceptable performance of topcoat against selected qualifying tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Polyurethane</th>
<th>PUrh + PEI-F</th>
<th>PUrh + PEI-aliph.</th>
<th>PUrh + PE-F</th>
<th>PUrh + PEI-Quat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Gloss</td>
<td>1.3/1.1</td>
<td>1.2/1.1</td>
<td>1.2/0.8</td>
<td>1.2/1.0</td>
<td>1.3/1.1</td>
</tr>
<tr>
<td>DFT</td>
<td>3.1-3.6</td>
<td>3.1-3.7</td>
<td>2.1-2.9</td>
<td>2.5-2.7</td>
<td>2.7-3.7</td>
</tr>
<tr>
<td>MEK Dbl Rub</td>
<td>200+</td>
<td>200+</td>
<td>200+</td>
<td>200+</td>
<td>200+</td>
</tr>
<tr>
<td>Impact Resistance, lb-in, direct/reverse</td>
<td>40/20</td>
<td>40/20</td>
<td>40/20</td>
<td>40/20</td>
<td>40/20</td>
</tr>
<tr>
<td>Cross-cut adhesion</td>
<td>5B/5B</td>
<td>5B/5B</td>
<td>5B/5B</td>
<td>5B/5B</td>
<td>5B/5B</td>
</tr>
<tr>
<td>WET/DRY</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QUV (cyclic test) 600 h</td>
<td>Pass/no change</td>
<td>Pass/no change</td>
<td>Pass/no change</td>
<td>Pass/no change</td>
<td>Pass/no change</td>
</tr>
<tr>
<td>STB</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Flexibility/DFT</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Water Resistance</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
</tbody>
</table>
Integration into CARC coatings

- Negligible difference in appearance of coatings with and w/o HBP
  - Draw-down
  - Spray coat

- Acceptable coating properties
  - Gloss
  - Color
  - Adhesion

1 Component Polyurea CARC MIL-C-53039
2 Component Polyurethane CARC MIL-DTL-64159
2 Component Epoxy CARC MIL-P-53022
HBPs incorporated into reactive coatings exhibit variable activity, improved at 2% loading

<table>
<thead>
<tr>
<th>CARC</th>
<th>HBP &amp; Additive</th>
<th>% Reduct. <em>C. albicans</em></th>
<th>% Reduct. <em>E. Coli</em></th>
<th>% Reduct. <em>S. aureus</em></th>
<th>% Reduct. <em>MRSA</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy (primer)</td>
<td>PEI C10 C4 Q</td>
<td>X</td>
<td>18.54 (99.99)*</td>
<td>5.41 (100)*</td>
<td>X</td>
</tr>
<tr>
<td>Polyurea 1 wt%</td>
<td>PE C10 C4 Q</td>
<td>99.68</td>
<td>98.02 (99.54)*</td>
<td>100 (86.05)*</td>
<td>X</td>
</tr>
<tr>
<td>Polyurea 2 wt%</td>
<td>PEI C10 C4 Q</td>
<td>X</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PEI C10 C4 Q</td>
<td>X</td>
<td>18.29 (99.99)*</td>
<td>25.44 (100)*</td>
<td>X</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PE C10 C4 Q</td>
<td>X</td>
<td>NR (99.54)*</td>
<td>5.92 (86.05)*</td>
<td>X</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PEI B</td>
<td>94.26 (65.99)*</td>
<td>25.65 (99.93)*</td>
<td>43.66 (100)*</td>
<td>X</td>
</tr>
<tr>
<td>Int. Epoxy 2 wt%</td>
<td>PEI C10 C4 Q</td>
<td>X</td>
<td>90.26</td>
<td>100</td>
<td>X</td>
</tr>
</tbody>
</table>

* Q denotes quaternary ammonium salt (values in (x) from TPU system)
* B denotes biguanide group
* Reduced efficacy relative to TPU system overcome by loading increase

Approved for Public Release (JUN 2007)
XPS Analysis of HBP in COTS Paints

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition - Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>COTS Polyurethane Baseline 2-22-06</td>
<td>41.269</td>
</tr>
<tr>
<td>COTS Polyurethane Baseline 4-13-06</td>
<td>74.52</td>
</tr>
<tr>
<td>COTS Polyurethane PEIquat*</td>
<td>68.541</td>
</tr>
<tr>
<td>COTS Polyurethane PEQuat</td>
<td>69.60</td>
</tr>
<tr>
<td>COTS Oil/Alkyd Baseline 4-13-06</td>
<td>81.570</td>
</tr>
<tr>
<td>COTS Oil/Alkyd PEQuat</td>
<td>81.35</td>
</tr>
<tr>
<td>COTS Acrylic Latex Baseline 2-15-06*</td>
<td>74.687</td>
</tr>
<tr>
<td>COTS Acrylic Latex Baseline 4-21-06</td>
<td>73.8</td>
</tr>
<tr>
<td>COTS Acrylic Latex PEIquat*</td>
<td>73.764</td>
</tr>
<tr>
<td>COTS Acrylic Latex PEQuat</td>
<td>77.18</td>
</tr>
</tbody>
</table>

- COTS – Commercial off-the-Shelf.
- Good segregation of HBP only in acrylic latex
- HBP caused instant gelation regular latex

Licensing our patented technology to numerous paint and coating companies
E-Spinning permits significant surface migration.

➢ E-spinning performed by collaborators at Virginia Tech.

➢ E-spinning accomplished using 120K, 350K PMMA

➢ Fiber sizes unpertrubed by additive inclusion

➢ Initial experiment demonstrating Ag uptake met with some success (3 min exposure)

<table>
<thead>
<tr>
<th>XPS RESULTS</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 K PMMA</td>
<td>79.84</td>
<td>0</td>
<td>20.16</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>350K PMMA, 1% add.</td>
<td>71.38</td>
<td>5.67</td>
<td>15.5</td>
<td>7.45</td>
<td>0</td>
</tr>
<tr>
<td>350K PMMA, 3% add.</td>
<td>53.35</td>
<td>15.56</td>
<td>14.24</td>
<td>16.85</td>
<td>0</td>
</tr>
<tr>
<td>350K PMMA, Ag dip</td>
<td>77.42</td>
<td>0</td>
<td>22.05</td>
<td>0</td>
<td>0.53</td>
</tr>
<tr>
<td>350K PMMA, 1% add., Ag dip</td>
<td>78.18</td>
<td>2.33</td>
<td>14.83</td>
<td>3.09</td>
<td>1.57</td>
</tr>
<tr>
<td>350K PMMA, 3% add., Ag dip</td>
<td>70.24</td>
<td>8.08</td>
<td>11.2</td>
<td>8.44</td>
<td>2.04</td>
</tr>
</tbody>
</table>

• E-spinning performed by M. Hunley; T.E. Long at Virginia Tech.
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Conclusions

• Demonstrated repeatable >30 X self segregation of active components to the air/polymer interface in coatings

• HBP scaffold universal. Favorable for attachment of a myriad of reactive species through straightforward chemistry.

• Transitioned to low VOC TPU coating systems

• Demonstrates strong activity (99.9999 % kill) towards environmental hazards: S. aureus, C. albicans, E. Coli, MRSA

• Preliminary evidence: Compatible with existing coating systems

• Potential in coated fabrics, latex paints, etc
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• ISN 6.2 Research Program
• Triton Systems, Inc.