กระบวนการเชิงนวัตกรรมสำหรับผลิตน้ำยางคงรูปอิสระ

นาย กำจรเดช กิจมั่นเจริญกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

INNOVATIVE PROCESS FOR FREE-VULCANIZED RUBBER LATEX PRODUCTION

Mr. Kumjorndej Kitmancharoenkul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2009

Thesis Title	INNOVATIVE PROCESS FOR FREE-VULCANIZED RUBBER LATEX PRODUCTION
By	Mr. Kumjorndej Kitmancharoenkul
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Professor Pattarapan Prasassarakich, Ph.D.
Thesis Co-Advisor	Pienpak Tasakorn, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

S. Hannongbua

....Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.... Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

.... Thesis Advisor
(Professor Pattarapan Prasassarakich, Ph.D.)

.... Thesis Co-Advisor
(Pienpak Tasakorn, Ph.D.)

Warinthorn Chavasiri

.... Examiner
(Assitant Professor Warinthorn Chavasiri, Ph.D.)

.... External Examiner
(Polpatr Pruksananont, Ph.D.)

กำจรเดช กิจมั่นเจริญกุล : กระบวนการเชิงนวัตกรรมสำหรับผลิตน้ำยางคงรูปอิสระ (INNOVATIVE PROCESS FOR FREE-VULCANIZED RUBBER LATEX PRODUCTION.) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ.ดร. ภัทรพรรณ ประศาสน์สารกิจ , อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ดร.เพียรพรรค ทัศคร, 93 หน้า

น้ำยางธรรมชาติผ่านกระบวนการเกิดครีมเพื่อทำให้ข้นขึ้น โดยการเติมสารก่อครีม คือ คาร์บอกซีเมทิลเซลลูโลส, ไฮดรอกซีเอทิลเซลลูโลส และไฮดรอกซีโพรพิลเมทิลเซลลูโลส ได้ศึกษาชนิดของสารก่อครีม, ความเข้มข้นของสารก่อครีม, เวลา และอุณหภูมิที่มีผลต่อปริมาณเนื้อยางแห้งในน้ำยางข้น เพื่อหาภาวะที่เหมาะสมต่อกระบวนการเกิดครีมของน้ำยางธรรมชาติ น้ำยางข้นที่ได้จะถูกทำให้คงรูปโดยกระบวนการวัลคาไนเซชัน โดยการใช้ซัลเฟอร์และเททราเมทิลไทยูแรมไดซัลไฟด์เป็นสารเชื่อมขวาง น้ำยางคงรูปอิสระที่ได้จาการแปรเปลี่ยนอุณหภูมิ, เวลา และความเข้มข้นของสารเชื่อมขวางจะถูกทำให้เป็นฟิล์มและปล่อยให้แห้งที่อุณหภูมิห้อง เพื่อนำมาวัดสมบัติเชิงกลต่างๆ เช่น การทนต่อแรงดึง, ค่าของความยืดเมื่อขาดและค่าความแข็ง นอกจากนี้ยังทดสอบค่าความหนาแน่นของการเชื่อมขวาง, เลขคลอโรฟอร์มและดัชนีการบวมตัว โดยพบว่าภาวะที่เหมาะสมต่อการทำน้ำยางข้นนั้นใช้ ไฮดรอกซีโพรพิลเมทิลเซลลูโลส ความเข้มข้น 0.6% ที่อุณหภูมิห้องเป็นเวลา 24 ชั่วโมง สำหรับการคงรูปของน้ำยางข้น ค่าความต้านทานแรงดึงสูงสุด ได้จากการใช้เททราเมทิลไทยูแรมไดซัลไฟด์ ความเข้มข้น 2 ส่วนในเนื้อยาง 100 ส่วน ทำปฏิกิริยาที่อุณหภูมิ 50 องศาเซลเซียส นาน 3 ชั่วโมง โดยปฏิกิริยาของการคงรูปที่อุณหภูมิต่ำนั้นต้องการเวลาสำหรับทำปฏิกิริยาเพิ่ม เลขคลอโรฟอร์มและดัชนีการบวมตัวแสดงให้เห็นถึงยางคงรูปอิสระนั้นไม่เกิดการเชื่อมขวางอย่างสมบูรณ์

สาขาวิชา : ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต กำจรเดช กิจมั่นเจริญกุล
ปีการศึกษา : 2552 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

4972222823 : MAJOR PETRO CHEMISTRY AND POLYMER SCIENCE

KEYWORDS : CREAMED NATURAL RUBBER LATEX / CREAMING METHOD / CREAMING AGENT / VULCANIZATION / SULFUR

KUMJORNDEJ KITMANCHAROENKUL: INNOVATIVE PROCESS FOR FREE-VULCANIZED RUBBER LATEX PRODUCTION. THESIS ADVISOR: PROF.PATTARAPAN PRASASSARAKICH, Ph.D., THESIS CO-ADVISOR: PIENPAK TASAKORN, Ph.D., 93 pp.

Field natural rubber latex was concentrated by creaming method via addition of creaming agents, namely carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) and hydroxypropyl methyl cellulose (HPMC). The effects of creaming agent concentration, creaming time and temperature on dry rubber content (DRC) were studied to determine the optimum condition for latex creaming process. Creamed latex was cured by vulcanization in a stirred reactor with sulfur elements and tetramethylthiuram disulfide as curing agent. Free-vulcanized latex obtained from the reaction with varying temperature, cure time and curing agent concentration were made into films and dried at room temperature. Tensile properties, elongation at break, hardness of the film products were measured. Crosslink density, chloroform number and swelling index of latex were also investigated. It was found that optimum condition for latex concentrate was using HPMC as creaming agent at 0.6% concentration, at room temperature, for 24 hours. For vulcanization of creamed latex, the maximum tensile strength was obtained from TMTD 2 phr at vulcanization temperature of 50°C and cured time of 3 hours. At lower vulcanization temperatures, longer cured time was required. Chloroform number and swelling index showed that the latex compounds were not completely vulcanized.

Field of Study : Petrochemistry and Polymer Science Student's Signature K. Kitmancharoenkul
Academic Year : 2009 Advisor's Signature
Co-Advisor's Signature

ACKNOWLEDGEMENTS

The author would like to express his gratitude to his advisor, Prof. Dr. Pattarapan Prasassarakich and his co-advisor, Dr.Pienpak Tasakorn for their encouraging guidance, supervision, support and helpful suggestion throughout this research. The author also would like to acknowledge Assoc. Prof. Dr. Supawan Tantayanon, Assist. Prof. Dr. Warinthorn Chavasiri and Dr. Polpatr Pruksananont for serving as chairman and members of thesis committee, respectively.

Many thanks also go to the Department of Chemical Technology, Faculty of Science, Chulalongkorn University for providing research facilities throughout this research work.

The authors also gratefully acknowledged the funding support from Center for Petroleum, Petrochemical and Advanced Materials and the Graduate School of Chulalongkorn University.

Finally, the author wishes to express his deep gratitude to his family for their love, inspiration, support and encouragements throughout graduate study.

CONTENTS

Page

Page

LIST OF FIGURES

Figure Page

Figure Page

Figure Page

LIST OF TABLES

Table Page

LIST OF ABBREVIATIONS

ASTM : American standard testing method

°C : Degree celsius

CMC : Carboxymethyl cellulose

DRC : Dry rubber content

EB : Elongation at break

h : Hour

HEC : Hydroxyethyl cellulose

HPMC : Hydroxypropyl methyl cellulose

Mpa : Mega pascal

MW : Molecular weight

MWD : Molecular weight distribution

NR : Natural rubber

NRL : Natural rubber latex

phr : Part per hundred

S : Sulfur

TSC : Total solid content

TMTD : Tetramethylthiuram disulfide

VFA : Volatile fatty acid

ZDEC : Zinc diethyl dithiocarbamate

ZnO : Zinc oxide

CHAPTER I

INTRODUCTION

1.1 The Purpose of the Investigation

Natural rubber is one of the most important commodities of Thailand that it has become the world's largest producer and exporter since 1991. Especially natural rubber latex, Thailand produces about 600,000 tons annually [1]. Natural rubber latex is normally concentrated to remove excess water and so increase its rubber contents. Latex concentrate is used as a raw material for many dipped products such as gloves, balloon, condom, etc. The production of natural rubber latex concentrate usually employs centrifugation. Although, this method can achieve high dry rubber content in latex but the disadvantages are high energy used, complex process and therefore high cost.

Creaming process is an alternative method for the concentration of natural rubber latex that is performed by adding water-soluble hydrocolloid called creaming agents to increase the buoyant density of latex, such as alginate and cellulose type polymers. The rubber particles in latex rise slowly to the top to form a creamed rubber layer on the liquid. This method is not as commonly used industrially as centrifugation but the requisite equipment is simple and easy to operate, i.e. labor cost is low, power requirement is negligible, and the proportion of rubber lost in the skim latex is small.

Use only natural rubber latex concentrate can not achieve products that have a desire mechanical property. Vulcanizing agents are needed to initiate reaction at appropriate time and temperature yielding chemical crosslink between rubber molecules. In this research work, natural rubber latex is concentrated with the use of creaming agent and followed by vulcanization for improved properties of rubber products.

1.2 Objectives

The objectives of this research can be summarized as follows:

1. To investigate the creaming of natural rubber latex and the effect of operating parameters on such creaming.
2. To study the effect of vulcanization parameters on properties of free-vulcanized rubber latex.

1.3 Scopes of the Investigation

1. Literature survey and in-dept study for this research work.
2. The design and preparation of experimental procedure.
3. Preparation of natural rubber latex concentration by creaming method with varying parameters as follows:
    a) Type of creaming agent: carboxymethyl cellulose (CMC), hydroxy ethyl cellulose (HEC) and hydroxypropyl methyl cellulose (HPMC).
    b) Concentration of creaming agent: 0.2 – 1.0%.
    c) Time of creaming process: 12 – 72 hours.
    d) Temperature of creaming process: room temperature to 60°C.
4. Determination of dry rubber content (DRC) of creamed latex.
5. Preparation of free-vulcanized rubber latex film by varying parameters as follows:
    a) Source of curing agent: sulfur and TMTD.
    b) Vulcanization temperature: 40 -70°C.
    c) Vulcanization time: 1 – 6 hours.
6. Measurement of the mechanical properties of free-vulcanized rubber film: tensile strength, elongation at break and hardness.
7. Determination of the crosslink in free-vulcanized rubber by chloroform test, swelling index and degree of crosslink.
8. Determination of free sulfur in sulfur free-vulcanized rubber film.
9. Summarization of the results and suggestion for future work.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber Latex

2.1.1 Properties of Natural Rubber Latex

Natural rubber (NR) is obtained from the milky secretion (latex) of various plants, but the only important commercial source of natural rubber is the tree, *Hevea brasiliensis.* Natural rubber latex (NRL), collected by tapping from *Heavea* rubber trees, is a colloidal suspension of rubber particles in an aqueous phase. The latex exuding from the tapping cut is called as fresh natural rubber latex or fresh field latex. Fresh field latex is composed of approximately 25-40% dry rubber content (DRC) and 5-10% non-rubber substances. These non-rubber components are including proteins, carbohydrates, lipids and inorganic salts. The chemical and physical properties of the fresh latex are influenced by clone, age of rubber [1], tapping intension [2] and seasoning of tapping. The composition of typical fresh field latex is presented in Table 2.1.

Table 2.1 Composition of fresh NRL [3].

Composition	Percentage (by weight)
Total solid content	36
Dry rubber content	33
Proteinous substance	1-1.5
Resinous substance	1-2.5
Ash	Up to 1
Sugars	1
Water	Add to 100

In general, fresh latex is density between 0.975 and 0.980 g/cm^3 with pH ranging from 6.5 to 7.0 and a refractive index of 1.5910. The viscosity is depending on total solid content in NR Latex. Rubber does not dissolved in water, alcohol, or acetone but it swells and dissolves or partly solubilizes in benzene, toluene, gasoline, carbon disulfide, turpentine, chloroform, carbon tetrachloride and other halogen containing solvents.

For the preservation of field latex, ammonia is normally added at levels of 0.3 to 0.8% by weights based on the weight of latex, depending on such thing as the length of time preservation is required, the condition of the latex when the ammonia is added, and the like, when used in combination with other bactericides, as follows:

Formaldehyde

Formaldehyde is an excellent bactericide; a combination of formaldehyde pre-treatment to sterilize the latex, followed by ammoniation is the basis of the so-called McGavack system of preservation. Typically, fresh natural rubber latex is treated with 0.15-0.2% w/w formaldehyde at the collecting station, as soon as possible after tapping. This quickly kills all the bacteria. The latex is then allowed to stand for a period of 15-30 hours at the factory, during which time the formaldehyde interacts with the proteins in the latex, and a consequent fall in pH occurs. Ammonia is added to bring the pH up to a little above 6. Formaldehyde has also been used as an anticoagulant at the cup and bucket stage. The usual amount used for this purpose is about 0.02% w/w added as 1% w/v aqueous solution.

Sodium sulfite

Sodium sulfite is used as an anticoagulant at the cup and bucket stage, especially when the latex is to be used for the production of a form of dry natural rubber known as pale crepe. As the name of this product implied, it is essential to keep discoloration of this type of natural rubber to a minimum. In this connection, it may be noted that sodium bisulfite is used as an enzyme inhibitor in the manufacture of pale crepe; the objective is to minimize discoloration. About 0.05% w/w of sodium sulfite on the whole latex is recommended as an anticoagulant, added as 3% w/v aqueous solution. Of this amount, a few drops are added in the cup at the time of tapping, and the balance is added to the buckets during collection.

Potassium hydroxide

The only practically-important alternative to ammonia as a sole preservative for natural rubber latex is potassium hydroxide. It is an effective bactericide by virtue of its high alkalinity. For the same reason, it gives latex which is colloidal very stable.

2.1.2 Chemical Structure of Natural Rubber

Natural rubber is a high molecular-weight hydrocarbon. The chemical structure of rubber is mainly composed of isoprene units, C_5H_8, linked at C1 and C4 carbon atoms, as shown in Figure 2.1. Here, the double bond can be either in the *cis*- or *trans*-configurations. In the early stage of X-ray diffraction studies, the double bonds of isoprene units in rubber chain were oriented in the *cis*-configuration, known as *cis*-1,4-polyisoprene [4].

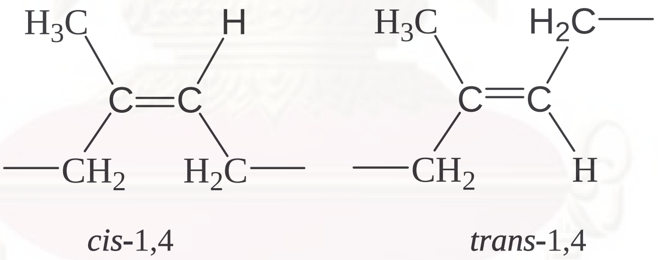


Figure 2.1 Structure of *cis*- and *trans*- in polyisoprene.

In fact, the natural rubber molecules is not a pure *cis*-1,4 polyisoprene. Besides, it contains very small amount of functional groups in rubber chain termed as abnormal groups, such as aldehyde groups, ester or lactone group and epoxides. Structural studies using ^{13}C-NMR spectroscopy disclosed that the rubber molecule contains about two to three *trans*- isoprene unit. Recently, the detailed structure characterization of natural rubber was investigated by means of ^{13}C-NMR and ^{1}H-NMR spectroscopy. From the relative intensity of the signal and the degree of polymerization of highly purified natural rubber, the number of *trans*- isoprene existing at the initial terminal of the rubber molecule is estimated to be two. Accordingly, the structure of natural rubber is assumed to be as shown in Figure 2.2.

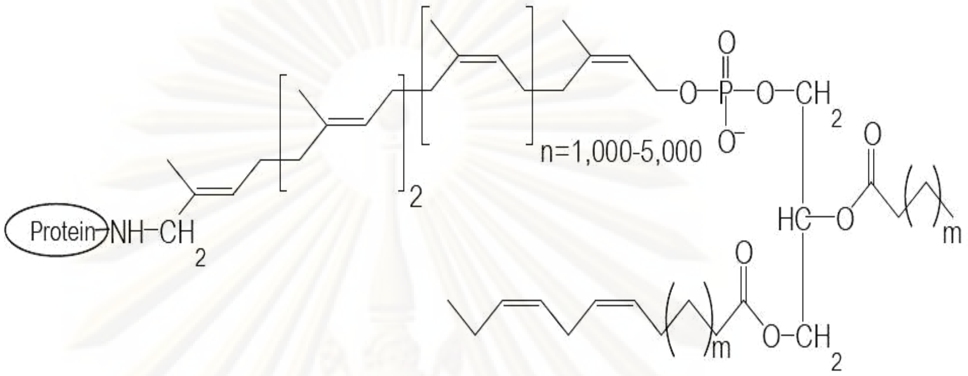


Figure 2.2 Presumed structure of natural rubber [5].

2.1.3 Constitutions of Natural Rubber Latex

By high speed centrifugation, the freshly tapped latex can be separated into four main fractions; an upper layer of rubber, an orange or yellow layer containing Frey-Wyssling particles, a colorless serum phrase and a bottom fraction consisting of mainly lutoid particles as illustrated in Figure 2.3.

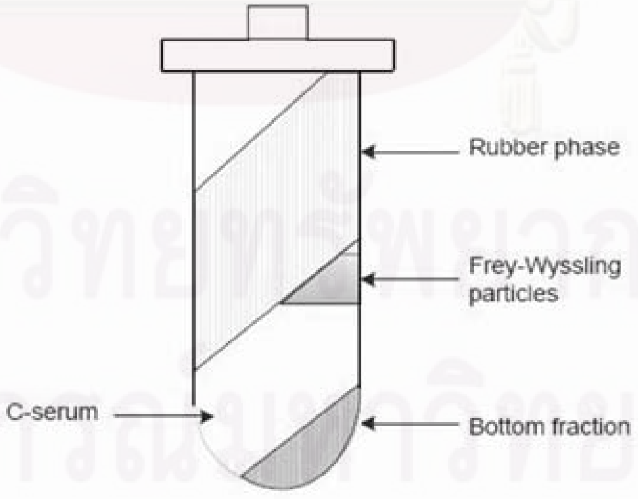


Figure 2.3 Four main fractions of fresh NRL obtained by using high speed centrifugation [8].

a) Rubber Matters Composition

(1) Rubber Particles

Rubber particles in natural rubber latex are spherical droplets of hydrocarbon, which are stabilized by the negative charge of surface-absorbed proteins and lipids [6] as shown in Figure 2.4.

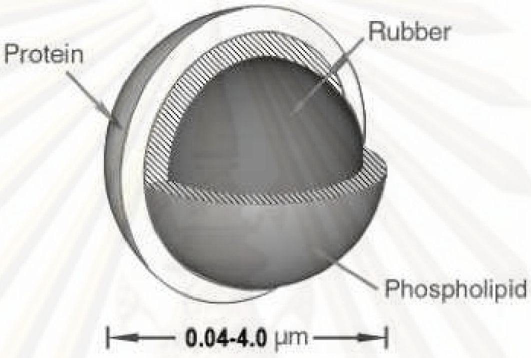


Figure 2.4 Schematic representations of rubber particles [6].

(2) Lipids

Lipids are water insoluble components, which are mainly concentrated in the rubber phase with minor quantities in the bottom fraction and in the Frey-Wyssling particles. Lipids can be classified into neutral and polar lipids. The neutral lipids such as sterols, sterol esters, tocotrienols and others lipids are able to dissolve in rubber particles. Tocotrienol is a derivative of Vitamin E which is the most important neutral lipid in NR. This is because tocotrienol is recognized as the most effective neutral antioxidant in NR [9,10]. It is reported that the polar lipids, phospholipids and glycolipids were strongly adsorbed onto the surfaces of rubber particles in which proteins are intermediate and anchored on the rubber particles. Phospholipids was claimed to be an activator in sulfur vulcanization [12].

(3) Proteins

Proteins coating at the outer layer of rubber particle is about 25% of all proteins in latex. In addition, 50 and 25% of proteins are in water and lutoid fraction, respectively. Almost all proteins at the outer layer of rubber particle are known as alpha-Globulin, and the residual proteins are known as Hevien alpha-Globulin [13]. It does not dissolve in distilled water, yet it dissolves in acid, alkali and salt; furthermore, its iso-electric point is pH 4.8, so rubber particles always coagulate at this pH. On the other hand, Hevien dissolves in distilled water, and its iso-electric point is pH 4.5. Hevien protects coagulation when dehydration occurs like filling either alcohol or acetic acid into latex.

The effect of proteins on raw rubber had long been studied in the past. It has been reported that proteins at the outer layer of rubber particle consists of crystine disulfide linkage, which is sulfur compound about 5 percent. Therefore, when coagulation occurs, protein at this part degrades into hydrogen sulfide and mercaptan compound giving bad smell [14]. In addition, amino acids derived from decomposition of proteins cause storage hardening of NR by crosslinking reaction of amino acids and the abnormal groups on NR molecules, such as carbonyl and epoxide groups [15,16]. For the effects on vulcanizates, the neutral and basic amino acids give certain improvements in properties such as modulus, compression set and heat build-up compared to purified NR, while proteins and acidic amino acids improve only the heat build-up properties [17].

b) Non-Rubber Matters Compositions

(1) Water and Serum

This fraction consists of two types of substances, carbohydrates; proteins and amino acids.

Carbohydrates are sugar and starch substances, and they present in latex about 1 percent. Almost sugars in serum fraction are called quebrachitol as illustrated in Figure 2.5 and the residual sugars are glucose, fructose and sucrose, respectively.

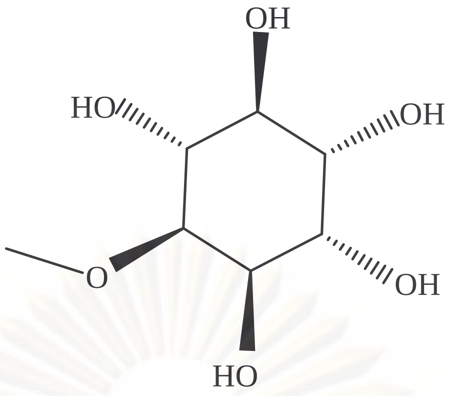


Figure 2.5 Chemical structure of quebrachitol sugar.

Furthermore, these sugars can be fed by bacteria causing degradation of sugar into short chain fatty acids called volatile fatty acid (VFA) such as formic, acetic and propionic acid, which brings coagulation to latex.

Almost protein in serum fraction is alpha-globulin which is between water-air and oil-water interface.

(2) Lutoid and Others

This fraction is composed of two types, which are lutoid and Frey-Wyssling.

Lutoid

The lutoid particles are almost numerous of the large organelles in latex next to rubber particles. They are vacuoles, which are usually between 0.5-3 μm in diameter, bound to a unit membrane of about 80 Å in thicknesses [18]. The pH of lutoid is 5.5. Inside of lutoid particle, there is an aqueous containing substances such as acids, mineral salts, proteins, sugar and polyphenol oxidase, which causes rubber more yellow or brown when it is oxidized by oxygen in air.

Besides, osmosis can occur easily on lutoid because of both encapsulations by one thin layer and hot weather. When lutoid swells, latex viscosity increases, and when lutoid breaks down, latex viscosity decreases. Furthermore, breaking down of lutoid releases positive charge colloids and metal ions such as calcium and magnesium. These ions, coming out from lutoid to latex, causes coagulation. Moreover, adding ammonia into latex causes brown or purple precipitate at the bottom layer of latex because both magnesium ion and residual pieces of breaking lutoid combine with ammonia.

Frey-Wyssling

The size of Frey-Wyssling particles is bigger than rubber particles. However, its density is less than rubber particle. The Frey-Wyssling is spherical with encapsulation by two carotenoid layers, which make rubber to be dark yellow or orange. Frey-Wyssling can also combine with ammonia and precipitates into serum fraction.

The non-rubber matters are composed of many constituents as shown in Table 2.2.

Table 2.2 Non-rubber constituents in latex [19].

Constituents	Percentage by weight of latex
Fatty acid soap (e.g. ammonium oleate)	0.5
Sterols and sterol esters	0.5
Proteins	0.8
Quebrachitol	0.3
Choline	0.1
Glycerophosphate	0.1
Water-soluble carboxylicacid salts (acetate, citrate, etc.)	0.3
Amino acids and polypeptides	0.2
Inorganic salts (ammonium and potassium carbonate and phosphate, etc.)	0.2

2.1.4 Particle Size of Natural Rubber

The particle size of rubber particles in the fresh field latex depends on the age and clone of rubber trees. Natural rubber latex from the mature trees was found to contain large and small rubber particles. The average size of large rubber particles (LRP) was about 0.04 – 4 µm with mean diameter of 1.03 µm. On the other hand, the size distributions of small rubber particles (SRP) in the serum phase ranging between 0.05 – 0.3 mm. The total latex shows a similar particle size distribution to that of the LRP rubbers as can be seen from Figure 2.6.

