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นางสาวณัฐญา ตันเรืองศรี

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PREPARATION OF COMPOUNDED RUBBER FROM NATURAL RUBBER MODIFIED WITH CARDANOL AND FORMALDEHYDE

Miss Nataya Tunruangsri

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
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ณัฐญา ตันเรืองศรี : การเตรียมยางคอมพาวด์จากยางธรรมชาติดัดแปรด้วยคาร์ดานอลและฟอร์แมลดีไฮด์ (Preparation of Compounded Rubber from Natural Rubber Modified with Cardanol and Formaldehyde) อาจารย์ที่ปรึกษาวิทยานิพนธ์ : รศ. ดร.โสภณ เริงสำราญ ; 146 หน้า. ISBN 974-347-115-4

งานวิจัยนี้ศึกษาการเตรียมยางคอมพาวด์จากยางธรรมชาติดัดแปรด้วยคาร์ดานอล-ฟอร์แมลดีไฮด์เรซิน คาร์ดานอลได้จากของเหลวจากเปลือกเมล็ดมะม่วงหิมพานต์ เรซินนี้ถูกสังเคราะห์โดยใช้การพอลิเมอไรเซชั่นแบบควบแน่นของคาร์ดานอลกับฟอร์แมลดีไฮด์โดยใช้เบสเป็นตัวเร่งปฏิกิริยา เรซินนำไปพิสูจน์เอกลักษณ์ด้วยอินฟราเรดและนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโครสโคปี สำหรับการเตรียมยางคอมพาวด์ สารแขวนลอยของสารเติมแต่งถูกเตรียมด้วยเครื่องบอลมิลเป็นเวลา 3 ชั่วโมง หลังจากนั้นน้ำยางข้นและคาร์ดานอล-ฟอร์แมลดีไฮด์เรซินอิมัลชั่นถูกเติมและผสมตามเวลาที่เหมาะสม น้ำยางคอมพาวด์ถูกทำให้จับตัวกันด้วยกรดฟอร์มิก 5 เปอร์เซ็นต์โดยปริมาตรและทำการวัลคาไนซ์ยางที่ 150 องศาเซลเซียสเป็นเวลา 10 นาที ความเข้ากันได้ของสารเติมแต่งกับน้ำยางข้นในยางคอมพาวด์นำไปศึกษาด้วยเทคนิคทางกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) และกล้องจุลทรรศน์ (OM) ศึกษาสมบัติเชิงกลเช่น ความต้านแรงดึง มอดูลัส ความยืดที่จุดขาด และความแข็ง นอกจากนี้ยังศึกษาสมบัติทางความร้อนด้วยการบ่มเร่งและเครื่องวิเคราะห์ทางเคมีด้วยความร้อนภายในเครื่อง (TGA) ผลของปริมาณกำมะถัน (0.5–2 ส่วนในยาง 100 ส่วน) ปริมาณคาร์ดานอล-ฟอร์แมลดีไฮด์เรซิน (0-6 ส่วนในยาง 100 ส่วน) และเวลาที่ใช้ผสม (0.5-2 ชั่วโมง) ที่มีต่อสมบัติดังกล่าวของยางคอมพาวด์ถูกศึกษา ผลการวิจัยพบว่าสูตรของยางคอมพาวด์ที่ให้สมบัติดีที่สุดคือ กำมะถัน 2 ส่วนในยาง 100 ส่วน คาร์ดานอล-ฟอร์แมลดีไฮด์เรซิน 2 ส่วนในยาง 100 ส่วน และเวลาผสมที่เหมาะสมคือ 0.5 ชั่วโมง สูตรยางคอมพาวด์นี้ให้ค่าความต้านทานแรงดึง 17.26 เมกกะพาสคาล ความยืดที่จุดขาด 2183 เปอร์เซ็นต์ ค่าความแข็ง 34.5 และสมบัติทางความร้อนได้รับการปรับปรุงเมื่อเติมคาร์ดานอล-ฟอร์แมลดีไฮด์เรซิน

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต.....ณัฐญา ตันเรืองศรี.........

หลักสูตร...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่ออาจารย์ที่ปรึกษา...........................

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NATAYA TUNRUANGSRI: PREPARATION OF COMPOUNDED RUBBER FROM NATURAL RUBBER MODIFIED WITH CARDANOL AND FORMALDEHYDE. THESIS ADVISOR: ASSOC. PROF. SOPHON ROENGSUMRAN, Ph.D. 146 pp. ISBN 974-347-115-4

This research studied the preparation of compounded rubber from natural rubber (NR) modified with cardanol-formaldehyde (CF) resin. The cardanol was obtained from cashew nut shell liquid. This resin was synthesized using a condensation polymerization of cardanol with formaldehyde in the presence of a base catalyst. The resin was characterized by infrared and nuclear magnetic resonance spectroscopies. For the preparation of compounded rubber, the aqueous dispersion of the additives was prepared using ball mill for 3 hours. Then the concentrated latex and cardanol-formaldehyde resin emulsion were added and mixed at appropriate time. The latex compounds were coagulated by 5%v/v formic acid and then vulcanized at 150°C for 10 minutes. The compatibility of additives and rubber latex in rubber compounds was determined by scanning electron microscopy (SEM) and optical microscope (OM). The mechanical properties, such as tensile strength, modulus, elongation at break, and hardness were also determined. Furthermore, the rubber compounds were studied for thermal properties by aging and thermogravimetric analysis (TGA). The effects of the sulfur quantity (0.5-2 phr), cardanol-formaldehyde resin quantity (0-6 phr), and mixing time (0.5-2 hour) on those properties of rubber compounds were studied. The result indicated that the formulation of compounded rubber, which gave the best properties, were 2 phr sulfur, 2 phr cardanol-formaldehyde resin, and the appropriate mixing time was 0.5 hour. This formulation gave tensile strength of 17.26 MPa, elongation at break of 2183 percent, hardness value of 34.5, and the thermal properties were also improved by incorporation of cardanol-formaldehyde resin.

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LIST OF SCHEMES

ABBREVIATIONS

Ave. : Average

°C : Degree Celsius

CF : Cardanol-Formaldehyde

CNSL : Cashew Nut Shell Liquid

cps : Centipoise

CU : Chulalongkorn University

MBT : 2-Mercaptobenzothiazole

NR : Natural Rubber

OM : Optical Microscope

PCNSL : Phosphorylated Cashew Nut Shell Liquid

PCP : Phosphorylated Cardanol Prepolymer

phr : Parts per Hundred Rubber

rpm : Rounds per minute

SEM : Scanning Electron Microscope

TGA : Thermogravimetric Analysis

TISI : Thai Industrial Standards Institute

CHAPTER I

INTRODUCTION

The Rubber Research Institute of Thailand reported that Thailand produced 2,065,202 tons of natural rubber and exported 1,839,396 tons or 89.07% of total production in 1998, the remaining 10.93% were used in the country [1]. However, the export of ribbed smoke sheet and block rubber has had the tendency to decrease. Therefore, it is extremely necessary to find new ways to use more natural rubber products.

The excellent combination of physicomechanical properties of natural rubber has made it a versatile material that is capable of meeting the challenging demands of the present times. Natural rubber has established an enviable position in the industrial market as an excellent engineering polymer. Two of its most important properties that need to be considered for any engineering applications are its mechanical strength and aging behavior. However, it is often found necessary to modify it with various additives. The properties of modified natural rubber are dependent on the judicious selection of additives.

In this research, phenolic resin was chosen to improve mechanical and thermal properties of natural rubber combined with other additives such as vulcanizing agent, accelerator, activator, and surfactant. This phenolic resin was synthesized from cardanol, phenolic nature, and formaldehyde via condensation polymerization with a basic catalyst. For this reason cardanol was chosen because it is renewable resource. It is obtained from cashew nut shell liquid (CNSL), which is a byproduct of the cashew industry. The major components of CNSL is anacardic acid. Upon heating, anacardic acid will decarboxylate to yield cardanol. Moreover, cardanol is cheaper than phenol, a synthetic material. Thus, the use of cardanol in phenolic resins may be of immense interest in the days of dwindling petroleum deposits.

This investigation concerned with the preparation of compounded rubber from natural rubber, concentrated latex, modified with cardanol and formaldehyde. The ball mill mixer was used to prepare compounded rubber. Various proportions of sulfur, cardanol-formaldehyde resin and various mixing time were studied. Furthermore, the mechanical and thermal properties were investigated.

Objectives

1. To study the preparation of compounded rubber from natural rubber modified with cardanol and formaldehyde.
2. To study the mechanical properties and thermal properties of the prepared rubber compounds.

Scope of the Investigation

For the preparation of the natural rubber compound modified with cardanol-formaldehyde resin, the appropriate formulations were studied. Cardanol-formaldehyde resins were synthesized by base catalyzed reaction. In preparing rubber compounds, the aqueous dispersions of additives, concentrated latex, and cardanol-formaldehyde resin emulsion were mixed together in a ball mill mixer at an appropriate time. The formulations of compounded rubber were changed with respected to the sulfur quantity, cardanol-formaldehyde resin quantity, and the mixing time. Mechanical and thermal properties of compounded rubber were investigated according to the ASTM and ISO standards. Compatibility of additives and rubber latex was determined by scanning electron microscopy (SEM) and optical microscope (OM).

CHAPTER II

THEORY AND LITERATURE REVIEWS

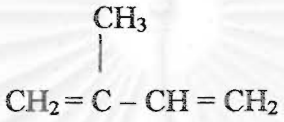
2.1 Natural Rubber [2,3]

Natural rubber can be isolated from more than 200 different species of plants, including even such surprising examples as dandelions or goldenrod. However, only one tree source, *Hevea Brasiliensis,* is commercially significant. At one time, early in the century, a large tree *Funtumia elastica* was exploited in tropical Africa, as was the *Landolphia species*, a climbing shrub. In Mexico, the large tree, *Castilloa elastica* also provides rubber. In South America, the Ceara Rubber tree, *Manihot glaziovii*, was another source. None could compete with *Hevea Brasiliensis* in yield, frequency of tapping, or longevity.

About 7-10% of the world's natural rubber is converted into latex concentrate. Concentration is achieved by centrifugation (most commons), by creaming, or by evaporation. The centrifuged latex is shipped as latex concentrate containing 60% dry rubber content. The remainders of latex and field coagulum are processed into conventional types of rubber such as ribbed smoke sheets (RSS), pale crepes, and brown crepes, into the newer forms of technically specified 'block' rubber (TSR). These are the basic raw materials for all types and grades of natural rubber.

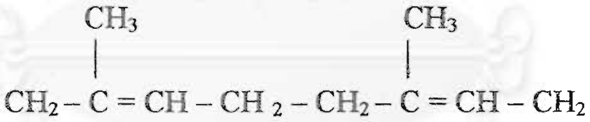
2.2 Properties of Natural Rubber [2,4]

Natural rubber is a polymer of isoprene, in which essentially all the isoprene units are linked together at carbon atoms 1 and 4 in a head-to-tail arrangement.



$$CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2$$

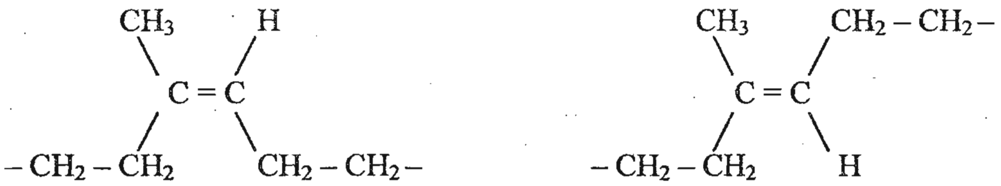
Figure 2.1 The structure of isoprene.



$$CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2$$

Figure 2.2 Head-to-tail arrangement

Commercial grades of *Hevea* natural rubber contain 93-94 %wt. cis-1,4 configuration, which means that carbon atoms 1 and 4 are both on the same side of double bond. In the trans-1,4 configuration, these two carbon atoms are on opposite sides of the double bond.



cis- polyisoprene *trans* - polyisoprene

Figure 2.3 C*is*- and *trans*- configuration of polyisoprene.

2.2.1 Composition [2]

Commercial raw natural rubber has a small, but highly important number of non-rubber constituents. These may compromise as much as 5-8% of the total composition. Most important are the natural-occurring antioxidants and activators of cureing, represented by the proteins, sugars, and fatty acids. Typical composition is shown in Table 2.1.

Table 2.1 Analysis of representative natural rubber

Ingredient	Ave.%	Range%
Moisture	0.5	0.3-1.0
Acetone Extract	2.5	1.5-4.5
Protein	2.5	2.0-3.0
Ash	0.3	0.2-0.5
Rubber Hydrocarbon	94.2	-
Total	100.0	-

Trace elements present in rubber include potassium, and phosphorus, as well as copper, manganese, and iron. Although usually present only to the extent of 2-3 parts per million, the latter are important as catalysts to promote the oxidation of vulcanized rubber. Amounts higher than 8-10 parts per million are not tolerated.

Table 2.2 outlines in detail the complex variety of chemical substances present in the dry rubber and latex.

Table 2.2 Approximate concentrations of non-rubber constituents in centrifuged latex concentrates

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 salts (acetate, citrate, etc.)	0.3
Amino acids and polypeptides	0.2
Inorganic salts (ammonium and potassium carbonate and phosphate, etc.)	0.2

2.2.2 Physical Properties

Physical properties of natural rubber may vary slightly due to the non-rubber constituents present and to the degree of crystallinity. When natural rubber is held below 10°C, crystallization occurs, resulting in a change of density from 0.92 to about 0.95. Listed in Table 2.3 are some average physical properties.

Table 2.3 Some physical properties of natural rubber

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 power factor is reduced to 0.0015 and the resistivity substantially increased in deproteinized rubber.

2.3 Natural Latex [2]

Natural latex is produced in special vessels outside the cambium layer of the *Hevea brasiliensis* tree. Latex as it comes from the tree has a solid content of about 36%, a surface tension of 40.5 dyn/cm (30°C), and a pH of 6. Latex fresh from the tree is stabilized by naturally occurring proteins and phospholipids. It also contains other materials such as resins, sugars, mineral salts, and alkaloids. The protein stabilizer is very susceptible to bacterial action and would be destroyed within a few hours if ammonia were not immediately added. Soap-forming fatty acids are formed when the ammonia hydrolyzes the lipids. This ammonia soap then becomes the primary stabilizer, displacing the adsorbed protein from the particle surface.

If latex is preserved entirely by ammonia (high ammonia latex), a portion of the ammonia is usually removed before application. Other preservatives, such as sodium pentachlorophenate, sodium salt of ethylenediamine tetraacetic acid, boric acid or zinc alkyl dithiocarbamate, may be used with smaller amounts of ammonia. This is known as low ammonia latex and has advantages of lower cost and elimination of the need to deammoniate the latex before processing into products.

Latex is concentrated to greater than 60% rubber solids before leaving the plantation, and this is accomplished either by centrifuging or creaming. Creamed latex is usually produced by treating the dilute latex with small amounts of sodium or ammonia salts of alginic acid. The migration or creaming of particles to the upper portion of the latex takes place over a period of several days, increasing the rubber solids in this area. The lower portion of the latex, containing some very small rubber particles and other chemicals mentioned above, is then separated from the cream and is either discarded or is coagulated to salvage the small quantity of rubber remaining in it. The upper portion is usually referred to as the concentrate and the lower portion as the skim or serum.

2.4 Vulcanization [4,5]

2.4.1 Definition of Vulcanization

Vulcanization is a process by which elastomeric materials are generally prepared; it consists of the formation of a molecular network by a chemical tying together of independent chain molecules. The resulting rubbers retract forcibly to their approximately original shape after large mechanically imposed deformations. Vulcanization thus is an intermolecular reaction which increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force, i.e., increases elasticity while it decreases plasticity.

According to the theory of rubber elasticity, the retractive force resisting a deformation is proportional to the number of network-supporting polymer chain per unit volume of elastomer. A supporting chain is a segment of polymer backbone between network junctures. An increase in the number of junctures gives an increase in the number of supporting chains. In an unvulcanized high polymer, above its melting point, only molecular chain entanglements constitute junctures and their number per molecule increases with molecular weight. Vulcanization usually produces network junctures by the insertion of chemical crosslinks between polymer chains. These crosslinks may be chains of sulfur atoms, single sulfur atoms, carbon-carbon bonds, polyvalent organic radicals, or polyvalent metal ions.

2.4.2 The Effects of Vulcanization on Vulcanizate Properties

Major effects of vulcanization are illustrated by the idealization in Figure 2.4. It should be noted that the properties of Figure 1 are not functions of crosslink density only. They are also affected by the type of crosslink, the nature of the polymer, the type and amount of filler, etc.

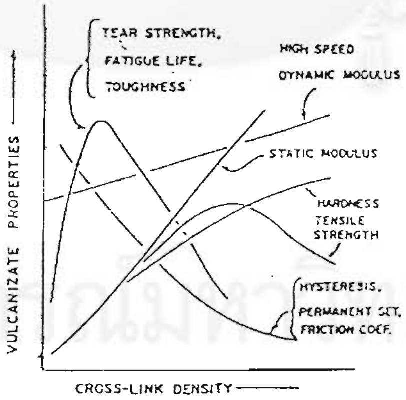


Figure 2.4 The effects of vulcanization.

2.4.3 Parameters of the Vulcanization Process

Critical parameters related to the process of vulcanization are the time elapsed before it starts, the rate at which it occurs, and the extent. There must be sufficient delay (called scorch time or scorch resistance) before the outset of vulcanization to permit mixing, forming, and molding. Afterward, the formation of cross-links should be rapid and its extent controlled.

Scorch resistance is usually measured by the time at a given temperature required for the onset of crosslink formation as measured by an abrupt increase in viscosity. In recent years, specialized rheometers (or cure meters) have been used. These devices are capable of measuring the extent of cure of a single sample at a given temperature on a continuous basis. The most popular of these instruments are of the oscillating disk variety. An instrument of this type is illustrated schematically in Figure 2.5.

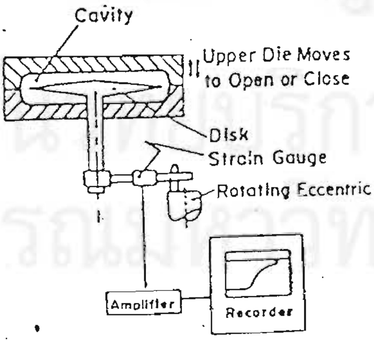


Figure 2.5 Schematic diagram of cure meter.

The resistance to oscillation is measured and recorded as a function of time on a so-called rheometer chart like the one shown in Figure 2.6.

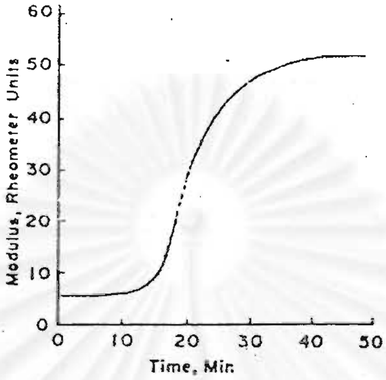


Figure 2.6 Rheometer chart.

2.5 Sulfur Vulcanization [4,5,6]

Sulfur was the first agent used to vulcanize the first commercial elastomer, natural rubber. The chemistry of sulfur vulcanization is so complex that it is only with in the few years that a coherent theoretical treatment has been possible. Even today, only the main stage are proven and there is still much to be learned about the effect of additives of various types.

This complex reaction is an excellent example of the combined efforts of physical and organic chemists. It starts with measurement in 1910-1912, of the rate of the sulfur reaction, followed by the examination of the apparent loss of unsaturation by rubber in 1938-1945. The use of methyl iodide as a ‘chemical probe’ increased knowledge of the crosslinking reactions further. These latter workers used 'model olefines' of low molecular weight to follow crosslinking reactions. These model substances were easier to handle than vulcanized rubber and enabled intelligent guesses to be made as to the nature of the crosslinks themselves. The various chemical structures present in a vulcanized natural rubber network are shown schematically in Figure 2.7.

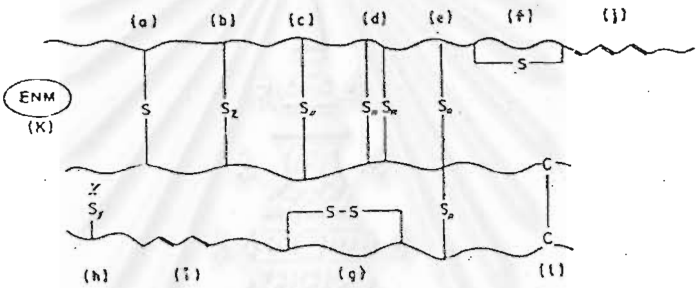


Figure 2.7 Typical chemical groupings present in a sulfur-vulcanized natural rubber network. (a) Monosulphide crosslink; (b) Disulphide crosslink; (c) Poly sulphide crosslink (x = 3-6); (d) Parallel vicinal crosslink (n = 1-6) attached to adjacent main chain atoms and which have the same influence as a single crosslink; (e) Crosslinks attached to common or adjacent carbon atom; (f) Intra-chain cyclic monosulphide; (g) Intra-chain cyclic disulphide; (h) Pendant sulphidic group terminated by moiety *X* derived from accelerator; (i) Conjugated diene; (j) Conjugated triene; (k) Extra-network material; (l) Carbon-carbon crosslinks (probably absent).

2.5.1 Accelerated Sulfur Vulcanization [7]

The form of 'sulfur-only' vulcanization, while alleviating many of the disadvantages of uncrosslinked elastomers, does not provide an optimum product. Around 1910 it was discovered by Oenslanger in Germany that the addition of aniline to a rubber/sulfur formulation greatly increase the rate of vulcanization and improved the final vulcanizate properties. These amines were the first accelerators for vulcanization.

Presently there are a wide range of accelerator systems available for elastomers, providing a range of cure rates, scorch times and final properties. These accelerators include the thiurams, sulfenamides, mercaptobenzothiazoles, amines and more recently sulfenimides; several common accelerators are shown in Table 2.4 Additionally, there are combination systems (i.e., thiuram sulfenamides) also available. The variety of accelerators accounts for the wide applicability of elastomers to material applications. Also of increasing utility are binary accelerator systems, which utilize two or more accelerators in a synergistic manner. Mixed in the proper proportions, binary systems can lead to significant improvement in curing behavior and mechanical properties.

2.5.2 The Chemistry of Accelerated Sulfur Vulcanization [5]

Accelerated sulfur vulcanization is thought to proceed by the following steps:

(a) The accelerator reacts with sulfur to give monomeric polysulphides of the type Ac-S_x-Ac, where Ac is an organic radical derived from the accelerator. Certain initiating species may be necessary to start reaction, which then appears to be autocatalytic.

Table 2.4 Typical accelerators used in conjunction with sulfur for the vulcanization of diene rubbers.

