Rheological, Chemical, Mechanical Properties of Re-refined Engine Oil Bottoms (REOB) Modified Binder

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The Story!

• Background
• Objectives/Scope
• Methodology
  - Binder Experiment
    • Gel permeation Chromatography (GPC)
    • X-ray fluorescence spectroscopy (XRF)
    • Fourier transform infrared (FTIR) spectroscopy
    • Atomic Force Microscopy (AFM)
  - Mixture Experiment
    • Semi-circular bend (SCB) test

• Results
• Summary and Conclusion
**Use of REOB: Concern**

- Inconsistent and conflicting conclusions

<table>
<thead>
<tr>
<th>Detrimental</th>
<th>Not Detrimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor field performance</td>
<td>Equal field performance</td>
</tr>
<tr>
<td>Adverse effect on binder properties</td>
<td>Equal or improved binder and mixture properties</td>
</tr>
</tbody>
</table>

- Limitations with current Superpave testing/specification
  - Need for additional aging/testing protocols
  - Sometimes requires other analysis approaches (e.g., GPC, FTIR, XRF etc.)
Objectives

- Evaluate rheological, chemical, micro-mechanical and mechanical properties of aged binders containing
- Correlate binder properties to mixture intermediate temperature cracking performance
Scope

- 12.5 NMAS asphalt mixture
- Four Binders
  - PG 70-22
  - 0-, 5-, 10-, and 15% REOB
- Binder Experiment
  - Rheological tests
  - Micro-mechanical properties
    - atomic force microscopy
  - chemical properties
    - GPC, FTIR, and XRF
- Mixture Experiment
  - SCB at intermediate temperature
  - ASTM D 8044
Binder Experiment • Gel Permeation Chromatography (GPC)

GPC Analysis Principle

PMAC

Increasing Elution Volume

MW (Daltons x 10^-3)

ΔRI (Relative Units)

73.6% MW 1,000

4.9% MW 3,150

17.8% MW 7.5K

3.4% MW 125K

0.3% MW 185K

0.20.51251020501000 5020 10 5 2 1 0.5 0.2
Binder Experiment

- Quantification of GPC curves by integration
Binder Experiment

• X-ray Fluorescence Spectroscopy (XRF)
  - To identify elemental composition of binder samples generally found in REOB
    - Calcium (Ca)
    - zinc (Zn)
    - molybdenum (Mo)
    - copper (Cu)

EDXRF PANalytical Epsilon 1Spectrometer
Binder Experiment

- Fourier Transform Infrared (FTIR) Spectroscopy
  - To identify chemical functional groups
  - Carbonyl Index (CI): presence of REOB and aging change

Bruker Alpha FT–IR spectrometer)
**Binder Experiment**

- **Atomic Force Microscopy (AFM)**

Reduced Elastic modulus

\[
E_{\text{reduced}} = \frac{\pi}{2} \frac{F}{\delta^2 \tan(\alpha)}
\]

Total energy needed to separate AFM tip from a sample

\[
E_{\text{bonding}} = \int_{z_0}^{z_1} F \, dz \approx \frac{\Delta z}{2N} \sum_{i=1}^{N} [F(z_{i+1}) + F(z_i)]
\]

- \(F\): measured force
- \(\delta\): indentation depth
- \(\alpha\): half-opening angle of the AFM tip
- \(d\): cantilever deflection
- \(z\): piezo-driver displacement
Mixture Experiment

• Semi-Circular Bend Test
• ASTM D8044
• Temperature: 25°C
• Half-circular Specimen
  – Laboratory prepared
  – 150mm diameter X 57mm thickness
  – simply-supported and loaded at mid-point
• Notch controls path of crack propagation
  – 25.4-, 31.8-, and 38.0-mm
• Aging: 5 days, 85°C
• Loading type
  – Monotonic
  – 0.5 mm/min
  – To failure
• Record Load and Vertical Deformation
• Compute Critical Strain Energy: $J_c$
Results

