

Polymer-Modified Asphalt 101

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AZ DOT + Local Agency Training Seminar – 4/10/14

Outline

- Reasons for Asphalt Modification
 - Primary Distresses in Asphalt Pavements
- Polymers for Asphalt + Emulsion Modification
 - “Plus” Testing for Polymer Modification
 - Chip Seal and Micro Surfacing
- Polymer Morphology and Compatibility
- PMA Storage and Handling

Reasons for Asphalt Modification

- The perception that asphalt cement has changed since the 1970's.
- Traffic factors have increased: including heavier loads, higher volumes and radial tires with higher tire pressures. (Twofold increase in truck traffic from 1974-1989.)
- Deferred maintenance because of funding shortages.
- Higher costs have created a tendency to construct thinner pavements, thus reducing the service life of the pavement.
- To meet new Superpave design specifications.

Distresses in Asphalt Pavements

- High Temperature Permanent Deformation
- Low Temperature Thermal Cracking
- Load-Associated Fatigue Cracking
- Aging
- Stripping

High Temperature Permanent Deformation

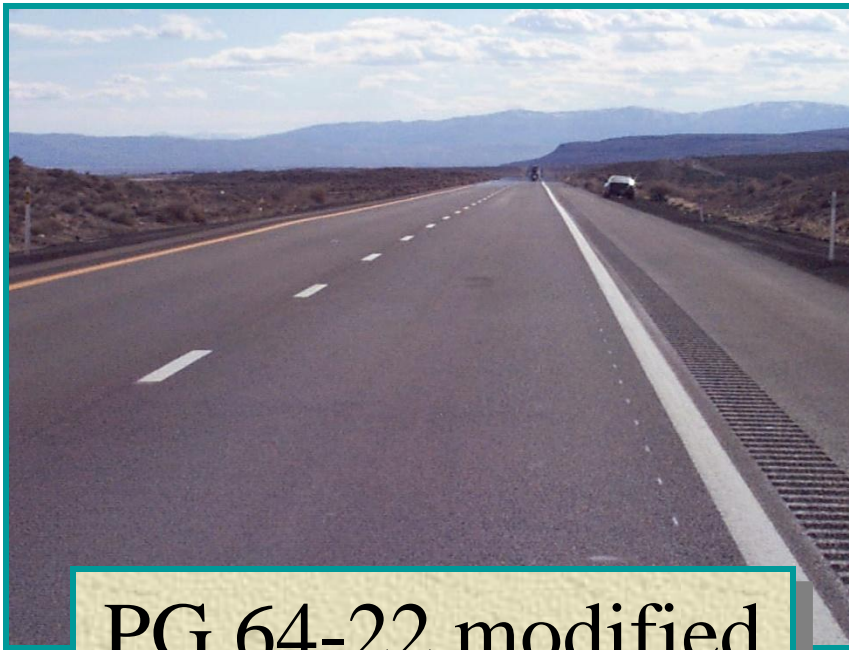


High Temperature Permanent Deformation (Rutting)

- Rutting is caused by the accumulated plastic deformation (flow) in the asphalt mixture with repeated application of loads at upper pavement service temperatures.
- Rutting is predominantly influenced by the aggregate and mix design.
- **Modifiers can stiffen the binder and provide a more elastic material.**

High Temperature Performance I-80, Nevada (FHWA)

- Same gradation - different binders.

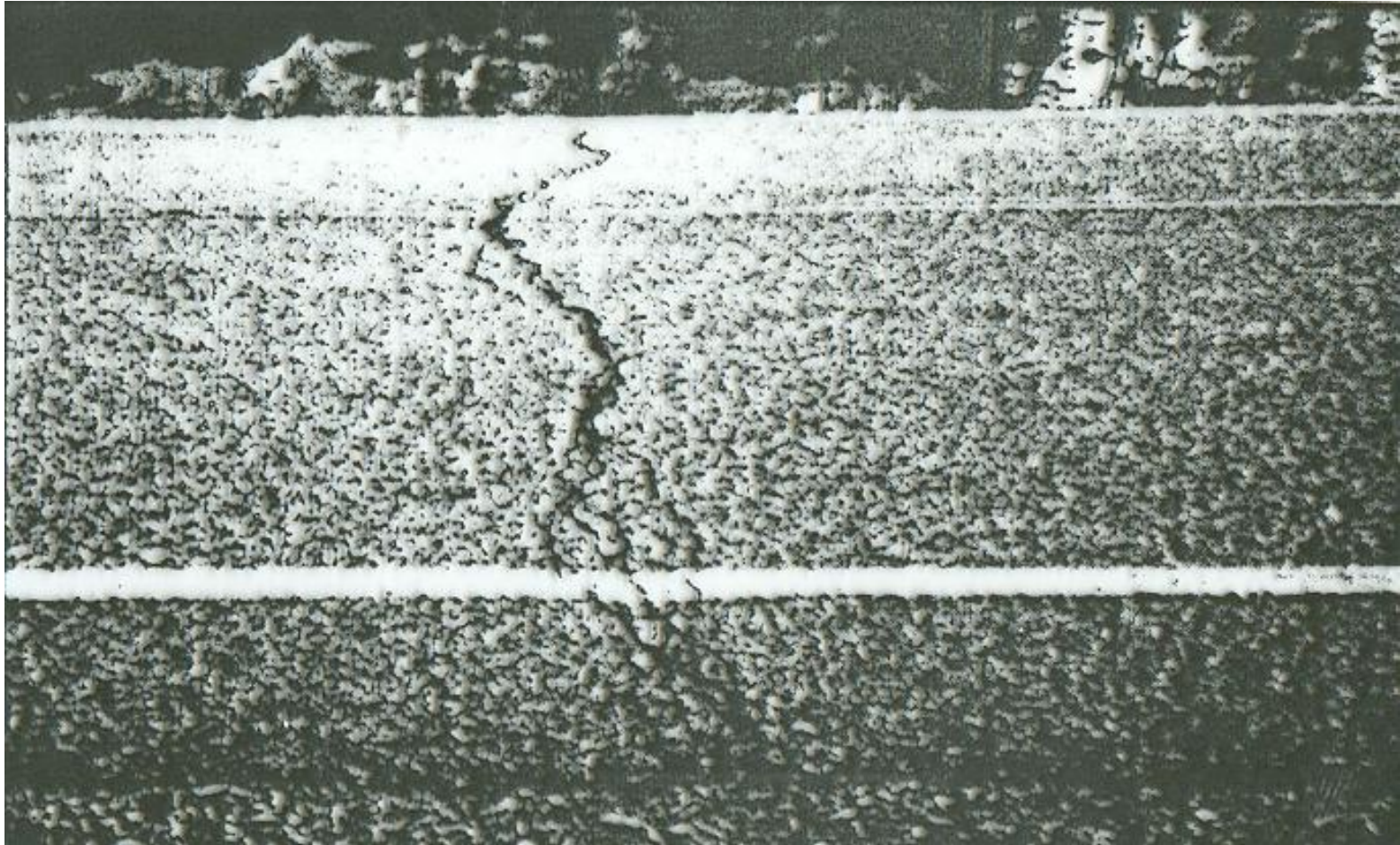


PG 64-22 modified
No rutting TG63



PG 64-22 unmodified
15mm of rutting TG67

Low Temperature Thermal Cracking



Low Temperature Thermal Cracking

- Thermal shrinkage cracking results from either a single thermal cycle where the temperature reaches a critical low temperature (Single Event Thermal Cracking) or from thermal cycling above the critical low temperature (Thermal Fatigue).
- Low Temperature Thermal Cracking is predominantly influenced by the binder properties.
- **Modifiers can improve the low temperature flexibility of the mixture.**

Load-Associated Fatigue Cracking



Load-Associated Fatigue Cracking

- Load-associated fatigue cracking is caused by continuous application of loads over a period of time.
- **Load-associated fatigue cracking is influenced by both binder and mixture properties.**

Aging

- Aging or embrittlement occurs during the mixing and laydown process and during the service life of the asphalt. The asphalt binder displays large increases in stiffness due to oxidation and volatile loss in the binder.

Carboxylic Acids



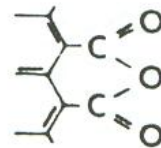
Ketones



Sulfoxides



Anhydrides



Stripping

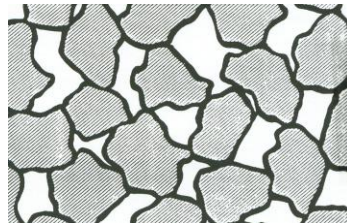
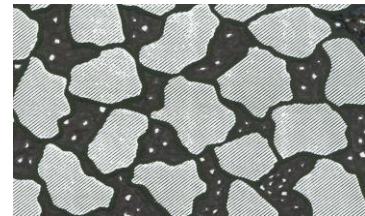
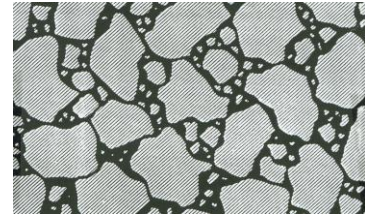
- Stripping is loss of bond between the aggregates and asphalt binder which typically begins at the bottom of the HMA layer and progresses upward.
- Stripping is driven by the aggregate's surface affinity for water.
- Additives can change the surface of the aggregate from hydrophilic (water-loving) to hydrophobic (water-hating).

Ideal Asphalt Binder and Asphalt Mixture

- Displays improved resistance to previously mentioned distresses.
- Improves lifecycle cost of the asphalt pavement.
- Improved Safety.

