Understanding the Use and Availability of Polymers for Hot Mix Asphalt

36th Annual Rocky Mountain Asphalt Conference
Denver, CO
February 19, 2009

Presented by: Ron Corun
Manager – Asphalt Technical Services
NuStar Asphalt Refining, LLC
Types of Modification

- Chemical
- Polymer
  - Block Copolymers (SB, SBS, SEBS)
  - SBR Latex
  - Polyolefins
- Crumb Rubber
Chemical Modification

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

- Polyphosphoric Acid consists of higher molecular weight species with a distribution of chain lengths.
- Concentration ranges based on equivalent $P_2O_5$ content
- Various types used:
  - 105
  - 115
Polyphosphoric Acid – What Does it Do?

• Increases PG high temperature grade
  – Example: PG 58-28 + PPA = PG 64-28
  – Typically, 0.50% - 1% PPA increases PG high temperature by one grade
What Is a Polymer?
Some Examples

Polymers are everywhere… You eat them, You wear them, You work with them, You use them all the time!

- carbohydrates
- proteins
- nucleic acids
- wood
- cotton
- silk
- nylon
- polyester

- polystyrene
- PVC
- adhesives
- coatings
- fibers
- elastomers
- foams
What Is a Polymer?

A polymer is a long string (or net) of small molecules connected together through chemical bonds.

A polymer is made of distinct monomer units all connected together.

**OK, but why is that important?**
The chain connectivity of the polymer can give the chain great strength...and at the same time they can be very flexible.

It also make the polymer viscosity high in both the solution and melt state ...
Now liquids behave elastically to some degree ... they are viscoelastic.

They are easily moldable, castable, soluble, spinnable, etc. ... and so many useful objects can be made from them.
Styrenic Polymers (Elastomers)

- Polystyrene is hard and brittle
- Commonly co-polymerized with butadiene

Disposable fork

POLY-STYRENE

B

POLY-BUTADIENE

Rubber band
SB and SBS

Block
Copolymer
(SB & SBS)

- Butadiene
- Styrene
SBR Latex

Random Copolymer (SBR)

- Butadiene
- Styrene
Predominate Modifiers

- SB, SBS and SBR are most widely used in US and around the world
  - Excellent performance – case studies
  - Long history of success – since 1970’s in Europe
  - SB and SBS produce a stable, compatible system easily used in today’s construction practices
How is PMA Produced?

• Start with a neat asphalt
  – Dissolve and Cross-link SBS Molecules
    • High shear mill
    • Reaction Time
    • Constant Agitation
    • Constant Heat

• Test Asphalt Properties
  – Performance Properties
  – Homogenous Material
  – Stable Material
Flourescence Microscopy

- SBS milled into asphalt
- High shear mill
- Early in process
Flourescence Microscopy

- Forming physical entanglement network
Flourescence Microscopy

• Addition of compatibilizer (cross-linking agent) improves dispersion and creates chemical bonds
Flourescence Microscopy

- Completed cross-linking
Polymer Modified Asphalt – What Does it Do?

- Addition of rubbery material allows asphalt to recover after loading.
- Recovery allows asphalt to withstand pavement distresses.

Results of repeated creep-recovery tests at 40°C
Polymer Modified Asphalt – What Does it Do?

- Pavement distresses addressed by PMA
  - Improved resistance to rutting
  - Reduce fatigue cracking
  - Mitigate thermal cracking
  - Resist top-down cracking

- Improve durability with thicker asphalt binder films
  - Higher asphalt contents
  - Reduce moisture damage
Polymer Modified Asphalt – What Does it Do for Rutting?

- Laboratory Data
  - Asphalt Pavement Analyzer
  - Hamburg Device
- Field Trials
- National study
Polymer Modified Asphalt – What Does it Do for Rutting?

