กระบวนการรีไซเคิลเชิงกลร่วมเคมีของยางธรรมชาติวัลคาไนซ์

นายพิพัฒน์ ไทยเจริญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

MECHANO-CHEMICAL RECYCLING PROCESS OF VULCANIZED NATURAL RUBBER

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2008

Thesis Title	MECHANO-CHEMICAL RECYCLING PROCESS OF VULCANIZED NATURAL RUBBER
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อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ดร.ศิริลักษณ์ พุ่มประดับ, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร. พัชณิตา ธรรมยงค์กิจ, 63 หน้า

งานวิจัยนี้ศึกษากระบวนการดีวัลคาไนเซชันในยางธรรมชาติที่ผ่านการวัลคาไนซ์ด้วยวิธีเชิงกลร่วมเคมีในยางธรรมชาติวัลคาไนซ์ โดยใช้กรดไทโอซาลิไซลิกเป็นตัวดีวัลคาไนซิ่งเอเจนต์ เปรียบเทียบกับการใช้กรดไทโอซาลิไซลิก/นอมอลบิวทิลเอมีน หรือไดฟีนิลไดซัลไฟด์ซึ่งเป็นดีวัลคาไนซิ่งเอเจนต์ ภาวะที่เหมาะสมสำหรับกระบวนการดีวัลคาไนเซชั่นของยางธรรมชาติที่ผ่านกระบวนการวัลคาไนซ์ คือการนำยางคงรูปที่ได้ไปบดให้มีขนาดอนุภาคที่เล็ก และนำยางที่ได้มาผสมกับดีวัลคาไนซิ่งเอเจนต์ ที่ 140 องศาเซลเซียส เป็นเวลา 48 ชั่วโมง ความก้าวหน้าในกระบวนการดีวัลคาไนเซชั่นสามารถบ่งบอกได้จากค่าสัดส่วนโซล-เจลในยางดีวัลคาไนซ์ที่ได้ ยางรีวัลคาไนซ์ถูกผลิตขึ้นมาจากการนำยางธรรมชาติมาผสมกับยางดีวัลคาไนซ์ที่ได้ ในอัตราส่วน 95/5, 90/10, 85/15, 80/20, 60/40, 40/60 และ 20/80 ตามลำดับ หลังจากนั้นเติมสารคงรูปแล้วนำไปขึ้นรูปอีกครั้ง ค่าทนต่อแรงดึงของยางรีวัลคาไนซ์ที่ใช้ระบบการคงรูปแบบดั้งเดิมที่ปริมาณการผสมยางดีวัลคาไนซ์ 5-15 ส่วนในเนื้อยางร้อยส่วนจะลดลงร้อยละ 5-10 ในขณะที่ร้อยละของการยืดที่จุดขาดจะได้รับการปรับปรุงให้ดีขึ้นประมาณร้อยละ 5-10 เมื่อยางรีวัลคาไนซ์ถูกเตรียมโดยยางดีวัลคาไนซ์ที่มีการเติมกรดไทโอซาลิไซลิกเป็นดีวัลคาไนซิ่งเอเจนต์ 1 ส่วนในเนื้อยางร้อยส่วน ผลที่ได้จากการศึกษานี้แสดงให้เห็นว่าสมบัติเชิงกลในยางรีวัลคาไนซ์สามารถกลับคืนมาได้มากกว่าร้อยละ 90 เมื่อเทียบกับยางธรรมชาติคงรูป

สาขาวิชา....ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.....ลายมือชื่อนิสิต.......พิพัฒน์ ไทยเจริญ.......
ปีการศึกษา....................2551............ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก..........
ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม........................

497 24179 23: MAJOR MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: DEVULCANIZATION / DEVULCANIZED RUBBER / DEVULCANIZING AGENT /MECHANO-CHEMICAL DEVULCANIZATION / VULCANIZATION

PIPAT THAICHAROEN: MECHANO-CHEMICAL RECYCLING PROCESS OF VULCANIZED NATURAL RUBBER. ADVISOR : SIRILUX POOMPRADUB, Ph.D., THESIS COADVISOR : Asst.Prof. PATCHANITA THAMYONGKIT, Dr.rer.nat., 63 pp.
ISBN:

Mechano-chemical devulcanization process for vulcanized natural rubber (NR) was investigated in this study. A novel devulcanizing agent used in this study was thiosalicylic acid. Thiosalicylic acid/*n*-butylamine and diphenyl disulfide were used as the references. Optimum condition for devulcanization of NR vulcanizate was found to be grinding of the rubber vulcanizate and subsequent mixing with a selected devulcanizing agent at 140 °C for 48 h. Degree of devulcanization was indicated by using sol-gel fractions of devulcanized rubber. Revulcanized rubber was made by using virgin rubber blend with devulcanized rubber at various ratios: 95/5, 90/10, 85/15, 80/20, 60/40, 40/60 and 20/80, and the mixture were further revulcanized. Tensile strength of the conventional revulcanized rubber (5-15 phr) was decreased by 5–10%, while an elongation at brakes was improved by 5–10% when the revulcanized rubber was prepared by the devulcanized rubber in the presence of 1 phr thiosalicylic acid. These results showed that mechanical properties of the revulcanized rubber were recovered more than 90% compared with the vulcanized rubber.

Field of study:.Petrochemistry and Polymer Science..Student's Signature....Pipat T............
Academic year ....2008.......................Advisor's Signature..............P..
Co-Advisor's Signature...Patchanit T.

ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude to many people without whom this work could have never been accomplished. First of all, the author would like to thank his advisor and co advisor, Dr. Sirilux Poompradub and Assistant Professor Dr. Patchanita Thamyongkit for their discerning suggestion encouragement, sacrifice, and forbearance through his course of study for the past years. Thanks are also extended to Professor. Dr. Pattarapan Prasassarakich, Assistant Professor Dr. Warunee Ariyawiriyanan and Assistant Professor Dr. Varawut Tangpasuthadol for being members of the thesis committee and for their worthy comments and suggestions.

The author gratefully acknowledge the funding support from Program of Petrochemistry and Polymer Science, National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, (NCE-PPAM), and CU Graduate School Thesis Grant, Chulalongkorn University.

Finally, the author would like to express deep gratitude to his family for their understanding and encouragement. Also, special thanks are expanded to his friends for friendship and cheerful moral support. Without them, he would not have withstood many difficulties.

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LIST OF ABBREVIATIONS

ASTM : American society for testing and materials
°C : Degree celsius
min : minute
h : Hour
mm : Millimeter
MPa : Megapascal
CBS : *n*-Cyclohexyl-2-benzothiazyl sulfenamide
TS : Thiosalicylic acid
DD : Diphenyl disulfide
BU : *n*-Butylamine
PO : Process oil
N : Newton
CV : Conventional vulcanization
Semi EV : Semi-efficient vulcanization
EV : Efficient vulcanization
NR : Natural rubber
NV : Natural rubber vulcanizate
DR : Devulcanized rubber
phr : Part by weight per hundred part of rubber
SEM : Scanning electron microscopy
TGA : Thermal gravimetric analysis
ZnO : Active zinc oxide

CHAPTER I

INTRODUCTION

1.1 Statement of Problems

Process of vulcanization by sulfur enables us to manufacture tires for automobiles and aircrafts, which are indispensable for our modern society. Chemically combined sulfur bridges between rubber molecules from this process construct an elastic three-dimensional network structure. However, the sulfur bridges can not be naturally removed or decomposed. Attempts to reverse the change in the three-dimensional structure have been proved difficult, expensive and energy-consuming. Currently, the amount of used rubber waste is drastically increased, leading to global environmental problems. The devulcanization is the process of the intermolecular bonds cleavage of, such as, carbon-sulfur and/or sulfur-sulfur bonds. The polymer chain length of the resulting devulcanized rubber product was generally found to be shorter compared to that of the originals resulting in poorer rubber properties [1]. In general, the devulcanization of the used rubber products is carried out through physical, chemical, or biotechnological processes. In the physical process, rubber products are devulcanized with the help of external energy, for examples, mechanical devulcanization process [2], cryomechanical devulcanization process [3,4], microwave method [5,6], or ultrasonic energy [7-11]. However, these processes were a random scission of crosslinks and main chain which were responsible for crosslinking during revulcanization.

