

A Biosourced Janus molecule

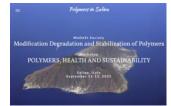
for sustainable elastomeric nanocomposites

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MoDeSt Society Workshop Polymers Health and Sustainability Salina, September 11-13



M. Galimberti – A biosourced Janus molecule

Workshop Polymers, Health and Sustainability

Salina, September 11-13, 2022

1

- Elastomers and Rubbers
- Rubbers and sustainability
- Focus on the main application of rubbers
- An example from ISCaMaP @Polimi

Elastomers and Rubbers

Elastomer

"A natural or synthetic polymer which at room temperature can be stretched repeatedly to at least twice its original length and which after removal of the tensile load will immediately and forcibly return to approximately its original length" Compilation of ASTM Standards Definitions, sponsored by ASTM committee E8, ASTM, Philadelphia PA, 1976

Rubber

"Family of polymeric materials which are flexible and elastic. Rubber can be substantially deformed under stress, but recovers quickly to near its original shape when the stress is removed"

ISO 1382 (1982) "Rubber - Vocabulary"

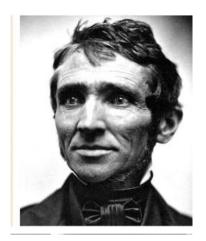




ελ

"There is probably no other inert substance the properties of which excite in the human mind an equal amount of curiosity, surprise and admiration.

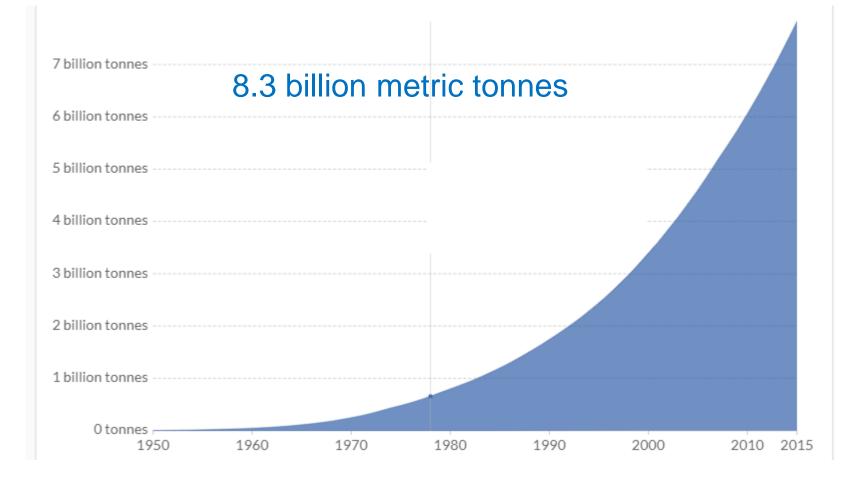
Who can examine and reflect upon this property of gum-elastic without adoring the wisdom of the Creator?"



Charles Goodyear

Goodyear, C. "Gum elastic and its variation with a detailed account of its applications and uses" 1855, 1, New Haven

Cumulative global plastic production 1950 - 2015



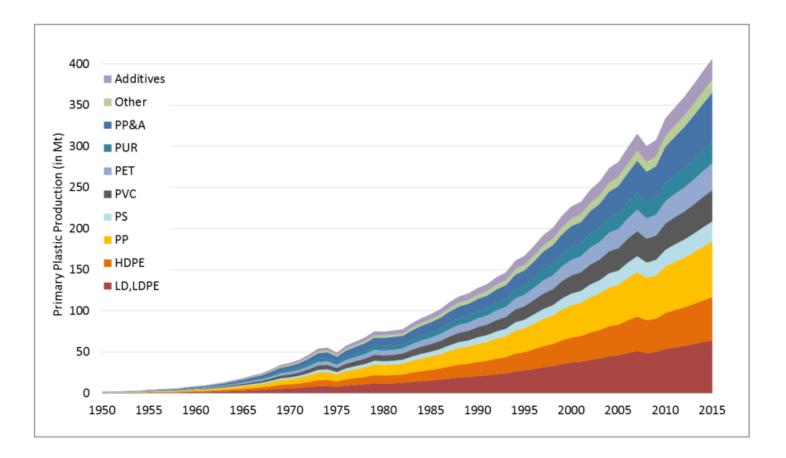
https://ourworldindata.org/plastic-pollution

Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Science Advances, 3(7), e1700782. Available at: http://advances.sciencemag.org/content/3/7/e1700782.

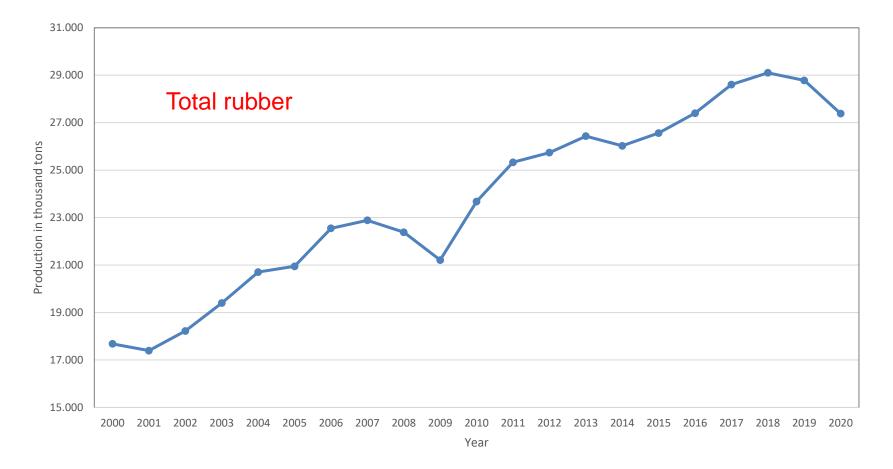
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By polymer type

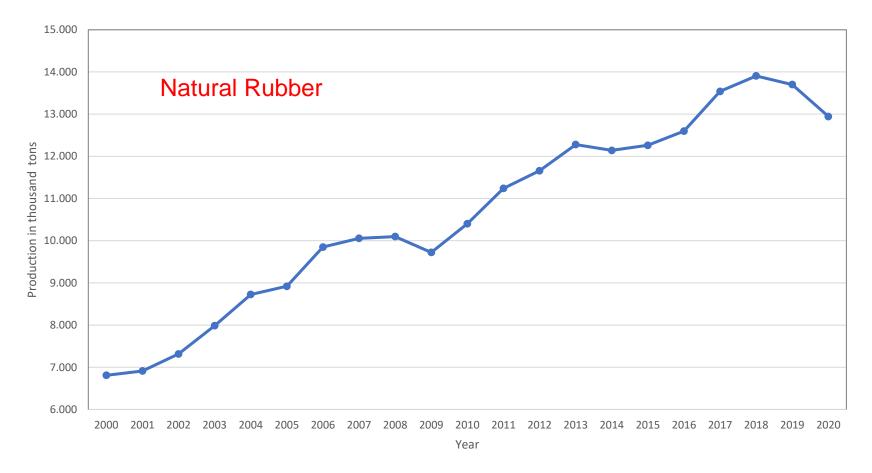


Production of rubber worldwide from 2000 to 2020 (in 1,000 metric tons)



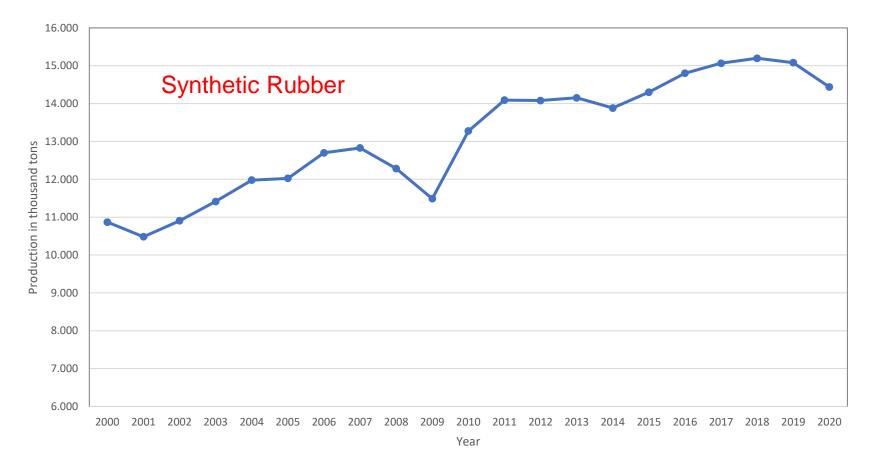
max: $29 \cdot 10^6$ metric tons

Natural rubber production worldwide from 2000 to 2020 (in 1,000 metric tons)



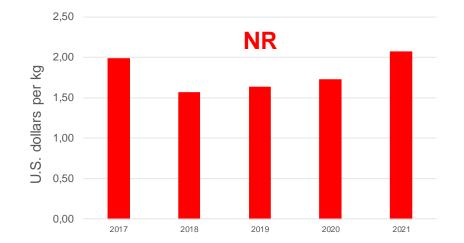
max: $14 \cdot 10^6$ metric tons

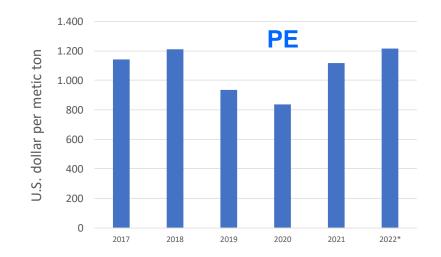
Synthetic rubber production worldwide from 2000 to 2020 (in 1,000 metric tons)

