CHAPTER I

INTRODUCTION

1.1 General consideration

Hevea brasiliensis or para rubber is one of the important
economic plants of Thailand. In 1990 Thailand produced 1,249,921 tons
of natural rubber (NR), of which only 99,131 ton were used by the local
rubber industry and the rest were exported (Rubber Research Institute,
Thailand 1991).

It is still considered to be unsatisfactory in terms of economic
value added returns of national product, because most of the exported
solid rubber products are ribbed smoked sheet (RSS). The disadvantage
of RSS compared to other rubber is its low-price due to contamination
and discoloration,so that the price of rubber are usually sold at the
cheapest grade. The specification for the best quality RSS is light and
uniform color.

In some high grade rubber industries such as footwear industry,
one major problem is the dark and variable color of the raw rubber
input. Currently this problem is solved by minimizing the composition
of NR, and replacing NR as much as possible with synthetic rubber such
as SBR 1502, SBR 1205 and BR 01 which have consistent light color and
other physical properties. At present the manufactures gain benefit

Table 1.1 Total production of Thailand's rubber in 1990 (Rubber

Research Institute, 1991)

Type of rubber	Total production (Tons)	Domestic consumption (Tons)	Exports (Tons)	Price[*] (Baht/kg)
RSS[1]	965,608	27,634	937,974	21.30
TTR[2]	161,584	31,275	130,309	22.17
Brown crepe	24,553	10,333	14,220	25.90
Conc. latex	65,011	18,851	46,160	14.50
ADS[3]	19,495	5,144	14,395	-
Other	13,626	5,894	7,732	-
Total	1,249,921	99,131	1,150,790	-

where   1. RSS   = Ribbed smoked sheet

2. TTR   = Thai trade rubber

3. ADS   = Air dried sheet

* Source : Bangkok Rubber Company, Ltd. (1991-1992)

because synthetic rubbers imported as raw materials for exporting products are tax refunded, but this is not a good long term economic solution, especially for the Thai rubber planters. So, if we could specify our raw rubber products according to their color, and be able to achieve this quality consistently, the manufacturers will consume more NR. In terms of raw rubber exports, our technically specified NR would be more value added, and compete better in the world market for wider range of rubber based industries besides tyres such as foundation garment and footwear.

One of the consideration in light rubber product is the clone of natural rubber latex because each clone may contain different amount of non-rubber substances which are involved in the darkening of solid rubber. Carotenoid pigments are mostly claimed as discolorating factor in previous reports (Nadarajah and Karunaratne, 1971), however there is no experimental work which carried out on the discoloration of latex, compound rubber, until the final form which is rubber vulcanizate, especially starting with the rubber latex clones which were grown dominantly in Thailand.

1.2 Rubber clones recommended for planters in Thailand

Clone of NR is one of the important factor in improving the quality of rubber. Generally, rubber clones recommended for planters in Thailand have been changing every 4 year depending on environment and clonal characteristics such as volume and distribution of rain, wind power, yield of latex and disease resistance, however the new clones recommended are always the same as the old clones

Rubber clones recommended in Thailand were divided into 2 classes : the first class rubber are clone : RRIM 600, GT 1, PB 255 and PB 261, the second class rubber are clone : PB 235, PB 260, PB 217, PB 28/59 and RRIM 623,

1.3 Composition of natural rubber latex

Hevea brasiliensis latex is a cytoplasmic system containing rubber and non-rubber particles dispersed in an aqueous serum phase (HO et al., 1975). Fresh latex, after tapping from the tree, may be divide into four main fractions by ultracentrifugation at 59,000 x g ; these are a white rubber fraction, a yellowish-orange layer containing the Frey-Wyssling particles, a C-serum fraction and a grayish-yellow gelatinous bottom fraction (B fraction) containing lutoids, as shown in Figure 1.1 (Cook and Sehar, 1953 ; Moir, 1959).