Use of Modified Asphalts

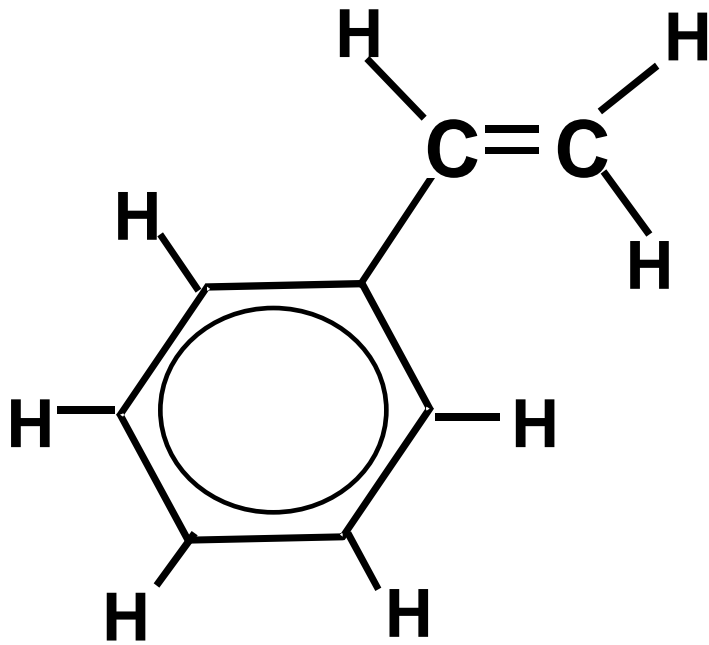
- Hot Mix Asphalt (HMA)
 - Dense Graded Mix
 - Stone Matrix Asphalt (SMA)
 - OGFC



What are **P**olymers?

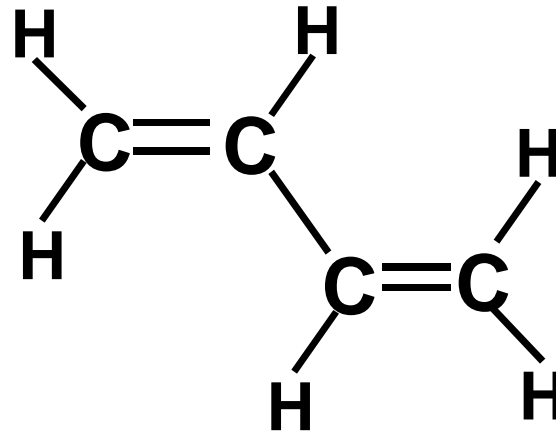
- Comprised of many small molecules
 - **Poly** = many
 - **Monomers** = small molecules or repeat units
- Monomers chemically react \longrightarrow larger molecules
 - **Water-based polymers** – latex form (SBR)
 - **Solvent-based polymers** – pellets, bale (SB-,SBS)
- Properties are determined by:
 - **Types and sequence of monomers**
 - **Molecular weight**

Typical Monomers



Styrene

$M_w \sim 104 \text{ g/mol}$

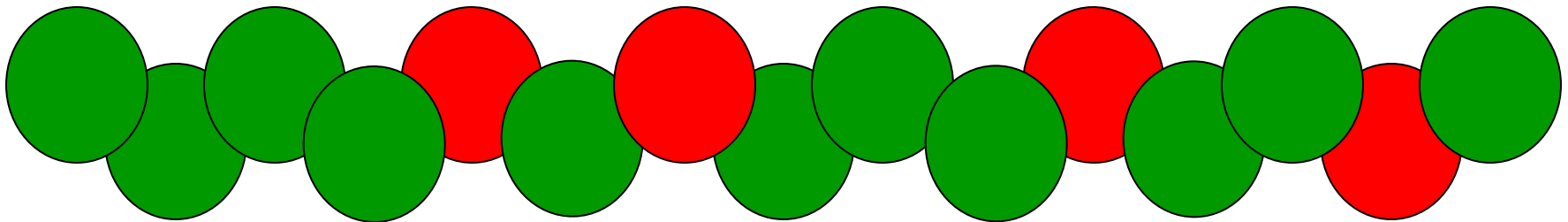


Butadiene

$M_w \sim 54 \text{ g/mol}$

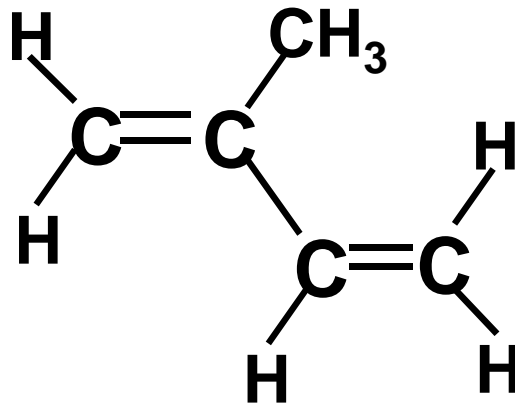
Polymers for Asphalt Modification

- 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



Polymers for Asphalt Modification

- 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

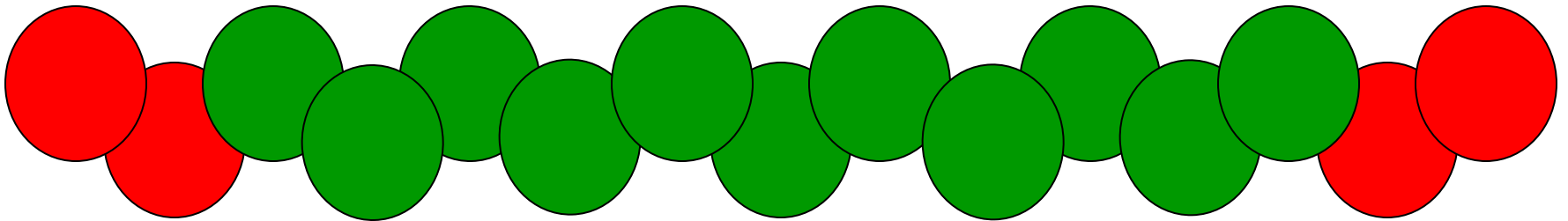


Isoprene
 $M_w \sim 68 \text{ g/mol}$

Polymers for Asphalt 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**

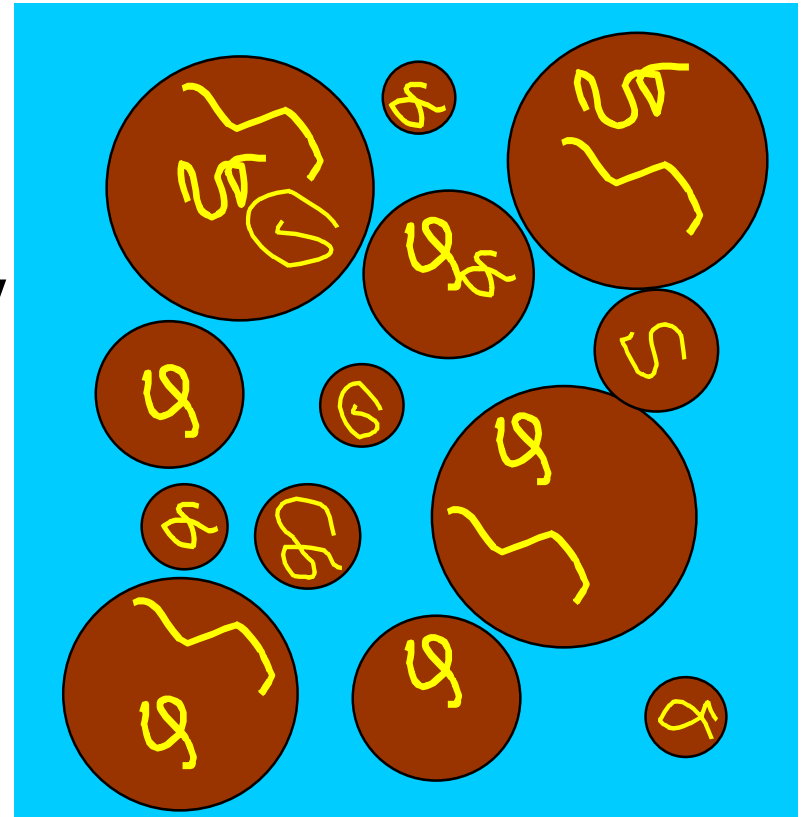
- Ethylene vinyl acetate (EVA) resin
- Vinyl acetate content ~ 20% to 40%
 - Low Tg, high melt temp due to crystallinity

- **Thermoset**

- Ground tire rubber (GTR)
- Mixtures of E-SBR, S-SBR, PBd, natural rubber
 - Depends on tire component
 - Tread, sidewall, innerliner (halobutyl),...

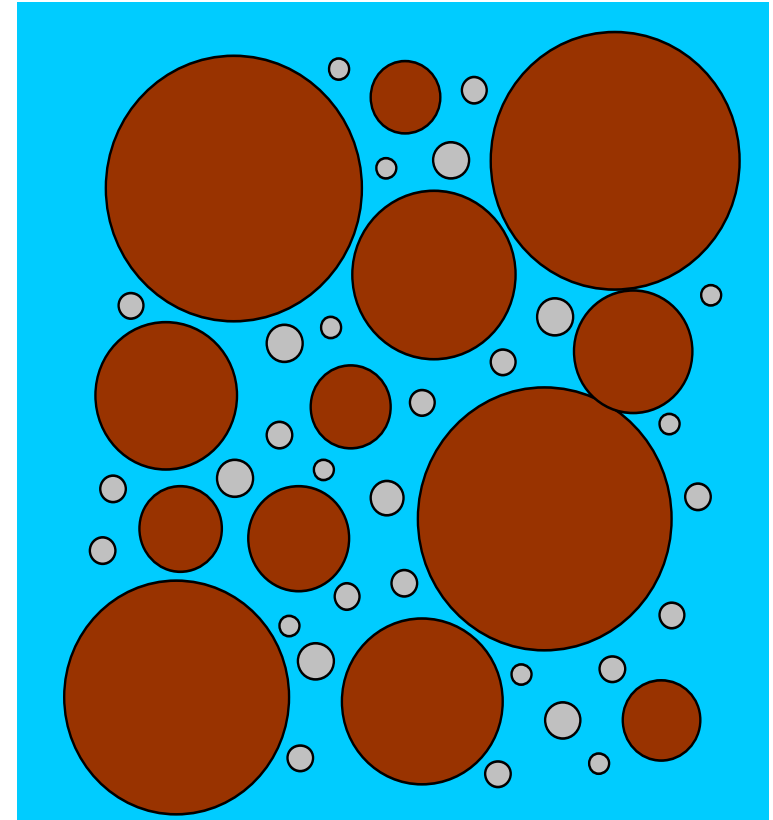
Polymer Modification of Asphalt Emulsions

