

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Background of chlorinated rubbers

The first preparation of chlorinated rubber was generally attributed to Roxburgh, in 1801, who passed a stream of chlorine gas into a solution of rubber in carbon disulphide. However, as chlorine reacts with carbon disulphide to form sulphur monochloride, which is itself highly reactive towards rubber, the nature of the reaction product is open to doubt. Parkes (1846) later mentioned that chlorine be used as a vulcanising agent in the cold. Englehard and Day (1859) described a series of chlorinated rubber in the absence of air, or by bubbling chlorine through a solution of rubber in an organic solvent. The products ranged from flexible leather-like materials to brittle white masses. Since then, many different techniques have been used for producing chlorinated rubber.

A solution method is the most important which is treatment of a solution of rubber in organic solvent such as chloroform or carbon tetrachloride with chlorine. When performing the chlorination by solution method, not only expensive chlorine-containing organic solvent must be used in large quantities, which is uneconomic, but also complete separation and recovery of the chlorine-containing solvent from the product are difficult, and if it is admixed with the product or it is volatilized it will escape into the atmosphere. It is also known that the chlorine-containing organic solvent represented by carbon tetrachloride is injurious to the human body and it has a danger to destroy the ozone layer as well, so it very probable that it can not be used in the future. The chlorination by solution method adopted traditionally has therefore serious problems as described above.

On the other hand, according to the conventional process in which a polyisoprene rubber is dispersed or emulsified in water before its chlorination, even chlorination is difficult. In addition, rubber particles tend to aggregate in the course of the chlorination, and there is a problem that the resultant chlorinated rubber is hard to be dissolved in a traditional solvent such as toluene.

Since 1992 the chlorination of rubber in an aqueous medium without causing aggregation of particles has been suggested to prepare highly chlorinated rubber.

## **2.2 Application of chlorinated rubbers [5]**

### **a) Paints and varnishes**

The main use of chlorinated rubber has been in the field of chemical and heat resistant paints, varnishes, and lacquers. For this purpose the chlorinated rubber is dispersed in an organic solvent, such as ethyl or buthyl acetate, toluene, xylene, together with appropriate plasticisers and pigments. Such paint and varnishes can be applied by brushing or dipping and, in most cases, by spraying. The maximum concentration of chlorinated rubber of spraying is ca. 10-12 % and the total solid content may be 30-40 %. The finishes adhere well to, and are used for the protection of, wood, stone, cement, plaster, and steel. Protection is particularly good against severe weathering conditions, seawater, chemical fumes, and in some cases, against attack by fungi, termites, etc. Among specific uses are the protection of structural steelwork against many chemicals. Properly compounded paint films are claimed to resist the action of 5-50 % sodium hydroxide, 5-95 % sulphuric acid, 85 % phosphoric acid, chlorine, sulphur dioxide, and ammonia.

b) Chemical-resistant finishes [6]

Protective coatings based on chlorinated rubber are particularly adapted to those industries where the problems of corrosion is of paramount important, as pulp and paper mills, where equipment is continuously exposed to high humidities, acid vapors, alkalies and other destructive agents. Chlorinated rubber finishes are also becoming standard materials in the petroleum, steel, textile, gas, mining, good, and other industries where maximum resistance to corrosive agents is required. Owing to the excellent bacterial attacked resistant properties of chlorinated rubber, the food industry will undoubtedly find the use of this type of coating an excellent means of solving some of its most annoying problems. Properly formulated chlorinated rubber coating have amply demonstrated their chemical resistance to both dilute and concentrated solutions of the following: caustic soda, up to 75 %, sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, lactic acid, formic acid, and many others.

c) Films and impregnated materials

Chlorinated rubber has been used for the manufacture of unsupported film and for impregnating fabrics and paper. Such materials are waterproof, flame resistant, and petro-resistant. They also possess electrical properties, which render them attractive. Electrical strengths of the order of 2,500 V/mm (4mm sheet) with a power factor of 0.003 at 1,000 c/s and permittivity ca. 3.0 have been reported. Water permeability figures of 0.12 mg/h/in<sup>2</sup>.

d) Expanded chlorinated rubber

Porous slabs and sleeves have been used for thermal insulation, particularly at low temperature. Thermal conductivity valued compare satisfactory with those of glass wool and granulated cork, while apparent densities are appreciably

lower than for these materials. Such expanded products are made by heating under a pressure which is reduced suddenly.

