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MODIFICATION OF NATURAL RUBBER WITH CASHEW NUT SHELL LIQUID

Miss Lalita Rodthongkum

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ไกลซิดิล 3-เพนทาดีซินิลเฟนิลอีเทอร์ สังเคราะห์ได้จากการทำปฏิกิริยาของคาร์ดานอลและอีพิคลอโรไฮดรินโดยมีโซเดียมไฮดรอกไซด์อยู่ด้วย พิสูจน์เอกลักษณ์ด้วยอินฟราเรดสเปกโทรสโกปีและนิวเคลียร์แมคเนติกเรโซแนนซ์สเปกโทรสโกปี ยางธรรมชาติดัดแปรด้วยไกลซิดิล 3-เพนทาดีซินิลเฟนิลอีเทอร์เตรียมได้โดยการผสมน้ำยางธรรมชาติเข้มข้น ไกลซิดิล 3-เพนทาดีซินิลเฟนิลอีเทอร์ และสารเติมแต่งโดยตรงด้วยเครื่องบอลมิล เตรียมแผ่นยางวัลคาไนซ์มาตรฐานเพื่อนำผลิตภัณฑ์ยางไปทดสอบสมบัติเชิงกลและสมบัติทางความร้อน ศึกษาอิทธิพลของความเข้มข้นของไกลซิดิล 3-เพนทาดีซินิลเฟนิลอีเทอร์ ชนิดและปริมาณสารลดแรงตึงผิว และเวลาที่ใช้ในการผสมที่มีต่อสมบัติเชิงกลของยางที่เตรียมได้ ตรวจสอบสมบัติทางความร้อนของผลิตภัณฑ์ยางด้วยเทอร์โมกราวิเมตริกอะนาไลซิสและความทนต่อการบ่มเร่ง ตรวจสอบการกระจายตัวของไกลซิดิล 3-เพนทาดีซินิลเฟนิลอีเทอร์และสารเติมแต่งด้วยกล้องจุลทรรศน์และกล้องจุลทรรศน์อิเลคตรอนแบบส่องกราด เปอร์เซนต์การเชื่อมขวางโมเลกุลของผลิตภัณฑ์ยางสามารถหาได้โดยการสกัดด้วยเครื่องซอกฮ์เลท

ผลการศึกษาสมบัติเชิงกลของผลิตภัณฑ์ยางธรรมชาติดัดแปรด้วย ไกลซิดิล 3-เพนทาดีซินิลเฟนิลอีเทอร์ แสดงให้เห็นสูตรที่เหมาะสมสำหรับใช้เตรียมผลิตภัณฑ์ยางคือ น้ำยางธรรมชาติเข้มข้น 100 ส่วนโดยน้ำหนักแห้ง ซิงค์ออกไซด์ 5 ส่วนในยาง 100 ส่วน กำมะถัน 2 ส่วนในยาง 100 ส่วน กรดสเตียริก 2 ส่วนในยาง 100 ส่วน เอ็มบีที 1 ส่วนในยาง 100 ส่วน ไกลซิดิล 3-เพนทาดีซินิลเฟนิลอีเทอร์ 2 ส่วนในยาง 100 ส่วน และ เทอร์จิตอลเอ็นพี10 1.5 ส่วนในยาง 100 ส่วน ผลิตภัณฑ์ยางมีอุณหภูมิของการสลายตัวอยู่ที่ 393 องศาเซลเซียส มีการเชื่อมขวางโมเลกุลของผลิตภัณฑ์ยาง 95 เปอร์เซ็นต์ ผลิตภัณฑ์ยางที่เตรียมได้มีสมบัติเชิงกลที่ดีกว่าผลิตภัณฑ์ยางธรรมชาติดัดแปรด้วยอนุพันธ์ของของเหลวสกัดจากเปลือกเมล็ดมะม่วงหิมพานต์อื่นบางชนิดและสามารถนำไปเตรียมเป็นผลิตภัณฑ์ยางบางประเภทได้

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา...............................
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KEY WORD: RUBBER MODIFICATION / RUBBER COMPOUNDING / CASHEW NUT SHELL LIQUID

LALITA RODTHONGKUM: MODIFICATION OF NATURAL RUBBER WITH CASHEW NUT SHELL LIQUID. THESIS ADVISOR: ASSOC. PROF. SOPHON ROENGSUMRAN, Ph.D. 141 pp. ISBN 974-347-231-2

Glycidyl 3-pentadecenylphenyl ether was synthesized from the reaction of cardanol and epichlorohydrin in the presence of sodium hydroxide and characterized by infrared spectroscopy and nuclear magnetic resonance spectroscopy. The glycidyl 3-pentadecenylphenyl ether (GPPE) modified natural rubber was prepared by direct mixing the natural rubber latex, GPPE, and additives in a ball mill. The standard vulcanized sheets were prepared for thermal and mechanical properties testing. The effect of GPPE concentration, type and concentration of surfactant, and mixing time on the mechanical properties of vulcanized sheets were studied. Thermogravimetric analysis and thermal aging were used to determine the thermal properties of vulcanized sheets. The dispersion of GPPE and additives were investigated by optical microscope and scanning electron microscope. The percent crosslinking of vulcanized sheets was also studied by soxhlet extraction.

The results of mechanical properties indicated that the suitable formulations of the GPPE modified natural rubber were 100 parts by dry weight of concentrated rubber latex, 5 phr zinc oxide, 2 phr sulfur, 2 phr stearic acid, 1 phr MBT, 2 phr GPPE, and 1.5 phr Tergitol NP10. The rubber product had thermal decomposition temperature at 393.13°C. The percent crosslinking of rubber containing of 2 phr GPPE were 95%. This rubber product had mechanical properties better than some other CNSL modified natural rubbers and suitable for preparing some rubber products.

Department……Petrochemistry and polymer science…… Student's signature……………………...

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Finally, my deepest gratitude goes to my family for their encouragement and support to make my study successful.

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
Ave.	Average
°C	Degree Celsius
cal./c.c.	Calorie per cubic centimeter
cal.g.	Calorie. gram
cal./sec/cm^2/°C	Calorie per second per square centimeter per degree Celsius
^{13}C-NMR	Carbon Nuclear Magnetic Resonance
cm.	Centimeter
cm^{-1}	Unit of wave number
cm^3	Cubic centimeter
cP	Centipoises
°F	Degree Fahrenheit
g.	Gram
g./ml.	Gram per milliliter
g.mol^{-1}	Gram per mole
^{1}H-NMR	Proton Nuclear Magnetic Resonance
in.	Inch
ISO	International Organization for Standardization
kg./cm^2	Kilogram per square centimeter
MHz	Megahertz

ABBREVIATIONS (continued)

min. : Minute

ml. : Milliliter

mm. : Millimeter

MPa : Mega Pascal

ohms./c.c. : Ohms per cubic centimeter

phr : Part per hundred parts of rubber

ppm. : Part per million

psi. : Pound per square inch

rpm. : Rounds per minute

sec : Second

wt. : Weight

w/v : Weight by volume

μm : Micrometer

CHAPTER I

INTRODUCTION

Thailand is the leader in production and exporting of natural rubber in the world. Major export items of natural rubber products are latex thread, compound rubber, reclaimed rubber and unvulcanized rubber, respectively. However, at present, the export of ribbed smoke sheet rubber and block rubber has the tendency to decrease due to the competition of exporting by other countries, which is increasing [1]. Therefore, it is extremely necessary to find a new approach of natural rubber modification to increase production and exporting values of rubber products. The modified rubber has some special qualities and properties such as heat resistance, abrasion resistance, tensile strength, hardness. Furthermore, the modified rubber is capable to compete with other exporting country's rubber products.

Natural rubber from *Hevea brasilliensis*, is a natural polymer, which has been commercially available for over a hundred years [2]. *Hevea* rubber has attractive properties, which is unmatched by most synthetic rubber. The backbone unsaturations make certain types of chemical modification relatively easy. The modification of natural rubber by blending with a cheap and easily available material is one of many methods. This method is very attractive because it is easy to handle and gives a ready to use product for the rubber industry.

Cashew nut shell liquid (CNSL), a material from natural resource, is a by-product from cashew industry. CNSL and its derivatives have found a wide range of industrial applications due to their higher thermal stability and mechanical strength [3]. Glycidyl 3-pentadecenylphenyl ether (GPPE) is a derivative of CNSL, derives from the reaction of cardanol and epichlorohydrin. GPPE is a monoepoxy compound, which has both of an epoxy group and unsaturated side chain. The GPPE molecule can be polymerized or crosslink with other unsaturated molecules. From these advantages, CNSL and its derivatives are used as potential candidates to be incorporated into natural rubber.

Therefore, the objective of this research is to produce rubber product, which contains natural rubber latex, additives, CNSL derivative (GPPE), which are ready to be used in the rubber industry. The method of preparing this compound is mixing in a ball mill, in emulsion condition. The advantages of this method are the reduction of processing, time, and cost for the factory if this compound is used as raw material. Many different parameters, such as the amount of CNSL derivatives, time of mixing, type and concentration of surfactant, were taken into account to achieve the proper ingredients, which make products with good properties.

This research is very attractive because the resulting product is expected to have good thermal and mechanical properties, which is a combination of the advantage from CNSL derivatives and natural rubber.

Objectives

1. To obtain the suitable condition for modification of natural rubber with modified cashew nut shell liquid.
2. To study the mechanical and thermal properties of the prepared rubber compound.

Scope of the Investigation

The preparation of a natural rubber product containing CNSL and its derivative, glycidyl-3-pentadecenylphenyl ether (GPPE), was carried out. The suitable formulation, which yielded the best mechanical and thermal properties, was determined. The investigation procedures were carried out as follows:

1. Literature survey and in-depth study of this research work.
2. Design and preparation of experimental procedures.
3. Synthesis of glycidyl-3-pentadecenyl phenyl ether (GPPE) from the reaction of cardanol and epichlorohydrin.
4. Characterization of GPPE by infrared spectroscopy (IR), and nuclear magnetic resonance spectroscopy (NMR).
5. Mixing of the concentrated latex, additives, and GPPE. The appropriate condition and factors effecting on the mechanical properties were determined by changing the following parameters:
    a. The optimum concentration of GPPE
    b. The types and concentration of surfactant
    c. The effect of mixing time

6. Coagulation of compounded rubber, vulcanization and preparation of vulcanized sheets for rubber testing.
7. Study of the compatibility and dispersion of GPPE in rubber product by optical microscopy (OM) and scanning electron microscopy (SEM).
8. Study of the effect of GPPE on the percent of crosslinking.
9. Testing of mechanical properties such as tensile strength, elongation at break, hardness and testing of thermal properties by thermogravimetric analysis (TGA).
10. Summarization of the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber

Natural rubber is a milky aqueous serum, which can be isolated from more than 200 different species of plant. However, only the tree source, *Hevea brasilliensis*, is commercially significant. The *Hevea* tree has the story of natives in South America, discovered by Christopher Columbus in 1496[4]. From that discovery, natural rubber has been used and applied to various products, such as waterproof articles for clothing and footwear, tires, and others. In 1877, the natural rubber was first shipped to Singapore and planted. According to Southeast Asia has a hot, damp climate with equable distribution of rainfall and temperature, which is appropriate for rubber tree growth.

Today, it is known that the rubber tree was not indigenous to South America alone. The rubber tree widely grew in many regions of Africa and mainly in Southeast Asia, especially in Thailand, Indonesia, and Malaysia.

2.2 Production of Natural Rubber in Thailand

Thailand is currently the world leader in the production and export of natural rubber with exporting volume of approximately 2,031,166 tons of rubber and the total value exported 43,937.37 million Bahts in the year 1999 as shown in Tables 2.1 and 2.2[1].

Table 2.1 Thailand natural rubber exporting volume and value*

Year	Volume (tons)	Value (million Bahts)
1995	1,747,269	61,261
1996	1,922,042	63,370
1997	1,919,640	57,458
1998	1,998,247	55,413
1999	2,031,166	43,937

* Source: http://www.oae.go.th

Table 2.2 Natural rubber production in 1999 [5]

Country	Volume (tons)
Thailand	2,150
Indonesia	1,621
Malaysia	850
India	595
China	464
Vietnam	235
Sri Lanka	103
Philippines	60
Nigeria	80
Rest of the World	522
Total	6,680

Thailand exports different types of rubber for example, ribbed smoked sheet rubber, block rubber, crape rubber, concentrated rubber, and others.

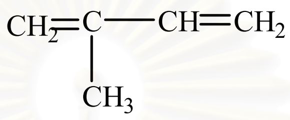
2.3 Natural Rubber Latex

By means of tapping the *Hevea brasiliensis* tree, natural rubber latex exudes, which is a colloidal dispersion consisting of rubber particles and non-rubber substance in an aqueous serum phase [2]. The rubber hydrocarbon constitutes between 30% and 45% of the whole latex, while the non-rubber substances account for between 3% and 5%. The variation of rubber content is due to factors such as the type of tree, the tapping method, the soil condition, and the season. The latex is normally called "field" latex, and it contains only 30% dry rubber content (DRC) [6]. This material is not utilized in its original form due to its high water content and susceptibility to bacterial attack. From these reasons, it is necessary both to preserve and concentrate the field latex to increase its dry rubber content. Three concentration methods are available: creaming, centrifugation, and evaporation. Of these, centrifugation is most widely used. Concentration by centrifugation also removes concomitantly about two-thirds of the field latex. Dry rubber content of commercial NR latex concentrate is 60% or more. The latex concentrates must be preserved to inhibit bacterial growth that could destabilize the latex and result in spontaneous coagulation. Centrifuged latex concentrates are usually preserved with 0.7% (w/v) of ammonia, known as high ammonia (HA) latex concentrate.

2.4 Properties of Natural Rubber Latex

2.4.1 Chemical Formula

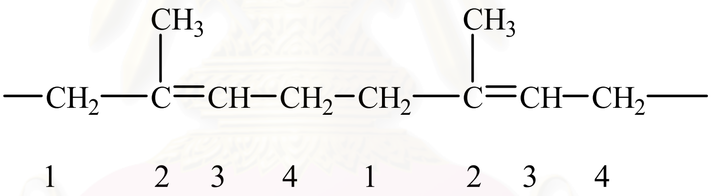
The rubber in natural latex is a homopolymer of polyisoprene [7]. Isoprene was found to have the formula C_5H_8, which has the following structure:



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2$$

Figure 2.1 Isoprene unit

The isoprene units in natural rubber are linked together at carbon atom 1 and 4 in a head-to-tail arrangement.



$$-\underset{1}{CH_2}-\underset{2}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{=}\underset{3}{CH}-\underset{4}{CH_2}-\underset{1}{CH_2}-\underset{2}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{=}\underset{3}{CH}-\underset{4}{CH_2}-$$

Figure 2.2 Head-to-tail arrangement of polyisoprene

Most commercial natural rubber contains 93-94% wt of *cis*-1,4-polyisoprene. In this configuration, carbon atom 1 and 4 are both on the same side of double bond.

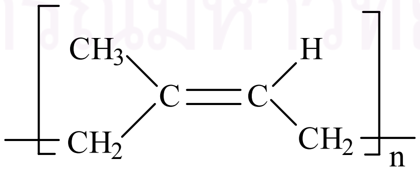


Figure 2.3 *cis*-polyisoprene

2.4.2 Composition

The rubber particles in natural latex are polydispersed and have a wide range of diameters from 0.01 to 5 μm [2]. The average size is usually considered to be between 0.25 and 0.8 μm with a molecular weight distribution of $10^5 – 10^7$ g.mol^{-1}

Freshly-tapped natural rubber latex is a whitish fluid with a density between 0.975 and 0.980 g/ml and a pH of 6.5 to 7.0 [4]. Because of latex is a natural product so the composition varies widely depending on its source [6]. Typical composition of natural rubber latex is shown in Table 2.3

Table 2.3 Typical composition of natural rubber latex [4, 6]

Composition	Average (%)
Total solid content	36
Dry rubber content	33
Moisture	0.3 – 1.0
Proteinous substances	1 – 1.5
Resinous substances	1 – 2.5
Ash	<1
Sugar	1
Water	60

Trace elements present include potassium, magnesium, and phosphorus, as well as copper, manganese, and iron. Although usually present only to the extent of 2–3 ppm, the latter are impact as catalysts to promote the oxidation of vulcanized rubber. Amounts higher than 8–10 ppm are not tolerated.

Table 2.4 shows in detail the complex variety of chemical substances present in the dry rubber and latex.

Table 2.4 Approximate concentration of non-rubber constituents in centrifuged latex concentrates [4]

Constituent	Percentage by weight of latex
Fatty acid soaps (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 carboxylic acid salt (acetate, citrate, etc.)	0.3
Amino acids and polypeptides	0.2
Inorganic salts (ammonium and potassium carbonate and phosphate, etc.)	0.2

2.4.3 Physical Properties

Physical properties of natural rubber vary slightly depending on the clone mix, non-rubber constituents present, degree of crystallinity, and storage hardening. Average physical properties of natural rubber are shown in Table 2.5

Table 2.5 Some physical properties of natural rubber [4]

Properties	Value
Density	0.92
Refractive index (20 °C)	1.52
Coefficient of cubical expansion	0.00062/°C
Cohesive energy density	63.7 cal./c.c.
Heat of combustion	10,700 cal.g
Thermal conductivity	0.00032 cal./sec/cm^2/°C
Dielectric constant	2.37
Power factor (1,000 cycles)	0.15 – 0.2
Volume resistivity	10^{15} ohms./c.c.
Dielectric strength	1,000 volts/mil

The properties of concentrated latex used in this experiment are shown in Appendix A.

2.5 Rubber Compounding

The basic principle of compounding is to minimize the number and amount of additives used to achieve the desired processing behavior and product properties [2, 4]. Compounding transforms raw natural rubber into a range of materials suitable for applications, which the objectives are [8,9]:

a) to facilitate processing and fabrication

b) to ensure a rapid puttrough with minimal reject rate

c) to achieve the required balance in vulcanizate properties

d) to provide durability, all at the lowest possible cost

All ingredients used are normally given in amounts based on a total of 100 parts of the rubber or combinations of rubbers used. This notation is generally listed as PHR (parts per hundred of rubber).

The major ingredients of most natural rubber compounds are:

2.5.1 Vulcanizing Agents

Vulcanizing agents are the chemicals that produce network junctures by insertion of crosslinks between polymer chains, which gives the desired physical properties in the final product. The crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process usually carried out by heating the rubber (mixed with vulcanizing agents) in a mold under pressure.

Sulfur

The most common vulcanizing agent used is sulfur due to several reasons: low cost, ease of availability, fast vulcanization, minimal interference with other compounding ingredients, and an excellent balance of vulcanizate properties.

Two forms of sulfur used as vulcanizing agents are rhombic and amorphous. The rhombic form is normally used for vulcanization, it exists as a cyclic structure composed of eight atoms of sulfur, S_8. The amorphous form is actually polymeric in nature; it is a metastable high polymer with a molecular weight of 100,000 to 300,000. It is insoluble in most solvents and rubber, hence the name “insoluble sulfur”. Because of this property, amorphous sulfur is used to prevent blooming on uncured rubber surfaces. Insoluble sulfur must not be processed above 210 - 220°F or it will revert to the rhombic form.

Sulfur is combined in the vulcanization network in a number of ways as monosulfide, disulfide, or polysulfide. It is also present as pendant sulfides, or cyclic monosulfide and disulfides as shown in Figures 2.4 a, b, and c respectively.

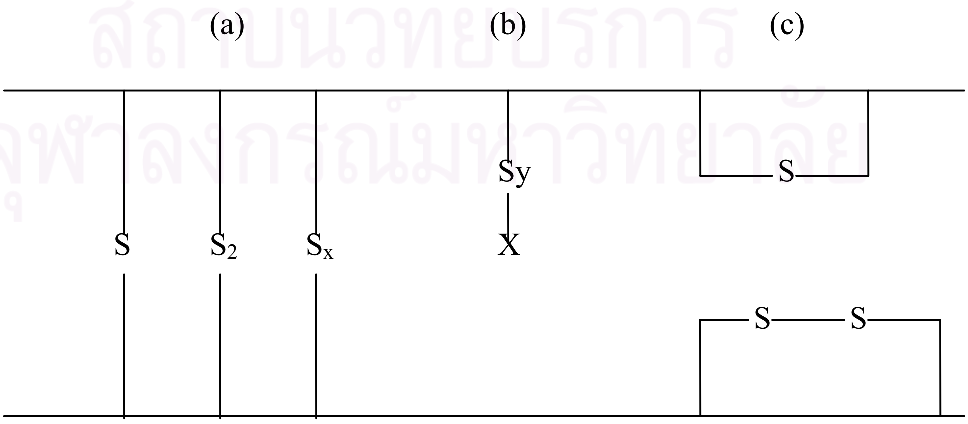


Figure 2.4 Structural features of vulcanizate network

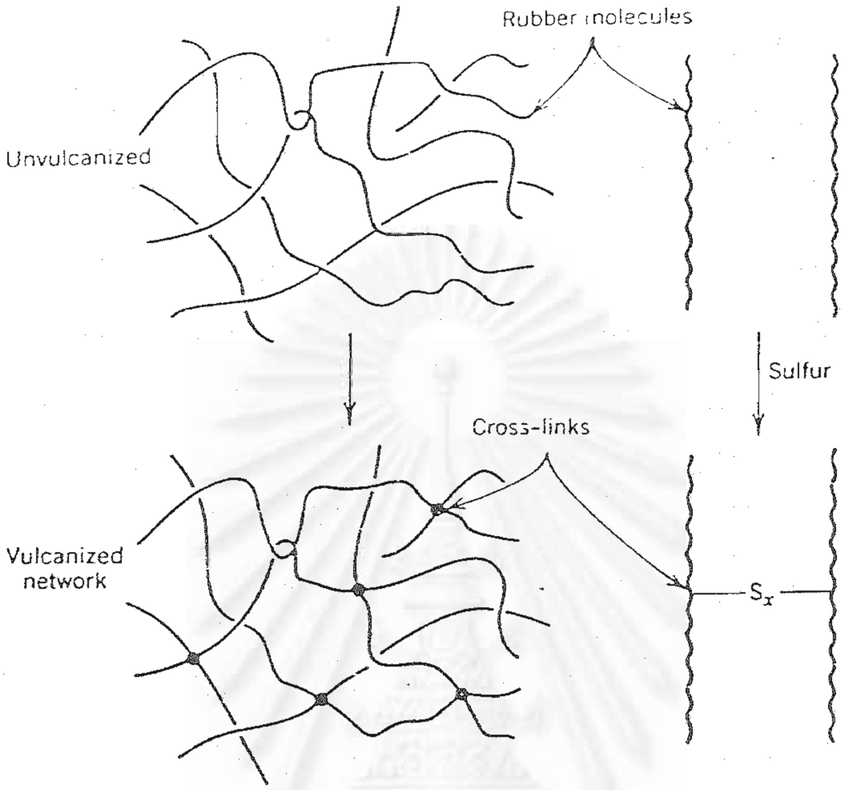


Figure 2.5 Network formulation

In general, about 1.0 to 3.0 phr of sulfur is used for most rubber products.

Difunctional compounds are also used as nonsulfur vulcanizing agents. Certain difunctional compounds form crosslinks with rubbers by reacting to bridge polymer chains into three-dimensional networks, examples are epoxy resins, quinone dioximes, diamines, and dithio compounds.

2.5.2 Accelerators

The main reasons for using accelerators are to aid in controlling the time and/or temperature required for vulcanization and thus improve the properties of the vulcanizate. The reduction in the amount of time required for vulcanization is generally accomplished by changing the amounts and/or types of accelerators used.

There are wide ranges of accelerator systems available to obtain the specific vulcanization characteristics:

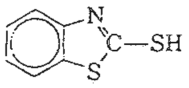
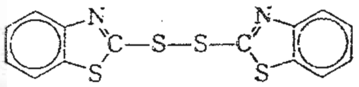
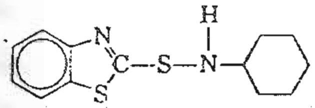
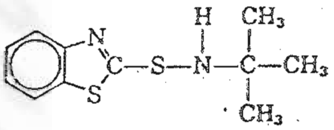
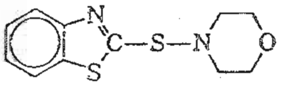
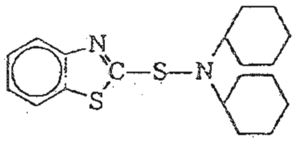
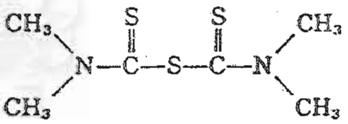
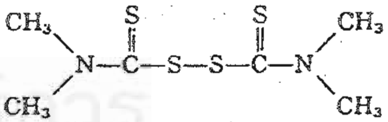
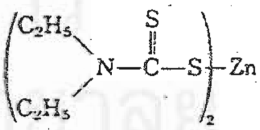
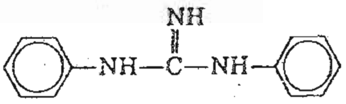
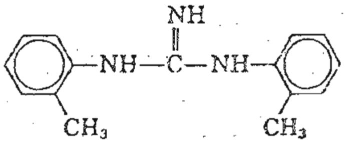
a) Single accelerator systems (primary accelerators), which have sufficient activity to produce satisfactory cures within specified times.

b) Combinations of two or more accelerators, consisting of the primary accelerator which is used in the largest amount, and the secondary accelerator which is used in smaller amounts (10 to 20% of the total) in order to activate and to improve the properties of the vulcanizate. Combinations of this type usually produce a synergistic effect as the final properties are somewhat better than those produced by either accelerator separately.

c) Delayed action accelerators, which are not affected by processing temperature but produce satisfactory cures at ordinary vulcanization temperatures.

Several common accelerators used in sulfur vulcanization are shown in Table 2.6.

Table 2.6 Accelerators in sulfur vulcanization

Compound	Abbreviation	Structure
Benzothiazoles		
2-mercaptobenzothiazole	MBT	
2,2′-dithiobisbenzothiazole	MBTS	
Benzothiazolesulfenamides		
N-cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-*t*-butylbenzothiazole-2-sulfenamide	TBBS	
2-morpholinothiobenzothiazole	MBS	
N-dicyclohexylbenzothiazole-2-sulfenamide	DCBS	
Dithiocarbamates		
tetramethylthiuram monosulfide	TMTM	
tetramethylthiuram disulfide	TMTD	
zinc diethyldithiocarbamate	ZDEC	
Amines		
diphenylguanidine	DPG	
di-*o*-tolylguanidine	DOTG	

2.5.3 Accelerator Activators

These components are used to increase the vulcanization rate by activating the accelerators to perform more effectively. It is believed that they react in some manner to form intermediate complexes with the accelerators. The complex is more effective in activating the sulfur present in the mixture, thus increasing the cure rate.

Accelerator activators are grouped as follows:

a) *Inorganic compounds* (mainly metal oxides) used include zinc oxide, hydrated lime, litharge, red lead, white lead, magnesium oxide, alkali carbonates, and hydroxides. The majority of metal oxides are used in coated or treated forms in order to disperse more readily in the rubber mixtures. From 2 to 5 phr are normal usages.

b) *Organic acids*, they are generally high molecular weight monobasic acids or mixtures which are normally used in combination with metal oxides such as, stearic, oleic, lauric, palmitic, and myristic acids, and hydrogenated oils from palm, castor, fish, and linseed oils. The usage of each particular type depends on the accelerator used and the amounts of other compounding ingredients present. Normally from 1 to 3 phr are used.

In natural rubber compounding, zinc oxide and the fatty acid are normally used in combination to form the most common vulcanization activators. A rubber-soluble soap is formed in the rubber matrix that can be formed complexes with accelerators and reaction products between accelerators and sulfurs.

Typically, a recipe for the vulcanization system for rubber contains:

	phr
Zinc oxide	2 – 5
Fatty acid	1 – 3
Sulfur	1 – 3
Accelerator	0.5 – 2

Furthermore, other components such as age-resistors, fillers, softeners, and miscellaneous material are also used in rubber compounding to achieve the optimum properties for rubber products. These rubbers mostly function as engineering elastomers.

2.6 Modification of Natural Rubber

Natural rubber comes from the tree with a pre-determined structure form, which derives its excellent physical properties for serving as a general-purpose elastomer. Moreover, the natural rubber endows with a unique combination of physicomechanical properties, has established an enviable position in the industrial market as an excellent engineering polymer [2, 8].

However, there is an ever-present demand for improvement in areas such as vulcanization, ageing, bonding, processability, and abrasion resistance and adhesion. Also, properties such as gas permeability, oil and flame resistance have to be adjusted to fit certain applications.

The objectives of modification are:

1. To improve the behavior of natural rubber during the manufacture of rubber articles and to improve the performance of those articles in service.
2. To alter the properties of natural rubber in such a way that it could compete in areas of application outside its traditional ones.

Improvements based on compounding alone are not always sufficient to meet these targets. Therefore, other methods such as modification of the natural rubber molecule itself have to be pursued.

The presence of a double bond in each natural rubber repeating unit means that, it can be treated as a simple olefin, and therefore, should under some of the many and various chemical reactions of this class of compounds. Many reactions involving the double bond in natural rubber have been investigated with some success, but others have failed, principally because of the presence of non-rubber solids, which con complete, or interfere with the particular reaction.

Three types of chemical modification of natural rubber can be distinguished:

a) Changing the structure, or geometry of the natural rubber molecule without introducing new material; examples are carbon-carbon crosslinking, cyclization, *cis, trans*- isomerization, and depolymerization.
b) Functionalization by attaching of groups having specific physical characteristics or chemical reactivities to the natural rubber chain, though addition or substitution reactions at the olefinic double bonds; examples is epoxidized natural rubber (ENR).

c) Grafting short or long chains of a different polymer type on the natural rubber hydrocarbon; examples are grafting natural rubber with polystyrene or polymethyl metacrylate.

