Performance Resins in Tire Compounding

J. Guiliams*, T. Carvagno, A. van Bennekom, S. Basu, G. van Ruler
April 2014
Clemson University Global Tire Conference
* speaker
Who we are

- A global specialty chemicals company headquartered in Kingsport, Tennessee
- Over 13,000 employees and 44 manufacturing sites around the globe
- A company dedicated to environmental stewardship, social responsibility and economic growth
- 2012 ENERGY STAR® Partner of the Year
- Sales revenue of $9.3 billion in 2011
Our product platforms & strategy in tires

*Post Solutia acquisition*

- **Insoluble Sulfur**
  - No. 1 global position
  - Crystex®
  - Broad capability to evolve product line

- **Antidegradants**
  - No. 2 global position
  - Santoflex®

- **Hydrocarbon Resins**
  - No. 1 global position in portfolio
  - Broad line of PMRs, C5s, C9s, Rosin esters

- Leading position provides revenue to invest in R&D
- Application Development experience helps us understand customer problems and how to fix them
- Having platforms that span industries give the deep understanding of our technology required to innovate

*We are committed to continuing investments in innovation to meet the evolving needs of the tire industry*
Outline

- Resins in rubber applications
- Traditional phenolic tackifying resins vs. performance hydrocarbon (HC) resins
- Benefits of performance hydrocarbon resins
- How to choose the correct performance resin
  - It’s complicated
Resins in rubber applications

- Resin is a very generic term applied to polymeric materials with:
  - Relatively small molecular weight, $M_n$ range: $\sim 500 – 1500 \text{ g/mol}$
  - High $T_g$ in comparison to molecular weight

- Curing & reinforcing resins
  - Phenol-Formaldehyde resol + HMT/HMMM: Crosslinking
  - Phenol-Formaldehyde novolak + HMT/HMMM: Reinforcing - modifying tear/abrasion resistance

- Tackifying resins
  - Phenol-Formaldehyde novolak: Tack for green tire
  - Hydrocarbon
  - Rosin: Tack for green tire, Modifying viscoelastic profile of rubber

"Traditional"

"Performance"
# Resins in Rubber Applications

<table>
<thead>
<tr>
<th>Reactive Resins</th>
<th>Non-Reactive Resins</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Curing Resins</strong></td>
<td><strong>Reinforcing Resins</strong></td>
</tr>
<tr>
<td>Phenol-Formaldehyde</td>
<td>Phenol-Formaldehyde</td>
</tr>
<tr>
<td>resol type</td>
<td>novolak type</td>
</tr>
<tr>
<td></td>
<td>High Styrene resins</td>
</tr>
<tr>
<td></td>
<td>Methylene donors</td>
</tr>
<tr>
<td></td>
<td>Resorcinol(-formaldehyde)</td>
</tr>
<tr>
<td></td>
<td>Poly-butadiene</td>
</tr>
<tr>
<td></td>
<td>Styrene-Acrylonitrile</td>
</tr>
<tr>
<td></td>
<td>Poly-vinyl-chloride resins</td>
</tr>
</tbody>
</table>

Rubber Technology, John S. Dick
What are non-reactive resins?

- Materials that modify the visco-elastic profile of polymers, resulting in compounds with specific properties other than the polymer itself (e.g. adhesion, stiffening)

- Produced from petrochemical or natural feedstock
  - C5 or C9 streams
  - Coal coke
  - Styrene and/or AMS
  - Natural
  - Hydrocarbon resin
    - aliphatic, aromatic, mixed aliphatic-aromatic
  - Coumarone-Indene
  - Pure monomer resin (PMR)
  - Rosin and Polyterpene resin
Novolak phenol formaldehyde resin: non-reactive, tackifying

- Phenol / formaldehyde >1
- Acidic catalyst

- Linear
- R is often t-butyl, octyl
- Softens the rubber to get better surface contact
- Used as Tackifying resin

B. Stuck, et. al. (May, 1997) "Phenol-Formaldehyde Resins in Tire Applications" Educational Seminar at ACS Rubber Division Meeting, Anaheim, CA
Hydrocarbon resins
possible structures

- Aliphatic C5 resins
  - Linear, similar to natural rubber

- Aliphatic-aromatic C5/C9 resins

- Aromatic C9 resins
  - Similar to polystyrene

- Many can be fully and partially hydrogenated (H2) to change aliphatic-aromatic balance

Each resin structure has a different effect on the visco-elastic properties of polymers
Impact of Performance Resins on rubber properties

