Thermoplastics

Early history of rubber

- The early source of rubber was the sap of the tree Hevea Brasiliensis from the Amazon rain forest.
- A Scotsman, Charles Macintosh found that an excellent waterproof fabric could be made by coating a cotton fabric with rubber latex in 1824.
- 1844 - Charles Goodyear discovered that the strength of a molded piece of rubber was greatly increased if some sulfur was mixed into it before it was molded in a hot press. Termed “Vulcanising.
- 1888 – John Dunlop invented the pneumatic tire.
- 1895 - Andre Michelin first put a pneumatic tire on an automobile.

Latex; Source of Rubber.

Use as is for dipped goods

Natural Rubber in Malaysia

- 1870’s - Henry Wickham collected 70,000 rubber-tree seeds from the Amazonian rain forest in Brazil, and sent them to London's Kew Gardens to be germinated.

- The seedlings were sent out to the British colonies and used to start the first plantation. For this, credit must go to a "crazy Englishman" Henry Nicholas Ridley then director of the Singapore Botanic Gardens. One of nine seedlings brought by Ridley in 1877 is still standing.

- This tree signalled the start of the rubber plantation era in the late 19th-20th Century, and turned Malaysia into the world's largest producer of natural rubber.

After World War 1

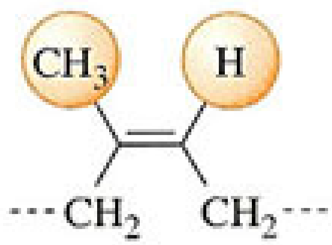
- Large need for rubber for tires because of the growth of the automobile industry.
- Security of the rubber supply became a concern, both in the US and Germany. Both set out to find an alternative in the chemistry lab.

Edison

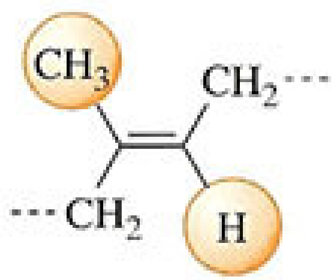
- In 1927 Thomas Edison, Henry Ford and Harvey Firestone founded the Edison Botanical Research Co of Fort Myers, FLA.
- One project at the Fort Myers laboratory was the search for a new botanical source of rubber.
- The best one found was Solidago, or Goldenrod

Solidago – Golden Rod

Structure of Natural Rubber



cis- polyisoprene



trans- polyisoprene

Also occurs naturally as chicle; used as chewing gum in S America. Not as resilient as the cis.

Isoprene is the repeat unit, the monomer. The natural polymer would be at least 15,000 repeat units.
Many other isoprene derivatives in the plant world: camphor, basil, bayberry, turpentine, menthol, lemon oil, rose oil, geraniol, citronella, etc

- But isoprene monomer is not easy to make and is expensive.
- It does not polymerise readily
- The laboratory made polymer made was not useful.

Wallace Carothers (1896-1937)