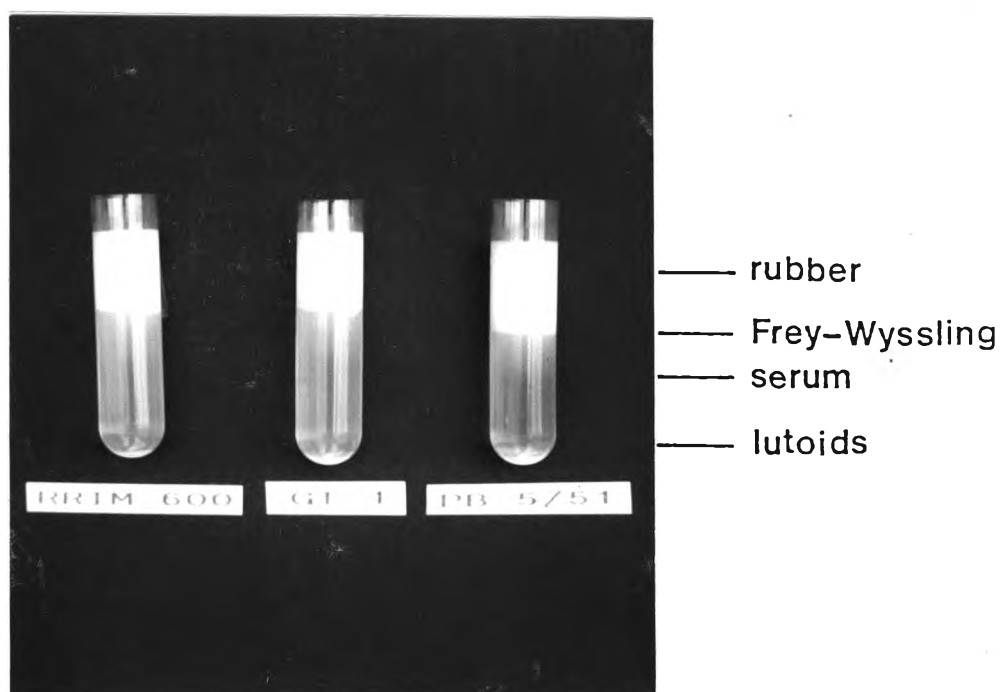──── rubber

──── Frey-Wyssling
──── serum

──── lutoids

Figure 1.1 Fractionation of fresh Hevea latex after ultracentrifugation

The rubber hydrocarbon constitutes about 30-45% of the whole latex while the non-rubber substances account for 3-5%, the rest being water. The rubber particles in fresh latex are protected by a complex film containing proteins and lipids. The non-rubber substances consist of proteins, amino acids, carbohydrates, lipids, amines, inorganic constituents, nucleic acid and nucleotides. Many of these substances are dissolved in the C-serum, while others are associated with the rubber or non-rubber particles in B fraction (Archer et al., 1963). During the coagulation of rubber, some of these substances are lost in the aqueous serum, but many of them, especially the water insoluble lipids and the precipitated proteins are retained in the rubber phase. Some of the retained non-rubber substances significantly influence the properties of rubber both in the raw and the vulcanized state. Their effects can be advantageous or deleterious to the rubber.

1.4 Enzymatic discoloration

1.4.1 Polyphenol oxidase (PPO)

Among several factors causing discoloration of latex and of rubber, one enzymatic factor is polyphenol oxidase (PPO) which is a copper-protein, and has been known by various names, such as phenolase, 3-hydroxytyrosine oxidase, catechol oxidase and tyrosinase, because this enzyme oxidizes a variety of phenolic substrates (Roberts, 1971). PPO is responsible for the discoloration of plant tissues following mechanical damage. PPO is frequently mentioned in literature as present in Hevea latex. De Haan-Homans (1949) has shown that latex contains a complicated system of oxidizing enzymes, namely catalase, tyrosinase, peroxidase and at least one other oxidase. These enzymes catalyze the oxidation of phenols and aminophenols by atmospheric oxygen to

orthodihydroxy phenols and then to orthoquinones, which react with naturally occurring amino acids and proteins present in latex to give color products (Borgstrom, 1968; Nadarajah and Karunaratne, 1971). Hsia (1958) has reported the presence of PPO in the lutoid fraction of fresh field latex accompanied by natural substrates. The method of enzyme isolation is based on the evidence that in <u>Hevea</u> latex, PPO is localized in lutoid particles. By mixing the latex with Tris-Manitol buffer, the lutoids are kept intact. A browning discoloration is shown during and immediately following the liberation of the bottom lutoids fraction indicating the presence of PPO (Karunaratne, 1970). Addition of 0.1% Triton X-100 at the beginning of isolation has been suggested by Roberts (1971) to increase the PPO activity.