Several chemical reclaiming agents are used for the manufacture of devulcanized rubber for the chemical process. Typical examples include organic disulfides or mercaptans. Apart from these, the use of inorganic compounds has also been reported [12]. Initially, the rubber to be treated is subject to be swollen in common organic solvents, e.g., toluene, benzene, and cyclohexane. However, such solvents are difficult to remove after the reaction. Recently, Kojima et al. reported the effectiveness of supercritical CO_2 as a swelling solvent for the chemical reclaiming process of unfilled and carbon black-filled polyisoprene rubber vulcanizates [13-16]. Residual CO_2 in the rubber matrix is easily and rapidly removed by releasing pressure. Moreover, applications of supercritical *n*-butanol and toluene have been reported for the decomposition of used rubber into fuel oil [17]. However, a major drawback of the chemical devulcanization process is its high cost.

In the biotechnological process, biodegradation of the rubber powder was performed by oxidation-reduction reaction driven by different species of *Thiobacillus Acidithiobacillus* and *Nacardia* [18-22]. However, the efficiency and rate of devulcanization was found to be a function of particle size because this process was exclusively or primarily limited to the surface layers of the elastomers [18].

The mechano-chemical process, which consist the use of the rubber sample followed by the addition of the devulcanizing agent, has been proven as a more efficient approach by many studies [23-25]. In this content, the mechano-chemical method starting from grinding of the natural rubber (NR) vulcanizate followed by treating the resulting rubber sample by thiosalicylic acid is studied. Structurally, the molecule of thiosalicylic acid combines the functionality of thiophenol and benzoic acid. Thiophenol is usually used as devulcanizing agent to break the sulfur crosslinked bond and benzoic acid is used as retarder for vulcanization in order to prevent the fast curing. Therefore, thiosalicylic acid is supposed to act as the bifunctional devulcanizing agent, which is prepared by mixing with virgin rubber and devulcanized rubber. Moreover, to our knowledge, the use of thiosalicylic acid has not yet been reported for a mechano-chemical devulcanizing process. The aim of this study is to investigate the efficiency of thiosalicylic acid for the mechano-chemical process. Effects of devulcanization time and the amount of thiosalicylic acid on the mechanical properties of the resulting rubber were studied in order to find the optimum condition for the devulcanization. The mechanical properties of revulcanized rubber were examined and compared with that obtained from the conventional process using well-known diphenyl disulfide as a devulcanizing agent. The devulcanization of truck tire by the developed mechano-chemical process was also demonstrated for the possible practical industrial use.

1.2 Objectives

1. To optimize devulcanization condition of vulcanized rubber.
2. To investigate mechanical properties of virgin rubber/devulcanized rubber blend (revulcanized rubber).

1.3 Scopes of Work

1. Reviews related previously published research.
2. Design and plan experimentals.
3. Prepare the formulation for rubber compounding with various three systems, including:
    - conventional vulcanization (CV)
    - semi-efficient vulcanization (Semi-EV)
    - efficient vulcanization (EV)
4. Study physical and mechanical properties of vulcanized rubber, including tensile strength, sol-gel fraction, cross links density and hardness.
5. Study the vulcanized rubber mixed with devulcanizing agent and process oil. After mixing, the rubber powder was processed in the following conditions:
    - oven temperature was varied in the range of 120-140^{o}C for 30 min
    - mixing time of rubber and devulcanizing agent at ambient temperature 0-48 hr
    - amount of devulcanizing agent was varied in the range of 0-2 phr
6. Study physical properties of devulcanized rubber in terms of sol-gel fraction and cross links density.
7. Study the physical and mechanical properties of NR blended with devulcanized rubber (revulcanized rubber) in terms of sol-gel fraction, cross links density, tensile strength, and hardness.
8. Study the morphology of revulcanized rubber by using Scanning Electron Microscope (SEM).
9. Study the thermal properties and dynamic mechanical analysis (DMA) of revulcanized rubber.
10. Compare the mechanical, morphology and themal properties of revulcanized rubber with NR vulcanizates.
11. Analyze data and summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber.

Natural rubber (NR) is a biological homopolymer of isoprene and has the general structure in Figure 2.1. Polyisoprene, especially when chemically modified by vulcanization, has the remarkable ability to substantially return to its original shape after being stretched considerably. To obtain NR, the Hevea brasiliensis tree is tapped for its sap. An off-white sap is collected and is coagulated by the addition of a strong acid. Hevea brasiliensis is a native of tropical rain forest of the Amazon basin in Brazil. Nowadays world's NR come from South-East Asia, mainly Thailand, Malaysia and Indonesia [26].

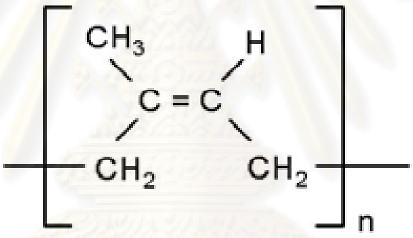


Figure 2.1 Structure of natural rubber (cis-1, 4-polyisoprene).

A picture of *Hevea brasiliensis* is shown in Figure 2.2. In the wild, the tree can reach a height of up to 44 m. It is a monoecious species belonging to the Euphorbiaceae family, which has 11 *Hevea* species presently known [27]. It is a very important species, because it is the principal source of commercial natural rubber. Latex is a high molecular weight polymer whose structure is cis-1,4-polysoprene, produced in a specialized system (latex vessels) present in all organs of the plant [28]. The white or yellow latex occurs in latex vessels in the bark, mostly outside the phloem. These vessels spiral up the tree in a right-handed spiral which forms an angle of about 30 degrees with the horizontal. Once the trees are 5-6 years old, the harvest can begin: incisions are made orthogonal to the latex vessels, just deep enough to tap the vessels without harming the tree's growth, and the sap is collected in small buckets. This process is known as rubber tapping. Older trees yield more latex, but they stop producing after 26-30 years [28].

Figure 2.2 Leaf and seed from the Hevea brasiliensis tree.

2.2 Vulcanization.

Vulcanization is a chemical process of crosslinking the chain-like rubber molecules to form an elastic three-dimensional network which prevents permanent deformation after removal of the deforming force. In order to develop the full potential of rubbers, they must be crosslinked. For rubbers containing unsaturated carbon-carbon bonds in the backbone, a variety of curing agents are available to choose with some common ones being sulfur [29-30], peroxides [31], and phenolic resin. Among them, sulfur is the most popular one employed in rubber vulcanization industry. In most cases, the cure reaction is achieved by a chemical reaction between the rubber and curing agent [32]. The first method of vulcanization was based on the discovery of Charles Goodyear in U.S. and Thomas Hancock in England [33]. It was found that addition of sulfur to rubber, followed by heating, led to an improvement in the properties. Vulcanization results in the increase of tensile strength, modulus (stiffness), hardness, and rebound, and the decrease of elongation, hysteresis (heat buildup), compression set and solubility. It also makes rubber impermeable to gases and resistant to heat, electricity and chemical action. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network as shown in Figure 2.3.

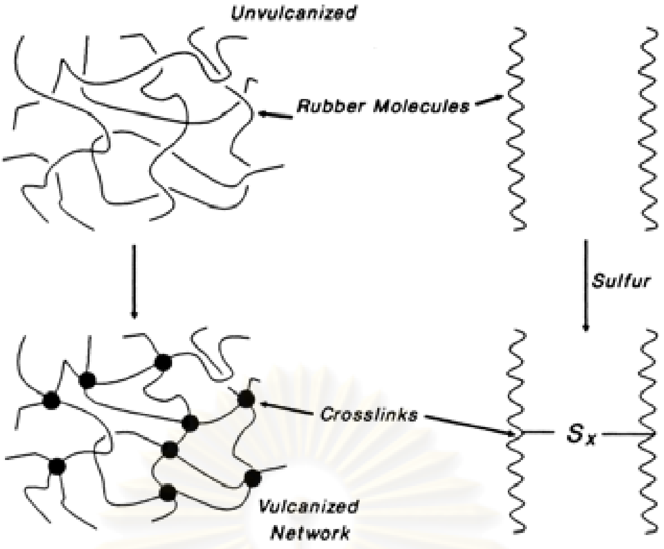


Figure 2.3 The formation of a crosslinked molecular network [34].