#### e) Moulding

Although chlorinated rubber is not sufficiently thermoplastic alone, the addition of a plasticiser, particularly tricresyl phosphate, gives a material, which can be moulded under pressure at 120-150 °C. Such mouldings are opaque if the pressure is released before cooling. If cooled under pressure, these mouldings are translucent, although normally pale brown in color. Almost colorless products are obtainable from the moulding of chlorinated deproteinised rubber. Useful moulding powders have also been made by treating a solution of chlorinated rubber with phenol and formaldehyde. The properties of moldings can be also varied by the addition of fillers.

#### f) Adhesives [7]

The chlorinated rubber has become an important ingredient in various types of adhesives. Preparations using this base are unusually specialized owing to their chemical resistance, water resistance, and mildew resistance.

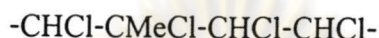
### 2.3 Chemical structure of chlorinated rubbers

By analogy with chlorine and simple olefins, it might be thought that direct addition of the halogen to the isoprene double bond take place, thus;



This would give a product containing 51% of chlorine but since chlorinated rubber invariably contains ca. 65% of chlorine. This simple reaction can not be true.

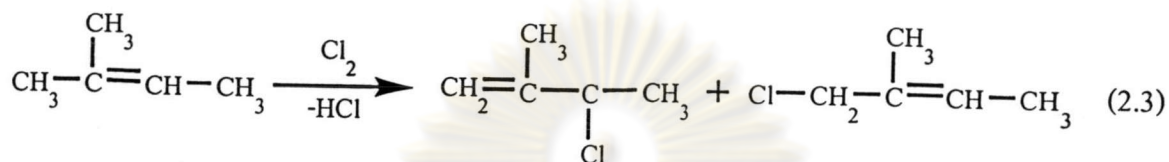
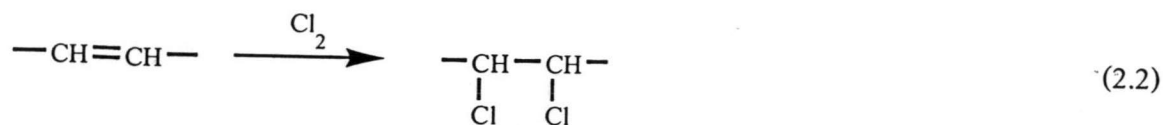
Gladstone and Hibbert (1888) first noticed that halogen chloride gas was evolved in the initial stages of the reaction. As hydrogen chloride evolution is normally diagnostic of a substitution process, they suggested that the reaction involved both addition and substitution, and allotted the following structure to their product, which contained 68% chlorine.



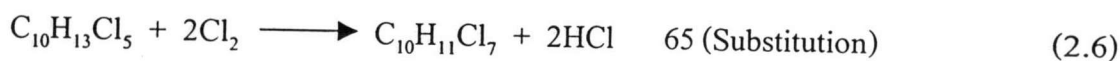
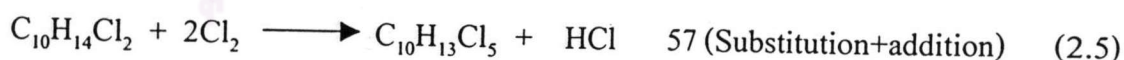
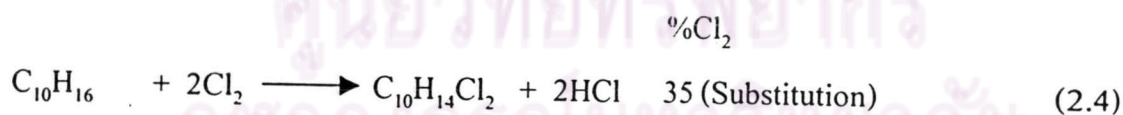
MacGavack (1923) later carried out a more systematic investigation of the process. He measured the amount of chlorine adsorbed and hydrogen chloride evolved in the course of reaction and showed that the first stage was almost exclusively one of substitution and addition with chloroform as solvent, the final product contained 65% of chlorine and as the empirical formula  $\text{C}_{10}\text{H}_{13}\text{Cl}_7$ . These results were confirmed by Baxter (1936) [8], who carried out a cursory kinetic investigation of the reaction in solution at  $60^\circ\text{C}$ . Under this condition, it was found that substitution was the only reactions occur during the first two hours. This was followed by rapid simultaneous substitution and addition until each  $\text{C}_{10}\text{H}_{16}$  unit had taken up three chlorine atoms by substitution and four chlorine atoms by addition. At this stage, reaction was virtually complete (65% of chlorine) and any further changes were slow and of a minor character.