- 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

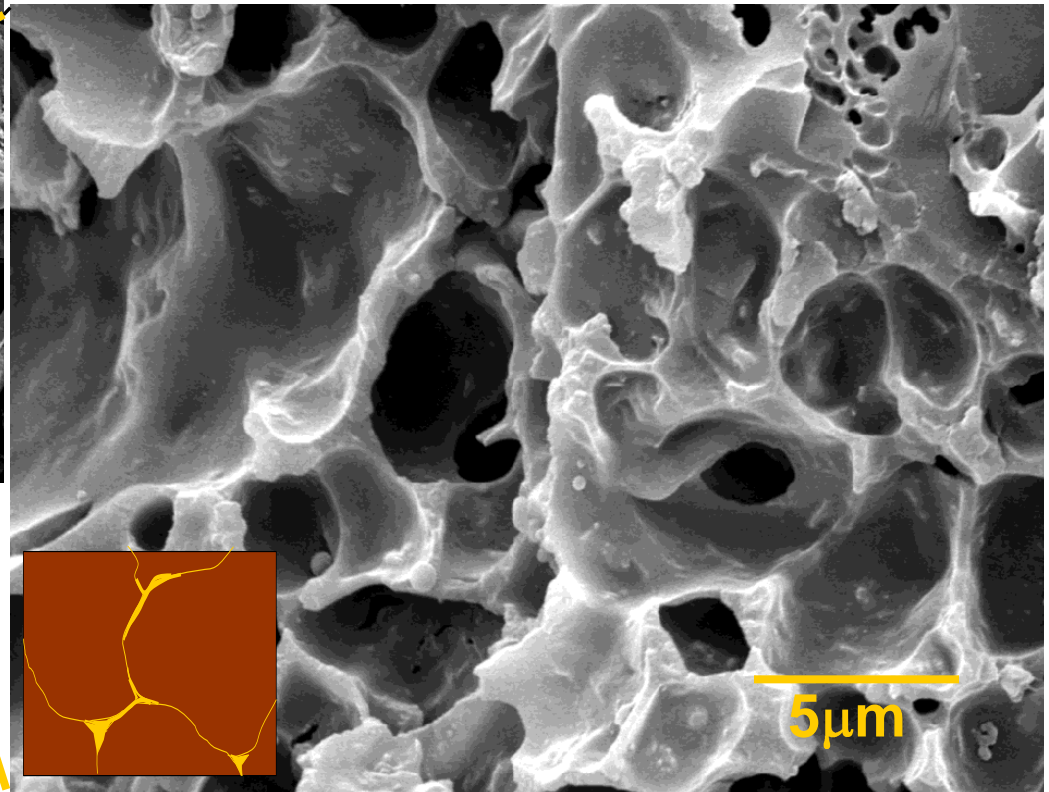
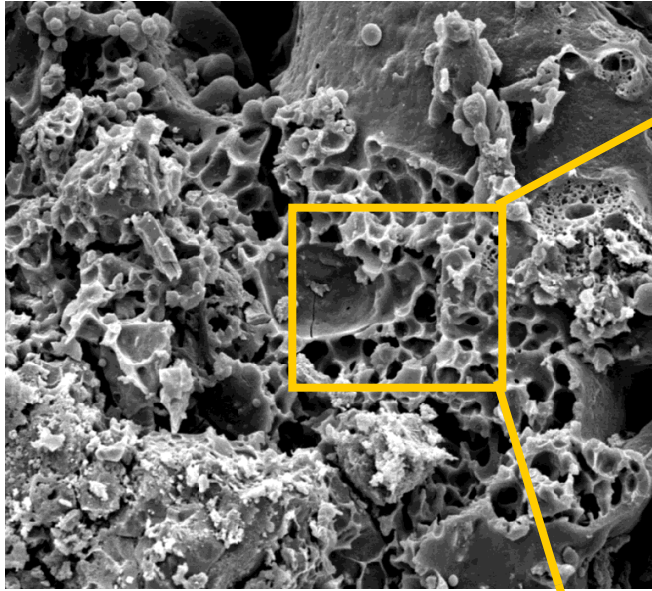


Polymer Modification of Asphalt Emulsions

- 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



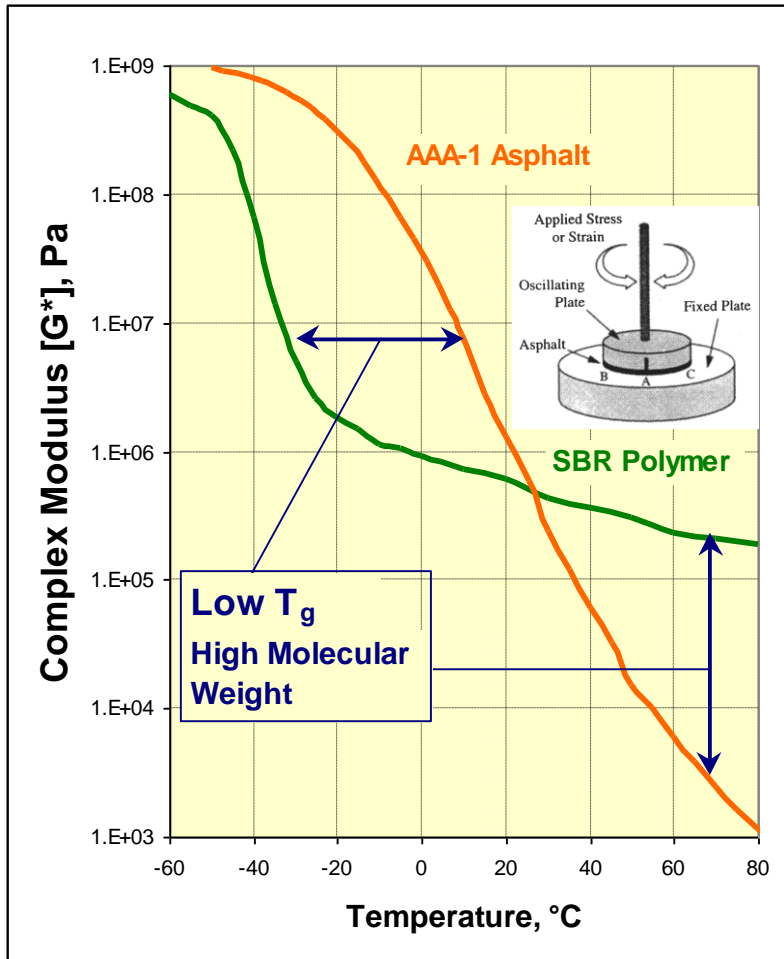
Micro Surfacing Polymer Morphology in Field



Texas State Highway 84

- Near Waco, TX
- Paved in 1998
- Samples taken in 2001

Viscoelastic Behavior Polymers + Asphalt

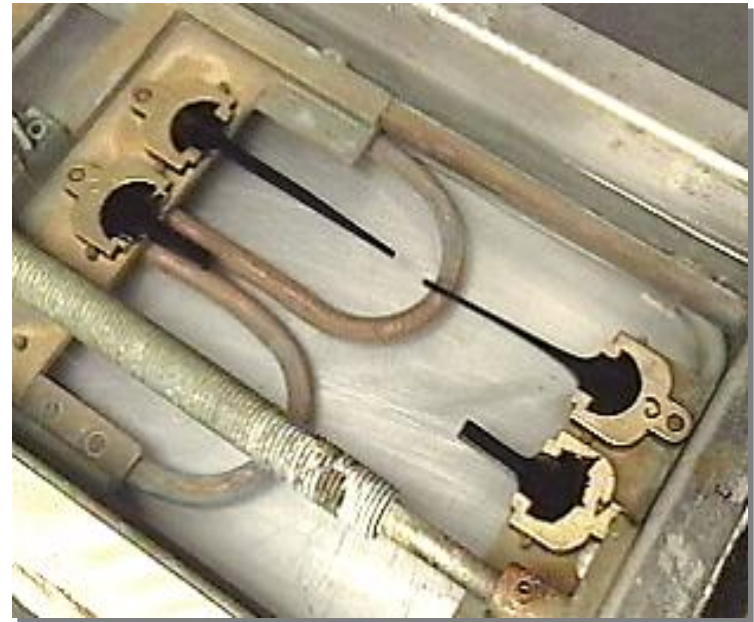
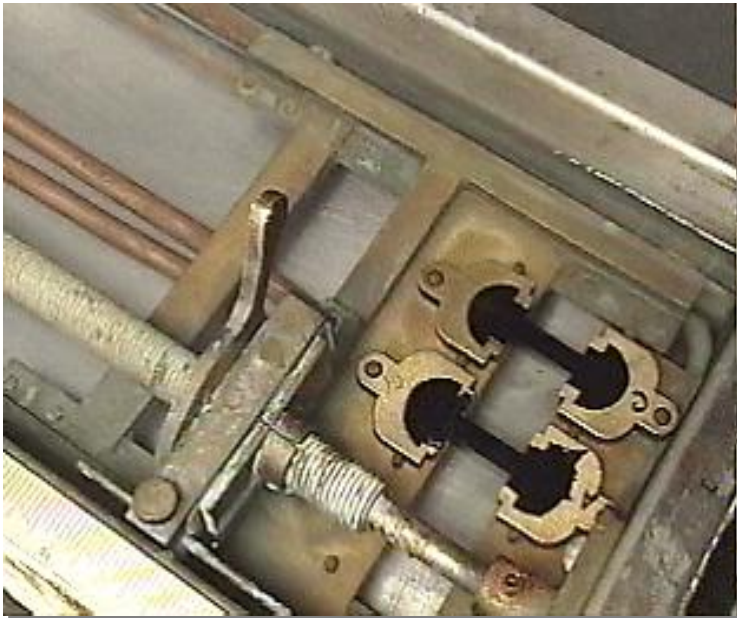
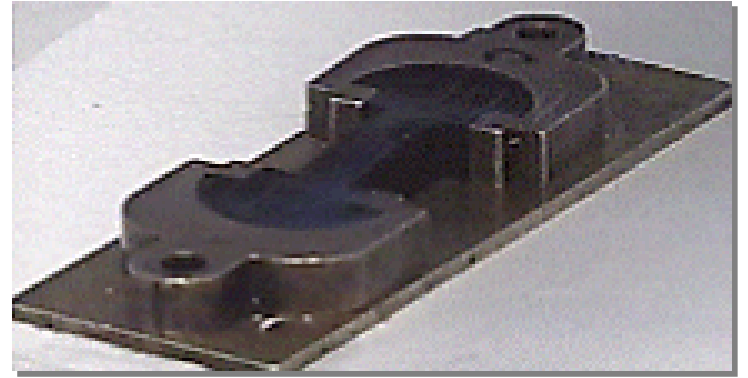