The improved frictional properties of rubber by vulcanization are highly desired for pneumatic tire application. Tensile and tear strength usually show a specific optimum crosslink density. Vulcanization-induced changes are proportional to the number of crosslinks and their length. Excessive crosslinking can convert the elastomer to a hard and brittle solid [34].

Vulcanization, thus, is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. A crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon to carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber, mixed with vulcanizing agents, in a mold under pressure [34].

2.2.1 Vulcanization Reagents for Sulfur Vulcanization.

Many reagents which are associated with the sulfur vulcanization of polydienes, e.g. NR, have been developed. These reagents are classified into vulcanization agents, accelerators, activators, retarders, and prevulcanization inhibitors. Vulcanization agents include elemental sulfur (insoluble sulfur, colloidal sulfur) or an organic sulfur donor such as tetramethylthiuram disulfide (TMTD) or 4,4'-dithiobismorpholine (DTDM). The most important classes of accelerators are those based on sulfenamides, benzothiazoles, guanadines, and dithiocarbamic acid. The classification of these accelerators, in terms of their chemical composition and speed of vulcanization, is shown in Table 2.1. Activators (sometimes called secondary accelerators) may be used to potentiate accelerators. Useful activators include metal oxides (usually zinc oxide), fatty acids, and nitrogen-containing bases. Retarders and prevulcanization inhibitors are added to obtain longer processing times by avoiding premature vulcanization (scorch). Retarders include acidic compounds (phthalic anhydride, salicylic and benzoic acids) and nitroso compounds (N-nitrosodiphenylamine). The most widely used prevulcanization inhibitor is N-cyclohexylthiophthalimide (CTP) [35].

Table 2.1 Accelerator type comparison [35].

Type	Scorch safety	Curing speed	Abbreviations Relative
None	-	Very slow	-
Sulfenamides	Long	Fast	CBS, MBS
Guanidines	Moderate	Moderate	DPG
Mercaptobenzothiazoles	Moderate	Moderate	MBT, MBTS, ZMBT
Thiurams	Short	Very fast	TMTD, TMTM
Dithiocarbamates	Lesat	Very fast	ZDBC

Rubber vulcanization by sulfur with no accelerators takes several hours and is no longer of commercial importance. With the use of accelerators, optimum curing can now be accomplished in periods as short as 2-5 min. Accelerated sulfur vulcanization is suitable for not only NR and its synthetic counterpart (IR), but also for other synthetic rubbers such as polybutadiene rubber (BR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber (IIR), and ethylene-propylene-diene rubber (EPDM). A typical basic recipe for accelerated sulfur vulcanization includes sulfur and/or a sulfur donor (0-4 phr), an accelerator or a mixture of accelerators, zinc oxide (2-10 phr), and stearic acid (1-4 phr) [35].

2.2.2 Cure System.

There are three generally recognized classifications for sulfur vulcanization: conventional, efficient (EV) cures, and semiefficient (semi-EV) cures. These differ primarily in the type of sulfur cross-links that form as shown in Figure 2.4, which in turn significantly influences the vulcanizate properties and crosslink bond energy in Table 2.2. The term efficient refers to the number of sulfur atoms per cross-link. The use of sulfur as a crosslinking agent by itself generates a considerable amount of main-chain structural modifications. Cyclic sulfide structures and cis-to-trans chain isomerization are detected in addition to polysulfidic crosslinks which are found attached to different carbons of the NR repeat unit. When the amount of accelerator is high proportional to the amount of sulfur used, the network structure appears to be simpler with less crosslinking, less main chain structural modification, and fewer cyclic sulfide structures. Polysulfidic crosslinks have been detected in addition to accelerator terminated polysulfides [36].

Table 2.2 Crosslink bond energy [36].

Linkage Type	Bond energy (kJ mole^{-1})
-C-C-	351
-C-S-C-	285
-C-S- S-C-	267
-C-S_x-C-	< 267

The major variables, in terms of type and level, are the sulfur donors and accelerators. Vulcanization systems are classified as conventional, semi-efficient (semi-EV), and efficient (EV), based on the level of sulfur and the ratio of accelerator to sulfur, as shown in Table 2.3. EV systems use low or even zero (with a sulfur donor) levels of sulfur and a relatively high level of accelerators. As illustrated in Table 2.4, the resultant vulcanizate efficiently utilizes sulfur to form networks in which the crosslinks are mainly monosulfidic, and which exhibit a low degree of main-chain modifications. The use of EV systems in NR reduces or eliminates reversion, except at very high curing temperatures. Thus, the resulting vulcanizate exhibits a high resistance to thermal and oxidative ageing [36].

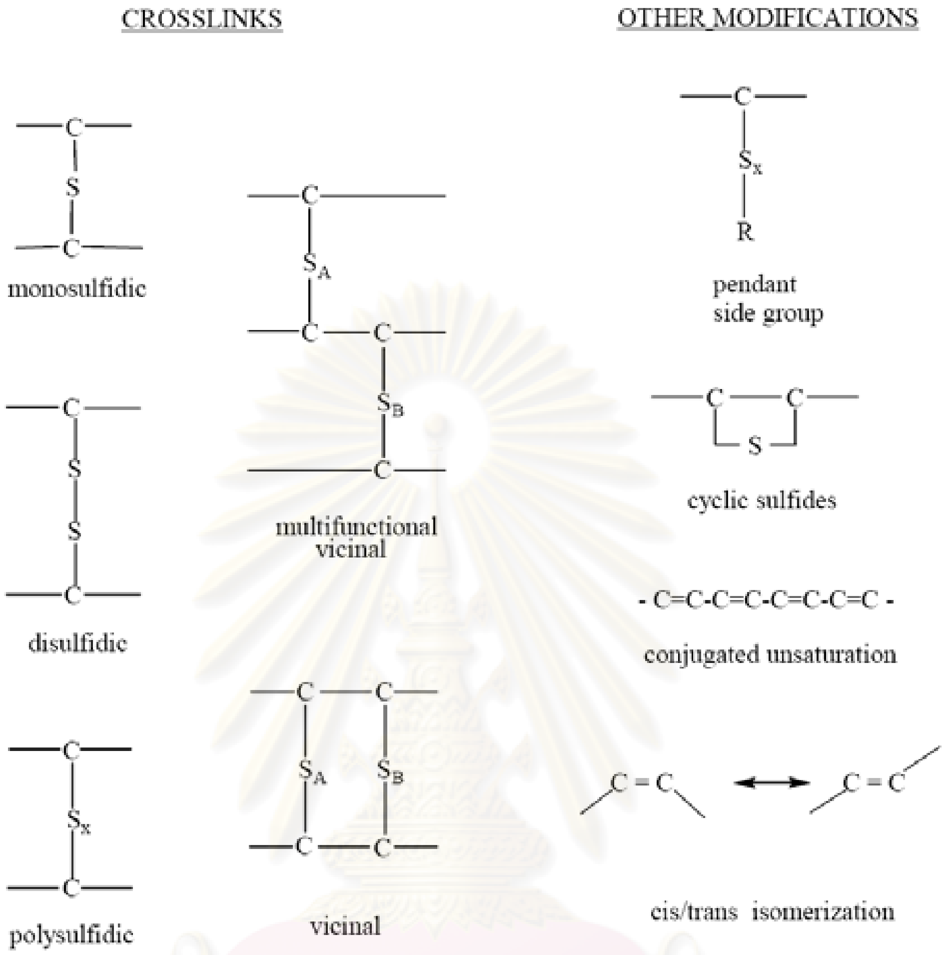


Figure 2.4 Sulfur-based cure system designs where conventional systems are polysulfidic, EV systems are mono- to disulfidic, and semi-EV is di- to polysulfidic [37].

Table 2.3 Compositions of conventional, semi-EV and EV vulcanization systems [38].

Type	Sulfur (S, phr)	Accelerator (A, phr)	A/S ratio
Conventional	2.0-3.5	1.2-0.4	0.1-0.6
Semi-EV	1.0-1.7	2.5-1.2	0.7-2.5
EV	0.4-0.8	5.0-2.0	2.5-12

Table 2.4 Vulcanizate structure and properties of three different sulfur-curing systems [38].