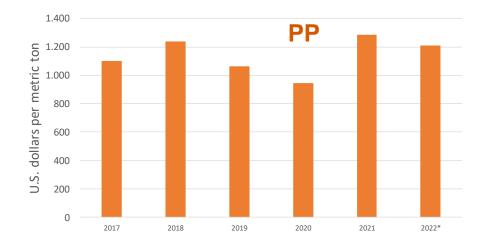


max: $15 \cdot 10^6$ metric tons

Price from 2017 to 2021



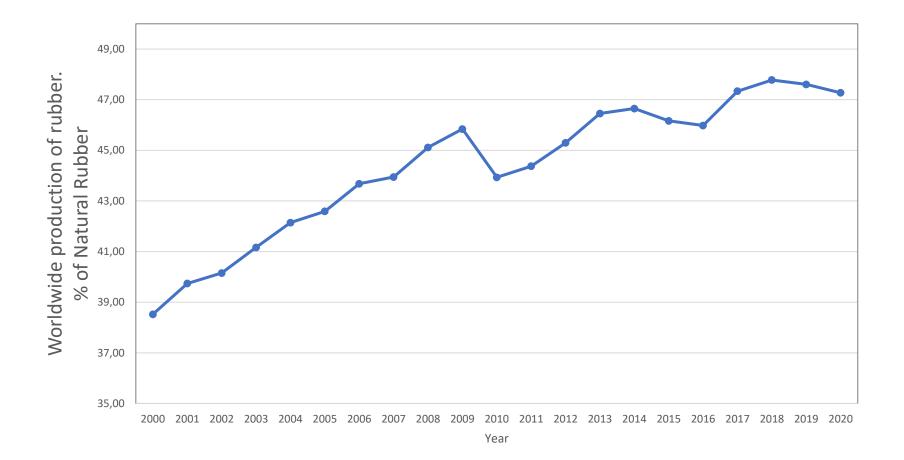




Source: Bloomberg; Krungsri Research

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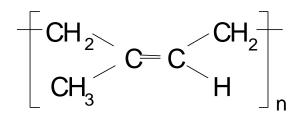
Relative amount of Natural Rubber



Source: Statista

Natural Rubber. Poly(1,4-cis-isoprene)





Almost 100% cis - 1,4- poly-isoprene



hevea brasiliensis



partenium argentatum



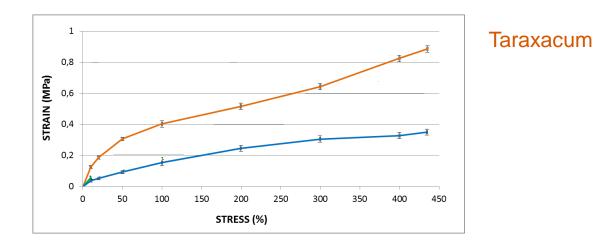
taraxacum kok-saghyz

Why Natural Rubber is such a great material?

Low Tg: - 64°C Chain mobility Good behavior at low T

Steric purity: 1,4-cis Molecular order: enough to crystallize under stretching

Strain Induced Crystallization (SIC)



High tensile strength High Elasticity High resilience Low hysteresis Low heat build up The best building tack High dynamic fatigue resistance High tear and abrasion resistance





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.

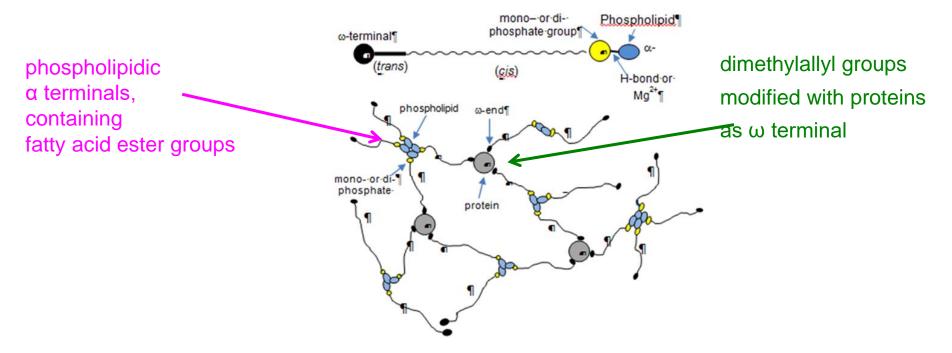
Eng, A.H., Ong, E. L. in: Hevea Natural Rubber Handbook of elastomers Eds., CRC Press, 2000, 29-60.

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.

NR. The Strain Induced Crystallization (SIC). The new interpretation



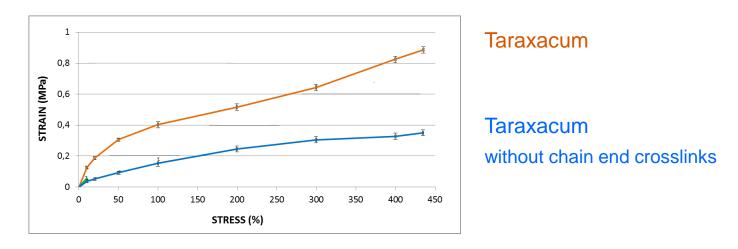
branch-points are formed, by hydrogen bond, ionic bond or through the formation of micelles.

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

Kakubo, T., Matsuura, A., Kawahara, S., & Tanaka, Y. RCT, 1998, 71, 70-75.

Tanaka, Y., & Tarachiwin . RCT, 2009, 82, 283-314

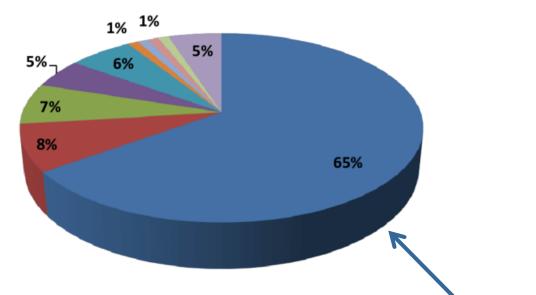
Strain Induced Crystallization (SIC)



Musto, S., Barbera, V., Maggio, M., Mauro, M., Guerra, G., & Galimberti, M. (2016). Crystallinity and crystalline phase orientation of poly (1, 4-cis-isoprene) from Hevea brasiliensis and Taraxacum kok-saghyz. *Polymers for Advanced Technologies*, *27*(8), 1082-1090.

NR. World Applications

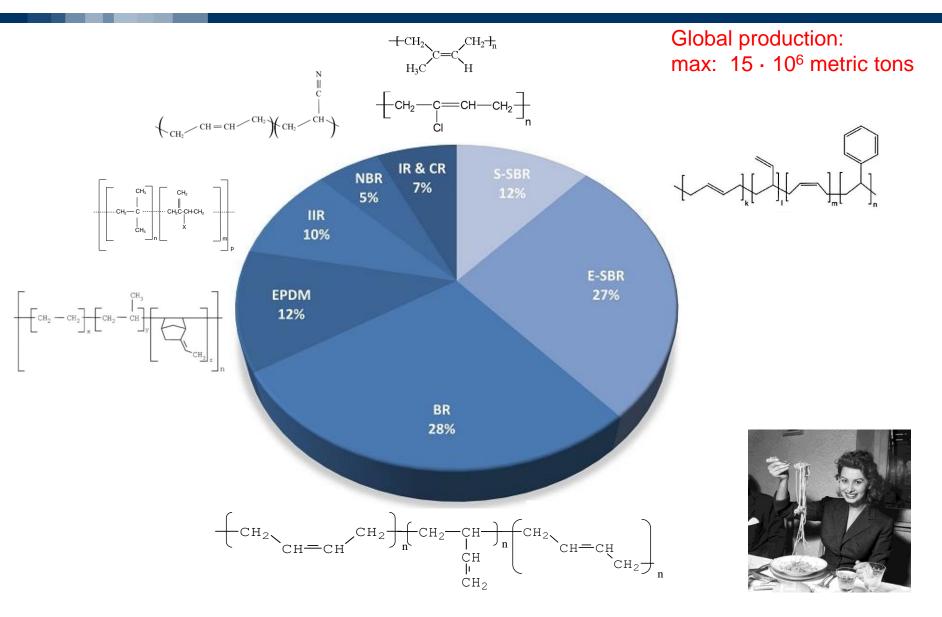
- Tyres
- Hoses & Belts
- Automotive
- Footwear
- Medical Gloves
- Threads
- 🔳 Foam
- Adhesives
- Other Latex
- Other GRG





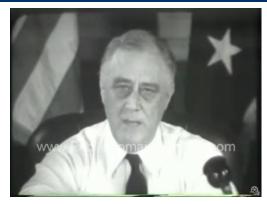
Blengini et al. Assessment of the Methodology for Establishing the EU List of Critical Raw Materials. 2017

