

CHAPTER I

INTRODUCTION

1.1 General aspects

Thailand is the largest natural rubber producing country with a NR production of more than 1.5 million tons in 1994. The world production is shown in Table 1.1. It is rapidly increasing every year. In 1998, Thailand produced 2,075,950 tons of natural rubber, but only 186,379 tons were used by the local rubber industry, the rest as exported. The major exported rubber products in 1998 were rubber tires 37% and rubber gloves 36%, valued in excess of 25,000 million baht, or 75% of export.

Table 1.1: World production of natural rubber (1994) [1]

Country	Tons ($\times 10^3$)	% of world production
Thailand	1.50	27.62
Indonesia	1.35	24.86
Malaysia	1.07	19.71
India	0.425	7.83
China	0.325	5.99
Philippines	0.172	3.17
Sri Lanka	0.106	1.95
Others	0.482	8.87
Total	5.43	100.00

The world price of NR is greatly depending on the demand for rubber for the tire industry. This situation is not favorable for the NR exporting countries because the tire industries fluctuate due to the fluctuation of the world economy.

To avoid the crises and instabilities caused by this situation which strongly affects our NR production and in order to get the maximum foreign exchange earning from NR, research and development are necessary for the continued prosperity of NR plantation in Thailand. One way of doing this is to chemically modify NR, thus opening up a new field in the development of rubber derivatives.

Chlorinated rubber is one of rubber modifications which had long been used in the paint, adhesive, and printing ink industries. It is imported from Europe and America. Thailand uses approximately 120 tons per year and cost more than 12 million baht.

1.2 Reactions of natural rubber

NR is obtained by the coagulation of the milky aqueous dispersion of rubber called latex which is produced by the tree *Hevea Basillensis*. The formula of NR molecules is $(C_5H_8)_n$, when n is about 40,000-50,000 and C_5H_8 is isoprene monomer. Because of the unsaturated nature of polyisoprene, NR must be considered as a chemical compound which can be attacked by other reactive molecules and the reactions can be cationic, anionic or free radical. Among the oldest known reactions concerning natural rubber, the attention must be drawn to vulcanization. Its principle is based on the creation, mainly on the double bond neighbouring atoms, of intermolecular sulphur linkage. Various interpretations of vulcanization have been proposed in literature; either a radical type (Figure 1.1) or anionic type process (Figure 1.2). [2]

