Basics of tire manufacturing

BME - Guest lecture, 2021

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Tartalom

- 1.) Hankook Tire & Technology Hungary
- 1.) Az abroncsok csoportosítása
- 2.) Az abroncs felépítése
- 3.) Az abroncsgyártás folyamata
- 4.) A gumikeverékek alapanyagai
 - 4.1) Vulkanizáció
- 5.) A gumikeverékek vizsgálata
- 6.) Követelmények / EU Labeling System



Hankook Tire & Technology



- ➢ 8 plants worldwide
 - Korea (2), China (3), Indonesia, USA, Hungary (Rácalmás)
- Total annual capacity: 102 million tires
- Almost 21,000 employees
- ➢ 5 R&D centers
- Official suplier of DTM and Formula Renault Eurocup, Formula E



Hankook Tire & Technology - Hungary

Product portfolio – Rácalmás

OE (Original Equipment)



RENAULT

- RE (Replacement Equipment)
- Advanced technologies



1.) Classification of tires; requirements



5

Classification of tires

1. Groups by vehicle type

Passenger car (PC)



Agriculture (AG)



2. Groups by season

Ventus V12 Evo2

Summer

Light truck (LT)



Off-the-Road (OTR)



Truck and bus (TB)



Industrial (ID)



Aircraft (AC)



Motorcycle (MC)





Winter



Optimo 4S Négyévszakos



Requirements – Functions of tire



Transmission of forces to the road surface



Decreasing vibration from road surface

Handling, cornering





Requirements





2.) Structure of radial tires



9

Structure of radial tires





Cross-section of radial tires





3.) Tire manufacturing process



Tire manufacturing process



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Raw materials

- Rubber compound
 - Rubber (natural, synthetic)
 - Filler (carbon black, silica, other inorganic fillers)
 - Oil (natural, synthetic)
 - Curatives (sulfur, accelerators, retarders)
 - Processing aids
 - Antidegradants
- Textile cord
- Steel cords and wires



















Mixing

 Disperse the ingredients of the rubber compound in the polymer matrix

• Equipments:

Open mills

- Internal mixers
- batch production
- (Mixing extruders \rightarrow continous production)

Mixing stages:

- Non-pro: all of the ingredients, except curatives
- Final: dispersion of vulcanizing agents







Mixing - Internal mixers

Main parts:

- Chamber
 - A space closed by the ram on top and the drop door on the bottom where the mixing happens

• Rotors

 Rotating parts of the mixer that crush and disperse the raw materials

• Drop door

 Openable part at the bottom of the chamber to discharge the compound





Mixing - Rotor types

Intermeshing

- Constant gap
- More cooled surface
- Better filler dispersion
- Silica compounds!



High-shear zone: between rotor tips

Tangential Different gap along the axis

- Higher mixer capacity
- Worse filler dispersion
- Carbon compounds





High-shear zone: between the rotor tip and the chamber wall



Extrusion

- Pressing the plasticized comp'd through a die to give it a profile
- **Extruded semi-finished materials:**
 - 0
 - 0
 - 0





Calendering

- > Topping the textile or steel cords with a thin layer of rubber.
- For better adhesion cords are treated and/or coated with special materials.
- **Textile** \rightarrow **Carcass** the base of the tire
- Steel → Belt reinforcement







Cutting

- Cutting the calendered material to the right size (defined by the specification)
- Changing the orientation of cords in the semi-finished product



Building







Curing



- Main parameters: time, temperature, pressure
- **150-178°C**, **10-25** mins, **8-17** bar
- Application of mold release agents
- Silica compounds: formation of bonds between silica – coupling agent - polymer





4.) Raw materials of rubber compounds



Formulation

PHR: Parts per Hundred Rubber

Non-pro compound

- Rubber (Natural, Synthetic)
- Filler (Carbon black, Silica)
- Processing aids (Oil, Additives)
- Tackifiers
- Antidegradants (Waxes)
- Activator (ZnO, Fatty acid)

Final compound

- Vulcanizing agents
 - Sulfur
 - Accelerator
 - (Retarder)

