MY UNDERSTANDING OF GUTTA PERCHA

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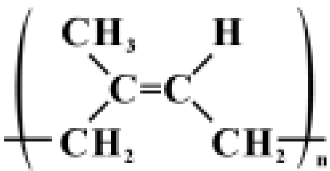
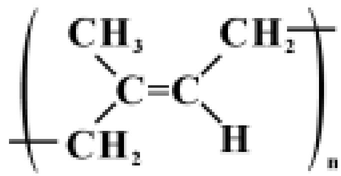
I learnt . . .

in the secondary school in the early 1950s, that
"Hydrofluoric acid must be stored in a gutta percha bottle as it erodes glass."

In the university in the early 1960s, I learnt that gutta percha is poly-*trans*-isoprene, an stereo-isomer of natural rubber, and the only thermoplastic natural polymer.



poly-*trans*-isoprene



poly-*cis*-isoprene

In the laboratory, a gutta percha bottle existed, and I used hydrofluoric acid for putting marks on glassware.

http://www.ingenious.org.uk/

When I was in Bandung . . .

from 1990 - 1992, I asked people about gutta percha but nobody knew.

Just before the end of my stay, someone told me that gutta percha sample was shown in a local products exhibition.

I rushed the venue and was informed that it was from Cipetir.

I wrote a letter to PT Perkebunan XI and visited the plantation for the first time.

Subsequently I visited Cipetir several times, one occasion with participants to the International Workshop on Green Polymers - Bandung/Bogor 1996.

Photographed by M. Iguchi 2002

What I saw at Cipetir

From harvested leaves/twigs to Crude Gutta (Physical process)

Harvested leaves

Milling (to destruct cells)

75C hot-water (Gutta comes out, dirt sediments)

Crude gutta
(to be fragmented and dried)

What I saw at Cipetir - continuation

From Crude Gutta to White Gutta (Chemical process)

Extraction of resin in ice-cold benzin

Dissolution in benzin

Whitening with clay

Steam distillation

Taking out separated gutta

Weighing and moulding

The products (sealed in a tin for shipping)

Gutta-percha Plantation

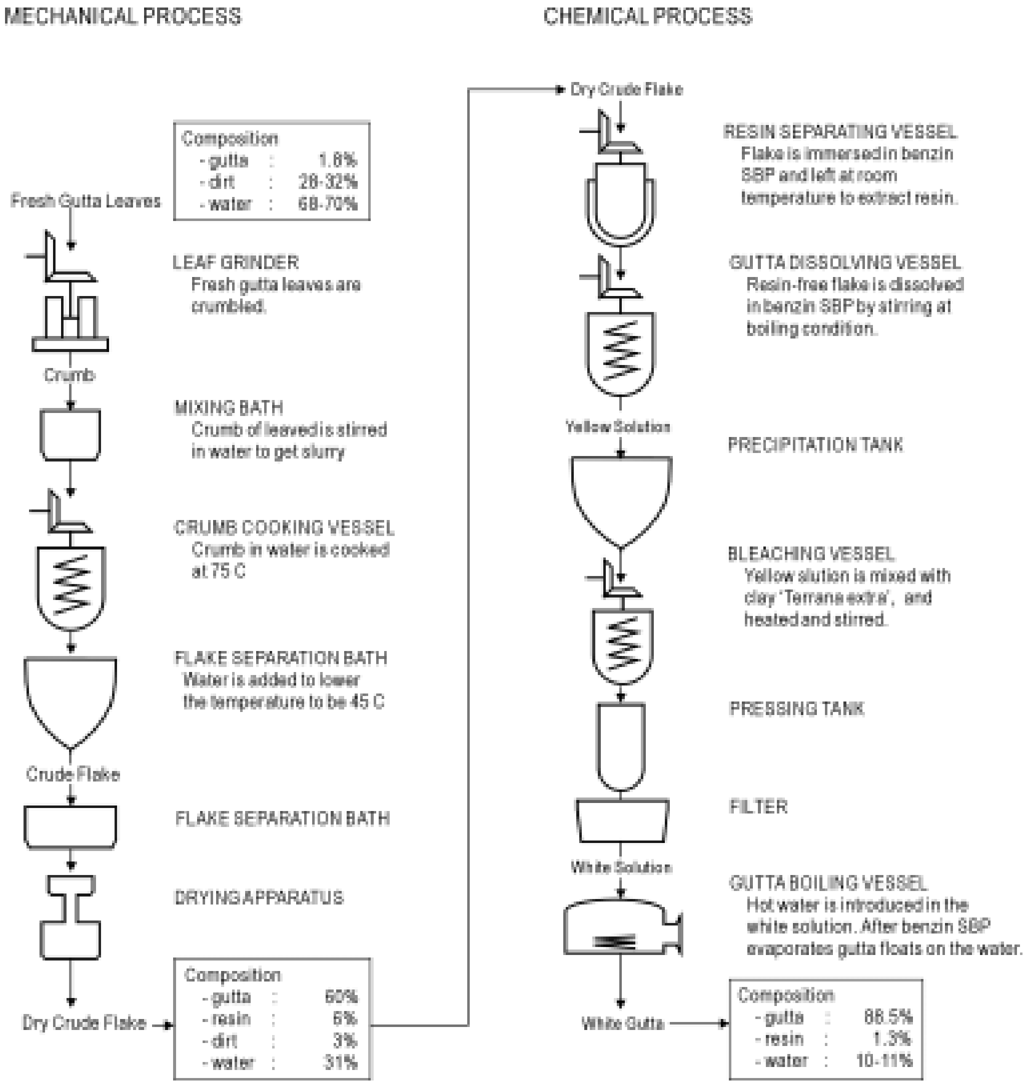
-1880 Relentless felling jeopardised the existence of gutta trees in the forests.

