UNIVERSITY OF ZAGREB

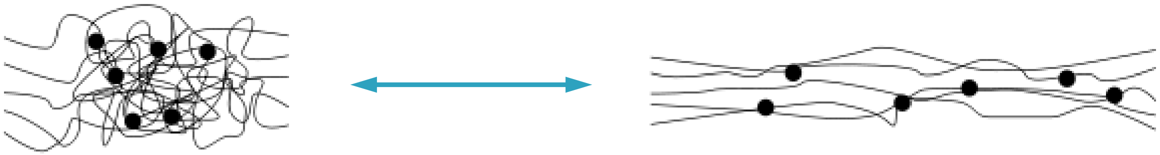
FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

Polymer science and technology

Assoc. prof. Zvonimir Katančić
katancic@fkit.unizg.hr

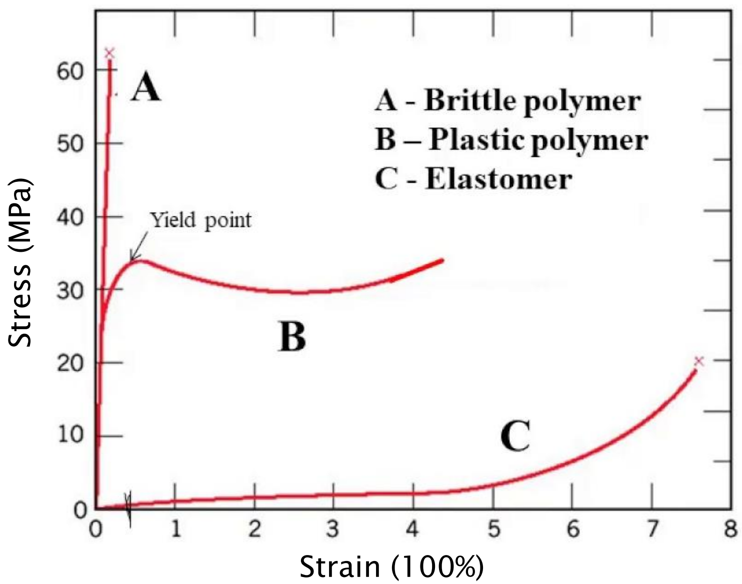
ELASTOMERS

- IUPAC definition: Polymers that displays rubber-like elasticity
- **Elastomers are usually chemically crosslinked** but may also be **thermoplastic** (**thermoplastic elastomers** – mPP, PU)
- Elasticity is derived from the ability of the long chains to reconfigure themselves to distribute an applied stress and **covalent cross-links enable the return to its original size when stress is removed**
- As a result, elastomers can reversibly **extend up to 1000%**
- Without the cross-links the applied stress would result in a permanent deformation

