EMAC 276

Lecture 15: Polydienes

from Natural Rubber to Synthetic Rubber

Part 1: Natural Rubber, Polyisoprene

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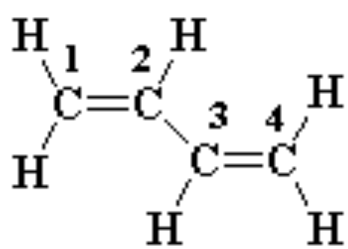
February 24, 2025

What is a diene?

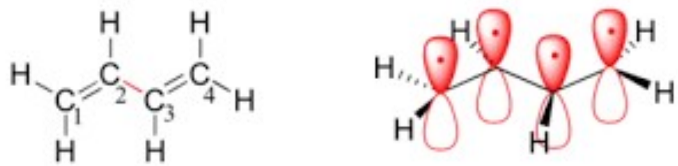
A diene is an unsaturated hydrocarbon containing two double bonds between carbon atoms.

Butadiene is the simplest diene:



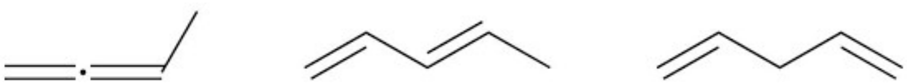
Butadiene has two carbon-carbon double bonds, in the 1 and 3 positions, that is, starting at the carbon atoms numbered 1 and 3.

Dienes and Polydienes can Adopt Numerous Configurations



1,3-butadiene

The placement of the double bond.



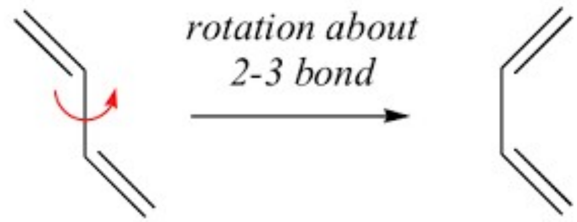
Cumulated Conjugated Isolated

Cumulated – pi bonds are adjacent.

Conjugated – pi bonds are separated by exactly ONE single bond.

Isolated – pi bonds are separated by any distance greater than ONE single bond.

Rotation around the single bond.



s-trans s-cis

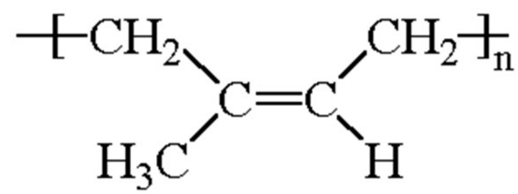
Isolated

s-trans *s-cis*

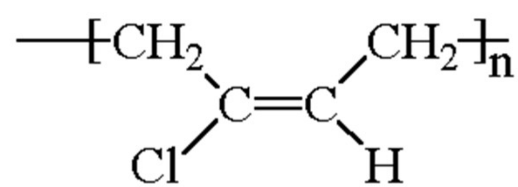
Monomer

Diene Based Polymers that We Will Consider

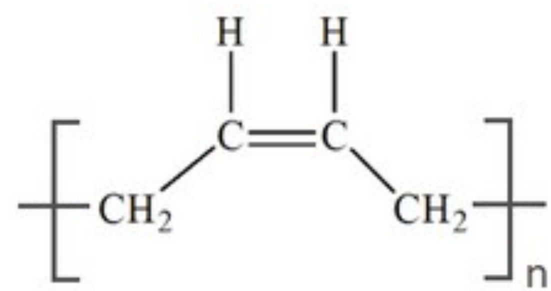
Polyisoprene



Polychloroprene (Neoprene)



Polybutadiene



Caotchouc is the Origin of Rubber

caou·tchouc/*noun*
ˈkouˌCHo͞ok,-ˌCHo͞o(k)/noun:
unvulcanized natural rubber.

Natural rubber, also called by other names of **India rubber**, **latex**, **Amazonian rubber**, *caucho* or ***caoutchouc***, as initially produced, consists of polymers of the organic compound **isoprene**, with minor impurities of other organic compounds, plus water. Forms of **polyisoprene** that are used as natural rubbers are classified as elastomers.

Origin of “Rubber”: Material and Name

The first use of rubber was by the indigenous cultures of Mesoamerica. The earliest archeological evidence of the use of natural latex from the *Hevea* tree comes from the Olmec culture, (1200 BCE) in which rubber was first used for making balls for the Mesoamerican ballgame. Rubber was later used by the Maya and Aztec cultures.

1736 – Charles Marie de la Condamine 1751 introduced samples of rubber to the French, Academie Royale des Sciences.

1751 – He presented a paper on the properties of rubber.