Nevertheless, any chemical modification of natural rubber must comply with certain criteria to succeed in the marketplace as follows:

- The reagents should be specific and not induce unintended changes.
- The reaction should be able to take place with high efficiency in the latex from or during dry mixing or curing.
- No catalyst poisoned by non-rubber components should be used.
- The reagents and processes should, ideally, be low cost.

The modification of natural rubber with a variety of natural resins has long been practiced to improve their properties. This method has been very attractive, since the resins are easily available in natural resource.

2.7 Cashew Nut Shell Liquid (CNSL)

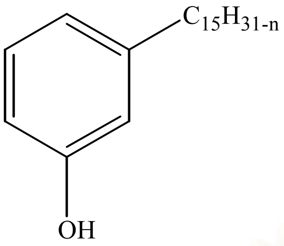
Cashew nut shell liquid is an abundant agricultural by-product of cashew industry. CNSL occurs as a reddish brown viscous liquid in soft honeycomb structure of the shell of cashew nut, a plantation product obtained from the cashew tree, *Anacardium occidentale* L [11]. Native to Brazil, the tree grows in the coastal areas of Asia and Africa. Cashew nut attached to cashew apple is gray colour, kidney shape and 2.5-4 cm long. The shell is about 0.3 cm thick, having a soft leathery outer skin and thin hard inner skin (Figure 2.7). Between these skins is the honeycomb structure containing the phenolic material popularly called CNSL. Inside the shell is the kernel wrapped in a thin brown skin, known as the testa.

a b

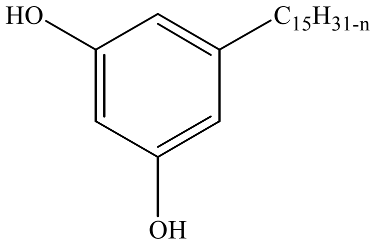
Figure 2.7 Illustration of a) cashew apple and b) cross-section of cashew nut

2.7.1 Chemical Composition

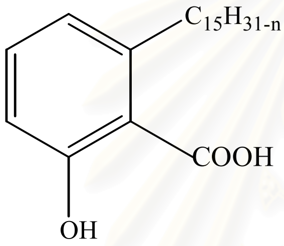
Natural cashew nut shell liquid contains four major components namely cardanol (3-pentadecenyl phenol), cardol (5-pentadecenyl resorcinol), cardol (2-methyl, 5-pentadecenyl resorcinol), and anacardic acid (6-pentadecenyl salicylic acid) [12]. The chemical formulas of these components are shown in Figure 2.8.



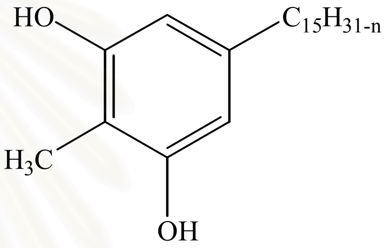
cardanol
(3-pentadecenyl phenol)



cardol
(5-pentadecenyl resorcinol)



anacardic acid
(6-pentadecenyl salicylic acid)



2-methyl cardol
(2-methyl,5-pentadecenyl resorcinol)

Figure 2.8 chemical structures of major components in natural CNSL

In the roasting process, some polymerization as well as decarboxylation occurs. Thus, a technical CNSL could contain cardanol (60-65%), cardol (10–12%), and other minor components. The specifications of technical CNSL are shown in Table 2.7.

Table 2.7 IS Specification* for CNSL [11]

Characteristic	Requirement
Specific gravity, 30/30°C	0.95-0.97
Viscosity at 30°C, cP (max)	550
Moisture, % by wt (max)	1.0
Matter insoluble in toluene, % by wt (max)	1.0
Loss in wt on heating, % by wt (max)	2.0
Ash, % by wt (max)	1.0
Iodine value (max)	
a) Wij's method	250
b) Catalytic method	375
Polymerization	
a) Time, min (max)	4
b) Viscosity at 30°C, cP (min)	30
c) Viscosity after acid washing At 30°C, cP (min)	200

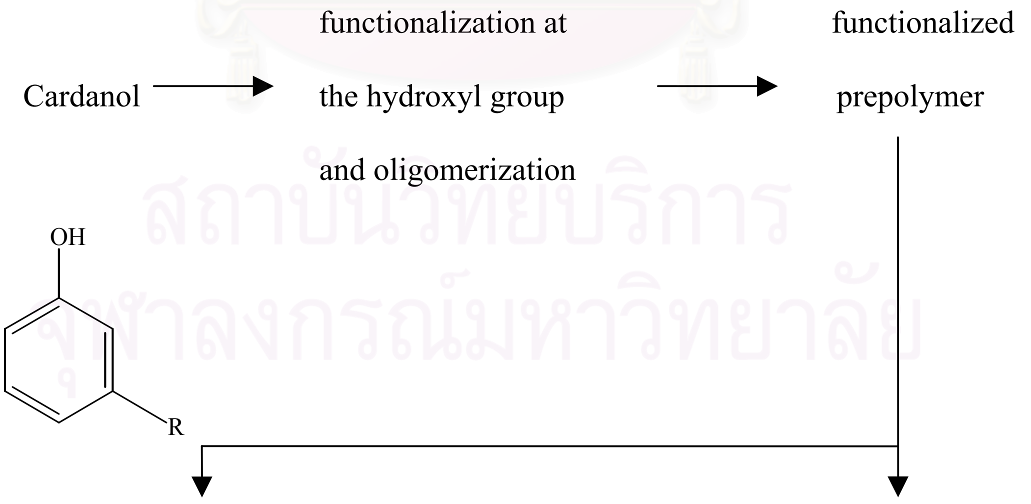
* IS 840: 1964

2.7.2 Applications

CNSL is a source of a long chain *m*-substituted phenol, which promises to be an excellent monomer [11]. This monomer can be polymerized to get various polymeric products and/or can be suitably modified to chemical intermediates for industrial use [14].

Unsaturated hydrocarbon phenols of CNSL could be polymerized either by step- or chain- reaction mechanism or combination of these techniques. They could also be suitably chemically modified to introduce specific functional groups and polymerized to make polymers with specific properties. Thus especial polymer could possibly be produced from a monohydric phenol with an unsaturated side chain R at the *meta*- position through either (a) a prepolymer route or (b) a dimer route as follows [15]:

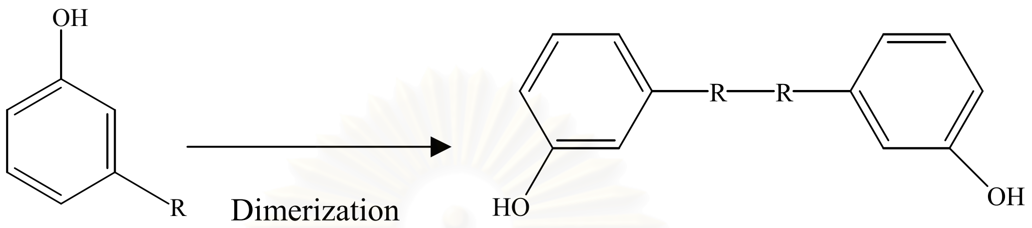
a) *Prepolymer route:*



can be used in variety of ways such as ion-exchange resins, polymeric fire-retardants, depending on the

can be further polymerized and processed into thermoset plastic products having higher impact functional groups. properties than phenolics resin.

b) *Dimer route:*



Dimer

↓

Condensation polymerization
with highly polar and rigid
bifunctional monomers.

↓

Linear chain polymers with
repeating sequences of hard
and soft segments. Possibility
for liquid crystal polymers
or thermoplastic elastomers.

Furthermore, the polymer from CNSL and cardanol has been prepared either by condensation with electrophilic agents such as formaldehyde or by chain polymerization at the unsaturation sites in the side chain using acid catalysts.

CNSL in its raw and chemically modified form find a wide range of industrial application due to it is a by-product from the industrial, it is easily available, and it has a low cost. The special properties of CNSL are high thermal stability and mechanical strength. CNSL and cardanol are used as friction material, surface coatings and laminating resins. Cardanol functionalized with orthophosphoric acid and oligomerized result in prepolymers acting as multifunctional additive for natural rubber vulcanizates [16]. Cardanol when used as a plasticizer in natural rubber improves its tear strength, solvent resistance and ageing properties.

2.8 Natural Rubber Modified with CNSL and Its Derivatives

CNSL and its derivatives have long been used as rubber compounding additives in various roles as plasticizers, anti-oxidants, vulcanizate property modifiers, processing aids, and adhesion promoters [16, 17]. Incorporation of CNSL has been found to improve the performance of rubber products, and increase its resistance of moisture. Cardanol used as a plasticizer in natural rubber improved its tear strength, solvent resistance and ageing properties [18].

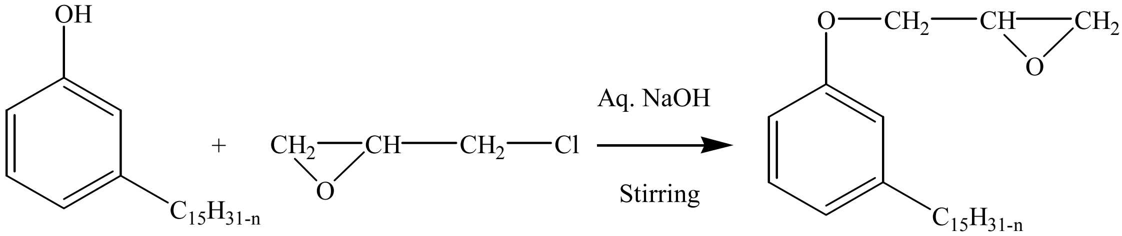
Cardanol and other components from CNSL are very viscous liquids and slightly acid. These properties cause them to blend together with natural rubber latex with difficulty, due to partial coagulation of rubber molecules. The reaction, which causes a more reactive cardanol is very interesting. One of the reactions is reacting cardanol or CNSL derivatives, which molecule possessing active hydrogen, with epichlorohydrin in the presence of sodium hydroxide to obtain compounds containing both an epoxy group and unsaturation in the molecules [19, 20].

The sodium hydroxide used in this process has a double role to play:

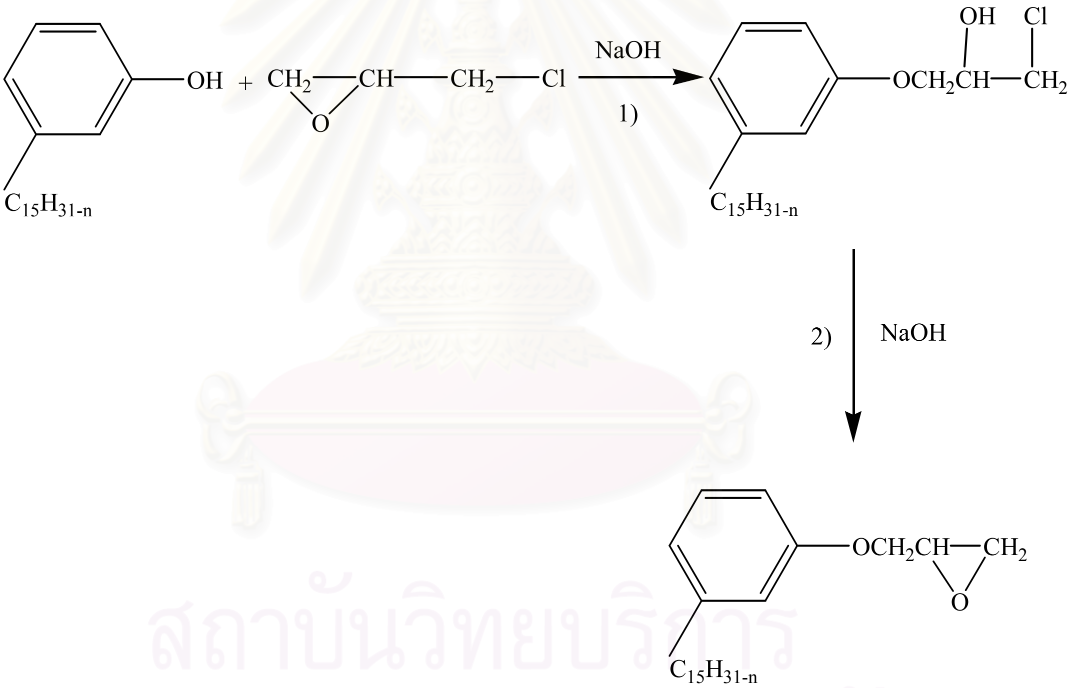
a) As catalyst for the epoxide/phenolic hydroxyl reaction

b) As the means of dehydrochlorination

In this work, the reaction of cardanol and epichlorohydrin to obtain glycidyl-3-pentadecenyl phenyl ether (GPPE) is mentioned as follows:



The reaction generally occurs in two steps: 1) the formation of a chlorohydrin intermediate and 2) the dehydrohalogenation of the intermediate to the glycidyl ether:



GPPE is a monoepoxy compound that contains both an epoxy group and unsaturated side chain. The presence of the unsaturation indicates that the molecule may be polymerized in two steps: the first step consisting of reaction through the epoxy group, and the second consisting of reaction through the unsaturation [18]. Polymers increase the crosslink density in the cure polymer network, which maintain their properties at higher temperatures.

2.9 Literature Reviews

Shinoda et al. studied a rubber composition for automotive tires comprised of specific proportions of carbon black, a modified novolak phenolic resin, hexamethylenetetramine, a polymeric cardanol derived from the thermal polymerization of cashew nut shell liquid, and other additives including vulcanizing agent and accelerator [21]. Mixing of the components was carried out by B-type Banbury mixer. Various compositions of rubber sheets were compared with the inventive composition. The formulation and product properties are shown in Table 2.8.

Table 2.8 Formulation and product properties of Shinoda's work.

	Comparative Rubber Compositions				Inventive Rubber Composition	Comparative Rubber Composition
	1	2	3	4		
NR/SBR	70/30	70/30	70/30	70/30	70/30	70/30
ZnO	10	10	10	10	10	10
Stearic acid	2	2	2	2	2	2
CCR[1*]	10	10	10	10	10	10
HAF	60	60	60	60	60	60
Cashew oil	-	15	-	-	-	-
Cardanol	-	-	15	-	-	-
PC[2*]	-	-	-	15	-	-
PC[3*]	-	-	-	-	15	25
Sulfur	5.5	5.5	5.5	5.5	5.5	5.5
Accelerator	3.5	3.5	3.5	3.5	3.5	3.5

Table 2.8 Formulation and product properties of Shinoda's work (Continued)

	Comparative Rubber Compositions				Inventive Rubber Composition	Comparative Rubber Composition
	1	2	3	4		
Hexamethylene tetramine	1.2	1.2	1.2	1.2	1.2	1.2
Mooney viscosity ML_{1+4} (100°C)	85.4	52.0	55.2	63.2	69.2	64.3
JIS hardness (25°C) (JISA)	92.0	93.0	93.0	94.0	96.0	96.0
Modulus (20°C, MPa)	59.2	55.3	40.5	51.9	84.8	88.4

CCR^{1*} : Cashew modified cresol resin

PC^{2*} : Polymeric cardanol (viscosity 4000 cps)

PC^{3*} : Polymeric cardanol (viscosity 37000 cps)

They summarized that smaller amounts than 5 weight parts of cardanol would reduce the softening effect at the vulcanized stage, whilst larger than 20 weight parts would invite bleeding before vulcanization.

Pillai et al. synthesized phosphorylated cardanol prepolymer (PCP) by simultaneous phosphorylation and oligomerization of cardanol [15]. From thermogravimetric analysis data it was shown that PCP has higher thermal stability when compared to cardanol-formaldehyde (novolak)-type resins. Completely cured

PCP was highly resistant to hydrolysis by water, improved the bonding characteristics, and showed good fire-retardant properties.

Menon et al. studied the chemical crosslink density (CLD) and network structure of natural rubber vulcanizates, modified with phosphorylated cardanol prepolymer (PCP), which was obtained from the reaction of cardanol with orthophosphoric acid [22]. The rubber compounding was carried out by two-roll mill. From the experimental data of the PCP modified natural rubber vulcanizates showed lower CLD as compared to the unmodified natural rubber sample. In contrast, the superior tensile characteristic of the PCP modified vulcanizates was presumed to be partly due to the presence of an entangled network structure between the aliphatic segment of PCP and the isoprene chain.

Menon studied the tensile stress-relaxation characteristics at room temperature of gum natural rubber vulcanizates containing phosphorylates cashew nut shell liquid (PCNSL) prepolymer at various strain rates and strain levels, in comparison with the unmodified sample [23]. Modification of natural rubber with PCNSL resulted in improvements in tensile properties along with a lower degree of stress relaxation at the higher strain rates and strain levels. The compound formulation is shown as follows:

- natural rubber	100	parts by dry weight
- ZnO	10	phr
- stearic acid	2	phr
- sulfur	2	phr

- MBT	1.5	phr
- TMTD	0.5	phr
- PCNSL	0, 10, 15, 20	phr

The physical properties of vulcanizated sheet are shown in Table 2.9.

Table 2.9 The physical properties of vulcanizated sheet from Menon's work

Properties	PCNSL (phr)			
	0	10	15	20
Modulus 300% (MPa)	-	1.65	1.30	0.55
Tensile strength (MPa)	2.16	16.70	15.67	7.26
Elongation at break (%)	240	1060	1170	1370

Bhunia et al. synthesized and characterized glycidyl 3-pentadecenylphenyl ether (GPPE) was obtained from the reaction of cardanol and epichlorohydrin [14]. A novel polyether was synthesized by cationic polymerization of GPPE in the presence of a latent thermal initiator, *N*-(benzyl)*N,N*–dimethyl anilinium hexafluoroantimonate (BDAHA). The resulting polymer had low molecular weight with a polydispersity index of 1.148. The thermal stability of GPPE and the polyether was also studied.

Laongsri studied the optimum formulation to produce premixed raw rubber, which contained carbon black and vulcanizing agents that was ready to be used [24]. Ball mill was used for preparing rubber compound. Carbon black and the additives were directly mixed with concentrated latex in aqueous dispersion system. The formulation of compounded sheets which give the best properties in the experiment are shown as follows:

- Rubber latex	100 phr
- carbon black type N330	25 phr
- sulfur	2 phr
- ZnO	5 phr
- stearic acid	2 phr
- MBT	1 phr
- Tergitol NP10	3 phr

The properties and carbon black dispersion of the vulcanized sheets are shown in Table 2.10.

Table 2.10 Properties and carbon black dispersion of vulcanized sheet from Laongsri's work.

Properties	Result
Tensile strength (MPa)	16.49
Elongation (%)	1538
Modulus 500% (MPa)	8.23
Hardness (shore A)	60.4
Tear strength (kN/m)	57.15
Solvent swelling (%)	250
Dispersion rating	5.0

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Natural rubber latex: Thai Rubber Latex Corporation (Thailand) Co. Ltd.
2. Cashew nut shell liquid (CNSL) : Parktai Import
3. Sulfur : Ajax Chemical
4. Stearic scid : Ajax Chemical
5. Zinc oxide (ZnO) : Ajax Chemical
6. 2-Mercaptobenzothiazole (MBT) : Fluka
7. Tergitol NP10 : Union Carbide
8. Sodium dodecyl sulphate (SDS) : Fluka
9. Formic acid : Merck
10. Epichlorohydrin : Fluka
11. Sodium hydroxide : Carlo Erba
12. Anhydrous sodium sulphate : Merck
13. Diethylenetriamine : Fluka
14. Formaldehyde : Merck
15. Hexane : Merck
16. Methylene chloride : Merck
17. Methanol : Merck
18. Petroleum ether : Lab Scan

3.2 Instruments and Apparatus

1. Ball mill
2. Mechanical stirrer : Janke & Kunkel, RE16
3. Compression molding : Lab Tech. Engineering Co. Ltd.
4. Universal testing machine : Instron Corporation, Model 1011
5. Hardness testing machine : Shore Instrument & MFG. Co., Model 716
6. Thermogravimetric Analyzer : Perkin Elmer, TGA 7
7. Optical Microscope : Olympus, BH-2
8. Scanning Electron Microscope : JEOL, JSM-5800LV
9. Infrared Spectrophotometer : Perkin Elmer, Nicolet (Impact 410)
10. Nuclear Magnetic Resonance Spectrophotometer : Bruker, ACF 200 MHz

3.3 Experimental Procedure

3.3.1 Preparation of Glycidyl 3 – pentadecenylphenyl Ether (GPPE)

3.3.1.1 Decarboxylation of CNSL

Natural CNSL was decarboxylated catalytically with calcium hydroxide and stirred while immersed in an oil-bath at 135°C for 2 hours. The mixture was allowed to cool to ambient temperature and extracted with hexane, filtered and concentrated to give a dark-brown oil.

3.3.1.2 Purification of Cardanol

The decarboxylated CNSL 60 g, 19.4 g of 40% formaldehyde solution, and 2.57 g of diethylenetriamine were mixed in 200 cm^3 methanol. After mixing for 30 min., phase separation occurred. The upper phase was decanted and treated with 40 cm^3 water followed by petroleum ether. The petroleum ether extract was dehydrated by anhydrous sodium sulphate and evaporated to give purified cardanol [25].

3.3.1.3 Synthesis of Glycidyl 3–pentadecenylphenyl Ether (GPPE) from Cardanol

Cardanol 100 g and 50 ml of hexane were placed in a stainless steel reactor and 43.5 ml of epichlorohydrin was added dropwise using an additional funnel while stirring with mechanical stirrer. Then 8% sodium hydroxide solution was added dropwise to the mixture during a period of 9 hours at the ambient temperature. The stirring was continued for 18 hours and the mixture was kept aside for 24 hours at room temperature. The product was extracted into hexane, which was washed with deionized water and dried over anhydrous sodium sulphate. The hexane solution was filtered, evaporated and then characterized by IR and NMR techniques.

3.3.2 Preparation of Natural Rubber Product Containing Glycidyl 3-pentadecenylphenyl Ether (GPPE) and Other Additives.

The natural rubber latex containing glycidyl 3-pentadecenylphenyl ether and other additives was prepared by ball mill under the ambient temperature. ZnO, sulfur, MBT, and stearic acid were mixed with deionized water in ball mill at 1300 rpm. for

90 min, and then emulsion of GPPE and surfactant was added and mixed till 180 min. After that, the natural rubber latex was added and mixed for 30 min. The compounded rubber latex was poured into a stainless steel tray and coagulated by 5% formic acid. The compounded sheet was washed with running water and compressed by compression mold under a pressure of 50 kg/cm^2 for 1 hour. The sheet was spread out at room temperature for 24 hours. The water retained in the product was finally removed by keeping the sheet in an air oven at 60°C for 24 hours.

The compounded sheets were prepared and subjected to various investigations as following:

1) Effect of GPPE Concentration

The natural rubber products were prepared by varying the GPPE concentrations of 0, 1, 2, 3, 4, and 5 phr. The formulations of compounded sheets are shown in Table 3.1.

2) Effect of Surfactant Type and Concentration

These effects were investigated by varying the surfactant type such as NP10 and sodium dodecyl sulphate (SDS) which refer to nonionic and anionic surfactant respectively. The effect of surfactant concentration was also studied by variation the concentration of 1, 1.5, and 2 phr. The compounded sheets formulations were changed as shown in Table 3.2.

3) Effect of Mixing Time

The mixing time was followed by varying the time of 0.5, 1, and 2 hours to obtain the appropriate time of mixing.

Table 3.1 Compounded sheets formulations

Ingredient	Quantity of mix (phr)
Natural rubber latex*	100
ZnO	5
Sulfur	2
Stearic acid	2
MBT	1
GPPE	0, 1, 2, 3, 4, 5

* The properties of natural rubber in this experiment are shown in Appendix A

Table 3.2 The range of parameters investigated in compounded sheets

Amount Code*	Surfactant (phr)	GPPE (phr)	Mixing time (hr.)
A1	1.0	0, 1, 2, 3, 4, 5	0.5, 1.0, 2.0
A2	1.5		
A3	2.0		
B1	1.0		
B2	1.5		
B3	2.0		

* series A, and B represented the surfactant NP10 and SDS respectively

3.3.3 Preparation of Vulcanized Sheets (ASTM D3182)

The compounded sheets were placed on a flat, dry, clean metal surface. Then the sheets were cut (4.5 ± 1.5 mm.) shorter in width and length than the corresponding dimensions of the mold cavity.

The mold was brought to curing temperature (150^{o}C) in the closed press and held at this temperature for at least 20 min before the unvulcanized pieces were inserted. The press was opened, then the unvulcanized pieces were inserted into the mold, and the press was closed in the minimum time possible. The mold was held under the pressure of 120 kg/ cm^2 (1700 psi) for 10 min. After the required vulcanization time, the press was opened. The vulcanized sheets were removed from the mold and cooled on metal surface, which used water-cooling for 15 min. The vulcanized sheets were conditioned at 23 ± 2^{o}C for at least 16 hours before preparation and testing.

3.4 Characterization

3.4.1 The Characterization of Cardanol and GPPE

IR spectrophotometer, H^1 NMR and C^{13} NMR spectrophotometer were used to characterize cardanol and GPPE. The chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. Deuterated chloroform ($CDCl_3$) was used as a solvent for recording the NMR spectra. All spectra are presented in Appendix B.

3.4.2 Determination of Dispersing Property

The dispersing property of GPPE and other additives were studied by optical microscopy and scanning electron microscopy techniques.

a) Optical Microscopy

The compounded rubber latex was dropped on flat slide, and then covered with cover glass. Olympus, BH-2 optical microscope was used to investigate the dispersion of emulsion system. The sample slides were photographed at magnification of 400X.

b) Scanning Electron Microscopy

Vulcanized rubber sheets were examined for dispersion in a cross-section area. Samples were prepared by dipping the small piece of vulcanized sheets in liquid nitrogen. The sheets broke and were coated at the cross-section site with gold. Then, the samples were introduced into JSM-5800LV scanning electron microscope. The determination was carried out in vacuum condition with magnification of 600X.

3.4.3 Determination of Thermal Properties of the Rubber Product

a) Thermogravimetric Analysis (TGA)

A Perkin Elmer TGA7 thermogravimetric analysis system was used to follow the weight loss of 2-3 mg sample between 50-650°C. The heating rate was 20°C/min.

b) Ageing Properties (ISO 188)

The dumb-bell test pieces were prepared by dieD cutting machine (ASTM D412-98a). The test pieces were placed in the air oven, which has been preheated at the operating temperature. The test pieces shall be stationary free from strain, freely exposed to air on all sides, and not exposed to light. The conditions in testing are shown as follows:

Temperature : $70 \pm 1^{o}C$

Duration of test : 72 hours

When the heating period was complete, the test pieces were removed from the oven and conditioned for no less than 16 hours and no more than 6 days in a strain-free condition before mechanical testing.

The test results of both the unaged and aged test pieces shall be reported together with the percentage change in the value of the property measured as calculated from the formula:

$$\frac{x_a - x_0}{x_0} \times 100$$

where:

x_a is the value of the property before ageing

x_0 is the value of the property after ageing

The change in hardness shall be expressed as a difference calculated from the formula:

$$x_a - x_0$$

3.4.4 Determination of Percent Crosslinking

Soxhlet Extraction

The vulcanized rubber was cut to make the small pieces and kept in an oven to obtain the constant weight. Then, 2.0 g. of sample was placed on cotton gauze and tied. Extraction of the sample with hexane was operated in soxhlet-type extractor for 8 hours. The sample was removed, and kept in oven at 70°C for 12 hours and allowed to cool to ambient temperature in a dessicator. The percent crosslink density was calculated from the percent weight loss of the sample from the formula:

$$\% \text{ crosslinking} = \frac{w_1 - w_2}{w_1} \times 100$$

where:

w_1 is the weight of sample before extraction

w_2 is the weight of sample after extraction

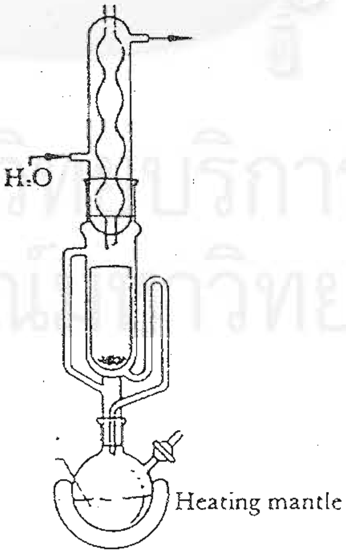


Figure 3.1 Soxhlet-type extractor

3.5 Mechanical Testing

Mechanical properties of the vulcanized rubber were investigated by the ASTM and the ISO test methods as following:

a) Hardness

(ASTM D2240: Standard test method for rubber property. Durometer Hardness)

The type A durometer was used to determine hardness of the compounded rubber in this experiment. The test specimens shall be at least 6 mm (0.25 in.) in thickness and the lateral dimensions of the specimen shall be sufficient to permit measurements at least 12 mm (0.5 in.) from any edge. The surfaces of the specimen shall be flat and parallel over a sufficient area to permit the presser foot to contact the specimen over an area having a radius of at least 6 mm (0.25 in.) from the indenter point. In this experiment, the test specimens were composed of 2 plied pieces to obtain the necessary thickness. The condition in testing are shown as following:

Temperature : 25 °C
Number of plied pieces : 2 pieces
Duration of testing : 15 sec.

Five measurements of hardness testing were used at different positions to obtain a reliable average.