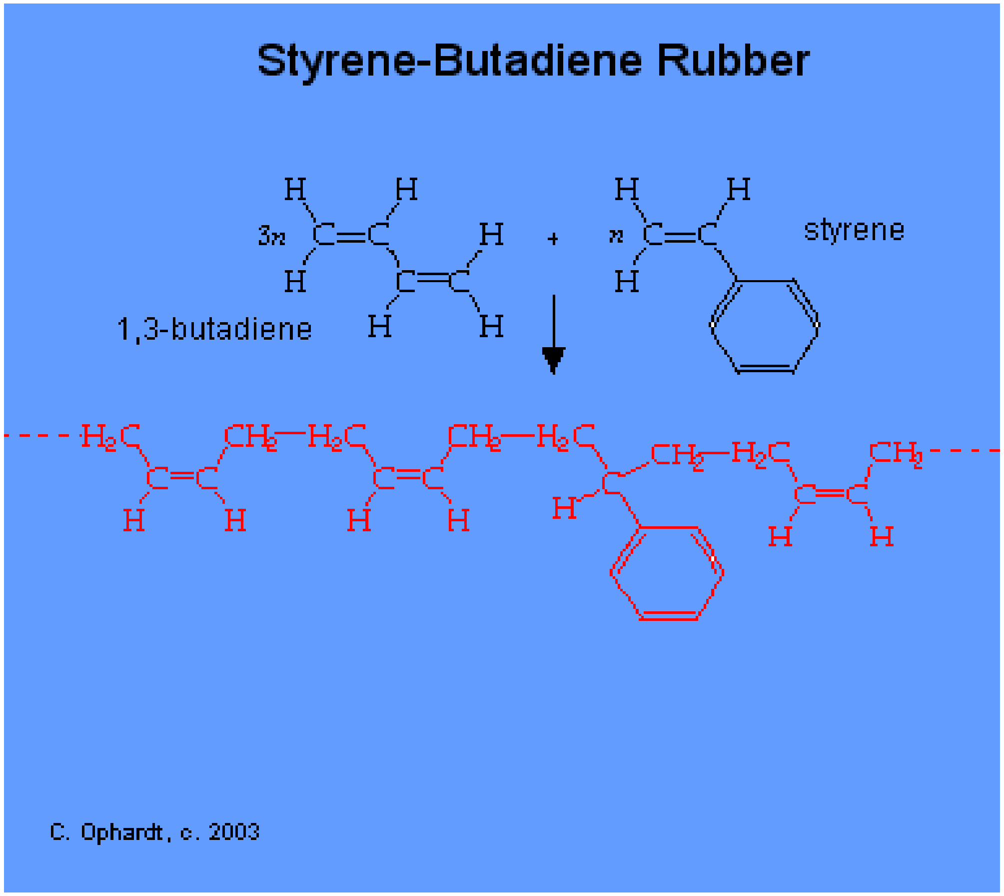
- Brilliant DuPont scientist.
- Made Neoprene in 1932, the first US made synthetic rubber.
- But Neoprene not resilient enough for tires. Still used for oil/solvent resistant gloves and hoses.
- He also invented Nylon in 1935, and contributed to theoretical understanding of polymers.
- Germans ahead at this time; made Buna rubber in 1927. Still used for tire sidewalls.

•Government sponsored R&D in the late 30’s found a copolymer of styrene and butadiene (1:3 ratio) to be the best candidate for use in tires, called SBR.

•Manufacturing process was as latex.

•Mfg plants estab-lished during WWII.

•After the war we found the Germans had discovered and used the same composition and process.



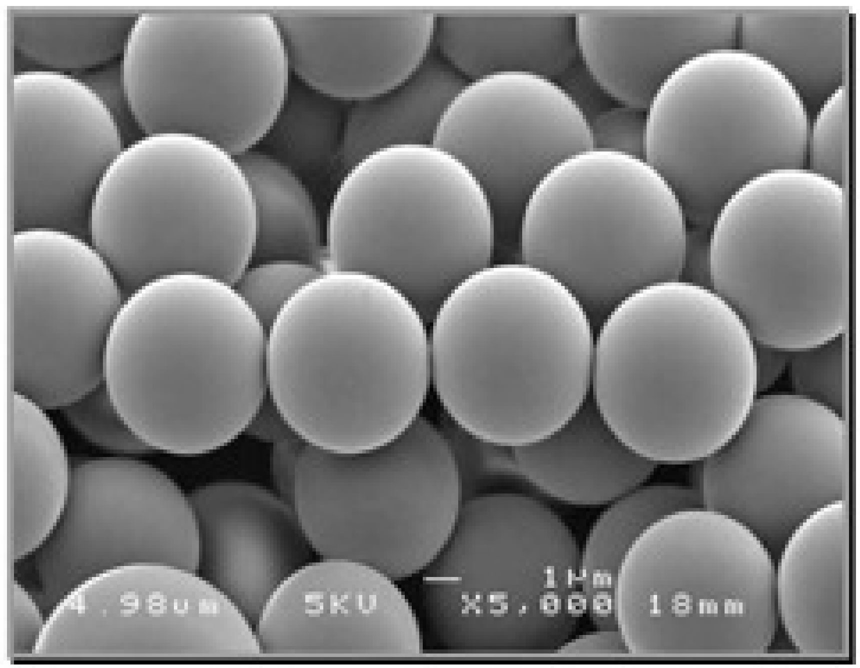
Polymerisation by Free Radical Chain Reaction

- A free radical is an extremely reactive species.
- After formation, it adds to a monomer immediately and randomly,
- But this creates a new radical.
- And so the process continues over and over; a chain reaction,
- It can easily add 15,000 monomer units in less than a second,
- Random, and both cis and trans.

Latex Polymerisation Process

- Water, soap, monomers and source of free radicals added to a reactor. Stir and cool.
- Tiny rubber particles form in the water from each radical.
- Soap is adsorbed onto the growing particle, stabilising it.
- After the monomer is used up, acid or alum added to destroy the soap and precipitate the polymer, and an antioxidant to destroy the free radicals.
- Wash polymer, filter and dry.