• Field Trials
  – MD Intersection – 1993
    • Reduced rutting from 1.5” per year to .25” TOTAL RUTTING after 13 years
    – Duplicated all over US since

1993

2006
Polymer Modified Asphalt – What Does it Do for Rutting?

• National study conducted by ARA Engineering
  – Principal investigator Harold Von Quintus
  – Objectives
    • Quantify the effect of using PMA as compared to conventional-unmodified HMA mixtures
    • Identify conditions that maximize effect of PMA to increase HMA pavement & overlay life
  • Asphalt Institute Publication ER-215
Von Quintus Study Test Sections - Experiments

- LTPP: Core & Supplemental Sections
  - SPS-1; SPS-5; SPS-6; SPS-9
  - GPS-1; GPS-2; GPS-6; GPS-7
- MTO Modifier Study
- Accelerated Pavement Tests
  - FHWA ALF, Turner Fairbanks
  - NCAT Test Road
  - California HVS Studies
  - Ohio Test Road
  - Corp of Engineers
Von Quintus Study Distress Comparisons - Rutting

Graph showing the relationship between Rut Depths on PMA Sections and Rut Depths on Companion Sections.
Polymer Modified Asphalt – What Does it Do for Fatigue Cracking?

- Laboratory Data – Rutgers University (Courtesy of Tom Bennert)
  - Flexural Beam Fatigue Test
    - Cyclic loading of the asphalt beam
    - Measure stiffness throughout test
    - When stiffness drops to 50% of initial stiffness – considered failure
  - Test conditions
    - 1,000 micro stain
    - 15°C
    - 10 Hz
Flexural Beam Fatigue (AASHTO T321)
Short-term Oven Aged in Accordance with AASHTO R30

Fatigue Life ($N_f_{50\%}$)

- PG64-22 STOA
- PG76-22 STOA

Tensile Strain (in/in)
Von Qunitus Study Distress Comparisons – Fatigue Cracking

Fatigue Cracking - PMA Sections, %

Fatigue Cracking - Companion Sections, %
Polymer Modified Asphalt – What Does it Do for Low Temperature Cracking?

- Laboratory Testing – MTQ (Courtesy of Michel Paradis)
  - Thermal Stress Restrained Specimen Test (TSRST)
Polymer Modified Asphalt – What Does it Do for Low Temperature Cracking?

- Thermal Stress Restrained Specimen Test (TSRST) – test parameters
  - Length of Sample – 250mm
  - Diameter of Sample – 60mm
  - Cooling Rate - 10°C per hour
  - Initial Load – 50N
- Sample attached to load cells to maintain constant sample length
- Maximum Stress and Minimum Temperature are obtained at fracture
Polymer Modified Asphalt – What Does it Do for Low Temperature Cracking?

### MTQ Test Results

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PG 58-28</th>
<th>PG 58-34</th>
<th>PG 58-40</th>
</tr>
</thead>
<tbody>
<tr>
<td>True Grade</td>
<td>59.7-28.6</td>
<td>58.4-36.6</td>
<td>62.6-38.0*</td>
</tr>
<tr>
<td>Elastic Recovery (%)</td>
<td>-</td>
<td>58</td>
<td>81</td>
</tr>
<tr>
<td>Cracking T°(°C)</td>
<td>-31.2°</td>
<td>-38.7°</td>
<td>-46.7° **</td>
</tr>
<tr>
<td>(1 year outdoor conditioning)</td>
<td>-27.4°</td>
<td>-36.9°</td>
<td>-45.6° **</td>
</tr>
</tbody>
</table>

* - did not meet PG grade

** - could not crack at 10°C per hour cooling rate
Polymer Modified Asphalt – What Does it Do for Top Down Cracking?

- Top Down Cracking
  - Cracking starts at top of asphalt pavement – not fatigue cracking starting at bottom
  - Recent phenomena – theories on cause
    - Thermal gradient in pavement
    - Stresses at edge of radial truck tires
Polymer Modified Asphalt – What Does it Do for Top Down Cracking?