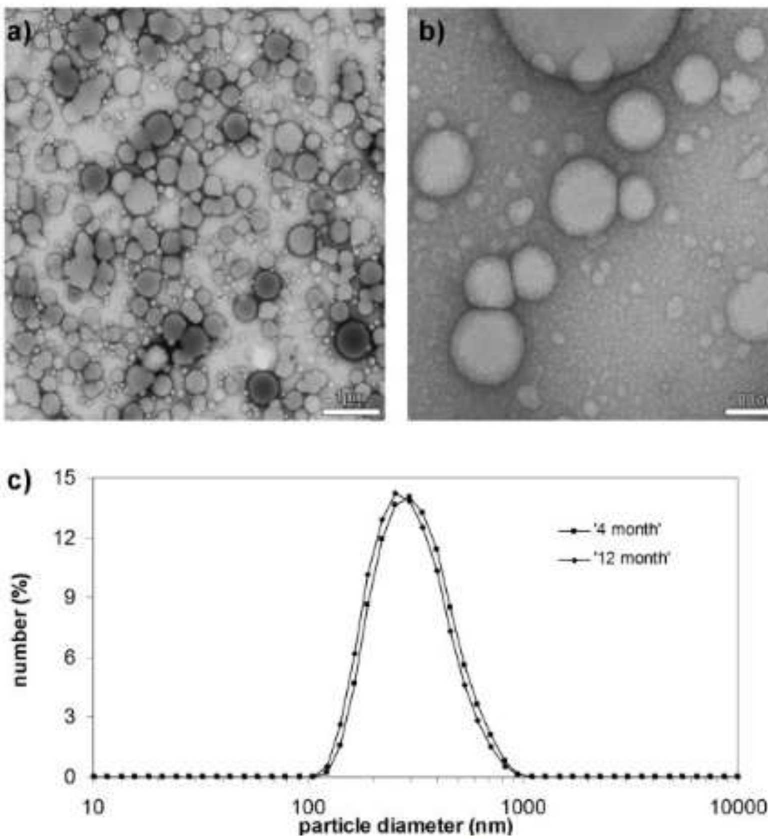
Origin of “Rubber”: Material and Name

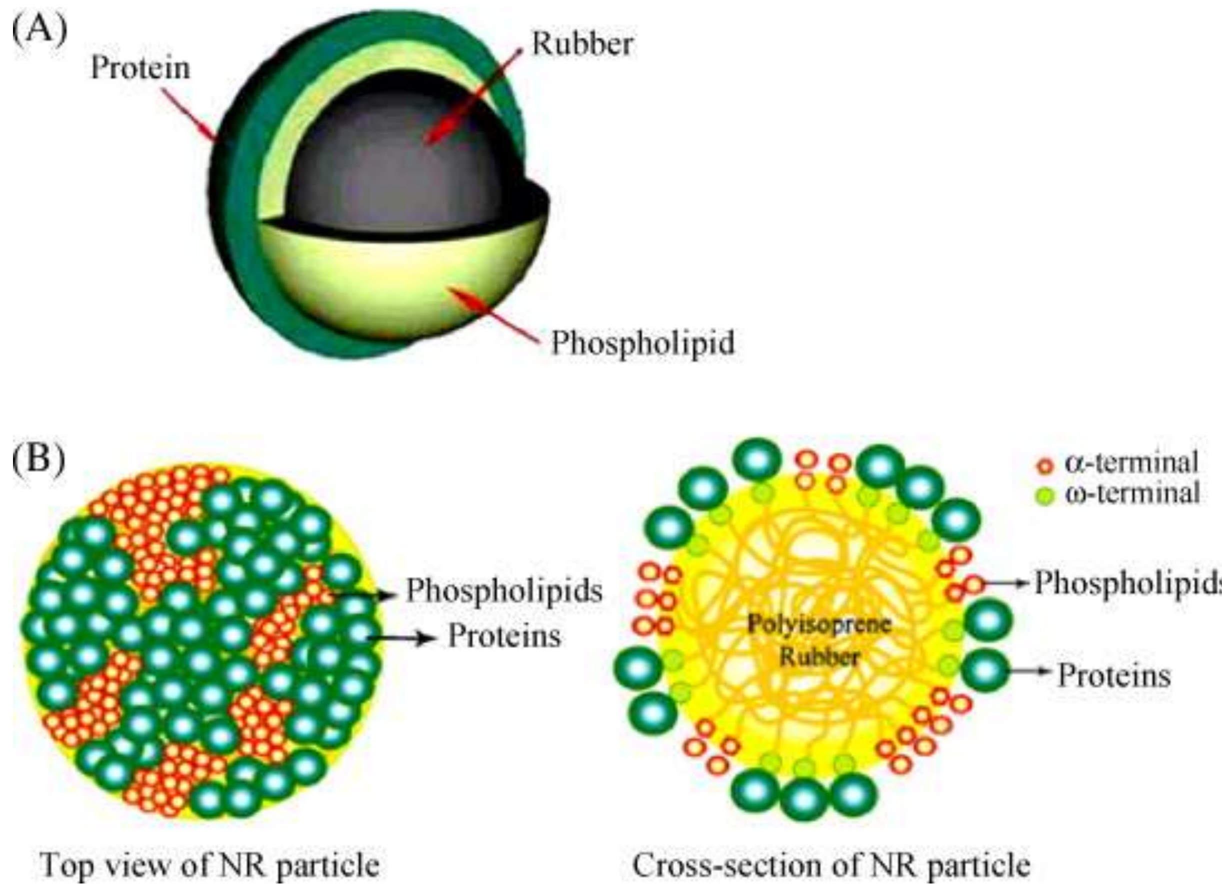
Ancient rubber was made from latex of the rubber tree (*Castilla elastica*), which is indigenous to the tropical areas of southern Mexico and Central America. The latex was made into rubber by mixing it with the juice of what was likely *Ipomoea alba* (a species of morning glory), a process which preceded Goodyear's vulcanization by several millennia. The resultant rubber would then be formed into rubber strips, which would be wound around a solid rubber core to build the ball.

Origin of the term “Rubber”

In England, Joseph Priestley, in 1770, observed that a piece of India gum (i.e., natural rubber) was extremely good for rubbing off pencil marks on paper, hence the name "rubber".

Composition of Rubber Latex and Natural Rubber





Composition of Rubber Latex and Natural Rubber

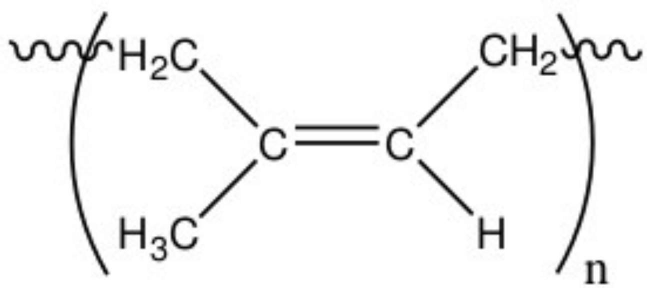
	Latex[a]		*Dry rubber*[c]
	% w/v fresh latex[a]	*% w/w dry matter of latex*[b]	*% w/w dry matter*
Rubber hydrocarbon	35.0	87.0	94.0
Proteins	1.5	3.7	2.2
Carbohydrates	1.5	3.7	0.4
Lipids	1.3	3.2	3.4
Organic solutes	0.5	1.1	0.1
Inorganic substances	0.5	1.2	0.2

Approximate values only (highly dependent on clone, season and physiological status of the tree).
[a]averaged from data published by Wititsuwannakul, 2001.[100]
[b]calculated.
[c]Sainte-Beuve, 2006.[115]

Latex, **colloidal suspension**, either the milky white liquid emulsion found in the cells of certain flowering plants such as the rubber tree (Hevea brasiliensis) or any of various manufactured **water emulsions** consisting of synthetic rubber or plastic

Composition of Rubber Latex and Natural Rubber

Polyisoprene (Natural Rubber)



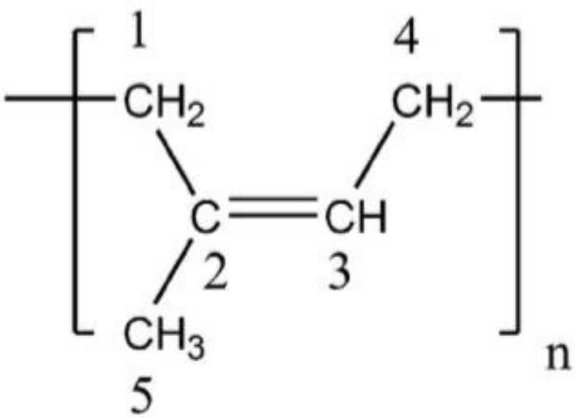
Cis- Polyisoprene

Natural Rubber contains 98% cis 1,4-Polyisoprene

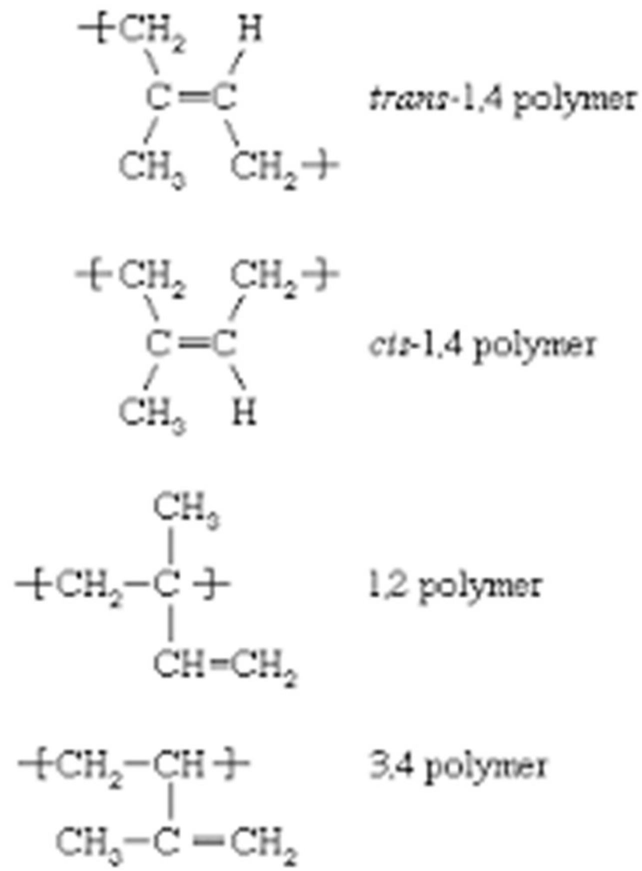
Natural rubber is characterized to have

- **Good elastic properties, amorphous in nature**
- **Good Resilience and damping behavior**
- **Mw ranging from 1 to 2.5 x 10^6.**
- **But poor resistance to heat, oxygen and ozone due to presence of high no. of unsaturation.**

