Polymer Modified Asphalt Emulsions

Dr. Koichi Takamura
BASF Corporation
Charlotte Technical Center
Charlotte, NC 28273
Takamuk@basf.com
Asphalt: Flexible Pavement

- Dissipate Applied Energy without permanent damage
- Combination of **Viscous** and **Elastic** Behaviors
Automotive Suspension System

Shock Absorber = Viscous
Spring = Elastic
Automotive Suspension System

- Dissipate Applied Energy quickly without permanent damage to your car
- Combination of Shock Absorber and Spring
Time Effect on Elastic Materials

- Time has no effects on total deformation
  - Deformation (Strain) ≠ Time
  - Deformation (Strain) ∝ Weight (Stress)
Time Effect on Viscous Materials

- Continue to deform until Stress is removed
  - Deformation (Strain) $\propto$ Weight (Stress) and time
  - Slow Traffic = More Rutting
Time Effect on Elastic Materials

- Time has no effects on total deformation
  - Deformation (Strain) ≠ Time
  - Deformation (Strain) ∝ Weight (Stress)

- Polymers improves elasticity of the cured asphalt emulsion

- How?
Pure Polymer and Unmodified Asphalt Properties

- **SBR Polymer**
  - High Elasticity and High Elongation at wide range of temperature
  - $G^*$ changes only factor 10 between −20 and 80°C

- **Asphalt**
  - Adequate properties at 0-40°C
  - Brittle at low and limited strength at high temperature.
  - 100,000 times change in $G^*$ at the same temp. range

- **How to Achieve “Maximum Improvement with Minimum Level “?**
SEM Photo of the Latex Foam

200 µm
Latex Foam

- 95% air and 5% Polymer
- Softness from Air
- Desired Strength from Polymer Network

Polymer Aerosol

- 95% air and 5% Polymer
- Mix as Air
- No Physical Strength from Polymer

Latex
Latex Foam vs Polymer Modified Asphalt

- Strong Contrast in Physical Properties between Continuous (Polymer) and Dispersed (Air or Asphalt) Phases
  - “Softness from Air” vs Hardness from Asphalt
  - Elasticity/Strength from Polymer Network
    - Dispersed Polymer would give only minimum effects on physicals
Asphalt Emulsion

- Latex Particles
- Asphalt droplets
<table>
<thead>
<tr>
<th>Latex Modified Emulsion</th>
<th>Cured Bitumen Emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen</td>
<td>Bitumen</td>
</tr>
</tbody>
</table>

- **Optimum for Fine Polymer Network Formation**

Diagram: Latex film surrounds bitumen droplets in the modified emulsion, leading to a fine polymer network in the cured emulsion.
Microsurfacing

SBR polymer/cement complex form honeycombs

10 µm
How to make fine, stable asphalt emulsions?
**Conditions for droplet break-up**

- **Viscosity ratio** and **Flow type** are two critical parameters for emulsion preparation.
  - No droplet break-up under simple shear flow at the droplet viscosity > 4x of the suspending medium viscosity.
  - Need the **Extensional Flow** to produce fine emulsions.

\[
G^* = \frac{G}{\gamma} \frac{\eta_c b}{\eta_d}, \quad \lambda = \frac{\eta_d}{\eta_c}
\]

- \( G = \) shear rate
- \( b = \) droplet radius
- \( \gamma = \) interfacial tension
- \( \eta_c, \eta_d = \) viscosity of continuous and dispersed phases

**Diagram:**
- Break-up under simple shear flow
- Break-up under extensional flow
- Stable

**Legend:**
- Orange region: Conditions for asphalt emulsion production
- Green region: Break-up only under extensional flow
- Yellow region: Break-up under simple shear flow
Asphalt Emulsion Production

Colloid Mill Tooth

Colloid Mill Tooth
Mechanism of emulsion formation

- Latex polymer particles remain in the water phase
  - Does not affect the asphalt emulsion production
  - Easy to produce asphalt emulsion with fine particle size
- **Emulsifiers (surfactants)** prevent coalescence of droplets created
Surfactant = Surface Active Agent

How to make oil droplets like to be in water?

- Cover with one layer of molecules having two parts
  - Like to be in Water (hydrophilic)
  - Like to be in Oil or don’t like to be in water (hydrophobic)
How to Maintain Stable Oil Layer on Water?