- Florida DOT
  - 90% of pavements scheduled for rehab:
    - Deficient crack rating
    - Top-down cracking
- FDOT – University of Florida embarked on a multi-year study to identify causes and solutions.
Top Down Cracking – University of Florida Research

Cycles to Failure

- Used the HMA Fracture Model to calculate $N_f$ for crack to propagate 2 in
- Mixtures with $N_f<6000$ performed poorly
Top Down Cracking – University of Florida Research

Dissipated Creep Strain Energy

- $\text{DCSE}_{\text{min}}$ is the minimum energy required to produce $N_f = 6000$

Based on the $M_R$ and Strength tests
Top Down Cracking - University of Florida Research

- **Conclusions**
  - $\text{DSCE}_{\text{HMA}}$ must be greater than $\text{DSCE}_{\text{min}}$ for good top down cracking performance
  - PMA consistently gives higher DSCE values

- Based on this research and on accelerated loading tests for rutting, FL DOT now uses PMA in top 4” of interstate and heavily trafficked primary highways
Polymer Modified Asphalt – What Does it Do for Top Down Cracking?

- Top Down Cracking
  - Not limited to Florida
  - New Jersey I-287
    - 20 year old full-depth asphalt pavement
    - Severe cracking – thought to typical bottom-up fatigue cracking
    - Forensics found cracking to be top-down
Polymer Modified Asphalt – What Does it Do for Top Down Cracking?

- New Jersey I-287
  - Milled 4” to remove cracked HMA
  - Repaved with 4” HMA using polymer modified asphalt
  - Picture at left is I-287 11 years after milling and paving
Polymer Modified Asphalt – What Does it Do for Durability?

- Asphalt Content
  - Higher asphalt content = longer pavement life
  - Higher asphalt content may also = rutting
    - PMA ability to resist rutting allows higher AC% without rutting
- NCAT Test Track
  - Two companion sections – same aggregate gradation
    - One – built at design AC% using PG 67-22
    - Two – built at design AC% + 0.5% using PMA PG 76-22
  - Results – PMA section rutted less
Polymer Modified Asphalt – What Does it Do for Durability?

- NCHRP 9-9 - NCAT Research Project
  - Verifying gyration levels
  - Lower # of gyrations = higher AC% in mix

<table>
<thead>
<tr>
<th>20 Year ESALs</th>
<th>$N_{\text{design for binders}} &lt; \text{PG -76-XX}$</th>
<th>$N_{\text{design for binders}} &gt; \text{PG -76-XX}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 300,000</td>
<td>50</td>
<td>NA</td>
</tr>
<tr>
<td>300,000 to 3,000,000</td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td>3,000,000 to 10,000,000</td>
<td>80</td>
<td>65</td>
</tr>
<tr>
<td>10,000,000 to 30,000,000</td>
<td>80</td>
<td>65</td>
</tr>
<tr>
<td>&gt; 30,000,000</td>
<td>100</td>
<td>80</td>
</tr>
</tbody>
</table>
Polymer Modified Asphalt – What Does it Do for Durability?

- **Asphalt Content**
  - Higher asphalt content = Thicker asphalt films on aggregate
  - Increasing asphalt content by 0.5% increases film thickness by 3 to 4 microns (2003 TRB paper by Boris Radovskiy)
  - Greater film thickness and stickiness of PMA typically leads to better asphalt-aggregate adhesion and higher TSR numbers
Summary – What Do Polymer Modified Asphalts Do?

• Improved Pavement Performance
  – Reduced rutting
  – Reduced fatigue cracking
  – Improved low temperature cracking resistance
  – Reduced top down cracking
  – Improved durability
    • Higher asphalt contents
    • Improved TSR results – more resistant to stripping
• Von Quintus Study – Quantified Enhanced Performance of PMA
  – 25 to 100 % increase in service life
  – 3 to 10 years increase in service life
Polymer-Modified Asphalt Supply Outlook

36th Annual Rocky Mountain Asphalt Conference
Denver, CO
February 19, 2009

Ronald Corun
Manager – Asphalt Technical Services
NuStar Asphalt Refining, LLC

DeWitt & Company
Acknowledgements

• Polymer Supply Information
  – De Witt & Company
  – Tom Brewer
Why is SBS Currently in Short Supply?

• Styrene-Butadiene-Styrene (SBS) polymer capacity is not short
• Shortage of raw materials - Butadiene
• Ethylene production is the problem
Why is Ethylene Production the Problem?