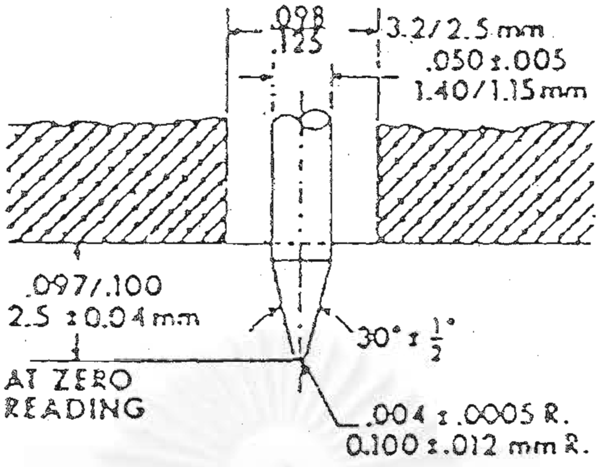


Figure 3.2 Indenter for Type A durometer

b) Tensile Properties

(ASTM D412-98a: Standard test methods for vulcanized rubber and thermoplastic elastomers-tension)

Tensile strength, the elongation, and the modulus were determined. The test specimen dimension (Type D) is shown in Figure 3.3.

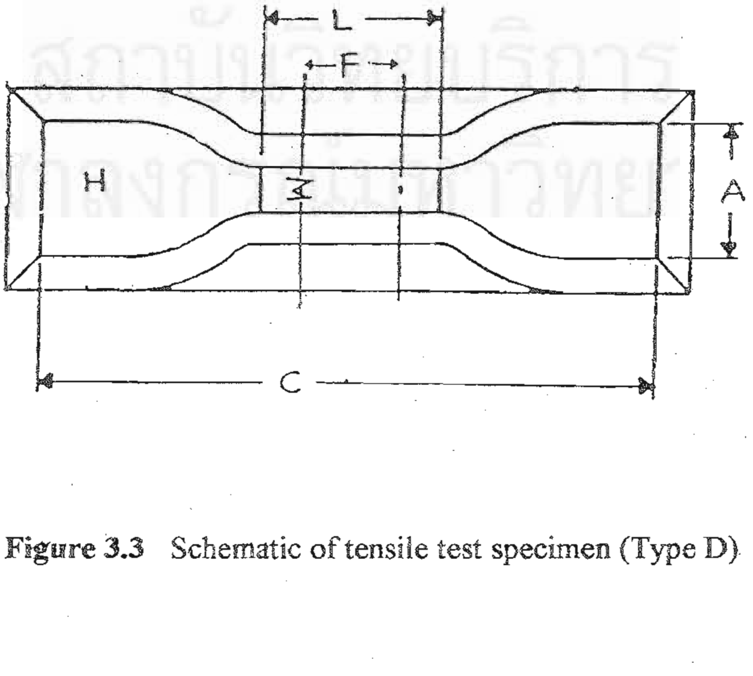


Figure 3.3 Schematic of tensile test specimen (Type D)

	Dimension	Type D (mm.)
A	Width of ends	16 ± 1
C	Overall length	100
F	Length of testing	19 ± 2
H	Transition radius inside	16 ± 2
L	Length of narrow portion	33 ± 2
W	Width of narrow portion	3

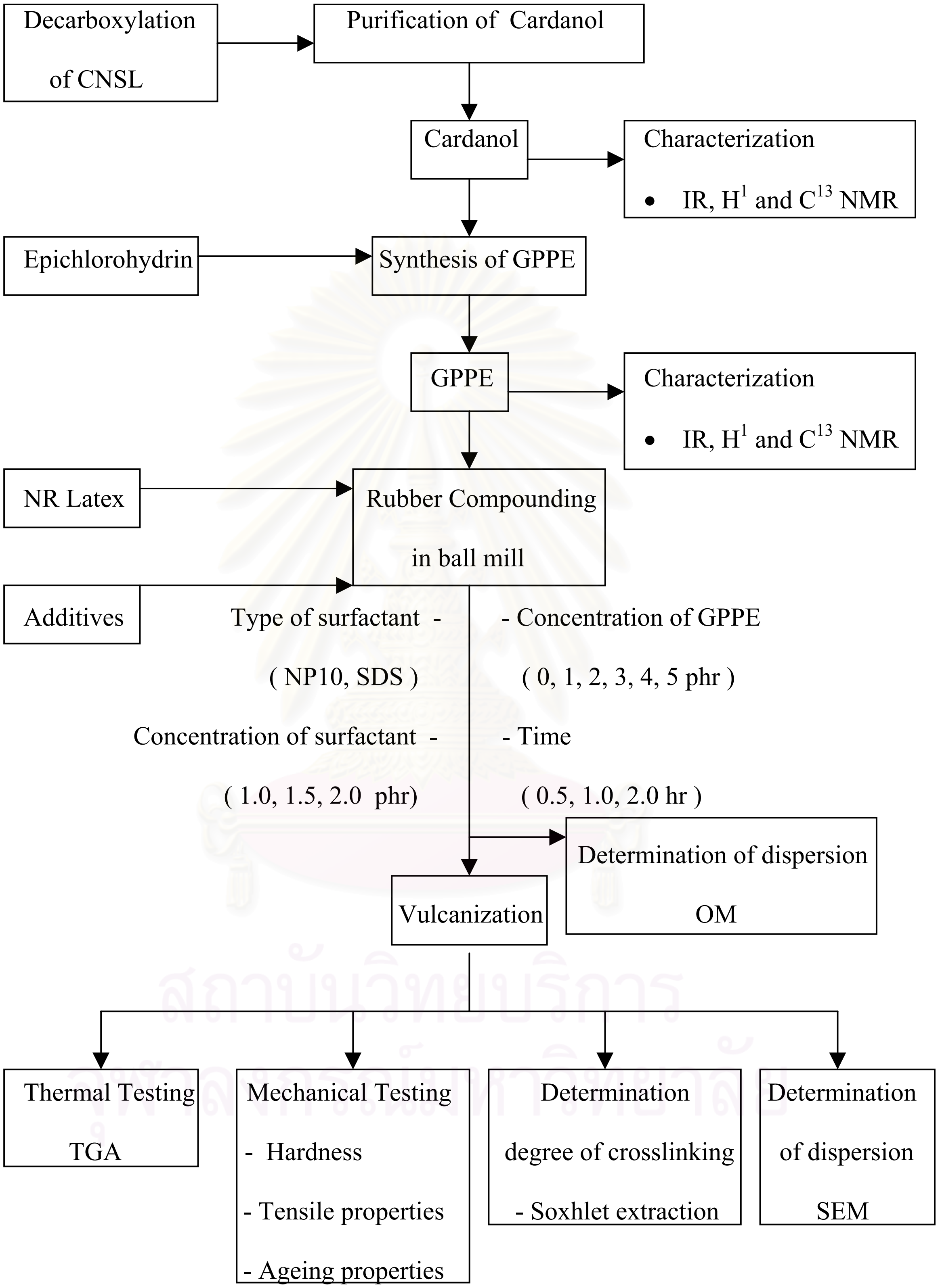
The tensile testing condition

Temperature : 25^{o}C

Humidity : 60%

Crosshead speed : 500 mm/min.

Sample rate : 10 pts/sec.



Flow diagram 1 Experimental scheme of preparation the rubber product

CHAPTER IV

RESULTS AND DISCUSSION

The modification of the natural rubber product was carried out in two steps: step one, glycidyl 3-pentadecenylphenyl ether (GPPE) was synthesized from cardanol and epichlorohydrin in the presence of sodium hydroxide, then the GPPE product was characterized by infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR); step two, the rubber compounding was prepared by directly mixing the concentrated latex with GPPE and other additives in a ball mill. Many different parameters, which consist of GPPE concentration, type and concentration of surfactant, and mixing time, have been taken into account. The dispersion of GPPE and other additives were determined by optical microscopy (OM) and scanning electron microscopy (SEM). Soxhlet extraction was used to determine the crosslink density of the rubber products. Thermal and mechanical properties were investigated to give optimum ingredients and conditions for preparation of the good properties of the modified natural rubber product.

4.1 Preparations and Characterization of GPPE

The glycidyl 3-pentadecenylphenyl ether (GPPE) was synthesized from the reaction of cardanol and epichlorohydrin in the presence of sodium hydroxide. The reaction was carried out at room temperature for 9 hours. The GPPE was extracted by hexane and the hexane was evaporated, yielding a slightly viscous yellowish brown liquid. IR and NMR were used for GPPE characterization.

4.1.1 Infrared Spectra

Perkin Elmer, Nicolet (Impact 410) infrared spectrophotometer was used for characterization of cardanol and GPPE. The IR spectra of cardanol and GPPE are given in Appendix B. Table 4.1 provides the important peaks and their assignments.

Table 4.1 Infrared spectral data of cardanol and GPPE

Vibration Assignments	Absorption Frequency (cm^{-1})	
	Cardanol	GPPE
Phenolic (–OH) group	3416	-
CH- aromatic	3011	3013
CH- aliphatic	2863– 2960	2926, 2854
C=C ring stretching	1588, 1470	1601, 1495, 1451
Ar-O-R aryl alkyl ether	-	1267, 1055
C-O stretching	1157	1166

From IR spectra of GPPE compared with cardanol, the phenolic (–OH) group at approximately 3416 cm^{-1} of GPPE was decreased due to the presence of ether function of C-O-C asymmetric and symmetric stretching vibration in GPPE molecule at 1267 and 1055 cm^{-1}, respectively.

4.1.2 Nuclear Magnetic Resonance Spectra

Bruker, ACF 200 MHz nuclear magnetic resonance spectrophotometer was used for characterization of cardanol and GPPE. The ^{1}H-NMR and the ^{13}C-NMR spectra of cardanol and GPPE are shown in Appendix C.

4.1.2.1 ^{1}H-NMR spectra

The ^{1}H-NMR spectrum of cardanol in $CDCl_3$ showed the chemical shifts at δ_H 7.13 ppm 1H, *t*, J=7.96 Hz, c), 6.76 ppm (1H, *d*, J=7.71 Hz, d), 6.69 ppm (1H, *s*, a), and 6.67 ppm (1H, *d*, J=7.13 Hz, b). All of the chemical shifts referred to the proton in the benzene ring.

The ^{1}H-NMR spectrum of GPPE in $CDCl_3$ showed the chemical shifts at δ_H 7.19 ppm (1H, *t*, J=7.67 Hz, c), 6.81 ppm (1H, *d*, J=7.21 Hz, d), 6.79 ppm (1H, *s*, a), 6.75 ppm (1H, *d*, J=8.30 Hz, b), 4.15 ppm (1H, *dd*, J=5.48 Hz, e), 3.95 ppm (1H, *dd*, J=5.42 Hz, f), 3.32 ppm (1H, *m*, g), and 2.75 ppm (2H, *m*, h). The signals at δ_H 4.15 and 3.95 ppm referred to the two germinal protons of $-CH_2-$, which were effected by the magnetical asymmetry of the proton between a phenoxy moiety and an epoxy moiety, respectively.

Table 4.2 ^{1}H-NMR spectral data of GPPE in $CDCl_3$

Positions	δ_H (ppm), *multiplicity*, J (Hz)
a	6.79, *s*
b	6.75, *d*, 8.30
c	7.19, *t*, 7.67
d	6.81, *d*, 7.21
e	4.15, *dd*, 5.48
f	3.95, *dd*, 5.42
g	3.32, *m*
h	2.75, *m*

4.1.2.2 ^{13}C-NMR spectra

The ^{13}C-NMR spectrum of cardanol in $CDCl_3$ showed the chemical shift at δ_C 155.97 ppm attributed to a carbon position *a*, the peaks at 144.58 and 136.70 ppm referred to the carbon in position *e*, the peaks at 129.43, 120.81, 115.70, and 112.93 ppm referred to the carbon in position *c*, *d*, *f*, and *b*, respectively. All the ^{13}C-NMR spectra of cardanol referred to the carbon in an aromatic ring system.

The ^{13}C-NMR spectrum of GPPE in $CDCl_3$ also revealed the presence of a carbon in aromatic ring at δ_C 158.67 ppm, which referred to the carbon position *a*. The peaks at 144.46, and 136.74 ppm corresponded to the carbon position *e*. The peaks at 129.21, 121.33, 114.98, and 111.50 ppm corresponded to the carbon position *c*, *d*, *f*, and *b*, respectively. Moreover, the ^{13}C-NMR spectrum of glycidyl moiety prominently presented at δ_C 68.69 ppm referred to the carbon in position *g*. The peaks at 50.07 and 44.40 ppm indicated the carbon of an epoxy group in the position *h* and *i*, respectively.

Dept-135 NMR was also used for providing more information of ^{13}C-NMR spectra by comparing with ^{13}C-NMR spectrum of GPPE. Dept-135 NMR of GPPE showed the absence of quaternary carbons at the *a* and *e* positions. Positive signals of –CH resonance in aromatic ring referred to the carbons at *c*, *d*, *f*, and *b* positions. Prominently negative signals of -CH_2 resonance at the *g* and *i* positions referred to the resonance of carbons on the glycidyl moiety of GPPE molecule.

From, ^{13}C-NMR spectra, and dept-135 NMR spectrum of GPPE apart from the characteristic signals for the aromatic nucleus and C_{15} side chain, the presence of the glycidyl moiety was confirmed by the appearance of the proton on –CH_2 group by signaling the peaks at 4.15 and 3.95 ppm of ^{1}H-NMR spectrum and corresponding to the peaks at δ_C 40 – 80 ppm of ^{13}C-NMR spectrum.

4.2 Preparation of Natural Rubber Product Containing Gylcidyl 3-pentadecenylphenyl Ether (GPPE) and Other Additives

The rubber product containing GPPE, zinc oxide (ZnO), sulfur, stearic acid, and 2-mercaptobenzothiazole (MBT) was prepared in a ball mill for investigation the effects of GPPE concentration, type and surfactant concentration, and the mixing time.

4.2.1 Effect of GPPE Concentration

The effect of GPPE concentration was observed by varying the GPPE concentration corresponding to 0, 1, 2, 3, 4, and 5 phr (part per hundred of rubber), while the other additives are fixed as follows:

- Rubber latex	100	parts by dry weight
- ZnO	5	phr
- Sulfur	2	phr
- Stearic acid	2	phr
- MBT	1	phr
- Tergitol NP10	1.5	phr

From the result of vulcanized sheet preparation at 150°C for 10 minutes, the little air bubble occurred on the vulcanized sheet at a high concentration of GPPE. The result of this behavior is due to the high level of moisture in the rubber product. The lone pair of electrons of oxygen atoms in the GPPE molecule can form hydrogen bonds with water molecules leading to difficulties in releasing the moisture from the rubber product matrix. This problem was solved by compressing the compounded sheet after coagulation for longer than 1 hour to give a thinner sheet size. Finally the retained water was removed by keeping the prepared sheet in an air oven at 60°C for 24 hours before vulcanization.

4.2.1.1 Effect of GPPE Concentration on Thermal Property

Thermal stability of the rubber product in various concentrations of GPPE was determined by thermogravimetric analysis technique (TGA) over a temperature range from 60-650°C. The temperature, which the percentage of weight loss rapidly occurred during transformation, was determined and referred to as "onset temperature". All of the TGA curves are shown in Appendix D. The correlation of GPPE concentration and the onset temperature is presented in Figure 4.1.

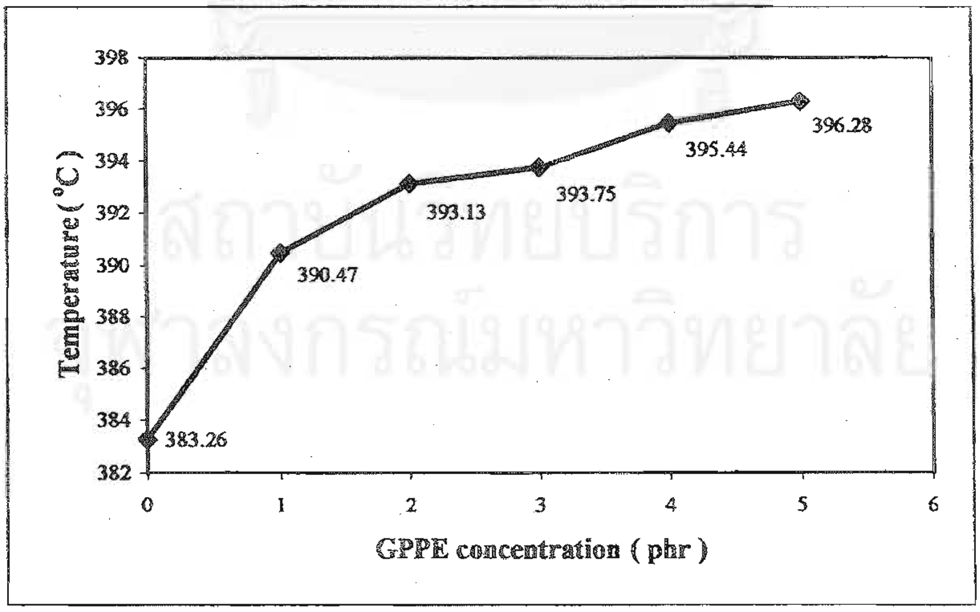


Figure 4.1 The correlation of GPPE concentration and the onset temperature

From Figure 4.1, it was indicated that the onset temperature was affected by the concentration of GPPE in the vulcanized rubber. The onset temperatures increased with increasing GPPE concentration. Notably at 1 and 2 phr of GPPE compared with a non-GPPE content rubber (at 0 phr), the onset temperature significantly increased, and still increased slowly from 3 to 5 phr of GPPE. It can be explained that, GPPE can improve the thermal stability for the modified rubber products, which was probably due to either a long unsaturated side chain or an epoxy group in GPPE molecule that could be polymerized during the temperature of vulcanization. The polymerization may occur together, with GPPE or with the unsaturated site in polyisoprene, to result in the phenolic resin backbone, which provided high temperature stability characteristics, due to the fact that resonance stabilization of resins contains an aromatic ring system in molecules that possess the highest bond strength the thermal stability thus increased.

4.2.1.2 Effect of GPPE Concentration on Mechanical Properties

The vulcanized sheets were prepared for studying the effect of GPPE concentration on mechanical properties. The mechanical properties, including tensile strength, elongation, modulus, and hardness, were determined in this research. Table 4.3 shows the mechanical properties of vulcanized rubber in various GPPE concentrations at 1 hour mixing and 1.5 phr of NP10 as the surfactant. All of the mechanical properties of vulcanized sheets in this experiment are shown in Appendix E.

Table 4.3 The mechanical properties of vulcanized rubber in various GPPE concentrations

Mechanical Properties	GPPE Concentration (phr)					
	0	1	2	3	4	5
Tensile strength (MPa)	8.82	16.71	16.52	12.15	10.34	9.41
Elongation (%)	861.75	1466.75	2315.00	1333.90	1224.85	960.95
Modulus 300% (MPa)	0.9648	1.2259	1.1321	1.0893	0.9351	0.7984
Hardness (shore A)	32.85	35.95	32.50	30.05	27.20	24.25

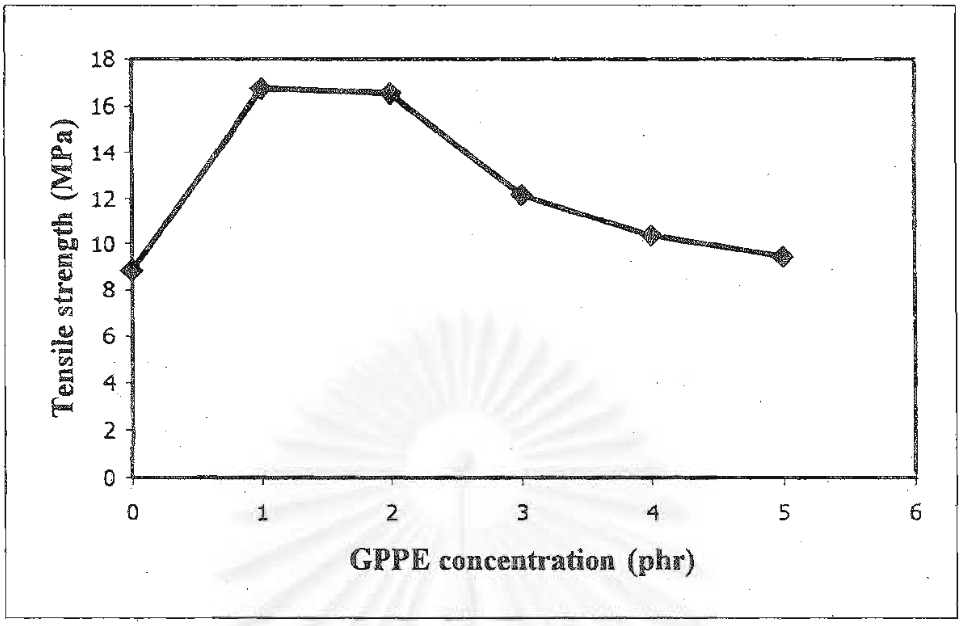


Figure 4.2 Effect of GPPE concentration on tensile strength

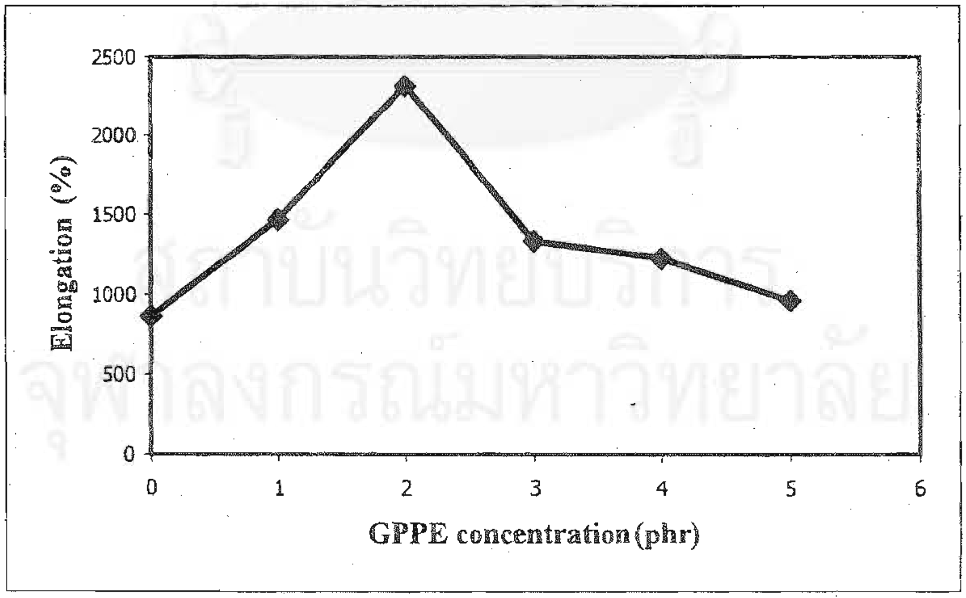


Figure 4.3 Effect of GPPE concentration on elongation

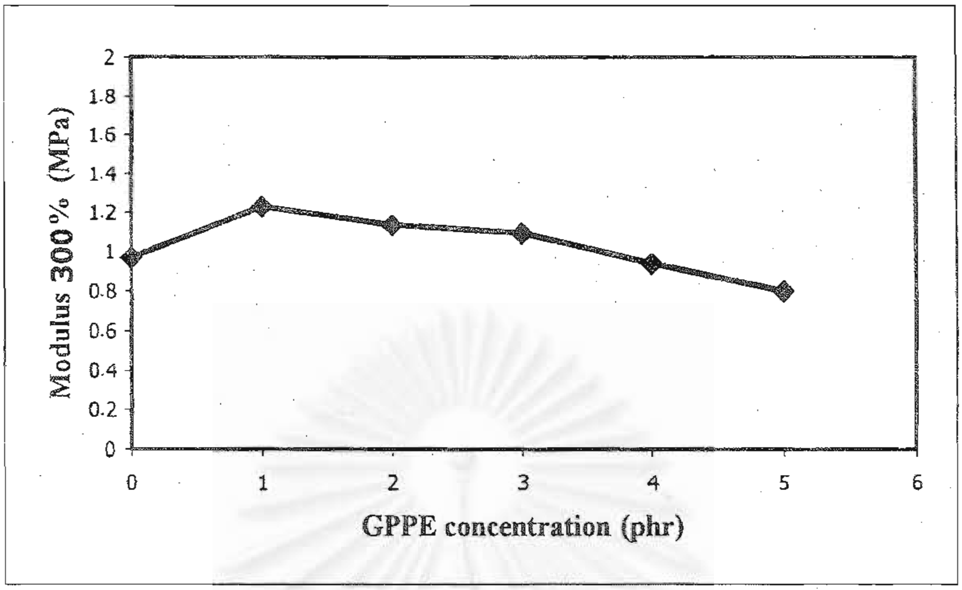


Figure 4.4 Effect of GPPE concentration on modulus 300%

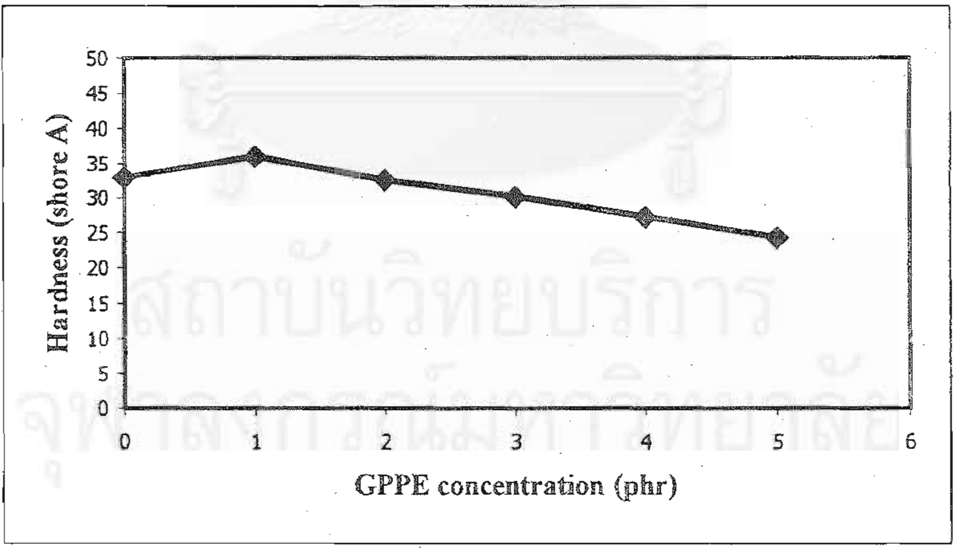


Figure 4.5 Effect of GPPE concentration on hardness

Figure 4.2 illustrated the effect of GPPE concentration on the tensile strength, which is a stress required to rupture the sample. It was found that when GPPE was added to a compounding system at 1–2 phr, the tensile strength rapidly increased, partly due to the probable formation of crosslink structure between the unsaturated side chain of GPPE and the isoprene chains of natural rubber molecules. Increasing the GPPE concentration to higher than 2 phr caused the tensile strength slowly decreased due to the increasing of GPPE concentration in the compounding system, which may be enough to a gel formation. The result from the formation of high molecular weight GPPE prepolymer demonstrated that when the molecules were agglomerated together, an interaction between the agglomerated molecules and other different molecules was difficulty occurred. Therefore, the crosslink between the GPPE and natural rubber tended to decrease.

Effect of GPPE concentration on the elongation is presented in Figure 4.3. The elongation significantly increased as the concentration of GPPE was increased to 2 phr and decreased when the GPPE concentration was increased to higher than 2 phr. This was due to similar reasons with the tensile strength, which was explained in the above paragraph.

In Figures 4.4 and 4.5, the modulus 300% and hardness of vulcanized sheets were studied. The modulus at 300% and the hardness slightly decreased with the increasing of the GPPE concentration to higher than 1 phr. These effects showed the efficiency of GPPE, which could reduce the stiffness of the vulcanizate.

The thermal and mechanical properties of vulcanized the rubber products were investigated in various GPPE concentrations. The GPPE could improve the thermal property and some mechanical properties of the vulcanized rubber in a limited range of GPPE concentration. Therefore, the optimum GPPE concentration of 2 phr was used to obtain the best thermal and mechanical properties for the rubber product.

4.2.2 Effect of Type and Surfactant Concentration

Tergitol NP10, a nonionic surfactant, was used to stabilize the aqueous dispersions of the compounding system. In this experiment, sodium dodecyl sulfate, an anionic surfactant, was also used. The effect of surfactant type and concentration were investigated by varying the NP10 and SDS concentrations to 1.0, 1.5, and 2.0 phr. The aqueous dispersion of additives, including zinc oxide, sulfur, stearic acid, and MBT were prepared by ball mill at 1300 rpm for 1.5 hours, and then the emulsion of GPPE 2 phr and surfactant was added and the mixture was mixed for 3 hours. Finally, the rubber latex was added and mixed further for 1 hour. The formulations of the compounded sheets are shown as follows:

- Rubber latex	100	parts by dry weight
- ZnO	5	phr
- Sulfur	2	phr
- Stearic acid	2	phr
- MBT	1	phr
- GPPE	2	phr

It was found that if Tergitol NP10 of 1.0 phr was used in the system, some of additives, GPPE, and the rubber particles were not dispersed. The rubber latex was coagulated after mixing with the GPPE and additives, due to the surfactant concentration, which was too low to result in micelle formation. Therefore, the aqueous dispersions system of rubber molecule, GPPE and additives were unstabilized. When the concentration of 2.0 phr of NP10 was used, it resulted in the coagulation of the compounded rubber taking more quantity of formic acid than in the case of using NP10 of 1.5 phr.

The air bubbles were generated fully in compounded rubber when SDS with a concentration of 1.5 and 2.0 phr were used. It was found that the coagulation of the system using formic acid was not performed if the concentration of SDS was higher than 1.0 phr.

The mechanical properties of compounded sheets containing NP10 of 1.0, 1.5, 2.0 phr, and 1.0 phr of SDS were determined. Table 4.4 shows the mechanical properties of vulcanized rubber in various surfactant concentrations in 1 hour mixing.