- $G^* = f(T) = \text{res. to deform.}$
- **Asphalt**
 - High G^* at low T – brittle
 - Low G^* at high T – viscous
 - $\Delta G^*(80^{\circ}\text{C} - 20^{\circ}\text{C}) = 1000x$
- **SBR Polymer**
 - Lower G^* at low T – flexible
 - Higher G^* at high T – elastic
 - $\Delta G^*(80^{\circ}\text{C} -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

Force Ductility & Elastic Recovery

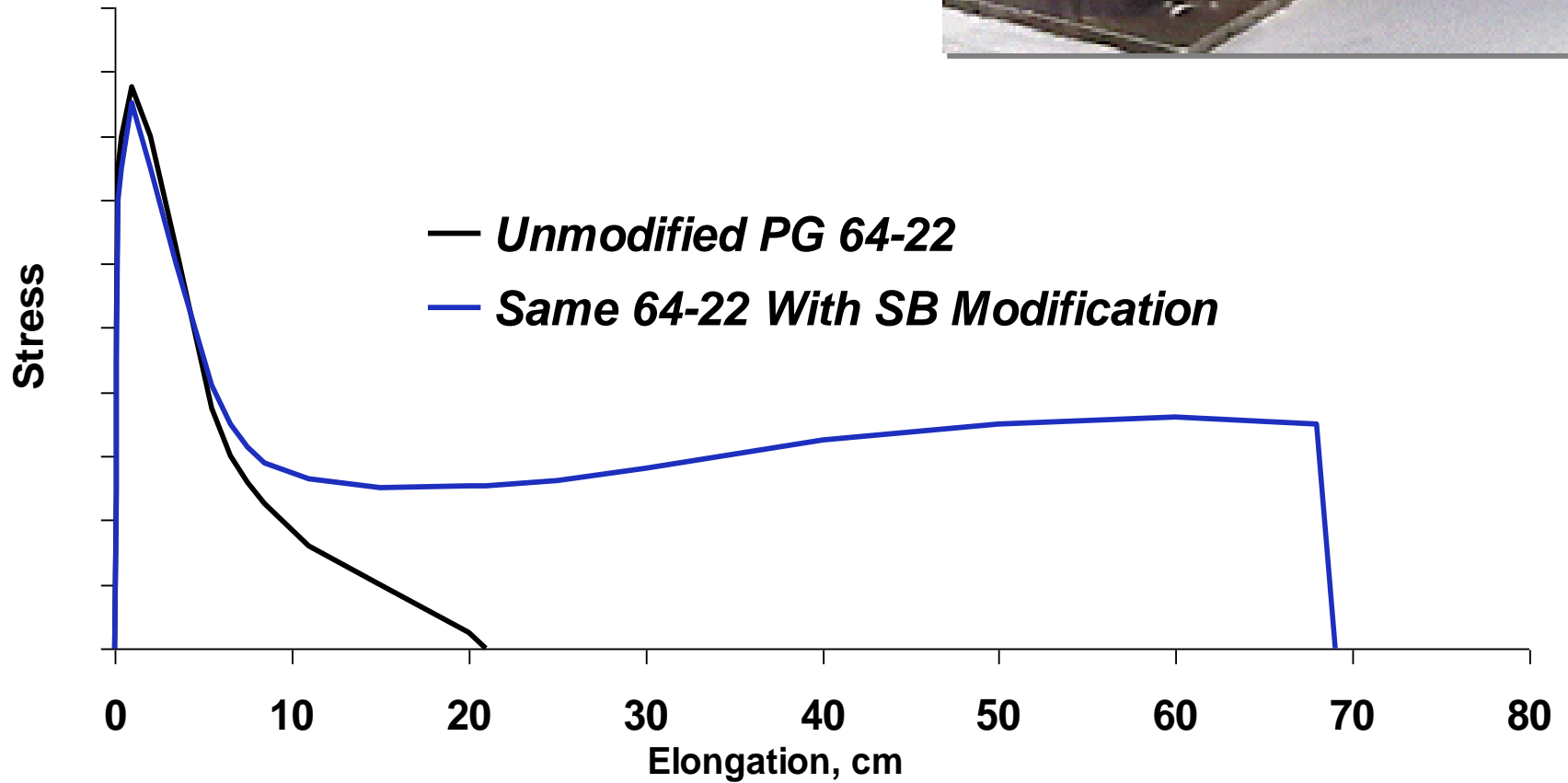
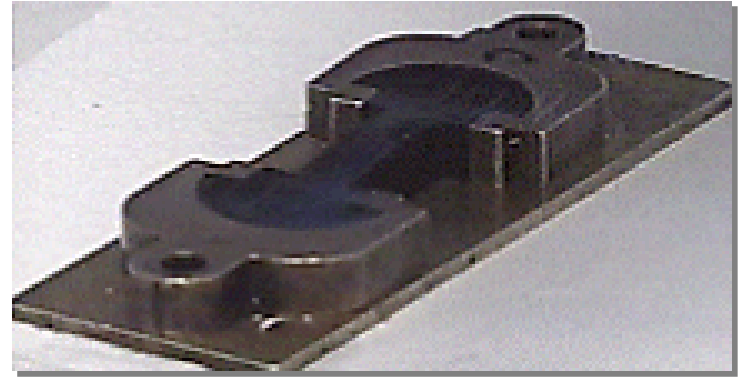


Force Ductility

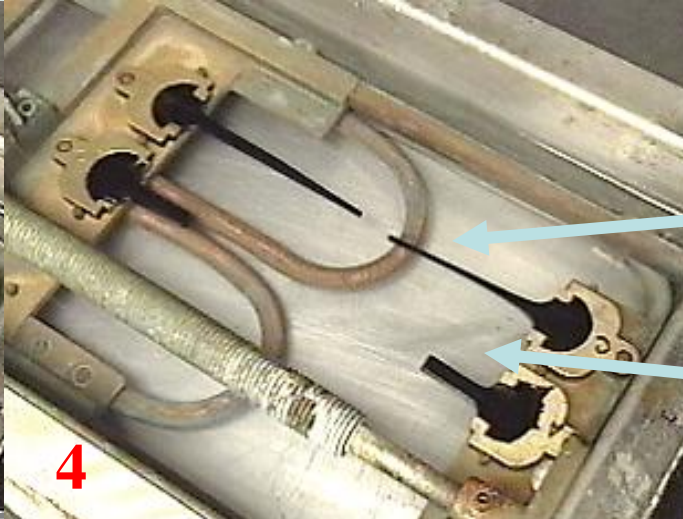
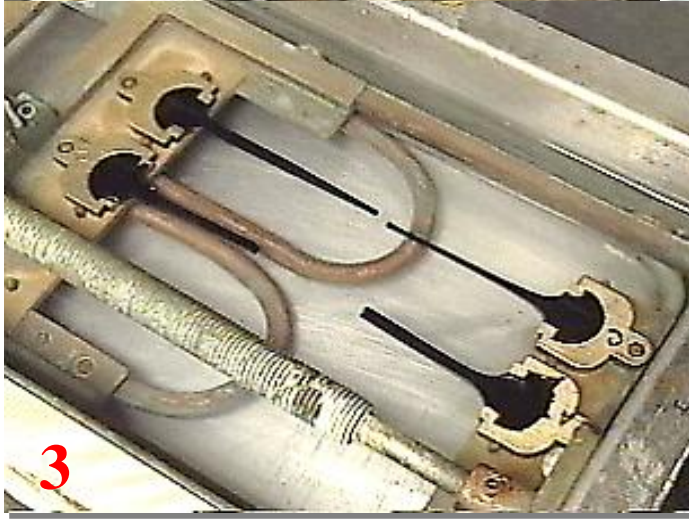
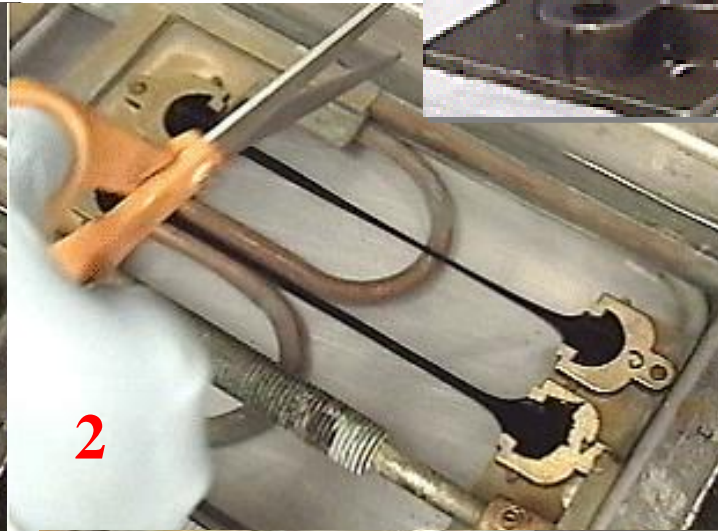
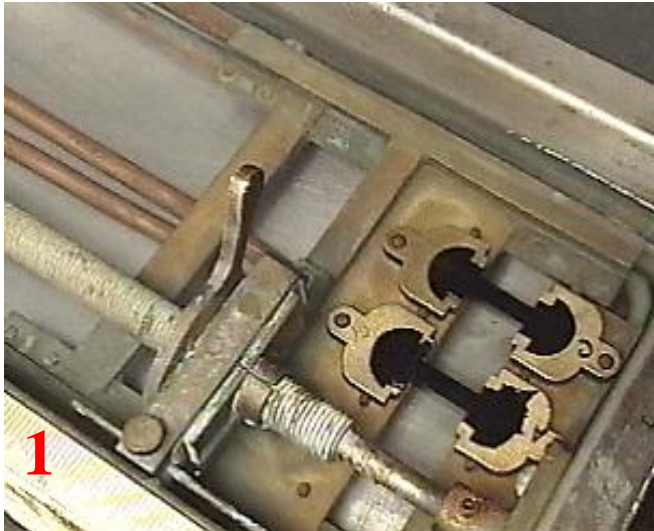
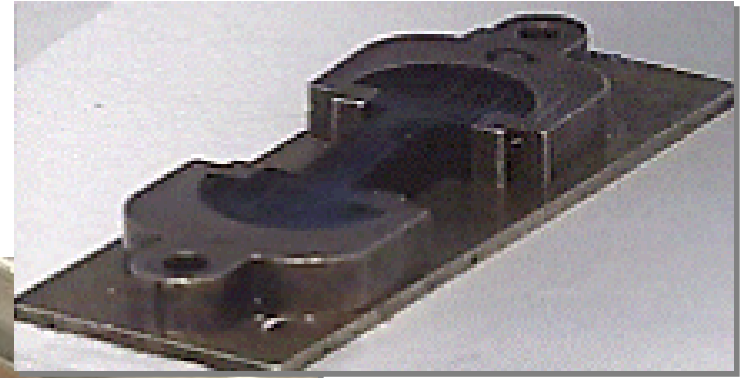