- By-products of Ethylene Production
  - Styrene
  - Propylene
  - Butadiene
  - Isoprene
  - Pentadiene
  - Cyclopentadienes
  - Aromatic Resin Formers
  - Isobutylene
  - Amylenes
  - Hydrogen
  - Benzene
Ethylene & Butadiene Market Comparison

- **Ethylene Market**
  - 120 million tons per year
  - Primary use – packaging materials
    - Plastic wrap
    - Trash bags
    - Milk jugs

- **Butadiene Market**
  - 14 million tons per year
  - Primary use – tires (70%)
  - Multiple other automotive and durable good uses
  - SBS polymer for asphalt (6%)
How Is Ethylene Made?

- Basic ethylene production technology is called a steam cracking process
  - Process heats feed up to 1700 degrees, then injects steam that cracks the molecules
  - Cracker unit cost $2 billion
- Choice between gas feeds like ethane, propane and butane and liquid feeds like naphtha and gas oils.
- Output is a mixture of ethylene and other products
- Requires a downstream purification processes to separate products
What’s Important to Know About Ethylene Production

- Ethylene
- Propylene
- Benzene
- Butadiene
- Pentadiene
- Isoprene
- Cyclopentadiene
- Aromatics

Produced by both Gas and Liquid Feed

Only a by-product of cracking Liquid Feeds

Gas Feed

Liquid Feed

Steam Cracking Process
Choosing Feeds to Produce Ethylene

- Each producer runs an economic model

- Feed availability and costs for the producer at their location
  - Yield of each feed – varies considerably
  - Demand for each product
  - Alternatives to buy versus make that product

- Ethylene and propylene are the prime products
  - Evaluate netback of all products
  - Liquid feeds generally produce 15:1 ethylene to butadiene
  - Economic impact of butadiene is not large
  - Based on the conditions producers set a feed slate for the “Cracker”
  - Butadiene shortage is not a primary consideration for feed slate
Model Output

- Liquids are always in the slate due to the facilities being built to be liquid crackers
- Crackers modified in the 80’s to be flexible
- Flexibility depends on producer, but varies from ~10% to ~50%
- Producing 3-5 million pounds a day a few pennies makes a big difference
What’s Changed

- Structural change - natural gas producers installed facilities to separate ethane
  - Ethane higher value than natural gas
- Ethane prices didn’t increase with the crude oil run-up
- Economic incentive to run more ethane feed
Feed Slate Change in 2008

2008 Liquid Cracking Down 23% vs. 2007/6
Ethylene General Trends

• Little to no capacity additions in Western World
• Significant ethylene capacity additions in Middle East and Asia
  – Most of the Middle East is gas cracking
  – Most of Asia is liquid or naphtha cracking
• New trend for ethylene units outside of US to be more flexible to be able to run more gas feeds
  – Historically have been naphtha crackers
• Expect more flexible cracking; hence, more variable Butadiene supply
Global Rubber Perspective

- Global rubber demand in 2008 is 21.4 million tons, or 47 billion pounds
- Tires are the major consumer of synthetic and natural rubber
- Butadiene is a major component in most synthetic rubber: SBR, PBR, SBS, etc
- Decreased tire demand will significantly improve butadiene supply
July 2008 - Butadiene (Bd) Supply

• Globally tight due to lighter cracking and higher demand
  – 2008 Bd supply estimated at 75% of 2007

• New Bd and ethylene capacity due on-stream in Asia

• Expected capacity utilization to be lower than 90% for the foreseeable future

• Regional differences
  – US crude Bd supply tight due to light cracking in first half
  – US has excess purification capacity and buys crude Bd from Europe to fill capacity
  – Europe tight on supply due to somewhat lighter cracking; thus, less crude Bd to export to US
North American Butadiene Consumption

- SBS (For Asphalt) 6%
- Nitrile Butadiene Rubber 3%
- Acrylonitrile Butadiene Styrene 5%
- Adiponitrile 13%
- Other 3%
- Poly Butadiene Rubber 28%
- Poly-chloroprene Rubber 2%
- SBR Latex 12%
- SBR (crumb form) 28%
July 2008 - What Factors Will Influence Supply?