1883 Dr. William Burck commenced botanical study for the development of plantations (with the Director, Dr. Melchiol Treub).

1900 Cipetir plantation was opened at Tjipetir, planting *Palaquium* oblongifolium, *Palaquium* gutta and *Palaquium* borneense (the latter two eliminated in later years).

http://www.biotox.cz/botanicus/jpg/bph_0237.jpg

Gutta-percha Process (by Dr. Burck, 1890s)



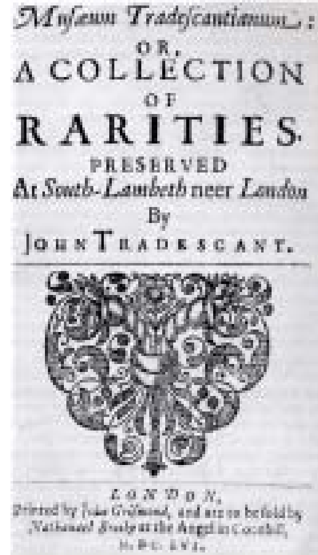
Didn't Burck know that gutta percha and rubber consisted of large molecules which were later called macromolecules or polymer?

With new knowledge accumulated during the subsequent 100 years, no better process was conceived by myself.

Early history (1)

1656

John Tradescant who visited the Far East wrote:
"The pliable mazer wood, being warmed in water will work to any form, such as of knife grips, small furniture, toys, etc".



Musæum Tradescantianum:
OR,
A COLLECTION
OF
RARITIES
PRESERVED
At South-Lambeth neer London
By
JOHN TRADESCANT.

LONDON,
Printed by John Grismond, and are to be sold by
Nathanael Brooke at the Angel in Cornhill,
M.DC.LVI.

http://www.porthcurno.org.uk/html/guttapercha.html

The tree was locally known as getah taban merah or getah taban sutra.
They felled down the trees found in the tropical forests and collected the gutta percha latex from the core parts of the wood because incision given on the bark did not yield much latex and the exuding latex itself quickly dried.

Early history (2)

1843

Dr. William Montgomerie and Dr Jos d'Almeida independently brought samples to London.

