

Rubber

Maurizio Galimberti

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

Lesson for UniPD, 14 November 2025

Politecnico di Milano, Rubber, Lesson for UniPD, 6 November 2026

Rubber. List of contents

Plastics and Rubbers

Entropic elasticity. Molecular requisites for an ideal elastomer

Most important rubbers

Rubber products. The environmental impact

Rubber from biosources

EOL thermoset rubber

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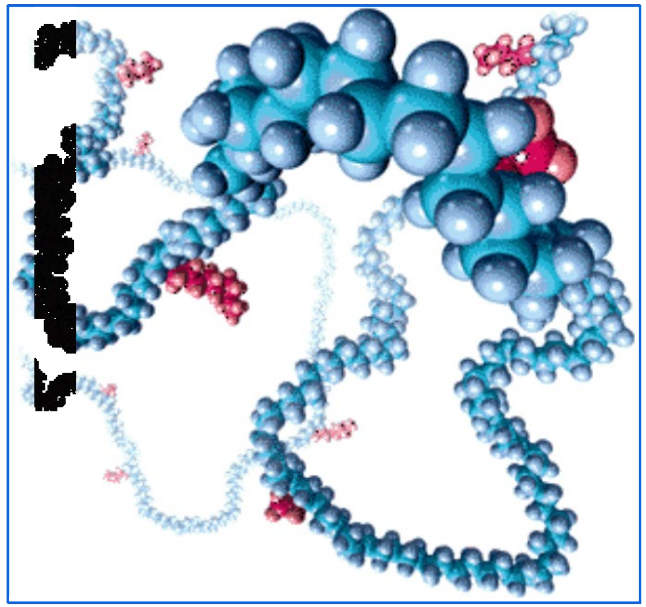
What is a polymer

A substance composed of macromolecules characterized by
the multiple repetition of one or more species of atoms (monomeric units),
connected covalently in such a way
that the molecule has a high relative molecular mass,
and the difference in molecular mass between molecules
is primarily due to differences in the number of repeating units.

IUPAC



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Polymer – ISO Definition

A substance composed of molecules

characterized by

the multiple repetition of one or more species of atoms (constitutional units),

linked to each others in amounts sufficient

to provide a set of properties

that do not vary markedly

with the addition or removal of one or a few of the constitutional units

ISO 472

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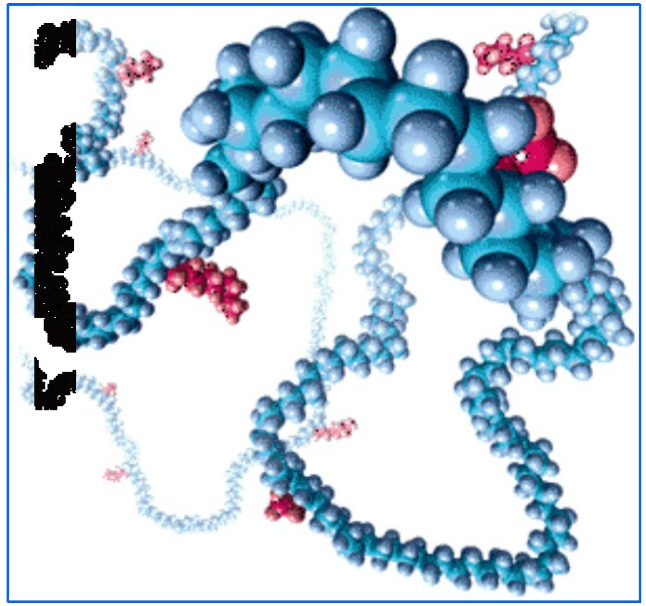
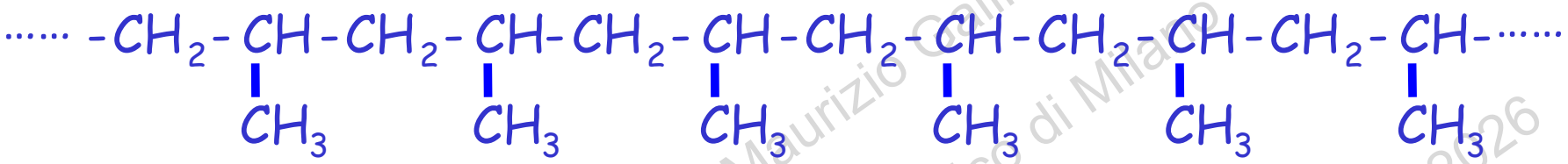
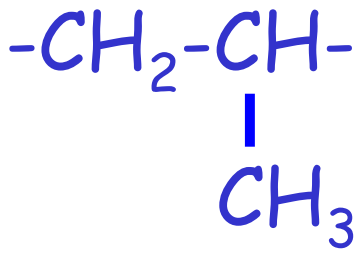


A polymer: polypropylene

The polymer: polypropylene



The repeating unit



Also said: constitutional unit

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Polymers

Thermoplastics and thermosets

Plastics and Rubbers

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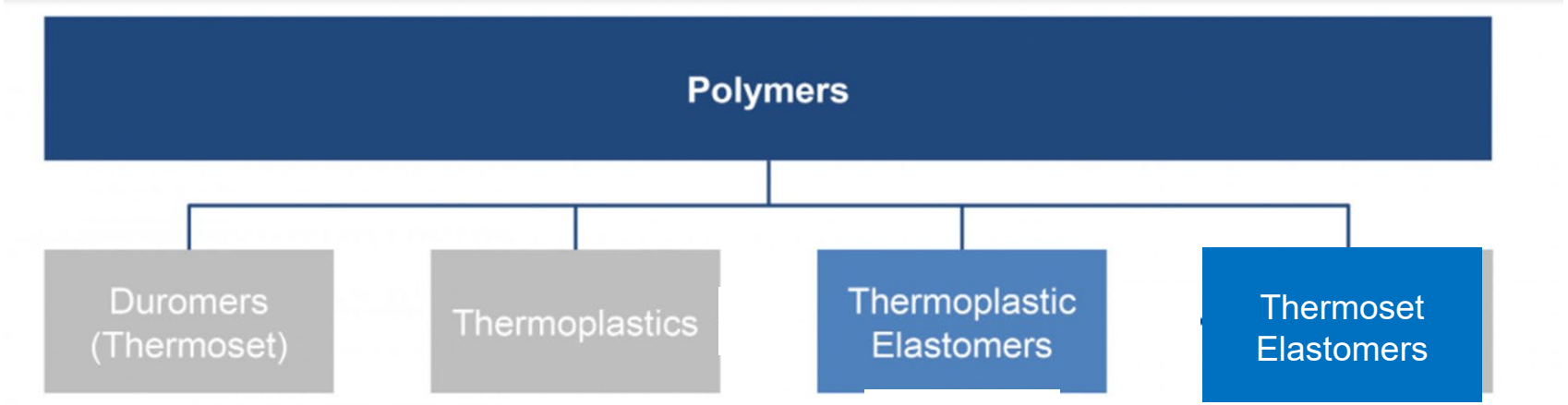
Polymers. Thermosets and thermoplastics



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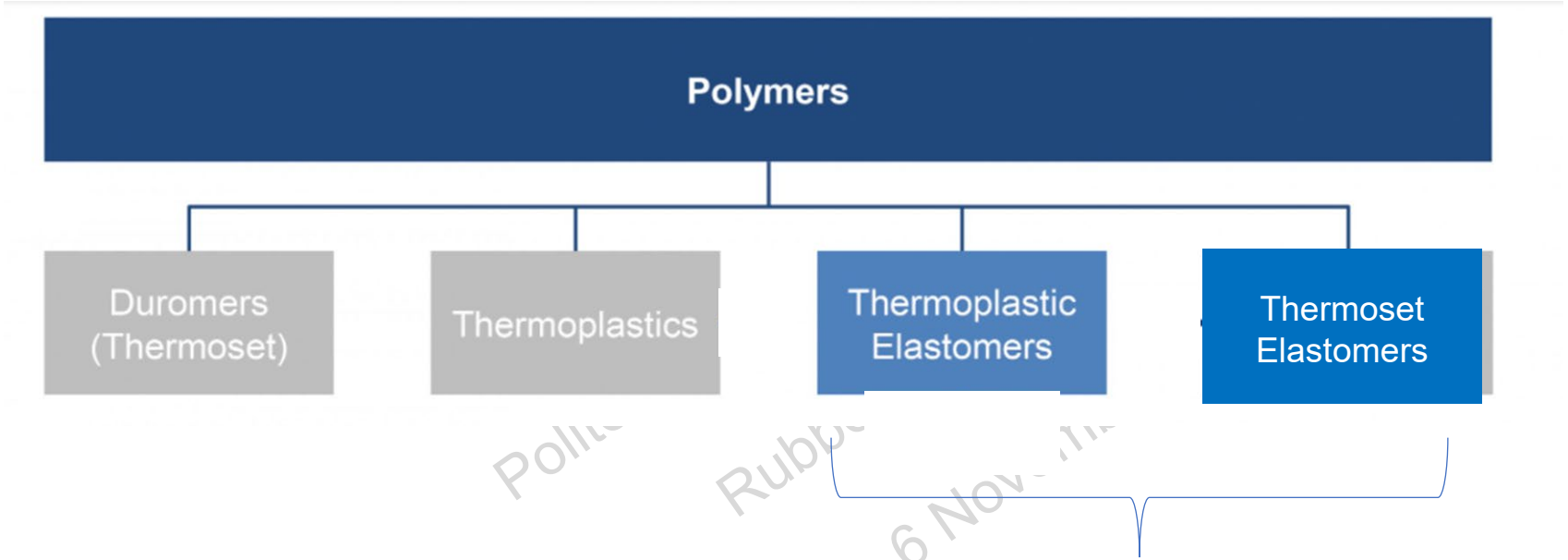
Polymers. Thermosets and thermoplastics



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Thermoset and thermoplastic polymers

Thermoplastic polymer

A polymer that softens when exposed to heat and returns to its original condition when cooled to room temperature.

IUPAC Compendium of Chemical Terminology (“Gold Book”), entry T06370.

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Thermoset polymer

A polymer that, once hardened by heat or other means, cannot be remelted or reshaped by reheating.

IUPAC Compendium of Chemical Terminology (the “Gold Book”), entry T06374.

Rubber and elastomers

Rubber

A material that can be stretched to at least twice its original length and,
upon immediate release of the stress,
returns with force to approximately its original length.

IUPAC Compendium of Chemical Terminology ("Gold Book"), entry R05351.

Elastomer

Polymer that displays rubber-like elasticity

IUPAC Compendium of Chemical Terminology ("Gold Book"), entry E02188.

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Thermoset rubber and thermoplastic elastomers

Thermoset rubber

Definition of thermoset rubber

+

Definition of thermoset polymer

IUPAC definitions

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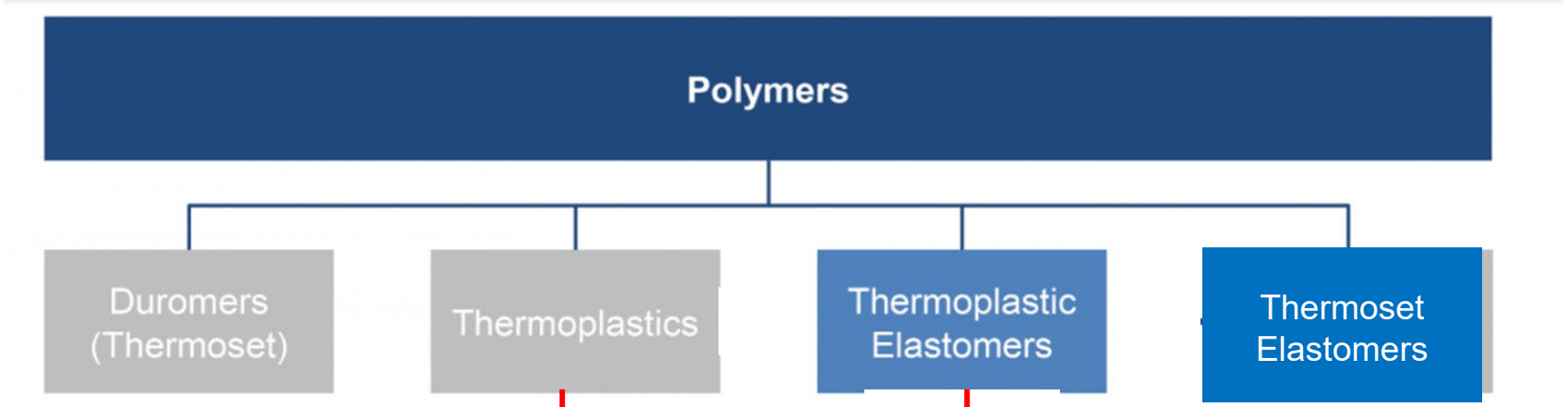
Thermoplastic elastomer (TPE)

A polymer or blend of polymers that, above its softening temperature, can be shaped by flow and that, below this temperature, behaves like an elastomer.

IUPAC Compendium of Chemical Terminology ("Gold Book"), entry **T06373**.

Polymers. Thermosets and thermoplastics



Thermoplastic polymer

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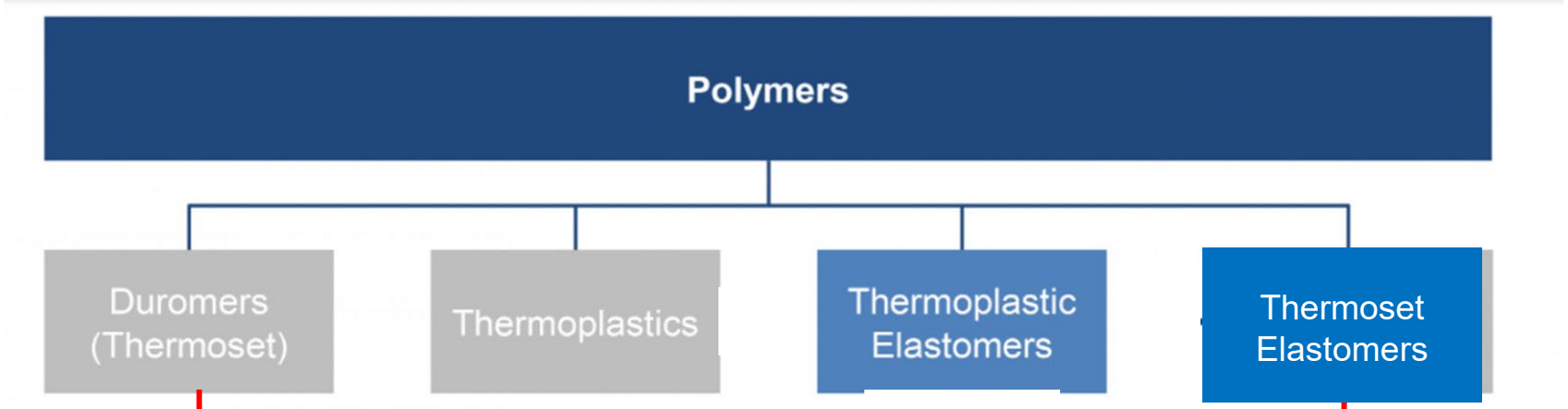
IUPAC Compendium of Chemical Terminology ("Gold Book"), entry T06370.

Entropic elasticity

Polymers. Thermosets and thermoplastics



Thermoset polymer

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IUPAC Compendium of Chemical Terminology (the "Gold Book"), entry T06374.

Entropic elasticity

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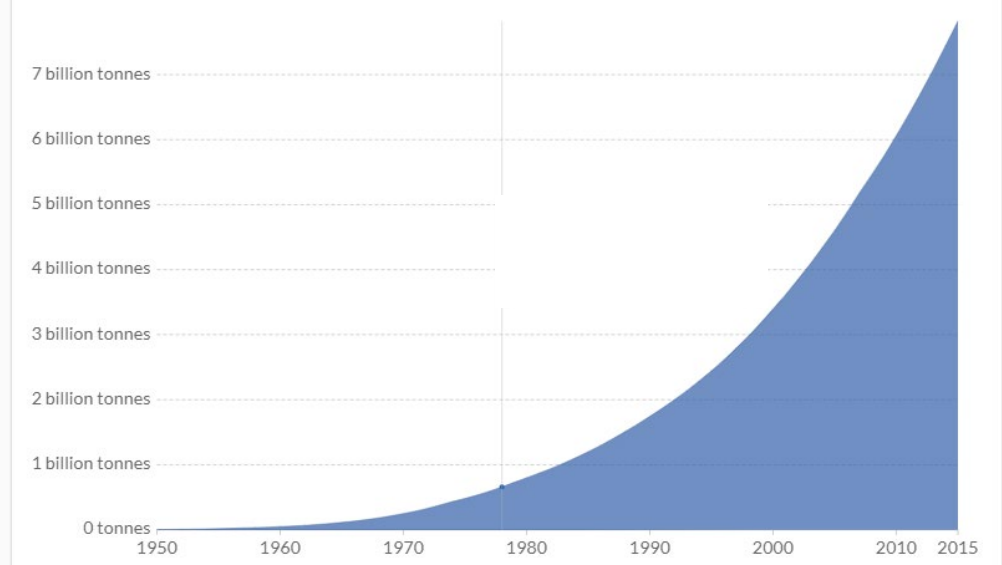
Plastic. Worldwide production

Cumulative global production 1950 - 2017



9.2 billion tons in 2017

Forecast to grow to 34 billion tons by 2050

Yearly production. 2022

400.3 million metric tons

iPP. Market value. 2022

120 billion US Dollars

0.2% of gdp of the earth

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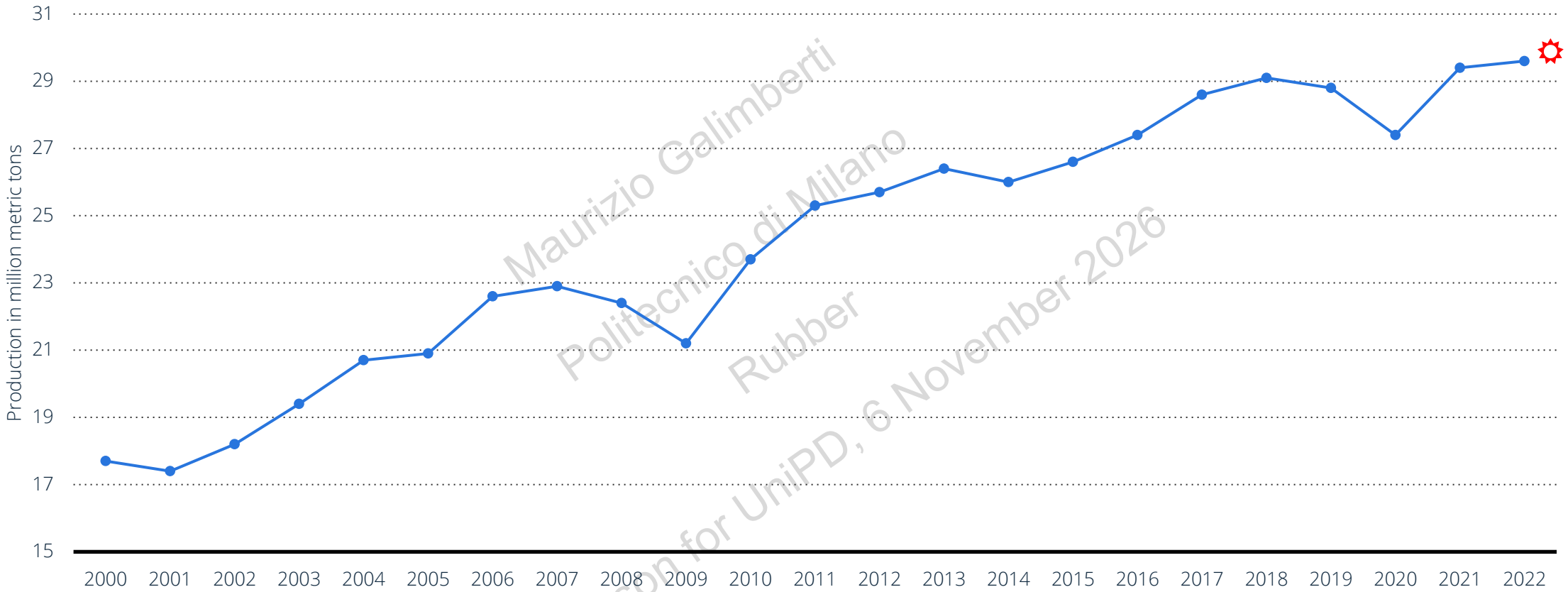
Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Science Advances, 3(7), e1700782.

