

Asphalt Binder Modification

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Asphalt Binder Modification

- Background
 - How Asphalt Behaves
 - Use of Modified Asphalt Binders
 - Types of Polymer Modification
 - Laboratory Handling
- Modified Asphalt Binder Testing
- Mixture Performance Testing

Background: How Asphalt Behaves

- Behavior is affected by :
 - Temperature
 - Time of Loading
 - Age of pavement or service life



Time-Temperature Superposition



How Asphalt Behaves: High Temperature

- High Temperature
 - desert climate
 - summer
- Sustained Loads
 - slow moving trucks
 - intersections





High Temperature Asphalt Pavement Behavior

- Rutting and depressions
- Depends on...
 - Asphalt binder (some)
 - Mineral aggregate (some)
 - Volumetric proportioning (some)





Principles of Rutting in Asphalt Mixtures

- Mohr-Coulomb Failure Theory
 - Described by Nijboer in 1948
 - Simplification of the rutting model considered in SHRP
 - Separated shear strength of asphalt mixture into three components
 - $\circ~$ Internal friction of the aggregate structure ($\varphi)$
 - Initial resistance or cohesion (c) independent of deformation rate
 - Viscous, or rate-dependent, cohesion
 - Cohesion (c)
 - Largely a function of asphalt binder characteristics
 - \circ Angle of internal friction (ϕ)
 - Largely a function of aggregate structure including gradation, particle shape (angularity), and texture

Principles of Rutting in Asphalt Mixtures



Aggregate Structure (Angular) Asphalt Binder Stiffness (Modification)

- Low Temperature
 - cold climate
 - winter
- Rapid Loads
 - \circ fast moving trucks



- Thermal Cracks
 - internal stresses induced by temperature change
 - $^{\rm o}$ stresses exceed strength
- Mixture is Brittle
 - transverse cracks
- Depends on...
 - asphalt cement (lots)
 - mineral aggregate (little)
 - volumetric proportioning (some)



Low Temperature Cracking



Binder Behavior - Aging

- Asphalt Reacts with Oxygen
 - "oxidative" or "age" hardening
 - During Construction Short Term
 - hot mixing
 - placement and compaction
 - In Service Long Term
 - hot climate worse than cool climate
 - Volatilization Short Term
 - volatile components evaporate during construction

Pavement Behavior - Aging

- Durability Cracks
 - Mixture is brittle
 - Random, wandering cracks
 - Longitudinal
 - Depends on...
 - asphalt cement (some)
 - mineral aggregate (little)
 - volumetric proportioning (some)



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Fatigue Cracking



Background: Use of Modified Asphalt Binders

Historical Paving Asphalt Usage in United States



Historical Paving Asphalt Usage in United States



- Interstate highways 1956
- AASHO Road Test 1958-62

still widely used for pavement design
legal truck load - 73,280 lbs

- Legal load limit to 80,000 lbs 1982
 10% load increase
 - 40-50% greater stress to pavement
- Radial tires, higher contact pressure



Modified Asphalt Usage



Modified Asphalt Usage



• Reasons for Use

 modification of neat asphalt binder to enhance its performance characteristics has occurred in the United States for more than 50 years

• Reasons for Use

- In a survey of 20 experts representing 18 states, 70% responded that there was a definite benefit in using polymer-modified asphalt mixtures to extend the pavement's service life.
 - Nearly 60% responded that the use of polymer-modified asphalt mixtures significantly reduced maintenance costs
 - insufficient performance data to quantify that benefit or enhancement.

- Reasons for Use
 - primary reason why users chose to use polymer-modified asphalt was to increase the mixture's resistance to rutting.
 - Secondary reasons were to increase resistance to thermal cracking and to increase durability of the mixture.

- Reasons for Use
 - Not all asphalt pavements need to be constructed using modified asphalt mixtures.
 - Each project should be evaluated to determine if the environmental conditions, traffic loading, expected service life and performance warrant the use of modified asphalt materials

Quantifying the Effects of Polymer Modification

- Report on 2005 study
- "The use of PMA definitely extends the service life of flexible pavements and HMA overlays."
 - Harold Von Quintus (ARA) –
 Principal Investigator



- Types of Modifiers and Additives
 - Generically referred to as "polymer-modified asphalts" or PMAs.
 - In actuality modified asphalt binders may be produced in a number of ways
 - polymer modification (most prevalent)
 - chemical modification