Configurations of Polyisoprene

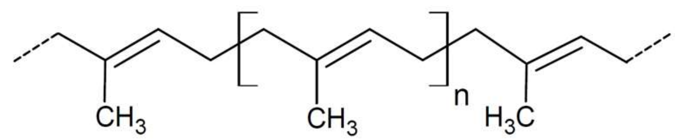


cis-1,4-polyisoprene

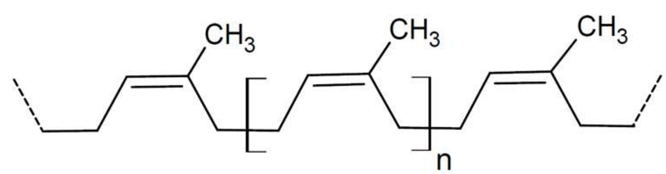


Two Configurations for 1,4-Polyisoprene

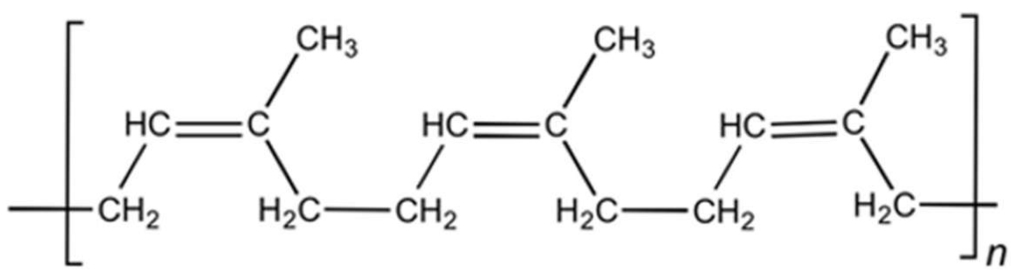
trans-1,4-Isoprene:



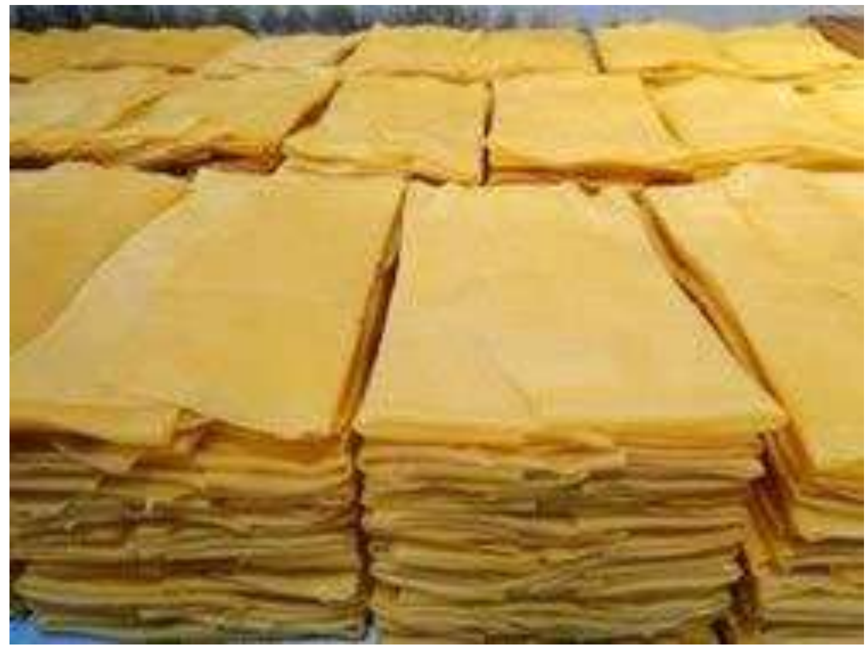
cis-1,4-Isoprene:



Natural Rubber is Poly-Isoprene in Cis configuration.



Composition of Rubber Latex and Natural Rubber



Dry natural rubber does not have good elastomeric properties.

The History of Charles Goodyear

In 1834 Charles Goodyear visited the Roxbury India Rubber Company In New York. The manager showed Goodyear a warehouse where Shelves held heaps of misshapen blobs, their folds stuck together. Goodyear began his work to make this material suitable for industrial Use. Moving from New York, to Massachusetts, to Philadelphia and to Connecticut Goodyear continued his experiments working primarily In his kitchen.

In 1839 while working at the Eagle India Rubber Company Goodyear accidentally combined on a hot stove natural rubber and sulfur. The resulting mixture didn't melt and flow as does natural rubber but kept it's shape, hardening further when additional heat was applied.

Charles Goodyear patented the process in 1844 after establishing the Naugatuck India-Rubber Company. He named the discovery vulcanization, after Vulcan, the Roman god of fire.

Goodyear's Vulcanization Patent

UNITED STATES PATENT OFFICE.

CHARLES GOODYEAR, OF NEW YORK, N.Y.

IMPROVEMENT IN INDIA-RUBBER FABRICS.

Specification forming part of Letters Patent No. 3,633, dated June 15, 1844.

U.S. Patent No. 3633; Issued June 15, 1844

Charles Goodyear died in 1860 at age 59, $200,000 in debt. The Goodyear Tire and Rubber Co., was founded in Akron, Ohio, in 1898, and was named in his honor.

- **Charles Goodyear never lived in Akron, Ohio.**
- **Charles Goodyear did not start the Goodyear Tire and Rubber Company**

I do claim—

1. The combining of the said gum with sulphur and with white lead, so as to form a triple compound, either in the proportions herein named or in any other within such limits as will produce a like result; and I will here remark that although I have obtained the best results from the carbonate of lead, other salts of lead or the oxides of that metal may be substituted therefor, and will produce a good effect. I therefore under this head claim the employment of either of the oxides or salts of lead in the place of the white lead in the above-named compound.

2. The formation of a fabric of the india-rubber by interposing layers of cotton-batting between those of the gum, in the manner and for the purpose above described.

3. In combination with the foregoing, the process of exposing the india-rubber fabric to the action of a high degree of heat, such as is herein specified, by means of which my improved compound is effectually changed in its properties so as to protect it from decomposition or deterioration by the action of those agents which have heretofore been found to produce that effect upon india-rubber goods.

CHARLES GOODYEAR.