Positive
• New capacity
• Bd pricing itself out of some applications
• High gas prices:
  – Less driving mean fewer replacement tires
  – Smaller vehicles/smaller new car tires
• Slowing economy; less growth

Negative
• Higher natural rubber prices driving consumers to synthetic rubbers based on Bd
• Lighter cracking
  – Higher naphtha prices
  – Structural change in US ethane market
• Low cost gas-based ethylene capacity coming on-stream in Middle East.
July 2008 - Tire Demand Data

- New Tire Demand
  - June vehicle production down 8% and falling
  - Vehicle production skewed towards smaller vehicles
  - Tire demand could be down over 12%

- Replacement Tires
  - Higher gas prices are reducing miles driven
  - Expect reduced tire demand over time
  - May take 3-6 months to play out.
October 2008

- Spread between gas and liquid feeds now down to $.05
- Demand is shrinking – tire demand is down
  - Asian market price drop of $0.10-$0.15 per lb
October 2008

- Tire Demand is down – Frees up Butadiene for SBS Suppliers
  - **Result** – 100% Bd available to SBS producers for now
  - SBS suppliers will be able to build up substantial inventory this winter
  - **Should be adequate SBS supply in 2009**
4Q 2008 Economic Decline – Makes Bd Supply Longer

- Economy progressively shut down during the fourth quarter
- Housing industry started years before
- Tire industry was the first 4Q casualty
- Adhesive industry followed quickly behind tires
- Followed by general chemicals/Ethylene
- The sequence helped increase Bd supply
Low Natural Rubber Prices Push Out Synthetic

SICOM Natural Rubber and NYMEX WTI
(Prompt Month)
February 2009 - Outlook

• Expect demand to be lower than 2008 across all market segments
  – Ethylene is expected to be 10-20% lower than 2008
  – Tire demand expected to be 20% lower than 2008

• Butadiene supply should be adequate in 2009.
Alternatives to SBS Polymer

- SBS polymer-modified asphalts are typically cross-linked systems
  - Contractor friendly
    - Terminal blend supply
    - Do not require agitation
    - Storage stable
    - No major changes to HMA plant operation
    - No major changes to HMA laydown and compaction
- State DOT agencies have developed specifications specifically for SBS systems
- Alternative modification systems may require changes for both DOT agencies and contractors
Alternatives to SBS Polymer

• SBR Latex – butadiene based polymer that is not in short supply at this time
  – Not storage stable
  – Must be blended at HMA plant
  – Contractor now becomes asphalt modifier and must test and certify product

• Non-butadiene polymers
  – Reactive Ethylene Terpolymer (Elvaloy)
  – Ethyl Vinyl Acetate (EVA)
    • Used in warm climates
    • Blended with SBS in cold climates

• Polyphosphoric Acid (PPA)
  – An extender, not an alternative
  – Can be blended with SBS to reduce SBS content
Alternatives to SBS Polymer

• Ground Tire Rubber (GTR) – wet process
  – 18-22% GTR melted and swelled into asphalt
  – No cross-linking occurs
  – Not storage stable
  – Not a terminal blend process
  – AR binder cannot be PG graded in a meaningful way
  – Recipe specification
Alternatives to SBS Polymer

• Ground Tire Rubber (GTR) – terminal blend
  – Typically proprietary process
  – 10-12% GTR may be added at high temperature and processed with high shear milling
  – Chemical stabilizer added
  – SBS is sometimes used to stabilize the system
  – GTR contains non-rubber materials
    • Carbon black
    • Calcium carbonate
  – Meeting solubility specification may be an issue
  – Settlement of inert materials in contractors tank may occur
  – Cannot be PG graded under current DSR test procedures
Alternatives to SBS Polymer

• Hybrid Binders
  – Blend of SBS and GTR
  – Cross-linked system
  – Storage stable
  – Terminal blend system
  – Current research sponsored by FL DOT at University of Florida
Alternatives to SBS Polymer

- ‘NOTHING’ is not an option
  - PG Grading system is based on climate and traffic
  - Using the wrong grade will lead to poor performance
  - We have enough historical data to prove that PMA does improve pavement performance
  - Flexibility and creativity are needed to come up with answers
DON’T SHOOT THE MESSENGER
Questions?