- PG test results
Results

• Atomic Force Microscopy

Reduced Elastic modulus

Total energy needed to separate AFM tip from a sample
Results -- AFM

- Relationship between $E_{\text{reduced}}$ and $G^* \sin \delta$

\[ y = 0.46x - 864.58 \]

$R^2 = 0.76$
## SARA data of original and aged REOB

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>1000-300K (%)</th>
<th>300-45K (%)</th>
<th>45-19K (%)</th>
<th>Asphaltenes %</th>
<th>Maltenes % &lt; 3K</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOB</td>
<td>0.36</td>
<td>5.54</td>
<td>3.37</td>
<td>18.33</td>
<td>72.4</td>
</tr>
</tbody>
</table>

## Determination of maltenes, asphaltenes and polymer content based on the molecular weight regions
## Compositional analysis

- Gel Permeation Chromatography

<table>
<thead>
<tr>
<th>Sample</th>
<th>HMW* Polymer 300-45K, %</th>
<th>Associated Asphaltenes 45-19K, %</th>
<th>Asphaltenes 19-3K, %</th>
<th>Maltenes &lt; 3K, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOB</td>
<td>5.9</td>
<td>3.37</td>
<td>18.33</td>
<td>72.4</td>
</tr>
<tr>
<td>Unaged base binder</td>
<td>3.96</td>
<td>1.63</td>
<td>21.33</td>
<td>73.08</td>
</tr>
<tr>
<td>Aged base binder</td>
<td>3.16</td>
<td>3.76</td>
<td>24.87</td>
<td>68.27</td>
</tr>
<tr>
<td>Aged 5% REOB modified binder</td>
<td>2.8</td>
<td>3.59</td>
<td>23.66</td>
<td>69.95</td>
</tr>
<tr>
<td>Aged 10% REOB modified binder</td>
<td>4.57</td>
<td>3.95</td>
<td>24.69</td>
<td>66.79</td>
</tr>
<tr>
<td>Aged 15% REOB modified binder</td>
<td>5.1</td>
<td>3.71</td>
<td>23.96</td>
<td>67.23</td>
</tr>
</tbody>
</table>
**Results – Compositional analysis**

- Gel Permeation Chromatography

**Determination of maltenes and asphaltenes content of 64-CO binder based on the molecular weight regions**

**Determination of maltenes and asphaltenes content of 64-CO binder by deconvolution of the GPC curve**
Results -- Compositional analysis

- Gel Permeation Chromatography

Gel Permeation Chromatography results:

- Asphaltenes
  - 16.7% MW 9,6K
  - 4.2% MW 35.0K
  - 55.7% MW 1,025
  - 19.4% MW 3,1K
  - 4.0% MW 115K

- Maltenes
  - 4.7% MW 34K

- Polymer
  - 15.1% MW 3.9K
  - 1.9% MW 108K

- REOB
  - 9.6% MW 9.3K

Graphs showing the composition of aged 0% REOB and aged 15% REOB modified binders.
**Compositional analysis**

- Gel Permeation Chromatography
  - Distribution of molecular species showing peak molecular weights

<table>
<thead>
<tr>
<th>Sample</th>
<th>HMW* Species %/MW</th>
<th>Associated Asphaltene Species %/MW</th>
<th>Asphaltenes 2 %/MW</th>
<th>Asphaltenes 1 %/MW</th>
<th>Maltenes %/MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aged base binder</td>
<td>1.9 /109K</td>
<td>4.7 /34K</td>
<td>15.1 /9.3K</td>
<td>9.6 /3.9K</td>
<td>68.8 /1,050</td>
</tr>
<tr>
<td>Aged 5% REOB modified binder</td>
<td>1.5 /90.5K</td>
<td>4.4 /39K</td>
<td>17.8 /8.5K</td>
<td>7.6 /3.5K</td>
<td>68.7 /1,050</td>
</tr>
<tr>
<td>Aged 10% REOB modified binder</td>
<td>4.1 /110K</td>
<td>3.7 /32K</td>
<td>14.6 /10.8K</td>
<td>14.8 /3.8K</td>
<td>62.8 /1,050</td>
</tr>
<tr>
<td>Aged 15% REOB modified binder</td>
<td>4.0 /115K</td>
<td>4.2 /35K</td>
<td>16.7 /9.6K</td>
<td>19.4 /3.9K</td>
<td>55.7 /1,025</td>
</tr>
</tbody>
</table>
Compositional analysis • Gel Permeation Chromatography

