

THE MANUFACTURE OF RUBBER GOODS

Rubber has the properties of flexibility, strength and elasticity. Natural rubber is obtained from the rubber tree and is poly-*cis*-1,4-isoprene. Several kind of synthetic rubbers are also imported.

Vulcanisation is the process whereby the polymer chains of the rubbers are cross-linked, making use of the double bond present. Sulphur is the most common cross-linking substance.

A variety of other compounds are added to give the final rubber product the required properties.

INTRODUCTION

Rubber is a widely used material having properties of flexibility, strength and elasticity. The basic raw material, either natural rubber or synthetic rubber, is imported into New Zealand in latex or solid form, and processed into many different products.

The raw rubbers, composed essentially of long polymer chains, are joined together with "crosslinks" in a process called vulcanisation to give the final material its characteristic properties.

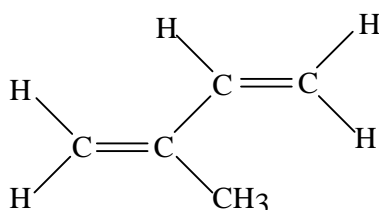
RAW MATERIALS

Natural rubber

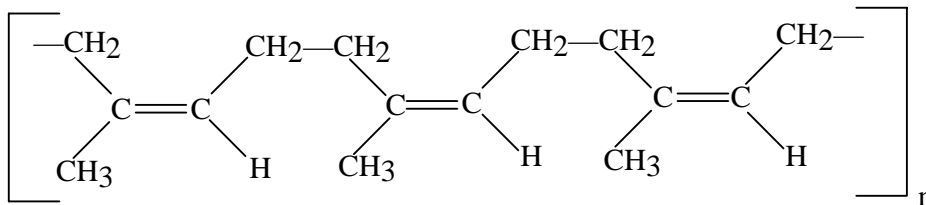
Natural rubber is obtained from the rubber tree *Hevea brasiliensis* by tapping the bark. 50-60 g of the sticky liquid or latex is obtained from each established tree per day (30 trees would produce about 100 kg of dry raw rubber per year). The rubber content of this latex is 30-45%. If it is to be exported in latex form it is concentrated by centrifugation and stabilised by the addition of ammonia. The latex is a lyophobic sol with the latex particles negatively charged. Polyvalent ionic salts, water soluble organic compounds and acids, e.g. formic or acetic acid solutions, cause the latex to coagulate and precipitate out.

Latex imported into New Zealand is about 60% rubber and the solid is imported as slabs, sheets or fine crumb.

Natural rubber is poly-*cis*-1,4-isoprene, and is highly stereoregular. Isoprene (2-methyl-1,4-butadiene) has the structure



and the polymer is



At least 97% of the rubber has isoprene units in the cis configuration and the molar mass varies between 10^5 and $4 \times 10^6 \text{ g mol}^{-1}$. Natural rubber has two features which influence its physical properties and hence its uses.

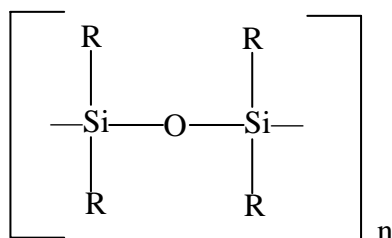
- Rotation about the C-C single bond is possible. In normal rubber the polymer chain is coiled up by rotation about these bonds into random structures. Under stress the molecular chain uncoils and a more regular folded structure results. On release of the stress the molecules rapidly recover their coiled up randomness.
- For each isoprene unit there is one double bond which imparts chemical reactivity.

Natural rubber hardens below 0°C and softens and weakens above 80°C , losing its strength and becoming tacky. In between these temperatures it can flow under stress and permanent deformation occurs under prolonged strain.

These undesirable properties are reduced by vulcanisation, in which the reactivity the double bonds impart to the molecule is utilised to make it react with added material to form crosslinks between the chains. The crosslinking increases the useful temperature range of the rubber and hardens the rubber so that it becomes much stronger and does not creep but returns to its original shape on release of stress. Its surface properties are improved and its solubility decreased. Sulphur is still the most important vulcanising compound for natural rubber, but not the only one.

Synthetic rubber

The many raw synthetic rubbers imported into New Zealand have been made overseas by the polymerisation of appropriate monomers. The raw rubbers include butadiene rubber, butyl rubber (isobuteneisoprene copolymer), synthetic isoprene rubber, ethylene-propylene rubbers, chloroprene rubber (the methyl group of isoprene is replaced by chlorine), nitrile rubbers (acrylonitrile-butadiene copolymer), styrene-butadiene rubber, and silicone rubbers which are polysiloxanes,



Rubbers suitable for many different jobs can be made from the appropriate raw material.

New Zealand's annual imports of raw rubber exceed 20 000 tonnes, with the ratio of synthetic to natural rubber now approaching two to one.

GENERAL RUBBER TECHNOLOGY

From latex

Compounds added to the raw latex must be in the form of emulsions or dispersions. They are prepared by milling the substances with distilled or softened water in ball or gravel mills (cylinders half to two-thirds filled with a grinding charge, glass or porcelain balls, or flint gravel), which revolve for anything from a few hours up to several days. Gelatin, casein, glues, soaps etc. are used as wetting or dispersing agents. Substances added are softeners, fillers, pigments for colour, the vulcanising agents and antioxidants.

The latex itself has to be stabilised with surface-active agents to prevent coagulation which can be irreversible. These agents act by imparting a charge (negative or positive) to the surface of the minute rubber particles or by holding an envelope of water around the particle, thereby preventing any mixing.

The compounding materials and the latex are mixed and are then ready for dipping, moulding, foaming or spreading.

- *Dipping* - In this process a "former" the shape of the article to be produced is dipped into the compounded latex (often more than once) and the film that coats the former is dried, cured (in an oven or by a stream of hot air) and stripped from the former. Gloves, testtubes, teets, bathing caps, bladders for balls etc. are made this way.
- *Moulding* - Plastic or metal moulds are used to make solid articles.
- *Foaming* - Air is usually beaten into the latex mechanically, the latex set by a sensitising agent (e.g. ammonium acetate) and immediately cured.
- *Spreading* - The latex mixture is applied to cloth or other surfaces (e.g. raincoats). The degree of penetration must be exactly right and the viscosity finely controlled. Carpet backings and adhesive surfaces are important examples. Here, the curing occurs at room temperature.

From dry rubbers

The production sequence is mixing, forming and vulcanising. The solid rubber and the other materials (similar to those emulsified or dispersed in the latex process) have to be mixed. This is done with two basic machines, a two-roll mill in which the material is passed between two heavy metal rollers mounted horizontally, and a Banbury mixer, an internal mixer in which the materials are sheared between the internal rollers and the inside of the casing. The machines are driven by powerful electric motors and water cooling is necessary because much heat is produced in the mixing materials. This could cause premature vulcanisation, called "scorching".

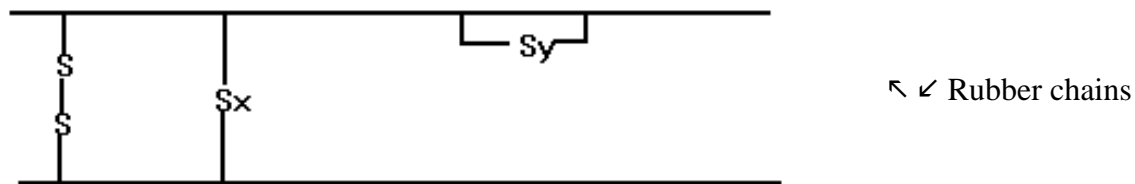
There are four basic methods of forming the material to the required shape; spreading onto fabric from solution, extruding, calendering (passing between rollers) and moulding. Examples of products from the different methods are - spreading: waterproof sheeting; extrusion through a dye: tubes, cords or profiled shapes; calendering: sheeting or coated fabric; moulding: solid rubber articles. The production of car tyres involves all four processes.

Vulcanising from the manufacturers point of view is applying heat at a given temperature for a given time to cure the product so it takes up its shape. Curing involves the chemical reactions which occur in the rubber mixture to produce the crosslinking. Heating can be done in the mould using steam, or in autoclaves, ovens, using hot gases etc.

THE CHEMISTRY OF VULCANISATION

Vulcanisation

Sulphur vulcanisation, the most common form, involves the formation of polysulphide crosslinks between the chains. Both crosslinks and cyclic structures can form:

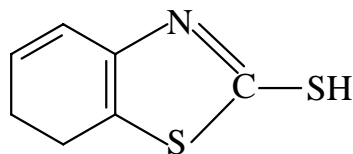


If sulphur only is used, curing times of 8 hours are necessary. Modern methods using "activators" and "accelerators" reduce the curing time, eliminate cyclic structures and can shorten the sulphur links down to one or two sulphur atoms. Shorter sulphur links give greater stability to heat and improve the ageing properties.

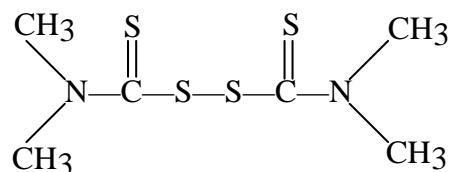
The activators and accelerators are used up in the process and some accelerators can replace elemental sulphur altogether. A typical vulcanising system in parts by weight would be:

Raw rubber	100	
Zinc oxide	6.0	} activators
Stearic acid	0.5	
Mercaptobenzthiazole	0.5	accelerator
Sulphur	3.5	

Mercaptobenzthiazole has the structure shown below and is just one of many accelerators in use.



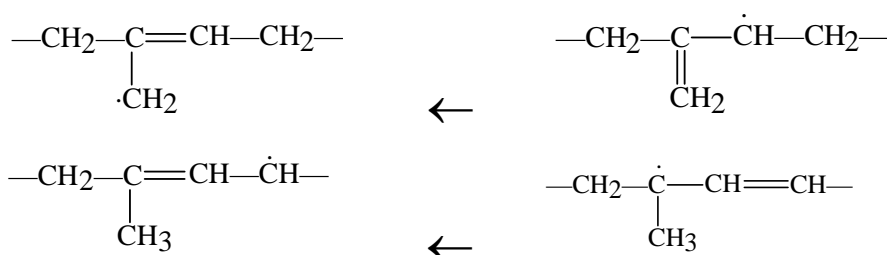
Tetramethylthiuramdisulphide (TMTD),



can function alone without sulphur, but it is a powerful accelerator with sulphur.

If acceleration is too great, vulcanisation can occur before the material is shaped - "scorching".

The chemistry of the process is not well understood. Possibly the stearic acid reacts with the zinc oxide to give a zinc soap which leads to the formation of zinc salts of the activators, and these in turn attack the rubber chains, probably at the allylic hydrogen. The allylic hydrogen is attached to a carbon atom next to the double bond, and is reactive because free radicals formed by hydrogen atoms being lost are resonance stabilised.



Other compounding agents

Fillers

Fillers range from inert dilutants such as whiting, talc, clays, CaCO₃, etc. which "cheapen" the product and make it go further, to reinforcing fillers which increase tensile strength and abrasion resistance.

Carbon black is a most important reinforcing agent in tyres and tubes and is usually produced by burning oil or natural gas in a limited supply of oxygen. It is imported and it makes up to 30% of the tyre composition.

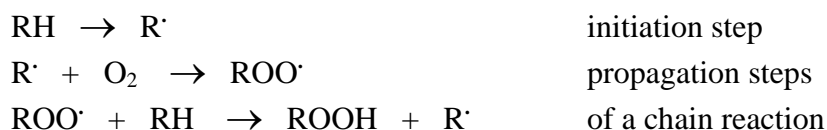
For white or coloured products, silica, china clays and light magnesium carbonate are useful reinforcing agents, but inferior to carbon black in abrasive resistance.

Fibrous fillers such as cotton flock, asbestos and synthetic resins can be used for special purposes.

Colour can be imparted by the addition of pigments.

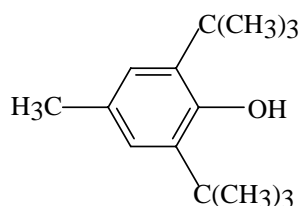
Protective agents

Protective agents prevent ageing or deterioration, which comes about mainly by oxidation. One important reaction is autoxidation resulting in replacing allylic H's by —OOH groups in a chain reaction:



The hydroperoxides can break down in reactions giving scission of the polymer chains and producing more free radicals which can initiate further autoxidation. Thus, ageing can be "autocatalytic".

Antioxidants react preferentially with the ROO· radicals to give stable free radicals, thus breaking the chain reaction. They are usually aromatic amines and ring-substituted phenols, e.g.



Ozone attacks the double bonds of the polymer chains breaking them at these bonds and "antiozonants" are known. Trace amounts of certain metal ions can hasten oxidation, partially by reaction with the hydroperoxide to give free radicals. Sequestering agents added form complexes with these metal ions, rendering them unreactive.

Softeners and lubricants

Softeners and lubricants, in the form of stearic acid, waxes, mineral oils, tars, etc. are added to plasticise or increase self-adhesion of the rubber mix. Certain resins increase the tackiness of the rubber for use on adhesion tapes.

TYPICAL FORMULATIONS

The following are two typical formulations.

For dipping (latex formulation) - relative dry weight.

NH ₃ - preserved latex	100	
stabiliser	0.2	
sulphur	1.0	vulcanising agent
zinc oxide	1.5	activator
zinc dithiocarbamate	1.0	accelerator
trialkylphenol	1.0	antioxidant
pigment	1.0	

Cure: 30 minutes at 100°C in air

For tyre manufacture - relative weights

natural rubber	100	
zinc oxide	4	acticator
stearic acid	3	activator
carbon black	50	reinforcer
process oil	5	processing acid
N-phenyl-N-t-butyl-p-phenylenediamine	1	antioxidant
cyclohexyl thiazyl-sulphenamide	0.5	accelerator
sulphur	2.5	vulcanising agent

Cure: 30 minutes at 148°C.

This is the original article written by John Packer from essays by J. Little and S.J. Kast (Chemistry 100 students) who visited U.E.B. Shack Rubber and Reidrubber in Auckland, and from J. Mills (Christ's College) who visited Empire Rubber Mills in Christchurch. The help from these three companies is gratefully acknowledged.