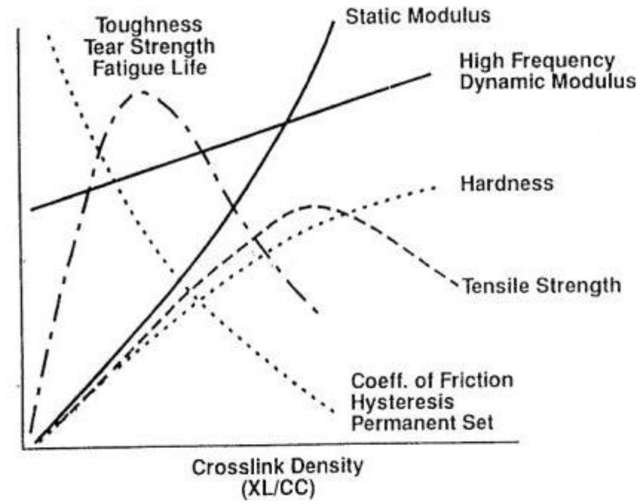


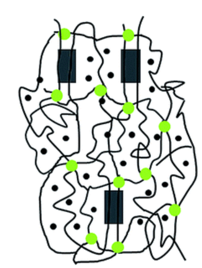
ELASTOMERS

Stress – strain curve of polymer materials



Mechanical properties of elastomer (rubber) depend on crosslink density



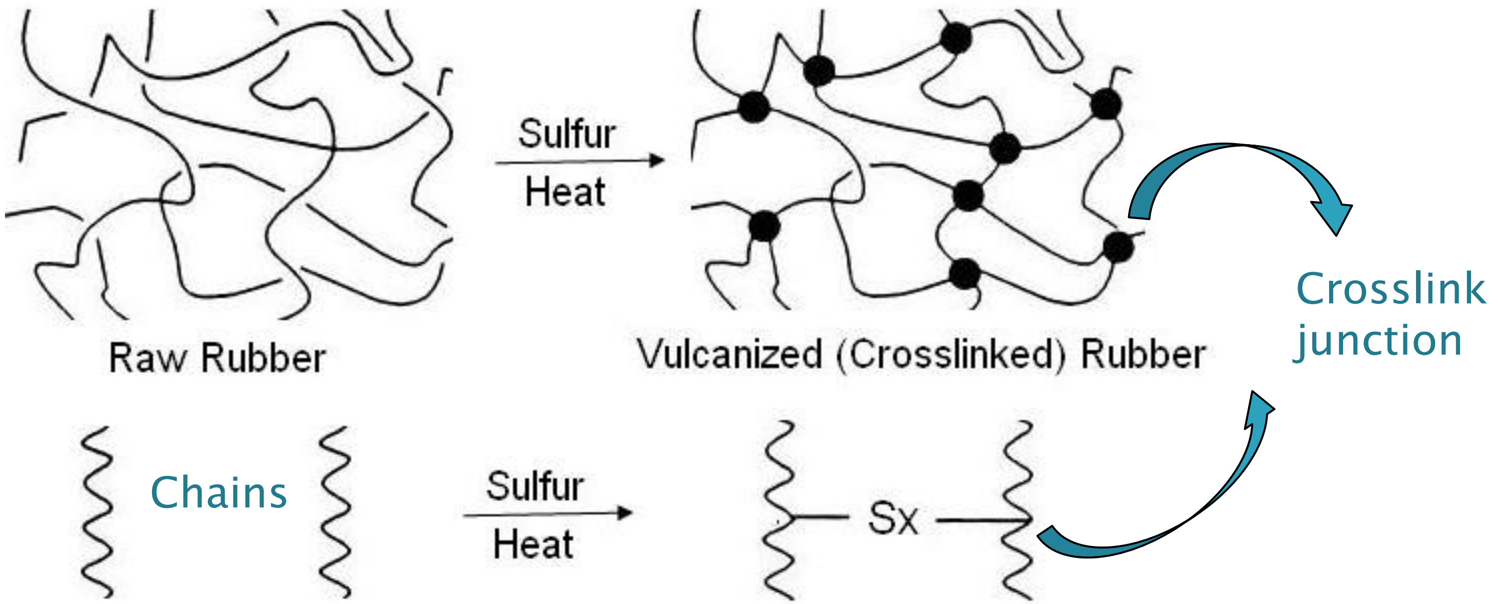


Low crosslink density

High crosslink density

Synthetic rubber

- After polymerization elastomers are **mold-shaped and** simultaneously **vulcanized**
- **Vulcanization** is **crosslinking** process where **polymer chains** are **chemically bonded,** forming cross-links and are converted into a **three-dimensional network**



Synthetic rubber

- Vulcanization was **discovered in 1839 by** Charles **Goodyear** in USA and Thomas **Hancock** in England
- Word „vulcanization” derives from the word volcano, due to the smell of sulfur
- **Crosslinking agents**
  - **Sulfur** (S_8)
  - **Organic Peroxide** (Dibenzoyl peroxide)
  - **Metallic oxide** (MgO, ZnO, …)
  - **Thiourea**
  - **Microwave**
- **Sulfur** has **limitation** because the **elastomers must contain chemical unsaturation** (**C=C double bonds**) for sulfur crosslinking process
- For example, EPR (ethylene propylene rubber) does not contain C=C double bonds and are usually crosslinked by organic peroxide

Synthetic rubber

- **Sulfur vulcanization is very slow,** and sulfur **accelerators** are used to speed up the process, from **2 or 3 hours to 10 minutes**
- Accelerators are added in **very low concentration 0.5 to 3 %** together with S_8 (<5 %), usually combination of two or more accelerators is used, important to synchronize the rate of crosslinking

Classification of Accelerators:

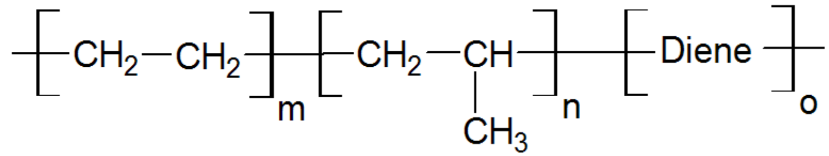
Accelerators	*Chemical Group*	*Vulcanization Speed*
BA, HMT	Aldehyde Amine	Slow
DPG, DOTG	Guanidine	Slow
MBT, MBTS, ZMBT	Thiazole	Semi Ultra fast
ZBDP	Thiophosphate	Ultra fast
CBS, TBBS, MBS, DCBS	Sulfenamides	Fast-Delayed action
ETU, DPTU, DBTU	Thiourea	Ultra fast
TMTM, TMTD, DPTT, TBzTD	Thiuram	Ultra fast
ZDMC, ZDEC, ZDBC, ZBEC	Dithiocarbamate	Ultra fast
ZIX	Xanthates	Ultra fast

Synthetic rubber

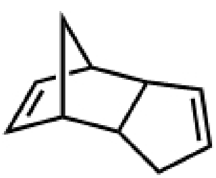
- **Ethylene Propylene Diene (EPDM)**
- **Styrene Butadiene (SBR)**
- **Silicone Rubber (SI)**
- **Nitrile Rubber (NBR)**
- Polybutadiene (BR)
- Polyisoprene (IR)
- Butyl Rubber (IIR, Isobutene-isoprene)
- Chloroprene (CR, Neoprene®)
- Fluorocarbon (FMK, Viton®)
- Fluorosilicone (FSI)

Ethylene Propylene Diene Rubber (EPDM)

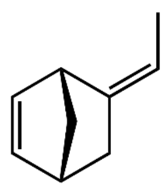
- EPDM is a **copolymer**
  - **ethylene**
  - **propylene**
  - **diene** monomers (3-9%)



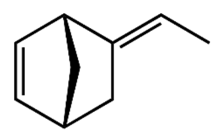
- **Diene** – provide **cross-linking sites** for vulcanization due to double bonds (predecessor EPR can be crosslinked only by peroxides)
  - dicyclopentadiene (DCPD)
  - ethylidene norbornene (ENB)
  - vinyl norbornene (VNB)
  - 1,4-hexadiene



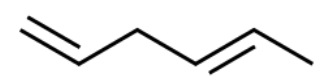
DCPD



ENB



VNB



1,4-hexadiene

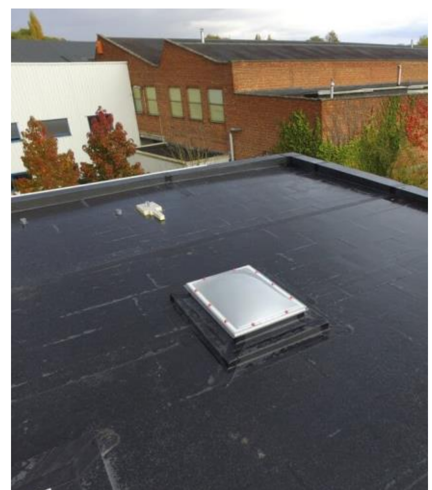
Ethylene Propylene Diene Rubber (EPDM)

- **Ethylene content** from 45% to 75%
- The higher the **ethylene content –** the more filler loading is possible
- Propylene increases crystallinity and hardness