AGED SAMPLES

0% REOB
5% REOB
10% REOB
15% REOB

0%
5%
10%
15%

NORMALIZED CURVES

HIGH MW POLYMERS REGION

MW >200K 100K 50K 20K

UNAGED REOB
**Compositional analysis**

- Gel Permeation Chromatography
  - Comparison of theoretical data calculated according to percentage of REOB content with experimental results

<table>
<thead>
<tr>
<th>Sample</th>
<th>&gt;45K, %</th>
<th>Asphaltenes, %</th>
<th>Maltenes, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>5% REOB modified binder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>3.3</td>
<td>28.22</td>
<td>68.48</td>
</tr>
<tr>
<td>Integrated</td>
<td>2.8</td>
<td>27.25</td>
<td>69.95</td>
</tr>
<tr>
<td>De-convoluted</td>
<td>1.5/90.5K</td>
<td>29.75</td>
<td>68.75</td>
</tr>
<tr>
<td><strong>10% REOB modified binder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>3.4</td>
<td>27.89</td>
<td>68.68</td>
</tr>
<tr>
<td>Integrated</td>
<td>4.6</td>
<td>28.64</td>
<td>66.79</td>
</tr>
<tr>
<td>De-convoluted</td>
<td>4.1/110K</td>
<td>33.10</td>
<td>62.80</td>
</tr>
<tr>
<td><strong>15% REOB modified binder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>3.6</td>
<td>27.51</td>
<td>68.89</td>
</tr>
<tr>
<td>Integrated</td>
<td>5.1</td>
<td>27.67</td>
<td>67.33</td>
</tr>
<tr>
<td>De-convoluted</td>
<td>4.0/115K</td>
<td>40.30</td>
<td>55.70</td>
</tr>
</tbody>
</table>
Compositional analysis

- X-ray fluorescence spectroscopy
Compositional analysis

- Fourier transform infrared spectroscopy
Results

- Relationship between mixture cracking performance and binder properties

\[ y = 0.00x - 0.56 \]
\[ R^2 = 0.77 \]

\[ y = -1.62x + 0.38 \]
\[ R^2 = 0.85 \]
Summary and Conclusion

- Evaluated rheological, chemical, micro-mechanical and macro-mechanical properties of aged binders containing REOB contents (0-, 5-, 10-, and 15 %)
- In general, binders containing 5% REOB did not adversely affect binder and mixture performance
- ∆Tc increased (-) with an increase in REOB content
  - More pronounced for 2 PAV and 4 PAV aged binders
- Addition of REOB softened the binder
  - low PG decreased with increased REOB content.
- Microscale AFM test results exhibited a decrease in stiffness and bonding energy with an increase in REOB content.
- XRF and FTIR spectroscopy successfully identified REOB in binders
Summary and Conclusion

• Residual polymer content in REOB influenced the distribution of maltenes and asphaltenes when REOB concentrations were greater than 5%.

• Good correlation was observed between microscale AFM stiffness and PG parameter, G*\sin\delta as well as between AFM bonding energy of binders and SCB $J_c$ mixture cracking performance.

• Good correlation between FTIR CI of binders and SCB $J_c$ mixture cracking performance was found up to REOB content 10%.
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Total High MW %</th>
<th>Asphaltenes %</th>
<th>Maltenes %</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOB</td>
<td>16.00</td>
<td>20.97</td>
<td>63.03</td>
</tr>
<tr>
<td>REOB-RTFO</td>
<td>16.66</td>
<td>21.7</td>
<td>61.64</td>
</tr>
<tr>
<td>REOB-PAV</td>
<td>18.84</td>
<td>21.61</td>
<td>59.55</td>
</tr>
</tbody>
</table>

![Graph showing RI response/relative amount vs. Molecular Weight for REOB, REOB-RTFO, and REOB-PAV](image)