1.4.2 Polyphenol

Quantitation of polyphenols present in the bottom fraction of latex in various rubber clones has been performed by using the colorimetric method (Nadarajah and Karunaratne, 1971). Their results indicated that the amount of natural polyphenols vary considerably from clone to clone. Thus the latex of clone RRIC 7 is very prone to enzymatic discoloration and has been found to have a very high phenolic content. However, on the whole, there is no clear relationship between phenolic content and enzymatic discoloration. Furthermore, they have roughly measured the amount of discoloration produced after adding excess amount of phenols (0.1% v/w), such as; catechol, resorcinol and pyrogallol to the various clones of latex which do not give a discolored coagulum or only a slightly discolored coagulum obtained after formic acid coagulation.

1.5 Non-enzymatic discoloration

Nadarajah and Karunaratne (1971) have suggested that discoloration of latex occurs even if the PPO had been destroyed which indicated for other mechanisms in the discoloration of latex. The main pathway to non-enzymatic browning seems to begin with the reaction between carbonyl and amino groups to give an unsaturated carbonyl amino derivative. Most natural substances contain phenolic compounds and some polyphenols enter into reaction leading to discoloration, and it is claimed into melanin formation. Rinderknecht and Jurd (1958) have reported that polyphenols can combine with amino acids in aqueous solution at low temperature to give a yellow color. The color was obtained on heating phloroglucinol with glycine. The yellow color of rubber can be possibly formed by similar reaction. An increase in the pH of the solution or higher alkalinity resulted in an enormous increase in the browning (Burton, McWeeny and Biltcliffe, 1962) formed by carbonyl amino reactions. It is also known that alkaline treatment cause rapid autoxidation of polyphenols to give dark colored polymers.

1.6 Effect of some lipids on discoloration

There are factors other than oxidase and phenolic content of lattices which have a bearing on discoloration. The natural latex lipids are mostly concentrated in the rubber phase with smaller quantity in the bottom fraction and the Frey-Wyssling particles. Ho et al. (1975) have shown that there are thirteen spots on thin layer chromatography plate of neutral lipids of NR, two of which are carotenoid pigments and tocotrienols.

1.6.1 Carotenoid pigments

The crystalline yellow pigment carotenoid was first isolated in 1831 by Wackenvoder. Carotenoid pigments are compounds basically consisting of eight isoprenoid units. The color of the Frey-Wyssling particles of rubber latex is due to the presence of carotenoid pigments which is the cause of yellow color of some lattices (Nadarajah and Karunaratne, 1971). Ascher et al., (1963) have suggested that carotenoid pigments can be found in the bottom fraction from ultracentrifuged latex and also appeared as a yellow layer immediately below the rubber cream. The yellow color of latex is a clonal characteristic depending on the amount of carotenoid pigments existed in the latex.

1.6.2 Tocotrienol

Tocotrienols are currently a very important natural antioxidant in the food industry and cosmetology. Its antioxidant activity has been shown in NR by several investigators. Tocotrienols played an important role in the oxidisability of raw and vulcanized rubber assessed by the plasticity retention index (PRI); a measure of the extent of deformation of rubber to thermal oxidative degradation, and by retention of tensile strength; a measure of the stress and strain property in tension under specified condition (Nadarajah et al., 1972; Morimoto, 1985; Hasma and Othman, 1990). In addition to these effect, tocotrienols can retard the enzymatic discoloration by competing with polyphenol substances to react with oxygen, thus giving an end-product which have no effect on color of NR. Hasma (1984) has shown that about 3% of neutral lipids are tocotrienols in fresh latex clone RRIM 501. Dunphy et al. (1965) and Whitte et al. (1966) reported a surprisingly large amount of free and esterified α-, γ- and δ-tocotrienols together

with a much smaller amount of α-tocopherol in ammonia preserved latex concentrate. The γ-tocotrienol is predominant over α- and δ-tocotrienol both in the free and esterified form.

1.7 Structure of natural rubber and its vulcanizate

Solid raw rubber is normally obtained by coagulating the latex with acid followed by washing and drying. It contains a high proportion of rubber hydrocarbon, mixed with some non-rubber constituents.