Table 4.4 The mechanical properties of vulcanized rubber in various surfactant concentrations

Mechanical Properties	Surfactant Concentration (phr)			
	NP10 1.0	NP10 1.5	NP10 2.0	SDS 1.0
Tensile strength (MPa)	10.78	16.52	13.01	0.89
Elongation (%)	2231.50	2315.00	2077.50	777.74
Modulus 300% (MPa)	1.0682	1.1321	1.2635	0.3828
Hardness (shore A)	27.75	32.50	27.80	16.50

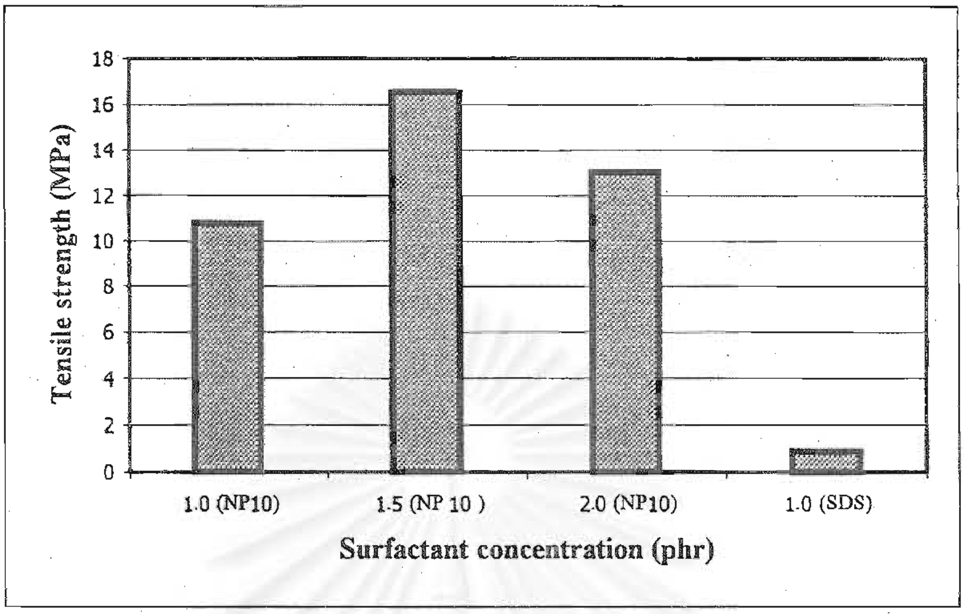


Figure 4.6 The type and concentration of surfactant effects on tensile strength

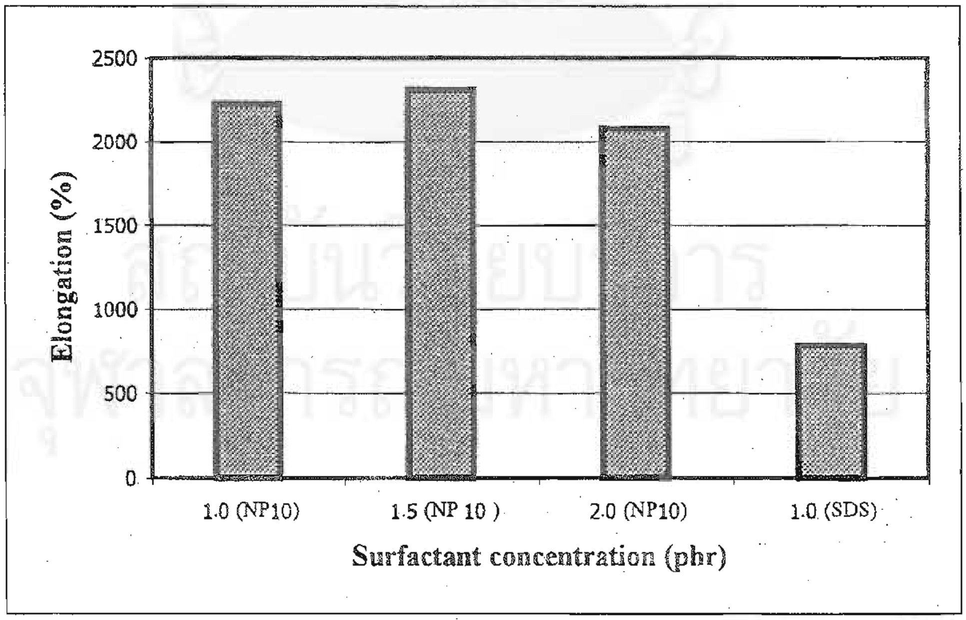


Figure 4.7 The type and concentration of surfactant effects on elongation

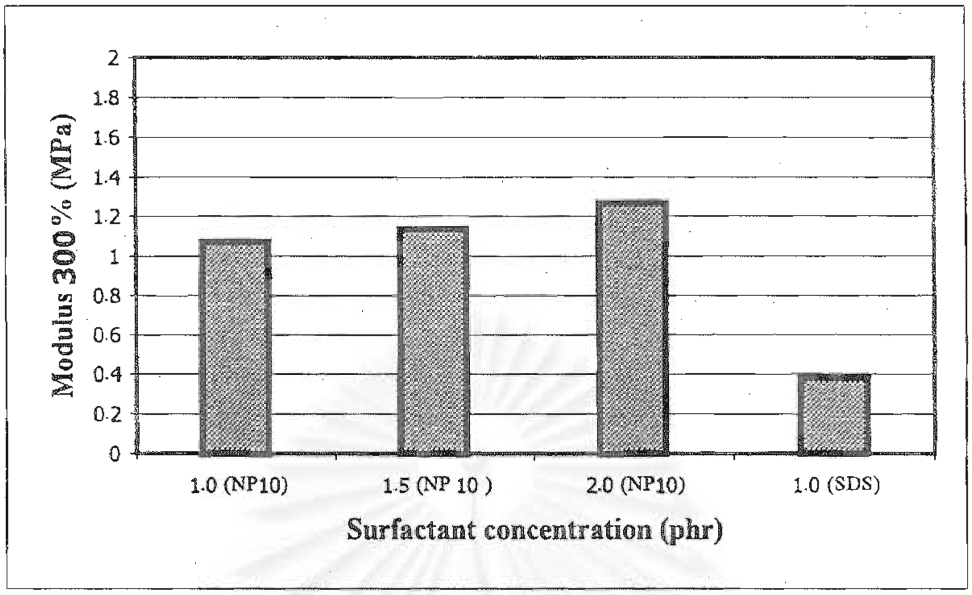


Figure 4.8 The type and concentration of surfactant effects on modulus 300%

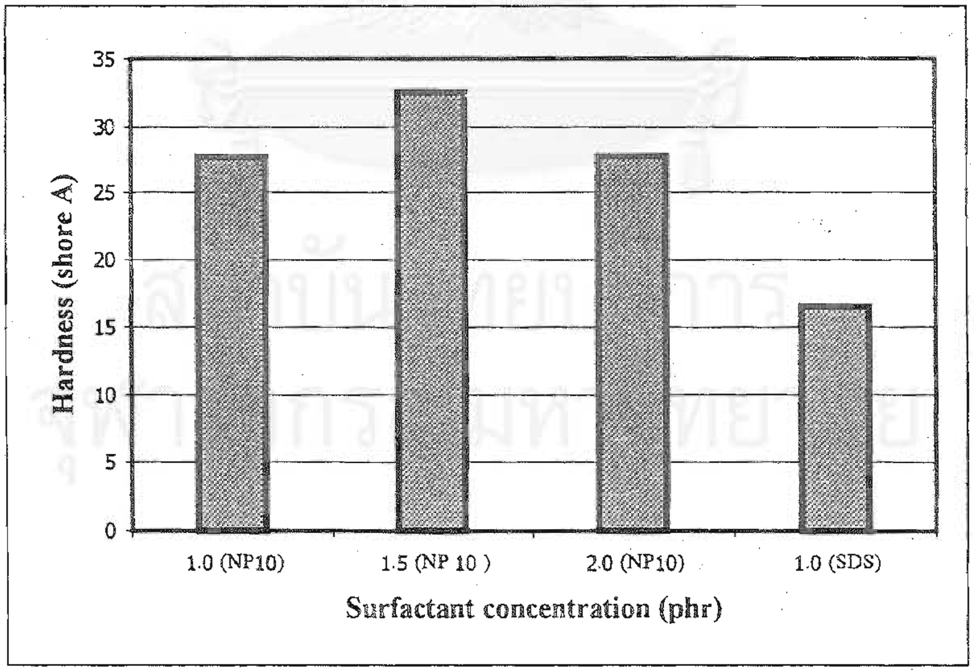


Figure 4.9 The type and concentration of surfactant effects on hardness

The mechanical properties of compounded rubber from the process containing SDS concentration of 1.0 phr showed the lowest properties, which compared to the same product generated from those process containing NP10 instead of SDS. The lowering of mechanical properties on rubber products might be due to a generating of air bubble or foam in the rubber product when SDS was used as a dispersing agent for additives and GPPE. Another reason was that SDS, an anionic surfactant, was generally suitable for stabilizing low pH rubber latex. But in case of this experiment, a high ammonia concentrated rubber latex with the pH of approximately 11 was used. In general, the rubber particles in a high pH medium had a negative charge, which was incapably stabilized by anionic molecules of SDS.

In the opposite direction, the product had good mechanical properties when the nonionic surfactant, NP10, was used in the process instead of SDS. The important reason might be due to the structure of NP nonionic surfactant (Figure 4.10), which was capable with rubber particles in rubber latex by forming the hydrogen bonding between water molecule and aliphatic site of rubber particles, GPPE and also the additive molecules.

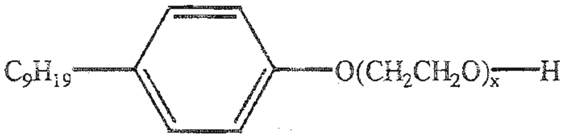


Figure 4.10 General structure of NP surfactants

The result indicated that the rubber products had the highest mechanical properties, such as tensile strength, elongation, and hardness, when 1.5 phr of NP10 was used.

Only the 300% modulus of the compounded rubber containing NP10 of 2.0 phr was higher. But at the concentration using NP10 of 2.0 phr, it was difficult for the compounded rubber was to coagulate and took more quantity of formic acid than when using NP10 of 1.5 phr. Therefore, the NP10 concentration of 1.5 phr was used as the optimum quantity for stabilizing the aqueous dispersion system in this experiment.

4.2.3 Effect of Mixing Time

The mixing time of the compounded rubber was another important factor. Usually the production cost depends on a period of mixing time. In this work, the time for preparing the compounded rubber (after the rubber latex was added) was investigated by varying the mixing time to 0.5, 1.0, and 2.0 hours. The formulations of compounded sheets, which was used to determine the effect of mixing time are shown as follows:

- Rubber latex	100	parts by dry weight
- ZnO	5	phr
- Sulfur	2	phr
- Stearic acid	2	phr
- MBT	1	phr
- GPPE	2	phr
- Tergitol NP10	1.5	phr

The mechanical properties of the vulcanized sheets were observed to obtain the appropriate time for rubber compounding. Table 4.5 illustrates the effect of mixing time on the mechanical properties of the vulcanized rubber sheets.

Table 4.5 The mechanical properties of vulcanized rubber in various mixing time

Mechanical Properties	Mixing Time (hr)		
	0.5	1.0	2.0
Tensile strength (MPa)	10.41	16.52	16.20
Elongation (%)	1527.90	2315.00	2278.50
Modulus 300% (MPa)	0.9621	1.1321	1.2485
Hardness (shore A)	31.50	32.50	30.55

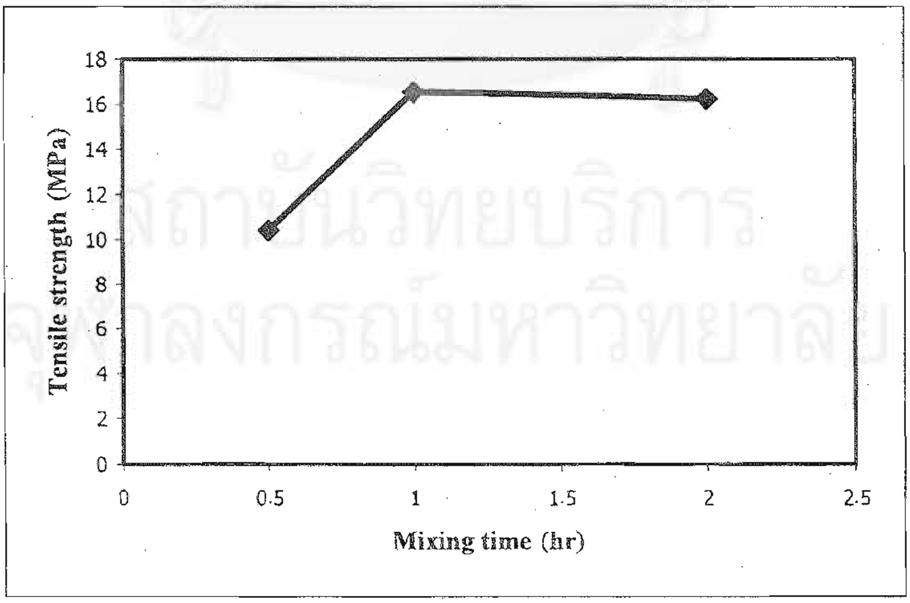


Figure 4.11 Effect of mixing time on tensile strength

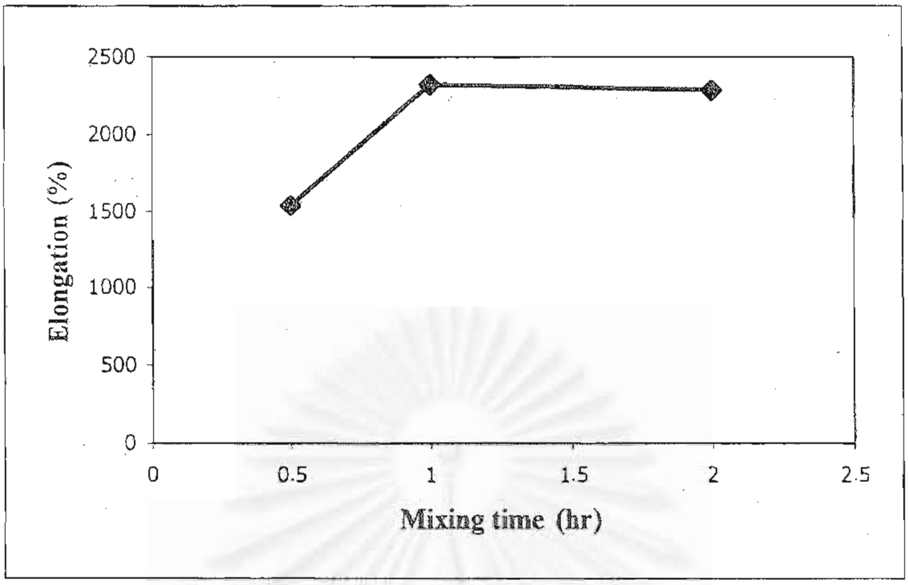


Figure 4.12 Effect of mixing time on elongation

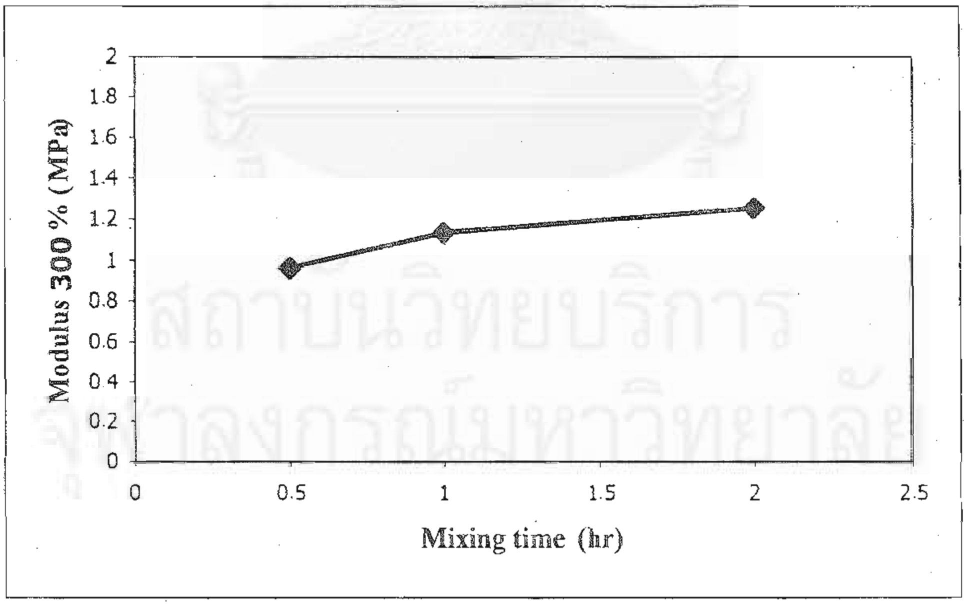


Figure 4.13 Effect of mixing time on modulus 300%

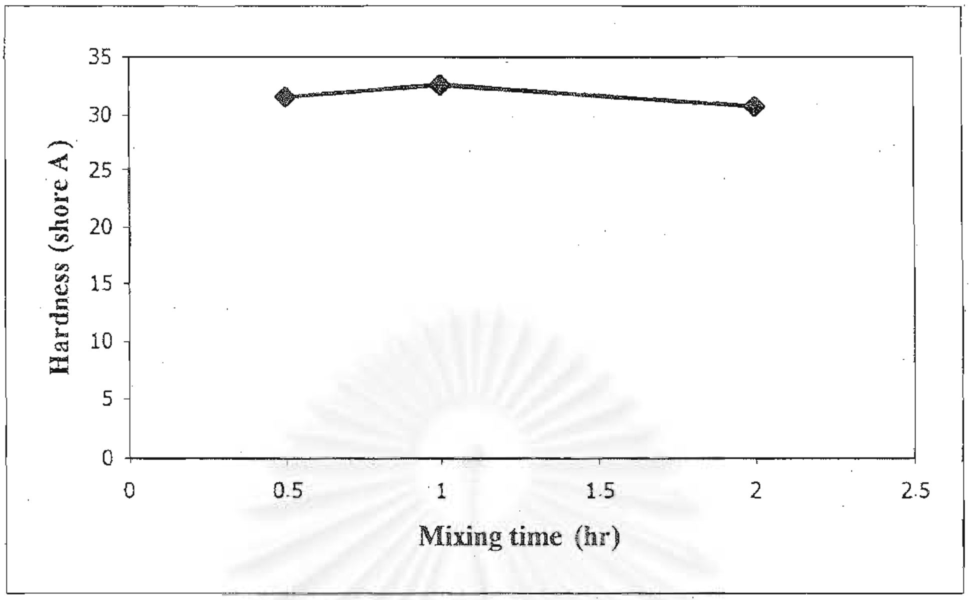


Figure 4.14 Effect of mixing time on hardness

From the mechanical properties of vulcanized rubber in various mixing time, the tensile strength and the elongation increased with increasing mixing time from 0.5 to 1 hour. When the time of mixing was increased to higher than 1 hour, the tensile strength and the elongation were nearly constant. The modulus 300% of the vulcanized sheets was slightly increased with increasing the mixing time. The hardness was nearly constant at all of the mixing time. Then the mixing time of 1 hour was used as the optimum mixing time for preparation of the compounded rubber latex.

4.3 Determination of Dispersing Property

In this experiment, the dispersing of GPPE and additives were observed by optical and scanning electron microscopy techniques. A good dispersing of all ingredients shows a unique property of the rubber product, which introduces a good benefit to compete in the industrial market.

4.3.1 Determination of Dispersing Property by Optical Microscopy

Olympus, BH-2 optical microscope was used to investigate the dispersing of GPPE and additives in an emulsion system. Effects of type and surfactant concentration and mixing time were studied. The dispersing of the emulsion system was carried out by dropping the emulsion from the compounding process on the glass slide, covered with cover glass. Then the sample was photographed by transmission of the light beam through a sample. Figures 4.15 and 4.16 are used to explain the effects of the surfactant type on the dispersing property of GPPE and additives at 3 phr of GPPE and 2 hours of mixing.

The Tergitol NP10 was used to stabilize the emulsion system of rubber latex, containing GPPE, and additives. The small droplet referred to the GPPE and additives. In Figure 4.15, the GPPE and additives dispersed thoroughly as small droplet particles formed in the rubber matrix. In Figure 4.16, the SDS was used, the emulsion showed a low characteristic of dispersion. In this case, it might be due to an aggregation of GPPE and additives. Therefore, the Tergitol NP10 has better efficiency in stabilizing the emulsion system in this experiment than the SDS.

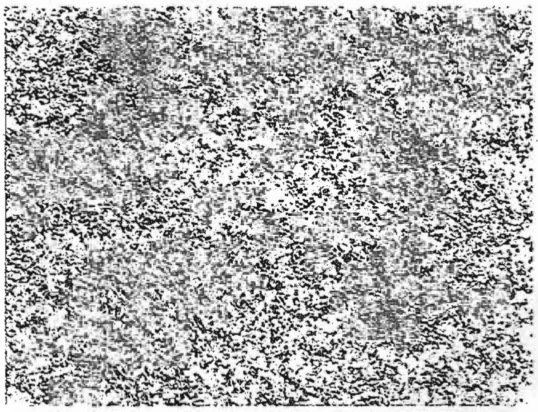


Figure 4.15 Emulsion of series A surfactant (400X)

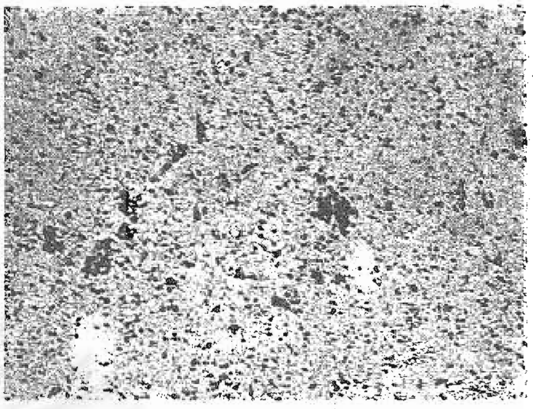


Figure 4.16 Emulsion of series B surfactant (400X)

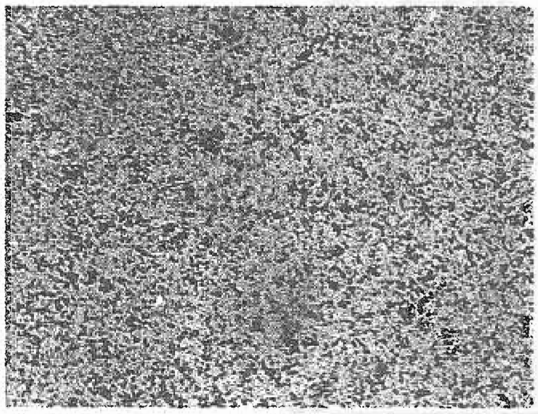


Figure 4.17 Emulsion of A1 of 1 phr of GPPE at 0.5 hr of mixing (400X)

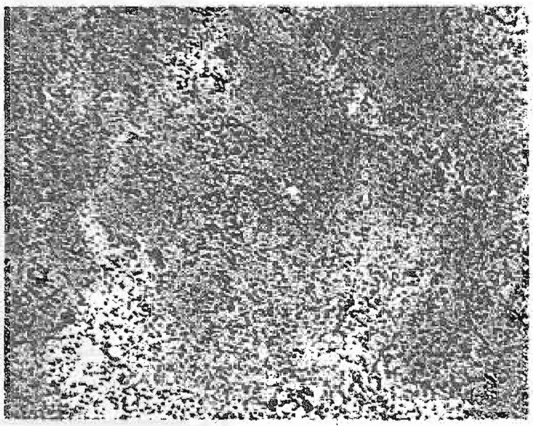


Figure 4.18 Emulsion of A1 of 1 phr of GPPE at 1.0 hr of mixing (400X)

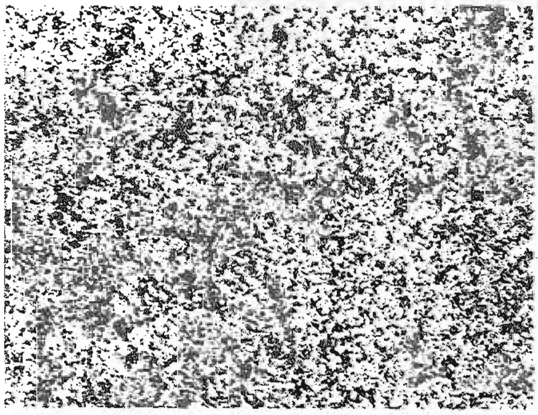


Figure 4.19 Emulsion of A1 of 1 phr of GPPE at 2.0 hr of mixing (400X)

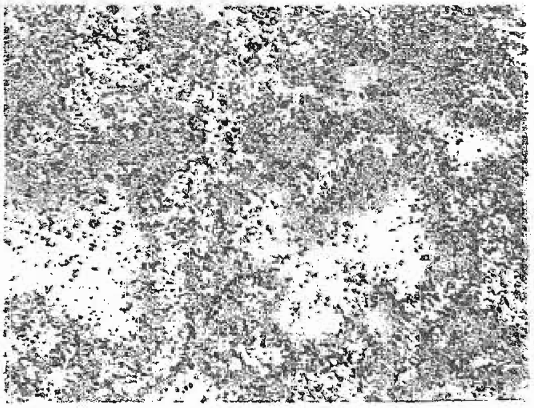


Figure 4.20 Emulsion of A1 of 3 phr of GPPE at 1.0 hr of mixing (400X)

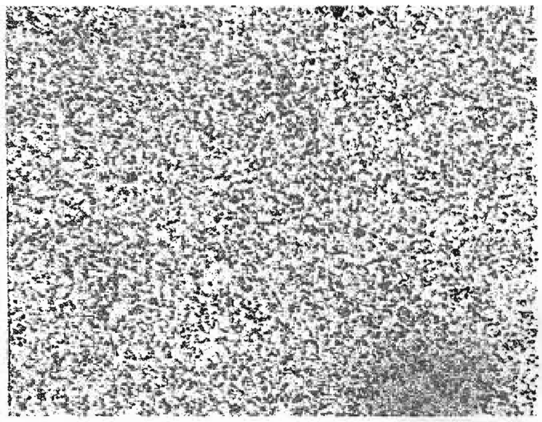


Figure 4.21 Emulsion of A2 of 1 phr of GPPE at 0.5 hr of mixing (400X)

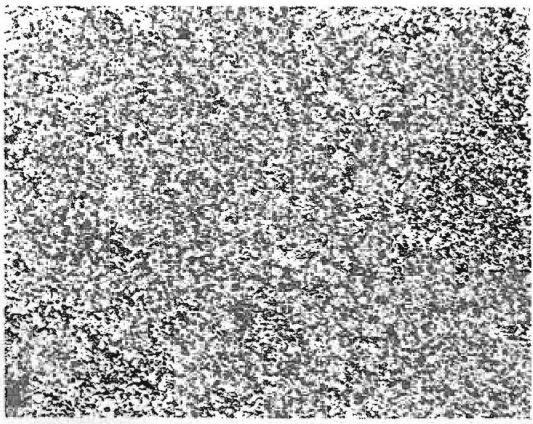


Figure 4.22 Emulsion of A2 of 1 phr of GPPE at 1.0 hr of mixing (400X)

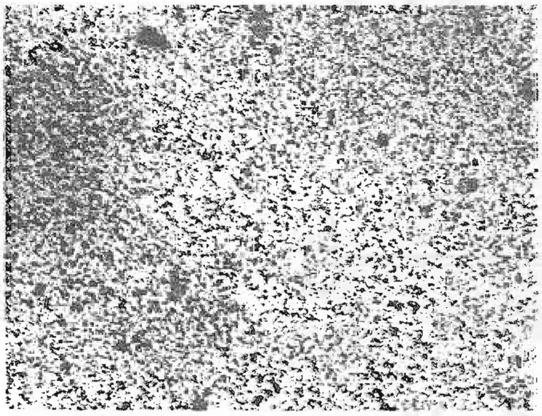


Figure 4.23 Emulsion of A2 of 1 phr of GPPE at 2.0 hr of mixing (400X)

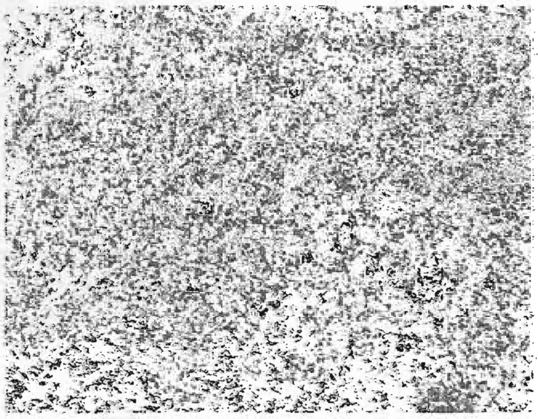


Figure 4.24 Emulsion of A2 of 3 phr of GPPE at 2.0 hr of mixing (400X)

When the Tergitol NP10 concentration of 1.0 phr was used, the aggregation of the droplet particles increased with increasing mixing time as shown in Figures 4.17-4.19. In Figure 4.18, the mixing time of 1.0 hour was set, the droplet particles dispersed quite well. However, when increasing the concentration of GPPE to 3 phr (Figure 4.20), a heterogeneous phase was occurred, due to a good dispersion characteristic limitation based on the low GPPE concentration only.

For Figures 4.21–4.23, the concentration of 1.5 phr Tergitol NP10 was used. The GPPE and additives show steady uniform dispersion for every period of mixing time. Because the amount of surfactant was appropriate to form micelles thoroughly throughout the emulsion system. The dispersion still had good characteristic when the GPPE concentration was increased to 3 phr.

Therefore, the optical microscopy micrograph revealed that the A2 group of the 1.0 hour mixing had the best characteristic of dispersion in the emulsion system and was used for further investigation by scanning electron microscopy technique.