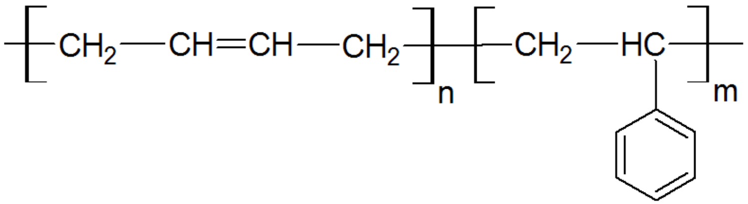
- EPDM has saturated polymer backbone – **excellent resistance to heat, steam, light and ozone (weathering)**, suitable to be used outdoors for many years or decades without degradation
- EPDM can be formulated to be resistant to **temperatures up to 150 °C**, has good low temperature properties, with **elastic properties** to temperatures **up to −40 °C**
- **Compatible with polar substances**, ketones, hot and cold water, and alkalis (**the most water-resistant rubber available**)
- **Incompatible with most hydrocarbons**, oils, kerosene, aromatic compounds, gasoline and halogenated solvents
- It is an electrical insulator

Ethylene Propylene Diene Rubber (EPDM)

- Application
- **Automotive industry – door, window and trunk seals**, cooling system circuit hoses, blends with other polymers as impact modifier for car bumpers
- **Seals on doors for refrigerators and freezers** (where it also acts as an insulator), garden and appliance hose, cable electrical insulation
- **Major applications** are **roofing and waterproofing, geomembranes**
- EPDM granules mixed with PU binders and sprayed onto concrete or asphalt to create a non-slip, soft, safety surface for wet-deck areas (pool decks)
- Surfacing under playground play equipment



Styrene Butadiene Rubber (SBR)



- SBR – random **copolymer**
  - butadiene (BR) (75–90%)
  - styrene (St) (10–25%)
  - with higher styrene content, the rubbers is harder
- Two major types of SBR with different properties based on their manufacturing process:
  - **emulsion SBR** (e-SBR) – **Hot SBR or Cold SBR**
  - **solution SBR** (s-SBR)

- Emulsion (**free-radical** polymerization)
- a) **hot polymerization**
  - **at 50 °C**
  - **branched molecules** are created, the rubber is **harder with lower tensile strength**

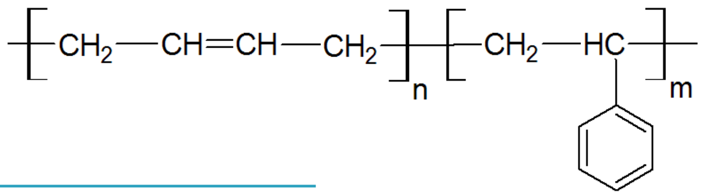
  b) **cold polymerization**
  - **at 5–10 °C**
  - smaller number of branches, **higher tensile strength**, better abrasion resistance, ageing resistance and flex resistance

Styrene Butadiene Rubber (SBR)

- Solution (**anionic** polymerization)
  - **Lithium and alkyl lithium** are catalysts
  - Mixture of **monomers** in a **hydrocarbon** solvent (hexane or cyclohexane) with a **modifier** which provides a good distribution of styrene units within the polybutadiene segments
  - The process is homogeneous (all components are dissolved), which provides greater control over the process, allowing tailoring of the polymer
- **Emulsion SBR** grades still account for **more than 75%** of the total world production
- **The most widely used synthetic rubber**
  - Low cost compared with those of all other synthetic rubbers
  - Ability to accept high filler levels
  - Overall properties on a cost/performance basis

Styrene Butadiene Rubber (SBR)

- Properties – **similar to natural rubber** (NR) (1st lecture)
- Excellent abrasion resistance
- **Poor ozone and weathering resistance**
- SBR is vulnerable to thermal and oxidative degradation due to the presence of double bonds in the polymer backbone



*S– solution, *E–**emulsion** polymerization	*S–SBR	*E–SBR
Tensile strength (MPa)	36	20
Elongation at break (%)	565	635
Glass transition temperature (°C)	−65	−50
Polydispersity index	2.1	4.5

- The typical **working temperature range is −25 °C to 100 °C**

Styrene Butadiene Rubber (SBR)

➢ Application

- **car tires** (**blended** with NR)
- **conveyor belts**
- footwear
- hoses
- toys
- molded rubber goods
- waterproof materials
- adhesives

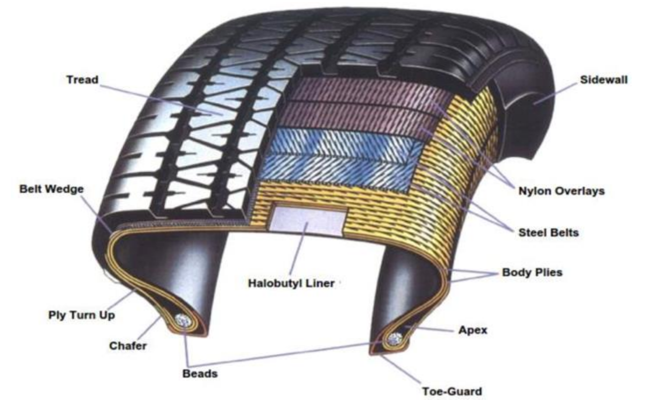






Car and truck tires

- **Composition**
- **Rubber (NR/SBR blend)**
- **Stabilizer** – UV, thermal
- **Crosslinking agent** – S_8 and accelerators, peroxides
- **Filler** – carbon black
- **Reinforcements** – fabric and metal