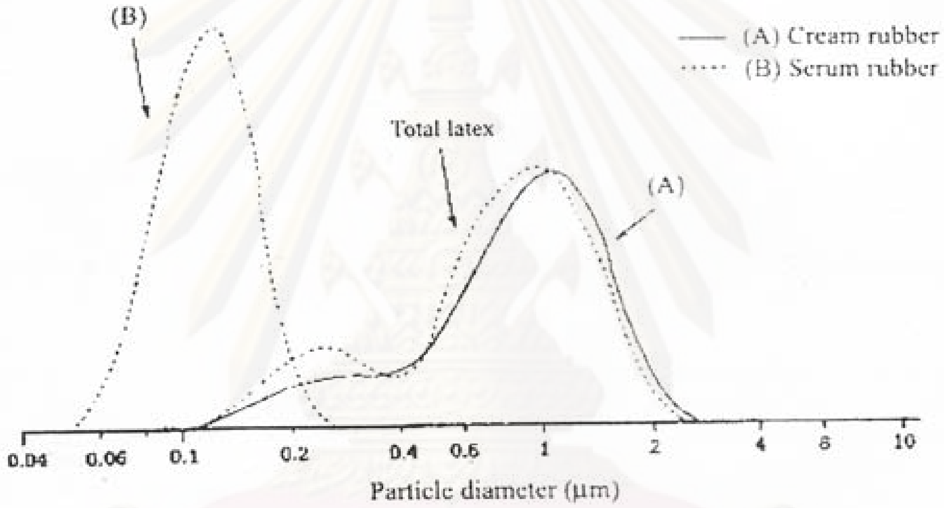


Figure 2.6 Particle size distribution of fresh field latex [7].

2.1.5 Molecular Weight (MW) and Molecular-Weight Distribution (MWD) of Natural Rubber from *Heavea brasileinsis*

NR obtained from *Hevea brasiliensis* is a polymer of a very high molecular-weight and wide MWD. The variation of MWD depends on the clone from which the rubber is obtained, the age of tree, soil and climatic conditions. It was reported that NR have a bimodal distribution. An exhaustive study of the MWD of NR in latex by the use of size exclusion chromatography (SEC or GPC) was reported by Subramaniam [20]. The distribution of all clonal rubbers can be classified into one of three types as shown in Figure 2.7.

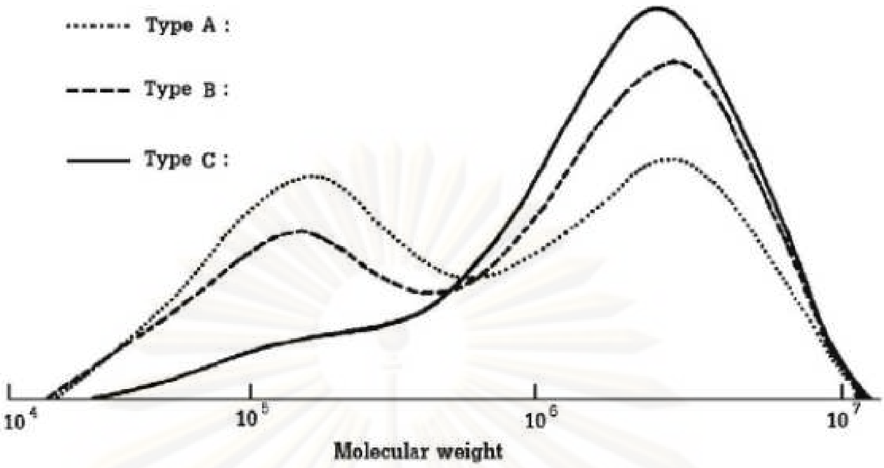


Figure 2.7 Types of molecular-weight distribution curves of natural rubber [20].

Type A. Distinctly bimodal distribution where the peak height in the low molecular-weight region is nearly equal or slightly less than the peak height at the high molecular-weight region.

Type B. Bimodal distribution where the height of the low molecular-weight peak is only half or less the height of the high molecular-weight peak.

Type C. Skewed unimodal distribution with a “shoulder” or a “plateau” in the low molecular-weight region.

The polydispersity of molecular-weight by the M_w/M_n value is extremely high in NR ranging from 2.5 to 10. The range of molecular-weight is approximately the same in rubber from all clones, although the shapes of MWD curve are different, usually from about 3 x 10^4 to 1.2 x 10^7. The high molecular-weight peak appears between 1 x 10^6 for different rubbers. The peak top of the low molecular-weight peak is appeared between 1 x 10^5 and 2 x 10^5. The high molecular-weight rubber fraction has been presumed to be derived from branching, presumably found by the reaction of abnormal groups [21].

2.2 Manufacturing of Natural rubber latex

Natural rubber latex exudes from the *Hevea brasiliensis* tree having rubber content between 25 and 40% w/v, the average being 33%. The remainder of the latex is mainly water. There are four principal reasons why it has become common practice to concentrate natural rubber latex before transportation:

1. It is uneconomical to transport preserved field natural rubber latex over large distances, because this would necessitate transporting a mass of water equal to approximately twice the mass of the dry rubber.

2. Several of the industrial processes which use natural rubber latex require it in a more concentrated form than 33%.

3. Natural rubber latex concentrates tend to be more uniform in quality than the field lattices from which they were obtained. This is mainly a consequence of the bulking and concomitant blending which precede and follow the concentration process. Differences between batches of field latex therefore tend to be mitigated.

4. The ratio of non-aqueous non-rubber substances to dry rubber is reduced in the course of some of the concentration processes, because the non-rubber substances are preferentially eliminated. The product is in consequence a closer approximation to a colloidal dispersion of natural rubber in water than is preserved field natural rubber latex. As such, it more closely approximates to what is perceived to be ideally required in several industrial processes.

The various methods which have been proposed for concentrating natural rubber latex, have received serious attention as practicable processes. These are evaporation, electro-decantation, centrifugation and creaming.

2.2.1 Concentration by Evaporation

The concentrating natural rubber latex by evaporation appears to have been patented by the K.D.P. Ltd [22]. One particular way of carrying out this process is illustrated schematically in Figure 2.8.

In a typical example of this process, the latex to be concentrated is heated to 90°C and introduced through suitable nozzles into an evaporation chamber in which the air pressure has been reduced to about 10 kPa. The corresponding boiling-point of water at such a pressure is 46°C. At the moment of entering the evaporator, a rapid fall in temperature of about 44°C occurs, and at the same time the water content of the latex is reduced by 7%. In this case, the operation must be repeated about 11 times if it is required to increase the total solids content of the latex from 35% to 75%.

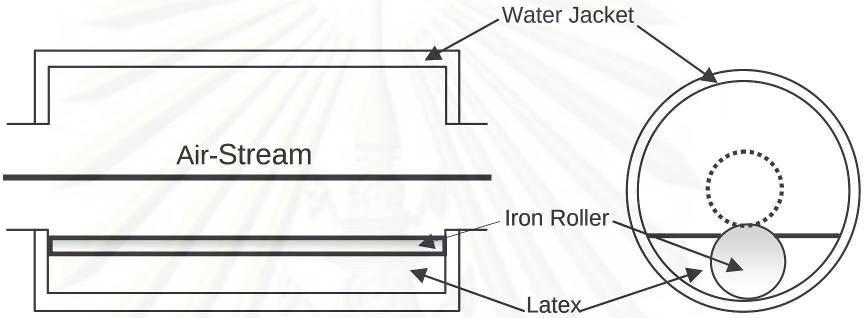


Figure 2.8 Schematic illustration of typical equipment for concentrating natural rubber by evaporation [22].

2.2.2 Concentration by Electro-decantation

The principle of the concentration of natural rubber latex by electro-decantation is illustrated in Figure 2.9 [23]. An electrical potential difference is applied between the two electrodes. Being negatively-charged, the rubber particles tend to move towards the anode. The separation rate of latex into the cream and skim is accelerated by increasing semi-permeable membrane unit between the two electrode compartments. In practically, anionic surface-active substances increase the magnitude of the negative charge carried by rubber particles, so the efficiency of process is improved.

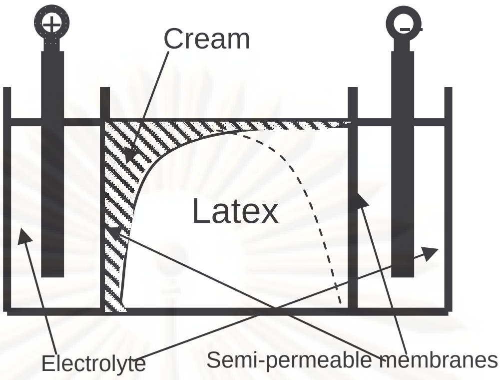


Figure 2.9 Concentration of natural rubber latex by electro-decantation [23].

2.2.3 Concentration by Centrifugation

Centrifugation is by far the most important method currently used for the concentration of natural rubber latex. Very roughly about 90% of the natural rubber latex concentrate used industrially is produced by centrifugation, most of it by subjecting the latex to a single stage of centrifugation. Centrifugation is in effect a type of accelerated creaming process, in which the motion of the rubber particles relative to the aqueous phase is affected by means of a centrifugal field rather than a gravitational field. The successful concentration by centrifugation depends upon there being a significant difference between the density of the rubber particles and that of the aqueous phase. The centrifuge concentrate is also known as cream, and the dilute latex obtained as a by-product is known as skim. Skim rubber contains about 5 -10% of the total rubber after centrifugation. Other non-rubbers remain in the serum phase. The product process of concentrated latex by centrifugation is shown in Figure 2.10.

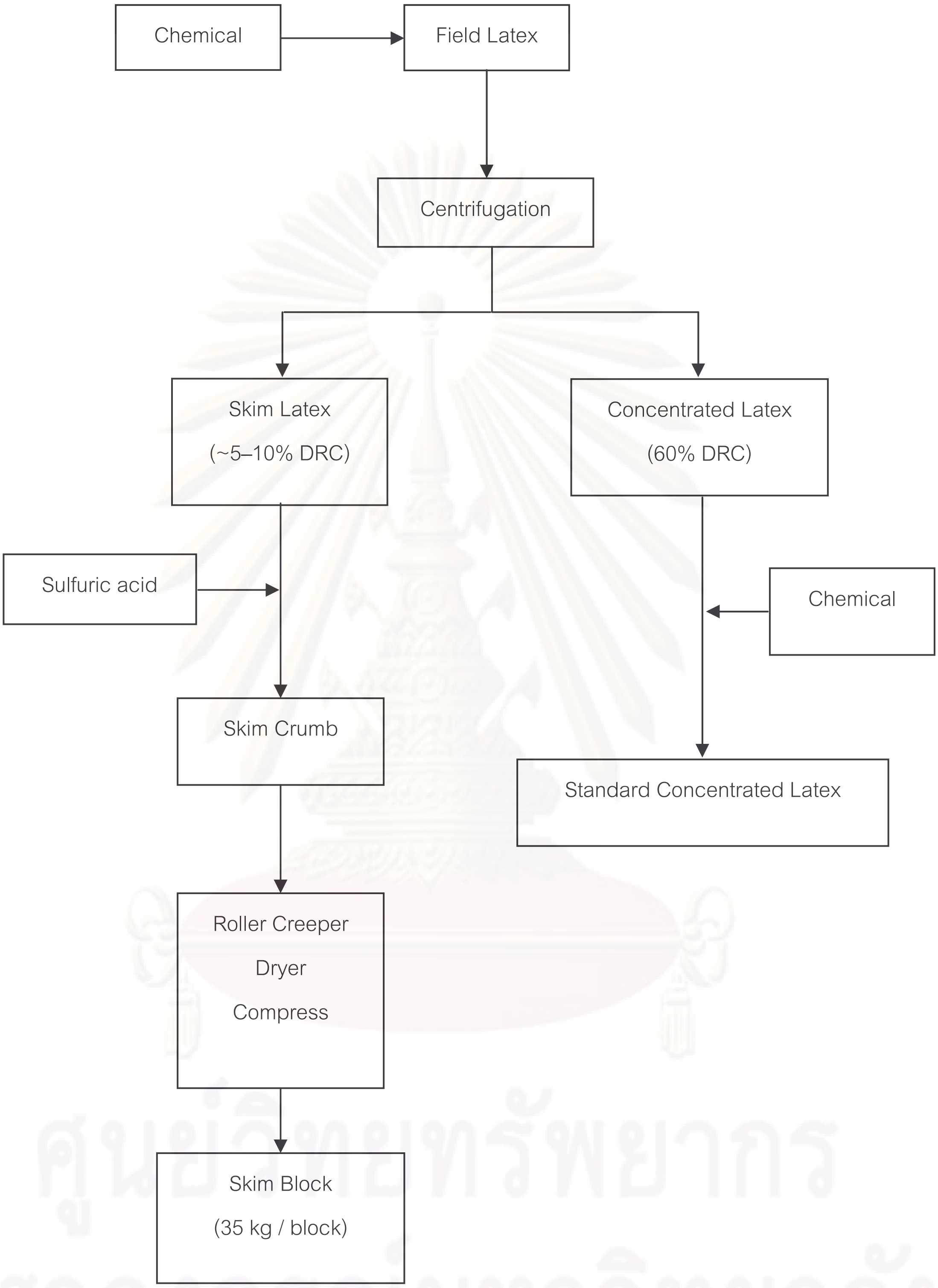


Figure 2.10 Commercial production of concentrated latex, skim latex and skim rubber [20].

According to theory of centrifugation, the motion of a centrifuging latex particle relative to its serum is confined to the radial direction, while the lateral movement relative to the serum may be neglected. The equilibrium radial velocity of a particle is determined by the balance between two forces, centrifugal buoyancy and viscous drag. The rate of movement of a suspended spherical particle under centrifugal field is predicted by Stokes' law [21], as shown in equation (2.1)

$$V = (\rho_s - \rho_p)\omega^2 R\phi / 18\eta \tag{2.1}$$

where V : particle velocity

ρ_s : density of serum (1.02 g/cm^3)

ρ_p : density of particle (0.93 g/cm^3)

ω : angular velocity

ϕ : particle diameter

R : radius path of centrifugator

η : viscosity of serum

The type, de Alfa Laval, is the most common commercial type of centrifugation. The important factors affecting the composition of the cream phase are as follows:

- Feed rate: The reduction of feed rate increases the efficiency of concentration and rubber content.
- Angular velocity of centrifugation: The increasing centrifugation speed promotes the efficiency of the separation.
- Length of the regulating screw: The regulating screws of various lengths into the skim discharge orifice can control the equilibrium difference between the density of the discharging skim and cream phases.

2.2.4 Concentration by Creaming

Particles dispersed in a fluid medium and subjected to a gravitational field have a tendency to move relative to the dispersion medium if the density of the particles differs from that of the dispersion medium. If particles are less than the dispersion medium, as it is for natural rubber latex, then the latex particles will move upwards with the passage of time. This process is known as creaming, and the concentrate as cream. The dilute latex which forms as the lower layer when latex cream is known as skim as shown in Figure 2.11. The rate of movement of a suspended spherical particle under gravity is predicted by Stokes' law, as shown in equation (2.2)

$$V = (\rho_s - \rho_p) g \phi^2 / 18\eta \tag{2.2}$$

where g : gravitational force

In practice, the rate of creaming of natural rubber latex can be markedly increased by small additions of water-soluble hydrocolloids to the latex, e.g. sodium alginate. Various explanations of mechanism by which creaming agents operated have been proposed, but it seems likely that loose and reversible aggregation of the particles occurs. This leads to an increase in particle size, and then the Brownian movement and the intensity of the negative electric charge on the particle surface are reduced remarkably. Thus the effective size of particles size increases, favoring faster creaming. This evidence is resulting in a creaming rate. A wide range of water-soluble hydrocolloids will act as creaming agent in NR latex, if they were added at the optimum condition. The method of concentration has several important advantages over other methods. The requisite equipment is simple and easy to operate, *i.e.*, labor costs are low, power requirements are negligible, and the loss of rubber in the skim latex is small.

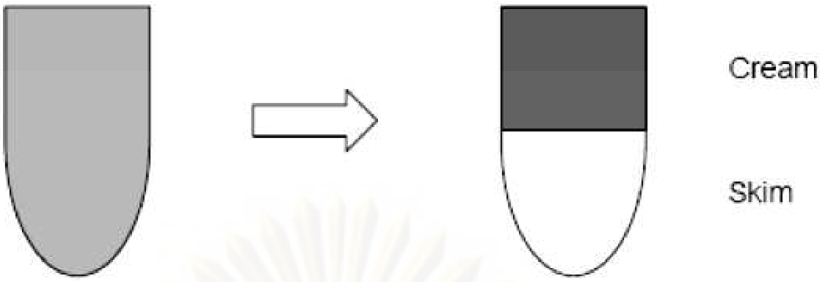


Figure 2.11 Creaming process of natural rubber latex.

After centrifugation or creaming to concentrate the latex, the concentrated latex is then preserved by further additions of ammonia, usually at 0.60 to 0.75% weight based on the weight of latex, if used alone to produce what is called high ammonia (HA) latex or at 0.15 or 0.25% if used in combination with secondary bactericides to produce is low ammonia (LA) latex.

2.3 Destabilization of Natural Rubber Latex

2.3.1 Chemical Destabilization [28]

Chemical coacervants function mainly by reducing the zeta-potential, which is associated with the electrical double layer surrounding the latex particle.

- neutralization of electrical charge of latex particle, e.g., acid, metallic ions, cationic surface-active substances
- compression of the electrical double layer, e.g. electrolyte
- dehydration of rubber molecule, e.g. acetone, ethyl alcohol
- surface phase separation of polymer and aqueous phase, e.g., toluene, benzene, carbon tetrachloride
- heat-sensitizing effect, e.g., polypropylene glycols, zinc amide
- viscosity induced gelation, e.g., salt of hydrofluorosilicic acid
- radiation induced photochemical oxidation, e.g., UV light

2.3.2 Physical Destabilization [29]

Physical factors are able to destabilize the latex, if they increase either frequency or/and violence of the collision between particles.

- maturation of latex
- electrical field
- high concentration of latex
- dilution of latex (desorption of stabilizing substance)
- high temperature of latex
- low freezing temperature of aqueous phase
- evaporation of aqueous phase
- vigorous mechanical agitation

2.4 Vulcanization of Natural Rubber Latex

Useful rubber articles, such as tyres and mechanical dipped goods, cannot be made without vulcanization because raw rubber (unvulcanized) is in general mechanically weak, deficient in elastic recovery, sensitive to temperature (becoming stiff when cold and soft when hot) and greatly swollen or dissolved by many organic liquids. Also all rubbers require vulcanization to improve strength and elastic recovery, reduce temperature sensitiveness and improve resistance to liquids. Vulcanization is carried out by using sulfur, peroxide or high energy radiation. The most widely used method for vulcanization of natural rubber latex is sulfur vulcanization.

Sulfur Vulcanization

Vulcanization process of NR latex using sulfur as crosslinking agent can be made in two ways; prevulcanization and post-vulcanization. In the first method, natural rubber latex is vulcanized with the rubber still remaining in the dispersed phase. Prevulcanized latex may be carried out by mixing suitably stabilized latex with vulcanization ingredients (sulfur, accelerators and activators). The crosslink reaction takes place over maturation at temperature 20°C to 90°C for appropriate periods. The rate of prevulcanization varies with different vulcanization systems and the extent of prevulcanization has influence on the final vulcanization properties. After drying the latex, a vulcanized film with good strength properties is obtained without further heating because the rubber particles in prevulcanized latex have already chemically crosslinked.

For the latter method, the compounded latex is vulcanized after it has been dried down to give a film with better resistance to oils, greases and solvents when compared to prevulcanized film. Furthermore, the mechanical properties of post-vulcanized latex film are similar to or better than those of the film prepared from prevulcanization. In addition, the thickness of the compounded latex film has influence on the temperature and vulcanization time to achieve the required degree of crosslinking.

Various types of chemical grouping which have been so far deduced to be present in sulfur vulcanizates of NR are shown in Figure 2.12 of course not all the grouping are present in every case and the relative concentrations of each may vary widely, depending particularly on the molar ratio of accelerator to sulfur (A/S) used which can be classified as in Table 2.3 [43]. The first is conventional (CV) or high sulfur vulcanizing system, which polysulfidic crosslink combined in the network for each chemical crosslink. Whereas disulfidic linkages are predominantly form in this rubber vulcanized by using semi-EV system. Finally, the efficient vulcanizing system (EV) presents monosulfidic crosslink.

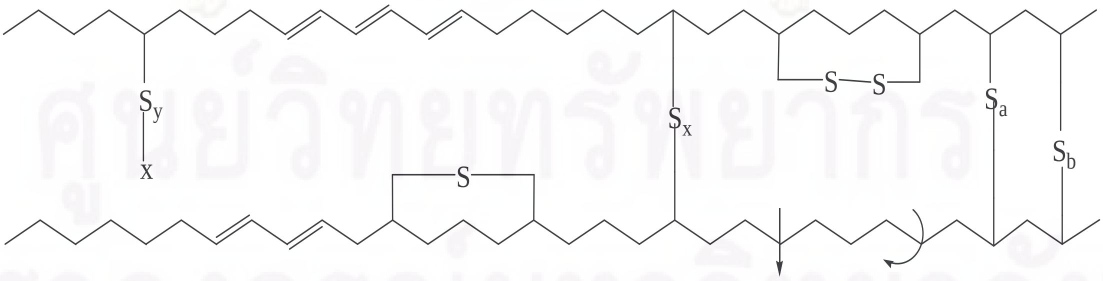


Figure 2.12 Diagrammatic representation of network structure of sulfur vulcanizate (x,y, a and b = 1-9, x = accelerator fragment, curly arrow denotes *cis-*, *trans-*isomerized double bond, and downward arrow denotes main chain scission) [43].

Table 2.3 Classification of sulfur vulcanization systems [50].

Class	Sulfur (S) (phr)*	Accelerator (A) (phr)*	A/S ratio
Conventional (CV)	2.0-3.5	1.0-0.5	0.1-0.5
Semi-EV	1.0-1.8	2.5-1.0	0.6-2.5
Efficiency (EV)	0.3-0.8	6.0-2.5	3.0-25.0

*phr: parts per hundred rubber

2.5 Compounding of Natural Rubber

Regularly, compounding transforms NR into a range of materials suitable for applications. Such transformation is accomplished by an addition of a number of ingredients for instance, carbon black or non-black fillers or both, activators, accelerators, vulcanizing agents, suitable antidegradants and sometimes retarders or prevulcanization inhibitors. The objectives of compounding are

(a) to facilitate processing and fabrication.
(b) to ensure a rapid throughput with minimal rejection rate.
(c) to achieve the required balance in vulcanizate properties.
(d) to provide durability, all at the lowest possible cost [24].

2.5.1 Accelerators

The vulcanization process can generally be accelerated by adding small amounts of chemicals known as accelerators. The classification of these accelerators, in terms of their chemical composition and speed of vulcanization, is shown in Table 2.4.

Table 2.4 Classification of accelerator groups and their relative curing speeds [25].

Type	Example	Relative curing speed
Guanidines	DPG	Slow
Dithiocarbamates	ZDEC, ZDBC	Very fast
Thiurams	TMTD, TMTM	Very fast
Thioureas	ETU	Fast
Thiophosphates	DIP, DIS	Semi-fast
Thioazoles	MBT, MBTS, ZMBT	Moderate
Sulfenamides	CBS, MBS	Fast with delay-action

Functionally, accelerators are typically classified as primary or secondary accelerators. The former usually provides considerable medium to fast cure and good modulus development. The latter usually produces scorchy, very fast curing stocks. The secondary accelerators are seldom use alone, but generally are found in a combination with primary accelerators to gain faster cures or greater product properties.

2.5.2 Activators

Activators are chemical used to activate or extract the full potential from the organic accelerators. Useful activators include metal oxides (usually zinc oxide; ZnO), fatty acids and nitrogen containing bases. ZnO is the most widely used inorganic activator (lead and magnesium oxides are also used, but less often). For ZnO to be fully effective, ZnO must be present in a form that can react with the accelerators system [26].

2.5.3 Antidegradants

Antidegradants are commonly used to protect rubber both in uncured and cured states. Normally, there are many kinds of antidegradants widely used in the rubber industries. The types of antidegradant can be classified by their duties, namely antiozonants and antioxidants, which are used to protect the rubber from ozone attack and oxidation of rubber, respectively. Types and applications of elastomer are the principle factor in considering the antidegradant used.

2.5.4 Reinforcing Fillers

Reinforcing fillers are used to reinforce or enhance properties of elastomer while reduce cost the compounds. In black-filled compounds, carbon blacks are used. For non-black compounds, silicas, clays, calcium carbonate, etc. can be used depending on the properties required. The most commonly known reinforcing fillers are carbon blacks and silicas. Silicates, clays, whiting (calcium carbonate), and other mineral fillers are used extensively where a high degree of reinforcement is not essential.

2.5.5 Organic Peroxides

Organic peroxides are curing agents that posses one or more oxygen-oxygen (R-OO-R) bonds. These chemicals are used commercially to produce free radicals, yielding the desired crosslinked networks in elastomer via hydrogen abstraction and/or addition at double bonds. The structure of the peroxides affects strongly their thermal and chemical stabilities, as well as the energy level of the free radicals generated [27]. These are generally seven major classes of organic peroxides as shown in Table 2.5.

Table 2.5 Major commercial organic peroxide classes [30].

Organic peroxide	10 h half life
Diacyl peroxides	21-75°C
Peroxydicarbonates	49-51°C
t-Alkyl peroxyesters	38-107°C
Peroxyketals	92-112°C
Dialkyl peroxides	115-13°C
Tert-Alkyl hydroperoxides	Not applicable
Ketone peroxides	Not applicable

Four classes of organic peroxides are used commercially for crosslinking and polymer modification of polyethylene and elastomers: diacyls, peroxyesters, peroxyketals, and the dialkyl type peroxides [31,32]. Each class of peroxide has a distinctive half life (thermal stability). The most common peroxide used in the crosslink industry has traditionally been the dialkyl classes. However, there are several other peroxide types, which provide distinctive advantages, such as aromatic odorless, non-bloom, and liquid form, in many manufacturing operations.

2.6 Latex Film Formation

The term ‘latex film’ normally refers to a film formed from soft latex particles where the forces accompanying the evaporation of water are sufficient to compress and deform the particles into transparent, void free-films. Three steps can be distinguished in the process of film formation from latex considering only pure, unfilled polymeric films as shown in Figure 2.13.

