Rubber Synthesis & Processing
Overview

INTRODUCTION (BRIEF HISTORY & CLASSIFICATION)

THE FUTURE OF THE RUBBER INDUSTRY IN SAUDI ARABIA (HIGH INSTITUTE, SABIC & ARAMCO)

SYNTHESSES AND PROPERTIES OF RUBBER (EPDM, B R & SBR)

FILLER AND ADDITIVES AND COMPOUNDING (OILS, CARBON BLACK, CARBONATE, CLAY, SILICA, MINERAL FILLERS & COMPOUNDING)

VULCANIZATION (SULFUR & PEROXIDE)

PROCESSING (EXTRUSION, INJECTING, MOULDING & CALENDARING)
Elastomers have relatively long chains, high degree of flexibility in room temperature, linked by network between the chains. Joints are linked together by network, and become solid-like structures, chains cannot slip past each other under external stresses.

Deal rubber can stretched up to 10 times and at least twice from its primary length, and quickly return to its original length.

Network is achieved chemical or physical crosslinks, physical reversible and unstable with high temperature.
1. BRIEF HISTORY

Eraser was the first use for rubber by Magellan.

American indigenous peoples used it as waterproof and footwear.

In England were produced as waterproof fabrics and snow-boots.

In cold weather became brittle, and when leave it in the sun became gum-like.

Many trying to improvement rubber qualities, Goodyear discovered vulcanization in 1840, accident.

Hancock in 1842 try to find and discovery the secret way of vulcanization.

In 1850, used rubber as toys, also hollow balls for golf and tennis.

In 1895, Michelin had the bold idea have get used to the tire to the automobile.

The Russians and the Germans start to synthesize rubber. In 1914-1918, the drop in natural rubber production in Brazil matched with first world war, causing the need for lower cost products with vegetable supplies in order to manufacture tires.
2. CLASSIFICATION OF RUBBER

2.2.1. SYNTHESIS AND NATURAL

NATURAL NR known as Latex, from the large woods tree Hevea Brasiliensis. Now latex collected from Brazil, India, Malaysia, Indonesia, Sri Lanka, Vietnam, Cambodia.

Natural product as a milky liquid, 0.98 g/cm3 and 6.5 to 7.1 pH, molecular weight between $10^4 – 10^7$, and Mw/Mn 2.5 to 10, structures cis-1,4,- poly isoprene.

<table>
<thead>
<tr>
<th>CONSTITUENT</th>
<th>CONTENT %</th>
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<tbody>
<tr>
<td>Rubber</td>
<td>30 – 40</td>
</tr>
<tr>
<td>Proteins</td>
<td>1.0 – 1.5</td>
</tr>
<tr>
<td>Resins</td>
<td>1.5 – 3.0</td>
</tr>
<tr>
<td>Minerals</td>
<td>0.7 – 0.9</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>0.8 – 0.1</td>
</tr>
<tr>
<td>Water</td>
<td>55 – 60</td>
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SYNTHETIC RUBBER, World War II, was causes of developments in Germany production of a polymer as a replacement for the natural rubber for general-purpose application.

Many kind of synthetic rubber for example Styrene Butadiene Rubber (SBR), polybutadiene rubber (PR) and nitrile rubber (NBR).

Synthesis by poly-reactions such as radical and ionic or coordinating polymerization and copolymerization, synthesis by some types emulsion, solution and suspension.
2.2. GENERAL, SPECIAL & SPECIALTY PURPOSE

GENERAL-PURPOSE ELASTOMERS, good physical properties, process ability and compatibility, generally economical, good abrasion resistance and tensile properties. Constitute the largest volume of polymer used. For example, Natural rubber (NR), Polyisoprene rubber (IR), Styrene-butadiene rubber (SBR) and Butadiene rubber (BR).

SPECIAL PURPOSE ELASTOMERS, have all unique properties, which cannot be matched by the general-purpose types and are very important for manufacturing industrial and automotive rubber products. For example, Ethylene-propylene rubber (EPM and EPDM), Chloroprene rubber (CR) and Acrylonitrile-butadiene rubber or Nitrile rubber (NBR).
SPECIALTY ELASTOMERS great number of polymers with very specific properties, in many cases of great importance for the automotive, aircraft, space, and offshore industries. For example, Chlorosulfonated Polyethylene (CSM), Acrylic Rubber (ACM), Silicone Rubber (PMQ/PV/MQ/VMQ), Floursilicone Rubber (FPQ), Fluor elastomers (FPM/FFKM/FEPM), Urethane Rubber (AU/EU), Epichlorohydrine Rubber (CO/ECO/GECO).
THE FUTURE OF THE RUBBER INDUSTRY IN SAUDI ARABIA

2.1. HIGH INSTITUTE FOR ELASTOMER INDUSTRIES

Located in Yanbu city, world's class first institute specializes in the education and training for Elastomer conversion industry.