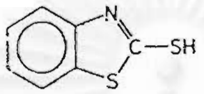
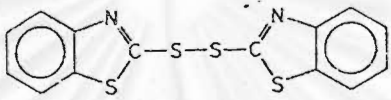
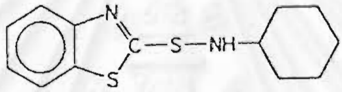
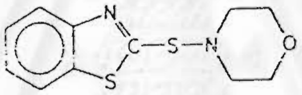
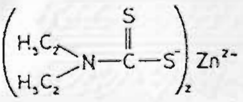
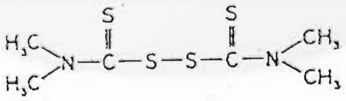
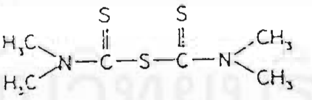
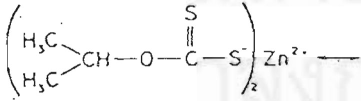
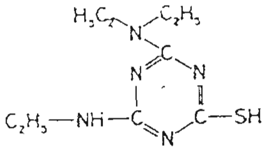
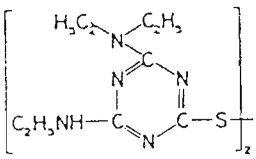
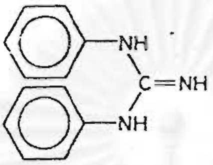
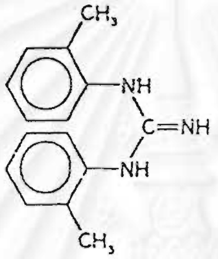
Type and examples	Chemical formula	Comments
Thiazoles Mercaptobenzothiazole (MBT)		MBT and its derivatives form the dominant group of accelerators used with dienes. MBT is powerful but tends to be scorchy
Dibenzothiazyl disulphide (MBTS)		
Sulphenamides N-cyclohexyl benzo thiazyl sulphenamide (CBS)		Delayed action semi-ultra accelerator. Widely used
N-oxydiethylbenzothiazyl sulphenamide (NOBS)		Similar to CBS
Dithiocarbamates Zinc diethyl dithiocarbamate (ZDC or ZDEC)		Ultra-accelerator. This and other dithiocarbamates usually too fast for dry rubber technology. Used in latex work
Thiuram sulphides Tetramethyl thiuram disulphide (TMT or TMTD)		Ultra-accelerator. Also vulcanizing agent.
Tetramethyl thiuram monosulphide (TMTM)		Ultra-accelerator. Like TMTD often used in small quantities in conjunction with other accelerators
Xanthates 	Zinc isopropyl xanthate (ZIX)	Ultra-accelerator
Triazines 2-Ethylamino-4-diethyl amino-6-mercaptotriazine		
Disulphide oxidation product of above		Similar delayed action as CBS —improved reversion resistance

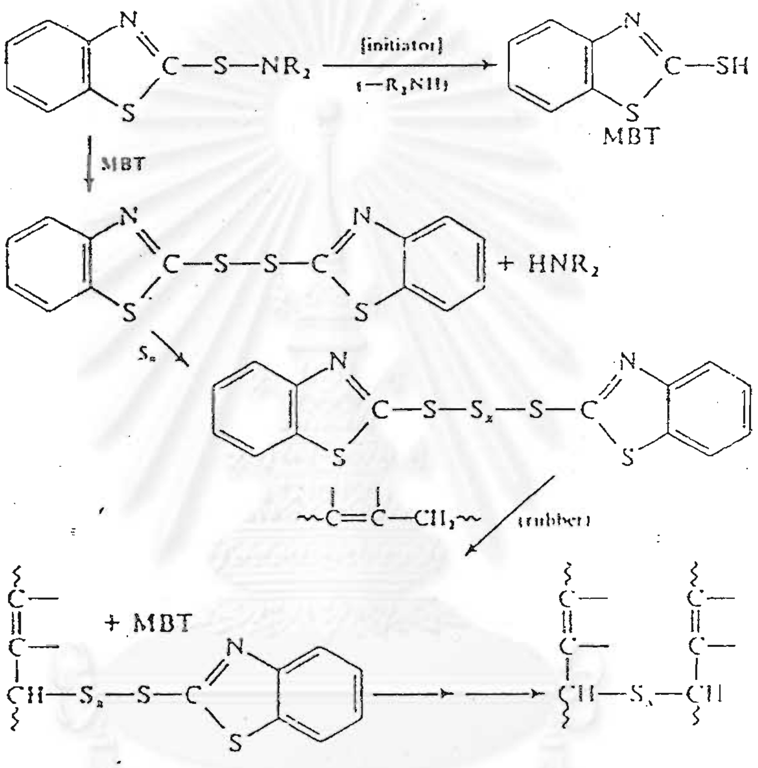
Table 2.4 (continued)

Type and examples	Chemical formula	Comments
Guanidines		
Diphenyl guanidine (DPG)		Medium-speed accelerator Now largely used in conjunction with other accelerators. Strong synergism with MBT
Di-*o*-tolyl guanidine (DOTG)		Medium-speed accelerator. Also used as 'plasticizer' for polychloroprenes.
Water-soluble accelerators There are several examples of accelerators from many of the above classes that are water soluble and which are used in latex technology. They are usually sodium salts and include the sodium salt of MBT (SMBT), sodium diethyl dithiocarbamate (SDC or SEDC) and sodium isopropyl xanthate (SIX).		

(b) The polysulphides can interact with rubber to give polymeric polysulphides of the type rubber-S_x-Ac. During this reaction, the formation of mercaptobenzothiazole (MBT) was observed when an accelerator derived from MBT had been used. When MBT itself is used, it first disappears, then reappears during the formation of rubber polysulphides.

(c) The rubber polysulphides then react, either directly or through a reactive intermediate, to give cross-links or rubber polysulphides of the type rubber-

S_x-rubber. It a sulfenamide accelerator is used, the reaction can be represented as in Scheme 2.1.

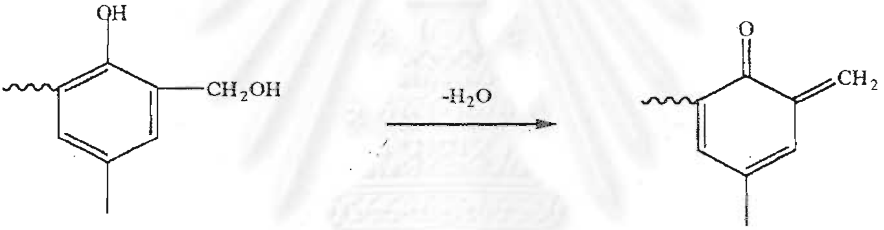


Scheme 2.1 The mechanism of accelerated sulfur vulcanization.

2.6 Vulcanization by Phenolic Resin [4,5]

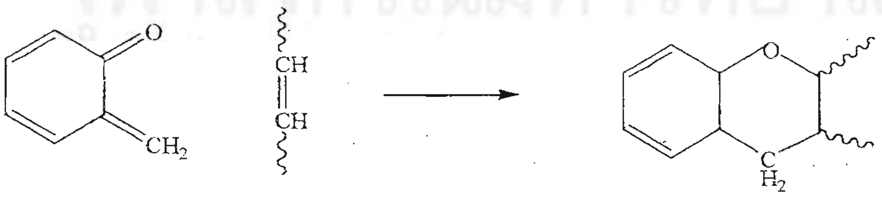
The first work on phenolic resins as vulcanizing agents for diene rubbers was undertaken over 40 years ago. Such resins are potentially interesting since they may be reacted with natural rubber in any proportion to give products of widely different hardness. In addition, at least in principle, the resin may also be modified to be an antioxidant as well as a vulcanizing agent for the rubber. Subsequent studies have also shown that the system has good resistance to reversion.

The first systematic study on the vulcanization of rubber with phenolic resins was undertaken at the Dutch research institute Rubber-Stichting during World War II. Whilst the mechanism of cure remains to be fully established it is generally considered that the first stage involves the formation of a methylene quinone structure by elimination of water from an *o*-methylol phenol.



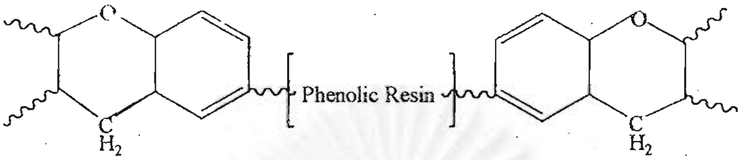
Scheme 2.2 The formation of methylene quinone structure.

The initial material may be *o*-methylol phenol itself or a phenolic resin containing several such groups. In the case of the *o*-methylol phenol it has been found that condensation with a double bond occur, presumably after elimination of water, to produce a chroman ring.



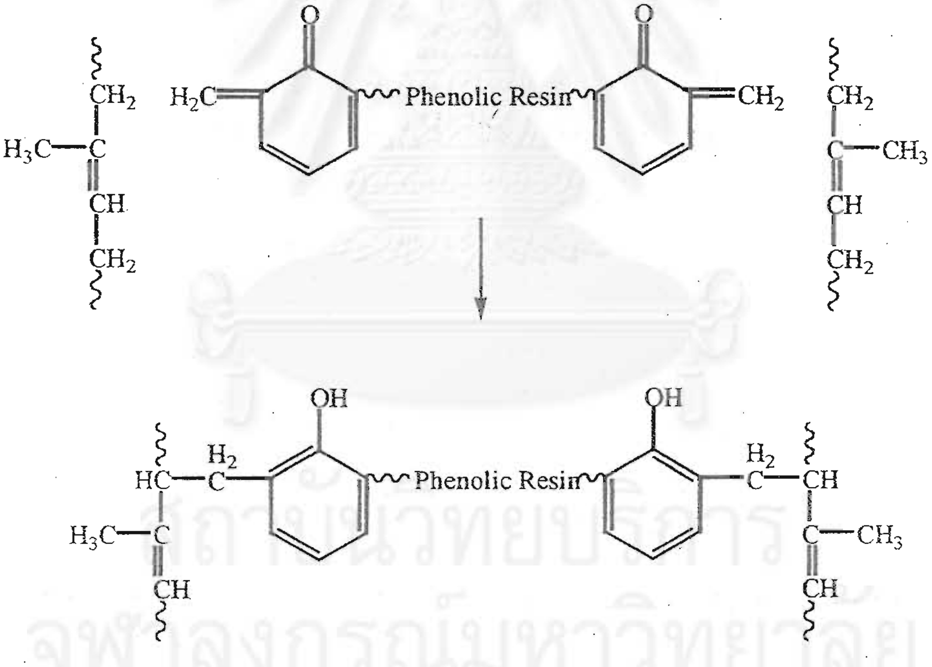
Scheme 2.3 The formation of chroman ring.

Hence it has been assumed that in the case of a polyfunctional phenolic resin, crosslinking occurs via the resin and two such chroman rings:



Scheme 2.4 Crosslinking of phenolic resin with chroman ring.

An alternative theory suggests that reaction occurs at the α-methylene group with, once again, methylene quinone or a derivative as a reactive intermediate:



Scheme 2.5 The vulcanization of rubber with phenolic resin.

Whilst the first mechanism would involve a reduction in phenolic hydroxyl concentration as cure proceeds together with the generation of ether linkage, the second mechanism does not. Results of tests to differentiate between the two possibilities are somewhat ambiguous.

2.7 Anacardium Occidentale

2.7.1 The Cashew Tree [8,9]

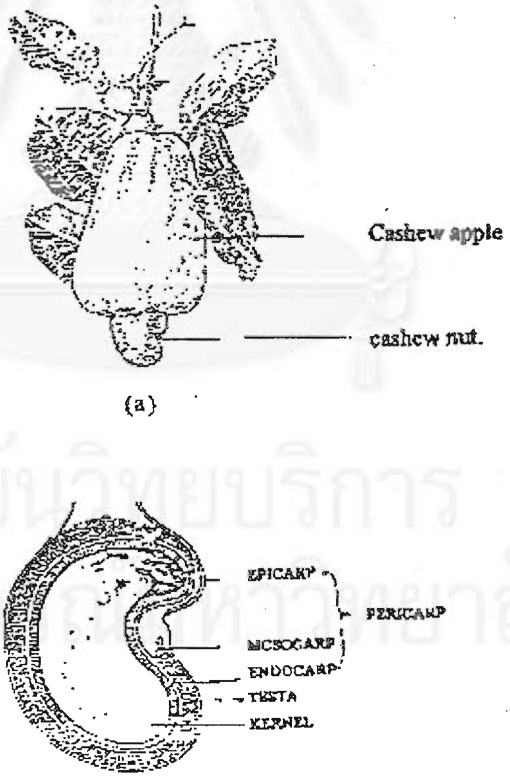
The cashew tree, Anacardium occidentale Linn., is a native of Brazil and was introduced into Asia and Africa by the Portuguese in the 1600's. It is now found widely in other part of tropical South and Central America, Mexico and West Indies. The generic name, *Anacadium*, was bestowed upon it because it described the heart-like shape of the nut. The specific name, *occidentale*, was used because the nut came from the Western America.

The cashew plant is a jungle or semi-jungle tree by nature. The tree, which is an evergreen, naturally grows up to 12 meters high and has a spread of 25 meters. They are readily recognized by their light colored foliage. The yellow-green leaves, revealing distinct veins, are elliptic in shape and approximately 4 to 6 inch in length and 2 to 3 inch in width. They feel leathery to the touch.

2.7.2 Cashew Apple and Cashew Nut [8,9,10,11]

The cashew nut is attached to the bottom of the cashew apple, false fruit, developed from the receptical. The cashew apple varies in size from 2 to 4 inch length and 1.5 to 2 inch in width. It is yellowish-red in color and possess a thin waxy skin. Broadly conical or pear-likes in shape, it is called a cashew "pear" or cashew "apple" (Figure 2.8 a)

The whole cashew nut is from 2.5 to 3.2 cm long; 1.9 to 2.2 cm broad at the base; and 1.3 to 1.6 cm thick at the steam-end. It is gray brown in color and shaped more like the kidney than the heart from which its generic name is derived. The shell of the nut is hard, about an eight of an inch thick. It consists of two layers. The outer layer, which is smooth surface, thin and tough. The inner layer is hard. Between the two layers is a honeycomb structure, which contains a phenolic material known as "Cashew Nut Shell Liquid (CNSL)". It is commercially and importance in economic growing. Inside the shell is the kernel, wrapped in a thin brown skin, know as the "testa" (Figure 2.8 b)



(a)

(b)

Figure 2.8 (a) Cashew apple and cashew nut.

(b) Section of a cashew nut.

2.8 Cashew Nut Shell Liquid (CNSL)

2.8.1 Introduction [9,12]

Cashew nut shell liquid is contained in the honeycomb structure between the soft outer skin of the nut and the harder inner shell. It is a dark brown viscous liquid and is reported to occur in the fresh shell to the extent 15 to 20 and 20 to 30 percent by weight for African nuts and Indian nuts, respectively. CNSL is extremely caustic and is a strong desiccating agent. Table 2.5 shows the Indian and Irvington specification.

Table 2.5 Specification for Cashew Nut Shell Liquid

Properties	Indian 840-1964	Irvington specification[a]
Specific gravity 30/30°C	0.950-0.970	-
50/60°F	-	0.95-0.97
Viscosity at 25°C, cps	-	max 600
30°C, cps	max 550	-
Moisture, w/w, percent	max 1.0	max 1.00
Matter insoluble in toluene, w/w, percent	max 1.0	-

Table 2.5 (continued)

Properties	Indian 840-1964	Irvington specification[a]
Dirt and foreign matter, w/w, percent	-	max 1.00
Loss in weight on heating, w/w, percent	max 2.0	-
Color	-	Brown
Iodine value (Wij's method), percent	min 250	min 250
Ash, w/w, percent	max 1.0	-
Polymerization		
(a) Time, min	max 4.0	max 19
(b) Viscous, at 30°C, cps	min 30	min 30

[a] Irvington Varnish and Insulator Co., Irvington, New Jersey, USA.

2.8.2 Extraction [13]

Traditionally, Indian processors of cashew nuts roast them in an open perforated drum. CNSL either leaks away or is burnt in the fire. With increase in the price of CNSL, many refined extraction techniques have come into vogue.

Hot oil bath method

This is the most common method of commercial extraction largely used in Quilon and other areas in Kerala. The raw nuts are passed through a bath of hot CNSL (180-200°C) itself, when the outer part of the shell bursts open and releases CNSL (50% recovery). Another 20% could be extracted by passing the spent shells through an expeller and the rest by solvent extraction techniques. The expeller oil, however, does not satisfy IS specifications and needs upgrading. This can be done by acid washing followed by centrifugation and heating.

Expeller method

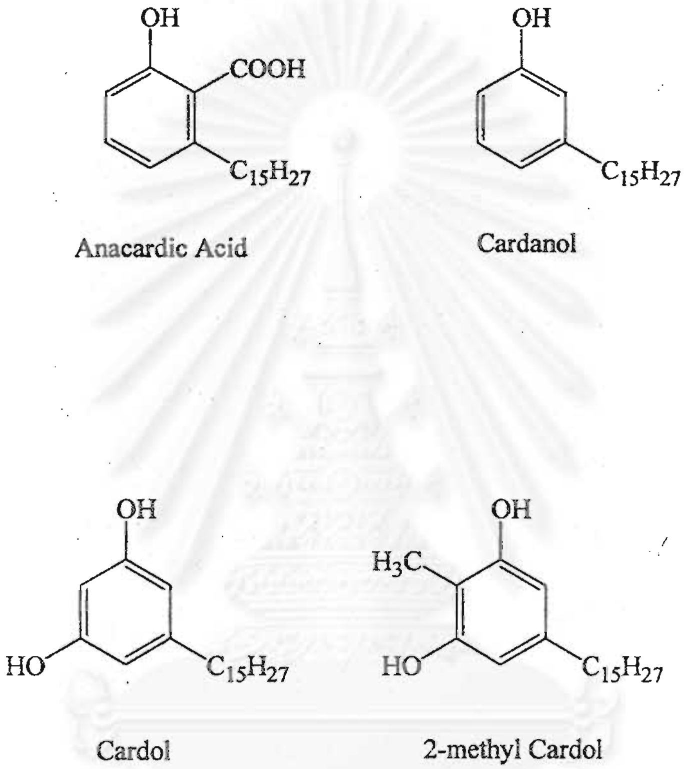
In Mangalore area, some factories have introduced manually operated cutting machines in which shells of lightly roasted nuts are cut, keeping the kernel intact. The shells are then fed to an expeller to recover 90% of the oil.

Kiln method

In this method (extensively employed in Panduritti, Tamil Nadu), the nuts are shelled after sun drying or after drum roasting. The liquid obtained is, however, crude and contaminated.

2.8.3 Composition of CNSL [8,9,14,15]

CNSL, is mixtures of phenolic compounds, consists of two principal constituents, anacardic acid and cardol. Both belong to the group of chemicals classified as higher phenols. In its natural state, the composition of CNSL is shown in Scheme 2.6. In each fraction, it has a side chain of 15 carbon atoms with different degree of unsaturation (Scheme 2.6)



Scheme 2.6 Composition of naturally occurring CNSL.

Anacardic acid readily loses carbon dioxide to yield a meta-substituted phenol, "cardanol" on heating. For commercial usage the CNSL is obtained from the cashew nut shell by a process that involves heating the shells to a high temperature for several minutes in a vat of previously obtained the liquid. During this process the liquid is held at the high temperature for several hours. Considerable decarboxylation of the anacardic acid takes place, as well as some polymerization of the phenolic bodies to yield a commercial CNSL, which is mainly monophenolic in character, but contains a small amount (approximately 16%) of anacardic acid, cardol and polymerized material.

2.8.4 Polymerization Characteristics [13]

CNSL can be polymerized in a variety of ways.

Addition polymerization at the side chain unsaturation

Polymerization can be effected through the double bonds of the side chain employing either free radical or ionic initiators. CNSL responds easily to acidic catalysts like H_2SO_4, HCl, diethyl sulphate, etc., which induce polymerization through the formation of an allylic carbonium ion from the more reactive double bonds of the triene. (A rubbery polymer was obtained on heating with diethyl sulphate for 1 hour at 180°C.) For the production of friction – dust for brakelinings, generally a preliminary acidic polymerization of the side chain is carried out with dimethyl or diethyl sulphate. The semipolymerized material is then polymerized with formaldehyde and the resultant product is comminuted.

Metal activated polymerization

CNSL was found to acquire drying characteristics on activation with a metal or metallic compound. Thus, CNSL heated in contact with copper, aluminium, lead, etc., was found to acquire superior drying characteristics than when heated alone. These form good media for paints on further cooking with drying oils.

Heat polymerization

CNSL, when heated at 160-300°C in the presence of certain accelerators, gave excellent staving enamels.

Oxidation polymerization

When CNSL is oxidized, its iodine number may be quickly reduced to zero, and the reaction product dries very quickly at ordinary and elevated temperatures. Acid oxidizers (e.g. HNO_3) and oxidizers in the presence of acid are valuable. The product when dissolved in solvents, such as turpentine, naphtha or kerosene, give an excellent coating material, useful for making paints, varnishes, etc., and for impregnating paper and woven fabrics.

Condensation polymerization

CNSL can be condensed with active hydrogen-containing compounds, such as formaldehyde, furfural, etc., at the *ortho* and *para* positions of the phenolic ring under acidic or alkaline conditions to yield a series of polymers of 'novolac' and 'resol' types. Condensation polymers of CNSL are finding use as coating materials (paints, lacquers, cements, etc.), adhesives, plastic and rubber compositions and automobile brakelinings.

2.9 Literature Reviews

Misra and Pandey [16] studied the kinetics of reaction between cardanol and formaldehyde when catalyzed by an alkali, sodium hydroxide. They investigated the effects of processing parameters, e.g., cardanol formaldehyde molal ratio, catalyst concentration, and temperature. The addition reaction has been shown to be a second-order reaction when the concentration of active positions of reactants is used instead of their molar concentrations. Specific reaction rate constants have been determined for various cardanol-formaldehyde molal ratio, catalyst concentrations, and reaction temperatures. The energy of activation, E, is found to be 67.541 MJ/kg-mol (16.132 kcal/mol). The correlation between overall reaction rate constant and the process parameters has also been developed.

Misra and Pandey [17] investigated the mechanism of the reaction between cardanol and formaldehyde when catalyzed by an alkali, sodium hydroxide. It was observed that only three individual rate constants, k_{11}, k_{12}, and k_{13}, out of 12 appearing in the mechanism could be quantitatively estimated due to poor separation of the intermediates. The equation for the rate of overall chemical reaction has been developed and found to agree well with the experimental data.