Global demand for synthetic elastomers. 2020



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

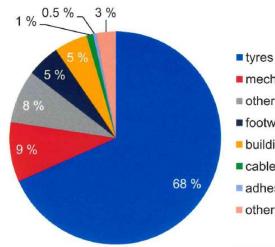
Unsaturated rubbers. BR, SBR. Main applications



https://www.youtube.com/watch?v=c-JKYRSzu0s



E-SBR



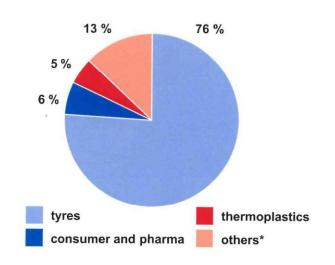
mechanical goods other automotive goods footwear building cable and wire

adhesives

others



S-SBR + BR + IIR



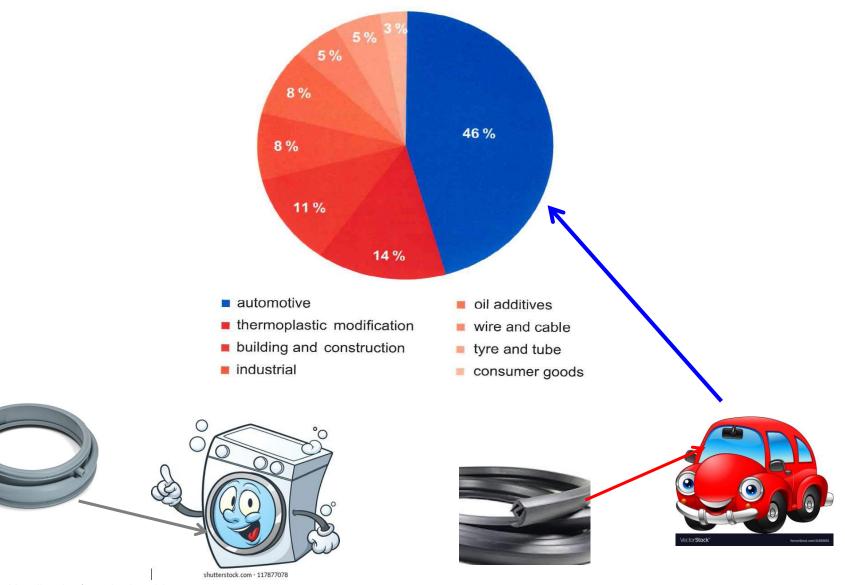
Arlanxeo. Handbook of synthetic rubber

Arlanxeo. Handbook of synthetic rubber

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Saturated rubber. EPDM. Main applications

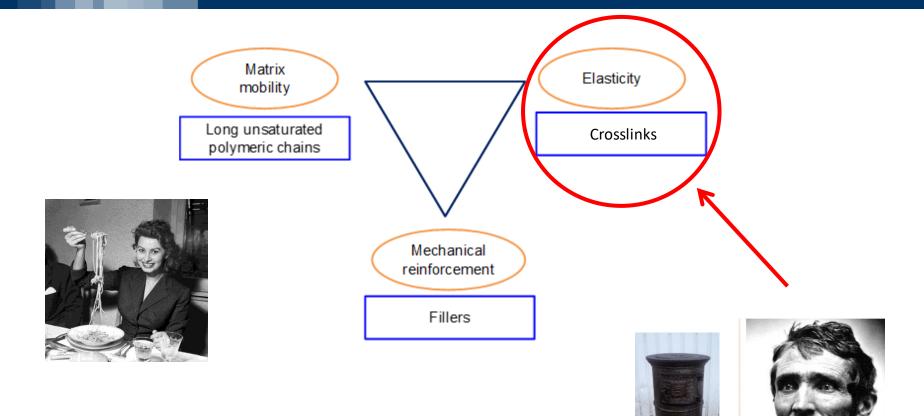


Arlanxeo. Handbook of synthetic rubber

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Rubbers need to be crosslinked



Rubbers need to be crosslinked

Ipomoea alba





Castilla elastica tree



Rubber processed in ancient Mesoamerica, MIT researchers find - MIT News Office

Rubbers need to be crosslinked

Ipomoea alba





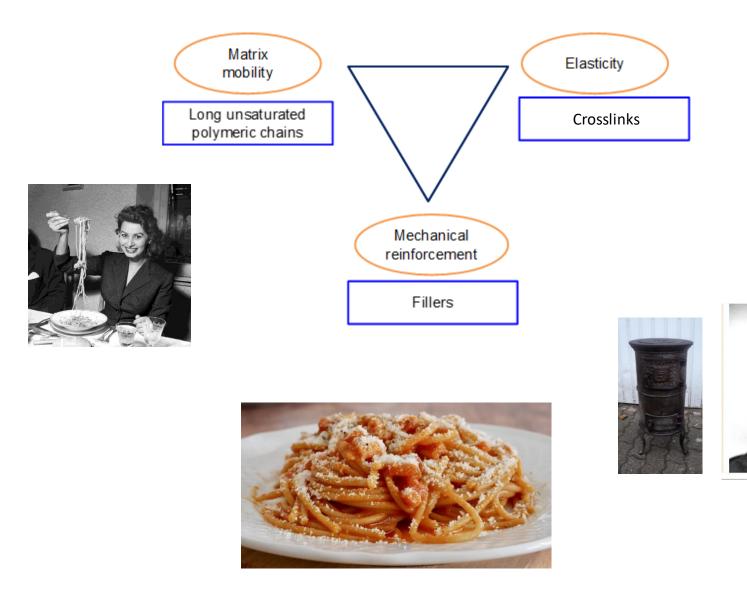
Castilla elastica tree



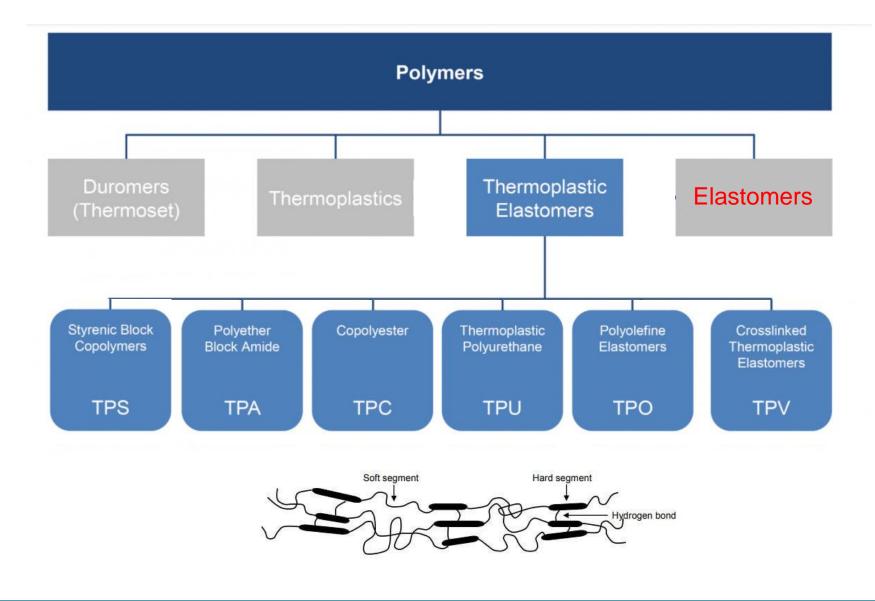
Crosslinked rubbers are thermoset materials

Rubber processed in ancient Mesoamerica, MIT researchers find - MIT News Office

Rubbers in the real world are rubber compounds



Thermoplastic Elastomers ! - TPE



ISO 18064

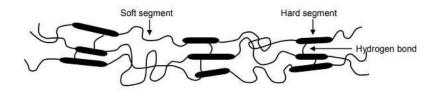
Polymer or blend of polymers

that has properties at its service temperature

similar to those of vulcanized rubber

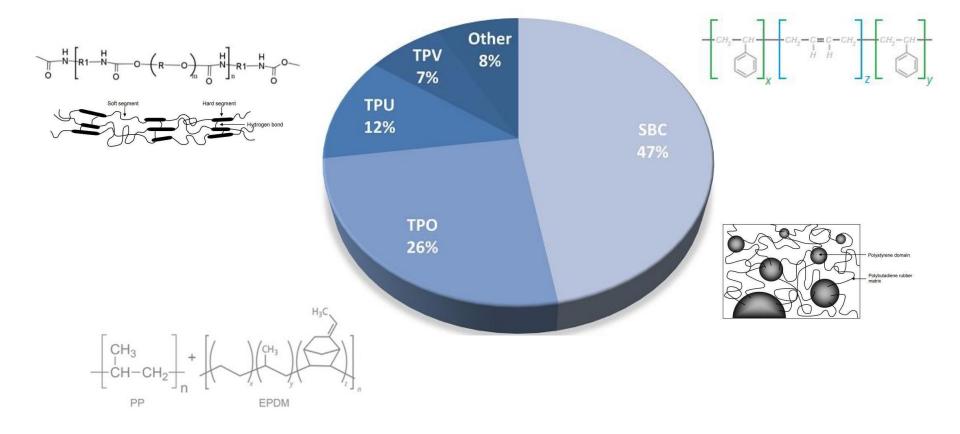
but can be processed and reprocessed at elevated temperature

like a thermoplastic



Thermoplastic rubber is a commonly used term for thermoplastic elastomer.

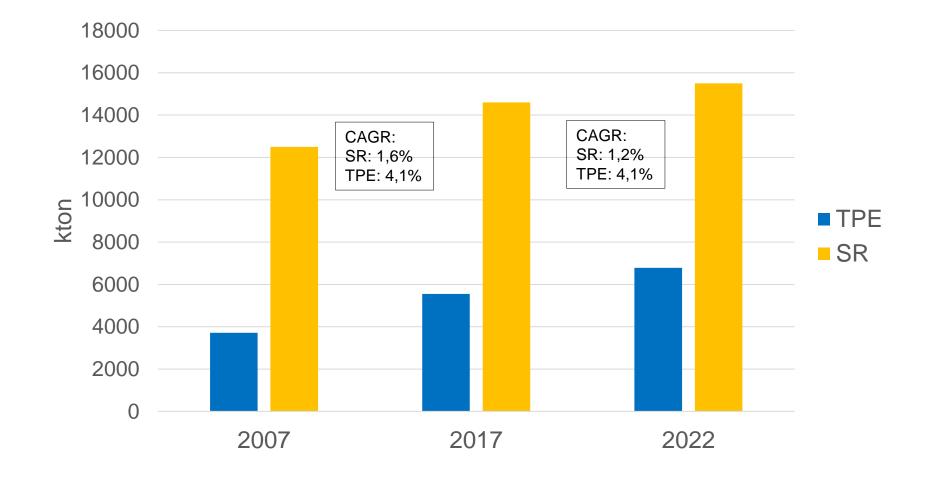
TPE. The market



Source: Ceresana

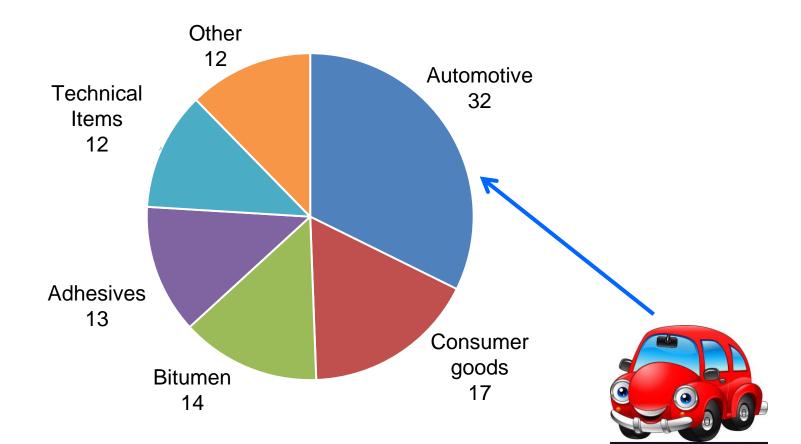
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TPE vs Synthetic rubbers