	Conventional	Semi-EV	EV
Poly- and disulfidic crosslinks (%)	95	50	20
Monosulfidic crosslinks (%)	5	50	80
Cyclic sulfide concentration	high	medium	low
Low-temperature crystallization resistance	high	medium	low
Heat-ageing resistance	low	medium	high
Reversion resistance	low	medium	high
Compression set, 22 h at 70°C	30	20	10

The reason for the greater loss in properties with conventional cure systems can be understood by examining cross-link bond strengths. Polysulfide bond strengths are significantly lower than are the bond strengths from the shorter cross-links obtained with EV cure systems. The relatively unstable S_x bonds break and rearrange to form mono- and disulfide linkages plus non-cross-linking cyclic and accelerator-terminated fragments. These reactions are observed as changes in properties with increased aging severity. However, conventional systems in NR do provide better flex life than EV cures, and this is one of the limitations of EV curing. The short monosulfide bonds are less able to rearrange to relieve localized stresses which can build during flexing, whereas the longer S_x bonds can rearrange. This ability for stress relief is thought to be one mechanism for the superior flex life of conventional cures. If NR compounds are subjected to thermal aging plus fatigue, the conventional systems perform no better than EV systems. The compromise obtained by using semi-EV systems involves the balance between heat aging and flex life [38].

2.2.3 Effects of Vulcanization on Vulcanization Properties.

Vulcanization causes profound changes at the molecular level. The long rubber molecules (molecular weight usually between 100,000 and 500,000 daltons) become linked together with junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 4,000 to 10,000 daltons. As a result of this network formation, the rubber becomes essentially insoluble in any solvent, and it cannot be processed by any means which requires it to flow, e.g., in a mixer, in an extruder, on a mill, on a calender, or during shaping, forming, or molding. Thus, it is essential that vulcanization occur only after the rubber article is in its final form [32].

Major effects of vulcanization on use-related properties are illustrated by the idealization of Figure 2.5. It should be noted that static modulus increases with vulcanization to a greater extent than does the dynamic modulus. (Here, static modulus is more correctly the equilibrium modulus, approximated by a low strain, slow-strain-rate modulus. Dynamic modulus is generally measured with the imposition of a sinusoidal, small strain at a frequency of 1–100 Hz.) The dynamic modulus is a composite of viscous and elastic behavior, whereas static modulus is largely a measure of only the elastic component of rheological behavior [32-33,39].

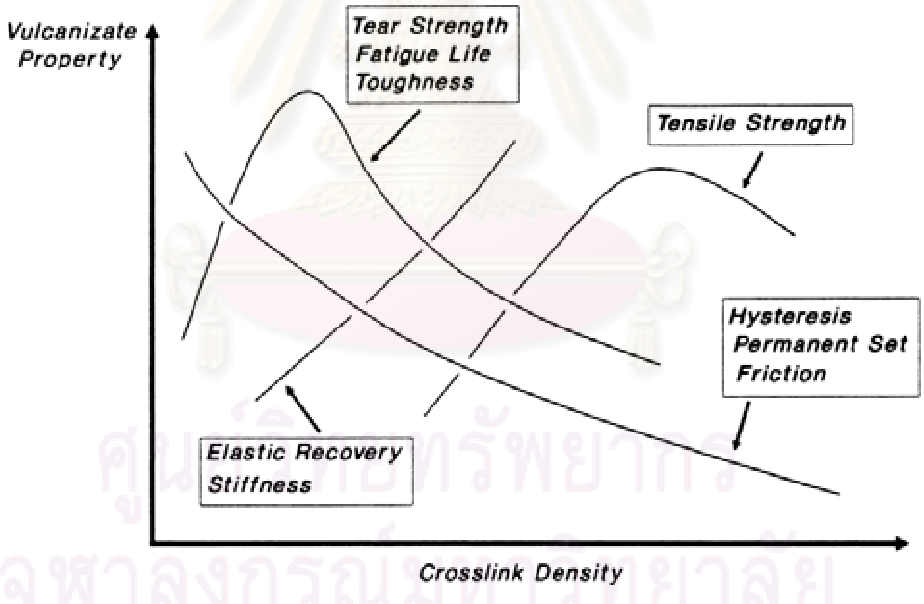


Figure 2.5 Vulcanizate properties as a function of the extent of vulcanization

Hysteresis is reduced with increasing crosslink formation. Hysteresis is the ratio of the rate-dependent or viscous component to the elastic component of deformation resistance. It is also a measure of deformation energy that is not stored (or borne by the elastic network) but that is converted to heat. Vulcanization then causes a trade-off of elasticity for viscous or plastic behavior. Tear strength, fatigue life, and toughness are related to the breaking energy. Values of these properties increase with small amounts of crosslinking, but they are reduced by further crosslink formation. Properties related to the energy-to-break increase with increases in both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are developed, the energy-to-break related properties are maximized at some intermediate crosslink density [39].

It should be noted that the properties given in Figure 2.5 are not functions only of crosslink density. They are also affected by the type of crosslink, the type of polymer, and type and amount of filler, etc.

2.3 Recycling Processes.

Vulcanization is the reason that gum rubber is useful in the tire industry. Unfortunately, it has also created a serious environmental problem as tremendous amount of waste rubbers dumped and stockpiled. Unlike the thermoplastic polymers which can be easily reprocessible by heating, the thermoset polymers, such as vulcanized elastomers can not be simply reused once they form the three-dimensional network. However, there cycling of such materials is demanding due to the environmental and economic factors resulted from the ever-increasing amount of waste rubbers, especially scrap tires. Rubber recycling processes keep developing, aiming at the reutilization of rubber as close as possible to its virgin form. This type of recycling method where rubber is reused like in its virgin form is called devulcanization (or reclaiming). There have been many efforts to recycle waste rubbers during the past several decades [40]. Those methods are generally divided into two categories. One is at the physical level. It involves grinding the material mechanically into smaller pieces without breaking the chemical bonds. The end result is the size reduction. Another category of methods attempts to break the three-dimensional network chemically with the aid of various forms of energy (mechanical, thermal, chemical, biological interaction, microwave, ultrasound, etc.). It has to convert the three-dimensional, insoluble and infusible thermoset into a soft, tacky, reprocessable and revulcanizable product simulating the properties of the virgin rubber. Recovery and recycling of rubber from the used rubber products will solve the waste rubber disposal problem. However, a selective process that only breaks the cross-links without main chain scission is still unavailable at the moment. The devulcanized rubber will have a different molecular structure compared to the unvulcanized rubber (see Figure 2.6). Due to the broader molecular weight distribution, the revulcanized product will have lower mechanical properties in comparison with the product from virgin rubber. Moreover, the revulcanization conditions might also be influenced by the change in molecular weight [22].

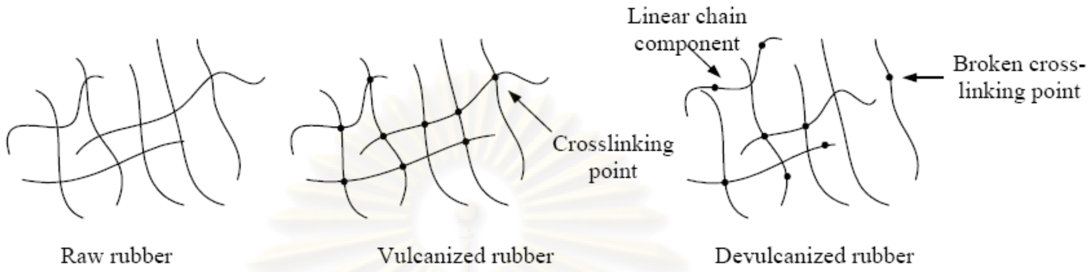


Figure 2.6 The difference of molecular structures between virgin rubber,vulcanizate and devulcanized rubber [22].

2.3.1 Landfills Waste Rubber.

Landfills have been, over the years, an easy way to dispose of waste rubber. However, fires at dumpsites, lack of space, and the increasing costs associated with the land-filling operations have made this a non-viable solution [12]. Landfills provide breeding grounds for mosquitoes and rodents when waste tires are stockpiled or illegally dumped. Another problem associated with the dumping of waste rubber is the leaching of toxic chemicals into the surrounding soil, which makes it a huge threat to agriculture and human health. Consequently, a majority of the states in America banned whole tires from landfills since 2003 due to fire hazards and human health hazards.