Geyer, R. (2020). Production, use, and fate of synthetic polymers. In Plastic waste and recycling (pp. 13-32). Academic Press

https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/#:~:text=The%20worldwide%20production%20of%20plastics,percent%20from%20the%20previous%20year.

Worldwide production of rubber. 2000 - 2022



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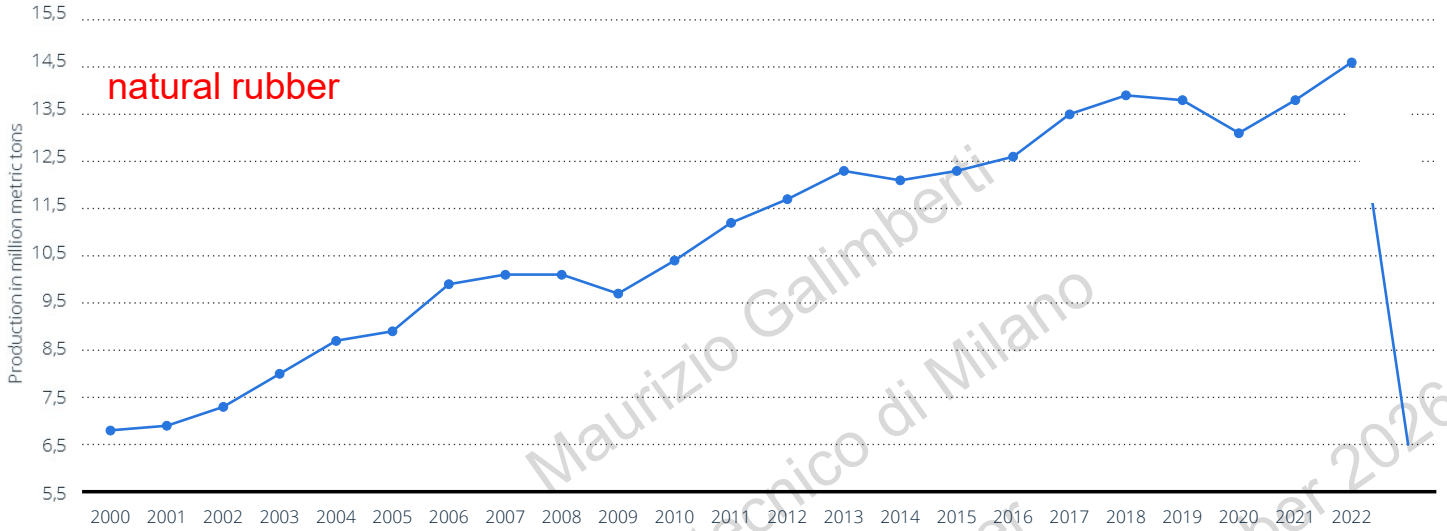
☼ $29.6 \cdot 10^6$ metric tons

https://www.statista.com/statistics/618804/total-global-natural-and-synthetic-rubber-production/

Worldwide production of natural and synthetic rubber. 2000 - 2022



14.6 million metric tons

17 billion dollars

% of NR

2000: 39 2020: 47



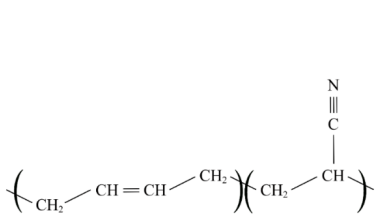
15.1 million metric tons

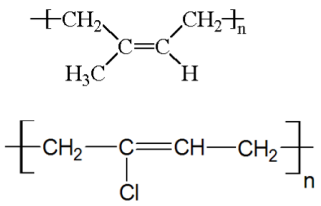
23 billion US Dollars

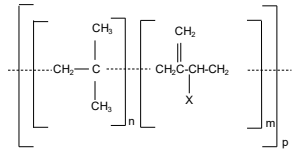
https://www.statista.com/statistics/275387/global-natural-rubber-production/

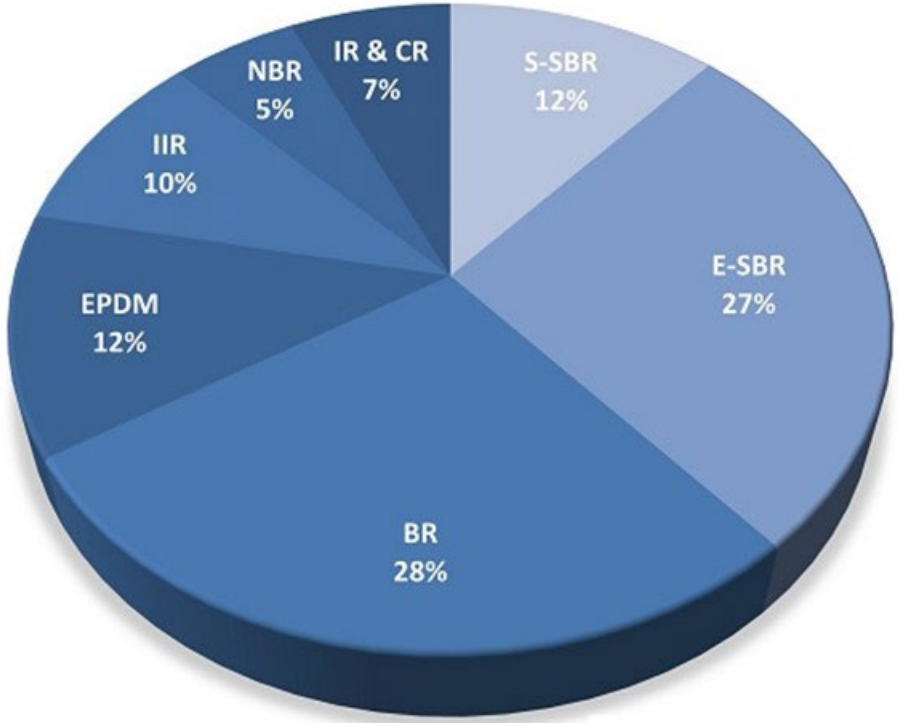
https://www.statista.com/statistics/280536/global-natural-rubber-production/#:~:text=The%20production%20of%20synthetic%20rubber,million%20metric%20tons%20in%202022.

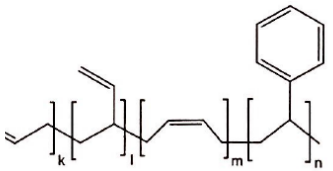
Synthetic rubber. Global demand. 2020

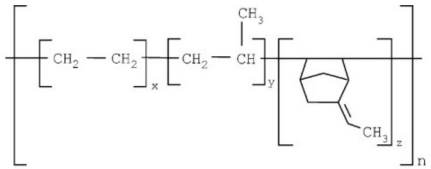




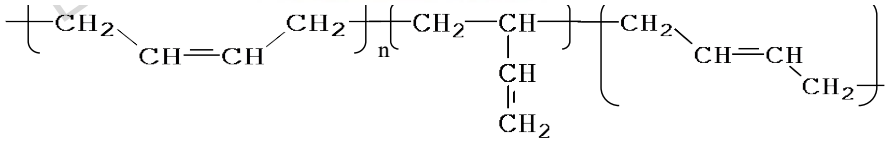


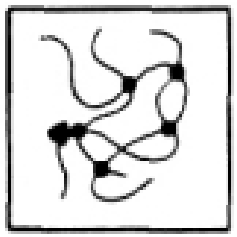






Mainly unsaturated rubbers

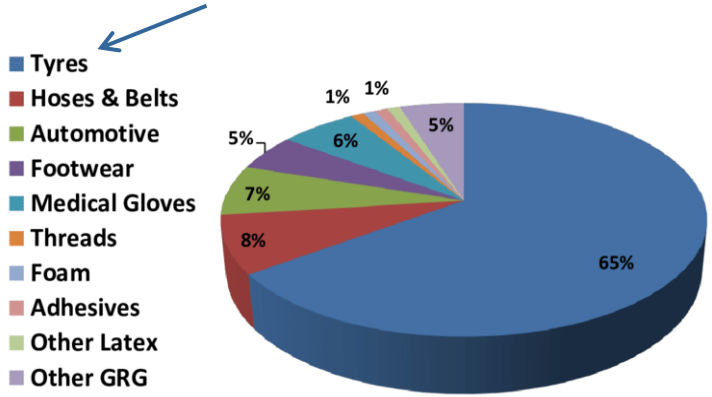




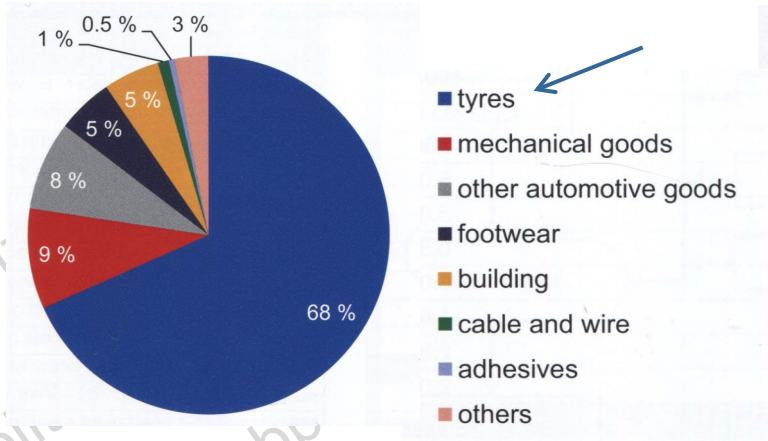
https://www.ceresana.com/en/market-studies/plastics/synthetic-rubber/

Rubber. Applications. Tyres and automotive

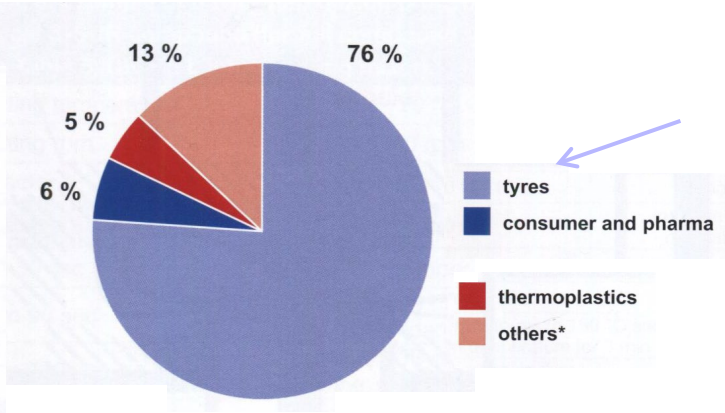
NR



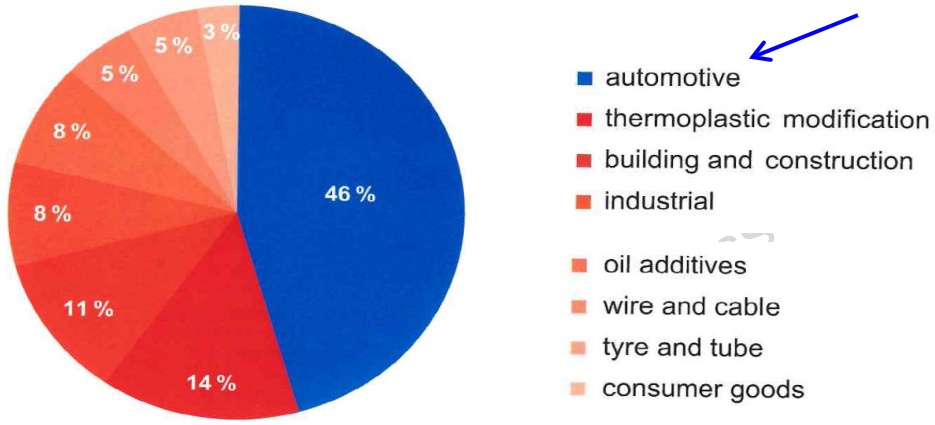
E-SBR



S-SBR + BR



EPDM



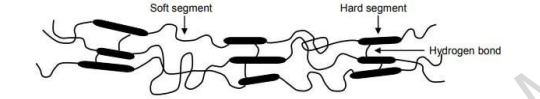


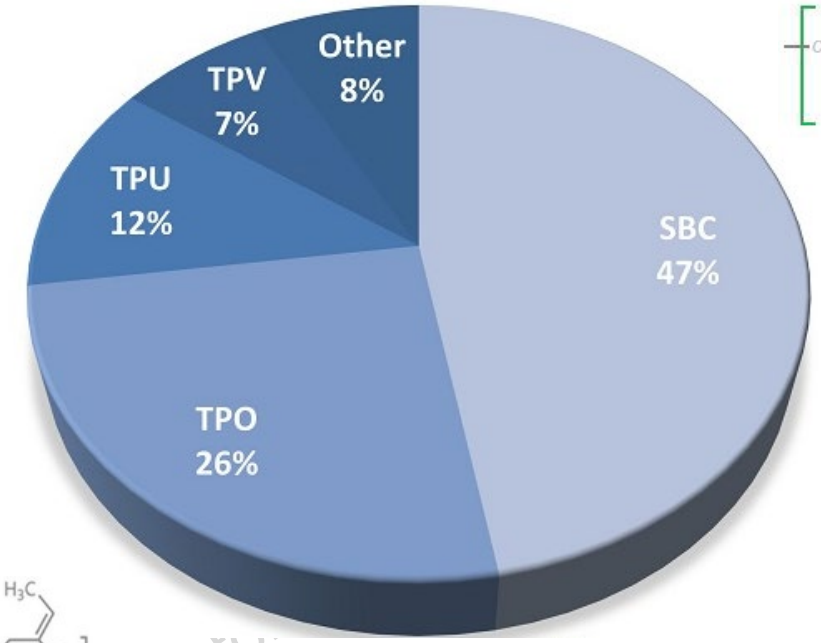
Rubbers are key materials to move people and things

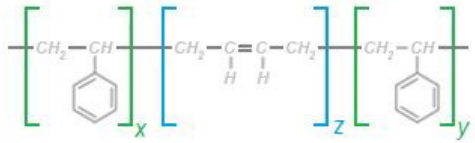
Blengini et al. Assessment of the Methodology for Establishing the EU List of Critical Raw Materials. 2017

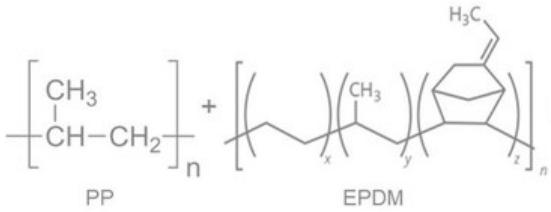
Arlanxeo. Handbook of Synthetic Rubber

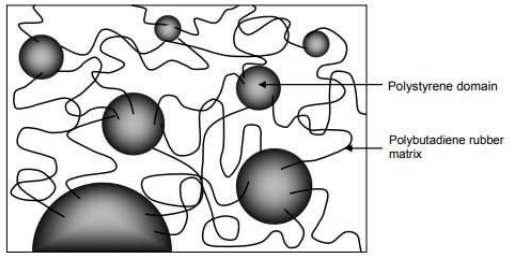
Thermoplastic elastomers (TPE). The market







