Clay Tolerant Superplasticizer for Concrete

Robert Baumann, Marc Schmitz, Sudhir Mulik
Value Proposition

• Opportunity Statement
  • PCE based on a styrene maleic anhydride (SMA) copolymer backbone reduce the sensitivity to clay impurities significantly

• Key benefits of this technology will address the following aspects
  • Intensive washing of aggregates is avoided to lower consumption of clean water
  • Addition of more PCE to compensate for the intercalated quantity will add to cost
  • Retain concrete strength
State of the Art

• Deactivation of PCE in the presence of swellable clays
  • Polyethylene glycol chain get intercalated in montmorillonite layer structure

• Possible countermeasures
  • Extensive washing of aggregates
  • Use of scavengers
    EP 1838643 B1 describes the use of cationically charged polymers to inert clay impurities
  • Use of superplasticizers without side chains is less effective and does not provide slump retention
Structural Elements of PCE

• **Backbone Chemistry**
  • Polymethacrylic acid
    Mn 3000, Mw 5000
  • Styrene / maleic anhydride copolymer

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Mw</th>
<th>ratio styrene : maleic anhydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMA 1000</td>
<td>2000</td>
<td>5500</td>
<td>1:1</td>
</tr>
<tr>
<td>SMA 2000</td>
<td>3000</td>
<td>7500</td>
<td>2:1</td>
</tr>
<tr>
<td>SMA 3000</td>
<td>3800</td>
<td>9500</td>
<td>3:1</td>
</tr>
</tbody>
</table>

• **Sidechain chemistry**
  • Polypropylene glycol (NH₂-PPG)
    O- (2-aminopropyl)-O’ (2-methoxyethyl) polypropylene glycol (Mn 600)
  • Polyethylene glycol monomethyl ether
    MPEG 550, 1000, 2000
Superplasticizer Overview

- SMA-Estes

\[ \text{Grafting Ratio is the molar ratio of maleic half ester to maleic acid} \]

- PMAA-Estes
  - Produced using sodium hyperphosphite catalysis
- Commercial PMAA-Ester
- Beta Naphthalene Sulfonate Condensate
Structural Variations

• Backbone Chemistry
  • Acrylic
  • Styrene/Maleic Anhydride – Monomer ratio

• Side Chain Architecture
  • Side Chain Chemistry – EO vs. PO
  • Side Chain Length – 550 to 2000
  • Grafting density
## MORTAR FORMULATION

<table>
<thead>
<tr>
<th>Component</th>
<th>(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement OPC CEM I 42,5 R*</td>
<td>500</td>
</tr>
<tr>
<td>Quarzsand H 32</td>
<td>500</td>
</tr>
<tr>
<td>Sand particle size 0.2 - 1 mm</td>
<td>600</td>
</tr>
<tr>
<td>Sand particle size 1 - 2 mm</td>
<td>400</td>
</tr>
<tr>
<td>Superplasticizer (as solid)</td>
<td>1.9</td>
</tr>
<tr>
<td>Bentonite clay</td>
<td>8.0</td>
</tr>
<tr>
<td>Water</td>
<td>288.1</td>
</tr>
</tbody>
</table>

W/C ratio 0.58  
Superplasticizer 0.38% bwc  
Clay contamination 0.4% based on solids

We tested for  
- Initial flow with/without clay  
- Slump retention (1 hour)  
- Cement setting retardation
## Performance Results