Interesting Patent found During the Goodyear Search

Nathaniel Hayward, U.S. Patent No. 1090, Issued: **February 24, 1839**

UNITED STATES PATENT OFFICE.

NATHANIEL HAYWARD, OF WOBURN, ASSIGNOR TO CHARLES GOODYEAR, OF BOSTON, MASSACHUSETTS.

IMPROVEMENT IN THE MODE OF PREPARING CAOUTCHOUC WITH SULPHUR FOR THE MANUFACTURE OF VARIOUS ARTICLES.

Specification forming part of Letters Patent No. **1,090**, dated February 24, 1839.

What I claim as my invention, and desire to secure by Letters Patent, is—

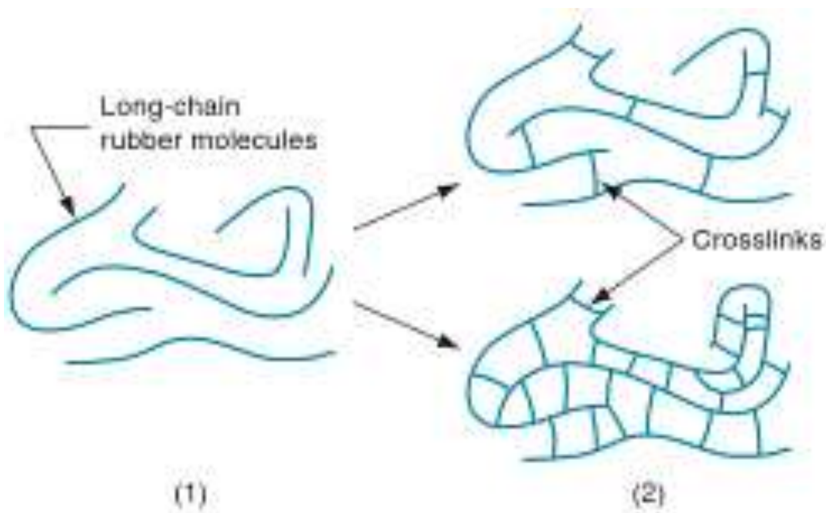
The combining of sulphur with gum-elastic, either in solution or in substance, either in the modes above poined out or in any other which is substantially the same, and which will produce a like effect.

In witness whereof I, the said NATHANIEL HAYWARD, have hereunto set my hand this 23d day of November, A. D. 1838.

NATHANIEL HAYWARD.

IMPROVEMENT IN THE MODE OF PREPARING CAOUTCHOUC WITH SULPHUR FOR THE MANUFACTURE OF VARIOUS ARTICLES

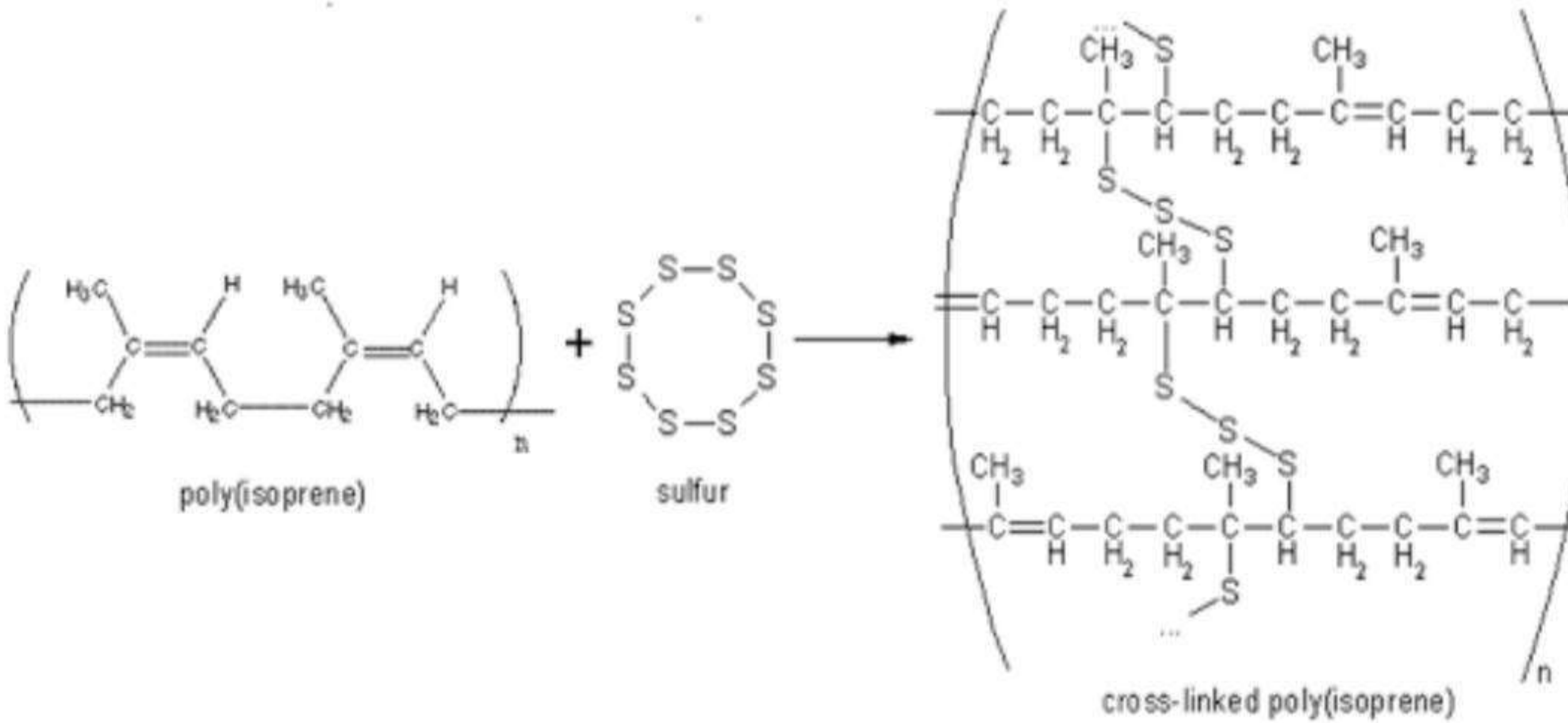
What Happens Molecularly During Vulcanization?



Vulcanization’s effect on rubber molecules:
1. Raw rubber;
2. Vulcanized (cross-linked) rubber

Advantages of Vulcanization:
•It has good tensile strength and extensibility.
•It has excellent resilience i.e.it returns to the original shape, when the deforming load is removed.
•It possesses low water absorption tendency.
•It has higher resistance to oxidation, wear and tear abrasion.
•It is better electrical insulator.
•It is resistant to organic solvents (petro, benzene), fats and oils.
•It has slight tackiness.
•It has useful temperature range of -40.C to 100.C

What Happens Chemically During Vulcanization?



Vulcanisation

What Happens Mechanically After Vulcanization?

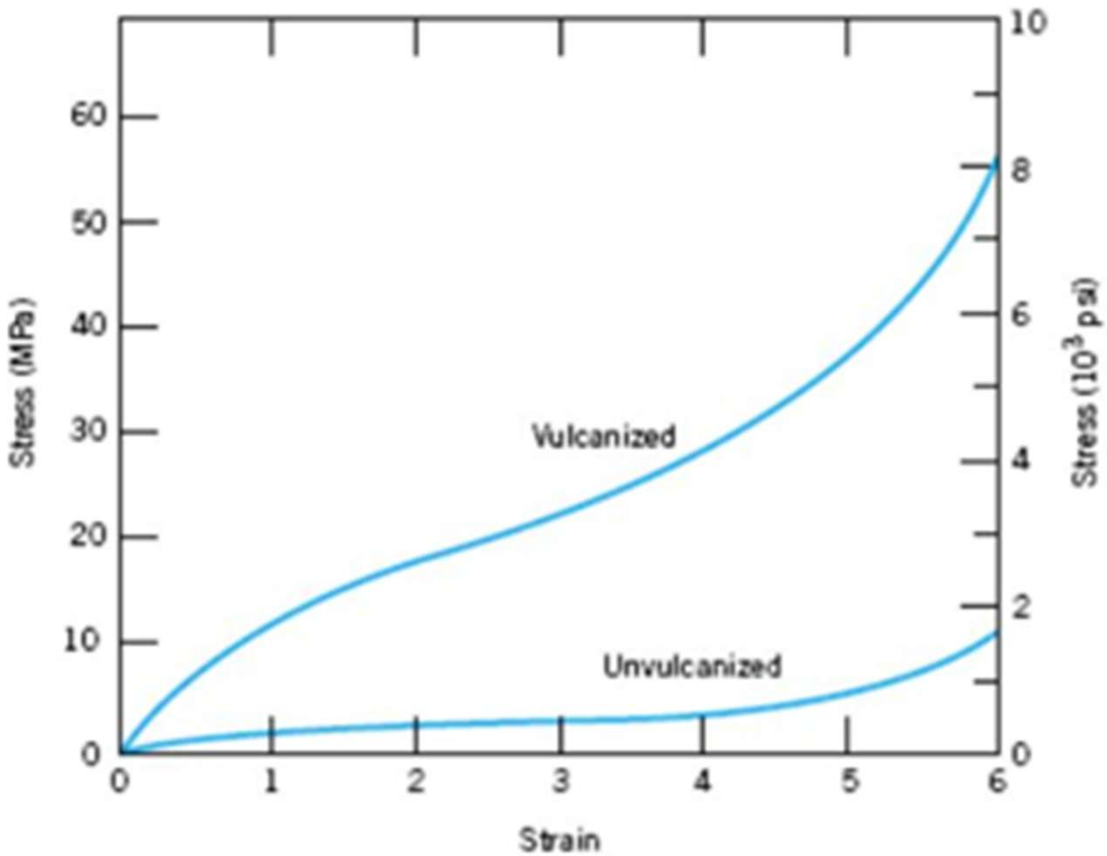
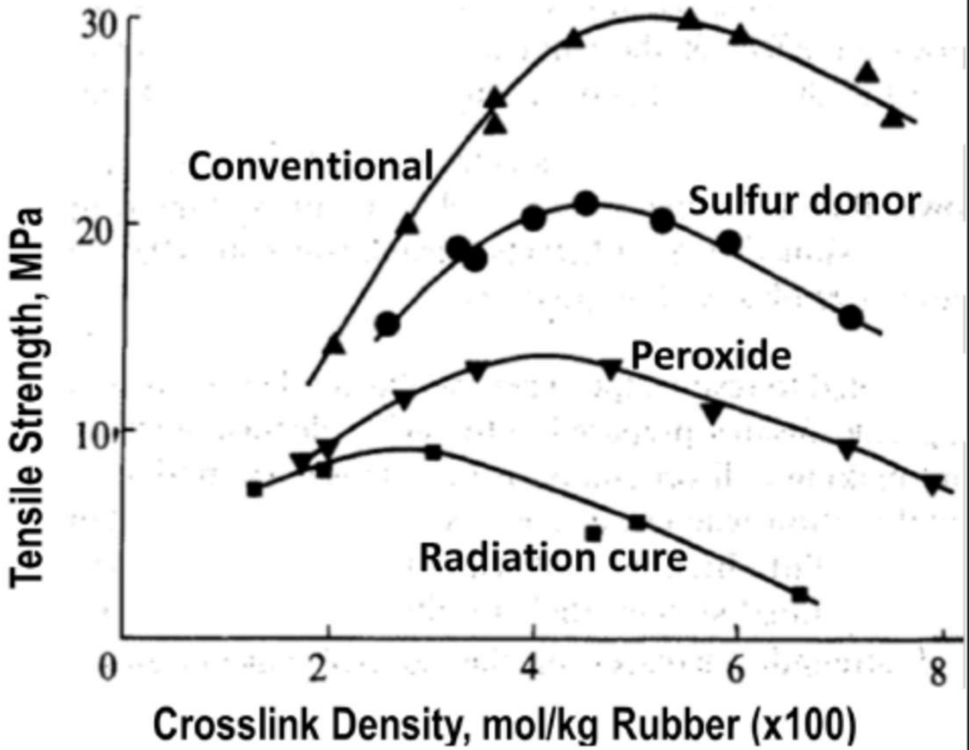
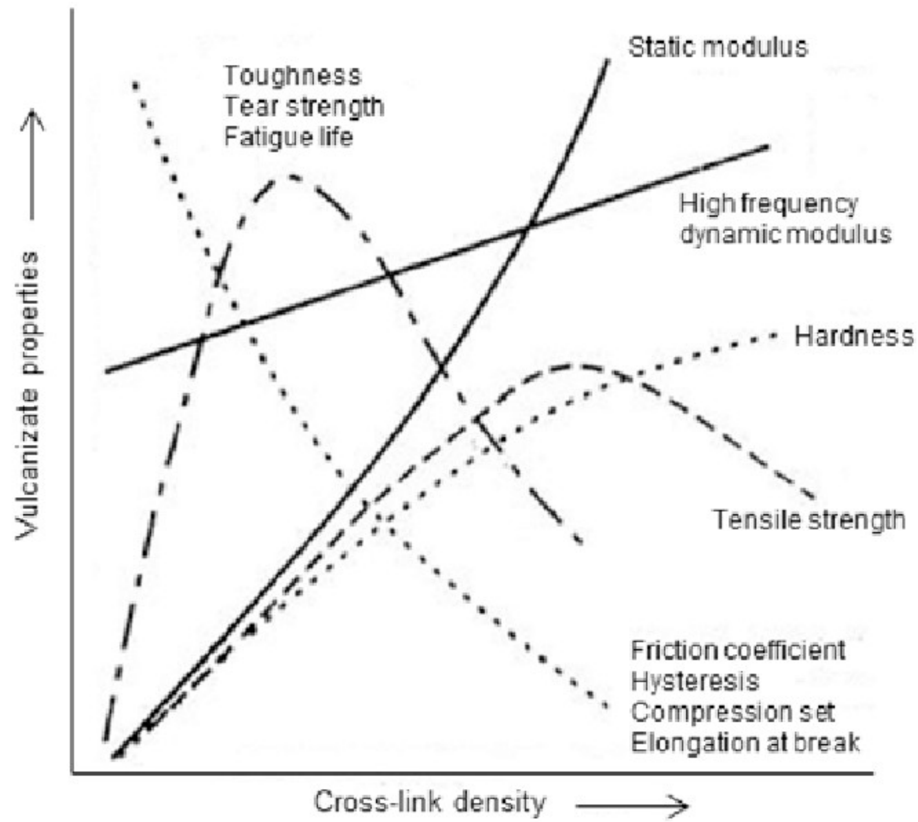