Misra and Pandey [18] suggested a quick method for the determination of composition of the resin formed by alkali-catalyzed cardanol-formaldehyde reaction. The complete analysis of the product could be carried out by determining experimentally the concentration of only one reactant, viz., formaldehyde present in the reaction mixture at any time.

Menon, Pillai, and Nando[19] studied the chemical crosslink density (CLD) and network structure of natural rubber (NR) vulcanizates, modified with phosphorylated cardanol prepolymer (PCP) by equilibrium swelling and other chemical methods. The PCP-modified NR vulcanizates showed lower CLD, as compared to the unmodified NR samples, the decrease being lesser for the semiefficient vulcanization (SEV) system, as compared to the conventional (CV) and efficient (EV) vulcanization systems. The superior tensile characteristics of the PCP-modified vulcanizates of the SEV system is presumed to be partly due to the presence of an entangled network structure between the aliphatic segment of PCP and the isoprene chains, as evident from X-ray diffraction studies. The critical role of Zn^{++} ions in the crosslinking reaction, especially at higher concentrations of PCP, was evident from the increase in CLD at higher concentrations of ZnO.

Connor and Blum [20] synthesized a variety of crosslinked phenol-, or derivatized phenol-formaldehyde polymers and studied the thermal stability of the cure resins. The phenol derivatives included *o*– and *p*- cresol, *p*-nonylphenol, *m*-pentadecylphenol, and raw and distilled cashew nut shell liquid. The derivatives were copolymerized with phenol and formaldehyde using sulfuric acid as catalyst to yield novolak-type prepolymers, which were then cured with hexamethylenetetramine. Thermogravimetric analysis was used to evaluate the thermal stability of the cured resins. It was found that the thermal stability of the resins decreased with increasing amounts of cashew nut shell liquid, with distilled cashew resins being slightly more thermally stable than raw cashew resins. The thermal stability of resins containing substituted phenols with alkyl chain was observed to increase from *n*-

pentadecylphenol to cresol to phenol. The trend in thermal stability of the resins may be explained on the basis of alkyl groups being less thermally stable than aromatic rings. The amount of hexamethylenetetramine used to cure the prepolymers also influences the thermal stability of the resin. It appears that a level of 10 to 15% hexamethylenetetramine maximizes the thermal stability of the resin.

Menon [21] studied the tensile stress-relaxation characteristics at room temperature of gum natural rubber (NR) vulcanizates containing 10-20 phr of phosphorylated cashew nut shell liquid (PCNSL) prepolymer in various strain rates and strain levels, in comparison with that containing the same dosage of 2-ethyl hexyl diphenyl phosphate and the unmodified sample. Modification of NR with 10-15 phr of PCNSL resulted in improvements in tensile properties along with a lower degree of stress relaxation at the higher strain rates and strain levels.

Menon, Pillai, and Nando [22] studied the effect of fillers like carbon black, silica, and china clay on the cure characteristics and physicomechanical properties of natural rubber (NR) modified with phosphorylated cashew nut shell liquid (PCNSL) in various proportions. Prominent cure retardation has been observed with progressive increase on concentration of PCNSL from 0 to 20 phr. The softening effect of PCNSL on the vulcanizate has been displayed by the linear decrease in hardness and tensile modulus and the increase in elongation at break with the increase in concentration of PCNSL. The results on the tensile and tear strengths of the vulcanizates showed that the reinforcing effects of the fillers were maximized at concentrations of PCNSL ranging from 5 to 10 phr. Also, the PCNSL-modified NR vulcanizates showed improved resistance to thermo-oxidative aging and decomposition, especially at the higher concentration of 20 phr.

Bunthoon [23] studied the preparation of natural rubber product containing carbon black by directly mixing the concentrated latex with the additives. The effect of amount of carbon black (25-45 phr), sulfur (0.5-4 phr), accelerator (0.5-2 phr MBT), activator (2-10 phr ZnO and 1-4 phr stearic acid), type of carbon black (N220 and N330) and type of surfactants (SDS, Tergitol NP 9 and Tergitol NP 10) on the mechanical properties were studied. The compounded rubber was also assessed of carbon black dispersion by optical microscope and scanning electron microscope. The optimum formulation of compounded rubber, which give the best properties, are 100 parts by dry weight concentrated latex, 25 phr carbon black type N 330, 2 phr sulfur, 1 phr MBT, 5 phr ZnO, 2 phr stearic acid, and 3 phr Tergitol NP 10. The degree of carbon black dispersion is 5.0.

Vu, Mark and Pham [24] studied blends of natural rubber with cardanol-formaldehyde resins to improve mechanical properties (such as toughness) and thermal properties (such as high-temperature resistance). Cardanol was obtained from cashew nut shell liquid, which then was used to prepare cardanol-formaldehyde resole and novolak resins. The resins were found to be compatible with natural rubber in various formulations. The cure behavior of natural rubber blended with either the CF resole or novolak was investigated. The blended materials showed improved mechanical properties and good thermal stability, with an increase in the resinleading to increase in tensile strength and thermal stability. Aging studies showed that these modified elastomers also had improved oxidative stability.

CHAPTER III

EXPERIMENT

3.1 Chemicals

1. Natural rubber latex : Thai Rubber Latex Corporation
2. Sulfur : Ajax Chemicals
3. Zinc oxide (ZnO) : Ajax Chemicals
4. Stearic acid : Fluka
5. 2-Mercaptobenzothiazole (MBT) : Fluka
6. Tergitol NP 10 : Union Carbide
7. Formic acid : Merck
8. Sodium sulphate anhydrous : Merck
9. Formaldehyde : M & B Laboratory Chemicals
10. Sodium hydroxide : Carlo Erba Reagent
11. Petroleum ether : Lab-Scan Analytical Sciences
12. Hexane : Merck
13. Methanol : Merck

14. Cashew nut shell liquid : Obtained locally
15. Diethylenetriamine (DETA) : Fluka
16. Calcium hydroxide : Fluka

3.2 Instruments and Apparatus

1. Ball mill
2. Rheometer : Gibitre Rheocheck OD 2000
3. Universal testing machine : Instron Corporation Series IX
4. Hardness testing machine : The Shore Instrument & MFG.Co
5. Infrared spectrophotometer : Perkin Elmer, Nicolet (Impact 410)
6. Nuclear magnetic resonance spectrometer : Bruker, AC-F 200 MHz
7. Thermogravimetric analyzer : Perkin Elmer, TGA 7
8. Scanning electron microscope : JSM-5800 LV
9. Optical microscope : Olympus, BH-2

3.3 Procedures

3.3.1 Preparation of Cardanol [25]

Cardanol was obtained by decarboxylation of cashew nut shell liquid (CNSL). A mixture of CNSL (300 g), calcium hydroxide (6 g), and hexane (200 ml) was placed in a 1-L two necked flask equipped with a reflux condenser, stirrer, and thermometer. The flask was placed in an oil bath maintained at 135-140°C for 2 hours. Then calcium hydroxide was removed by filtration and hexane was removed by evaporation.

3.3.2 Purification of Cardanol [26]

Cardanol (120 g), diethylenetriamine (5.42 ml), and 40% formaldehyde solution (35.92 ml) were mixed in methanol (400 ml). The reaction was carried out at 135-140°C for 2 hours. An exothermic reaction took place after mixing the reactants and after thirty minutes a phase separation occurred into an upper, slightly reddish, solution and a lower phase which solidified and was dark in colour. The upper phase was decanted and treated with water (80 ml) followed by petroleum ether. The petroleum ether was removed by evaporation.

3.3.3 Preparation of Cardanol-Formaldehyde Resin

A resole form of cardanol-formaldehyde (CF) resin was prepared by the reaction of cardanol and 40% formaldehyde solution with a mole ratio of 1:2 in the presence of 10% w/v sodium hydroxide (NaOH) as the catalyst. The reaction mixture was heated under constant stirring at 80°C for 2 hours. The reaction time was begun count down when NaOH solution was added.

3.3.4 Preparation of Natural Rubber Product Modified with Cardanol Formaldehyde Resin

The natural rubber latex modified with cardanol-formaldehyde resin and additives was prepared by ball mill mixer. All additive ingredients such as sulfur, stearic acid, zinc oxide, MBT, and Tergitol NP 10 were used without further purification. Aqueous dispersion of additives was prepared by ball mill mixer under room temperature for 3 hours. The rate of ball mill mixer was 1300 rpm. The quantity of additives were used according to the work of Bunthoon [23]. Then the natural rubber latex and cardanol-formaldehyde resin emulsion were added and mixed for required time. The compounded rubber latex was coagulated with 5% formic acid by volume. The compounded sheet was washed with running water and after that it was compressed in a mold in order to remove remaining water.

The compounded sheets were prepared and subjected to various investigations as follows.

1. Effect of the sulfur quantity

The aqueous dispersions of the additives were prepared by ball mill mixer for 3 hours. The sulfur was used with varying the quantity from 0.5, 1, 1.5, to 2 phr. The formulation of compounded sheets is shown in Table 3.1.

Table 3.1 Compounded sheets formulations

Ingredients	Quantity (phr)
Natural rubber	100
MBT	1
ZnO	5
Stearic acid	2
Tergitol NP 10	1.5
Sulfur	0.5, 1.0, 1.5, 2.0
CF resin	0, 1, 2, 4, 6
Mixing time [a] (hour)	0.5, 1, 2

[a]Mixing time is the time to mix rubber latex with CF resin after milling aqueous dispersion of additives for 3 hours.

2. Effect of the cardanol-formaldehyde resin quantity.

Before adding cardanol-formaldehyde resin into the aqueous dispersions of the additives, the resin must be in an emulsion form. The resin emulsion was made by stirring the mixture of Tergitol NP 10 (1.0 g) and water (30 ml) for 2 hours. The quantity of resin was varied by changing the quantity from 0, 1, 2, 4, to 6 phr. The formulation of compounded sheets were the same as shown in Table 3.1.

3. Effect of the mixing time

The mixing time for natural rubber latex and cardanol-formaldehyde resin emulsion mixed with the aqueous dispersion was studied by varying the time to 0.5, 1, and 2 hours so as to obtain the appropriate time. The formulations of compounded sheets were the same as shown in Table 3.1.

3.3.5 Determination the Vulcanization Characteristics of Compounded Rubber

The vulcanization characteristics of natural rubber compounds were measured on an oscillating disk cure meter, Gibitre Rheocheck OD 2000, as per ASTM D 2084-95. The time required to obtain a cure curve was a function of the characteristics of the rubber compound and of the test temperature.

Test condition :

Temperature	150°C
Testing time	20 min
Rotational amplitude	3°

3.3.6 Preparation of Vulcanized Sheets (ASTM D 3182)

Preparation of Sheets

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

Vulcanization Procedure

The vulcanized sheets were prepared by hot press process. The mold was brought to curing temperature (150°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. The press was closed in the minimum time possible. Precautions were then taken to prevent excessive cooling by contact with cool metal surfaces or by exposure to air drafts. The mold was held under a pressure of 120 kg/cm^2 (1700 psi) on the cavity areas during vulcanization. After the required vulcanization time, the press was opened. The vulcanized sheets were removed from the mold and cooled on metal surface by using water cooling for 10 to 15 min. The vulcanized sheets were conditioned at 23 ± 2°C for at least 16 hours and for no greater than 96 hours before preparing and testing.

3.4 Determination of the Compatibility

3.4.1 Optical Microscope (OM)

An Olympus BH-2 was used in order to observe the dispersion of the emulsion of additives and rubber latex.

3.4.2 Scanning Electron Microscope (SEM)

A JSM-5800LV scanning electron microscope was used to determine the dispersion of vulcanized rubber. The samples were prepared by dipping in liquid nitrogen for a few minutes and then they were broken. After that the fracture surface was coated with gold vapor.

3.5 Mechanical Testing

Mechanical properties of the vulcanized rubber, i.e., tensile properties and hardness, before and after aging were measured following ASTM and ISO test methods as follows:

3.5.1 Tensile Properties

The tensile strength, tensile modulus, and elongation at break of rubber compounds were measured in a universal testing machine (Instron Corporation Series IX) according to ASTM D 412-87.

The dumb-bell test pieces (type D) shall have the outline shown in Figure 3.1.

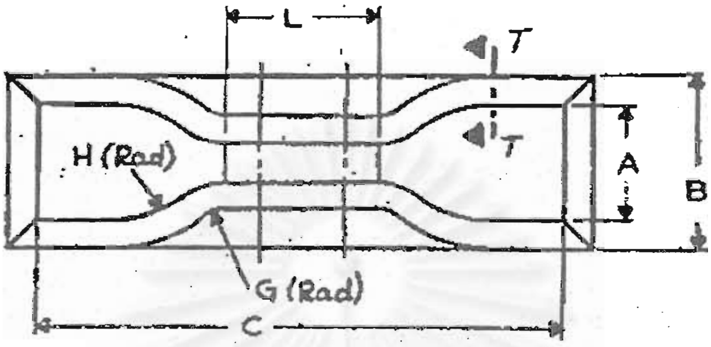


Figure 3.1 Schematic of tensile specimen

Dimension	Type D (mm)
A Width of ends	16 ± 1
C Overall length (minimum)	100
G Transition radius outside	14 ± 1
H Transition radius inside	16 ± 2
L Length of narrow portion	33 ± 2

The condition of tensile testing

Temperature	25 °C
Humidity	60 %

Crosshead Speed	500.0 mm/min
Gauge Length	20.0 mm

3.5.2 Hardness

Hardness property was measured using an indentation hardness tester (Durometer type A) as per ASTM D 2240-95. This test method is based on the penetration of a specific type of indentor when forced into the material under specified conditions. The shape of indentor for type A durometer is shown in Figure 3.2.

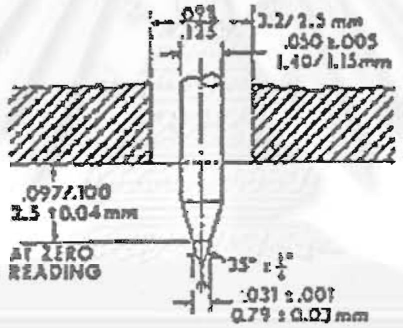


Figure 3.2 Indentor for type A durometer.

The hardness specimen shall be at least 6mm (0.25 in.) in thickness unless it is known that results equivalent to the 6 mm values are obtained with a thinner specimen. The surface 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 from the indentor point.

3.6 Thermal Analysis

3.6.1 Thermal Aging

Thermal aging of the vulcanizates were carried out in an air oven, at 70°C for 72 hours, as per the standard ISO 188.

3.6.2 Thermogravimetric Analysis

Thermogravimetric analysis was performed on a TGA 7 thermogravimetric analyzer (Perkin Elmer). The heating rate used was 20°C per min and the runs were from 50°C to 650°C in a nitrogen atmosphere.

3.7 Solvent Swelling

A specimen was cut from vulcanized sheets and weighed about 0.1 g then it was immersed in the test liquid, toluene (100 ml), for 22 hours at ambient temperature according to ASTM D 471. After the immersion test has proceeded for the required length of time, the specimen was removed. Loose liquid was quickly removed by blotting with filter paper and the swollen weight was immediately measured. Calculation the percent change in mass is as follows:

$$\Delta M, \% = [(M_2 - M_1) / M_1] \times 100$$

where: ΔM = change in mass, %,

M_1 = initial mass of specimen, g, and

M_2 = mass of specimen after immersion, g.

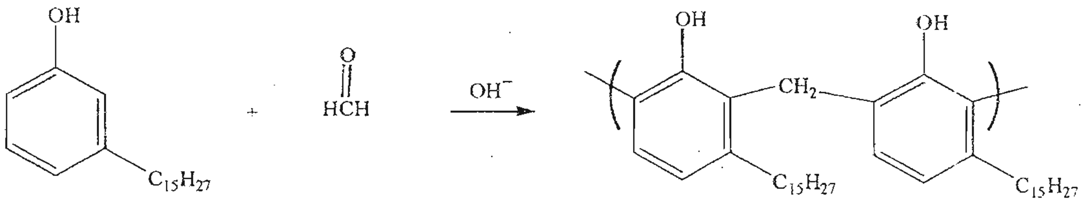
CHAPTER IV

RESULTS AND DISCUSSION

In this investigation, the compounded rubbers were prepared by direct mixing the concentrated natural rubber latex with the cardanol-formaldehyde (CF) resin and other additives. The ball mill mixer was used for preparing the compounded rubber. Then the compatibility of additives and rubber latex in the vulcanized rubbers were determined. Finally, the mechanical properties and thermal properties were investigated.

4.1 Characterization of Cardanol-Formaldehyde Resin

Cardanol-formaldehyde resin was obtained from a reaction between cardanol and formaldehyde with a mole ratio of 1:2 in the presence of NaOH as the catalyst. A reaction temperature of 78-80°C was used and maintained for 2 hours. The chemical equation of condensation reaction was represented as follows:



Scheme 4.1 The formation of cardanol-formaldehyde resin.

The ^{1}H-NMR and IR spectroscopies were used for characterization of CF resin. The ^{1}H-NMR spectrum of resin was determined in $CDCl_3$. The NMR spectrum showed the presence of aromatic protons and methyl protons. Aromatic protons appeared as a multiplet in the range of 6.64-7.25 ppm. Olefinic protons appeared in the range of 4.61-5.43 ppm. Methylene protons appeared in the range of 0.89-2.79 ppm. The peak at 3.35 ppm was due to methylene proton between aromatic ring. The ^{1}H-NMR spectrum of cardanol in $CDCl_3$ also showed the presence of aromatic protons and methyl protons similar to those of the CF resin, which all of chemical shifts refered to the protons in the benzene ring and alkyl side chain. Unlike CF resin, the spectrum of cardanol showed the absence of the peak around 3.35 ppm. Thus, the formation of CF resin was confirmed by the appearance of the peak at 3.35 ppm. The ^{1}H-NMR spectra of CF resin and cardanol are shown in Appendix A.

The IR spectrum of cardanol was similar to CF resin. The broad band at the 3300 cm^{-1} indicated the presence of the hydroxyl group. The peaks between 2980cm^{-1} and 3020 cm^{-1} were belonged to –CH– stretching of alkyl side chain and –CH– stretching of aromatic, respectively. The peak at 1580 cm^{-1} was due to the vibration of the aromatic –C=C– linkage. The peak at 1230 cm^{-1} was due to –CO– stretching of phenol and the peak at 1050 cm^{-1} showed –CO– stretching of primary alcohol. For CF resin, the intensity of the peak at 1050 cm^{-1} was stronger than cardanol. The IR spectra of CF resin and cardanol are shown in Appendix A.

4.2 Vulcanization Characteristics

The compounded rubbers that obtained from the coagulation procedure were used for preparing the vulcanized sheets for mechanical properties investigation. The temperature and the appropriate cure time of this compounded rubber were determined by rheometer.

The rheograph for the compounded rubber at 150°C is given in Appendix B. Table 4.1 showed some of the vulcanization parameters of the compounded rubber.

Table 4.1 Vulcanization parameters of the compounded rubber.

Parameters	Values
Scorch time, t_2 (min)	3.64
Optimum cure time, t_{90} (min)	8.81
Minimum torque, M_L (dNm)	17.72
Maximum torque, M_H (dNm)	21.15
Cure rate index, CRI (min^{-1})	19.34

The cure rate index (CRI) was estimated according to the method reported by ASTM D 2084. From Table 4.1, 90% of cure time required was 8.81 min. in this compounded rubber. The appropriate cure time was 10 min because after the 90% of cure time, the cure curve was almost unchanged at about 22 dNm. From the curve, it was suggested that the mechanical properties slightly changed after the 90% of curing time. This compounded rubber was slowly cured because the slope of the curve increased slightly.

4.3 Effect of the Sulfur Quantity on the Mechanical Properties

Sulfur was the first and a common agent used to vulcanize the natural rubber. The effect of the sulfur quantity on the properties of the vulcanized rubbers was determined by varying the quantity of sulfur from 0.5, 1.0, 1.5, to 2.0 phr. The other additives were kept constant. The formulations of compounded rubber were obtained as follows :

• Natural rubber	100 parts by dry weight
• ZnO	5
• Stearic acid	2
• MBT	1
• Tergitol NP 10	1.5
• CF resin	2

The aqueous dispersion of ZnO, stearic acid, MBT, sulfur, and Tergitol NP 10 (0.5 phr) were prepared by ball mill mixer for 3 hours. After that, rubber latex and CF resin emulsion (Tergitol NP 10 1 phr was used to make emulsion) were added and mixed for 0.5 hour.

Table 4.2 and Figure 4.1 summarize the effect of the amount of sulfur on the mechanical properties. The details of all data are shown in Appendix C.

Table 4.2 Effect of the sulfur quantity on the mechanical properties

Properties	Sulfur quantity (phr)			
	0.5	1.0	1.5	2.0
Tensile Strength (MPa)	12.05 ± 0.74	12.33 ± 0.08	16.01 ± 0.10	17.26 ±0.91
Elongation at Break (%)	2302.0 ± 48.1	2252.5 ± 500.9	2251.0 ± 53.7	2183.0±236.2
300% Modulus (MPa)	1.114 ± 0.037	1.202 ± 0.038	1.277 ± 0.141	1.310 ± 0.274
500% Modulus (MPa)	1.867 ± 0.127	2.341 ± 0.046	2.475 ± 0.214	2.674 ± 0.687
Hardness (shore A)	27.8 ± 1.3	32.9 ± 0.8	33.8 ± 0.3	34.5 ± 0.1
Solvent Swelling (%)	598.57 ± 2.73	430.77 ± 8.54	416.67 ± 6.26	284.62 ± 11.06

The variations in the tensile properties of the vulcanized rubber, such as modulus at 300% elongation, modulus at 500% elongation, elongation at break, and tensile strength with the quantity of sulfur are given in Table 4.2 and Figure 4.1.

