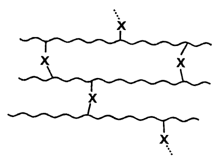
ELASTOMER TECHNOLOGY

- 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 depends on the type and number (density) of crosslinks.

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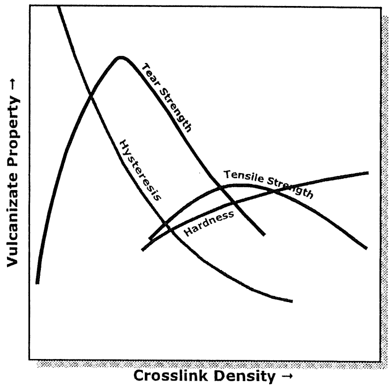
Rubber Compound Components

- **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, $CaCO_3$, TiO_2)**

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.**



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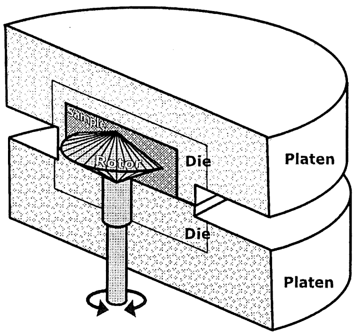
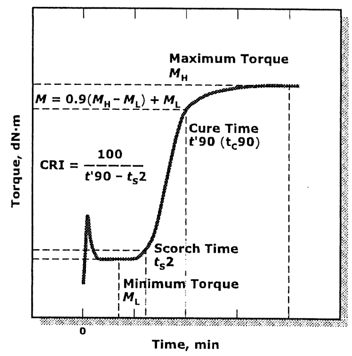
Effects of Crosslink Type & Distribution

- **Crosslink distribution: in sulfur vulcanization, the molar densities of monosulfide (C-S-C), disulfide (C-S-S-C), and polysulfide ($C-S_x-C$) 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: $-COO^- \; M^{2+} \; ^-OOC-$; di- or polysulfide bonds: $C-S_x-C$) 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





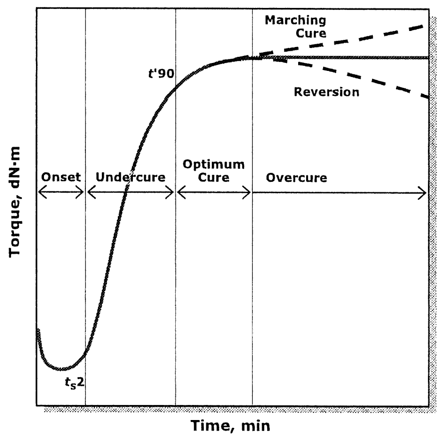
ISO 3417, ASTM D2084

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)**

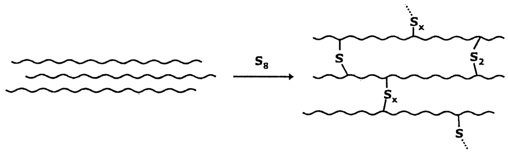
    $$CRI = \frac{100}{t'90 - t_S2}$$
  - **Goal: rapid, controllable rate**
- **The extent and type of crosslinking**
  - **Maximum torque (M_H), crosslink density, crosslink distribution (sulfur vulcanization: monosulfide, disulfide, polysulfide)**
  - **Goal: desired physical properties**