- Modified Binder should outperform neat binders by breaking at larger deformation

Force Ductility



Elastic Recovery



Neat doesn't recover

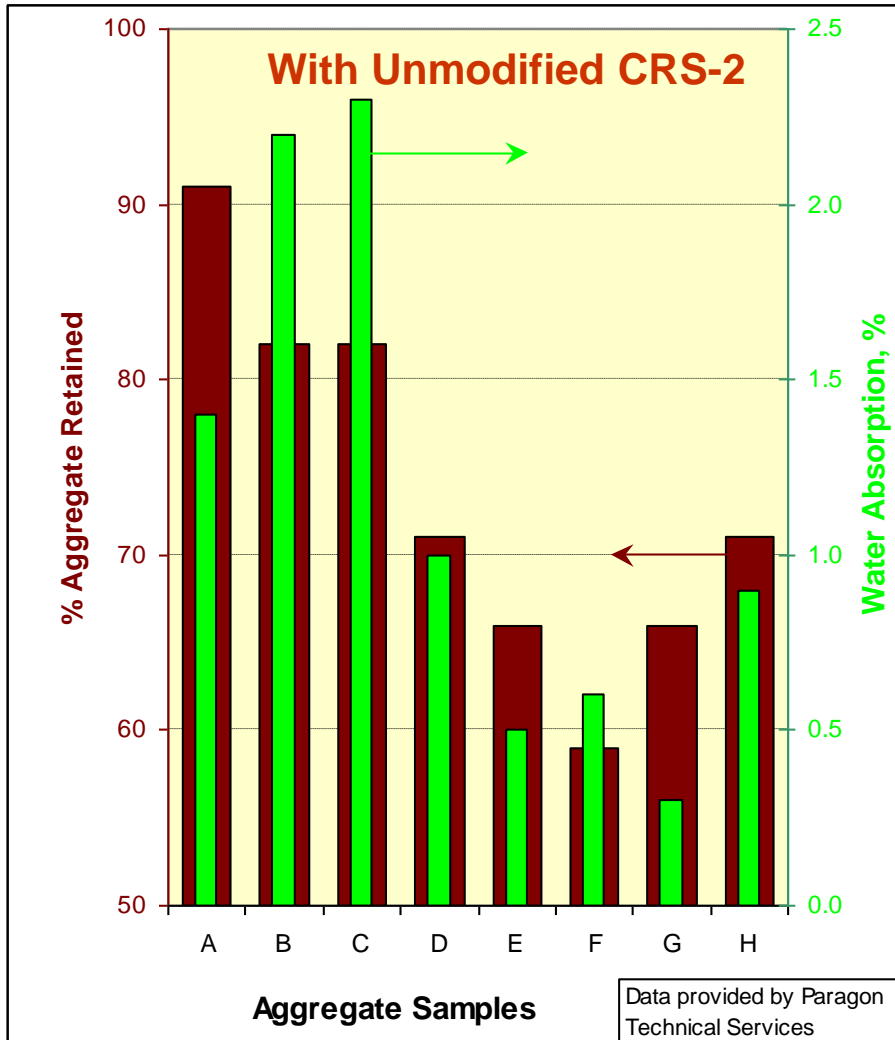
Modified recovers

Typical PG “Plus” Specs – PG 76-22

- Force Ductility Ratio, Spec. 0.30-0.35 min.
 - Break stress / Maximum stress
 - Tested at 4C
- Elastic Recovery, Spec. 65-75% minimum
 - ASTM D6084 – 10 cm pull, cut immediately
 - AASHTO T301 – 20 cm pull, wait 5 min.
 - Hybrid ASTM D6084/AASHTO T301
 - Original or RTFO-aged binder
 - Tested at 10C or 25C