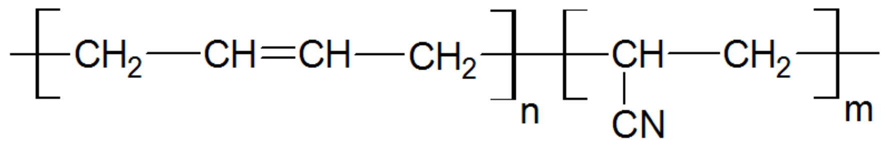


Type of tire	car	truck
Natural rubber (NR)	15–20%	**25–30%**
Synthetic rubber (SBR)	**25–30%**	15–20%
Carbon black	22–28%	20–28%
Metal/steel	12–16%	**20–27%**
Textile (nylon, rayon, polyester)	4–6%	0–10%
Additives	10–12%	7–10%
S_8 and accelerators	1–2%	1–2%

Nitrile rubber (NBR)

- Also known as **nitrile butadiene rubber** and **acrylonitrile butadiene rubber**

- NBR is **copolymer**
  - acrylonitrile (ACN)
  - butadiene (BR)



- **Emulsion free-radical polymerization**
  - temperature: 5–15 °C (cold NBR) or 30–40 °C (hot NBR)
  - lower polymerization temperature, lower branching
  - emulsifier: alkaline salts of saturated fatty acids
- Properties can be adjusted by varying the acrylonitrile content
- **ACN content – 15 to 50%**
- Higher ACN content: **greater resistance to** swelling by hydrocarbon oils, **less flexible at lower temperatures**, due to higher glass transition temperature (Tg) of polyacrylonitrile

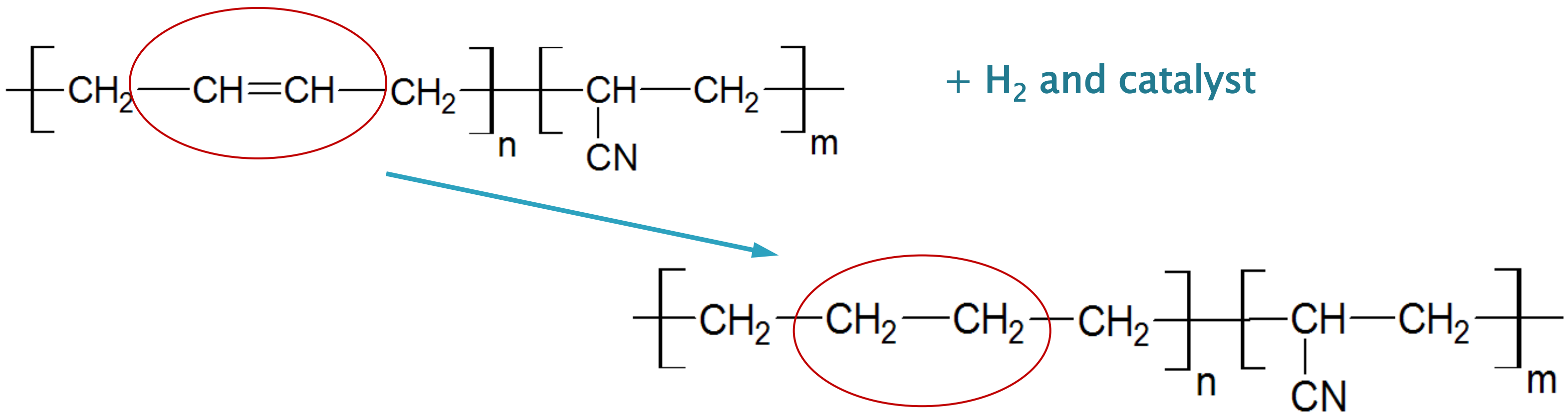
Nitrile rubber (NBR)

- Properties
- **Highly resistant to oil, fuel, and other chemicals**
- **Poor ozone and weathering resistance** (unsaturated bonds in backbone)
- Working temperature range is -40 °C to 100 °C

- Application
- Used in the **automotive and aeronautical industry to make fuel and oil handling hoses**, seals, O-rings
- Used to produce molded goods, footwear, adhesives, sponges, expanded foams
- Its resilience makes NBR a useful material for **disposable lab, cleaning, and examination gloves**
- More resistant than natural rubber to oils and acids, and has superior strength, NBR gloves are therefore more puncture-resistant than natural rubber (latex) gloves, NBR is less likely to cause an allergic reaction than natural rubber

Nitrile rubber (NBR) – modification

- **Hydrogenated nitrile rubber (HNBR)**
- It is hydrogenated in solution using precious metal catalysts. During this process, the carbon–carbon double bonds in nitrile rubber convert into more stable single bonds



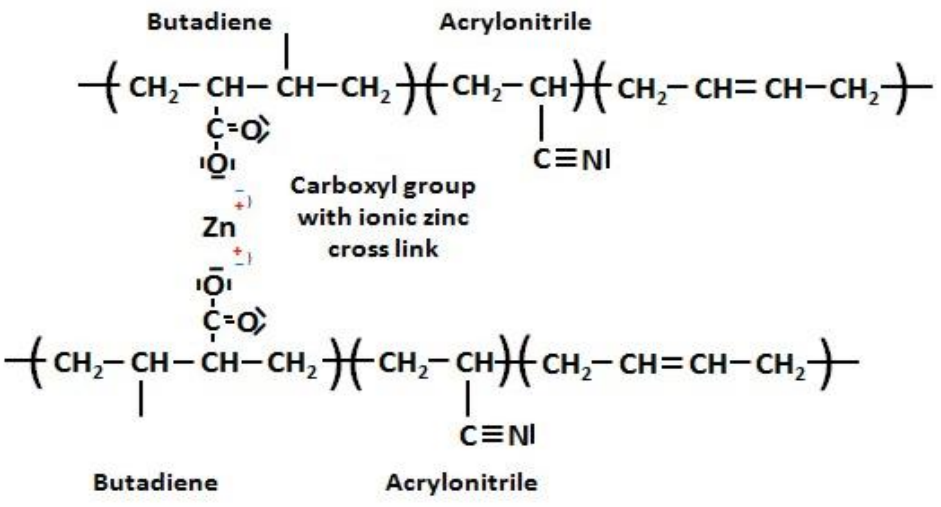
Saturated rubber HNBR

- **Excellent** resistance **to ozone and weathering,** industrial **lubricants, sour gases** (H_2S), **hot water**/steam up to 160 °C

- **Gaskets and seals, especially for the oil and gas industry and automobile industry** , higher temperature resistance, excellent resistance to common automotive fluids (engine oil, coolant, fuel etc.)