Source: Freedonia, Versalis

2022. 6.7 Mton



Rubbers are key materials to move people and things







Rubber and Sustainability

by 2030

- 2.4 billion cars will be on the road
- annual passenger traffic and global freight volumes
 will grow by 50% and 70% with respect to 2015

Global Mobility Report 2017, Tracking Sector Performance. Sustainable mobility for all. 2017

by 2025

the global market for tires is forecasted to reach
 2.7 billion units.
 Total weight: 27 billion kg.

https://www.reportlinker.com/p05379599/?utm_source=GNW. Access: July 2022

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in 2016

global greenhouse emissions GHG

were 49.4 billion tonnes CO₂ equivalent

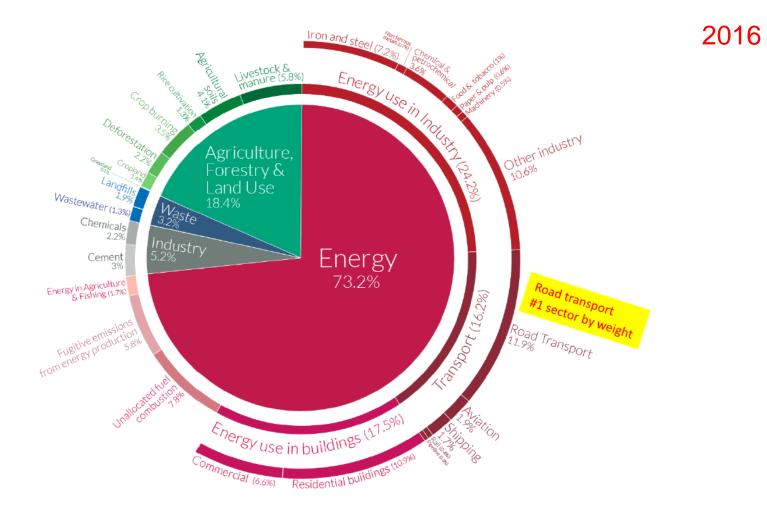
Energy is the sector that most contributes

to global greenhouse emissions: more than 70%

What about the road transport in environmental perspective?

Global Mobility Report 2017, Tracking Sector Performance. Sustainable mobility for all. 2017

Global grrenhouse gas emissions by sector



OurWorldinData.org – Research and data to make progress against the world's largest problems. Source: Climate Watch, the World Resources Institute (2020). Licensed under CC-BY by the author Hannah Ritchie (2020).

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in 2016

global greenhouse emissions GHG

were 49.4 billion tonnes CO₂ equivalent

Energy is the sector that most contributes

to global greenhouse emissions: more than 70%

The road transport gives the highest contribution: about 12%.

Global Mobility Report 2017, Tracking Sector Performance. Sustainable mobility for all. 2017

Our world in data. 2020

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Sustainable Transport

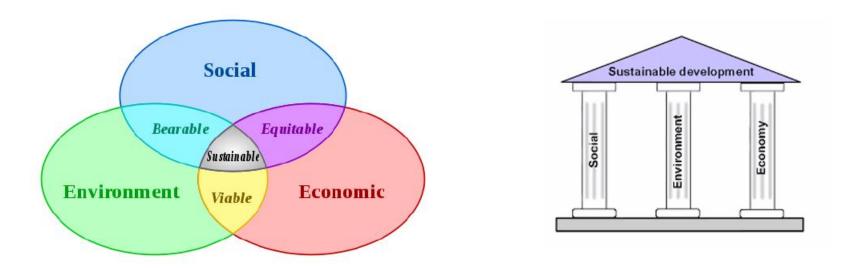


Sustainable transport is integrated in several Sustainable Development Goals in the 2030 Agenda for Sustainable Development

United Nations, sustainable development knowledge platform, sustainable development goals. https://sustainabledevelopment.un.org/sdgs. [Accessed August 2022].

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Meeting the needs of the present without compromising the ability of future generations to meet their own needs



Bruntland Report for the World Commission on Environment and Development (1992) - https://www.globalfootprints.org/sustainability/) Purvis, B., Mao, Y. & Robinson, D. Three pillars of sustainability: in search of conceptual origins. *Sustain Sci* **14**, 681–695 (2019).

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Applied Sustainability

FINITE, FOSSIL FUEL



LINEAR ECONOMY



MAKE

TAKE

DISPOSE



ENERGY FROM FINITE SOURCES



NATURAL SOURCES

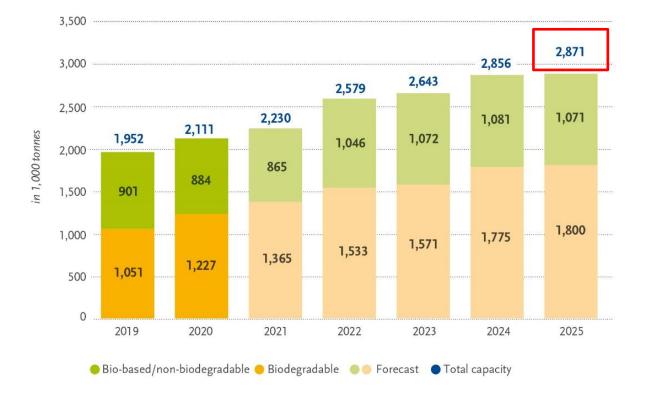
CIRCULAR ECONOMY



ENERGY FROM RENEWABLE SOURCES

CARBON CAPTURE AND UTILIZATION

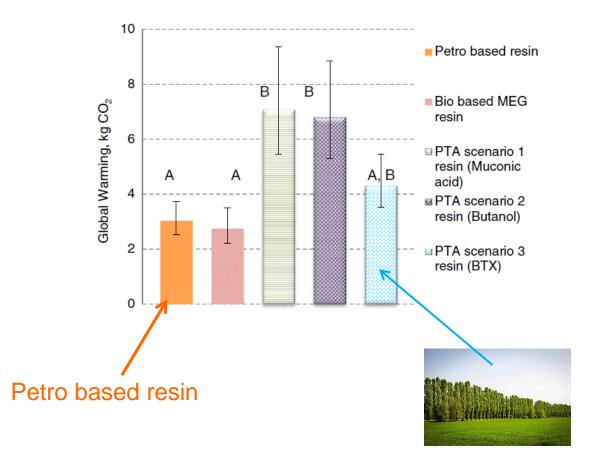
Bioplastics are less than 1% of the plastics' market



Source: European Bioplastics, nova-Institute (2020) More information: www.european-bioplastics.org/market and www.bio-based.eu/markets

Cradle to gate LCA for terephtalic acid. Oil based vs biobased

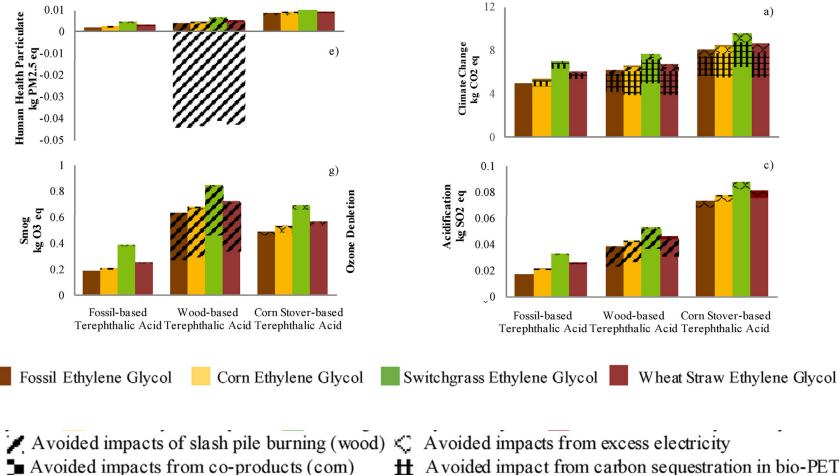
Global warming



Akanuma, Y., Selke, S. E., & Auras, R. (2014). A preliminary LCA case study: comparison of different pathways to produce purified terephthalic acid suitable for synthesis of 100% bio-based PET. *The International Journal of Life Cycle Assessment*, *19*(6), 1238-1246.