Vulcanization Profiles

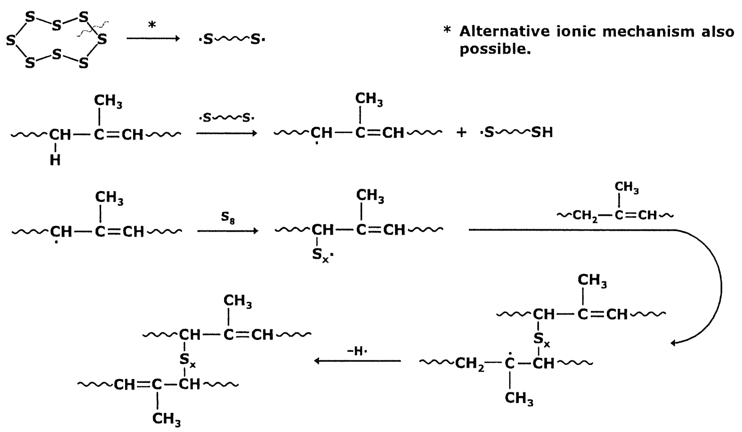


Sulfur Vulcanization

- 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

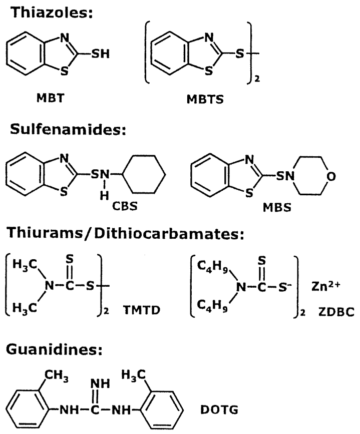


Sulfur Vulcanization: Basic Rxn

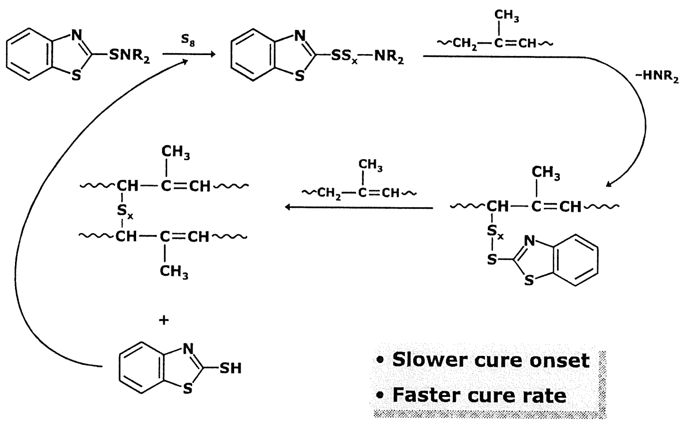


Sulfur Vulcanization: Accelerators

- **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 poly-sulfide).**

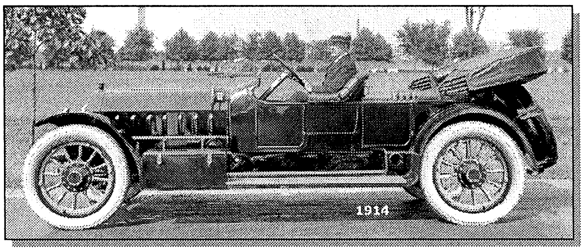


Sulfur Vulcanization: Accelerated Rxn



- **Slower cure onset**
- **Faster cure rate**

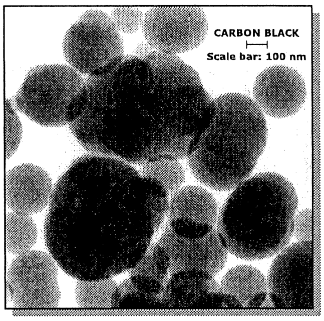
Adapted from M.H.S. Gradwell & N.R. Stephenson, 2004, *Rubber Chem. Technol.* 77 931-946.



- **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



Non-Reinforcing	Reinforcing
Clay (kaolin) $CaCO_3$ $BaSO_4$	Carbon black Silica (precipitated)

Image adapted from S.-L. Kim & D.H. Renecker, 1993, *Rubber Chem. Technol.* 66, 559-566.

Rubber Compounds: Carbon Black-filled

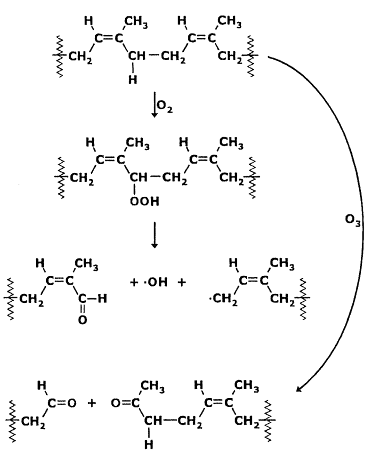
		Elastomer					
		SBR		EPDM		NBR	
	Component[a]	gum	black	gum	black	gum	black
	Elastomer	100	100	100	100	100	100
Reinforcing Filler:	Carbon black		50		50		50
	ZnO	4	4	5	5	5	5
	Stearic acid	2	2	1	1	1	1
	Sulfur	1.8	1.8	1.0	1.0	1.0	1.0
	Accelerators	1.25	1.25	1.5	1.5	0.6	0.6?[c]
	Processing aids	10	10	25	25	10	10
	Antioxidant	2	2			1.5	1.5
	Performance						
	Cure time, min[b]	25	20	25	25	25	20
	Tensile str., MPa	1.3	23.6	1.6	15.4	1.4	19.3
	Elongation, %	310	520	310	410	590	610

[a] Parts per hundred (phr) of rubber. [b] Optimum cure at 153°C. [c] Assumed; no accelerator shown in source table.

Adapted from J.R. Beatty & M.L. Studebaker, 1975, *Rubber Age* 107(8) 20-35.

Antidegradants

- **Elastomers with many carbon-carbon double bonds (NR, IR, BR, SBR, NBR, CR) are attacked by oxygen and ozone.**
- **Halogenated elastomers (CR, BIIR, CIIR) 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.**



Adapted from G.-Y. Li & J.L. Koenig 2005 *Rubber Chem. Technol.* 78, 355-390; S. Commereuc *et al.* 1997 *Polym. Degrad. Stabil.* 57, 175-182.

Antidegradants (cont.)

- **Contain functional groups (OH, NH, SH) that act as chain terminators.**
- **Antioxidants**
  - **Peroxy scavengers react with peroxy radicals ($RO_2\cdot$)**
  - **Hydroperoxide scavengers react with ROOH.**
  - **Types:**
    - **Hindered phenols**
    - **Alkyldiphenylamines**
    - **Dihydroquinolines**
    - **Organophosphites**
- **Antiozonants**
  - **Function depends on ability to migrate to rubber surface**
  - **Types:**
    - **Dialkyl- or diaryl-*p*-phenylenedi-amines**
    - **Dihydroquinolines**