This situation at this period was intriguing, since it suggested that each isoprene residue is chemically combined with a fractional number of chlorine atoms (i.e.  $3\frac{1}{2}$ ). This, in term, could only mean that the rubber molecule behaves chemically as if it obtains repeating functional units of  $\text{C}_{10}\text{H}_{16}$  instead of the accepted  $\text{C}_5\text{H}_8$  residue. Fully chlorinated natural rubber contains about 65% chlorine compared with the 51% that would be obtained if the only reaction were one of addition. Hence at some stage some substitution is necessary. This is not altogether surprising since

although linear alkenes give predominantly addition products (1), alkenes branched at the double bond give predominantly allylic substitution, for example as with 2-methyl-2-butene (2). [8]



This aspect of the problem was not solved until Bloomfield (1943) [9] investigated the reaction under better controlled conditions. In general, his results confirmed the conclusions of previous workers and he showed that the first molecule of chlorine (per isoprene residue) was taken up exclusively in substitution. The second molecule, in simultaneous substitution and addition, and the third molecule in substitution only; this last stage was slow, and became progressively more difficult as the reaction proceeded. In order to avoid fractional numbers of chlorine atoms in the empirical formula, the following series of equations, involving the double isoprene unit  $\text{C}_{10}\text{H}_{16}$  was postulated:



Careful analysis of the product established its empirical formula as  $C_{10}H_{11}Cl_7$ ; this differs somewhat from the results of previous workers. Bloomfield further showed that in the first stage of the reaction, although one molecule of halogen chloride was liberated for each molecule of chlorine absorbed, there occurred a considerable drop in unsaturated bond in the rubber. This observation was important, since it contradicts simple substitution of the molecule. He therefore suggested that the drop in unsaturated was partly due to a cyclization reaction, although not exclusively so.

A scheme involving a polar mechanism has been proposed for the cyclization reaction. This is summarized in Figure 2.1, where the curved arrows represent electron-pair transformations resulting in covalent-bond transfer. It can be seen that the proposed scheme satisfied the experimental requirements, in that (1) one molecule of hydrogen chloride is produced for every molecule of chlorine consumed, (2) the loss of unsaturated molecule is qualitatively explained, and (3) it provides a new structural unit, the cyclic  $C_{10}H_{15}Cl$  unit and thus overcomes the original theoretical objection to assigning half a chlorine atom to each isoprene residue.

Ramakrishnan, Raghunath, and Pande (1935) measured the reaction in unsaturated molecules during the initial stage of chlorination in unsaturated molecules during the initial stage of chlorination, by technique of ozonolysis. Their results established quantitatively that one double bond is lost for every two isoprene residues that cyclize. This result accords well with the above mechanism of Bloomfield.

Later, Farmer (1946) subsequently proposed a series of reactions involving cyclization by a free radical mechanism. However, this mechanism seem to be not wholly correct, since Bloomfield showed that the first stage of the reaction is

unaffected by light and oxygen, and hence is probably not a free radical reaction. The chlorination mechanism proposed by Bloomfield is shown in Figure 2.2.