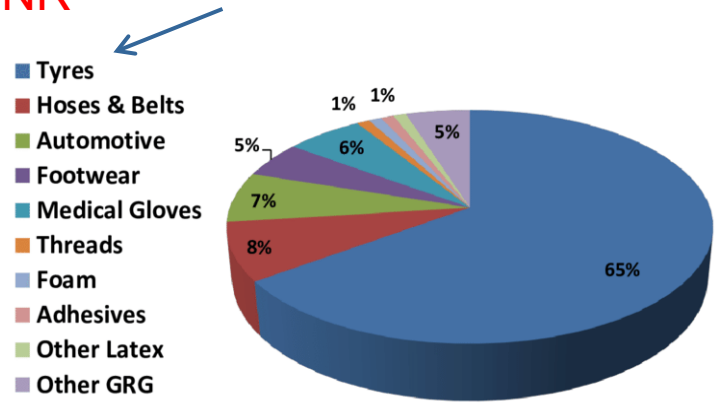




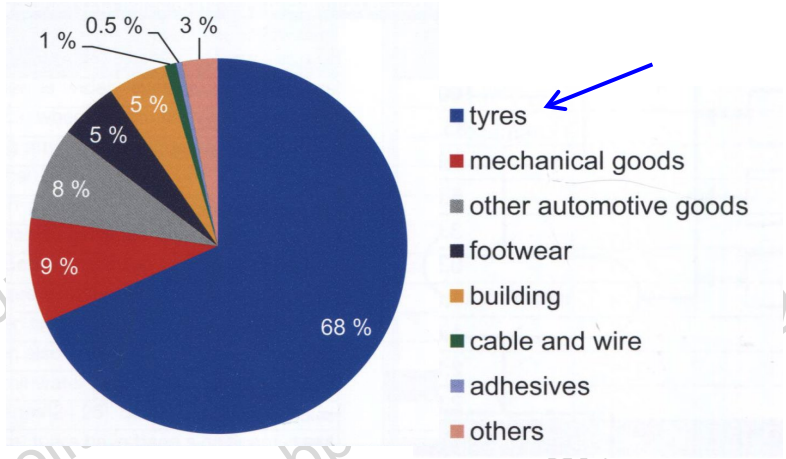
Source: Ceresana

Rubber and TPE. Applications. Tyres and automotive

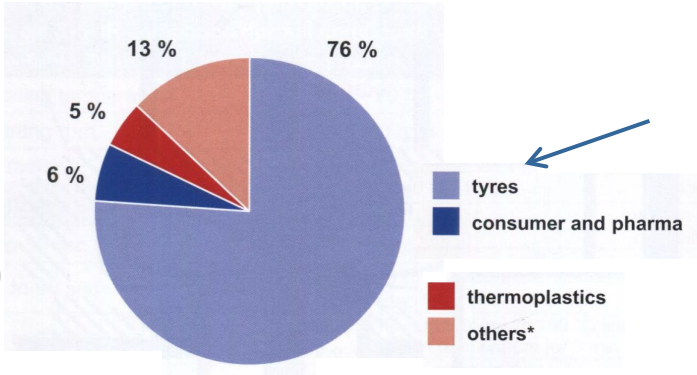
NR



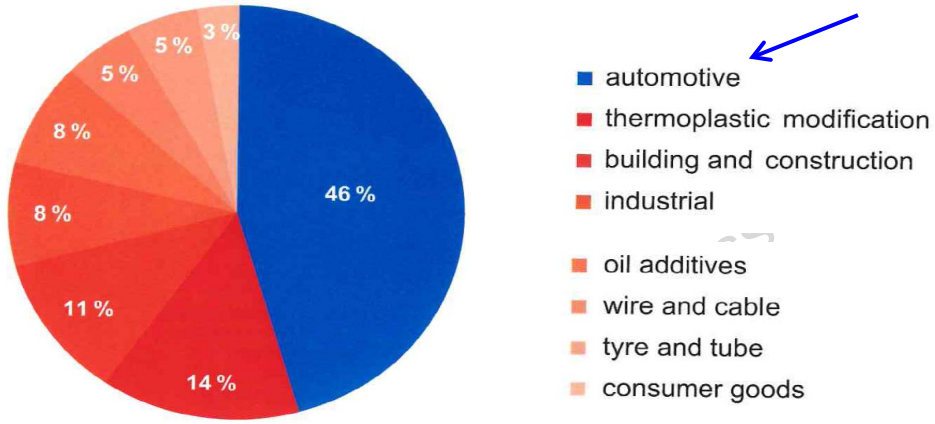
E-SBR



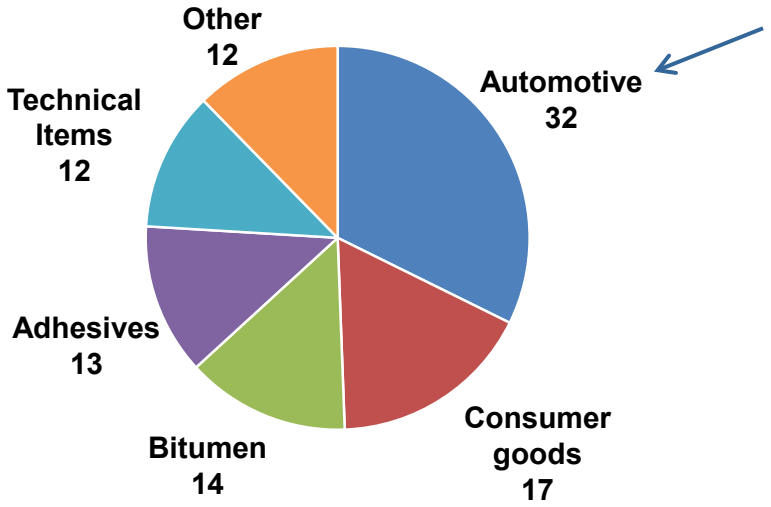
S-SBR + BR



EPDM



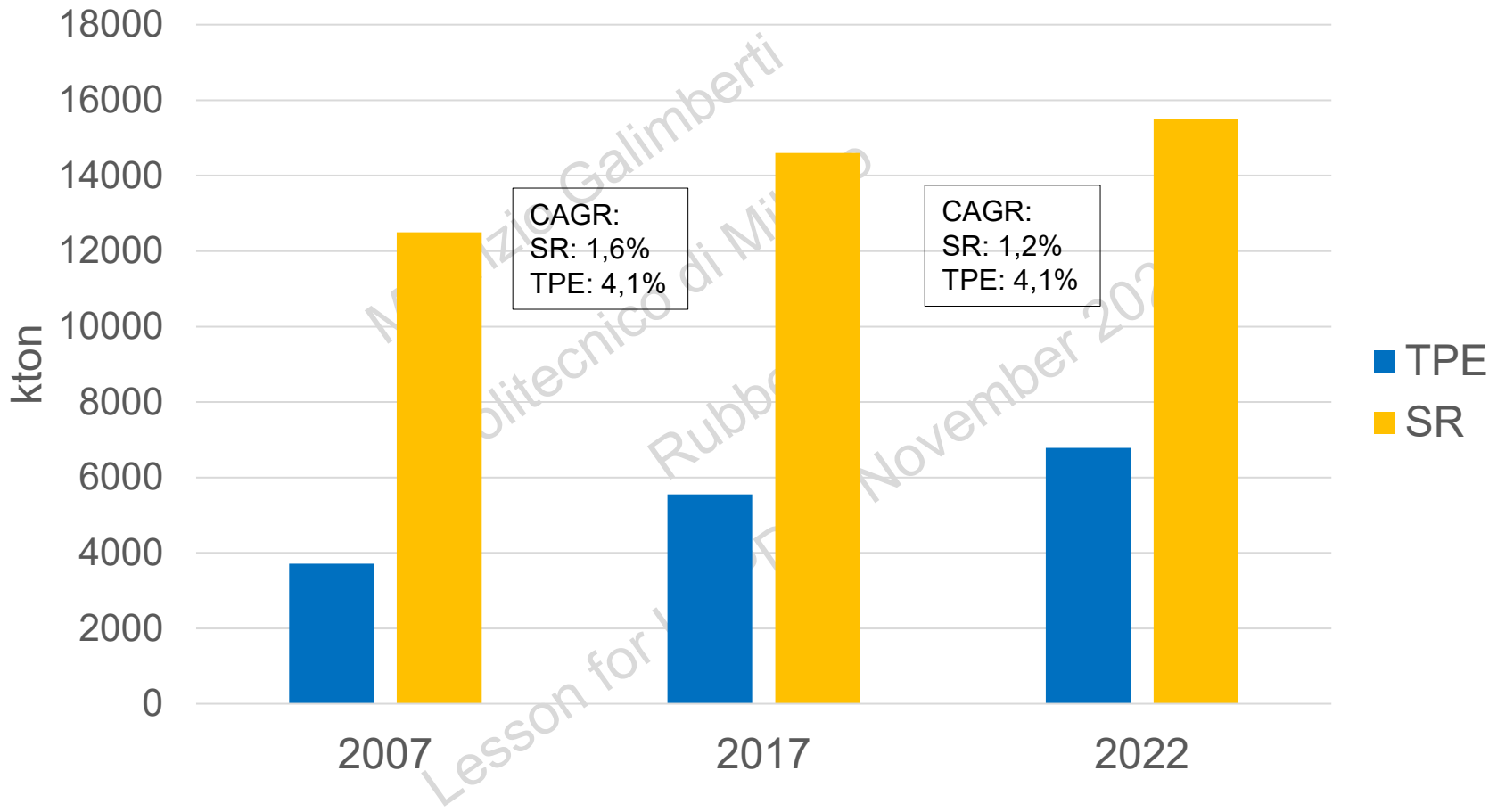
TPE



Blengini et al. Assessment of the Methodology for Establishing the EU List of Critical Raw Materials. 2017

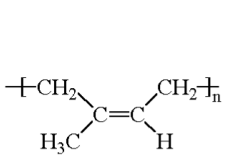
Arlanxeo. Handbook of Synthetic Rubber

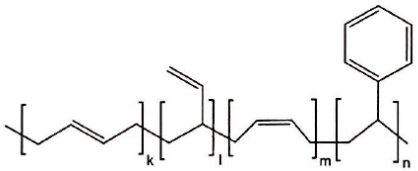
Synthetic rubbers vs TPE

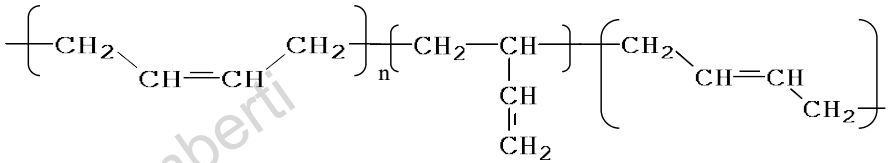


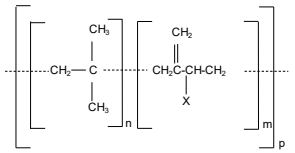
Source: Freedonia, Versalis

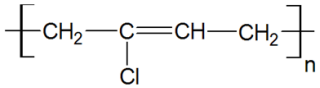
Rubber. Thermoset vs Thermoplastic

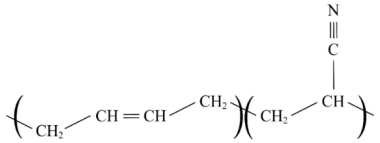


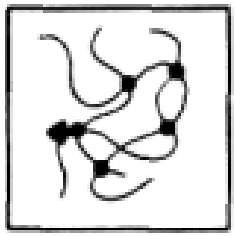


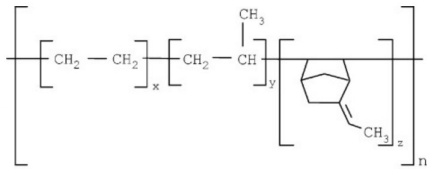






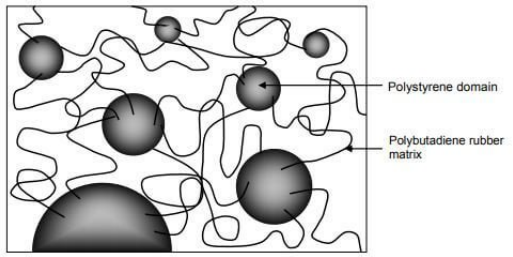


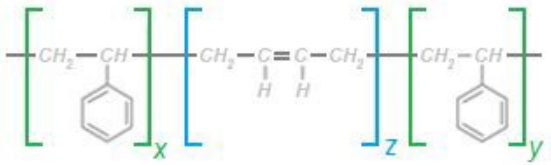


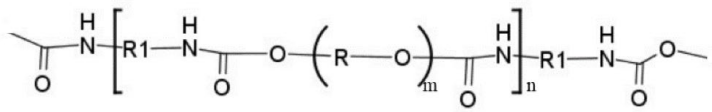


crosslinked

with sulfur or peroxides







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Blengini et al. Assessment of the Methodology for Establishing the EU List of Critical Raw Materials. 2017

Entropic elasticity

Molecular requisites for an ideal elastomer

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Enthalpic and entropic elasticity

The basic differences in the behaviour of elastomers and ideal elastic solids are governed by specific mechanisms of energy storage during deformation.

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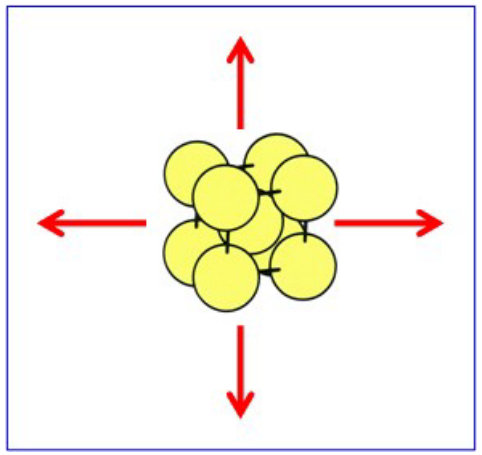
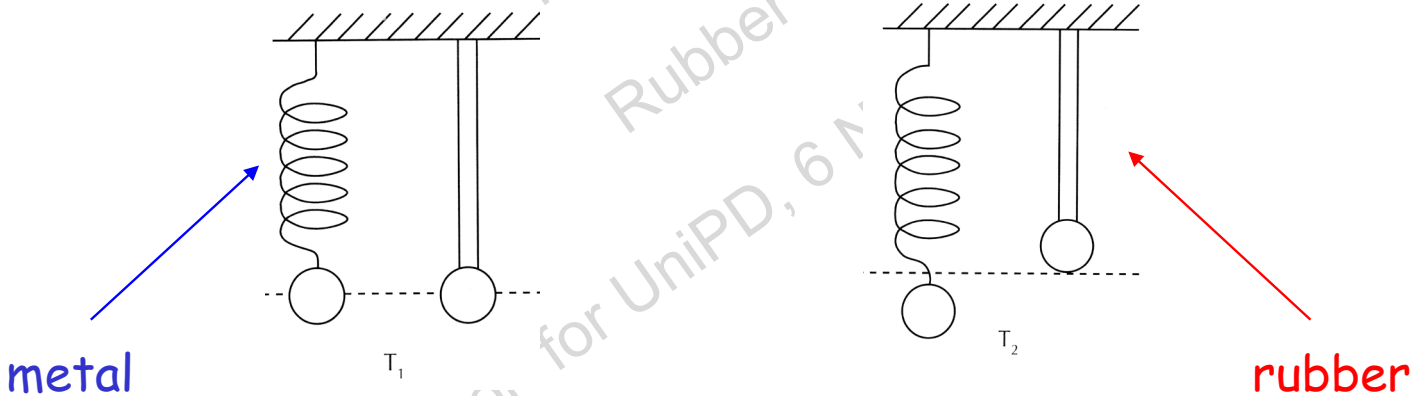
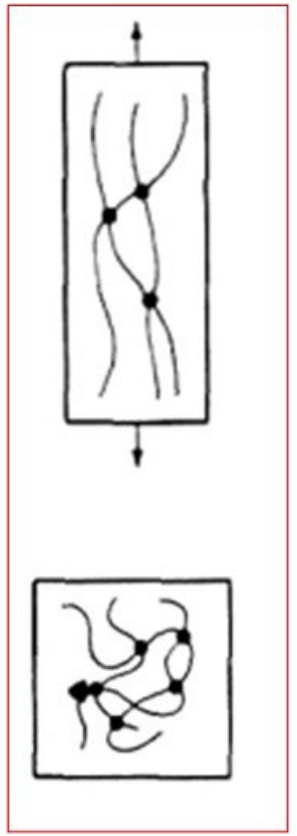




T2 > T1



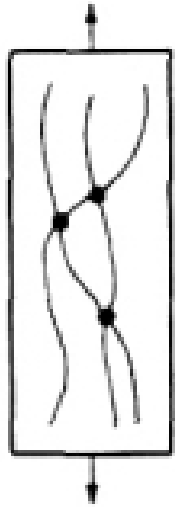
Entropic elasticity

$$\Delta G_{all} = \Delta H_{all} - T\Delta S_{all} \cong -T\Delta S_{all}$$

No molecular creep

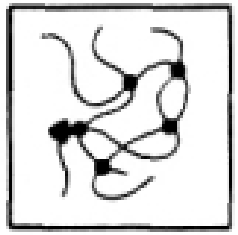
No dissipation of energy

$$\Delta H_{(2a\text{-}2b)} = 0$$



For an elastomer:

$$dW = -fdL$$



f = force

L = length

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Entropic elasticity

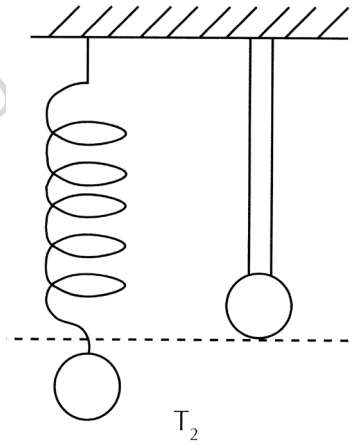
Retractive force

$$f = \left(\frac{\partial G}{\partial L}\right)_{P,T} \cong -T\left(\frac{\partial S}{\partial L}\right)_{P,T}$$

L = length of the sample

If $\delta S/\delta L < 0$,

retractive force increases as T increases



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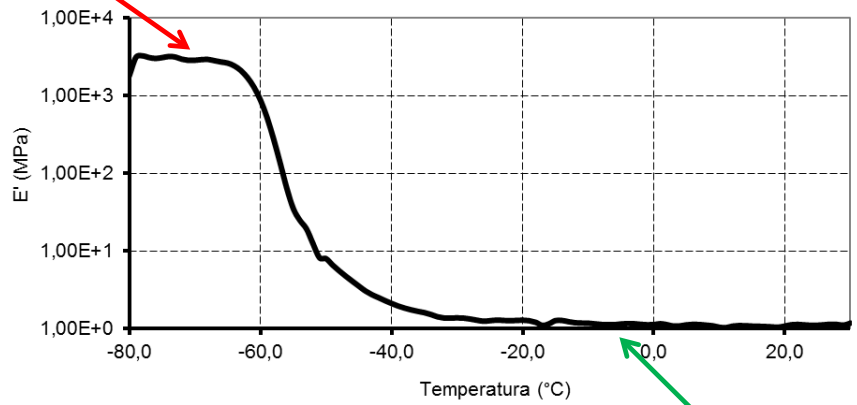
Enthalpic and entropic elasticity

$\sigma = Y\,\varepsilon$



$$f = \left(\frac{\partial G}{\partial L}\right)_{P,T} \cong -T\left(\frac{\partial S}{\partial L}\right)_{P,T}$$

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Molecular requisites for an ideal elastomer

the material MUST

- ☞ **be a high polymer**
- ☞ **be above its glass transition temperature: high local segment mobility**
- ☞ **be amorphous in the unstressed state**
- ☞ **contain a network of crosslinks to restrain gross mobility of chains**

F.W. Billmeyer, Textbook of Polymer Science, J. Wiley & Sons

Molecular requisites for an ideal elastomer

What about the structure of the polymer?

- High molecular mass
- Linear structure of extremely flexible macromolecular chains
- Disorder of intramolecular structure

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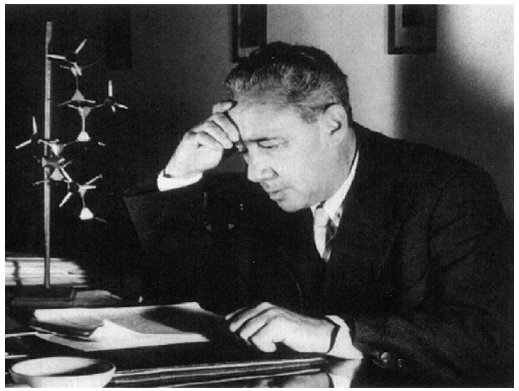


G. Natta, presentation at

"XVI Congres International de Chimie Pure et Appliquè" , Paris (F), 1957

Molecular requisites for an ideal elastomer

Macromolecular Chains

"The linear chains
must be very long
to prevent viscous creep ……



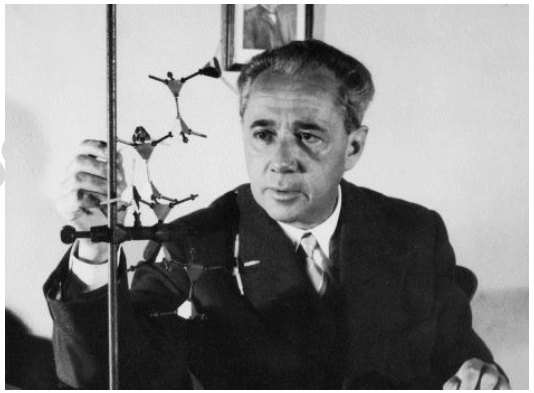
…… and they must be highly disjoined
so that they can preserve certain properties of liquids."

… be flexible and also "disjoined" …

Molecular requisites for an ideal elastomer

Macromolecular Chains

… modify their conformation overcoming potential energy …



It is necessary for the bond of the chain atoms
to oscillate with low deformation works
in a shallow hole of energy,
included between not too high energy maxima. “

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Molecular requisites for an ideal elastomer

Difficult crystallization

"The elements of the chain and their successions should show some dissimmetries, such as to make crystallization difficult."

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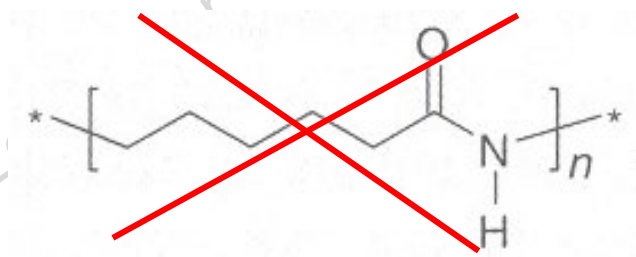
No associations among chains

"No causes (for example polar groups or hydrogen bonds) which promote associations between molecules or reduce their mobility should be present."



