An Introduction to Modified Asphalt Binders

Presented by:

The Association of Modified Asphalt Producers

Alaskan Asphalt Pavement Summit
Anchorage, AK – Nov, 2013

Modified Asphalt Binders

The Basics covered include:

- ✓ Background
- ✓ Chemistry
- ✓ Polymer modification
- ✓ Modified Emulsions
- ✓ Handling
- ✓ Lay down
- ✓ Field Experience
- ✓ Testing for Modified
- ✓ Testing to AASHTO M320
- ✓ Rheology Basics

Outline

- Introduction to Asphalt Modification
- Polymer Chemistry/Modifier Basics
- Polymer Compatibility/Dispersion in Asphalt
- PMA Storage and Mixing/Compaction Temps
- PMA Benefits – AI Study
- Superpave M320 “Plus” Testing and MSCR

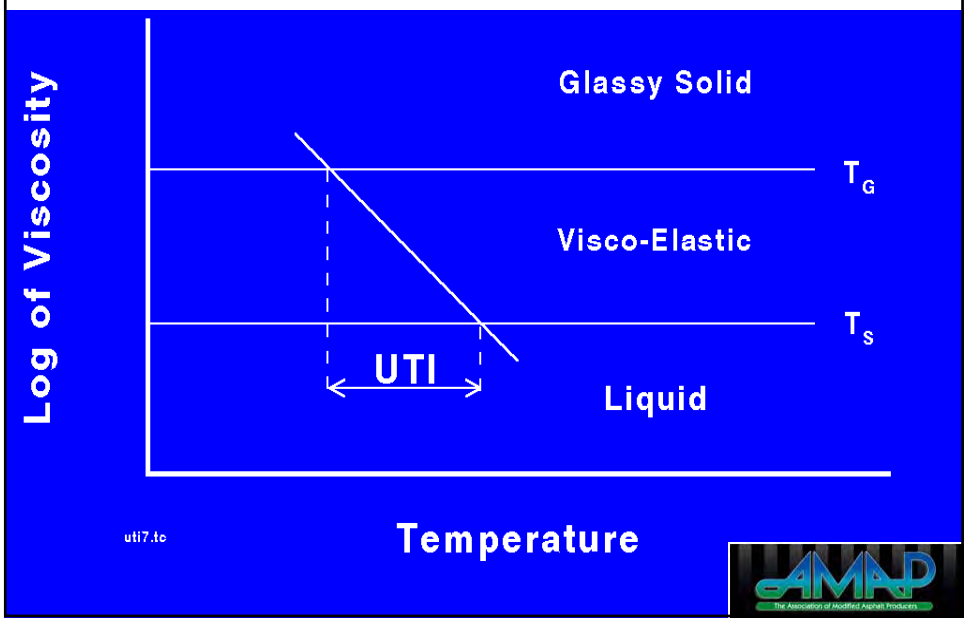
Reasons for Asphalt Modification

- 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.

Useful Temperature Interval

- Maximum to Minimum temperature range where the binder is expected to perform properly.
- Often referred to as the 'True Grade' or "Continuous Grade" of the binder.
- The Rule of '92'.

Useful Temperature Interval (UTI)



Distresses in Asphalt Pavements

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

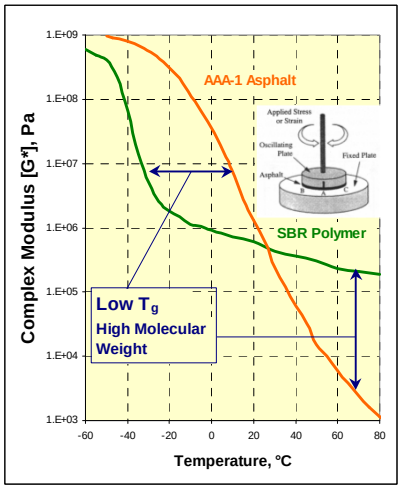
High Temperature Permanent Deformation (Rutting)