Anselme Payen (French chemist) proved gutta percha contained a 75-82% hydrocarbon compound after hot water treatment. Hot water contained oxygen compounds, 4-16% alban, and 4-6% fluavi.

Contemporary chemists determined that the formula of gutta percha as $(C_{10}H_{16})_n$, $C_{20}H_{32}$, $(C_4H_7)_n$, etc. with no clear image for the polymeric structure.

1848

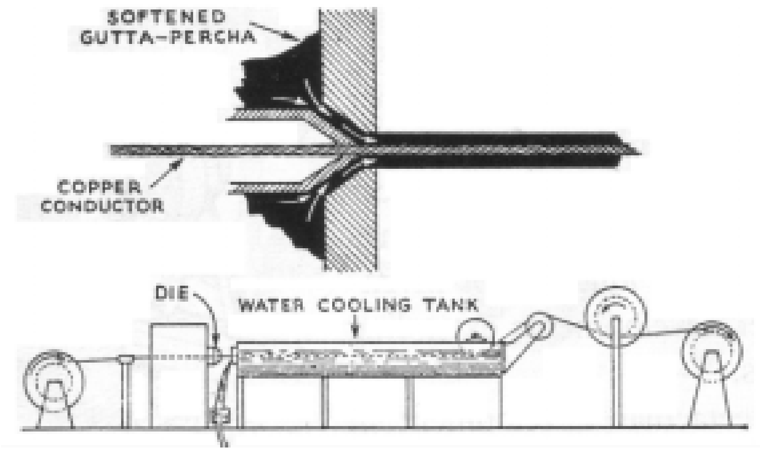
Michael Faraday found the fact that gutta percha had an excellent insulating properties in water (*Philosophical Magazine*, 9 February 1848)

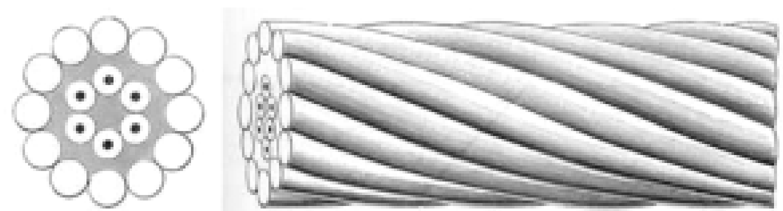
Application for cable covering

1848

Thomas Hancock, who formed The Gutta Percha Company in 1845, invented an extruder machine to extrude gutta percha and continuously cover wires.

Barlow and Foster patented the method as well as a machine to cure a compound of gutta percha and sulphur. *No idea of cross-link formation*!





From: C. Singer, E. J. Holmyard, A. R. Hall and T. L. Williums (Ed.), *A History of Technology Vol.V*, Oxford University Press, New York and London 1958

1851

The first submarine cable was laid from Dover (England) to Calais (France).

Application for cable covering - continuation

1895

Giuseppe Marconi invented wireless telecommunication1895

1930

Polythene (polyethylene) was invented by I. C. I.

~1950

Demands of Gutta percha for cable covering diminished.

Various applications

The only thermoplastic material made the world excited!

Great Central Fair Philadelphia, 1864
www.lcpgraphics.org/inventories/sanitaryfair/

http://www.atlantic-cable.com/Article/GuttaPercha/index.htm

Why "Pahang Jelai"
in Japanese alphabet?

Various applications - continuation

(Feathery cube)

The first gutta-percha ball (1848)

Hand hammered gutta-percha ball

Bramble ball

http://www.thedesignshop.com/history.htm

http://www.tias.com/stores/raljel/

http://www.vintagebuttons.net/rubber.html

Dental filler
(still of use today)

Scientific aspects

K. H. Stokes's historic observation

An Electron Diffraction Examination of Some Linear High Polymers, K. H. Storks, J. Am. Chem. Soc. 1938, **60**, 1753

It is surprising that most of the crystallites are oriented with their fibre axis directions normal to the plane of a film the thinckness of which is much less than the length of a macromolecule. . . . The gutta-percha molecule may possibly fold by a mechanism of rotation around the single bonds. The chemical repeating units of this polymer is short and relatively few folds per macromolecule are required in a film of 200Å thick. . . .