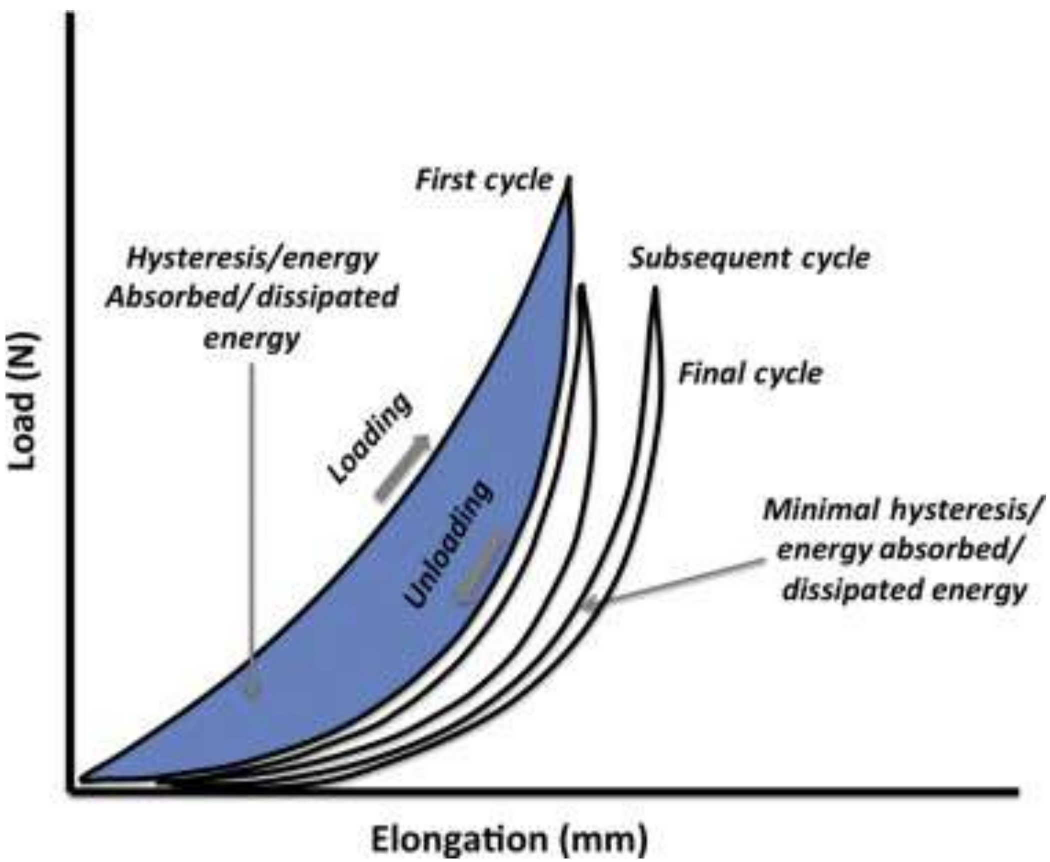
FIGURE 15.15
Stress–strain curves to 600% elongation for unvulcanized and vulcanized natural rubber.

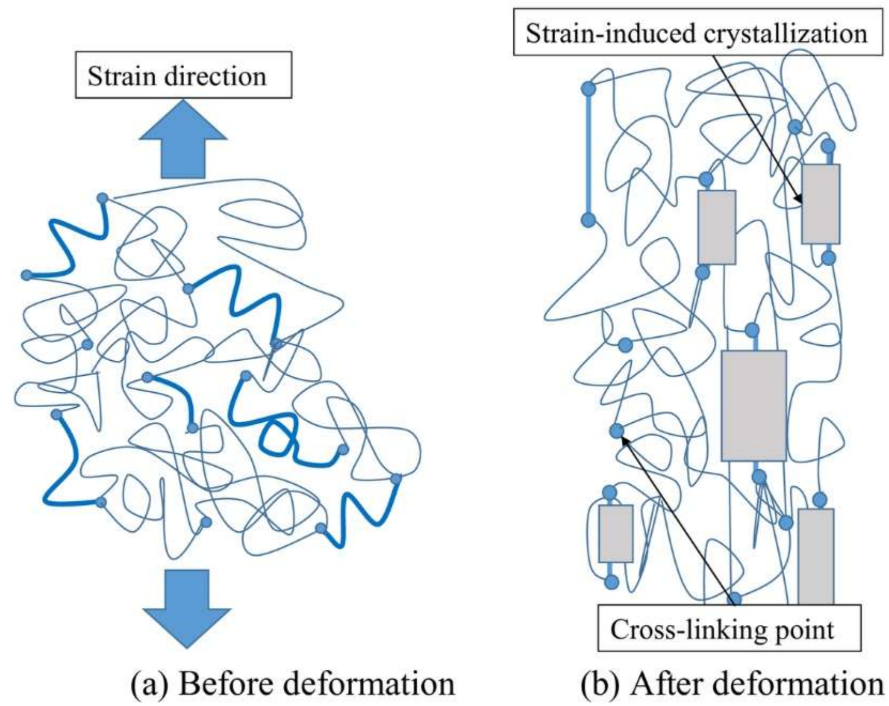
What Happens Mechanically as a Function of Vulcanization?





Hysteresis and Strain Induced Crystallization





Commercial Production of Polyisoprene

The preparation of an all *cis*-1,4-polyisoprene, a duplicate of natural rubber, continued to elude the most extensive efforts of scientists for many more years.

It was not until the mid 1950's that two independent catalyst systems, each capable of polymerizing isoprene to a *cis*-1,4-polymer, were disclosed.

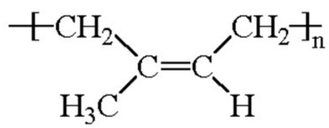
1) Home and coworkers, employing a Ziegler-type catalyst prepared from trialkylaluminum and titanium tetra-chloride, polymerized isoprene to an essentially all *cis*-1,4-polyisoprene.

2) The other catalyst, based on lithium metal, was discovered by a Firestone Tire and Rubber research team.

In 1960, just a few years after the discovery of the stereospecific catalysts, the first commercial plant for the production of *cis*-polyisoprene with a lithium catalyst was on stream.

Commercial Production of Polyisoprene

- The only configuration of polyisoprene that is of commercial importance is cis-1,4 polyisoprene.