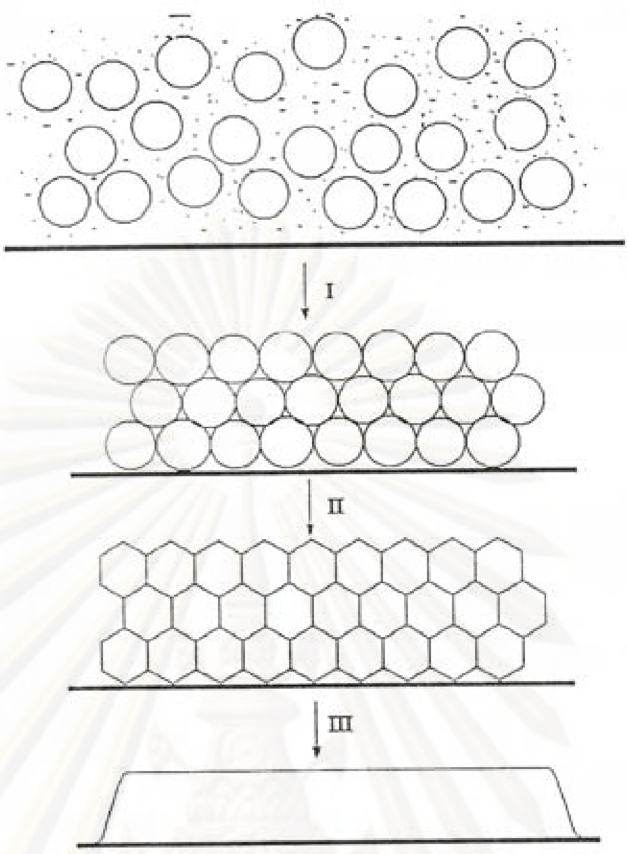


Figure 2.13 Schematic of latex film-formation process showing the three main steps:

I) Concentration of latex.

II) Deformation of particles.

III) Interdiffusion of chains across particle boundaries.

Step I

In the first step, water evaporates at a constant rate until the particles from a dense packing of spheres. For a monodispersed latex, the highest solids volume faction is then to 0.74. An additional condition for high packing fraction is sufficient colloidal stability.

Step II

At the beginning of the second step, particles appear at the surface of latex, and the rate of water evaporation decreased. Forces start to act and ensure the deformation of the particles in such a way that polymeric materials fill all the space.

The forces acting have to overcome the mechanical resistance of the particles to deformation. Later, the spherical particles are transformed into rhombic dodecahedra. At this stage, interfaces between particles still exist.

Step III

The final step corresponds to evolution of the interfaces between particles. They tend to disappear by interdiffusion of the macromolecular chains from one particle to its neighbors. It is sometimes called maturation. A film property like mechanical strength is altered during this step.

2.7 Literature Reviews

Dafader *et al*. [33] studied the creaming of field natural rubber latex by using sodium alginate as creaming agent. It was found that 64.37% of total solid contents (TSC) in creamed rubber latex was obtained by using concentration of creaming agent as 6 parts per hundred of rubber (phr), creaming time of 24 hours and temperature of 40°C. The physico-chemical properties of creamed latex were consistent with ASTM specification.

Loykulnant *et al*. [34] studied the recovery of skim natural rubber latex (SNRL) by using water-soluble biopolymers and their derivatives, N,O-carboxymethyl chitosan (CMCh) and hydroxypropylcellulose (HPC), as creaming agent. It was found that creaming of skim natural rubber latex could be achieved by using both agents. Phase separation between cream and serum phases depend on concentration of creaming agents and creaming time. The concentration of CMCh between 7.34 to 10.3 g/L provided the recovered skim rubber more than 90%. Using of various concentrations of HPC, 3.37 -11.8 g/L, the phase separation of SNRL could be occurred similar to the case of using CMCh. HPC could be recovered from the serum phase by heating at 50°C. More than 90% of HPC could be recovered and reused effectively.

Moonprasith *et al*. [35] studied the recovery of residual rubber from skim natural rubber (SNR) latex, based on using hydroxypropyl methyl cellulose (HPMC) as a thermo-responsive flocculants. The SNR particles were completely separated to form high concentrated latex as cream phase within only 5 hours. Almost 100% of SNR was recovered when using HPMC 0.7%w/w. HPMC could be precipitated from the serum phase by heating the serum phase at about 70°C.

Werathirachot *et al*. [36] studied the creaming of skim natural rubber latex by using water soluble chitosan as creaming agent. When adding chitosan solution to the neutral skim rubber latex with a rubber content of 5.3% w/v until the concentration of chitosan in the dispersion was 0.107%, the phase separation between rubber particles and yellow serum was clearly observed.

Gorton and Pendle [37] reported the effect of particle size of sulfur, zinc diethyl dithiocarbamate (ZDEC) and zinc oxide (ZnO) dispersions upon the sulfur vulcanized ammonia-preserved NR latex at vulcanization temperature of 60°C for period of time 1 to 6 hours. It was found that over the range of particle sizes of sulfur, ZDEC and ZnO appeared to have almost no effect upon the tensile properties.

Claramma *et al*. [38] studied the sulfur vulcanization of natural rubber latex at 60, 70, 80 and 90°C for different period. For the ratio of S : ZDEC : ZnO dispersion in formulation of latex compound as 3 : 2 : 0.4 phr, maximum of crosslink density of latex film was achieved when the vulcanized rubber latex was conducted at 80°C for 2 hours or 90°C for 1 hour. At lower temperatures, the rate of vulcanization was slow. At each temperature, the tensile strength and elongation at break decreased when the vulcanization time increased.

Ho *et al*. [39] studied the effect of maturation duration of vulcanized natural rubber latex on the properties and morphology of latex films by atomic force microscopy. It was found that crosslink density of latex films increased when maturation duration was increased. The maximum crosslink density of 6.14 x 10^{-6}

mol/cm^3 was achieved under maturation for 8 days. The results of surface morphology of latex films presented the vulcanization mechanism controlled by the relative rates of the diffusion of vulcanizing reagents and the crosslink reaction within the latex particle as shown in Figure 2.14.

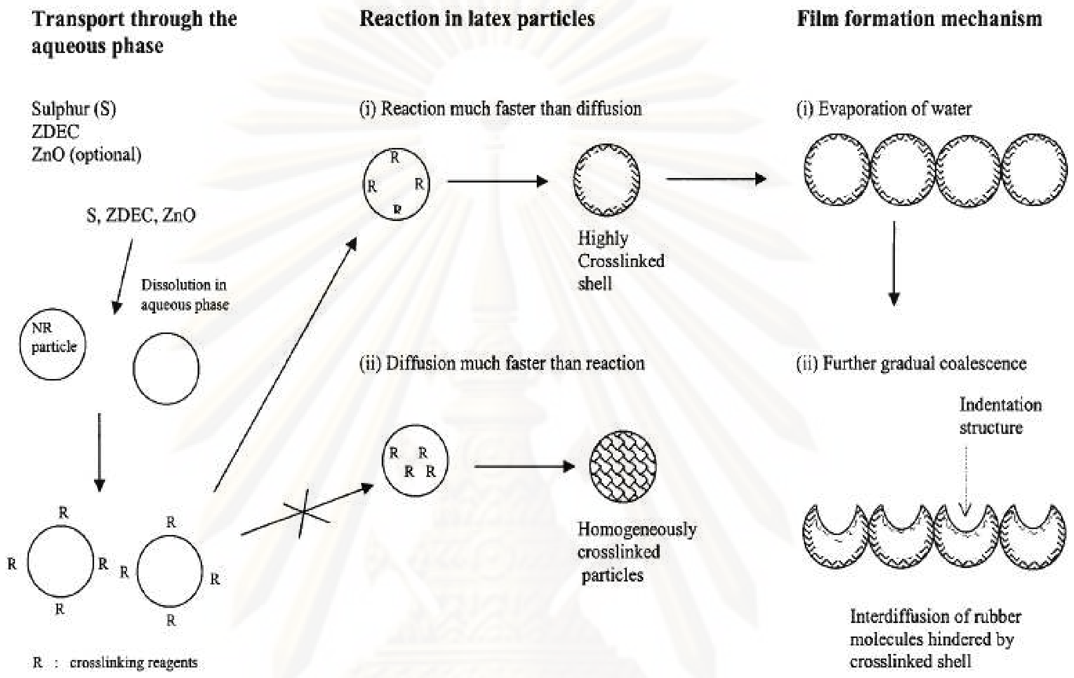


Figure 2.14 Proposed mechanisms of vulcanization of latex and its film formation [39].

Sasidharan *et al.* [40] studied effect of vulcanization time and storage on the stability and physical properties of sulfur-vulcanized natural rubber latex. It was found that as vulcanization time increased, the mechanical stability time (MST), the tensile strength and modulus increased and the elongation at break decreased. The change in the stability and physical properties were due to the crosslinking of rubber particle during vulcanization. At periods of storage between 0 to 300 days, the MST values of all vulcanized latex increased during storage for 120 days, and thereafter MST gradually decreased.

CHAPTER III

EXPERIMENTALS

3.1 Materials and Chemicals

3.1.1 Material

Field natural rubber latex was obtained from N.Y. Rubber Company in Chonburi, Thailand.

3.1.2 Chemicals

No.	Chemicals	Supplier	Grade
1	Ammonia	BDH Chemicals Ltd.	Analytical
2	Carboxymethyl cellulose	Honghuad Ltd.	Commercial
3	Hydroxyethyl cellulose	Honghuad Ltd.	Commercial
4	Hydroxypropyl methyl cellulose	SR Lab	Commercial
5	Lauric acid	Earth Chemical Ltd.	Analytical
6	Potassium hydroxide	Earth Chemical Ltd.	Analytical
7	Sulfur	Pan Innovation Ltd.	Commercial
8	Zinc oxide (ZnO)	Pan Innovation Ltd.	Commercial
9	Zinc diethyl dithiocarbamate (ZDEC)	Pan Innovation Ltd.	Commercial
10	Tetramethylthiuram disulfide (TMTD)	Pan Innovation Ltd.	Commercial
11	Acetic acid	Earth Chemical	Analytical
12	Chloroform	BDH Chemicals Ltd.	Analytical
13	Toluene	SR Lab	Analytical
14	Sodium sulfite	SR Lab	Analytical

3.2 Procedures

3.2.1 Creaming of Natural Rubber Latex

The creaming agent was dissolved in deionized water. Field natural rubber latex preserved with 0.4% ammonia solution was charged in a beaker then creaming agent and 0.4% ammonium laurate were added. The mixture was gently stirred for 1 hour to ensure thorough mixing of the system. The mixture was transferred to a separating funnel then allowed to stand for phase separation (Figure 3.1). The cream phase and the serum phase were separated. Dry rubber content (DRC) of cream rubber latex was determined.

Creamed natural rubber latex was weighed approximately 5 g into a watch glass and then latex is coagulated by sufficient 6% w/v of acetic acid. The glass was stand at room temperature until a clear serum appeared. Coagulum latex was picked up with the main body of the coagulum. The coagulum was washed with running water for 10 minutes, passed between rolls to a thickness of 2 mm and dried at 70±20°C in a hot air oven atmosphere. The dried rubber was cooled in desiccator to room temperature and weight. Drying and weighing was repeated until the mass was constant. The percentage of DRC was calculated by using equation (3.2)

$$\%DRC = \frac{W_c}{W_0} \times 100 \tag{3.2}$$

where W_c = weight of dry coagulum (g)

W_0 = weight of creamed latex sample (g)

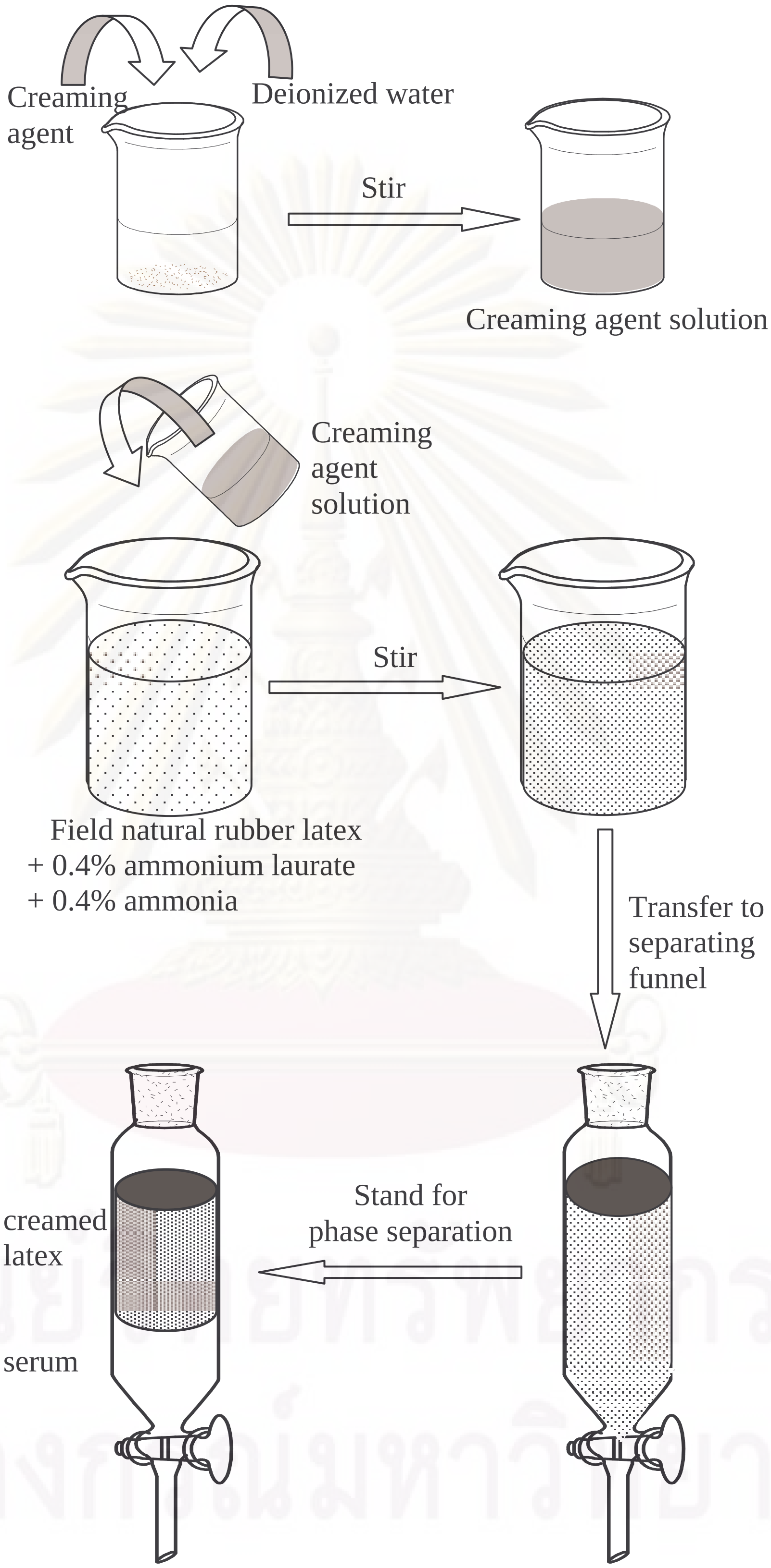


Figure 3.1 Procedure for creaming process of creamed latex.

3.2.2 Free-vulcanized Rubber Latex

Free-vulcanized rubber latex was prepared by using creamed natural rubber latex and ingredients according to the formulation given in Table 3.1. The procedure was shown in Figure 3.2. The insoluble compounding ingredients such as vulcanizing agents (sulfur, ZDEC, ZnO and TMTD) were prepared in dispersion. The materials were dispersed in water by grinding action and the dispersing agent prevented the dispersed particles from reaggregating. A ball mill was used for making the dispersions for 48 h. Ammonium luarate was prepared by neutralizing lauric acid with ammonium hydroxide. All ingredients were added to creamed latex and stirred in water bath set at constant temperature for 1-6 h and cooled to room temperature. Films were prepared by casting the vulcanized latex onto glass substrates to a thickness of about 2 mm, drying was done at room temperature.

Table 3.1 Formulation of free-vulcanized rubber latex.

Ingredients	Part by Weight (Dry) phr*
Creamed natural rubber latex	100
Potassium hydroxide solution (10%)	2.5
Potassium laurate solution (20%)	2.0
Sulfur dispersion (50%)/TMTD dispersion (33%)	1.0-3.0
ZDEC dispersion (50%)	3.0
Zinc oxide dispersion (50%)	3.0

*phr = part per hundred

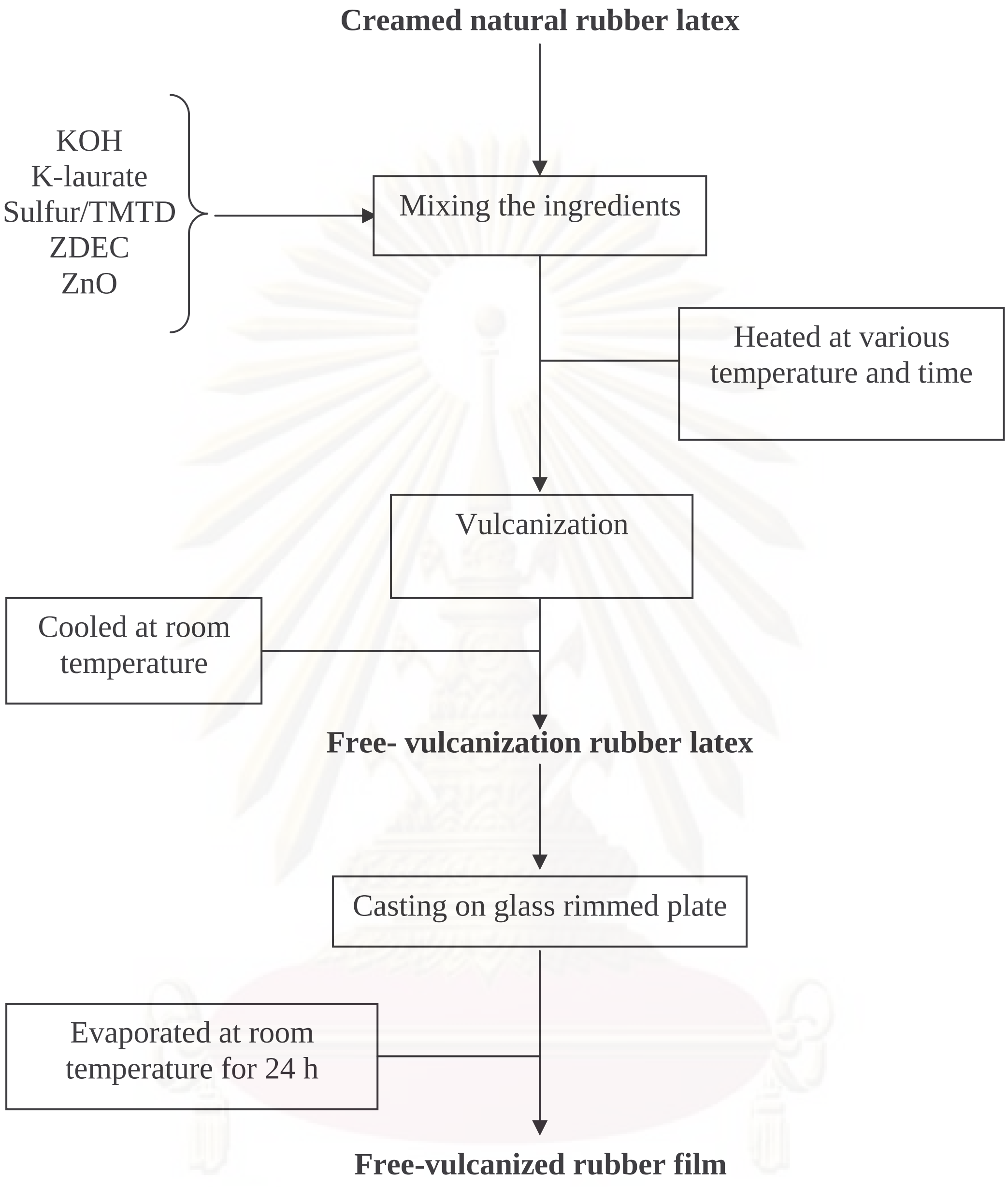


Figure 3.2 Production of free-vulcanized rubber film.

3.3 Measurement of Mechanical Properties

3.3.1 Tensile Properties

The free-vulcanized film samples were cut into tensile specimens using a die C. The cutting die punched the specimen into dumbbell test piece as shown in Figure 3.1. The dumbbell samples used were 25 mm in gauge length, 25 mm in width and 2.0 mm in thickness. Testing were carried out on LLOYD Universal Testing Machine model LR5K in accordance with ADTM D412. The crosshead speed of 500 mm/min was used with a full scale force at 5 kN. Five specimens were used for each tensile measurement. The elongations at break were also measured.

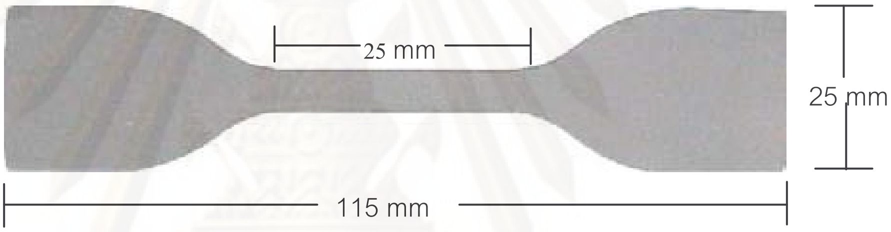


Figure 3.3 Tensile test specimens**.**

3.3.2 Hardness

The hardness testing was measured using Durometer Shore-type-A according to ASTM D2240. The test temperature was room temperature. The measurements were taken from five different points distributed over the sample and the reported values were based on an average of five measurements.

3.4 Determination of Chloroform Number

The chloroform test was performed by mixing equal part (ca. 5 g) of free-vulcanized latex and chloroform and then stirring with a glass rod until coagulation is complete. The coagulum was allowed to stand for 2-3 minutes. The state of vulcanization could therefore be judged from the appearance of the coagulum. An arbitrary number, known as the chloroform number, is assigned to the latex on the basis of appearance. Four stages of latex vulcanization are usually distinguished by this test, and are assigned as chloroform numbers as follows, the perceived degree of vulcanization increased with increasing chloroform number as follows:

	State	Coagulum form
No.1	uncrosslinked rubber	tacky lump
No.2	lightly vulcanized rubber	tender lumps, breaks short
No.3	moderately vulcanized rubber	non-tacky crumbs
No.4	fully vulcanized rubber	fine dry crumbs

3.5 Determination of Equilibrium Swelling

The equilibrium swelling of a vulcanized rubber in a solvent is dependent on the density of crosslink, the nature of the solvent, and the rubber. With a given rubber solvent system, therefore, the equilibrium swelling value becomes a measure of the crosslink density of the vulcanizate. Equilibrium swelling values are determined by immersing a thin film of the rubber (10 x 10 x 20 mm) in the solvent, usually toluene, for 48 hours and measuring the increase in weight at equilibrium. Equilibrium swelling ratios are usually calculated in the following equation (3.4)

$$\mathrm{Q} = \frac{W_2 - W_1}{W_1} \tag{3.4}$$

where Q = swelling index
W_1 = initial weight
W_2 = equilibrium swelling weight

The variation of 'Q' with crosslink density, for conventionally-cured natural rubber in toluene, may be broadly described as follows:

Unvulcanized rubber, Q = >15
Lightly vulcanized, Q = 7-15
Moderately vulcanized, Q = 5-7
Fully vulcanized, Q = <5

3.6 Determination of Crosslink Density

The crosslink density efficiency of the specimens was evaluated in terms of crosslink density using an equilibrium solvent swelling test method. The specimens (10 x 10 x 20 mm) with accurately weight were immersed in toluene and allowed to swell in close vessels for 7 days. Then, the surface of the swollen samples was quickly wiped and weighted (w_1). After drying at 40^{o}C for 48 h, the dried rubber samples were weighed again (w_2) to determine the amount of absorbed toluene inside the samples. The volume fraction of polymer in the swollen specimens (v) was calculated using equation (3.5)

$$v = \frac{w_2(\delta_r)^{-1}}{w_2(\delta_r)^{-1} + (w_1 - w_2)(\delta_s)^{-1}} \qquad (3.5)$$

where δ_r and δ_s are the density of rubber and solvent, respectively. The crosslink density of the specimens was calculated based on the Flory-Rhener equation (3.6)

$$-[\ln(1-v)] + v + \chi v^2 = V_0 n[v^{1/3} - \frac{v}{2}] \qquad (3.6)$$

where n is the number of elastically active chains per unit volume (mol/cm^3). V_0 is the molar volume of the solvent (106.3 cm^3/mol for toluene) and χ is the Flory-Huggins polymer solvent interaction term (0.39 for NR-toluene).

3.7 Determination of Free Sulfur

The sulfur in a rubber compound available for further vulcanization is extractable by sodium sulfite. This sulfur is determined by titrating, the thiosulfate resulting from extraction with sodium sulfite solution (50 g/dm^3). It represents essentially the elemental sulfur, but will include small amounts of coordinately bound sulfur (such as some of the polysulfide sulfur) and organically bound sulfur in some cases, particularly in the presence of thiuram disulfide compounds. Free sulfur shall be determined in accordance with ASTM D297-81.

Free-vulcanizate samples were treated with sodium sulfite solution; sodium sulfite reacted with sulfur to form sodium thiosulfate, which was, in turn, determined idiomatically.