- 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.**

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.**

Viscoelastic Behavior – Asphalt vs SBR Polymer Film

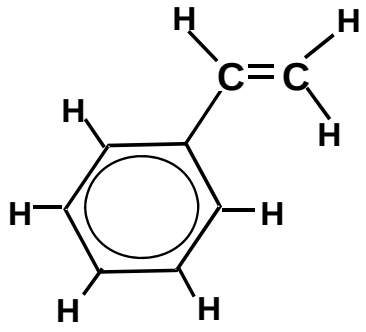


- G* = f(T) = res. to deform.
- **Asphalt**
  - **High G* at low T – brittle**
  - **Low G* at high T – viscous**
  - **ΔG*(80°C – 20°C) = 1000x**
- **SBR Polymer**
  - **Lower G* at low T – flexible**
  - **Higher G* at high T – elastic**
  - **ΔG*(80°C – 20°C) = 10x**

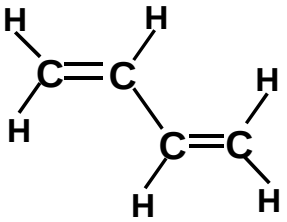
What are **Polymers**?

- Comprised of many small molecules
  - **Poly = many**
  - **Monomers = small molecules or repeat units**
- Monomers chemically react ➡ 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



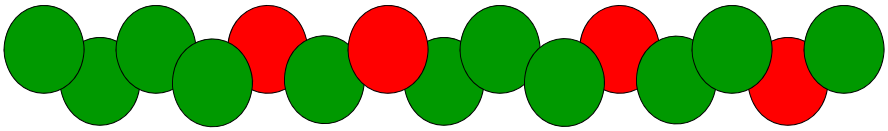
Styrene
M_w ~ 104 g/mol



Butadiene
M_w ~ 54 g/mol

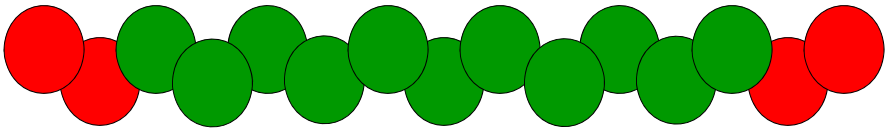
Polymers for Asphalt Modification

- **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

- **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**



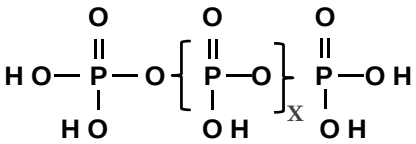
Polymers for Asphalt Modification

- **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),…**

Chemical Modification

- Polyphosphoric Acid (PPA)
- Air Blown or catalytically blown.
- Others

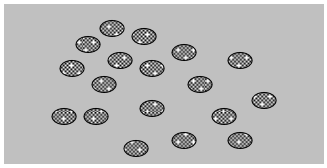
Polyphosphoric Acid (PPA)



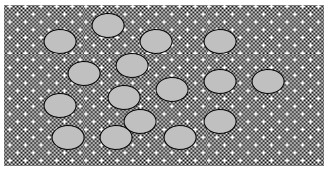
- PPA Chemical Attributes
  - Different from Orthophosphoric acid
  - No Free Water
- 105% and 115% most common
- Increases asphalt stiffness, improves rutting resistance, expands PG range to meet Superpave specs
- Does not affect low-temperature grading
- Modification does NOT involve oxidation and actually slows it down
- Retards binder aging

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.

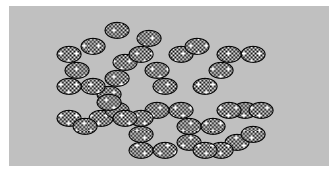


The asphalt is dispersed in the polymer phase. This usually happens at much higher loadings of polymer ~>7 wt%.

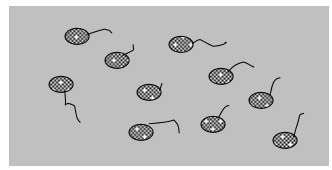


Physical and Chemical Polymer Networks

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.