- **Surfactant = Surface Active Agent**
  - Molecules preferentially accumulate at the surface
    - Hydrocarbon tail doesn’t like to be in water
      - Hydrophobic (lipophilic) group
    - A head makes strong interaction (i.e. hydrogen bonding) with water
      - Hydrophilic (lipophobic) group
Surfactant = Surface Active Agent

- Classified based on charge nature of the hydrophilic group
  - Anionic Surfactant
    - Soap: i.e. Potassium salt of fatty acid (K-Oleate)
    - Sodium salt of Dodecyl sulfonate (SDS)
    - with Ethylene Oxide group (EO)ₙ
Surfactant = Surface Active Agent

- **Cationic Surfactant**
  - Hydrocarbon chain with Amines

- **Non-ionic Surfactant**
  - Ethylene Oxide chains
  - Could be a large molecule (10<n<50)
Preventive maintenance with asphalt emulsion

- Chip Seal
  - Rural Highways
- Microsurfacing
  - Interstate and Urban Highways
Chip Seal (Surface Seal)
Chip Seal

- Cationic rapid setting (CRS) Emulsion with Soft Asphalt
- Spray “Hot” emulsion, cover with “Clean” aggregate, then roll
- Could be second aggregate for smooth surface
Chip Seal
Chip Seal
CRS for Chip Seal

Typical CRS Emulsion

<table>
<thead>
<tr>
<th>Composition</th>
<th>Level, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>65</td>
</tr>
<tr>
<td>Water</td>
<td>35</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>0.10</td>
</tr>
</tbody>
</table>

0.15% against asphalt

- Total surface area of asphalt droplets ≈120m²/100g emulsion
- Emulsifier molecules need to cover this surface ≈2.3x10²⁰
- Total emulsifier molecules added = 2.6x10²⁰
  - ~90% emulsifier on the asphalt surface
  - ~10% in the water
- Particle size and emulsifier type affect this valance
Industry Perception
- Positively charged asphalt particles adhere to negatively charged aggregates
Asphalt Emulsion = An Elephant, 30 Cats and 1 million Fleas
(asphalt droplet, latex particles and surfactant molecules)
The Elephant is too slow to move, thus you (aggregates) would immediately be covered with fleas
**Surfactants in Chip Seal**

**Optimum Surfactant Level**
- Cationic surfactants adsorb head-on and make aggregate oil-wet
  - Neutralize aggregate surface charge

**Excess Surfactant Level**
- Second surfactant layer forms to make aggregate water-wet
  - Cationic surface charge
### Surface Area and Size

<table>
<thead>
<tr>
<th>Size</th>
<th>Each Vol., m³</th>
<th>Total Number</th>
<th>Total Surface Area, m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1m</td>
<td>1m =1x1x1</td>
<td>1</td>
<td>=1x1x6</td>
</tr>
<tr>
<td>0.5m</td>
<td>0.5m =0.5x0.5x0.5</td>
<td>0.125</td>
<td>=0.5x0.5x6x8</td>
</tr>
<tr>
<td>0.125m</td>
<td>0.125</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>10cm</td>
<td>0.1x10⁻³</td>
<td>1/1000</td>
<td>=0.1x10⁻³x1000</td>
</tr>
<tr>
<td>1cm</td>
<td>1.0x10⁻⁶</td>
<td>1.0x10⁵</td>
<td>600</td>
</tr>
<tr>
<td>1mm</td>
<td>1.0x10⁻⁹</td>
<td>1.0x10⁵</td>
<td>6000</td>
</tr>
<tr>
<td>100µm</td>
<td>1.0x10⁻¹²</td>
<td>1.0x10¹²</td>
<td>6x10⁴</td>
</tr>
<tr>
<td>10µm</td>
<td>1.0x10⁻¹⁵</td>
<td>1.0x10¹⁵</td>
<td>6x10⁵</td>
</tr>
<tr>
<td>1µm</td>
<td>1.0x10⁻¹⁸</td>
<td>1.0x10¹⁸</td>
<td>6x10⁶</td>
</tr>
<tr>
<td>100nm</td>
<td>1.0x10⁻²¹</td>
<td>1.0x10²¹</td>
<td>6x10⁷</td>
</tr>
</tbody>
</table>

- **Fines in aggregate in chip seal**
  - 99% aggregate of 1cm cube = ~ 600m²
  - 1% fines (dust) of 100µm cube = 600m²
  - 0.1% fines of 10µm cube = 600 m²

- **Fines in Chip Seal and Slurry Seal Control**
  - Surfactant Distribution, thus Asphalt Emulsion Stability
How to Initial Setting of the Chip Seal Emulsion?

- Emulsifier adsorption to aggregate, road surface
  - Neutral charge of these surfaces
  - Slightly less emulsifiers on the asphalt surface
- Increase in emulsion pH
  - $\text{RCOOH} \Rightarrow \text{RCOO}^- + \text{H}^+$ (on the asphalt surface)
  - Neutral asphalt particles when $\text{RCOO}^- = \text{RN}^+$
- Reduction in emulsion temperature
  - Reduce emulsifier solubility at below Kraft Point
  - Less emulsifier on the asphalt surface

* Kraft Point = The minimum temperature for the micelle formation of ionic surfactant
Microsurfacing

AUTOBAHN near LUDWIGSHAFEN

Paved in Oct. 2001
Photo taken in Sept. 2003
Microsurfacing (Slurry Seal)

- Big Scale Blade Coating Operation
  - 2m wide and <1cm thick
  - 4-5km/hour
  - Open to traffic within 1 hour
- Rut filling capability, up to 5cm deep
  - Graded aggregate of fines to 1cm in diameter
  - Stable cationic asphalt emulsion
    - 1.5-2.5% emulsifiers
      - A large amount of free surfactants in the water phase
    - 1.0<pH<2.5
Paving Machine
Microsurfacing Operation

Portland cement (lime or Alum)
Micro-Surfacing

60sec < Mix Time < 180sec

Cohesion Development < 1 hr
**Setting Mechanism**

- **Bitumen Emulsion (1.5<pH<2.5)**
  - Positively Charged due to Adsorbed Cationic Surfactant at low pH

- **Cement addition increases slurry pH to above 10**
  - Organic acids start to dissociate as RCOO⁻ with Increasing pH
  - RCOO⁻ and adsorbed cationic surfactants determine total surface charge of bitumen droplets
  - Some surfactants are also adsorbed on fines surface

- **Setting characteristics are very sensitive to aggregate and asphalt**
Surface Charge of Bitumen Droplets

- Amines from Cationic Surfactants: RN⁺
- Organic Acids from Bitumen: RCOO⁻
- Total Charge on Bitumen Surface

K. Takamura et al. J. Colloid Interface Sci. 125, 212, 1988
Three years under wheels in Texas

Polymer Network

Microsurfacing

Latex Foam
Microsurfacing: SEM Photo

Latex Polymer-Cement composite

10 µm
Microsurfacing: Emulsion Residue

![Graph showing the relationship between curing time and rutting resistance temperature.](graph-image)

- **Emulsion Only**
- **Emulsion+Cement**
- **Emulsion+Cement+SBR**

Bar chart showing the phase angle at $G^*$ for different conditions:
- **Emulsion only**
- **+ Cement**
- **+3% Latex**

Rutting resistance temperature, °C

Curing Time, day
Microsurfacing: Curing Process

- 1 day at Ambient Temperature, then Cured at 60°C
- Additional 2 PG Improvement within 10 days
- Additional 3 PG Improvement after One Month
  - Total 5 PG Improvement
Transverse Shear Stress by Radial Tire

- **Bias-Ply Tire** generates vertical contact stresses to the pavement
  - Fracture initiates at bottom of the pavement layer and penetrates to the surface

- **Radial Tires** Exert Excess Transverse Shear Stresses to the Asphalt Pavement Layer
  - Longitudinal pavement crack at the pavement surface

Byron Ruth et al. U. of Florida
Binder Requirements for Preventive Maintenance

Radial Tire

- Excess shear stresses to thin Surface Treatments (Chip Seal & Microsurfacing)
  - Need to withstand higher strain/stress levels than the hot mix binder, especially under fully loaded radial truck tires
Fatigue Resistance Test

1. Strain sweep from low to high strain (i.e. 0.1 to 5%)
2. Repeated stresses at constant strain (i.e. 5%) for 30 min
3. 0.1% strain for 15 min to monitor potential recovery
4. Repeat 2 and 3 to monitor reduction in binder strength under repeated high strain-stresses
   - Choose temperature at $G^* = 1 – 10$ MPa
The emulsion residue is weaker than the original asphalt
- Asphalt droplets do not fully coalesce even after cured for 1 day at 60°C
Flexible SBR latex polymer honeycombs absorb excess stresses without permanent deformation.
Earthquake Resistant Building

Stress Absorbing Rubber Pads

Foundation
Advantages of Polymer Network

- SBR latex polymer honeycombs remain flexible, and take stresses without permanent deformation
Conclusions

- Latex polymer remains in the water phase of the asphalt emulsion
- Transfer to Polymer Honeycombs surrounding asphalt particles only when needed (upon curing)
  - Improve elasticity of asphalt binder
    - Provide enhanced fatigue resistance under repeated high strain stresses (i.e. high load traffics with radial tires)
  - Honeycombs of cement/polymer complex to improved rut filling capability
- Current residue recovery procedures by distillation & evaporation do not reproduce the polymer morphology
  - Only tell Polymer modified or not