1.7.1 Molecular structure of natural rubber

Natural rubber is a polymer of very high molecular weight (MW) and wide molecular weight distribution (MWD). The molecular weight distribution of NR in freshly tapped lattices of different clones has been extensively studied by Subramanium (1980). By gel permeation chromatography (GPC), bimodal distribution of 10^4-10^7 Dalton have been observed in several clonal rubbers which can be classified roughly into 3 types as shown in Figure 1.2. Although the shape of the distribution curves are different, the range of molecular weight (MW) is approximately the same in rubber from all clones, usually from about 3×10^4 to 10^7. The highly molecular weight peak appears between 1×10^6 and 2.5×10^6 for different rubbers. The position of the low molecular weight peak appears between 1×10^5 and 2×10^5 for all clones studied (Nair, 1970). The characteristic type of molecular weight distribution (MWD) shown by each clonal rubber is shown in Table 1.2.
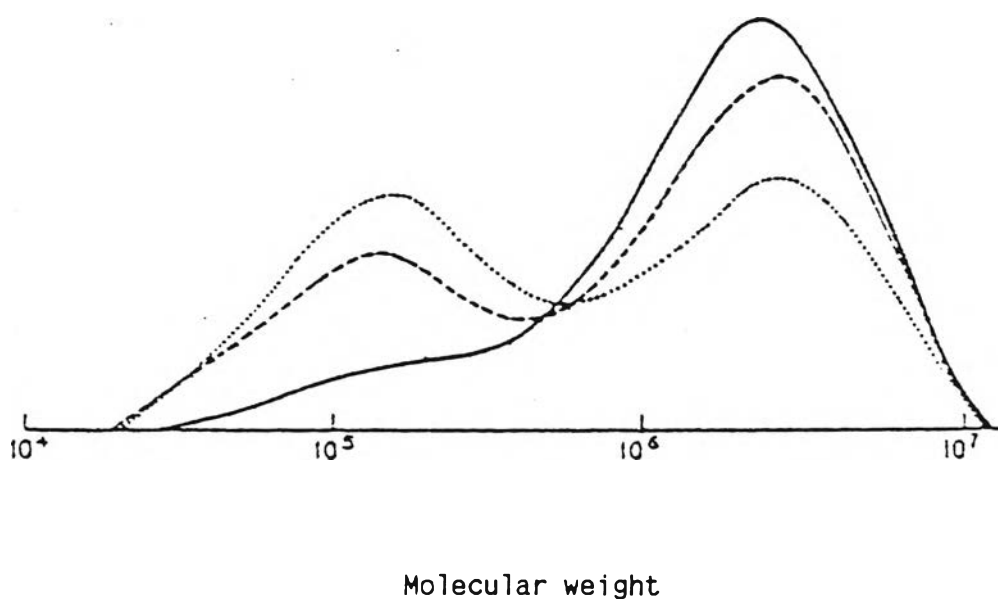
Molecular weight

Figure 1.2   Types of molecular weight distribution curves of

natural rubber (Subramamium, 1980)

● Type 1. (....) Distinctly bimodal distribution where the peak height in the low molecular wight region is nearly equal or slightly less then the peak height at the high molecular weight region.

● Type 2. (----) Distinctly bimodal distribution where the height of the low molecular weight peak is only half or less than the height of the high molecular weight peak.

● Type 3. (_____) Skewed unimodal distribution with a "shoulder" or a "plateau" in the low molecular weight region.

Table 1.2 Types of molecular weight distribution and fraction of

low molecular weight in clonal rubbers (Subramanium, 1980)

Clone	Usual type of MWD curve	Weight fraction below molecular weight 5×10^5 (%)
Tjir 1	3	20
PB 5/51	3	1
PB 28/59	3	18
PB 5/63	3	21
RRIM 628	2	24
RRIM 701	2	30
RRIM 623	2	23
RRIM 600	2	33
GT 1	2	30
PR 251	2	34
RRIM 605	1 or 2	36
RRIM 703	1 or 2	39
RRIM 501	1 or 2	40

The structure of these high molecular weight polymers have been studied by many scientists. The polymer consists of isoprenoid as the monomer unit (Figure 1.3). Using NMR spectra, Golub et al.(1962) showed that the 1, 4 - polyisoprenoid unit of NR exists at least 99% in cis 1, 4-configuration. By ^{13}C -NMR spectra, the number of trans per polymer chain units is roughly estimated to be 2.0-3.9 for various Hevea rubber samples by calculating of relative intensity of the trans signals combined with the degree of polymerization as determined by GPC (Tanaka, 1989). These finding suggest that Hevea rubber has the fundamental structure as shown in Figure 1.4, however the structure of both terminal units has yet to be identified.
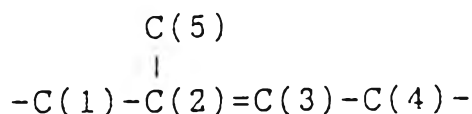
$$
\begin{array}{c}
\text{C(5)} \\
|\\
-\text{C(1)}-\text{C(2)}=\text{C(3)}-\text{C(4)}-
\end{array}
$$

