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SYNTHESIS OF NEW VULCANIZING AGENT FROM CASHEW NUT SHELL LIQUID

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คาร์ดานอลพอลิซัลไฟด์ (ซีพีเอส) เป็นสารวัลคาไนซ์ประเภทสารให้กำมะถัน ซึ่งสังเคราะห์ได้จากสารสกัดจากเปลือกเมล็ดมะม่วงหิมพานต์ ที่ผ่านการกำจัดหมู่คาร์บอนซิลแล้วกับธาตุกำมะถัน ที่อณหภูมิและระยะเวลาในการทำปฏิกิริยาต่าง ๆ สภาวะที่เหมาะสมสำหรับการเตรียมซีพีเอสทำได้ที่อุณหภูมิ 140 องศาเซลเซียส โดยปราศจากตัวทำละลายเป็นเวลา 3 ชั่วโมงและใช้ธาตุกำมะถันมากเกินพอ ให้ปริมาณกำมะถันร้อยละ 30 โดยน้ำหนัก

ผสมซีพีเอสกับยางธรรมชาติ และสารเติมแต่งที่ใช้ทั่วไป ด้วยเครื่องบดสองลูกกลิ้ง โดยใช้ซีพีเอสแทนที่ปริมาณกำมะถันโดยการควบคุมปริมาณกำมะถันทั้งหมด และโดยการผสมซีพีเอสด้วยปริมาณกำมะถันที่คงที่ ศึกษาการพิสูจน์เอกลักษณ์ของการวัลคาไนซ์และสมบัติเชิงกล พบว่าเวลาที่ใช่ในการบ่มที่เหมาะสมของยางที่ประกอบด้วยซีพีเอสลดต่ำลงและสมบัติเชิงกลส่วนใหญ่ของยางที่ประกอบด้วยซีพีเอสดีขึ้น ได้ทำการทดสอบการเร่งอายุ และเปรียบเทียบผลกับชิ้นงานที่ไม่ได้เร่งอายุพบว่า ยางที่ประกอบด้วยซีพีเอสเกิดการผันกลับน้อยกว่า งานนี้ได้แสดงว่าการใช้ซีพีเอสเป็นสารวัลคาไนซ์ จะปรับปรุงสมบัติเชิงกลพื้นฐานและลดการเกิดการผันกลับของยางคอมพาวด์

ภาควิชา.............................. .... ลายมือชื่อนิสิต....................................

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา.......................

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Cardanol polysulfide (CPS) is a sulfur donor type vulcanizing agent which was obtained from the reaction of decarboxylated cashew nut shell liquid and elemental sulfur at various of temperature and reaction time. The appropriate conditions for the preparation of CPS were carried out at 140 ^{0}C with no solvent for 3 hrs and an excess elemental sulfur was used to give 30 %wt of sulfur content.

The CPS was mixed with natural rubber and common additives by two-roll mill using CPS in place of sulfur content by controlling total sulfur content and combining with constant sulfur content. The vulcanization characteristic and mechanical properties of rubber compounds were studied. It was observed that most of the mechanical properties of rubber containing CPS compounds were improved. Accelerated aging test was investigated and the results were compared to unaged specimens. It was observed that the rubber containing CPS have lower reversion in the ultimate vulcanizates. This work shows that the use of CPS as vulcanizing agent improved basic mechanical properties and reduced the reversion of rubber compounds.

ภาควิชา................................ .... ลายมือชื่อนิสิต...................................

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา........................

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ABBREVIATIONS

ASTM = American Society for Testing and Materials
^0C = Degree Celsius
cm = centimeter
CU = Chulalongkorn University
CLD = caprolactamdisulfide
DPTT = dipentamethylene thiuramtetrasulfide
DTDM = dithiodimorpholine
g = Grams
GY = Goodyear (Thailand) Public Company Limited
hrs = hours
in = Inch
ISO = International Organization for Standardization
JIS = Japanese Industrial Standard
MBSS = 2-morpholino-dithio-benzothiazole
MHz = Mega Hurtz
min = Minutes
mm = Millimeter
Mod 500% = Modulus 500%
OTOS = N-oxydiethylene dithiocarbadipentamyl-N’-oxydiethylene thiuramtetrasulfide
phr = Parts per hundred parts of rubber
PTT = The Petroleum authority of Thailand
psi = poise
rpm = Rounds per minute
sec = Second
S_{25} = 25% of torque
S_{90} = 90% of torque
T-rise/1 = Torque rise per 1 unit
T_{25} = Time that the torque value reach to 25%

T_{50} = Time that the torque value reach to 50%

T_{90} = Optimum cure time

TMTD = tetramethyl thiuramdisulfide

wt% = Weight percent

τ = Torque

CHAPTER I

INTRODUCTION

Rubber Compounding is the art and science of selecting and combining elastomers and additives to obtain an intimate mixture that will develop the necessary physical and chemical properties for a finished product.

The objectives of rubber compounding are threefold. [1]

1) To secure certain properties in the finished product in orders to satisfy service requirements.

2) To attain processing characteristics necessary for efficient utilization of available equipment.

3) To achieve the desirable properties and processibility at the lowest possible cost.

Each additive has its specific function and impact on properties, processibility, and price. In order to reduce the cost of investment of compound that is suitable for certain applications, knowledge on the function and effectiveness of compounding ingredients is indispensable.

Vulcanizing agent is one of the important additive ingredients in compounds, which must be present to cause chemical reaction in its molecular structure, converted from a thermoplastic to a thermoset having improved elastic properties. Sulfur is the most popular vulcanizing agent because of its predominant properties. However there are many disadvantage of sulfur such as reversion. The reversion increases when the amount of sulfur increases. Furthermore, it is easy to bloom because sulfur has low solubility in rubber at room temperature. A sulfur donor is used to replace sulfur in order to solve this problem.

The cashew, (*Anacardium occidentale*), is a member of the *Anacardiceae* family. It is indigenous to South America, especially in Brazil. The Cashew has a long history as a useful plant, but only in the present century it has become an important tropical tree crop. The CNSL is by-product from cashew nuts industry and it is cheap, comprising mainly 90% of anarcardic acid [2]. It is treated by a heating process, which results in decarboxylation of the acids so that it becomes cardanol. Cardanol is an unsaturated *m*-alkyl phenol. The *ortho*- and *para*- that have suitable positions are available to react with sulfur, which could be used as the sulfur donor for vulcanizing rubbers.

This investigation was concerned with the preparation of cardanol polysulfide (CPS) from cashew nut shell liquid. The reaction was carried out under different conditions such as reaction temperature and reaction time. The CPS was used as vulcanizing agent by mixing it with natural rubber and other additives. Finally, the vulcanization characteristics, mechanical properties, accelerated aging were also considered.

Therefore, the objective of this research is to synthesize of new sulfur donor vulcanizing agent, which has low cost and effectiveness for vulcanization.

Objective

1. To synthesize the new vulcanizing agent from cashew nut shell liquid.
2. To study mechanical properties of rubber which prepared from new vulcanizing agent.

Scope of Investigation

For the preparation of cardanol polysulfide (CPS), the appropriate conditions were studied. The reaction temperature and reaction time, which yield high %wt of sulfur content, were determined. Then CPS, which used as vulcanizing agent, was mixed with natural rubber and other additives. The vulcanization characteristics, mechanical properties and accelerated aging test were investigated.

The investigation procedures were carried out as follows:

1. Literature survey and in-depth study of this research work.
2. Design and prepare of apparatus and chemical substances.
3. Prepare CPS by CNSL. The appropriate reaction was determined by changing the following parameters:

   3.1 The effect of reaction temperature

   3.2 The effect of reaction time
4. Study the effect of parameters on %wt of sulfur content.
5. Characterize the structure of CPS by Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR).
6. Use CPS as vulcanizing agent by mix CPS with natural rubber and other additives.
7. Test vulcanization characterization such as optimum cure time, scorch time and delta torque etc.
8. Test mechanical properties such as tensile strength, elongation at break, modulus, hardness and rebound resilience.
9. Test accelerated aging and compared the results to unaged species.
10. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Cashew Nut Shell Liquid (CNSL) [2-5]

Cashew Nut Shell Liquid (CNSL) is a by product of cashew industry, which is extracted from the outer shell of the cashew nut obtained from the cashew nut tree. The Cashew nut has a shell of about 1/8 inch thickness with an inside that is a soft honeycomb structure containing a dark brown viscous liquid, which is the pericarp fluid of the cashew nut. The characteristics of CNSL is governed by IS 840. The picture of cashew nut is shown in Figure 2.1 and the specification of CNSL is shown as in Table 2.1.

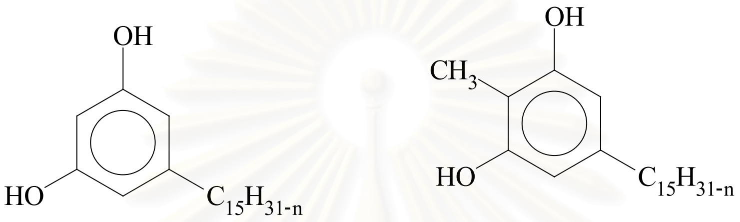
Figure 2.1 Picture of cashew nuts

Table 2.1 IS Specifications for Cashew Nut Shell Liquid

Characteristic	**Requirement**
Specific gravity 30/30°C	0.950 to 0.970
Viscosity at 30°C, in centipoises	300 (max)
Moisture, % by weight, Max	1.0
Loss in weight on heating, Max	2.0
Ash, % by weight, Max	1.0
Iodine value, a) Wij's method b) RK method	 250 290
Polymerization time in min, Max	4

CNSL, extract with low boiling petroleum ether, contains about 90% anacardic acid, together with cardanol, 2-methyl cardol and cardol which are a mixture of biodegradable unsaturated *m*-alkyl phenols. By the heating process, anacardic is decarboxylated to obtain cardanol. The structures of each component are shown in Figure 2.2.

Anacardic acid cardanol



2-methyl cardol cardol

Where n = 0, 2, 4 or 6

Figure 2.2 Structures of components in cashew nut shell liquid

2.2 Vulcanization

The uncured rubber must be transformed from a soft, tacky, stretchy substance into a tough, hard tread that will resist abrasion and provide excellent mileage and traction.

Treatment of rubber is to give its certain qualities, e.g., strength, elasticity, and resistance to solvents, and to render it impervious to moderate heat and cold. Chemically, the process involves the formation of cross-linkages between the polymer chains of the rubber's molecules. In 1839, vulcanization was accomplished usually by a process invented by Charles Goodyear, involving a combination with sulfur and heating. Mr. Goodyear stumbled upon a way to harden molded rubber without losing its flexibility. In 1846, Alexander Parkes developed a method of cold vulcanization (treating rubber with a bath or vapors of a sulfur compound). Rubber for almost all ordinary purposes is vulcanized; exceptions are rubber cement, crepe-rubber soles, and adhesive tape. There are many vulcanization methods, the compound is usually placed in molds and subjected to heat and pressure. The heat may be applied directly by steam, by steam-heated molds, by hot air, or by hot water. Vulcanization can also be accomplished with certain peroxides, gamma radiation, and several other organic compounds. The finished product is not sticky like raw rubber, does not harden with cold or soften much except with great heat, is elastic, springing back into shape when deformed instead of remaining deformed as unvulcanized rubber does, is highly resistant to abrasion and to gasoline and most chemicals, and is a good insulator against electricity and heat.

2.2.1 Theory of Vulcanization [6-7]

Vulcanization is the process, which convert plastic rubber into the elastic-rubber or hard rubber state. The process is brought by the linking of macromolecules at their reaction sites. It is also known as crosslinking.

Following ASTM definition, vulcanization is " An irreversible process during which a rubber compound through a change in its chemical structure (for example, cross-linking) becomes less plastic and more resistance to swelling by organic liquid while elastic properties are conferred, improved, or extended over a greater range of temperature."

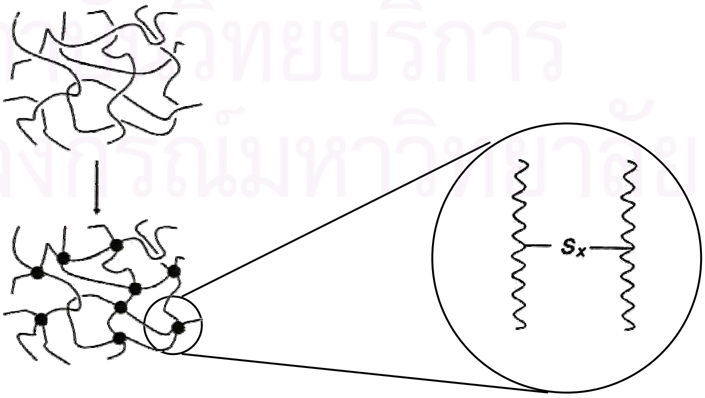


Figure 2.3 Network of sulfur vulcanization

The properties of the vulcanized rubber, or vulcanizate, depend on

a) The nature and distribution of the crosslinks
b) The crosslink density
c) Non-crosslink modifications introduced along the polymer chain
d) Extra-network material, that is the unattached residual reaction products of the vulcanizing system

2.2.2 Degree of vulcanization or crosslink density [8]

The number of crosslinks formed depends on the amount of vulcanizing agent, its activity and the reaction time. In sulfur vulcanization, the most commonly used, various types of crosslink are formed depending on the quantity and activity of the other additives, particularly accelerators. Sulfur can be combined in the vulcanization network in a number of ways between monosulfide to polysulfide, but it also present as pendent sulfides, or cyclic sulfur structure as shown in Figure 2.4.

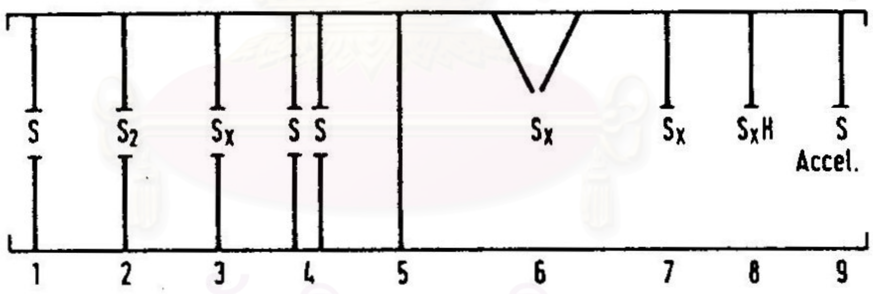
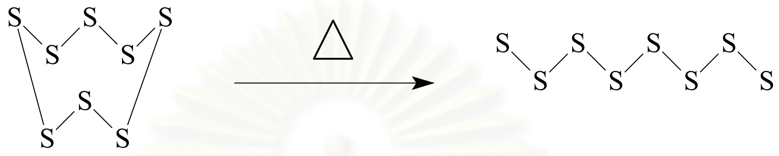


Figure 2.4 Structural features of vulcanizates network: 1) monosulfidic, 2) disulfidic, 3) polysulfidic, 4) when X ≥ 3, vinical, 5) C-C crosslinking, 6) chain modifications, cyclic sulfur structures, 7) sulfur chains, 8) thiol groups, and 9) bound accelerator residues

2.2.3 Mechanism of sulfur vulcanization [7,9]

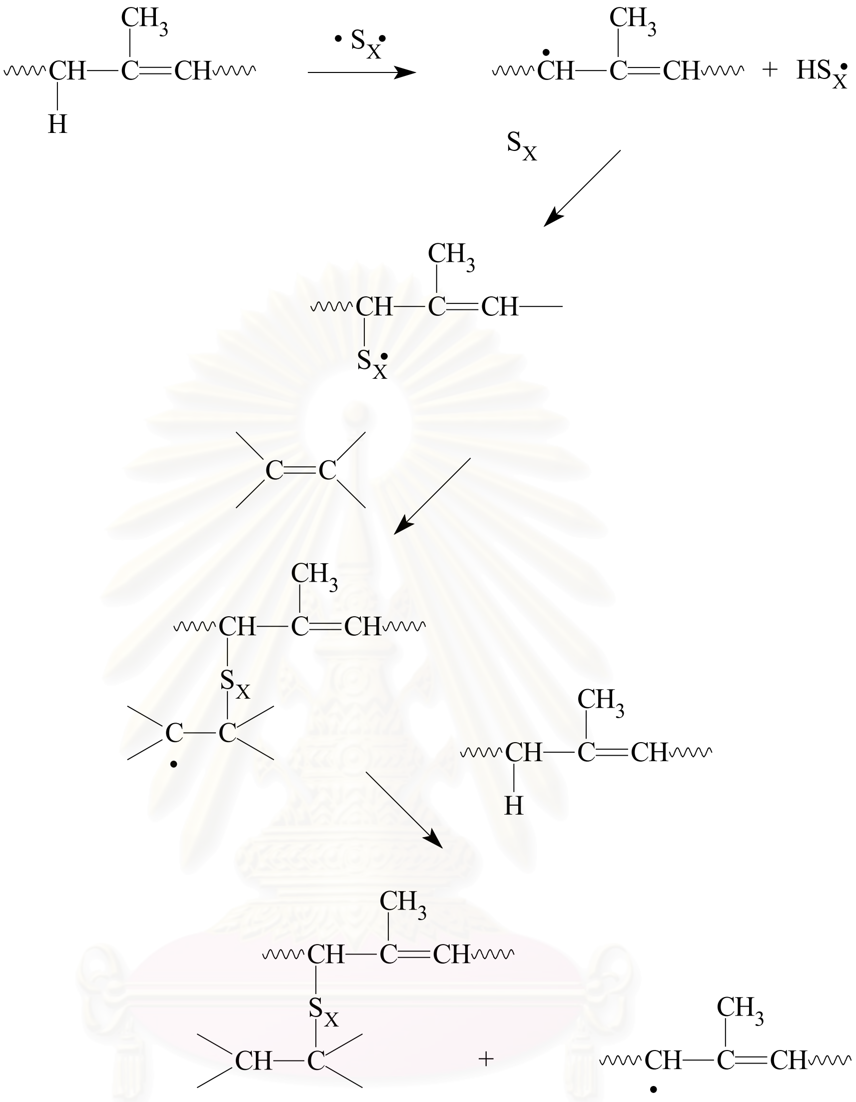
The initial step of vulcanization seems to be the splitting of the sulfur ring. It can crosslink or vulcanize directly even at room temperature.



Scheme 2.1 Splitting of sulfur ring

After being activated by ring splitting, the sulfur is able to react with an accelerator, zinc oxide and also with reactive sites on the rubber molecule, whether these are α-methylene groups, double bonds, or other sites, in such a way that no intermolecular crosslinks are formed initially.

With sulfur vulcanization, the vulcanization structures formed are of great importance to crosslink yield; moreover, the structures formed in accelerator-free vulcanization are many different types. To begin with, therefore, the chemical mechanism of unaccelerated sulfur vulcanization will be considered in some detail.



Scheme 2.2 Mechanism of sulfur vulcanization of rubber

2.2.4 Vulcanizing System [10-11]

The vulcanizing system is the combination of sulfur with accelerators needed to convert the rubber compound from an essentially plastic state to a shaped elastomeric thermoset. The system is added to the rubber polymer during mixing and remains inactive during subsequent processing and fabrication operations. Vulcanization then takes place, usually by the application of heat to activate the system. Crosslinks are inserted between adjacent polymer chains to form a three-dimensional network, which prevents further flow.

The vulcanizing system determines the type and concentration of crosslinks.

Sulfur is used in combination with one or more accelerators and an activator system comprising zinc oxide and a fatty acid (normally stearic acid). Part or all of the sulfur may be replaced by a sulfur donor. In the presence of a vulcanization accelerator, the side reactions are surpressed and, depending on activity and amount of accelerator used, the average number of sulfur atoms per crosslink is decreased. The proportion of sulfur and accelerator and the range of E values of each system are shown in Table 2.2.

Table 2.2 Classification of sulfur vulcanizing system

System	Sulfur concentration (phr)	Accelerator concentration (phr)	Approximate range of E values obtained
EV	0.3-1.0	6.0-2.0	1.5-4
Semi-EV	1.0-2.0	2.5-1.0	4-8
Conventional	2.0-3.5	1.0-0.5	10-25
Very inefficient	3.5-10	0.5-0	25-100

2.2.5 Vulcanization Methods [9]

Systems for vulcanizing rubber can be broken down into five different methods i.e. vulcanization in the press, open cure, vulcanization in water, vulcanization in lead and continuous vulcanization. Each method can be subdivided into minor methods such as the vulcanization in water, which can be used for very large articles, can be carried out in two ways, i.e. vulcanization under atmospheric pressure and under pressure. Almost all rubber products are vulcanized by one or more of these.

For this research, the vulcanization of thick-walled articles, a type of vulcanization in the press was chosen because it is the simplest method. The heat is transferred from the metal of the mold to the articles to be vulcanized. The size of the mold, the type of press, the mold material and other factors greatly affect the curing time and temperature. The higher the mold, the more efficiently it must be protected against loss of heat.

2.3 Vulcanizing agents [8-9, 12]

Vulcanizing agents are ingredients, which must be present to cause chemical reaction, resulting in crosslink of elastomer molecules. The most importance ones are sulfur, sulfur donors, peroxides and metal oxides.

Vulcanizing agent can be grouped in 3 categories.

2.3.1 Sulfur and related elements.

2.3.1.1 Sulfur

Sulfur is one of the practical rubber-vulcanizing agents. It is a critical additive. When chemically combined with rubber, sulfur develops basic properties in the vulcanized compound such as tensile strength, elongation, modulus and hardness. Sulfur suitable for vulcanizing has to be at least 99.5% pore and it must not contain more than 0.5% of ash.

The most stable molecule form of sulfur at ambient conditions is a ring structure containing eight sulfur atoms. Depending on conditions these molecules orient into one of two crystalline structures. At room temperature, the crystals sulfur are rhombic (α-sulfur) and above 95 ^{0}C they arrange to monoclinic (β-sulfur). Less than 1.5% of either crystalline structure of sulfur is soluble in any rubber at room temperature. The second common molecular form of sulfur is polymeric sulfur (γ-sulfur), made up of unbranched chains of atoms. It is commonly referred to insoluble sulfur.

Classification of Sulfurs

a) Rhombic sulfur

Rhombic is the ordinary form of sulfur under normal conditions. Sulfur is insoluble in water but can dissolve easily in natural rubber at room temperature and increases as the temperature of the rubber rises. The proportion of sulfur soluble at a high mixing temperature, which exceeds the proportion soluble at room temperature tends, once the products have cooled, to crystallize out of the over-saturated soluble, the crystal being formed either inside or on the surface of the products called blooming. The rate of crystallization depends on the over-saturation of the compound and on the rate of diffusion of the sulfur in polymers. The fact that blooming thus depending on the over-saturation of the compound means that the mixing temperature, which governs the amount of sulfur dissolved, is very important.

To prevent blooming in unvulcanized rubber compounds (which would make bonding or welding difficult) the sulfur is incorporated at the lowest possible temperature. The other way is use a special modified sulfur such as insoluble sulfur.

b) Insoluble sulfur

Insoluble sulfur or polymeric sulfur (γ-sulfur) available on the market contains about 65-85% of material which is insoluble in carbon disulfide is also insoluble in rubber and therefore has no tendency to blooming. However, insoluble sulfur is not stable. Instead it changed into the normal soluble form, which is again capable of blooming, doing so very slowly at room temperature, faster when the temperature is raised. Insoluble sulfur, therefore, has to be stored at the lowest possible temperature.

Attempts have been made to stabilize insoluble sulfur against conversion into the soluble form e.g. by adding a small amount of chlorine, bromine, iodine, sulfur monochloride, or of a terpene, which have been found to reduce the rate of transformation.

When insoluble sulfur is properly dispersed in the rubber compound, its use (instead of normal soluble sulfur) causes practically no change in the coarse of vulcanization or in the properties of the vulcanizates. However, its insolubility sometimes makes uniform dispersion difficult.

c) Colloidal sulfur

Normal vulcanization sulfur is very difficult to disperse because of its coarse particles and it is therefore no at all easy to incorporate it uniformly in latex. To ensure uniform incorporation and prevent sedimentation in latex mixes it is advisable to use colloidal sulfur, which can be obtained by grinding sulfur in a colloidal mill or by precipitation from colloidal sulfur solutions.

The physical properties of sulfur such as color, odor and molecular weight, etc. are shown in Table 2.3.

Table 2.3 Physical properties of sulfur

Physical properties	
Apparent Color	yellow; impurities may cause color to be yellow shades of green, gray and red.
Odor	Pure sulfur is odorless, but traces of hydrocarbon impurity may impart an oily and/or rotten egg odor; +FAINT ODOR
Boiling Point	444.6 ^{0}C
Melting Point	112.8 to 120 ^{0}C
Molecular Weight	32.06
Density	112.400 lb/cu ft at 255 deg F
Hardness	1.5 to 2.5
Sensitivity Data	May cause irritation of skin, mucous membranes. May cause irritation to eye. If spilled on clothing and allowed to remain, may cause smarting and reddening of the skin.

2.3.1.2 Selenium and Tellurium.

Selenium and Tellurium are elements, which are close to sulfur in the periodic system. They are used analogously to sulfur for rubber vulcanization. Their action is somewhat less powerful than that of sulfur. Because of their price and toxicity they are not of practical importance. In some cases small amounts of selenium or tellurium are used as additives to sulfur or to sulfur liberating accelerators. The proportion of sulfur can then be considerably reduced. Vulcanizates produced in this way are characterized by particularly good heat resistance in steam or hot air and by a high modulus. The difference between sulfur, selenium and tellurium are illustrated in Table 2.4.

Table 2.4 Physical Properties of sulfur, selenium and tellurium

	sulfur	**Selenium**	**Tellurium**
Atomic Weight	32.06	78.96	127.61
Appearance	Yellow powder	Metallic powder	Metallic powder
Specific Gravity	2.07	4.08	6.24
Melting Point (^{0}C)	112.8-120	217.4	449.8
Price			

2.3.2 Sulfur-Bearing Chemicals.

Sulfur Donors, aside from elemental sulfur that contain sulfur in a heat-labile form, can also be used. The compounds used can decompose at the vulcanization temperature and release radicals, which combine with the chain to form crosslinks. The details of sulfur donors are described in section 2.4.

2.3.3 Nonsulfur Vulcanization.

2.3.3.1 Metal Oxides.

Normally, they are used as accelerators. However, carboxylated nitrile, butadiene, and styrene-butadiene rubbers may be crosslinked by the reaction of zinc oxide with carboxylated groups on the polymer chain. Polychloroprenes (Neoprenes) are also vulcanized by reaction with metal oxides, zinc oxide being normally used. Chlorosulfonated polyethylene (Hypalon) is crosslinked in the same way. Litharge (PbO), litharge/magnesia (MgO), amd magnesia/pentaerthritol combinations are used.

2.3.3.2 Difunctional Compound.

Certain difunctional compounds form crosslinks with rubbers by reacting to bridge polymer chains into three-dimensional networks. For example, epoxy resin are used with nitrile, quinone dioximes with butyl and diamines or dithio compounds with fluororubbers.

2.3.3.3 Peroxides

Organic peroxides can be used to vulcanized rubbers that are saturated or those that do not have any reactive groups capable of forming crosslnks. They do not enter into the polymer chains but produces radicals, which form carbon-to-carbon linkage with adjacent polymer chains. The peroxide crosslinking has the following advantages:

1) better heat stability
2) better reversion resistance
3) lower high temperature compression set
4) absence of sulfur avoids corrosion in cable metals

Peroxide initiates crosslinking through a free radical reaction. In essence, thermally liberated peroxy radical abstracts labile hydrogen from the polymer chain and then crosslinking is effected by the combination of two adjacent polymer free radicals. In practice the reaction is more complicated because coagents are often used with the peroxide to enable a reduction in peroxide levels and improve processing safety.

2.4 Sulfur Donors [8]

Sulfur donor used decomposed at the vulcanization temperature and released radicals, which combined with the chains to form crosslinks. Consequently, this form of vulcanization produces products, which resist aging processes at elevated temperatures much more efficiently than those produced with normal curing systems. However, due to the large amounts of the sulfur donors used, these systems are more expensive than normal sulfur cured.

Theoretically, total sulfur content could be given from sulfur donors to incorporate with the molecules of rubbers, however, usually only active sulfur becomes activate. Practically, this means that the equivalent quantities of sulfur donors that are required in order to obtain the same crosslink density are calculated by the active sulfur content. Weight percentage of total sulfur and active sulfur content of commercial sulfur donors are shown in Table 2.5.

Table 2.5 Total sulfur content and active sulfur content of commercial sulfur donors.

	Total sulfur (wt%)	**Active sulfur (wt%)**
DTDM	27.1	13.6*
CLD	22.2	11.1*
MBSS	22.5	11.3*
DPTT	33.3	16.6**
OTOS	12.9	12.9*
TMTD	26.6	13.3*

* Refers to one available S atom (monosulfidic structure)

** Refers to one available S atom (disulfidic structure)

Sulfur donor can be prepared from many organic compounds and sulfur. For this research, cardanol polysulfide (CPS) is synthesized from CNSL and elemental sulfur was used as a sulfur donor type vulcanizing agent.

2.5 Vulcanization state [1,9,13]

The vulcanization time affects the modulus in many ways. It shows that vulcanization consists of several reaction phases that are the scorch or onset of vulcanization, undervulcanization, optimum vulcanization and overvulcanizaiton. The various states are shown in Figure 2.5.

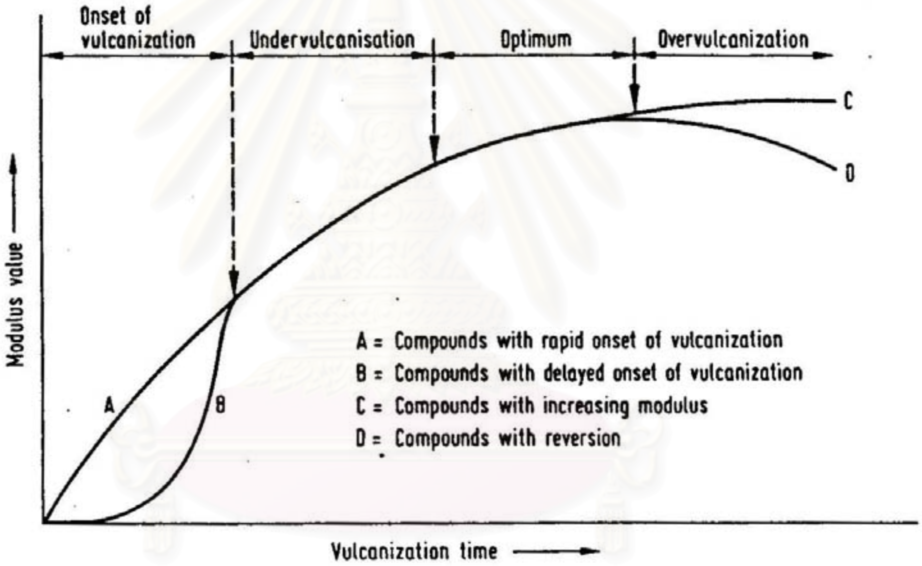


Figure 2.5 States of vulcanization

2.5.1 Onset of vulcanization

This is the point of time at which the compound first begins to stiffen, thus becoming incapable of flowing thermoplastically; in the case of a press cure it is the point of time at which the compound ceases to flow in the mold. Depending on the vulcanization auxiliaries chosen, it may occur early or late.

2.5.2 Undervulcanization

This is the stage between the onset of vulcanization and the vulcanization optimum. As the degree of crosslinking is still small at this stage, most of the properties required in a rubber article are still so little evident that a highly undervulcanization articles is of no technical value.