Туре	Raw material	PHR
Polymer	Elastomers	100
Filler	Carbon black	55
Processing aid	Oil	35
Activators	Stearic acid	2
	Zinc oxide	4
	Antioxidant	1
Antidegradants	Wax	1
	Antiozonant	2
Curatives	Accelerator	1.5
	Sulfur	1.5
тс	203	



Raw materials - NR

Natural rubber (NR)

- Cis-1,4-polyisoprene
- ~5% other components (proteins, fatty acids, resins etc)





Production

Collecting latex → coagulation with formic acid → washing → smoking → baling

Production

- Good processability
- Good green tackiness
- Medium wear resistance
- Easily oxidizes (aging resistance ↓)
- Crystallization (stretching, 15°C)





Raw materials - SBR

Styrene-butadiene rubber (SBR)

- Cis-, trans- and vinyl content, branching, molecular weight, polydispersity
- Styrene content; importance of production method

Production

Emulsion or solution polymerization

	E-SBR	S-SBR	Effect	
Styrene content [wt%]	0 - 60	0 - 45	Traction, wear resistance, rolling resistance	
Vinyl content [wt%]	~ 18	10 - 90	Traction, wear resistance, rolling resistance	
Molecular weight dispersion	Wide	Narrow	Narrow: better RR and wear resistance	
Monomer dispersion	random	random or block	Random: lower rolling resistance	
Branching	random	Controlled (linear or brached)	Decrease in dynamic performance	
Functionalization	None	Can be functionalized easily	Low rolling resistance	

• Styrene content \uparrow : Elasticity \downarrow , $T_g \uparrow$ (Wet traction \uparrow)

Properties

- Can be easily modified based on requirements (S-SBR)
- Good processability
- Good wear resistance and wet traction

High heat generation, low green tackiness



Raw materials - BR

Butadiene rubber (BR)

- Cis, trans and vinyl content, branching, molecular weight, polydispersity
- Importance of catalyst

Catalyst	Nd	Со	Ni	Ti	Li
Microstructure					
1.4-cis content (%)	98	97	97	93	38
1.2-vinyl content (%)	0,5	1,7	1,8	5	11
Glas Transition Temperature Tg (°C)	-109	-107	-107	-104	-93
Branching (%)	< 5	20	20	15	< 5
Polydispersity PDI (Mw / Mn)	2,1	3,1	4,2	3,4	2,0

Production

• Solution polymerization, anoionic or Ziegler-Natta catalyst



- **Properties**
 - Low T_g
 - Good wear resistance, fatigue resistance
 - Poor processability, low green tackiness
 - Low traction \rightarrow usually it is used for NR or SBR blends



Raw materials – IIR

- Butyl rubber (IIR, Isobutilene-Isoprene rubber)
 - Isobutylene (98%) and isoprene (2%) copolimer
 - Preferably used type: halo-butyl (CI, Br)
- Production
 - Batch cationic solution polymerization (Friedel-Crafts)



Properties

- Good chemical resistance
- Very low air-permeability
- Good fatigue resistance
- Very low tensile strength
- Incompatible with other polymers
- \circ Few unsaturation \rightarrow Application of special curing system



Raw materials - Fillers

Properties

- Insoluble in rubber, make solid phase
- Functions
 - Better processability
 - Favorable mechanical properties
 - Cost reduction





Carbon black:

- Cheap
- Physical interaction with polymers
- Used for all of semi-finished products

Not reinforcing filler:

Calcium-carbonate (white sidewall)

Silica:

- Expensive
- Chemical bond with polymers → needs a coupling agent
- Usage: cap tread
 - Improved wet traction
 - Lower rolling resistance



Raw materials – Carbon black

Carbon black (CB)

• Organic filler. Physical-chemical interaction with polymer

Production

- Pirolysis (Furnace method Furnace Blacks)
- Main properties
 - Partical size
 - Structure
 - Specific surface area
 - Surface activity / surface chemistry





Raw materials – Carbon black

Property	Effect
•	<u>Small partice size:</u> Better reinforcement, conductivity, low viscosity. Poor dispersibility
?	<u>Higher structure:</u> Better reinforcement, higher viscosity. Smaller rheological swelling. Increases dispersibility
	<u>Higher porosity:</u> Higher conductivity and viscosity. Decreases specific gravity
	Surface chemistry: Higher oxygen content improves wetting (better dispersion). Decreases conductivity



Raw materials – Silica

Silica

- Precipitated silicium-dioxide. Chemical bond with the polymer.
- Coupling agent is required.