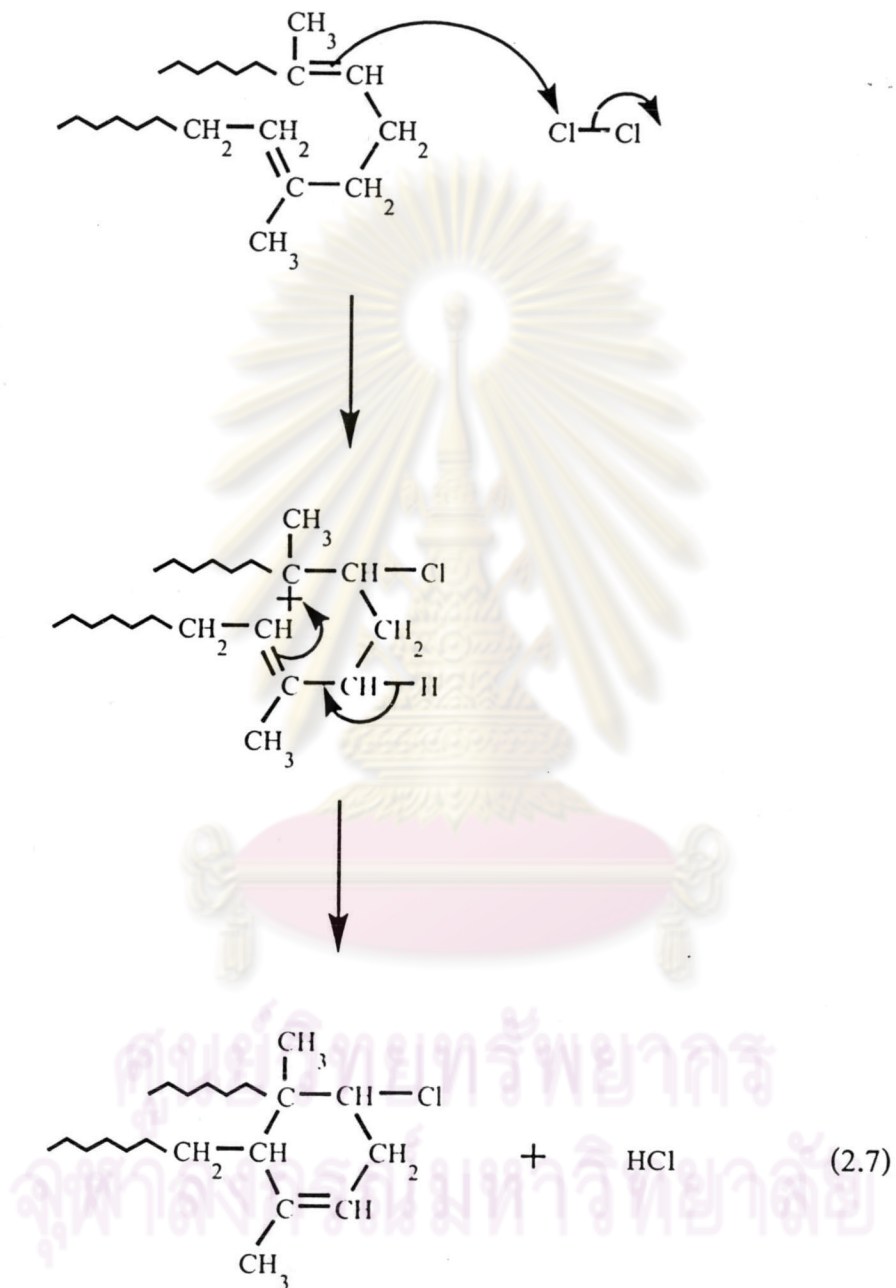


Figure 2.1 Cyclization during primary stage of rubber chlorination



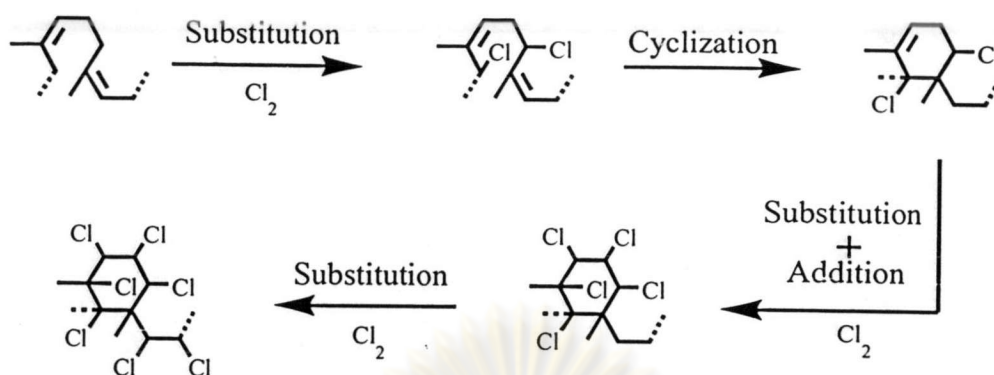


Figure 2.2 The chlorination mechanism of natural rubber

Although many theories have been put forward to explain the experimental facts, neither the detailed structure nor the mechanism of formation of chlorinated rubber is known explicitly.