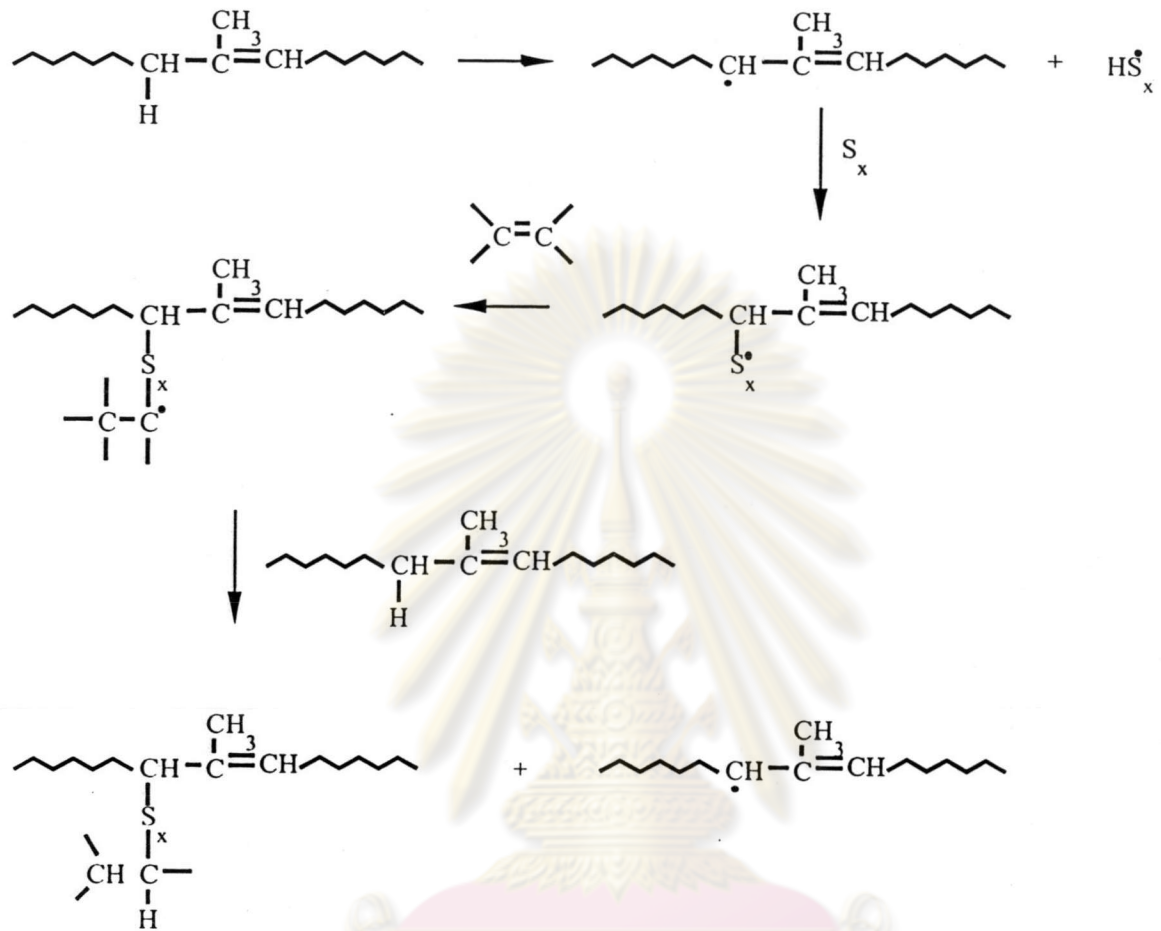


Figure 1.1 Mechanism involving free radicals

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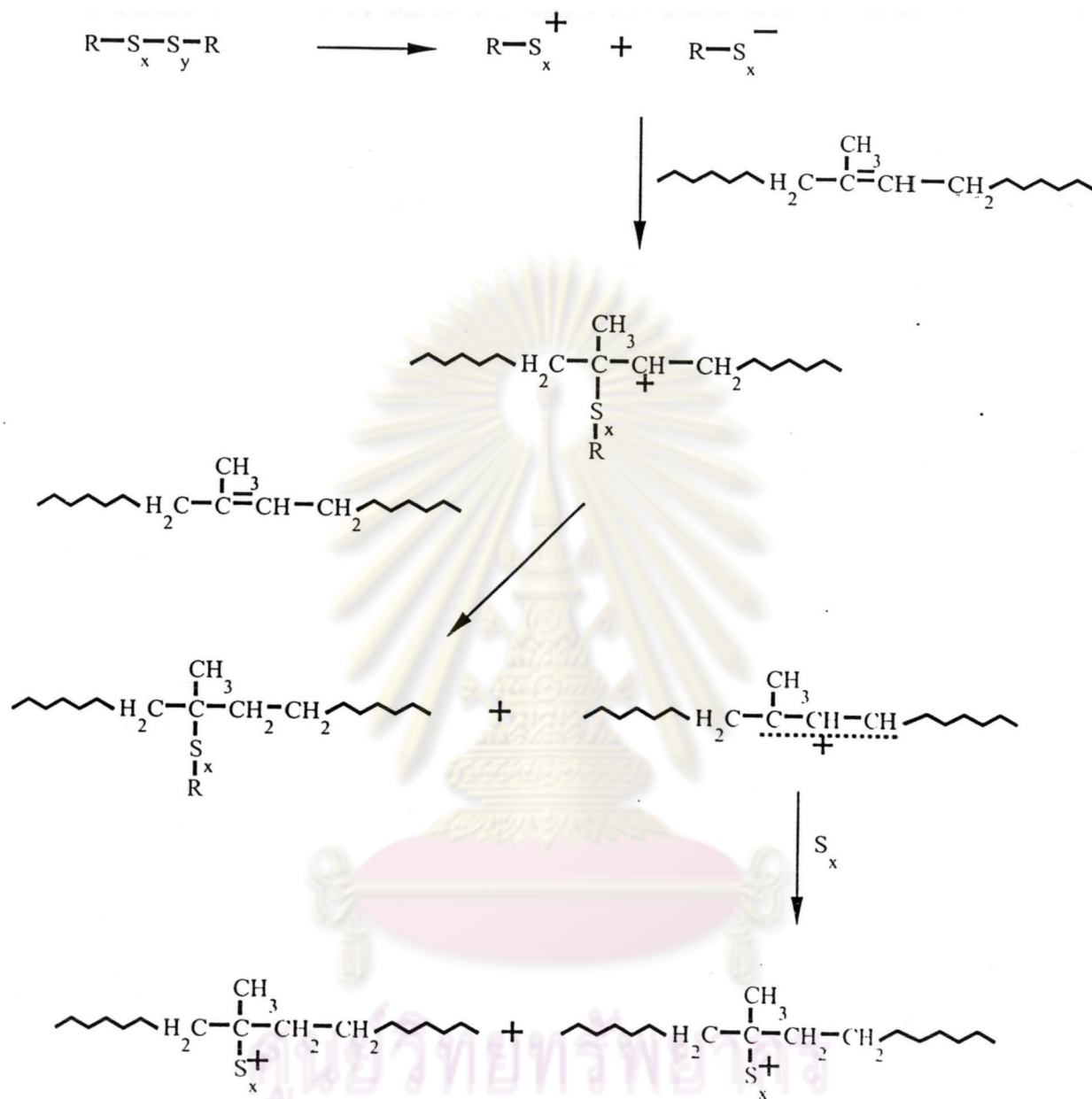