Molecular requisites for an ideal elastomer

A certain degree of order

"The chains should have a sufficiently regular structure
so that
in spite of the asymmetries of monomeric units
or of those caused by irregularities in their succession
and in spite of the "disarticulation" of the bonds, ……

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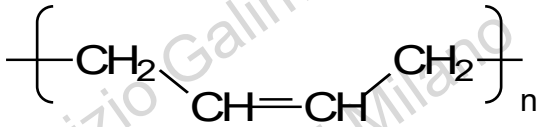
Orientation and crystallization under stretching

by stretching, they
can be oriented
and
associated in crystalline aggregates"

Molecular requisites for an ideal elastomer

Mobility of the macromolecular chain



polibutadiene 1,4-cis

linear chains, containing double bonds, are highly disjoined

Role of the DOUBLE BOND in the main chain

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November 2026

Molecular requisites for an ideal elastomer

Mobility of the macromolecular chain

"If the mobility of the neighbouring single bonds is not greatly hindered by bulky side groups, rubbers with a high resilience can be obtained"

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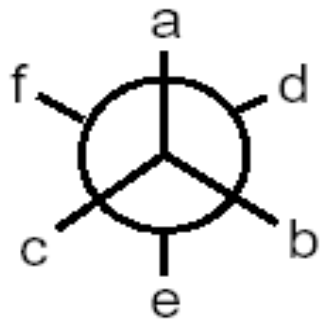
UniPD, 6 Novembe 2026



a,e : chain

c,b - f,d: small groups

Most important rubbers

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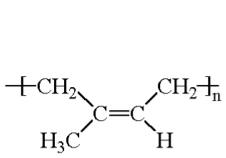
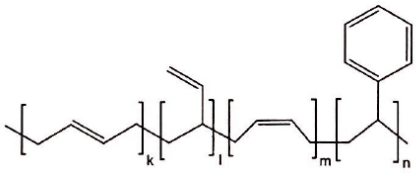
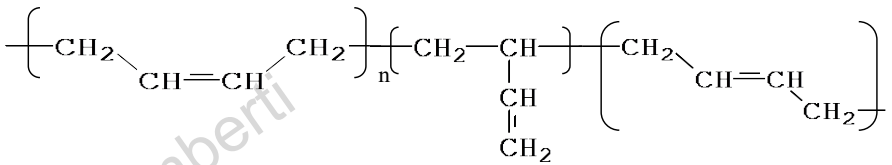
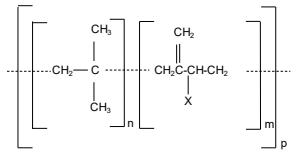
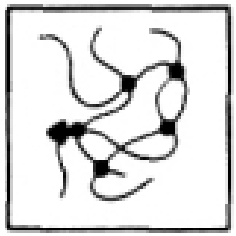
Rubber. Thermoset

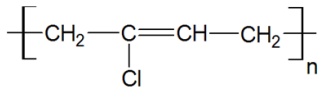


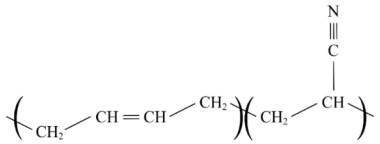


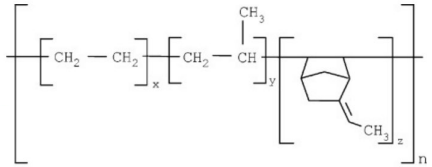












crosslinked

with sulfur or peroxides

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Poly(1,4-cis-isoprene)

Natural Rubber







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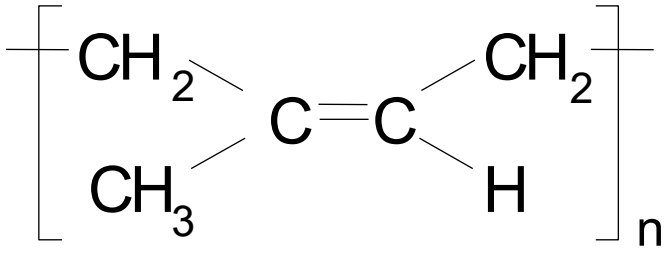
Lesson for UniPD
2026

NR. Poly(1,4-cis-isoprene)

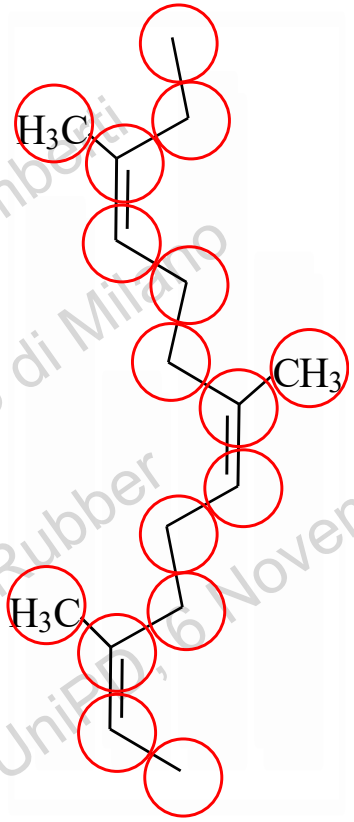






	%
Polyisoprene	93.2
Proteins	2.2
Neutral lipids	2.4
Polar lipids	1.0
Carbohydrates	0.4
Inorganic salts	0.3
Others	0.1
Moisture	0.4

"Pure rubber" can be in the range 93 – 97 %



Poly-isoprene
1,4-cis

- High molecular mass
- Internal double bond with amost 100% 1,4-cis configuration
- Low Tg: about – 64°C
- m.p. = 20°C
- Amorphous at rest
- Crystallization under stretching

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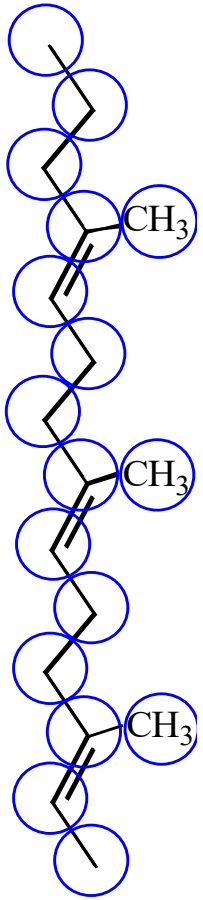
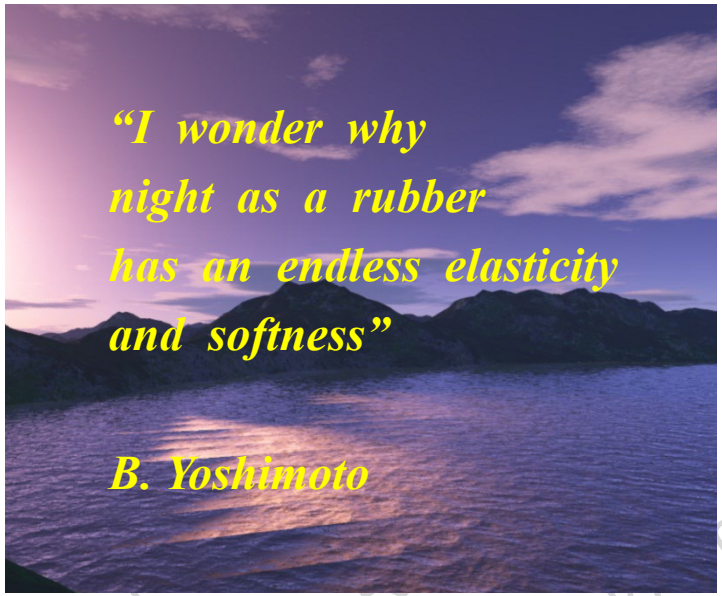
Poly(isoprene): 1,4-cis vs 1,4-trans



Poly-isoprene-1,4-trans

d = 0.98 kg/dm^3

m.p. = 60°C



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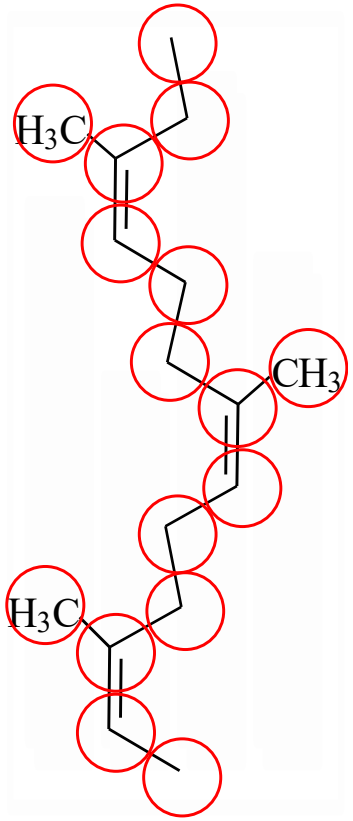


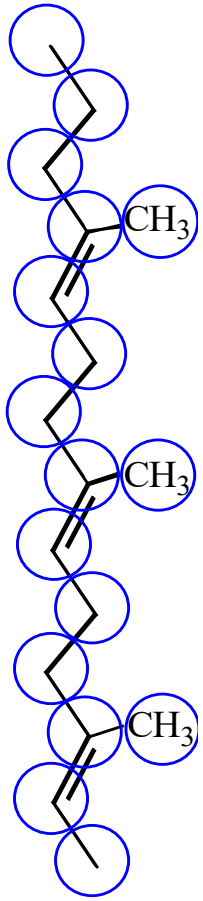
Poly-isoprene-1,4-cis

d = 0.93 kg/dm3 (at rest)

0.95 kg/dm3 (stretched)

m.p. = 20°C

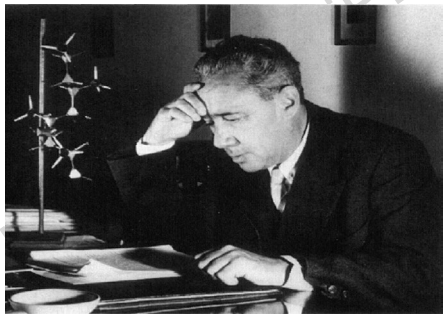
High cis polydiene. The ideal structure for elasticity

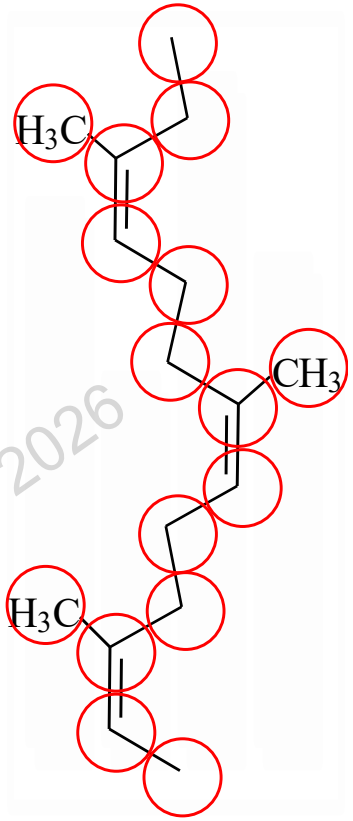


1,4-diene polymers

"with complete 1,4-trans arrangement, chain takes a more linear form,

crystallization is easier: pure crystalline product with a melting point too high for a rubber"





d = 0.98 kg/dm³

m.p. = 60°C

d = 0.93 kg/dm³ (at rest)

0.95 kg/dm³ (stretched)

m.p. = 20°C

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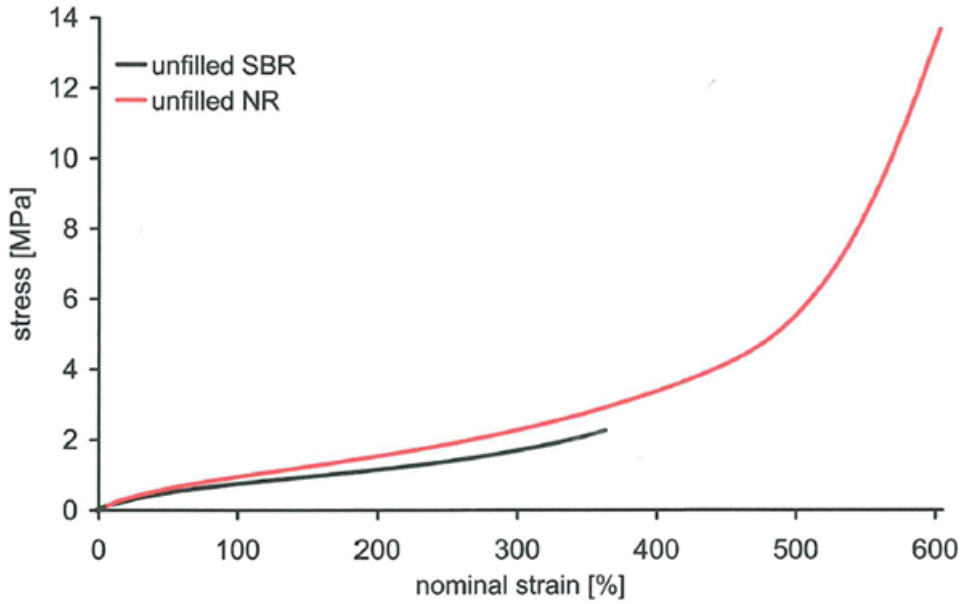
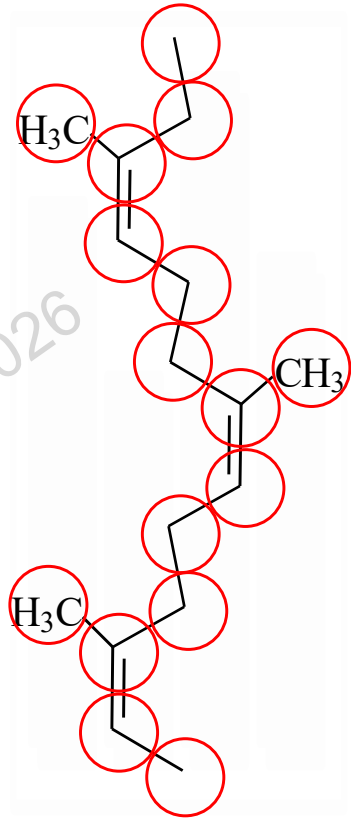
Natural rubber. Strain induced crystallization





by stretching, they
can be oriented
and
associated in crystalline aggregates”

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Natural rubber. Strain induced crystallization

SIC has been prevailingly explained

with the high stereoregularity of poly(isoprene) chains:

1,4-cis units close to 100%

Brock, M. J., & Hackathorn, M. J. *Rubber Chemistry and Technology,* **1972,** *45,* 1303-1314.

Burfield, D. R., & Tanaka, Y. *Polymer,* **1987,** *28*, 907-910.

Eng, A.H., Ong, E. L. in: Hevea *Natural Rubber Handbook of elastomers Eds., CRC Press,* **2000**, 29-60.

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Small melting entropy per statistical segment

was reported to be an important factor

for controlling the crystallization of the rubber network.

Corradini, P. In: *J. Polym. Sci., Polym. Symp.*, **1975,** *50*, 327-344. Wiley Subscription Services, Inc.

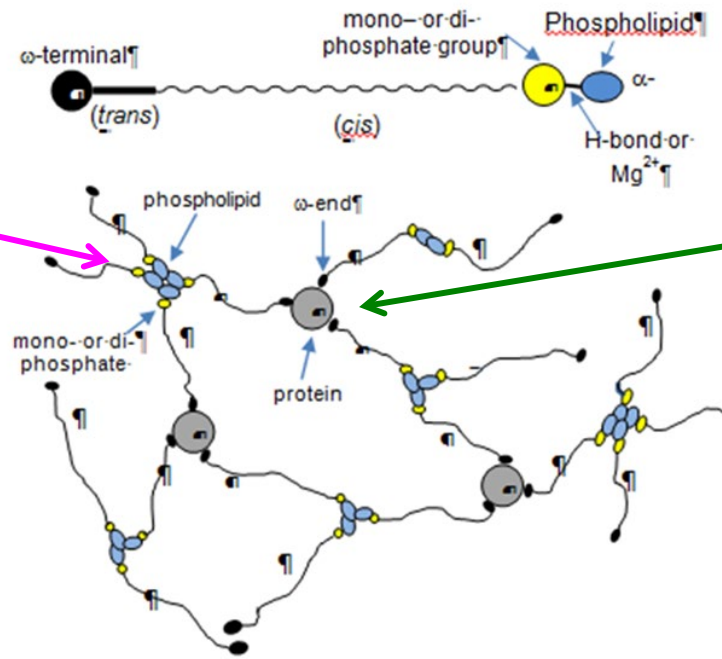
Allegra, G., & Bruzzone, M. *Macromolecules,* **1983,** *16*, 1167-1170.

$$\Delta G_m = \Delta H_m - T\,\Delta S_m = 0$$

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

Natural rubber. Strain induced crystallization

phospholipidic
α terminals,
containing
fatty acid ester groups



dimethylallyl groups
modified with proteins
as ω terminal

☞ branch-points are formed, by hydrogen bond, ionic bond or through the formation of micelles.

☞ Linked and free saturated fatty acids: nucleating effect
Free unsaturated fatty acids: plasticizers

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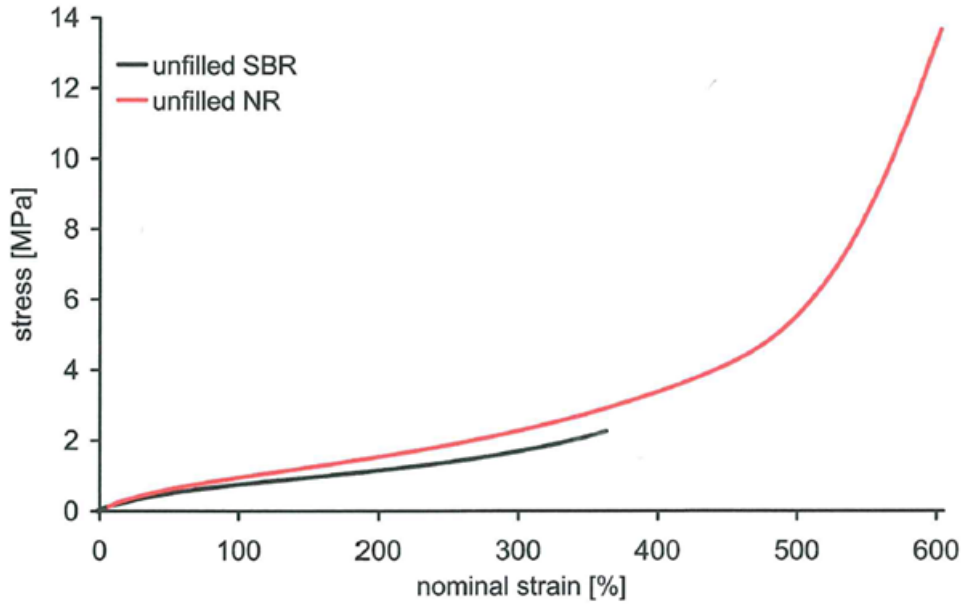
Kakubo, T., Matsuura, A., Kawahara, S., & Tanaka, Y. *RCT,* **1998,** *71*, 70-75.
Tanaka, Y., & Tarachiwin . *RCT*, **2009**, *82*, 283-314

NR: good properties and applications

- CHAIN MOBILITY
- LOW Tg = - 65°C

  GOOD BEHAVIOUR AT LOW T
- MOLECULAR ORDER:

  ENOUGH TO CRYSTALLIZE UNDER STRETCHING



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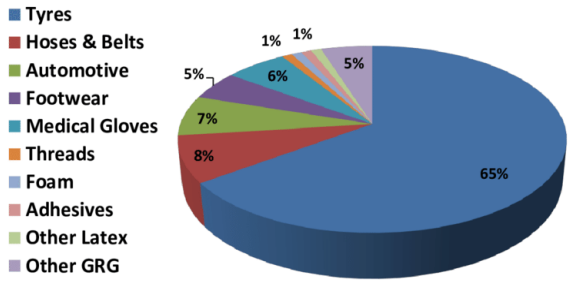
- HIGH ELASTICITY
- HIGH TENSILE STRENGTH
- HIGH RESILIENCE
- LOW HYSTERESIS



NR: good properties

- LOW HEAT BUILD UP
- HIGH DYNAMIC FATIGUE RESISTANCE
- HIGH RESISTANCE TO TEAR (Propagation)
- HIGH ABRASION RESISTANCE
- BUILDING TACK: THE BEST !