Established by (Yanpet) an affiliate of SABIC and Exxon Mobil and (TVTC) under the supervision of the (MPMR).

Collaboration agreement with the (UARF) in USA to be the education partner responsible for the preparation of training programs and training of Saudi cadres to work for the institute as instructors and operation technicians as well as preparing all technical specifications for Elastomer equipment and training devices.

100 students every year and work at sabic affiliates.
2.2. SABIC'S PRODUCTS FOR RUBBER

SABIC is committed to producing 100,000 tonnes per year of rubber (including SBR, BR, and EPDM), and carbon black.

The KEMYA elastomers plant started up in 2015, to support Kingdom customer needs. SABIC and ExxonMobil for rubbers products, carbon products with continuous carbon company.

SABIC’s customers will be supported by SABIC’s Application Development Centre in Riyadh to develop rubber products used in construction, automotive and industrial applications such as roof sheeting, building profiles, tires, weather seals, gaskets, hoses and conveyor belts.
3. LANXESS AND ARAMCO

LANXESS and Aramco signed Aramco beyond the seas for "Saudi Aramco" and the company "Lanxess" Germany Chemical.

LANXESS holds 50% of rubber Processing, which includes 3,700 employees and over 20 production facility. For Research Centers of global research.

The most important brands and products:

- Ethylen-propylen-elastomers (EPMs and EPDMs)
- Chloroprene rubber (CR)
- Ethylene-vinyl acetate rubber (EVM)
- Hydrogenated nitrile rubber (HNBR)
- Nitrile butadiene rubber (NBR)
SYNTHESES AND PROPERTIES OF RUBBER

1. EPDM (ETHYLENE PROPYLENE DIENE MONOMER)(SP)

Ethylene and propylene copolymers (EPM) and ethylene, propylene and suitable diene monomer (EPDM),

DIENE type:
- ENB (5-ethylenenorbonene)
- DCPD (dicyclopentadiene)
- HD (1,4- hexadiene)

EPM haven’t unsaturated bonds. So resistant to O2, O3 and chemicals.
EPDM have unsaturated bonds as side groups only and low content 10 % wt, most of them will disappear by vulcanization.

Coordination polymerization used, in aliphatic hydrocarbon solution (pentane and hexane) in the presence vanadium salts (VCl₄, VOCl₃) and ethyl chloraluminum, (EPM) vulcanized by peroxide systems, (EPDM) sulfur mix with fast ultra-accelerators, growing fast with the increasing of double bond content.
Lowest density rubber, $T_g = -70^\circ C$

EPDM: Introduce Diene Monomer (crosslink site, 4-5%)

$E/P$ ratio = 50/50 to 75/25

Automotive rubber products: weather strip, hose
2. BR (POLYBUTADIENE RUBBER)(GP)

Macromolecules may be present in of cis-1,4, trans-1,4 and 1,2-vinyl units, vinyl group isomeric forms (syndiotactic, isotactic and atactic).

Coordination the most or anionic alkyl lithium the most used anionic polymerization.

Polymerization in solution method, non-polar medium used of benzene, toluene and aliphatic. molecular weights of around 250,000 to 300,000 g.mol-1

In Li-BR initiators, easier for processing, they can be extruded in higher ratio under lower temperature, have higher strength.
Structural units mostly depend on type of ed initiator & determines basic properties. 2-vinyl does not have elastic properties, more than 95% of cis-1.4 are the best elastic properties.

Polymerization in low temperatures, linear polymers, increased temperature possibility of their branching is increased.

of non-polar solvents (hexane) used, cis- and trans-1.4 units, low content of 1,2 units, polar medium solvent (tetrahydrofuran) around 90% of 1.2 units and practically does not contain cis-1.4 units.
\[ \text{C}_4\text{H}_9\text{Li} \leftrightarrow \text{C}_4\text{H}_9^-\text{Li}^+ + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \rightarrow \text{C}_4\text{H}_9^-\text{CH}_2^-\text{CH}=-\text{CH}-\text{CH}^-\text{Li} \]

**initiation**

\[ \text{n CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{n CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \rightarrow \text{C}_4\text{H}_9^-\text{CH}_2^-\text{CH}=-\text{CH}-\text{CH}^-\text{Li}^+ \]

**propagation**

\[ \text{H}_2\text{O} + \text{C}_4\text{H}_9^-\text{CH}_2^-\text{CH}=-\text{CH}-\text{CH}_2^-\text{Li}^+ \rightarrow \text{C}_4\text{H}_9^-\text{CH}_2^-\text{CH}=-\text{CH}-\text{CH}_2^-\text{Li}^+ + \text{LiOH} \]

**termination**

polybutadiene
BR reacts slower with oxygen and ozone, however necessary presence of aegradants additives.

The requires containing of proper softeners the most often of aromatic aphthenic.

Sulfur systems most often cured. Mostly sulfonamides or their combinations with thiazyls are used as accelerators.