Production

- Precipitation of sodium-silicate with sulfuric acid
- $SiO_2 + Na_2CO_3 \xrightarrow{\sim 1350^{\circ}C} Na_2O \cdot SiO_2 + CO_2$ (sand)



• $Na_2O \cdot SiO_2 + H_2SO_4 \rightarrow Silica + H_2O + Na_2SO_4$

Main properties

- Specific surface area
- Moisture content
- Structure
- pH



Primary particle (~10-100nm) Aggregate (~50-300nm) Agglomerate (> ~200nm)



Raw materials – Silica





Raw materials – Fillers

Chemical reaction of silanization:



- Main parameters:
- Time (3~15 mins)
- Temperature (135~155°C)



Alapanyagok - Adalékok

Processing aids / Oils

- Softening
- Wetting (fillers)
- Homogenization

Tackifiers

- Natural / synthetic
- Resins:
 - Increase hardness and stickiness
 - Support vulcanization

Adhesion promoters

Improved adhesion between rubber and steel (cords, wires)

Antidegradants

- Antioxidants, antiozonants
- Waxes: prevent degradation of polymer chains (heat, UV, O₂)









Raw materials – Curatives

Sulfur

- Grounded sulfur, S₈ (oil coated)
 - Cheap
 - Can migrate to surface!
- Insoluble sulfur, S_∞ polymer
 - Expensive
 - Insoluble in CS₂
 - Prevents migration



• Reverts to $S_8 \rightarrow$ temperature control during storage and usage

Zinc oxide

- IIR (butyl-rubber): lack of double bonds → sulfur curing doesn't work
- Accelerated ZnO crosslinking:
 - Using ZnO to remove halogen atoms from the chain and create active spots to crosslink (in the presence of sulfur)



Raw materials – Curatives

• Accelerators:

- Increase the speed of vulcanization
- Sulfur compounds
 - Dithiocarbamates
 - Thiazoles
 - Benzothiazole sulfenamides
 - Guanidines

Activators:

- Activation of accelerators
- ZnO + Stearic acid (forming Zn-stearate)

Retarders:

Prevent premature vulcanization (scorching)





Vulcanization

- Forming of chemical crosslinks between polymer chains
- Vulcanization curve: MDR (Moving Die Rheometer)
- Vulcanization (curing) of a sample between a still & an oscillating plate
- Registration of torque needed to keep fix deformation







The double bond activates the hidrigens on the α carbon \rightarrow The vulcanizing complex attacks here. The double bond remains!



Vulcanization - Curing

- The Rheo curve & the properties of cured rubber are determined by the curing system
 - Sulphur / Accelerator ratio
 - Accelerator(s) type





5.) Compound Analysis



Compound Analysis

Cured & Uncured Rubber Compound

Uncured (not vulcanized):

- In correlation with processability of compound
 - Viscosity, Scorch time
 - Rheology (MDR, vulcanization times)

Cured (vulcanized):

- In correlation with properties of finished tire
 - Modulus, Elongation at break, tensile sthrenght
 - Hardnes (Shore A)
 - Viscoelastic properties

Specific Gravity:

In correlation with raw materials (quality & quantity)



Viscoelasticity

- Rubber Compound is a Viscoelastic material
 - Deformation Reversion: Energy dissipates (Hysteresis)
 - Fuel economic = Low Rolling Resistance, LRR



Viscoelasticity



Viscoelasticity



Rolling resistance(RR)

- Lower, if we can win back back more energy after deformation (low hysteresis)
- Lower tanδ @ 60°C →
 lower rolling resistance



Wet traction

 Traction is better, if we loose more energy after deformation (high hysteresis)

High tan δ / Loss Modulus (G") @ 0°C \rightarrow Better wet traction

Magic triangle!

wet traction

abrasion resistance 🖌

HD Silica, bifunctional silane

-standard Carbon Black

rolling resistance



6. EU labeling system



EU Labeling