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Backbone</th>
<th>Sidechain</th>
<th>grafting ratio</th>
<th>Slump Value w/o Clay (mm)</th>
<th>Slump Value w/ Clay (mm)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial PCE</td>
<td>MAA</td>
<td>MPEG 1000</td>
<td>0.3</td>
<td>300</td>
<td>214</td>
<td>29</td>
</tr>
<tr>
<td>Commercial BNS</td>
<td>MAA</td>
<td>MPEG 550</td>
<td>0.42</td>
<td>248</td>
<td>210</td>
<td>15</td>
</tr>
<tr>
<td>MPEG-PMAA</td>
<td>MAA</td>
<td>MPEG 550</td>
<td>0.42</td>
<td>277</td>
<td>212</td>
<td>23</td>
</tr>
<tr>
<td>NH2-PPG PMAA</td>
<td>MAA</td>
<td>NH2-PPG</td>
<td>0.42</td>
<td>246</td>
<td>229</td>
<td>7</td>
</tr>
<tr>
<td>NH2-PPG-SMA A4</td>
<td>SMA 1000</td>
<td>NH2-PPG</td>
<td>0.11</td>
<td>245</td>
<td>222</td>
<td>9</td>
</tr>
<tr>
<td>NH2-PPG-SMA A5</td>
<td>SMA 1000</td>
<td>NH2-PPG</td>
<td>0.5</td>
<td>252</td>
<td>234</td>
<td>7</td>
</tr>
<tr>
<td>MPEG-SMA A2</td>
<td>SMA 1000</td>
<td>MPEG 550</td>
<td>0.67</td>
<td>300</td>
<td>283</td>
<td>6</td>
</tr>
<tr>
<td>MPEG-SMA A3</td>
<td>SMA 1000</td>
<td>MPEG 1000</td>
<td>0.67</td>
<td>282</td>
<td>269</td>
<td>5</td>
</tr>
<tr>
<td>MPEG-SMA A5</td>
<td>SMA 1000</td>
<td>MPEG 2000</td>
<td>0.67</td>
<td>267</td>
<td>260</td>
<td>3</td>
</tr>
</tbody>
</table>

The presence of clay causes:

- Strong deactivation of acrylic MPEG PCE
- Strong deactivation of beta naphthalene sulfonate condensate
- Acrylic PPG PCE shows low clay sensitivity, but low plasticizing effect
- SMA based comb polymer with PPG side chain show low clay sensitivity, but low plasticizing effect
- SMA based comb polymer with MPEG side chains show strong plasticizing effect and are clay tolerant
- SMA based comb polymers with MPEG are more effective with shorter side chains
At a given grafting density the shorter side chains perform better. This is contrary to acrylic PCEs.
Best results could be achieved with a backbone of S/MA ratio of 1:1, MPEG 550 and a grafting density of 1 (1:1 ratio of half ester to bi-acid)
Other Properties

- Impact on cement setting rate (without clay)

![Setting process with ultra sonic graph](image)

- Impact on concrete strength (without clay)

<table>
<thead>
<tr>
<th>Sample</th>
<th>W/C Ratio</th>
<th>Tensile Strength after 1 day (N/mm²)</th>
<th>Tensile Strength after 7 days (N/mm²)</th>
<th>Compressive Strength after 1 day (N/mm²)</th>
<th>Compressive Strength after 7 days (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic PCE</td>
<td>0.50</td>
<td>3.1</td>
<td>5.1</td>
<td>13</td>
<td>29.2</td>
</tr>
<tr>
<td>SMA PCE</td>
<td>0.50</td>
<td>3.2</td>
<td>6</td>
<td>13</td>
<td>32.5</td>
</tr>
</tbody>
</table>
Other Properties – Stability

Acrylic PCE
W/C ratio 0.57

- Without clay: 273 mm
- With clay: 204 mm

SMA PCE
W/C ratio 0.57

- Without clay: 283 mm
- With clay: 248 mm
Other Properties – Slump Retention (without clay)

W/C ratio 0.5

Slump Retention [mm]

- acrylic PCE
- SMA PCE
Summary

- PCEs with SMA polymer backbone have shown surprising robustness as concrete superplasticizers in the presence of clay.
- Their effect on concrete rheology, slump retention, cement setting and strength development is comparable to acrylic PCE.
- The bulky, hydrophobic polymer backbone seems to prevent intercalation of the brush polymer.
- The dispersion mechanism apparently is different to traditional PCE as low Mw side chains enable improved flow properties.
- More work is required to completely understand their mode of action as concrete superplasticizers.
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