Polymers in Modified Asphalt

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Kraton Polymers
Polymers in Modified Asphalt

- Types of Polymers
- Compatibility of Polymers
- Effects of Polymers
- Analysis of polymers
- Recovery of PMA
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.
Differing Monomers (Repeat Units)

**Homopolymer**

AAA

**Copolymers**

**Random**

BABABBABABABABABBAB

**Alternating**

ABABABABABABABABABABABABAB

**Block**

BBBBBBBBBBBBBBBBBBBB

**Grafted**

BBBBBBBBBBBBBBBBBBBB

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Polymer Synthesis

- **Condensation Polymerization**
  - Splits off a small molecule (usually water)
  - Requires at least di-functional monomers

\[ x \underbrace{\ldots x}_{n} + y \underbrace{\ldots y}_{n} \rightarrow (\underbrace{\ldots}_{n} xy) \]

- **Addition Polymerization**
  - No molecule split off
  - Involves the opening of a double bond

\[ \equiv \underbrace{_R}_{x} \rightarrow (\underbrace{\underbrace{\ldots y}_{R}}_{x}) \]
Condensation Polymers

Polyamides

\[ \text{H}_2\text{N} - \text{R}' - \text{NH}_2 + \text{HO} - \begin{array}{c} \text{C} - \text{R}' - \text{C} - \text{OH} \end{array} \rightarrow \]

\[ \left\{ \text{H} - \begin{array}{c} \text{N} - \text{R}' - \text{NC} - \text{R}' - \text{C} \end{array} \right\}_x + \text{H}_2\text{O} \]

Polyesters

\[ \text{HO} - \text{R}' - \text{OH} + \text{HO} - \text{C} - \text{R}' - \text{COH} \rightarrow \]

\[ \left\{ \text{O} - \text{R}' - \text{OC} - \text{R}' - \text{C} \right\}_x + \text{H}_2\text{O} \]

Polycarbonates

\[ \text{Cl} - \text{C} - \text{Cl} + \text{HO} - \text{R}' - \text{OH} \rightarrow \]

\[ \left\{ \text{R}' - \text{OC} - \text{O} \right\}_x + \text{HCl} \]
Addition Polymerization

Cationic

\[ \text{RI}^+ + \text{M} \rightarrow \text{RMI}^+ \xrightarrow{\text{M}} \text{RMMMMI}^+ \]

Coordination Polymerization
Ziegler Natta

\[
\begin{array}{c}
\text{R}_1 \\
\text{R}_2 - \text{M} \\
\text{R}_3
\end{array}
\]

\[
\begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3
\end{array}
\]
Structures of Common Polymers

ABS
\[ \left[ \begin{array}{c}
  \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}=:\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2 \n  \end{array} \right]_n
\text{C}=\text{N}
\]

\[ T_g = 110^\circ \text{ to } 125^\circ \text{C} \]

Nylon 6,6
\[ \left[ \begin{array}{c}
  \text{N}-\text{(CH}_2\text{)}_6-\text{N}-\text{C}-\text{(CH}_2\text{)}_4-\text{C} \n\end{array} \right]_n
\]

\[ \text{MP } = 240^\circ \text{ to } 265^\circ \text{C} \]
\[ T_g = 50^\circ \text{ to } 60^\circ \text{C} \]

Neoprene
\[ \left[ \begin{array}{c}
  \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \n  \text{H} \quad \text{C}=\text{C} \quad \text{C} \quad \text{C} \quad \text{C}=\text{C} \quad \text{C} \quad \text{H} 
\end{array} \right]_n
\]

\[ T_g = -40^\circ \text{ to } -20^\circ \text{C} \]

Polycarbonate
\[ \left[ \begin{array}{c}
  \text{CH}_3 \quad \text{C} \quad \text{C} \quad \text{O}-\text{C} \quad \text{O} \n  \text{CH}_3
\end{array} \right]_n
\]

\[ T_g = +140^\circ \text{ to } +150^\circ \text{C} \]
Structures of Common Polymers

**Polyethylene**
- $M_p = 130^\circ \text{C} \text{ to } 140^\circ \text{C}$
- $T_g = -125^\circ \text{C}$

**Polypropylene**
- $M_P = 165^\circ \text{C} \text{ to } 175^\circ \text{C}$
- $T_g = -20^\circ \text{C} \text{ to } -5^\circ \text{C}$

**Polyethylene Terephthalate (PET)**
- $M_p = 245^\circ \text{C} \text{ to } 265^\circ \text{C}$
- $T_g = 70^\circ \text{C} \text{ to } 80^\circ \text{C}$