Polystyrene Latex



What makes Rubber Resilient?

- It must have very long molecules
- These naturally become entangled, ie like a big tangle of thousands of pieces of string.
- When rubber is stretched, the polymer chains straighten out, when released they spring back to their natural non-linear shape.
- But the tangles prevent it stretching infinitely.
- Prolonged gentle stretching causes some tangles to slip; Vulcanisation prevents this.

Post war, SBR Latex technology led to a large number of new materials:

<u>Applications for latex:</u>

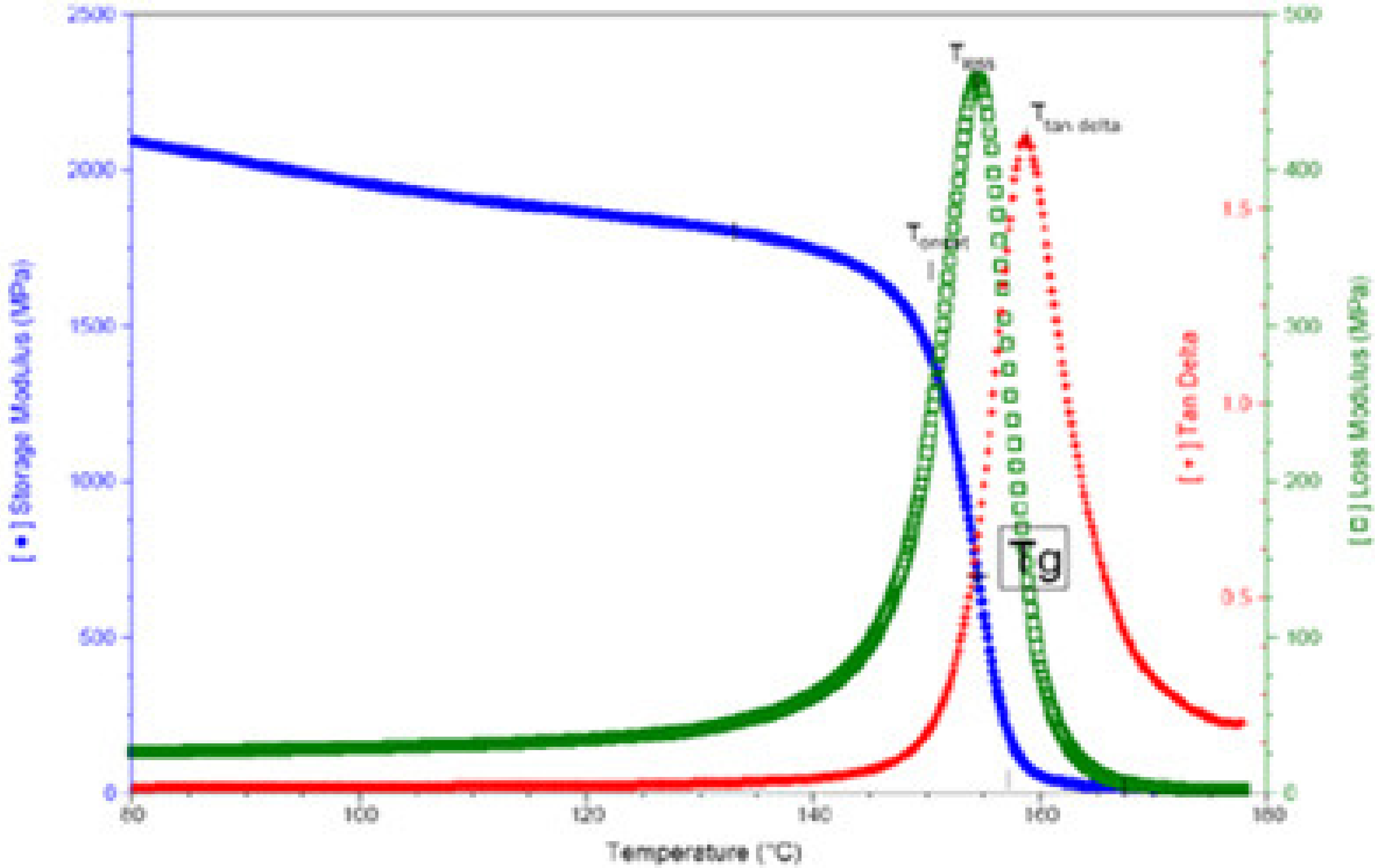
- Water-based coatings
- Water-based adhesives