Elvaloy (+PPA)
Reactive Elastomeric Terpolymer (RET)

Separation

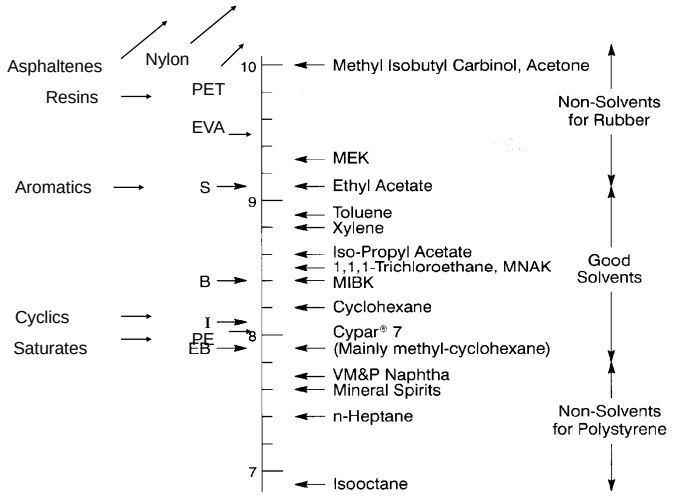
- My asphalt has waxes, asphaltenes, metals, salts, etc., yet it stays together. Why do my polymers separate?
- Because Flory-Huggins says so!

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

$\Delta G_{mix}/RT = (\varphi_A/X_A)\ln\varphi_A + (\varphi_B/X_B)\ln\varphi_B + \chi_{AB}\varphi_A\varphi_B$

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

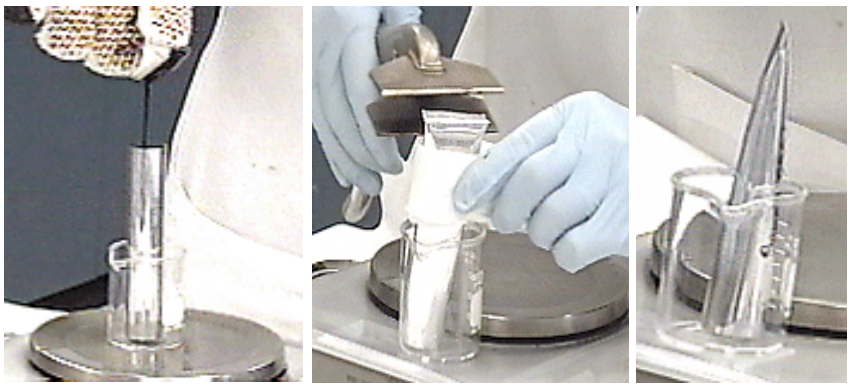
Solubility Parameters



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



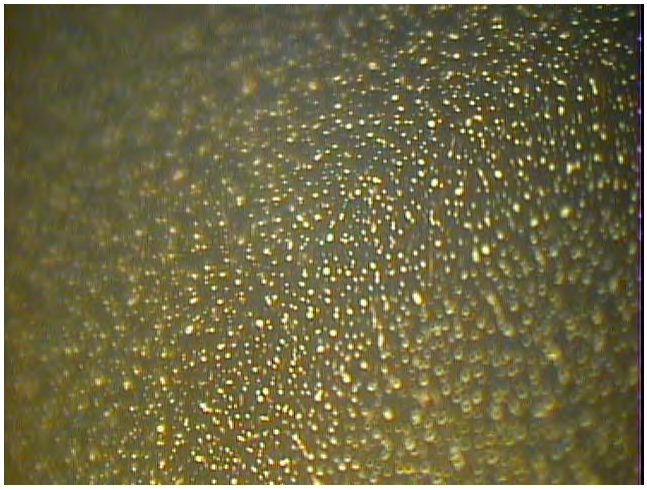
Vertical tube held at elevated temperature

Source Koch Materials

Microscopy of Various Types of Systems

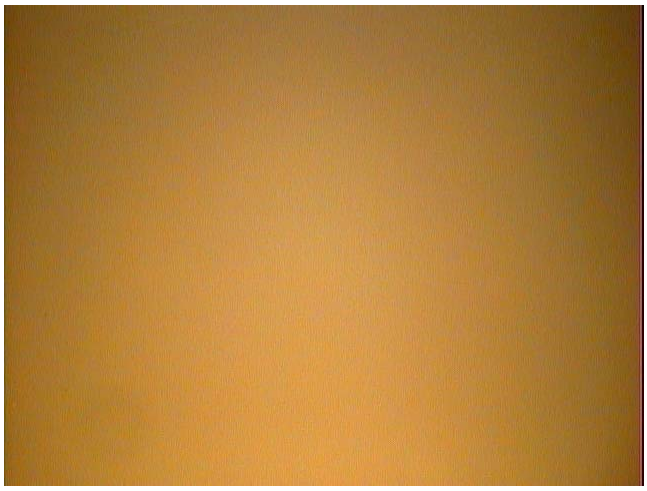
- There are numerous methods used to define the macro relationships of modified asphalt systems.
- These tests are more subjective than objective, but provide a clear visual indication of compatibility.

Fluorescence Microscopy



Initial Dispersion of Polymer in Asphalt

Fluorescence Microscopy



Fully Cured Polymer in Asphalt

“Dispersion” in Asphalt

- What is the appropriate scale?
- Millimeter scale – visible particles
- Micrometer scale – HMAC film thickness
- Nanometer scale – molecular size

- Working Premise – to truly be considered a binder modifier, the modifier must disperse at approximately the scale of HMAC film thickness and behave more as a liquid than as a solid at mixing and compaction temperatures.

Mix & Compaction Temperatures

- Current practice is to follow supplier recommendations

- NAPA & Asphalt Institute use EC101

General Guidelines for Storage and Mixing Temperatures

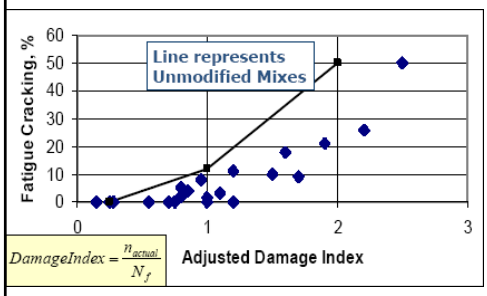
PG Binder	Storage Temperature (°F)	Mixing Temperature (°F)
64-22	285-315	265-320
70-22	300-325	280-330
76-22	315-340	285-335
Extended Storage	<275°F	

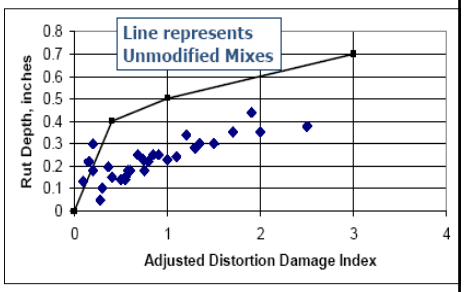
Source: EC-101

Asphalt Institute Study

- Titled “PMA for Enhancing HMA Performance”
- Two objectives:
  - Quantify the effect of using PMA as compared to conventional mixtures in terms of increasing pavement life and reducing the occurrence of surface distress.
  - Identify the conditions or site features (for example, traffic levels, layer thickness, climate, etc..) that maximize the effect of PMA on performance

Modified versus Unmodified Performance

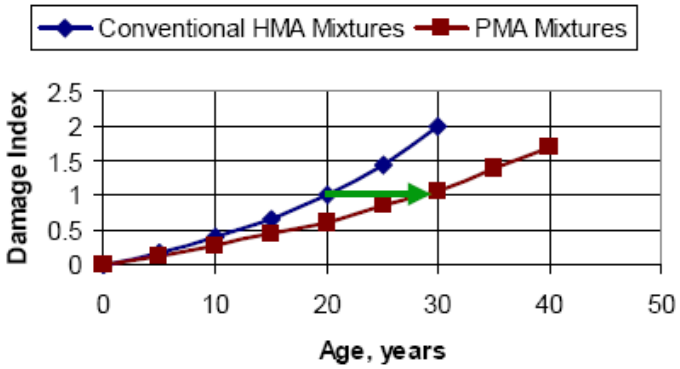




Polymer Modified HMA shows a substantially lower Rut Depth and less % Fatigue Cracking

*Harold von Quintus, "Polymer-Modified Asphalts- Enhancing HMA Performance," AMAP Annual Meeting, February 10, 2004

Expected Service Life Increase for a 20-year Design*



*Harold von Quintus, "Polymer-Modified Asphalts- Enhancing HMA Performance," AMAP Annual Meeting, February 10, 2004

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

Superpave Binder Specification AASHTO M320

Framework was developed as part of the Strategic Highway Research Program *(SHRP). Initially released as AASHTO MP1*

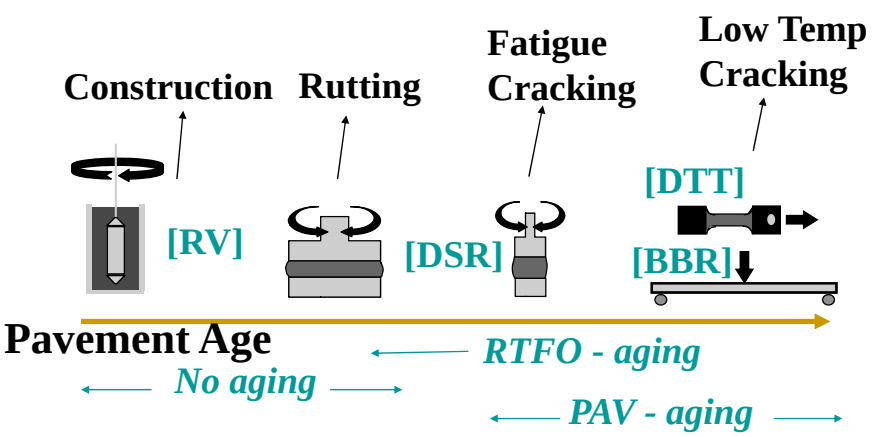
Performance-based specification for the purchase of asphalt binders used in hot-mix asphalt.

Measure of the rheological properties of the binders over a wide range of temperatures, loading, and aging conditions.

Background:
Pre-Superpave Shortcomings

- Viscosity Grading
  - Viscous effects only
- Penetration Grading
  - Empirical measure of viscous & elastic effects
- No low-temperature properties measured
- No consideration of long term aging
- Problems with modified asphalt characterization
- Specification proliferation

Superpave Binder Equipment



Empirical Tests for Binders

All used to identify “qualities” of specific modified asphalt binders

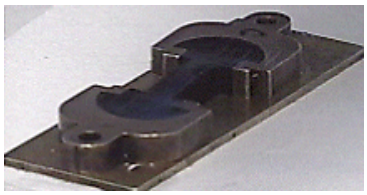
•Forced Ductility
•Elastic Recovery
•Toughness & Tenacity

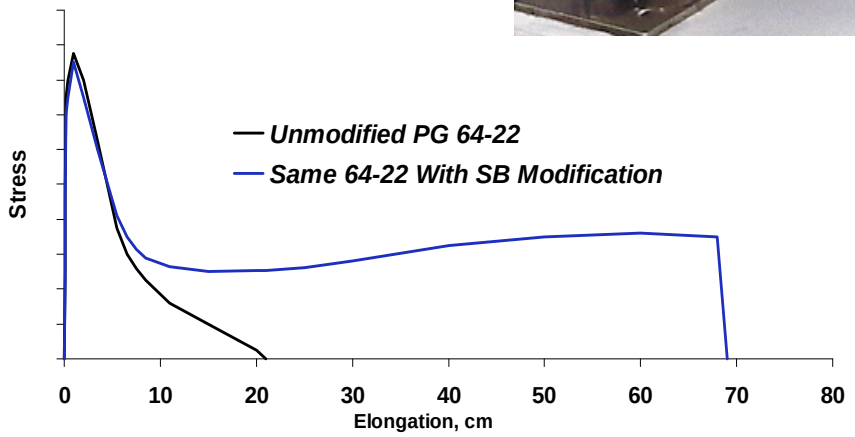
All have a non-uniform stress/strain relationship which make it impossible for true comparisons or understanding of engineering material properties.

Specification proliferation has become a costly problem.
- Many different procedures, temperatures, and loading times are used across the Country.
- The same tank is tested for all required procedures.
- Forced to formulate to the most difficult procedure

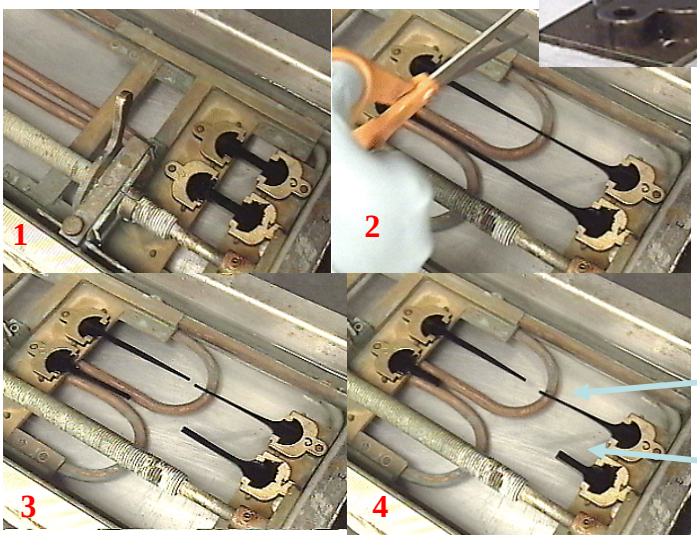
Forced Ductility & Elastic Recovery

Forced Ductility





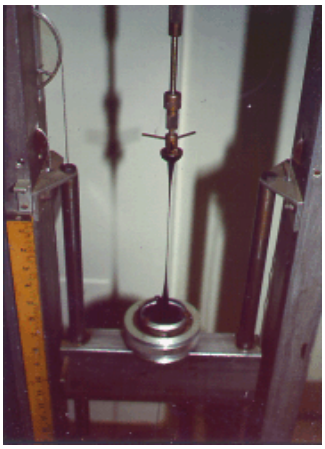
Elastic Recovery



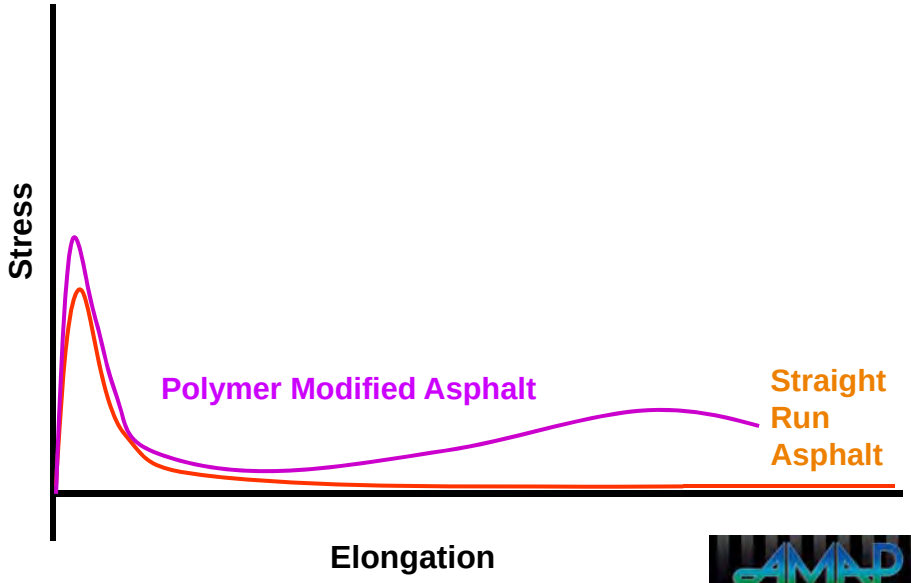
Neat doesn't recover

Modified recovers

Toughness & Tenacity



TNT



Typical “Plus” Results for Mod. Binder

Example - PG76-22

- Forced Ductility Ratio, Spec. 0.30-0.35 min.
  - Break stress / Maximum stress at 4C
- Elastic Recovery, Spec. 65-75% minimum.
  - Pull 10/20cm, wait/no wait 5 mins, cut, measure recovery after 60 mins, test at 10C or 25C, original or RTFO residue
- Toughness, 110 in-lbf min
  Tenacity, 75 in-lbf min
  T&T is normally specified for SBR.- in-lbf or N-m at 25C

MSCR (TP 70) vs. Modulus

Modulus

- $G = \frac{\text{Stress}}{\text{Strain}}$

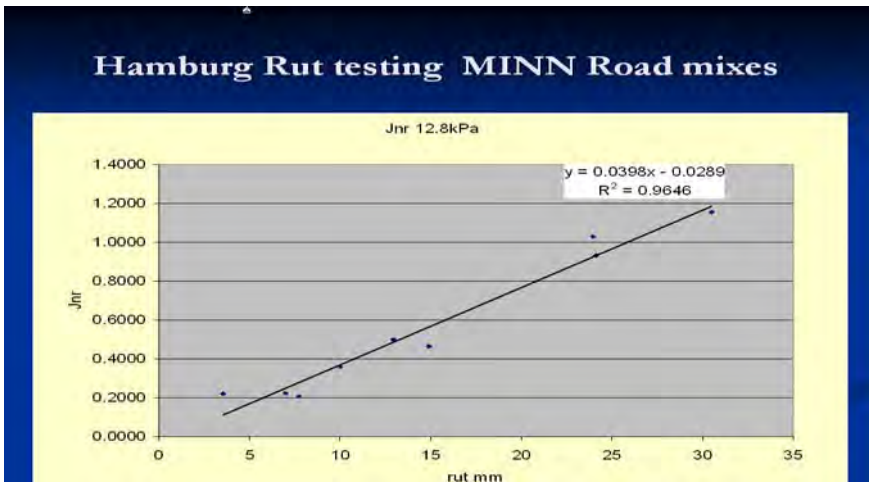
Compliance

- $J = \frac{\text{Strain}}{\text{Stress}}$

Multiple Stress Creep Recovery

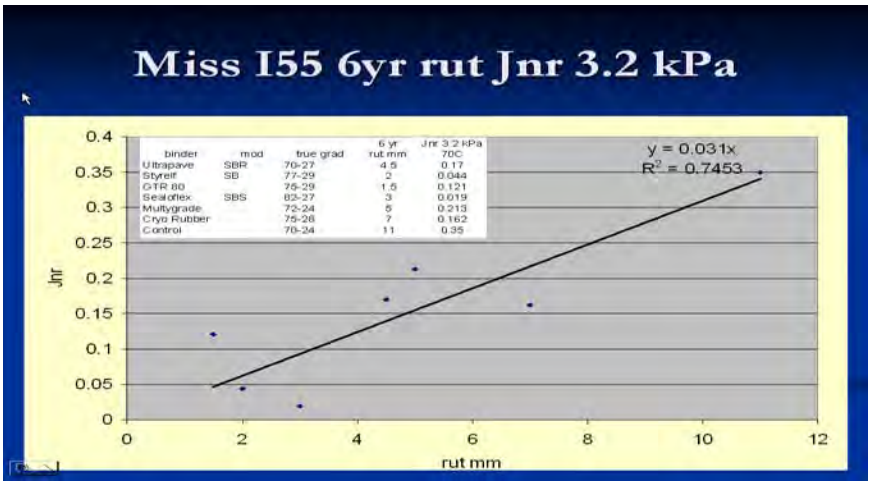
- MSCR Identifies beneficial elastic properties.
  - Rutting Performance
    - Direct measure of Non Recoverable Compliance
    - Goal is quantify the non-linear performance of the binder to predict Rutting Performance. (Jnr)
  - % Recovery Performance
    - Direct measure of Recoverable Compliance
    - Goal is investigate differences in linear & non-linear performance of the binder (% Difference)

Relationship: Compliance to Rut Depth MN Road



Excerpts from D'Angelo & Dongre'

Relationship: Compliance to Rut Depth Miss DOT



binder	mod	true grad	6 yr rut mm	Jnr 3.2 kPa 70C
Ultrapave	SBR	76-27	4.5	0.17
Styrelf	SB	77-29	2	0.044
GTR 80		75-29	1.5	0.121
Sealoflex	SBS	82-27	3	0.019
Multigrade		72-24	5	0.215
Cryo Rubber		75-26	7	0.162
Control		70-24	11	0.35

Excerpts from D'Angelo & Dongre'

MSCR Testing Specification

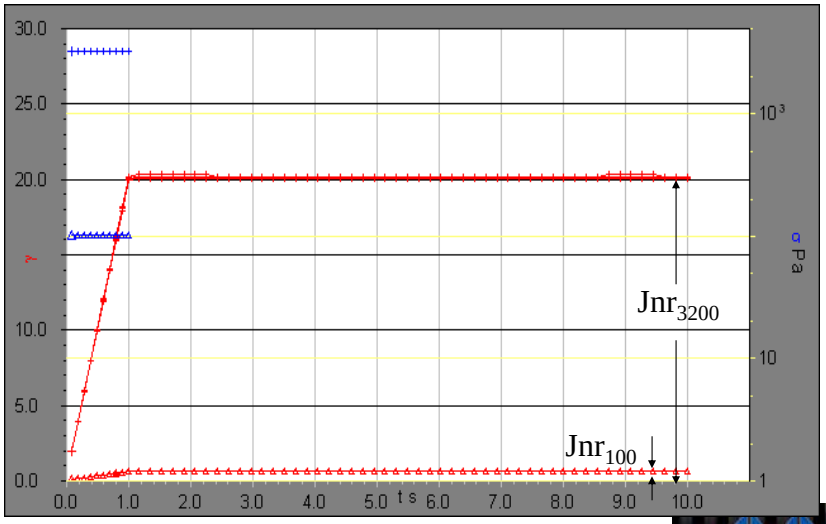
Determination of a Specification criteria.

- The existing binder specification works very well for neat binders.
- The grading for neat binders should not change.
- Establish new Jnr criteria based on response of neat binders at their continuous grade temp.
- Evaluate the binders near the end of their linear range. Most neat binders remain linear up to 3.2 kPa stress.

Excerpts from D'Angelo & Dongre'

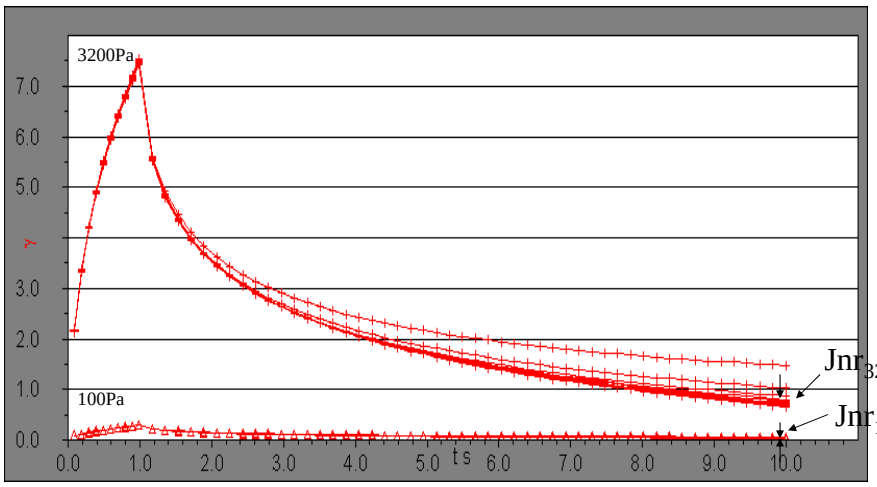
Example of a Newtonian Material

Neat binder PG64-28 tested to MSCR at 64°C



Example of a Visco-Elastic Binder

Modified binder PG70-28 tested to MSCR at 70°C



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