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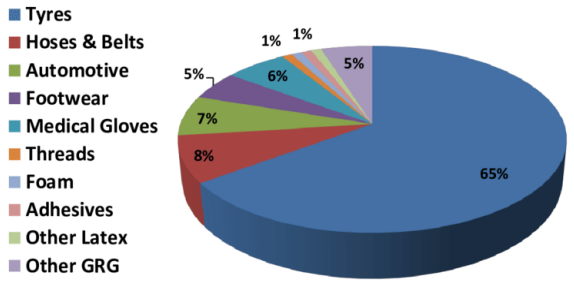
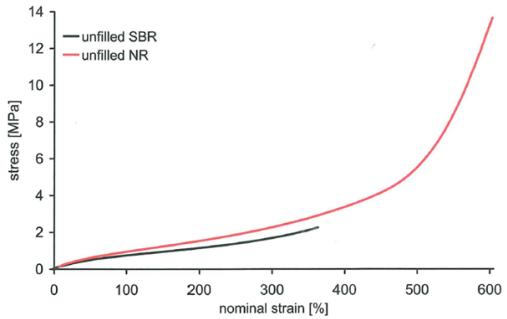


NR. Properties. Pay attention

- Difficult processability
- Low impermeability
- Low aging resistance
- Low oil resistance



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Poly(butadiene)

Mauri alimberti
Pr on for UniPD, b mber 2026

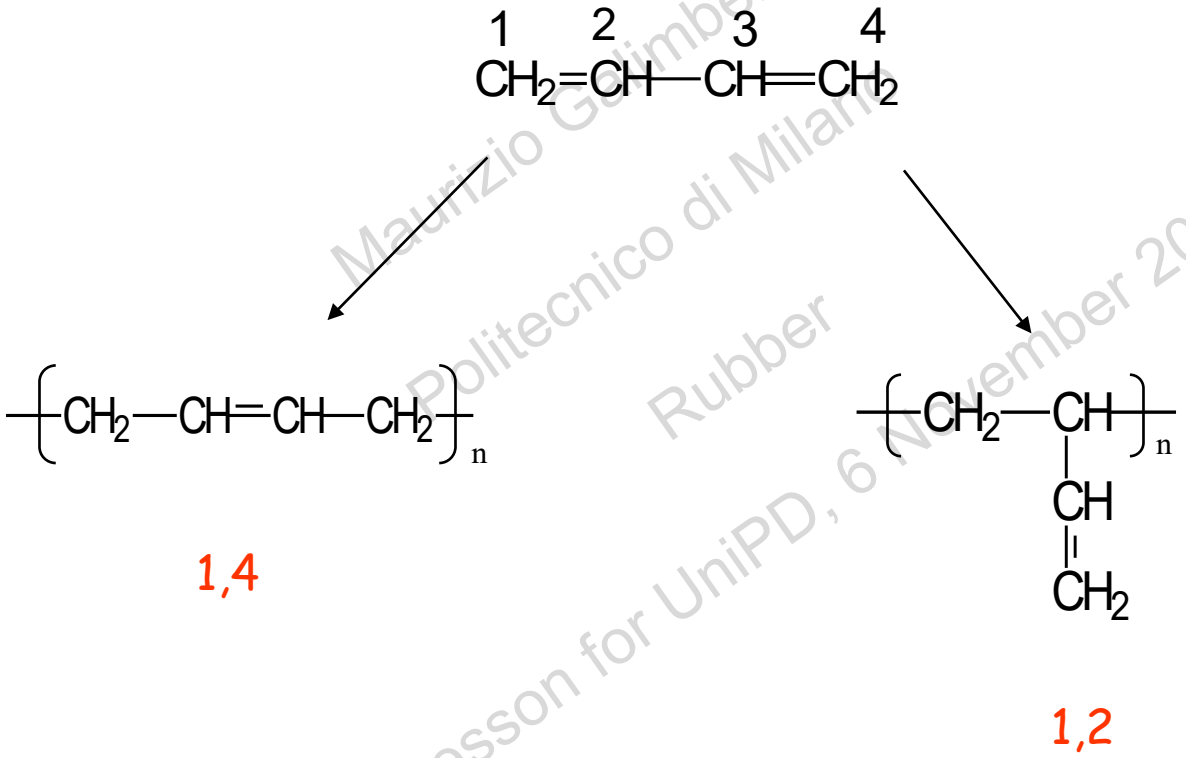






Poly(butadiene)

Constitutional units



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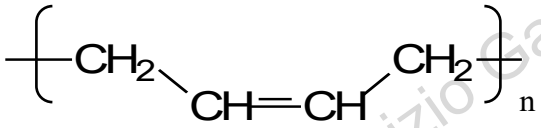
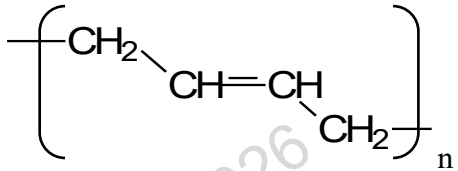
Poly(butadiene)

Poly-butadiene-1,4

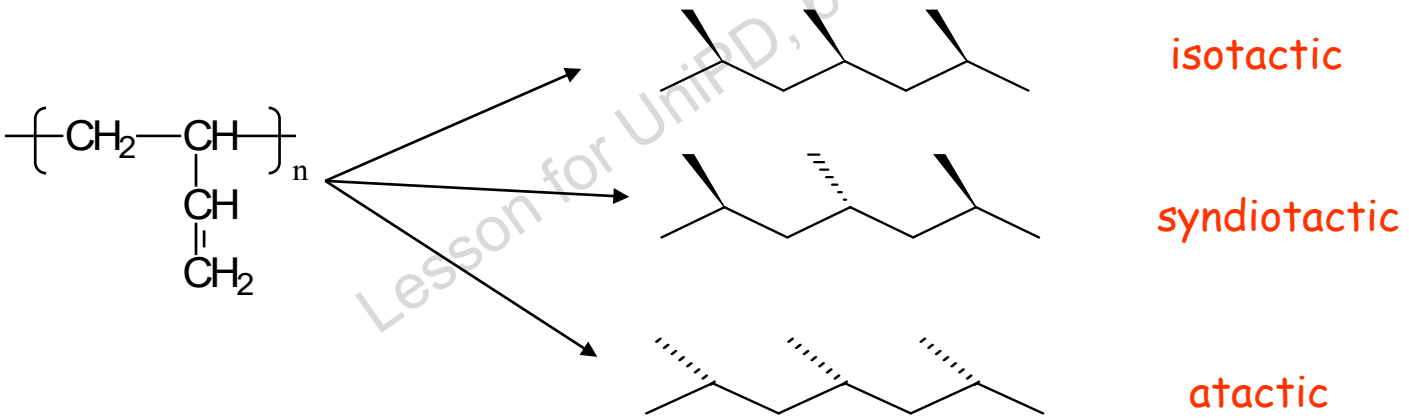
1,4-cis



1,4-trans



Poly-butadiene-1,2



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Polybutadiene. Catalysis and microstructure

Microstructure and Thermal Properties

Transition Metal	1,4 –cis %	1,4-trans %	1,2 %	Tg °C	Tm °C
Nd	98	1	1	-109	-67
Ni	96	2	2	-107	-65
Co	95	3	2	-107	-54
Ti	92	4	4	-105	-51
Li	38	52	10	-93	no

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Neodimium BR is the BR with the highest 1,4-cis content

BR. Good properties and applications

☞ VERY HIGH CHAIN MOBILITY

- ☞ VERY LOW Tg = - 100°C
- ☞ EXCELLENT PROPERTIES AT LOW T:
  CHAIN EXTREMELY FLEXIBLE
- ☞ FREEZING TEMPERATURE: LOWER THAN NATURAL RUBBER
- ☞ HIGH RESILIENCE
- ☞ HIGH RESISTENCE TO DYNAMIC FATIGUE
- ☞ VERY GOOD FOR DYNAMIC APPLICATIONS

pay attention !

- ☞ CRYSTALLIZATION FOR LONG STORAGE TIME

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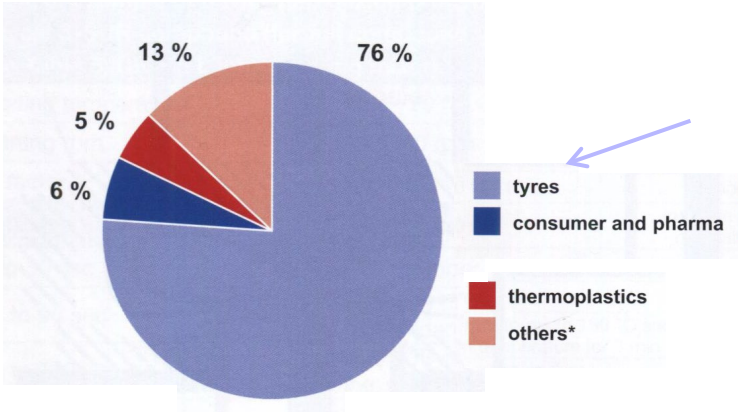

Poly(styrene-co-butadiene)

Styrene-Butadiene rubber

SBR



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Politecnico di Milano
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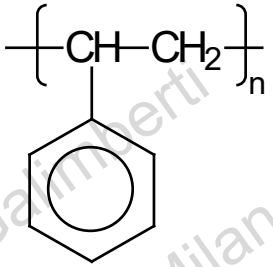
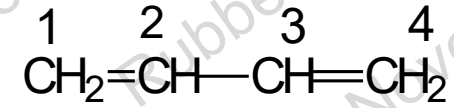
November 2026

Poly(styrene-co-butadiene). 4 comonomers

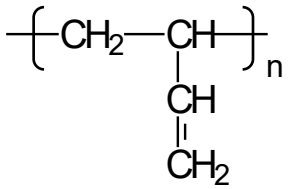
styrene



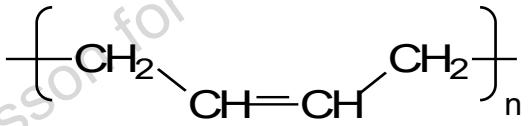
1,3-butadiene



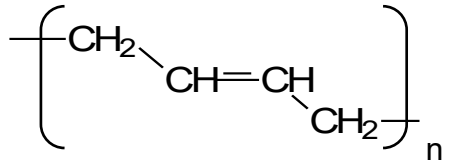
1,2



1,4-*cis*



1,4-*trans*



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SBR. Different polymerization techniques

Emulsion SBR

E-SBR

Radicalic Polymerization

Solution SBR

S-SBR

Anionic Polymerization

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Emulsion SBR

E-SBR

Radicalic
Polymerization

Polymerization	Initiator	°C
Hot	Thermal	40 - 60
Cold	Redox	5 - 15

Most important SBR

- E-SBR: born first
- Backbone of Synthetic Rubber Industry
- Limited number of commercial grades, unterchangeable

with respect to S-SBR:

- Better processability
- Lower cost

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Emulsion SBR. Typical features

Emulsion SBR

E-SBR

Radicalic Polymerization

Chemical composition (wt %)

Rubber: 92 Fatty Acid: 6 Ashes: 0.1 – 0.7 *without extension oil*

Extension Oil: 0 – 33

Chemical composition of pure E-SBR (wt%)

Styrene: 20 – 40

Butadiene: *1,4-cis*: 8 – 12 *1,4-trans*: 72 - 74 *1,2*: 16 - 18

Distribution of butadiene and styrene along the chain

$r_B r_S < 1$ (0.1 – 0.2), $r_B \approx r_S$ random

MW, Mooney Viscosity

30 – 60 Mooney units

Molecular Weight Distribution

Broad

Tg: -35 - -50°C amorphous copolymers

Color: Light, Dark

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Solution SBR.

Solution SBR

S-SBR

Anionic Polymerization

Why S-SBR consumption is increasing ?

- S-SBR: key rubber for silica based tires
- S-SBR: GREEN TIRES

Main recent technical developments:

- Control of copolymer microstructure
- High Molecular Mass
- Processability OK

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Solution SBR. Anionic polymerization. Organolithium as initiators

Control of copolymer microstructure

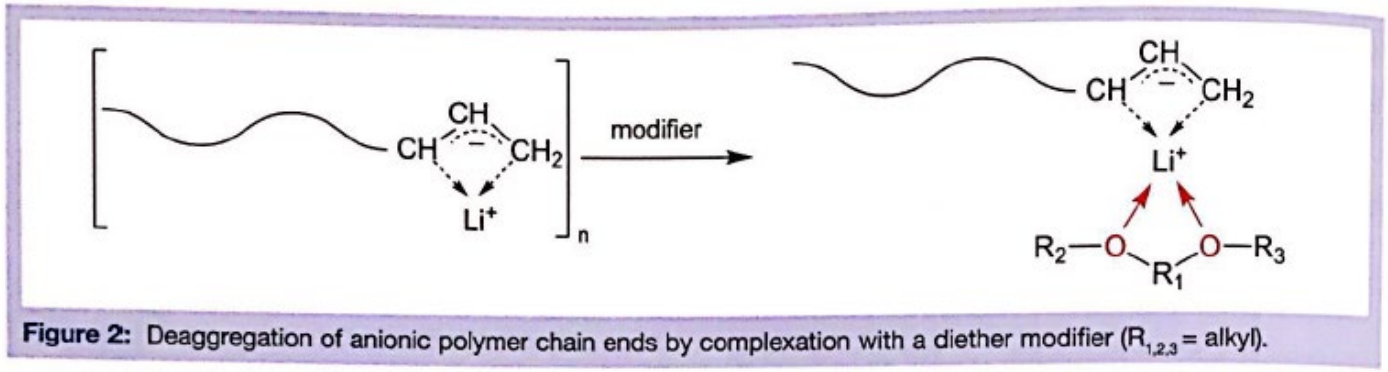

Figure 2: Deaggregation of anionic polymer chain ends by complexation with a diether modifier ($R_{1,2,3}$ = alkyl).

Effect on comonomer incorporation in SBR

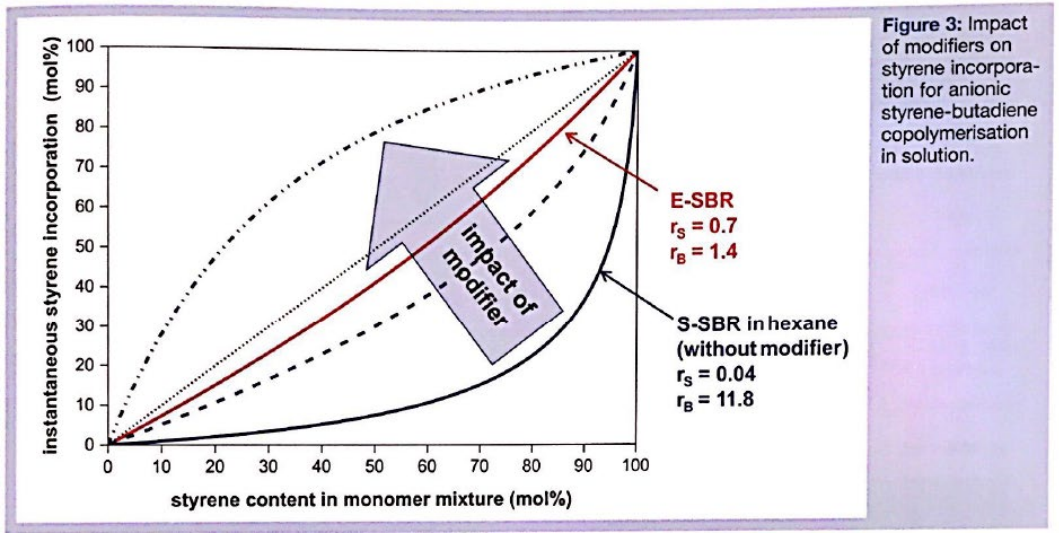

Figure 3: Impact of modifiers on styrene incorporation for anionic styrene-butadiene copolymerisation in solution.

HB-Arlanxeo

Solution SBR. Typical features

Solution SBR

S-SBR

Anionic Polymerization

Chemical composition (wt %)

rubber: 98 fatty acid: 0.5 ashes: 0.1 – 0.7

Oil: 0 / 33

Chemical composition of S-SBR rubber

Styrene: 10 – 40

Butadiene: *1,4-cis*: 30 – 50 *1,4-trans*: 20 - 60 *1,2*: 10 - 80

Distribution of butadiene and stirene along the chain

$r_B r_S < 1$, $r_B > r_S$ random - blocky

MW, Mooney Viscosity

40 – 60 Mooney units

Molecular Weight Distribution

Narrow

Tg: -20 - -70°C Amorphous copolymers

Color: Light, Dark

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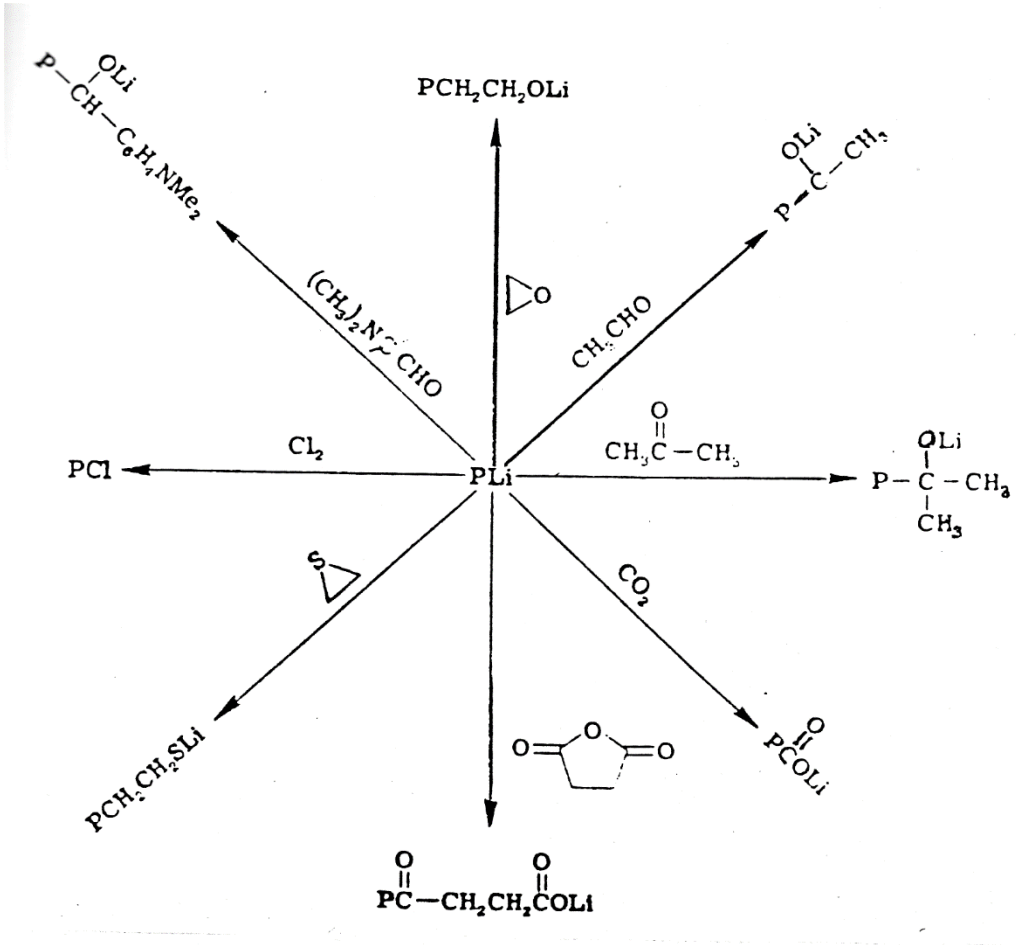
Solution SBR. Anionic polymerization. Organolithium as initiators