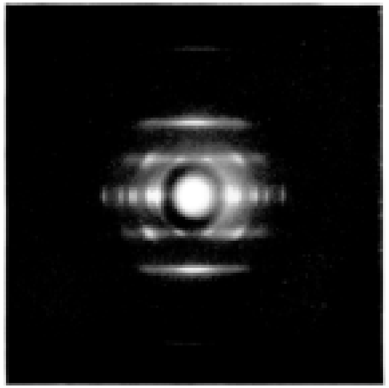


Fig. 4.—Electron diffraction pattern from stretched "Br-4" grade gutta-percha. ($L\lambda = 2.73_{(g)} \times 10^{-8}$ mm.[2])

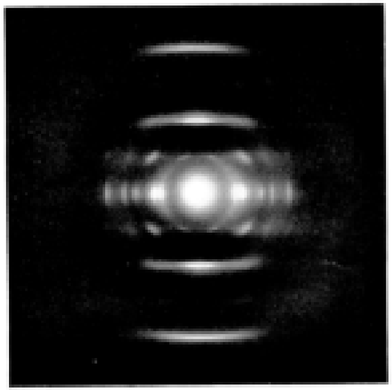


Fig. 5.—Electron diffraction pattern from stretched "white" gutta-percha. ($L\lambda = 2.70_{(g)} \times 10^{-8}$ mm.[2])

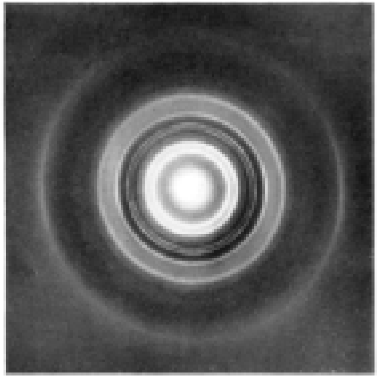


Fig. 8.—Electron diffraction pattern from unstretched "white" gutta-percha at normal incidence. ($L\lambda = 2.70_{(g)} \times 10^{-8}$ mm.[2])

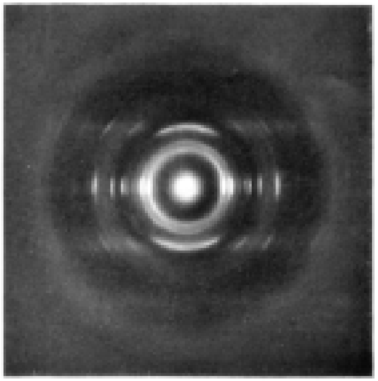
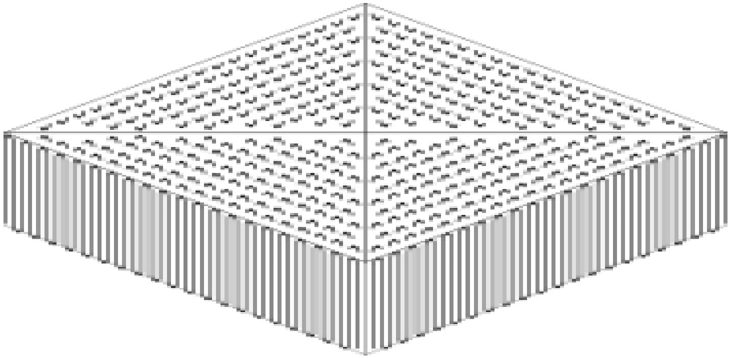


Fig. 9.—Electron diffraction pattern from unstretched "white" gutta-percha at 45° incidence. ($L\lambda = 2.70_{(g)} \times 10^{-8}$ mm.[2])