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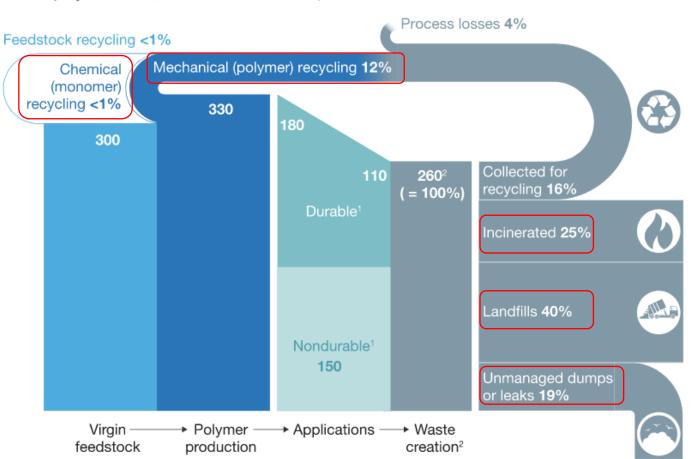




H Avoided impact from carbon sequestration in bio-PET

L. Chen et al. / Journal of Cleaner Production 137 (2016) 667e676

The majority of plastics waste goes to landfill and incineration



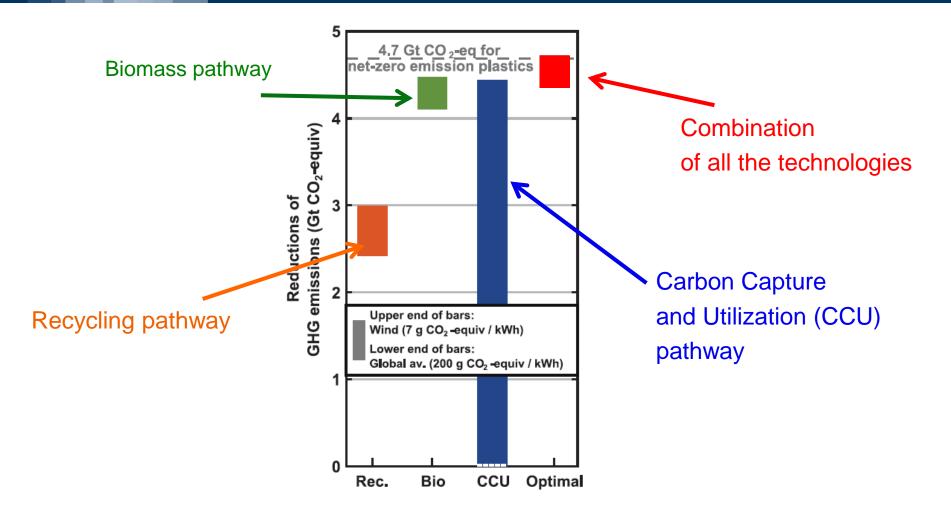
Global polymer flows, millions of metric tons per annum, 2016

¹Durable applications with an average lifetime >1 year will end up as waste only in later years; nondurable applications go straight to waste.

²150 million metric tons of mixed plastic waste from nondurable applications that end up as waste in same year, plus 110 million metric tons of mixed plastic waste from production in previous years.

https://www.mckinsey.com/industries/chemicals/our-insights/no-time-to-waste-what-plastics-recycling-could-offer

Net-zero greenhouse gas emission. For plastics



Reduction of GHG emissions. With respect to linear carbon pathway

Science 374, 71–76 (2021)

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Sustainable rubbers - Natural Rubber



hevea brasiliensis

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/m²·s other trees: 5–13 µmol/m²·s



partenium argentatum



taraxacum kok-saghyz

(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

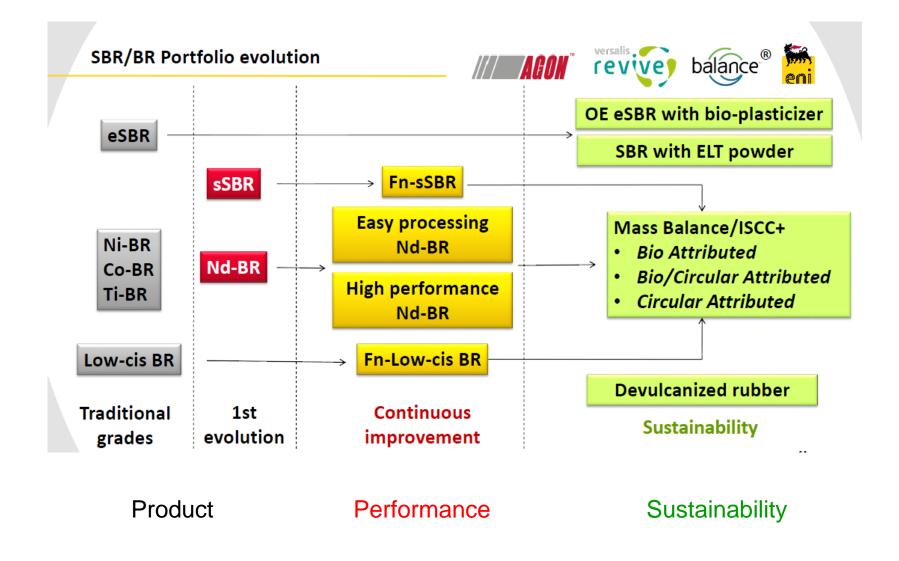
More sustainable synthetic rubbers



ELT = End of Life Tyres

F. Bacchelli. A multi-perspective model for sustainable synthetic rubber. Presentation at DKT IRC 2021

More sustainable rubbers



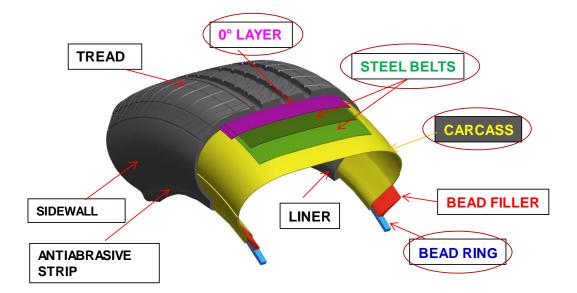
F. Bacchelli. A multi-perspective model for sustainable synthetic rubber. Presentation at DKT IRC 2021

Focus on the main application of rubbers

The main application of rubbers. Tyres. Not just black and round

A complex composite of different **semi-finished materials** made of rubber, textile and metal reinforcements





At least 9 Components in a Tyre

Complexity as an opportunity for sustainability

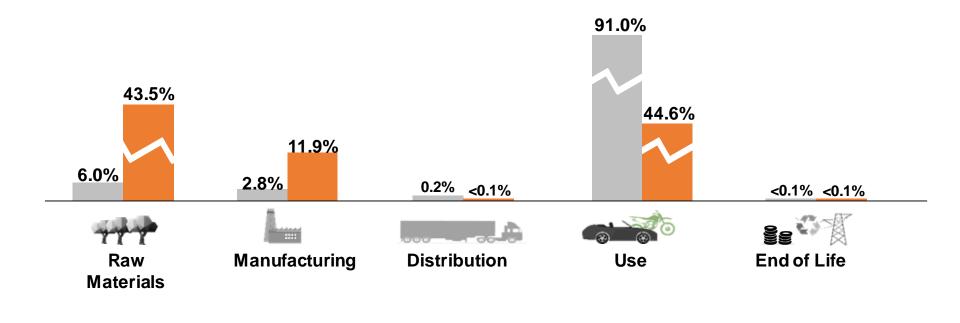
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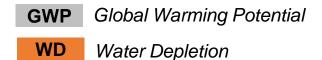
Tyres. Products driven by performance



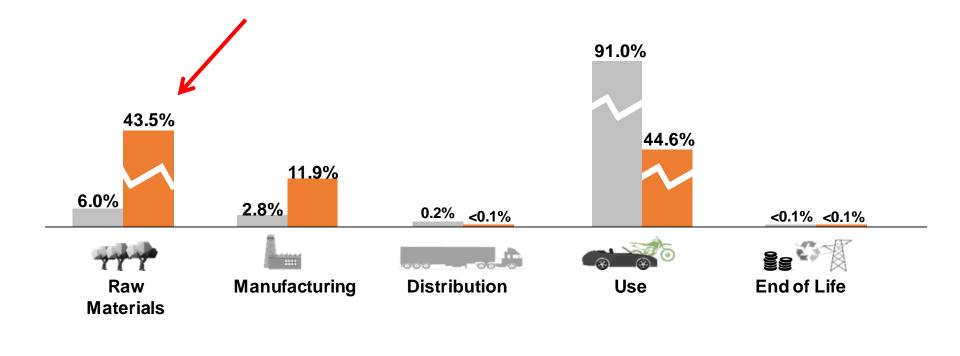
Electric vehicle will impact also: High Load Capacity Tyres, Aerodynamics

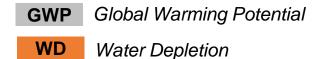
(As of today) sustainability must fit with performance