Addition of polar groups as chain ends



Polar SBR

Interaction with silica

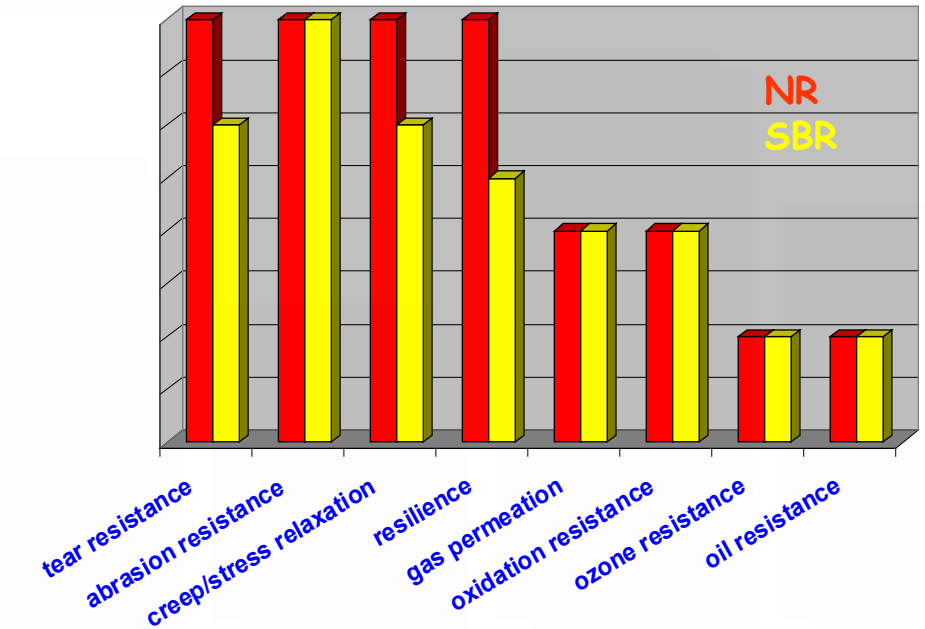
Silica as filler for tyre tread compounds with low hysteresis

Green tyres

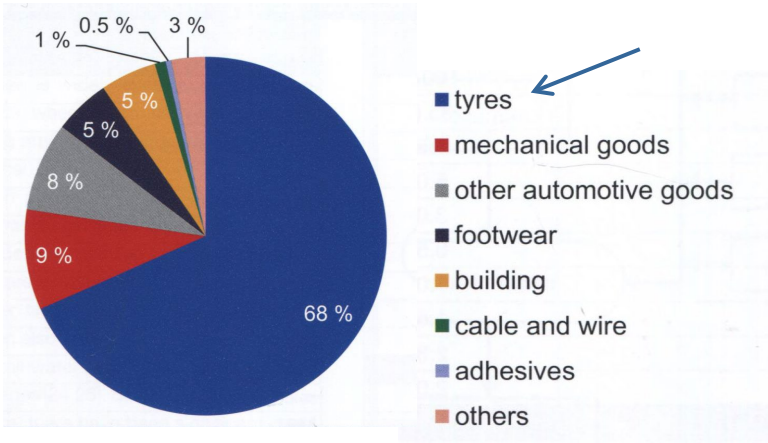
, 6 November 2026

NR vs SBR. Applications

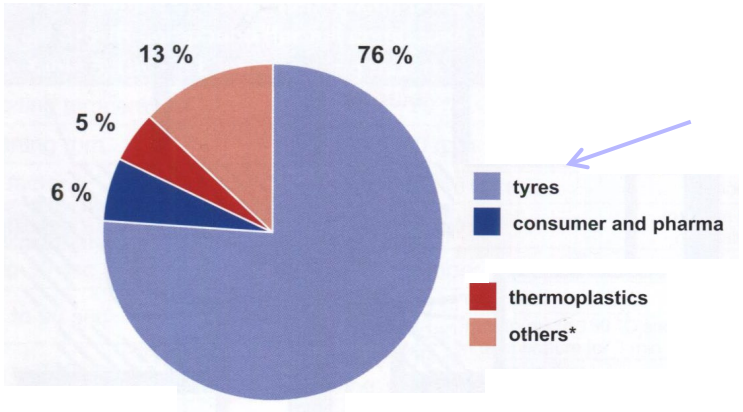
	NR	SBR
Glass transition	-70	-60
Service Temperature	-55 70 100	-45 70 100
Hardness Range(IRHD)	30-100	40-100
Tensile strenght(Mpa)	24	3



E-SBR



S-SBR + BR



Maurizio G
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Butyl rubber

IR, IIR, XIIR

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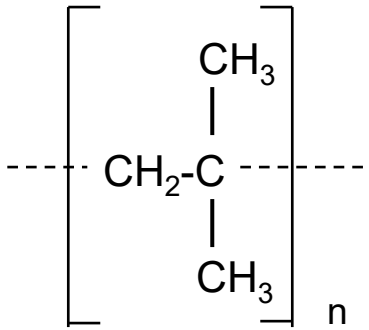
Automotive

Shock absorber



Hi-Fi: acustic case

Elastomers based on isobutene



Poly-isobutene

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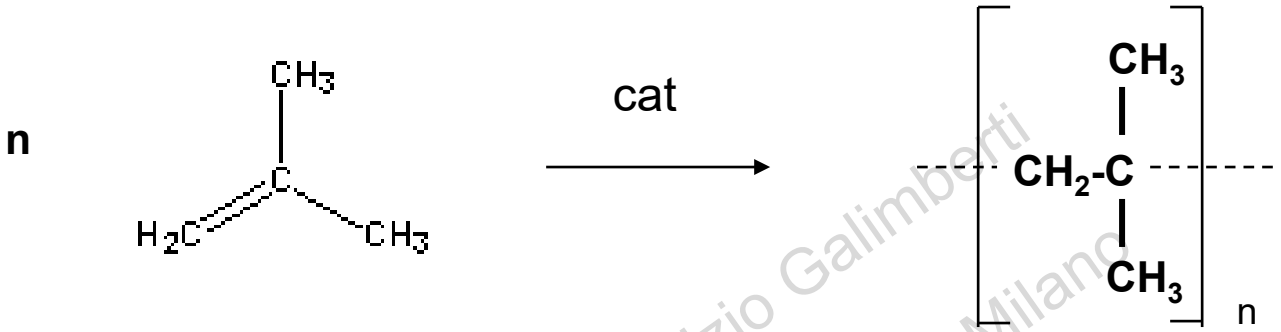
Poly-isobutene (PIB)



Isobutene

Poly Isobutene

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Cationic Polymerization

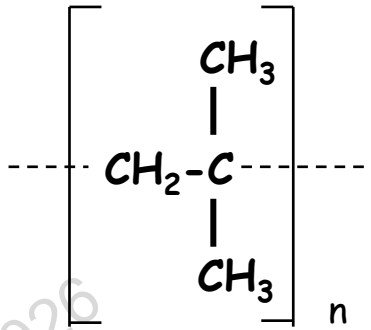
Catalysts: BF_3, $AlCl_3$, RX (X = F, Cl, Br, I)

Activators: HCl, H_2O, $(CH_3)_3C$-Cl.

Poly-isobutene (PIB)

Isobutylene polymerizes in a head-to-tail sequence

producing a rubber having no asymmetric carbon atoms.



The *geminal*-dimethyl group

has two methyl groups bonded to the same carbon atom

[-C(CH_3)$_2$)-CH_2-]

on alternative chain atoms along the polyisobutylene backbone

producing a steric crowding effect.

Distorting the hydrogen atoms of the methylene carbon (-CH_2-)

from the normal tetrahedral 109.5° to 124°,

and the dihedral angle of the carbon-carbon single bond backbone by about 25°

some strain is relieved.

The stereochemistry of the isobutylene unit thus results in

close packing along the polymer chain, low free volume fraction,

and consequently low permeability.

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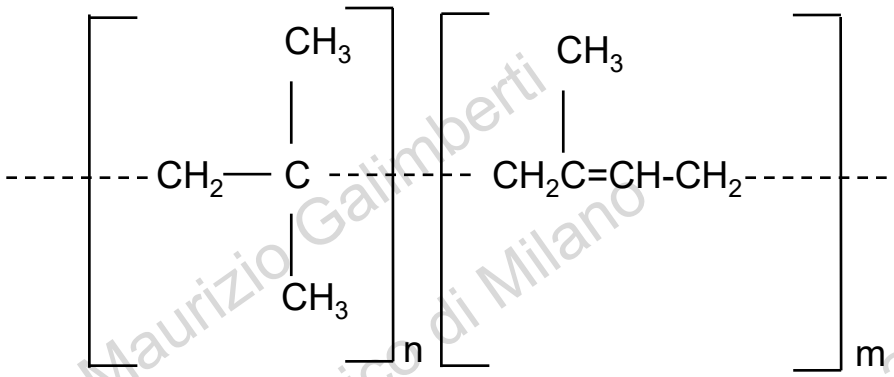
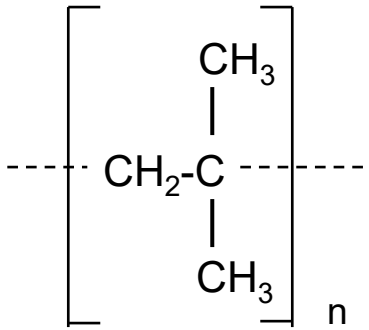
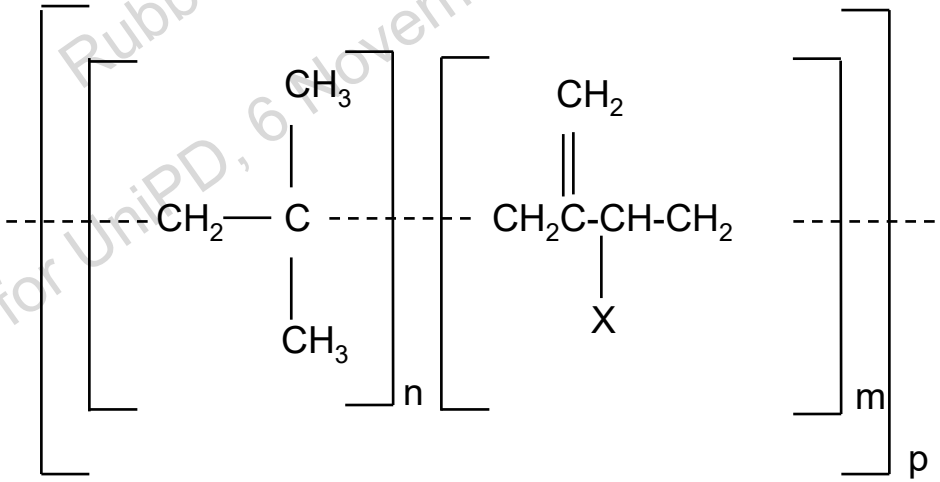
Elastomers based on isobutene



Butyl Rubber



Poly-isobutene



Halobutyl rubber

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Polyolefin elastomers

Ethylene Propylene copolymers

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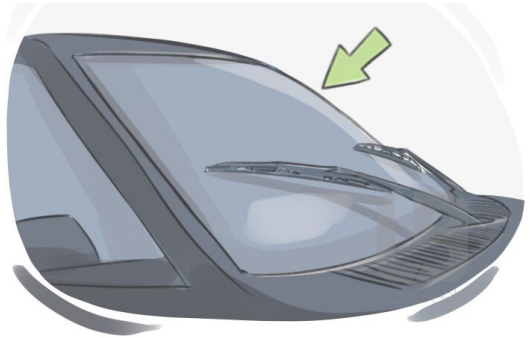
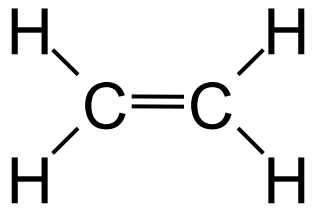


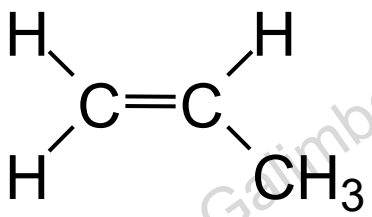




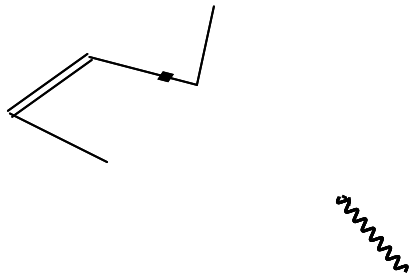
EPDM



ETHYLENE

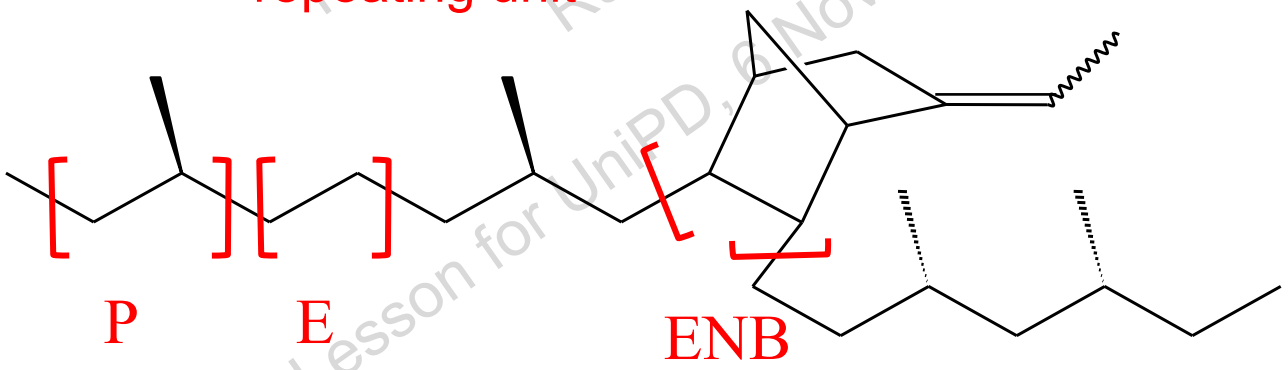


PROPYLENE



ETHYLIDENE-NORBORNENE
ENB

repeating unit



the polymer chain

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Rubber products

The environmental impact

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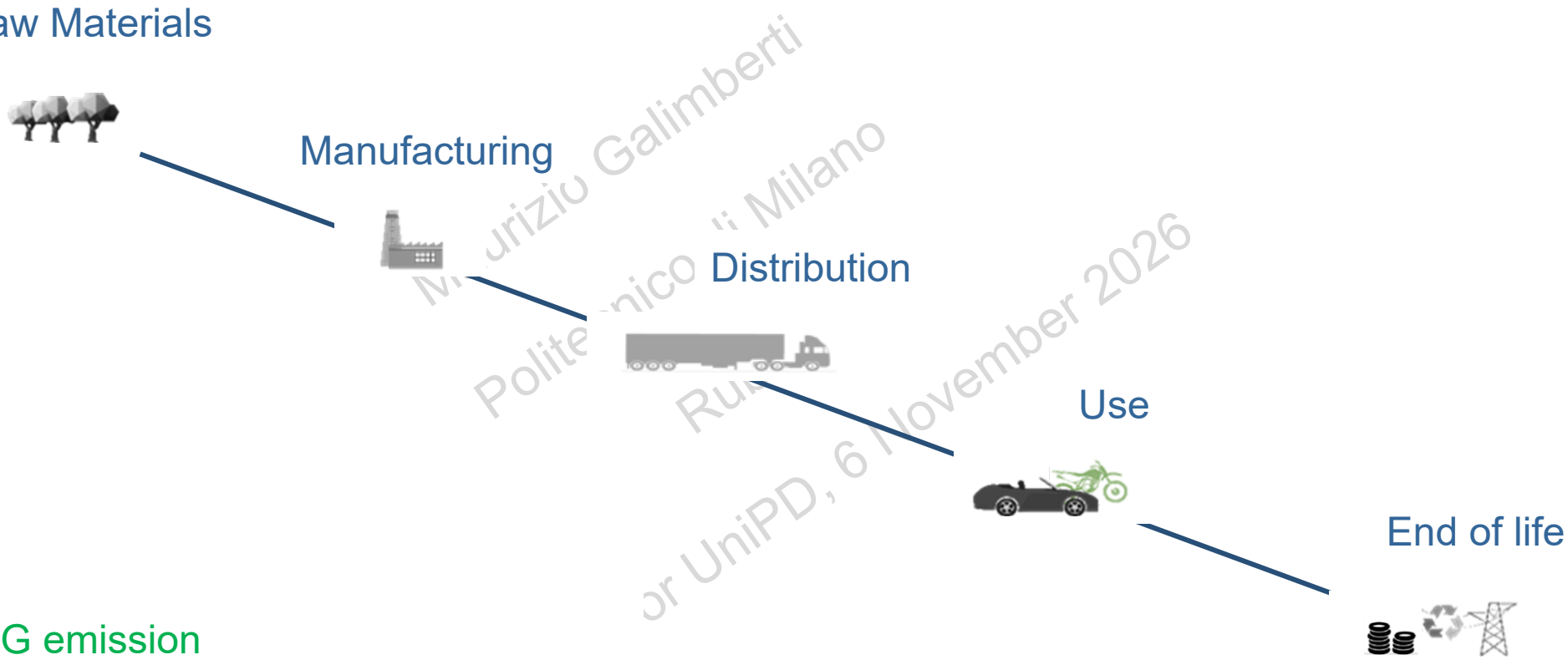
Life Cycle Assessment of a rubber product. A tyre



