SERVICE LIFE PREDICTION MODEL FOR TIRE BELTCOAT COMPOUNDS

Innovations in Rubber Design (RIEG organized)
London, UK

Edward R Terrill
Akron Rubber Development Laboratory, Inc.
2887 Gilchrist Rd. Akron, Ohio 44305
Ph: 330-794-6600  Fax: 330-794-6623

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Key Question

• Is it possible to predict service life of a beltcoat compound (asked by National Highway Safety Administration [NHTSA])?
Tire used for Oxidation Kinetics based Predictive Model Study

The BFGoodrich Touring T/A SR4 P-metric P195/65R15 89S tire (new tire provided by NHTSA)

The belt-coat compound was taken from between the belts, excluding the wedge compound.
Comparison of Predicted Elongation to Break Results to In-Service Tire Elongation to Break Data

Predicted Curve
In-service Tire Data
Outline

• Part 1 - Predict Beltcoat Compound Service Life
  – Elongation-to-break aging kinetics
  – Oxidation kinetics
  – Effect of Oxygen Partial Pressure on Oxygen Consumption Rate
  – Diffusion Limited Oxidation Model Predictions of Oxidation Rate in the belt-coat compound of a tire

• Part 2 – Determine Chemical Structure of the Crosslink Formed during Oxidation
  – Crosslink Distribution
  – $^{13}$C NMR
  – Triphenylphosphine (percentage of polysulfidic)
  – FTIR
Elongation to Break as a Function of Oven Aging Time for New Tire Belt-Coat Compound
Time-Temperature Superposition of Elongation to Break Data for Belt-Coat Compound
Oxygen Consumption Rate of Belt-Coat Compound
Integrated Oxygen Consumption as a Function of Aging Time of Belt-Coat Compound
Time-Temperature Superposition of Integrated Oxygen Consumption Results from Belt-Coat Compound
Summary of Shift Factors as a Function of Temperature

Empirical Shift Factors (at)

O₂ cons
CO₂ gen
CO gen
vol org

eₐ = 23 kcal/mole

eₐ = 30 kcal/mole
Comparison of Predicted Elongation to Break Results to In-Service Tire Elongation to Break Data

Shifted Aging Time, years at 22.6°C

Elongation to Break (%)
Proposal - The Missing Factors are the following:

• Beltcoat in a tire is subject to higher oxygen partial pressure (from inflation pressure) than provided by atmospheric oxygen pressure.
• In-service tire spends a portion of its time at running temperature. We assume average tire is running 4% while in service.
Effect of Oxygen Partial Pressure on Oxygen Consumption Rate for the New Tire

Oxygen Consumption Rate (moles O$_2$/g-s)

Oxygen Partial Pressure (cm Hg)

- 20°C
- 55°C
- 65°C
Dynamic Shoulder Component Temperatures
DLO Model Prediction for the Oxygen Consumption Rates in an Inflated Stationary Tire in Phoenix, AZ
DLO Model Prediction for the Oxygen Consumption Rates in a Running Tire

![Graph showing oxygen consumption rates in a running tire](image-url)
Comparison of Predicted Elongation to Break Results to In-Service Tire Elongation to Break Data
Part 2 - Key Question

• What is the chemical structure of the crosslink formed during oxidation (asked by National Highway Safety Administration [NHTSA])?
### Beltcoat Compounds (Tires provided by NHTSA)

<table>
<thead>
<tr>
<th>Tire Manufacturer</th>
<th>Tire Model</th>
<th>Tire Size</th>
<th>Load Range</th>
<th>Speed Rating</th>
<th>DOT</th>
<th>Max IP (kPa)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF Goodrich</td>
<td>T/A SR4</td>
<td>P195/6 5R15</td>
<td>89</td>
<td>S</td>
<td>APC6BB 113803</td>
<td>240</td>
<td>New</td>
</tr>
<tr>
<td>BF Goodrich</td>
<td>T/A SR4</td>
<td>P195/6 5R15</td>
<td>89</td>
<td>S</td>
<td>APC6BB 11455</td>
<td>240</td>
<td>Field – 7.38 yrs / 44,385 miles of service in Phoenix, Arizona</td>
</tr>
<tr>
<td>BF Goodrich</td>
<td>T/A SR4</td>
<td>P195/6 5R15</td>
<td>89</td>
<td>S</td>
<td>APC6BB 113803</td>
<td>240</td>
<td>Oven aged at 60°C for 6 weeks, max sidewall pressure, 42% O₂ inflation gas, capped</td>
</tr>
<tr>
<td>BF Goodrich</td>
<td>T/A SR4</td>
<td>P195/6 5R15</td>
<td>89</td>
<td>S</td>
<td>APC6BB 113803</td>
<td>240</td>
<td>Wheel tested for 168 hrs</td>
</tr>
</tbody>
</table>