Tyres and sustainability. Life Cycle Assessment for a tyre

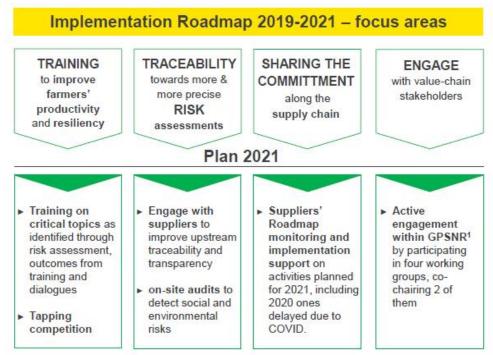




"Towards 100% sustainable raw materials" - Natural Rubber





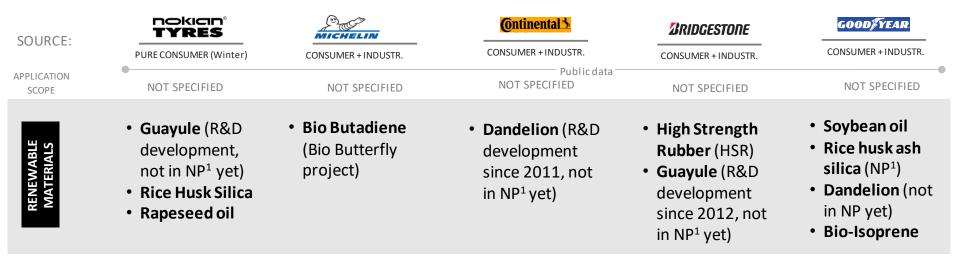


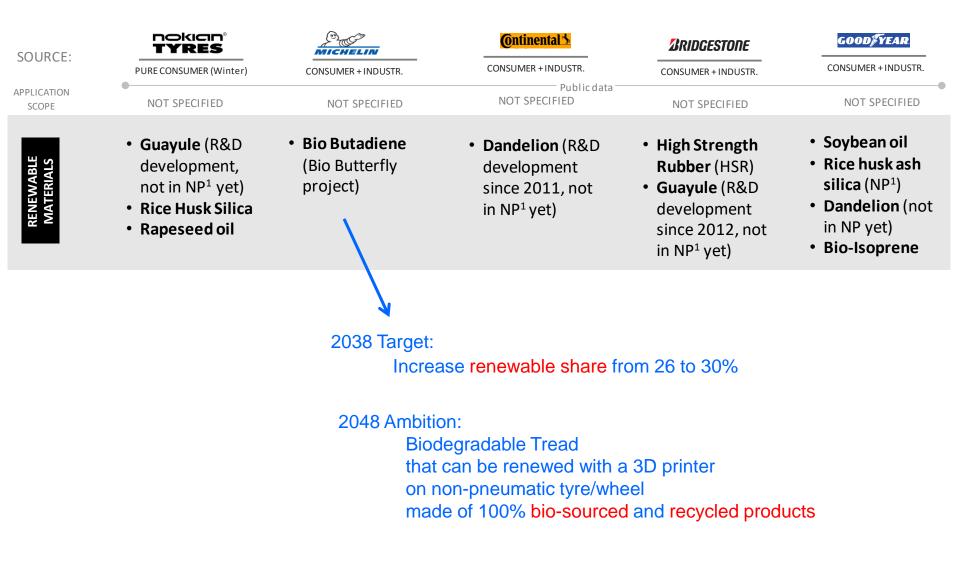
The Pirelli roadmap for NR sustainability

The new forward-looking plan will be released end 2021/early 2022

The Global Platform for Sustainable Natural Rubber

 Initiated by WBCSD's TIP Tyre makers, the Global Platform for sustainable Natural Rubber (GPSNR) was launched in 2018 and is today an independent multi-stakeholder initiative pursuing sustainable development of the natural rubber value-chain



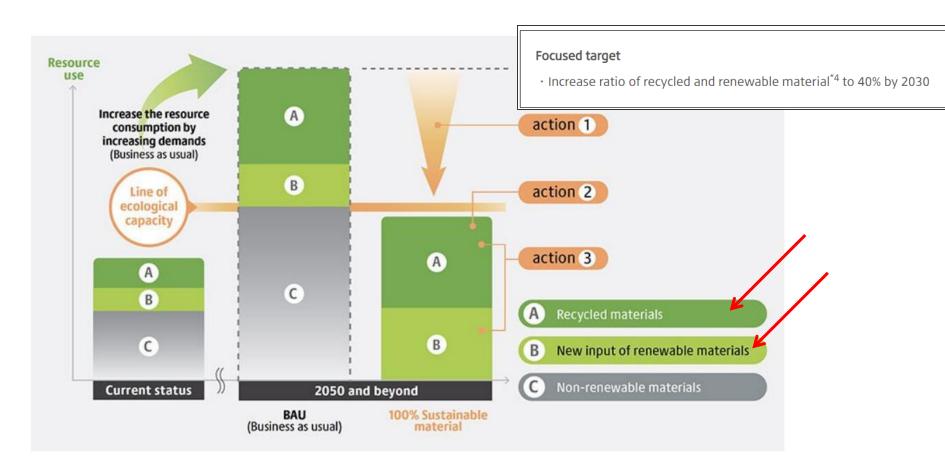


Bridgestone's view

| Today | Sustainable materials | | | |
|---|--|--|--|---|
| Natural Rubber from Para Rubber Tree | Expand the range of renewable resources | Conventional Natural Rubber + Guayule | | Guayule grown in arid regions will diversify the source of natural rubber |
| Synthetic Rubber from Petroleum | Replace fossil resources with renewable materials | Synthetic Rubber from Biomass | | Butadiene from bioethanol |
| Rubber Chemicals from Petroleum | | Rubber Materials from Biomass | | Curing agent and anti-aging chemical from biomass |
| Filler from Petroleum and Coal | | Filler from Biomass | | Reinforcing carbon black from vegetable fats and oils |

Internet site & IRC2020

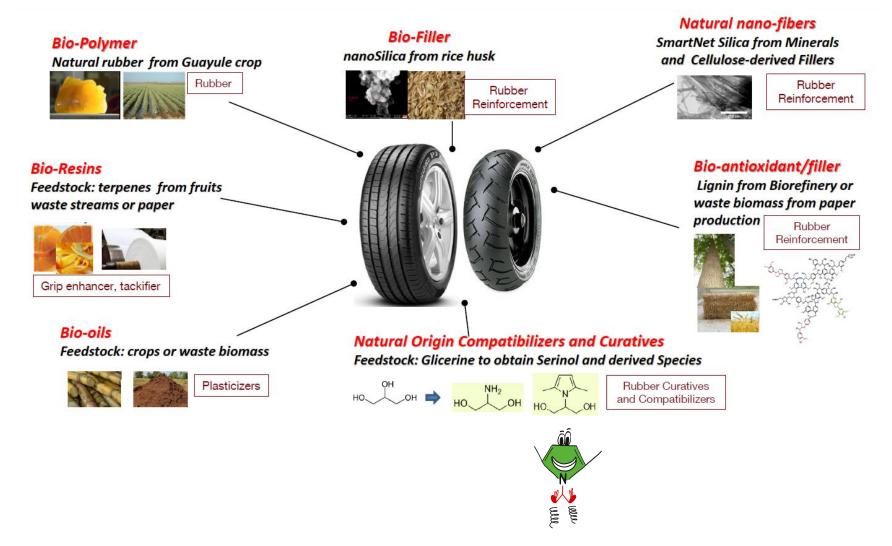
Bridgestone's view



Internet site

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The Pirelli's view



Luca Giannini – Pirelli Tyre - The Challenges of Sustainable Development in Tyre Materials - 2022

The Michelin's view. Concept tyre



Airless: a technology that eliminates the risk of flats and rapid pressure loss and reduces environmental impact

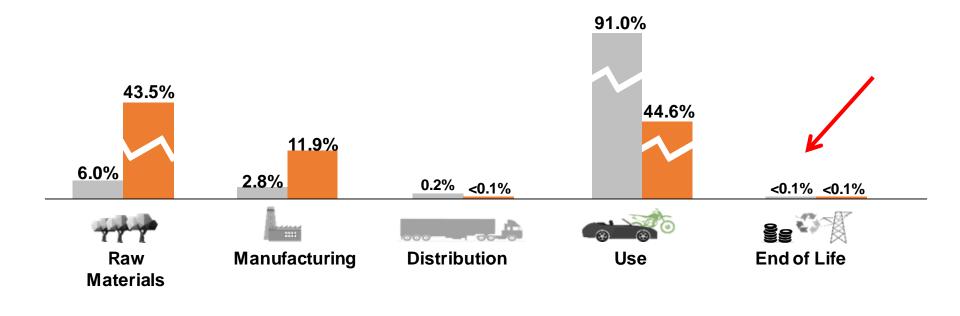
Rechargeable: a tread that can be 3D printed on demand

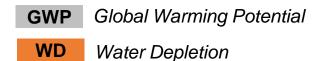
Connected: for a safe and personalized augmented driving experience

100% Sustainable: disruptive innovation in biosourced and recycled materials

https://www.michelin.com/en/innovation/vision-concept/

Life Cycle Assessment for a tyre





What about rubber recycling? What to do with waste tyres?

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

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Fort Lauderdale (FA). Osborne Reef. A tyre artificial reef

In 1972, a reef was created using 2 million of old tires.

Aim: to generate a new habit for marine life.

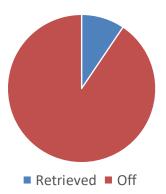




The steel in the tires has deteriorated,

dispersing into the waters destroying sea organisms and preventing the growth of new ones.





Only 73000 tires were retrieved

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Retreading tyres



A retreaded tyre enables saving...

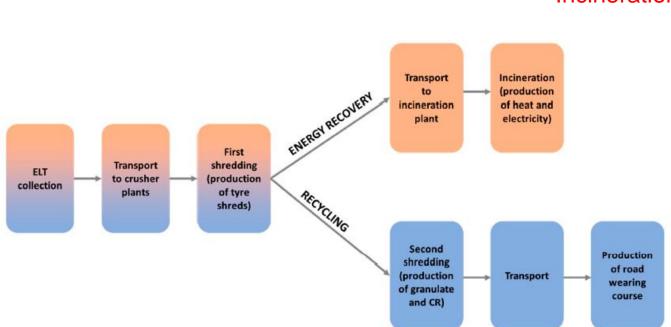


https://www.etrma.org/key-topics/circular-economy/

The R-imperatives

recover, recycle, redesign, reduce, refurbish, refuse, remarket, remanufacture, repair, replace, reprocess, reproduce, repurpose, resale, resell,

What to do with end of life tyres (ELFT)?