4.3.2 Determination of Dispersing Property by Scanning Electron Microscopy

The scanning electron microscopy (SEM) was used to analyze the dispersing properties of GPPE and additives in a cross-section area of a vulcanized rubber. The vulcanized sheets from A2 group of 1.0 hour mixing were investigated. Figures 4.25–4.30 show the SEM micrograph of the vulcanized sheets containing 0, 1, 2, 3, 4, and 5 phr of GPPE, respectively.

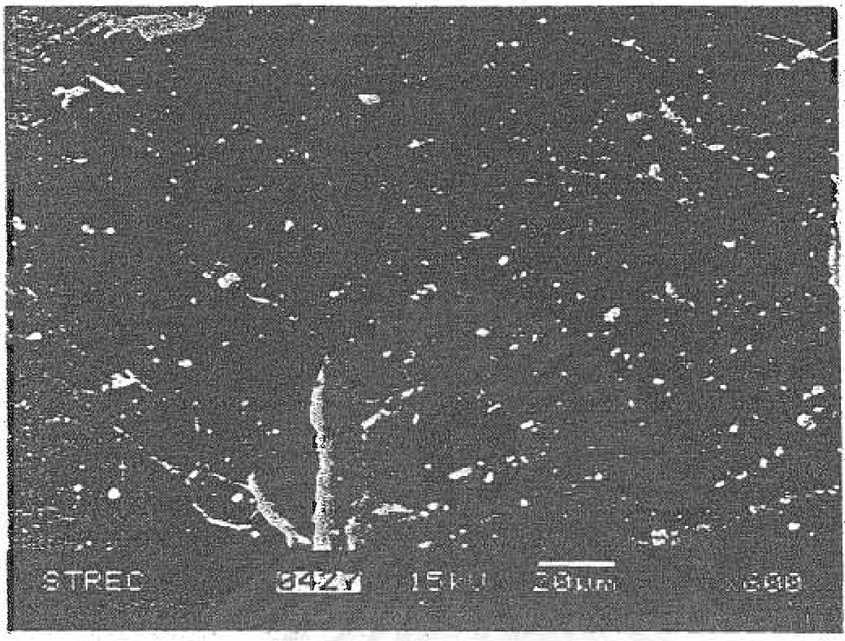


Figure 4.25 SEM photomicrograph of 0 phr of GPPE (600X)

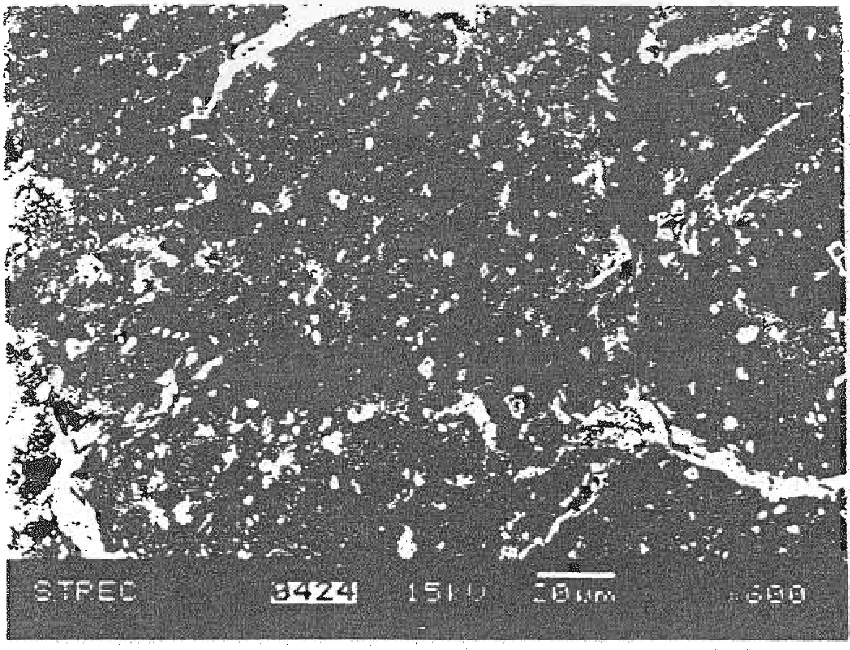


Figure 4.26 SEM photomicrograph of 1 phr of GPPE (600X)

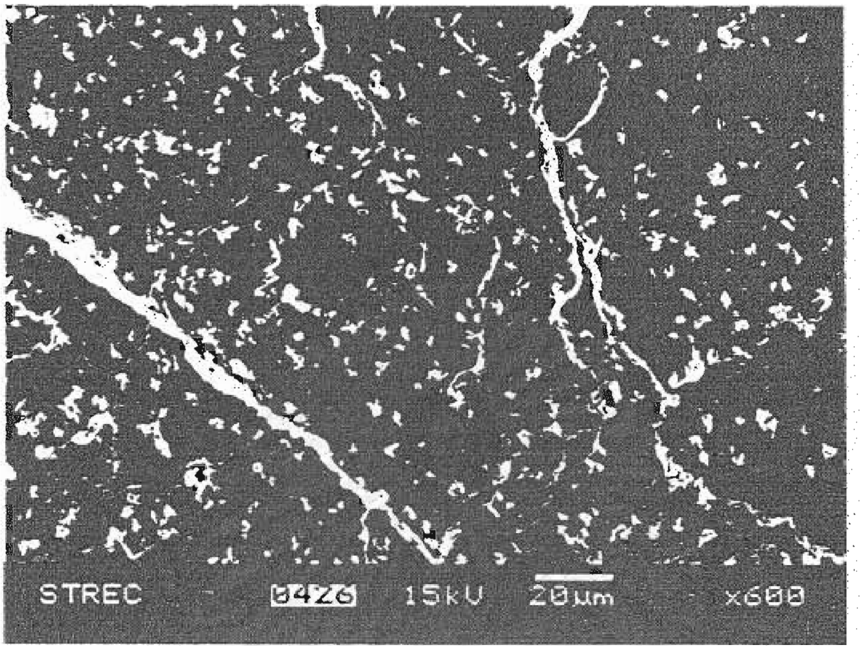


Figure 4.27 SEM photomicrograph of 2 phr of GPPE (600X)

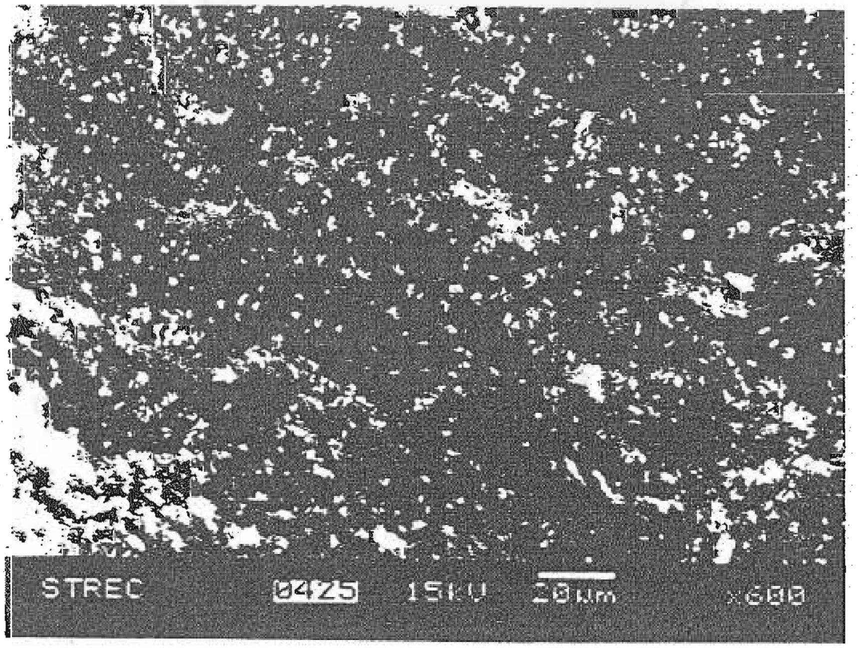


Figure 4.28 SEM photomicrograph of 3 phr of GPPE (600X)

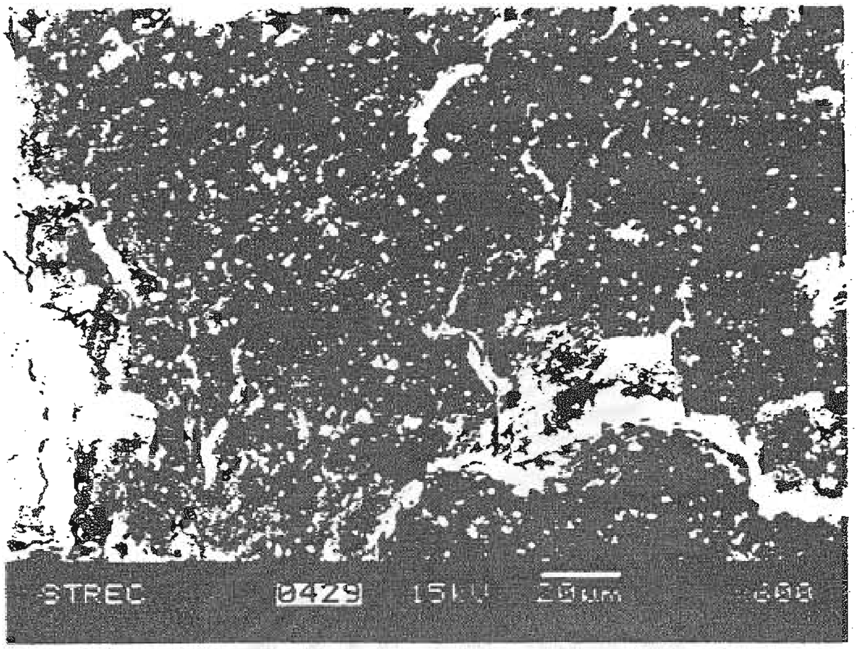


Figure 4.29 SEM photomicrograph of 4 phr of GPPE (600X)

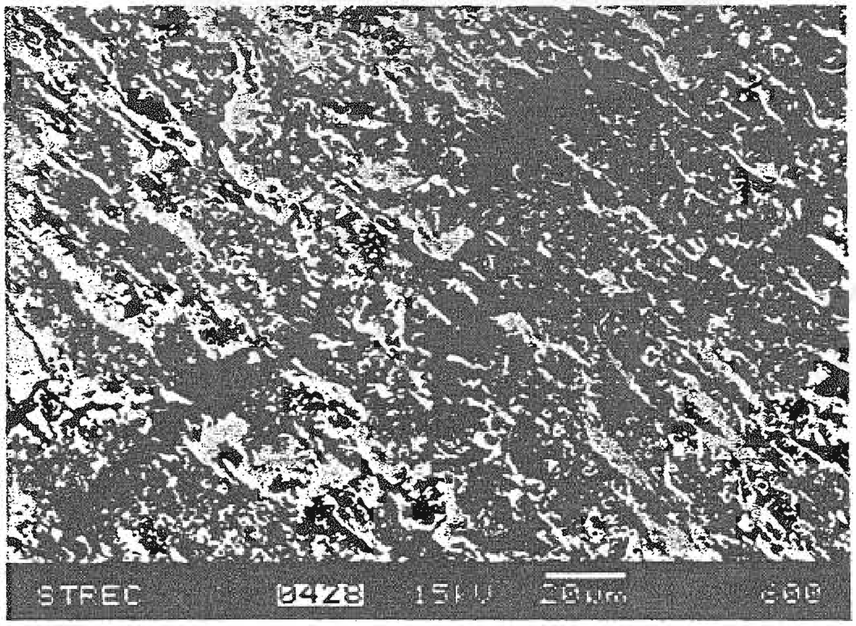


Figure 4.30 SEM photomicrograph of 5 phr of GPPE (600X)

In Figures 4.25 – 4.30, the dark points referred to the rubber matrix, and the bright spots were GPPE and additives. In Figures 4.25–4.29, the light spots increased with increasing GPPE concentration and steadily dispersed through the cross-section area of the sample. However, in Figure 4.30, small porous dispersed steadily through the sample surface, which was probably due to the evaporation of the retained water in the vulcanized sheet during the vulcanization process.

The OM and SEM photomicrographs were used to explain clearly about the correlation between the dispersion and the mechanical properties of vulcanized rubber containing GPPE and additives. When all ingredients were mixed, two-phase separation occurred, which GPPE, a minor phase, dispersed in the rubber matrix of a major phase. The good mechanical properties occurred with the steady dispersion of GPPE and additives molecules in the rubber matrix. At high concentrations of GPPE, dispersion characteristics were not good because of the aggregation of GPPE molecules and the strong hydrogen bonding of GPPE with retained moisture, which lead to micro porous formation after vulcanization. The appearances of micro porous formation caused the vulcanized rubber could easily break, and so the lowering of tensile strength and elongation property were observed.

4.4 Ageing Properties

Thermal ageing was used to determine the retention on mechanical properties of the vulcanized rubber after ageing in a hot air oven at 70°C for 72 hours. The mechanical properties, including tensile strength, elongation, modulus 300%, and hardness, were investigated in this experiment. The ageing resistances were calculated on the percentage change of the property for tensile strength, elongation, and modulus 300%. The hardness was reported in terms of the property change. All of the mechanical properties are presented in Appendix E. Table 4.4 shows the retention on mechanical properties of the A2 group at 1.0 hour mixing.

Table 4.6 The retention on mechanical properties after ageing of A2 group of 1 hour mixing

Mechanical Properties	GPPE Concentration (phr)					
	0	1	2	3	4	5
Tensile strength (%)	-23.40	0.04	1.39	2.06	2.23	2.56
Elongation (%)	0.73	2.81	6.57	11.33	11.77	11.24
Modulus 300% (%)	1.30	3.35	3.59	4.17	4.25	5.46
Hardness	-1.75	0.18	1.95	2.40	2.40	2.50

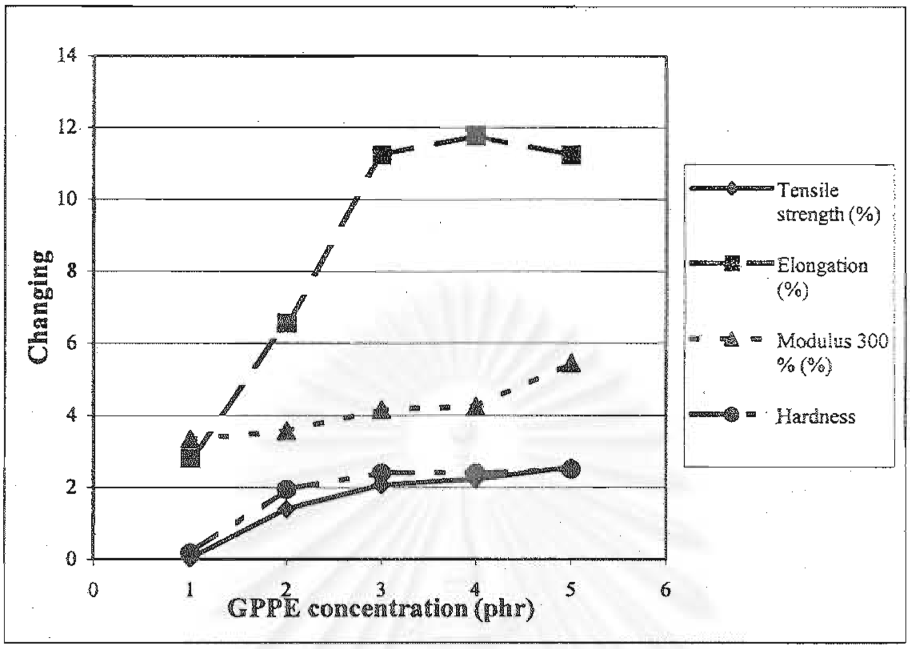


Figure 4.31 Changing of the mechanical properties after ageing

From Figure 4.31, the vulcanized rubber containing GPPE showed good retention on mechanical properties after ageing. The mechanical properties increased by ageing the vulcanized rubber, which may be due to a post-curing reaction during the ageing period. When the post-curing reaction occurred, the unsaturated side chain in GPPE molecules could probably crosslink along with the rubber molecule to form networks, which caused increasing on mechanical properties.

4.5 Determination of Percent Crosslinking

Soxhlet extraction was used to determine the percent crosslinking of the vulcanized rubber. In this experiment, the vulcanized rubber was cut to small pieces to increase surface area. The extraction was carried out in a soxhlet-type extractor for 8 hours. Hexane was used as a solvent, due to the solubility of rubber particle, GPPE, and additives. In this case, uncrosslinked molecules were extracted by hexane. The percent crosslinking was calculated from the percentage of weight loss sample after extracting. All of the percent crosslinks are shown in Appendix F. Figures 4.32–4.34 show the percent crosslinking of vulcanized rubber on various GPPE and Tergitol NP10 concentrations.

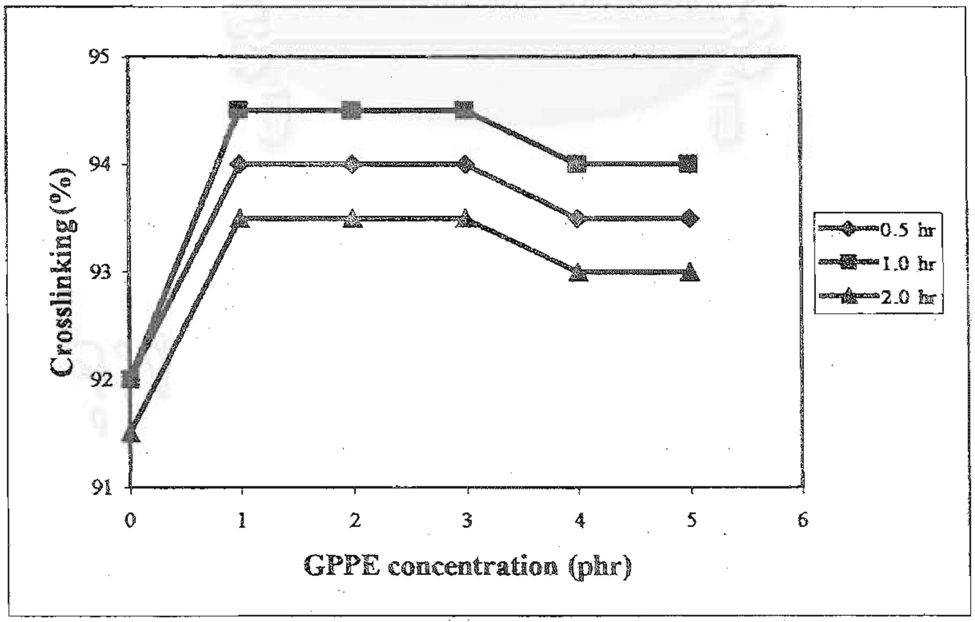


Figure 4.32 % Crosslinking of using Tergitol NP10 of 1.0 phr (A1 group)

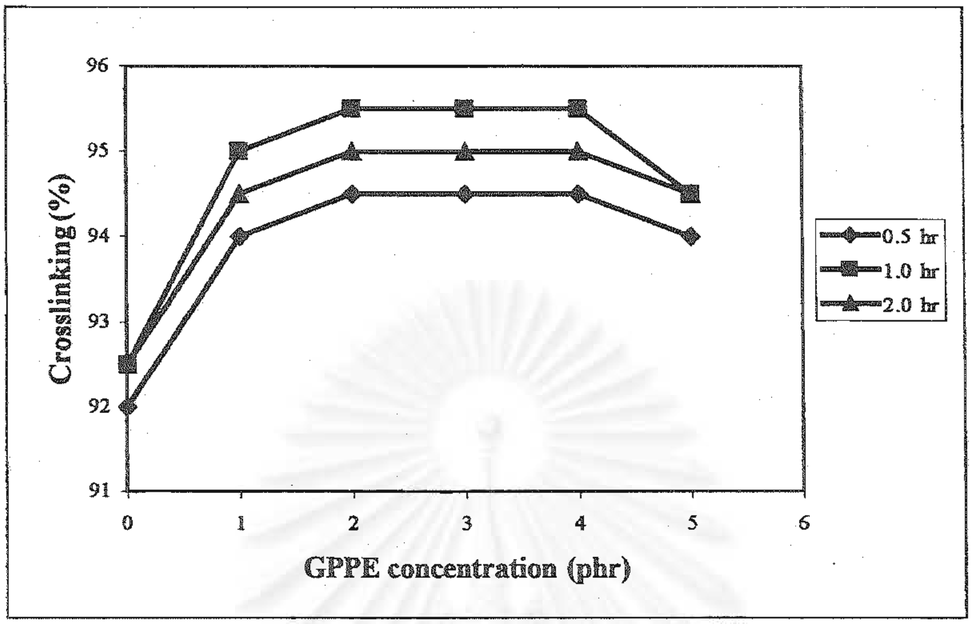


Figure 4.33 % Crosslinking of using Tergitol NP10 of 1.5 phr (A2 group)

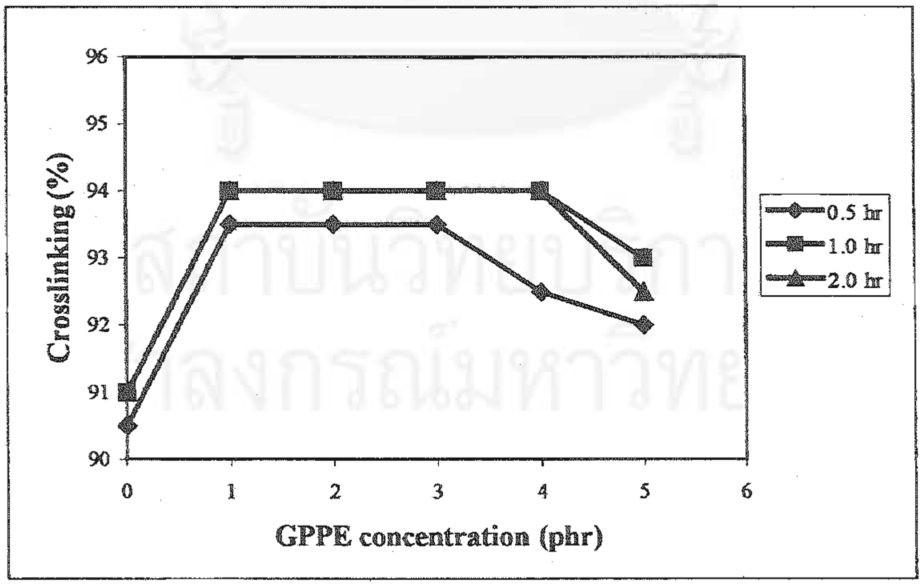


Figure 4.34 % Crosslinking of using Tergitol NP10 of 2.0 phr (A3 group)

The GPPE-modified natural rubber showed a higher percent of crosslinking than the unmodified natural rubber, which was due to GPPE behaved as a bifunctional group molecule. The bifunctional molecule could be formed through the crosslink structure either with other GPPE molecules or with the isoprene chains in natural rubber. From Figures 4.34-4.36, it was indicated that the GPPE concentration increased, whereas the percent of crosslinking was nearly constant or slightly decreased when the GPPE concentration was higher than 3 phr. The decreasing of percent crosslinking may be due to the aggregation of GPPE molecules at high GPPE concentrations. When 2.0 phr of NP10 was used to obtain the lowering percent crosslinking, the droplet particles in the emulsion system of high Tergitol NP10 concentration were found to be more stable. Therefore, some GPPE molecules inside the small droplet particles could not be polymerized or could not crosslink with other molecules during the vulcanization. The uncrosslinked molecules were extracted by hexane from the system.

4.6 The Mechanical Properties Comparison of GPPE Modified Natural Rubber Obtained from This Research with Some Natural Rubber Products

4.6.1 Comparison with Laongsri's Work

For the mechanical properties, as compared to Laongsri's work [24], carbon black type N330 was added necessarily to the GPPE modified natural rubber and the concentration of Tergitol NP10 was increased to 3.0 phr according to the concentration obtained from the optimum dispersion of ingredients. Tear strength of vulcanized rubber that gave the optimum properties was tested and compared with Laongsri's work. The comparison of ingredients and mechanical properties are shown in Tables 4.7 and 4.8, respectively.

Table 4.7 Comparison of ingredients with Laongsri's work

Ingredients (phr)	GPPE Modified NR (without filler)	GPPE Modified NR (with filler)	Laongsri's Work
Natural rubber	100	100	100
Carbon black type N330	-	25	25
Sulfur	2	2	2
ZnO	5	5	5
Stearic acid	2	2	2
MBT	1	1	1
Tergitol NP10	1.5	3.0	3.0
GPPE	2	2	-

Table 4.8 Comparison of mechanical properties with Laongsri's work

Mechanical Properties	GPPE Modified NR (without filler)	GPPE Modified NR (with filler)	Laongsri's Work
Tensile strength (MPa)	16.52	16.15	16.49
Elongation (%)	2315	2260	1538
Modulus 300% (MPa)	1.3121	1.4300	-*
Hardness (shore A)	32.50	46.25	60.4
Tear strength (kN/m)	83.03	82.72	57.15

* This property was not test.

From Table 4.8, the modulus 300% and hardness of the GPPE modified natural rubber with filler were higher than the GPPE modified natural rubber without filler. This was due to carbon black, which acted as reinforcing filler. Thus the modulus and hardness of rubber product were raised. But the tensile strength, elongation, and tear strength of the GPPE modified natural rubber with filler were slightly lower than the GPPE modified product without filler. This was partly due to a loss of rubbery properties of the GPPE modified natural rubber with filler.

The comparison of the GPPE modified natural rubber with filler and the rubber product from Laongsri's work showed that the elongation and tear strength of the GPPE modified natural rubber with filler was significant higher than Laongsri's product. This was probably due to the formation of network structure, which occurred in GPPE modified product. But the hardness of both GPPE modified natural rubber with and without filler showed lower values than Laongsri's product.

4.6.2 Comparison of GPPE Modified Natural Rubber with Rubber Product Containing Other CNSL Derivatives

Natural rubber modified with phosphorylated cashew nut shell liquid (PCNSL) and phosphorylated cardanol prepolymer (PCP), were reported by Menon [23]. Menon's work was summarized in the Literature Reviews (Chapter II). The rubber sheets were prepared by mixing the rubber with various amounts of PCNSL and other additives on a two-roll mixing mill.

The details of ingredients and mechanical properties of comparative compounded rubber sheets are presented in Tables 4.9 and 4.10, respectively.

Table 4.9 Comparison of ingredients of Menon's work and this research

Ingredients	Menon's work	This Research
Natural rubber (phr)	100	100
ZnO (phr)	10	5
Sulfur (phr)	2	2
Stearic acid (phr)	2	2
MBT (phr)	1.5	1.0
TMTD (phr)	0.5	-
PCNSL (phr)	15	-
GPPE (phr)	-	2

Table 4.10 Comparison of mechanical properties with Menon's work

Mechanical Properties	Menon's work	This Research
Tensile strength (MPa)	15.67	16.52
Elongation (%)	1170	2315
Modulus 300% (MPa)	1.3000	1.3121

From Table 4.9, the amount of ingredients used in this research such as, ZnO and MBT, were less than those in Menon's work. The compounded rubber sheet of this research did not contained TMTD. The tensile strength, elongation, modulus 300%, and hardness of this research product were higher than the mechanical properties of rubber product from Menon's work, especially the elongation.

4.6.3 The Properties Comparison of GPPE Modified Natural Rubber Obtained from This Research with Standard Properties Specified by Thai Industrial Standard Institute (TISI)

The properties of GPPE modified natural rubber without filler, which were obtained from this research, were compared with the properties of some rubber products [26, 27]. The standard specification of mechanical properties for automotive rubber mats and door weather strips for automobile were compared with modified natural rubber containing GPPE as shown in Table 4.11.

Table 4.11 The properties of GPPE modified natural rubber of this research and standard specification of rubber products

Properties	Automotive Rubber Mats (5th quality)	Door Weather Strips for Automobile	This Research Product
Hardness	65+5	60±5	32.50
Tensile strength (MPa), not less than	10.4	7.0	16.52
Elongation (%), not less than	250	300	2315
Tear strength (kN/m), not less than	52.5	15	83.03
Ageing - Hardness	+5	+10, -5	+1.95 (34.45)
- Tensile strength (%)	8.3	±25	+1.39 (16.75)
- Elongation (%)	200	±35	+6.57 (2407)

The results in Table 4.11 indicated that the mechanical properties of modified rubber product containing GPPE showed higher values of mechanical properties than that of standard mechanical properties of rubber products. This was true except for the hardness of the rubber product, which was lower than that of standard. This might be due to the dispersion of GPPE as determined and the filler was not used. In this case, carbon black N330 of 25 phr was used in GPPE modified rubber for comparison with the mechanical properties of other rubber product. The hardness of rubber product was lower than the standard hardness, but showed a higher value than rubber products without filler. It also tended to be high if the carbon black was used at a higher amount. Therefore, GPPE modified rubber could be used to produce these rubber products.

CHAPTER V

CONCLUSION

Glycidyl 3-pentadecenylphenyl ether (GPPE) was synthesized from the reaction of cardanol with epichlorohydrin in the presence of sodium hydroxide (NaOH). A product from the reaction was characterized by infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR).

GPPE modified natural rubber was prepared by direct mixing concentrated rubber latex with GPPE and additives. At the beginning, the additives were prepared in aqueous dispersions for 1.5 hours, and then an emulsion of GPPE at pH approximately 10 was added and further mixed for 1.5 hours. The ball mill was used for mixing at the speed of 1300 rpm. Finally, the rubber latex was added into the aqueous dispersions and let it mixed for 1 hour. Compounded natural rubber latex was coagulated by 5% (by volume) formic acid. Effects of GPPE concentration, surfactant type and concentration, and mixing time were studied. The dispersion of GPPE and additives were studied by optical microscopy (OM), and scanning electron microscopy (SEM).

The formulations of compounded sheets, which give the optimum properties in this research, consisted of 100 phr natural rubber latex, 5 phr zinc oxide, 2 phr sulfur, 2 phr stearic acid, 1 phr MBT, 2 phr GPPE, and 1.5 phr Tergitol NP10.

The properties of GPPE modified natural rubber are shown in Table 5.1.

Table 5.1 The properties of GPPE modified natural rubber

Properties	Results
Mechanical properties	
- Tensile strength (MPa)	16.52
- Elongation (%)	2315
- Modulus 300% (MPa)	1.3121
- Hardness (shore A)	32.5
Thermal properties	
- Onset temperature (ºC)	393.13
Percent crosslinking	95.0

The GPPE modified natural rubber obtained from this research had higher mechanical properties when compared with other cashew nut shell liquid derivatives modified natural rubbers. Furthermore, almost all of the mechanical properties of GPPE modified natural rubber were higher than the mechanical properties of contain rubber products.

Suggestion for Future Work

1. Preparation of filled GPPE modified natural rubber and studying the effect of filler on mechanical and thermal properties of vulcanized rubber products.
2. Preparation of the ready used products from the GPPE modified natural rubber and studying the possibility in industrial applications.

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APPENDICES

APPENDIX A

The Properties of Natural Rubber Latex in This Experiment

Table A.1 The properties of natural rubber latex in this experiment*

Properties	Value
Total solid content, %	61.96
Dry rubber content, %	60.18
Non-rubber solids, %	1.78
Ammonia content (on Total weight), %	0.71
Ammonia content (on Water phase), %	1.86
pH Value	10.53
KOH number	0.6356
Volatile fatty acid number (VFA)	0.0258
Mechanical stability time @ 55% TS.Sec	950
Specific gravity at 25°C	0.9447
CST (ml.)	2.8
Magnesium content (ppm.)	21
Viscosity (60% TS.Spindle no.1. 60 rpm.) cps.	87

Remark: Free from pentachlorophenol

*All test are performed according to the relevant ISO 2004-1997(E) Specification.

*Data from Thai Rubber Latex Cooperation (Thailand) Public Company Limited

APPENDIX B

Infrared Spectra

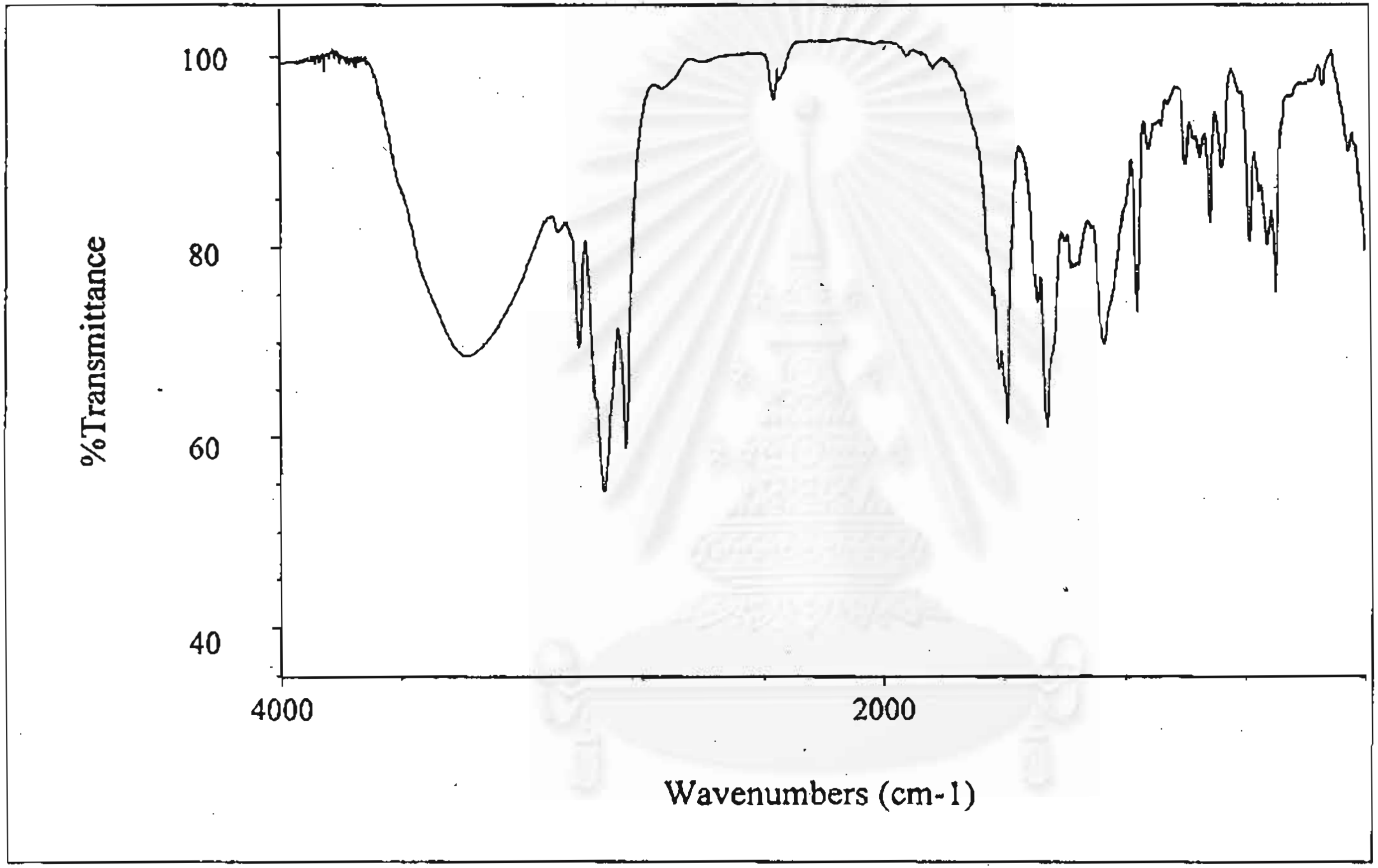

Figure B.1 Infrared spectrum of cardanol

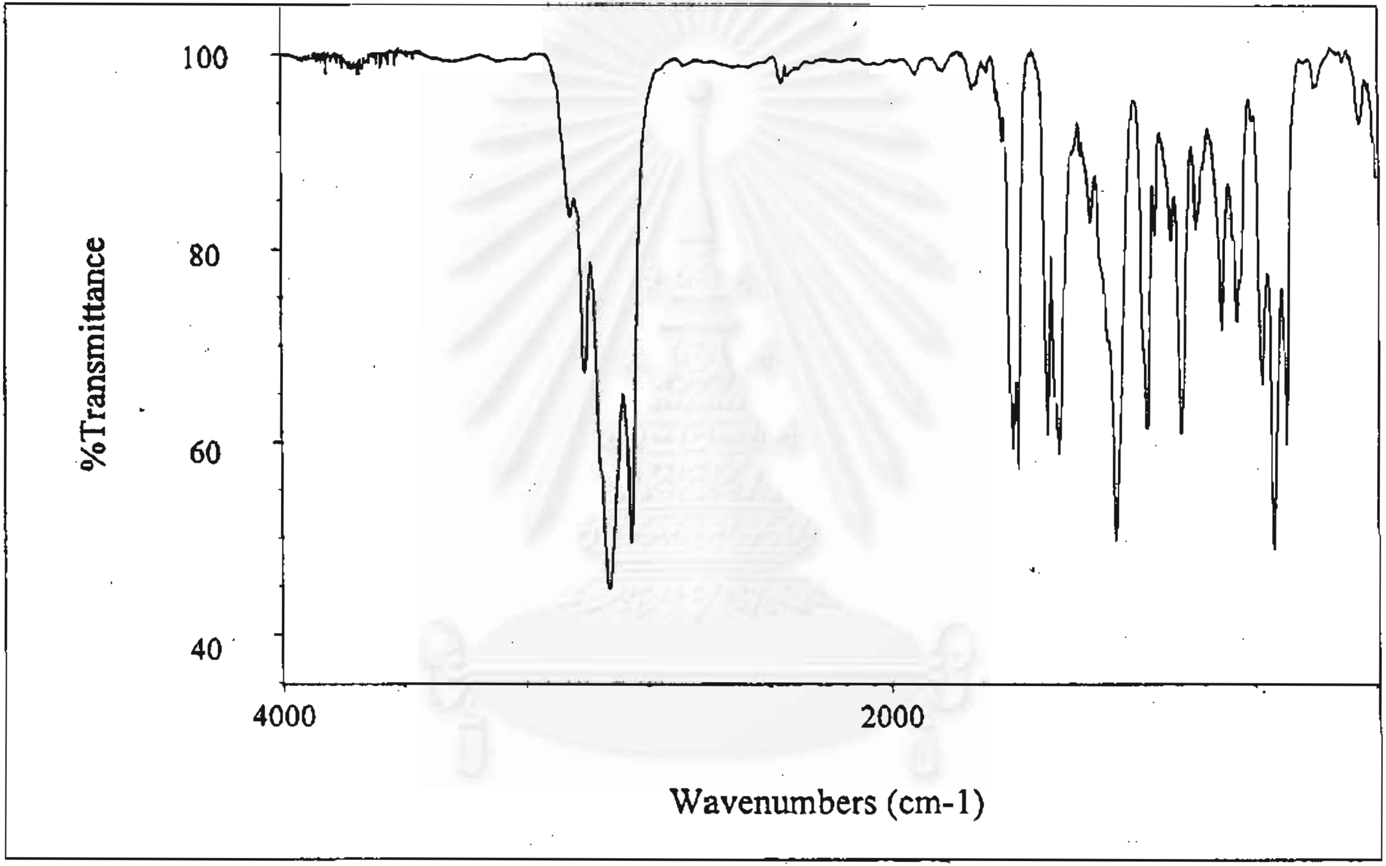

Figure B.2 Infrared spectrum of glycidyl 3-pentadecenylphenyl ether (GPPE)

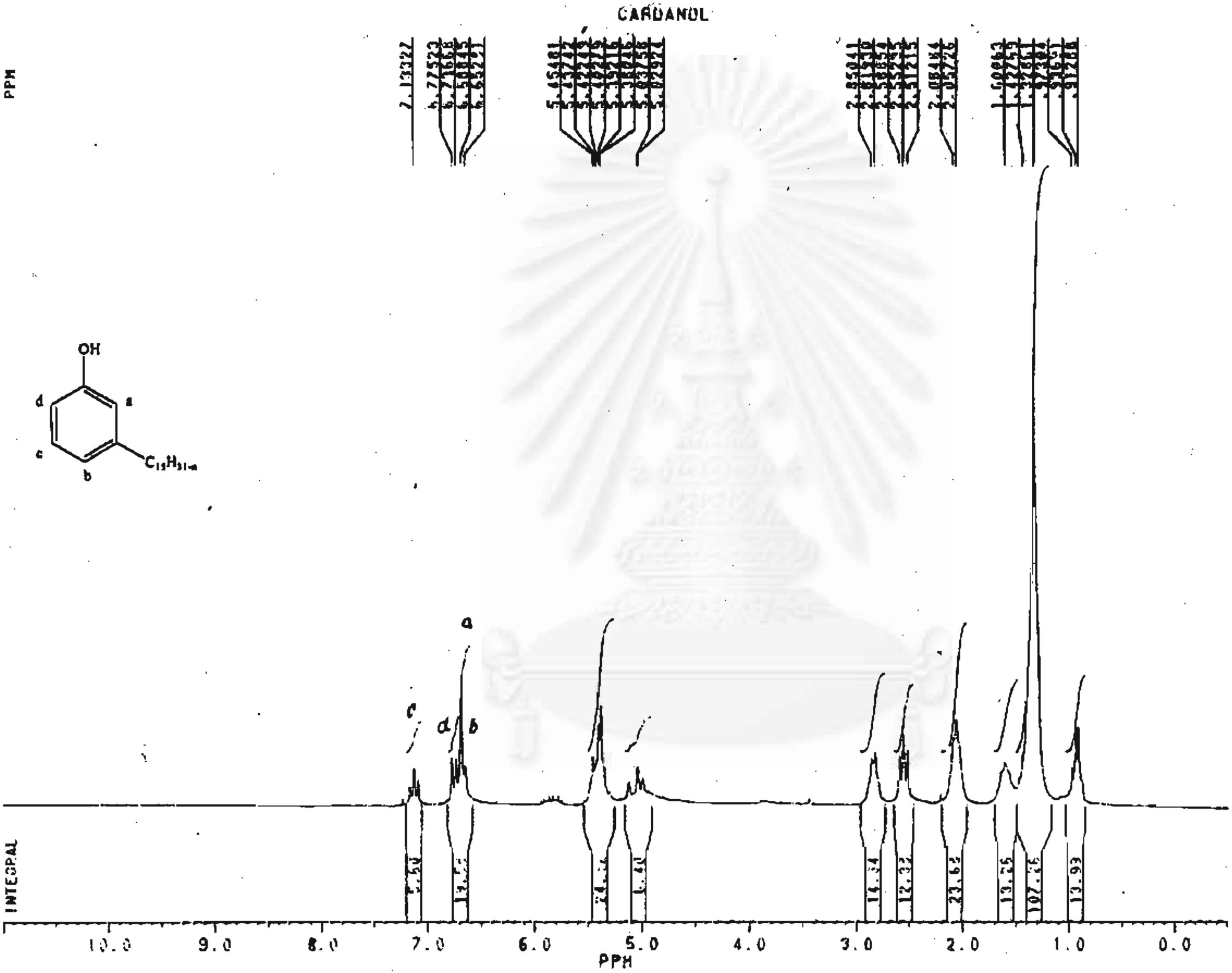

Figure C.1 ^{1}H-NMR spectrum of cardanol in $CDCl_3$

Nuclear Magnetic Resonance Spectra

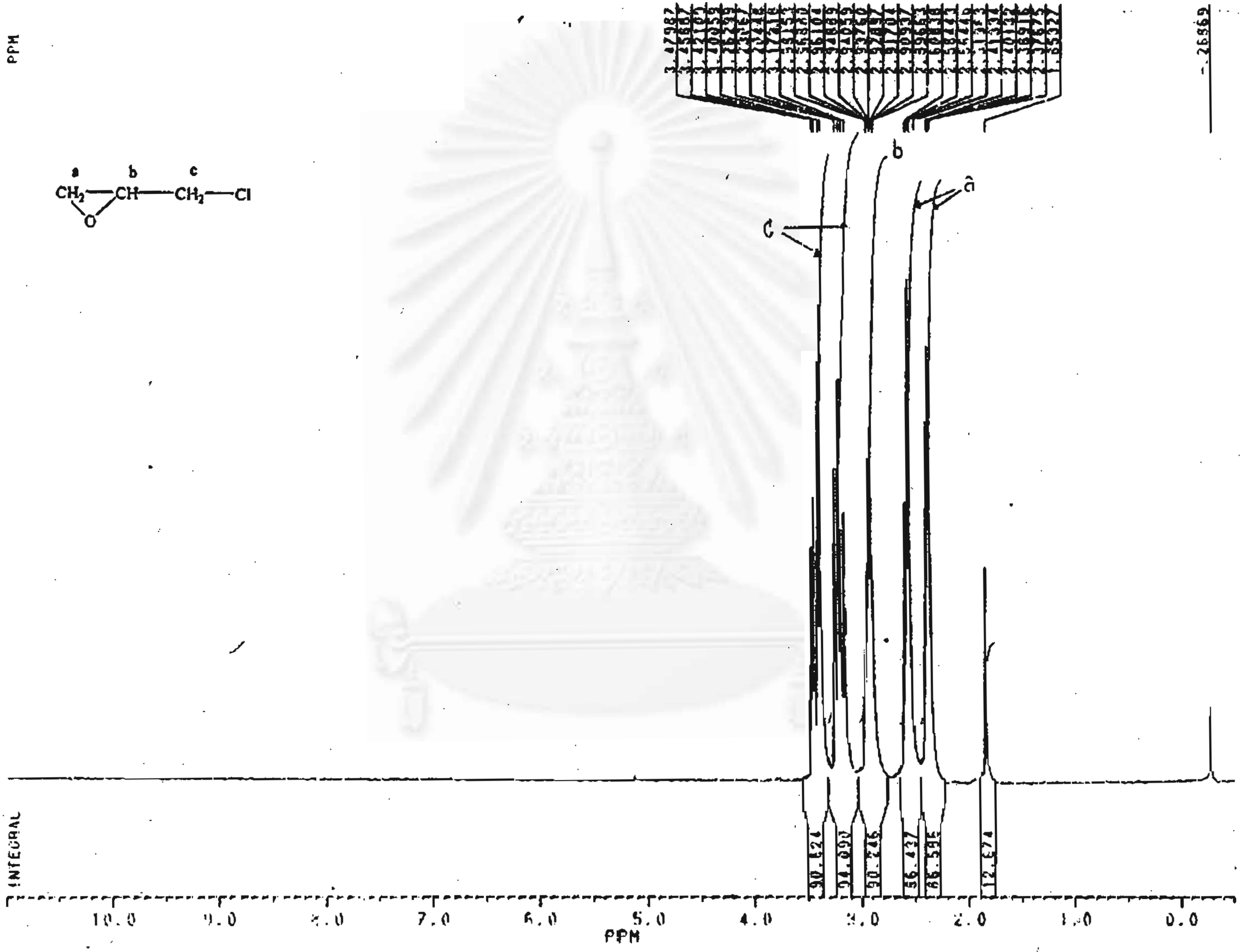

Figure C.2 ^{1}H-NMR spectrum of epichlorohydrin in $CDCl_3$

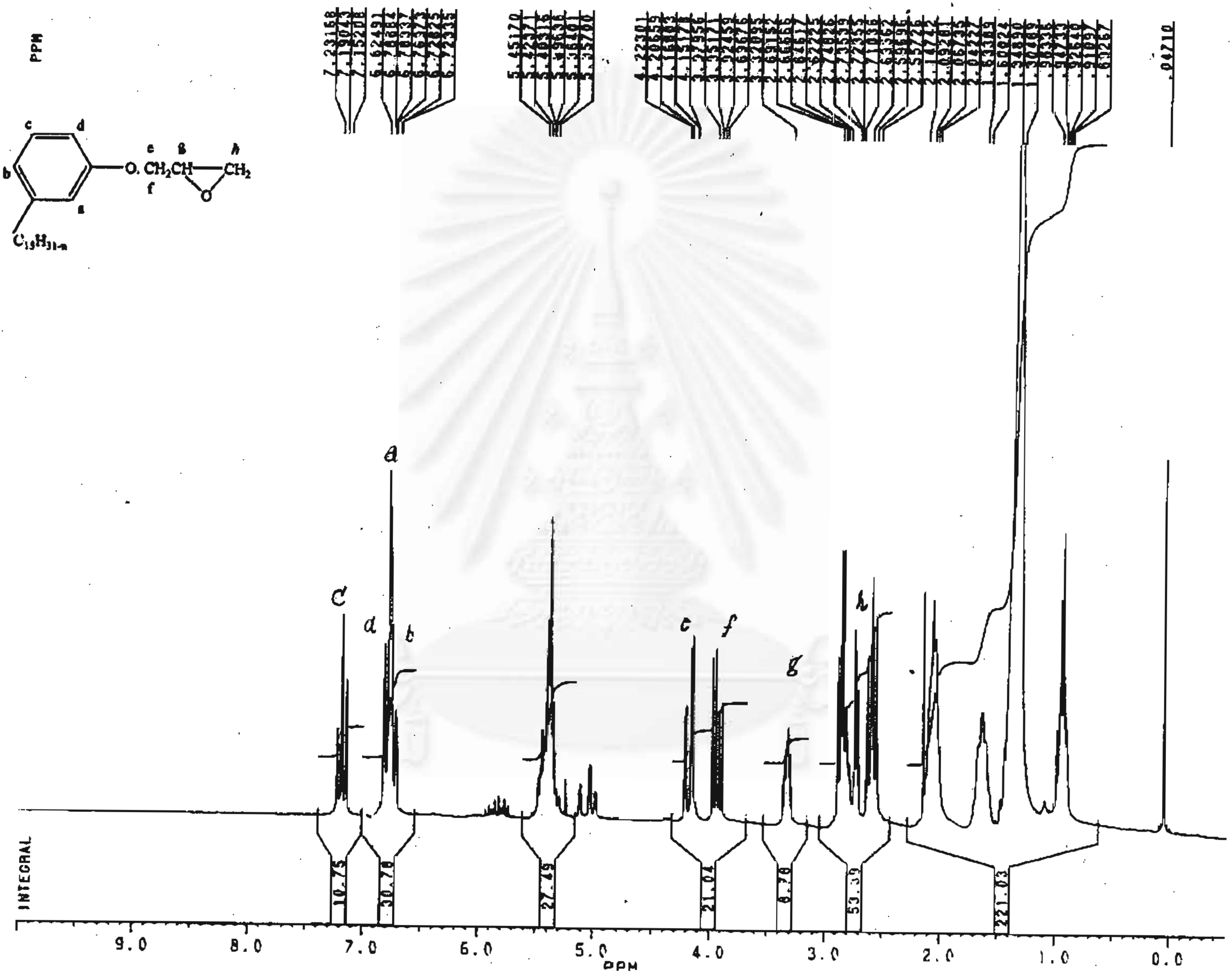

Figure C.3 ^{1}H-NMR spectrum of glycidyl 3-pentadecenylphenyl ether in $CDCl_3$

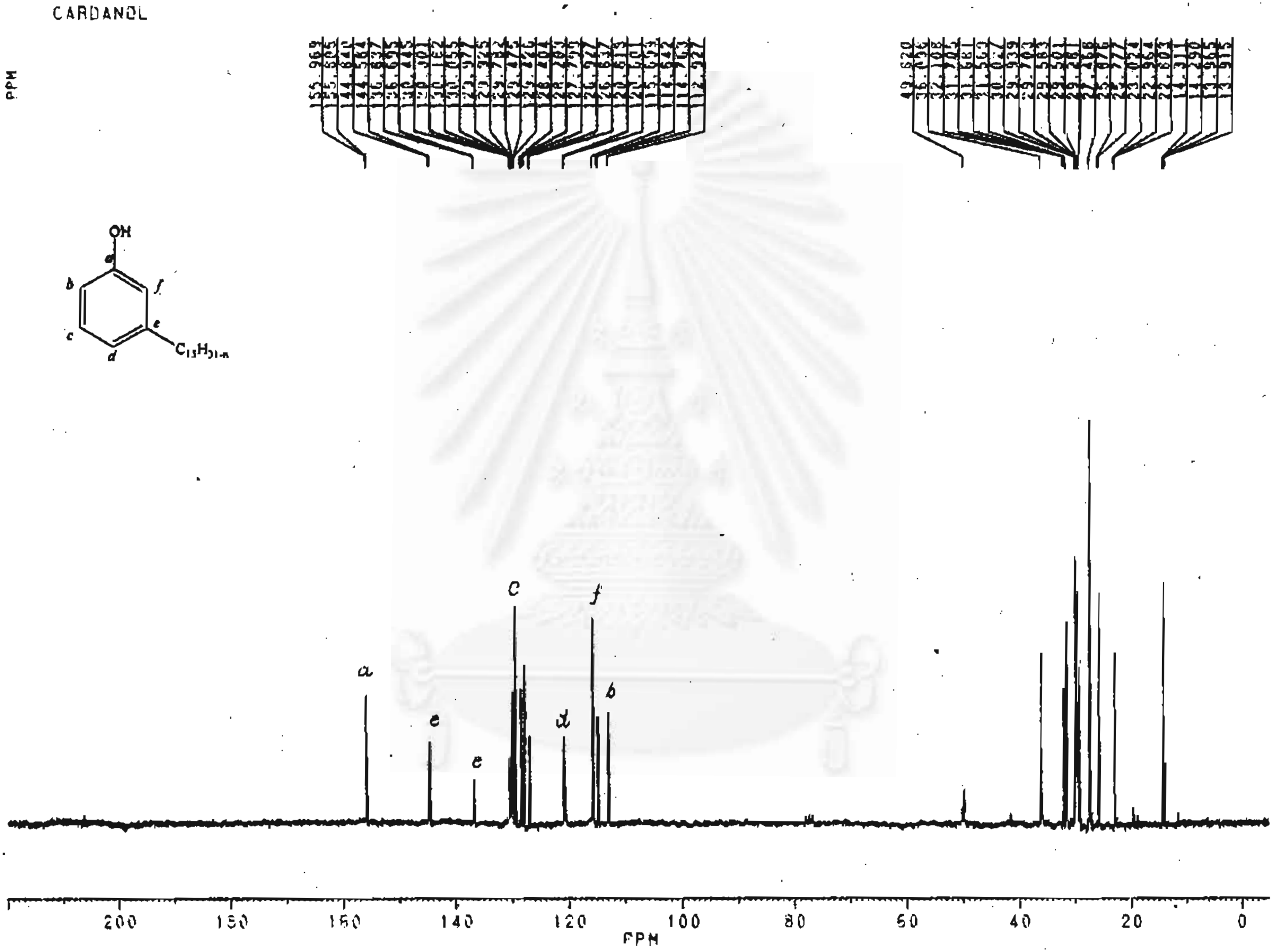

Figure C.4 ^{13}C-NMR spectrum of cardanol in $CDCl_3$

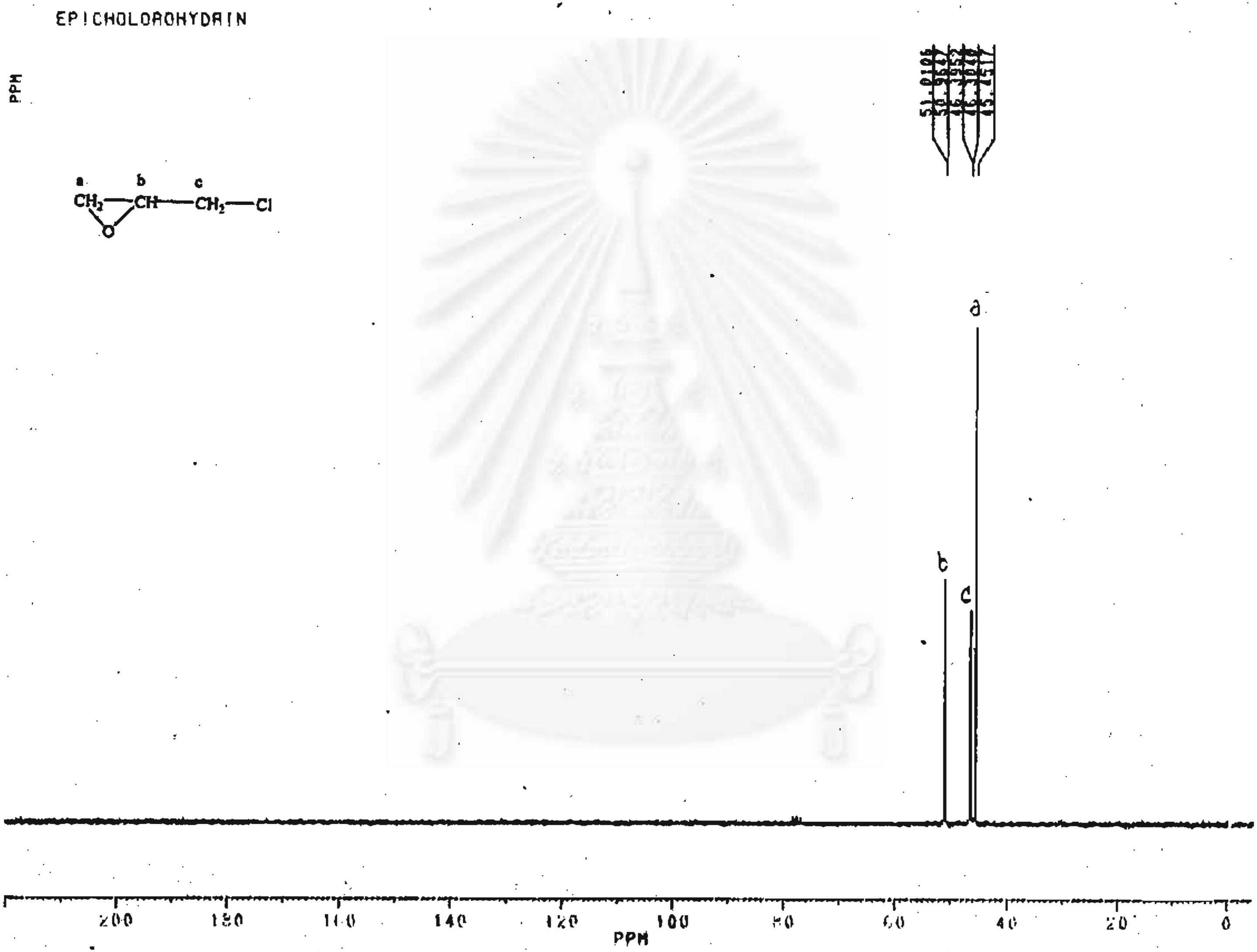

Figure C.5 ^{13}C-NMR spectrum of epichlorohydrin in $CDCl_3$

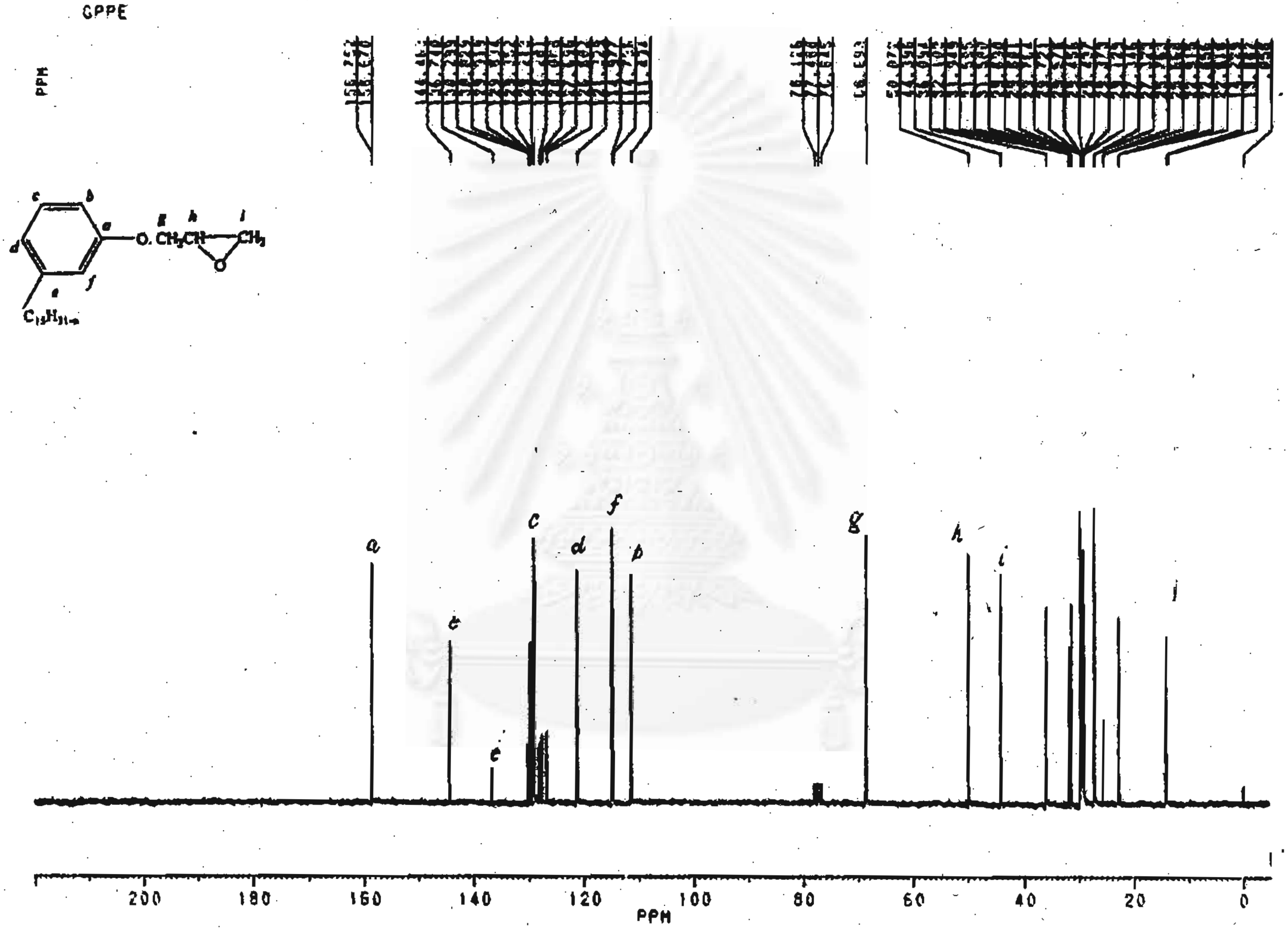

Figure C.6 ^{13}C-NMR spectrum of glycidyl 3-pentadecenylphenyl ether in $CDCl_3$