- Types of Modifiers and Additives
 - Polymers
 - Two broad classes of polymers used in asphalt modification are polyolefins and styrenic polymers.
 - Polyolefins
 - based on the polymerization of molecules containing a simple double bond or olefin.
 - include polyethylene, polypropylene, and ethylene vinyl acetate.
 - Styrenic polymers
 - based on polystyrene that has been co-polymerized with other small molecules most commonly butadiene

- Types of Modifiers and Additives
 - Polymers
 - Classified based on physical properties
 - Plastomers
 - Exhibit plastic behavior
 - will yield and remain in their stretched position when the load is released
 - most polyolefins behave as plastomers
 - Elastomers
 - Exhibit elastic behavior
 - will yield under load (stretch) but will return to their original shape when the load is released
 - styrene-butadiene copolymers behave as elastomers

- Types of Modifiers and Additives
 - Polymers
 - when blended into asphalt, polymers can behave in two different ways
 - If the polymer forms discrete particles...
 - it functions primarily as a thickener, which increases the viscosity of the asphalt binder
 - If the polymer forms a continuous network...
 - it functions as a homogeneous blend, which may impart some of the physical characteristics of the polymer to the asphalt binder

Impact of Polymer Network (Crosslinking)

Fluorescence Micro-graphs at 250 magnification show changes in morphology	
Discrete polymer	polymer strands
particles	developing
LC 4	LC 4P
More uniform	More uniform
dispersion	dispersion almost
some bulking	cross-linked
LOP 4	LOP 4P

- Elastic Modification (Elastomers)
 - Most common co-monomer to produce styrenic polymers is butadiene
 - When styrene and butadiene are polymerized in a random arrangement...
 - referred to as a "random copolymer"
 - called styrene-butadiene rubber (SBR)
 - may also be referred to as a synthetic latex
 - When styrene and butadiene are polymerized in discrete, connected blocks...
 - referred to as a "block copolymer"
 - called styrene-butadiene (SB) or styrene-butadiene-styrene (SBS)



- Polymer Modified Asphalt Specifications
 - Sought to characterize the elastic properties of a styrenic polymer-modified asphalt binder
 - use of tests that stretch the asphalt binder and measure...
 - stress-strain response
 - Force Ductility test
 - Toughness and Tenacity test
 - recovery
 - Elastic Recovery test
Asphalt Modification

- Plastic Modification (Plastomers)
 - When stretched, yield and remain in stretched position
 - Polyolefin polymers
 - Add to the high temperature stiffness
 - Do not have the elastic characteristics of styrenic polymers
 - Polyethylene
 - often the low density polyethylene identified as LDPE
 - Ethylene vinyl acetate (EVA)

Background: Laboratory Handling

Laboratory Handling and Storage

- The properties of asphalt binders can be altered during handling and storage
 - These changes may be reversible or non-reversible depending upon cause
- The causes include...
 - Damaged or partially open cans
 - Heating during handling
 - Proper long-term storage has minimal effect
- Other factors

Causes of Change – Oxidation

- Oxygen reacts with asphalt cement
 - Molecular size increases
 - Polarity increases
 - The binder becomes stiffer
 - This reaction is not reversible
- Rate of reaction is highly dependent upon temperature
 - Rule of thumb reaction rate doubles for every 10°C increase in temperature

- Steric hardening is a reversible process that occurs at room temperature
 - Polar molecules become structured with time
 - This structuring increase binder stiffness
 - Steric hardening starts immediately upon cooling and continues at a reduced rate for an extended period of time (months? years?)
- The amount of steric hardening that occurs is binder-specific

Some binders show relatively small amounts

Controlling Steric Hardening

- Steric hardening is destroyed by heating
 - Referred to as annealing in test methods
- Always control the amount of time between sample pouring and testing
 - Limit the amount of time asphalt binder is held in silicone molds before testing
 - Holding a DSR test specimen in a silicone mold for several hours or more may be sufficient to pass a binder that would otherwise fail

- Some polymers may degrade when heated at high handling temperatures
 - Temperature is polymer-specific
 - Use manufacturer recommendations for handling and do not overheat
- Polymer degradation cannot be reversed
 - Degradation causes a softening of the asphalt binder

- Separation during storage
 - Tendency is binder- and modifier-specific
 - Some systems are more stable than others
 - Separation may occur during storage
- Polymer tends to float to top giving "scum"
 - ° If this scum persists with stirring test results may not be representative
 - Removing "scum" removes polymer and test results are no longer representative

Heating Asphalt Binders – Precautions

- Always heat asphalt samples/cans in an oven
 Avoid hot plates, heating mantles, etc.
- Always heat at the lowest temperature and for the shortest time possible
 - Follow manufacturer's instructions
- Avoid heating in thin layers
 - e.g., near-empty cans, shallow tins
- Cover the heated container when possible
 - The cover may not be effective in reducing oxidation but it will help prevent contamination from dust, etc.