2.3.2 Rubber Pyrolysis.

The high calorific value of rubber, 32.6 mJ/kg, compared to that of coal, 18.6-27.9 mJ/kg [43], and the fact that rubber contains over 90% organic materials, makes burning scrap rubber a great resource for fuel [12]. However, burning scrap rubber for fuel brings with it the problem of air pollution due to emissions. Environmental concerns led to the development of a process that recycles rubber using an oxidation process, which results in the breakdown of the polymer by selective oxidative decoupling of C-C, C-S and S-S bonds by water as a solvent near its supercritical temperature. Another method of using waste rubber has been developed that adequately recovers oil, steel, and carbon black. This method involves heating the rubber at 700 ^{o}F for 10 min. to obtain the resulting by-products.

Pyrolysis provides another route for reuse of the waste tire rubbers due to their high potential energy values stored in the hydrocarbons. It involves in the thermal decomposition of organic materials such as rubbers in the absence of air and oxygen to produce valuable gases and oils to be reusable [44]. In this process, the carbon black and steel can be recovered. However the separation of the components of gases and oils could be an expensive operation and it also inevitably releases the toxic substances into the atmosphere.

2.3.3 Grinding Method.

Grinding tire rubber has been one of the most common methods used for recycling [44]. The end result of the process is the size reduction of the waste rubber, with the ability to control the average particle size. There are many grinding processes that have been developed to attain the particulate form of the rubber, namely, ambient grinding, cryogenic grinding and solution grinding.

2.3.3.1 Ambient Grinding.

Ambient grinding, unlike its name, does result in the generation of heat. In this process, vulcanized rubber is placed in a serrated grinder, reducing rubber to particles of size 10-30 mesh. The surface quality of the end product is highly dependant on the size of the particles. If an attempt is made to increase particle size, the smoothness of the particles decreases. The generation of heat during the process is higher for aged rubber, or rubber with a higher modulus, which in turn leads to increased degradation of the polymer chains [12].

2.3.3.2 Cryogenic Grinding.

In the cryogenic grinding process, small pieces of vulcanized rubber are placed in liquid nitrogen for a period of time and are then transferred into a ball mill, in the presence of liquid nitrogen, to form a fine powder [45]. The size of the particles is controlled by the change in the immersion time of the polymer in the liquid nitrogen [12]. An advantage of this process is the lack of heat generation, which avoids any likelihood of the degradation of polymer chains in the vulcanized products. Secondly, the ease of separation of the fiber and steel from the rubber, the resulting increase in the yield of rubber, and finally the decreasing costs of liquid nitrogen have led to a significant increase in the use of the cryogenic grinding process.

The cryogenic process produces fairly smooth fracture surfaces more than ambient ground products is shown in Figure 2.7 [12]. Little or no heat is generated in the process. This results in less degradation of the rubber. In addition, the most significant feature of the process is that almost all fiber or steel is liberated from the rubber resulting in a high yield of usable product and little loss of rubber. However, the process may be economical for expensive rubbers such as fluorocarbon rubbers. Little or no heat is generated in the process, resulting in less degradation of the rubber. In addition, the most significant feature of the process is that almost all fiber or steel is liberated from the rubber, resulting in a yield of usable product and little loss of rubber.

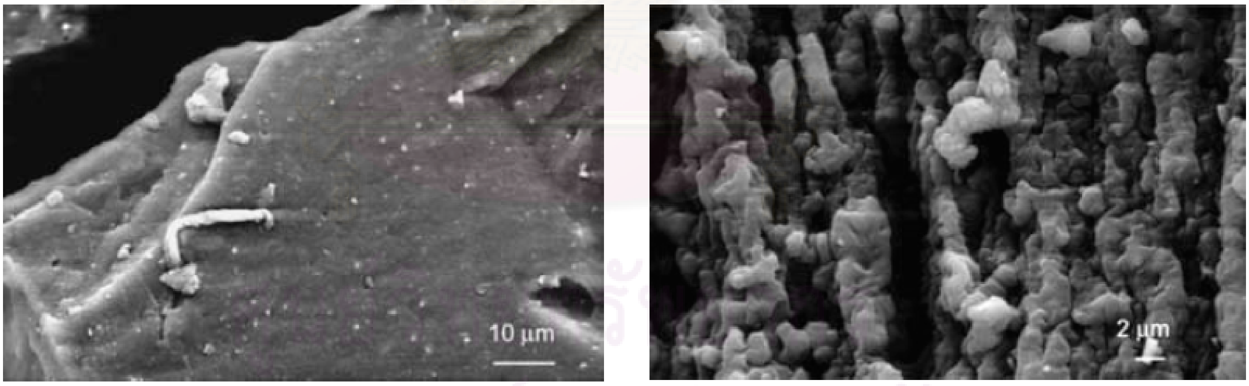


Figure 2.7 The surface structure of cryogenically ground powder (left) and ambiently ground powder (right)

2.3.3.3 Water Solution Grinding.

Wet or solution grinding is another grinding process that reduces the particle sizes by grinding in a liquid medium. The process requires the use of coarse ground particles, approximately between 10-20 mesh in size, which are ground between two closely spaced grinding wheels in a liquid medium [12]. An advantage of the process is the improved heat transfer during shearing and size reduction, which avoids degradation of the polymer chains; secondly, the sizes that can be obtained are as small as 400-500 mesh.

2.3.4 Physical Devulcanization Method.

In a physical devulcanization process scrap/waste rubber products are devulcanized with the help of external energy. Thus, in physical devulcanization process three-dimensional network of crosslinked rubber breaks down in presence of different energy source. Due to the breaking of network structure macromolecular rubber chain is transformed into small molecular weight fragments so that it can be easily miscible with the virgin rubber during compounding. So reclaim rubber produced by physical devulcanization process may be used as non-reinforcing filler. But if in this process a specific amount of energy is used which is sufficient to cleave only the crosslink bonds, then after devulcanization a good quality of reclaim rubber will be obtained which will be thermoplastic in nature and compare well with virgin rubber properties. Different types of physical devulcanization processes are mechanical, thermo-mechanical, microwave, and ultrasonic.

2.3.4.1 Mechanical Devulcanization Process.

In mechanical devulcanization process crumb rubber is placed in an open two-roll mixing mill and milling is carried out at high temperatures. In this process drastic molecular weight breakdown takes place due to mechanical shearing at high temperature. A physical process of devulcanization of vulcanized rubber and refining of the reclaimed rubber are described. The vulcanized rubber in particulate form (e.g. ground tire) is reclaimed with devulcanization agents by passing the rubber between an essentially smooth stator and an essentially cylindrical rotor arranged to provide an axial shear zone in which the rubber is frictionally propelled by the rotor action. The action may be assisted by mixing a suitable amount of previously reclaimed rubber or of vulcanized rubber with or in advance of the particulate vulcanized rubber, and/or by supplemental heating. In other aspects of the invention previously reclaimed and vulcanized rubber is similarly fed and acted upon as substitute for conventional refining operation. De *et al.* [46] reported the mechanical devulcanization process of vulcanized NR. The reclaimed NR was prepared by milling vulcanized sheets at about 80 ^{o}C. On a two roll laboratory mill it formed a band on the roll. Next, it was mixed with various rubber additives. In another case, mixing of reclaimed rubber (RR) with fresh rubber in various proportions and study of their curing characteristics, mechanical properties, etc., were done. However, the Mooney viscosity of the reclaimed rubber was very high indicating that the plasticity of rubber was very low due to the presence of higher percentage of crosslinked rubber. The extent of devulcanization, i.e. percentage of sol/gel fraction, molecular weight of the sol fraction, and the influence of milling parameters on the Mooney viscosity were not reported.

Study of the curing characteristics of the blends of fresh rubber with reclaim rubber indicated that with increase in the reclaim rubber content the cure rate increased but the scorch time, optimum cure time and reversion resistance decreased. As the proportion of reclaim rubber in the blends increases modulus, abrasion loss, compression set and hardness increase while tensile strength, elongation at break, tear strength, resilience and flex resistance decrease. The above result shows that increase in the proportion of reclaim rubber increases the crosslink density. As crosslink density is very high for the NR/RR (25/75) blend so modulus is high but tensile strength and flex properties are low. Thus, reclaim rubber appeared to perform as non-reinforcing filler in this study.

2.3.4.2 Thermo-Mechanical Devulcanization Process [47].

This process involves the thermo-mechanical degradation of the rubber vulcanizate network. The vulcanizate is swollen in a suitable solvent and then transferred to a mill to form a fine powder (0.20 mm diameter). This powder rubber is revulcanized with curing ingredients. The products thus obtained show slightly inferior properties to those of the original vulcanizates.

2.3.4.3 Microwave Devulcanization Process.

By carefully choosing the dosage of microwave energy, at a certain frequency, and at the desired energy level, elastomers can be devulcanized and thus be reprocessed. Hence, this is a process where the elastomer can be reclaimed to a material that is capable of being re-compounded and has the properties that are equivalent to the original vulcanizate. It was presumed that breakdown of chemical bonds in the vulcanizates only occured in carbon-sulfur and sulfur-sulfur bonds and it resulted in no significant main chain (carbon-carbon bonds) degradation [5].

However, one critical requirement of the microwave process is the presence of polar groups in the polymer. The availability of polar groups in the polymer results in an increase in the temperature of the material once it has been exposed to the microwave energy, which would result in the severing of the crosslinks.

2.3.4.4 Ultrasonic Devulcanization Process.

The most promising method of recycling elastomers is the ultrasonic method. Ultrasonic technology was first reported in 1973 by Pelofsky [7], in which rubber particles were immersed in a liquid medium, and then were exposed to ultrasonic energy, which resulted in the disintegration and dissolution of the polymer in the liquid medium. Ultrasonic irradiation with a frequency of 20 kHz, and the power intensity greater than 100 W was used in the process. The next step in the development of ultrasonic technology was the development of a process by Okuda and Hatano [48], in which a natural rubber vulcanizate was subjected to 50 kHz ultrasonic energy for approximately 20 min. to achieve devulcanization. The researchers claimed that the properties attained after the revulcanization process were similar to that of the original vulcanizate. Mangaraj and Senapati [49], in their patent on ultrasonic vulcanization, noted the possibility of degradation of rubber and the crosslinks by ultrasonic energy.

2.3.5 Chemical Devulcanization Method.

Research in using chemical method to devulcanize crosslinked rubber occurred at 1960-70’s. The original purpose of this method was to apply some specific chemical reagent as a probe to determine the structure and types of the sulfur crosslinks [50]. The chemical method was able to distinguish among the polysulfide, disulfide and monosulfide bonds in the sulfur cured rubber vulcanizates by measuring the crosslink density before and after the treatment of rubber with different chemical reagents specifically breaking particular types of crosslinks. For example, Saville *et al*. [37] used propane thiol/piperidine to cleave polysulfide linkages while leaving the mono-, disulfide and carbon-carbon linkages intact. Campbell [51] found that hexane-1-thiol was more reactive and could cleave both poly- and disulfide links while leaving the monosulfide and carbon-carbon bonds intact. Selker et al [52-54] reported the importance of methyl iodide to break only the monosulfide bonds in rubber vulcanizates. There were also other effective chemicals to cleave particular crosslinks. However, it was found that some of the chemical reagents such as methyl iodide were carcinogenic.

Although the chemical method is very powerful to distinguish among the different types of crosslinks and analyze the chemical structures, this process is very slow and it creates additional problems such as the removal of solvents and operation safety.

2.3.6 Biological Devulcanization Method.

There are also some trials to use microorganisms to devulcanize waste rubbers. It was reported that microorganisms were able to break sulphur-sulphur and sulphur-carbon bonds by digestion and thus they could be used to devulcanize waste rubber in order to make polymer chains on the surface more flexible and facilitate increased binding upon vulcanization [55].

Biodegradation of NR was achieved by Tsuchii and coworkers [56-57]. They used bacteria from the genus *Nacardia* and the process led to a substantial weight loss of different types of NR vulcanizates. A recent approach involves the utilization of a type of fungus to degrade the vulcanized NR sheets on a wood medium [22]. The fungus decreased the total sulfur content of the rubber by 29% in 200 days, accompanied by the cleavage of sulfide bonds between polyisoprene chains. Dipolar decoupling/magic angle spinning (DD/MAS) solid-state ^{13}C NMR revealed that the fungus preferentially decomposed monosulfide bonds linked to a *cis*-1, 4-isoprene backbone but the cleavage of polysulfide bonds was also observed.

Biotechnological method has advantages over the mechanical and chemical processes since it consumes little energy and does not require hazardous chemicals. However, an obstacle with the biotechnological processes is that it involves living organisms, which are affected by the environment they are cultivated in. Chemicals involved in vulcanization process (accelerators, antioxidants, etc.) might suppress the growth of microorganisms and thus inhibit the biodegradation of rubber materials [58]. Zinc oxide, mercaptobenzothiazole, dithiocarbamate accelerators and para-phenylenediamine type antioxidants are particularly strong anti-metabolites [47]. Besides, rubber biodegradation is a slow process, and the growth of bacteria utilizing rubber as a sole carbon source is also slow [58]. Therefore, incubation periods extending over weeks or even months are required to obtain enough cell mass or degradation products of the polymers for further analysis.

2.3.7 Mechano-Chemical Devulcanization Method.

Mechano-chemical is a branch of chemistry in which chemical phenomena, such as chemical reactions and changes in crystalline structures induced by mechanical actions like fracture and large deformation. The mechano-chemical process was the fact that strong mechanical action was accompanied by friction that produced heat.

Vulcanization rubber can be improved by using a revulcanizing accelerator while applying a mechanical force to the rubber powder. In general, a devulcanizing catalyst, devulcanizing oil and process oil are used jointly with the reclaiming agent. Disulfide and triphenyl phosphine were found to increase the plasticity of rubber reclaim. The fact that these reagents behave as devulcanizing agents for rubber is explained by their function as a radical acceptor for the rubber radicals that are formed in the mechano-chemical reaction.

Publications on mechano-chemical devulcanization date back to World War II. In these two studies, combinations of accelerator, zinc oxide, softening agents, and devulcanizing agents were used. The devulcanization was carried out on two-roll rubber mills at relatively low temperatures (>80 ^{o}C). Some of these basic rubber chemicals appear to attack the sulfur-sulfur bonds in combination with shear, reducing the cross-link density and increasing the plasticity. Since the process takes place on a two-roll mill in the presence of air, there would, in all likelihood, be a reduction in polymer molecular weight. This reduction in molecular weight would also increase plasticity. Relatively good properties were obtained.

Devulcanization using mechanical shear (i.e., a mill). The length of time of the process was quite long at 30 min.; temperature was not discussed. Thiols and disulfides were used. Besides main chain breakdown, cross-links were opened and the viscosity was reduced (increased plasticity). This is more like devulcanized rubber than straight devulcanization because of the level of polymer chain breakdown.

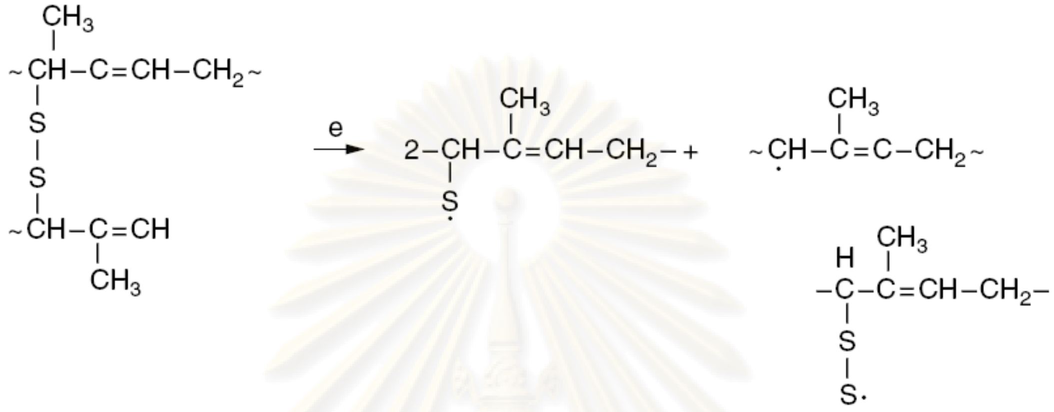
In 1980, another patent by Watabe [59] was issued for a process that used many chemicals in virtually the same manner, namely shear (mills and extruders), to chemomechanically devulcanize. Chemicals suggested were basically accelerators. As with the previous references, this was done in the presence of air; therefore, main chain scission could occur.