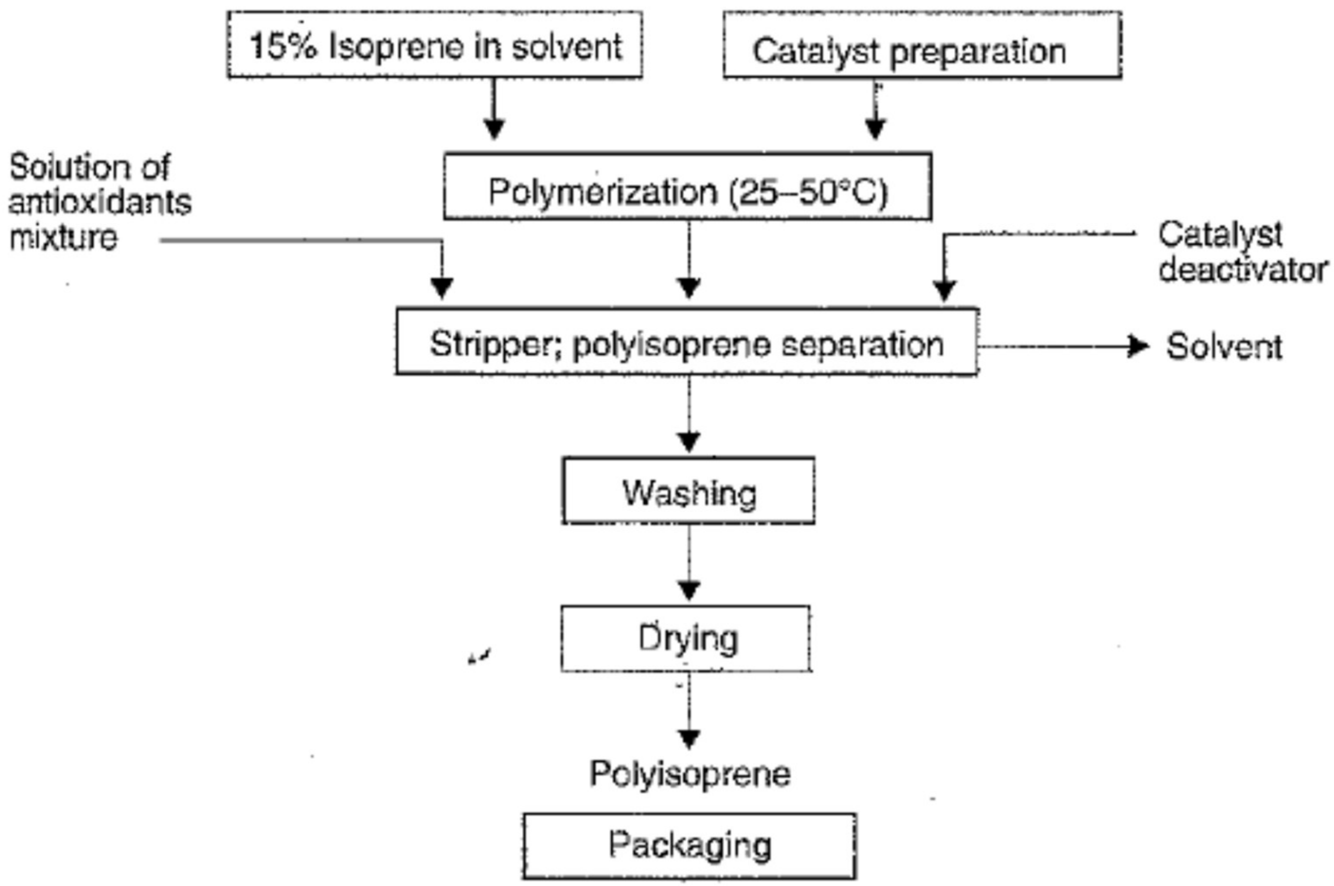


- Two major polymerization methods exist to commercially produce cis-1,4-Polyisoprene:
  - Ziegler-Natta: comprising trialkylaluminum and titanium tetrachloride,
  - Lithium and Lithium alkyl.

- The properties of synthetic cis-1,4 polyisoprene are very similar to those of cis-1,4 polyisoprene obtained from natural rubber.

- When vulcanized the mechanical properties also are similar.

Polymerization Sequence for Polyisoprene



Comparison of Chemical and Structural Properties of Naturally Produced and Synthetic Polyisoprene

Table 3.8 Analytical data of different polyisoprenes [28]. (Reprinted with permission of the publishers, Butterworth-Heinemann Ltd from *Rubber Technology and Manufacture* edited by C.M. Blow and C. Hepburn, 1982)

	Synthetic polyisoprene		
Property	*Ziegler–Natta*	*Lithium*	*Natural rubber*
1,4 *cis* units (% wt)	96	92	98–100
Limiting viscosity number (dl/g)	2.5–4.5	8–11	6–7
Gel content (% wt)	10–20	0	High level depending on age
Geometric shape	Branched	Linear	Branched
Stabilizer content (pphr)	1	0.5	2–3
Ash content (% wt)	0.15–0.30	0.05	Approx. 0.5
Total metal content (ppm)	400–3000	70	Approx. 1000
Mooney viscosity [ML(1+4) 100°C]	60–90	–	Approx. 120
Color	White	White	Dark

Mechanical Properties of Naturally Produced and Synthetic Polyisoprene

Table 3.9 Some vulcanizate properties [28]. (Reprinted with permission of the publishers, Butterworth-Heinemann Ltd from *Rubber Technology and Manufacture* edited by C.M. Blow and C. Hepburn, 1982)

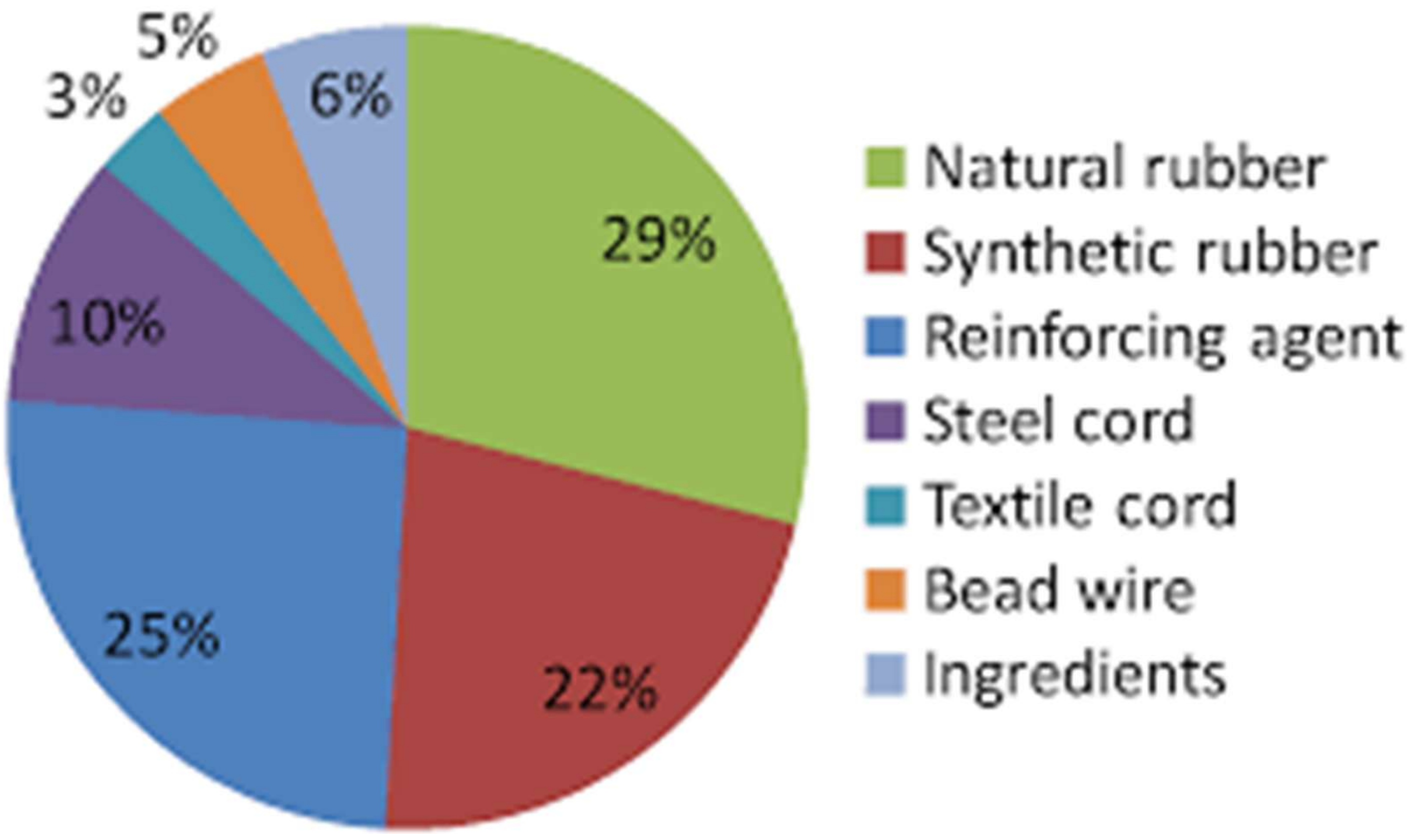
	Type of polymer				
Property	*Ziegler–Natta PI*	*Lithium PI*	*Natural PI*	*SBR*	*PB*
Tensile strength (MPa)	30	25	31	25	17
Tear strength (N/mm)	70	60	110	45	35
Heat build-up (°C)	23	21	23	40	33