**Polystyrene**
- $T_g = 90^\circ \text{C} \text{ to } +110^\circ \text{C}$
Stereoisomerism

- **Isotactic**
- **Atactic**
- **Syndiotactic**
Polymer Structures

Linear

Branched

Cross-linked
Types of Branching

LDPE

0.910-0.925

HDPE

0.941-0.965

LLDPE

0.910-0.940
Molecular Weight Growth

- **Addition**
- **Condensation**

**R = Slope**

**R = constant implies no termination**

**Molecular Weight**

**Time -->**
Molecular Weight Distributions

**ANIONIC**

- Polydispersity index $d = M_w/M_n$
- Typical KRATON $d = 1.05$

**ZIEGLER-NATTA FREE RADICAL**

- $d \sim 10$ heterogeneous Z-N
- $\sim 4$ homogeneous
- $\sim 2$ metalloocene

Type of reaction determines molecular weight distribution. Measured by GPC.
Thermoplastic vs. Thermoset

Cool

Heat

Heat

Thermoset

Thermoplastic

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Physical States of Polymers

- Amorphous
  - Glass Transition Temperature ($T_g$)

- Semi-crystalline
  - Glass Transition Temperature and melting point ($T_m$)
  - Regular Structure
  - Hydrogen Bonding or Dipole Interactions
**Glass:**
Not ordered on a molecular scale, sometimes very brittle, easily penetrated by solvents/plasticizers

**Crystal:**
very strong local order, not easily penetrated by solvents, Tm can be relatively high
Separation

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

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \]

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

- where

\[ \chi_{AB} = (\delta A - \delta B)^2 / RT \]
Solubility Parameters

- Asphaltenes
- Resins
  - Nylon
  - PET
- Aromatics
  - EVA
  - S
- Cyclics
- Saturates

Non-Solvents for Rubber:
- Methyl Isobutyl Carbinol, Acetone

Good Solvents:
- MEK
- Ethyl Acetate
- Toluene
- Xylene
- Iso-Propyl Acetate
- 1,1,1-Trichloroethane, MNAK
- MIBK
- Cyclohexane
- Cypar® 7
- (Mainly methyl-cyclohexane)
- VM&P Naphtha
- Mineral Spirits
- n-Heptane
- Non-Solvents for Polystyrene
- Isooctane
“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.
Polymer Requirements for Asphalt

- Requirements for Dispersion in Asphalt
  - Thermoplastic
  - Suitable Polarity
  - Minimal Ionic Interactions
  - Minimal Crystallinity
- Requirements for Processing in Asphalt
  - Suitable Molecular Weight
  - Suitable Stability
  - Suitable Dispersibility at Processing Temp
So What Does That Leave?

- Low Crystallinity Polyolefins (LDPE, APP, etc.)
- Styrene Diene Polymers
  - Styrenic Block Polymers (SBS)
  - Random Styrene Diene Polymers (SBR)
- Olefin Vinyl Polymers (EVA, PVC)
- Olefin Acrylic Polymers (Ethylene Acrylates)
Asphalt Compatibility – SBS Example

- Too low asphaltene content: low softening point
- Too high aromaticity: domain weakening
- Too low aromaticity: insufficient solvency power
- (High TR content)
- (Low TR content)

Asphaltene content, %
Physical Effects of Polymers in Asphalt

- Reduce Temperature Susceptibility
- Increase Tensile Strength
- Increase Elasticity
Analysis of Polymers in Asphalt

- Infrared Analysis
- NMR Analysis
- GPC Analysis
- Microscopy
IR Analysis of Polymer in Asphalt
\(^1\)H NMR of Polymer in Asphalt
GPC of Polymer in Asphalt

Roofing Compound 12% SBS

Time (Min)

RI Response

Unaged 1 Mo. 2 Mo. 3 Mo.

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Micrograph of SBS Polymer in Asphalt
Recovery of PMA from Hot Mix

- Polymers may crosslink
- Polymers may adhere strongly to aggregate
- Polymers may be less soluble in the extraction medium than they are in hot asphalt
- There is no guarantee that extracting 98+% of asphalt will also extract 98+% of the polymer modifier.
Recovery of PMA from Hot Mix

- Asphalt and polymers age.
- The chemical changes may alter the thermodynamic minimum morphology.
- The semi-rigid matrix of PMA may not allow morphological changes to accommodate the change in thermodynamically favored morphology.
- Dissolving, then reprecipitating, the PMA will most definitely allow morphological rearrangement.
- Thus the morphology of extracted PMA, and thus the rheological properties of extracted PMA, may be different from those in in situ PMA in hot mix.
Thank you for your kind attention!

Questions? Comments?
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