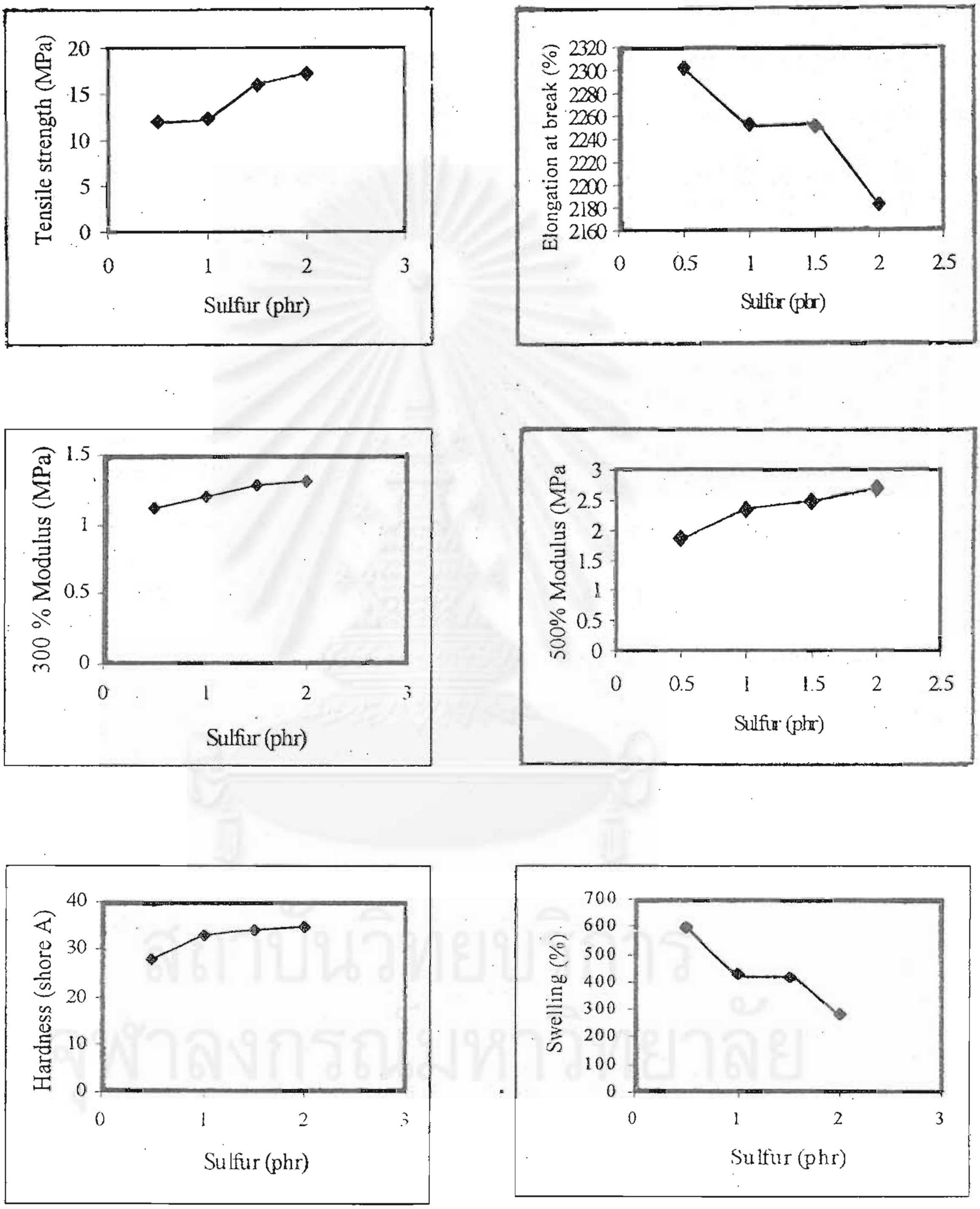


Figure 4.1 Effect of the sulfur quantity on the mechanical properties.

The modulus at 300% and 500% elongation and the tensile strength increased with the increasing of sulfur quantity. This was attributed to the presence of higher proportions of the number of crosslinks. The elongation at break decreases with increasing sulfur quantity. The hardness increased continuously with the number of crosslinks. The more compacting of network, the shorter of molecular segments between the crosslink, hence the tighter of network, which caused an increase in hardness [27].

From Figure 4.1, the solvent swelling of vulcanized rubber was also decreased with an increase in sulfur quantity. The swelling parameter was not influenced much by the degree of crosslinking. It depended mainly on the chemical structure of the compounded rubber and the solvent [7]. Therefore, the best properties were obtained with 2 phr of sulfur and this quantity of sulfur was chosen to prepare compounded rubber.

4.4 Effect of the Cardanol-Formaldehyde Resin Quantity

In this investigation, CF resin was synthesized via condensation reaction between cardanol and formaldehyde containing base as catalyst. The effect of CF resin quantity on the mechanical properties was evaluated by varying CF resin quantity to 0, 1, 2, 4, and 6 phr. The CF resins were prepared as an emulsion before mixing with rubber latex. The formulation of compounded rubber was obtained as follows:

Natural rubber	100 parts by dry weight
ZnO	5
Stearic acid	2
MBT	1
Tergitol NP 10	1.5
Sulfur	2
Mixing time (hour)	0.5

Table 4.3 and Figure 4.2 summarize the effect of CF resin quantity on the mechanical properties. The details of all data are shown in Appendix C.

Table 4.3 Effect of the cardanol-formaldehyde resin quantity

Properties	The CF resin quantity (phr)				
	0	1.0	2.0	4.0	6.0
Tensile Strength (MPa)	7.72 ± 0.91	11.05±0.23	17.26±0.91	14.05±0.27	12.93±1.48
Elongation at Break (%)	2020.8 ± 122.7	2072.8 ± 43.5	2183.0 ± 236.2	2134.5 ± 19.1	2053.2±9.5
300% Modulus (MPa)	1.134 ± 0.044	1.233 ± 0.016	1.310 ± 0.274	1.391 ± 0.017	1.428 ± 0.008
500% Modulus (MPa)	2.161 ± 0.770	2.540 ± 0.031	2.674 ± 0.687	3.306 ± 0.023	3.411 ± 0.098
Hardness (shore A)	29.2 ± 0.1	32.0 ± 0.3	34.5 ± 0.1	34.2 ± 0.1	36.9 ± 0.3
Solvent Swelling (%)	742.86 ± 3.69	392.86 ± 11.12	284.62 ± 11.06	300.00 ± 3.39	323.08 ± 3.72

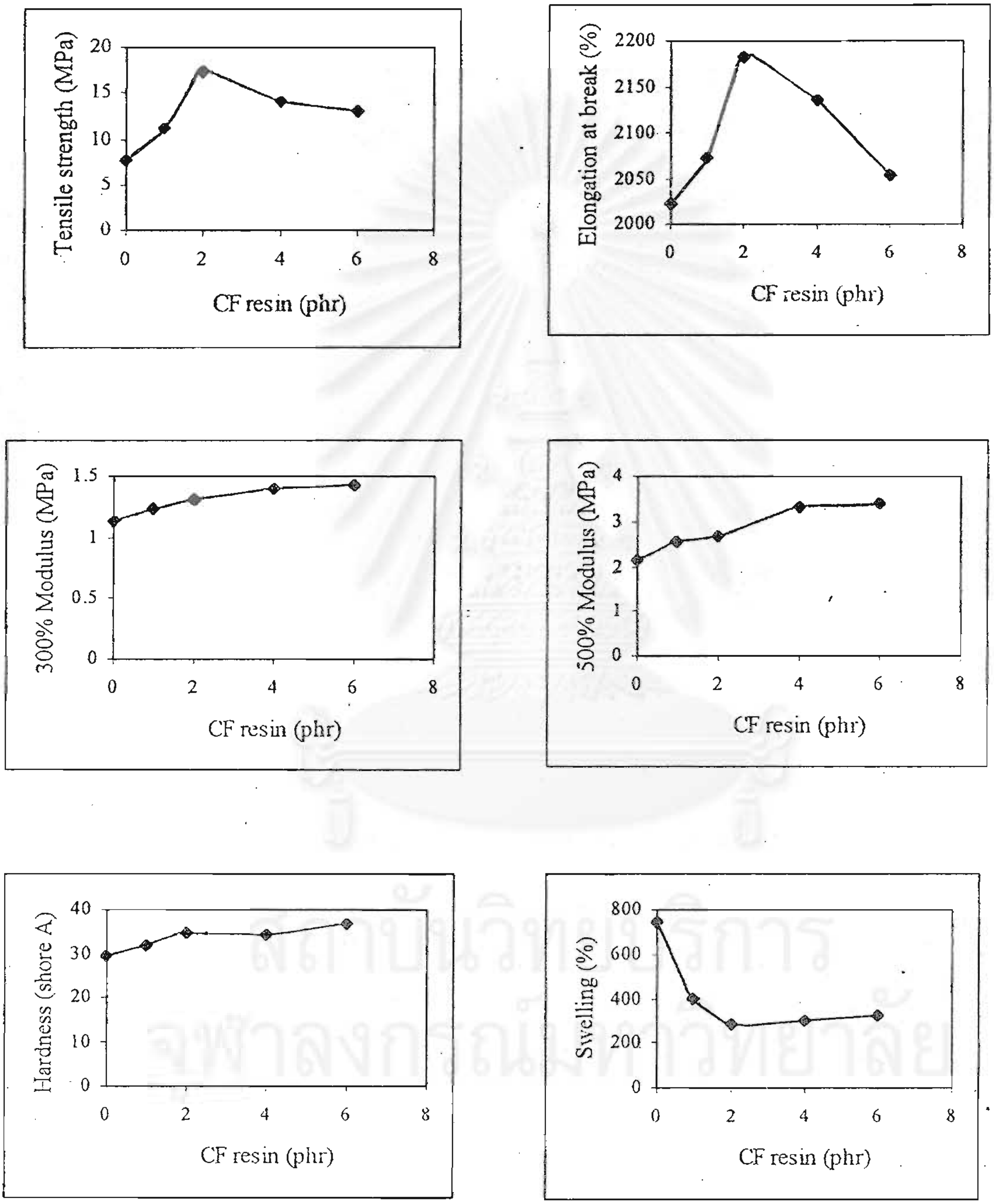


Figure 4.2 Effect of the cardanol-formaldehyde resin quantity.

From Table 4.3 and Figure 4.2, the tensile strength of the vulcanized rubber reached a maximum (17.26 MPa) with the presence of 2 phr of CF resin. This may be due to better dispersion of the additives in the NR matrix, which is evident from the optical micrograph of the latex compound containing 0-6 phr of CF resin (Figure 4.10-4.14). It is also presumed that there is interaction between active functional groups of additive particles with phenolic hydroxy groups of CF resin. The lower tensile strength value at higher dosage of CF resin (4-6 phr) may be due to the plasticization effect. Normally, plasticizers are known to lower the tensile strength of the base polymer [21].

The modulus at 300% and 500% elongation and hardness increased with increasing the CF resin quantity. This was attributed to the formation of an entangled network structure between CF resin and the isoprene chains of natural rubber [21]. The minimum solvent swelling parameter of CF-modified rubber was observed with 2 phr of CF resin in the vulcanized rubber, according to the tensile strength. Thus, the amount of CF resin of 2 phr was chosen for preparing the compounded rubber.

4.5 Effect of the Mixing Time

Except for the study of the effect of sulfur and CF resin quantity on mechanical properties, the mixing time of aqueous additive dispersion with rubber latex and CF resin emulsion was also determined. This was due to the fact that the time of rubber production was a very important factor. If a short time was used to produce rubber product, it would reduce the cost of production. The effect of mixing time was determined by varying the time from 0.5, 1.0, to 2.0 hours. The compounded rubber formulations were obtained as follows:

• Natural rubber	100 parts by dry weight
• ZnO	5
• Stearic acid	2
• MBT	1
• Tergitol NP 10	1.5
• CF resin	2
• Sulfur	2

Table 4.4 and Figure 4.3 summarize the effect of the mixing time on the mechanical properties. The details of all data are shown in Appendix C.

Table 4.4 Effect of the mixing time on the properties.

Properties	The mixing time (hour)		
	0.5	1.0	2.0
Tensile Strength (MPa)	17.26±0.91	16.42±0.54	16.62±0.71
Elongation at Break (%)	2183.0±236.2	2261.2±15.2	2468.0±295.6
300% Modulus (MPa)	1.310±0.274	1.315±0.132	1.308±0.113
500% Modulus (MPa)	2.674±0.687	2.774±0.373	2.724±0.131
Hardness (shore A)	34.5±0.1	34.4±0.1	34.7±0.3
Solvent Swelling (%)	284.62±11.06	366.67±29.66	385.71±11.98

From Table 4.4, the tensile strength and modulus at 300% and 500% elongation of the vulcanized rubber at any time were almost constant. The elongation at break and hardness increased somewhat with the increasing of mixing time. Furthermore, the minimum swelling parameter of vulcanized rubber was obtained at 0.5 hour. Thus, the mixing time of 0.5 hour was chosen as an optimum time for preparing the compounded rubber.

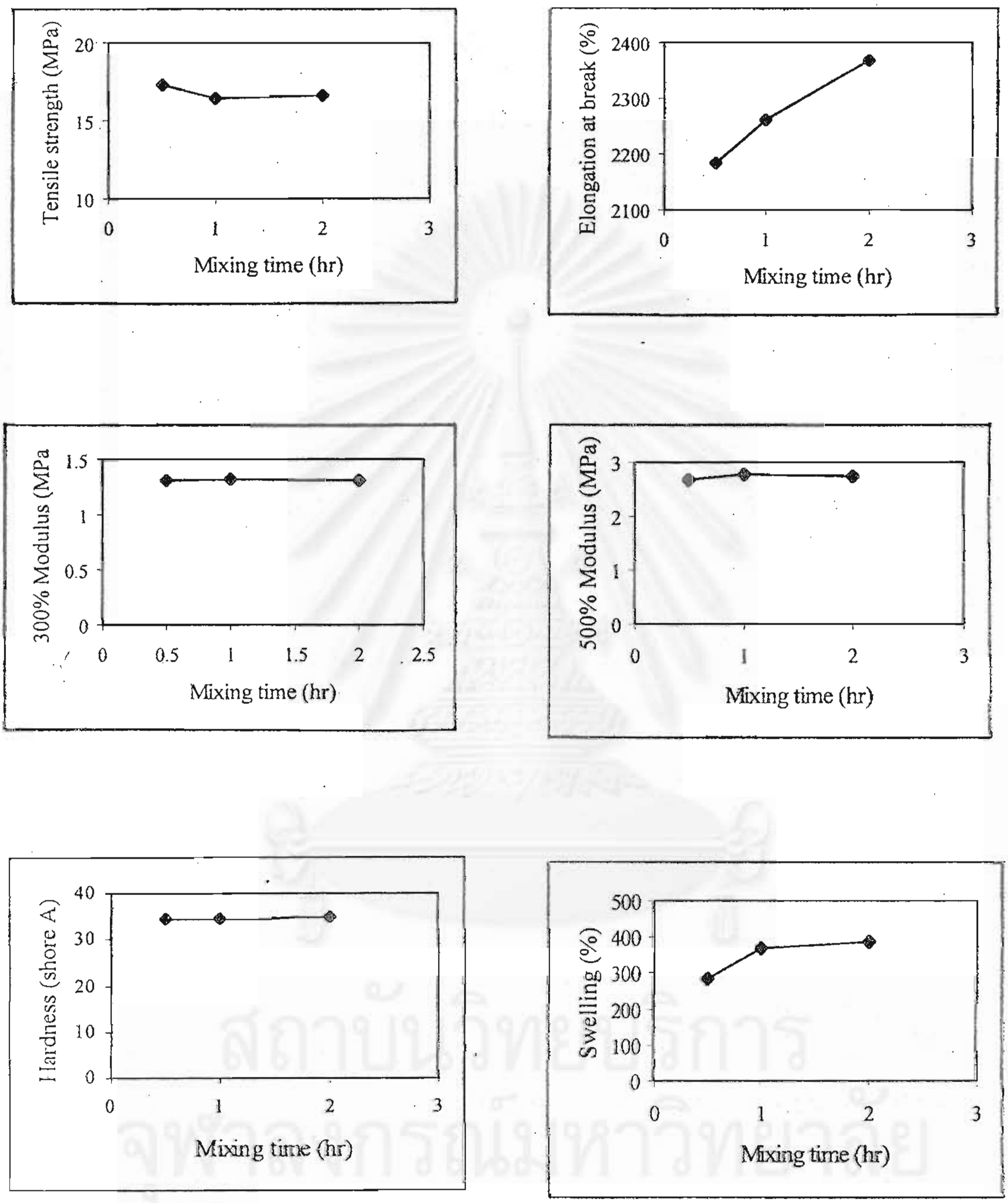


Figure 4.3 Effect of mixing time on the properties.

4.6 Resistance to Aging

The changing in mechanical properties of the vulcanized rubber (2 phr sulfur, 0.5 hr mixing time) after aging in a hot air oven at 70°C for 72 hours are presented in Table 4.5. The details of all data are shown in Appendix D.

Table 4.5 The mechanical properties of vulcanized sheet after aging.

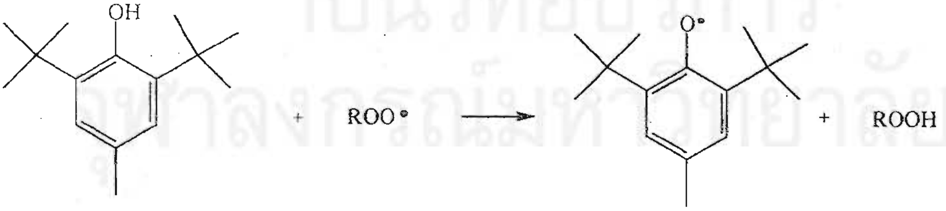
CF resin	The changing in mechanical properties		
	Hardness (value)	Tensile strength (%)	Elongation at break (%)
0	12.7	-30.5	-22.2
1	3.2	-9.4	-16.9
2	1.1	-3.7	-7.1
4	2.6	-8.4	-9.8
6	3.0	-11.3	-9.8

From Table 4.5, the increasing in hardness and the decrease in tensile strength and elongation at break of CF-modified samples, after aging, may be attributed to the formation of additional crosslinks during postvulcanization. The renewed crosslinking also took place similarly to crosslinking processes. The changing of properties could be acceptable when compared with Thai Industrial Standards Institute (TISI) of some rubber products. For example, properties changing after aging of some rubber products are shown in Table 4.6.

Table 4.6 The properties changing after aging of some rubber products according to TISI

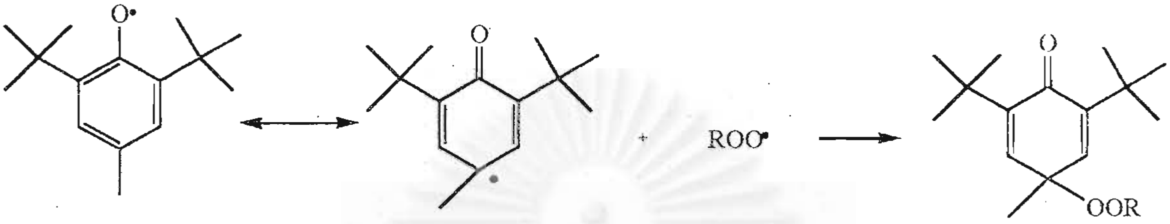
Properties	Rubber hose for coolant system	Automotive rubber mats	This study
Hardness (IRHD)	+15	+10, -5	+1.1
Tensile strength (%)	-20	-25	-3.7
Elongation at break (%)	-50	-35	-7.1

Phenolic compounds are antioxidants, which function by "trapping" or "scavenging" free radicals, such as peroxy radicals, chain radicals, and hydroperoxides to produce inactive decomposition products. Hindered phenolic antioxidants were used to scavenge radicals, especially oxygen radicals, by the following simplified model process:



Scheme 4.2 The formation of phenoxy radical (donor process).

Phenoxy radical was reacted further to accept other radicals through recombination as follows:



Scheme 4.3 The inactive mechanism of phenoxy radical (acceptor process).

Thus, two peroxy radicals could be inactivated by one phenolic molecule. CF resin could also be considered to be this type of antioxidant and this indicated that CF resin, which is a long alkyl-substituted phenol at the meta position, was a very good stabilizer in natural rubber compounds.

4.7 Thermogravimetric (TG) Analysis

The theory of thermogravimetry was simple: as a material decomposes on heating, it loses volatile materials which escape from the sample causing a decreasing in weight. Thus, the successive decomposition reactions occur with increasing temperature, a TG curve showed a series of sharp weight-losses separated by plateaus of constant weight. Therefore, CF-modified rubbers were heated at a constant rate of 20°C/min from 50-650°C for analyzing their degradation behavior at elevated temperatures. All of the decomposition curves were shown in Appendix E and

Figure 4.4 showed the initial decomposition temperature of unmodified and CF-modified rubbers. All of samples were heated under nitrogen atmosphere.

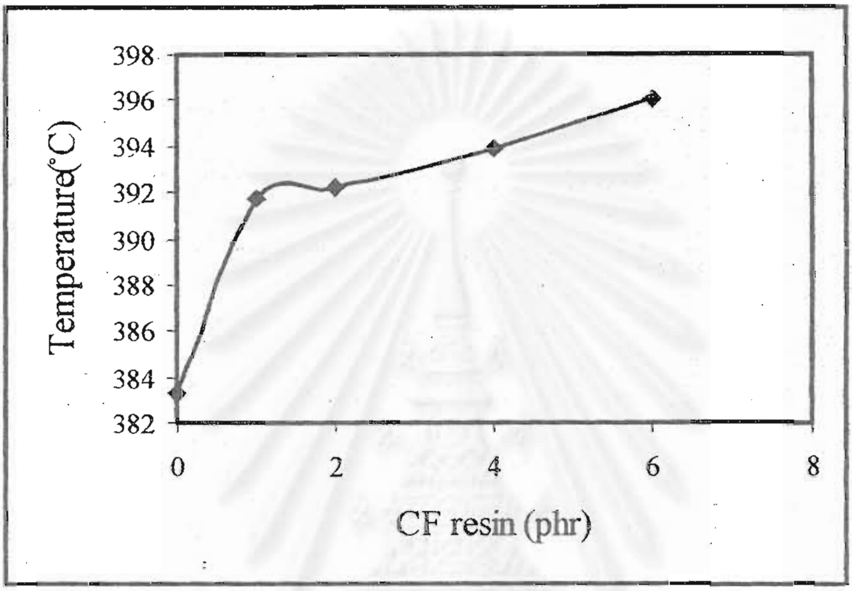


Figure 4.4 The initial decomposition temperature of vulcanized rubber.

The initial decomposition temperature of unmodified rubber started to degrade at lower temperature than those of the CF-modified rubbers. The trend observed in CF resin series was observed that the CF resin quantity was increased to result in a higher thermal stability of the vulcanized rubber. This was attributed to the inherent rigidity of the dihydroxydiphenylmethane unit as a whole.

4.8 Scanning Electron Microscope (SEM)

The fracture surface of vulcanized rubbers for the unmodified and CF-modified samples were examined by SEM with a magnification of 600x. Figure 4.5, 4.6, 4.7, 4.8, and 4.9 showed morphology for 0, 1, 2, 4, and 6 phr of CF resin with 2 phr sulfur and the mixing time of 0.5 hour, respectively. These micrographs displayed some cavities in the structure, probably due to water evaporation during the vulcanization, but the material itself seemed to be homogeneous. Furthermore, the material appears to have no phase separation and shows homogeneous microdispersion of additives and CF resin emulsion in rubber matrix.