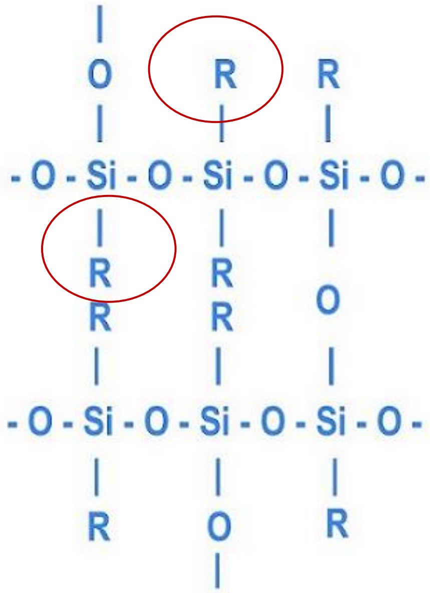
Nitrile rubber (NBR) – modification

- **Carboxylated Nitrile rubber (XNBR)**
- Carbon–carbon double bonds in butadiene part are converted into single bonds and **carboxyl groups (R–COO–) are bonded**
- 10% or less carboxyl groups are distributed randomly
- These groups make ionic crosslinks through the addition of zinc (Zn^{2+}) additives
- This **increases crosslink density** and **improves tensile properties**, tear and abrasion properties and allows higher continuous service temperature compared to NBR



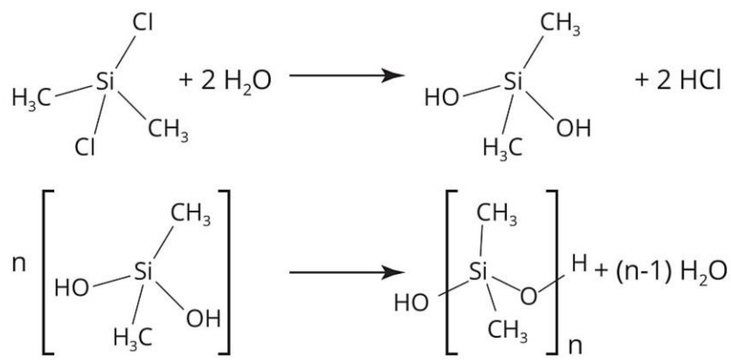
Silicone rubbers (SIR)

- 3rd lecture – silicone resins
- Inorganic or semi-organic polymers
- Backbone made up entirely of silicon-oxygen bonds with organic substituents attached to each silicon atom
- By varying the −Si−O− chain lengths, side groups, and crosslinking, silicones can be synthesized with a wide variety of properties and compositions, **can vary in consistency from liquid to gel to rubber to hard plastic**



Silicone rubbers (SIR)

- Silicone rubber is polysiloxane or **polydimethylsiloxanes (PDMS)**
- Obtained via hydrolysis–condensation polymerization of the **dimethyldichlorosilane** in the presence of an excess of water



- The polymer is **manufactured in multiple viscosities**, ranging from a thin **pourable liquid** (n is very low – **silicone oil**), to a **thick rubbery solid** (n is very high)
- More flexible than the carbon backbone due to **large bond angles and bond lengths** (C–C backbone bond in PE length 1.54 Å, bond angle 112°, Si–O backbone bond length 1.63 Å, bond angle 130°), **side groups are spaced farther apart** so polymer segments can change conformation easily

Silicone rubbers (SIR)

- **Crosslinking of silicone rubber is** performed in **three** different ways
- **Platinum-catalyzed** addition curing
- **Peroxide** curing
- **Condensation** curing

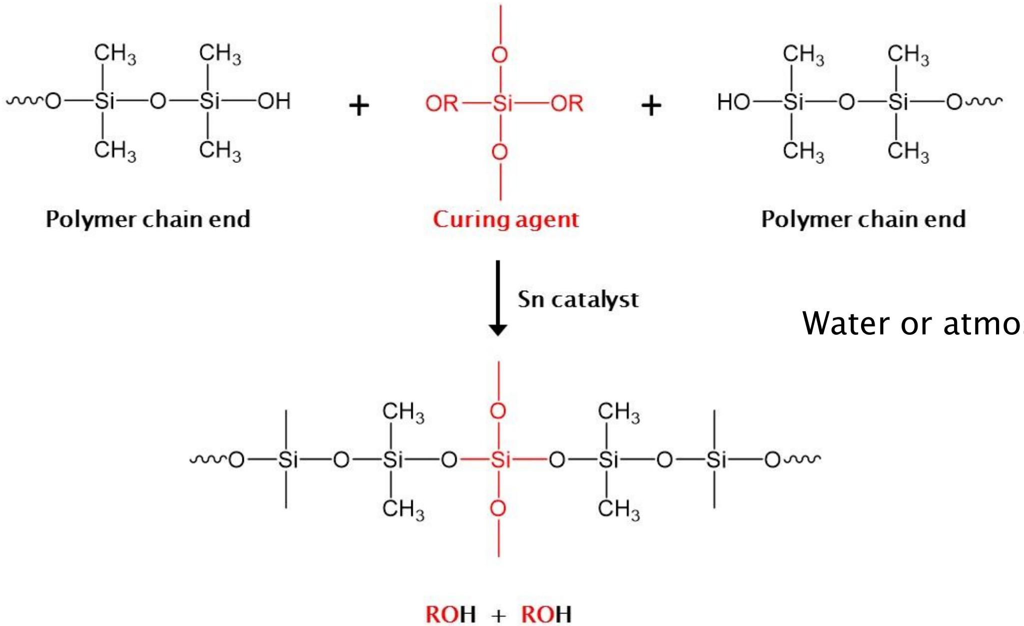
- In each of these three processes**, specific curing agents, side groups on the polymer** and **catalysts** are used in the formulation of the silicone rubbers

- **Platinum-catalyzed**
- **Hydroxy-** functionalized siloxane reacts in the presence of a Pt complex catalyst, creating an ethyl bridge between the two chains
- The reaction has no byproducts and rubber cures quickly

Silicone rubbers (SIR)

➢ **Condensation curing**

- Terminal **hydroxyl groups** of the polymer react with a **siloxane curing agent** (alkoxy, acetoxy, ester silanes)

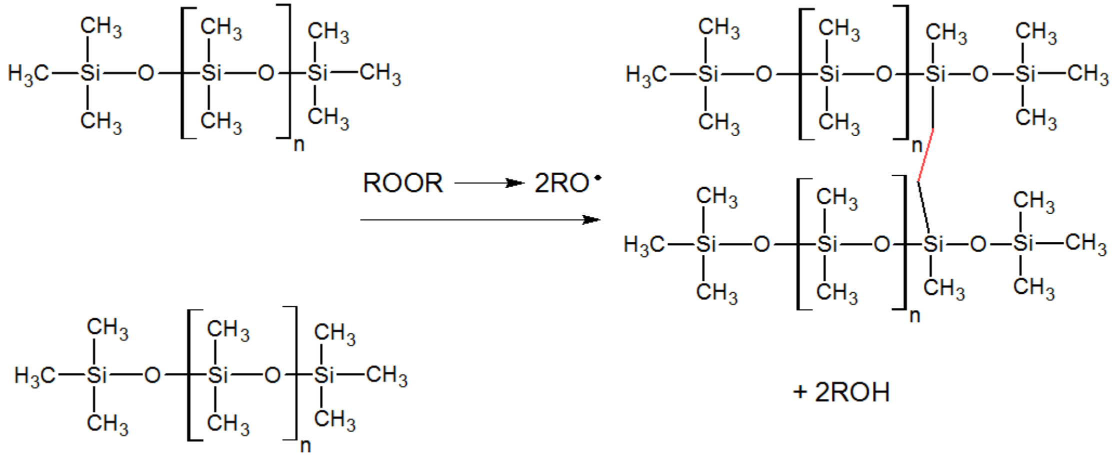


Water or atmospheric humidity

- Catalyzed by **tin (Sn)** or **organotitanium** compounds in the presence of small amounts of water, at room temperature
- Acetoxy-tin condensation is used in household bathroom caulk

Silicone rubbers (SIR)

- **Peroxide curing**
- **Organic peroxides**, at **elevated temperatures**, form highly reactive radicals that chemically crosslink the polymer chains



- The curing process leaves behind byproducts, which can be an issue in food contact and medical applications.
- These products are usually treated in a post-cure oven which greatly reduces the peroxide breakdown product content

Silicone rubbers (SIR)

- **Properties**
- **Resistant to extreme temperature (operating range -100 to 300 °C),** flexible at low temperatures, high thermo-oxidative stability
- **High resistance to heat aging, ozone and weathering**
- Good **biocompatibility**
- **Low physical strength**
- Poor resistance to tearing poor abrasion resistance

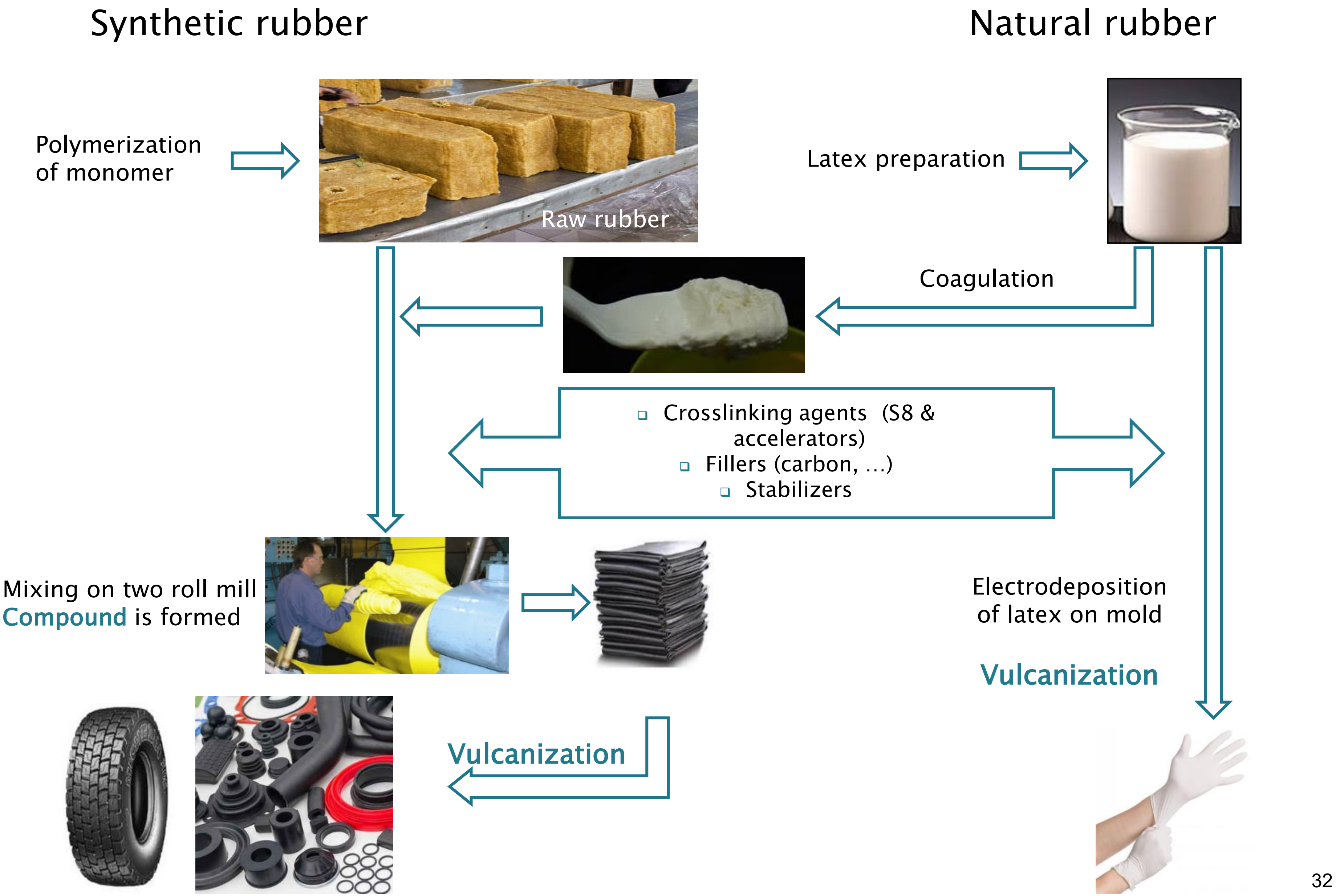
- **Applications**
- Automotive applications
- Home goods (cooking, baking and food storage products)
- Electronics
- Medical devices and implants (respiratory masks, soft contact lenses)