CHAPTER IV

RESULTS AND DISSCUSSION

4.1 The Effect of Operating Parameters on Creaming

Three different cellulose derivatives were used in this process; carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) and hydroxypropyl methyl cellulose (HPMC). The influences these creaming agents were studied by varying their concentrations, creaming time and temperature. Details are described below:

4.1.1 Characteristics of Creaming with Type and Concentration of the Chemicals

Natural rubber latex is a dispersion of rubber particles in water. In the experiment, field latex was mixed with a creaming agent and left standing to allow phase separation. The cream and serum phases separated to the top and bottom layers, respectively as shown in Figure 4.1.

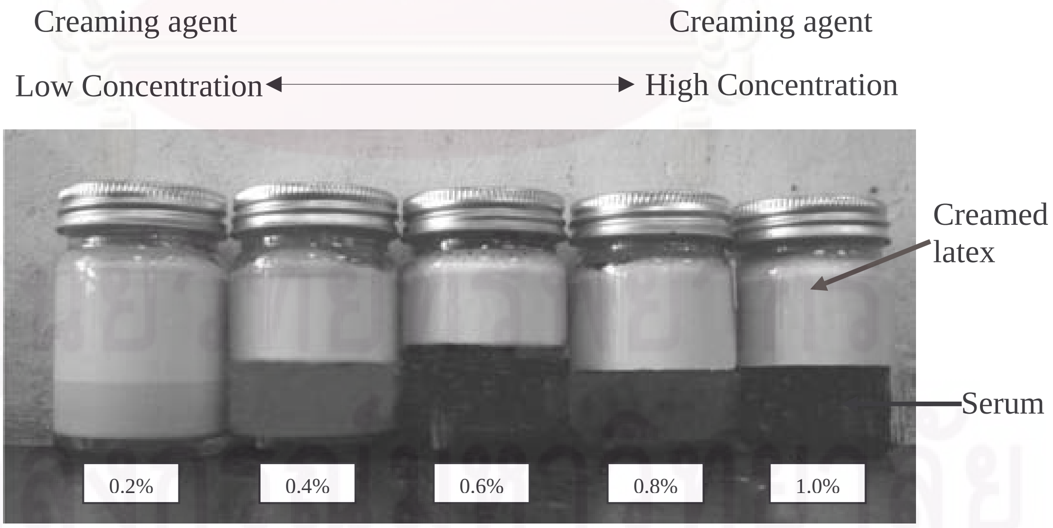


Figure 4.1 Varying separations with creaming agent concentration (using HPMC as creaming agent).

The creaming latex was left standing at room temperature for 24 h; the rubber particle formed the cream phase and floated to the top since the density of NR particles (0.93 g/cm^3) is lower than the serum. The effect of creaming agent concentration on dry rubber content (DRC) obtained was studied over the range of 0.2 to 1.0 %.

Results shown in Figure 4.2 indicate that higher DRC of the cream phase was achieved with higher molecular weight of creaming agent, i.e. from HPMC, HEC and CMC, respectively. It was due to the fact that the higher molecular weight of alkyl group in HPMC would collect higher number of runner particles resulting in larger aggregates than others. This effect also made it possible for the aggregates of rubber particles to move faster upward to the cream phase [44]. The effectiveness of alkyl groups on creaming was methyl < ethyl < propyl.

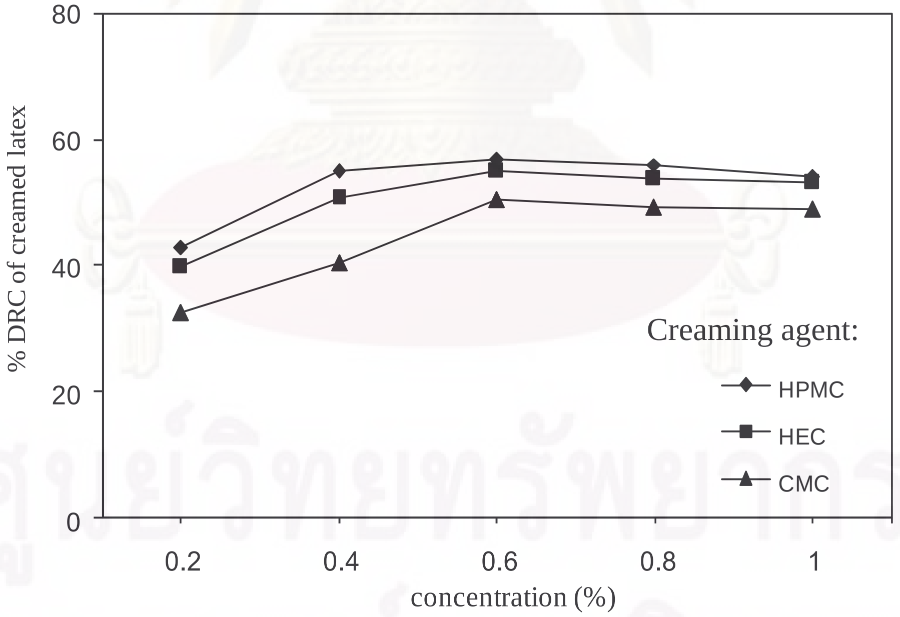


Figure 4.2 Creamed characteristic with different types of creaming agent and concentrations (creaming time 24 h, at room temperature).

All creaming agents showed similar results at lower concentration of 0.2 to 0.6% that the DRC of creamed latex increased with the increasing concentration to the maximum value at 0.6%. The dry rubber contents of creamed latex obtained from CMC, HEC and HPMC were 50.35%, 54.98 and 56.78%, respectively.

On further increase of creaming agent concentration, DRC of creamed latex decreased slightly. At higher concentration of 0.8 to 1.0%, the high amount of creaming agent would increase the viscosity of the mixture thus possibly hinder movement of smaller aggregates upward to cream phase resulting in less compaction, and therefore such decrease of DRC.

4.1.2 Creaming Time

From the previous section, it is concluded that HPMC is the most efficient among creaming agents used, and it works best at a concentration of 0.6%. The next important parameter is creaming time. The effect of creaming time on DRC was studied by analyzing samples taken at an interval of 12 up to 72 h of settling at room temperature. The results were shown in Figure 4.3.

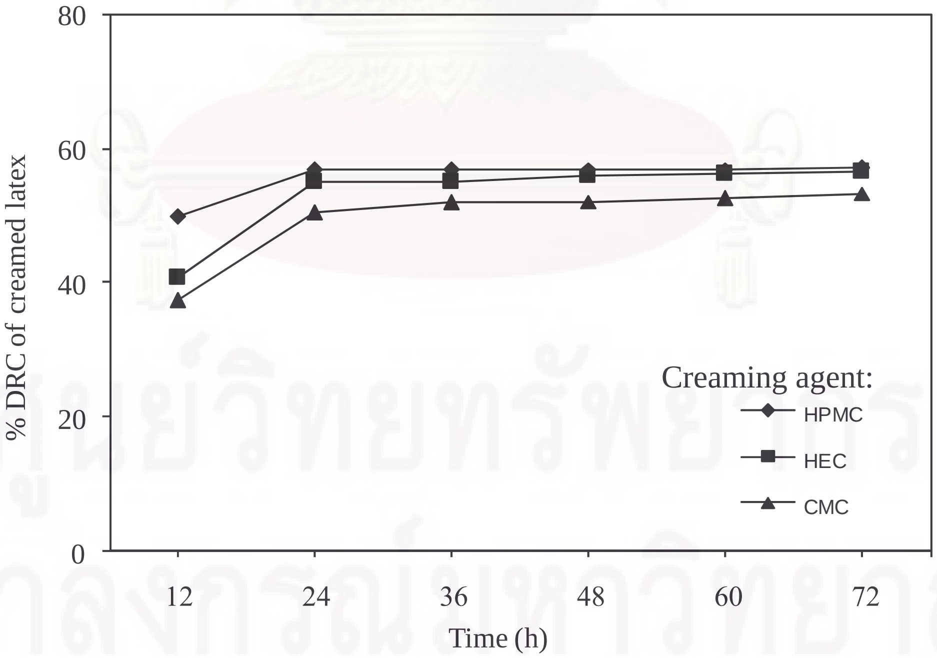


Figure 4.3 Variation of DRC with creaming time (creaming agent concentration 0.6%, at room temperature).

It can be seen that DRC of creamed latex increases with settling time. At 72 h, the final DRC observed is highest for HPMC being 57.07%. Furthermore, it exhibits a faster recovery of rubber particles with higher DRC than other agents. The rapid settling rate was observed up to 24 h, after that the increment was slight. It is obvious that settling is virtually completed within 24 h for all agents used, however, compaction may followed but with much slower rate. Similar result was observed elsewhere for sodium alginate as creaming agent [33].

4.1.3 Temperature

The effect of temperature on creaming was investigated over the range of room temperature to 60°C, while keeping a concentration of creaming agent at 0.6% and settling time of 24 h. Two effects were expected: the lowering of latex viscosity, and the suppression of hindrance effect on the part of the creaming agents. The results are shown in Figure 4.4.

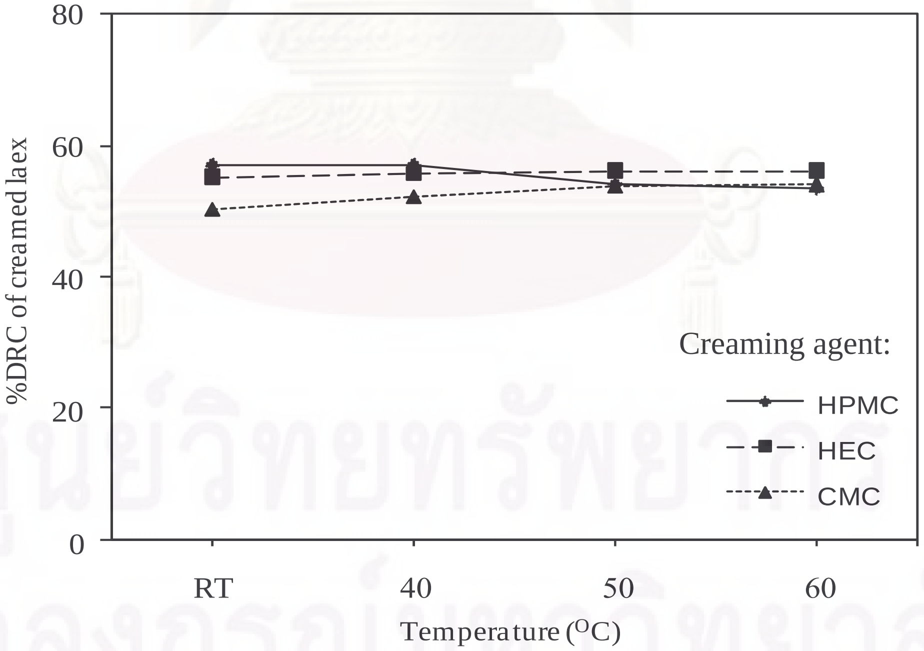


Figure 4.4 Influence of temperature on creaming agent performances (creaming agent concentration 0.6%, creaming time 24 h).

It has been observed by Peethambaran *et al.* [44], that when heating the mixture of latex with CMC, the viscosity of the mixture was reduced. Coupling with the difference of phase densities, this will affect creaming in such a way that the aggregates of rubber particles move upward easier thus facilitate the phase separation.

For CMC, the lowest molecular weight of creaming agents used, DRC of creamed latex increases steadily with temperature which indicates that lowering of viscosity prevail. As for HEC, with a slightly higher molecular weight, DRC changes in similar manner as CMC but with less prominence. Hence lowering of latex viscosity was not enough to markedly take effect on settling rate. Whereas HPMC, with its superior hindrance effect on aggregate forming, exhibits the temperature influence differently. DRC obtained with HPMC decreases with temperature.

Kita *et al*. [46] reported that HPMC has a cloud-point temperature about 55°C and phase separation of HPMC and water nearly occurred. In this research it is postulated that temperature reduces polymer’s hindrance effect due to the kinetic energy of water molecules surrounding it, thus the high molecular weight polymer tends to group away from water resulting in cloud point. In turn, soluble polymer available for rubber particle aggregate formation is less resulting in smaller aggregates. The settling rate is retarded. Therefore, DRC exhibits a gradual decrease toward the cloud point of the creaming agent. Evidently, it is noted that temperature may not exceed 70^{o}C or degradation of NR will commence and eventually impair rubber product properties.

The conclusion for this section is that creaming is suitably performed at room temperature and additional heating in the process is unnecessary. For process design point of view, it is worth to mention that heating may be required in later stage when recovery of the polymer from the serum is needed. It is also noted that, for industrial practice, several creaming aids may be employed together with other means of creaming techniques to shorten production time while attaining the latex concentrate with 65% DRC. The product is used in rubber thread manufacture.

4.1.4 Properties of Creamed Latex

In this work, the best conditions chosen for creaming is by using HPMC at 0.6% as creaming agent with creaming time 24 h and operating at room temperature. Properties of the creamed latex can be compared to ISO 2004-1997 specifications, as presented in Table 4.1 and Figure 4.5. The ISO standard is for commercial latex concentrate produced by centrifugation.

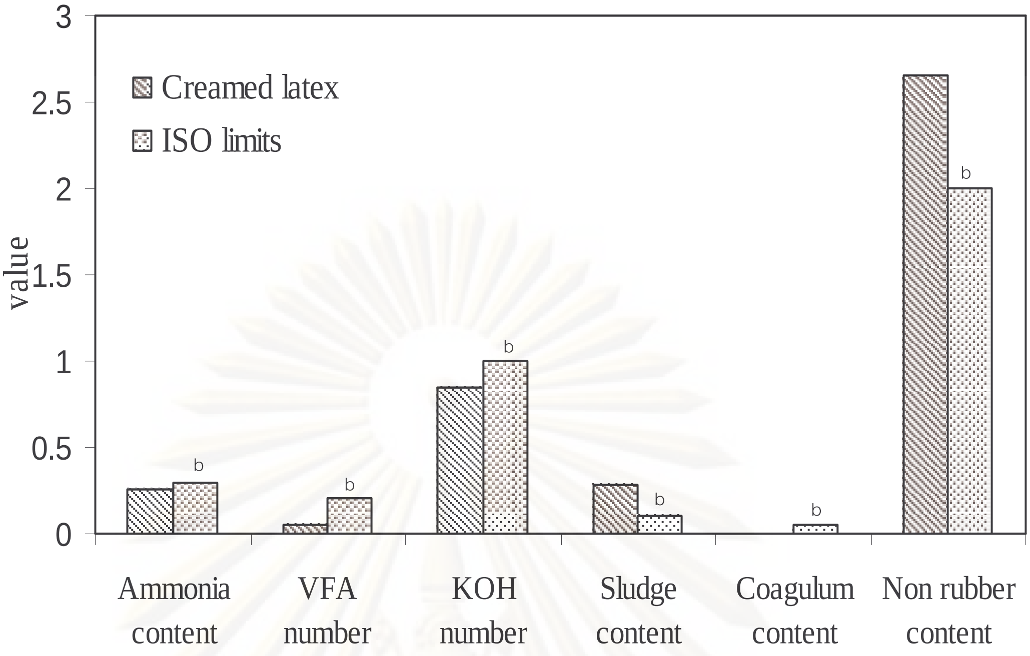
Table 4.1 Properties of creamed latex as compared to ISO limits requirement

Properties	Values	ISO limits*
Total solid content (% by wt.)	59.24	61.50[a]
Dry rubber content (% by wt.)	56.59	60.00[a]
Non rubber content (% by wt.)	2.65	2.0[b]
Ammonia content (on total weight) (% by wt.)	0.26	0.29[b]
Ammonia content (on water phase) (% by wt.)	0.54	
Mechanical stability time @ 50% TS ,second	667	650[a]
Volatile fatty acid number (VFA number)	0.046	0.20[b]
Potassium hydroxide number (KOH number)	0.84	1.0[b]
pH of latex	9.86	
Specific gravity at 25°C	0.96	
Sludge content, %	0.28	0.1[a]
Coagulum content, %	0.003	0.05[a]

a = minimum, b = maximum

Even though, a field latex of similar properties (Appendix A), with 0.95 and 0.08 for non-rubber content and sludge content, respectively, is used as starting materials. It is not unexpected that TSC, DRC, non rubber content and sludge content are lower than ISO standard since creaming process differs from centrifugation in that there is no magnesium removal and washing of latex in the process. In centrifugation process, more NH_3, TMTD and ZnO are added prior to processing to preserve the field latex; di-ammonium phosphate (DAP) is also added to remove phosphate, follows by washing in the first centrifuge. Non rubber content such as protein and carbohydrate will be removed along as well. Further removal of protein can be achieves, if so required, by adding urea in ammonia solution in further centrifugation stage.

Such purification is needed for latex concentrate use in glove production. However, it is not required for creamed latex to be used for rubber thread or as raw materials for others where protein allergy is not essential. It is suggested also that creaming is economical pre-treatment prior to storage and transportation to other factories making of block rubber or latex concentrate by centrifugation [45].



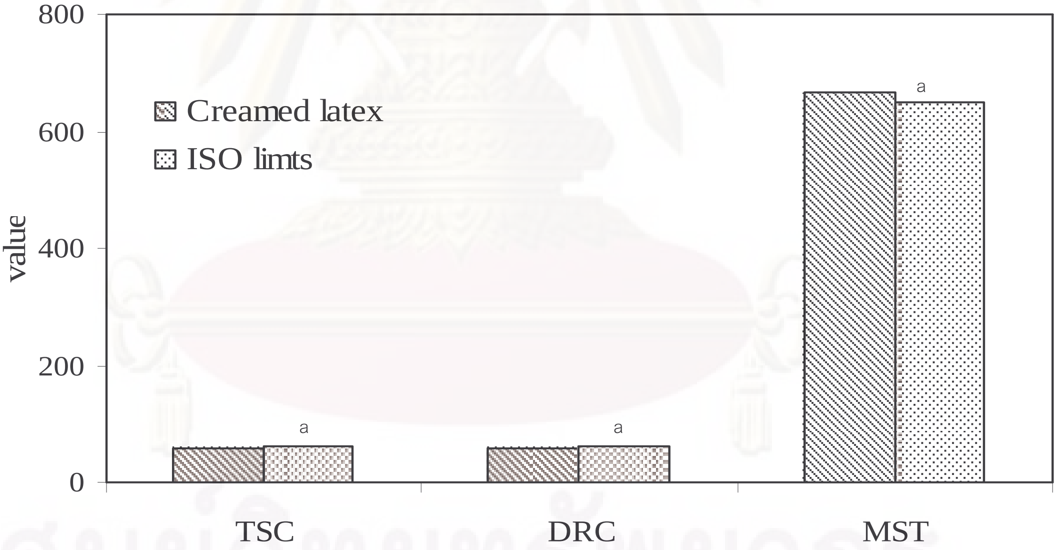


Figure 4.5 Properties of creamed latex as compared to ISO specifications of latex concentrate (a = minimum, b = maximum).

For creamed latex, the contribution of residual HPMC in creamed latex would also add to a higher non rubber content, all other properties are within ISO limits. Although the values of TSC and DRC may be less than ISO specifications, the creamed latex with DRC about 50-55% are, in practice, produced for mattress, rubberized coir, balloon and adhesives manufacturing manufacturers in India [47,48]. The creamed latex obtained in this work is equally suitable for those products.

4.1.5 Cost Estimation

The cost of production for any product will need to be considered whether it is worthwhile for investment. The cost estimation is a simple calculation of the cost per kilogram of creamed latex. The cost of creamed latex with various creaming agents is presented in Table 4.2.

Table 4.2 Cost calculation of creamed latex with different creaming agents.

Creaming agent	Cost of creaming agent (Baht per kg.)	Cost of creamed latex* (Baht per kg.)
CMC	90	35.40
HEC	180	35.80
HPMC	230	36.10

*Based on field rubber latex cost of 58.50 Baht/kg.

A creaming agent costs more with increasing number of alkyl group resulting in higher production cost of creamed latex. Although the cost of creamed latex with HPMC is highest, the polymer can be recovered from remaining serum phase after separation. Moonprasith *et al.* [35] has reported that HPMC can precipitate from serum phase at a temperature about 70°C. Loykulnant *et al.* [34] has also investigated HPMC recovery by heating serum phase at about 80°C and obtained more than 90% recovery. Therefore, the manufacturing cost of creamed latex can be reduced as such.

4.2 Free-vulcanized Rubber Latex

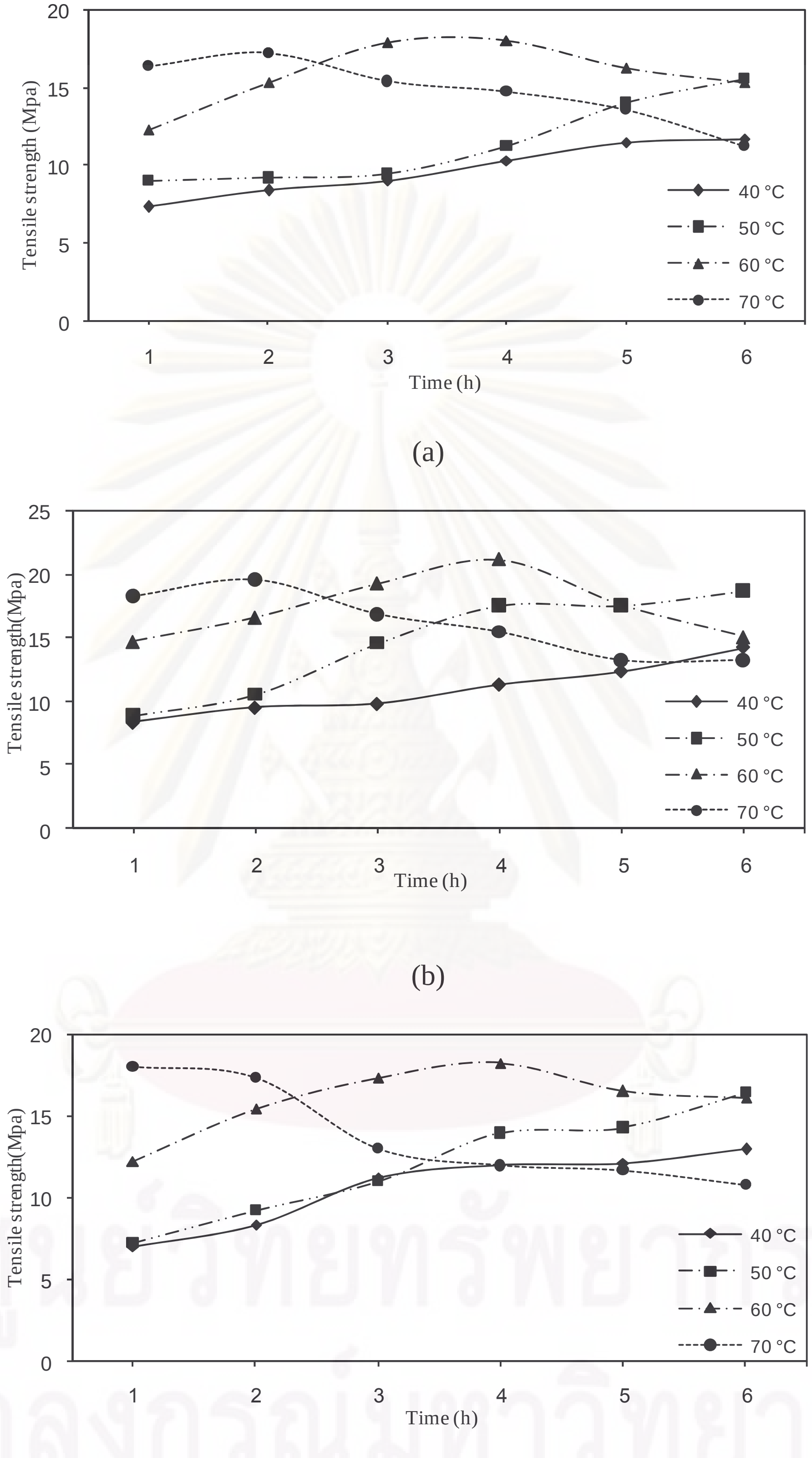
In order to facilitate product manufacturing, creamed latex need free-vulcanization for long storage and can be used without further vulcanization. The vulcanization of latex involves chemical reaction taking place in the heterogeneous system. In the experiment, latex was mixed with vulcanizing agent and reaction was conducted by heating at various vulcanization temperatures for a range of 1 to 6 h. The free-vulcanized products were made into films for testing. Films were cast on glass-rimmed plate and allowed to dry at room temperature. The effect of vulcanization parameters such as concentration of curing agent, time and temperature on properties of free-vulcanized rubber were investigated.

4.2.1 Mechanical Properties

(1) Sulfur vulcanization

Mechanical properties of free-vulcanized rubber film were measured in term of tensile strength according to ASTM method. The variations of tensile strength of sulfur vulcanized rubber films from various operating parameters were shown in Figure 4.6.

Generally, all tensile strength variations of rubber films cured by sulfur concentration of 1 to 3 phr exhibit a similar trend, however, the curves with vulcanization at 70^{o}C interestingly stand out from the rest. At this temperature, tensile strength shows high value at short reaction time, and drops off with prolong heating. This implies that one hour or less is sufficient for vulcanization. For long heating, natural rubber latex will only degrade. Degradation is also observed for vulcanization at 60^{o}C that after 4 h the tensile strength appears to drop as well. For vulcanization temperature of 40^{o}C and 50^{o}C, tensile strength steadily increased suggesting that better cross-linking of rubber chain takes longer time to achieve.



(a)

(b)

(c)

Figure 4.6 Variation of tensile strength of sulfur vulcanized rubber film using sulfur concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

Claramma *et al.* [38] has reported that the rate of NR latex vulcanization, with sulfur elements as curing agent, was slow at low vulcanization temperature and the process required more reaction time to achieve a higher value of tensile strength. Natural rubber latex can be over-cured and loose its strength if vulcanization takes place at high temperature [43].

Due to a limitation on operating time with cost involved, it would be desirable to keep reaction time as short as possible, though the highest tensile strength (21.16 MPa) was obtained for 60^{o}C heating for 4 h and sulfur 2 phr. It is therefore concluded that, for sulfur cure, a suitable production of free-vulcanized latex is at 70^{o}C with vulcanization time of 1- 2 h using sulfur concentration 2 phr. For application where long time may be required, such as in adhesive, it would be on the safe side to use vulcanization temperature of 60^{o}C and sulfur concentration of 2 phr.

(2) TMTD vulcanization

Sulfur donor such as TMTD cans also the effectively used for free-vulcanization of latex. Variations of tensile strength of rubber films, using TMTD as curing agent is shown in Figure 4.7.

Generally, for all concentration of TMTD used (1-3 phr), the variations exhibit similar pattern that tensile strength of rubber films for vulcanization temperature of 50°C is superior than at 40°C, 60°C and 70°C, respectively. This is due to the behavior of vulcanization system using TMTD. Kurien *et al.* [41] has reported that TMTD will form complex with ZnO and the complex is unstable at 45°C resulting in decomposition to ZnO which causes a thickening effect on latex compound. Thus high value of tensile strength was observed at 50°C but prolong heating or higher vulcanization temperature resulted in inferior mechanical properties. For vulcanization temperature of 40°C, TMTD slowly released sulfur available for cross-linking, therefore prolong heating steadily improved tensile strength.

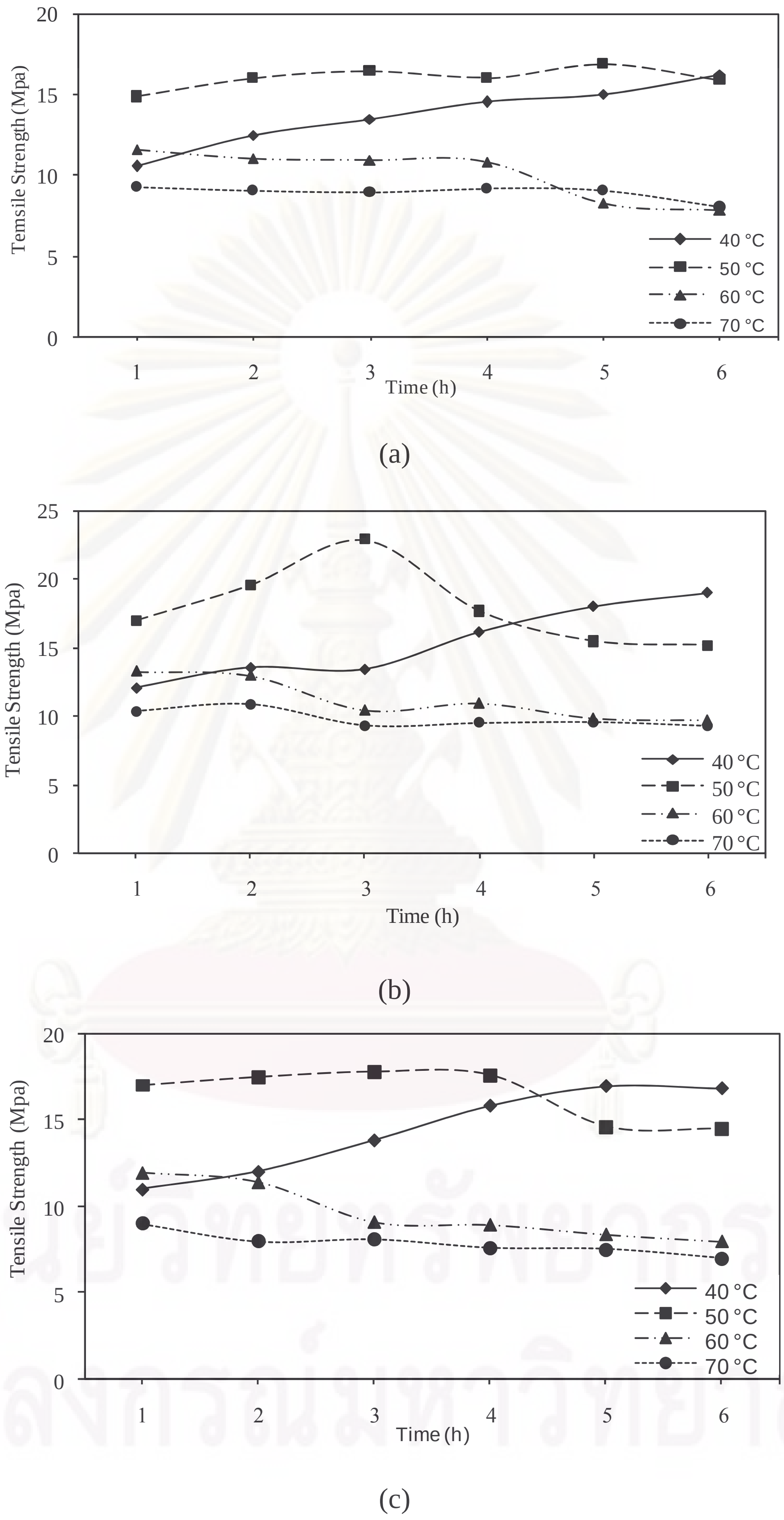


Figure 4.7 Variation of tensile strength of TMTD vulcanized rubber film using TMTD concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

Comparison of the concentration of TMTD indicated that 2 phr offer better results, however, the best tensile strength was observed to be heating at 50°C for 3 h (22.86 MPa). In light of the evidence, a conclusion can be drawn that this vulcanization system is best obtained at between 40°C to 50°C and 2 phr.

When compared with sulfur curing, TMTD being released from a complex with ZnO offers better tensile strength than sulfur which is not readily dissolved in the system. This is because vulcanization with sulfur donors entails a splitting of S_x (x = predominantly 1 or 2) from the sulfur donors, resulting in sulfur crosslink of shorter average length x than classical sulfur vulcanizations (S_8). This leads to better mechanical properties of the rubber films. The mechanism of TMTD curing has been proposed in Figure 4.8 [49].

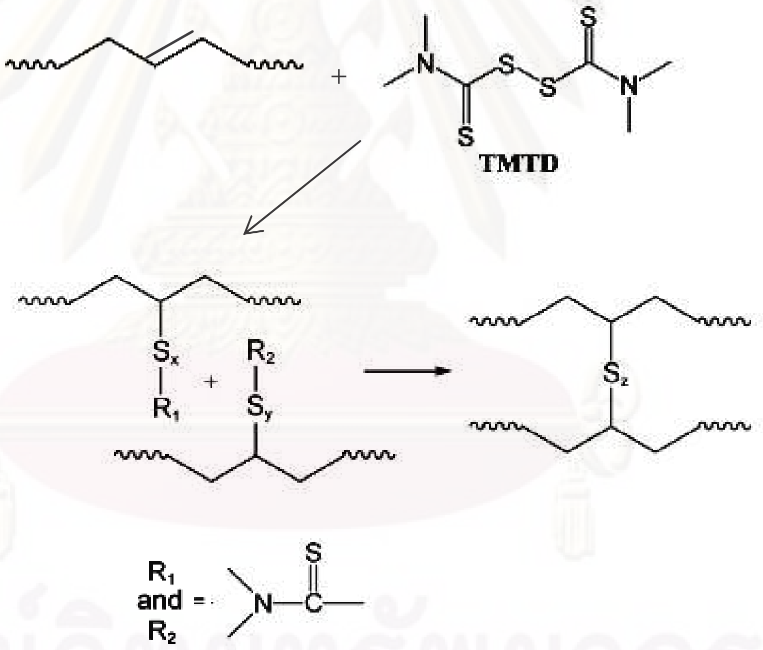
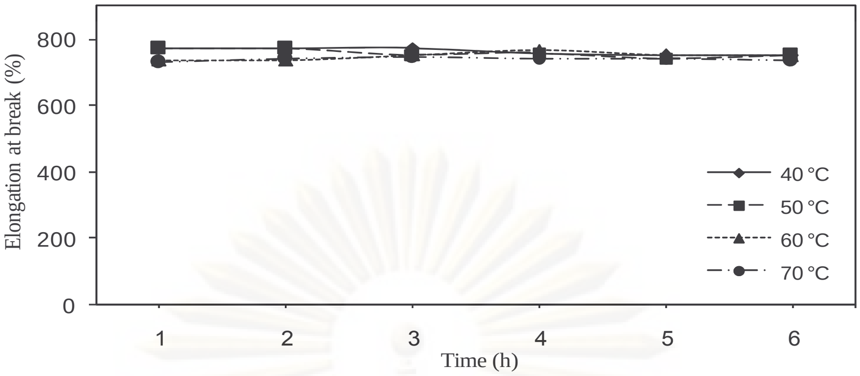
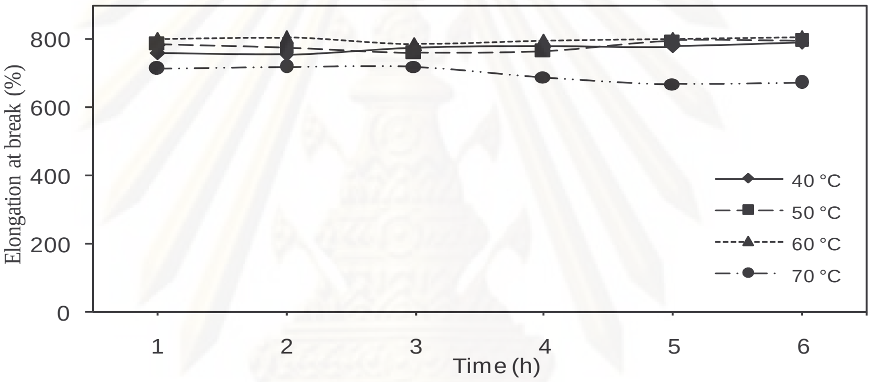


Figure 4.8 Mechanism of TMTD vulcanization [49].

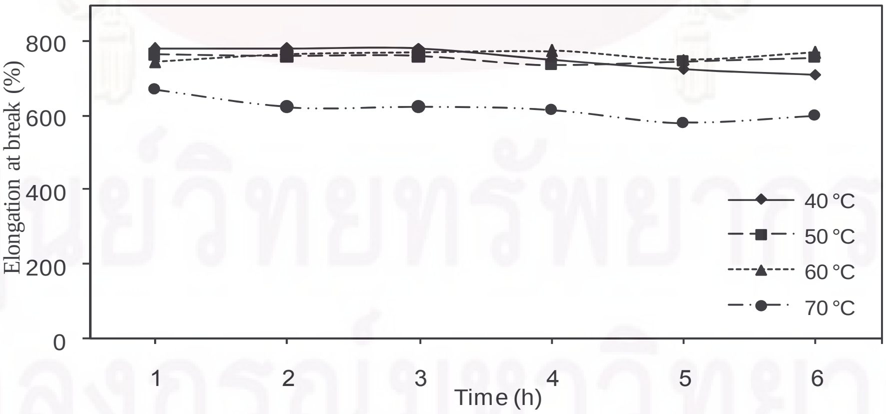
Elongation at break (EB) is another mechanical property of interest. It is normally expressed as a percentage of the original length of test sample upon straining until it breaks. Results are shown in Figures 4.9 and 4.10 for sulfur and TMTD curing, respectively.



(a)

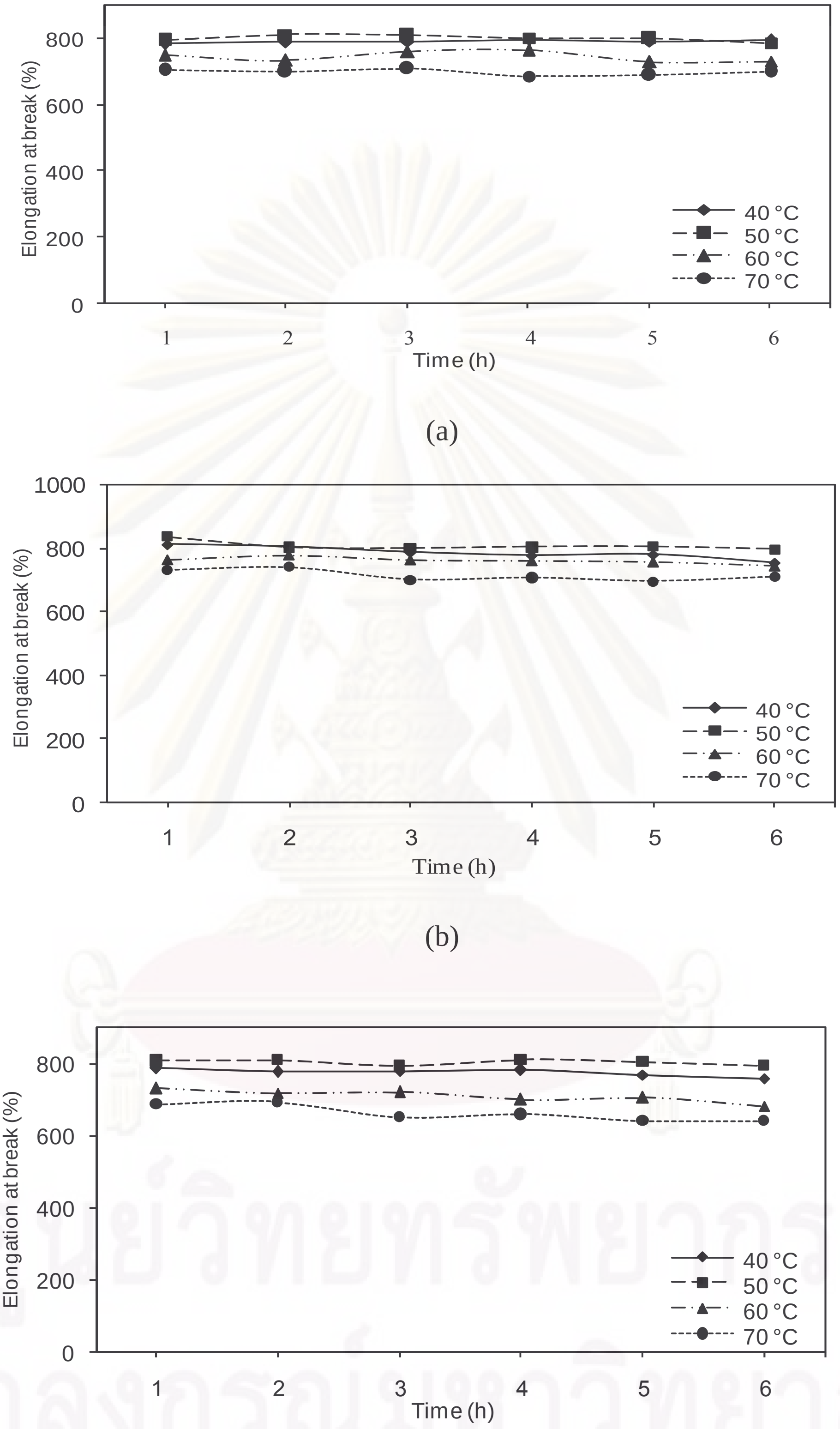


(b)



(c)

Figure 4.9 Elongation at break of sulfur vulcanized rubber film using sulfur concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.



(a)

(b)

(c)

Figure 4.10 Elongation at break of TMTD vulcanized rubber film using TMTD concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

All conditions exhibit a similar pattern that EB appears to be about 700-800% with little change with vulcanization time. The value is slightly less than rubber glove made from latex concentrate reported in literature. This is probably due to the inclusion of non rubber content in the creamed latex.

EB results confirm same conclusions as that of tensile strength that best conditions result in relatively high values of EB. However, high vulcanization temperature, 70°C, yields inferior EB owing to degradation of rubber particularly upon prolong heating. EB of sulfur cured films is generally less than TMTD cured. For TMTD, high value of EB is observed for vulcanization temperature of 40°C and 50°C and concentration of 2 phr.

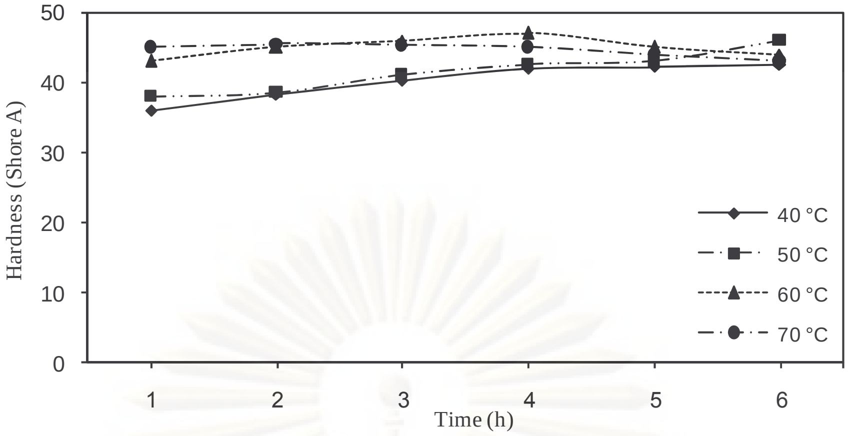
4.2.2 Hardness

Hardness of rubber is defined as the resistance to indentation under conditions which do not puncture the rubber. Test results of rubber films, formed from free-vulcanized cream latex, are presented in Figures 4.11 and 4.12 for sulfur curing and TMTD curing, respectively.

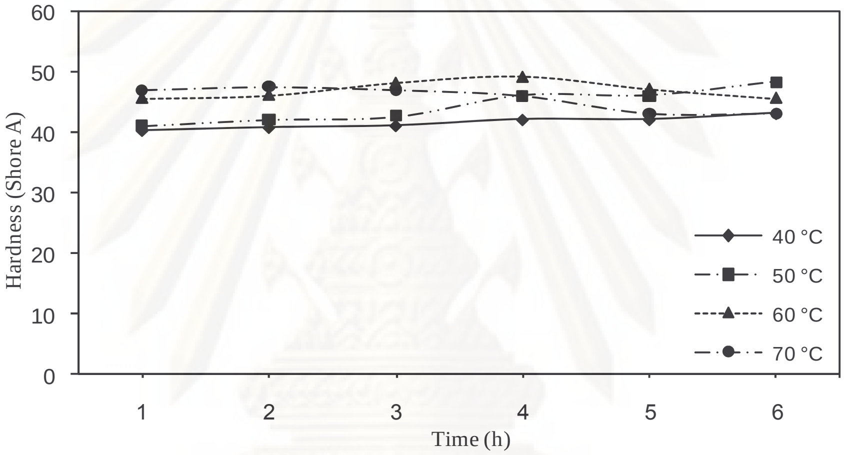
The hardness of film rubber made from sulfur curing is generally higher for vulcanization temperature of 70°C and 60°C than lower temperatures, as shown in Figure 4.11. However, prolong heating time reduced hardness slightly due to degradation. Whereas, longer heating time improved hardness for vulcanization temperature of 40 and 50°C owing to better curing.

On the other hand, TMTD curing offers better hardness with vulcanization temperature of 50 and 40°C than higher temperature, as shown in Figure 4.12. This indicates better cured films. Prolong heating also favors 40°C results, similar to other mechanical properties discussed previously.

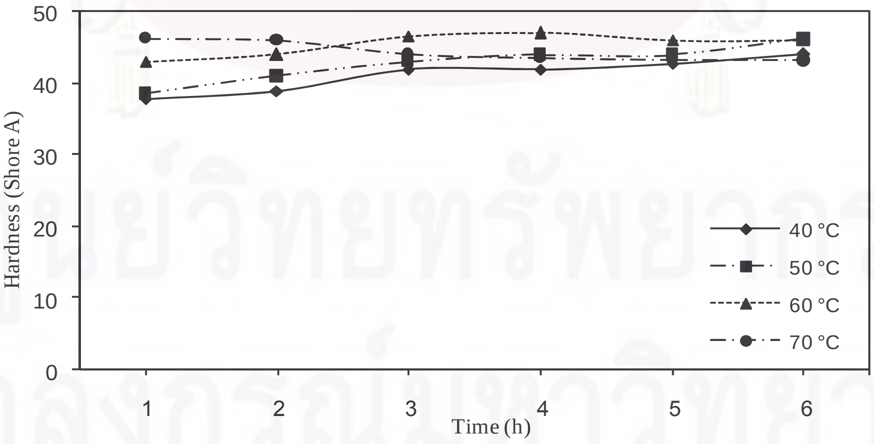
It should be noted also that a concentration of 2 phr curing agent shows better hardness for both vulcanization systems, though the difference is marginal.



(a)

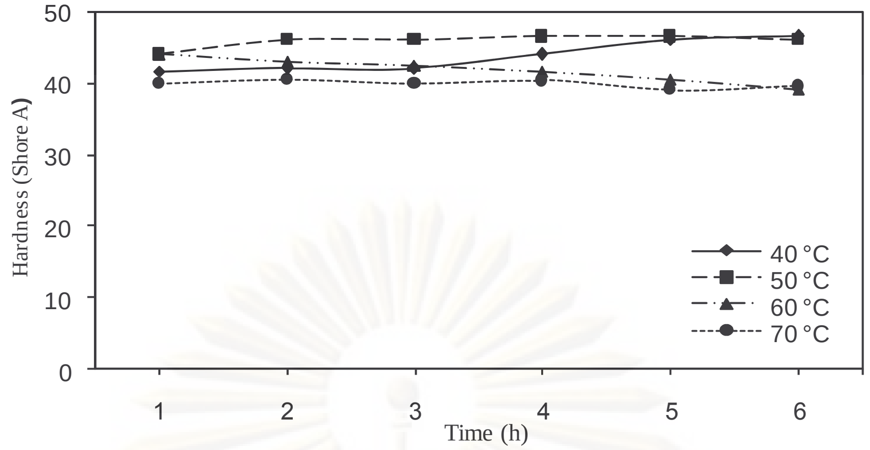


(b)

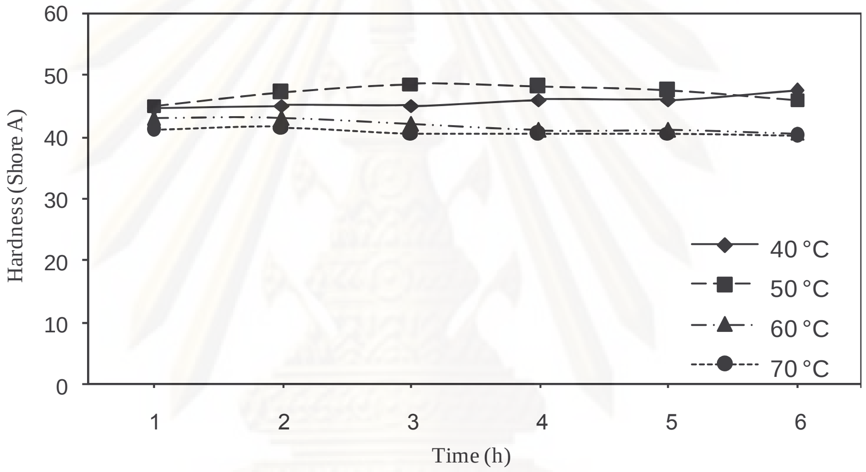


(c)

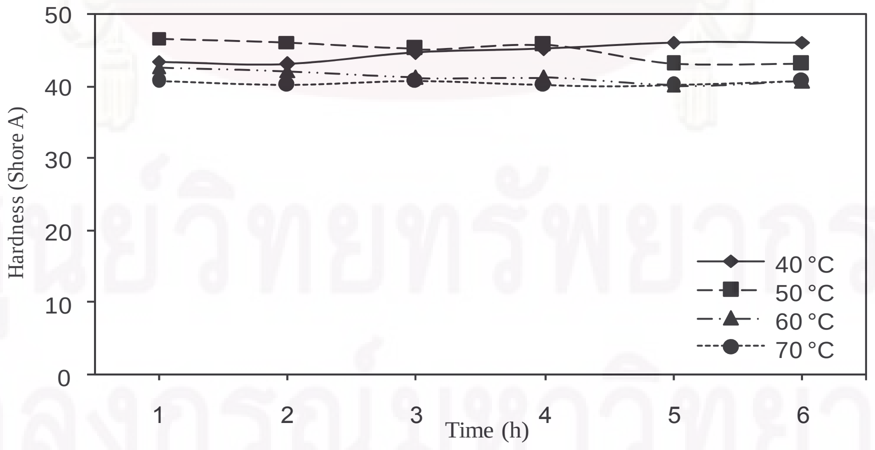
Figure 4.11 Hardness of sulfur vulcanized rubber film using sulfur concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.



(a)



(b)



(c)

Figure 4.12 Hardness of TMTD vulcanized rubber film using TMTD concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

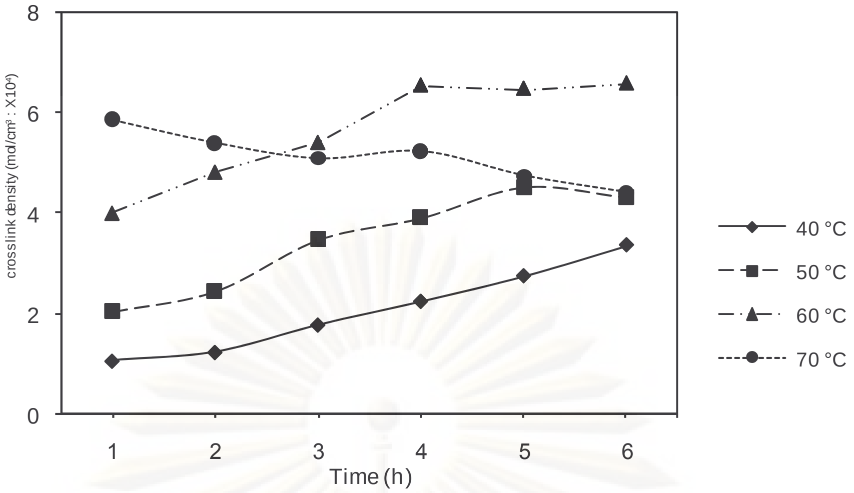
4.2.3 Crosslink Density

The total crosslink density of the vulcanized rubber films were determined by using the toluene swelling method developed by Flory-Huggins. Results are presented in Figures 4.13 and 4.14 for sulfur and TMTD vulcanization, respectively. Crosslink densities confirm vulcanization conditions of both systems.

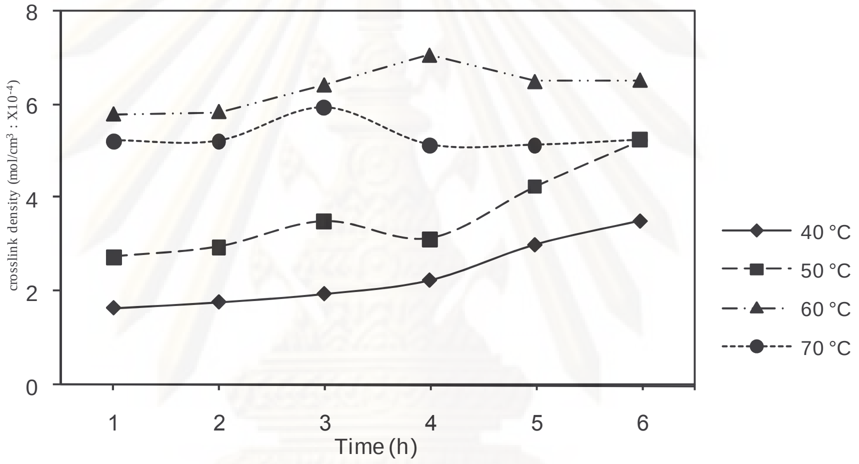
Sulfur vulcanization system indicated that crosslink density was better obtained with high vulcanization temperatures, particularly at 60°C. Prolong heating impairs crosslink density for vulcanization temperature of 70°C due to degradation of rubber, but improves those from lower vulcanization temperatures. Results also indicate that high crosslink density is achieved under the same condition as for tensile strength.

TMTD vulcanization system shows better crosslink density for 50°C but the vulcanization time must not be longer than 3 h. Prolong heating improves crosslink density of 40°C though after 3-4 h. At high vulcanization temperature degree of crosslink is all inferior. The curing agent concentration of 3 phr appears to be suitable for this system.

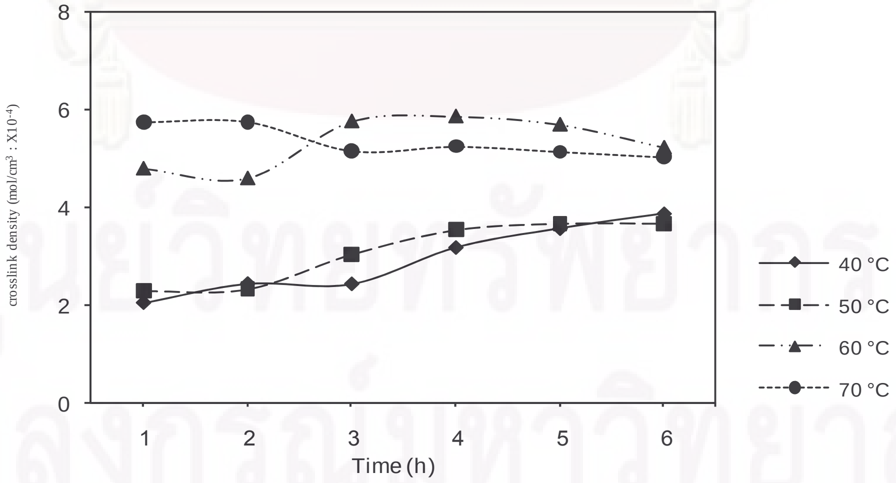
It should be noted also that tensile strength of sulfur vulcanized film is governed not only by the introduction of crosslink but also by the ability of particles to coalesce among them. When latex is vulcanized, the rubber particles are internally cross-linked. By increasing vulcanization temperature or heating time, the rubber particles become more and more link up by attaching on others, and hence, become bigger aggregates and harder. Thus, when the film is formed from highly cross-linked latex, joining of the rubber aggregates becomes more and more difficult, resulting in lower tensile strength [38].



(a)

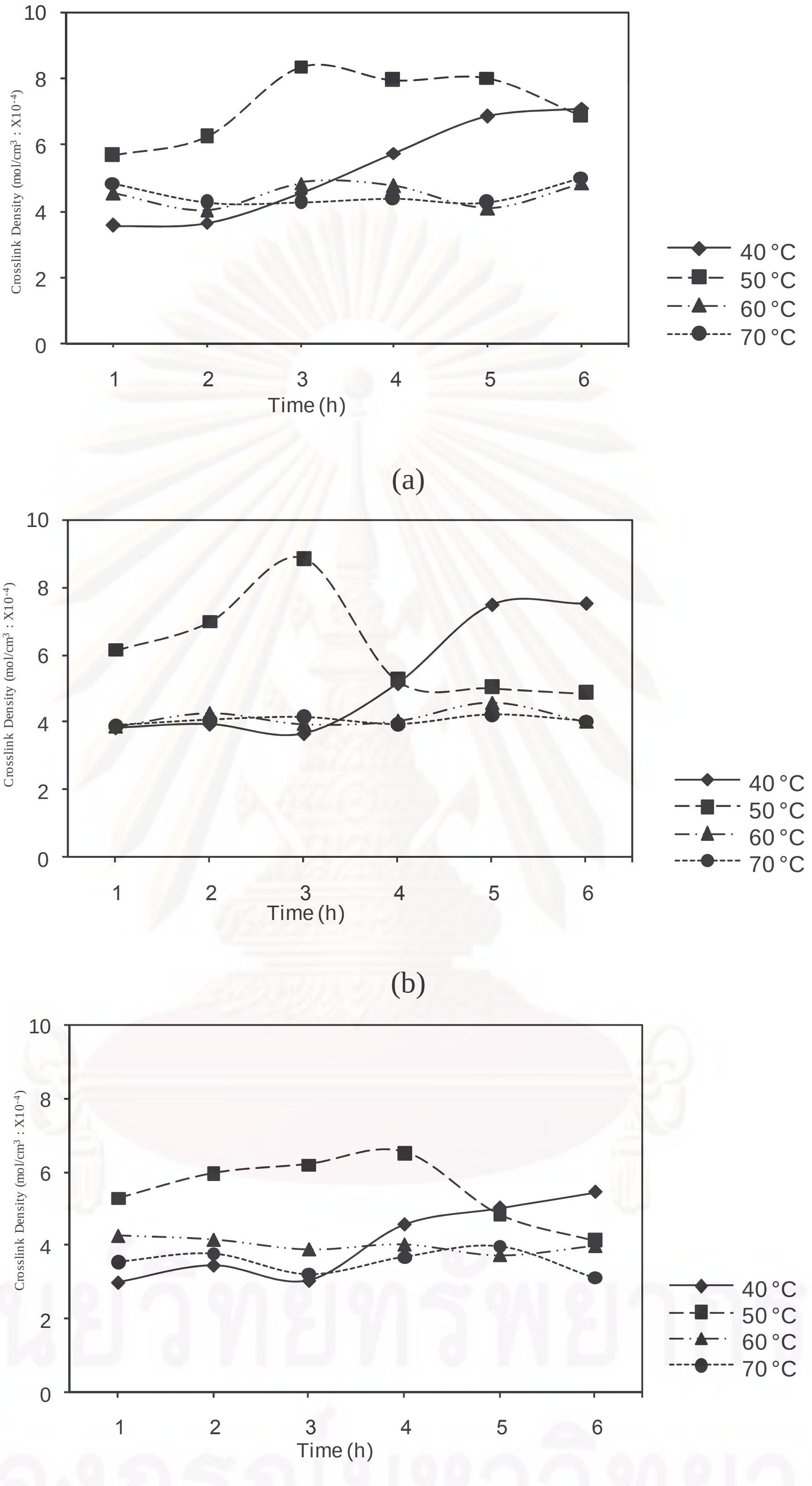


(b)



(c)

Figure 4.13 Effect of parameters on crosslink density of sulfur vulcanized rubber film using sulfur concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.



(a)

(b)

(c)

Figure 4.14 Effect of parameters on crosslink density of TMTD vulcanized rubber film using TMTD concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

4.2.4 Chloroform Number

Chloroform number is used to indicate the extent of crosslink in compound latex. To determine such number the free-vulcanized latex was mixed with chloroform in equal part and observed the appearance of coagulum to which a chloroform number could be assigned. Results are shown in Figures 4.15 and 4.16.

For sulfur vulcanization system, it can be seen that the chloroform number ranges from 1 to 3. At vulcanization temperature of 40°C, chloroform number reached up to a level of 2 which indicates that the latex was lightly vulcanized. At higher vulcanization temperature of 50, 60 and 70°C, chloroform number increased with increasing of time. However, as curing agent is increased high chloroform number could be reached in a shorter time, as in Figure 4.15.

For TMTD vulcanization system, shown in Figure 4.16, the pattern is similar to that of sulfur vulcanization. At low vulcanization temperature of 40°C, chloroform number increased when time until it reached number 3. At higher vulcanization temperature, however, chloroform number reached number 3 at shorter time of 1 h, indicating a quick vulcanization.

Nevertheless, the highest chloroform numbers of free-vulcanized latex in this experiment was only 3, a moderately vulcanized. Sasidharan *et al.* [41] reported that the chloroform number of vulcanized latex reached a maximum of number 4, a fully vulcanization, for a vulcanization time not less than 10 hours.

It is advisable therefore that, if storage of free-vulcanized latex is not contributing to appreciable cost, the vulcanization should be carried out at 40°C using only 1 phr curing agent and the latex stirred at all time for more than 10 h before use.

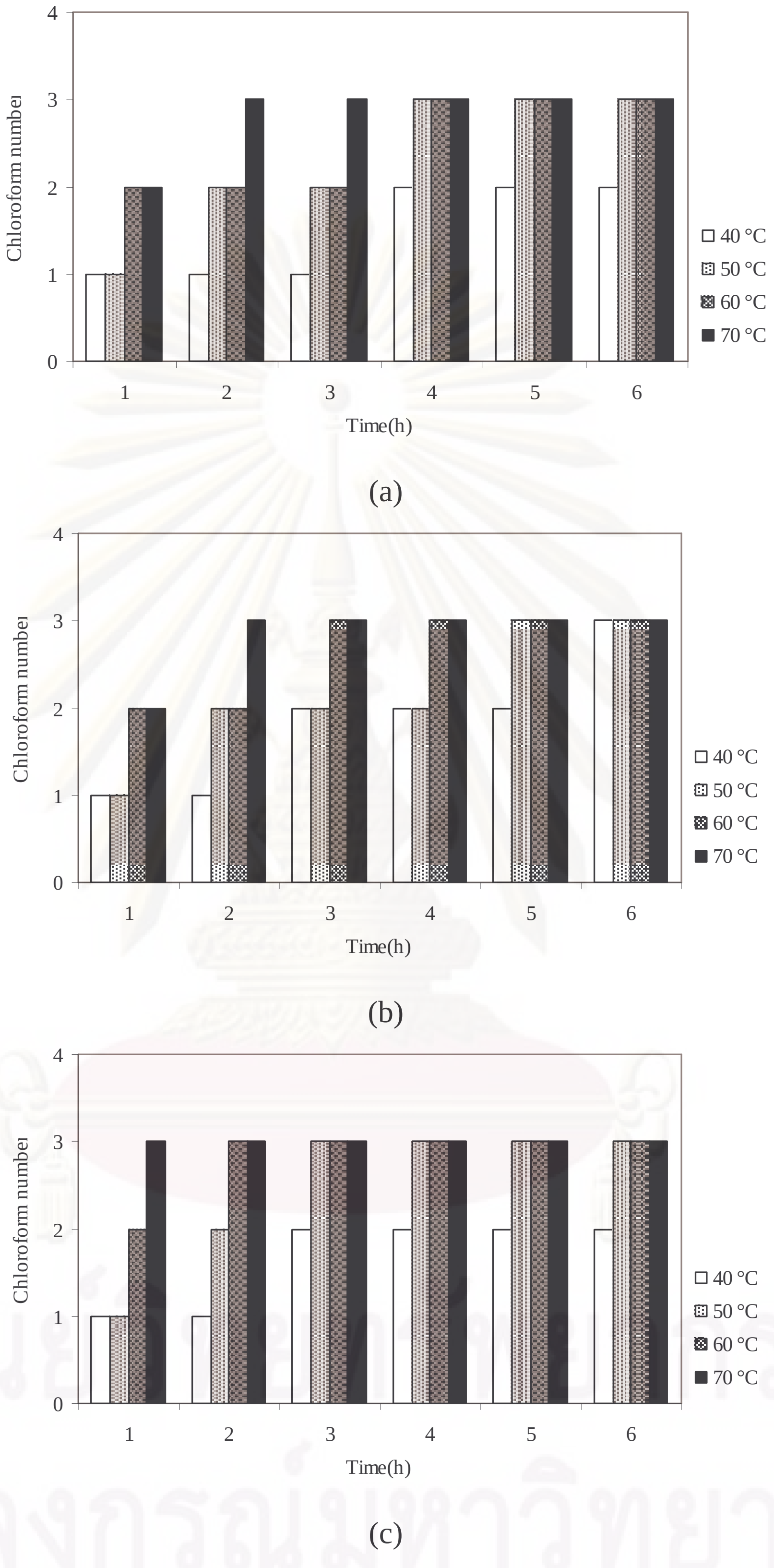


Figure 4.15 Chloroform number of sulfur vulcanized latex using sulfur concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

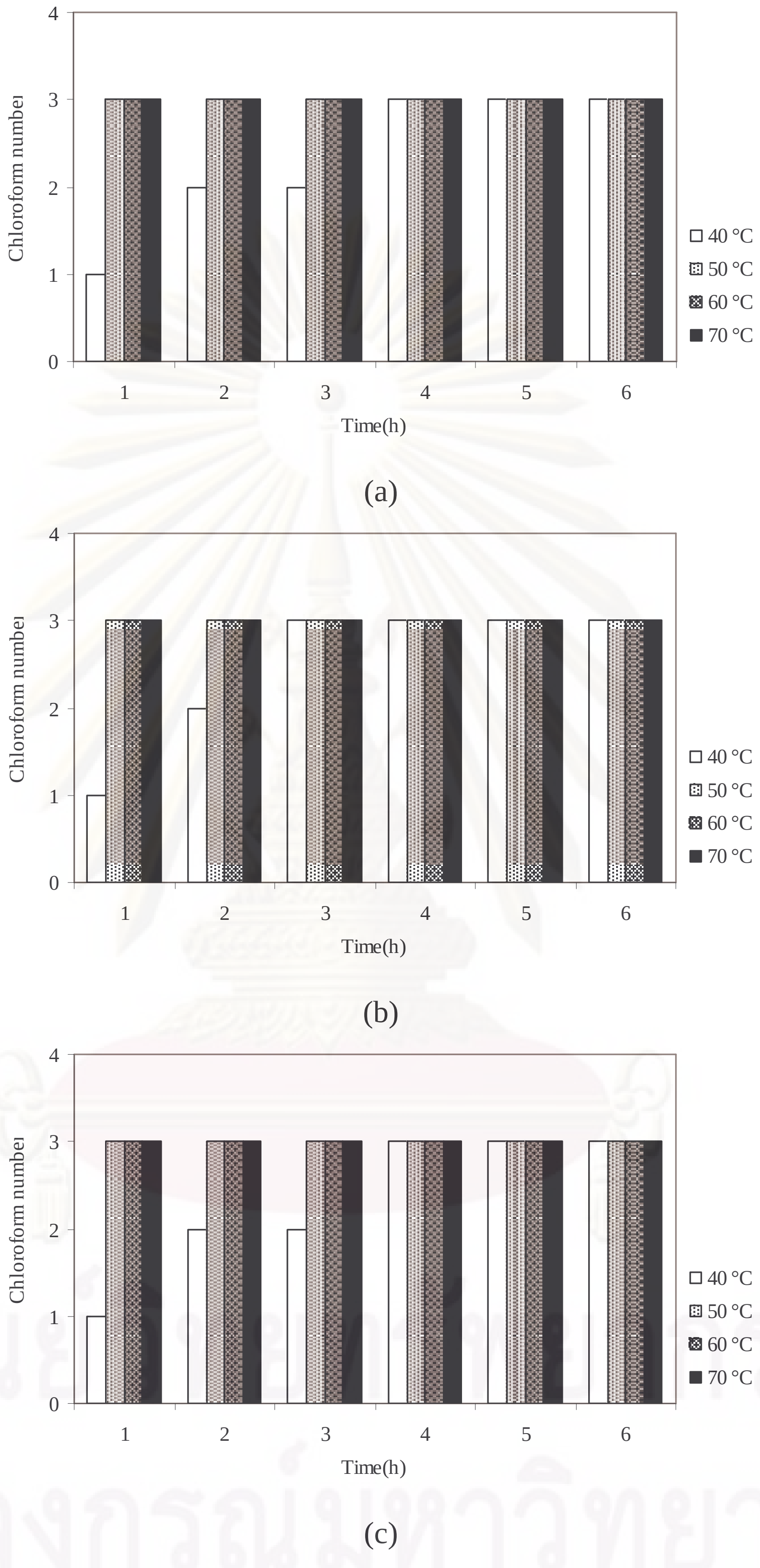


Figure 4.16 Chloroform number of TMTD vulcanized rubber film using TMTD concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

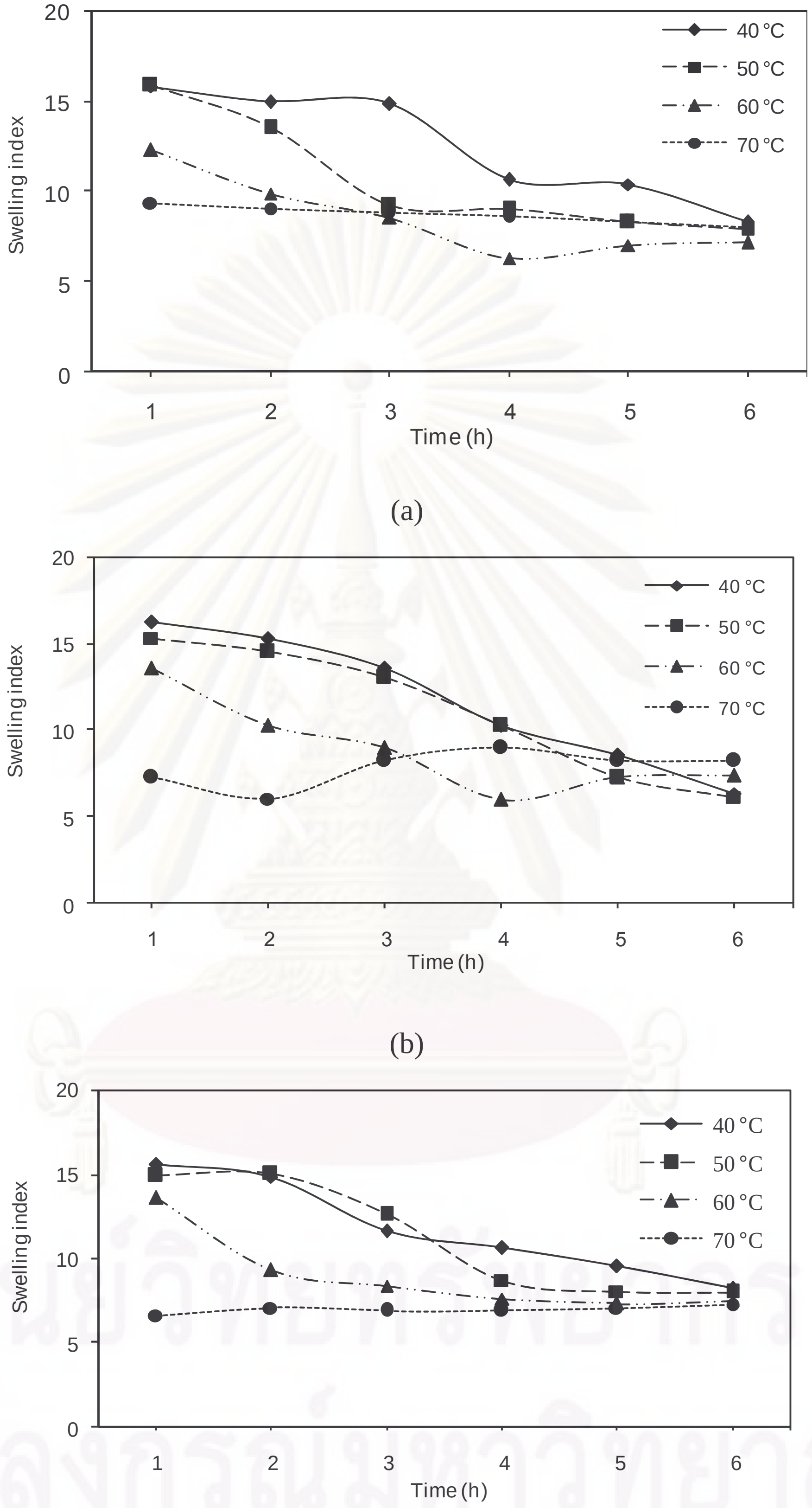
4.2.5 Swelling Index

Swelling index also indicates the extent of vulcanized rubber. The results are shown in Figures 4.17 and 4.18 for sulfur and TMTD curing, respectively.

For sulfur vulcanization system, it can be seen from Figure 4.17 that at vulcanization temperature of 40 to 60°C the swelling index decreased as heating time increased. It can be explained that at low vulcanization temperature, the crosslinking increases with vulcanization time. At vulcanization temperature of 70°C, however, the value of swelling index was already low from vulcanization time of 1 h indicating no further vulcanization required.

For TMTD vulcanization, the swelling index at 40°C decreased with increasing vulcanization time. At higher vulcanization temperature, low swelling index was observed and the trends of swelling index were slightly changed with vulcanization time. It can be clearly seen that at high vulcanization temperature the cross-linking of rubber was already achieved at short period.

Results of swelling index in this work support the previously found from the results of chloroform number that a complete vulcanization of rubber film does not occur because of a maximum value of swelling index should be more than 5.0.

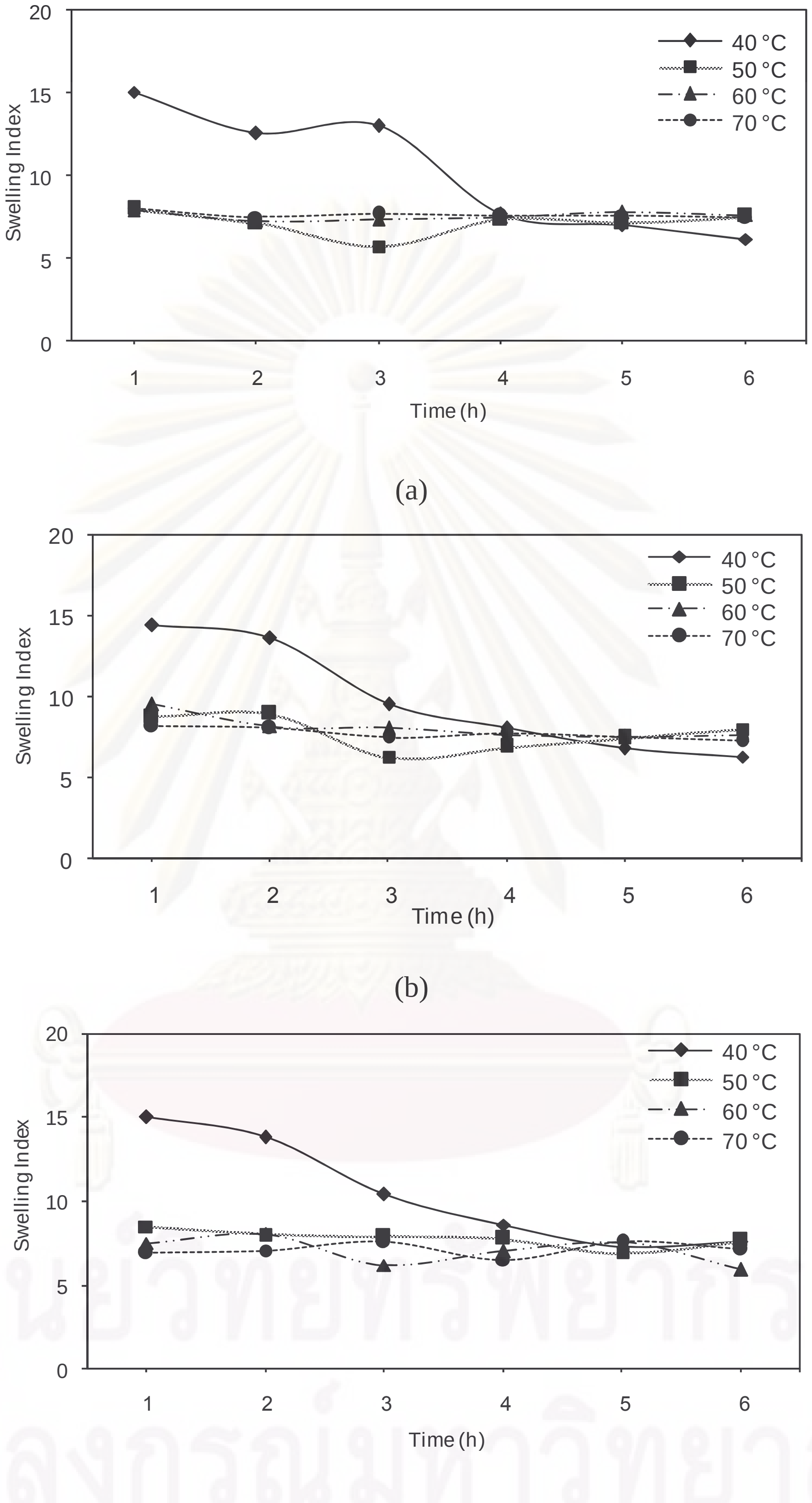


(a)

(b)

(c)

Figure 4.17 Swelling index of sulfur vulcanized rubber film using sulfur concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.