Incineration

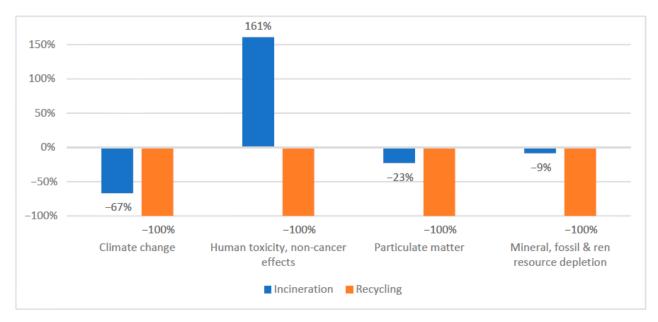
Shredding and new life

Appl. Sci. 2021, 11, 3599

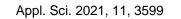
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LCA of end of life tyres

Impact of recycling and incineration



Negative values are OK



"In Europe every year, more than three million tonns end-of-life tyre are collected and treated through various recycling and recovery processes."

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

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Civil Engineering

Concrete

Bitumen and Asphalt

Railway maintanance

Playground and Sporting Surface

Geotechnical Engineering

Soil stabilization

Unbound pavements

Sub-ballast layers

Seismic isolation systems

Whole-tyre enbankements

LCA comprises:

- vulcanization of rubber, tire manufacturing,
- waste tire transportation to the thermolysis plant, and the thermolysis process.

Avoided impacts!

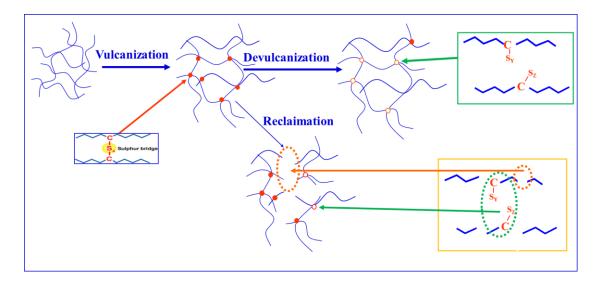
"The overall impacts associated with the production of CB are compensated by the production of other valuable outputs: heavy and light oil, steel, syngas.



Journal of Elastomers & Plastics 2019, Vol. 51(7-8) 740-754

Devulcanization

is the process of cleaving the monosulfidic, disulfidic, and polysulfidic crosslinks (carbon-sulfur or sulfur-sulfur bonds) of vulcanized rubber.

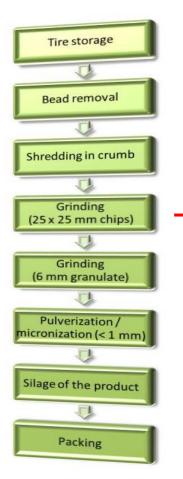


Reclaiming

is a procedure in which scrap (tire) rubber or vulcanized rubber waste is converted - using mechanical and thermal energy and chemicals – into a state in which it can be mixed, processed, and vulcanized again.

DEVULCANIZATION OF WHOLE TIRE RUBBER. V.K. Rajendran*, L. Reuvekamp, J.W.M. Noordermeer, W. Dierkes, A. Blume

Grinding



Technologies for devulcanization / reclaiming

| Technology | Basis of Processing | Zone of Reaction |
|-----------------------|--|----------------------|
| Thermo- mechanical | Mechanical (squeezing) Steam (thermal) TSE | Surface of particles |
| Physical | Ultrasonic waves | Throughout particles |
| Physical | Microwaves | Throughout particles |
| Physical | Supercritical CO ₂ | Throughout particles |
| Chemical | Chemicals/chemical reactions | Surface of particles |
| Biological | Microorganisms | Surface of particles |

Results?

Ebonite from scrap NR - BUCT Beijing









TPE vs Thermoset rubbers



shoes



Bitumen





adhesives



Door seal



SBC, TPU, TPO, TPV



https://www.pin-365.com/

IUCN. Primary Microplastics in the Oceans: A Global Evaluation of Sources. 2017

Primary microplastics into the environment. Tyre debris



of synthetic textiles & tyres



https://www.pin-365.com/

IUCN. Primary Microplastics in the Oceans: A Global Evaluation of Sources. 2017

Primary microplastics into the environment. Tyre debris



are from the erosion of synthetic textiles & tyres

Total release to the environment of microplastics

- Optimistic 1.8 Mtons/year
- Central 3.2 Mtons/year
- Pessimistic 5.0 Mtons/year



https://www.pin-365.com/

IUCN. Primary Microplastics in the Oceans: A Global Evaluation of Sources. 2017

6PPD: a powerful protective agent for tyre

6PPD



Recently, concerns raised for a product of the reaction of 6PPD with ozone: **6PPD quinone**. This product has been reported to be **very toxic and highly lethal** to Coho salmon .

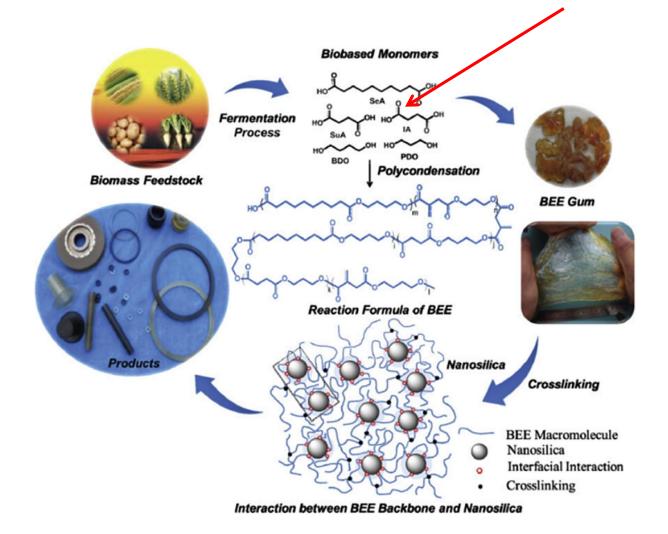


6PPD

6PPD-quinone

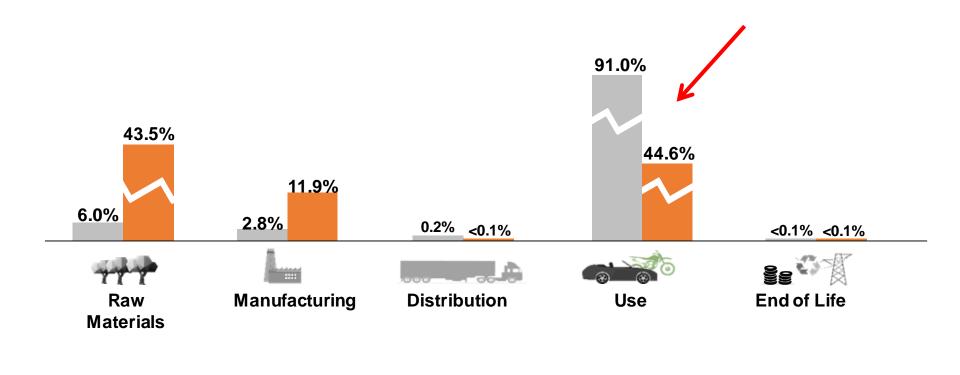
Z Tian et al, Science, 2020, DOI: 10.1126/science.abd6951 C J Walsh et al, J. N. Am. Benthol. Soc., 2005, 24, 706. DOI: 10.1899/04-028.1 A. Agua, R. Stanton, & M. Pirrung, 2021. DOI: 10.26434/chemrxiv.13698985.v1

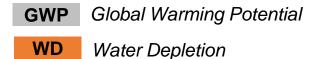
Towards biodegradable rubbers



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

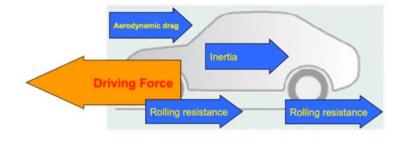
Tyres and sustainability. Life Cycle Assessment for a tyre





Luca Giannini – Pirelli Tyre - The Challenges of Sustainable Development in Tyre Materials - 2022

Impact of a tyre on the environment during its use



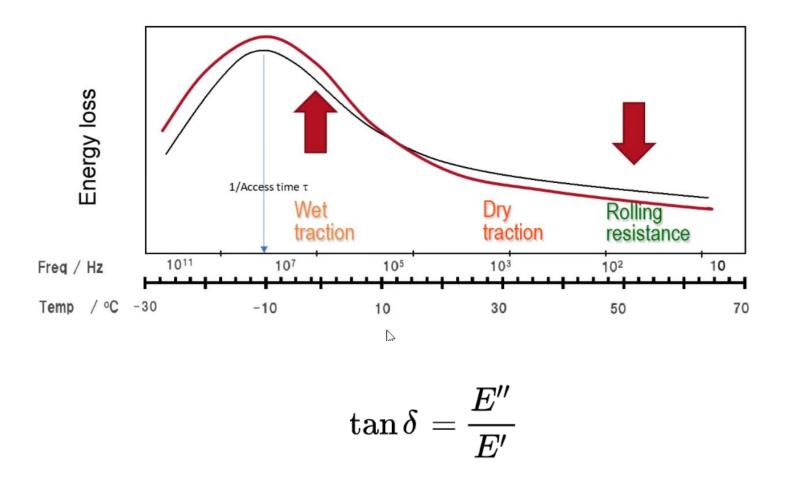
Fuel consumption = Power train \cdot (Weight \cdot **Tyre rolling resistance** + Air Drag) + Heat management

Tyre rolling resistance = *Tyre rubber volume*
$$\cdot$$
 Strain energy \cdot *tank*

With 20% reduction for each of the terms one can get 50% reduction of RR

$$an \delta = rac{E''}{E'}$$

Impact of a tyre on the environment during its use. The role of Tan delta



Electrical vehicles



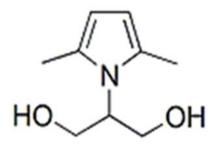
https://www.compositesworld.com/articles/what-is-the-role-of-composites-in-electric-vehicles

- A particularly low rolling resistance: one battery charge
- As quiet as possible
- To suit the higher masses of electric vehicles.
- To handle very high levels of torque without generating excessive wear.