2.5.3 Vulcanization optimum

In the most cases goods have to be vulcanized to a fairly high degree of crosslinking. Within the range of tensile strength, which is designated the vulcanization optimum, the manufacturer (depending on the requirements, which the rubber articles have to fulfill) will aim to get either a relatively low tensile stress or a relatively high degree of vulcanization. Not at all the properties are optimal at a given degree of vulcanization.

2.5.4 Plateau and over vulcanization

In the case of natural rubber when the vulcanization optimum is exceeded, the crosslinking is reversed at a rate, which depends on the chosen vulcanization system, and this reversion causes the mechanical properties to suffer.

2.5.5 Postvulcanization

In connection with overvulcanization mentioned should also be made of postvulcanization, which occurs during prolonged storage, e.g. at room temperature.

Whilst the modulus curve is rising rapidly, vulcanization is occurring. ‘Cure time’ can therefore be defined as the sum of the scorch time and the vulcanization time, although the definition of ‘optimum cure’ time is not so simple. In the first place, distinction must be made between a full cure, such might be required for experimental process, and the ‘technological optimum’ which would be given under production conditions. Under factory and laboratory conditions, it has paramount importance to measure this quantity with the minimum of time and effect whilst the rubber is actually curing. It is possible to put the uncured stock into a hot mold, transfer to the press, and heat for the required time at the temperature of cure by a machine which automatically records the result in a convention form as shown in Figure 2.6.

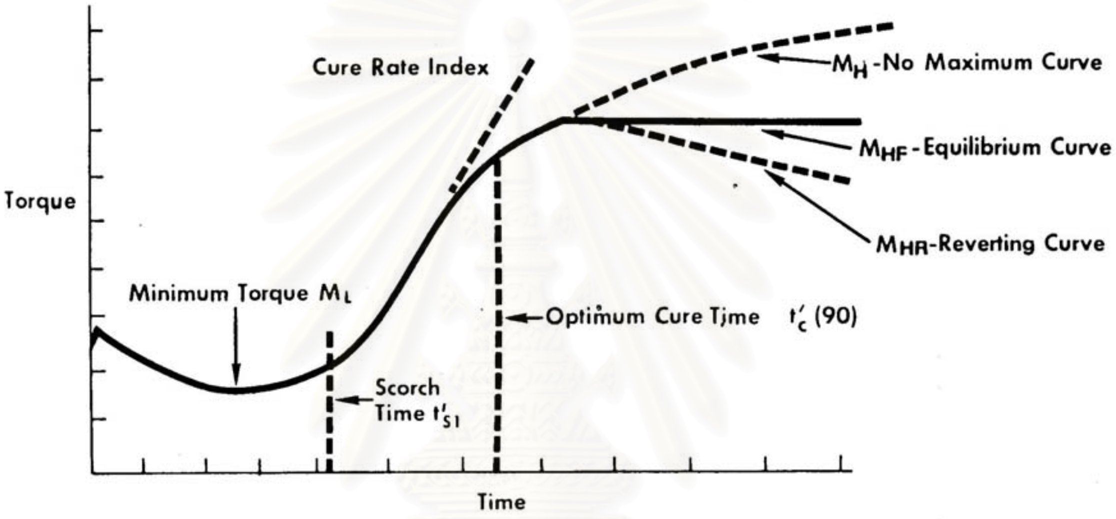


Figure 2.6 Rheograph

From Figure 2.6, the torque is plotted against time to give a so-called rheometer chart, rheograph, or cure curve.

2.6 Processing Technique [1]

For rubber mixing processed, the most widely used equipments are internal mixer, banbury, brabender mixer and two-roll mill.

The objective of the mixing process is to produce a compound with its ingredients sufficiently and thoroughly incorporated and dispersed so that it will process easily in the subsequent forming operations. Also, it is necessary for cure efficiency and to develop the necessary properties for end-use; all with the minimum expenditure of machine time and energy.

\ A banbury and two-roll mill are selected for mixing natural rubber and additives for this research. First, the natural rubber and common additives were mixed by banbury except vulcanization ingredients (sulfur, accelerator and sulfur donor), called non-productive compounds. Then it was mixed with vulcanization ingredients by two-roll mill, which usually heated at 60-80 ^{0}C. Thus, the long time of mixing should be avoided because scorching may occur.

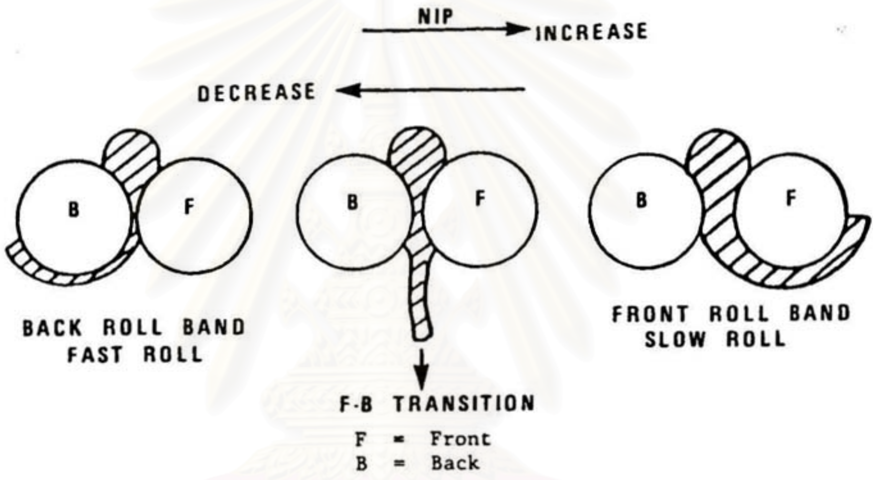


Figure 2.7 Behavior of rubber on the two-roll mill

2.7 Literature Reviews

Sulfur donors have been used as vulcanizing agents for a long time. One of the oldest sulfur donors is sulfur dichloride, which was discovered in 1846. It makes vulcanization of thin natural rubber articles possible at room temperature or better at slightly elevated temperatures (cold temperature). It was of little importance because of poor aging properties of vulcanizates. Afterwards, sulfur dichloride was improved by use incorporation with organic compounds to be transformed into sulfur bearing compounds. One important organic compound is alkyl phenol.

Para-tertiary amyl phenol disulfide, the most popular phenol sulfide resin, has been used as a vulcanizing agent for the improvement properties of rubber. It was prepared from *para-tertiary* amyl phenol and disulfur dichloride or sulfur dichloride known as Vultac®. There are developments for using alkyl phenol sulfide as a vulcanizing agent in many ways as shown below:

In 1947, W. M. George et al. [14] studied the treatment of butadiene polymerizates, including polymerizates of various butadiene derivatives and vulcanization of butadiene polymerizate with the material added to impart tack and with such other materials as are desired for incorporation in the ultimate product. They found that phenol sulfides are valuable as primary vulcanizing agents in the treatment of synthetic elastomers. The sulfur contained in the phenol sulfide apparently enters into the vulcanization reaction, and in cases in which large quantities of sulfur are made available for use in vulcanization through the phenol sulfide, in addition to the quantities of sulfur normally used in the vulcanization. When, however, it was recognized that the phenol sulfide served as a primary vulcanizing agent and the quantity of sulfur separately incorporated in the mixture to be vulcanized is corresponding by reduced or eliminated to take account of the sulfur available from the phenol sulfide. It was found that these factors of tear resistance upon aging, elongation at breaking and heat embrittlement are actually improved by inclusion of the phenol sulfides as compared to products obtained by vulcanizing operations in which the phenol sulfide was omitted.

Then 1976, E. N. Robert [15] improved a process for preparing chlorobutyl rubber composition employing *para-tertiary* butyl phenol sulfide as curing agent. The reaction was carried out using approximately 11:10 moles of phenol to monochloride It has a sulfur content in excess of about 27 %wt and a softening point not less 80 ^{0}C. This *para-tertiary* butyl phenol disulfide, unlike other commercially employed alkyl phenol sulfides, is a non-tacky solid substance, which does not deteriorate as by coalescing under normal storage conditions.

And in 1976, M. R. Le [16] synthesized friable *tertiary* amyl phenol sulfides as vulcanizing agents. They are made in flaked form by reacting *tertiary* amyl phenol with sulfur monochloride at a mole ratio 0.7 to 0.95 moles of the phenol to one mole of sulfur monochloride. The alkyl phenol was introduced to the reactor in a molten condition or else it is introduced as a solid and then melted or at least practically method. The hot liquid reaction product was then flaked on a cooled surface. They are facilitated by its ease of shipping and handling in flaked form.

In 1999, N. Rabindra et al. [17] studied the anti-reversion coagent and sulfide resin of vulcanization of rubber. This invention was related to the vulcanization process, which is carried out in the presence of an anti-reversion coagent and a sulfide resin and the use of an anti-reversion coagent in combination with a sulfide resin in the vulcanization of rubber. The anti-reversion coagents comprised at least two groups selected from citraconimide and itaconimide. The resulting vulcanized rubbers have significantly improved physical and mechanical properties.

For the last related literature, in 1999, Dohhen K., C. et al. [18] prepared the process of calcium phenate detergents from cashew nut shell liquid which may advantageously be employed in a lubricant so as to impart suitable properties of detergency, heat resistance and acid neutralization. Distilled or hydrogenated distilled CNSL was reacted with calcium salt and sulfur in the presence of promoters selected from alcohol, glycol and mineral oil to obtain a reaction mixture. The reaction mixture was subjected to the step of carbonation to obtain basic sulfurized calcium phenate and, if required, further overbasing with carbon dioxide, in the presence of an acid.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Cashew nut shell liquid (CNSL)	: Pharktai Import Co., Ltd., CU
2. Ethyl acetate	: Merck,CU
3. Natural rubber STR20	: Tek Bee Hang, GY
4. Elemental sulfur	: Fluka, GY
5. Stearic acid	: Ajex Chemicals, GY
6. Zinc oxide (ZnO)	: Ajex Chemicals, GY
7. N-cyclohexyl-2-benzothiazole sulfenamide (CBS)	: Ajex Chemicals, GY
8. Carbon black	: Ajex Chemicals, GY
9. Aromatic oil	: Merk,GY
10. Resorcinol	: Fluka, GY
11. Peptizer	: Ajex Chemicals, GY
12. $CDCl_3$	: Merk, CU
13. CD_3COCD_3	: Merk, CU

3.2 Glasswares

1. Beaker
2. Centrifuge tube
3. Glass funnel
4. Two-neck round bottom
5. Condenser
6. Other general laboratory glasswares

3.3 Instruments and Apparatus

1. Mechanical stirrer : Model RW20DZM, GmbH & Co., CU
2. Hot plate and magnetic stirrer : Model 34532, Snijderes, CU
3. Centrifuge : Model 4206, ALC, CU
4. Two-roll mill : Lab Tech Engineering Co. Ltd., GY
5. Internal mixer (Banbury) : Kobelco Stewart Bolling Inc., GY
6. Sulfur Analyzer : LECO, PTT
7. FT-IR : Nicolet Impact 410, CU
8. NMR : Bruker ACF 200, CU
9. Rheometer : Alpha Technologies, GY
10. Mooney viscometer : Monsanto, GY
11. Tensile tester : Instron Calibration Laboratory, GY
12. Compression molding : Lab Tech. Engineering, GY
13. Hardness testing machine : Zwick, GY
14. Rebound tester : Zwick, GY

3.4 Experimental procedures

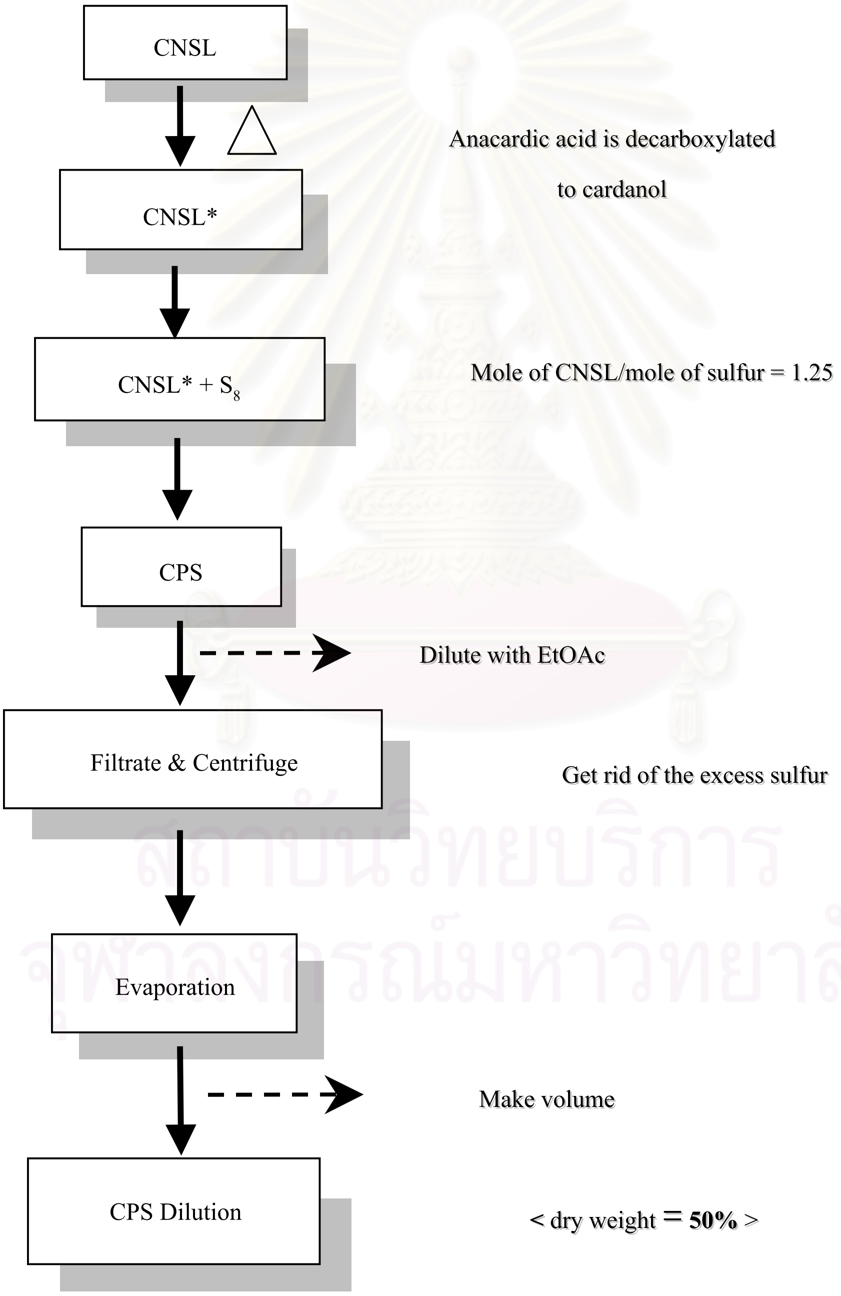
3.4.1 Preparation of CPS

3.4.1.1 Decarboxylation of CNSL [x]

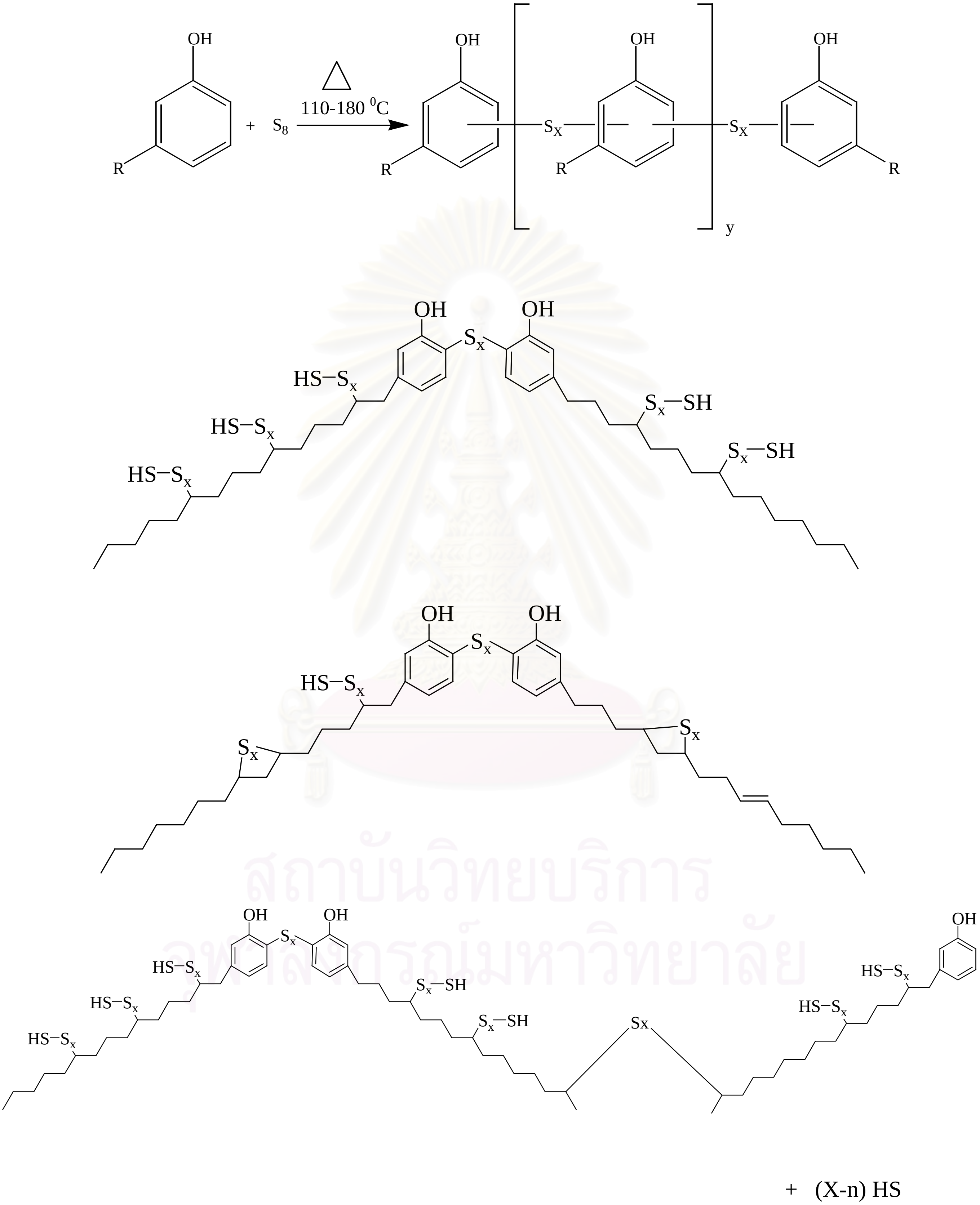
CNSL was decarboxylated to give cardanols in the presence of calcium hydroxide as a catalyst. In a 1000 ml 2-neck round bottom flask, equipped with condenser and thermometer 200 g of natural CNSL, 40 g of calcium hydroxide and 200 ml of hexane as solvent were charged. The mixture was refluxed with stirring. After 3 hrs, the reaction was stopped, cooled down and calcium hydroxide was filtrated off.

3.4.1.2 Synthesis of CPS

A portion of decarboxylated CNSL (75 g) and excess elemental sulfur (45 g) were added to a 250 ml beaker. The mixture was heated to 110-180 ^{0}C with various mediums and stirring for 2, 3, 4 and 5 hrs. The reaction mixture becomes viscous resin. After stopping the reaction, the viscous resin was diluted with ethyl acetate with continuous stirring for 0.5 hr. The dilute mixture was stood for at least 3 hrs to let non-reacted elemental sulfur precipitate. Then the mixture was filtrated and centrifuged to get rid of excess elemental sulfur. The dilution mixture was evaporated. Ethyl acetate was added to make up to 150 ml with ethyl acetate. Dry weight of the dilution was calculated following JIS K 6909 as shown in Appendix A.



Flow diagram 3.1 Experiment scheme of CPS preparation


OH
R
+
S_8
110-180 ^{0}C
OH
R
S_X
OH
R
S_X
OH
R
y
OH
OH
S_x
HS−S_x
HS−S_x
HS−S_x
S_x−SH
S_x−SH
OH
OH
S_x
HS−S_x
S_x
S_x
OH
OH
S_x
HS−S_x
HS−S_x
HS−S_x
S_x−SH
S_x−SH
Sx
OH
HS−S_x
HS−S_x
+ (X-n) HS

Where R = $C_{15}H_{31-n}$

n = 0, 2, 4 or 6

x = integer from 1-8

y = integer from 0-10

Scheme 3.1 Reaction of CPS

3.4.1.3 Characterization of CPS

The product, cardanol polysulfide (CPS), is a dark brown resin. The characterization of CNSL and CPS was carried out by FT-IR, ^{1}H NMR and ^{13}C NMR. The chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. Deuterated chloroform ($CDCl_3$) or deuterated acetone (CD_3COCD_3) was used as a solvent for recording the NMR spectra. The exact structure of this product is not known; it is believed that CPS is a complex mixture of polysulfide, which was postulated in U.S. Pat. No. 2,422,156. CPS has a sulfur content of about 30 %wt, which was investigated by sulfur analyzer. The operational conditions are as follows:

Oxygen gas pressure	400	psi
Instrument gas pressure	400	psi
Furnace temperature	1350	^{0}C

3.4.2 Preparation of rubber compounds

3.4.2.1 Preparation of non-productive compounds

Non-productive compound is, normally called, a compound, which is mixed, from rubber and additives except vulcanization ingredients.

For this research, conventional rubber additives were employed in usual amounts. In the following compounds, base compounds were mixed by the banbury mixer. Non-productive compound can be stored for a long time without scorch because vulcanizing ingredients were not mixed into it.

Mixing condition

Rotor speed	60	rpm
Volume	270	liter
Pressure	5	Bar
Temperature	160	^{0}C
Mixing time	130	sec

The ingredients of non-productive compound are shown in Table 3.1.

Table 3.1 Ingredients in non-productive compound.

Ingredients	Quantity of mix (phr)
NR STR20	100
Peptizer	0.07
Resorcinol	1.1
High straining aromatic oil processing	3.5
Carbon Black	24
Stearic acid	2
ZnO	3
	133.67

3.4.2.2 Preparation of productive compounds

Vulcanization ingredients were added to non-productive compound and mixed by a two-roll mill.

Mixing condition

Friction ratio	1:1.2
Temperature	60-70 ^{0}C
Mastication time of non-productive compound	2 min
Mixing time	8 min

CPS was used to partially replace sulfur by controlling the total sulfur at 2 phr. Normally, the amount of sulfur donor, which was used to replace sulfur, is estimated from active sulfur. The CPS has 30 %wt of sulfur content but the wt% of active sulfur cannot be determined, thus 30 %wt of sulfur in CPS was used to calculate the required level of sulfur. The CPS was varied at 1.66, 3.33, 5.00 and 6.67 phr.

For study the effect of CPS when using combination between sulfur and sulfur donor for vulcanization, condition B was chosen to represent this system. The amount of CPS was varied from 0-6 phr when sulfur was kept constant at 1.5 phr (**series B**). For study the effect of CPS when only sulfur donor for vulcanization, condition E was chosen to represents their system. The amount of CPS was varied from 0-12 phr without using any sulfur (**series E**). The vulcanization ingredients of rubber compounds are shown in Table 3.2.

Table 3.2 Vulcanization ingredients of rubber compounds

Compounds	Vulcanization ingredients		
	CBS	sulfur	CPS
A	1.5	2.0	-
B	1.5	1.5	-
B1	1.5	1.5	1.67
B2	1.5	1.5	4.0
B3	1.5	1.5	6.0
C	1.5	1.0	-
C1	1.5	1.0	3.33
D	1.5	0.5	-
D1	1.5	0.5	5.0
E	1.5	-	6.67
E1	1.5	-	9.0
E2	1.5	-	12.0
E3	1.5	-	15.0

3.5 Determining vulcanization characteristics of the rubber compounds

ASTM D 2084 : Standard Test Method for Rubber Property-Vulcanization using Oscillating Disk Cure Meter

The Alpha Technologies Rheometer MD2000 was used to determine the vulcanization characteristics of rubber compounds.

Test condition

Temperature	150 ^{0}C
Testing time	60 min
Arc	0.5 ^{0}

The Monsanto viscometer was used to determine the vulcanization curve of the rubber compounds.

Test condition

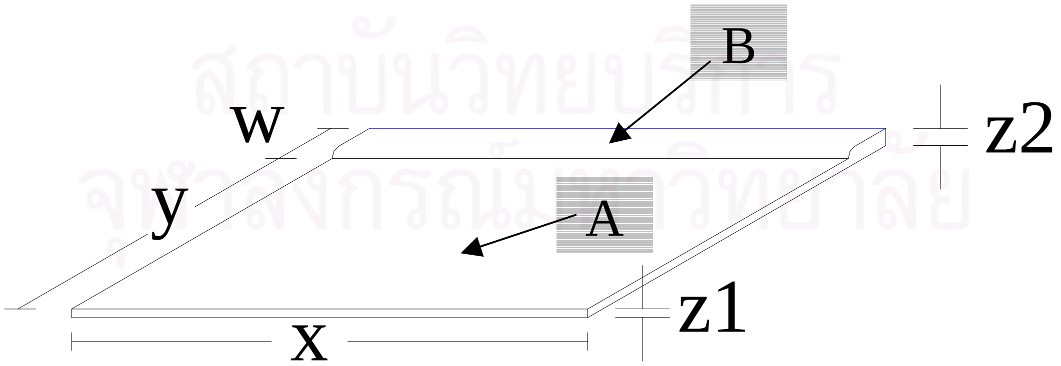
Temperature	121 ^{0}C
Testing time	60 min
Arc	0.5^0

3.6 Preparation of vulcanized sheets

3.6.1 The preparation of sheets

a) The preparation of sheets for tensile tester and hardness tester

For preparation of sheets, the unvulcanized rubbers were cut with specific dimension as Figure 3.1. Then the unvulcanized rubbers must be dried and cut smoothly to avoid flashing-over resulting from point discharges, or burning inside the unvulcanized rubbers.



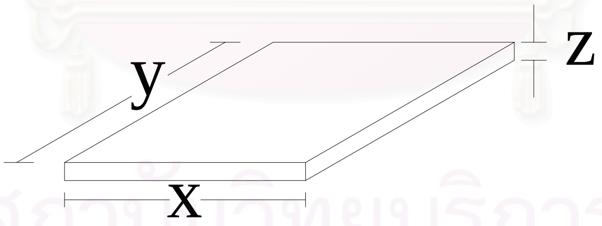
Where w = 1 cm
x = 10 cm
y = 8 cm
z1 = 2 mm
z2 = 4 mm

Figure 3.1 Vulcanized sheet for tensile and hardness tests.

As seen in Figure 3.1, the vulcanized sheet was subdivided into 2 parts. Part A (2 mm in thickness) was used for a tensile test and part B (top cap, 4 mm in thickness) was used for a hardness test.

b) The preparation of sheets for rebound resilience test

For the preparation of sheets for rebound resilience, the green rubbers were cut with specific dimension as in Figure 3.2.



Where x = 8 cm
y = 10 cm
z = 6 mm

Figure 3.2 Vulcanized sheet for rebound resilience test

3.6.2 Vulcanization procedures

The vulcanized rubber sheets were prepared by the compression molding. The mold was preheated to avoid the long curing times at relatively low temperatures, which are necessitated by the poor thermal conductivity of rubber. The mold was brought to curing temperature (150 ^{0}C) in the closed press and held at this temperature for at least 20 minutes before the green rubber pieces were inserted. After preheating the mold, green rubbers were inserted into mold and the press was closed. The mold was held under a pressure of 120 Kg/cm^2 (1700 psi) on the cavity at 150 ^{0}C to a required vulcanization time for each pieces. The vulcanized sheets were conditioned at 23 ± 2 ^{0}C for at least 16 hrs before preheating and testing.

3.7 The mechanical testing

The ASTM and ISO test methods were used to investigate the mechanical properties of the rubber compounds.

3.7.1 Durometer hardness

ASTM D2240: Standard Test Method for Rubber Property-Durometer Hardness

From Figure 3.1, the top cap of vulcanized sheets was used to observe hardness. The shape of the indentor is shown in Figure 3.3.

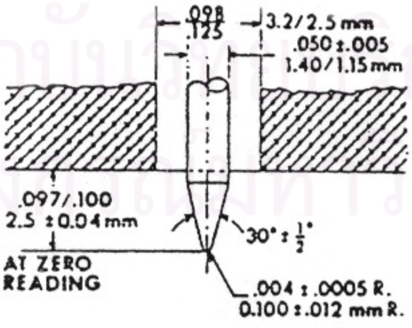


Figure 3.3 Indentor for type D durometer

The test specimens for this research were 4 mm in thickness. The minimum requirement for the thickness of the specimen was dependent on the extent of penetration of indentor into the specimen. For materials having hardness above 50, type D durometer was used. The thickness of the specimen was at least 3 mm.

The surface of the specimen was flat and parallel over a sufficient area to permit the presser foot to contact the specimen. The specimen was placed on a hard, horizontal surface. The durometer was held in a vertical position with the point of the indentor at least 12 mm from any edge of the specimen. The presser foot was applied to the specimen without shock while keeping the foot parallel to the surface of the specimen. The conditions in testing are shown as in the following:

Temperature	25	^{0}C
Relative humidity	50	%

For all of the properties measured, at least 5 samples were tested to obtain the median values.

3.7.2 Tensile tester

ISO 37: Rubber, Vulcanized or Thermoplastic-Determination of Tensile Stress-Strain Properties

A tensile tester is basically a simple device. The tensile tester, the elongation and the stress at a given elongation (modulus) were determined.

The test specimen (type1) is shown in Figure 3.4.

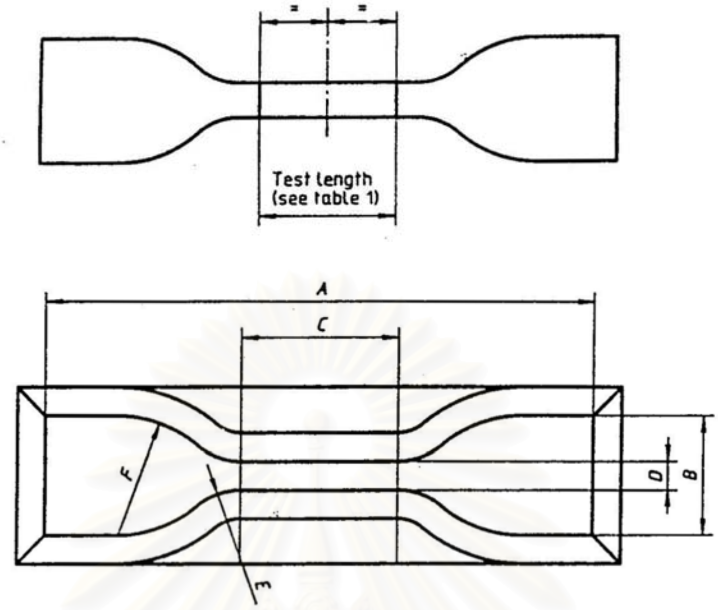


Figure 3.4 Schematic of tensile test specimen (type1)

	Dimension	**Type1 (mm)**
A	Overall length (minimum)	115
B	Width of ends	25.0 ± 1.0
C	Length of narrow portion	33.0 ± 2.0
D	Width of narrow portion	6.0 + 0.4
E	Transition radius outside	14.0 ± 1.0
F	Transition radius inside	25.0 ± 2.0

Temp	25 ^{0}C
Relative humidity	50%
Speed of testing	20.00 in/min
Test length	6.35 cm.

3.7.3 Rebound resilience

ASTM D 1054: Standard Test Method for Rubber Property-Resilience using a Rebound Pendulum

Deflection is determined by measuring the depth of penetration of the rebound ball into the rubber block under testing. The testing device for rebound resilience is shown in Figure 3.5.