(a)

(b)

(c)

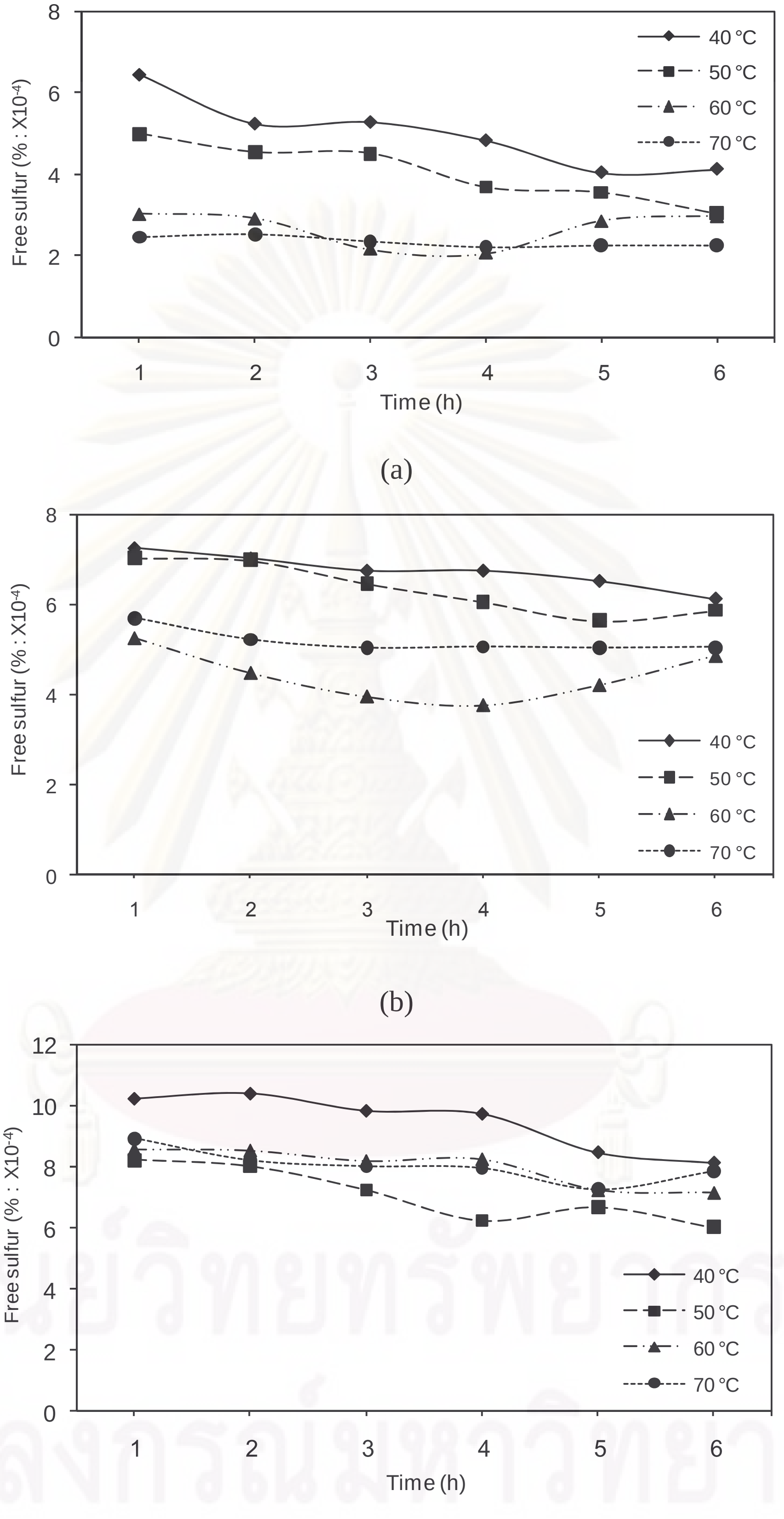
Figure 4.18 Swelling index of TMTD vulcanized rubber film using TMTD concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

4.2.6 Free sulfur

Free sulfur is residual sulfur in rubber film that is not used up in the crosslink reaction. The results on the percentage of free sulfur are shown in Figure 4.19. At vulcanization time of 40 and 50°C, free sulfur decreases with increasing vulcanization time. It can be mentioned that on extending time of vulcanization at low temperature, the consumption of sulfur elements in the process continues on [50]. This leads to the reduction of free sulfur in the vulcanizates.

At vulcanization temperature of 60°C with sulfur concentration of 1 and 2 phr, the percentages of free sulfur decreased as heating time increased from 1 to 4 h. The percentage of free sulfur was least at the same conditions of maximum tensile strength. For sulfur concentration of 3 phr, the percentage decreased with time. At vulcanization temperature of 70°C, the percentages of free sulfur slightly decreased with increasing time. This showed that the efficiency of sulfur consumption was obtained in a short time at high vulcanization temperature.

It can be seen that at the concentration of 3 phr, the percentage of free sulfur is higher than 1 and 2 phr, respectively. This indicates that all sulfur molecules have not crosslink with rubber. These support the previous results of tensile strength that high residual sulfur affects mechanical properties of rubber film products.



(a)

(b)

(c)

Figure 4.19 Free sulfur in vulcanized rubber film using sulfur concentration: (a) 1 phr, (b) 2 phr, (c) 3 phr.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The major conclusions of this study can be highlighted and further elaborated as follows:

1) The natural rubber latex concentrate was prepared by creaming method. The most suitable creaming agent for creamed latex in this study was HPMC. The optimum condition for creaming was 0.6% creaming agent concentration at room temperature for 24 hours of creaming time. The reduction of cost of production creamed latex can be achieved by recovery of HPMC by heating the serum phase at approximately 70°C.

2) For free-vulcanization of creamed rubber latex with sulfur curing system, the maximum mechanical properties of rubber films were achieved under conditions of sulfur concentration of 2 phr, temperature of 60°C and reaction time of 4 hours. At vulcanization temperature of 40 and 50°C with all sulfur concentrations, the rate of vulcanization required longer time to react. At vulcanization temperature of 60 and 70°C, the mechanical properties increased after appropriate vulcanization time and then decreased due to overvulcanization.

3) For TMTD curing system, the maximum mechanical properties of rubber film were achieved under conditions of TMTD concentration of 2 phr, vulcanization temperature of 50°C and curing time 3 hours. At vulcanization temperature of 50, 60 and 70°C, high tensile strength needed short vulcanization time to prevent destabilized of creamed rubber latex.

4) The crosslink density increased with increasing vulcanization time at low vulcanization temperature. For higher vulcanization temperature, crosslink density did not change at longer curing time. Chloroform number and swelling index of rubber in this research indicated that the vulcanization of rubber was not complete.

5) The high amount of free sulfur in sulfur vulcanization caused the reduction in mechanical properties of rubber films.

5.2 Suggestions for Further Studies

Future investigations of creamed natural rubber latex and free-vulcanization of creamed latex should be carried out in the following directions:

1. Improvement of creaming method.

Investigations should be conducted in creaming agent of other cellulose derivatives that contain a large alkyl group, such as butyl, with the aim of using less amount of agent, shorter time, and obtaining higher DRC in creamed latex.

2. Improvement of free-vulcanized system.

Investigations should be conducted in the use of other accelerators, such as binary or combined accelerator system, to improve properties of film products or the use of potassium xanthate for vulcanization at room temperature to reduce energy and cost of vulcanization process.

REFFERENCES

[1] Thai Rubber Associate. World production of NR [Online]. Available from http://www.she.com.cn/e27.pdf [2009, May 29].

[2] Yip E. Clonal Characterization of latex and rubber properties. J. nat. Rubb. Res. 5, 1 (1990): 52.

[3] Yew F. K. Pushpapasah E. Influence of soil conditions and growth of Hevea: Glasshouse Evaluations. J. nat. Rubb. Res. 6, 1 (1991): 62.

[4] Bunn, C. W. Molecular structure and rubberlike elasticity. I. The crystal structure of β-gutta-percha, rubber and polychloroprene. Proc.Roy. Soc. A180 (1942): 40.

[5] Eng, A.H., Kawanara, S., Tanaka, Y. *Tarns*-isoprene units in natural rubber. Rubb. Chem. Technol. 67 (1993): 159.

[6] Nyburg, S.C. A statistical structure for crystalline rubber. Acta. Cryst. 7 (1954): 385.

[7] Verhaar, G. Natural latex as a colloid system. Rubber Chem. Technol. 32 (1959): 1627-1659.

[8] Sakdapipanich, J., Susujaritporn, S., Tanaka, Y. Structural characterization of the small rubber particles in fresh *Hevea* latex. J. Rubb.Res. 2, 2 1999): 160.

[9] Cook A., Sekhar B.C. Fraction from *Hevea brasiliensis* latex centrifuged at 59,000g. J.Rubb.Res.Inst. 14 (1953): 163-167.

[10] Othman A.B. and Hasma H. Role of non-rubber constituents on thermal oxidation aging of natural rubber. J.nat. Rubb. Res. 5, 1 (1990): 1-11.

[11] Morimoto M. Effect of non-rubber ingredients in natural rubber on aging properties. Proc. Int Rubb. Tech. Conf. 4, 62 (1975).

[12] Cerejido M., Rotunno C.A. Introduction to the study of biological membrane. New York: Gordon and Breach Science Publisher Inc., 1970.

[13] Chanmanit A. A study of variability in processing properties of Thai rubber. Master's Thesis, Department of Polymer Science, Faculty of Graduate Studies, Mahidol University, Thailand, 2000.

[14] Hasma H., Amir-hashim M.Y. Change to NR latex proteins on properties of the latex to its products. J. nat. Rubb. Res. 12, 1(1997) 21-32.

[15] Silpsamrith W. Effect of Cassava Strach on physical properties of natural rubber blends. Master's Thesis, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Thailand, 2000.

[16] Gregory M.J. and Tan A.S. Some observation on storage hardening of natural rubber. Proc. Int. Rubb. Tech. Conf. 74 (1975): 28.

[17] Burfield D.R., Gran S.N. Non-oxidative crosslinking reactions in natural rubber. J. Polym. Sci. Polm. Chem. 13 (1975): 272.

[18] Othman A.B., Hasma H. Influence of *Hevea* proteins and amino-acid on properties of natural rubber. Proc. Int. Rubb. Tech. Conf. (1988): 166.

[19] Dickenson P.B. The ultrastructure of the latex vessel of *Hevea brasiliensis* Proc. Nat. Rubb. Prod. Res.Ass. Jubilee Conf.: Cambridge.(1964): 52.

[20] Semegen, S.T. Rubber technology. 2nd ed. New York: Van Nostrand Reinhold, 1973.

[21] Blackley, D. C. Polymer lattice science and technology: vol. 2 Type of lattices. 2nd ed. London: Chapman & Hall, 1997.

[22] Blackley D.C. High polymer lattices, vol 1. London: Maclaren & Sons, 1996.

[23] K.D.P. company. Concentrated latex by evaporation process., 1926.

[24] Rosen, S. L. Fundamental principles of polymeric materials. 2nd ed. New York: John Wiley and Sons, Incs., 1993.

[25] Roberts, A.D. Natural rubber science and technology. Oxford: Oxford University Press, 1988.

[26] Quirk, R.P. Vulcanization and crosslinking in elastomers. Rubber Plast. Technol. 4, 1 (1988): 31.

[27] Trievette C.D., Motita, E. and Young, E.J. Rubber Chem. Tech. 35 (1962): 1370.

[28] Sanchez, J. and Myers, T.N. Organic Peroxides. 4th ed., 1996.

[29] Hary, B.W. Textbook of colloid chemistry. New York: John Wiley & Sons, 1939.

[30] Yoyutsky, S. Colloid chemistry. Moscow: English translation Mir Publishers, 1978.

[31] Myers, T.N. Polymeric materials encyclopedia., 1996.

[32] Kamath, V.R. and Palys, L.H. Polyethylene Melt Flow Modification. SPE Regional Technical Conference (RETEC), Plastics Waste Management Paper No.6, October. 1990.

[33] Dafader, N. C., Haque, M. E., Akhtar, F, Ahmad, M. U. and Utama M. Evaluation of the properties of natural rubber latex concentrated by creaming method for gamma ray irradiation. Macromolecular Reports. 33,2 (1996): 73-81.

[34] Loykulanant, S., Kongkaew C., Chaikumpoolert, O. and Suchiva, K. Efficient recovery of skim natural rubber. Proceeding of The 1st Thailand-Japan Rubber Symposium., Chonburi, Thailand. 20-22 August, 2007.

[35] Moonprasith, N., Sa-nguanthummarong, P., Kongkeaw, C. and Loykulnant, S. Effect of surfactant on gelation of hydroxypropylmethyl cellulose in skim Natural rubber latex serum. J. Metals, Materials and Minerals. 18, 2 (2008): 89-91.

[36] Werathirachot, R., Danwanichakul, P., Kongkeaw, C. and Loykulanant, S. Water soluble chitosan as an environment-friendly coagulant in removal of rubber particles from skim rubber latex. J. Metals, Materials and Minerals. 18, 2 (2008): 93-97.

[37] Gorton, A.D.T., and Pendle, T.D., Dispersion particle size in natural rubber latex technology. NR Technology. 12, 2 (1981): 21-26.

[38] Claramma N. M., Mathew N. M. Effect of temperature on sulfur prevulcanization of natural rubber latex. J. Appl. Polym. Sci. 65 (1997): 1913–1920.

[39] Ho, C.C., and Khew, M.C. Surface morphology of prevulcanized natural rubber latex films by atomic force microscopy: New insight into the prevulcanization mechanism. Langmuir. 15 (1999): 62085-6219.

[40] Sasidharan, K.K., Joseph,R., Palaty, S. Gopalakrishnan, K.S., Rajammal, G., Pillai, P.V. Effect of the vulcanization time and storage on the stability and physical properties of sulfur-prevulcanized natural rubber latex. J. Appl. Polym. Sci. 97 (2005): 1804–1811.

[41] Kurien M., Claramma, N.M., Kuriakose, A.P. A new secondary accelerator for the sulfur vulcanization of natural rubber latex and its effect on the rheological properties.. J. Appl. Polym. Sci. 93 (2004): 2781-2789.

[42] Robert AD, editor Natural rubber science and technology. Oxford: oxford university press, 1988.

[43] Chen, M.,Ao, N., Zhang, B., Den, C., Qian, H. and Zou. H. Comparison and Evaluation of the thermooxidative stability of medical natural rubber latex products prepared with a sulfur vulcanization system and a peroxide vulcanizaion system.. J. Appl. Polym. Sci. 98 (2005): 591-597.

[44] Peethambaran, N.R., Kurikose, B., Rajan, M. and Kurikose, A.P., Rheological behavior of natural rubber latex in the presence of surface-active agents. J. Appl. Polym. Sci. 41 (1990): 975-983.

[45] Office of Industrial and Economics, Ministry of Industry, Development guidelines for the value creation of rubber products for competitions' enhancement, 2007.

[46] Kita, R., Kaku, T., Kubota, K. and Dobashi, T. Pinning of phase separation of aqueous solution of hydroxypropylmethyl cellulose by gelation. Physics Letetrs A. 259, 3-4 (1999): 302-307.

[47] R K Latex. Latex Products. [Online] Available from http://www.rklatex.com/products.html [2009, July 16].

[48] Alleppey Latex (P) Ltd. Latex Products. [Online] Available from http://www.alleppeylatex.com/products.html [2009, July 16].

[49] Viriyakantichok, K. Enhanced dispersion of rubber particles in free vulcanized latex for rubber film. Master Thesis, Department of Chemical Technology, Chulalongkorn University, Thailand, 2006.

[50] Choi, S., Han, D., Ko, S. and Lee, H.S. Thermal aging behaviors of elemental sulfur-free polyisoprene vulcanizates. Bull. Korean Chem. Soc. 26, 11 (2005): 1853-1855.

[51] Travas-sejdic, J., Jelencic, J. Bravar, M. and Frobe, Z. Characterization of the natural rubber vulcanizates obtained by different accelerators. Eur. Polm. J. 32, 12 (1996): 1395-1404.

APPENDICES

APPENDIX A

Properties of Field Natural Rubber Latex

Table A-1 Properties of field natural rubber latex.

Properties	Values
Total solid content (% by wt.)	31.95
Dry rubber content (% by wt.)	30.48
Non rubber content (% by wt.)	1.47
Ammonia content (on total weight) (% by wt.)	0.25
Ammonia content (on water phase) (% by wt.)	0.47
Mechanical stability time @ 50% TS ,second	Cannot test
Volatile fatty acid number (VFA number)	0.036
Potassium hydroxide number (KOH number)	0.84
pH of latex	9.08
Specific gravity at 25 °C	0.97
Coagulum content, %	0.0005

APPENDIX B

Specification of Creaming Agents

Table B-1 Specification of carboxymethyl cellulose.

Characteristics	Specification		Results
	Min	Max	
Viscosity 1%, mPa.s	1500	2500	1580
Degree of substitution	0.65	0.90	0.71
pH	6.5	8.0	7.3
Moisture as packed, %	0	8	6

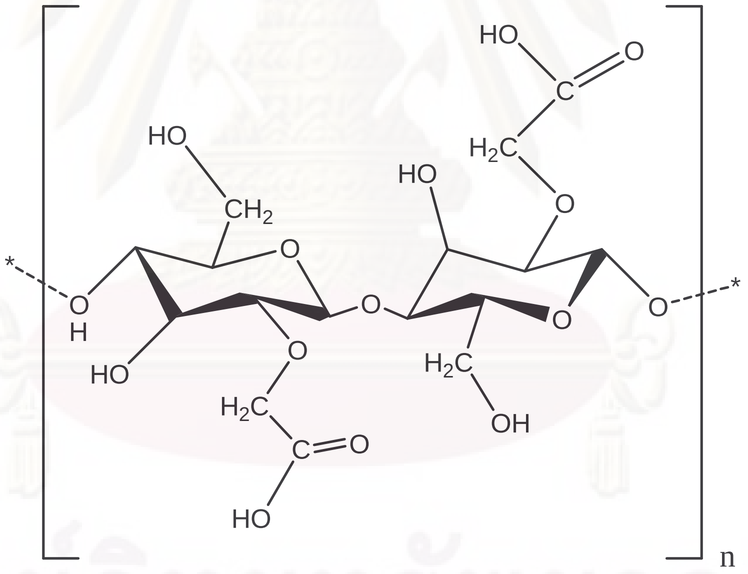
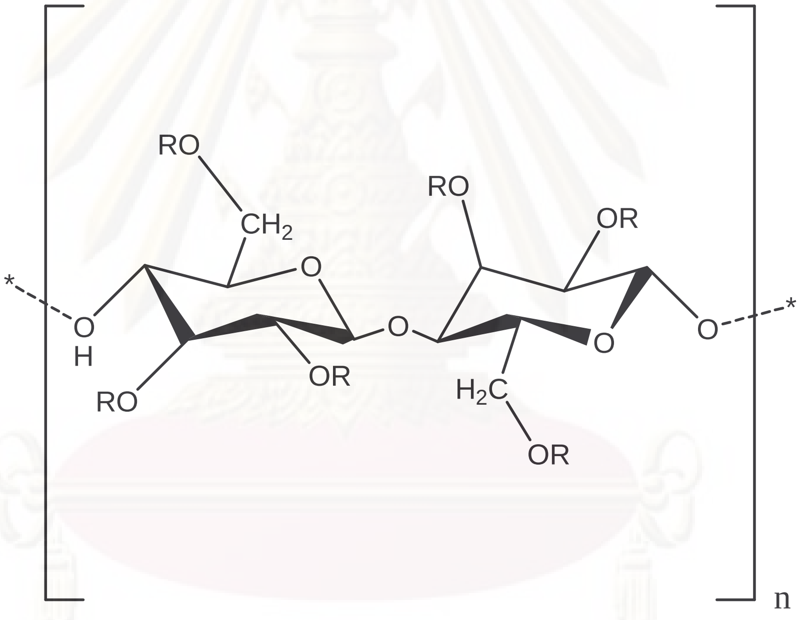


Figure B-1 Chemical structure of carboxymethyl cellulose.

Table B-2 Specification of hydroxyethyl cellulose.

Characteristics	Specification		Results
	Min	Max	
Viscosity 1%, mPa.s	2400	3000	2960
Degree of substitution	0.65	0.90	0.71
pH	6.0	7.0	6.2
Hydration time, minutes	5	15	7

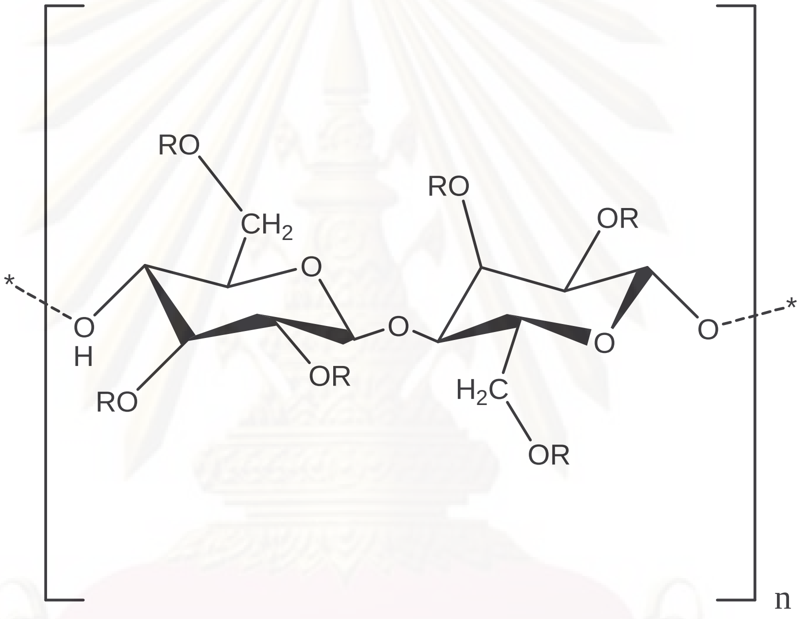


$R = H$ or CH_2CH_2OH

Figure B-2 Chemical structure of hydroxyethyl cellulose.

Table B-3 Specification of hydroxypropyl methyl cellulose.

Characteristics	Specification		Results
	Min	Max	
Viscosity 2%, mPa.s	60000	90000	74297
Degree of substitution	0.65	0.90	0.71
Moisture as packed, %	0	7	2.9



$R = -H, -CH_3, -CH_2-CHOH-CH_3$

Figure B-3 Chemical structure of hydroxypropyl methyl cellulose.

APPENDIX C

Determination of Free Sulfur

Reagents and Materials:

1. Cadmium Acetate Solution (30 g/dm^3)
2. Cadmium Acetate Wash Solution (1.2 g/dm^3)
3. Formaldehyde Solution (40%)
4. Glacial Acetic Acid
5. Iodine, Standard Solution (0.05 N) — Add 6.35 g of iodine and 20 g of potassium iodide (KI) to a beaker and just cover with water. Let stand with occasional stirring until dissolved, adding a small additional amount of water if necessary. When dissolved, dilute to 1 dm^3, filter through a filter crucible, and store the solution in a stoppered, brown glass bottle.
6. Paraffin.
7. Sodium Stearate Suspension in Water (1 g/dm^3).
8. Sodium Sulfite Solution (50 g Na_2SO_3/dm^3).
9. Starch Solution (10 g/dm^3).
10. Strontium Chloride Solution (5 g $SrCl_2$/dm^3).

Procedures:

1. Place 2 g of a sample thinly sheeted (0.5 to 0.75 mm (0.02 to 0.03 in.)) in a 400 cm^3, thin-walled, chemically resistant glass flask. Add 100 cm^3 of Na_2SO_3 solution, 5 cm^3 of a sodium stearate suspension in water, and approximately 1 g of paraffin. Cover the flask with a small watch glass and gently boil for 4 h, or digest just below the boiling point for 16 h. Remove the flask and add 100 cm^3 of $SrCl_2$ solution and 10 cm^3 of cadmium acetate solution. Separate the rubber and precipitate by filtration, using a Buchner funnel with suction. Wash with two 75 to 100 cm^3 portions of cadmium acetate wash solution.
2. To the filtrate add, while stirring, 10 cm^3 of formaldehyde solution, 10 cm^3 of glacial acetic acid, and 5 cm^3 of starch solution. Add enough crushed ice to

bring the temperature of the solution below 15°C, and titrate with 0.05 N iodine solutions to a blue end point.