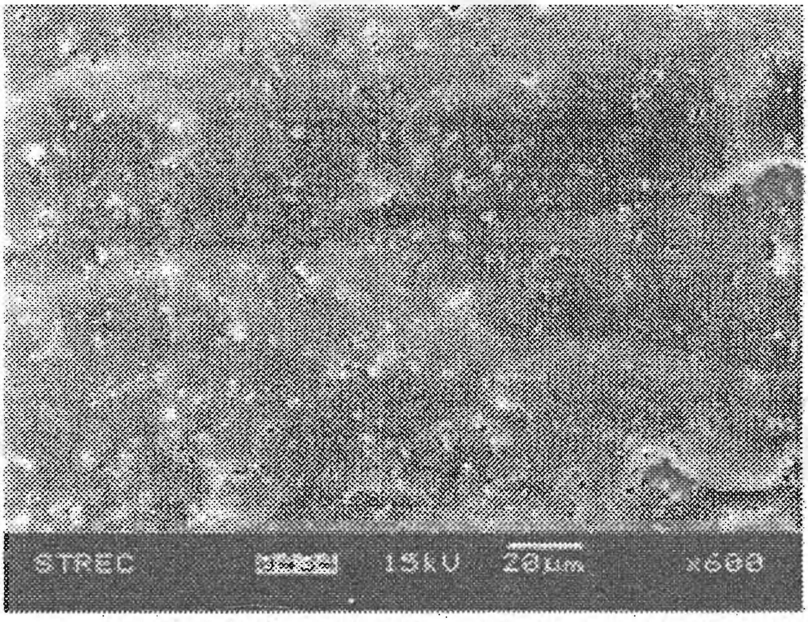


Figure 4.5 Scanning electron micrograph of the fracture surface on the unmodified rubber.

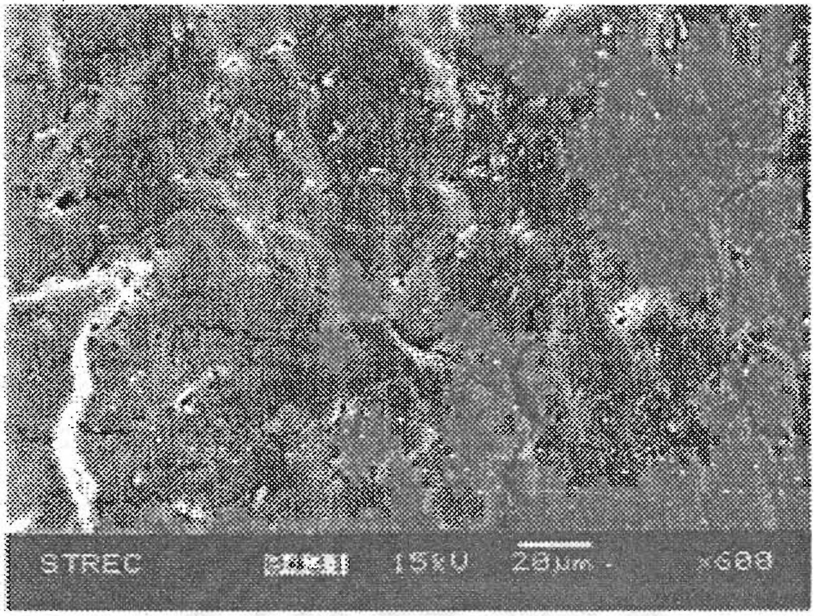


Figure 4.6 Scanning electron micrograph of the fracture surface on the CF-modified rubber (1 phr).

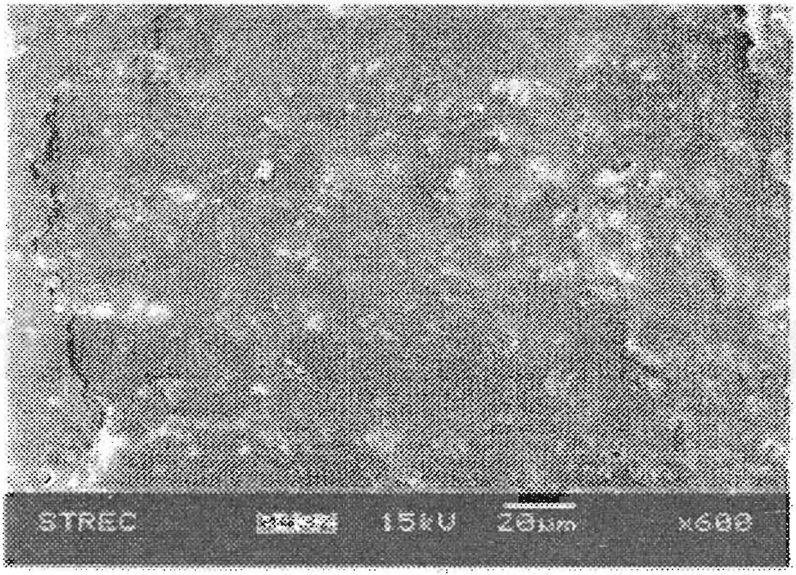


Figure 4.7 Scanning electron micrograph of the fracture surface on the CF-modified rubber (2 phr).

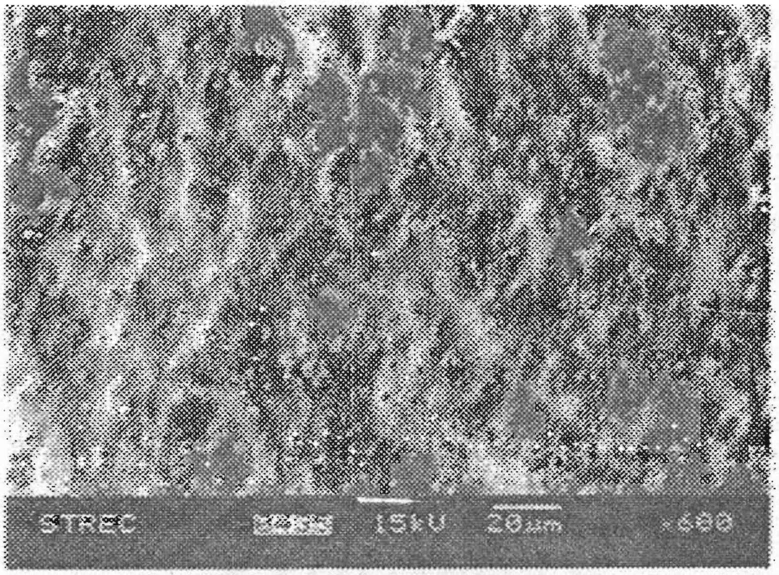


Figure 4.8 Scanning electron micrograph of the fracture surface on the CF-modified rubber (4 phr).

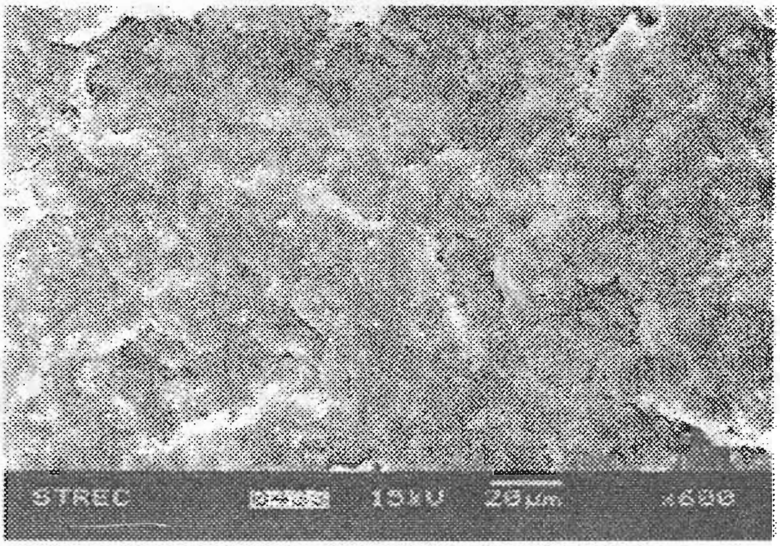


Figure 4.9 Scanning electron micrograph of the fracture surface on the CF-modified rubber (6 phr).

4.9 Optical Microscope (OM)

An optical microscope was used to observe particles dispersion of latex compounds at a magnification of 400x. Optical micrographs for unmodified and CF-modified samples with 1, 2, 4, and 6 phr of CF resin are shown in Figures 4.10, 4.11, 4.12, 4.13, and 4.14. For unmodified sample, it showed a good dispersion of additives. Similar to the low CF resin quantity, all of the additives were dispersed in rubber matrix and showed homogeneous microdispersion. In the case of higher quantity of CF resin it indicated the agglomeration of CF resin to produce higher molecule.

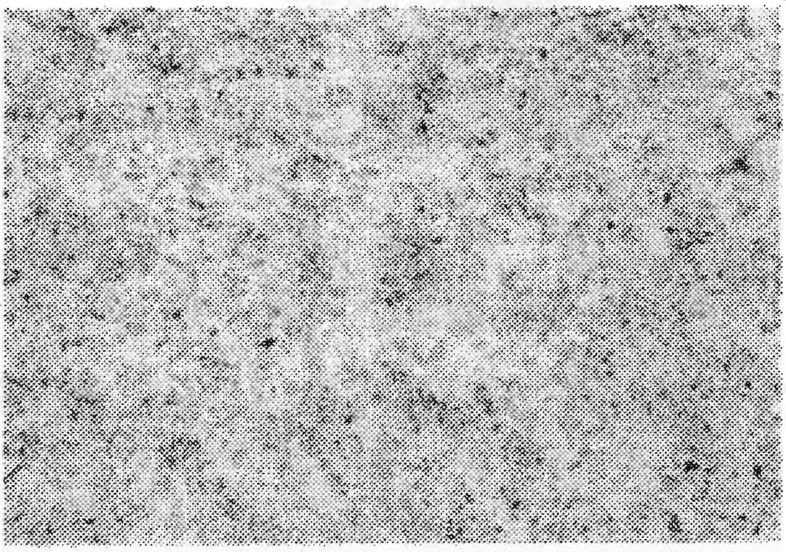


Figure 4.10 Optical micrograph of latex compound for unmodified rubber.

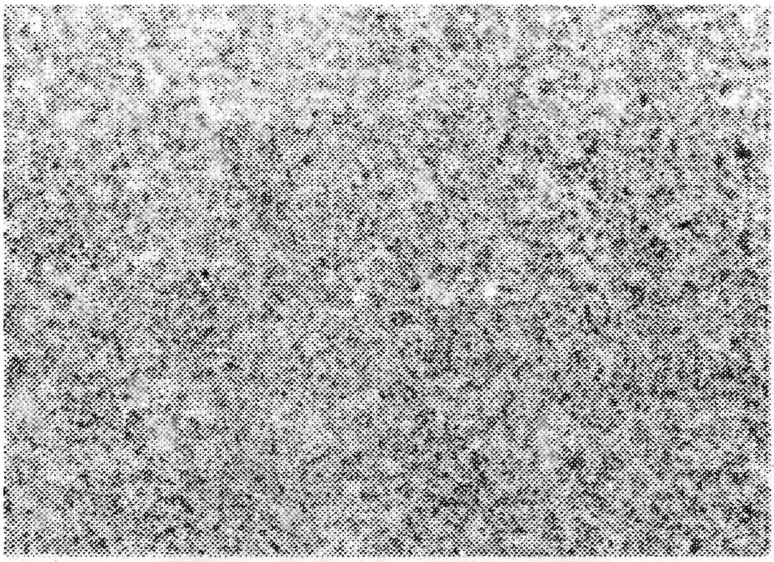


Figure 4.11 Optical micrograph of latex compound for CF-modified rubber (1 phr).

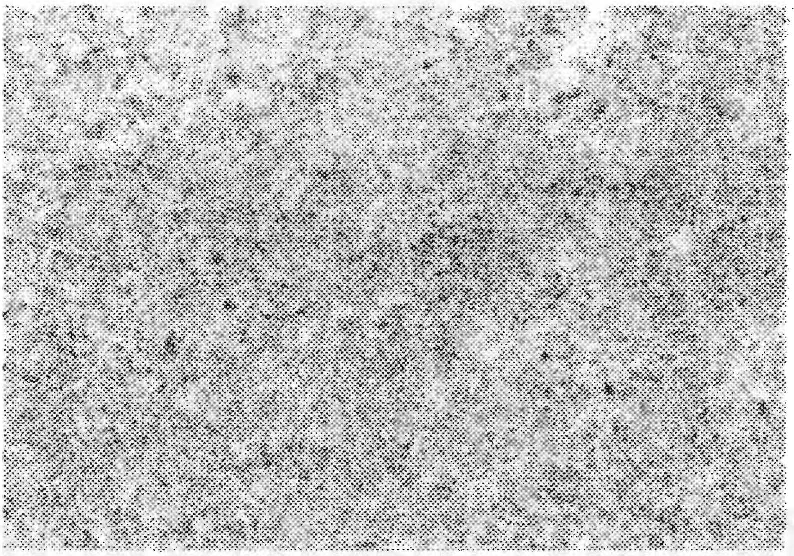


Figure 4.12 Optical micrograph of latex compound for CF-modified rubber (2 phr).

Figure 4.13 Optical micrograph of latex compound for CF-modified rubber (4 phr).

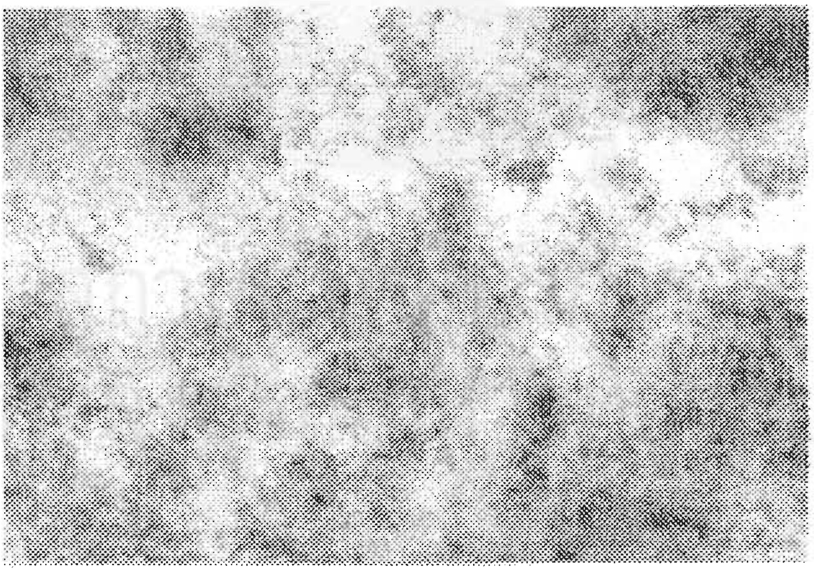


Figure 4.14 Optical micrograph of latex compound for CF-modified rubber (6 phr).

4.10 The Comparison of the Properties with the Work of Bunthoon

The work of Bunthoon was summarized in the Literature Reviews (Chapter II) [23]. The formulation of compounded rubber that were used in his work are presented in the following Table 4.7 :

Table 4.7 The comparison of the formulation of compounded rubber from this research with the work of Bunthoon.

Ingredients	Quantity (phr)	
	Work of Bunthoon	This work
Natural rubber	100	100
ZnO	5	5
Stearic acid	2	2
MBT	1	1
Tergitol NP 10	3	1.5
Sulfur	2	2
Carbon black	25	-
CF resin	-	2
Mixing time (hour)	0.5	0.5

The comparison of the mechanical properties of compounded rubber from this work with those from the work of Bunthoon is shown in Table 4.8.

Table 4.8 The comparison of the mechanical properties of compounded rubber from this work with those from the work of Bunthoon.

Properties	Results	
	Work of Bunthoon	This work
Tensile strength (MPa)	16.49	17.26 ± 0.91
300% Modulus (MPa)	-	1.310 ± 0.274
500% Modulus (MPa)	8.23	2.674 ± 0.987
Elongation at break (%)	1538	2183 ± 236.2
Hardness (shore A)	60.4	34.5 ± 0.1
Tear strength (MPa)	57.15	-
Solvent swelling (%)	250	284.62 ± 11.06
Aging	-	
-Tensile strength (%)		-3.7
-Elongation at break (%)		-7.1
-Hardness (value)		+1.1

From Table 4.8, the tensile strength and elongation at break of vulcanized rubber that were obtained from this investigation showed better properties than those from the work of Bunthoon, especially elongation at break. This may be attributed to the plasticization effect of CF resin. The lower in hardness value of this investigation may be due to the softening effect of CF resin. This disadvantage, perhaps could be overcome by the incorporation of appropriate filler into compounded rubber.

4.11 The Comparison of the Properties with the Work of Vu.

The work of Vu was summarized in the Literature Reviews (Chapter II)[24]. The formulations of compounded rubber that used in their work different from this investigation. Moreover, the previously report dry rubber was used as a raw material whereas this investigation used rubber latex. The formulations of compounded rubber of the previous work are presented in Table 4.9.

Table 4.9 Natural rubber formulary index of Vu.

Ingredients	Formulation (phr)								
	U^a	R^b_5	R_{10}	R_{15}	R_{20}	N^c_5	N_{10}	N_{15a}	N_{15b}
CF resole resin	0	5	10	15	20	0	0	0	0
CF novolak resin	0	0	0	0	0	5	10	15	15
HMTA[d]	0	0	0	0	0	0.5	0.1	1.5	2.25
Natural rubber	100	100	100	100	100	100	100	100	100
Sulfur	3	3	3	3	3	3	3	3	3
Zinc oxide	1	1	1	1	1	1	1	1	1
Zinc stearate	4	4	4	4	4	4	4	4	4
MBT	1	1	1	1	1	1	1	1	1

[a] Unmodified rubber, [b] Resole resin-modified rubber, [c] Novolak resin-modified rubber, [d] Hexamethylene tetramine.

Table 4.9 Natural rubber formulary index of Vu.(continued)

Ingredients	Formulation (phr)			
	U_s	S^a_{10}	S_{20}	S_{30}
CF novolak resin	0	10	20	30
HMTA	0	15	15	15
High *cis*-1,4 poly (isoprene)	100	100	100	100
Sulfur	3	3	3	3
Zinc oxide	1	1	1	1
Stearic acid	4	4	4	4
MBT	1	1	1	1
SiO_2 (VN_3)	20	20	20	20

[a]Novolak resin-modified isoprene rubber

The comparison of the mechanical properties of some formulations with our research is shown in Table 4.10.

Table 4.10 The comparison of the mechanical properties of our result with the work of Vu.

Properties	R_{15}	N_{10}	S_{30}	This study
Tensile strength (MPa)	6.00	6.38	2.93	17.26 ± 0.91
300% Modulus (MPa)	0.75	0.65	-	1.310 ± 0.274
500% Modulus (MPa)	1.47	1.02	-	2.674 ± 0.987
Elongation at break (%)	750	659	163	2183 ± 236.2
Hardness (shore A)	-*	-*	-*	34.5 ± 0.1
Solvent swelling (%)	-*	-*	-*	284.62 ± 11.06

* These properties were not studied.

From Table 4.10, the tensile strength, modulus, and elongation at break of vulcanized sheets that obtained from this investigation showed better properties than the work of Vu, especially tensile strength and elongation at break. This may be attributed to the fact that smoked rubber sheet must undergo mastication before use, which the latex rubber is used directly, thus retaining its original high molecular weight which results in higher modulus product. Moreover this investigation gives better properties, with less CF resin less than in the work of Vu [24].

4.12 The Comparison of the Properties with Thai Industrial Standards Institute

The properties of vulcanized rubber, which were obtained from this investigation, are compared with the properties of some rubber products of the Thai Industrial Standards Institute (TISI). The mechanical properties for rubber hoses for compressed air, rubber ring for pressured water pipe, and bicycle rubber inner tubes compiled with the TISI standard are shown in Table 4.11.

Table 4.11 The mechanical properties of rubber products.

Properties	Rubber hoses for compressed air	Rubber ring for pressured water pipe	Bicycle rubber inner tubes	Compounded rubber from this study
Tensile strength (MPa)	6.0	12.5	9.81	17.26
Elongation at break (%)	250	325	450	2183
Aging (change in)			-*	
-Tensile strength (%)	±35	-15		-3.7
-Elongation at break (%)	±35	-25		-7.1

* This property was not studied.

The mechanical properties of vulcanized rubbers, which were obtained from this study, were higher than the rubber standard of TISI (Table 4.11).

CHAPTER V

CONCLUSION

The compounded rubbers from natural rubber modified with cardanol-formaldehyde resin were prepared with the appropriate formulation, for the best properties. The appropriate obtainable formulation consists of 100 parts by dry weight concentrated latex, 5 phr ZnO, 2 phr stearic acid, 1 phr MBT, 1.5 phr Tergitol NP 10, 2 phr sulfur, and 2 phr CF resin. The appropriate mixing time is 0.5 hour. The modification of natural rubber with CF resin could improve the mechanical properties, especially tensile property. Furthermore, the resins acted as very effective antioxidant for natural rubber. The thermal stability of the CF-modified rubber depends on the quantity of CF resin used. The increasing of CF quantity in the rubber matrix improves the thermal stability of the system. The properties of the vulcanized rubber are shown in Table 5.1.

In Table 5.1, the properties of vulcanized rubber, which were obtained from this investigation, are compared with the properties of some rubber products of the Thai Industrial Standards Institute (TISI). Thus, compounded rubber from this investigation has good potential to be use to produce rubber hoses for compressed air, rubber ring for pressured water pipe, and bicycle rubber inner tubes.

Table 5.1 The properties of the vulcanized rubber.

Properties	Results
Tensile strength (MPa)	17.26 ± 0.91
300% Modulus (MPa)	1.310 ± 0.274
500% Modulus (MPa)	2.674 ± 0.987
Elongation at break (%)	2183 ± 236.2
Hardness (shore A)	34.5 ± 0.1
Solvent swelling (%)	284.62 ± 11.06
Aging	
-Tensile strength (%)	-3.7
-Elongation at break (%)	-7.1
-Hardness (value)	+1.1

Suggestion for Future Work

1. Investigating the properties, especially thermal properties of vulcanized rubbers, which can be obtained from this method but using the other hindered phenolic compounds.

2. Investigating the effect of filler additives, such as carbon black, silica, and china clay, on this compounded rubber.

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APPENDICE

APPENDIX A

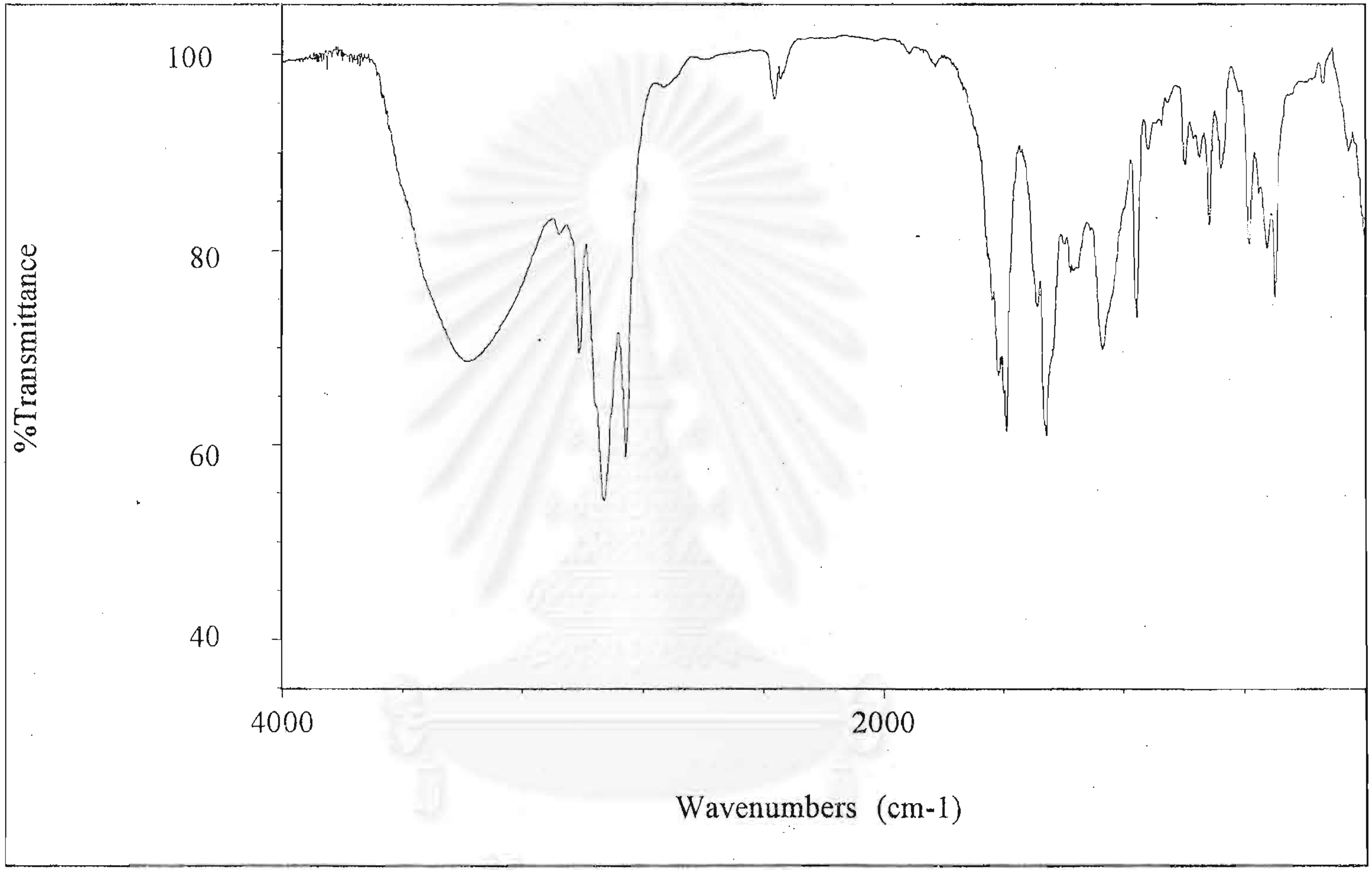


Figure A.1 Infrared spectrum of cardanol.

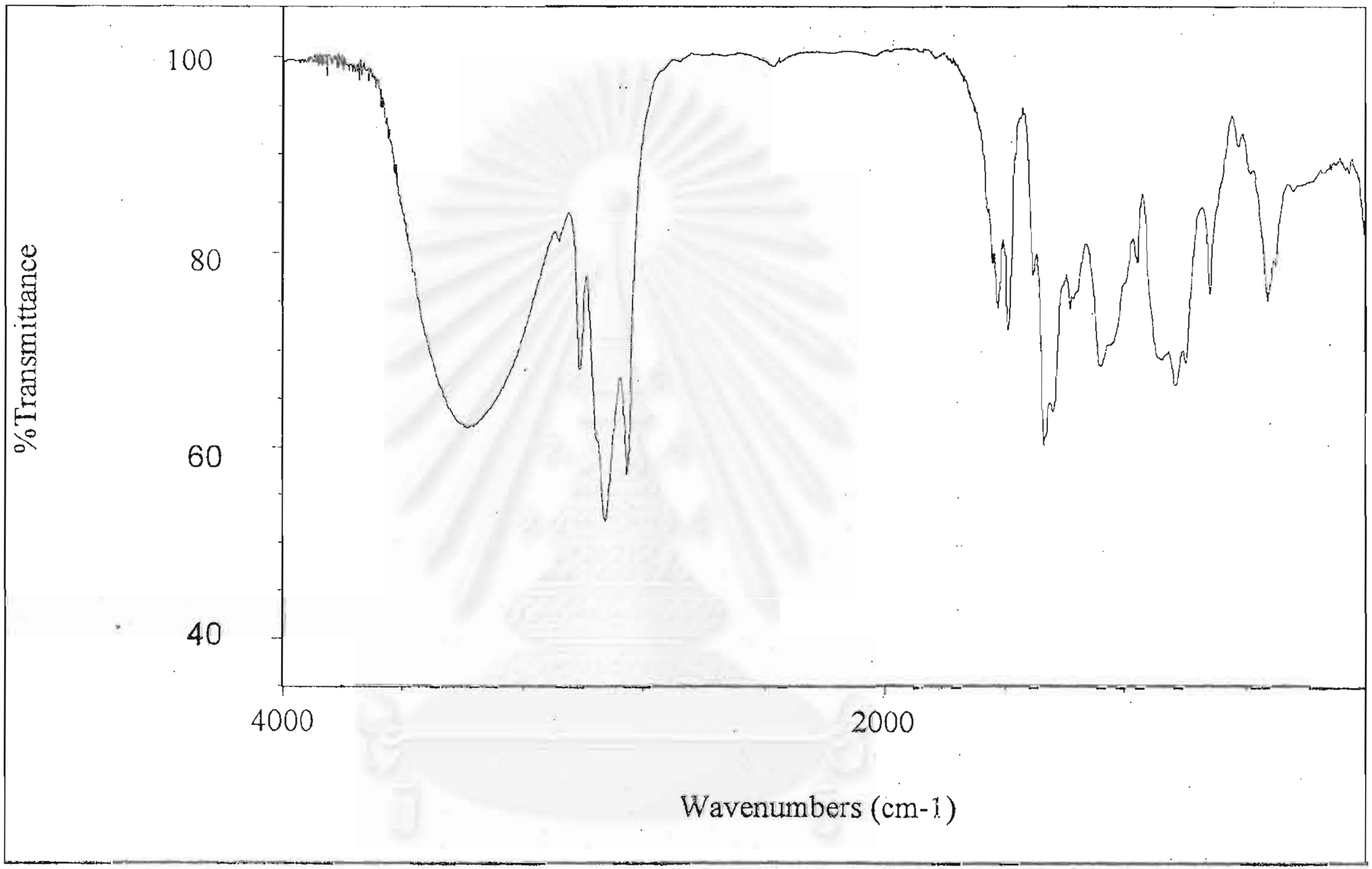


Figure A.2 Infrared spectrum of cardanol-formaldehyde resin.

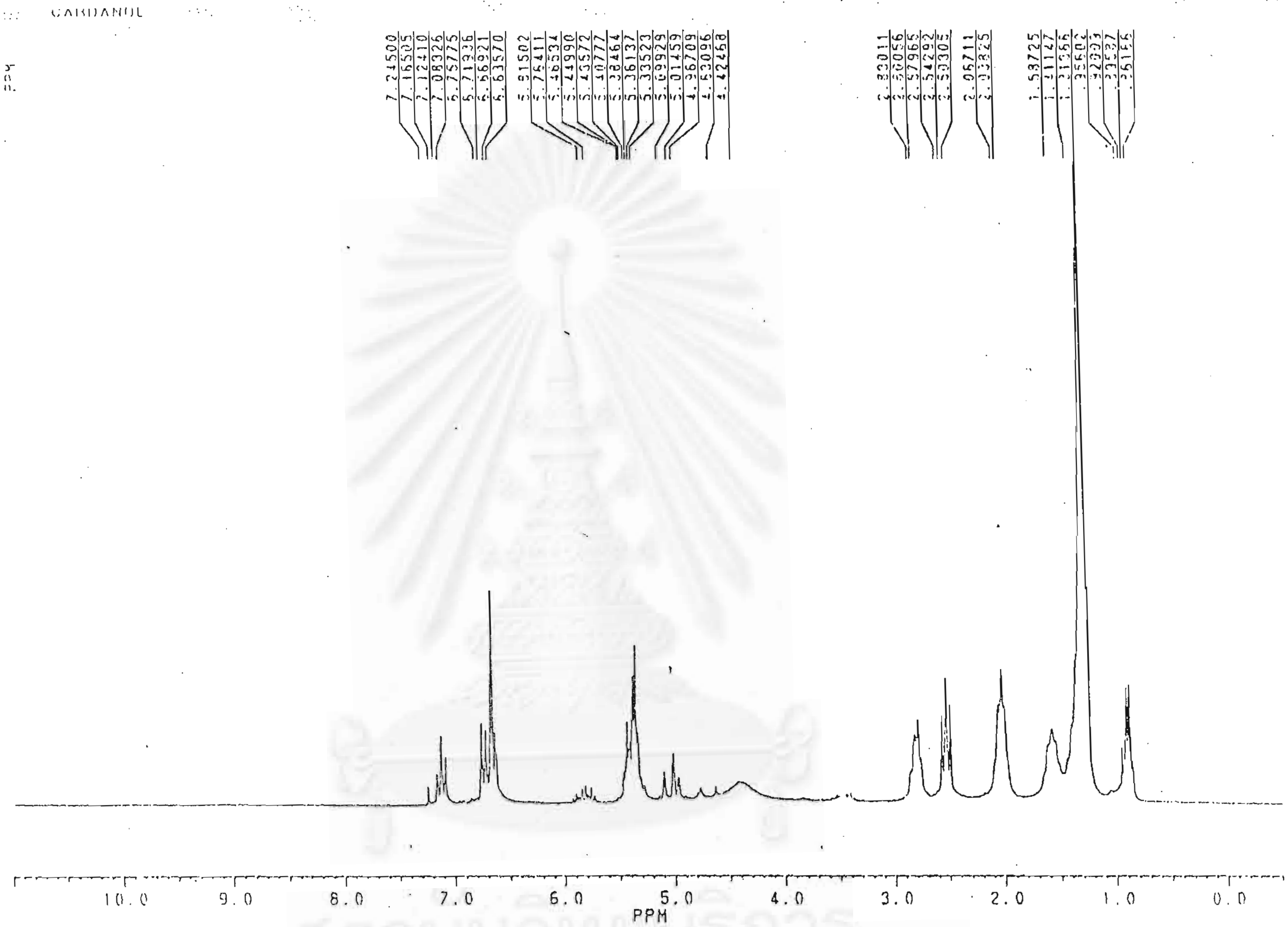


Figure A.3 Proton NMR spectrum of cardanol.

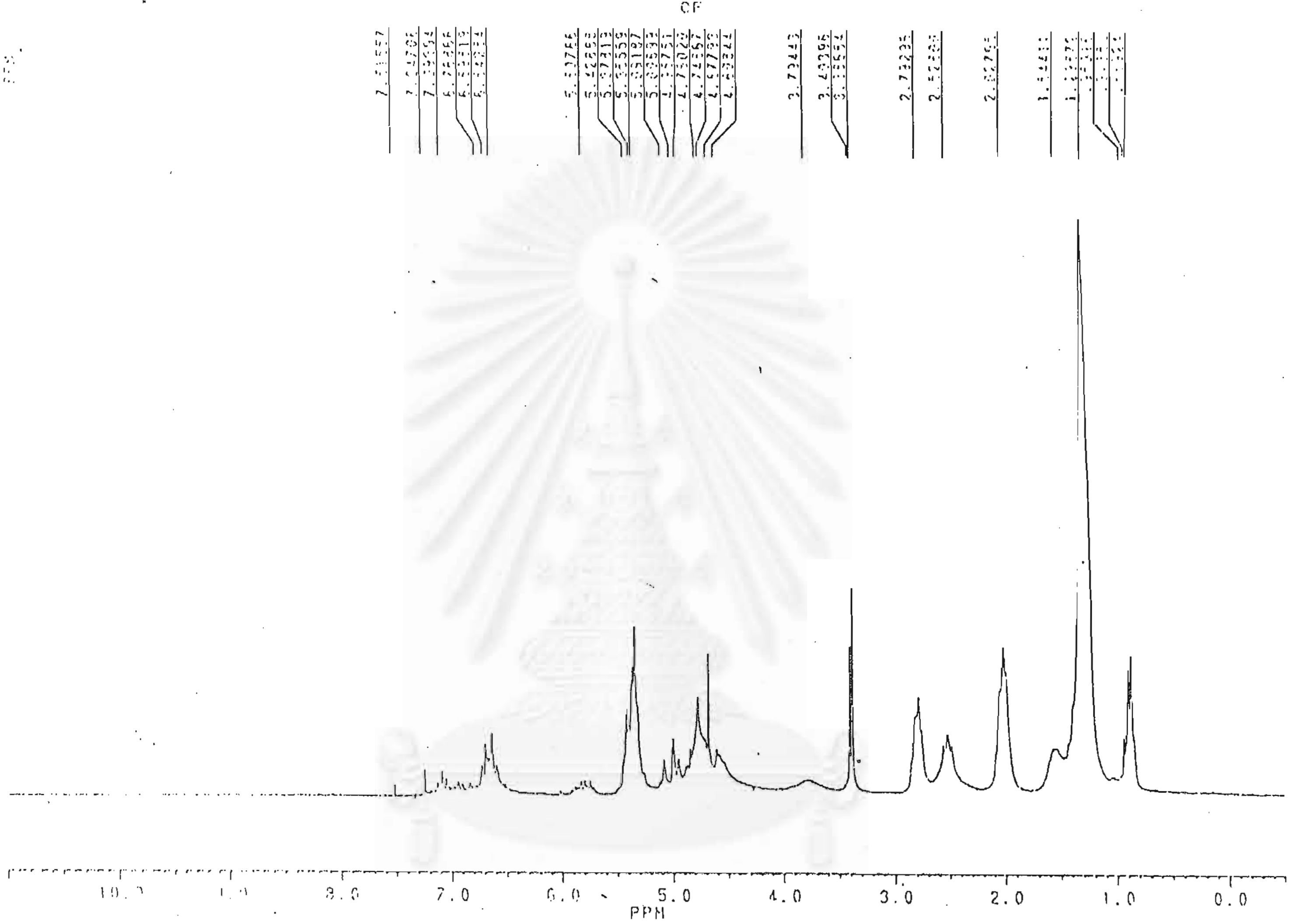


Figure A.4 Proton NMR spectrum of cardanol-formaldehyde resin.

APPENDIX B

Rheometer Summary Report

Rubber Technology Division

Tuesday March 14, 2000. REHO Page:

COMPOUND ID: R-27
R CHART RANGE: 50 dNm
R DIE TYPE: MPC

R DESCRIPTION: NATAYA CHULA
R CHART SPEED: 20 min.
R TEMPERATURE: 150 C

R DEGREE ARC: 3.00

MIXDATE	TESTID	MAX TORQ	MIN TORQ	ts1	ts2	tc10	tc50	tc90	P/F
*03/14/00	2	21.15	17.72	2.47	3.64	1.86	3.25	8.81	P

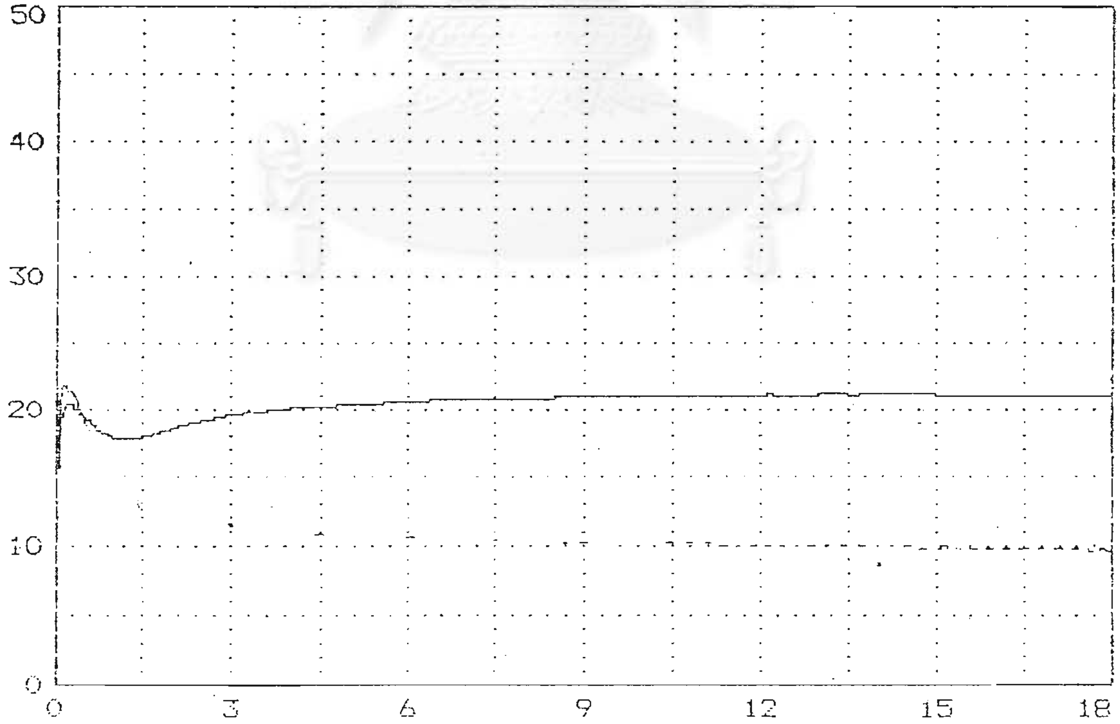


Figure B.1 Rheometer chart of sample.

APPENDIX C

1. Tensile strength of vulcanized rubbers

Table C.1 Tensile strength of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Tensile strength (MPa)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	4.302	4.426	4.3640	0.088
1		9.779	9.144	9.4615	0.449
2		12.570	11.520	12.0450	0.742
4		11.360	11.115	11.2375	0.173
6		11.920	11.490	11.7050	0.304
0	1	4.633	4.224	4.4385	0.275
1		9.039	10.340	9.6895	0.920
2		12.870	13.086	12.9780	0.153
4		11.670	10.162	10.9160	1.066
6		9.098	9.014	9.0560	0.059
0	2	4.713	3.896	4.3045	0.578
1		11.930	10.079	11.0035	1.310
2		13.433	13.694	13.5635	0.185
4		12.471	11.140	12.3055	0.234
6		10.870	9.991	10.4305	0.622

Table C.2 Tensile strength of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Tensile strength (MPa)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	6.848	6.829	6.8385	0.013
1		11.040	10.970	11.0050	0.049
2		11.380	11.270	11.3250	0.078
4		9.484	9.690	9.5870	0.146
6		9.384	9.468	9.4260	0.059
0	1	5.454	6.005	5.7295	0.390
1		12.291	12.434	12.3625	0.101
2		14.054	14.623	14.3385	0.402
4		14.859	13.770	14.3145	0.770
6		10.593	10.390	10.4915	0.144
0	2	6.046	5.438	5.7420	0.430
1		11.500	10.550	11.0250	0.672
2		12.670	10.380	11.5250	1.619
4		13.210	12.881	13.0455	0.233
6		9.018	9.597	9.3075	0.409

Table C.3 Tensile strength of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Tensile strength (MPa)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	7.017	7.588	7.3025	0.404
1		17.003	15.120	16.0615	1.331
2		16.080	15.940	16.0100	0.099
4		15.803	15.390	15.5965	0.292
6		14.170	13.760	13.9650	0.290
0	1	8.442	5.720	7.0810	1.925
1		16.930	16.400	16.6650	0.375
2		12.970	10.960	11.9650	1.421
4		11.270	10.780	11.0250	0.346
6		11.440	10.630	11.0350	0.573
0	2	8.036	8.171	8.1035	0.095
1		16.490	14.160	15.3250	1.648
2		14.150	14.555	14.3525	0.286
4		14.808	14.900	14.8540	0.065
6		11.530	12.060	11.7950	0.375

Table C.4 Tensile strength of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Tensile strength (MPa)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	7.076	8.360	7.7180	0.908
1		10.890	11.210	11.0500	0.226
2		16.620	17.900	17.2600	0.905
4		13.863	14.241	14.0520	0.267
6		13.980	11.880	12.9300	1.485
0	1	8.699	8.002	8.3505	0.493
1		13.98	11.610	12.7950	1.676
2		15.800	15.040	15.420	0.537
4		14.130	13.760	13.9450	0.262
6		12.520	11.590	12.0550	0.658
0	2	8.117	7.871	7.9940	0.174
1		16.740	13.020	14.8800	2.630
2		17.120	16.120	16.6200	0.707
4		16.050	14.460	15.2550	1.124
6		12.350	12.220	12.2850	0.092

2. Hardness of vulcanized rubbers

Table C.5 Hardness (shore A) of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Hardness (shore A)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	25.1	22.1	23.6	2.121
1		23.3	27.8	25.6	3.182
2		26.9	28.8	27.8	1.344
4		30.3	31.5	30.9	0.849
6		31.8	32.6	32.2	0.566
0	1	24.4	23.2	23.8	0.849
1		26.5	29.3	27.9	1.980
2		29.8	30.2	30.0	0.283
4		32.4	30.8	31.6	1.131
6		32.8	32.0	32.4	0.566
0	2	26.6	28.3	27.4	1.202
1		28.9	29.8	29.4	0.636
2		29.2	31.3	30.2	1.485
4		31.6	32.0	31.8	0.283
6		32.6	33.4	33.0	0.566

Table C.6 Hardness (shore A) of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Hardness (shore A)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	28.3	29.5	28.9	0.849
1		34.6	34.9	34.8	0.212
2		33.5	32.3	32.9	0.849
4		35.3	34.9	35.1	0.283
6		36.4	36.8	36.6	0.283
0	1	29.1	30.0	29.6	0.636
1		33.8	34.2	34.0	0.283
2		34.7	34.3	34.5	0.283
4		36.0	36.4	36.2	0.283
6		37.7	37.1	37.4	0.424
0	2	26.9	24.9	25.9	1.414
1		32.9	32.1	32.5	0.566
2		33.4	33.8	33.6	0.283
4		34.9	35.3	35.1	0.283
6		38.8	39.0	38.9	0.141

Table C.7 Hardness (shore A) of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Hardness (shore A)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	29.7	28.5	29.1	0.849
1		32.3	33.7	33.0	0.990
2		33.6	34.0	33.8	0.283
4		35.6	35.8	35.7	0.141
6		36.3	37.3	36.8	0.707
0	1	32.9	31.0	31.9	1.344
1		33.3	33.7	33.5	0.283
2		34.6	34.2	34.4	0.283
4		36.1	36.5	36.3	0.283
6		37.0	37.8	37.4	0.566
0	2	29.8	31.4	30.6	1.131
1		33.4	33.8	33.6	0.283
2		34.7	34.3	34.5	0.283
4		36.7	36.5	36.6	0.141
6		37.4	38.0	37.7	0.424

Table C.8 Hardness (shore A) of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Hardness (shore A)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	29.1	29.3	29.2	0.141
1		31.8	32.2	32.0	0.283
2		34.6	34.4	34.5	0.141
4		34.1	34.3	34.2	0.141
6		36.7	37.1	36.9	0.283
0	1	27.7	26.9	27.3	0.566
1		33.6	33.2	33.4	0.283
2		34.3	34.5	34.4	0.141
4		34.6	34.2	34.4	0.283
6		36.7	36.3	36.5	0.283
0	2	27.1	27.7	27.4	0.424
1		33.7	33.3	33.5	0.283
2		34.5	34.9	34.7	0.283
4		35.0	35.4	35.2	0.283
6		36.1	35.5	35.8	0.424

3. Elongation at break of vulcanized rubbers

Table C.9 Elongation at break of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Elongation at break (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	2146.0	2011.3	2078.7	95.2
1		2112.0	1977.0	2044.5	95.5
2		2268.0	2336.0	2302.0	48.1
4		2259.0	2122.0	2190.5	96.9
6		1034.0	1849.0	1441.5	576.3
0	1	2466.0	2517.0	2491.5	36.1
1		2617.0	2860.0	2738.5	171.8
2		2590.0	2458.0	2524.0	93.3
4		2443.0	2392.0	2417.5	36.1
6		2951.0	2546.0	2748.5	286.4
0	2	2350.0	2140.0	2245.0	148.5
1		2052.0	2078.0	2065.0	18.4
2		2530.0	2144.5	2337.3	272.6
4		2393.0	2256.0	2324.5	96.9
6		2562.0	2478.0	2520.0	59.4

Table C.10 Elongation at break of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Elongation at break (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	1567.0	1632.0	1599.5	46.0
1		2134.0	1983.0	2058.5	106.8
2		2606.7	1898.3	2252.5	500.9
4		2207.0	2063.0	2135.0	101.8
6		2277.0	2165.0	2221.0	79.2
0	1	1545.0	1829.5	1687.3	201.2
1		2055.7	1991.3	2023.5	45.5
2		2113.7	2111.0	2112.4	1.9
4		2110.0	2158.0	2134.0	33.9
6		1980.2	2206.0	2093.1	159.7
0	2	2051.0	1991.0	2021.0	42.4
1		2158.0	2187.0	2172.5	20.5
2		2147.7	2086.0	2116.9	43.6
4		1716.0	1656.7	1686.4	41.9
6		1213.0	1277.0	1245.0	45.3

Table C.11 Elongation at break of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Elongation at break (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	2204.0	1962.0	2083.0	171.1
1		2629.5	2173.0	2401.3	322.8
2		2289.0	2213.0	2251.0	53.7
4		2268.0	2350.0	2309.0	58.0
6		2186.2	2098.0	2142.1	62.4
0	1	1801.0	1644.5	1722.8	110.7
1		2474.3	1941.0	2207.7	377.1
2		2242.2	2493.0	2367.6	177.3
4		2123.5	2120.0	2121.8	2.5
6		2123.0	2239.0	2181.0	82.0
0	2	1879.0	1950.2	1914.6	50.3
1		2186.0	2350.0	2268.0	116.0
2		2022.0	2290.0	2156.0	189.5
4		1996.0	2245.0	2120.5	176.1
6		2434.0	2374.0	2404.0	42.4

Table C.12 Elongation at break of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Elongation at break (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	1934.0	2107.5	2020.8	122.7
1		2103.5	2042.0	2072.8	43.5
2		2350.0	2016.0	2183.0	236.2
4		2121.0	2148.0	2134.5	19.1
6		2046.5	2060.0	2053.3	9.5
0	1	2008.0	2214.0	2111.0	145.7
1		2213.0	2112.0	2162.5	71.4
2		2250.5	2272.0	2261.3	15.2
4		2541.7	2318.0	2429.9	158.2
6		2333.7	2668.0	2500.9	236.4
0	2	2008.0	1896.0	1952.0	79.2
1		2186.0	2003.0	2094.5	129.4
2		2259.0	2677.0	2468.0	295.6
4		2166.7	2289.3	2228.0	86.7
6		2279.0	2109.0	2194.0	120.2

4. Swelling of vulcanized rubbers

Table C.13 Swelling of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Swelling (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	880.72	892.62	886.67	8.41
1		665.93	676.93	671.43	7.78
2		600.50	596.64	598.57	2.73
4		536.48	509.68	523.08	18.95
6		570.34	563.00	566.67	5.19
0	1	849.65	864.63	857.14	10.59
1		580.20	586.46	583.33	4.43
2		564.72	535.28	550.00	20.82
4		511.23	503.05	507.14	5.78
6		591.12	580.30	585.71	7.65
0	2	838.79	846.93	842.86	5.76
1		516.40	498.98	507.69	12.32
2		525.43	531.71	528.57	4.44
4		512.60	502.78	507.69	6.94
6		557.94	565.14	561.54	5.09

Table C.14 Swelling of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Swelling (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	818.25	824.61	821.43	4.50
1		492.64	474.02	483.33	13.17
2		424.73	436.81	430.77	8.54
4		566.49	590.65	578.57	17.08
6		580.20	573.64	576.92	4.64
0	1	878.63	888.03	883.33	6.65
1		466.87	486.97	476.92	14.21
2		509.42	523.92	516.67	10.25
4		465.81	477.05	471.43	7.95
6		457.31	471.25	464.28	9.86
0	2	846.72	869.94	858.33	16.42
1		405.68	378.94	392.31	18.91
2		516.48	529.68	523.08	9.33
4		538.46	547.26	542.86	6.22
6		460.74	446.96	453.85	9.74

Table C.15 Swelling of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Swelling (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	787.13	799.53	793.33	8.77
1		415.62	401.04	408.33	10.31
2		412.24	421.10	416.67	6.26
4		398.67	416.71	407.69	12.76
6		448.23	451.77	450.00	2.50
0	1	765.43	791.71	778.57	18.58
1		408.75	424.59	416.67	11.20
2		440.87	425.79	433.33	10.66
4		418.96	427.20	423.08	5.83
6		437.89	447.83	442.86	7.03
0	2	743.68	756.32	750.00	8.94
1		395.25	404.75	400.00	6.72
2		410.00	420.76	415.38	7.61
4		418.36	424.50	421.43	4.34
6		438.79	444.55	441.67	4.07

Table C.16 Swelling of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	Swelling (%)			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	740.25	745.47	742.86	3.69
1		385.00	400.72	392.86	11.12
2		276.80	292.44	284.62	11.06
4		302.40	297.60	300.00	3.39
6		320.45	325.71	323.08	3.72
0	1	700.00	733.34	716.67	23.57
1		385.20	399.42	392.31	10.06
2		345.70	387.64	366.67	29.66
4		340.65	332.07	336.36	6.07
6		312.54	304.12	308.33	5.95
0	2	754.80	768.28	761.54	9.53
1		382.92	367.08	375.00	11.20
2		377.24	394.18	385.71	11.98
4		348.53	351.47	350.00	2.08
6		369.87	396.79	383.33	19.04

5. 300% Modulus of vulcanized rubbers

Table C.17 300% Modulus of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	300% Modulus			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	0.819	0.944	0.882	0.088
1		0.807	1.115	0.961	0.218
2		1.088	1.140	1.114	0.037
4		0.978	1.138	1.058	0.113
6		1.089	0.896	0.993	0.136
0	1	0.881	1.016	0.949	0.095
1		1.182	1.017	1.100	0.117
2		1.321	1.247	1.284	0.052
4		0.891	1.097	0.994	0.146
6		0.911	0.986	0.949	0.053
0	2	0.867	0.859	0.863	0.005
1		1.329	1.164	1.247	0.117
2		1.072	1.163	1.118	0.064
4		0.973	0.898	0.936	0.053
6		0.775	0.932	0.854	0.111

Table C.18 300% Modulus of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	300% Modulus			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	1.051	1.049	1.050	0.001
1		1.358	1.386	1.372	0.020
2		1.229	1.175	1.202	0.038
4		1.281	1.327	1.304	0.033
6		0.900	1.022	0.961	0.086
0	1	1.180	1.043	1.112	0.097
1		1.352	1.134	1.243	0.154
2		1.267	1.442	1.355	0.124
4		1.268	1.124	1.196	0.102
6		1.157	1.204	1.181	0.033
0	2	1.041	1.147	1.094	0.075
1		1.188	1.103	1.146	0.060
2		1.383	1.241	1.312	0.100
4		1.273	1.236	1.255	0.026
6		1.264	1.120	1.192	0.102

Table C.19 300% Modulus of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	300% Modulus			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	0.999	0.913	0.956	0.061
1		1.154	1.187	1.171	0.023
2		1.277	1.078	1.178	0.141
4		1.162	1.202	1.182	0.028
6		1.145	1.198	1.172	0.037
0	1	1.237	1.103	1.170	0.095
1		1.250	1.278	1.264	0.020
2		1.200	1.414	1.307	0.151
4		1.316	1.235	1.276	0.057
6		1.282	1.238	1.260	0.031
0	2	1.049	1.063	1.056	0.010
1		1.225	1.451	1.338	0.160
2		1.106	1.146	1.126	0.028
4		1.184	1.317	1.251	0.094
6		1.088	1.101	1.095	0.009

Table C.20 300% Modulus of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	300% Modulus			
		1^{st} Experiment	2^{nd} Experiment	Average	Standard deviation
0	0.5	1.103	1.165	1.134	0.044
1		1.243	1.220	1.232	0.016
2		1.116	1.503	1.310	0.274
4		1.378	1.402	1.390	0.017
6		1.422	1.434	1.428	0.008
0	1	1.269	1.087	1.178	0.129
1		1.032	1.521	1.277	0.346
2		1.221	1.408	1.315	0.132
4		1.127	1.133	1.130	0.004
6		0.833	0.949	0.891	0.082
0	2	1.083	1.254	1.169	0.121
1		1.157	1.308	1.233	0.107
2		1.228	1.388	1.308	0.113
4		1.351	1.208	1.280	0.101
6		1.209	1.224	1.217	0.011

6. 500% Modulus of vulcanized rubbers

Table C.21 500% Modulus of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	500% Modulus			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	1.605	2.002	1.804	0.281
1		2.429	2.322	2.376	0.076
2		1.957	1.777	1.867	0.127
4		1.620	1.818	1.719	0.140
6		1.343	1.089	1.216	0.180
0	1	1.830	1.540	1.685	0.205
1		2.296	2.002	2.149	0.208
2		2.069	1.787	1.928	0.199
4		1.708	1.585	1.647	0.087
6		1.619	1.545	1.582	0.052
0	2	2.040	1.553	1.797	0.344
1		1.333	2.196	1.765	0.610
2		1.148	2.365	1.757	0.861
4		1.643	1.767	1.705	0.088
6		1.406	1.611	1.509	0.145

Table C.22 500% Modulus of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	500% Modulus			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	2.604	1.989	2.297	0.435
1		3.243	2.784	3.014	0.325
2		2.373	2.308	2.341	0.046
4		2.351	2.352	2.352	0.001
6		1.687	2.199	1.943	0.362
0	1	2.811	2.628	2.720	0.129
1		2.404	2.624	2.514	0.156
2		2.201	3.105	2.653	0.639
4		2.354	2.217	2.286	0.097
6		2.125	2.290	2.208	0.117
0	2	2.142	2.220	2.181	0.055
1		2.084	2.202	2.143	0.083
2		2.303	2.616	2.460	0.221
4		2.841	3.062	2.952	0.156
6		2.120	2.618	2.369	0.352

Table C.23 500% Modulus of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	500% Modulus			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	1.404	1.756	1.580	0.249
1		2.191	2.263	2.227	0.051
2		2.061	2.048	2.055	0.009
4		2.259	2.717	2.488	0.324
6		2.569	2.761	2.665	0.136
0	1	1.797	1.503	1.650	0.208
1		2.511	2.843	2.677	0.235
2		2.228	2.063	2.146	0.117
4		2.805	2.453	2.629	0.249
6		2.731	2.314	2.523	0.295
0	2	2.004	2.296	2.150	0.206
1		2.553	3.016	2.785	0.327
2		2.171	2.488	2.330	0.224
4		2.103	3.012	2.558	0.643
6		1.817	1.993	1.905	0.124

Table C.24 500% Modulus of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin (phr)	Mixing time (hr)	500% Modulus			
		1st Experiment	2nd Experiment	Average	Standard deviation
0	0.5	1.616	2.705	2.161	0.770
1		2.562	2.518	2.540	0.031
2		2.188	3.159	2.674	0.687
4		3.290	3.322	3.306	0.023
6		3.342	3.480	3.411	0.098
0	1	1.765	2.130	1.948	0.258
1		2.477	2.429	2.453	0.034
2		2.510	3.038	2.774	0.373
4		3.072	2.179	2.626	0.631
6		2.706	2.483	2.595	0.158
0	2	1.994	2.712	2.353	0.508
1		2.102	2.957	2.530	0.605
2		2.632	2.817	2.725	0.131
4		3.229	2.366	2.798	0.610
6		2.616	2.569	2.593	0.033

APPENDIX D

Mechanical Properties of Vulcanized rubbers after Aging

1. Tensile Strength

Table D.1 Tensile strength of sulfur 0.5 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	3.350	4.364	-23.2%
1	8.694	9.462	-8.1%
2	11.070	12.045	-8.1%
4	10.323	11.238	-8.1%
6	9.997	11.705	-14.6%

Table D.2 Tensile strength of sulfur 0.5 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	3.069	4.439	-30.9%
1	8.850	9.690	-8.7%
2	11.279	12.978	-13.1%
4	10.213	10.916	-6.4%
6	8.494	9.056	-6.2%

Table D.3 Tensile strength of sulfur 0.5 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	3.390	4.305	-21.3%
1	10.036	11.004	-8.8%
2	12.388	13.564	-8.7%
4	10.969	12.306	-10.9%
6	9.850	10.431	-5.6%

Table D.4 Different of tensile strength before and after aging of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	-23.2%	-30.9%	-21.3%
1	-8.1%	-8.7%	-8.8%
2	-8.1%	-13.1%	-8.7%
4	-8.1%	-6.4%	-10.9%
6	-14.6%	-6.2%	-5.6%

Table D.5 Tensile strength of sulfur 1.0 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	4.983	6.839	-27.1%
1	10.675	11.005	-3.0%
2	10.488	11.325	-7.4%
4	8.821	9.587	-8.0%
6	9.260	9.426	-1.8%

Table D.8 Different of tensile strength before and after aging of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	-27.1%	-38.1%	-55.6%
1	-3.0%	-20.1%	-14.7%
2	-7.4%	-6.4%	-7.7%
4	-8.0%	-7.7%	-12.8%
6	-1.8%	-10.4%	-11.3%

Table D.9 Tensile strength of sulfur 1.5 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	3.600	7.303	-50.7%
1	14.840	16.062	-7.6%
2	13.814	16.010	-13.7%
4	13.265	15.597	-14.9%
6	13.695	13.965	-1.9%

Table D.10 Tensile strength of sulfur 1.5 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	4.649	7.081	-34.4%
1	14.570	16.665	-12.6%
2	10.440	11.965	-12.7%
4	9.073	11.025	-17.7%
6	9.579	11.035	-13.2%

Table D.11 Tensile strength of sulfur 1.5 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	5.026	8.104	-38.0%
1	14.109	15.325	-7.9%
2	12.420	14.353	-13.5%
4	14.100	14.854	-5.1%
6	9.272	11.795	-21.4%

Table D.12 Different of tensile strength before and after aging of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	-50.7%	-34.4%	-38.0%
1	-7.6%	-12.6%	-7.9%
2	-13.7%	-12.7%	-13.5%
4	-14.9%	-17.7%	-5.1%
6	-1.9%	-13.2%	-21.4%

Table D.13 Tensile strength of sulfur 2.0 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	5.368	7.718	-30.5%
1	15.638	17.260	-9.4%
2	10.645	11.050	-3.7%
4	12.870	14.052	-8.4%
6	11.473	12.930	-11.3%

Table D.14 Tensile strength of sulfur 2.0 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	5.311	8.351	-36.4%
1	11.985	12.790	-6.3%
2	13.750	15.420	-10.8%
4	12.675	13.945	-9.1%
6	11.365	12.060	-5.8%

Table D.15 Tensile strength of sulfur 2.0 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Tensile Strength (MPa) (aged)	Tensile Strength (MPa) (unaged)	Different
0	6.344	7.994	-20.6%
1	13.835	14.880	-7.0%
2	14.860	16.620	-10.6%
4	14.195	15.260	-7.0%
6	11.085	12.280	-9.7%

Table D.16 Different of tensile strength before and after aging of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	-30.5%	-36.4%	-20.6%
1	-3.7%	-6.3%	-7.0%
2	-9.4%	-10.8%	-10.6%
4	-8.4%	-9.1%	-7.0%
6	-11.3%	-5.8%	-9.7%

2. Hardness

Table D.17 Hardness (shore A) of sulfur 0.5 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	36.8	23.6	13.2
1	27.8	25.6	2.2
2	30.9	27.8	3.1
4	28.7	30.9	-2.2
6	21.8	32.2	-1.4

Table D.18 Hardness (shore A) of sulfur 0.5 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	32.7	23.8	8.9
1	30.0	27.9	2.1
2	25.6	30.0	-4.4
4	26.6	31.6	-5.0
6	31.8	32.4	-0.6

Table D.19 Hardness (shore A) of sulfur 0.5 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	38.3	27.4	10.9
1	31.6	29.4	2.2
2	31.4	30.2	1.2
4	28.6	31.8	-3.2
6	31.4	33.0	-1.6

Table D.20 Different of hardness (shore A) before and after aging of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	13.2	8.9	10.9
1	2.2	2.1	2.2
2	3.1	-4.4	1.2
4	-2.2	-5.0	-3.2
6	-1.4	-0.6	-1.6

Table D.21 Hardness (shore A) of sulfur 1.0 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	37.3	28.9	8.4
1	35.4	34.8	0.6
2	36.9	34.6	2.3
4	30.2	35.1	-4.9
6	32.5	36.6	-4.1

Table D.22 Hardness (shore A) of sulfur 1.0 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	34.0	29.6	4.4
1	35.7	34.0	1.7
2	34.0	34.5	-0.5
4	32.9	36.2	-3.3
6	37.9	37.4	0.5

Table D.23 Hardness (shore A) of sulfur 1.0 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	38.4	25.9	12.5
1	38.7	32.5	6.2
2	33.9	33.6	0.3
4	36.8	35.1	1.7
6	25.9	38.9	-13.0

Table D.24 Different of hardness (shore A) before and after aging of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	8.4	4.4	12.5
1	0.6	1.7	6.2
2	2.3	-0.5	0.3
4	-4.9	-3.3	1.7
6	-4.1	0.5	-13.0

Table D.25 Hardness (shore A) of sulfur 1.5 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	40.2	29.1	11.1
1	37.2	33.0	4.2
2	36.3	33.8	2.5
4	38.9	35.7	3.2
6	40.3	36.8	3.5

Table D.26 Hardness (shore A) of sulfur 1.5 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	39.1	31.9	7.2
1	34.9	33.5	1.4
2	32.9	34.4	-1.5
4	35.0	36.3	-1.3
6	32.7	37.4	-4.7

Table D.27 Hardness (shore A) of sulfur 1.5 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	38.3	30.6	7.7
1	33.4	33.6	-0.2
2	38.6	34.5	4.1
4	35.3	36.3	-1.0
6	34.3	37.7	-3.4

Table D.28 Different of hardness (shore A) before and after aging of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	11.1	7.2	7.7
1	4.2	1.4	-0.2
2	2.5	-1.5	4.1
4	3.2	-1.3	-1.0
6	3.5	-4.7	-3.4

Table D.29 Hardness (shore A) of sulfur 2.0 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	41.9	29.2	12.7
1	36.1	32.9	3.2
2	33.1	32.0	1.1
4	36.8	34.2	2.6
6	40.9	36.9	4.0

Table D.30 Hardness (shore A) of sulfur 2.0 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	38.6	31.9	6.7
1	36.3	33.5	2.8
2	41.1	34.4	6.7
4	31.6	36.3	-4.7
6	31.9	37.4	-5.5

Table D.31 Hardness (shore A) of sulfur 2.0 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Hardness (aged)	Hardness (unaged)	Different
0	37.6	30.6	7.0
1	37.3	33.6	3.7
2	31.4	34.5	-3.1
4	37.7	36.3	1.4
6	37.5	37.7	-0.2

Table D.32 Different of hardness (shore A) before and after aging of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	12.7	6.7	7.0
1	1.1	2.8	3.7
2	3.2	6.7	-3.1
4	2.6	-4.7	1.4
6	4.0	-5.5	-0.2

3. Elongation at break

Table D.33 Elongation at break of sulfur 0.5 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	2197	2078	5.7%
1	2045	2044	0.0%
2	2003	2302	-13.0%
4	2088	2190	-4.7%
6	1135	1441	-21.3%

Table D.34 Elongation at break of sulfur 0.5 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1641	2491.5	-34.1%
1	2074	2738.5	-24.3%
2	2016.5	2524	-20.1%
4	2192	2417.5	-9.3%
6	2396	2748.5	-12.8%

Table D.35 Elongation at break of sulfur 0.5 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	2005	2245	-10.7%
1	1700	2065	-17.7%
2	2312	2337	-1.1%
4	2140	2324	-7.9%
6	2339	2520	-7.2%

Table D.36 Different of elongation at break before and after aging of sulfur 0.5 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	5.7%	-34.1%	-10.7%
1	0.0%	-24.3%	-17.7%
2	-13.0%	-20.1%	-1.1%
4	-4.7%	-9.3%	-7.9%
6	-21.3%	-12.8%	-7.2%

Table D.37 Elongation at break of sulfur 1.0 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1693	1599	5.9%
1	1881	2058	-8.6%
2	2119	2252	-5.9%
4	1991	2135	-6.7%
6	2278	2221	2.6%

Table D.38 Elongation at break of sulfur 1.0 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1660	1687	-1.6%
1	2091	2023	3.3%
2	1829	2112.	-13.4%
4	2220	2134	4.1%
6	1777	2093	-15.1%

Table D.39 Elongation at break of sulfur 1.0 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1832	2021	-9.4%
1	1937	2172	-10.8%
2	1878	2116	-11.3%
4	1582	1686	-6.2%
6	1000	1245	-19.6%

Table D.40 Different of elongation at break before and after aging of sulfur 1.0 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	5.9%	-1.6%	-9.4%
1	-8.6%	3.3%	-10.8%
2	-5.9%	-13.4%	-11.3%
4	-6.7%	4.1%	-6.2%
6	2.6%	-15.1%	-19.6%

Table D.41 Elongation at break of sulfur 1.5 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1718	2083	-17.5%
1	1791	2401	-25.4%
2	1708	2251	-24.1%
4	1766	2309	-23.5%
6	2006	2142	-6.3%

Table D.42 Elongation at break of sulfur 1.5 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1331	1722	-22.7%
1	1719	2207	-22.1%
2	2043	2367	-13.7%
4	1995	2121	-6.0%
6	1894	2181	-13.1%

Table D.43 Elongation at break of sulfur 1.5 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	longation at Break (aged)	Elongation at Break (unaged)	Different
0	1373	1914	-28.3%
1	1774	2268	-21.8%
2	2029	2156	-5.9%
4	2161	2120	1.9%
6	2198	2404	-8.5%

Table D.44 Different of elongation at break before and after aging of sulfur 1.5 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	-17.5%	-22.7%	-28.3%
1	-25.4%	-22.1%	-21.8%
2	-24.1%	-13.7%	-5.9%
4	-23.5%	-6.0%	1.9%
6	-6.3%	-13.1%	-8.5%

Table D.45 Elongation at break of sulfur 2.0 phr and mixing time 0.5 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1571	2020	-22.2%
1	1815	2183	-16.9%
2	1926	2072	-7.1%
4	1926	2134	-9.8%
6	1852	2053	-9.8%

Table D.46 Elongation at break of sulfur 2.0 phr and mixing time 1.0 hour at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1588	2111	-24.8%
1	1817	2162	-16.0%
2	2004	2261	-11.4%
4	2240	2429	-7.8%
6	2314	2500	-7.5%

Table D.47 Elongation at break of sulfur 2.0 phr and mixing time 2.0 hours at various CF resin quantities.

CF resin	Elongation at Break (aged)	Elongation at Break (unaged)	Different
0	1746	1952	-10.5%
1	1749	2094	-16.5%
2	2136	2468	-13.5%
4	2077	2228	-6.8%
6	1804	2194	-17.8%

Table D.48 Different of elongation at break before and after aging of sulfur 2.0 phr at various CF resin quantities and various mixing time.

CF resin	Different (0.5 h)	Different (1 h)	Different (2 h)
0	-22.2%	-24.8%	-10.5%
1	-7.1%	-16.0%	-16.5%
2	-16.9%	-11.4%	-13.5%
4	-9.8%	-7.8%	-6.8%
6	-9.8%	-7.5%	-17.8%

APPENDIX E

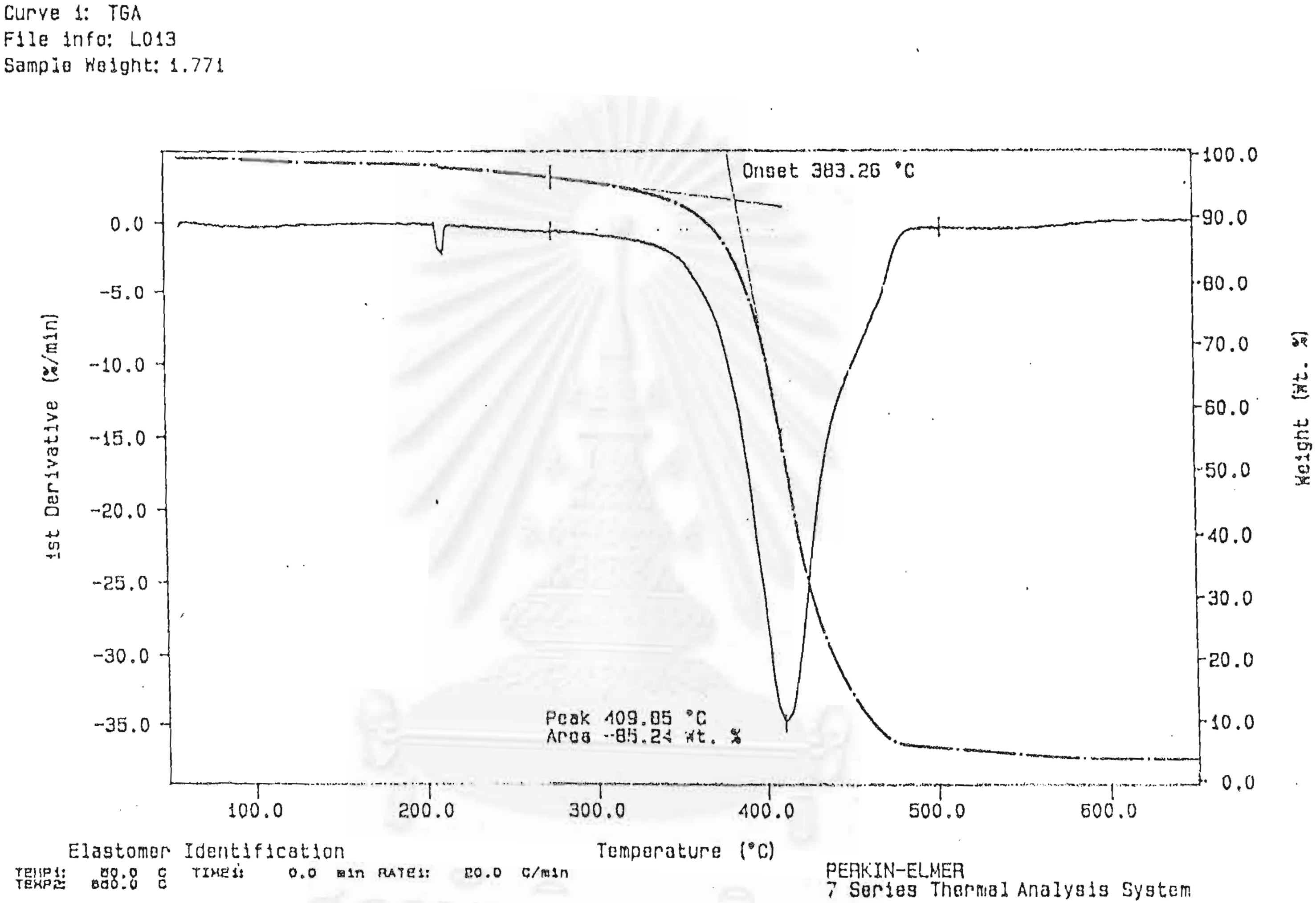
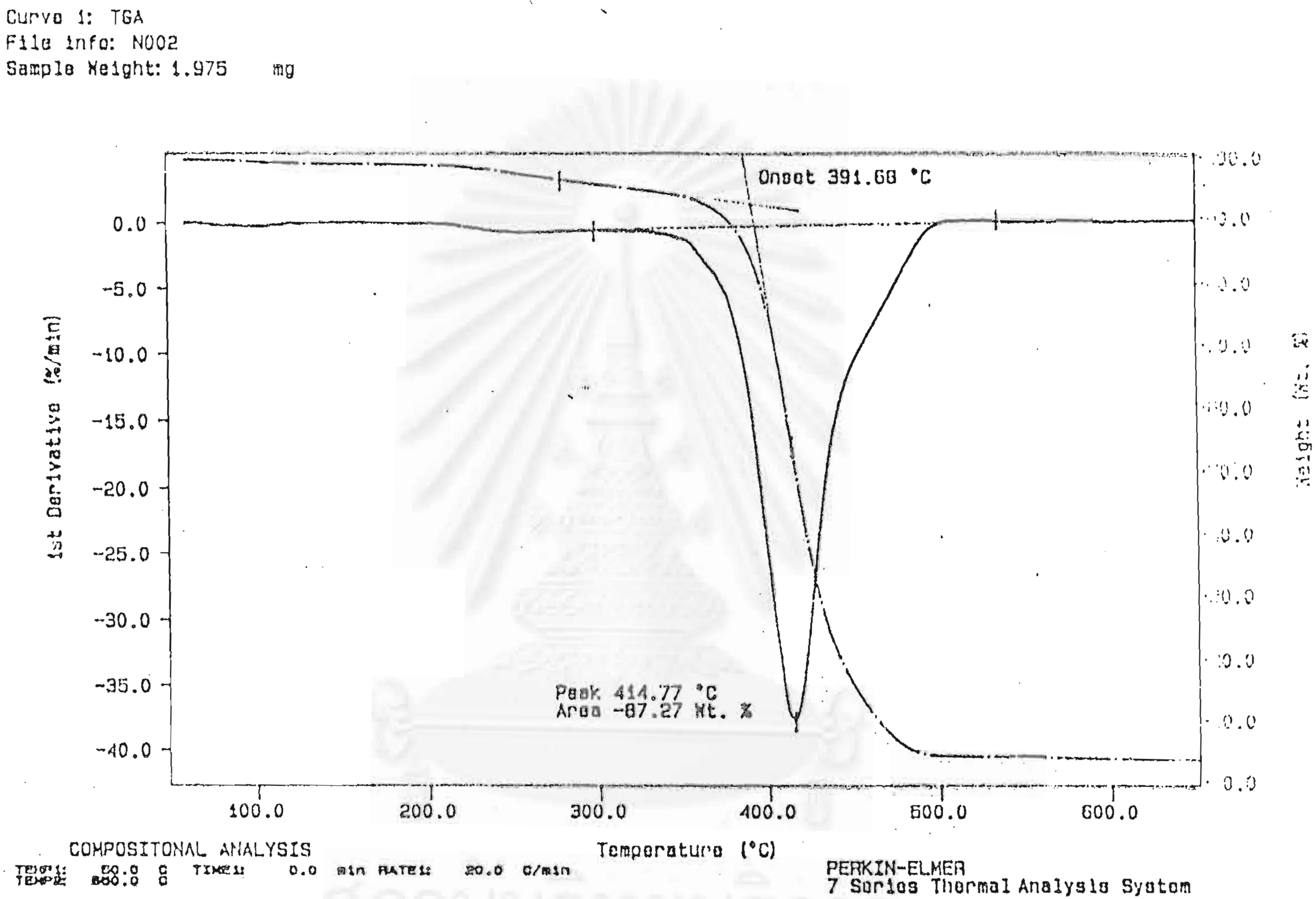


Figure E.1 TGA decomposition curve of sulfur/CF resin 2/0.

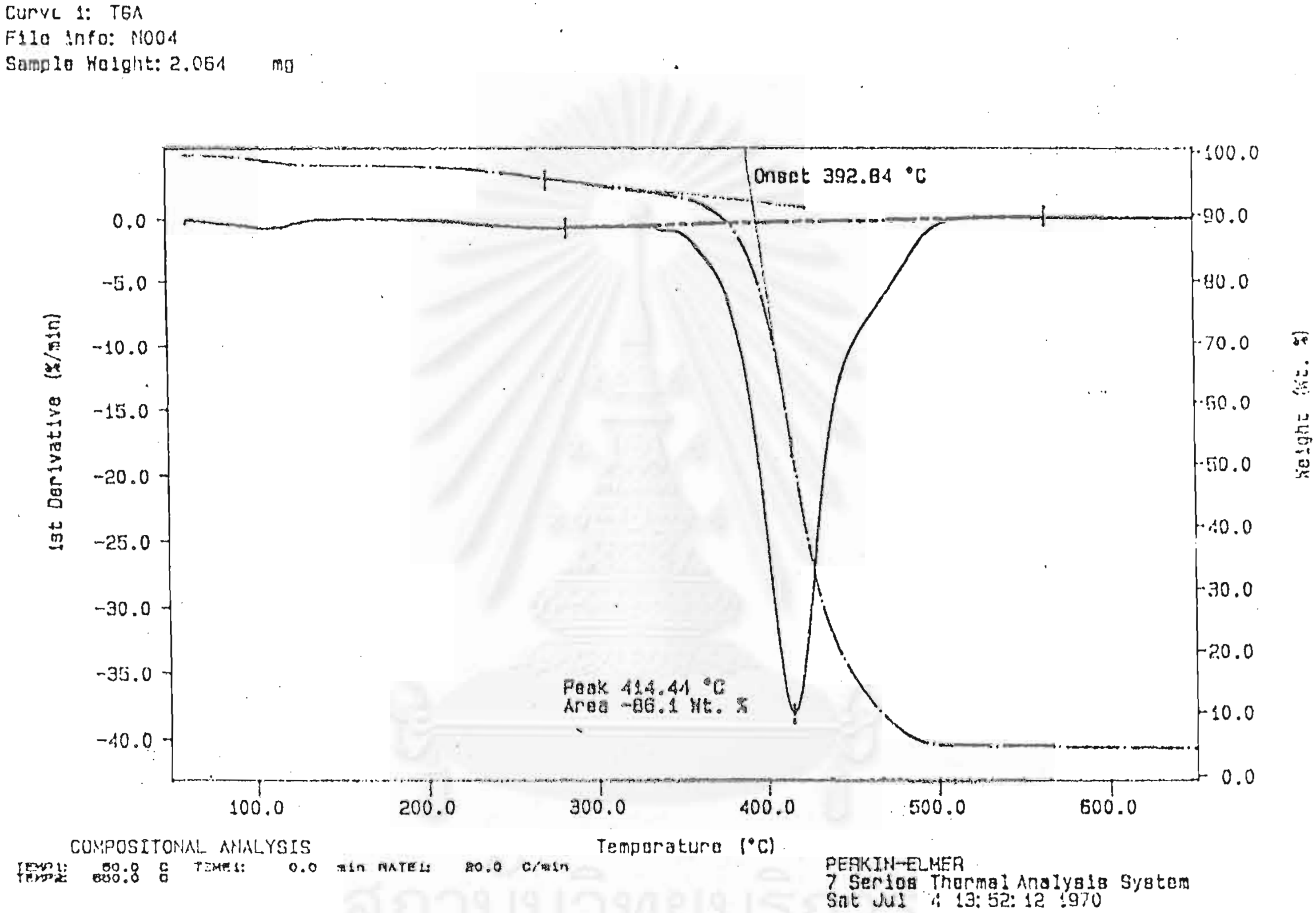


Curve 1: TGA
File info: N002
Sample Weight: 1.975 mg

COMPOSITONAL ANALYSIS
TEMP1: 50.0 C TIME1: 0.0 min RATE1: 20.0 C/min
TEMP2: 600.0 C

PERKIN-ELMER
7 Series Thermal Analysis System

Figure E.2 TGA decomposition curve of sulfur/CF resin 2/1.



Curve 1: TGA
File Info: N004
Sample Weight: 2.064 mg

COMPOSITONAL ANALYSIS
TEMP1: 50.0 C TIME1: 0.0 min RATE1: 20.0 C/min
TEMP2: 800.0 C

PERKIN-ELMER
7 Series Thermal Analysis System
Sat Jul 4 13:52:12 1970

Figure E.3 TGA decomposition curve of sulfur/CF resin 2/2.

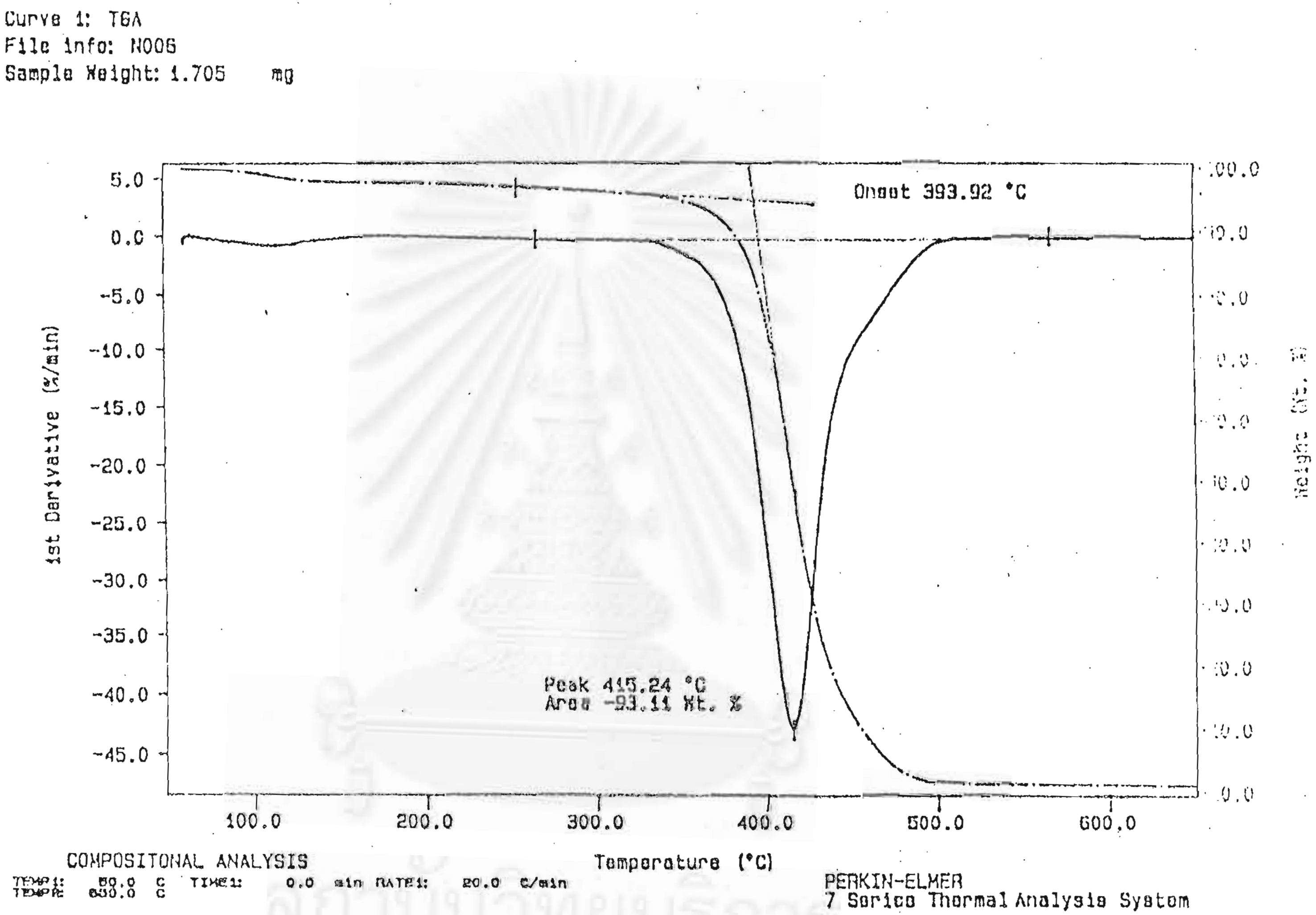


Figure E.4 TGA decomposition curve of sulfur/CF resin 2/4.

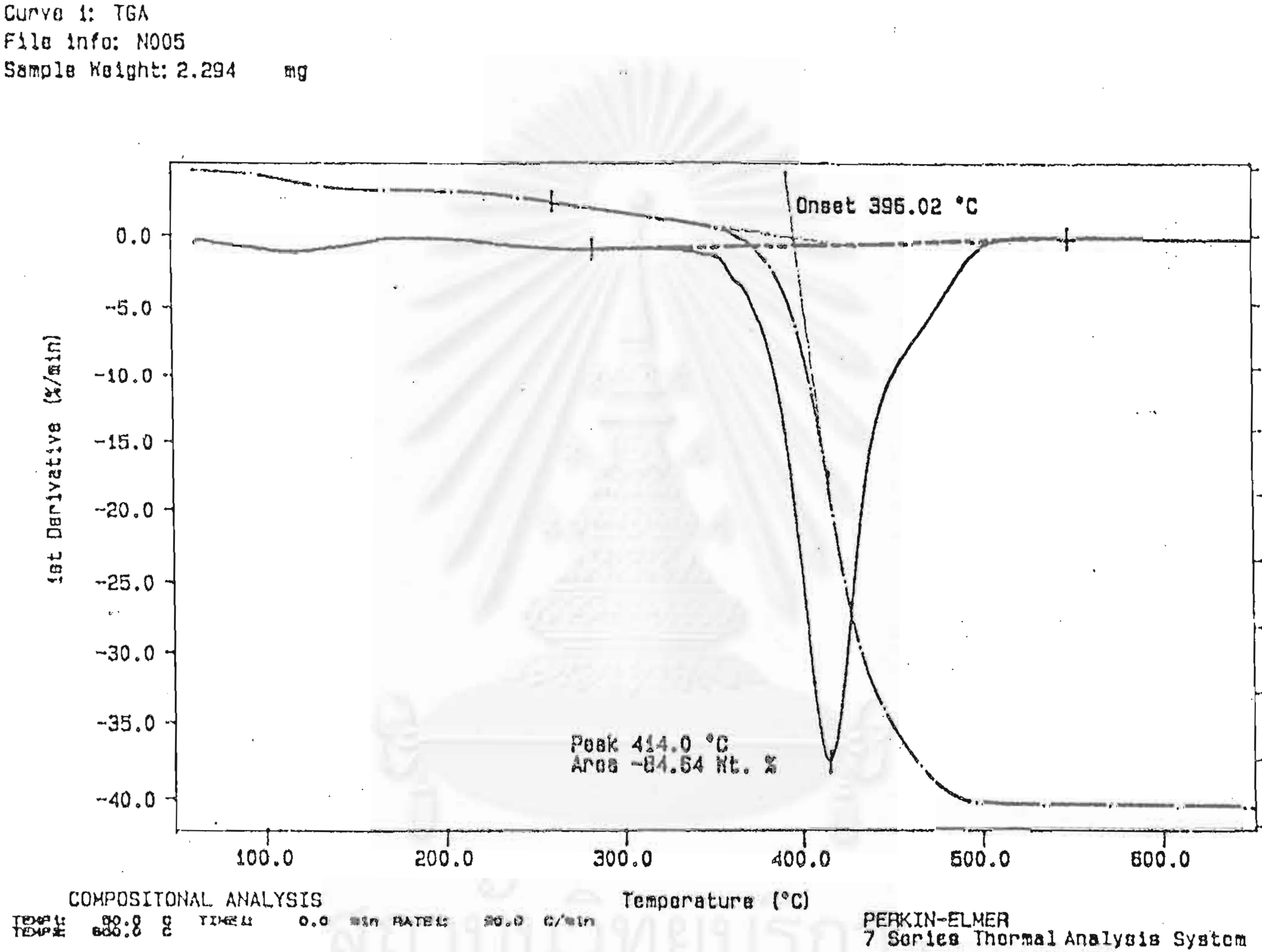


Figure E.5 TGA decomposition curve of sulfur/CF resin 2/6.

VITA

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