Source: Nokian Tyres

An example from ISCaMaP @Polimi

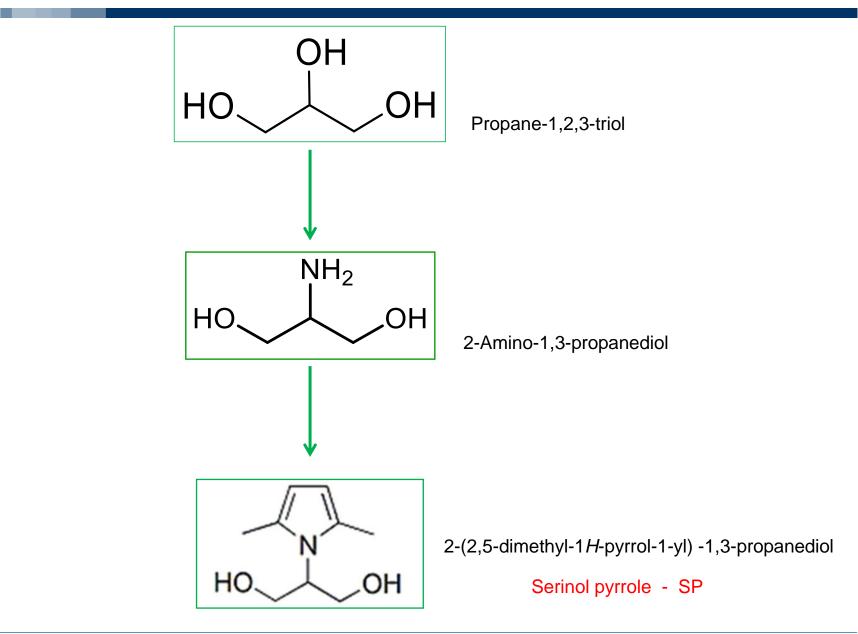
Innovative Sustainable Chemistry and Materials and Proteins



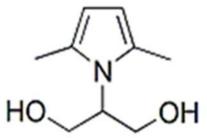
From glycerol

to universal coupling agent for carbon black and silica

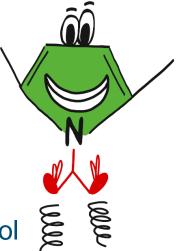
Glycerol as the C3 building block. From glycerol to serinol to serinol pyrrole



From glycerol to universal coupling agent for carbon black and silica





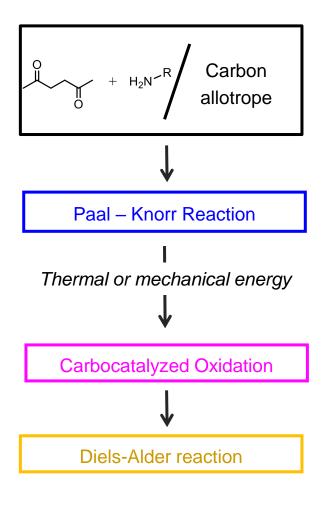


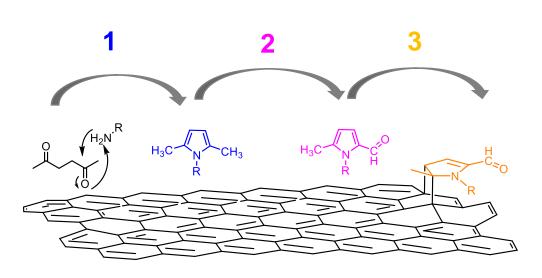
Serinol pyrrole - SP



Mechanism for the formation of CA/PyC adducts

Domino reaction





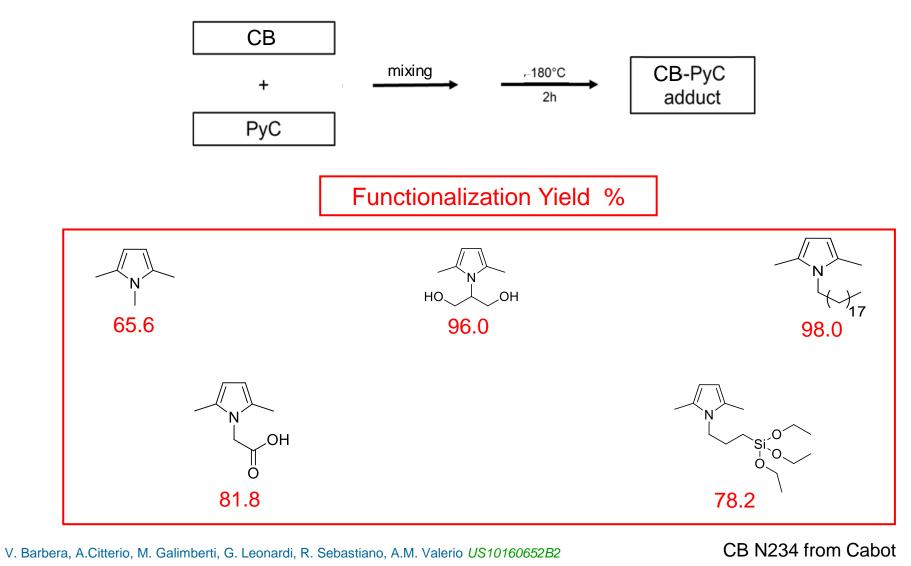


V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, 2019. Nanomaterials, 9(1), p.44.

M. Galimberti - A biosourced Janus molecule

Workshop Polymers, Health and Sustainability

Adducts of PyC with carbon black



M. Galimberti, V. Barbera WO 2018/087685 A1

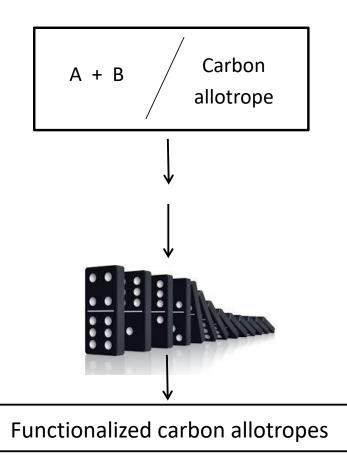
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253-270

M. Galimberti – A biosourced Janus molecule

Workshop Polymers, Health and Sustainability

Salina, September 11-13, 2022 86

The CA/PyC adducts



Functional group:from few % to 20%

- Functionalization yield: from 85% to quantitative
- Covalent bond
 between functional group
 and carbon allotrope
- Bulk structure of graphitic materials:
 substantially unaltered



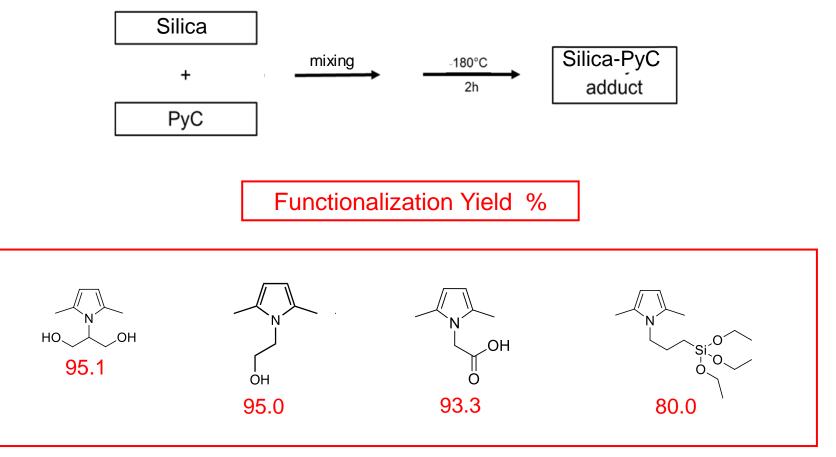
V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. US10329253B2
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. US10160652B2
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio. EP3180379B1

M. Galimberti, V. Barbera, EP3538511A1

M. Galimberti, V. Barbera, EP3538481A1

M. Galimberti – A biosourced Janus molecule

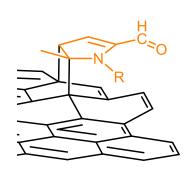
Adducts of Pyrrole compounds with silica

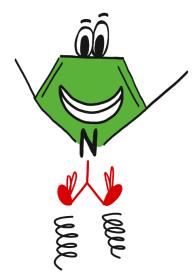


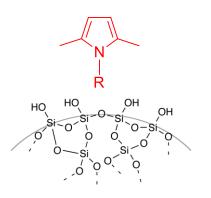
Silica: Zeosil® 1165 from Solvay

M. Galimberti,, A. Bernardi, V. Barbera, D. Locatelli WO2019162873A1

Univerasal coupling agents for carbon black and silica







In rubber compounds

Adducts reactive

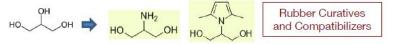
with the crosslinking system

with the rubbers

- Better crosslinking efficiency
- Higher dynamic rigidity
- Lower hysteresis at high T



Natural Origin Compatibilizers and Curatives Feedstock: Glicerine to obtain Serinol and derived Species

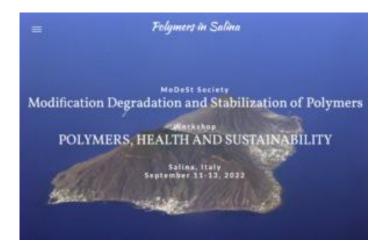


Pirelli Tyre; Annual Report: The Human Dimension. 2020, 106. https://corporate.pirelli.com/var/files2020/EN/PDF/PIRELLI_ANNUAL_REPORT_2020_ENG.pdf



instagram: @ismaterials.polimi

Thanks for your attention!



M. Galimberti – A biosourced Janus molecule