<u>Other Useful Polymers:</u>

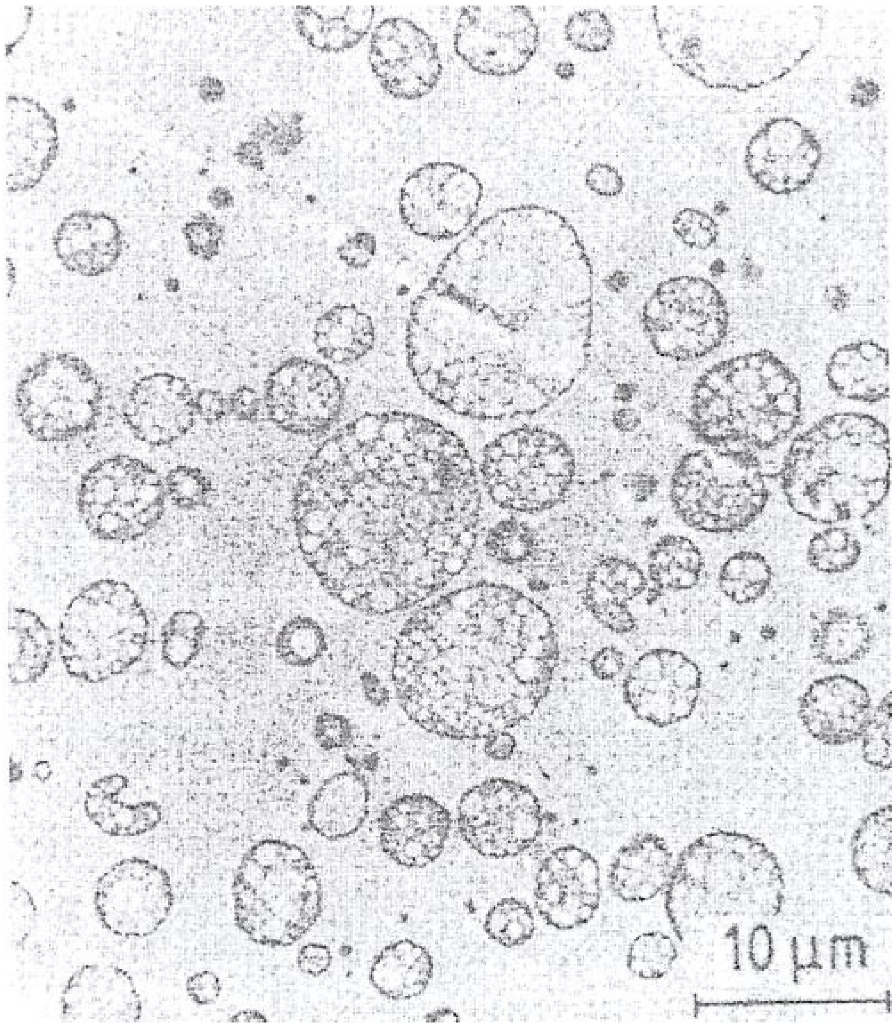
- Often tailored for specific uses or properties
- Next chart

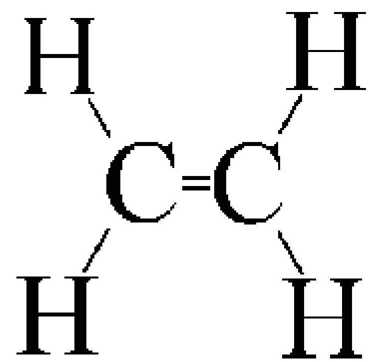
Name	Glass Transition Temperature, ^{0}C	Uses
Natural Rubber	-200	Tires, Latex gloves
Chloroprene	-40	Solvent resistant hose and gloves, Contact adhesive.
Polyvinyl acetate	32	Interior paint, Elmers glue
Polyacrylonitrile	97	Acrylic fiber
Polystyrene	100	Foamed Insulation, disposable cups.
Styrene-butadiene	-192 and -58	Tires, Paper coating, Carpet backing.
ABS and HIPS	Multiple	Football players helmets, auto parts
Polymethyl methacrylate	105	Plexiglas, exterior paint,
Polyethyl acrylate	-24	

Dynamic Mechanical Analysis Scan - Stiffness and Resilience versus Temperature



High Impact Polystyrene



But ethylene, 

the simplest, cheapest, most readily available monomer, does not polymerise this way. Requires high temperature and pressure.