Figure 1.2 Mechanism involving ions

Rubber has been modified in many ways, and modified forms have been available commercially since 1915. The best known types of modification can be divided into 6 groups.

a) Cyclized rubber [3]

The first one is called cyclized rubber is probably the oldest known modification of rubber. In 1791, Leonhardi discovered that rubber becomes hard and brittle when treated with sulfuric acid. Similar observations were made at the beginning of the 1920s, but only in 1927 did Fischer investigate thoroughly the reaction of rubber with organic sulfonic acids, sulfonyl chloride, and sulfates. At the same time Bruson, Sebrell, and Calvert found that cyclized rubber is also obtained from reaction of rubber with zinc chloride. The mechanism of this internal cyclization is not completely understood. A suggestion based on the results of M. Fordon was worked out in 1956 by Bloomfield and Stokes. The reaction employs the unsaturated isoprene unit of natural rubber, the protonation reaction occurs in the acid environment. Cyclized rubber has been applied in the fields of emulsion paints and reinforcing filler. The cyclization mechanism of polyisoprene is shown in Figure 1.3.

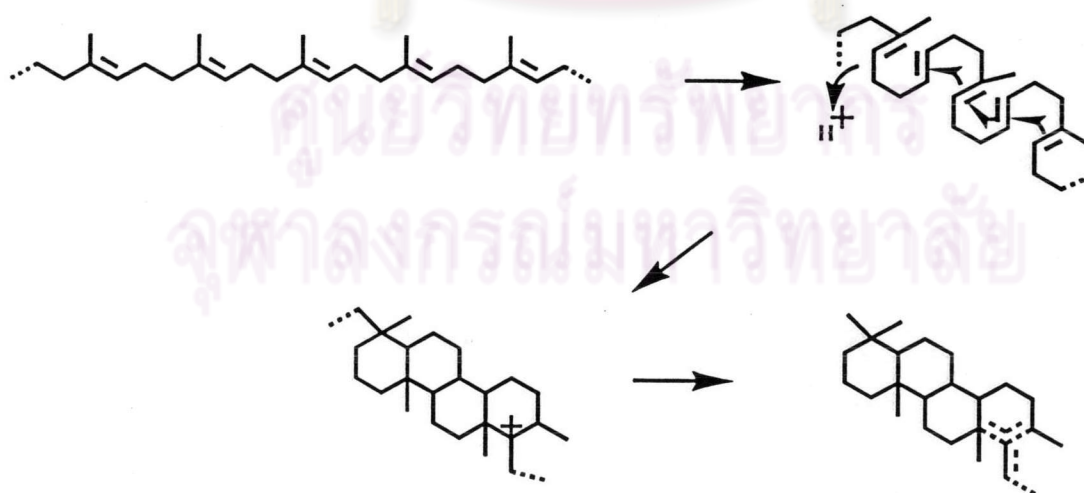


Figure 1.3 Cyclisation mechanism of polyisoprene

b) Epoxidised rubber

The second type of modification is epoxidised rubber which is used industrially. Epoxidising natural rubber leads to a certain number of advantages such as oil resistant products, adhesives, inner tubes, tyre liners and belting. The reaction of natural rubber epoxidation is shown in Figure 1.4.