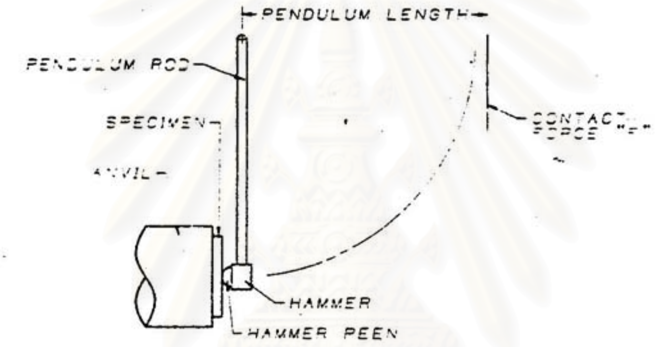


Figure 3.5 schematic representation of a testing device.

Specimen with a thickness of 12.5 ± 0.5 mm and a diameter of 41 ± 12 mm was used. Particle attention was give to a smooth surface and plane parallelism. A stacking of no more than three cylindrical discs of finished parts is possible, requiring no cementing or lubricating, or both, between specimens. This stacking, however, is permissible only in the case of plane parallel disc of uniform thickness over the entire area. The specimen should contain no fabric of any other reinforcing materials. At least two samples must be tested. The test is generally performed at a temperature of 23 ± 2 ^{0}C.

After the specimen has been placed on the anvil in the holder and the thermal conditioning completed, the pendulum is allowed to fall six times from the horizontal position onto the same place on the specimen and caught each time before it strikes the sample once more. The first of these three blows constitute the mechanical conditioning of the specimen. The rebound resilience is read on the fourth, fifth, and sixth strokes. The median of the three readings is recorded.

3.8 Accelerated aging

ASTM D 573: Standard Test Method for Rubber-Deterioration in an Air Oven

ISO 188: Rubber, Vulcanized-accelerated Aging or Heat Resistance Tests

Accelerated aging tests describe a procedure to determine the influence of elevated temperature on physical properties of vulcanized rubber. They are designed to ultimate the relative resistance of yellow rubbers to deterioration with the passage of time.

Specimens of vulcanized rubber are subjected to controlled deterioration by air at an elevated temperature and at atmospheric pressure for known periods of time.

3.8.1 Preparation of test pieces

The vulcanized sheets were cut into dumbbell-shaped specimens. If possible, markings should be carried out after heating as some marking inks can effect the aging of the rubber.

3.8.2 Aging procedure

Place the specimens for aging in the air oven after they have been preheated to 100 ^{0}C ± 1 ^{0}C for 1 and 3 days. The test pieces shall be placed free from strain, freely exposed to air on all sides and not exposed to light. Start the aging interval at the time the specimens are placed in the oven and continue for a measured time interval. At the termination of the aging interval, remove the specimens from the oven, cool to room temperature on a flat surface and condition them for not less than 16 hrs and not more than 6 days. After aging tests, their mechanical properties are measured and compared with those of original specimens. The physical properties concerned in the service application are used to measure the deterioration, but in the absence of any statement of these properties, it is recommended that tensile strength, stress at intermediate elongation, breaking elongation and hardness be measured.

Calculations of % reversion of properties changing are shown in Appendix F.

CHAPTER IV

RESULTS AND DISCUSSION

In this study, CPS is a sulfur donor type vulcanizing agent, which is prepared by decarboxylated CNSL and elemental sulfur. Three parameters; reaction temperature, medium and reaction time have been taken into account. The CPS was mixed with natural rubber sheet and other common additives. The preparation method for the non-productive compound was using banbury. The vulcanization ingredients comprising accelerator, sulfur and CPS were mixed with non-productive compounds by two-roll mill. The amount of CPS was varied to study the effect of CPS on vulcanizing the rubber compounds. Finally, the rubber compounds were determined and the vulcanization characteristics and the mechanical properties of rubber compounds were investigated.

4.1 Preparation of cardanol polysulfide (CPS)

The present study, based on the synthesis of CPS from cashew nut shell liquid as a vulcanizing agent, was carried out by varying reaction temperature, medium and reaction time. The appropriate conditions were evaluated in order to yield a high weight percent of sulfur content in CPS, which were determined by a sulfur analyzer.

4.1.1 Effect of the reaction temperature and medium on the preparation of CPS

The effect of reaction temperature on weight percent of sulfur content in CPS was studied by varying the temperature from 110-180 ^{0}C and toluene, ethylene glycol, cyclohexanol and non-solvent were used as a medium at each temperature.

The parameters were kept constant as follows:

Decarboxylated CNSL	70	g
Elemental sulfur	40	g
Reaction time	2	hr

The results of the effects of reaction temperature on weight percent of sulfur content in CPS were investigated by varying the medium and reaction temperature from 110-180 ^{0}C are shown in Table 4.1.

Table 4.1 shows the effects of reaction temperature and medium on weight percent of sulfur content in CPS. No solvent at 140 ^{0}C is the appropriate condition. It can be explained that the attainment of this condition is greatly influenced by the rising of temperature, resulting in an increased number of free radicals and increased rates of polymerization. But when the temperature is higher, the reaction cannot be controlled. And if there is no solvent diluting the reactant; the most concentrated reaction mixture, causing high weight percent of sulfur content in CPS (24 %wt).

Table 4.1 Effect of reaction temperature and medium on the %wt of sulfur content in CPS: reaction time = 2 hrs.

Temp (^{0}C)	**medium**	**%wt of sulfur content**	**Remark**
110	toluene	13	-
125	Ethylene Glycol	15	A lot of hydrogen sulfide gas was occurred.
140	-	24	-
168	Cyclohexanol	15	Cyclohexanol cannot be removed after the reaction was finished.
180	-	-	Reaction mixture becomes resin before 2 hrs.

4.1.2 Effect of the reaction time on the preparation of CPS

From Section 4.1.1 reaction temperature 140 ^{0}C, which gives appropriate condition was used in this experiment as follows:

Decarboxylated CNSL	70	g
Elemental sulfur	40	g
Reaction temperature	140	^{0}C

The effect of reaction time on weight percent of sulfur content in CPS was investigated by varying the reaction time to 2, 3, 4 and 5 hr, which are shown in Table 4.2 and Figure 4.1.

Table 4.2 Effect of reaction time on %wt of sulfur content in CPS: reaction temperature = 130-140 ^{0}C

Reaction time (hrs)	%wt of sulfur	Remark
2	24	-
3	30	The mixture was starting to be viscous resin.
4	31	-
5	-	The reaction can not reach 5 hrs because the mixture was too viscous for stirring.

From Table 4.2 and Figure 4.1, it can be seen that when the reaction time increases, the percentage by weight of sulfur content in CPS also increases. However, for more than 3 hours of the reaction time, the weight percent of sulfur content was not significantly increased. This means that the reaction was completed within only 3 hours with the 30 %wt of sulfur. Therefore, the appropriated time for this reaction is 3 hours.

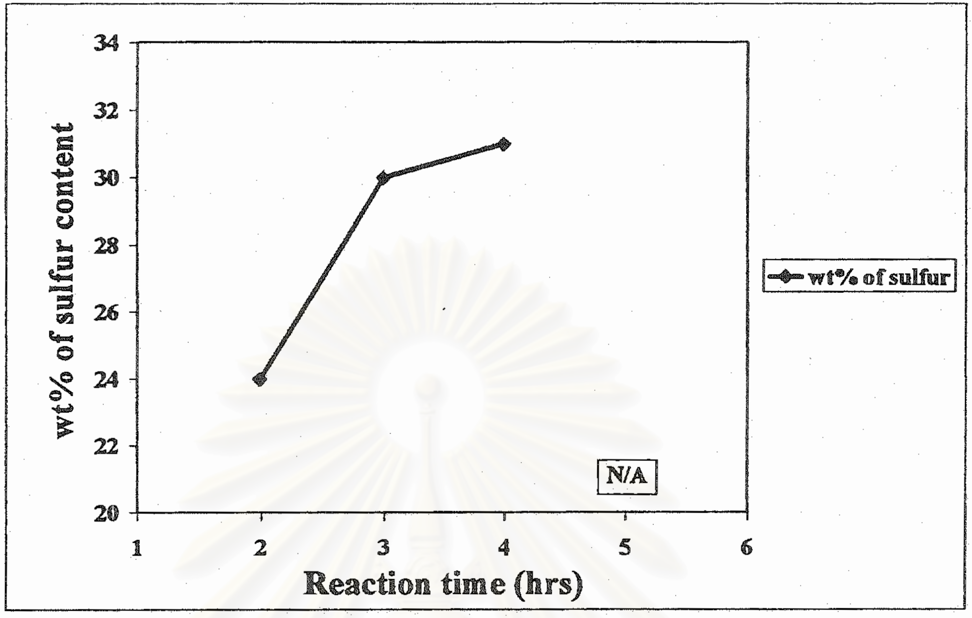
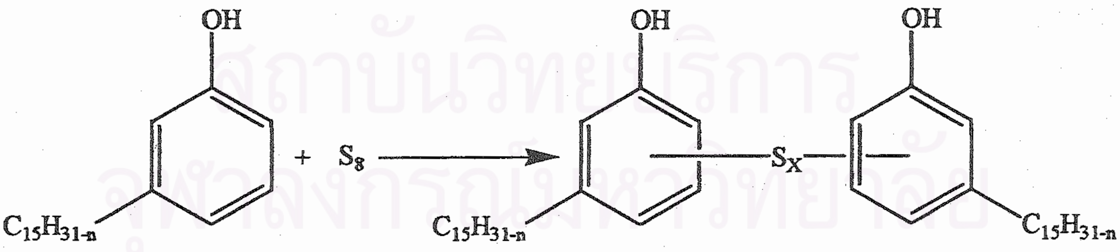
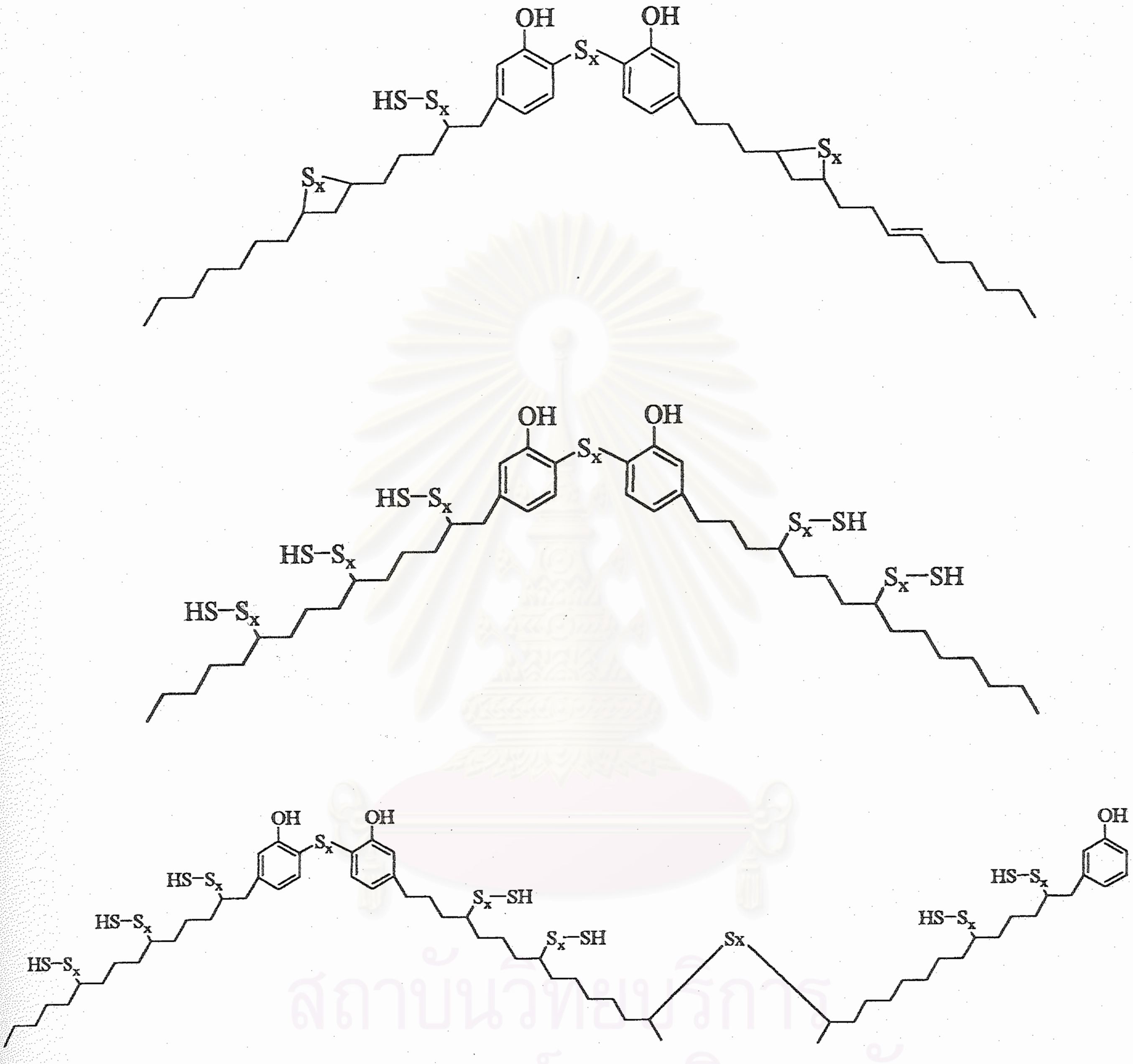


Figure 4.1 Effect of reaction time on %wt of sulfur content in CPS

4.2 Characterization of CPS

The FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopics were used to characterize the structure of CPS. The IR spectra of CNSL and CPS are shown in Figures 4.2 and 4.3, the ^{1}H NMR and ^{13}C NMR spectra of CNSL and CPS are shown in Figures 4.4, 4.5, 4.6 and 4.7, respectively.





Where n = 0,2,4 or 6

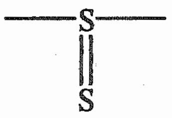
x is independently selected from an integer of 1 to 10

Scheme 4.1

Each sulfide link, S_x, in the above-mentioned structural formula may be a linear linkage of sulfur atoms, such as

—S— , —S—S— , —S—S—S— , etc.,

but also



$-\underset{\underset{S}{\|}}{S}-$,

$-\underset{\underset{S}{\|}}{S}-\underset{\underset{S}{\|}}{S}-$, etc.

The exact structure of this product is not known [14-17] because it comprises the various compositions. It is believed that it is a complex mixture of sulfide resin, comprising mono-, di- and polysulfide linkage, which are various chemical structures. However, FT-IR and NMR spectra point the difference between the reactant and product.

From Figure C.3 (^{13}C NMR spectrum of CNSL) there is a change at about 126-131 ppm, which is aromatic area, compared to Figure C.4 (^{13}C NMR Spectrum of CPS), This indicated that sulfur substituted was in aromatic ring.

Moreover, form the difference between Figure C.1 and C.2 (^{1}H NMR spectra of CNSL and CPS, respectively), it indicates that there are less double bonds in alkyl chain in CPS than in CNSL. This is meant that sulfur attacked some double bonds of side chain of cardanol as well.

4.3 Effects of CPS in rubber compounds on the vulcanization characteristics

Normally, vulcanizing agents can influence the vulcanization characteristics such as scorch time, optimum cure time (t_{90}) and delta torque, etc. Moreover, sulfur donors may be used in place of or in addition to sulfur in order to provide the required level of sulfur during the vulcanization process. The amount of sulfur donor, which may be compounded with the rubber, is an amount sufficient to provide an equivalent amount of sulfur as if sulfur itself was used. The detail of all data calculations are presented in Appendix D and the vulcanization curves of rubber compounds are illustrated in Appendix E. The data of vulcanization Characteristics are shown in Table 4.3.

Table 4.3 Vulcanization characteristics of **rubber compounds**

	Min τ	τ-rise/1	T_{25} (min)	S_{25} (dNm)	T_{90} (min)	S_{90} (dNm)	Rate	Delta τ	T_{50}	Max τ
A	1.51	3.55	3.70	4.93	6.80	12.69	0.64	12.51	4.30	13.92
B	1.58	3.65	3.75	4.59	6.90	11.31	0.61	10.76	4.25	12.33
B1	1.57	2.60	2.75	4.92	5.80	11.63	0.63	11.19	3.25	12.75
B2	1.46	2.15	2.25	4.78	5.50	12.16	0.59	11.89	2.75	13.35
B3	1.43	1.75	1.90	4.93	5.60	12.22	0.51	11.99	2.45	13.41
C	1.57	3.85	3.90	3.97	7.25	9.42	0.57	8.70	4.40	10.29
C1	1.49	2.40	2.50	4.34	6.55	10.24	0.46	9.74	3.00	11.22
D	1.51	4.25	4.20	3.04	8.20	6.76	0.48	5.84	4.80	7.35
D1	1.44	2.25	2.35	3.7	9.05	8.73	0.27	8.12	3.00	9.56
E	1.42	2.35	2.45	3.03	16.75	6.96	0.13	6.17	3.75	7.59
E1	1.48	1.80	2.05	3.32	16.3	7.71	0.12	6.92	3.25	8.40
E2	1.45	1.60	1.80	3.37	16.25	8.2	0.11	7.52	3.15	8.96
E3	1.32	1.40	1.60	3.33	11.95	8.13	0.18	7.64	2.75	8.96

4.3.1 Vulcanization characteristics of rubber compounds A-E (Using CPS in place of sulfur by controlling total sulfur at 2 phr)

The effects of CPS on vulcanization characteristics, when using CPS in place of sulfur were determined by rheometer and the vulcanization curve was obtained from a mooney viscometer. The results were compared between CPS containing rubbers when total sulfur was controlled at 2 phr (**compounds B1, C1, D1 and E**) and non-CPS containing rubbers (**compounds A, B, C and D**).

4.3.1.1 Extent of Crosslinking

The delta torques of compounds A-E are illustrated in Figure 4.1. The delta torque or extent of crosslinking is represented as of degree of crosslinking. It is seen from Figure 4.1 that the delta torque of CPS containing rubbers are more elevated than non-CPS containing rubbers. This indicated that CPS could liberate sulfur to crosslink with the molecules of rubber, hence the degree of crosslinking is increased. However, the delta torques of CPS containing rubbers are lower than delta torque **compound** A, which is the controller compound. Because the active sulfur content was not known, the total sulfur content was used to calculate for replacing the elemental sulfur.

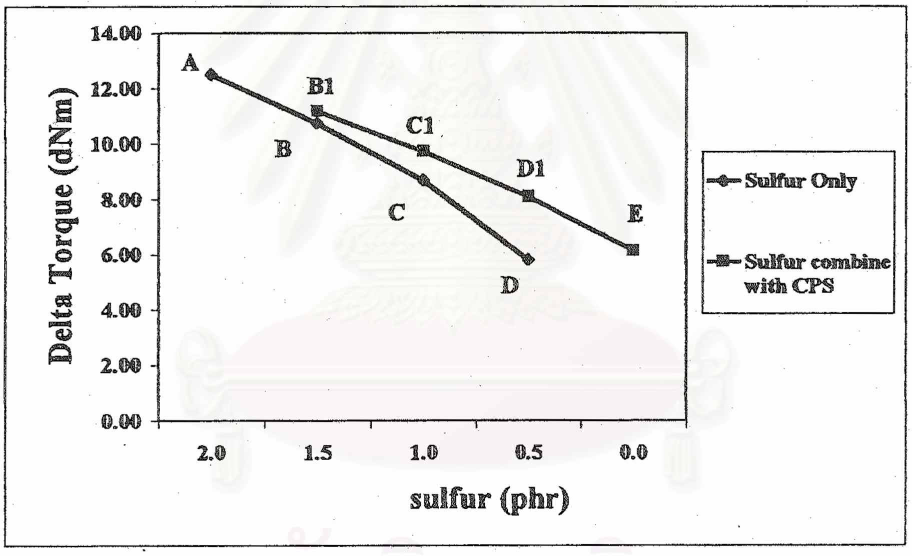


Figure 4.2 Extent of crosslinking of **compounds** A-E

4.3.1.2 Optimum Cure Time (t_{90})

The optimum cure time and vulcanization curves were investigated for studying the effect of CPS to vulcanization characteristics. The result for optimum cure time is shown in Figure 4.3. The vulcanization curve of compounds A, C1 and E are picked for illustration in Figure 4.4 for comparison.

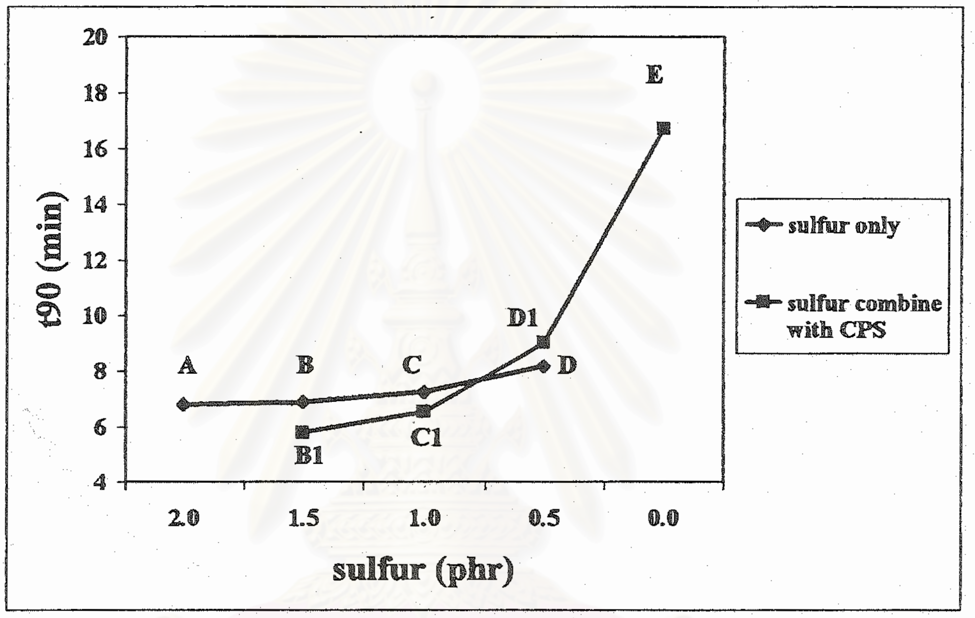


Figure 4.3 Optimum cure time of **compounds** A-E

From Figures 4.3 and 4.4, **compound** E (CPS only containing rubber) had the earlier onset of vulcanization, however it took a long time reach to the vulcanization optimum. On the other hand, **compound** A (only sulfur containing rubbers) had the longer onset of vulcanization, but it could reach the vulcanization optimum faster, which was indicated by a corresponding steep section of the vulcanization curve. In as much as **compound** C1, which consists of sulfur 1 phr and CPS 3.33 phr (sulfur : sulfur donor = 1 : 1), it had both the characteristics of sulfur and CPS. Therefore, **compound** C1 occurred early onset of vulcanization and reached the vulcanization optimum in a short time. Hence **compound** C1 had a short optimum cure time. Accordingly, when the large amount of CPS was used, the rate of vulcanization becomes lower, thus the optimum cure time is longer.

As before, this means that by changing a portion of sulfur and CPS in vulcanization system, the vulcanization behavior is affected.

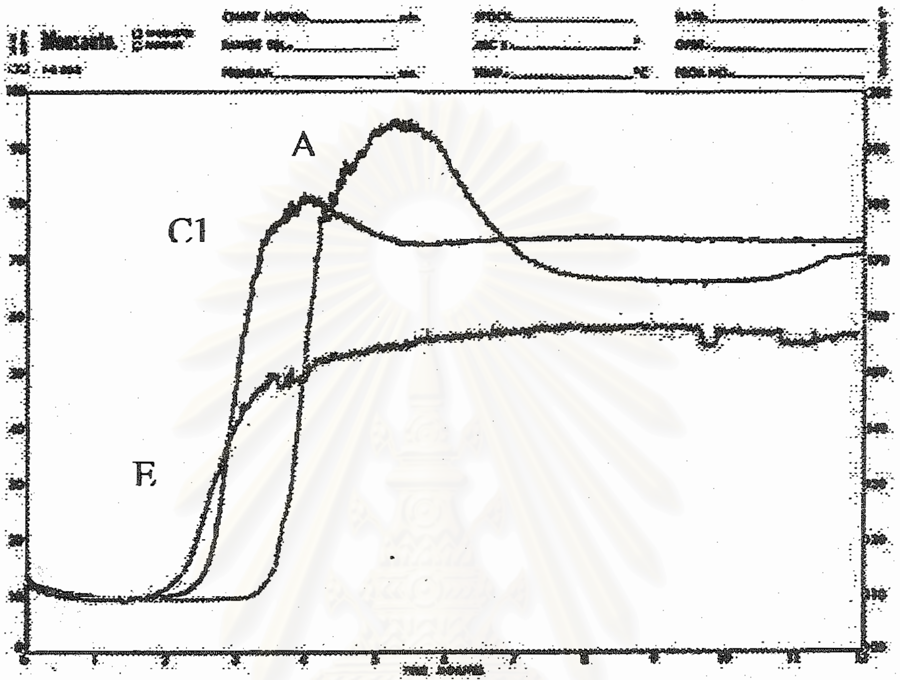


Figure 4.4 Vulcanization curve of **compounds A-E**

4.3.2 Vulcanization characteristics of series B (Using CPS combined with sulfur)

The vulcanization characteristics of **series B** were investigated to study the effect of CPS when CPS was used in combination with sulfur. The amount of CPS was varied from 0-6 phr when the amount of sulfur was constant at 1.5 phr. The data are presented in Table 4.4.

4.3.2.1 Extent of Crosslinking

From the study of the effect of CPS in **series B** on the vulcanization characteristics, the extent of crosslinking is shown in Figure 4.5. It can be seen from this figure that the extent of crosslinking of **series B** increased, as the amount of CPS raised. As reported earlier in section 4.3.1.1, the result supports that CPS can be used as a vulcanizing agent, leading to the increasing of the degree of crosslinking.

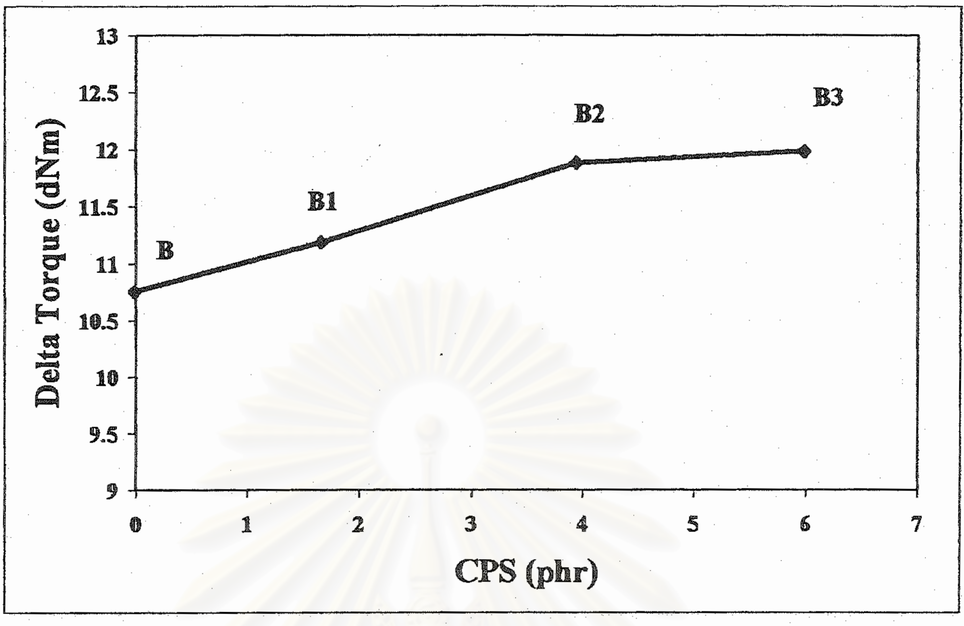


Figure 4.5 Extent of crosslinking of series B

4.3.2.2 Optimum Cure Time (t_{90})

From Figure 4.6, the optimum cure time reduced when the amount of CPS increased, except for **compound B3**. As vulcanization behavior of CPS that was observed in section 4.3.1.2, this is can be explained for **compounds B, B1 and B2** that when the amount of sulfur was controlled and the amount of CPS increased, the onset of vulcanization occurred early. The rate of vulcanization becomes faster, resulting in shorter optimum cure time. For **compound B3**, the amount of CPS was highest in **series B**. Even if it occurred onset of vulcanization in a short time, it took a long time to reach optimize cure. This is the reason for the cure time of **compound B3** that is not lower than other compounds in this series.

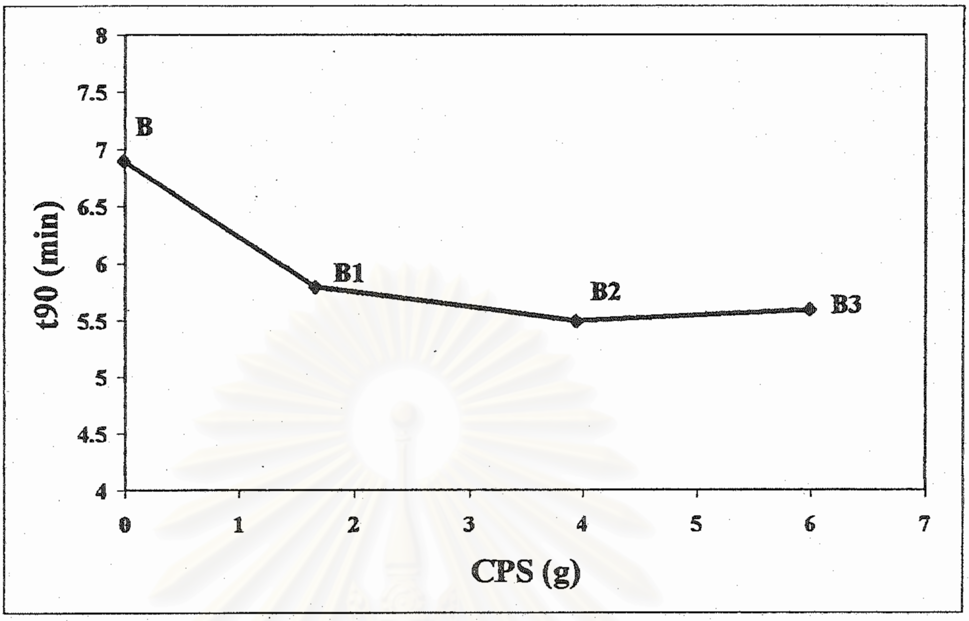


Figure 4.6 Optimum cure time of **series B**

4.3.3 Vulcanization characteristics of series E (only CPS containing rubbers)

The vulcanization by only CPS was studied in **series E**. The effects of CPS of **series E** on vulcanization characteristics were investigated and the data are illustrated in Table 4.5.

4.3.3.1 Extent of crosslinking

From the data in Table 4.3, the delta torque of series E was studied and presented in Figure 4.7. It can be seen that the extent of crosslinking of **series E** increased, as the amount of CPS raised. This is the same as those reported earlier in which CPS can elevate the degree of crosslinking. This is a drastic specification in the vulcanization capability of CPS to be used as vulcanizing agent. A similar trend is also noted with the vulcanization curve of compounds in series E as evident from Figures E.11, E.12 and E.13.

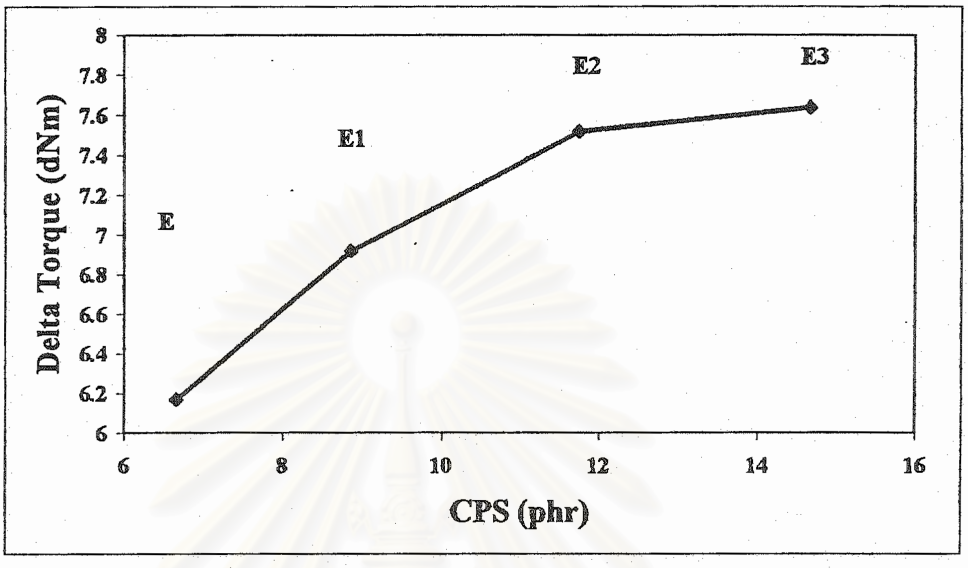


Figure 4.7 Extent of crosslinking of **series E**

4.3.3.2 Optimum Cure Time (t_{90})

The optimum cure times in **series E** are shown in Figure 4.8, showing that there is a drastic reduction in optimum cure time. It can be observed that this result is quite similar to those of **series B**. This indicates that when no effect from sulfur, CPS can reduce the cure time because it reaches the onset of vulcanization at an early state. It is confirmed that at the appropriated condition, the cure time can be reduced by CPS.

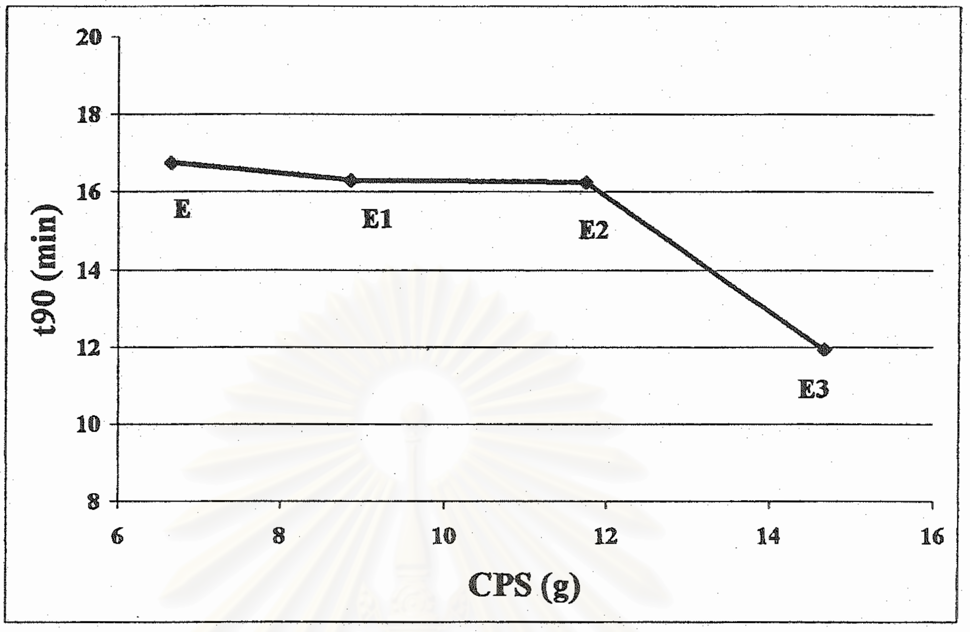


Figure 4.8 Optimum cure time of series E

4.4 Mechanical Properties of Rubber Compounds

Mechanical properties of rubber compounds were investigated to evaluate the value of tensile properties, hardness and rebound resilience. The effect of CPS on mechanical properties was observed by varied CPS in three systems, i.e. using CPS in place of sulfur, using CPS combined with sulfur and using only CPS for vulcanization. The details of all data calculations are shown in Appendix E. The results consist of tensile strength, modulus 500%, elongation, hardness and rebound resilience as shown in Table 4.4.

Table 4.4 Effect of CPS content on the mechanical properties of **rubber compounds**

	Tensile Strength (MPa)	Elongation at break (%)	Modulus 500% (MPa)	Hardness (Shore-D)	Rebound Resilience (W/mm)
A	31.31	575.12	24.41	56.0	62.60
B	30.60	594.65	22.84	54.0	62.40
B1	31.26	616.70	21.73	56.5	63.40
B2	29.30	615.80	20.39	56.5	66.80
B3	29.23	627.10	19.08	57.5	67.20
C	29.70	631.15	18.45	52.5	62.80
C1	30.23	647.97	17.80	55.0	62.40
D	23.23	645.85	13.36	45.5	61.00
D1	26.23	661.57	14.71	51.5	60.00
E	16.48	602.83	11.25	46.5	56.60
E1	18.68	638.71	11.28	49.5	58.80
E2	20.00	653.15	11.40	50.5	59.00
E3	22.57	679.65	11.63	52.0	59.40

4.4.1 Mechanical Properties of Compounds A-E (Using CPS in place of sulfur by controlled total sulfur at 2 phr)

The effect of CPS on the mechanical properties of CPS containing rubbers when total sulfur was controlled at 2 phr and non-CPS containing rubbers (COMPOUNDS A-E) were studied. The results were compared between CPS containing rubbers (**compounds B1, C1, D1 and E**) and non-CPS containing rubbers (**compounds A, B, C, D**).

4.4.1.1 Tensile Properties

The effect of CPS components on tensile properties of rubber compounds were compared between CPS containing rubbers **(Compounds B1, C1, D1 and E)** and non-CPS containing rubbers **(Compounds A, B, C and D)**. The results are shown in Figures 4.9, 4.10 and 4.11.

In Figure 4.9, the tensile strengths of CPS containing rubbers have the higher value than non-CPS containing rubbers. The tensile strength increases because degree of crosslinking increases from sulfur, which was liberated from CPS.

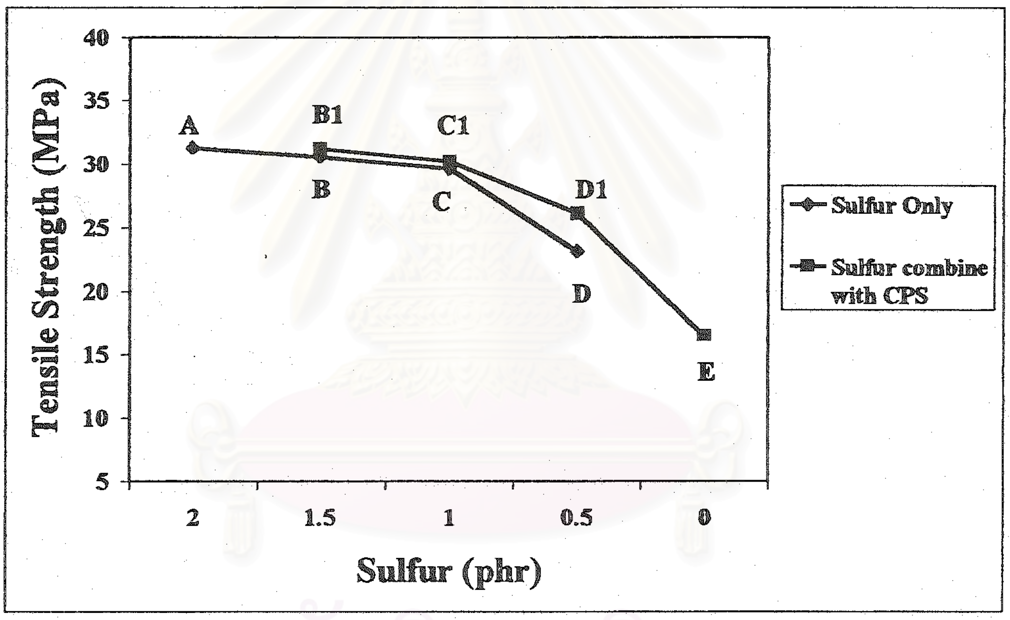


Figure 4.9 Tensile strength of **compounds A-E**

From Figure 4.10, the modulus 500% had the same trend. The reason for these observed effects of CPS containing compounds is CPS consists of cardanol that can crosslink with the molecules of rubber after it liberates sulfur atoms, leading to high mobility of molecular chains. Hence the modulus is not raised even it the degree of crosslinking increases.

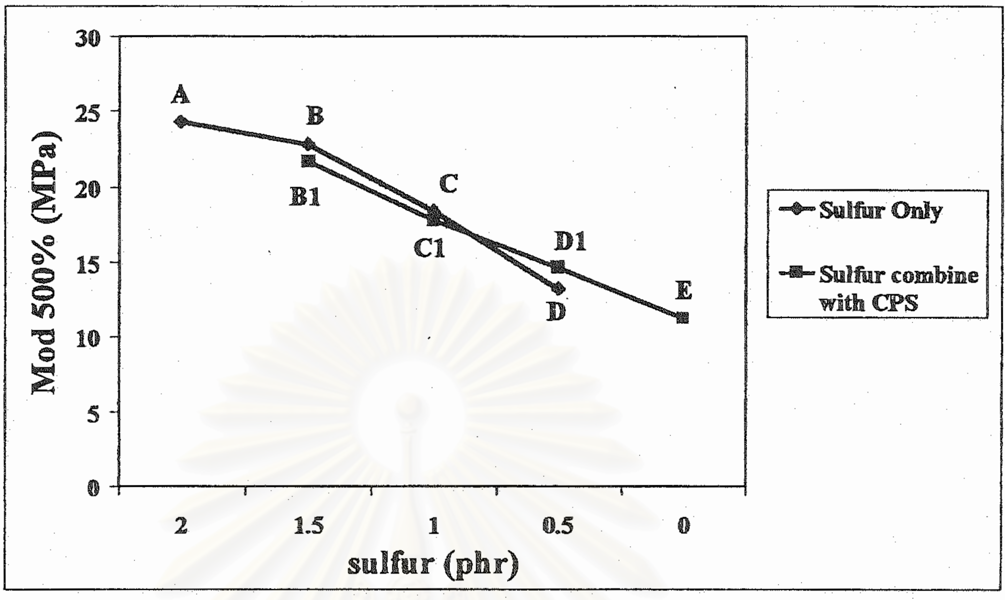


Figure 4.10 Modulus 500% of **compounds A-E**

In Figure 4.11, strong evidence for higher elongation in CPS containing rubbers compared to non-CPS containing rubbers are observed, except compound E. For the same reason in the modulus that CPS consists of cardanol that can crosslink with the molecules of rubber, leading to high mobility of molecular chains resulting in high elongation. However, for the low elongation of **compound** E, due to the long curing time, after a number of crosslinks has been formed during the vulcanization, they can be split up again by the vulcanization heat. The split crosslinks, which were mainly radical in nature, were then capable of forming new crosslinks. Then the degree of crosslinking increased, resulting in decreasing elongation.

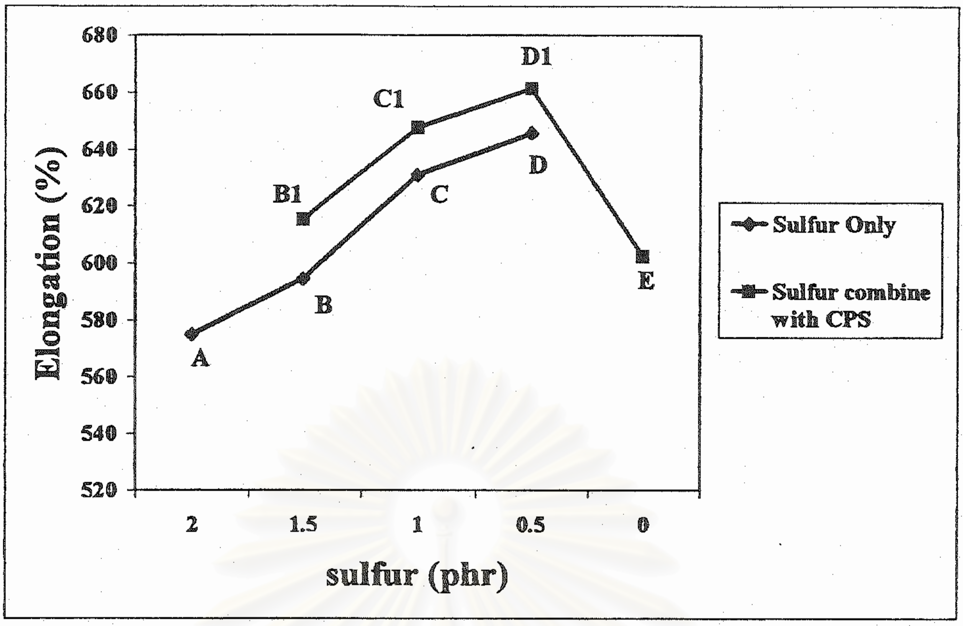


Figure 4.11 Elongation at break of compounds A-E

4.4.1.2 Hardness (Shore-D)

The hardness of rubber compounds is shown in Figure 4.12. It can be seen from this figure that the hardness of CPS containing rubbers is higher than non-CPS containing rubbers. This indicated that CPS could be used as a vulcanizing agent to crosslink with the molecules of rubber, also increasing the degree of crosslinking. As the degree of crosslinking rises, the hardness progressively increases.

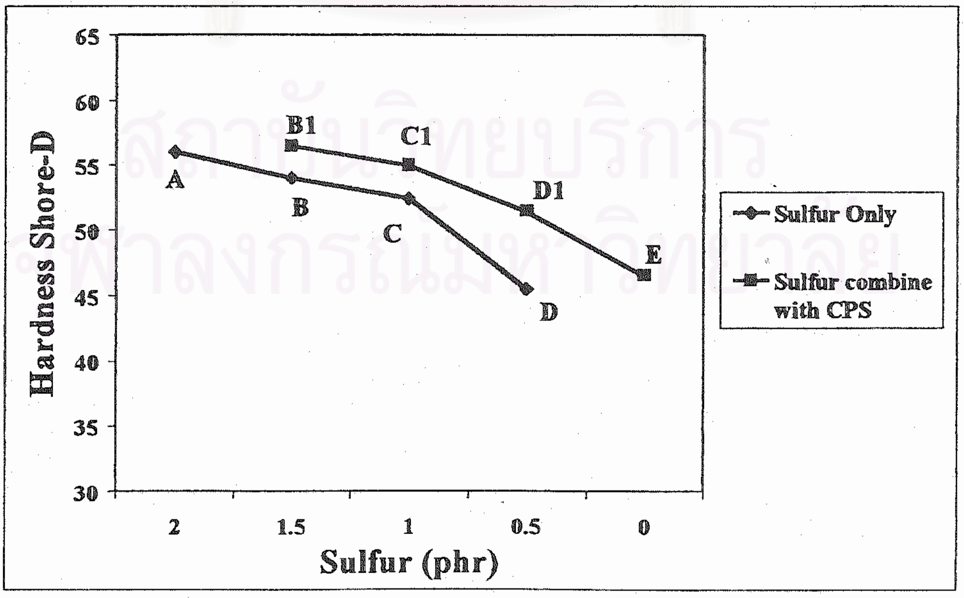


Figure 4.12 Hardness of compounds A-E

4.4.1.3 Rebound Resilience

The effect of CPS components on rebound resilience of rubber compounds is presented in Figure 4.13. Analysis of rebound resilience revealed that incorporation of large amounts of CPS resulted in the improvement of rebound resilience, but it decreased when the amount of CPS increased. The trend of rebound resilience is not dependent on the degree of crosslinking. This phenomenon can be explained as Figure in 4.14.

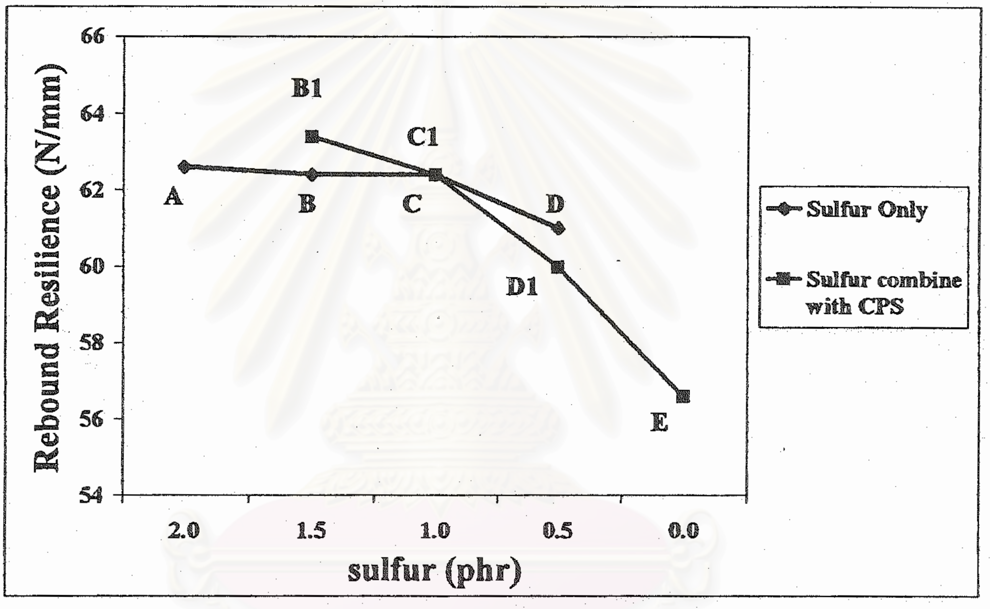


Figure 4.13 Rebound resilience of **compounds A-E**

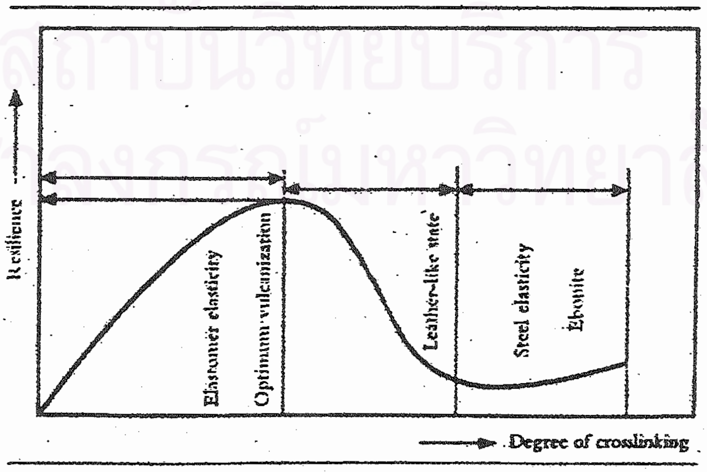


Figure 4.14 Relationship between rebound resilience and degree of crosslinking

Based on the degree of crosslinking, rubber elasticity is affected by the crosslink structure. Figure 4.14 illustrates that it is caused by reversible changes of positioning among the chain segments (Micro-Brownian movement) and its existence is indicated when even small forces produce highly elastic deformations. Elasticity increases with increasing Micro-Brownian movement with increased crosslinking, raising the rebound resilience to an optimum value. If the molecules, because of crosslinks, are in fixed locations in relation to one another, they tend to return to their initial positions after being displaced. As the number of crosslinks increase, the molecules or their segments become so firmly attached to one another that their tendency to return to the basic position after deformation cases, i.e. the elastomers-elasticity, becomes more pronounced.

4.4.2 Mechanical Properties of series B

The effects of CPS content in rubber compounds when the amount of sulfur was kept constant at 1.5 phr on the mechanical properties were investigated.

4.4.2.1 Tensile Properties

The effect of CPS content on tensile properties of rubber compounds in **series B** is shown in Figures 4.15, 4.16 and 4.17.

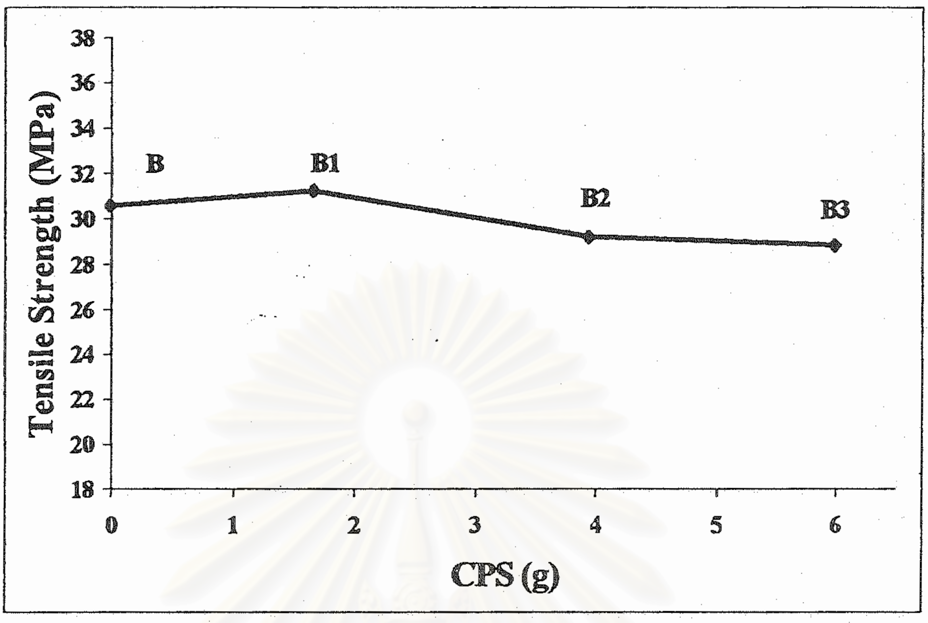


Figure 4.15 Tensile strength of series B

In Figure 4.15, the tensile strength did not rise continuously with the amount of CPS. Normally, the relationship between tensile strength and % of bond sulfur is shown in Figure 4.18, the tensile strength rises with the number of crosslinks until an optimum is reached, after which, if the crosslinking is continued, it initially falls steeply.

In Figure 4.16, the modulus decreased, it can be explained that the definite modulus or definite degree of crosslinking is decided by how long the crosslinking chain is built into each crosslink. CPS can liberate sulfide and then cardanol can also crosslink with the molecules of rubber. When the network structures were obtained from cardanol, which has a long chain of alkyl phenol, then it may be expected that the networks, which consist mainly of long bridge links, have free mobility of chain segments (Micro-Brownian motion); thus causing low modulus. On the other hand, if the network form from only sulfur atom, the distance between the chains is not large then the modulus is high.

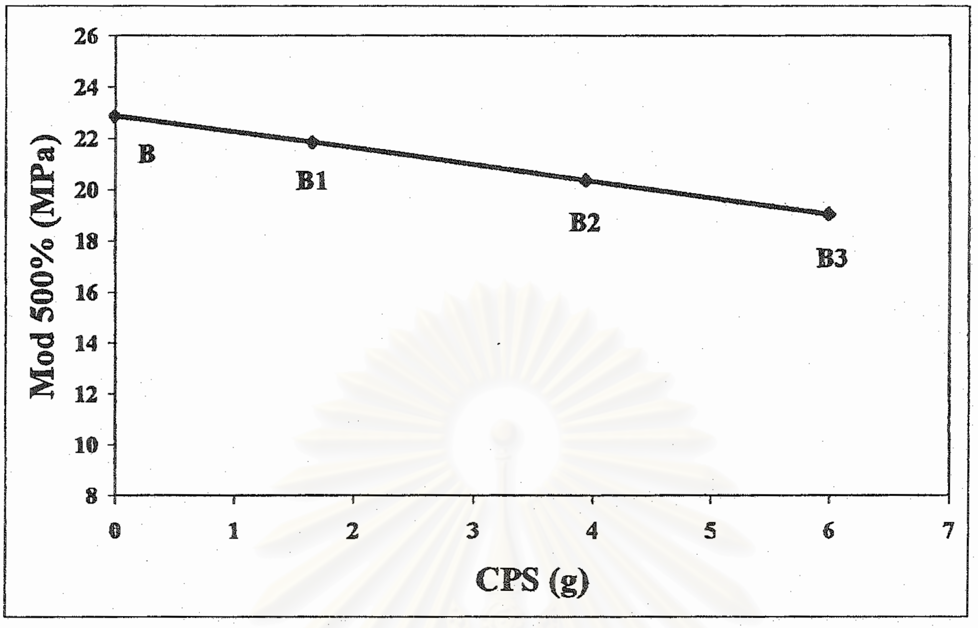


Figure 4.16 Modulus 500% of series B

In Figure 4.17, the elongation was improved by increasing the amount of CPS. This can be elucidated as seen in section 4.4.1.1, that when the proportion of CPS increases, the network was obtained from cardanol, leading to higher mobility of molecular chains. It is clear that it is the reason for higher elongation in compounds in series B.

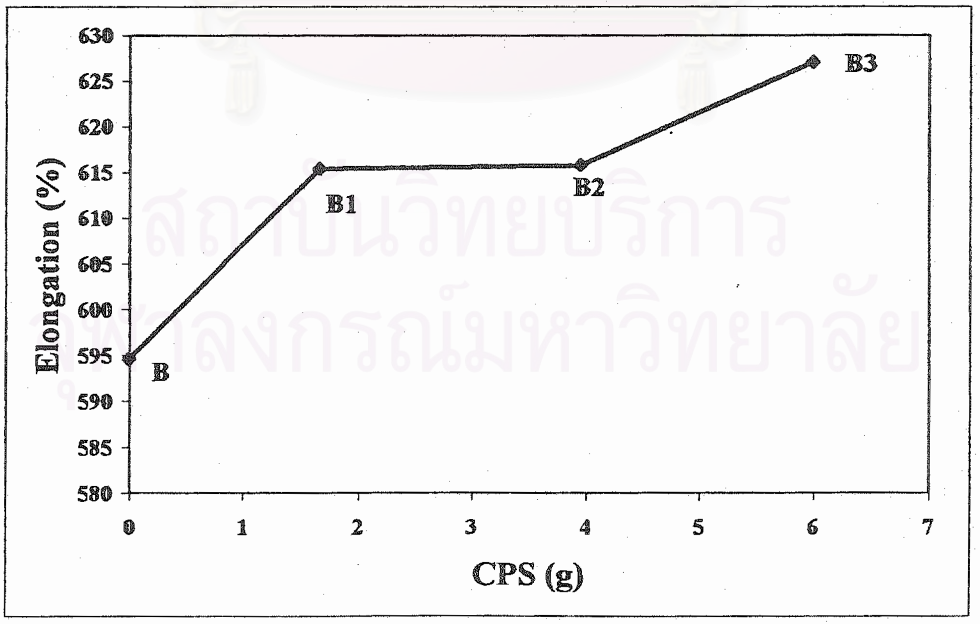


Figure 4.17 Elongation at break of series B

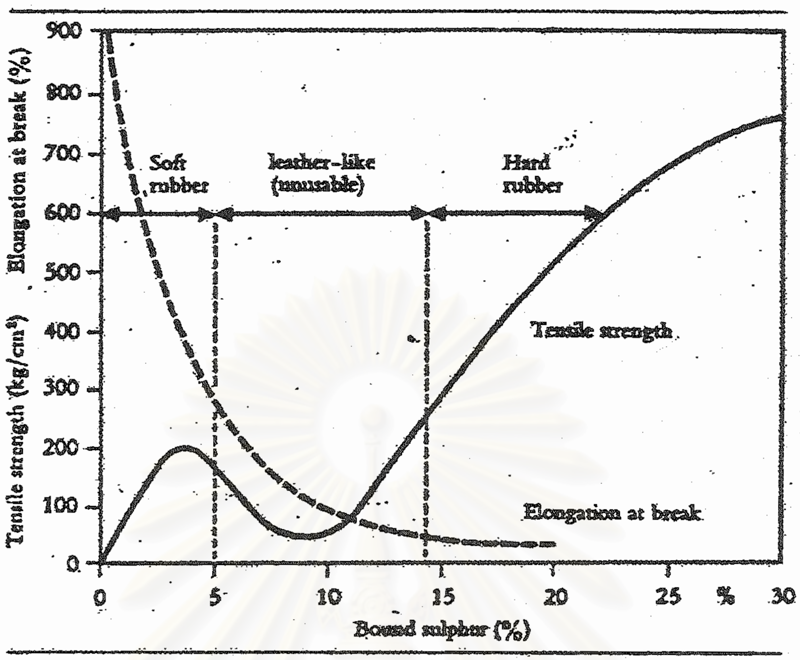


Figure 4.18 Relationship between tensile strength (kg/cm^2) and elongation (%) with bond sulfur (%)

4.4.2.2 Hardness

The hardness of series B is shown in Figure 4.19. The hardness of the rubber compounds improved when the CPS content was increased. This is due to the fact that the hardness increases depending on degree of crosslink. This shows the same results that support section 4.4.1.2.

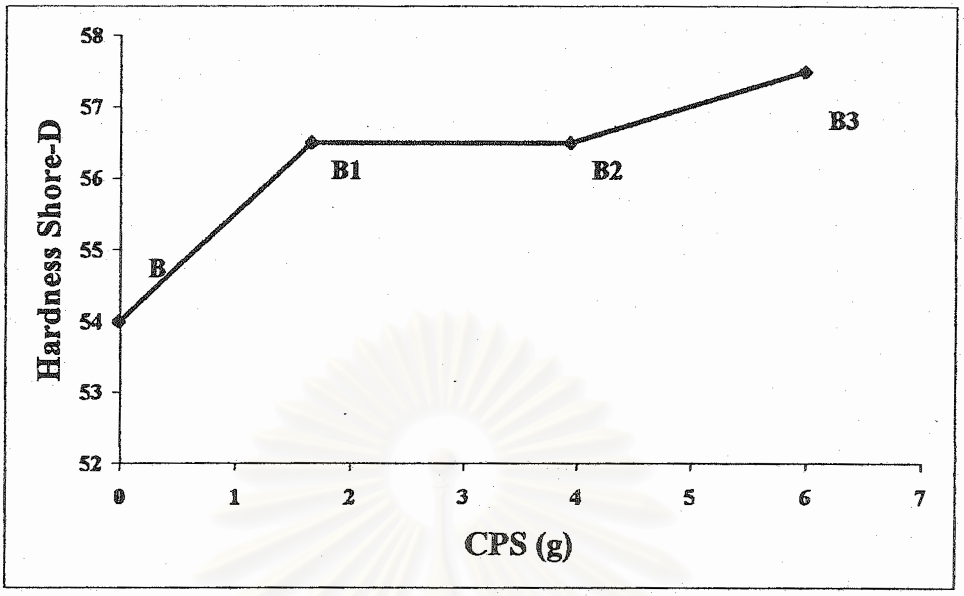


Figure 4.19 Hardness of series B

4.4.2.3 Rebound resilience

The effect of CPS content on rebound resilience in series B is revealed in Figure 4.20. The rebound resilience improved when the CPS content was increased. The result shows that the degree of crosslinking increased by CPS, thus the rebound resilience improved.

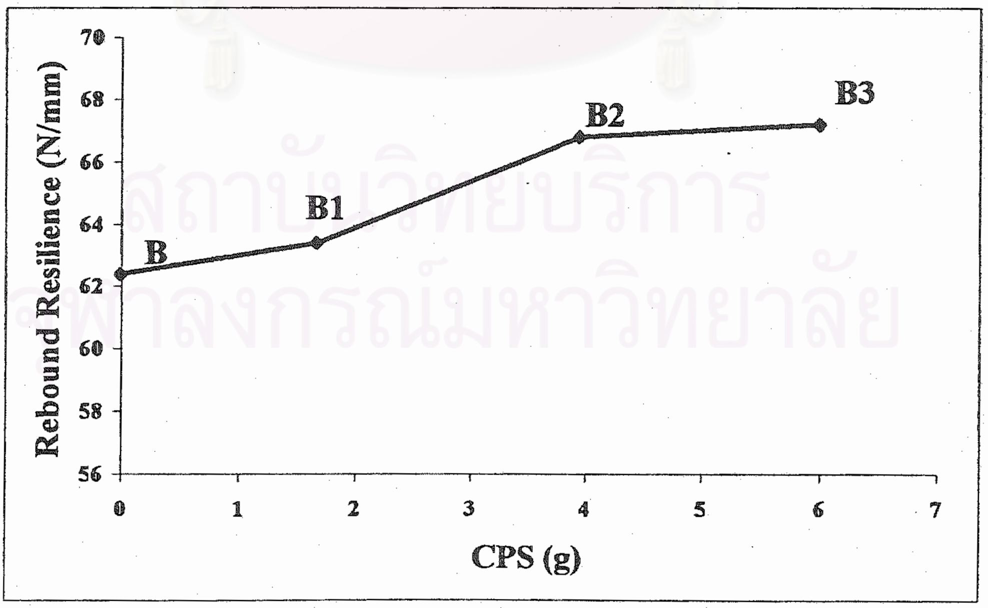


Figure 4.20 Rebound Resilience of series B

4.4.3 Mechanical properties of series E

The effects of CPS content in **series E** on mechanical properties were observed.

4.4.3.1 Tensile Properties

The effect of CPS content on tensile properties of rubber compounds in **series E** is shown in Figures 4.21, 4.22 and 4.23.

From Figure 4.21, the tensile strength was improved when the CPS content was increased. This is due to the CPS rise in the degree of crosslinking.

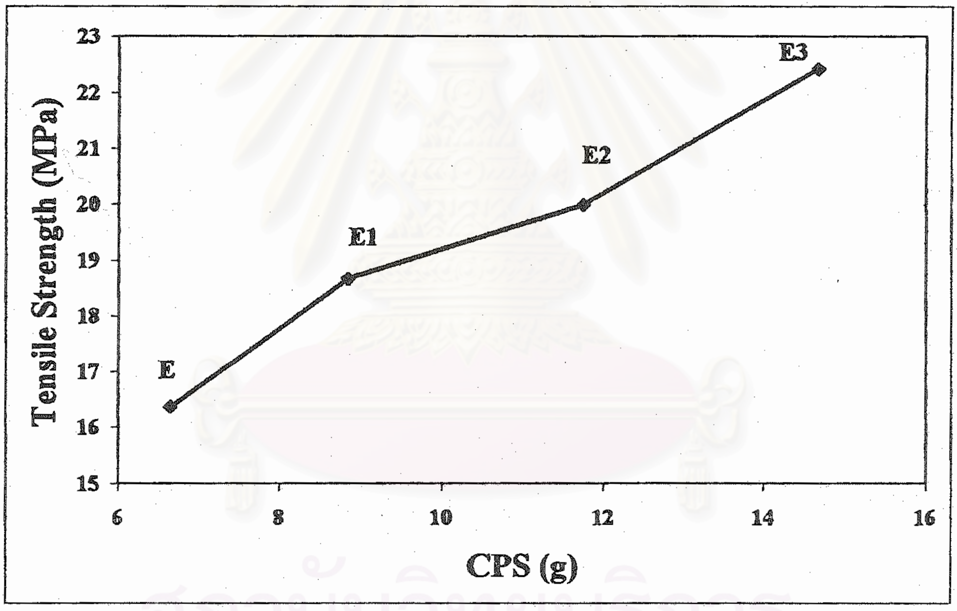


Figure 4.21 Tensile Strength of series E

In Figure 4.22, the modulus of series E is not significantly increased. This is because series E is the only CPS containing rubbers, hence, the distances of chain segments of each compound are near. Thus, the modulus was independent of the degree of crosslinking.

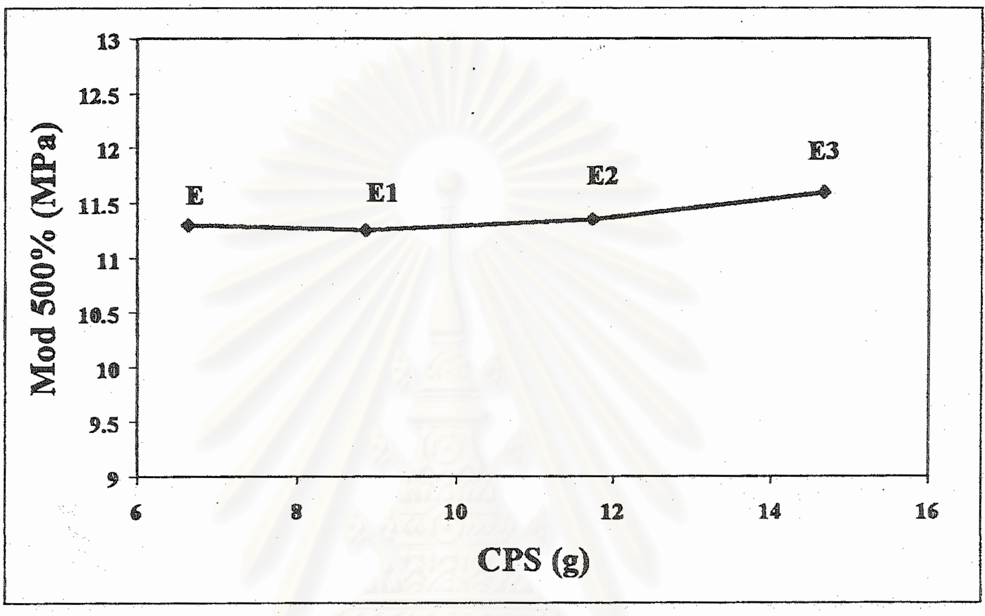


Figure 4.22 Modulus 500% of series E

From Figure 4.23, the elongation increased as the amount of CPS increased. As have been reiterated like the increasing elongation of series B, it is because the networks contain high proportion of cardanol linkage. Hence the mobility of the chains is high, resulting in high elongation.

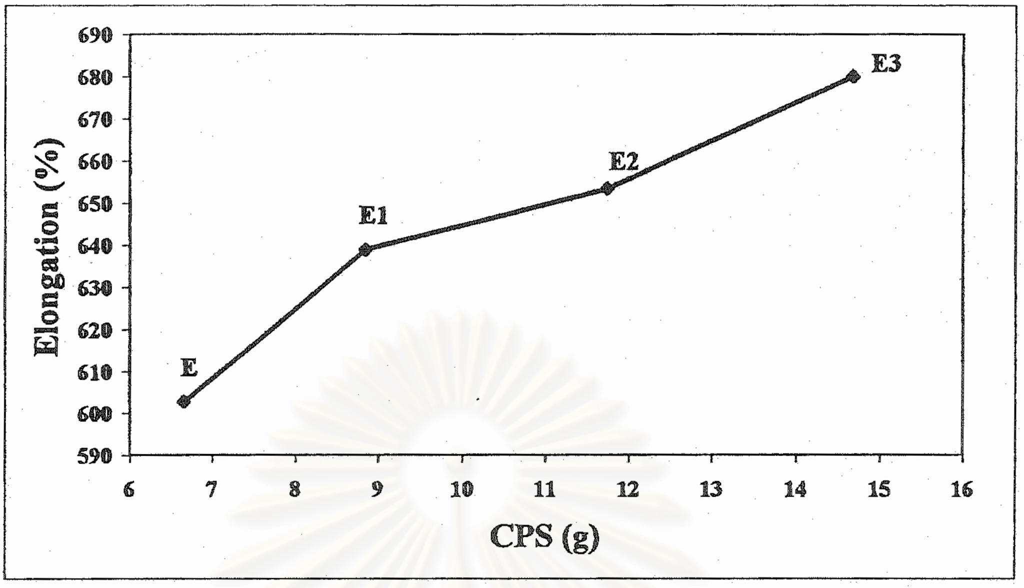


Figure 4.23 Elongation at break of series E

4.4.3.2 Hardness

The hardness of series E is presented in Figure 4.24, the hardness of series E improved with increasing CPS content. This is clear that the hardness increased following the degree of crosslinking. This is supported by the fact that the hardness is dependent on the degree of crosslinking as seen in sections 4.4.1.2 and 4.4.2.2 that show the same results.

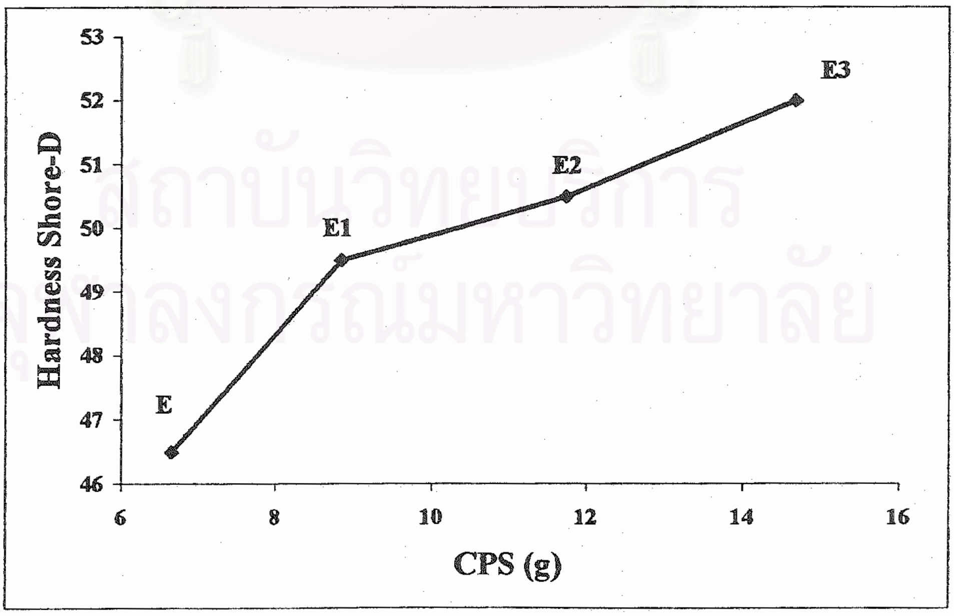


Figure 4.24 Hardness of series E

4.4.3.2 Rebound Resilience

In Figure 4.25, the rebound resilience of **series E** improved with the increasing amount of CPS. This indicates that the rising of rebound resilience was based upon the degree of crosslink. The result of this experiment is quite similar to Figure 4.26, which shows the increasing rebound resilience of **series B**.

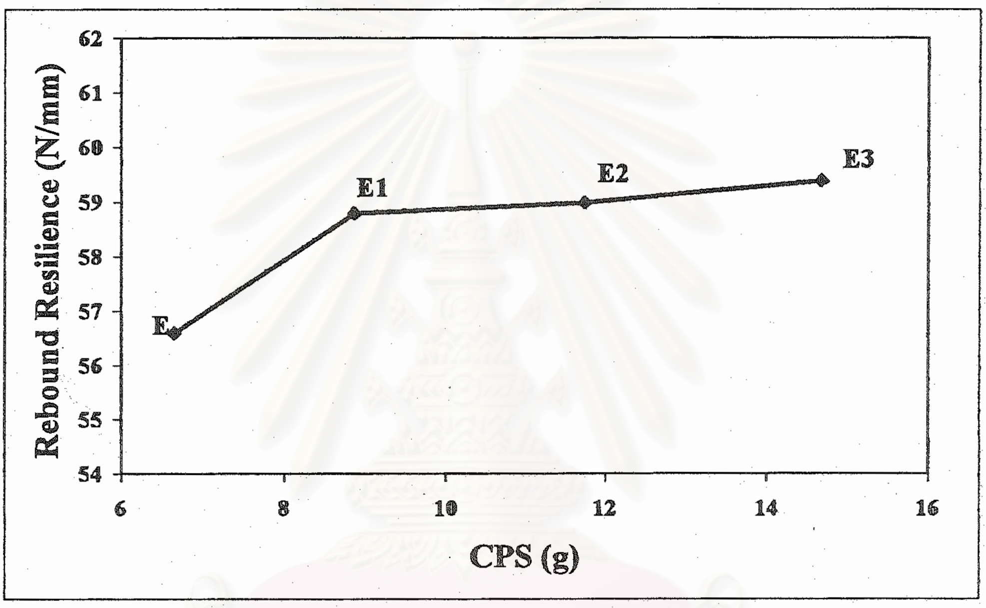


Figure 4.25 Rebound Resilience of **series E**

4.5 Effect of CPS on accelerated aging test of rubber compounds

The difference in ultimate elongation before and after heating is the most useful criterion for judging the durability of vulcanized rubbers. The ultimate elongation of practically all vulcanized rubbers decreases during aging; the rate of decrease depends on the temperature, time, and composition of the yellow rubbers. In this research, the specimens were aged at 100 °C in air oven for 1 and 3 days, then the mechanical properties aged specimens were investigated and shown in Appendix G. The percentage change in mechanical property i.e., tensile strength, modulus 500%, elongation and hardness or % reversion (compared to unaged specimens) was also calculated as shown in Appendix G. The data of %reversion of each of the mechanical properties are shown in Table 4.9.

Table 4.5 % Reversion of **rubber compounds**

% reversion	Tensile Strength (Mpa)		Elongation at break (%)		Modulus 500% (Mpa)		Hardness (Shore-D)	
	1day	3day	1day	3day	1day	3day	1day	3day
A	-30.13	-64.94	-30.77	-55.56	-	-	5.0	5.5
B	-12.95	-43.60	-36.77	-43.28	-	-	5.5	5.0
B1	-11.43	-37.35	-20.28	-34.79	-	-	4.5	5.5
B2	-6.89	-37.77	-18.92	-39.31	-	-	4.5	6.0
B3	-6.66	-35.18	-18.20	-38.38	34.58	-	5	7.5
C	-8.72	-28.87	-17.14	-26.87	41.06	-	2.0	2.5
C1	-6.66	-21.20	-16.20	-23.71	46.11	-	4.5	4.5
D	1.64	-18.94	-8.77	-20.81	42.94	24.65	4.0	4.0
D1	4.59	-6.78	-6.51	-18.54	51.57	45.97	3.0	5.5
E	46.15	21.28	-3.79	-12.27	37.20	52.32	6.0	7.0
E1	20.23	9.24	-3.82	-12.87	40.02	52.99	4.5	5.0
E2	20.99	14.45	-3.84	-11.13	42.44	58.23	4.5	5.5
E3	7.59	1.69	-7.78	-15.73	42.49	59.46	4.5	9.0

- cannot determine

4.5.1 Effect of CPS on accelerated aging test of compounds A-E

The effect of CPS on accelerated aging of **compounds A-E** was studied. The results of CPS containing rubbers were compared to non-CPS containing rubbers. All data of aged species are shown in Appendix G.

4.5.1.1 Reversion of Tensile Properties

From Table 4.9, Figures 4.26, 4.27 and 4.28, all % reversion of the tensile properties, i.e. tensile strength, elongation at break and modulus 500% show that CPS containing rubbers have lower reversion than non-CPS containing rubbers. It can be explained that CPS may have mono-, di- or polysulfide linkages, which is a stronger bond than polysulfide from elemental sulfur. Besidethis, CPS may crosslink with the molecules of rubber by carbon-carbon bond from unsaturated alkyl chains of cardanol. When bond energy is high, the compounds will have good heat stability (see Table 4.11). This indicates that CPS has anti-reversion properties.

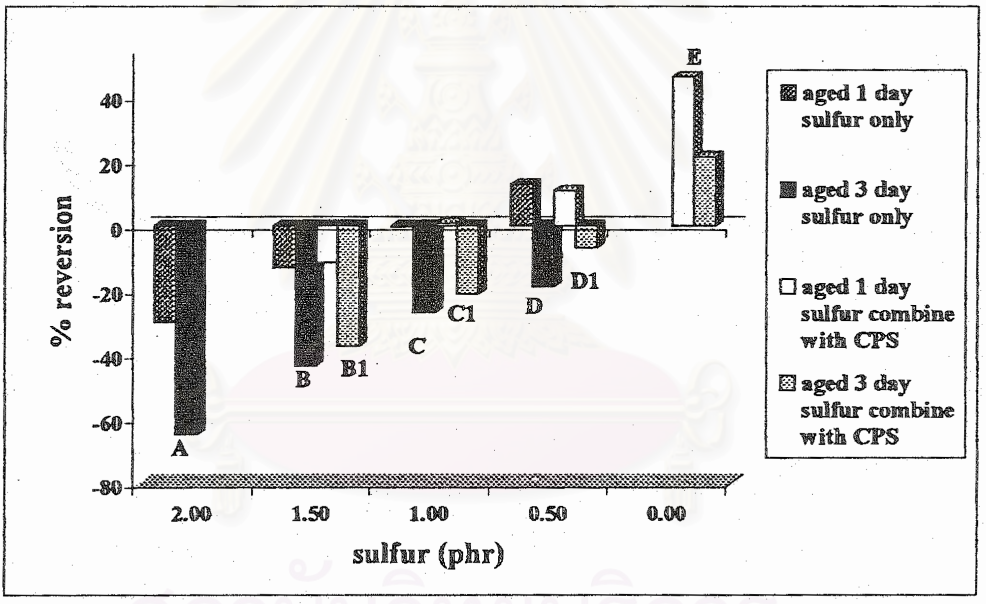


Figure 4.26 % reversion of tensile strength of compounds A-E

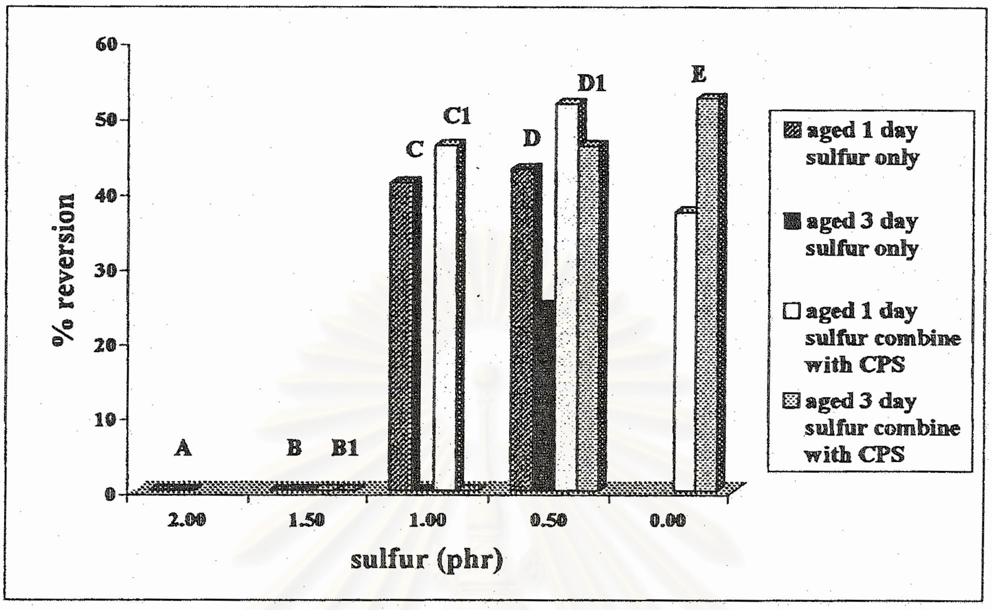


Figure 4.27 % reversion of modulus 500% of compounds A-E

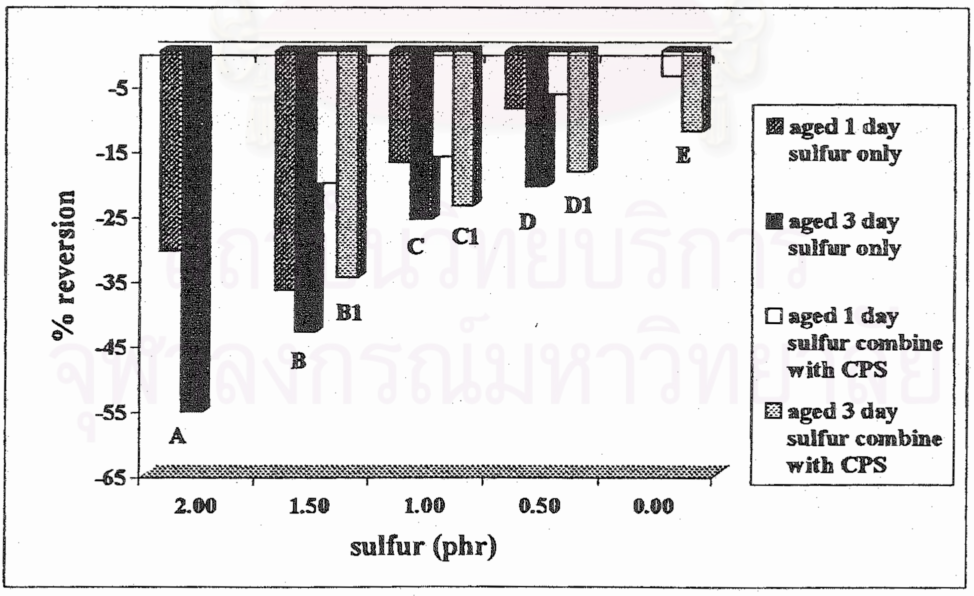


Figure 4.28 % reversion of elongation at break of compounds A-E

Table 4.6 Bond energy of various types of crosslink

Types of linkage	**Bond energy (kcal/mol)**
$-C-S_x-C-$	<64
-C-S-S-C-	64
-C-S-C-	68
-C-C-	84

4.5.1.2 Reversion of Hardness

From Figure 4.29, there were rising characteristics of modulus and hardness in accelerated aging or prolonged storage at room temperature. It should be explained that the postvulcanization which takes place by the accelerated aging test (or prolonged storaging at room temperature) is due not only to the incorporation of additional free sulfur after the vulcanization, but also some extent, as will be seen from Scheme 4.2, to the shortening of the polythioether bridges and the simultaneous formation of additional crosslinks. In this reaction a S_x bridge is of course split before being re-established after its shortening. In this splitting of the sulfur chains, which are incorporated as bridge links, the renewed crosslinking also takes place similarly to crosslinking processes. Accelerators, which able to activate free sulfur, are at any rate also capable as far as they survive the vulcanization process without being decomposed-of activating and splitting crosslinked polythio chains, leading to the hardness is rising after accelerated aging. Moreover, % reversion of hardness of CPS containing compounds is higher than non-CPS containing compounds. This confirms the anti-reversion properties of CPS.

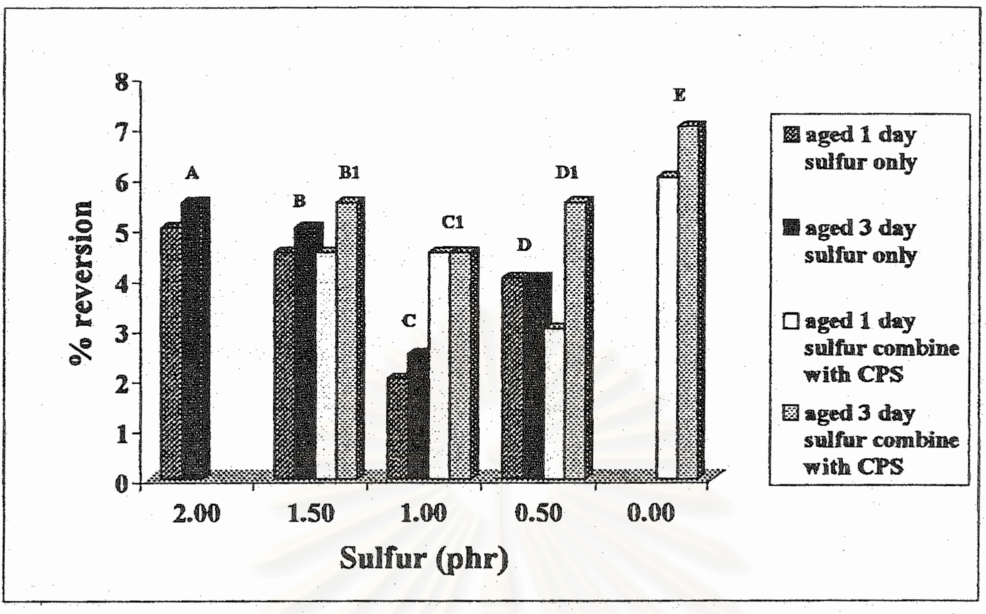
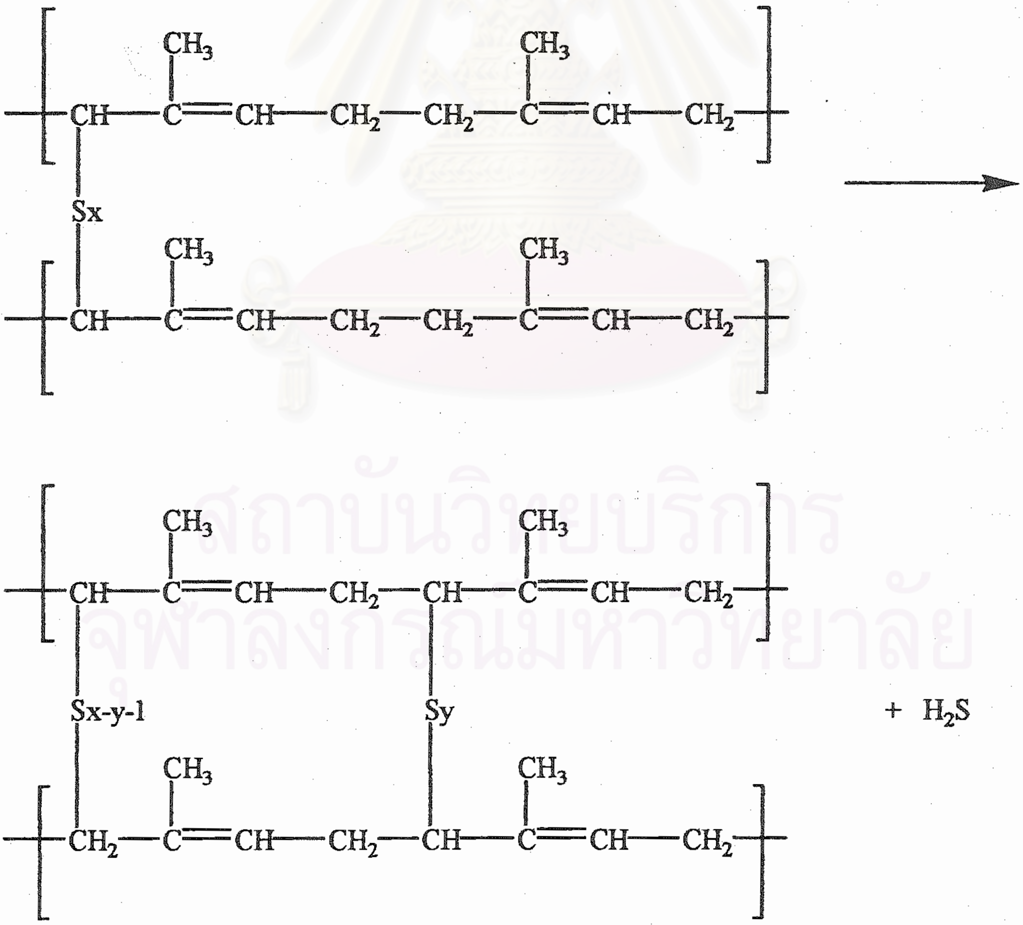


Figure 4.29 % reversion of hardness of **compounds A-E**



Scheme 4.2 Splitting of sulfur bond after vulcanization

4.5.2 Effect of CPS content on accelerated aging test of rubber compounds when sulfur was constant at 1.5 phr (series B)

The effects of CPS on accelerated aging test of **series B** were investigated. All data of aged species are shown in Appendix G.

4.5.2.1 Reversion of Tensile Properties

From Figures 4.30 and 4.32, it can be seen that % reversion of tensile strength and elongation of **series B** are in the vicinity value, even though the compounds had higher sulfur content; which caused increasing reversion of sulfur containing rubbers. This confirms the anti-reversion properties of CPS. But for Figure 4.31, compounds cannot obtain the modulus because the elongation is lower than 500% except for **compound B3**, which can show the modulus for aging 1 day. However, the data cannot be discussed.

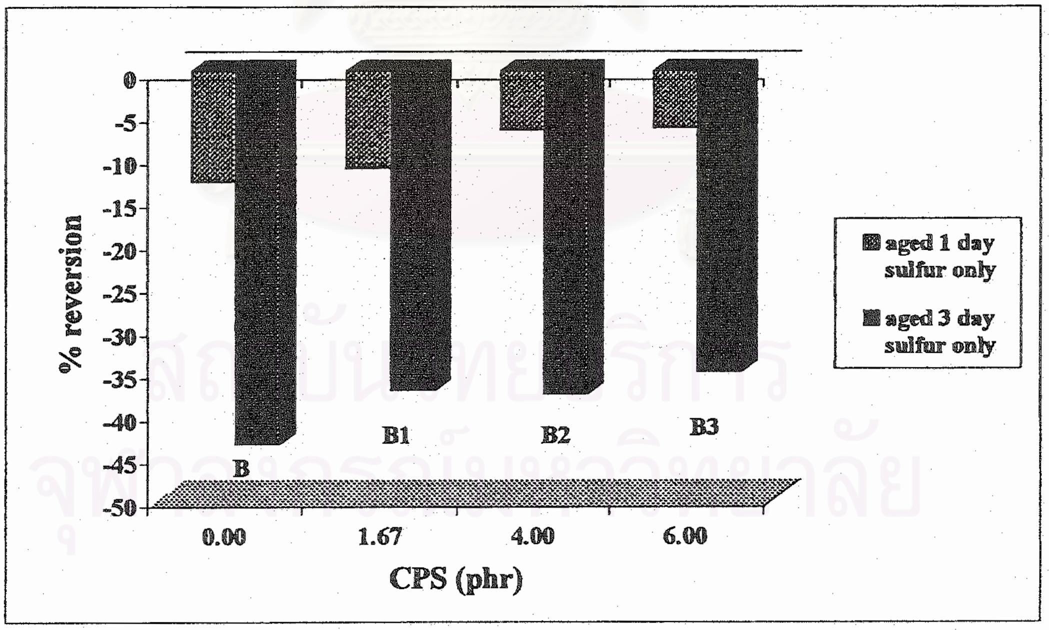


Figure 4.30 % reversion of tensile strength of **series B**

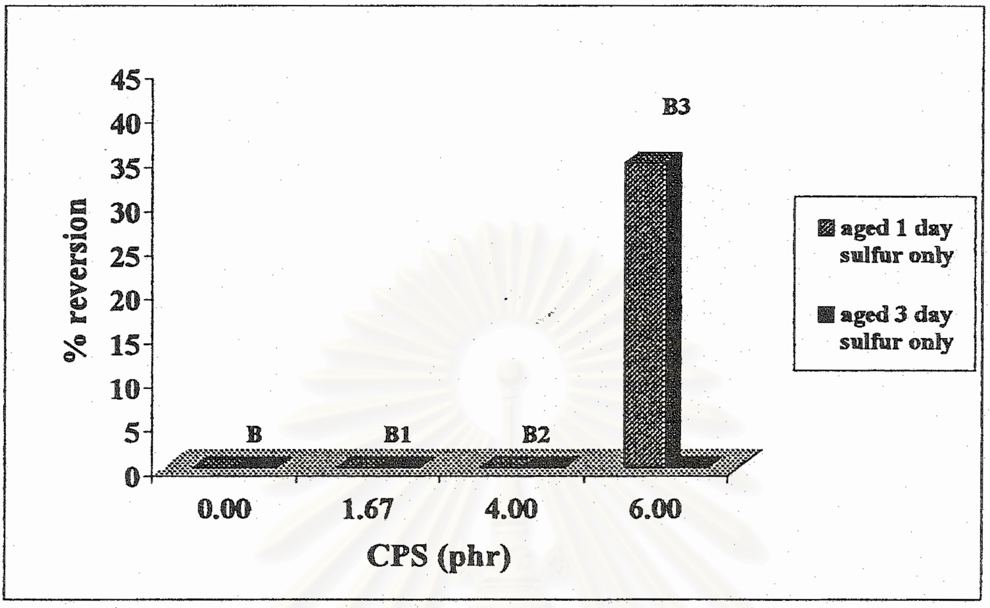


Figure 4.31 % reversion of modulus 500% of series B

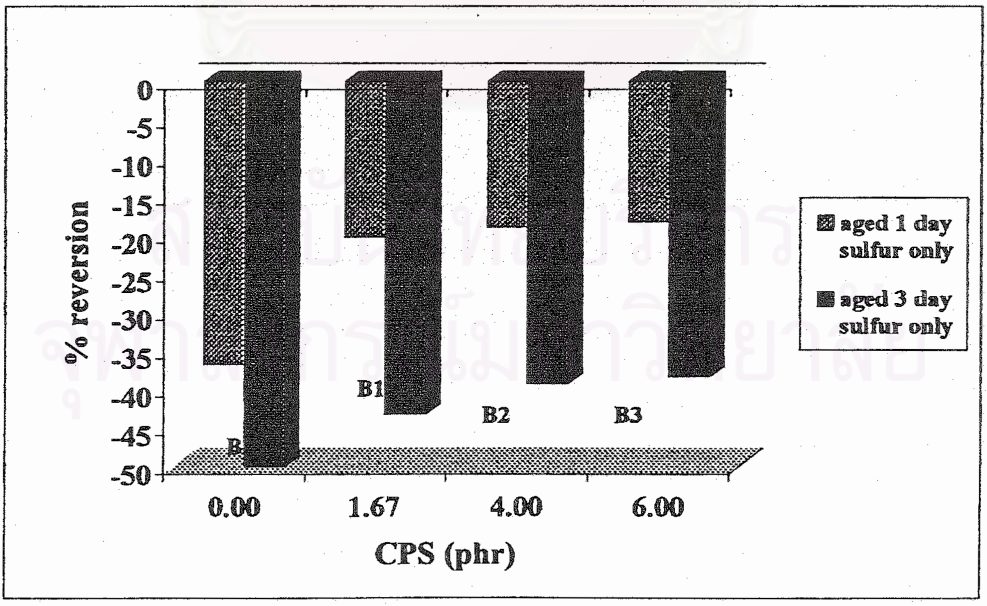


Figure 4.32 % reversion of elongation at break of series B

4.5.2.2 Reversion of Hardness

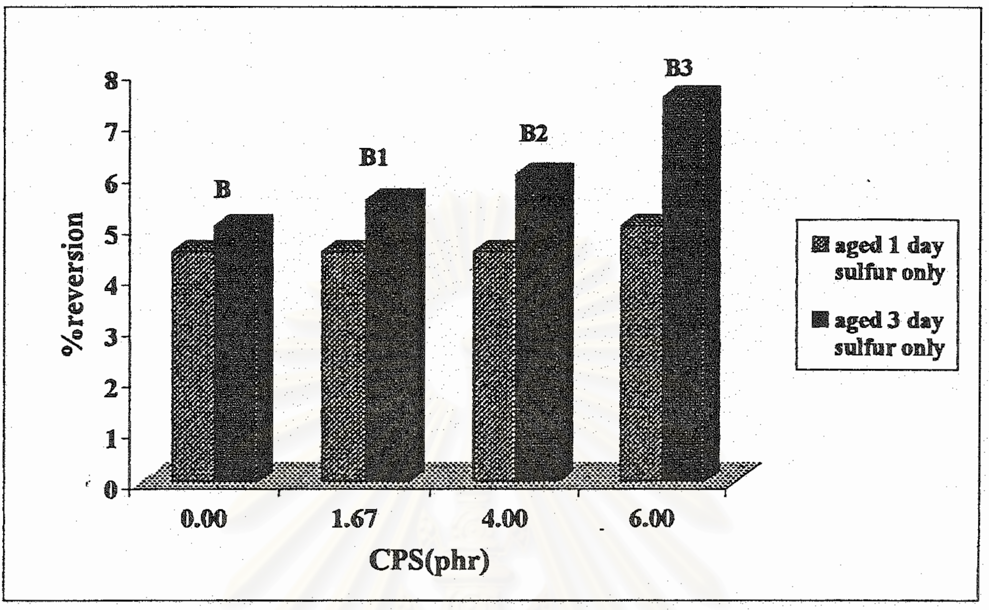


Figure 4.33 % reversion of hardness of series B

From Figure 4.33, as seen from section 4.4.2, the results show the nearly improved of hardness after aging even as the degree of crosslinking increases. It is clear that CPS can reduce the reversion of rubber compounds.

4.5.3 Effect of CPS content on accelerated aging test of rubber compounds with no sulfur (series E)

The effects of CPS on accelerated aging test of series E were observed. The details of all data of aged species are shown in Appendix G.

4.5.3.1 Reversion of Tensile Properties

In Figures 4.34, 4.35 and 4.36, it can be seen that **series E** has low % reversion of most of mechanical properties. However, % reversion of tensile strength and elongation is slightly increased. The reason for this result is the sulfur linkage also split and re-established again after aging, as evident from Scheme 4.2. From these data, it indicates that CPS can reduce the reversion.

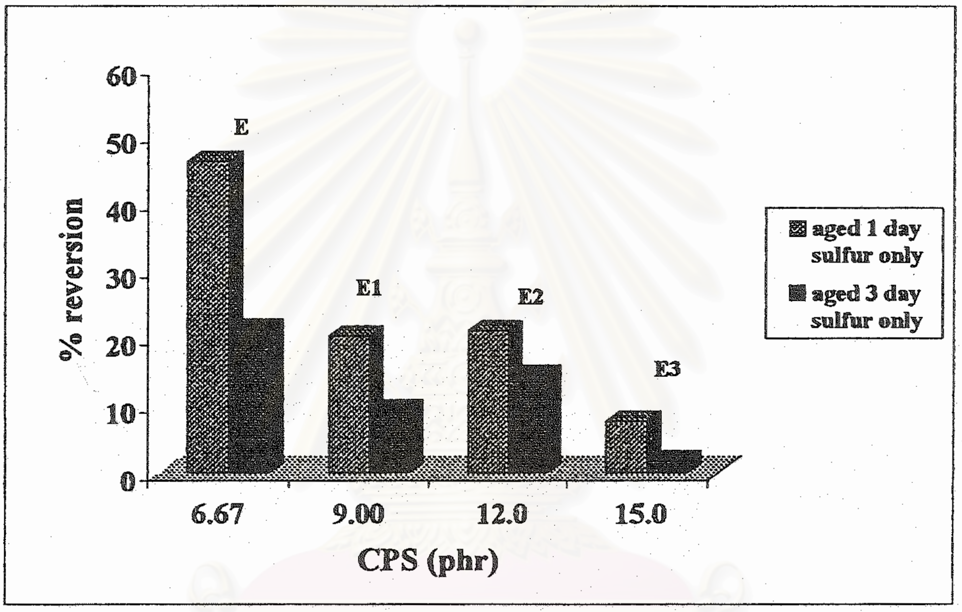


Figure 4.34 % reversion of tensile strength of series **E**

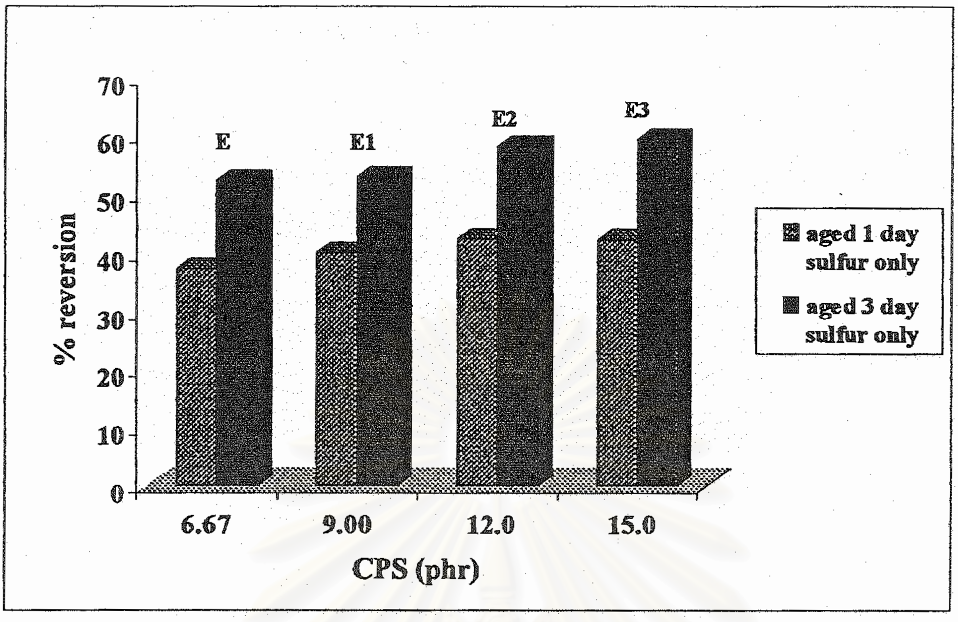


Figure 4.35 % reversion of modulus 500% of series E

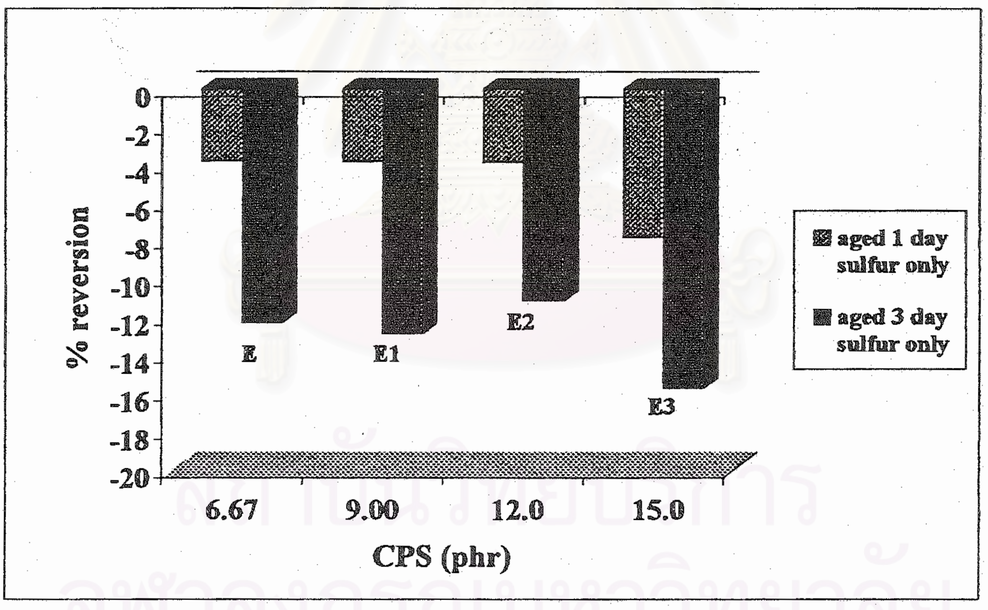


Figure 4.36 % reversion of elongation at break of series E

4.5.3.2 Reversion of Hardness

From Figure 4.37, the hardness improved after aging. This supports sections 4.4.2.2 and 4.4.3.2 with the same reason and this confirms that CPS can reduce the reversion of rubber compounds.

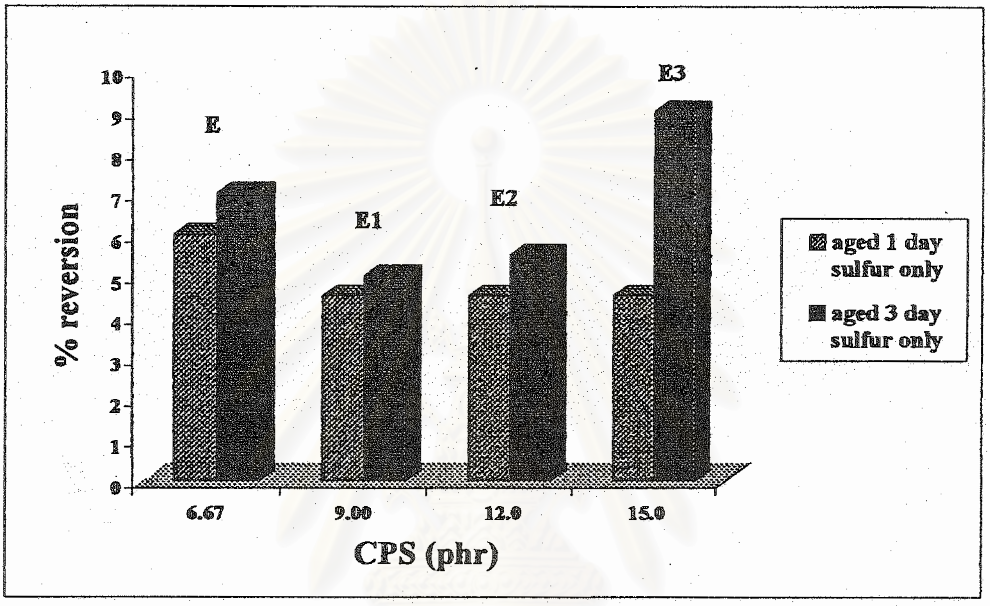


Figure 4.37 % reversion of hardness (Shore-D) of **series E**

4.6 Blooming

From Figure 4.38, it shows that CPS-containing rubbers had lower blooming than **compound A**, which is a sulfur-containing rubber. This is because the solubility of sulfur in rubber increases as the temperature rises. The proportion of sulfur soluble at a high mixing temperature, which exceeds the proportion soluble at room temperature, tends, once the products have cooled, to crystallize out of the over-saturated solution.

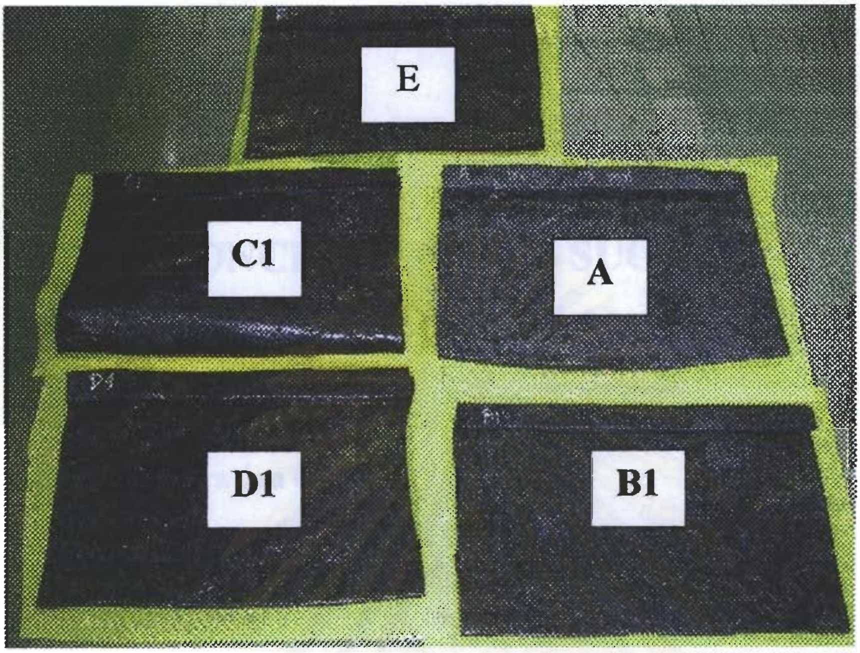


Figure 4.38 Picture of **compounds A, B1, C1, D1 and E**

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

5.1.1 Preparation of CPS

CPS was prepared from decarboxylated CNSL and elemental sulfur by condensation polymerization. The optimum condition was found and CPS was characterized to yield the highest weight sulfur content.

In this work, the appropriate conditions for the preparation of CPS were at 140 ^{0}C with non-medium for 3 hr and an excess elemental sulfur was used to give 30 %wt of sulfur content. FT-IR, ^{1}H NMR, ^{13}C NMR spectrometers and a sulfur analyzer were used to characterize CPS; however, the exact structure of this product was not known because it is a complex mixture of sulfide resin, comprising mono-, di-, polysulfide linkages, which are different chemical structure.

5.1.2 Mechanical Properties of CPS containing rubbers.

CPS were mixed with natural rubber and other additives to be used as vulcanizing agent. The vulcanization characteristics and mechanical properties of vulcanized rubbers were tested. The vulcanization characteristic such as delta torque and optimum cure time and mechanical properties ; tensile strength, modulus, elongation, hardness and rebound resilience, were investigated and compared to non-CPS containing rubbers. It was found that sulfur could be donated from CPS to crosslinks with the molecules of rubber. The optimum cure time reduced when a low content of CPS was used at a fixed amount of sulfur, because CPS can reach the onset of vulcanization in a short time. But at a high content of CPS, the cure time was longer. This is due to CPS, however it could reach the onset of vulcanization at an early stage, but it takes a long time to optimum cure. The reason for this phenomenon is because CPS consists of many sulfide linkages and cardanol, also forming crosslink with the molecules of rubber. Rubber compounds obtained from the use of CPS as a sulfur donor show improvement in most of the basic mechanical properties, because the degree of crosslinking increased from sulfur, which was donated from CPS. Then accelerated aging test was investigated and the results were compared to unaged specimens. It was observed that the CPS containing rubbers have lower reversion in the ultimate vulcanizates. This indicates that CPS could form stronger networks because of cardanol and shorter sulfide linkage, which have more bond energy than elemental sulfur. This work shows that CPS can be used as the vulcanizing agent and it improves mechanical properties and reduces the reversion of rubber containing CPS.

5.2 Suggestions

1) The presence of ethyl acetate that is used for solvent in the CPS dilution could effect the swell during processing. Therefore, CPS should be mixed with other additives such as carbon black or calcium silicate.

2) The effect of different processing methods such as mixing CPS with natural rubber latex by ball mill.

3) The blend of CPS with other rubbers such as synthesis rubber.

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APPENDICES

APPENDIX A

Calculations of dry weight of resin

JIS K 6909

Apparatus

a) *Weighing bottle* A 50 mm flat weighing bottle specified in JIS R 3503

b) *Drying Oven* Hot-air circulation type drying oven.

c) *Desiccator* A desiccator specified in JIS R 3503 containing silica gel as the desiccant.

Procedure

Approximately 1.5 g of sample was poured into weighing bottle specified in (a) and placed in the drying oven maintained at 135±1 ^{0}C for 1 hrs. Consequently, it was taken out of the oven and was allowed to cool down in the desiccator. The mass was weighted and the content of nonvolatile resin was calculated to an integral number by the equation below.

$$N = D/S \times 100$$

Where N: content of nonvolatile matter (%)

D: mass of sample after drying (g)

S: mass of sample (g)

APPENDIX B

Sulfur Analyzer Procedure

ASTM 1552-88

Testing Conditions:

Oxygen gas	40 psi
Instrument gas	40 psi
Furnace Temperature	1350 ^{0}C

Com-Aid about 3 g was put spread out over the boat. CPS dilution was dropped onto Com-Aid. Put the boat into furnace and operate the machine.