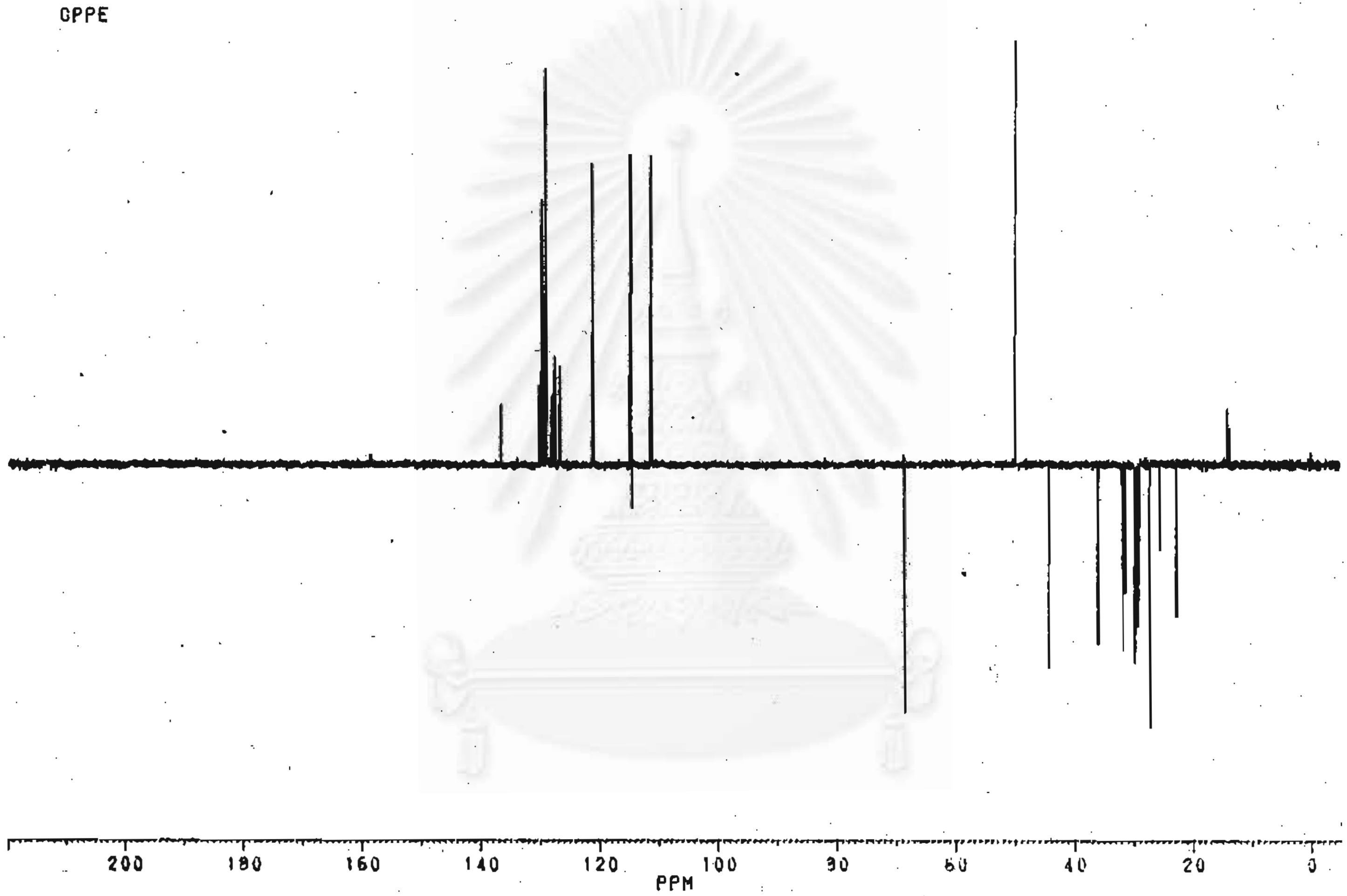

Figure C.7 Dept 135-NMR spectrum of glycidyl 3-pentadecenylphenyl ether in $CDCl_3$

APPENDIX D

Thermogravimetric Analysis Curves

Thermogravimetric analysis was used to determine the thermal stability characteristic of GPPE modified natural rubber. The conditions of testing are as follows:

Sample weight	1.7 mg
Temperature	50 - 650ºC
Heating rate	20ºC/min.

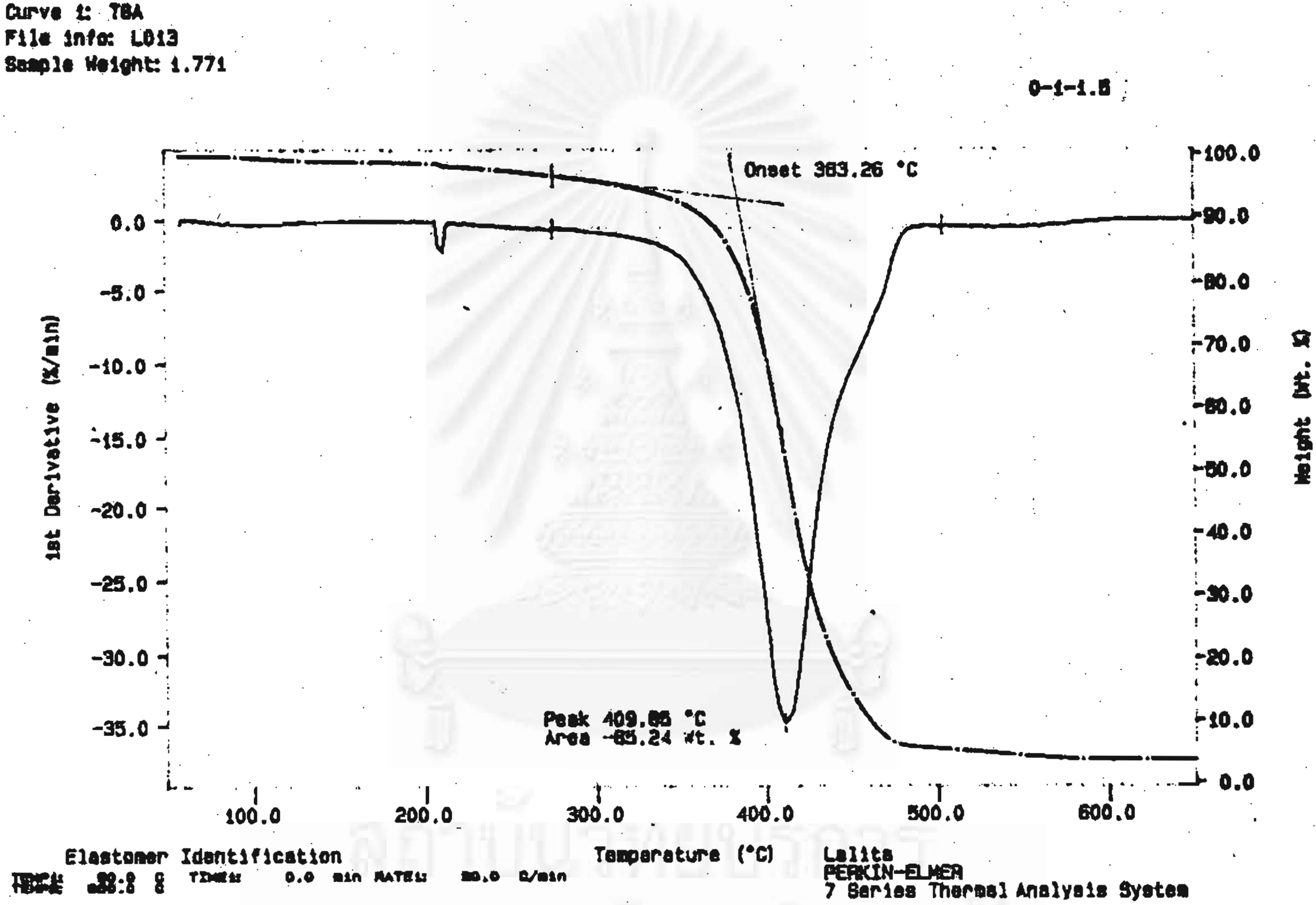

Figure D.1 Thermogravimetric analysis curve of unmodified natural rubber vulcanizate

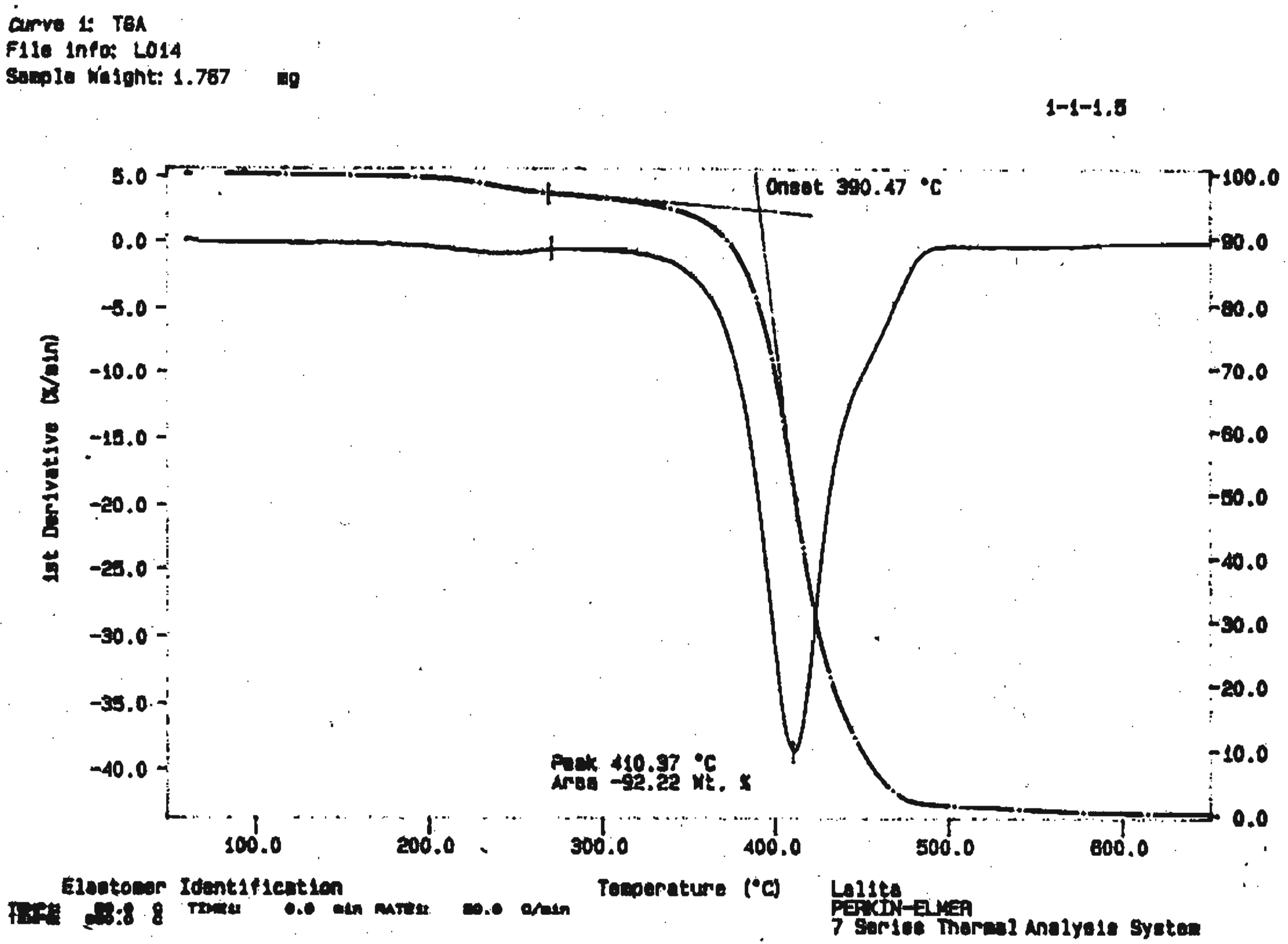

Figure D.2 Thermogravimetric analysis curve of GPPE 1 phr modified rubber vulcanizate

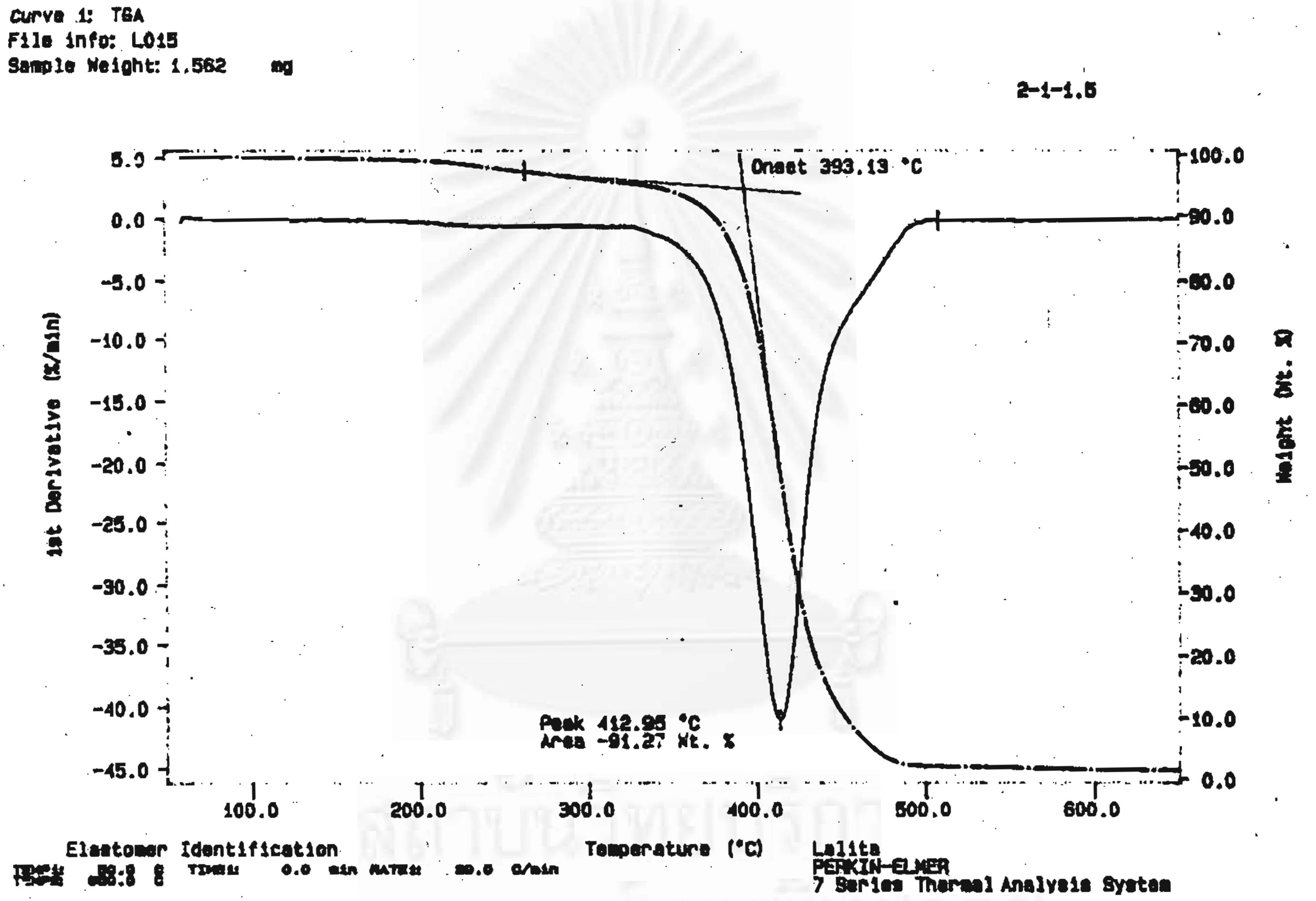

Figure D.3 Thermogravimetric analysis curve of GPPE 2 phr modified rubber vulcanizate

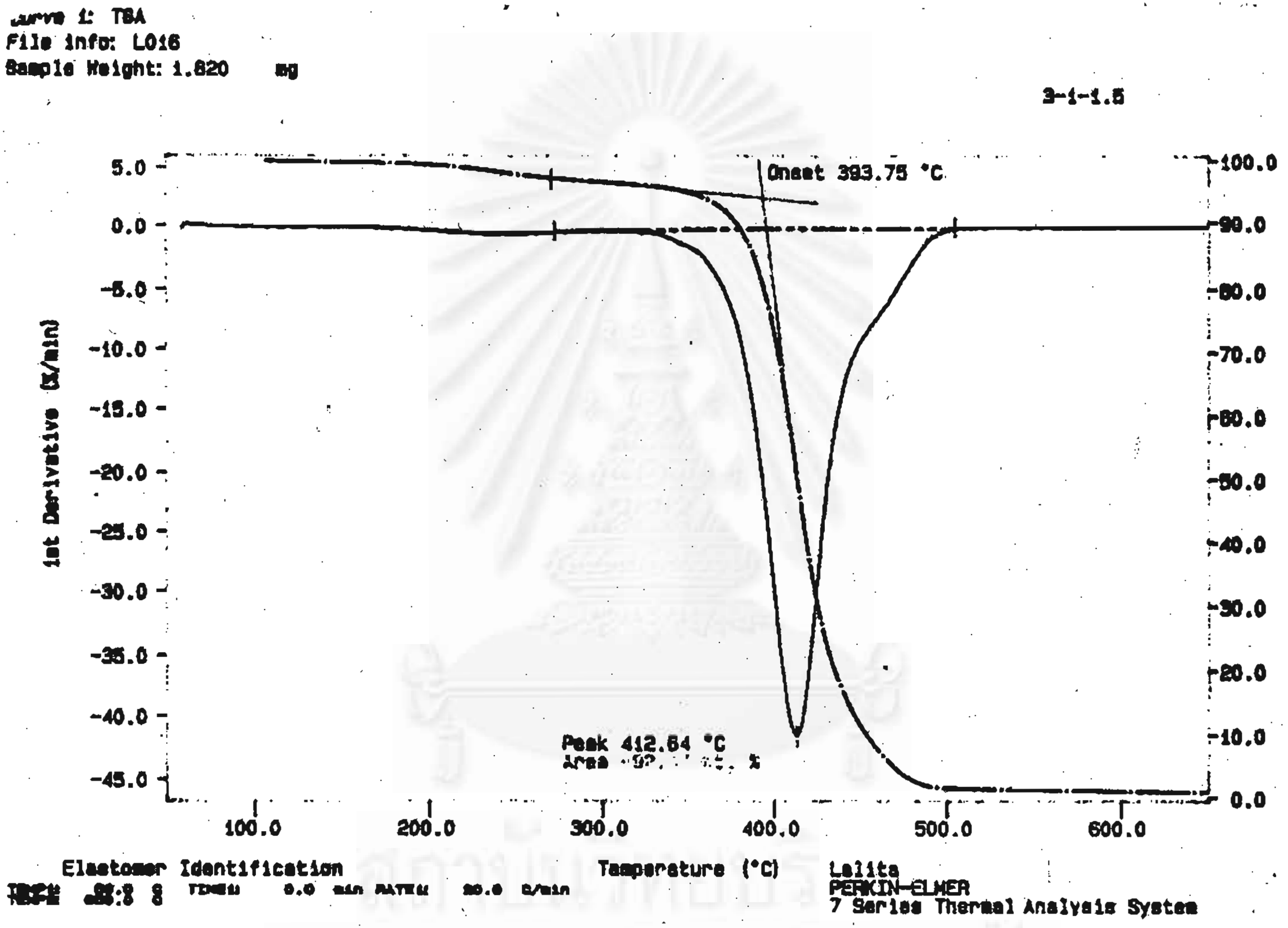

Figure D.4 Thermogravimetric analysis curve of GPPE 3 phr modified rubber vulcanizate

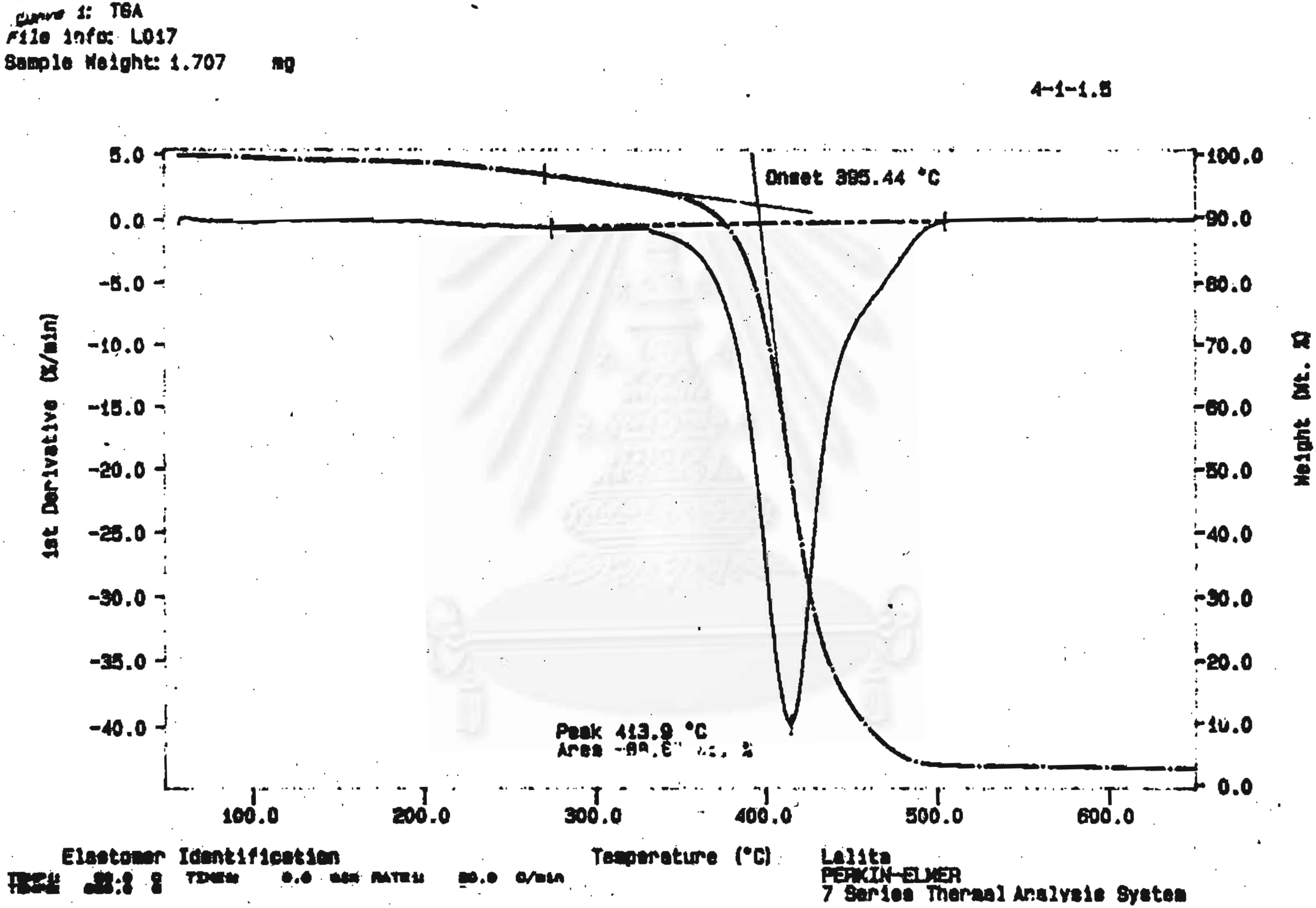

Figure D.5 Thermogravimetric analysis curve of GPPE 4 phr modified rubber vulcanizate

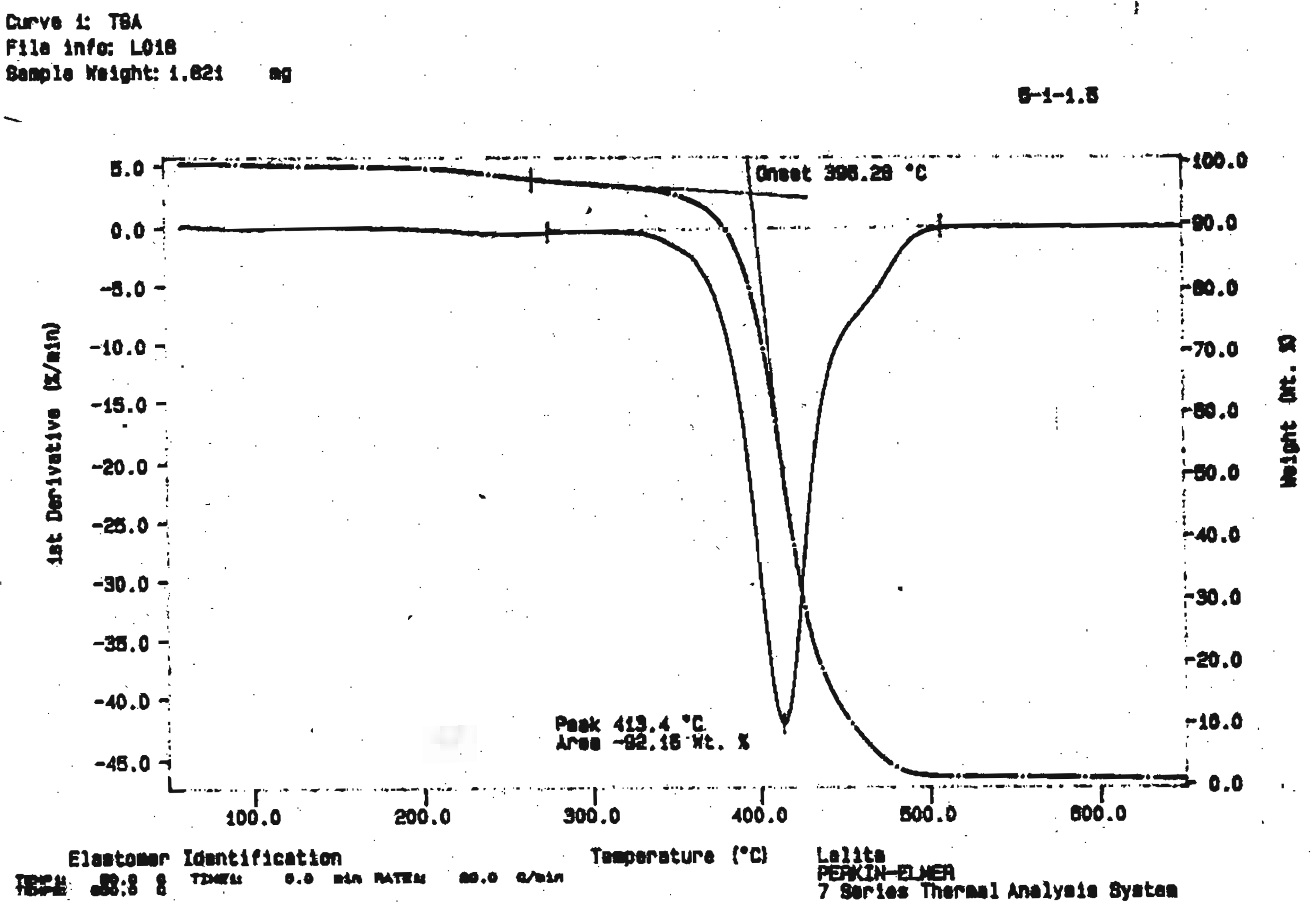

Figure D.6 Thermogravimetric analysis curve of GPPE 5 phr modified rubber vulcanizate

APPENDIX E

Mechanical Properties of Vulcanized Sheets

1. Tensile Strength of Vulcanization Sheets

Table E.1 Tensile strength of vulcanized sheets of using Tergitol NP10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Tensile Strength (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	8.32	8.46	8.39	±0.07
	1	10.45	9.78	10.12	±0.33
	2	10.48	10.45	10.47	±0.02
	3	7.15	7.05	7.10	±0.05
	4	6.87	6.68	6.77	±0.09
	5	1.18	1.23	1.21	±0.03
1.0	0	8.52	7.76	8.14	±0.38
	1	9.49	9.70	9.60	±0.10
	2	10.94	10.61	10.78	±0.17
	3	7.93	7.18	7.55	±0.37
	4	5.94	5.52	5.73	±0.21
	5	1.53	1.70	1.62	±0.09
2.0	0	8.12	8.27	8.20	±0.08
	1	9.12	9.18	9.15	±0.03
	2	6.78	6.50	6.64	±0.14
	3	4.99	4.85	4.93	±0.08
	4	3.30	3.08	3.18	±0.10
	5	1.65	1.71	1.68	±0.03

Table E.2 Tensile strength of vulcanized sheets of using Tergitol NP10 of 1.5 phr

Mixing Time (hr)	GPPE (phr)	Tensile Strength (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	8.65	8.55	8.60	±0.05
	1	9.62	8.92	9.27	±0.35
	2	10.48	10.33	10.41	±0.08
	3	9.95	8.65	9.30	±0.65
	4	8.74	9.15	8.95	±0.21
	5	7.45	8.88	8.16	±0.71
1.0	0	9.09	8.55	8.82	±0.27
	1	17.13	16.28	16.71	±0.43
	2	16.50	16.54	16.52	±0.02
	3	12.17	12.13	12.15	±0.02
	4	10.73	9.95	10.34	±0.39
	5	9.59	9.24	9.41	±0.17
2.0	0	8.30	8.36	8.33	±0.03
	1	12.72	11.16	10.94	±0.78
	2	16.00	16.40	16.20	±0.20
	3	11.50	11.97	11.73	±0.23
	4	9.38	10.82	10.10	±0.72
	5	6.99	6.66	6.83	±0.17

Table E.3 Tensile strength of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Tensile Strength (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	9.22	8.80	9.01	±0.21
	1	12.32	11.16	11.74	±0.58
	2	12.04	11.42	11.73	±0.31
	3	10.97	12.65	11.81	±0.84
	4	12.13	11.22	11.68	±0.46
	5	10.38	11.03	10.73	±0.35
1.0	0	9.63	8.28	8.95	±0.67
	1	13.96	14.14	14.05	±0.09
	2	12.82	13.20	13.01	±0.19
	3	12.63	12.37	12.50	±0.13
	4	10.47	9.28	9.88	±0.60
	5	8.43	9.45	8.83	±0.40
2.0	0	9.02	7.47	8.24	±0.77
	1	10.43	10.87	10.65	±0.22
	2	10.51	10.36	10.44	±0.08
	3	13.04	13.66	13.35	±0.31
	4	10.23	10.49	10.36	±0.13
	5	9.97	10.54	10.25	±0.28

Table E.4 Tensile strength of vulcanized sheets of using SDS of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Tensile Strength (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	1.27	1.15	1.21	±0.06
	1	1.62	1.63	1.63	±0.01
	2	1.22	1.16	1.19	±0.03
	3	0.55	0.56	0.56	±0.01
	4	0.29	0.35	0.32	±0.03
	5	0.26	0.27	0.27	±0.01
1.0	0	1.76	1.63	1.70	±0.07
	1	1.94	2.13	2.03	±0.09
	2	0.88	0.90	0.89	±0.01
	3	0.64	0.65	0.65	±0.01
	4	0.35	0.38	0.36	±0.02
	5	0.26	0.23	0.24	±0.02
2.0	0	1.35	1.28	1.32	±0.04
	1	2.00	1.72	1.86	±0.14
	2	1.79	1.79	1.77	±0.00
	3	0.80	0.78	0.79	±0.01
	4	0.32	0.39	0.36	±0.04
	5	0.29	0.27	0.28	±0.01

2. Elongation of Vulcanized Sheets

Table E.5 Elongation of vulcanized sheets of using Tergitol NP10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Elongation (%)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	798.70	799.00	798.85	±0.25
	1	1253.50	1255.70	1254.60	±1.10
	2	1887.00	1889.95	1888.48	±1.48
	3	853.00	854.00	853.50	±0.50
	4	811.00	813.90	812.45	±1.45
	5	813.40	807.00	810.20	±3.20
1.0	0	853.30	849.00	851.15	±2.15
	1	1817.00	1822.00	1819.50	±2.50
	2	2229.00	2234.00	2231.50	±2.50
	3	1212.80	1216.00	1214.40	±1.60
	4	854.50	860.00	857.25	±2.75
	5	780.60	784.30	782.45	±1.85
2.0	0	835.80	836.60	836.20	±0.40
	1	1785.70	1787.60	1786.65	±0.95
	2	1674.60	1678.20	1676.40	±1.80
	3	871.20	878.00	874.60	±3.40
	4	820.00	824.00	822.00	±2.00
	5	887.00	888.00	887.50	±0.50

Table E.6 Elongation of vulcanized sheets of using Tergitol NP10 of 1.5 phr

Mixing Time (hr)	GPPE (phr)	Elongation (%)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	772.50	768.20	770.35	±2.15
	1	1258.00	1262.00	1260.00	±2.00
	2	1526.00	1529.80	1527.90	±1.90
	3	1211.60	1213.00	1212.30	±0.70
	4	881.80	879.20	880.50	±1.30
	5	860.20	864.30	862.25	±2.05
1.0	0	860.90	862.60	861.75	±0.85
	1	1464.70	1468.80	1466.75	±2.05
	2	2314.00	2316.00	2315.00	±1.00
	3	1331.80	1336.00	1333.90	±2.10
	4	1222.00	1227.70	1224.85	±2.85
	5	902.90	911.00	906.95	±4.05
2.0	0	848.70	850.70	849.70	±1.00
	1	1806.00	1814.00	1810.00	±4.00
	2	2277.00	2280.00	2278.50	±1.50
	3	1752.20	1761.50	1756.85	±4.65
	4	1566.10	1570.40	1568.25	±2.15
	5	920.00	923.90	921.95	±1.95

Table E.7 Elongation of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Elongation (%)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	728.30	731.70	730.00	±1.70
	1	1724.00	1726.00	1725.00	±1.00
	2	2164.00	2167.00	2165.50	±1.50
	3	1364.70	1368.00	1366.35	±1.65
	4	924.20	923.50	923.85	±0.35
	5	917.60	919.70	918.65	±1.05
1.0	0	740.00	743.80	741.90	±1.70
	1	1424.00	1425.20	1424.60	±0.60
	2	2077.00	2078.00	2077.50	±0.50
	3	840.00	842.60	841.30	±1.30
	4	837.70	839.10	838.40	±0.70
	5	796.70	800.90	798.80	±2.10
2.0	0	765.80	767.00	766.40	±0.60
	1	1829.00	1825.67	1827.34	±1.67
	2	1367.27	1366.00	1366.64	±0.64
	3	853.00	858.97	855.99	±2.99
	4	835.20	842.00	838.60	±3.40
	5	840.00	842.50	841.25	±1.25

Table E.8 Elongation of vulcanized sheets of using SDS of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Elongation (%)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	877.30	870.70	874.00	±3.30
	1	796.60	801.70	799.15	±2.55
	2	729.38	727.50	728.44	±0.94
	3	636.90	637.10	637.00	±0.10
	4	601.67	605.00	603.34	±1.67
	5	404.67	410.60	407.64	±2.97
1.0	0	874.00	879.30	876.65	±2.65
	1	854.90	858.00	856.45	±1.55
	2	779.15	776.32	777.74	±1.42
	3	725.30	730.63	727.97	±2.67
	4	676.40	680.60	678.50	±2.10
	5	670.90	676.00	673.45	±2.55
2.0	0	841.40	846.20	843.80	±2.40
	1	866.80	870.00	868.40	±1.60
	2	777.03	780.70	778.87	±1.84
	3	638.00	632.40	635.20	±2.80
	4	575.10	578.00	576.55	±1.45
	5	515.07	518.63	516.85	±1.78

3. Modulus 300% of Vulcanized Sheets

Table E.9 Modulus 300% of vulcanized sheets of using Tergitol NP10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Modulus 300% (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	0.9076	0.9105	0.9091	±0.0015
	1	1.1360	1.2120	1.1740	±0.0380
	2	0.7921	0.7828	0.7875	±0.0047
	3	0.8346	0.8028	0.8187	±0.0159
	4	0.7483	0.7478	0.7481	±0.0003
	5	0.3955	0.3895	0.3925	±0.0030
1.0	0	0.9551	0.9391	0.9471	±0.0080
	1	1.0490	1.4390	1.2440	±0.1950
	2	0.9843	1.1520	1.0682	±0.0839
	3	0.8980	0.9126	0.9053	±0.0073
	4	0.7848	0.7139	0.7494	±0.0355
	5	0.5356	0.5462	0.5409	±0.0053
2.0	0	1.0916	0.8798	0.9857	±0.1059
	1	1.1143	0.9798	1.0471	±0.0673
	2	0.9856	0.9842	0.9849	±0.0007
	3	0.9015	0.9466	0.9241	±0.0226
	4	0.8952	0.8421	0.8686	±0.0265
	5	0.8880	0.7891	0.8386	±0.0495

Table E.10 Modulus 300% of vulcanized sheets of using Tergitol NP10 1.5 phr

Mixing Time (hr)	GPPE (phr)	Modulus 300% (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	1.2287	0.9022	1.0655	±0.1633
	1	1.2522	1.0680	1.1601	±0.0921
	2	0.9914	0.9327	0.9621	±0.0294
	3	0.9696	0.8718	0.9207	±0.0489
	4	0.8050	0.7522	0.7786	±0.0264
	5	0.7670	0.7860	0.7765	±0.0095
1.0	0	0.9405	0.9890	0.9648	±0.0243
	1	1.2258	1.2260	1.2259	±0.0001
	2	1.1242	1.1400	1.1321	±0.0079
	3	1.0590	1.1195	1.0893	±0.0303
	4	0.9496	0.9205	0.9351	±0.0146
	5	0.7920	0.8047	0.7984	±0.0064
2.0	0	1.1120	0.9710	1.0415	±0.0705
	1	1.1540	1.1650	1.1595	±0.0055
	2	1.1100	1.3870	1.2485	±0.1385
	3	1.2750	1.0730	1.1740	±0.1010
	4	1.1400	1.0560	1.0980	±0.0420
	5	0.7912	0.8606	0.8259	±0.0347

Table E.11 Modulus 300% of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Modulus 300% (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	1.0554	0.9871	1.0213	±0.0342
	1	1.1220	0.9437	1.0329	±0.0892
	2	0.9529	0.8664	0.9097	±0.0433
	3	0.9242	0.8531	0.8887	±0.0356
	4	1.1230	1.0470	1.0850	±0.0380
	5	0.9242	0.9782	0.9512	±0.0270
1.0	0	1.2350	1.3800	1.3075	±0.0725
	1	1.1620	1.2650	1.2135	±0.0515
	2	1.1750	1.3520	1.2635	±0.0885
	3	0.9764	0.9495	0.9630	±0.0135
	4	0.7659	0.8547	0.8103	±0.0444
	5	0.6793	0.7348	0.7070	±0.0277
2.0	0	1.0535	0.9944	1.0240	±0.0296
	1	1.5070	1.9030	1.7050	±0.1980
	2	1.0440	1.1780	1.1110	±0.0670
	3	0.8351	0.8360	0.8356	±0.0005
	4	0.6771	0.6819	0.6790	±0.0019
	5	0.7806	0.7540	0.7673	±0.0133

Table E.12 Modulus 300% of vulcanized sheets of using SDS of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Modulus 300% (MPa)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	0.4830	0.4783	0.4807	±0.0024
	1	0.5863	0.5686	0.5775	±0.0089
	2	0.4503	0.4591	0.4547	±0.0044
	3	0.4137	0.4088	0.4113	±0.0025
	4	0.2206	0.2160	0.2183	±0.0023
	5	0.2424	0.2663	0.2544	±0.0120
1.0	0	0.5010	0.4808	0.4909	±0.0101
	1	0.4303	0.5981	0.5142	±0.0839
	2	0.3694	0.3961	0.3828	±0.0134
	3	0.3295	0.3363	0.3329	±0.0034
	4	0.2737	0.2833	0.2785	±0.0048
	5	0.1894	0.1953	0.1924	±0.0030
2.0	0	0.5097	0.4705	0.4901	±0.0196
	1	0.4150	0.4500	0.4325	±0.0175
	2	0.4820	0.4215	0.4518	±0.0303
	3	0.3211	0.3228	0.3220	±0.0009
	4	0.2693	0.2766	0.2730	±0.0037
	5	0.2607	0.2719	0.2663	±0.0056

4. Hardness of Vulcanized Sheets

Table E.13 Hardness of vulcanized sheets of using Tergitol NP 10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Hardness (shore A)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	28.30	28.50	28.40	±0.10
	1	35.00	33.20	34.10	±0.90
	2	28.20	26.90	27.55	±0.65
	3	24.00	26.50	25.25	±1.25
	4	23.40	24.60	24.00	±0.60
	5	14.70	14.00	14.35	±0.35
1.0	0	27.20	28.10	27.65	±0.45
	1	32.70	33.50	33.10	±0.40
	2	27.50	28.00	27.75	±0.25
	3	27.60	27.20	27.40	±0.20
	4	25.50	24.90	25.20	±0.30
	5	20.00	19.50	19.75	±0.25
2.0	0	27.70	28.40	28.05	±0.35
	1	29.80	28.30	29.05	±0.75
	2	27.40	26.50	26.95	±0.45
	3	27.10	26.50	26.30	±0.20
	4	24.90	25.00	24.95	±0.05
	5	20.10	18.70	19.40	±0.70

Table E.14 Hardness of vulcanized sheets of using Tergitol NP10 of 1.5 phr

Mixing Time (hr)	GPPE (phr)	Hardness (shore A)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	33.40	32.20	32.80	±0.60
	1	34.50	32.80	33.65	±0.85
	2	31.90	31.10	31.50	±0.40
	3	30.00	31.40	30.70	±0.70
	4	27.20	27.40	27.30	±0.10
	5	23.20	22.10	22.65	±0.55
1.0	0	32.20	33.50	32.85	±0.65
	1	36.10	35.80	35.95	±0.15
	2	32.60	32.40	32.50	±0.10
	3	30.00	30.10	30.05	±0.05
	4	27.00	27.40	27.20	±0.20
	5	25.10	23.40	24.25	±0.85
2.0	0	32.70	33.40	33.05	±0.35
	1	32.60	33.20	32.90	±0.30
	2	30.40	30.70	30.55	±0.15
	3	29.40	29.90	29.65	±0.25
	4	28.60	27.90	28.25	±0.35
	5	23.20	24.70	23.95	±0.75

Table E.15 Hardness of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Hardness (shore A)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	30.00	30.80	30.40	±0.40
	1	30.60	30.90	30.75	±0.15
	2	29.60	29.80	29.70	±0.10
	3	27.30	26.90	27.10	±0.20
	4	27.70	27.00	27.35	±0.35
	5	26.50	25.90	26.20	±0.30
1.0	0	29.80	29.80	29.80	±0.00
	1	29.70	29.90	29.80	±0.10
	2	27.80	27.80	27.80	±0.00
	3	26.90	26.80	26.85	±0.05
	4	24.60	24.60	24.60	±0.00
	5	24.50	24.30	24.40	±0.10
2.0	0	30.20	28.70	29.45	±0.75
	1	29.80	30.10	29.95	±0.15
	2	27.70	27.30	27.50	±0.20
	3	26.60	26.90	26.75	±0.15
	4	25.10	25.70	25.40	±0.30
	5	26.10	25.70	25.90	±0.20

Table E.16 Hardness of vulcanized sheets of using SDS of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Hardness (shore A)		Average	SD
		1st Experiment	2nd Experiment		
0.5	0	16.10	16.50	16.30	±0.20
	1	17.10	17.40	17.25	±0.15
	2	16.20	16.70	16.45	±0.25
	3	11.80	12.20	12.00	±0.20
	4	9.90	10.30	10.10	±0.20
	5	9.80	9.60	9.70	±0.10
1.0	0	17.70	17.20	17.45	±0.25
	1	17.60	17.60	17.60	±0.00
	2	16.30	16.70	16.50	±0.20
	3	12.20	11.90	12.05	±0.15
	4	10.80	11.20	11.00	±0.20
	5	9.20	10.10	9.65	±0.45
2.0	0	17.80	17.50	17.65	±0.15
	1	18.10	17.70	17.90	±0.20
	2	18.40	17.60	18.00	±0.40
	3	12.60	12.60	12.60	±0.00
	4	11.00	11.30	11.15	±0.15
	5	8.80	8.90	8.85	±0.05

APPENDIX F

Ageing Properties

Thermal ageing was used to determine the retention in mechanical properties of the vulcanized sheets after ageing. The conditions of testing are shown as follows:

Temperature : 70 ± 1°C

Duration of testing : 72 hours

1. Tensile strength

Table F.1 Tensile strength of vulcanized sheets of using Tergitol NP10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Tensile strength (MPa)		
		Unaged	Aged	Percentage Change
0.5	0	8.39	6.71	-20.05
	1	10.12	9.78	-3.40
	2	10.47	10.40	-0.65
	3	7.10	7.42	4.45
	4	6.77	7.07	4.46
	5	1.21	1.28	7.87
1.0	0	8.14	6.44	-20.91
	1	9.60	9.64	0.41
	2	10.78	10.85	0.63
	3	7.55	7.43	-1.59
	4	5.73	5.34	-6.84
	5	1.62	1.57	-3.15
2.0	0	8.20	6.28	-23.43
	1	9.15	9.79	6.96
	2	6.64	6.74	1.48
	3	4.93	5.09	3.33
	4	3.18	3.20	0.75
	5	1.68	1.58	-5.95

Table F.2 Tensile strength of vulcanized sheets of using Tergitol NP10 of 1.5 phr

Mixing Time (hr)	GPPE (phr)	Tensile strength (Mpa)		
		Unaged	Aged	Percentage Change
0.5	0	8.60	6.49	-24.59
	1	9.27	9.25	-0.18
	2	10.41	10.56	1.51
	3	9.30	9.53	2.47
	4	8.95	9.23	3.21
	5	8.16	8.44	3.43
1.0	0	8.82	6.76	-23.40
	1	16.71	16.71	0.04
	2	16.52	16.75	1.39
	3	12.15	12.40	2.06
	4	10.34	10.57	2.23
	5	9.41	9.65	2.56
2.0	0	8.33	6.34	-23.92
	1	11.94	11.87	-0.56
	2	12.98	12.96	-0.11
	3	11.73	11.88	1.24
	4	10.10	10.23	1.31
	5	6.83	6.97	2.11

Table F.3 Tensile strength of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Tensile strength (Mpa)		
		Unaged	Aged	Percentage Change
0.5	0	9.00	8.36	-7.18
	1	11.74	11.35	-3.30
	2	11.73	12.49	6.49
	3	11.81	13.61	15.23
	4	11.68	13.38	14.60
	5	10.70	10.79	0.83
1.0	0	8.95	8.64	-3.49
	1	14.05	14.37	2.28
	2	13.01	13.40	3.00
	3	12.50	12.87	2.96
	4	9.88	10.58	7.12
	5	8.83	9.49	7.42
2.0	0	8.24	7.86	-4.63
	1	10.65	11.64	9.32
	2	10.44	11.41	9.34
	3	13.35	13.23	-0.90
	4	10.36	10.54	1.76
	5	10.25	10.27	0.16

2. Elongation

Table F.4 Elongation of vulcanized sheets of using Tergitol NP10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Elongation (%)		
		Unaged	Aged	Percentage Change
0.5	0	798.85	784.50	-1.80
	1	1254.45	1289.50	2.79
	2	1888.45	1884.00	-0.24
	3	853.45	926.50	8.56
	4	812.45	886.50	9.11
	5	810.20	832.80	2.79
1.0	0	851.15	818.50	-3.84
	1	1819.50	1942.50	6.76
	2	2231.50	2237.50	0.27
	3	1214.40	1235.50	1.74
	4	857.75	874.10	1.91
	5	782.95	813.40	3.89
2.0	0	836.20	807.50	-3.43
	1	1786.15	1815.50	1.64
	2	1676.90	1718.00	2.45
	3	847.60	965.00	10.34
	4	822.00	918.50	11.74
	5	787.50	807.00	2.47

Table F.5 Elongation of vulcanized sheets of using Tergitol NP10 of 1.5 phr

Mixing Time (hr)	GPPE (phr)	Elongation (%)		
		Unaged	Aged	Percentage Change
0.5	0	770.35	865.00	12.29
	1	1260.00	1437.00	14.05
	2	1527.90	1783.50	16.73
	3	1212.30	1262.50	4.14
	4	880.50	954.50	8.40
	5	862.25	908.00	5.31
1.0	0	861.75	868.00	0.73
	1	1466.75	1708.00	2.81
	2	2315.00	2407.00	6.57
	3	1333.90	1485.00	11.33
	4	1224.85	1369.00	11.77
	5	960.95	1069.00	11.24
2.0	0	849.70	989.50	16.45
	1	1810.00	1932.00	6.74
	2	2178.50	2307.50	5.92
	3	1756.85	1847.50	5.16
	4	1568.25	1611.50	2.76
	5	921.957	1064.50	15.46

Table F.6 Elongation of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Elongation (%)		
		Unaged	Aged	Percentage Change
0.5	0	730.00	639.90	-12.34
	1	1725.00	1836.40	6.46
	2	2165.50	2241.50	3.51
	3	1366.35	1507.20	10.31
	4	923.85	945.50	2.34
	5	918.65	929.40	1.17
1.0	0	741.90	639.90	-13.75
	1	1424.60	1307.70	-8.21
	2	2077.50	2187.00	5.27
	3	841.30	911.00	8.24
	4	838.40	904.00	7.82
	5	798.80	827.50	3.59
2.0	0	766.40	689.20	-10.07
	1	1827.34	1709.00	-6.47
	2	1366.64	1438.80	5.28
	3	855.85	872.00	1.89
	4	838.60	853.20	1.74
	5	841.25	815.70	-3.04

3. Modulus 300%

Table F.7 Modulus 300% of vulcanized sheets of using Tergitol NP10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Modulus300% (MPa)		
		Unaged	Aged	Percentage Change
0.5	0	0.9091	0.9213	1.34
	1	1.1740	1.2160	3.58
	2	0.7875	0.8173	3.78
	3	0.8187	0.8367	2.20
	4	0.7481	0.7777	3.96
	5	0.3925	0.3981	1.43
1.0	0	0.9471	0.9500	0.31
	1	1.2240	1.2924	3.89
	2	1.0682	1.1187	4.73
	3	0.9053	0.9274	2.44
	4	0.7494	0.7970	6.35
	5	0.5409	0.5920	9.45
2.0	0	0.9857	0.9880	0.23
	1	1.0471	0.1015	5.19
	2	0.9849	1.0280	4.38
	3	0.9241	0.9530	3.13
	4	0.8686	0.9100	4.77
	5	0.8386	0.8652	3.17

Table F.8 Modulus 300% of vulcanized sheets of using Tergitol NP10 of 1.5 phr

Mixing Time (hr)	GPPE (phr)	Modulus 300% (Mpa)		
		Unaged	Aged	Percentage Change
0.5	0	1.0655	1.0880	2.11
	1	1.1601	1.1820	1.89
	2	0.9621	0.9765	1.50
	3	0.9207	0.9464	2.79
	4	0.7786	0.8002	2.77
	5	0.7765	0.7982	2.79
1.0	0	0.9648	0.9773	1.30
	1	1.2259	1.2670	3.35
	2	1.1321	1.1727	3.59
	3	1.0893	1.2230	4.17
	4	0.9351	0.9748	4.25
	5	0.7984	0.8420	5.46
2.0	0	1.0415	1.0570	1.49
	1	1.1595	1.2070	4.10
	2	1.2485	1.2860	3.00
	3	1.1740	1.2080	2.90
	4	1.0980	1.1390	3.73
	5	0.8259	0.8680	5.10

Table F.9 Modulus 300% of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Modulus 300% (Mpa)		
		Unaged	Aged	Percentage Change
0.5	0	1.0213	1.0490	2.71
	1	1.0329	1.1000	6.50
	2	0.9097	0.9520	4.65
	3	0.8887	0.9320	4.87
	4	1.0850	1.1620	7.10
	5	0.9512	0.9579	0.70
1.0	0	1.3075	1.3040	-0.27
	1	1.2135	1.3840	14.05
	2	1.2635	1.2760	0.99
	3	0.9630	1.0480	8.83
	4	0.8103	0.9480	16.99
	5	0.7070	0.8290	17.26
2.0	0	1.0240	1.0190	-0.49
	1	1.7050	1.7630	3.40
	2	1.1110	1.2780	15.03
	3	0.8356	0.8636	3.35
	4	0.6790	0.7466	9.96
	5	0.7673	0.7912	3.11

4. Hardness

Table F.10 Hardness of vulcanized sheets of using Tergitol NP10 of 1.0 phr

Mixing Time (hr)	GPPE (phr)	Hardness (shore A)		
		Unaged	Aged	Hardness Change
0.5	0	28.40	29.40	1.00
	1	34.10	35.55	1.45
	2	27.55	31.75	4.20
	3	25.25	29.90	4.65
	4	24.00	28.30	4.30
	5	14.35	17.14	2.79
1.0	0	27.65	29.70	2.05
	1	33.10	34.85	1.75
	2	27.75	30.46	2.71
	3	27.40	30.15	2.75
	4	25.20	27.65	2.45
	5	19.75	22.55	2.80
2.0	0	28.05	30.25	2.20
	1	29.05	31.50	2.45
	2	26.95	29.80	2.85
	3	26.30	28.40	2.10
	4	24.95	27.80	2.85
	5	19.40	22.60	3.20

Table F.11 Hardness of vulcanized sheets of using Tergitol NP10 of 1.5 phr

Mixing Time (hr)	GPPE (phr)	Hardness (shore A)		
		Unaged	Aged	Hardness Change
0.5	0	32.80	29.60	-3.20
	1	33.65	35.15	1.50
	2	31.50	33.08	1.58
	3	30.70	32.45	1.75
	4	27.30	29.92	2.62
	5	22.65	25.45	2.80
1.0	0	32.85	31.10	-1.75
	1	35.95	36.13	0.18
	2	32.50	34.45	1.95
	3	30.05	32.45	2.40
	4	27.20	29.60	2.40
	5	24.25	26.75	2.50
2.0	0	33.05	31.00	-2.05
	1	32.90	34.30	1.40
	2	30.55	32.97	2.42
	3	29.65	32.40	2.75
	4	28.25	31.70	3.45
	5	23.95	27.15	3.20

Table F.12 Hardness of vulcanized sheets of using Tergitol NP10 of 2.0 phr

Mixing Time (hr)	GPPE (phr)	Hardness (shore A)		
		Unaged	Aged	Hardness Change
0.5	0	30.40	33.10	0.10
	1	30.75	34.95	0.35
	2	29.45	32.60	3.00
	3	27.10	31.70	4.40
	4	27.35	30.15	2.35
	5	26.20	28.65	2.15
1.0	0	29.80	32.35	2.55
	1	29.80	34.50	4.80
	2	27.80	32.50	4.70
	3	26.85	32.05	5.15
	4	24.60	27.00	2.40
	5	24.40	26.50	2.00
2.0	0	29.95	32.05	1.85
	1	29.95	34.04	4.24
	2	27.50	32.35	4.65
	3	26.75	30.74	4.14
	4	25.40	28.70	4.50
	5	25.90	27.20	1.10

APPENDIX G

Percent Crosslinking

Table G.1 Percent crosslinkimg of using Tergitol NP10 of 1.0 phr

GPPE Concentration (phr)	Crosslinking (%)		
	0.5 hr	1.0 hr	2.0 hr
0	92.0	92.0	91.5
1	94.0	94.5	93.5
2	94.0	94.5	93.5
3	94.0	94.5	93.5
4	93.5	94.0	93.0
5	93.5	94.0	93.0

Table G.2 Percent crosslinking of using Tergitol NP10 of 1.5 phr

GPPE Concentration (phr)	Crosslinking (%)		
	0.5 hr	1.0 hr	2.0 hr
0	92.0	92.5	92.5
1	94.0	95.0	94.5
2	94.5	95.5	95.0
3	94.5	95.5	95.0
4	94.5	95.5	95.0
5	94.0	94.5	94.5

Table G.3 Percent crosslinking of using Tergitol NP10 of 2.0 phr

GPPE Concentration (phr)	Crosslinking (%)		
	0.5 hr	1.0 hr	2.0 hr
0	90.5	91.0	91.0
1	93.5	94.0	94.0
2	93.5	94.0	93.5
3	93.5	94.0	93.5
4	93.5	93.5	93.0
5	92.0	93.0	93.0

VITA

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