TRC 1501: Performance of Asphalts Modified with Polyphosphoric Acid (PPA)

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Problem Statement

PPA is a hydrophilic and acidic material, which may have some adverse effects on the performance of binders and mixes.

ARDOT allows SB, SBS, and SBR. However, some suppliers may be using PPA as a modifier.

Performance of PPA-modified asphalt pavement is uncertain in Arkansas.

ARDOT needs to know how to manage the use of PPA to ensure high quality pavements.
Objectives

Find the current-state-of-practice of the use of PPA-modified asphalt binders

Analyze effects PPA on asphalt binders & mixes

Find possible issues of PPA modified asphalt binders

Propose recommendations to manage the usage of PPA in Arkansas
Review Pertinent Literature → Collect Unmodified and Modified Asphalt Binders → Collect Aggregates

Modify neat and PPA-modified binder with LAA → Conduct Binder Performance Tests → Conduct Chemical Test

Conduct Mixture Performance Test → Collect Field Performance Data

Analyze Test Results → Make Recommendations and Formulate Guidelines for DOTs
PPA improves binder’s Performance Grade (PG)

Required dosage of PPA to increase PG is crude source dependent.

Effects of lower amounts of PPA on binder’s chemical compositions are more significant than higher amounts.

Binders have more resistant to fatigue cracking with the addition of PPA.

Modification with only PPA is not equivalent to polymers in terms of performance against rutting and moisture damage.

In the continuous matrix, Aromatics and Saturates serve as a continuous phase and Asphaltenes remain as a dispersed phase stabilized by Resins.
27 agencies responded the survey

- 17 DOTs allow PPA
- 16 DOTs have concerns over PPA
- 8 DOTs are concerned with the use of amine based anti-stripping agents when PPA is used
- Other than PPA, SBS seems to be the most popular choice for asphalt modification
Survey Certified Asphalt Binder Suppliers in Arkansas

- Received responses from three (3) ARDOT approved binder suppliers
- Two of the respondents said they used PPA “just to follow the market.”
- PPA is used in tandem with other modifiers such as SBS or Elvaloy
- Caustic wash (done at the refinery) negates the effect of PPA modification
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Materials and Modifications

- Binder Source 1: PG 64-22 from Ergon@Memphis (Canadian Crude)
- Binder Source 2: PG 64-22 from Marathon@Catlettsberg, KY (Arabian Crude)
- PPA grade 105.
- SBS: Vector Dexco 2411
- Aggregates: Gravel and Sandstone from APAC Central Arkhola (Preston quarry) per ARDOT suggestion
- Liquid Anti-Stripping Agents –
  - Kao Gripper X2 from Kao Chemicals
  - AD-here® HP Plus™ from Akzo Nobel
  - PermaTac Plus® from Arr-Maz
  - Evotherm® M1 from Ingevity
  - PaveGrip® from PreTech
# Sample Nomenclature

<table>
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<th>Sample Nomenclature</th>
<th>Modification Details</th>
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<tr>
<td>S1B1</td>
<td>PG 64-22</td>
</tr>
<tr>
<td>S1B2</td>
<td>PG 64-22 + 0.25% PPA</td>
</tr>
<tr>
<td>S1B3</td>
<td>PG 64-22 + 0.5% PPA [PG 70-22]</td>
</tr>
<tr>
<td>S1B4</td>
<td>PG 64-22 + 0.5% PPA + 0.5% LAA</td>
</tr>
<tr>
<td>S1B5</td>
<td>PG 64-22 + 0.5% PPA (Foamed)</td>
</tr>
<tr>
<td>S1B6</td>
<td>PG 64-22 + 0.75% PPA</td>
</tr>
<tr>
<td>S1B7</td>
<td>PG 64-22 + 2% SBS [PG 70-22]</td>
</tr>
<tr>
<td>S1B8</td>
<td>PG 64-22 + 0.5% PPA + 2% SBS [PG 76-22]</td>
</tr>
</tbody>
</table>
Test Results

Penetration Test

- General trend - Reduced penetration value when PPA or SBS are added
- Higher pen value for PPA-modified binder than its SBS counterpart
- All LAAs except KaoGripper reduces pen values
Rotational Viscosity (RV) Test Results