Figure 1.3 Structure of isoprene unit (Tanaka, 1989)

$$
(\omega\text{-terminal})\!-\!\!(CH_2C\!\!=\!\!CCH_2)_3\!-\!\!(CH_2C\!\!=\!\!CCH_2)_n\!-\!(\alpha\text{-terminal})
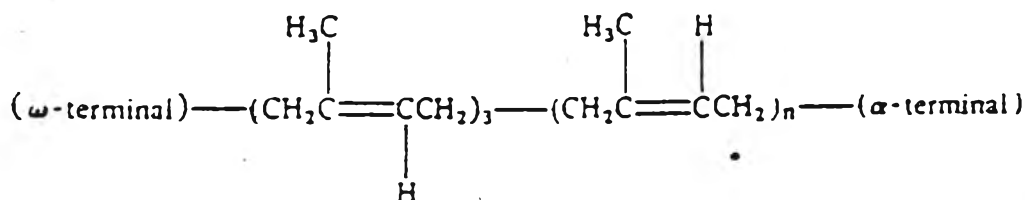$$

Figure 1.4 Structure1 of natural rubber (Tanaka, 1989)

The raw rubber is sensitive to hot and cold weather , and is liable to oxidation to a sticky product. These factors impose a severe limitation on the usefulness of this material. Today most of NR is used in vulcanized form which has better physical properties over a wider temperature range.

1.7.2 Vulcanization

Vulcanization is a process of crosslinking the essential linear rubber chains into a three-dimension network. Vulcanization can be roughly classified into 2 types : sulfur vulcanization and non-sulfur vulcanization.

1.7.2.1 Sulfur vulcanization

Sulfur is one of the most common vulcanizing agent of major industrial importance although many non-sulfur reagents are known. The continued popularity of sulfur can be attributed to several reasons : low cost, case of availability, fast vulcanization, minimal interference with other compounding ingredients, and an excellent balance of vulcanizate properties (Crowther, lewis and Mctherell, 1988). Usually sulfur alone or unaccelerated sulfur vulcanization system, is seldom used as it requires a very long cure time. The most common method of crosslinking NR is the accelerated sulfur vulcanization system, which requires the incorporation of one or more accelerators and activators. Analysis of a variety of accelerated sulfur curing systems has shown that the generalized structure of a vulcanizate is as depicted in Figure 1.5 (Hasma, 1984). The grouping identified comprise of mono-, di- and polysulfidic crosslinks, cyclic mono- and disulfide groups, pendent sulfide groups terminated by accelerator fragments and conjugated diene and triene units.
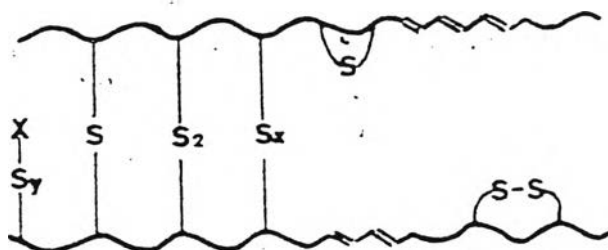
Figure 1.5 Structural features of an accelerated sulfur vulcanizate of

natural rubber

x = accelerator fragment; $x \geq 3$; $y \geq 1$

The properties of the various grouping present in

a given network generally depend on a sulfur donor, on the nature and

the concentration of the accelerators present, and on the temperature

and the time of cure.