Testing

How Asphalt Behaves: High Temperature



Apparent Viscosity

- Apparent Viscosity (ASTM D4957)
 - allows the user to better understand the behavior of non-Newtonian asphalt binders
- Procedure
 - Similar to absolute viscosity
 - Preheated asphalt sample poured into vacuum capillary viscometer tube until its level reaches the filling line.
 - Filled viscometer tube placed back in an oven for a short time.



- Rotational Viscosity
 - Provides viscosity of asphalt binders in the range of temperatures from 60°C to over 200°C
 - The measured values are used to grade binders in accordance with AASHTO M 320 and AASHTO R 29

Rotational Viscometer



Rotational Viscosity: Test Summary and Fundamentals

- Asphalt binder is placed between spindle and sample chamber
- Spindle rotates at constant speed
- Required torque is measured



- Background
 - MS-2
 - Recommended laboratory mixing and compaction temperature ranges for Marshall mix design based on viscosity (Saybolt Furol) as early as 1962
 - Changed to absolute and kinematic viscosity in 1974
 - 170 ± 20 centistokes for mixing
 - 280 ± 30 centistokes for compaction
 - Purpose
 - normalize the effect of asphalt binder stiffness on mixture volumetric properties
 - Aggregate packing and available void space

- Background
 - Modified Asphalt Binders in the Marshall Mix Design System
 - Produced higher air voids, lower density
 - Impact compaction with fixed energy input
 - Affected by mix stiffness = f(temperature/binder stiffness)
 - Should optimum asphalt binder content be adjusted?
 - Volume of asphalt for durability shouldn't be affected by binder stiffness
 - Higher asphalt binder content may be unnecessary

- Background
 - Modified Asphalt Binders in the Superpave Mix Design System
 - Adopted old (Marshall) standard in 1993
 - $\circ~$ 0.17 \pm 0.02 Pa-s (mixing)
 - $\circ~$ 0.28 \pm 0.02 Pa-s (compaction)
 - Manufacturer's recommendation for modified asphalt binders

- Background
 - Modified Asphalt Binders in the Superpave Mix Design System
 - Produced lower air voids, higher density
 - Shear compaction with fixed angle, pressure
 - Not affected by mix stiffness (i.e., not significantly affected by temperature)
 - Short-term Mix Conditioning
 - Four hours at 135°C or two hours at compaction temperature
 - Different absorption?

- Rotational Viscosity
 - 3 Temperatures
 - 105, 135, 165 used in research
 - Multiple shear rates
 - Typically 6.8 s⁻¹ (20 rpm)
- Cross-Williamson Model
 - Excel spreadsheet using SOLVER function
 - multiple iterations
 - Executed at each temperature to determine ZSV

NCHRP 9-10: Determining Temperatures

- Plot ZSV vs. Temperature
 - Determine Mixing Temperature
 - ZSV = 3 Pa-s
 - Determine Compaction Temperature
 - ZSV = 6 Pa-s

NCHRP 9-10: Mixing and Compaction Temperatures

• PG 76-22 (SBS)		
 Conventional 	202C	185C
° ZSV	165C	157C
• PG 76-22 (LDPE)		
 Conventional 	192C	176C
° ZSV	163C	155C

Research on Lab Mixing and Compaction Temperatures

- NCHRP 9-39, Procedure for Determining Mixing and Compaction Temperatures of Asphalt Binders in Hot Mix Asphalt
 - Purpose
 - Identify or develop a simple, rapid, and accurate laboratory procedure for determining the mixing and compaction temperatures of asphalt binder
 - NCHRP Report 648

NCHRP 9-39: Mixing and Compaction Temperatures





- Candidate Methods for Determining Laboratory Mixing and Compaction Temperatures
 - Steady Shear Flow (SSF) method
 - Reinke
 - Phase Angle method
 - Casola

Dynamic Shear Rheometer (DSR)



- Steady Shear Flow Test (Reinke)
 - \circ Uses DSR
 - High shear stress sweep
 - 50 to 1000 Pa
 - 5 data points per log decade
 - 8 total data points
 - Multiple temperatures
 - 88°C to 112°C
 - Parallel Plate
 - 25-mm plates
 - 0.5 mm gap

- Mixing Temperature Viscosity_{SS1000Pa} = 0.17 ± 0.02 Pa·s
- Compaction Temperature Viscosity_{SS1000Pa} = 0.35 ± 0.03 Pa·s