- RV test is done to determine the viscosity of asphalt binder at high temperatures

- PPA increases viscosity slightly
- All tested binders passed the Superpave requirements ($\leq 3\ Pa.s$ at $135^\circ C$)
- LAA (S1B4 and S2B4) decreases the viscosity of PPA modified PG 70-22 binder (S1B3 and S2B3)
### Mixing and Compaction Temperatures of PPA and SBS Modified Binders

Mixing viscosity of $270 \pm 20$ mPa.s and compaction viscosity of $280 \pm 30$ mPa.s

<table>
<thead>
<tr>
<th>Source 1 Binders</th>
<th>Mixing Temperature (°C)</th>
<th>Compaction Temperature (°C)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>S1B1</td>
<td>165</td>
<td>158</td>
</tr>
<tr>
<td>S1B3</td>
<td>170</td>
<td>164</td>
</tr>
<tr>
<td>S1B7</td>
<td>183</td>
<td>177</td>
</tr>
<tr>
<td>S1B8</td>
<td>191</td>
<td>186</td>
</tr>
</tbody>
</table>

Lower mixing and compaction temperatures of PPA-modified binders (S1B3 and S2B3) compared to the SBS-modified binders (S1B7 and S2B7)
• PPA increases the rutting factor of PG 64-22 binder
• SBS modified PG 70-22 binder had higher rutting factor than PPA modified PG 70-22 binder, but both meet Superpave specifications
• LLA decreases the rutting factor (S1B4 failed to meet Superpave Specification)
DSR Test Result (unaged PPA+LAA binders)

- S1B4-Pavegrip
- S1B4-PermaTac
- S1B4-Adhere
- S1B4-Evotherm
- S1B3
- S1B4-Gripper

Superpave Specification

• 4 out of 5 LAAs decreased the rutting factor of the S2B3 binder; they did not meet Superpave specifications
• Among the LAAs, Gripper (S1B4-Gripper) was found to be the most compatible, whereas Adhere HP Plus was the least compatible.
• The lowest stiffness was obtained from S1B8
• All met Superpave specifications for BBR stiffness
The highest “m”-value was obtained for S1B8
All met Superpave specifications for BBR m-value
Moisture Susceptibility Analysis by Surface Free Energy (SFE) Method

- Measure Contact Angles (Sessile Drop Method)
- Calculate Surface Free Energy Parameters
- Calculate Cohesive and Adhesive Energy
- Find the Compatibility

[Diagram showing liquid surface and contact angles: 95° (Bad wetting), 45° (Good wetting), 0° (Complete wetting)]
Moisture Susceptibility Analysis by Surface Free Energy (SFE) Method

Measuring Contact Angle by the OCA Device

A Typical Binder Sample for OCA Test
There are 3 SFE Components –
1. Acidic ($\Gamma^+$)
2. Basic ($\Gamma^-$)
3. Lifshitz-van der Waals ($\Gamma^{LW}$)

Total Surface Free Energy
$\Gamma_{total} = \Gamma^{LW} + \Gamma^{AB}$,

Where, $\Gamma^{AB} = 2\sqrt{\Gamma^+ \Gamma^-}$

Work of Cohesion,
$W_{CL} = 2\Gamma_{total}$

$\Delta G_{ad} = \Delta G^{LW}_{ad} + \Delta G^{AB}_{ad}$

$\Delta G^{AB}_{ad} = -2\left(\sqrt{\Gamma^+_L \Gamma^-_S} + \sqrt{\Gamma^-_L \Gamma^+_S}\right)$

$\Delta G^{LW}_{ad} = -2\sqrt{\Gamma^{LW}_L \Gamma^{LW}_S}$

Compatibility Ratio (CR) = $\Delta G_{dry}^{ad} / \Delta G_{wet}^{ad}$
• MMMC granite showed the highest compatibility among 4 aggregates.
• The two Arkansas aggregates showed very similar compatibility ratio with the binder samples; they are “good” compatible binder-aggregate systems.
Neat binder from **Source 1** is inherently **basic** and that from **Source 2** is **acidic**.

