Emulsions 101
Polymer-Modified Emulsions for Chip Seals and Slurry/Micro. Apps.

MPPP Meeting
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Outline

- Asphalt emulsion primer
- What are polymers?
- Why polymers for asphalt emulsions?
- Modification of asphalt emulsions
- Polymer networks in asphalt emulsions
- Impact on performance + properties
Asphalt Emulsions - Formulation

- **Components**
  - Asphalt
  - Surfactant (surface active agents, emulsifiers)
  - Water
  - Mechanical energy (colloid mill)

- **Other Ingredients**
  - Additives (calcium chloride, cutback agents, …)
  - Modifiers – *Polymers*
Dispersion of asphalt in water
- Water – continuous phase
- Asphalt – non-continuous or dispersed phase
  – Stabilized by surfactant

Surfactant → emulsion class.
- Cationic
- Anionic
- Nonionic
Asphalt Droplets

Particle Size, μm

Volume %
What are Polymers?

- Comprised of many small molecules
  - Poly = many
  - Monomers = small molecules or repeat units

- Monomers chemically react \( \rightarrow \) larger molecules
  - Water-based polymers – latex form (SBR)
  - Solvent-based polymers – pellets, bale (SB-, SBS)

- Properties are determined by:
  - Types and sequence of monomers
  - Molecular weight
Typical Monomers

Styrene

Butadiene
Polymers for Asphalt Emulsion Modification

- **Elastomer – Styrene-Butadiene Rubber - SBR**
  - Latex form – polymer particles dispersed in water
  - Random monomer addition – typ. 75/25 Bd/styrene
  - High molecular weight – 1,000,000 g/mole
    - 13,900 Bd “mers”, 2400 styrene “mers”
  - Broad distribution – chains many different lengths
Elastomer – Polyisoprene – Natural Rubber

- Latex form – polymer particles dispersed in water
- Homopolymer of isoprene – harvested from trees
- High molecular weight – 1,000,000 g/mole
- Broad distribution – chains many different lengths

Isoprene
Polymers for Asphalt Emulsion Modification

Thermoplastic Elastomers

- Styrene-Bd-Styrene block copolymer – SB-, SBS
- Monomers blocked in polymer backbone
  - Typically 70/30 Bd/styrene
- Lower molecular weight – 100,000 g/mole
  - 1300 Bd “mers”, 288 styrene “mers”
- Narrow distribution – all chains similar length
Polymers for Asphalt Modification

- **Thermoplastic**
  - Ethylene vinyl acetate (EVA) resin
  - Vinyl acetate content ~ 20% to 40%
    - Low Tg, high melt temp due to crystallinity

- **Thermoset**
  - Ground tire rubber (GTR)
  - Mixtures of E-SBR, S-SBR, PBd, natural rubber
    - Depends on tire component
    - Tread, sidewall, innerliner (halobutyl),…
Viscoelastic Behavior
Cured Latex Modified Asphalt Emulsion

- $G^* = f(T) = \text{deform. resist.}$
- **Asphalt**
  - High $G^*$ at low $T$ – brittle
  - Low $G^*$ at high $T$ – viscous
  - $\Delta G^*(80^\circ C - 20^\circ C) = 1000x$
- **SBR Polymer**
  - Lower $G^*$ at low $T$ – flexible
  - Higher $G^*$ at high $T$ – elastic
  - $\Delta G^*(80^\circ C - 20^\circ C) = 10x$
Polymer Modification of Asphalt Emulsions

- Emulsify polymer modified asphalt
  - “Pre-modified” emulsion
  - Polymers – SBS, SB-, EVA
  - Higher mod. asphalt viscosity
    - higher asphalt + mill temp.
  - Exit temp. > 100°C
  - Heat exchanger, back press.

- Polymer inside asphalt droplet
Polymer Modification of Asphalt Emulsions

- **Add latex external to asphalt**
  - Methods
    - soap batching
    - co-milling – asphalt line
    - co-milling – soap line
  - Polymers – SBR, NR latex
  - Lower asphalt process T
  - No special mill, handling

- **Polymer in water phase**

- **Continuous polymer film formation on curing**
Latex Polymer-Modified Asphalt Emulsion

- Optimum for Fine Polymer Network Formation
Chip Seal – Field Application
Chip Seal Surface Treatment

Near Taos, NM
## CRS-2 vs. CRS-2P (LM) – Physical Props.

<table>
<thead>
<tr>
<th>Test Method</th>
<th>CRS-2</th>
<th>CRS-2P</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;B Softening Point (°F)</td>
<td>ASTM D 36</td>
<td>115</td>
</tr>
<tr>
<td>Ductility (4°C, cm)</td>
<td>ASTM D 113</td>
<td>21</td>
</tr>
<tr>
<td>Elastic Recovery (10°C, %)</td>
<td>AASHTO T 301</td>
<td>5</td>
</tr>
</tbody>
</table>

### 3 wt.% SBR latex polymer (on asphalt)

- **Residue**
  - ASTM D 6934 - Oven evaporation at 163°C

- **Polymer**
  - Raises SP, drastically increases ductility and ER
Chip Seal – CRS-2
Early Strength Development

Water wicks agg. surface
Positive correlation
- early chip retention
- agg. H₂O absorptivity

Data provided by Paragon Technical Services
Early Strength Develop. – CRS-2P
ASTM D7000-04 - Sweep Test

% Aggregate Retained

Potential Chip Loss

Unmodified CRS-2
3 wt% SBR Latex Mod.