## 2.4 Properties of chlorinated rubbers

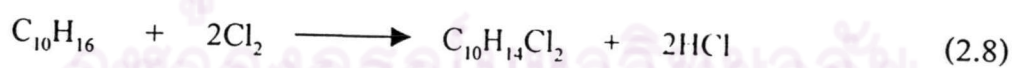
Chlorinated rubber is not a single, definite, and chemical compound. Its constitution and properties depend on the chlorine content of the polymer. In general, however, the commercial product contains 64-68% of the chlorine and available mainly in powder or fiber form. It is a white, granular powder of high specific gravity (1.66). Chlorinated rubber is non-flammable, non-thermoplastic and, when heated will darken and decompose, liberating hydrogen chloride. The thermal stability of the product depends on the chlorine content, and is at a maximum in the range 65-70% of chlorine. Chlorinated rubber is soluble in chlorinated and aromatic hydrocarbons, esters, and the higher ketones; it is insoluble but swells in ether and the lower ketones; it is completely insoluble in water, alcohol, and aliphatic hydrocarbons such as petrol.

## 2.5 Theoretical consideration

Previous studies of chlorinated rubbers have concentrated on high chlorine content product and the preparation methods leading to higher chlorine content were studied. The final product prepared was white powder. It can form brittle film by dissolving in toluene and drying. It never form film by using the final product which is viscous without solvent. The chlorinated rubbers with high chlorine content have the various prominent properties, especially high chemical resistance.

Hence, our work concentrated on film forming and some properties of chlorinated rubbers with low chlorine content. We prepared the chlorinated rubbers as viscous latexes with low chlorine contents, which led to the smaller amount of cracking of film. films of chlorinated rubber with a low chlorine content were as slippery as with a high chlorine content but retained the elasticity of unchlorinated natural rubber. The properties depend on chlorine content, thus the properties of chlorinated rubbers with different chlorine content were investigated.

We prepared chlorinated rubber with chlorine content below 30%, thus the reaction of product may involve the substitution reaction refer to Boomfield [9].



## 2.6 Literature survey

M. Lerdphatphaisan [5] studied the chlorination of various types of natural rubber (1989). The studies showed that chlorination in natural rubber latex have low chlorine content (30-40% by weight) and unacceptable thermal stability. Chlorination in solution, using carbontetrachloride as solvent, the reaction temperature of 78 °C and the reaction time between 21-24 hours. The chlorine contents reached is 63-65% by weight, depending on the types of starting natural rubber.

The patent [10] of method of producing chlorinated rubber (1992) described the method of chlorinating rubber latex with chlorine gas have 60 to 75% chlorine content in the aqueous medium. Nonionic or cationic surfactant is added to rubber latex and then acid is added to perform the acidifying treatment of latex. Rubber latex is chlorinated up to at least but not less than 30% chlorine content at a temperature of not higher than 50 °C, blocking off the light in the first step of chlorination. The remaining chlorination is performed while irradiating UV rays in the second steps of chlorination. The chlorination product is also claimed.

The patent [11] of preparation process of chlorinated rubber (1994) described the method of chlorinating rubber latex with chlorine gas in high-acidity aqueous dispersion of the polyisoprene rubber. Nonionic or anionic surfactant is added to rubber latex and then large amount of acid is added to perform acidifying treatment of latex. Rubber latex is chlorinated up to at least not less than 30% chlorine content at a temperature of 10-20 °C. Then raise the temperature to 40-70 °C and irradiate with UV rays or use a radical initiator in the second step. The chlorinated rubber is white solid.

Z. Jie-ping, L. Si-dong, W. Yong-cai, P. Zheng and P. He-peng [12] studied the effects of pH value of reaction system, reaction time, and reaction temperature on the chlorination reaction in the preparation of chlorinated natural rubber (CNR) from natural rubber latex (1999). It has been found from the thermal analysis that the thermal degradation of CNR in nitrogen is a one-step reaction, and 30% carbonide with a stable structure remained at 360 to 700 °C. Whereas the thermo-oxidative degradation of CNR in air is a multistep reaction, and the thermal degradation ratio reaches to 100% at 560 °C.



ศูนย์วิจัยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย