ELASTOMER TECHNOLOGY

- Understand the functions of the various components of rubber compound recipes.
- Explain the significance of vulcanization parameters, including scorch time, cure time, and cure rate index.
- Understand how crosslink structure (crosslink density and crosslink distribution) affects the mechanical properties of rubber compositions.
- Explain how fillers, particularly reinforcing fillers, affect the mechanical properties of rubber compositions.
- Identify the chemical systems most suitable for vulcanizing common elastomers.

Rubber Vulcanization

- Vulcanization is the process of forming a molecular network of linked polymer chains.
- Networks are formed by chemical crosslinks between chains:
  - Carbon-carbon bonds
  - Sulfur atoms or chains of sulfur atoms
  - Polyfunctional organic molecules
  - Polyvalent metal cations

- Goal: a thermoset product with desirable physical properties.
- Vulcanizate properties depend on the type and number (density) of crosslinks.
Rubber Compound Components

- Elastomer(s)
- Cure system
  - Crosslinking agent
  - Accelerator(s)
  - Cure activators (co-reactants with accelerator)
- Processing aids (improve post-cure processing properties)
  - Oils
  - Waxes
  - Tackifying resins
- Antidegradant(s)
  - Antioxidants
  - Antiozonants
- Pigments
- Particulate fillers and extenders
  - Reinforcing (carbon black, silica)
  - Non-reinforcing (clay, CaCO₃, TiO₂)

Crosslink Density:
Effects on Polymer Properties

- Crosslink density (degree of crosslinking) = number (mols) of crosslinks/unit volume.
- Crosslink formation affects elastomer properties:
  - Hardness increases.
  - Elastic behavior favored.
  - Hysteresis losses decrease.
  - Tensile and tear strength increase until crosslink density exceeds optimum levels.
Effects of Crosslink Type & Distribution

- Crosslink distribution: in sulfur vulcanization, the molar densities of monosulfide (C–S–C), disulfide (C–S–S–C), and polysulfide (C–Sₙ–C) crosslinks.
- Thermally stable crosslinks (C–C bonds, C–S–C bonds) contribute to
  - Low reversion (thermal stability)
  - Low compression set
- Thermally labile or flexible crosslinks (ionic bonds: -COO⁻⁻⁻M²⁺⁻⁻⁻OOC⁻⁻⁻; di- or polysulfide bonds: C–Sₙ–C) contribute to
  - Increased thermal reversion (crosslink cleavage)
  - Increased tear resistance
  - Increased fatigue resistance
- Crosslink structure affects the mechanical properties of NR vulcanizates more strongly than it affects those of synthetic elastomer vulcanizates.

Monitoring Vulcanization:
Oscillating Disk Rheometer

ISO 3417, ASTM D2084
Vulcanization Parameters

- The time until crosslinking starts
  - Scorch time, scorch resistance, scorch delay ($t_{s2}$)
  - Goal: adequate time for mixing, forming, or molding the rubber compound

- The rate of crosslink formation
  - Cure rate index (CRI)
    \[
    \text{CRI} = \frac{100}{t'_{90} - t_{s2}}
    \]
  - Goal: rapid, controllable rate

- The extent and type of crosslinking
  - Maximum torque ($M_max$), crosslink density, crosslink distribution
    (sulfur vulcanization: monosulfide, disulfide, polysulfide)
  - Goal: desired physical properties

Vulcanization Profiles

![Vulcanization Profiles Diagram]
Sulfur Vulcanization

- Suitable for diene-based elastomers:
  - NR, IR
  - BR
  - SBR
  - NBR
  - IIR
  - EPDM

- Low-cost
- Rate easily controlled
  - Accelerators
  - Retarders
- Crosslink distribution easily controlled (accelerators)
  - Monosulfides: heat resistance
  - Di-, polysulfides: tensile strength, elastic properties

Sulfur Vulcanization: Basic Rxn

* Alternative ionic mechanism also possible.
Sulfur Vulcanization: Accelerators

- Sulfur is a sluggish cross-linking agent, especially for synthetic rubber.
- Sulfur/amine-based accelerators allow faster vulcanization (ionic mechanism) at relatively low temperatures.
- Accelerated vulcanizations use lower levels of sulfur.
  - Aging properties improved
  - Overcuring reduced
- Cure onset (scorch) can be controlled.
- Crosslink distributions can be controlled (mono-, di-, or polysulfide).

Sulfur Vulcanization: Accelerated Rxn

- Slower cure onset
- Faster cure rate

• White tires → ZnO filler
• Starting in 1912, carbon black replaced ZnO and other filler materials in tires.
• Now: ~90% of all carbon black produced is used in the manufacture of tires and other rubber goods.

Reinforcing Fillers

• Synthetic elastomers have no inherent reinforcing properties
  - Low resistance to abrasion, tear
  - Low compound viscosity
  - Low hardness, toughness

• Non-reinforcing fillers
  - Show little or no physical interaction with polymer phase
  - Serve as extenders or pigments

• Reinforcing fillers
  - Create physical and chemical interactions with polymer phase
  - Affect performance characteristics of vulcanizates

• Reinforcement determined by
  - Particle size (upper limit: <1000 nm)
  - Particle surface area
  - Surface chemistry

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<tr>
<th>Non-Reinforcing</th>
<th>Reinforcing</th>
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<tr>
<td>Clay (kaolin)</td>
<td>Carbon black</td>
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<tr>
<td>CaCO₃</td>
<td>SiO₂ (precipitated)</td>
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Rubber Compounds: Carbon Black-filled

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<tr>
<th>Component</th>
<th>SBR</th>
<th>EPDM</th>
<th>NBR</th>
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</tr>
<tr>
<td>Antioxidant</td>
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<td>2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

**Performance**

- Cure time, min: 25, 20, 25, 25, 20
- Tensile str., MPa: 13, 23.6, 1.6, 15.4, 1.4, 19.3
- Elongation, %: 310, 520, 310, 410, 590, 610

* Parts per hundred (phr) of rubber. ① Optimum cure at 155°C. ② Assumed no accelerator shown in source table.


Antidegradants

- Elastomers with many carbon-carbon double bonds (NR, IR, BR, SBR, NBR, CR) are attacked by oxygen and ozone.
- Halogenated elastomers (CR, BIR, CIR) are susceptible to thermal decomposition (~HX).
- Outcomes:
  - Hardening or softening
  - Cracking
  - Loss of elastic properties
  - Reduced service life
- Antioxidants are added to rubber compounds to react with oxygen.
- Antiozonants are added to rubber compounds to react with ozone and oxygen.
Antidegradants (cont.)

- Contain functional groups (OH, NH, SH) that act as chain terminators.

- Antioxidants
  - Peroxy scavengers react with peroxy radicals (ROO$_2^·$)
  - Hydroperoxide scavengers react with ROOH.
  - Types:
    - Hindered phenols
    - Alkylidiphenylamines
    - Dihydroquinolines
    - Organophosphites

- Antiozonants
  - Function depends on ability to migrate to rubber surface
  - Types:
    - Dialkyl- or diaryl-p-phenylenediamines
    - Dihydroquinolines