Calculate the percentage of free sulfur as follows:

$$\text{Free sulfur (\%)} = (\text{A-B})\text{N}\times\frac{0.032}{\text{C}}\times 100 \qquad \text{(C-1)}$$

where A = volume of iodine solution required for titration of the sample (cm^3)

B = volume of iodine solution required for titration of the blank (cm^3)

N = normality of the iodine solution, and

C = grams of sample used

APPENDIX D

Data of Creamed Natural Rubber Latex

Table D-1 Effect of types and concentrations of creaming agent on DRC of creamed latex.

Creaming agent	Concentration (%)	Time (h)	Temp* (°C)	DRC (%)
CMC	0.2	24	RT	32.58
CMC	0.4	24	RT	40.55
CMC	0.6	24	RT	50.35
CMC	0.8	24	RT	49.36
CMC	1.0	24	RT	49.02
HEC	0.2	24	RT	39.85
HEC	0.4	24	RT	50.78
HEC	0.6	24	RT	54.98
HEC	0.8	24	RT	53.85
HEC	1.0	24	RT	53.10
HPMC	0.2	24	RT	42.78
HPMC	0.4	24	RT	54.97
HPMC	0.6	24	RT	56.78
HPMC	0.8	24	RT	55.99
HPMC	1.0	24	RT	53.97

*RT = Room temperature

Table D-2 Effect of creaming time on DRC of creamed latex.

Creaming agent	Concentration (%)	Time (h)	Temp* (°C)	DRC (%)
CMC	0.6	12	RT	37.23
CMC	0.6	24	RT	50.35
CMC	0.6	36	RT	51.85
CMC	0.6	48	RT	52.06
CMC	0.6	60	RT	52.55
CMC	0.6	72	RT	53.26
HEC	0.6	12	RT	40.58
HEC	0.6	24	RT	54.98
HEC	0.6	36	RT	55.02
HEC	0.6	48	RT	56.02
HEC	0.6	60	RT	56.08
HEC	0.6	72	RT	56.42
HPMC	0.6	12	RT	49.85
HPMC	0.6	24	RT	56.84
HPMC	0.6	36	RT	56.78
HPMC	0.6	48	RT	56.92
HPMC	0.6	60	RT	56.99
HPMC	0.6	72	RT	57.07

*RT = Room temperature

Table D-3 Effect of temperature on DRC of creamed latex.

Creaming agent	Concentration (%)	Time (h)	Temp* (°C)	DRC (%)
CMC	0.6	24	RT	50.35
CMC	0.6	24	40	52.25
CMC	0.6	24	50	53.85
CMC	0.6	24	60	53.98
HEC	0.6	24	RT	54.98
HEC	0.6	24	40	55.72
HEC	0.6	24	50	55.96
HEC	0.6	24	60	55.94
HPMC	0.6	24	RT	56.78
HPMC	0.6	24	40	56.92
HPMC	0.6	24	50	54.21
HPMC	0.6	24	60	53.48

*RT = Room temperature

APPENDIX E

Data of Properties of Free-vulcanized Rubber Films

Table E-1 Effect of vulcanization parameters on properties of free-vulcanized rubber films.

Curing agent	Conc (phr)	Temp (°C)	Time (h)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslink density (mol/cm^3 x10^{-4})	Chloroform number	Swelling index	Free sulfur (% x10^{-4})
S	1	40	1	7.28±1.75	774.33±12.35	36.0±0.00	1.06±0.06	1±0.00	15.79±2.24	6.46±0.15
S	1	40	2	8.37±0.14	772.25±52.85	38.2±0.29	1.23±0.03	1±0.00	14.96±1.02	5.24±0.08
S	1	40	3	8.96±2.05	773.15±20.36	40.3±0.58	1.78±0.06	1±0.00	14.82±0.87	5.29±0.45
S	1	40	4	10.26±0.48	756.35±3.58	42.0±0.00	2.25±0.18	2±0.00	10.64±0.34	4.83±0.26
S	1	40	5	11.44±0.09	750.36±19.28	42.2±0.29	2.75±0.34	2±0.00	10.39±1.52	4.04±0.40
S	1	40	6	11.68±1.59	749.25±75.24	42.5±0.00	3.37±0.02	2±0.00	8.25±0.95	4.13±0.17
S	1	50	1	8.99±0.56	770.52±20.17	38.0±0.00	2.05±0.06	1±0.00	15.85±2.36	5.01±0.30
S	1	50	2	9.15±0.78	771.36±36.28	38.5±0.00	2.46±0.00	2±0.00	13.53±1.05	4.56±0.85
S	1	50	3	9.41±0.02	752.54±25.10	41.0±0.00	3.48±0.06	2±0.00	9.22±0.87	4.52±0.95
S	1	50	4	11.26±1.74	758.25±10.36	42.5±0.00	3.91±0.12	3±0.00	8.99±0.47	3.69±0.24
S	1	50	5	13.99±0.96	742.96±20.36	43.0±0.00	4.52±0.03	3±0.00	8.26±0.69	3.55±0.10
S	1	50	6	15.59±1.44	750.36±19.87	46.0±0.00	4.32±0.17	3±0.00	7.85±1.04	3.03±0.24
S	1	60	1	12.26±2.58	737.58±37.58	43.0±0.00	4.02±0.08	2±0.00	12.26±0.12	3.03±0.17
S	1	60	2	15.36±0.48	738.25±86.54	45.0±0.00	4.83±0.56	2±0.00	9.85±2.08	2.91±0.29
S	1	60	3	17.89±0.47	752.77±24.87	46.0±0.00	5.41±0.00	2±0.00	8.52±0.15	2.16±0.47
S	1	60	4	18.03±0.95	769.24±10.69	47.0±0.00	6.55±0.50	3±0.00	6.29±0.47	2.06±0.08
S	1	60	5	16.26±1.63	752.57±3.86	45.0±0.00	6.48±0.06	3±0.00	6.99±1.36	2.85±0.28
S	1	60	6	15.35±1.24	750.55±70.14	43.0±0.00	6.59±0.08	3±0.00	7.13±0.95	2.97±0.08

Curing agent	Conc (phr)	Temp (°C)	Time (h)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslink density (mol/cm^3 x10^{-4})	Chloroform number	Swelling index	Free sulfur (% x10^{-4})
S	1	70	1	16.36±0.58	730.52±20.57	45.0±0.00	5.87±0.13	2±0.00	9.36±0.74	2.46±0.42
S	1	70	2	17.20±0.07	740.28±64.36	45.5±0.00	5.41±0.08	3±0.00	9.03±1.06	2.52±0.18
S	1	70	3	15.37±1.45	745.54±17.25	45.3±0.58	5.10±0.40	3±0.00	8.75±0.47	2.35±0.92
S	1	70	4	14.77±1.04	740.85±23.98	43.0±0.00	5.25±0.09	3±0.00	8.57±0.35	2.21±0.75
S	1	70	5	13.56±0.12	742.58±73.15	42.0±0.00	4.75±0.00	3±0.00	8.25±1.17	2.25±0.47
S	1	70	6	11.26±0.58	735.68±15.47	40.0±0.00	4.41±0.52	3±0.00	7.99±0.95	2.26±0.19
S	2	40	1	8.37±0.69	760.58±52.04	40.2±0.29	1.66±0.07	1±0.00	16.25±2.74	7.25±0.32
S	2	40	2	9.53±0.07	755.34±36.96	40.7±0.29	1.79±0.38	1±0.00	15.24±1.69	7.03±0.05
S	2	40	3	9.82±0.35	775.94±74.21	41.0±0.00	1.96±0.09	2±0.00	13.52±0.74	6.75±0.25
S	2	40	4	11.33±0.07	780.52±26.85	42.0±0.00	2.25±0.13	2±0.00	10.26±0.53	6.75±0.63
S	2	40	5	12.37±0.64	778.75±14.26	42.0±0.00	3.01±0.13	2±0.00	8.52±0.24	6.52±0.14
S	2	40	6	14.24±0.85	791.29±26.35	43.0±0.00	3.52±0.06	3±0.00	6.37±0.96	6.13±0.19
S	2	50	1	8.91±0.11	784.65±85.24	41.0±0.00	2.75±0.20	1±0.00	15.33±0.41	7.03±0.25
S	2	50	2	10.57±0.30	776.66±12.30	42.0±0.00	2.96±0.05	2±0.00	14.53±1.69	6.97±0.52
S	2	50	3	14.56±0.07	760.28±37.39	42.5±0.00	3.51±0.22	2±0.00	13.03±0.84	6.46±0.18
S	2	50	4	17.52±0.12	765.58±28.34	46.0±0.00	3.15±0.05	2±0.00	10.26±0.14	6.05±0.20
S	2	50	5	17.53±0.14	798.25±17.24	46.0±0.00	4.26±0.02	3±0.00	7.29±0.96	5.63±0.05
S	2	50	6	18.67±0.41	795.65±38.24	48.2±0.29	5.26±0.02	3±0.00	6.13±0.24	5.85±0.32
S	2	60	1	14.70±1.04	801.58±31.05	45.5±0.00	5.80±0.12	2±0.00	13.52±1.05	5.26±0.12
S	2	60	2	16.59±0.75	805.68±52.96	46.0±0.00	5.85±0.36	2±0.00	10.26±1.92	4.48±0.17
S	2	60	3	19.26±0.17	785.36±41.75	48.0±0.00	6.42±0.25	3±0.00	8.94±0.65	3.95±0.62
S	2	60	4	21.16±2.10	795.36±60.78	49.0±0.00	7.06±0.06	3±0.00	5.96±0.84	3.76±0.21
S	2	60	5	17.54±0.95	800.28±20.39	47.0±0.00	6.50±0.13	3±0.00	7.26±0.72	4.21±0.02
S	2	60	6	15.06±0.77	804.58±23.47	45.5±0.00	6.53±0.22	3±0.00	7.37±2.36	4.86±0.51

Curing agent	Conc (phr)	Temp (°C)	Time (h)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslink density (mol/cm^3 x10^{-4})	Chloroform Number	Swelling index	Free sulfur (% x10^{-4})
S	2	70	1	18.25±1.16	714.26±41.36	47.0±0.00	5.24±0.06	1±0.00	7.26±0.60	5.70±0.20
S	2	70	2	19.52±0.62	719.58±21.39	47.5±0.00	5.24±0.20	1±0.00	6.02±0.45	5.21±0.75
S	2	70	3	16.85±0.31	720.58±85.32	47.0±0.00	5.97±0.55	2±0.00	8.24±0.85	5.03±0.14
S	2	70	4	15.46±0.08	690.53±70.14	46.0±0.00	5.15±0.02	2±0.00	8.97±1.08	5.05±0.20
S	2	70	5	13.26±0.96	668.48±32.58	43.0±0.00	5.15±0.00	2±0.00	8.24±0.17	5.03±0.32
S	2	70	6	13.28±0.47	672.25±38.45	43.0±0.00	5.26±0.13	2±0.00	8.21±0.95	5.05±0.04
S	3	40	1	7.03±0.04	779.48±95.32	37.8±0.29	2.02±0.08	1±0.00	15.59±3.14	10.25±0.57
S	3	40	2	8.37±0.14	780.00±75.27	39.0±0.00	2.42±0.23	2±0.00	14.85±0.44	10.42±0.21
S	3	40	3	11.24±0.06	781.26±62.36	42.0±0.00	2.41±0.07	3±0.00	11.57±0.93	9.85±0.33
S	3	40	4	12.03±0.51	750.24±27.54	42.0±0.00	3.16±0.09	3±0.00	10.59±3.57	9.75±0.05
S	3	40	5	12.13±0.30	725.66±39.52	42.8±0.00	3.55±0.12	3±0.00	9.53±0.42	8.49±0.12
S	3	40	6	12.96±0.07	713.26±19.05	44.0±0.00	3.85±0.04	3±0.00	8.21±1.28	8.15±0.23
S	3	50	1	7.26±0.07	765.26±64.21	38.5±0.00	2.26±0.20	2±0.00	14.86±0.18	8.24±0.04
S	3	50	2	9.25±0.54	760.36±80.47	41.0±0.00	2.30±0.31	3±0.00	14.99±3.02	8.02±0.54
S	3	50	3	11.03±0.04	760.28±36.54	43.0±0.00	3.01±0.17	3±0.00	12.58±0.44	7.25±0.27
S	3	50	4	13.96±0.41	736.26±16.35	44.0±0.00	3.52±0.06	3±0.00	8.69±0.69	6.25±0.33
S	3	50	5	14.30±0.23	748.70±36.24	44.0±0.00	3.65±0.14	3±0.00	8.02±0.82	6.69±0.62
S	3	50	6	16.50±0.02	756.35±76.31	46.2±0.29	3.65±0.02	3±0.00	7.97±0.27	6.02±0.17
S	3	60	1	12.26±0.07	745.24±28.47	43.0±0.00	4.79±0.15	3±0.00	13.59±0.71	8.59±0.84
S	3	60	2	15.46±0.13	765.58±31.05	44.0±0.00	4.59±0.30	3±0.00	9.26±0.95	8.55±0.29
S	3	60	3	17.37±0.14	771.94±29.27	46.5±0.00	5.75±0.41	3±0.00	8.35±1.36	8.20±0.35
S	3	60	4	18.96±0.27	774.77±40.21	47.0±0.00	5.85±0.22	3±0.00	7.59±0.28	8.26±0.26
S	3	60	5	16.53±0.16	753.78±48.22	46.0±0.00	5.69±0.15	3±0.00	7.29±0.88	7.24±0.04
S	3	60	6	16.12±0.06	769.85±17.08	46.0±0.00	5.21±0.05	3±0.00	7.48±0.59	7.15±0.11

Curing agent	Conc (phr)	Temp (°C)	Time (h)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslink density (mol/cm^3 x10^{-4})	Chloroform Number	Swelling index	Free sulfur (% x10^{-4})
S	3	70	1	18.03±0.10	670.25±30.96	46.3±0.00	5.75±0.04	3±0.00	6.59±0.93	8.95±0.03
S	3	70	2	17.37±0.05	623.48±41.88	46.0±0.00	5.75±0.18	3±0.00	7.03±0.12	8.22±0.10
S	3	70	3	13.03±0.41	624.50±20.34	44.0±0.00	5.15±0.22	3±0.00	6.85±0.09	8.03±0.35
S	3	70	4	11.99±0.09	617.87±26.38	43.5±0.00	5.24±0.08	3±0.00	6.87±0.52	7.97±0.17
S	3	70	5	11.70±0.12	582.54±32.63	43.3±0.58	5.13±0.16	3±0.00	7.03±0.11	7.26±0.09
S	3	70	6	10.81±0.10	600.54±75.14	43.2±0.29	5.01±0.09	3±0.00	7.26±0.39	7.86±0.15
TMTD	1	40	1	10.52±0.17	782.15±56.31	41.5±0.00	3.56±0.31	1±0.00	15.09±0.17	-
TMTD	1	40	2	12.45±0.36	788.70±13.42	42.0±0.00	3.66±0.17	2±0.00	12.55±1.85	-
TMTD	1	40	3	13.44±0.08	790.66±34.85	42.0±0.00	4.56±0.21	2±0.00	12.99±0.47	-
TMTD	1	40	4	14.52±0.17	795.06±25.54	44.0±0.00	5.75±0.06	3±0.00	7.68±0.69	-
TMTD	1	40	5	14.99±0.04	790.26±20.14	46.0±0.00	6.85±0.30	3±0.00	6.99±0.44	-
TMTD	1	40	6	16.23±0.42	794.02±3.18	46.5±0.00	7.13±0.02	3±0.00	6.16±039	-
TMTD	1	50	1	14.85±0.13	792.35±92.22	44.0±0.00	5.66±0.11	3±0.00	7.99±1.33	-
TMTD	1	50	2	16.01±0.21	810.24±16.20	46.0±0.00	6.25±0.19	3±0.00	7.15±0.29	-
TMTD	1	50	3	16.42±0.06	807.37±45.74	46.0±0.00	8.36±0.27	3±0.00	5.69±0.26	-
TMTD	1	50	4	16.02±0.01	800.42±35.24	46.5±0.00	7.96±0.00	3±0.00	7.37±0.54	-
TMTD	1	50	5	16.85±0.32	798.02±19.54	46.5±0.00	8.03±0.08	3±0.00	7.16±0.15	-
TMTD	1	50	6	15.90±0.14	785.54±36.45	46.0±0.00	6.90±0.14	3±0.00	7.52±0.07	-
TMTD	1	60	1	11.59±0.09	745.66±25.47	44.0±0.00	4.53±0.09	3±0.00	7.90±0.14	-
TMTD	1	60	2	11.02±0.30	731.06±82.01	43.0±0.00	4.03±0.27	3±0.00	7.25±0.42	-
TMTD	1	60	3	10.95±0.04	758.37±17.41	42.5±0.00	4.85±0.11	3±0.00	7.32±0.63	-
TMTD	1	60	4	10.84±0.06	760.79±29.45	41.5±0.00	4.75±0.08	3±0.00	7.48±0.27	-
TMTD	1	60	5	8.24±0.31	726.96±27.88	40.5±0.00	4.10±0.35	3±0.00	7.78±0.18	-
TMTD	1	60	6	7.88±0.11	730.45±35.28	39.0±0.00	4.85±0.02	3±0.00	7.59±0.53	-

Curing agent	Conc (phr)	Temp (°C)	Time (h)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslink density (mol/cm^3 x10^{-4})	Chloroform number	Swelling Index	Free sulfur (% x10^{-4})
TMTD	1	70	1	9.26±0.18	702.41±12.65	40.0±0.00	4.86±0.24	3±0.00	8.03±0.85	-
TMTD	1	70	2	9.02±0.04	698.65±38.24	40.5±0.00	4.25±0.71	3±0.00	7.49±0.13	-
TMTD	1	70	3	8.95±0.03	705.62±64.27	40.0±0.00	4.26±0.25	3±0.00	7.63±0.37	-
TMTD	1	70	4	9.15±0.14	685.15±52..22	40.3±0.58	4.36±0.06	3±0.00	7.52±0.44	-
TMTD	1	70	5	9.03±0.09	688.15±18.27	39.0±0.00	4.25±0.24	3±0.00	7.59±0.08	-
TMTD	1	70	6	7.99±0.52	697.52±25.75	39.5±0.00	5.02±0.14	3±0.00	7.49±0.36	-
TMTD	2	40	1	12.05±0.74	811.21±60.85	44.5±0.00	3.86±0.39	1±0.00	14.40±0.45	-
TMTD	2	40	2	13.54±0.04	803.73±44.15	45.0±0.00	3.96±0.17	2±0.00	13.59±0.18	-
TMTD	2	40	3	13.41±0.15	786.38±38.74	45.0±0.00	3.69±0.14	3±0.00	9.49±0.96	-
TMTD	2	40	4	16.15±0.13	776.48±14.02	46.0±0.00	5.16±0.19	3±0.00	8.02±0.41	-
TMTD	2	40	5	18.02±0.09	779.67±85.27	46.0±0.00	7.49±0.39	3±0.00	6.79±0.69	-
TMTD	2	40	6	19.03±0.41	753.85±36.18	47.3±0.58	8.02±0.55	3±0.00	6.25±0.30	-
TMTD	2	50	1	16.94±0.36	835.10±38.42	45.0±0.00	5.73±0.18	3±0.00	8.75±0.45	-
TMTD	2	50	2	19.55±0.14	802.11±15.52	47.0±0.00	7.16±0.28	3±0.00	8.96±1.58	-
TMTD	2	50	3	22.86±0.05	799.00±38.17	48.5±0.00	9.15±0.41	3±0.00	6.25±0.18	-
TMTD	2	50	4	17.66±0.85	804.00±64.74	48.0±0.00	5.25±0.34	3±0.00	6.90±0.00	-
TMTD	2	50	5	15.44±0.53	804.24±9.74	47.5±0.00	5.02±0.95	3±0.00	7.48±0.95	-
TMTD	2	50	6	15.17±0.14	796.41±29.25	46.0±0.00	4.86±0.22	3±0.00	7.99±0.47	-
TMTD	2	60	1	13.26±0.52	763.20±43.85	43.0±0.00	3.85±0.74	3±0.00	9.53±0.39	-
TMTD	2	60	2	12.95±0.06	777.85±36.15	43.0±0.00	4.25±0.63	3±0.00	8.12±0.85	-
TMTD	2	60	3	10.44±0.18	762.52±27.33	42.0±0.00	3.93±0.14	3±0.00	8.06±0.24	-
TMTD	2	60	4	10.97±0.34	759.85±46.58	41.0±0.00	4.03±0.20	3±0.00	7.65±0.74	-
TMTD	2	60	5	9.82±0.25	755.97±52.07	41.0±0.00	4.56±0.32	3±0.00	7.46±0.18	-
TMTD	2	60	6	9.73±0.96	743.26±36.25	40.5±0.00	4.00±0.13	3±0.00	7.57±0.25	-

Curing agent	Conc (phr)	Temp (°C)	Time (h)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslink density (mol/cm^3:10^{-4})	Chloroform number	Swelling index	Free sulfur (%)
TMTD	2	70	1	10.35±0.36	732.02±40.15	41.0±0.00	3.90±0.42	3±0.00	8.15±0.28	-
TMTD	2	70	2	10.85±0.08	740.57±23.87	41.5±0.00	4.07±0.05	3±0.00	8.04±0.74	-
TMTD	2	70	3	9.26±0.55	700.57±42.19	40.5±0.00	4.15±0.09	3±0.00	7.45±0.23	-
TMTD	2	70	4	9.45±0.04	706.54±26.40	40.3±0.58	3.93±0.13	3±0.00	7.70±0.52	-
TMTD	2	70	5	9.52±0.32	695.54±38.52	40.5±0.00	4.22±0.13	3±0.00	7.49±0.21	-
TMTD	2	70	6	9.25±0.20	709.55±21.07	40.0±0.00	4.04±0.02	3±0.00	7.27±0.07	-
TMTD	3	40	1	11.02±0.05	788.75±68.21	37.8±0.58	2.99±0.37	1±0.00	14.99±0.33	-
TMTD	3	40	2	12.04±0.17	778.28±35.41	39.0±0.00	3.45±0.11	2±0.00	13.79±1.07	-
TMTD	3	40	3	13.85±0.09	780.54±96.18	42.0±0.00	3.04±0.06	2±0.00	10.36±0.36	-
TMTD	3	40	4	15.81±0.12	783.33±60.14	42.0±0.00	4.57±0.35	3±0.00	8.56±0.22	-
TMTD	3	40	5	16.98±0.58	769.69±85.32	42.8±0.58	5.02±0.15	3±0.00	7.22±0.41	-
TMTD	3	40	6	16.69±0.41	759.92±39.27	44.0±0.00	4.85±0.09	3±0.00	7.53±0.25	-
TMTD	3	50	1	17.06±0.36	807.65±25.64	38.5±0.00	5.29±0.52	3±0.00	8.46±0.36	-
TMTD	3	50	2	17.54±0.05	809.25±3.42	41.0±0.00	5.96±0.04	3±0.00	8.03±0.12	-
TMTD	3	50	3	17.84±0.09	792.00±29.47	43.0±0.00	6.21±0.06	3±0.00	7.86±0.05	-
TMTD	3	50	4	17.66±0.24	810.96±52.04	44.0±0.00	6.55±0.13	3±0.00	7.74±0.61	-
TMTD	3	50	5	14.65±0.18	804.97±21.38	44.0±0.00	4.85±0.44	3±0.00	6.90±0.22	-
TMTD	3	50	6	14.53±0.65	795.00±106.25	46.2±0.29	4.13±0.20	3±0.00	7.63±0.14	-
TMTD	3	60	1	12.01±0.05	730.59±17.78	43.0±0.00	4.26±0.17	3±0.00	7.45±0.69	-
TMTD	3	60	2	11.49±0.35	719.58±6.48	44.0±0.00	4.15±0.50	3±0.00	7.96±0.41	-
TMTD	3	60	3	9.15±1.02	720.64±27.85	46.5±0.00	3.90±0.12	3±0.00	6.15±0.22	-
TMTD	3	60	4	8.99±0.54	700.57±42.21	47.0±0.00	4.03±0.06	3±0.00	7.00±0.51	-
TMTD	3	60	5	8.42±0.06	705.65±42.15	46.0±0.00	3.74±0.12	3±0.00	7.49±0.63	-
TMTD	3	60	6	8.07±0.41	682.66±20.58	46.0±0.00	3.99±0.08	3±0.00	5.85±0.24	-

Curing agent	Conc (phr)	Temp (°C)	Time (h)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslink density (mol/cm^3:10^{-4})	Chloroform number	Swelling index	Free sulfur (%)
TMTD	3	70	1	9.02±0.14	687.25±18.35	46.3±0.00	3.56±0.10	3±0.00	6.85±0.15	-
TMTD	3	70	2	7.99±0.30	694.16±32.52	46.0±0.00	3.78±0.27	3±0.00	7.03±0.96	-
TMTD	3	70	3	8.12±0.07	650.52±45.65	44.0±0.00	3.22±0.04	3±0.00	7.52±0.71	-
TMTD	3	70	4	7.62±0.28	658.54±35.57	43.5±0.00	3.69±0.33	3±0.00	6.46±1.52	-
TMTD	3	70	5	7.56±0.22	642.02±40.21	43.3±0.58	3.99±0.06	3±0.00	7.55±0.25	-
TMTD	3	70	6	7.01±0.14	640.17±53.69	43.2±0.29	3.12±0.42	3±0.00	7.06±0.28	-

VITA

Mr. Kumjorndej Kitmancharoenkul was born on Febuary 25, 1985 in Chonburi, Thailand. He graduated with a Bachelor’s Degree of Science in Biology from Department of Zoology, Faculty of Science, Kasetsart University in 2006. He has continued his study in Master Degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2006 and finished his study in 2009.