- Entanglement density
  - Tensile properties
  - Hardness / low strain modulus
- Processability

- Wet & dry traction
- Rolling resistance
- Compound Tg

Based on resin rubber compatibility various compound performance balances can be achieved.
Study design
Formulation & processing

- Performance hydrocarbon and traditional phenolic resins were tested
  - 10 phr added to Ref
- Mixing done in 3 stages
  - Internal mixer
  - 2-roll mill
- Results from multiple studies conducted at several laboratories are included

### Passenger car light truck (PCLT) tread reference (Ref) formulation

<table>
<thead>
<tr>
<th>Components</th>
<th>Reference (phr)</th>
<th>Resin (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sSBR: 25% styrene, 42% vinyl, Mooney 65</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>BR: 44 Mooney, high-cis</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Silica: N\textsubscript{2} surface area 175 m\textsuperscript{2}/g, 6.5 pH</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Carbon Black N 234</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Si 69 (Silane)</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>TDAE Oil</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Santoflex\textsuperscript{®} (6PPD)</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>IPPD</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>TMQ</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>wax</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Resin</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>CBS</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>DPG</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Traditional phenolic tackifying vs. HC Performance Resins

- Performance resins provide similar Processability improvement
  - Trade-off Dry Handling when compared to traditional phenolic tackifying resins

- Performance resins provide significantly better Wet Grip / Rolling Resistance balance when compared to traditional phenolic tackifying resins

Performance Resins give improved tan delta 0°/60°C balance vs. traditional phenolic tackifying resins

DMA conditions: Simple shear, 10 Hz.
Temp sweep at 0.5% strain or strain sweep at 30°C
Benefits of performance hydrocarbon resins

Processability:
- Improved
  - Viscosity
  - Scorch time
- Trade-off
  - Cure time

Performance:
- Improved
  - Ice traction
  - Wet traction
  - Dry traction
- Trade-off
  - Dry handling
  - Rolling resistance

Indexed values. Higher is better.
(predictors from DMA and other lab measurements)

Hydrocarbon Performance Resins provide wide range of processing and performance benefits
How to choose performance HC resins

- Multiple types of hydrocarbon resins (HC) available
  - Aliphatic
  - Aromatic
  - Mixed aromatic-aliphatic
- Different performance balance from different HC resins
- HC resin attributes provide performance balance:
  - Resin molecular weight
  - Glass transition (Tg)
  - Aliphatic content
  - Resin loading

Typical performance trade-off: Wide range of WG/RR balance possible

DMA conditions: Temp sweep, Simple shear, 10 Hz, 0.5% strain

Knowledge of resin attributes and their impact on rubber is crucial to selection
How to choose performance resins: Attributes

- Resin attributes such as Tg, molecular weight and aliphatic content are interdependent and have complex relationships to each other.

Data from the resins tested in this study

Resin attributes change compatibility in different rubbers
Change the resulting effect on compound performance
Impact of resin attributes on properties of rubbers used in tires

Example system of four resins (A-D) with similar aliphatic content and with Tg ~ Mn were chosen
Model compounds: 30 phr resin, sSBR or BR

- Increasing resin Mn: A < B < C < D results in
  - Progressive shift in position & height of Tg peaks up to C
  - Beyond C, resin becomes partially incompatible at 30 phr resin
Impact of resin attributes on properties of PCLT tread compound

Tread compound: 10 phr resin, 80 phr Si, 70/30 sSBR/BR

- Like model compounds, similar trends with Mn observed
- Unlike model compounds at 30 phr, tread at 10 phr resin does not show incompatibility at high Mn (D)

For the simple example system, clear impact of resin attributes on compound performance is observed
How to choose Performance Resins
It's complicated

- For most resins, complicated structure-property relationships exist.
- Different resins impart different range and balance of compound performance.

Correct resin choice is critically important to achieve desired performance balance.
Summary

- Traditional phenolic vs. performance hydrocarbon resins
  - Performance hydrocarbon resins provide better rolling resistance and wet grip balance

- Benefits of performance hydrocarbon resins:
  - Processing benefits: Better viscosity, scorch safety, tack
  - Performance benefits: Better wet, dry, ice traction & tear

- How to choose the correct performance resin
  - It’s complicated - Resin choice depends on:
    - Rubber type & blend ratio
    - Resin loading
    - Resin type & molecular attributes

Selection of the appropriate resin for a rubber formulation is critically important to achieve desired performance
Thank you