1.7.2.2 Non-sulfur vulcanization

The search for an alternative vulcanization agent

to sulfur is usually undertaken for the purpose of improving heat

resistance (Lewis, 1984).   There are several kinds of non-sulfur

vulcanization such as peroxide vulcanization, using d-tert-butylperoxide

and dicumyl peroxide as the vulcanizing agent which gives carbon-carbon

crosslinks (Figure 1.6), and urethane vulcanization, using nitroso compound as the vulcanizing agent which link the NR chain via pendent amino group (Figure 1.7).
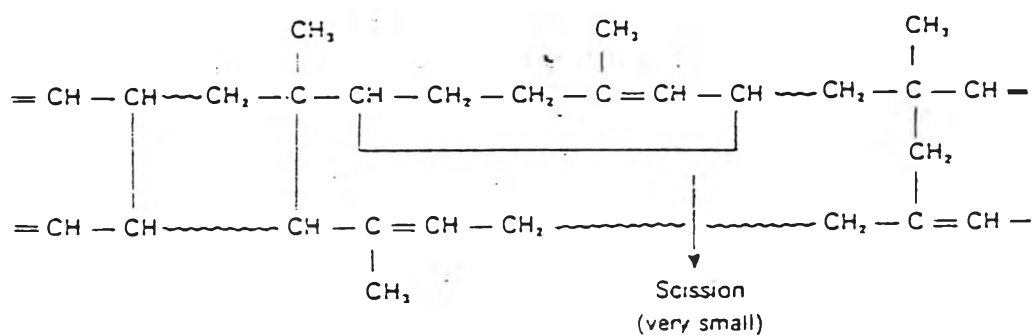

Figure 1.6   Example of carbon-carbon crosslink of peroxidic
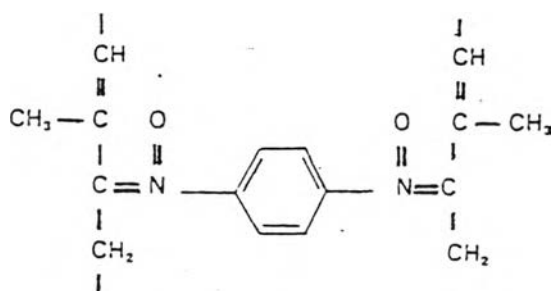
vulcanization (Baker, 1988)

Figure 1.7   Example of nitrone - phenyl - nitrone crosslink of

urethane vulcanization (Baker, 1988)

1.8   Physical properties of natural rubber

Two of the most significant properties of a raw rubber are its viscosity and the cure characteristics (Sullivan and wise, 1973). The

former establishes the amount of energy required to mix and form the compounded rubber, while the latter defines the time available for these operations. These characteristics are vitally important because they define the operating window available for converting uncured rubber compound into a usable product.

1.8.1 Mooney viscosity

Mooney viscosity is a measure of the flow property of raw rubber determined in a Mooney shearing disk viscometer. It is indicated by the torque required to rotate the disk embedded in a rubber specimen and enclosed in the die cavity under specified conditions. Viscosity values determined by this test method depend on the molecular structure of rubber particle and on non-rubber constituents attached to it. Subramanium (1975) has reported the diversity of Mooney viscosity ranging from 63 to 94, among which RRIM 501 has been classified as low viscosity clone (MV = 49). The variation between clones are greater than the standard deviation of the viscosity measurement within each clone. This investigation indicated that Mooney viscosity should be a clonal characteristic. Besides the source of latex, the method in which dry rubbers are produced from latex can affect Mooney viscosity of the raw rubber.

A very serious defect of NR is that it is mostly supplied at rather high and varying viscosities. Preliminary study of this thesis has shown that NR has higher Mooney viscosity than synthetic rubber (Table 1.3).

Table 1.3 Mooney viscosity variation in natural rubber and

synthetic rubber (Preliminary study of this thesis)

Type of rubber	Number of samples	Mooney viscosity (ML (1+4) 100°C)	
		Mean	Standard deviation
Natural rubber			
RSS 1	24	82.1	6.9
RSS 3	29	84.0	6.2
TTR 5L	31	75.2	7.5
Crepe	57	79.4	4.2
ADS	23	75.9	6.4
Synthetic rubber			
BR 01	21	46.0	2.3
S 1502	12	62.4	5.9

There are two problems associated with the high viscosity of NR. The first problem is that NR undergoes hardening during processing, shipment and storage, and the viscosity can rise by 10 to 40 Mooney units (Nadarajah et al., 1985). The higher Mooney viscosity is, the higher energy consumed in mixing the compound rubber. The second problem is that most clones give a variable viscosity rubber, only the constant viscosity grade (CV-NR), where consistent a Mooney viscosity of 60±5 or 80±5 can be obtained (Chin, 1969), therefore mixing time must be adjusted otherwise the quality of different lot can be different. There are several advantages of using rubber with low initial viscosity, one is to allow the elimination or reduction in

premastication and thus an important saving in energy cost. Another one is giving a good flow-ability in complicate molding process.