Figure 1.4 Epoxidation of natural rubber

The epoxidation reaction is interesting that it allows the introductions of polar chains and the rate of epoxidation can be easily controlled. It must be pointed out, however, that in the case of modifications over 50% several secondary reactions can be observed (Figure 1.5).

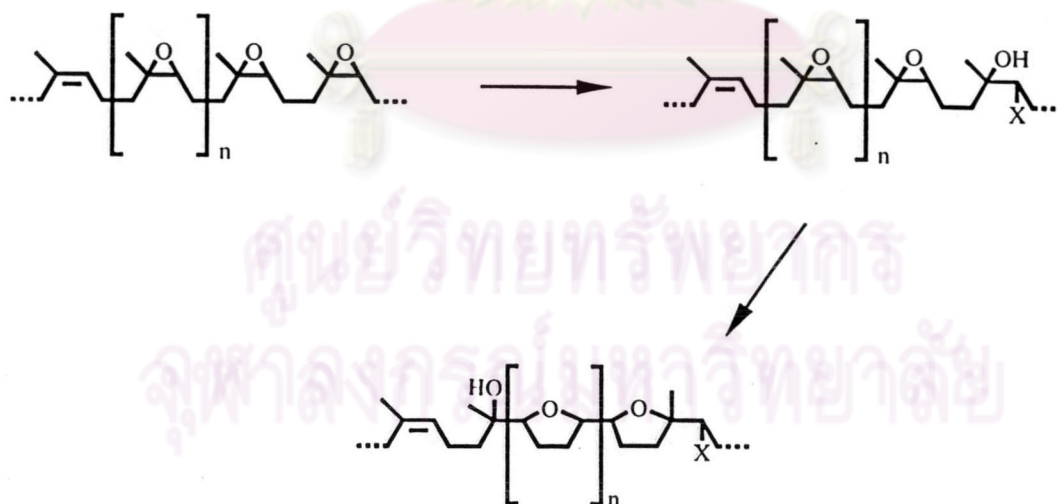


Figure 1.5 Epoxidation of natural rubber : secondary reactions

c) Grafting rubber

Amongst the products brought about by chemical modification of NR, are those which come from grafting on to the polyisoprene chain. This involves a chemical reaction of the C=C unsaturated atoms and in this case the grafting reaction is governed by a radical process.

An industrial development is "*Heveaplus*" obtained from NR by grafting with methylmethacrylate (MMA). Compared to vulcanized rubber, these materials present some interesting changes in hardness. They can be mixed with NR, improving its electrical characteristics, adhesive properties, and tear resistance.

d) Hydrogenated rubber [4]

Hydrogenated rubber is so far only a scientific curiosity, since it has never been product commercially on account of the experimental problems associated with its preparation. The early processes required either highly purified rubber in dilute solution or the use of very high temperature that caused degradation. In addition, hydrogenation requires its catalyst to come into contact with each double bond for the reaction, and thus relatively large amounts of catalyst are essential if the hydrogenation is to be completed in a reasonable period of time. In addition, all traces of catalyst must be removed to avoid rapid oxidation of the product.

Hydrogenated rubber is colorless and transparent. It is a plastic elastic waxy solid with the peculiar characteristics of pulling out into fine threads when stretched. Unfortunately, the limited scale of its preparation has so far precluded the serious measurement of any technological properties. It is known the fully hydrogenated NR is unaffected by the chemical reagents that normally attack unmodified natural rubber. This is due to the removal of the unsaturated molecules. However, this also results in it being difficult to vulcanize in the conventional manner. Potential applications to have been considered are tubes in the cable industry, which would utilize its insulation properties, and possibly in adhesives.

e) Hydrohalogenated rubber [4]

Natural rubber can be modified with hydrogen chloride, bromide, iodide, or fluoride to give rubber hydrochloride, rubber hydro bromide, rubber hydroiodide and rubber hydrofluoride, respectively. However, the latter three are of theoretical interest only, since the reaction with hydrogen chloride is the cheapest and by far the most feasible; the hydrobromide product is unstable, the HI addition has received only limited attention, and HF is highly toxic. The attraction of such a modification is the same as that of halogenation itself, to reduce the chemical reactivity of rubber by addition to its double bonds.

f) Chlorinated rubber

Another result of modification of NR, which has undergone and still receives attention is chlorination which gives rise to complex reactions, because of the possibility of the cyclisation as well as addition and substitution. The products resulting from these reactions are used industrially as anticorrosive paints, adhesive, printing, ink, etc..

The chemical structure and properties of chlorinated natural rubber will be discussed later in detail. Commercially available chlorinated rubber is produced by dissolving NR in a solvent chlorinating the solution. The toxicity of some of the solvents (e.g. carbon tetrachloride) is a major concern.

Chlorinated rubber was first marketed in Great Britain in 1921 as Duroprene. This was later followed by Tornesit, Alloprene, Parlon, etc. The main reasons for success of chlorinated rubbers are:

i) It forms hard, inert films that are resistant to alkaline and acidic agents and to mould growth. In surface coating it can either be modified with inert plasticisers or be used to increase the wear resistance of softer resins.

ii) Chlorination rubber films have high specific adhesion to many surfaces.

iii) The water-vapor permeability of the film is low, about one-tenth of that of alkyd resins.

iv) Chlorinated rubber has excellent solvent release properties, shown by its use in high-speed gravure inks.

v) The products can be fire retardant.

vi) Paints based on chlorinated rubber are extremely durable and can be overpainted with complete satisfaction even after 10 years.

The chemical modification of NR was received by Coe in a paper given at King Mongkut Institute of Technology (1997). In addition to established chemistry. The work in the present thesis was intended to explore one of these topics. [4]

Chlorinated rubber is useful and profitable chemical, would it be possible to make it by some other method-possibly in water?

It would be a potentially much cheaper route than that followed at present; there could however be some hazards if the ammonia present is not removed. If it were possible to use skim rubber or skim latex the cost savings would be even greater.

Partially halogenated natural rubber and Neoprene seem in the past to have been ignored for no obvious reason. Both should be relatively straightforward to do in solution-a good example of a probably uneconomic academic approach being cleaner, simpler and safer than the clearly preferable route direct from latex.

The addition of hydrogen chloride, hydrogen bromide or hydrogen iodide could be more attractive as there might be complications from having halogen atoms adjacent on the molecule. The chemistry of doing this is likely to be possible under pressure. The scientific literature should also provide some guidance.

It would be possible to exchange chlorine or bromine atoms for iodine which is far more reactive. An iodinated material would react with metals such as magnesium to give organo-metallic materials; they could be substituted by amines which would react with isocyanates, the possible route to reduce flammability.

In case of Neoprene it is possible that one might be able to make a direct substitution of existing halogen. Polychloroprene, to give Neoprene its more correct name exists in most of the various isomeric forms and one of these contains an allylic chlorine which is reactive. It makes up approximately 3.5% of the chlorine and is the species which enters into cross-linking reactions. It should be possible to substitute this chlorine by iodine by simple reaction with potassium iodide maybe even in latex. This would give the reactive species that was sought in the other reactions.

1.3 Objective and scope of this research

Commercial chlorinated rubbers have chlorine content 60-75%. The product obtained is white powder. However, nobody appears to have studied the properties of chlorinated rubbers with different chlorine content and their film forming character. Chlorinated rubber film with a high chlorine content usually has a cracking problem. Hence, we decided to study the properties of chlorinated rubber with low chlorine content to be prepared by a process avoiding solvents. Thus the following were studied.

a) Preparation of chlorinated rubbers

Partially chlorinated rubbers in different low chlorine contents were prepared from natural rubber latex, pre-vulcanized rubber latex and polychloroprene rubber latex. The chlorination took place at room temperature under nitrogen atmosphere by using chlorine gas.

b) Some properties of chlorinated rubbers

Some physical properties and chemical properties of partially chlorinated rubbers were studied i.e. film forming, solubility, water and chemical resistance, ozone resistance, thermal stability, permanent set, and morphology.



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