a) Cleavage of devulcanizing agent

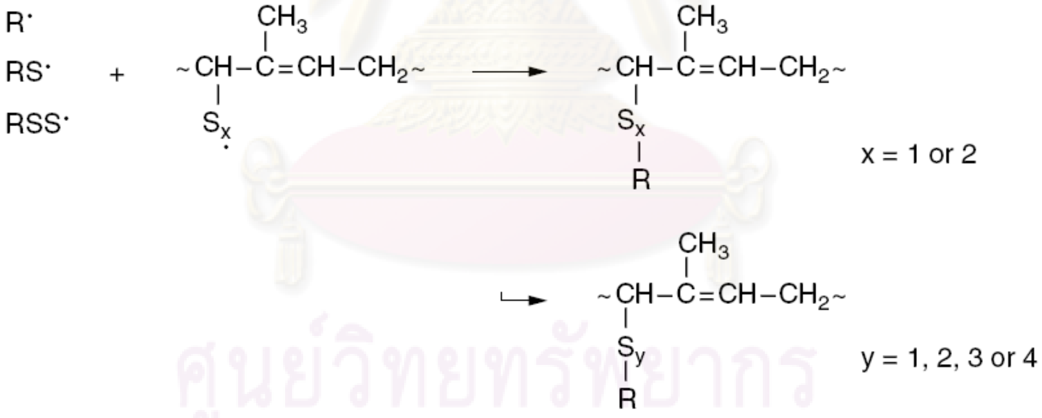
$$\text{R-S-S-R} \xrightarrow{e} 2\text{RS}^{\cdot}$$

$$\xrightarrow{e} \text{RSS}\cdot + \text{R}^{\cdot}$$

b) Cross-link scission



c) Reaction 1: between devulcanizing agent radical and vulcanized rubber radical



d) Reaction 2: between devulcanizing agent radical and vulcanized rubber radical

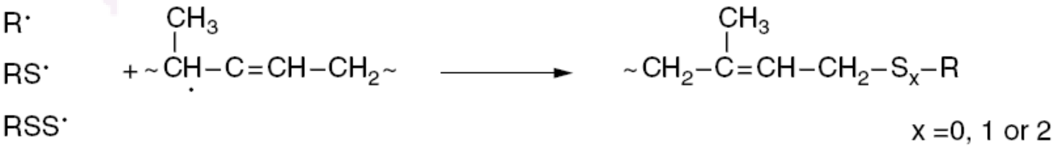


Figure 2.8 Mechano-chemical mechanisms.

In their article, De *et al.* [46] suggest that when devulcanizing with disulfides (a frequent occurrence), heat and mechanical energy do two things. First, they split the disulfide into free radicals. Second, the radicals formed by scission of the disulfide are capable of hydrogen abstraction or addition to the double bonds in natural rubber. Hydrogen abstraction is relatively easy because the protons in an allylic position are activated by the double bond (the resulting carbon radical is resonance stabilized), as shown in Figure 2.8.

The unusual aspect of work is that the devulcanizing agent is from natural sources. Temperature is also involved, but is relatively low at 40 to 60 ^{o}C. The natural material is not as efficient as the usual disulfides. More agents have to be used and the process time is rather lengthy.

2.4 Literature Reviews

In 2001, Yun *et al.* [9] investigated the ultrasonic devulcanization reactors for recycling of GRT: Comparative study. The present paper describes the comparative study of a continuous ultrasonic devulcanization of ground tire rubber (GRT) using two reactors. The devulcanization zone in the first reactor (coaxial reactor) was located at the exit from an extruder without imposition of additional shearing. In the second reactor (barrel reactor), the devulcanization zone was located in barrel where additional shearing takes place due to screw rotation. Gel fraction, crosslink density, cure behavior and physical properties of GRT obtained in these two reactors were measured. Also, the distributions of gel fraction and crosslink density at various locations in the devulcanization zone of the barrel reactor were determined. Gel fraction and crosslink density show that GRT in both reactors was partially devulcanized. A unique correlation between gel fraction and crosslink density obtained in both reactors indicated that additional shearing had a positive influence on improving the efficiency of devulcanization. Under the optimal devulcanization condition, the physical properties of revulcanized GRT and the output were higher in the barrel reactor. Power consumption density in the barrel reactor was found to be significantly higher.

In 2005, Kojima *et al.* [15] studied the devulcanization of sulfur-cured isoprene rubber in supercritical carbon dioxide. A new devulcanization process that utilizes supercritical CO_2 ($ScCO_2$) along with devulcanizing reagents was studied. Unfilled polyisoprene rubber samples (vulcanizates) with different crosslink distributions were prepared by controlling cure time and the curatives. Each of the vulcanizates was subjected to Soxlet Extraction using azeotropic acetone/chloroform to remove residual curatives. The devulcanization was preformed at various temperatures (140-200 ^{o}C) in the presence of $ScCO_2$ for 60 min. The product was fractionated into sol and gel compounds, and molecular weight of sol compound and the crosslink density of the gel component were determined. Thiol-amine reagent was found to be effective among several devulcanizing reagents. The molecular weight of the resulted sol component was about tens of thousands and the crosslink density of gel component decreased substantially from the initial ones. Yield of the sol component increased with the increase in the CO_2 pressure. In the supercritical fluid state of CO_2, the vulcanizate was more efficiently devulcanized than in an ordinary gaseous state of CO_2. The sol fraction depended considerably on the crosslink distribution in vulcanizate. These results suggest that the devulcanizing reagents penetrate and diffuse into the vulcanizate in the presence of Sc CO_2.

In 2005, Jana and Das [24] investigated the devulcanization of NR vulcanizates by mechanochemical process. Using a suitable disulfide-based devulcanizing agent, which cleaved the sulfur cross-links in vulcanized rubber at high temperature, devulcanization of gum NR was carried out. High sulfur and medium sulfur, as well as low sulfur-containing rubber vulcanizates were used to study the cleavage of sulfidic bonds. The cure characteristics and mechanical properties of vulcanized NR and revulcanized NR were studied. Thermal properties of the rubber were analyzed by thermogravimetric analysis (TGA), which indicates that the onset degradation temperature further increased on revulcanization with higher amount of disulfide. The properties of the revulcanized NR increased with increasing disulfide concentration, also the mechanical properties of the devulcanized NR were increased by decreasing the sulfur content in the original rubber vulcanizate. From the rheometric study increases in optimum cure time were observed when ground rubber vulcanizates were treated with higher amounts of disulfide. The scanning electronic microscopy (SEM) study suggested the change in failure mechanism as influenced by the type of cross-linking present and the devulcanizing agent used. From infrared (IR) spectroscopy it was observed that the oxidation of the main polymeric chain did not occur at the time of high temperature milling.

In 2006, Jana *et al.* [25] studied a novel devulcanization technology for vulcanized NR. Devulcanization of gum NR vulcanizate containing three different sulfur/accelerator ratios was carried out in 90 °C for 10 min with the help of open two-roll cracker cum mixing mill in the presence and absence of thiol acid as a devulcanizing agent. The vulcanizate properties markedly depended on devulcanizing agent and also devulcanization techniques. Revulcanized rubber obtained by devulcanizing with thiol acid offered better mechanical properties. Decrease in scorch time and increase in rheometric torque were observed for revulcanized rubber containing devulcanizing agent. The onset degradation temperature largely depended on presence of thiol acid. IR spectroscopic results revealed that the main polymeric chain did not oxidize at the time of milling above the room temperature. Increase in storage modulus and decrease in loss modulus were observed for revulcanized rubber from DMA study. The SEM was considered to study the failure mechanism and homogeneity of the vulcanizate. By adopting this devulcanization technique, more than 85% mechanical property of vulcanized NR was retained.

In 2006, Rajan *et al.* [60] investigated a mechanism of devulcanization of sulfur-vulcanized NR with aromatic disulfides and aliphatic amines using 2,3-dimethyl-2-butene (C_6H_{12}) as a low-molecular weight model compound. First, C_6H_{12} was vulcanized with a mixture of sulfur, zinc stearate and N-cyclohexyl-2-benzothiazylsulfenamide (CBS) as accelerator at 140 °C, resulting in a mixture of addition products (C_6H_{11}-S_x-C_6H_{11}). The compounds were isolated and identified by High Performance Liquid Chromatography (HPLC) with respect to their various sulfur ranks. In a second stage, the vulcanized products were devulcanized using the agents mentioned above at 200 °C. The kinetics and chemistry of the breakdown of the sulfur-bridges were monitored. Both devulcanization agents decompose sulfidic vulcanization products with sulfur ranks equal or higher than 3 quite effectively and with comparable speed. Diphenyl disulfide as devulcanization agent gives rise to a high amount of mono- and disulfidic compounds formed during the devulcanization, hexadecylamine, as devulcanization agent, prevents these lower sulfur ranks from being formed.