SSF Procedure: PG 64-34 (SBS-modified)



Temperature, C

- Determining the Laboratory Mixing and Compaction Temperature of Asphalt Binder Using a Dynamic Shear Rheometer: The Casola Method
 - DSR Mastercurve
 - 25-mm parallel plate
 - Minimum of three test temperatures
 - Reference temperature = 80°C
 - 31 frequencies
 - 0.1 to 100 rad/s
 - \circ Determine frequency (at $\mathsf{T}_{\mathsf{ref}}$) where phase angle (δ) equals 86 degrees

- Mixing Temperature
 - Mixing Temperature (°F) = $325\omega^{-0.0135}$
- Compaction Temperature
 - \circ Compaction Temperature (°F) = 300 $\omega^{-0.012}$

These relationships are purely empirical

NCHRP 9-39 Phase Angle Method: MasterCurve (PG 76-28)

G(t) 3.85E+02 J(t) 1.02E-03 m(ω) 9.39E-01 G*(ω) 1.41E+01 d(ω) 86.02 G'(ω) 9.74E-01 G"(ω) 1.40E+01 G*/sin(δ) 1.41E+01 J*(ω) 7.12E-02 J'(ω) 4.93E-03 J"(ω) 7.10E-02 Eta'(ω) 2.92E+02 0.048 rad/s ω

Mixing Temperature 339°F 170°C Compaction Temperature

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311°F 155°C



- Option of Steady Shear Flow or Phase Angle Methods
 - Both methods provide reasonable mixing and compaction temperatures (i.e. generally consistent with field experience) for modified and unmodified binders
 - Both are simple, use existing equipment, and take less than one hour of hands free operation.
 - For highly modified binders, an environmental temperature chamber or Peltier plate is needed.

Al Guidance Document

- For unmodified¹ asphalt binders...
 - laboratory mixing and compaction temperature may be determined using:

 (1) the rotational viscosity procedure (AASHTO T316) at two test temperatures; or
 (2) the rotational viscosity procedure at 135°C in combination with the dynamic shear rheometer procedure (AASHTO T315) at a single test temperature

¹ Also identified as: (a) AASHTO M320 asphalt binders that have a useful temperature interval (UTI) of < 92 degrees; or (b) AASHTO MP19 asphalt binders with an "S" designation

Al Guidance Document

- For modified² asphalt binders...
 - laboratory mixing and compaction temperature may be determined using:
 (1) the DSR Phase Angle Procedure; or
 (2) the DSR Steady Shear Flow Procedure, as recommended by NCHRP Report 648.

In addition, the recommendation of the supplier may be used, as many suppliers have determined mixing and compaction temperatures for their individual products that have proven to be appropriate.

² Also identified as: (a) AASHTO M320 asphalt binders that have a useful temperature interval (UTI) of \geq 92 degrees; or (b) AASHTO MP19 asphalt binders with an "H", "V", or "E" designation
Lab Mixing and Compaction Temperatures: Caveats

- Regardless of the selected procedure, recommend that laboratory mixing temperatures do not exceed 177°C (350°F).
- Not applicable to asphalt binders that have been modified with ground tire rubber (GTR)
 - The NCHRP 9-39 research did not evaluate GTR-modified asphalt binders
 - Unknown how the recommended procedures will work with this class of modified asphalt binder.
 - Refer to other existing practices for GTR-modified asphalt binders.

Additional Tests

- Separation
- Recovery and Stress-Strain Tests

- Elastic Recovery
- Force Ductility
- Toughness and Tenacity
- DSR Phase Angle
- MSCR Recovery

Separation

- Purpose
 - Used to assess polymer-asphalt compatibility
 - $\circ~$ generally referred to as the "ointment" or "cigar" tube test.
- Procedure
 - aluminum ointment tube is filled with 50 grams of modified asphalt binder
 - The filled tubes are then sealed and allowed to stand vertically in an oven operating at 163°C for 48 hours.

- Separation
 - \circ Procedure
 - The tubes are then transferred to a freezer for four hours
 - After freezing, the tubes are removed and cut into thirds
 - The top third and bottom third are separated into tins and tested
 - Using R&B softening point or DSR tests
 - $\circ~$ determine if a significant difference exists in the properties of the top and bottom thirds.

Separation Test



- Recovery and Stress-Strain Tests
 - Purpose
 - To evaluate whether an asphalt binder has been modified with an elastomer, specifically a block copolymer such as
 - designed to measure the ability of the asphalt binder to stretch when loaded and ultimately rebound to its original shape when unloaded

• Recovery and Stress-Strain Tests

- Common Tests
 - Elastic Recovery
 - Force Ductility
 - Toughness and Tenacity
 - DSR Phase Angle
 - Indicator of relative proportion of elastic and viscous components in asphalt binder

• Elastic Recovery

- Based on ductility equipment
 - Same molds, but different side pieces
 - Rectangular (parallel), not V-shaped
 - Sample preparation like ductility test
- Procedure
 - Load specimens at test temperature (usually 25°C)
 - Pull specimens to 10 or 20 cm
 - Defined by test procedure

• Elastic Recovery

- Procedure
 - Cut specimens in center
 - May have a 5-minute wait period before cutting
 - Allow specimens to relax for 1 hour
 - Push specimen back together until cut ends touch
 - Record elastic recovery as the difference between the stretched and final position divided by the stretched position
 - Express as a %

Elastic Recovery



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Elastic Recovery



Elastic Recovery



• Force Ductility

- Based on ductility equipment
 - Similar to Elastic Recovery Test
 - Uses a load cell to measure stress
 - Conducted at 4°C
 - Usually unaged binder
- Procedure
 - Load specimens at test temperature
 - Pull specimens to 30 cm
 - Measure stress

• Force Ductility



• Force Ductility



• Force Ductility



- Toughness and Tenacity
 - ° first introduced by Benson in the 1950s
 - Procedure
 - a metal hemispherical head is embedded in hot asphalt to a depth of approximately 11 mm
 - After cooling to 77°F (25°C), the head is attached to a tensile test machine and pulled from the asphalt binder at a rate of 51 cm/min.
 - The load is measured throughout the test
 - $\circ~$ a load-deformation curve is plotted
 - Toughness and tenacity values determined based on the area under different portions of the loaddeformation curve

• Toughness and Tenacity



• Toughness and Tenacity



• DSR Phase Angle

- Output from standard DSR testing
- Maximum phase angle ensures elastic component in asphalt binder
 - Influenced by stiffness of asphalt binder

Multi-Stress Creep Recovery (MSCR) Test

- Performed on RTFO-aged Binder
- Test Temperature
 - Environmental Temperature
 - Not Grade-Bumped
- 10 cycles per stress level
 - \circ 1-second loading at specified shear stress
 - 0.1 kPa
 - 3.2 kPa
 - 9-second rest period

MSCR: Calculating J_{nr}

0.1 kPa Shear Stress



• MSCR Recovery



Time, seconds

Validate Polymer Modification

PG 76-22 Binders: MSCR3.2kPa



Mixture Performance Testing

Hamburg Wheel Tracking

• MTE Rutting Study: WI E10 Fine Mix

PG Grade (M320)	PG Grade (M332)	Test Temp, °C	J _{nr3.2} , kPa ⁻¹	R _{3.2} , %	HWT Rut Depth (10,000 passes), mm
70-22	n/a	75	5.74	0.5	13.2
64-22	64S-22	64	3.40	3.4	7.1
70-22	70S-22	70	2.92	1.5	5.1
70-22	64H-22	64	1.35	4.4	3.6
76-22	64E-22	64	0.24	55.8	1.7
82-22	64E-22	64	0.08	78.5	1.6

SHRP Flexural Beam Fatigue





RH Aggregate, 7% Air Voids, MRL Binders



Flexural Beam Fatigue: Unmodified and Modified



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Flexural Beam Fatigue: PG 76-22



AMAP RAP and Modified Asphalt Study 2019

	RAP0-76	RAP30-76	RAP30-76H
SCB-IL at 25°C			
Flexibility Index	9.0	3.8	5.9
Texas Overlay Test at 25°C			
Cycles to Failure	80	17	72
DC(T)			
Fracture Energy at 0°C, J/m ²	1238	707	925
Fracture Energy at -6°C, J/m ²	720	530	570
Fracture Energy at -12°C, J/m ²	524	416	579
IDT Strength			
Average Failure Strength, MPa	4.03	3.78	3.81
IDT Creep and Strength			
Critical Cracking Temperature, °C	-33.1	-31.8	-32.1
Hamburg Wheel Tracking at 50°C			
Rut Depth at 20,000 Passes, mm	6.6	4.4	4.7

- Summary
 - Increased loading and a broader temperature range in which asphalt is expected to perform leads to a need for modified asphalt binders
 - Four-fold growth in use, as a percentage of the total amount of asphalt binder used, in the last 20 years
 - Proper handling in the lab is needed
 - User agencies typically focus testing on elastic properties of the modified asphalt binder
 - Benefits seen in mixture performance testing in the lab and in-service
 - Much more to learn!





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