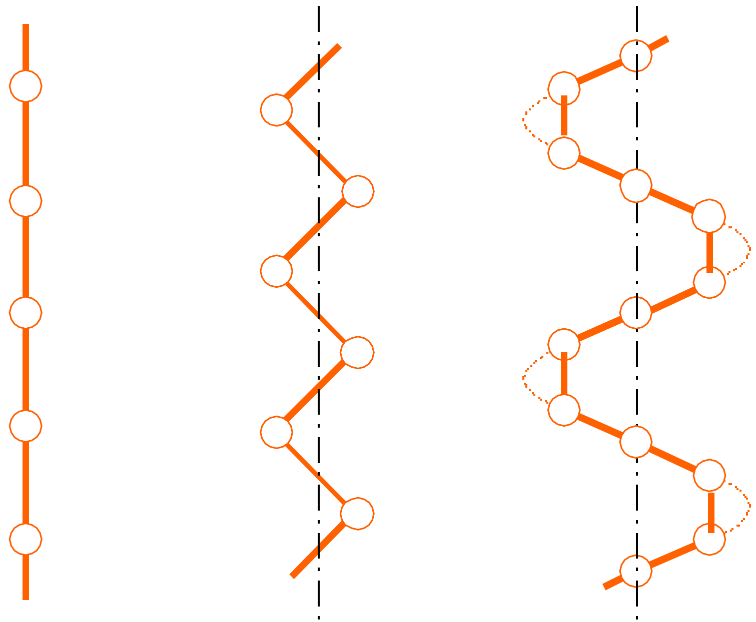
Scientific aspects - continuation

Stokes found the crystallization habit of linear crystalline polymers, in that chain molecules folds itself at a certain length and forms lamellar crystals, which became well known after Keller rediscovered the same habit with polyethylene single crystals in 1957.



Bulk polymer crystallised from the melt consists basically of lamellar crystallites.

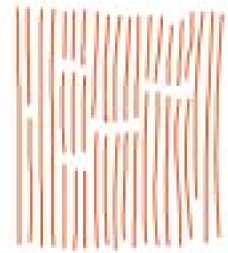
Primary Molecular Structure / Deformation Modes / Y-Modulus



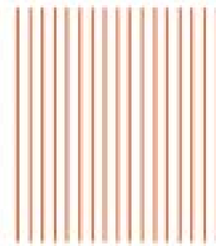
	Straight	Planar zig-zag	Helical
Bond rotation	No	No	Yes
Angular deform.	No	Yes	Yes
Bond stretching	Yes	Yes	Ye
Y-Modulus	**Large**	**Medium**	**Small**

Super-molecular structure models and stress-strain relationships (schematic illustration)