Rubbers comparison

Rubber	Natural (NR)	Styrene butadiene (SBR)	Ethylene propylene (EPDM)	Nitrile butadiene (NBR)	H-Nitrile butadiene (HNBR)	Silicone (SIR)
Price	$$	$	$	$	$$$$	$$$
Tensile strength	5	4	4	4	5	1
Maximum elongation (%)	700	600	600	600	340	800
Abrasion resistance	5	4	4	3	4	1
Weather resistance	2	3	5	3	4	5
Ozone resistance	1	1	5	1	4	5
Steam resistance	1	1	5	1	5	2
Chemical resistance (acid/alkali)	3	3	5	3	3	4
Oil resistance	1	1	1	5	5	3
Aliphatic solvents	1	1	1	4	4	1
Aromatic solvents	1	1	1	1	2	1

5: Excellent
4: Very good
3: Good
2: Poor
1: Very poor

Rubber processing & Vulcanization

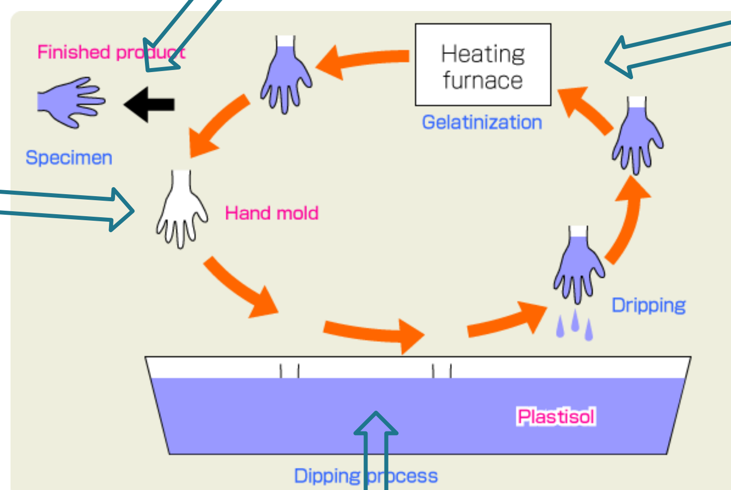


Rubber (nitrile & natural) gloves manufacturing

4

Molds get out to cool down and gloves are obtained

1



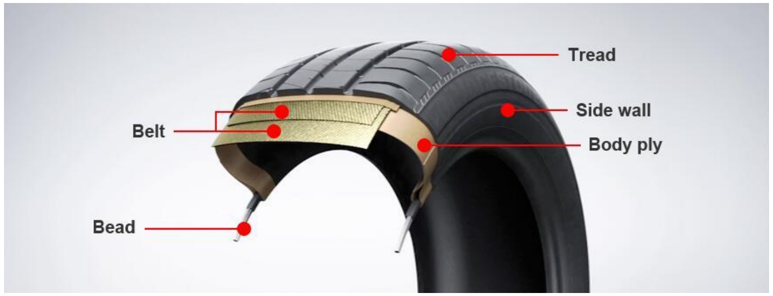
3

After 5 min vulcanization process is finished

2

Warm molds are immersed in bath with latex and glide through

Car and truck tires manufacturing

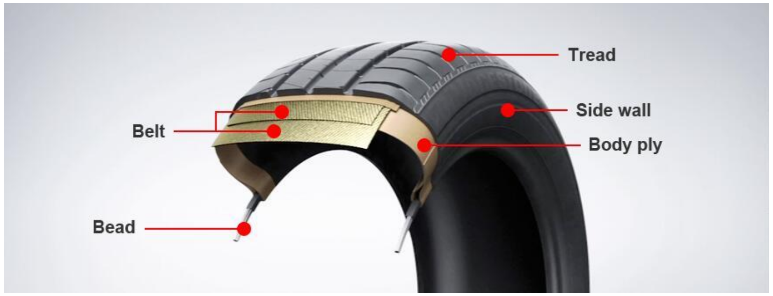


1) Mixing of raw materials to form the rubber compound. The chemical composition of each batch depends on the tire part—certain rubber formulations are used for the body, other formulas for the beads, and others for the tread

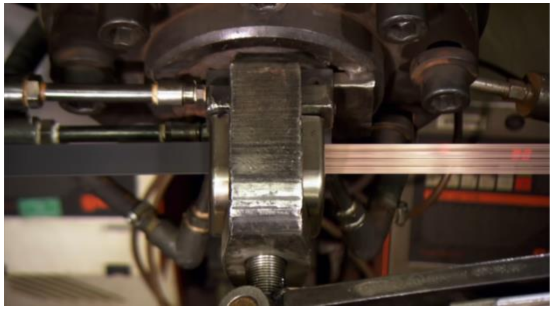
2) Rolling mills squeeze the batch into thick sheets. These sheets are used to make the specific parts of the tire

3) The tire body consists of strips of cloth-like fabric that are covered with rubber. Each strip of rubberized fabric is used to form a layer called a ply. A passenger car tire can have four plies in the body

Car and truck tires manufacturing

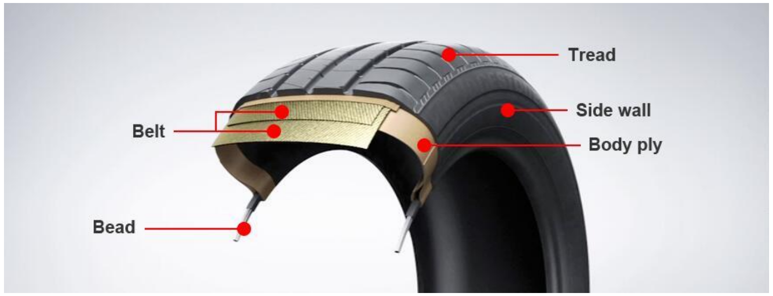


4) For the beads of a tire (give strength to stay on wheel rim), wire bundles are formed on a wire wrapping machine. Wires are covered with rubber and formed into rings

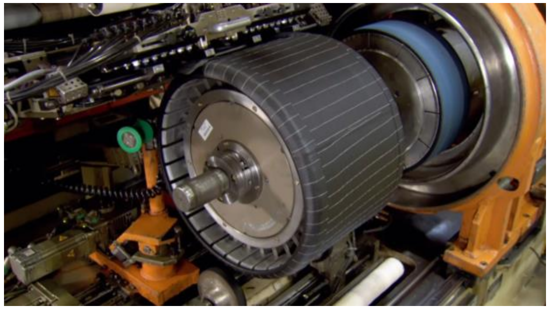


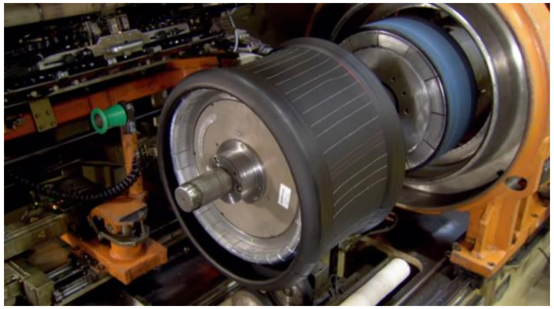
5) The rubber for the tire tread travels from the batch mixer to the extruder, the batch is further mixed and heated and is then forced out through a die to form a layer of rubber which are sliced into strips

Car and truck tires manufacturing

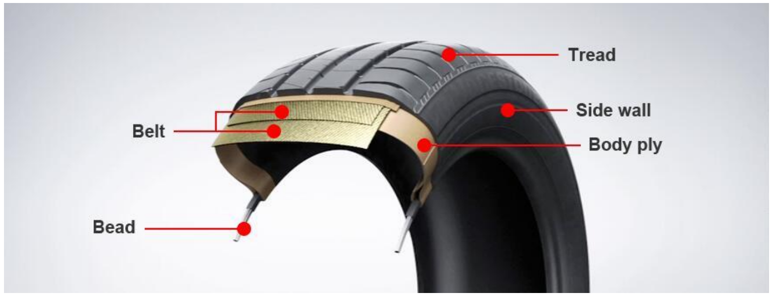


6) The rolls of sidewall rubber and the rings of beads are delivered to a tire-building machine (collapsible rotating drum that holds the tire parts). The tire assembler builds a tire by wrapping the rubber-covered fabric plies of the body around the machine drum. Ends of these plies are joined with glue, the beads are added and locked into place with additional tire body plies laid over the beads

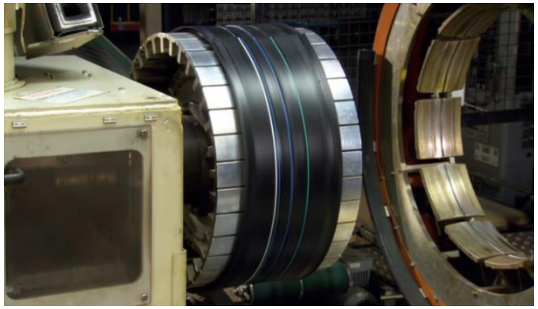


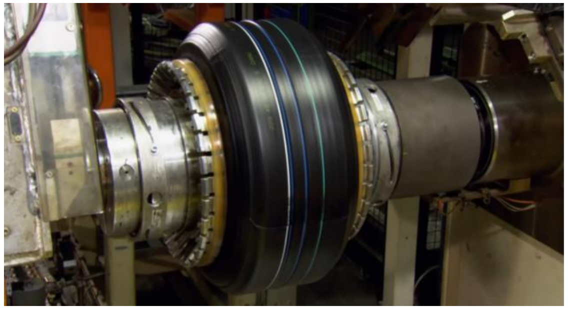


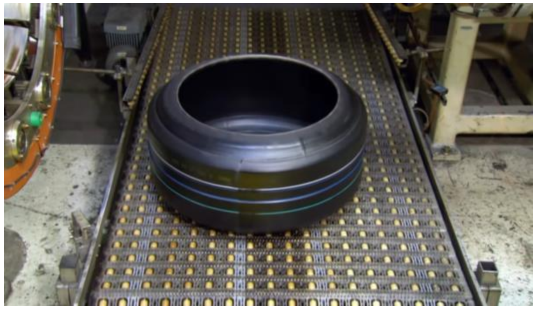
Car and truck tires manufacturing



7) The outer layer is assembled separately. Tread tire is applied to the ply and transferred to an inner layer and glued together







„Green" tire – uncured tire without tread pattern

Car and truck tires manufacturing

8) „Green” tire is transferred to a mold where tire is vulcanized, and it gets the tread pattern

https://www.youtube.com/watch?v=dLwsoM3WnuQ