Data Provided by Paragon Technical Services
Sweep Testing – CRS-2 vs CRS-2P
ASTM D7000 - 04

10/22/2007
Chip Seal with Latex Modified CRS

- Latex polymers accumulate at optimum location
  - Act to glue aggregate together!!!
Curing of CRS-2(LM) Emulsions

CRS-2(LM) (Unstable)

CRS-2(LM) (Stable)
Asphalt Emulsion ~ Surface Area

Surface area of asphalt = \(1200 \text{cm}^2 \approx 1.2 \times 10^{-1} \text{m}^2\) (10inch x 20inch)

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>2kg</td>
</tr>
<tr>
<td>Latex (65% solids)</td>
<td>90g</td>
</tr>
<tr>
<td>Cationic emulsifier</td>
<td>4.0g</td>
</tr>
<tr>
<td>HCl</td>
<td>3.0g</td>
</tr>
<tr>
<td>Water</td>
<td>900g</td>
</tr>
</tbody>
</table>

~ 1 gal emulsion

<table>
<thead>
<tr>
<th>Material</th>
<th>No of particles or molecules</th>
<th>Surface Area, m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>(3.1 \times 10^{13})</td>
<td>600</td>
</tr>
<tr>
<td>Latex (3% of asphalt)</td>
<td>(4.7 \times 10^{15})</td>
<td>330</td>
</tr>
<tr>
<td>Cationic Emulsifier</td>
<td>(1.2 \times 10^{22})</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>(1.5 \times 10^{22})</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>(3.0 \times 10^{25})</td>
<td></td>
</tr>
</tbody>
</table>
3% SBR Latex Polymer Modified CRS-2LM AC-5 (150 PEN) Asphalt

Chip Retention – ASTMD 7000-04

- Surf A
- Surf B
- Surf C
- Surf D

Retention percentages:
- Surf A: 70%
- Surf B: 75%
- Surf C: 80%
- Surf D: 90%
Curing of CRS-2LM Emulsion

- Water in asphalt emulsion wicks the aggregate surface.
  - Order of migration = Water, latex particles, asphalt droplets
Latex Polymer Distribution

- Latex particles migrate together with water???
  - Polymer rich regions around aggregate = NO
Latex Polymer Distribution

Latex particles migrate together with water!

- Polymer rich regions around aggregate = YES
Microsurfacing Operation

1 min < Mix Time < 3 min

Cohesion Development < 1 hr
Microsurfacing – High ADT + ESAL’s

AUTOBAHN

Paved in Oct. 2001
Photo from Sept. 2003
Microsurfacing Mix Formulation

- **Blade Coating Operation**
  - 2 m wide + <1 cm thick
  - 4-5 km/hour
  - Traffic within 1 hour

- **Latex Polymer Binds**
  - Asphalt
  - Fines to Aggregates

Latex Polymer = 3% of Asphalt (1/4 of Cement)

Emulsion
Water
Aggregate
Cement
Microsurfacing – Polymer Morphology
Field Application

Texas State Highway 84
- Near Waco, TX
- Paved in 1998
- Samples taken in 2001
Cured Latex Polymer Network

Microsurfacing

Latex Foam
SBR latex polymer

- 50% reduction in loss
  - one hour soak
- 67% reduction in loss
  - six day soak

- Surface of mix
  - tougher
  - more abrasion res.

- Adhesion + water resistance
  - improved

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**Graph:**

- X-axis: Unmod. SBR
- Y-axis: Loss (g/ft²)
- Bars: 1 Hour, 6 Day
- 3 wt% SBR (on asphalt)
Microsurfacing Residue – SHRP Grade

The diagram shows the effect of different types of materials on rutting resistance temperature and phase angle at G*\sin(\delta) = 1kPa.

- **Emulsion Only**: Shows a steady increase in rutting resistance temperature and a phase angle that remains relatively constant.
- **Emulsion+Cement**: Demonstrates a slight increase in rutting resistance temperature compared to Emulsion Only, with a more pronounced phase angle.
- **Emulsion+Cement+SBR Latex**: Displays a significant increase in rutting resistance temperature and a noticeable increase in phase angle compared to the other two options.

The graph on the right side of the page illustrates that 30 days after curing, the addition of cement or latex to the emulsion mixture significantly improves rutting resistance temperature, with latex showing the most substantial improvement in phase angle.
Advantages of Latex Polymer Network

- **Latex polymer honeycombs** remain flexible
  - Absorb stresses without permanent deformation
Summary – Polymer Modified Emulsions

- **Chip seals**
  - Early and long term chip retention
  - High temperature strength
  - Low temperature flexibility

- **Slurry seal and microsurfacing**
  - Improved mix cohesion
  - Reduction in abrasion loss of aggregate
  - Resistance to deformation
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Polymer-Modified Emulsions for Chip Seals and Slurry/Micro. Apps.

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Helping Make Products Better™
Polymer Modified Emulsion + GTR Modified Asphalt Producers

- **Producer - Pre-Modified Emulsion (SB-, SBS)**
  - SEMMaterials

- **Producers - Latex-Modified Emulsions (SBR/NRL)**
  - SEMMaterials ~ Ralumac® – NRL – Microsurfacing
  - All States Asphalt + GTR for Hot Applied Chip Seals
  - Hudson Companies + GTR for Hot Applied Chip Seals
  - SuitKote
  - Vestal Asphalt
  - Midland Asphalt
  - Gorman Brothers
  - Peckham Industries