- Acidity increases (pH decreases) with the addition of PPA.
- Foaming (S1B3 or S2B3) of the PPA-modified binder (S1B5 or S2B5) reduces its acidity.
Asphaltenes increase with increasing PPA dosage.
SBS does not increase Asphaltenes, but it alters the colloidal dispersion.
PPA may increase rutting resistance by reducing softening component (Aromatics)
PPA beyond the optimum level may cause excessive hardening in the long run, which is not desirable
Task 6: Evaluate Performance Properties of Asphalt Mixtures

Evaluation of Rutting and Stripping of Asphalt (ERSA) Test

- For each test, 2 samples of sat-cut slab specimen or a compacted core specimen is needed.
- Arkansas specifications (Section 407) for surface courses require a maximum rut depth of 8.000 mm at 8,000 cycles for an APA style wheel tracking tests.

Sample Setup for ERSA Testing

- For ERSA testing, the maximum cycle value of 8,000 cycles and a maximum rut depth of 8.0 mm is utilized.
ERSA Test Results

- All three modifications decreased rutting and moisture damage with similar improvement in performance.
- PPA-modified PG 70-22 showed less rut depth than SBS-modified PG 70-22.
Dynamic Modulus Testing

- To measure Dynamic Modulus of asphalt concrete sample, a dynamic load is applied at 0.1 Hz, 0.5 Hz, 1.0 Hz, 5 Hz, 10 Hz, and 25 Hz.
- Each of these frequencies is tested at five different temperatures: -10°C, 4°C, 21°C, 37°C, and 54°C.

For IDT Dynamic Modulus Testing, disc specimen are used.

- Loading of 25 Hz to 0.1 Hz is used at different temperatures (from -10°C to 54°C).

To measure Dynamic Modulus of asphalt concrete sample, a dynamic load is applied at 0.1 Hz, 0.5 Hz, 1.0 Hz, 5 Hz, 10 Hz, and 25 Hz.

- Each of these frequencies as tested at five different temperatures: -10°C, 4°C, 21°C, 37°C, and 54°C.

- Specimens of 100 mm diameter and 150 mm tall were used.
• Four mixtures very similar, except SBS-modified is stiffer at intermediate reduced frequencies and soften at high reduced frequencies
• All mixtures have TSR of more than 0.8

• Improved tensile strength of PPA-modified binders under both dry and wet conditions

• SBS-modified (S1B7) mixture shows higher tensile strength under wet and dry conditions.

• LAA-modified mixtures did not show any improvement from the results of PPA-modified mixtures, which is in agreement with the data obtained from the SFE analysis.
Field Performance Data

Acid Detection Test

Finding the Location of PPA-modified Mixture

Gather Field Performance Data from MMHIS

MMHIS Application Interface
Acid Detection Test

Figure Showing Acid detection test result. The left one (a) is negative in PPA detection, whereas (b) and (c) showing positive detection result.
Field Performance

Samples recovered from 10 sections as part of TRC 1404 was tested for detecting PPA

PPA was found in Job #B60115 *(Good Section; I-30, Arkadelphia)* and specific specimens are:
- LB65-8 (2nd Lift)
- LB65-28 (2nd Lift)
- LB65 - 27 (1st Lift)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Job Number</th>
<th>Interstate</th>
<th>Nearest City</th>
<th>Section Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB 65 (1st Lift)</td>
<td>B60115</td>
<td>I-30</td>
<td>Arkadelphia</td>
<td>Good Section</td>
</tr>
<tr>
<td>LB 65 (2nd Lift)</td>
<td>B60115</td>
<td>I-30</td>
<td>Arkadelphia</td>
<td>Good Section</td>
</tr>
</tbody>
</table>
Summary

- No adverse impact of PPA has been found.
- PPA seems to reduce the mixing and compaction temperatures.
- PPA increases high PG as well as low PG of the asphalt binder.
- PPA hardens the asphalt binder by reducing the Aromatic fractions.
- PPA improves the rutting resistance as well as cracking resistance of the asphalt mix.
- Improved moisture resistance (TSR) of PPA-modified mixture.
- PPA did not seem to have any adverse effect on I-30 section (Job #B60115 at Arkadelphia).
- ARDOT can conduct acid detection test (AASHTO TP 78) to check for the presence of PPA in asphalt binder or asphalt mix.
Questions, Comments???