90% of produced BR is used through production of tires. And largest volume synthetic rubber.
3. SBR (STYRENE-BUTADIENE-RUBBER)

Styrene-butadiene rubbers (SBR) are copolymers used two monomer styrene and butadiene. Butadiene structural units can be as cis-1.4, trans-1.4 or 1.2 (vinyl) units. Shared arrangement of styrene and butadiene units as a random block.

Increasing content of styrene and 1.2 vinyl increase of Tg temperature.

Usually used is free radical copolymerization emulsion in addition anion copolymerization solution.
Free radical copolymerization of butadiene and styrene in emulsion (E-SBR) do
not temperatures around 50°C (hot rubbers) or 5°C (cold rubbers).

At 50°C they are mainly peroxodisulfates, at 5°C they are reduction-oxidation
initiation systems consisting of hydroperoxide (p-menthane hydroperoxide).

Cold E-SBR are less branched and have more narrow distribution and Better
mechanical strength and hot E-SBR Very branched structure poor mechanical
strength.
FILLER AND ADDITIVES AND COMPOUNDING

Why Compounding is necessary? Raw rubber has very limited use, physical properties can be enhanced and Cost can be lowered.
Compounding is mixing process to addition many additives, fillers, polymers in uniform mixture to enhance properties.

Reinforcing fillers
Vulcanization: crosslinking
Process aids
Extenders: to reduce cost
Environmental resistors: O2, O3, heat, moisture
1. Vulcanization: Crosslinking or Curing

Vulcanization is the process of forming chemical bonds to connect the flexible long-chain rubber molecules into a three-dimensional network.

- Near to 3-D network
- Low strength to High strength
- Thermoplastic to Thermosetting
- Soluble to Insoluble

<table>
<thead>
<tr>
<th>TYPES</th>
<th>COMMON USE</th>
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<tbody>
<tr>
<td>Sulfur</td>
<td>Natural rubber, Isoprene, SBR, Butyl, Butadiene, EPDM, Nitrile</td>
</tr>
<tr>
<td>Organic Peroxides</td>
<td>Urethane, Silicone, Chlorinated Polyethylene, crosslinked Polyethylene, PVC/Nitrile</td>
</tr>
</tbody>
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Carbon Black

Carbon Black is a Reinforcement filler and aids to improve toughness and strength. Such as physical and chemical characteristics.

Effective of carbon black such as structure, particle size, surface activity, and porosity.

Ideal particle size of carbon black ranges from 8 nanometers for furnace blacks (crude oil), 300 nanometers for thermal blacks (natural gas).

Small particles size increase reinforcement, abrasion resistance, and increase tensile strength.
Accelerators

- increase **cross-linking rate** and efficiency.
- faster cure time and **less** sulfur needed.

Organic compounds are used in function as accelerators.

All accelerators compounds contain **sulfur** and **nitrogen** atoms in their molecules.

**Activator**

Activators are ingredients used to activate the accelerator and improve its **effectiveness**. Examples include Zinc oxide and Stearic acid.

**Retarder**

Reduce the **scorch** time of a compound. PVI (Cyclohexyl-n-thiophthalimide)
Process aids
Chemical plasticizer
Accelerate breakdown of MW by increasing oxidative chain scission, Sulfonyl acids.

Physical plasticizer
Softens compound by dilution effect, Fatty acid, oil.

Extenders
Additives that reduce the cost without great loss in physical property.
Solid fillers: clay, CaCO3

Age resistors
Antioxidants and antiozonants. Inhibit chain scission, cross-linking and chemical alteration of chain due to condition environment.
2. COMPOUNDING METHOD

Some stages must be flow before use in the processing & some thermal test.

First step is add the all the additives require in internal mixer at temperature 70-90 °C accept vulcanize and accelerators agents to avoid any crosslinked.

Note: mix the filler and additives with oil used firstly

Second step can add the vulcanize and accelerators agents at low temperature 30-40 °C.
The last step used two roll mill, the disparity of the compound ingredients confirmed. In the last step make a sheet compound for next processing.

After the preparation the rubber compound, few grams taken to do two thermal analysis (Mooney viscometer and Moving Die Rheometer), determining processing behavior.
Mooney viscometer

Measure of the viscosity of compound determined in a Mooney shearing disk viscometer. (at 100 to 125 oC).
Moving Die Rheometer (MDR) analysis the cure characteristics of Rubber Compound.
1. **EXTRUSION**

The rubber compound is extruded thru the extruder and then it get vulcanized. Then, the compound goes via a curing chamber to control the curing time. After that, it has to go thru a water bath for cooling and then the final product is ready.
2. INJECTING MOULDING

Rubber is injected into the mold using a large ram or screw. Heated & cured rubber compound is forced into the cavity using an injection nozzle. It is kept closed at a desired temperature to complete curing. After curing cycle, press opens and the cured rubber part is released.
3. **CALENDARING**

The rubber is passed through rotating rolls into the calendering nip to form fabric impregnated with rubber sheets or only rubber sheets.