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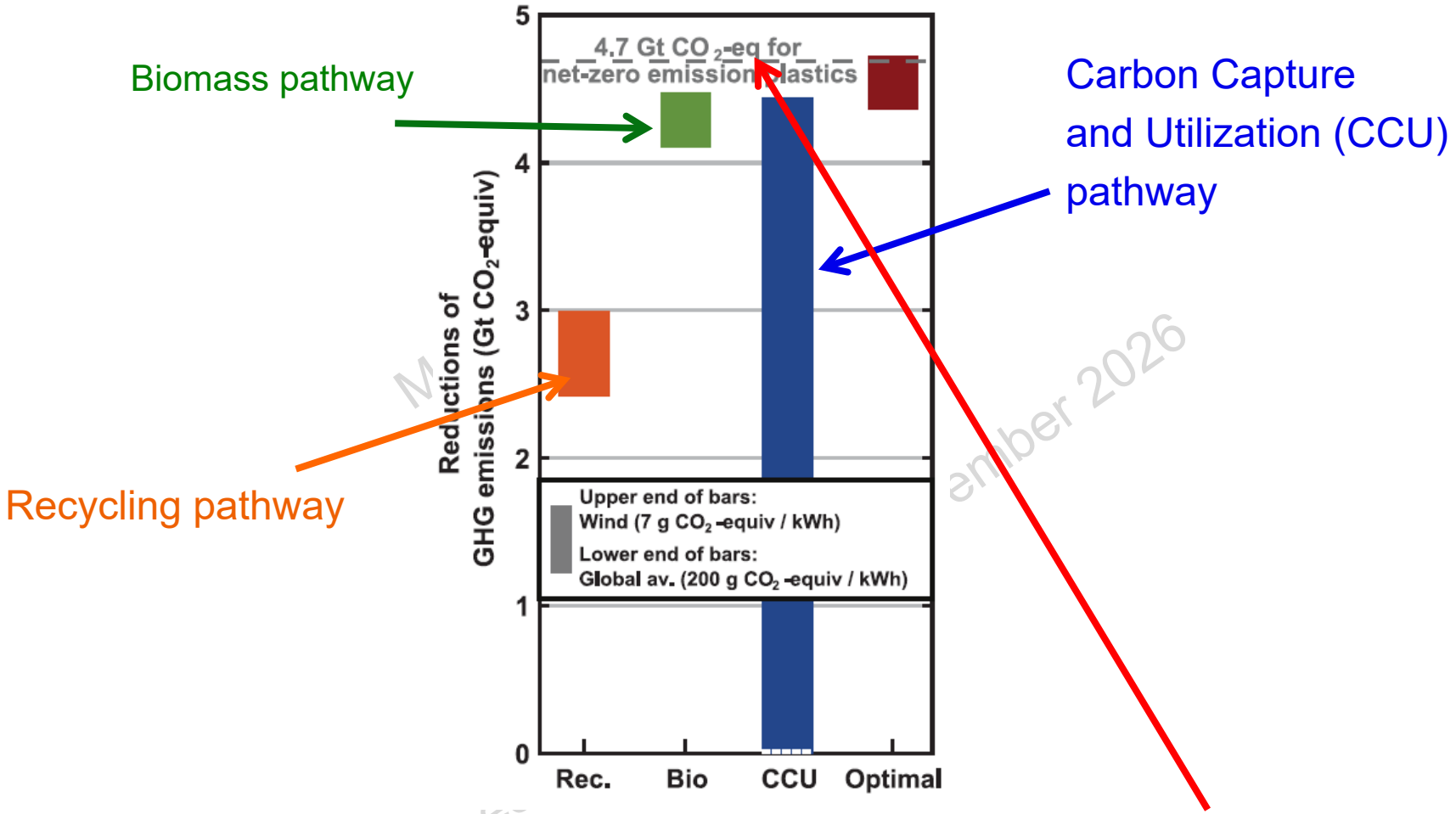
Rubber. Lesson for UniPD, 6 November 2026

GHG emission

Persistence in the environment

Net-zero greenhouse gas emission plastics



plastics solely based on either recycling, or biomass utilization, or CCU fail to reach net-zero GHG emissions, even for wind-based electricity production

Negative emission technologies are needed

Science 374, 71–76 (2021)

Circular rubbers

Rubber from biosources

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The carbon reservoir

Parameter	Value
Annual biomass production (NPP)	**~ 200 Gt dry biomass/year**
Agricultural dry biomass	~ 25 Gt/year
Agricultural dry residues	**~ 15 - 20 Gt/year**
Crude oil production	**~ 5 Gt/year**

Lesson for

Only a small fraction of the annual biomass production is harvested.

Agricultural residues represent a **huge underexploited renewable feedstock**

Biomass Matters for Rubber Materials

Annual Global Material Flows in the Rubber Industry

~ 32

Mt/y

Global rubber consumption

NR + SR elastomers

~ 60–70

Mt/y

Global compounded rubber materials

Estimated total compound flow

~ 18

Mt/y

Rubber used in tyres

NR + SR elastomers

~ 31

Mt/y

Materials used for tyre compounds

Estimated; excludes cords & bead wire

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2024 basis. Global NR + SR consumption = 31.544 Mt/y; tyre-sector rubber consumption = 18.013 Mt/y.
The ~60–70 Mt/y global compound figure is an order-of-magnitude estimate based on typical elastomer fractions in rubber compounds; it is not a directly reported IRSG statistics

Raw Materials. Natural Rubber



energy input for the production (1)

NR: 15-16 MJ/kg

synthetic rubber: 100 MJ/kg

carbon sequestration by the *Hevea* tree (2)

photosynthetic rate

Hevea leaves: about 11 μmol/m^2·s

other trees: 5–13 μmol/m^2·s

Cultivated areas 14.1 million ton hectar

Growth 1.8 times in the last 30 years





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(1) Chapman, A .V. Natural rubber and NR-based polymers: renewable materials with unique properties. In Proceedings of the 24th International H.F. Mark-Symposium, 'Advances in the Field of Elastomers & Thermoplastic Elastomers, Vienna, Austria, 15–16 November 2007.

(2) Jones, K.P. The paradoxical nature of natural rubber. Kautsch. Gummi Kunstst. 2000, 53, 735–742

Raw Materials. Natural Rubber

Biodiversity

Deforestation

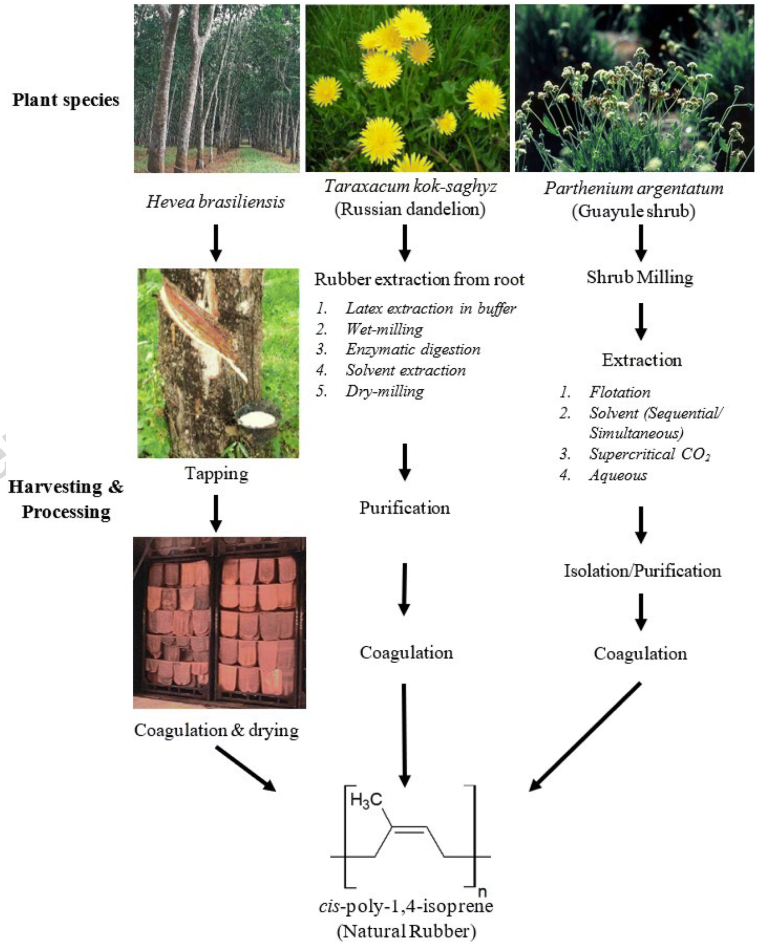
Impact on water cycle

Ammonia as the preservative

Price fluctuation

Small owners

The alternative natural rubbers are not yet ready



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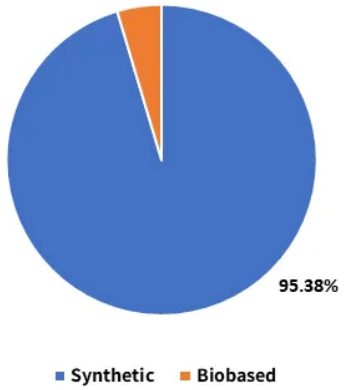
RSC Adv., 2022, 12, 34028

Synthetic rubbers. Raw materials. Bio-attributed rubbers

Monomer	Source	Synthetic route
Isoprene	Lignocellulosic	Fermentation
Butadiene	Lignocellulosic Sugar	Fermentation Chemical synthesis: from ethanol, from butandiol, metathesis
Styrene	Lignocellulosic	Chemical synthesis

butadiene



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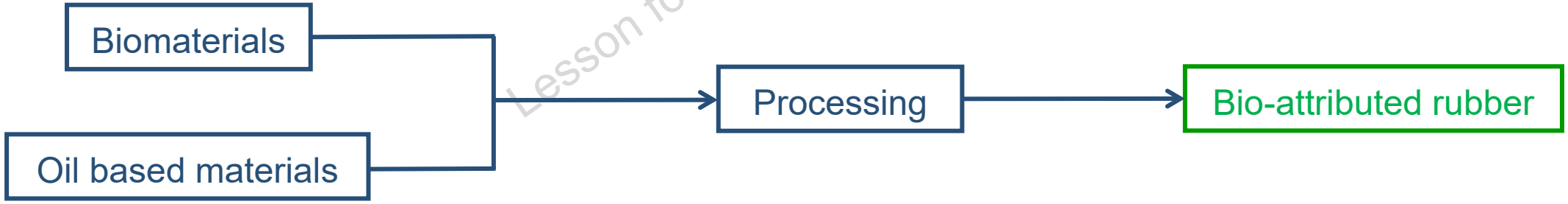
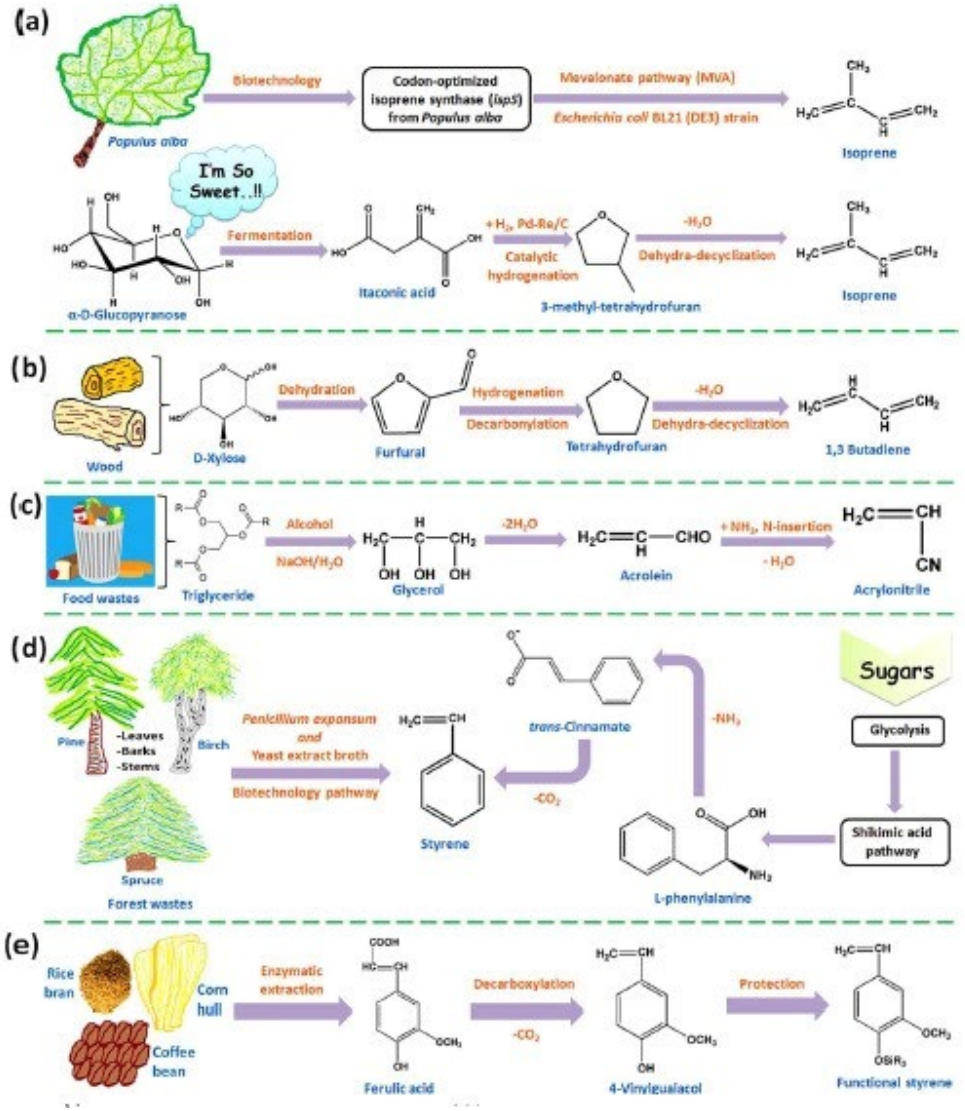


Journal of Applied Polymer Science Sept 2017 doi.org/10.1002/app.45701

Monomers from biosources



Journal of Applied Polymer Science Sept 2017 doi.org/10.1002/app.45701

Bio-based materials. 1930s

Giulio Natta, 1938

In reality, the farmer can also be regarded as a chemical worker,

since he looks after the most important of the organic syntheses known to man:

the chlorophyll synthesis,

in which the energy is supplied by the sun,

and the raw materials are water and carbon dioxide from the air,

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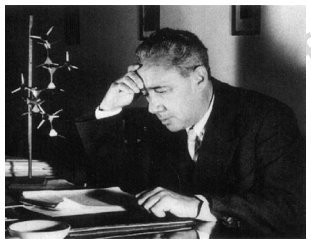
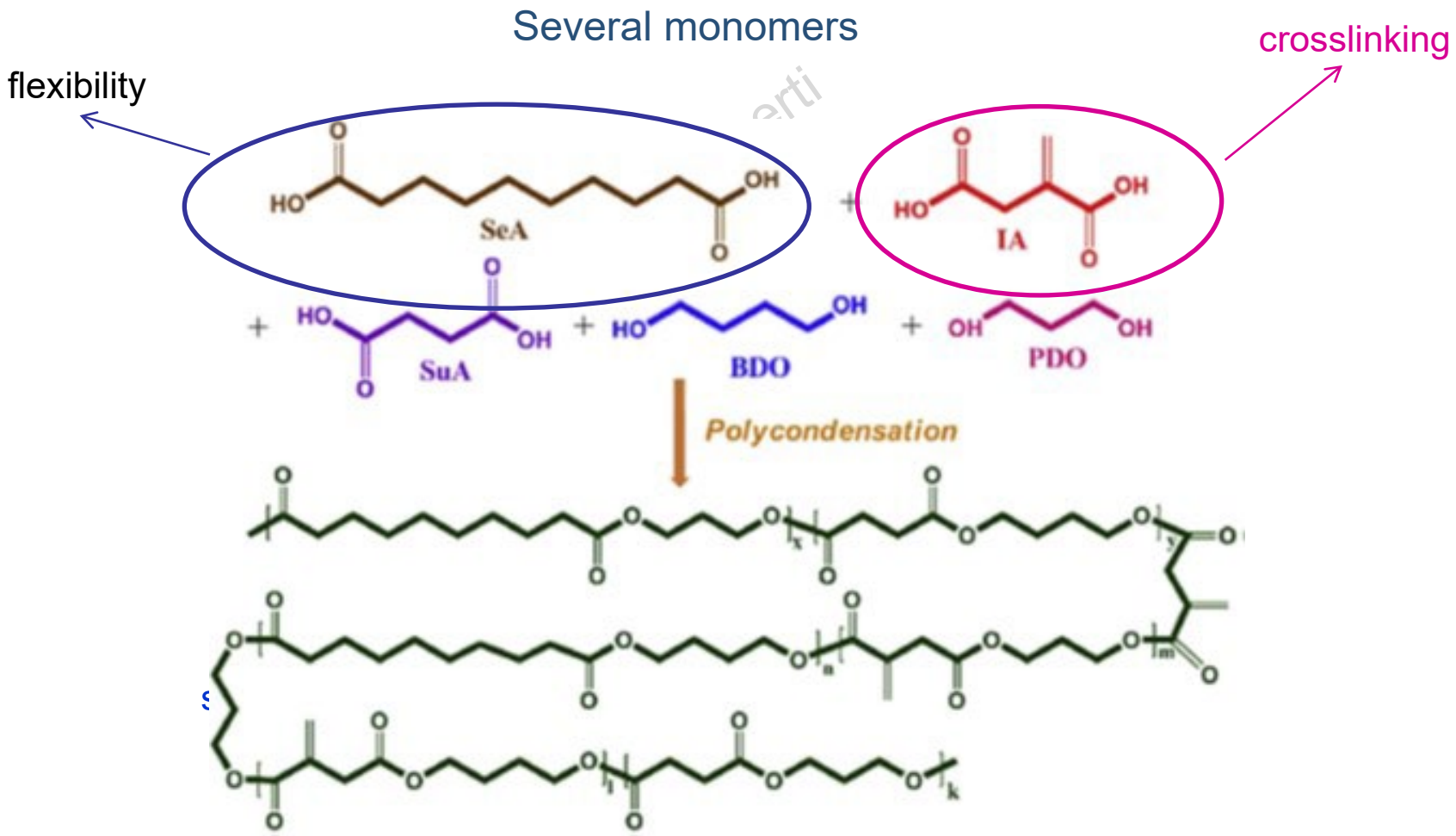