1.8.2 Cure characteristics

One of the important characteristics of an elastomer is the consistency in cure or vulcanization behavior. Cure behavior is most comprehensively followed by the cure curve derived from rheometer measurements. The important cure parameters are scorch time, cure rate, time to optimum cure and maximum modulus. Scorch time is the minimum safe time for processing the compounded rubber before the rubber is converted from a plastic to a vulcanized state where further processing is impossible. Rate of cure determines the time to cure a given product to its optimum state. So the presence of accelerators and activators will affect the consistency of cure rate, and NR is known to contain these natural accelerators and activators at different amount (Hasma, 1984).

In the production of a rubber compound, the technologist strives to balance these 3 stages : scorch, curing and overcure. Sufficient scorch time is mandatory to get the stock through the process to avoid scrap, yet not with so much residual scorch time that the cure time will be excessively long, thus tieing up expensive equipment. A fast cure rate is desired for the same reason, however it should not be so fast that insufficient mold flow occurs. Finally, one wants to achieve maximum utilization of the curing system by removing the product from the mold at the optimum time while avoiding the adverse effects of overcured (Sullivan and Wise, 1973).
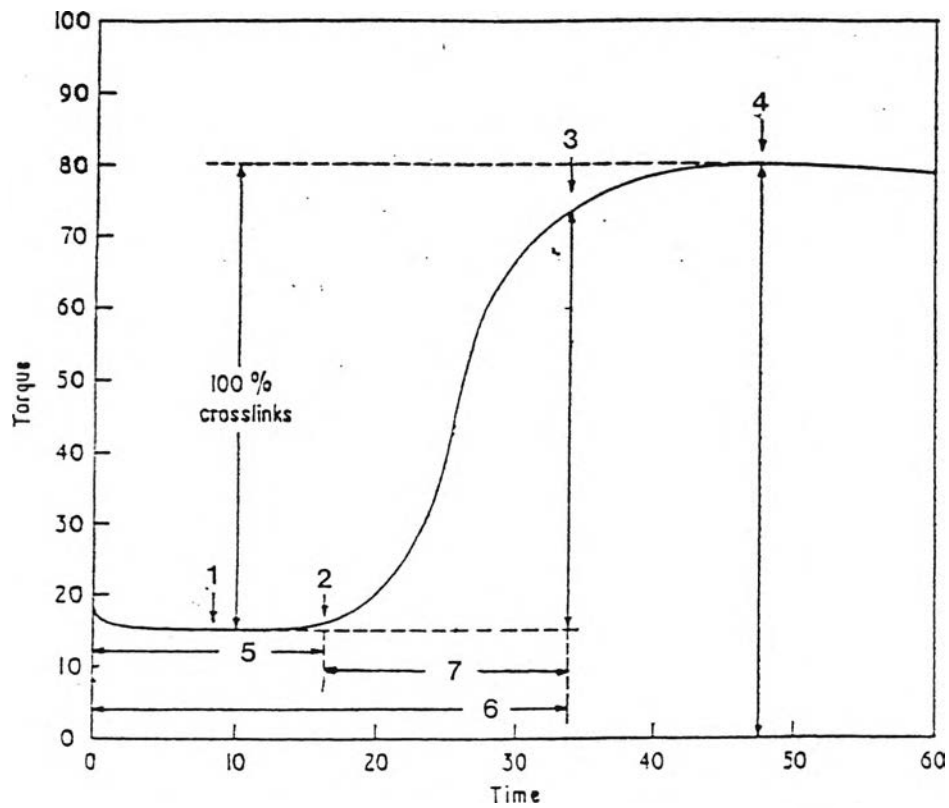
Figure 1.8   Rheometer curve

1 = minimum modulus (M_L)

2 = scorch point (1 torque unit rise above minimum
    viscosity)

3 = optimum cure

4 = maximum modulus (M_H)

5 = scorch time (T_S)

6 = time to optimum cure (T_{90})

7 = cure rate

1.9 Objectives

The hypothesis of this research is that discoloration of NR is dependent on the presence of some non-rubber ingredients namely carotenoid pigments, tocotrienols, polyphenols and polyphenol oxidase. Removal of discolorating factors should decrease the color index, whereas addition of each factor should reflect the importance of each factor on discoloration process. Three clones of rubbers : RRIM 600, GT 1 and PB 5/51 which are recommended clones for growing in Thailand are selected for this test. By following the development of color starting from raw rubber state, rubber compound and the final vulcanizate, the mechanism of discoloration can also be elucidated.