Chip Seal – CRS-2

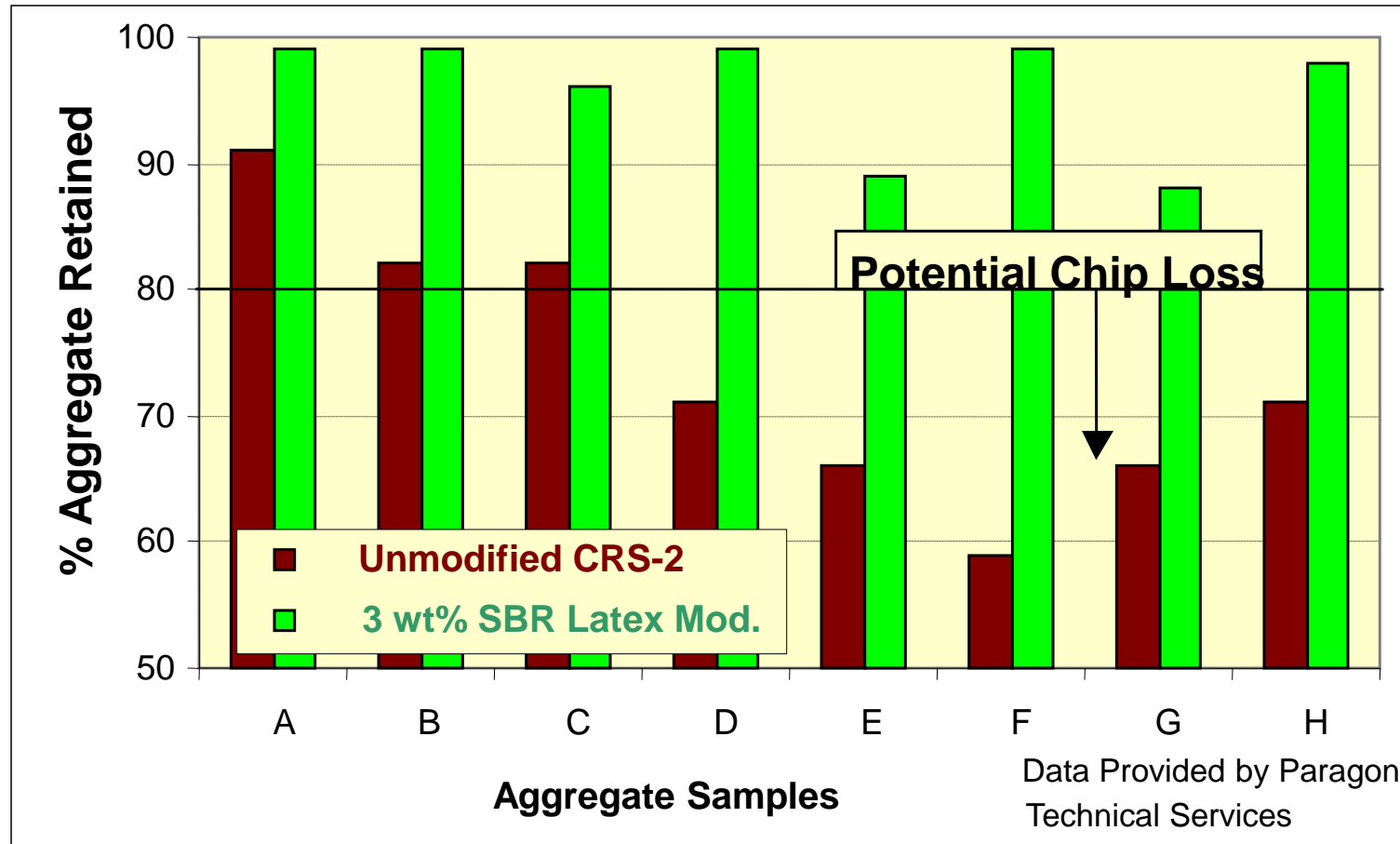
Early Strength Development



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

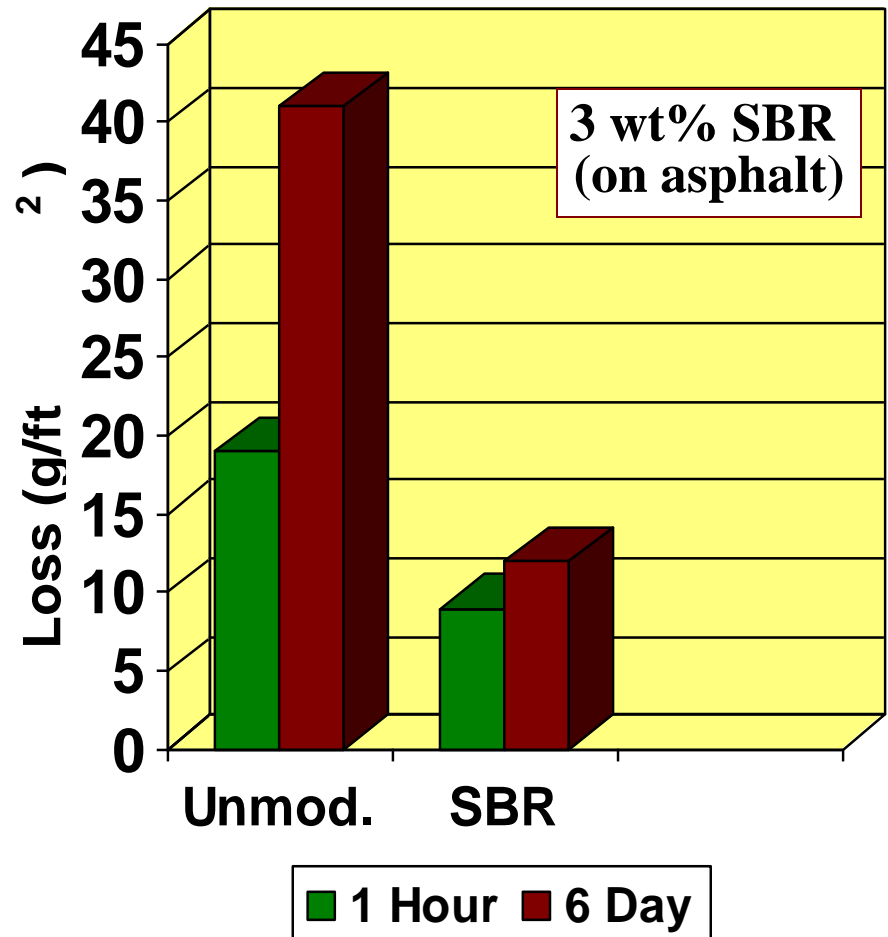
Early Strength Development – CRS-2P

ASTM D7000-04 – Sweep Test



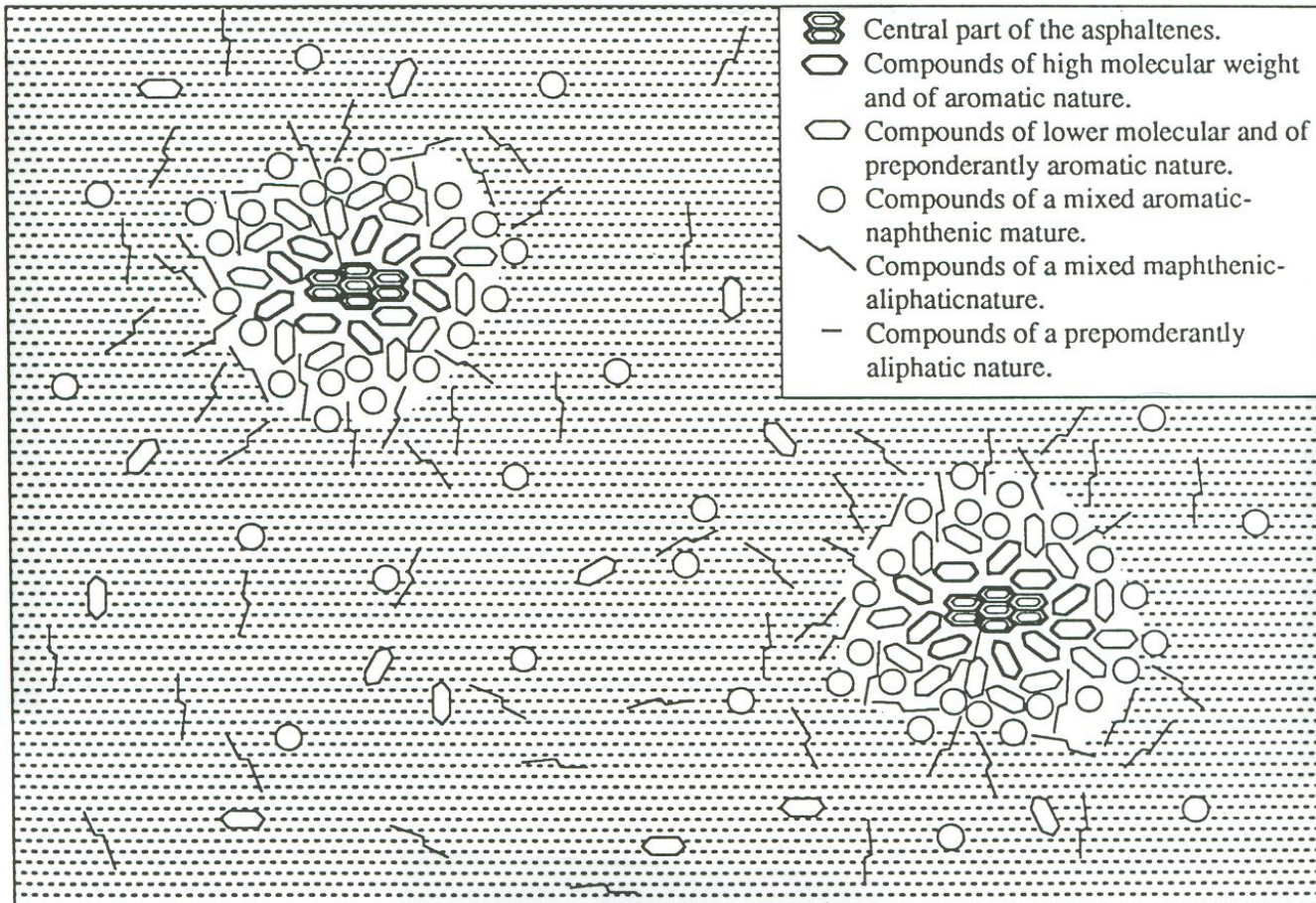
Wet Track Abrasion Loss – ISSA TB-100

- 50% reduction in loss
 - **one hour soak**
- 67% reduction in loss
 - **six day soak**
- Surface of mix
 - **tougher**
 - **more abrasion res.**
- Adhesion + water resist.
 - **improved**



Micellar Model for Asphalt

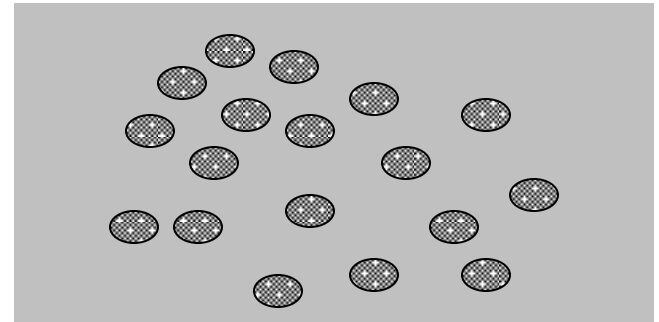
- Representation of peptized asphaltene micelles:



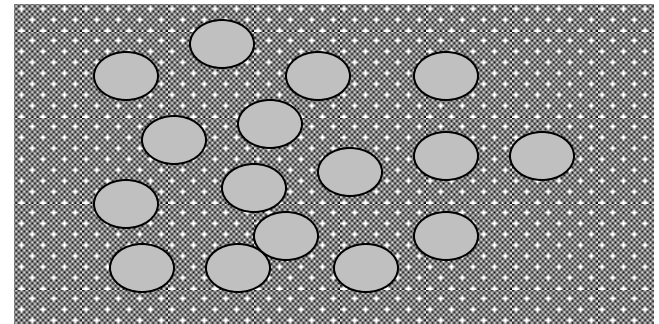
Hypotheses and Models Employed in SHRP Asphalt Research Program, SHRP-A/WP-90-008

Morphology of Polymer Modified Asphalt Cements

The polymer is a separate phase dispersed in the asphalt. (~1-5 wt% polymer) This is the most commonly observed system.

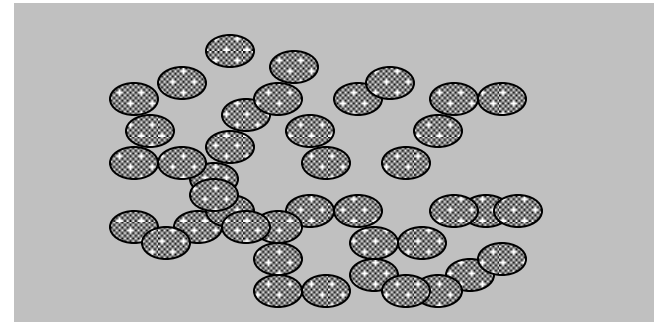


The asphalt is dispersed in the polymer phase. This usually happens at much higher loadings of polymer $\sim >7$ wt%.

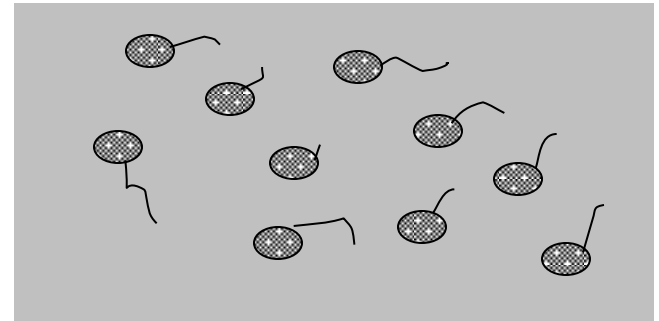


Physical and Chemical Polymer Networks

The polymer can form a network in the asphalt through physical entanglements. This behavior gives the polymer-modified asphalt more elastic behavior. An example of this would be a PMA with a high % of block polymers.



The polymer can be chemically bonded to certain functionalities on the asphalt molecule.



Separation

- My asphalt has waxes, asphaltenes, metals, salts, etc., yet it stays together. Why do my polymers separate?
- Because Flory-Huggins says so!

$$\square \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

$$\square \Delta G_{\text{mix}}/RT = (\phi_A/X_A)\ln\phi_A + (\phi_B/X_B)\ln\phi_B + \chi_{AB}\phi_A\phi_B$$

- where
- $\chi_{AB} = (\delta A - \delta B)^2/RT$

Compatibilities

- Compatibility can be defined several ways.
 - Compatibility can be defined as the state of dispersion between two dissimilar components.
 - For asphalt cements: The dispersion of the relatively aromatic, polar, associating molecules in a less aromatic, less polar solvent phase.
 - For Polymer Modified Asphalt Cements: The extent of dispersion between the asphalt cement and the modifier. This determines to a large extent the physical properties of the binder.