Comparative Mechanical Properties of Elastomers

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resis-tance
Natural rubber	20–100	1,000–4,000	100–700	–55–80	Fair
Styrene-butadiene rubber (SBR)	40–100	1,000–3,500	100–700	–55–110	Fair
Polybutadiene	30–100	1,000–3,000	100–700	–60–100	Fair
Polyisoprene	20–100	1,000–4,000	100–750	–55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	–55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	–70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	–55–100	Very good

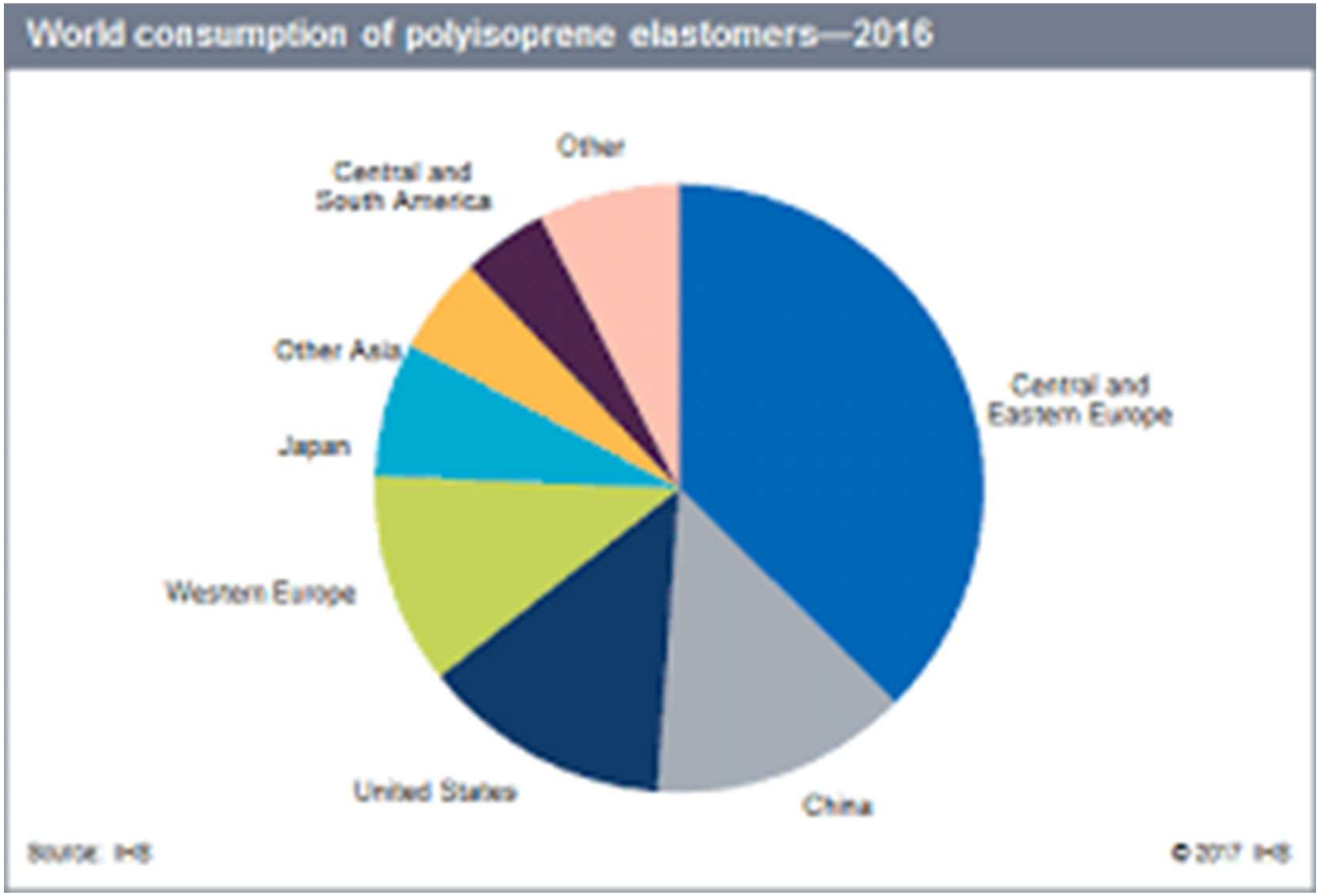
Table 1 Selected properties of some elastomers.

Applications for Polyisoprene - Tires



Additional Applications for Polyisoprene

Polyisoprene use Around the World



Alternate Sources for Natural Rubber Latex (Polyisoprene)

Guayule *(Parthenium Argentatum)*

Russian Dandelion
(*Taraxacum kiksaghyz* Rodin)

Fig Tree
(Ficus Carica)

Yield from the Alternate Latex Sources

Table 1. Properties and sources of natural rubber producing plants.

Natural rubber producing plant	Property	Source of rubber	Mw (kDa)	Production (Tones/Yr)	Content of rubber (%)
Hevea brasiliensis	*Hevea*, rubber yielding tree which is white or yellow latex occurs in latex vessels in the bark.	Bark	1,310	9,000,000	30-40
Guayule shrub *P. argentatum* Gray	A high protein guayule latex would also be a brown/green color	Root	1,280	10,000	3-12
Russian dandelion *Taraxacum (koksaghyz)*	It produces a milky fluid in its roots, which contains a high-quality rubber	Root	2,180	3,000	0-15
Fig tree (*Ficus carica*)	Natue of latex pale grey in colour.	Bark, leaf	190	--	4

Lesson 15: Polydienes –
From Natural Rubber to Synthetic Rubber
Part 1: Natural Rubber, Polyisoprene

Questions?

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"I don't care what you think you're good at, there's a 7-year-old kid on YouTube doing it better"