### Lab Mix Model Compounds (mixed at ARDL)

<table>
<thead>
<tr>
<th>Source</th>
<th>Polymer</th>
<th>Cure System</th>
<th>Filler Loading</th>
<th>Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab Mix (Compound #5)</td>
<td>Natural Rubber</td>
<td>Conventional</td>
<td>Unfilled</td>
<td>Aged and Un-aged for Infra-red Spectroscopy</td>
</tr>
<tr>
<td>Lab Mix (Compound #9)</td>
<td>Natural Rubber</td>
<td>Efficient</td>
<td>Unfilled</td>
<td>Aged and Un-aged for Crystallization Studies</td>
</tr>
</tbody>
</table>
Crosslink Density of Aged and Unaged Tires

![Bar chart showing crosslink density for new tire, field tire, oven-aged tire, and wheel-tested tire. The crosslink density is measured in moles/cc compound. Field tire has the highest density, followed by oven-aged tire, then new tire, and wheel-tested tire has the lowest density.]
Crosslink Distribution of Aged and Unaged Tires

- new tire
- field tire
- oven-aged tire
- wheel-tested tire

Crosslink Density (moles/cc compound)

- Poly
- Di
- Mono
Aerobic aging of tire belt-coat compounds led to increased crosslink densities. Changes in crosslink distribution were followed using wet chemistry (thiol cleavage agents). By this technique the new crosslinks formed could appear to be either polysulfidic type or monosulfidic type. The formed crosslinks in the field tire were mostly “polysulfidic” and during oven aging they were mostly “monosulfidic”.

Observation
Carbon-13 NMR Spectrum of Polyisoprene
$^{13}\text{C}$ NMR Spectrum of Carbons Bonded to Sulfur
Chemical and Physical Crosslink Densities

Crosslink Density by Swelling (moles/cc)

Total Sulfur Chemical Crosslink Percentage by 13C NMR
Observation

From $^{13}$C NMR spectroscopic analysis, no evidence was found for formation of more sulfur crosslinks in the field or oven-aged belt-coat compounds.
Triphenylphosphine-Extractable Sulfur in Oven-Aged and Un-aged Tires
Observation

The triphenylphosphine results of the extractable sulfur in the network suggest that the original sulfur network stays intact during these aging conditions (not thermally reverted).
## Infrared Results

<table>
<thead>
<tr>
<th></th>
<th>Percent increase absorbance at 1010 cm⁻¹ after aging</th>
<th>Percent increase absorbance at 1710 cm⁻¹ after aging</th>
<th>Percent increase absorbance at 3400 cm⁻¹ after aging</th>
<th>Overall Percent decrease in absorbance associated with cis alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Cure</td>
<td>89</td>
<td>470</td>
<td>215</td>
<td>-20</td>
</tr>
<tr>
<td>Efficient Cure</td>
<td>73</td>
<td>53</td>
<td>92</td>
<td>NC</td>
</tr>
<tr>
<td>Peroxide Cure</td>
<td>44</td>
<td>11</td>
<td>48</td>
<td>NC</td>
</tr>
</tbody>
</table>
Infrared Spectrum of Aged and Un-aged compound
(High sulfur, unfilled compound)

![Infrared Spectrum Graph]

- **Compound #5**
- Aged Compound #5
  (5 weeks at 70 °C)
Observation

By IR spectroscopy, the linkages formed during aerobic aging appear to be oxygenated species (sulfoxide, ether, epoxide, or peroxide). However, the sulfur linkages are probably participating in the formation of crosslinks in the form of sulfoxide linkages. At higher temperature (e.g., oven aging), the oxygenated linkages rearrange to carbon-carbon linkages with the evolution of CO$_2$ and SO$_2$ gases.
Crystallization Kinetics of Aged and Un-aged Compound

(Compound #9 - efficient cure, unfilled, high monosulfidic)

**Normalized Load**

- **unaged**
- **1 week at 70°C**
- **2 weeks at 70°C**
- **3 weeks at 70°C**
- **4 weeks at 70°C**
- **5 weeks at 70°C**

**Time (hours)**

0.1 to 1000
Summary and Conclusions

The crosslinks formed during aerobic aging of belt-coat compounds were found to be of two types. The following mechanism is proposed to explain the results from the various techniques. The chemical structure of one type is probably sulfoxide (sulfur-oxygen). The second type is probably carbon-carbon. The former was the primary crosslink structure formed during field service. The later was the primary crosslink structure formed during oven aging. Temperature, presumably, is the key factor governing the structure of the crosslinks formed.

The oven-aged tire belt-coat and the field-service tire belt-coat compounds were obtained with the same total crosslink density, differing in crosslink types. Thereby, these two samples provided a comparison of the role of the crosslink types formed during aerobic aging on physical properties. By tensile properties and crack growth rate, there was no significant difference between the field and oven-aged belt-coats.

The fundamental mechanism of property decay during aerobic aging was considered by examining crystallization kinetics before and after aging. The crystallization kinetic data suggest that oxidation of natural rubber is associated with loss of crystallizability on stretching. Crystallizability was presumably affected by pendant side groups and cis to trans rearrangements.