Separation Test

- Use to measure the separation of polymer from the asphalt.
- 50 grams, toothpaste tube, upright for 48 hours at 163C.
- Remove from oven, quench, run test on top third and bottom third of container.
 - G^* or viscosity
 - $G^*/\sin \delta$
 - Phase Angle
 - Softening Point

Separation Test



Vertical tube held at elevated temperature

Separation & Ring + Ball Test



- ***Tube cooled***
- ***Cut into thirds***
- ***Tested top & bottom (here, for ring & ball softening point or viscosity)***



Microscopy of PMA

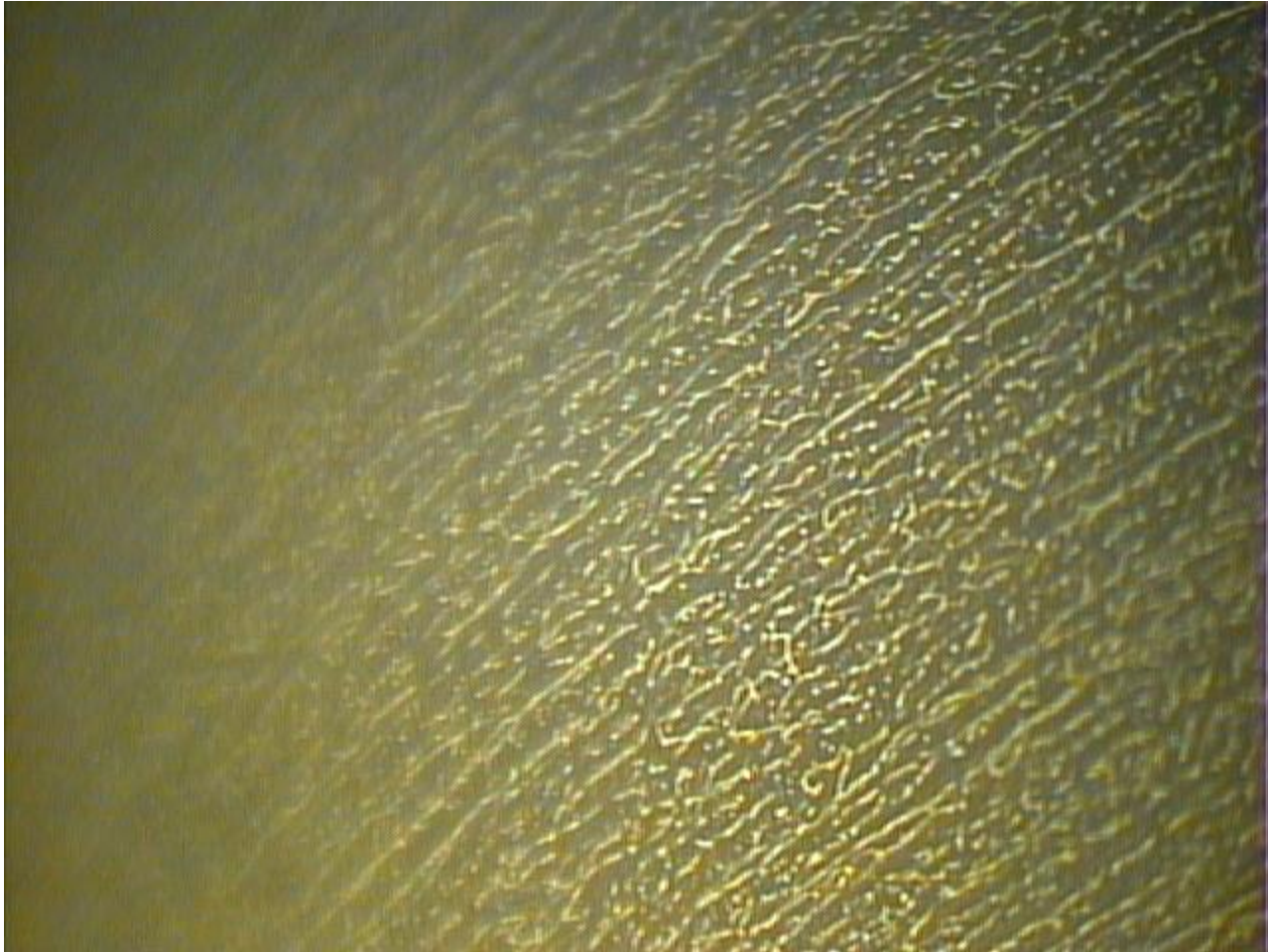
- There are numerous methods used to define the macro relationships of modified asphalt systems.
- These tests are more subjective than objective, but provide a clear visual indication of compatibility.

Fluorescence Microscopy



Initial Dispersion of Polymer in Asphalt

Fluorescence Microscopy



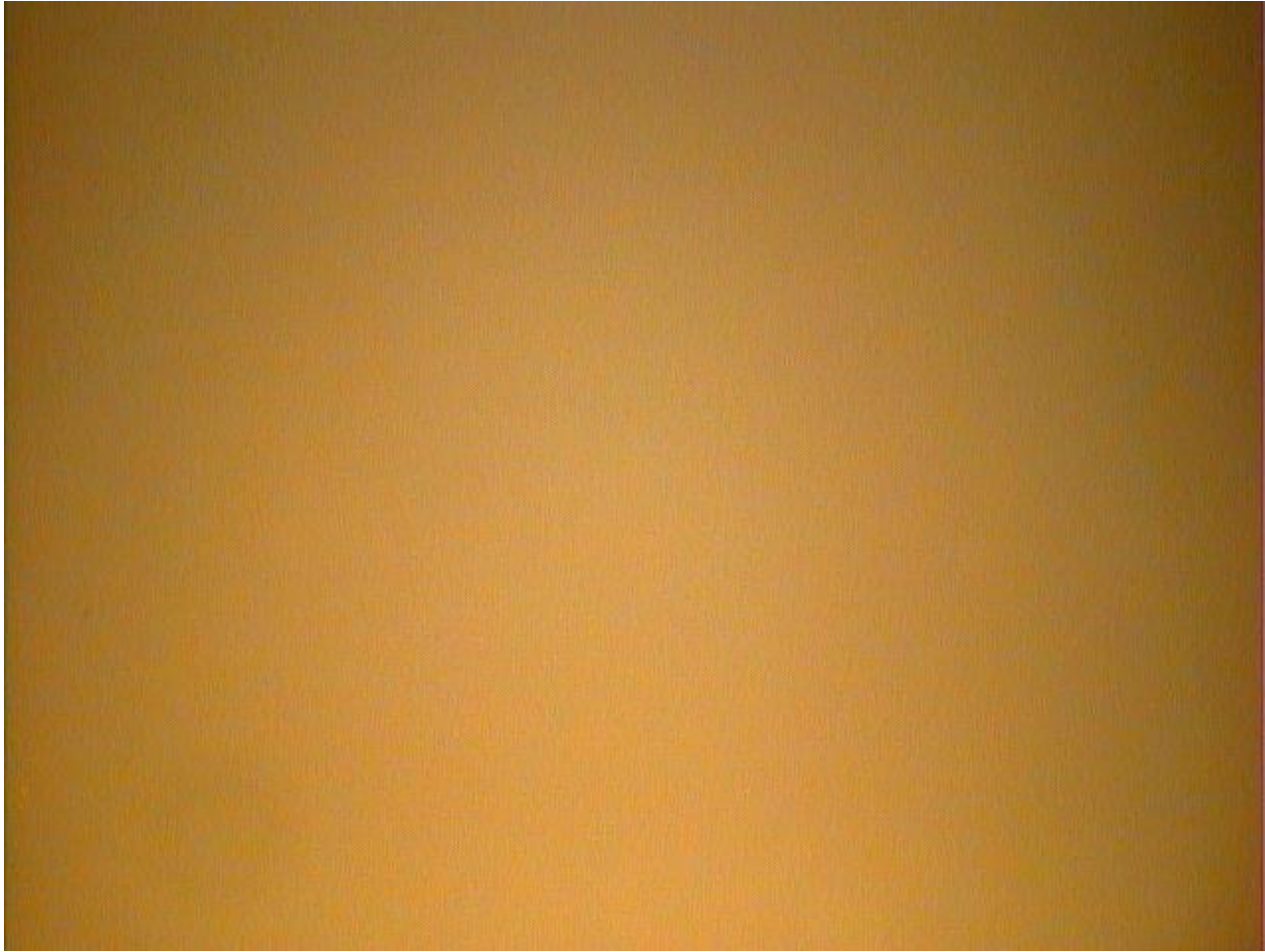
Formation of Polymer Networks in Asphalt

Fluorescence Microscopy

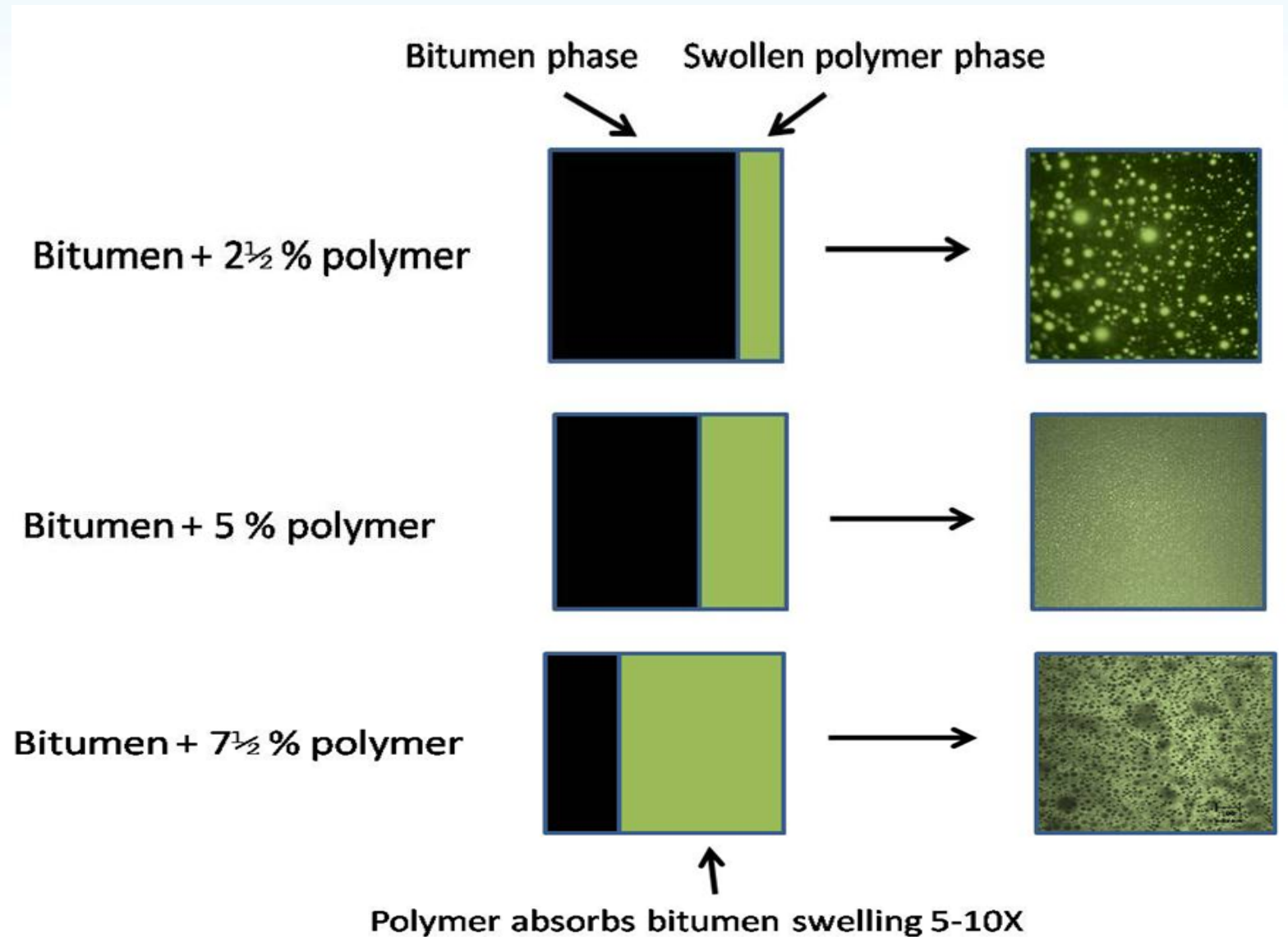


Maturing of Polymer Network in Asphalt

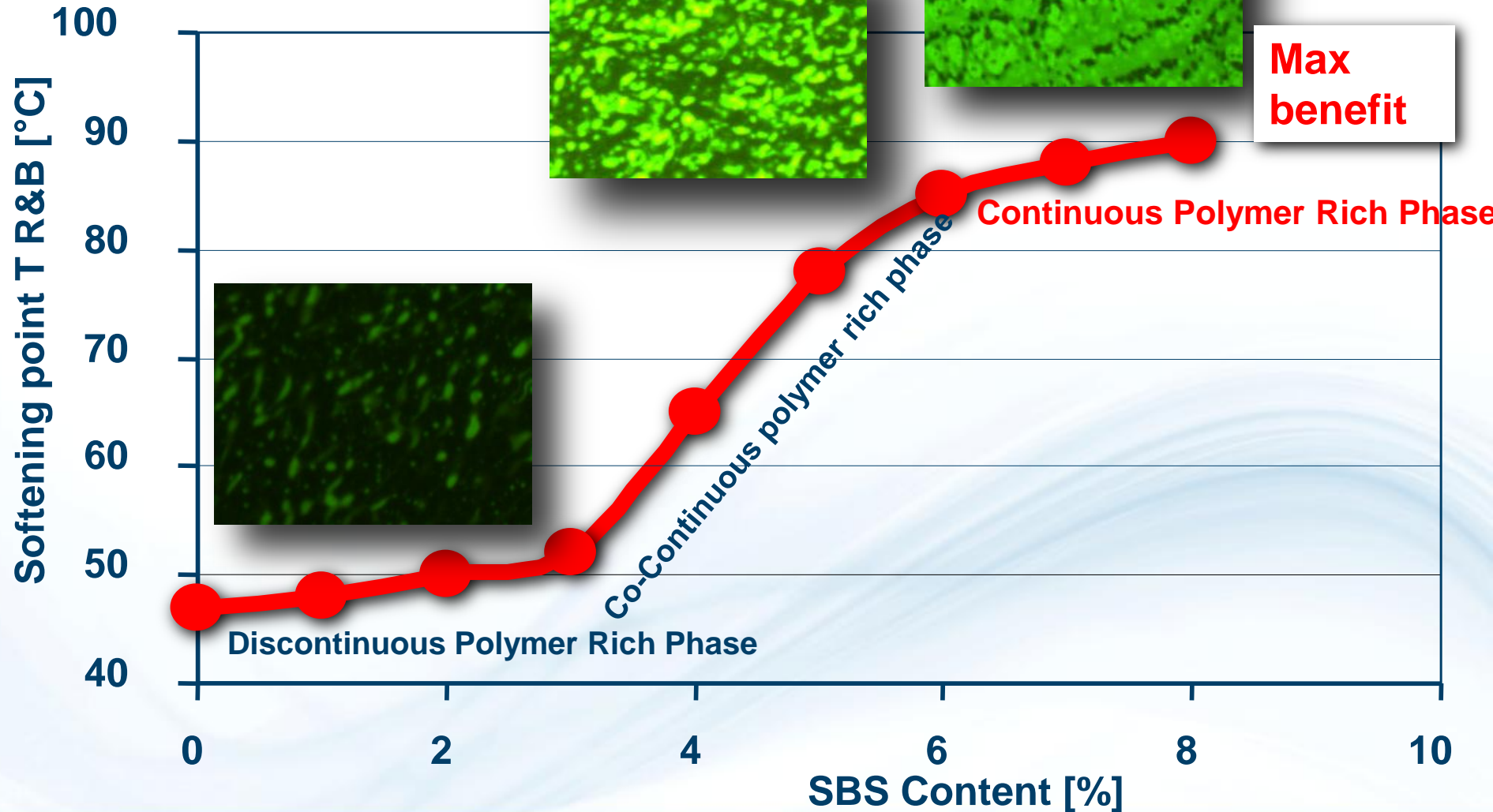
Fluorescence Microscopy



Fully Cured Polymer in Asphalt



Asphalt - Modified Polymer



Handling Modified Asphalts



- Between 5-20% of all asphalts are currently modified
- Most modified binders are in the PG 64-28 to 76-22 range
- Be safe and follow manufacturer's recommendations

Handling Modified Asphalts



- Mixing PMA with other asphalts can cause the asphalt to fail to meet the PG grade requirements
- Reduce contamination at the terminal
 - Tanker truck empty before loading at terminal
 - Load from correct loading arm at terminal

Handling PMA at the Plant

- Reduce contamination at the HMA plant
 - Pump into correct tank at HMA plant
 - Use dedicated tanks, if possible
 - If dedicated tank is not available
 - Empty tank as much as possible if previous material was different
 - Add 2 or 3 full loads of PMA before testing and/or using the material in the tank
- Diluted PMA may fail PG grade!!!

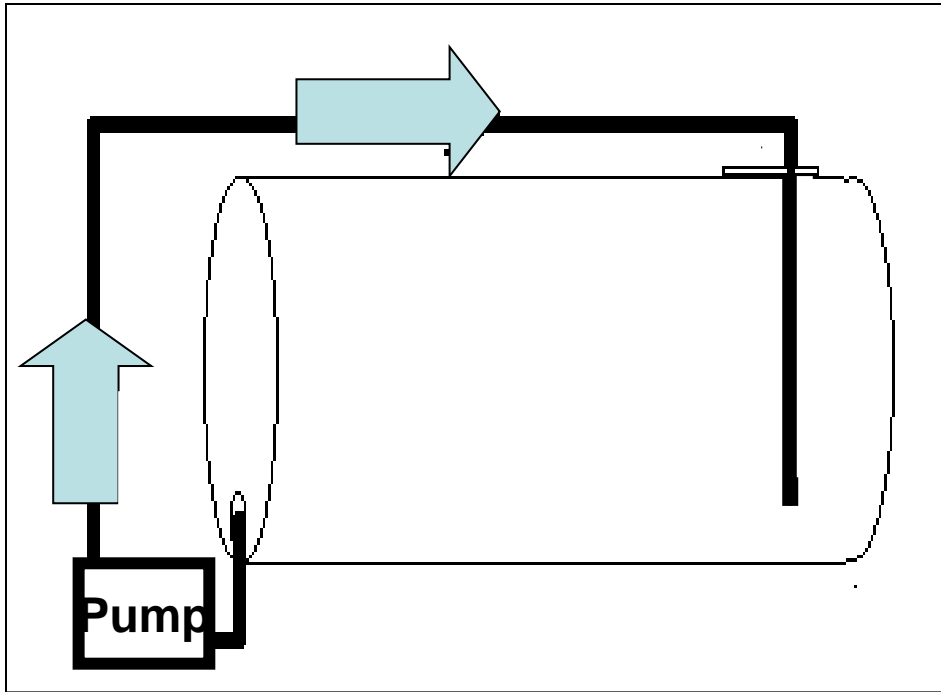


Handling PMA at the Plant



- Vertical or Horizontal tanks?
 - Very few PMAs requires agitation to prevent separation
 - Vertical tanks provide more efficient agitation
 - Check with supplier
- Check and maintain proper temperatures

Proper Circulation in Horizontal Tanks



- Suction and return lines at opposite ends of tank to completely circulate material
- Return line near bottom of tank to prevent oxidation

Handling PMA at the Plant

- **BEWARE OF MIXING MODIFIED ASPHALTS FROM DIFFERENT SUPPLIERS!!!**



- Different suppliers may use different polymer technologies
- Differing technologies may not be compatible
- Polymer separation may occur

Handling PMA at the Plant

- **BEWARE OF USING DIRECT-FIRE HEATERS WITH MODIFIED ASPHALTS!!!**



- Direct-fire heat tubes may develop hot spots
- Hot spots will immediately destroy the polymer network in the asphalt

General Guidelines for Storage and Mixing Temperatures

PG Binder	Storage Temperature (°F)	Mixing Temperature (°F)
64-22	285-315	265-320
70-22	300-325	280-330
76-22	315-340	285-335
Extended Storage	<275°F	

Source: EC-101

Long Term Storage of Modified Binders



- If storing PMA for longer than 60 days, turn heat down or off
- Lower temperatures minimize danger of damaging the PMA

Long Term Storage of Modified Binders



- Re-heating PMA binders
 - Bring temperature up slowly
 - If material has been held over the winter, heat incrementally 20 degrees increase at a time
 - Allow 3 or 4 days to get material up to circulation temperature
- As a precaution, you may want to test before using after winter shutdown

Contractor QC Plan



- Contractors need to establish QC plan to prevent PG asphalt contamination and failing test results
 - Identify all hardware – label or number
 - Tanks
 - Pumps
 - Piping
 - Valves
 - Sample points
 - Heat system
 - Establish standard procedures and hardware settings for asphalt flow into storage and into HMA plant