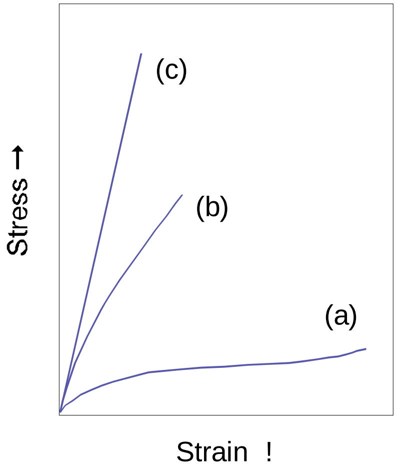
(a) Lamelae



(b) Fibrils

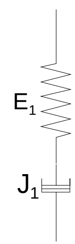


(c) Ideal

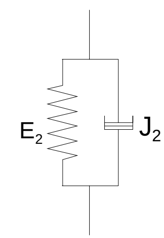


Young's modulus

<10% 60-70% 100%



Maxwell Model



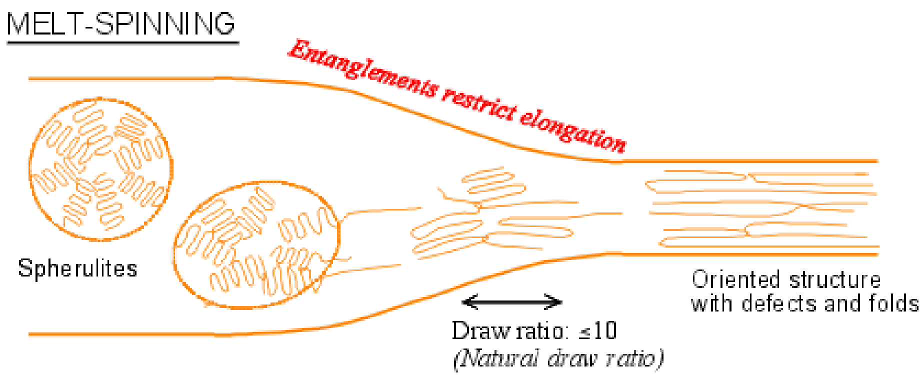
Voigt Model

Crystal structure and elastic modulus (by Prof. K. Tashiro, 2002)

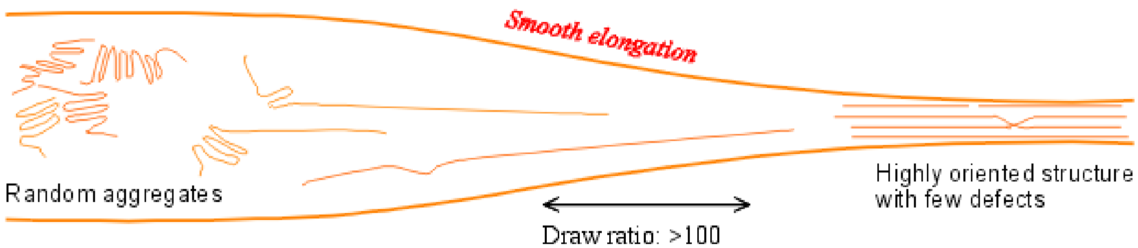
		Rubber	**Gutta percha** (α-form)	(β-form)
Crystal form		monoclinic	monoclinic	orthorhombic
Unit cell parameter	a	12.1566	8.0412	7.5901
	b	8.939	5.8656	11.7425
	c	8.0041	8.8461	4.7036
	α	90	90	90
	β	87.9923	104.1431	90
	γ	90	90	90
		869.2552	404.5922	419.216
Nr. of monomer units/cell		8	4	4
Density		1.041	1.1183	1.0793
Elastic modulus	bulk	8.9634	8.8925	9.0074
	x	8.8109	8.3734	8.8628
	y	8.857	8.232	9.0085
	z (fibre axis)	121.8575	118.5674	120.6373

What would be the properties of gutta percha if molecular chains were uniaxially oriented?

Chain orientation by Melt- and Gel-spinning processes



GEL-SPINNING (Spinnig from dilute solution → high drawability)



One important condition for enabling solution-spinning is usually Mw > 1,000,000.
Mw of fresh Yellow-gutta and White-gutta (measured in 1995) was 450,000.
Mw of old tinned white-gutta (measured recently) was 250,000.

Is solution-spinning possible with fresh gutta?

Crystallisation behaviour of natural rubber and gutta percha

The melting temperature of natural rubber is not well determined.

From our experience of stretching smoked sheet by “racking method”, we know that stretched specimens, containing 10-18% crystalline parts, are stable in room temperature in Bogor (28-33^{o}C).

It would mean that the melting temperature of rubber must be >30^{o}C).

Natural rubber is usually amorphous, and said to be slow to crystallise.

The phenomenon of crystallisation includes two mechanisms:
(1) Nucleation (i.e., formation of nucleus)
(2) Growth (i.e., attaching of molecules on the existing nucleous or crystal).

From our experience, we feel that the growth rate itself is rather fast, whereas nucleation does not occur easily.

It is said that such sort of foreign substances as stearic acid facilitate crystallisation. It is probable that stearic acid particles acts as nuclei.

Doesn’t gutta percha serve itself as a nucleus for natural rubber?
Doesn’t the properties of natural rubber change, if a small amount (<1%) of gutta percha is added.

Fin