APPENDIX C

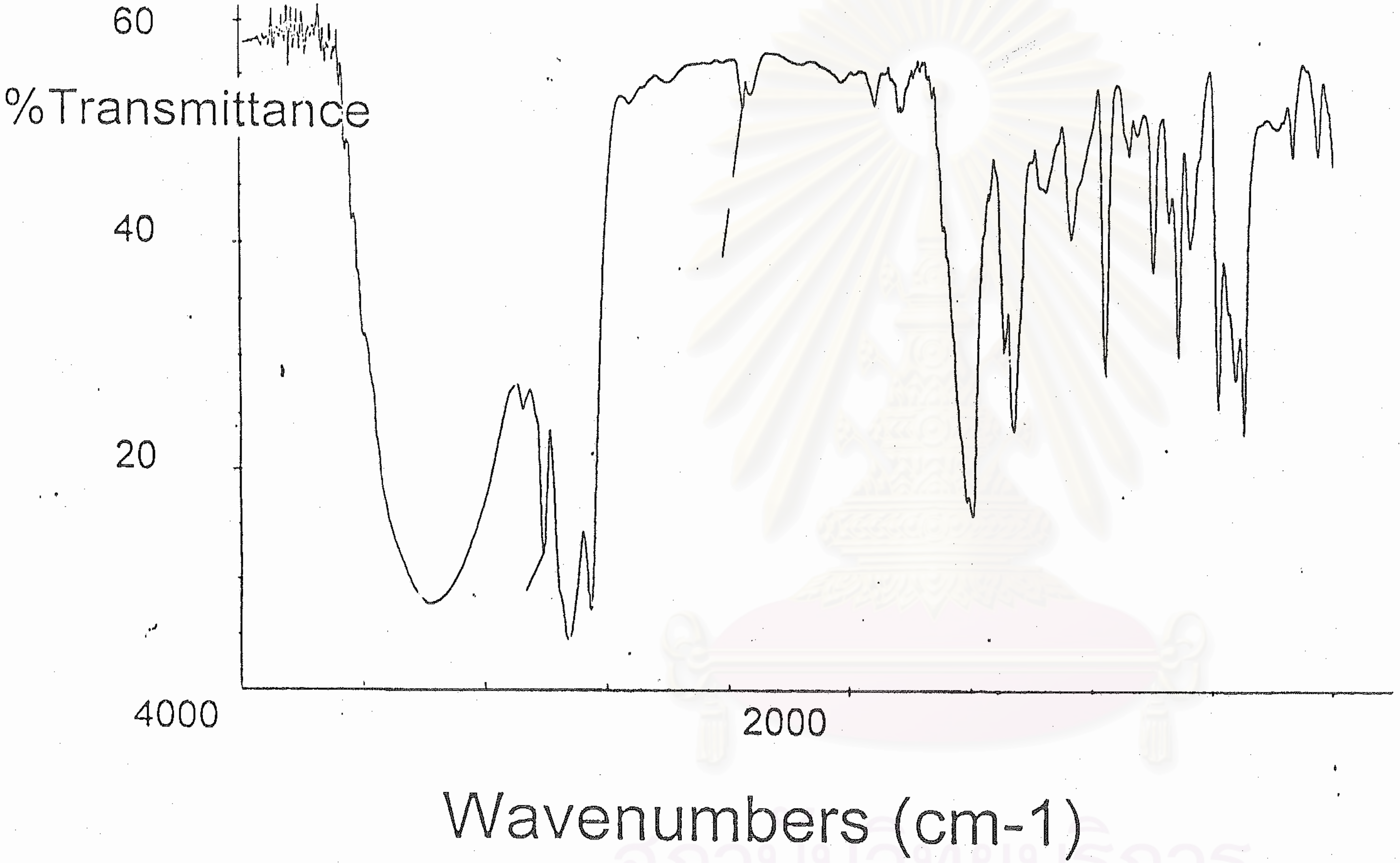


Figure C.1 IR spectrum of CNSL

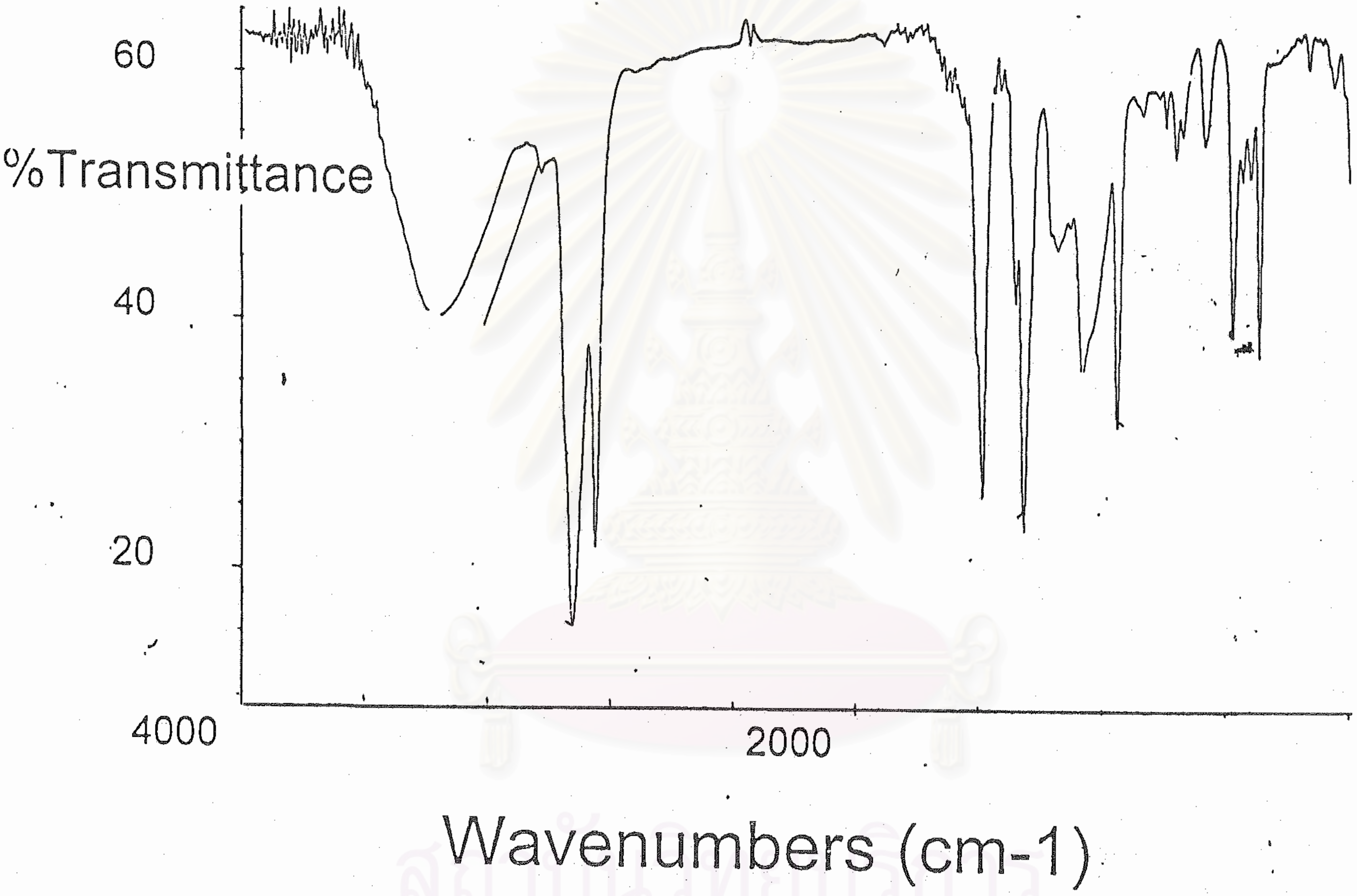


Figure C.2 IR spectrum of CPS

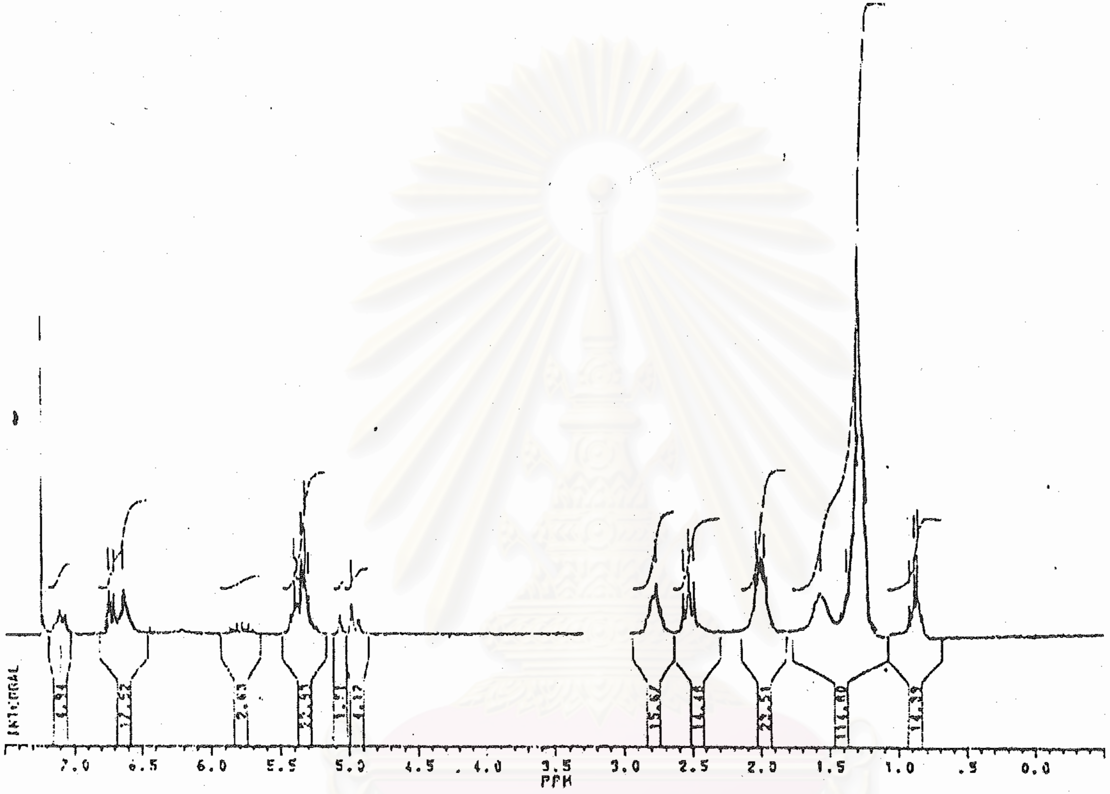


Figure C.3 ^{1}H NMR spectrum of CNSL

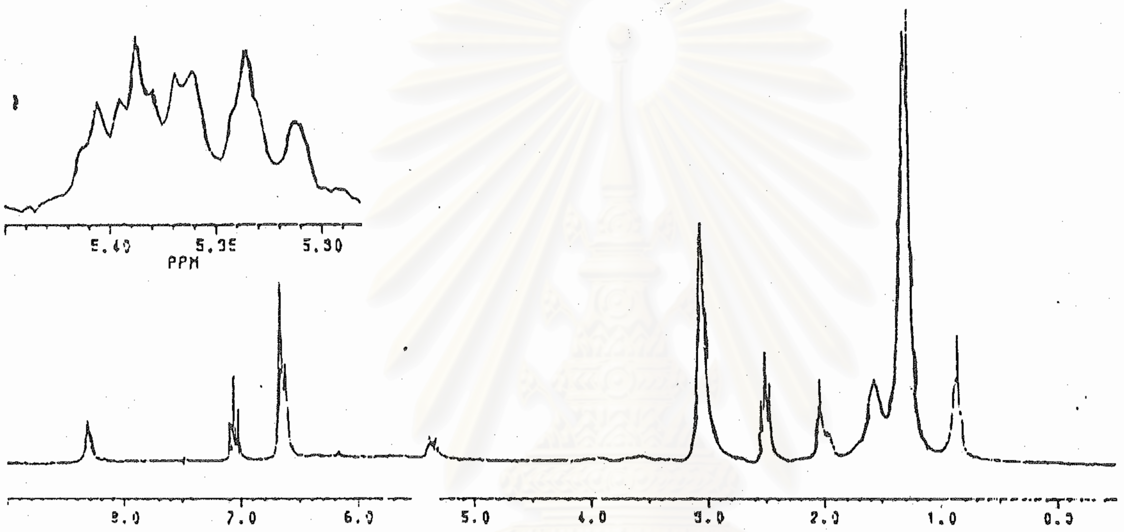


Figure C.4 ^{1}H NMR spectrum of CPS

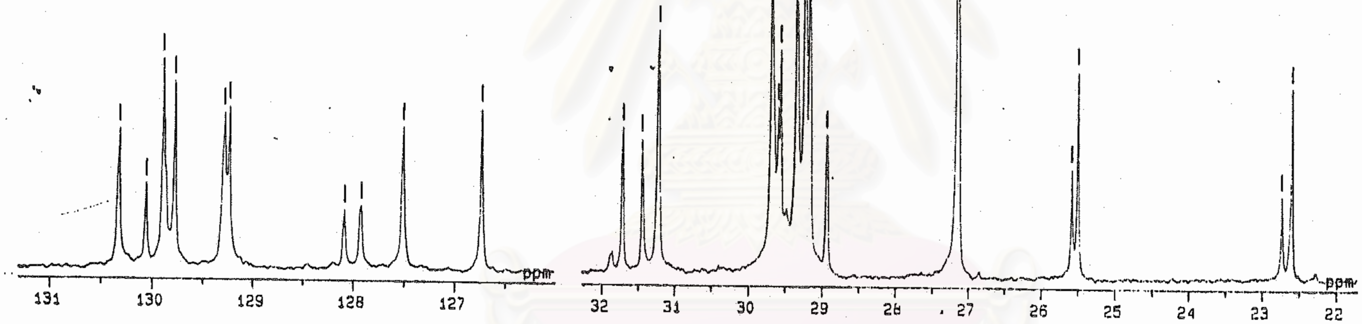


Figure C.5 ^{13}C NMR spectrum of CNSL

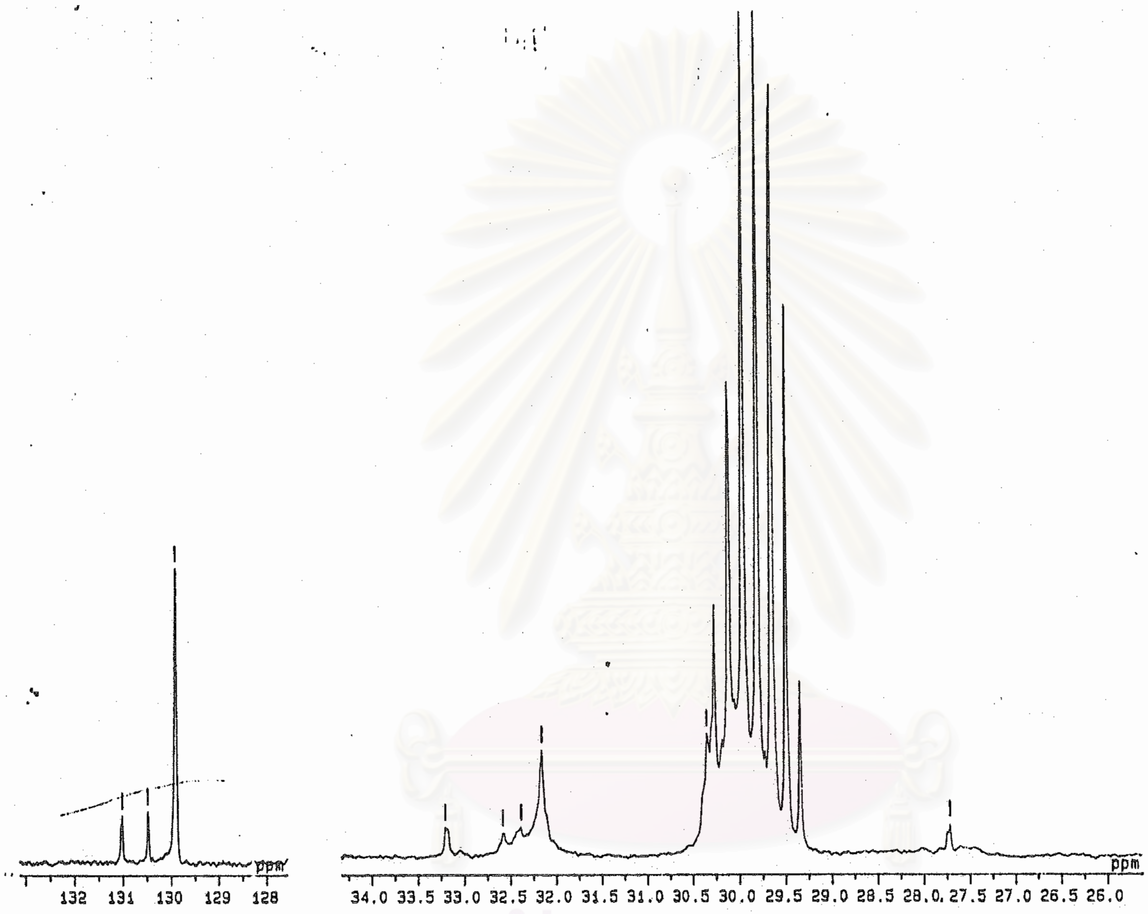


Figure C.6 ^{13}C NMR spectrum of CPS

APPENDIX D

In this research the rheometer and mooney viscometer were used for determination of vulcanization characteristic and vulcanization curve, respectively.

Table D.1 Vulcanization characteristics of rubber compounds

		Compounds												
		A	**B**	**B1**	**B2**	**B3**	**C**	**C1**	**D**	**D1**	**E**	**E1**	**E2**	**E3**
Min	1^{st}	1.56	1.70	1.67	1.46	1.48	1.70	1.55	1.60	1.52	1.51	1.48	1.45	1.31
τ	2^{nd}	1.45	1.45	1.46	1.46	1.37	1.44	1.42	1.42	1.36	1.33	1.47	1.44	1.33
τ-rise	1^{st}	3.70	3.80	2.60	2.20	1.80	3.90	2.50	4.30	2.20	2.30	1.80	1.60	1.40
/1	2^{nd}	3.40	3.50	2.60	2.10	1.70	3.80	2.30	4.20	2.30	2.40	1.80	1.60	1.40
T_{25}	1^{st}	3.90	3.90	2.80	2.30	1.90	4.00	2.60	4.20	2.30	2.40	2.00	1.80	1.60
	2^{nd}	3.50	3.60	2.70	2.20	1.90	3.80	2.40	4.20	2.40	2.50	2.10	1.80	1.60
S_{25}	1^{st}	4.96	4.59	5.00	4.69	4.94	4.21	4.38	3.03	3.67	3.13	3.31	3.39	3.32
	2^{nd}	4.90	4.59	4.84	4.87	4.91	3.72	4.29	3.05	3.72	2.93	3.33	3.35	3.33
T_{90}	1^{st}	7.00	7.10	5.90	5.50	5.60	7.20	6.70	8.00	9.00	17.30	16.40	16.20	11.70
	2^{nd}	6.60	6.70	5.70	5.50	5.60	7.30	6.40	8.40	9.10	16.20	16.20	16.30	12.20
S_{90}	1^{st}	12.69	11.43	11.76	12.07	12.25	9.42	10.34	6.79	8.76	7.15	7.69	8.20	8.06
	2^{nd}	12.68	11.18	11.50	12.25	12.19	9.42	10.14	6.72	8.70	6.76	7.72	8.19	8.20
Rate	1^{st}	0.64	0.60	0.62	0.60	0.50	0.60	0.45	0.50	0.27	0.12	0.12	0.12	0.18
	2^{nd}	0.64	0.62	0.64	0.57	0.52	0.54	0.46	0.45	0.26	0.13	0.11	0.10	0.17
Delta	1^{st}	12.53	10.71	11.21	11.77	11.94	8.59	9.78	5.78	8.06	6.28	6.91	7.52	7.63
τ	2^{nd}	12.48	10.80	11.16	12.00	12.03	8.80	9.69	5.90	8.17	6.05	6.93	7.51	7.65

Table D.1 Vulcanization characteristics of rubber compounds (continued)

		Compounds												
		A	**B**	**B1**	**B2**	**B3**	**C**	**C1**	**D**	**D1**	**E**	**E1**	**E2**	**E3**
T_{50}	1^{st}	4.50	4.40	3.30	2.80	2.40	4.50	3.10	4.80	3.00	3.70	3.20	3.10	2.70
	2^{nd}	4.10	4.10	3.20	2.70	2.50	4.30	2.90	4.80	3.00	3.80	3.30	3.20	2.80
Max	1^{st}	13.91	12.41	12.88	13.23	13.42	10.29	11.33	7.38	9.58	7.79	8.39	8.97	8.94
τ	2^{nd}	13.93	12.25	12.62	13.46	13.40	10.29	11.11	7.32	9.53	7.38	8.40	8.95	8.98

APPENDIX E

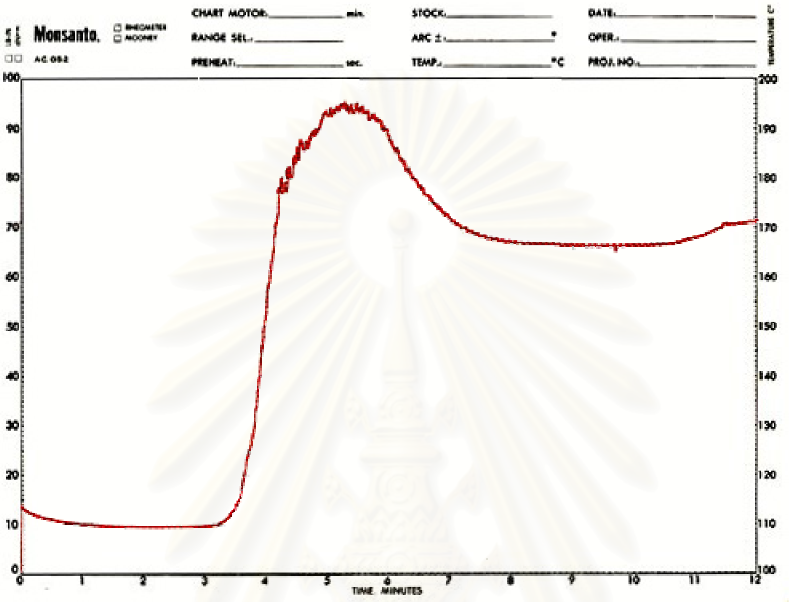


Figure E.1 Vulcanization curve of **compound A**

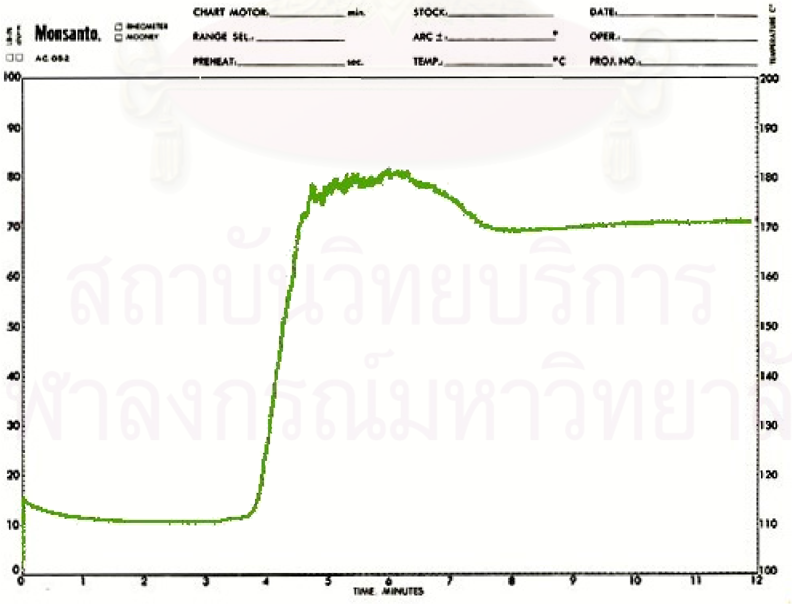


Figure E.2 Vulcanization curve of **compound B**

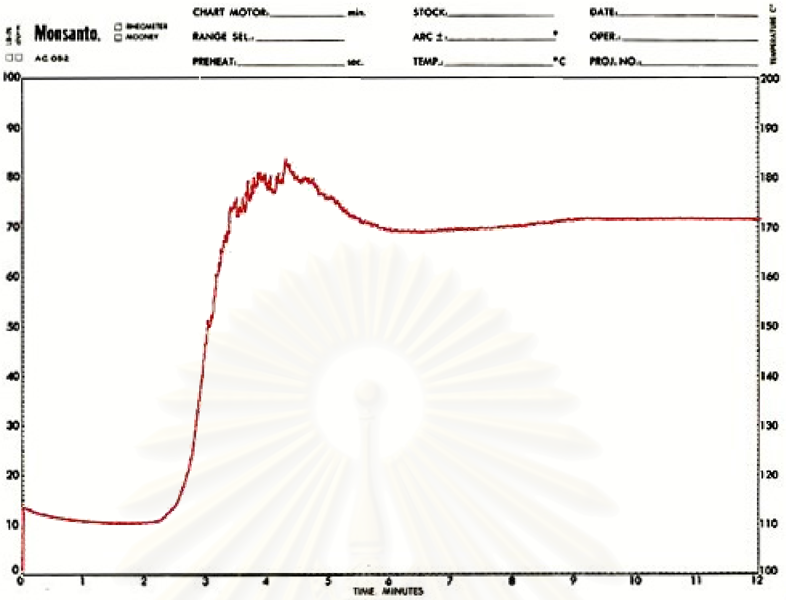


Figure E.3 Vulcanization curve of **compound B1**

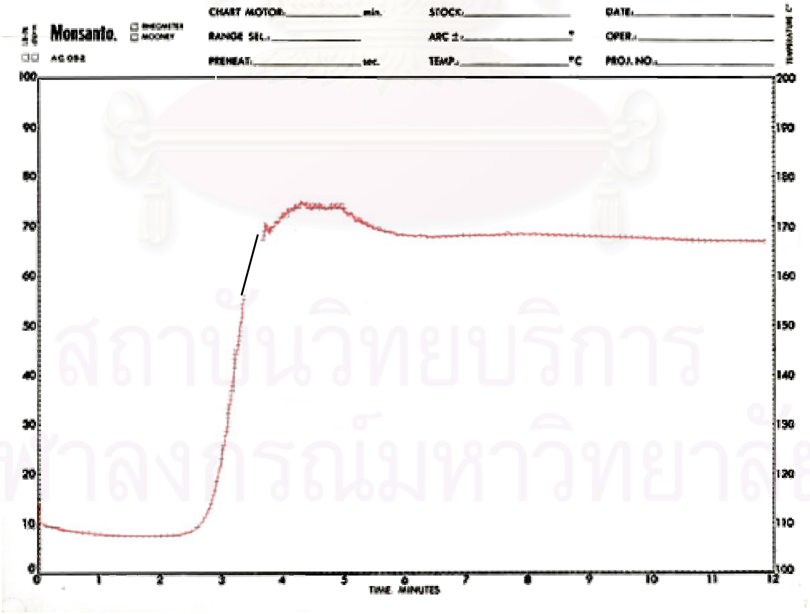


Figure E.4 Vulcanization curve of **compound B2**

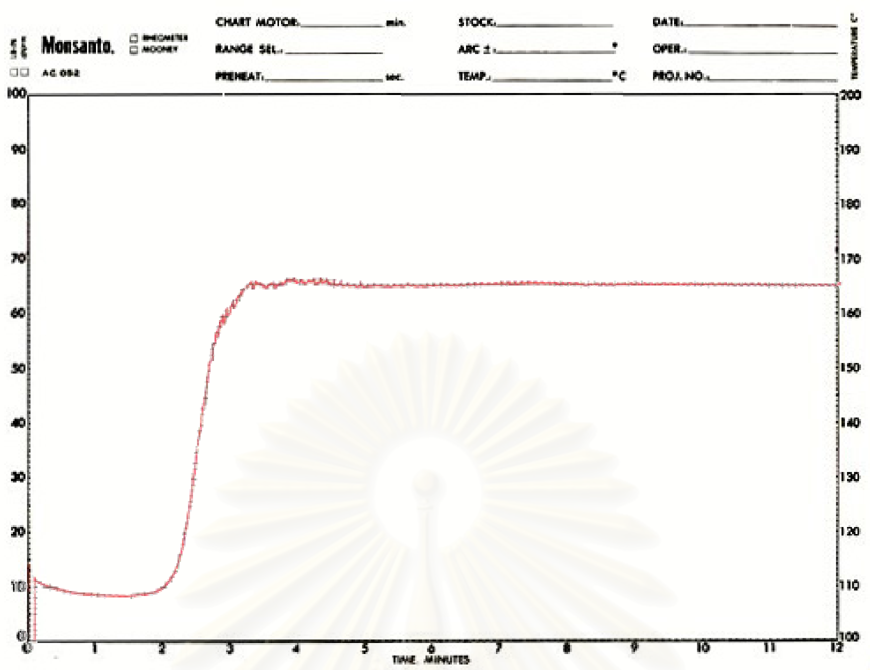


Figure E.5 Vulcanization curve of **compound B3**

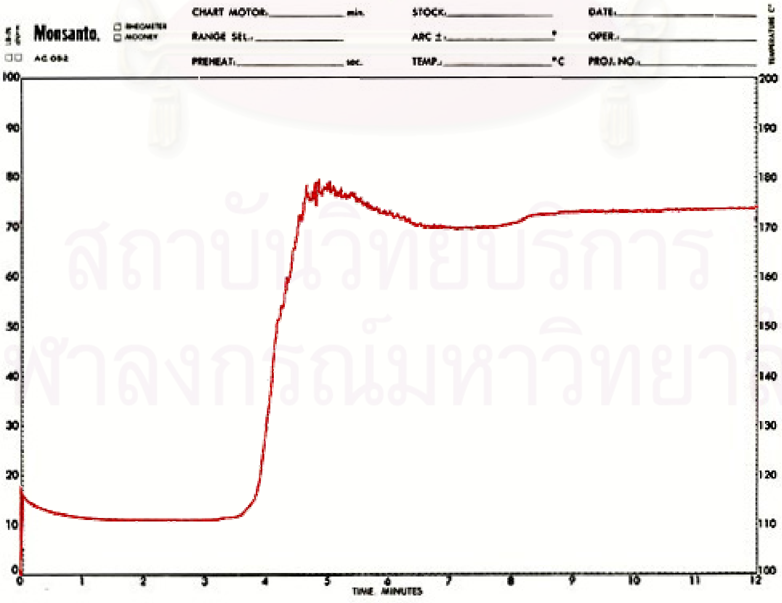


Figure E.6 Vulcanization curve of **compound C**

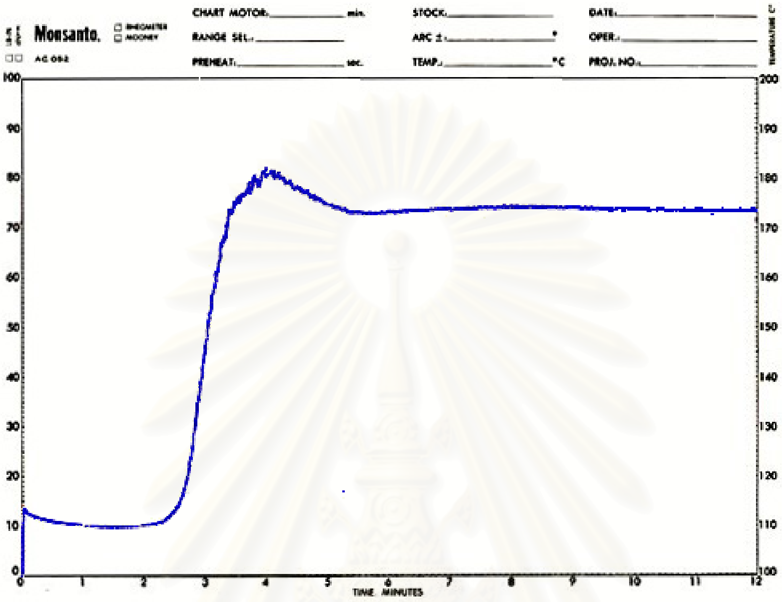


Figure E.7 Vulcanization curve of **compound C1**

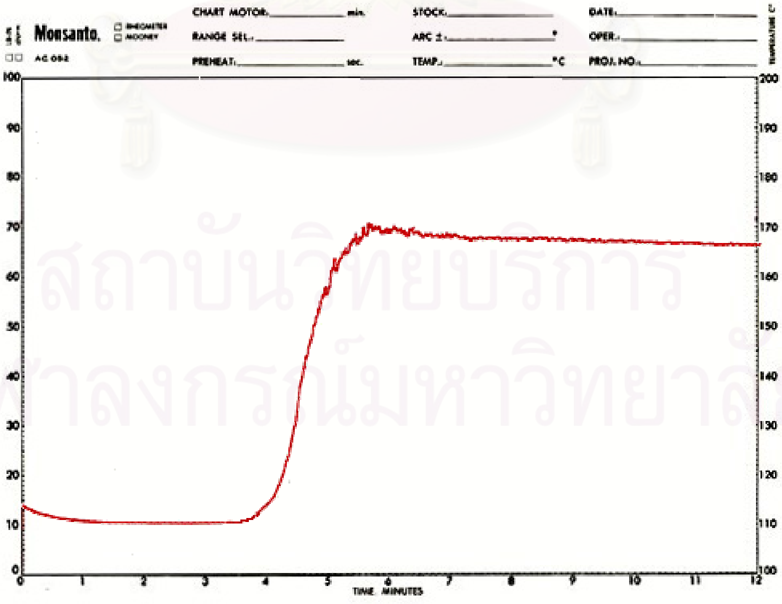


Figure E.8 Vulcanization curve of **compound D**

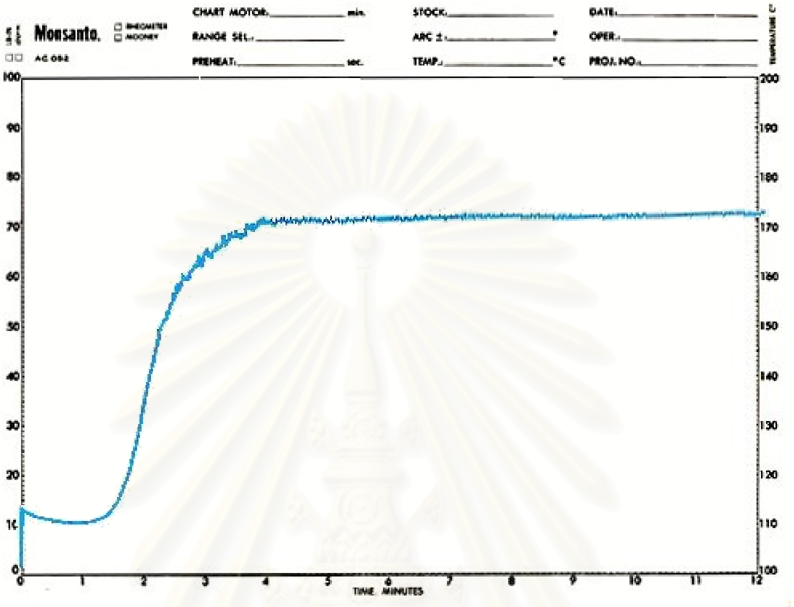


Figure E.9 Vulcanization curve of **compound D1**

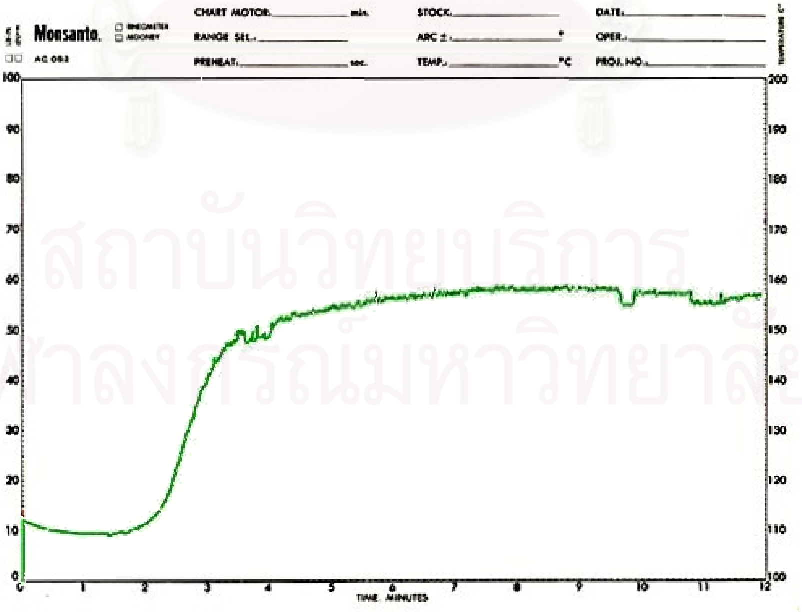


Figure E.10 Vulcanization curve of **compound E**

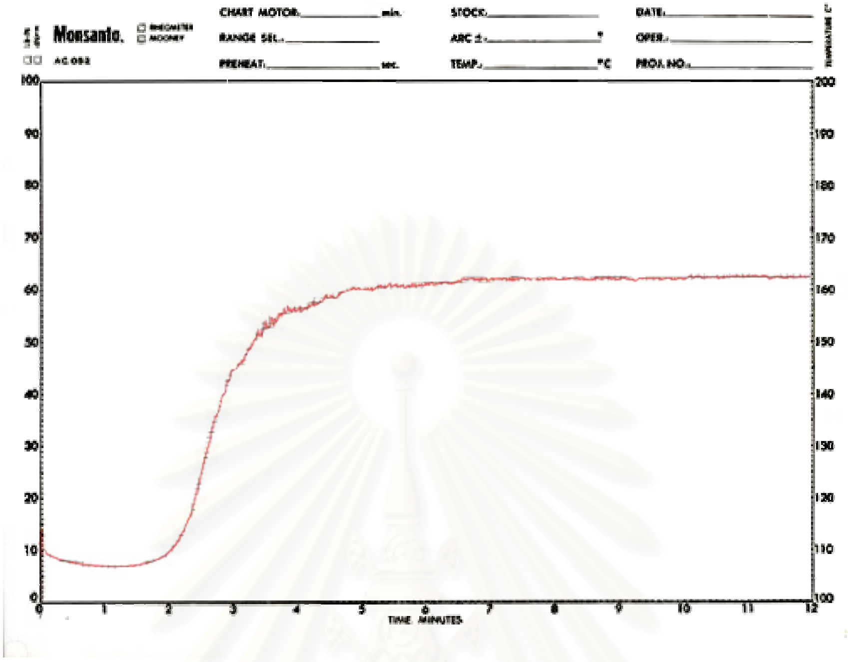


Figure E.11 Vulcanization curve of **compound E1**

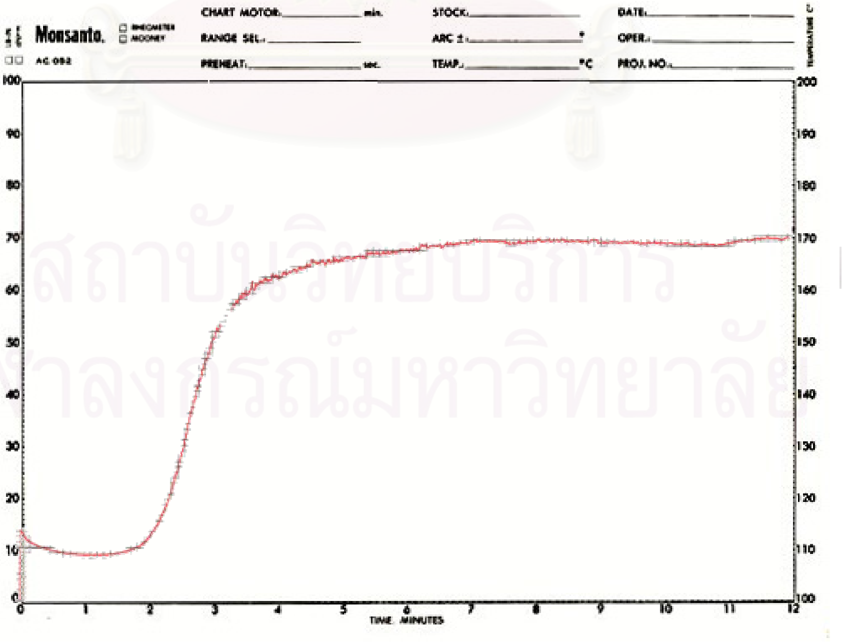


Figure E.12 Vulcanization curve of **compound E2**

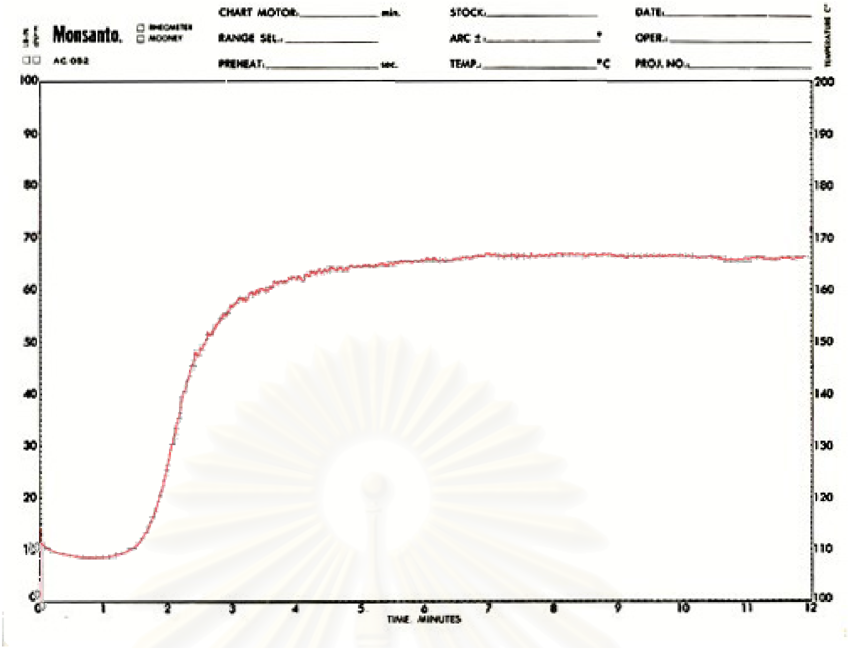


Figure E.13 Vulcanization curve of **compound E3**

APPENDIX F

Statistic of Mechanical Properties

The sampling distributions of mechanical properties data were calculated by standard deviation (SD)

$$SD = \frac{\Sigma (X_i - X_a)^2}{n-1}$$

When n is the number of sample

x_i is the sample

x_a is the sample mean

F.1 Mechanical Properties of Compounds A-E

Table F.1 Tensile strength of compounds A-E

Examples	Tensile strength (MPa)		Average
	1st Experiment	2nd Experiment	
A	27.5	34.7	
	29.6	31.7	
	29.3	31.9	
	31.9	33.9	
Mean	29.58	33.05	31.31
SD	1.56	1.28	

Table F.1 (continued)

Examples	Tensile strength (MPa)		Average
	1st Experiment	2nd Experiment	
B	**30.2** **28.4** **28.1** **29.9**	**31.3** **32.9** **31.1** **32.8**	
Mean	**29.18**	**32.03**	**30.60**
SD	**0.94**	**0.83**	
B1	**29.6** **30.7** **30.3** **30.7**	**33.9** **30.5** **31.5** **32.9**	
Mean	**30.33**	**32.2**	**31.26**
SD	**0.45**	**1.30**	
B2	**29.3** **29.2** **27.0** **31.1**	**30.6** **30.0** **27.1** **29.5**	
Mean	**29.15**	**29.3**	**29.23**
SD	**1.45**	**1.33**	

Table F.1 (continued)