Giulio Natta, La Chimica e l'Industria, XX, 10, 1938, 185-198

Novel bio-elastomers. Polyester elastomers

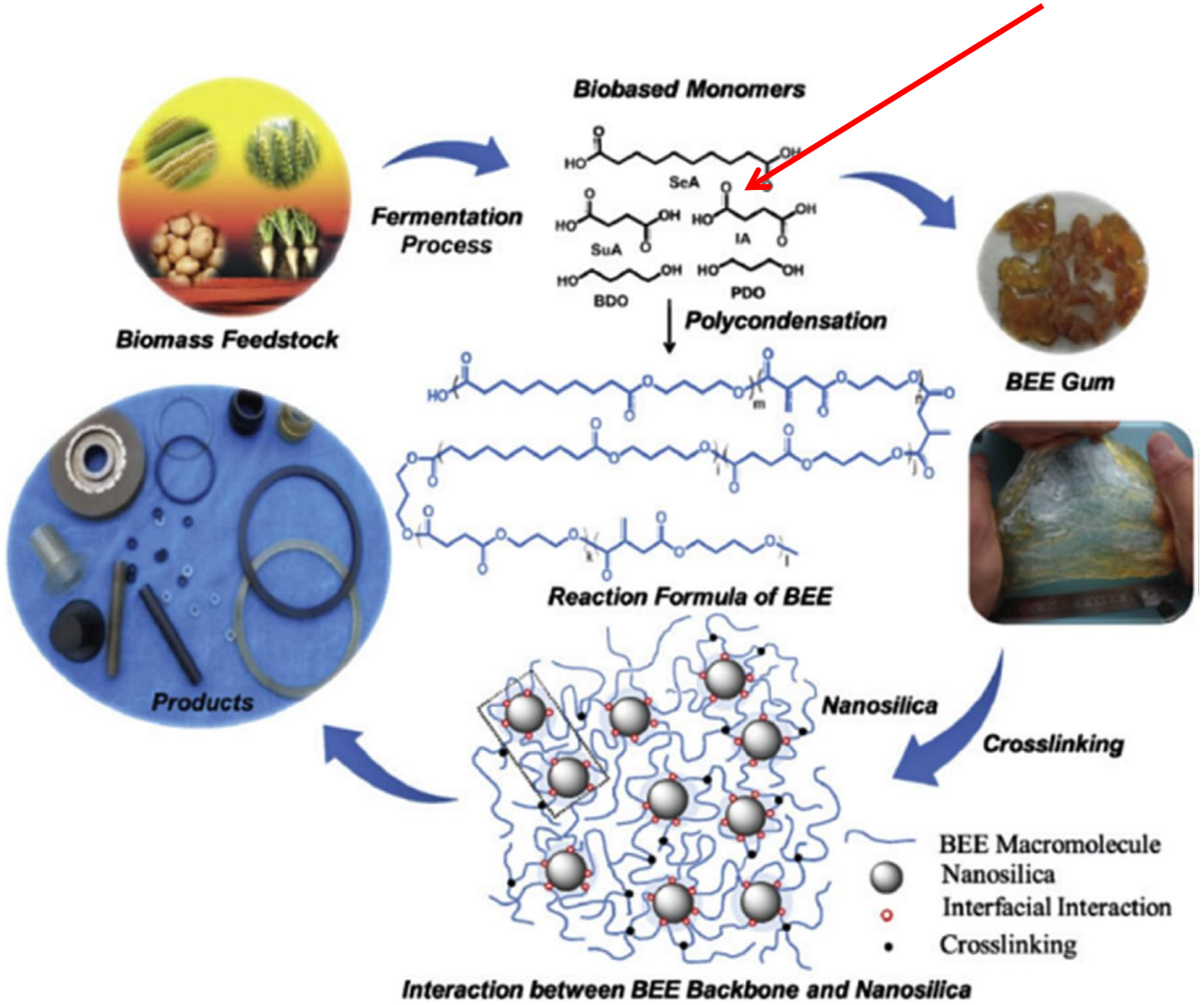


Mn = 35000 g/mol, PDI = 3.2

Tg = - 56°C

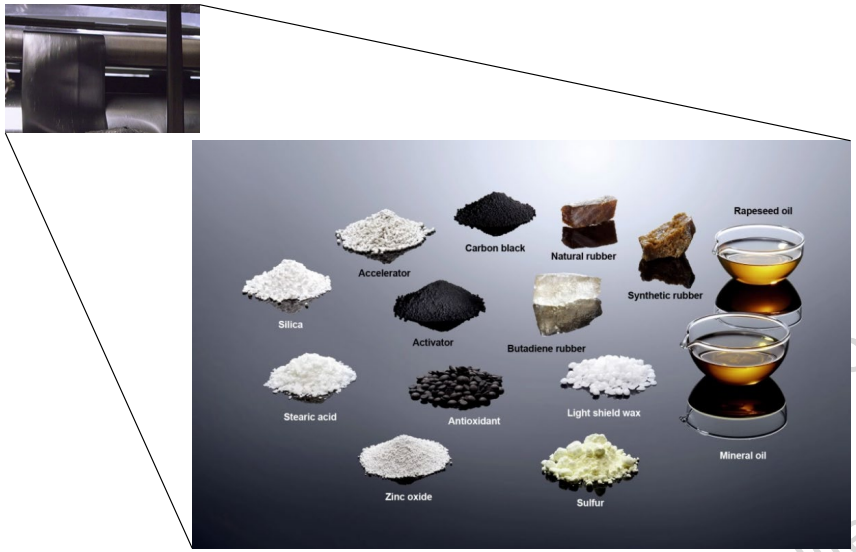
R. Wang et al. / Composites Science and Technology 133 (2016) 136-156

Novel bio-elastomers. Polyester elastomers



R. Wang et al. / Composites Science and Technology 133 (2016) 136-156

Rubber compounds





Ingredients (per hundred rubber)

Rubber	100
Reinforcing filler	30-80
Extension oil	10-30
Coupling agent	2-6
ZnO (zinc salt)	2-5
Stearic acid	1-3
Antiozone	2-8
Sulfur	1-5
Accelerator	1-4

Ingredients (per hundred scialatielli)

scialatielli	100
cozze (mussels)	219
vongole (clams)	219
pomodorini (cherry tomatoes)	63
spicchio d'aglio (garlic clove)	1
olio extravergine di oliva (extra virgin olive oil)	
prezzemolo (parsley)	
sale (salt)	

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https://acoustafoam.wordpress.com/2013/12/11/natural-synthetic-rubber-matting-sheeting-and-flooring/
https://www.pirelli.com/global/en-ww/road/cars/tyres/tyres-uncovered-the-secrets-of-the-compounds-which-help-us-travel-in-comfort-50391/

https://www.cucchiaio.it/ricetta/scialatielli-ai-frutti-di-mare/

Raw Materials. Alternatives from natural sources

Family	Traditional ingredient	Innovative ingredient
Reinforcing filler	Precipitated silica (p-Silica)	Silica from rice husk
	Carbon black (CB)	Recovered carbon black (rCB) Carbon materials from pyrolysis
	p-Silica, CB	Lignin, Sepiolite, Nano-cellulose, Cellulosic derivatives
Extension oil	Treated aromatic oil	Aliphatic oil, Biobased oil
Compatibilizer / Activators	Stearic acid	Vegetable fatty acids
Antioxidant, anti-ozone	Quinoline, p-phenylenedediamine	Bio-based antioxidants and antiozone: lignin, cardanol, (tea) polyphenols, hindered phenols, curcumin, derivatives of aldaric acids

Carbon Black, Recovered Carbon Black and Biochar

Carbon Black (CB)

Partial **combustion** or **thermal decomposition** of **hydrocarbons**.

Engineered material

Primarily elemental carbon.

Aggregates of fused, spheroidal primary particles with aciniform morphology: **structure, surface area, surface activity**

Recovered Carbon Black (rCB)

Thermal decomposition of **post-consumer rubber goods**

Semi-reinforcing filler derived from

Predominantly carbon,

Also contains **inorganic ingredients** from the feedstock.

Biochar

Thermochemical conversion of biomass in an **oxygen-limited environment.**

Biochar originates from biomass.
Solid material

Broad family
Not defined by performance.

Lesson for Uni

(1) ASTM D3053 — Standard Terminology Relating to Carbon Black. ICBA — What is Carbon Black?

(2) ASTM D8178 — Terminology Relating to Recovered Carbon Black. ASTM D8632-26 — Classification for rCB Used in Rubber Products.

(3) International Biochar Initiative (IBI), Biochar Standards. IBI: standardized definition used in its certification framework.

Silica from rice husk

SILICE da LOLLA di RISO

Non-food competitive / biomassa di scarto, sostituto della silice amorfa precipitata HDS

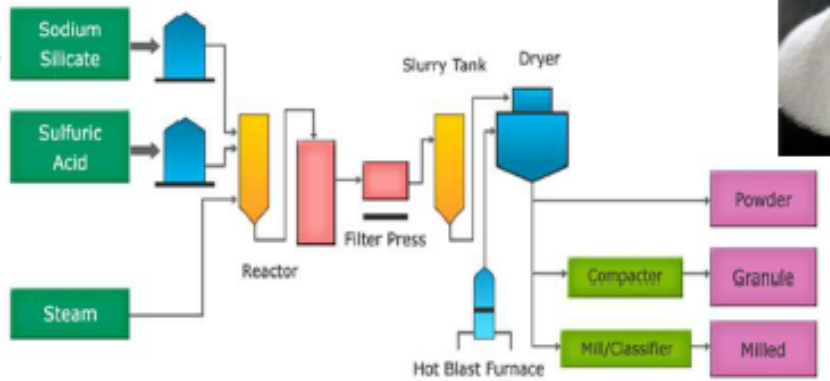


«guscio» del chicco di riso (silice: 20% in peso)

Combustione (generazione di energia)

Fusione alcalina della cenere con $NaOH$ o Na_2CO_3

SOLUZIONE DI SILICATO DI SODIO





Lesson for UniPD, 6 '

EOL thermoset rubber

Maurizio Galimberti
Politecnico di Milano
Rubber
Lesson for UniPD, 6 November 2026

End of life of a tyre

1.4 billion waste tyres every year

Waste tyre piles. They are visible from the space





west of Sulaibiya, Kuwait – 7 million tyre mountain

from space on the ground

Image on the left: © DigitalGlobe via Google Earth

End of life of a tyre. Devulcanization and reclaiming

Devulcanization

cleaving the monosulfidic, disulfidic, and polysulfidic crosslinks

Reclaiming

vulcanized rubber waste

is converted into a state in which it can be mixed, processed, and vulcanized again.

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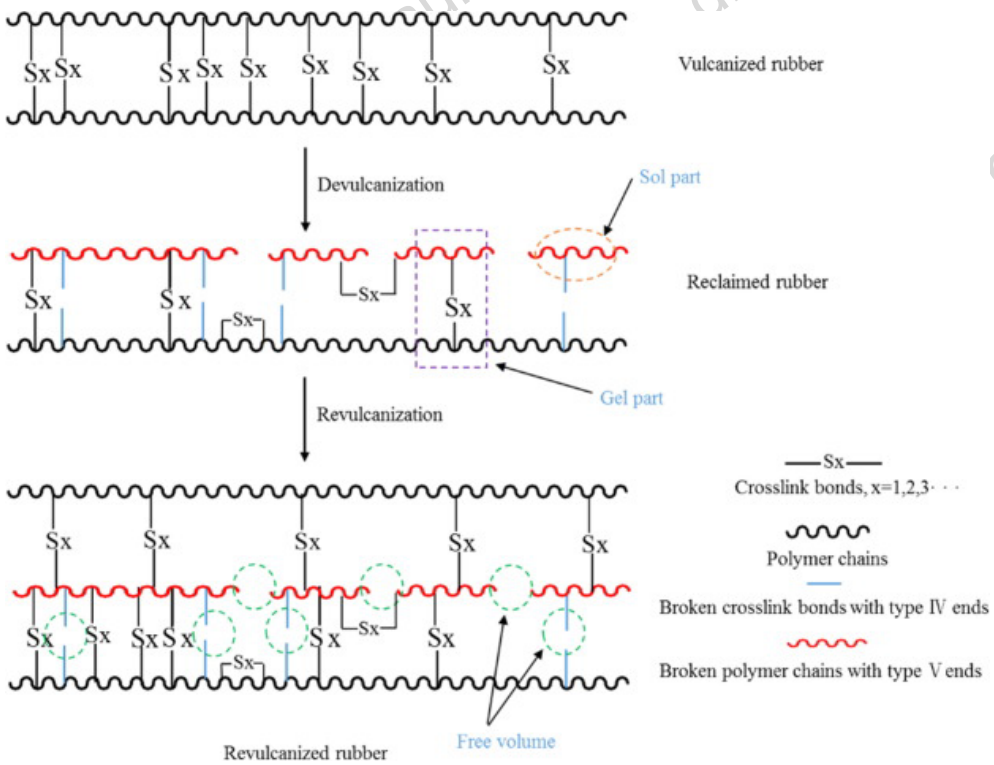
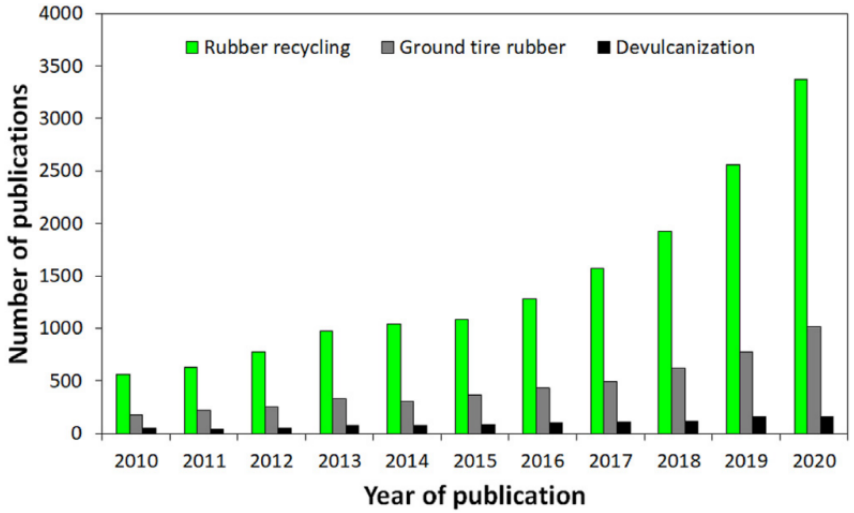
di Milano
ember 2026



Bond Type	Bond Energy, kJ/mol
–C–S_x–C–	<270
–C–S–S–C–	270
–C–S–C–	286
–C–C–	353

Waste Management (2018) 78, 980-991

Rubber recycling. Publications and patents



Advanced Industrial and Engineering Polymer Research 4 (2021) 209e222

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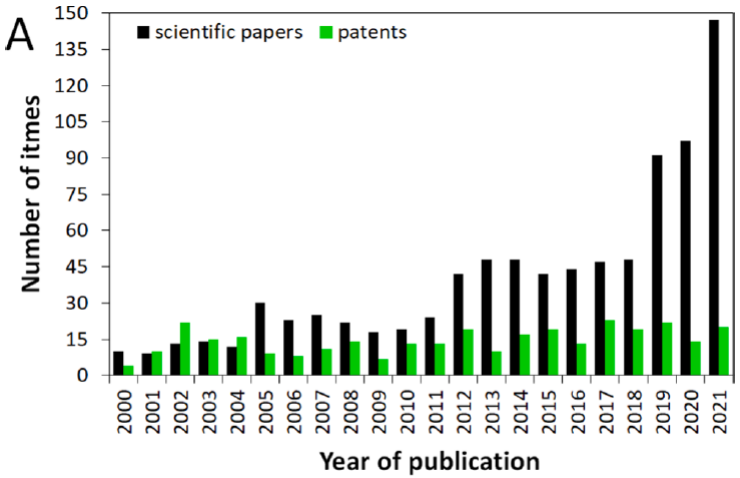
rubber recycling

A



Waste Management 150 (2022) 174–184

Technologies for reclaiming: what determines treatment depth?

Reaction depth is conditional – it is not fixed by the technology name alone.

Technology	Principal mechanism	Main controlling factors
Mechanical / thermal	Shear and heating	Mixing, temperature, particle size
Microwave	Electromagnetic heating	Dielectric/electric coupling, hot spots
Ultrasound	Acoustic energy and shear	Coupling, amplitude, local heating
Supercritical CO_2	Swelling and mass transport	Pressure, reagent solubility, time
Chemical	Bond-specific chemical reactions	Swelling, diffusion, reactivity
Biological	Microorganisms / oxidative action	Accessible surface, contact time

Across all routes: optimize crosslink scission while limiting polymer backbone damage.

Thermo - mechanical reclaiming

Description

A strong rise in temperature occurs.

This process is assumed to be a combination of

breaking of carbon-to-carbon bonds and sulphur crosslinks.

Soluble branched structures and gels are formed.

Chemicals and oils are frequently added (1% mass):

disulphides, thiols, amines and unsaturated compounds.

Advantages and disadvantages

Strongly depend on the type of the process.

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Thermo - mechanical reclaiming

- a completely thermo-mechanical process, based on the co-rotating twin-screw extruder
- starts from vulcanized rubber (e.g. scraps or post consume, traditionally considered as waste), based on NR, IR, EPDM, NBR, SBR.
- recycled material with properties similar to crude rubber.

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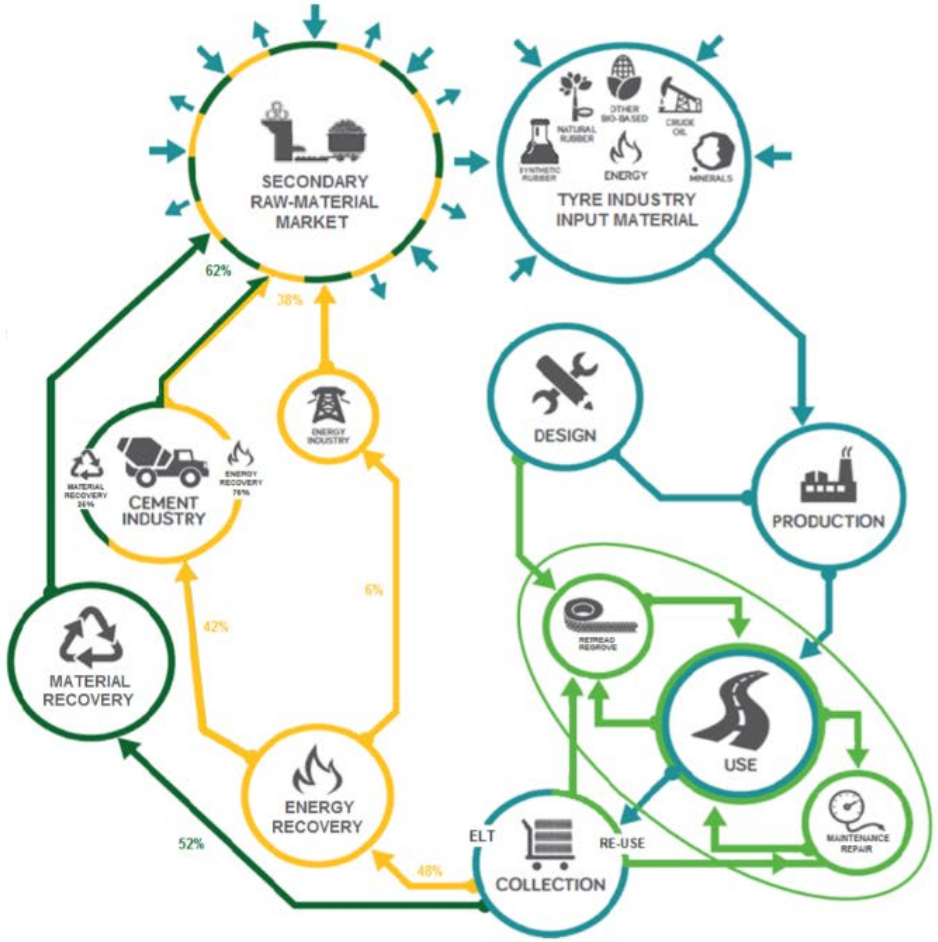
Tyres. Recycling

Secondary raw materials from end-of-life tyres (ELTs) are valuable resources for industries such as construction, automotive, and cement.



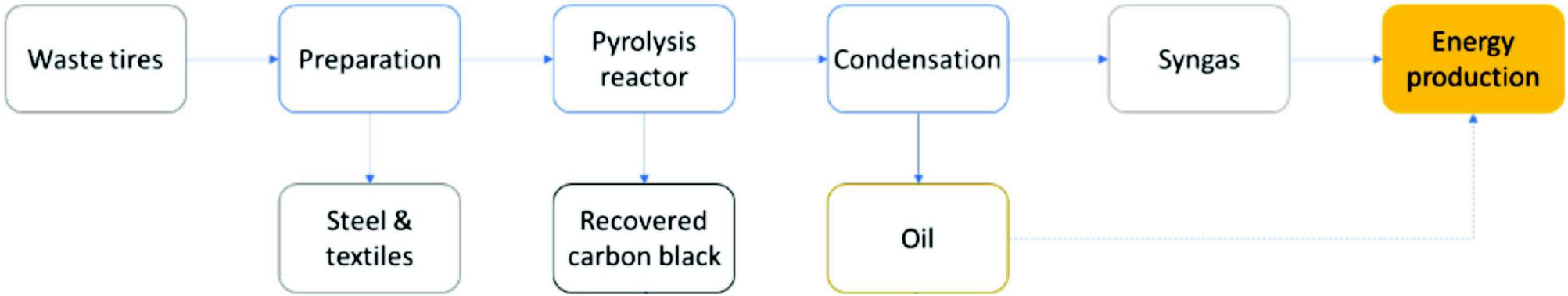
https://www.etrma.org/key-topics/circular-economy/

End of life of a tyre. Recovered carbon black (rCB)

Emerging recovery routes: Pyrolysis/Thermolysis

Technologies: Pyrolysis, thermolysis, and gasification.

Process: Thermal decomposition of tyres into gas, oil, and char.



rCB quality

depends on the feedstock composition

and pyrolysis conditions: type of reactor, temperature range, heating rate, and residence time.

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