Examples	Tensile strength (MPa)		Average
	1st Experiment	2nd Experiment	
B3	**29.7** **29.7** **27.8** **26.8**	**30.6** **29.4** **29.1** **27.8**	
Mean	**28.5**	**29.23**	**28.86**
SD	**1.25**	**1.00**	
C	**26.9** **27.6** **28.2** **28.5**	**27.7** **30.3** **29.5** **31.3**	
Mean	**27.8**	**29.7**	**28.75**
SD	**0.61**	**13.2**	
C1	**18.2** **17.7** **17.9** **18.3**	**31.0** **30.1** **30.0** **29.8**	
Mean	**18.03**	**30.23**	**28.76**
SD	**0.24**	**0.46**	

Table F.1 (continued)

Examples	Tensile strength (MPa)		Average
	1st Experiment	2nd Experiment	
D	13.2	22.4	
	13.4	24.2	
	13.1	22.0	
	13.8	24.3	
Mean	13.38	23.23	20.04
SD	0.27	1.04	
D1	15.5	26.0	
	14.2	25.0	
	14.7	26.4	
	14.5	27.5	
Mean	14.73	26.23	24.83
SD	0.48	0.90	
E	11.4	13.1	
	12.0	18.9	
	10.7	16.2	
	11.3	17.7	
Mean	11.35	16.48	21.38
SD	0.46	2.17	

Table F.1 (continued)

Examples	Tensile strength (MPa)		Average
	1st Experiment	2nd Experiment	
E1	19.8 17.3 18.6 19.0	17.6 19.8 18.1 19.6	
Mean	18.68	18.78	18.73
SD	0.90	0.94	
E2	21.0 20.1 19.6 19.3	17.6 19.8 18.1 19.6	
Mean	20.0	18.78	20.08
SD	0.64	0.94	
E3	23.9 20.5 22.3 23.0	20.7 19.8 20.9 19.2	
Mean	22.43	20.15	22.57
SD	1.25	0.69	

Table F.2 Modulus 500% of compounds A-E

Examples	Modulus 500% (MPa)		Average
	1st Experiment	2nd Experiment	
A	25.4 24.7 23.6 24.3	25.2 23.2 24.3 24.6	
Mean	24.5	24.33	24.41
SD	0.65	0.73	
B	23.2 23.4 22.4 22.6	23.2 23.0 23.1 22.2	
Mean	22.9	22.88	22.89
SD	0.41	0.40	
B1	22.3 22.1 21.4 22.3	22.0 22.2 21.7 21.0	
Mean	22.03	21.73	21.88
SD	0.37	0.45	

Table F.2 (Continued)

Examples	Modulus 500% (MPa)		Average
	1st Experiment	2nd Experiment	
B2	21.5	20.3	
	20.7	20.2	
	20.4	20.2	
	20.5	19.3	
Mean	20.78	20.0	20.39
SD	0.43	0.41	
B3	19.2	18.5	
	19.8	19.4	
	19.0	18.6	
	19.1	19.0	
Mean	19.28	18.88	19.08
SD	0.31	0.36	
C	19.0	19.2	
	18.5	18.3	
	18.4	18.0	
	18.9	18.1	
Mean	18.7	18.4	18.55
SD	0.26	0.47	

Table F.2 (continued)

Examples	Modulus 500% (MPa)		Average
	1st Experiment	2nd Experiment	
C1	18.2	18.1	
	17.7	17.9	
	17.9	17.5	
	18.3	17.8	
Mean	18.03	17.83	17.93
SD	0.24	0.22	
D	13.2	13.1	
	13.4	13.2	
	13.1	13.2	
	13.8	13.9	
Mean	13.38	13.35	13.36
SD	0.27	0.32	
D1	15.5	14.4	
	14.2	14.2	
	14.7	15.7	
	14.5	14.5	
Mean	14.73	14.7	14.71
SD	0.48	0.58	

Table F.2 (continued)

Examples	Modulus 500% (MPa)		Average
	1st Experiment	2nd Experiment	
E	11.4	11.1	
	12.0	11.5	
	10.7	10.9	
	11.3	11.7	
Mean	11.35	11.3	11.33
SD	0.46	0.32	
E1	11.7	11.6	
	10.8	10.9	
	11.1	11.2	
	11.4	11.5	
Mean	11.25	11.30	11.28
SD	0.34	0.27	
E2	11.2	11.2	
	10.7	12.1	
	11.3	11.6	
	12.2	10.9	
Mean	11.35	11.45	11.40
SD	0.54	0.45	

Table F.2 (continued)

Examples	Modulus 500% (MPa)		Average
	1st Experiment	2nd Experiment	
E3	12.0 11.4 11.2 11.8	12.0 11.4 11.2 11.8	
Mean	11.6	11.6	11.63
SD	0.32	0.32	

Table F.3 Elongation of compounds A-E

Examples	Elongation (%)		Average
	1st Experiment	2nd Experiment	
A	523.7 548.1 563.6 556.9	609.31 601.27 590.12 607.96	
Mean	548.08	602.17	575.12
SD	15.1083	7.59	

Table F.3 (continued)

Examples	Elongation (%)		Average
	1st Experiment	2nd Experiment	
B	594.5 578.2 564.4 587.9	595.97 613.82 599.43 622.77	
Mean	581.25	608.00	594.62
SD	11.32	10.84	
B1	588.1 618.3 610.3 601.8	636.84 603.96 622.48 641.75	
Mean	604.63	626.26	615.44
SD	11.18	14.69	
B2	599.61 632.89 589.04 637.11	631.81 620.64 586.87 628.80	
Mean	614.66	617.03	615.80
SD	20.73	17.89	

Table F.3 (continued)

Examples	Elongation (%)		Average
	1st Experiment	2nd Experiment	
B3	**636.44**	**651.26**	
	634.62	**627.83**	
	612.84	**640.78**	
	601.62	**611.46**	
Mean	**621.38**	**632.83**	**627.10**
SD	**14.71**	**14.87**	
C	**599.1**	**616.19**	
	624.5	**657.17**	
	620.5	**655.49**	
	603.9	**672.30**	
Mean	**612.0**	**650.29**	**631.14**
SD	**10.73**	**20.75**	
C1	**629.5**	**669.80**	
	639.7	**662.30**	
	625.0	**663.64**	
	637.7	**656.11**	
Mean	**632.98**	**662.96**	**647.97**
SD	**5.9839**	**4.86**	

Table F.3 (continued)

Examples	Elongation (%)		Average
	1st Experiment	2nd Experiment	
D	**655.2** **642.3** **628.0** **648.9**	**658.72** **688.77** **646.12** **670.76**	
Mean	**643.60**	**666.09**	**654.85**
SD	**10.10**	**15.73**	
D1	**641.8** **648.6** **674.1** **652.3**	**672.93** **665.49** **651.40** **685.92**	
Mean	**654.20**	**668.94**	**661.57**
SD	**12.08**	**12.49**	
E	**620.8** **591.1** **591.5** **601.5**	**543.78** **643.90** **610.66** **619.35**	
Mean	**601.23**	**604.42**	**602.82**
SD	**12.05**	**37.07**	

Table F.3 (continued)

Examples	Elongation (%)		Average
	1st Experiment	2nd Experiment	
E1	649.52	631.82	
	628.99	646.33	
	634.34	641.47	
	641.98	637.97	
Mean	638.71	639.40	639.10
SD	7.76	5.29	
E2	671.75	648.52	
	665.90	664.38	
	648.36	630.47	
	626.57	672.59	
Mean	653.15	653.99	653.60
SD	17.59	16.10	
E3	699.48	685.17	
	655.54	699.22	
	683.62	674.84	
	679.96	668.19	
Mean	679.65	680.75	680.20
SD	15.74	13.34	

Table F.4 Hardness (Shore-D) of compounds A-E

Examples	Hardness (Shore-D)		Average
	1st Experiment	2nd Experiment	
A	56	56	56
B	54	54	54
B1	56	57	56.5
B2	56	57	56.5
B3	57	58	57.5
C	52	53	52.5
C1	55	55	55
D	46	45	45.5
D1	51	52	51.5
E	46	47	46.5
E1	49	50	49.5
E2	51	50	50.5
E3	52	52	52

APPENDIX G

The accelerated aging test was investigated for studying the reversion of rubber compounds. The percentage of change in properties or % reversion was calculated as following :

$$\%\text{reversion} = \frac{X_a - X_o}{X_o} \times 100$$

$$= X_a - X_o \qquad \text{(for hardness)}$$

Where

X_o **is the value of the property before aging**

X_a **is the value of the hardness after aging**

G.1 Reversion of aged rubber compounds

G.1.1 Aging for 1 day

Table G.1 % reversion of tensile strength for 1 day aging of rubber compounds

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Tensile strength (MPa)	% reversion	Tensile strength (MPa)	% reversion	
A	19.4 22.4 19.9 23.0		24.8 22.7 21.4 21.7		
Mean	**21.18**	**-28.40**	**22.6500**	**-31.47**	**-29.93**
SD	**1.79**		**1.33**		
B	27.4 27.2 27.1 26.9		24.8 22.7 21.4 21.7		
Mean	**27.15**	**-10.37**	**22.6500**	**-15.53**	**-12.95**
SD	**0.21**		**1.3314**		
B1	26.7 27.5 27.2 28.0		28.1 25.7 27.2 27.2		
Mean	**27.35**	**-9.81**	**27.0500**	**-13.04**	**-11.43**
SD	**0.54**		**0.86**		

Table G.1 (continued)

Examples	1st Experiment		2nd Experiment		Average
	Tensile strength (MPa)	% reversion	Tensile strength (MPa)	% reversion	of % reversion
B2	26.9 26.8 22 26.8		27.0 29.5 26.5 28.2		
Mean	**25.63**	**-8.66**	**27.80**	**-5.119**	**-6.89**
SD	**2.09**		**1.16**		
B3	26.3 28.0 27.1 26.1		26 26.9 27.9 27.2		
Mean	**26.88**	**-5.70**	**27.00**	**-7.613**	**-6.66**
SD	**0.75**		**10.35**		
C	28.2 27.8 27.4 27.0		30.2 29.8 29.2 29.2		
Mean	**27.60**	**-0.72**	**29.6**	**-0.34**	**-0.53**
SD	**0.52**		**0.42**		

Table G.1 (continued)

Examples	**1st Experiment**		**2nd Experiment**		**Average of % reversion**
	Tensile strength (MPa)	**% reversion**	**Tensile strength (MPa)**	**% reversion**	
C1	29.1		29.7		
	28.3		30		
	28.1		30.2		
	27.2		29		
Mean	**28.18**	**3.21**	**29.7250**	**-1.65**	**0.78**
SD	**0.78**		**0.4548**		
D	24.7		27		
	23.6		24.6		
	24.0		24.8		
	22.9		27.1		
Mean	**23.80**	**14.15**	**25.8750**	**11.41**	**12.78**
SD	**0.75**		**1.1777**		
D1	27.8		28.3		
	27.1		27.2		
	27.3		27.7		
	26.6		27.5		
Mean	**27.20**	**16.12**	**27.6750**	**5.53**	**10.82**
SD	**0.50**		**0.4023**		

Table G.1 (continued)

Examples	**1st Experiment**		**2nd Experiment**		**Average**
	Tensile strength (MPa)	**% reversion**	**Tensile strength (MPa)**	**% reversion**	**of % reversion**
E	24.7 25.2 24.9 25.4		23.4 23 25.2 19.6		
Mean	**25.05**	**53.92**	**22.8000**	**38.39**	**46.15**
SD	**0.31**		**2.0248**		
E1	24 22.6 21 22.2		24.1 22.8 22.3 21.1		
Mean	**22.4500**	**20.21**	**22.5750**	**20.240**	**20.23**
SD	**1.0712**		**1.0756**		
E2	25.3 23.2 25.5 23.5		24.8 23.7 25.4 22.9		
Mean	**24.3750**	**21.88**	**24.2000**	**20.099**	**20.99**
SD	**1.0329**		**0.9670**		

Table G.1 (continued)

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Tensile strength (MPa)	% reversion	Tensile strength (MPa)	% reversion	
E3	27.5 22.9 23.2 24.7		26.5 23.1 24.1 22.2		
Mean	**24.5750**	**8.26**	**23.9750**	**6.912**	**7.59**
SD	**1.8212**		**1.6053**		

Table G.2 % reversion of modulus 500% for 1 day aging of rubber compounds

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Modulus 500% (MPa)	% reversion	Modulus 500% (MPa)	% reversion	
B3	25.8 27.6 26.5 25.1		24.1 24.9 25.5 25.9		
Mean	26.2500	36.19	25.1000	32.980	34.58
SD	0.9233		9.8238		

Table G.2 (continued)

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Modulus 500% (MPa)	% reversion	Modulus 500% (MPa)	% reversion	
C	25.6		28.3		
	24.9		27.4		
	26.8		24.2		
	25.5		26.6		
Mean	**25.70**	**37.43**	**26.625**	**44.70**	**41.07**
SD	**0.69**		**1.52377**		
C1	25.2		25.9		
	25.8		26.9		
	26.4		26.5		
	26.1		26.7		
Mean	**25.88**	**43.55**	**26.5000**	**48.67**	**46.11**
SD	**0.51**		**0.3742**		
D	18.7		18.2		
	18.9		19.3		
	19.4		19.3		
	19.3		19.7		
Mean	**19.08**	**42.62**	**19.1250**	**43.26**	**42.94**
SD	**0.33**		**0.5585**		

Table G.2 (continued)

Examples	1st Experiment		2nd Experiment		Average
	Modulus 500% (MPa)	% reversion	Modulus 500% (MPa)	% reversion	of % reversion
D1	22.1 22.7 22.6 22.0		22 22 22.7 22.3		
Mean	**22.35**	**51.78**	**22.2500**	**51.36**	**51.57**
SD	**0.9233**		**9.8238**		
E	16.7 15.4 14.8 15.6		15 16.5 14.9 15.4		
Mean	**15.63**	**37.67**	**15.4500**	**36.73**	**37.20**
SD	**0.79**		**0.6344**		
E1	15.6 15.2 16.0 16.3		16.0 15.6 15.3 16.3		
Mean	**15.7750**	**40**.22	15.8000	39.823	40.02
SD	0.4146		0.3808		

Table G.2 (continued)

Examples	**1st Experiment**		**2nd Experiment**		**Average of % reversion**
	Modulus 500% (MPa)	**% reversion**	**Modulus 500% (MPa)**	**% reversion**	
E2	16 16.2 16.9 16.4		15.9 16.7 15.2 16.6		
Mean	**16.3750**	**44.27**	**16.1000**	**40.61**	**42.44**
SD	**0.3345**		**0.6042**		
E3	16.4 16.6 16.8 16.6		16.7 16.4 16.8 16.1		
Mean	**16.6000**	**42.49**	**16.5000**	**42.24**	**42.37**
SD	**0.1414**		**0.2739**		

Example A, B, B1 and B2 cannot determine

Table G.3 % reversion of elongation for 1 day aging of rubber compounds

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Elongation at break (%)	% reversion	Elongation at break (%)	% reversion	
A	360.4 391.5 379.6 410.4		438.32 411.12 393.45 398.24		
Mean	**385.48**	**-29.67**	**410.2825**	**-31.87**	**-30.77**
SD	**20.98**		**17.4296**		
B	486.9 483.4 480.1 476.5		478.31 41.03 477.23 481.99		
Mean	**481.73**	**-34.33**	**369.6400**	**-39.20**	**-36.77**
SD	**4.45**		**189.7313**		
B1	494.4 490.3 486.6 482.7		499.28 491.84 470.97 508.07		
Mean	**488.50**	**-19.21**	**492.5400**	**-21.35**	**-20.28**
SD	**5.01**		**13.7146**		

Table G.3 % reversion of elongation for 1 day aging of rubber compounds

Examples	1^{st} Experiment		2^{nd} Experiment		Average of % reversion
	Elongation at break (%)	% reversion	Elongation at break (%)	% reversion	
B2	498.87		518.21		
	503.95		534.1		
	435.61		507.54		
	486.19		510.57		
Mean	**481.1550**	**-21.72**	**517.6050**	**-16.11**	**-18.92**
SD	**27.0792**		**10.2865**		
B3	502.8		502.21		
	508.24		520.66		
	507.94		534.9		
	502.27		525.17		
Mean	**505.3125**	**-18.68**	**520.7350**	**-17.71**	**-18.20**
SD	**2.7858**		**204.4552**		
C	551.7		527.26		
	540.5		530.49		
	528.1		569.03		
	517		539.23		
Mean	**534.33**	**-17.55**	**541.5025**	**-16.73**	**-17.14**
SD	**15.04**		**16.48523184**		

Table G.3 (continued)

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Elongation at break (%)	% reversion	Elongation at break (%)	% reversion	
C1	541.0 528.2 536.8 524.2		546.64 542.13 550.29 534.32		
Mean	**532.55**	**-15.87**	**543.3450**	**-16.53**	**-16.20**
SD	**7.71**		**5.9585**		
D	610.6 598.6 602.3 590.9		623.82 571.55 581.1 598.58		
Mean	**600.60**	**-6.68**	**593.7625**	**-10.86**	**-8.77**
SD	**8.18**		**19.8771**		
D1	621.2 609.4 619.6 607.4		587.54 566.83 565.26 570.74		
Mean	**614.40**	**-6.08**	**572.5925**	**-6.93**	**-6.51**
SD	**7.01**		**8.8576**		

Table G.3 (continued)

Examples	1st Experiment		2nd Experiment		Average
	Elongation at break (%)	% reversion	Elongation at break (%)	% reversion	of % reversion
E	535.2 545.7 539.9 550.3		627.23 603.47 664.48 574.26		
Mean	**542.78**	**-9.72**	**617.3600**	**-2.14**	**-3.79**
SD	**6.60**		**33.0464**		
E1	636.81 624.03 585.59 601.42		625.07 637.14 599.78 607.41		
Mean	**611.9625**	**-4.19**	**617.3500**	**-3.448**	**-3.82**
SD	**19.8096**		**14.6522**		
E2	649.75 610.76 624.46 617.53		641.56 622.58 621.1 639.82		
Mean	**625.6250**	**-4.21**	**631.2650**	**-3.475**	**-3.84**
SD	**14.7468**		**9.4595**		

Table G.3 (continued)

Examples	1st Experiment		2nd Experiment		Average
	Elongation at break (%)	% reversion	Elongation at break (%)	% reversion	
E3	671.1 598.17 603.89 627.02		669.72 603.12 608.93 636.54		
Mean	**625.0450**	**-8.03**	**629.5775**	**-7.52**	**-7.78**
SD	**28.7000**		**26.3923**		

Table G.4 % reversion of hardness for 1 day aging

Examples	**1st Experiment**		**2nd Experiment**		**Average**
	Hardness (Shore-D)	**% reversion**	**Hardness (Shore-D)**	**% reversion**	
A	61	**5**	61	**5**	**5**
B	60	**4**	59	**4**	**5.5**
B1	61	**5**	61	**4**	**4.5**
B2	61	**5**	61	**4**	**4.5**
B3	63	**6**	62	**4**	**5**
C	55	**3**	54	**1**	**2**
C1	60	**5**	59	**4**	**4.5**
D	49	**3**	50	**5**	**4**
D1	54	**3**	55	**3**	**3**
E	52	**6**	53	**6**	**6**
E1	54	**5**	55	**5**	**5**
E2	55	**4**	56	**6**	**5**
E3	56	**4**	56	**4**	**4**

G.1.2 Aging for 3 days

Table G.5 % reversion of tensile strength for 3 days aging of rubber compounds

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Tensile strength (MPa)	% reversion	Tensile strength (MPa)	% reversion	
A	8.1 9.7 8.5 10.2		18.2 17.4 18.6 17.7		
Mean	**9.13**	**-69.15**	**17.975**	**-60.74**	**-64.94**
SD	**0.99**		**0.5315**		
B	17.8 18.5 18.7 19.5		15.5 13.4 16.4 21.8		
Mean	**18.63**	**-39.59**	**16.775**	**-47.62**	**-43.60**
SD	**0.70**		**3.5781**		
B1	18.3 18.7 19.1 19.5		20.4 21 19.4 20.3		
Mean	**18.90**	**-37.68**	**20.275**	**-37.03**	**-37.35**
SD	**0.52**		**0.6602**		

Table G.5 (continued)

Examples	**1st Experiment**		**2nd Experiment**		**Average of % reversion**
	Tensile strength (Mpa)	**% reversion**	**Tensile strength (MPa)**	**% reversion**	
B2	19.8		18.9		
	17.9		21.1		
	18.4		14.3		
	14.8		20.3		
Mean	**17.7250**	**-39.19**	**18.6500**	**-36.35**	**-37.77**
SD	**1.8267**		**2.6320**		
B3	14.9		20.6		
	19.7		18.5		
	19.7		20.2		
	18.3		17.8		
Mean	**18.1500**	**-36.32**	**19.2750**	**-34.05**	**-35.18**
SD	**1.9615**		**1.1605**		
C	20.0		24.1		
	20.2		24.6		
	19.8		23.4		
	20.0		24.2		
Mean	**20.00**	**-28.06**	**24.075**	**-25.67**	**-26.87**
SD	**0.16**		**0.4992**		

Table G.5 (continued)

Examples	**1st Experiment**		**2nd Experiment**		**Average of % reversion**
	Tensile strength (MPa)	**% reversion**	**Tensile strength (MPa)**	**% reversion**	
C1	21.5		21.2		
	22.3		24.9		
	21.7		23.6		
	22.6		23.3		
Mean	**22.03**	**-19.32**	**23.25**	**-23.08**	**-21.20**
SD	**0.51**		**1.533**		
D	16.8		19		
	16.9		20.9		
	16.5		18.1		
	16.6		18.2		
Mean	**16.70**	**-19.90**	**19.05**	**-17.98**	**-18.94**
SD	**0.18**		**1.2974**		
D1	20.6		25.1		
	22.0		24.8		
	21.1		25.1		
	22.2		24.4		
Mean	**21.48**	**-8.32**	**24.85**	**-5.24**	**-6.78**
SD	**0.75**		**0.3317**		

Table G.5 (continued)

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Tensile strength (MPa)	% reversion	Tensile strength (MPa)	% reversion	
E	19.1 19.3 19.4 19.7		20.2 20.4 19.6 21.2		
Mean	**19.38**	**19.05**	**20.35**	**23.52**	**21.28**
SD	**0.25**		**0.6608**		
E1	21 21.4 20.2 19.3		19.4 20.8 21.1 20.5		
Mean	**20.4750**	**9.64**	**20.4333**	**8.83**	**9.24**
SD	**0.8043**		**0.7409**		
E2	22.1 23 22.1 24.3		24.1 23.1 22.5 22.6		
Mean	**22.8750**	**14.38**	**23.0750**	**14.52**	**14.45**
SD	**0.9010**		**0.6339**		

Table G.5 (continued)

Examples	1st Experiment		2nd Experiment		Average
	Tensile strength (MPa)	% reversion	Tensile strength (MPa)	% reversion	of % reversion
E3	22.7 21.6 23.3 23.9		23.4 22.8 22.1 23.7		
Mean	**22.8750**	**0.77**	**23.0000**	**2.56**	**1.67**
SD	**0.8496**		**0.6124**		

Table F.6 % reversion of modulus 500% for 3 days aging of rubber compounds

Examples	1st Experiment		2nd Experiment		Average
	Modulus 500% (MPa)	% reversion	Modulus 500% (MPa)	% reversion	of % reversion
D	15.4 15.2 14.5 14.8		18.7 18.9 - 17.4		
Mean	**14.98**	**11.96**	**18.33**	**37.32**	**24.65**
SD	**0.40**		**0.81**		

Table G.6 (continued)

Examples	**1st Experiment**		**2nd Experiment**		**Average**
	Modulus 500% (MPa)	**% reversion**	**Modulus 500% (MPa)**	**% reversion**	**of % reversion**
D1	20.1		23.1		
	19.7		22.8		
	20.3		23.1		
	19.4		23.3		
Mean	**19.88**	**34.97**	**23.08**	**56.97**	**45.97**
SD	**0.40**		**0.21**		
E	17.1		18.0		
	17.5		16.9		
	18.0		17.7		
	17.2		17.2		
Mean	17.45	50.22	17.45	54.42	52.32
SD	0.40		0.49		
E1	17.8		17.6		
	16.4		17.3		
	17.7		16.8		
	17.2		17.2		
Mean	17.28	53.56	17.2250	52.43	52.99
SD	0.5540		0.2861		

Table G.6 (continued)

Examples	**1st Experiment**		**2nd Experiment**		**Average**
	Modulus 500% (MPa)	**% reversion**	**Modulus 500% (MPa)**	**% reversion**	**of % reversion**
E2	17.6 18.1 17.9 18.5		18.2 17.5 17.9 18.6		
Mean	**18.03**	**58.81**	**18.0500**	**57.64**	**58.23**
SD	**0.3269**		**0.4031**		
E3	18.6 18.4 18.7 18.4		18.5 18.6 18.4 18.7		
Mean	**18.5250**	**59.01**	**18.5500**	**59.91**	**59.46**
SD	**0.1299**		**0.1118**		

Example A, B, B1, B2, B3, C, C1 cannot determine

Table G.7 % reversion of elongation for 3 days aging of rubber compounds

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Elongation (%)	% reversion	Elongation (%)	% reversion	
A	206.7 220.8 226.9 241.2		339.94 310.1 329.04 318.93		
Mean	**223.90**	**-59.15**	**324.5025**	**-51.96**	**-55.56**
SD	**14.30**		**12.87621**		
B	387.7 399.9 395.5 408.3		314.57 286.48 328.28 394.78		
Mean	**397.85**	**-41.02**	**331.0275**	**-45.55**	**-43.28**
SD	**8.601356482**		**45.92479**		
B1	392.4 398.2 412.8 419.5		385.36 379.75 369.6 371.47		
Mean	**405.73**	**-32.90**	**376.545**	**-36.68**	**-34.79**
SD	**12.57**		**7.347673**		

Table G.7 (continued)

Examples	**1^{st} Experiment**		**2^{nd} Experiment**		**Average**
	Elongation (%)	**% reversion**	**Elongation (%)**	**% reversion**	**of % reversion**
B2	403.75		387.74		
	367.12		420.46		
	370.63		317.87		
	312.37		410.14		
Mean	**363.4675**	**-40.87**	**384.0525**	**-37.73**	**-39.31**
SD	**32.7806**		**39.9993**		
B3	328.38		417.2		
	397.55		384.3		
	397.9		414.32		
	374.35		378.23		
Mean	**374.5450**	**-39.72**	**398.5125**	**-37.03**	**-38.38**
SD	**28.3105**		**17.4103**		
C	476.4		459.9		
	479		471.13		
	470.1		448.12		
	472.2		460.93		
Mean	**474.43**	**-22.48**	**460.02**	**-29.26**	**-25.87**
SD	**4.02**		**9.414255**		

Table G.7 (continued)

Examples	1st Experiment		2nd Experiment		Average of % reversion
	Elongation (%)	% reversion	Elongation (%)	% reversion	
C1	489.7		424.24		
	488.6		464.01		
	489.3		458.24		
	488.0		451.21		
Mean	**488.90**	**-22.76**	**449.425**	**-24.67**	**-23.71**
SD	**0.75**		**17.5869**		
D	563.3		507.55		
	560.9		534.85		
	552.7		490.6		
	550.7		505.31		
Mean	**556.90**	**-18.13**	**509.5775**	**-23.50**	**-20.81**
SD	**6.14**		**18.44963**		
D1	539.3		532.53		
	555.8		529.95		
	542.2		529.58		
	562.5		517.69		
Mean	**549.95**	**-15.94**	**527.4375**	**-21.15**	**-18.54**
SD	**11.03**		**6.629487**		

Table G.7 (continued)

Examples	1st Experiment		2nd Experiment		Average
	Elongation (%)	% reversion	Elongation (%)	% reversi0n	of % reversion
E	499.5 493.8 520.9 515.1		535.64 563.47 537.54 565.53		
Mean	**507.33**	**-15.62**	**550.545**	**-8.91**	**-12.27**
SD	**12.77**		**16.15441**		
E1	559.45 583.47 548.63 535.28		550.23 569.78 563.19 544.58		
Mean	**556.7075**	**-12.84**	**556.9450**	**-12.90**	**-12.87**
SD	**17.6645**		**10.0215**		
E2	574.53 581.31 571.03 592.25		584.28 574.58 590.12 578.69		
Mean	**579.7800**	**-11.23**	**581.9175**	**-11.02**	**-11.13**
SD	**8.0927**		**5.8549**		

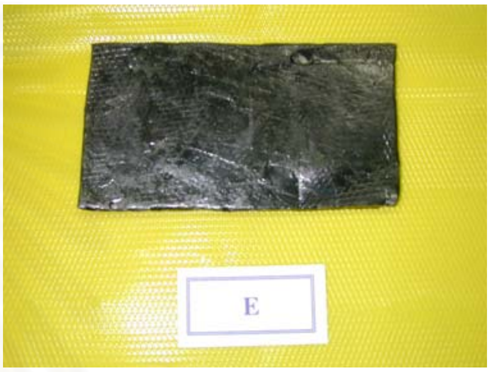
Table G.7 (continued)

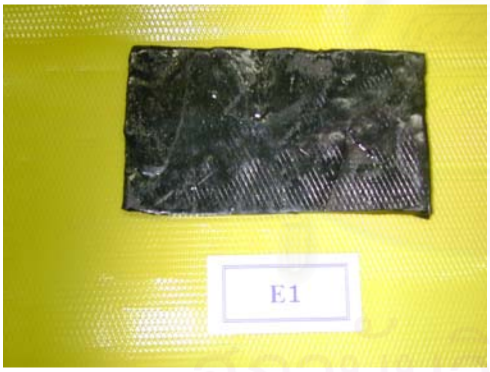
Examples	1st Experiment		2nd Experiment		Average
	Elongation (%)	% reversion	Elongation (%)	% reversi0n	of % reversion
E3	570.2		587.56		
	558.56		567.36		
	577.67		556.74		
	588.22		579.51		
Mean	**573.6625**	**-15.59**	**572.7925**	**-15.86**	**-15.73**
SD	**10.8173**		**11.7303**		

Table G.8 % reversion of hardness for 3 days aging

Examples	**1st Experiment**		**2nd Experiment**		**Average**
	Hardness (Shore-D)	**% reversion**	**Hardness (Shore-D)**	**% reversion**	
A	62	**-6**	61	**-5**	**-5.5**
B	60	**-6**	60	**-6**	**-6**
B1	62	**-6**	62	**-5**	**-5.5**
B2	63	**-7**	64	**-7**	**-7**
B3	65	**-8**	66	**-8**	**-8**
C	55	**-3**	55	**-2**	**-2.5**
C1	60	**-5**	59	**-4**	**-4.5**
D	50	**-4**	49	**-4**	**-4**
D1	57	**-6**	57	**-5**	**-5.5**
E	53	**-7**	54	**-7**	**-7**
E1	55	**-6**	56	**-6**	**-6**
E2	56	**-5**	55	**-5**	**-5**
E3	61	**-9**	61	**-9**	**-9**

APPENDIX H





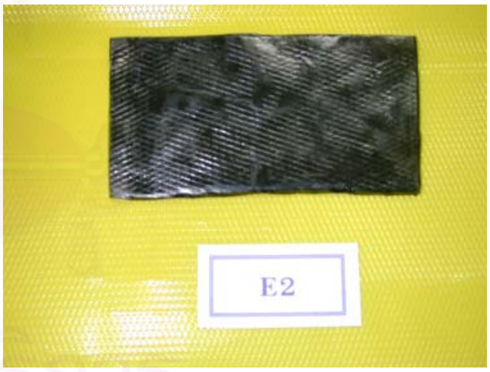


Figure H.1 Pictures of rubber compounds

VITA

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