CHAPTER III

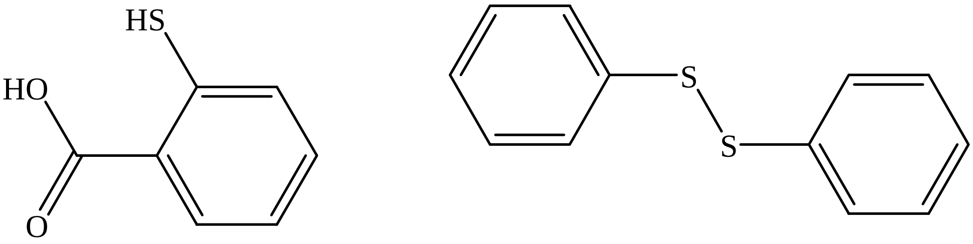
EXPERIMENTALS

3.1 Materials.

Materials for this study were obtained from the following commercial sources and used without further purification (Table 3.1) and structure of devulcanizing agents were shown in Figure 3.1.

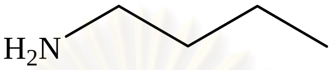
Table 3.1 Commercial sources for materials.

Chemicals	Company
Natural rubber (STR5L)	Thai Hua Chumporn Natural Rubber Co. Ltd.
Truck tire rubber powders (40 mesh)	Union Pattanakit Ltd.
Active zinc oxide (Commercial grade)	Pan Innovation Ltd.
Stearic Acid (Commercial grade)	Imperial Industrial Chemicals Co. Ltd.
Sulfur (Commercial grade)	PI Industry Limited.
n-Cyclohexyl-2-benzothiazyl sulfonamide (Commercial grade)	PI Industry Ltd.
Process oil	Pan Innovation Ltd.
Thiosalicylic acid	Merck
Diphenyl disulfide	Fluka
n-Butylamine	Fluka
Toluene	Fisher Scientific Ltd.



Thiosalicylic acid

Diphenyl disulfide



n-Butylamine

Figure 3.1 Structure of devulcanizing agents

3.2 Experimental Procedure.

3.2.1 Preparation of Vulcanized NR.

The compositions of rubber compounding in three types vulcanization are shown in Table 3.2. Mixing was done by a two-roll mill. The resulting rubber compound was then cured at 150°C for 15 min by compressing molding.

Table 3.2 Formulation in the unit of phr[a] for rubber compounding.

Ingredients (phr)	Conventional vulcanization (CV)	Semi-Efficiency vulcanization (semi-EV)	Efficiency vulcanization (EV)
NR (STR 5L)	100	100	100
ZnO^2	5	5	5
Stearic acid	2	2	2
Sulfur	3	1.9	0.8
CBS^3	1	2	3

[a] Part by weight per hundred part of rubber [b] Active zinc oxide

[c] *n*-cyclohexyl-2-benzothiazyl sulfenamide

3.2.2 Devulcanization Process.

NR vulcanizate was ground with a two-roll mill at 50°C for 15 min. The rubber powder was then mixed with devulcanizing agent and process oil at ambient temperature for 0-48 h. After mixing, the rubber powder was heated in the oven at various devulcanizing temperatures but at a fixed time of 30 min. The rubber product obtained was named devulcanized rubber. The formulations and conditions of devulcanization are shown in Table 3.3.

3.2.3 Revulcanization Process.

The virgin rubber was mixed with the devulcanized rubber at various ratios (95:5, 90:10, 85:15, 80:20, 60:40, 40:60 and 20:80) by two-roll mill. Then, the sample was revulcanized with the addition of proportionate amount of ZnO, stearic acid, sulfur, and CBS in the vulcanization system of CV at 150^{o}C for 10 min by compression molding. Only the ratios of (95:5, 90:10, and 85:15) were studied for both semi EV and EV systems.

3.3 Characterization Methods.

3.3.1 Determination of Cure Characteristics.

Curing properties including in terms of scorch and optimum cure time of the rubber compounding were measured by Rheometer MDR2000 (Monsanto, USA) at 150^{o}C. The typical cure curve as shown in Figure 3.2 was determined.

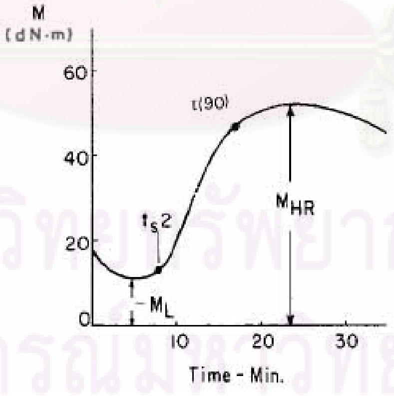


Figure 3.2 Cure characteristics curve from Rheometer

where M_L is minimum torque (N.m).

M_{HR} is maximum torque, (N.m).

Scorch time (t_2) in minute is the time taken for a two-unit rise above the minimum torque.

Optimum cure time (t_{90}) in minute is the time taken for attaining 90% of the maximum torque.

Table 3.3 Formulations in the unit of phr[a] of devulcanized rubber varies devulcanizing temperature, devulcanizing time, amount of devulcanizing agent and type of devulcanizing agent

Sample code	NV	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10
NR vulcanizate	100	100	100	100	100	100	100	100	100	100	100
Thiosalicylic acid	-	1	1	1	1	1	0.5	2	-	-	-
Diphenyl disulfide	-	-	-	-	-	-	-	-	1	-	-
Thiosalicylic acid/*n*-butylamine	-	-	-	-	-	-	-	-	-	1	-
Without the devulcanizing agent	-	-	-	-	-	-	-	-	-	-	-
Process oil	-	8	8	8	8	8	8	8	8	8	8
Devulcanization time (h)	-	0	0	24	48	72	48	48	48	48	48
Devulcanization temperature (^{o}C)	-	120	140	140	140	140	140	140	140	140	140

[a] Part by weight per hundred part of rubber

3.3.2 Tensile Measurement.

Tensile test was performed by a Universal Testing Machine LLOYD LR 5K, (Fareham, UK**)** in accordance with ASTM-D412 at room temperature and a crosshead seed of 500 mm/min. The average value of three measurements was reported as the result of the tensile test. Tensile strength and elongation at break were calculated as follows equations (1) and (2), respectively.

$$\text{Tensile strength (MPa)} = \frac{\text{force at rupture (N)}}{\text{cross - sectional area (m}^2\text{)}} \tag{1}$$

$$\text{Elongation at break (\%)} = \frac{\text{(length at rupture - original length)}}{\text{original length}} \times 100 \tag{2}$$

3.3.3 Hardness Determination.

Hardness testing was measured by using a Shore-type-A Lever Loader (REX GAUGE 2000 & OS-2 Stand) according to ASTM D 2240. The test temperature was carried out at room temperature. The measurements were taken from five different points distributed over the sample and the reported were based on an average of five measurements.

3.3.4 Sol-Gel Determination.

Sol and gel fractions were taken as the indication of degree of devulcanization and calculated by using equations (3) and (4) in the sample as described in appendix.

$$\text{Sol fraction (\%)} = \frac{(W_0 - W_1)}{W_0} \times 100 \tag{3}$$

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction (\%)} \tag{4}$$

where W_0 and W_1 is the dry sample mass before and after swelling, respectively.

3.3.5 Determination of Crosslink Density.

Crosslink density was determined by immersing the sample in 50 mL of toluene at room temperature for 72 h to attain equilibrium swelling. The sample was then taken out from toluene and the solvent was blotted from the sample surface. The resulting sample was weighted immediately and at 80 ^{o}C until the sample weight was constant. The study was repeated with other 2 samples. Then, the crosslink density was calculated by Flory-Rehner Eq. (5) [61] in the sample as described in appendix.

$$\nu = \frac{-[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2]}{V_0[\nu_r^{1/3} - (\nu_r/2)]} \tag{5}$$

where ν is the crosslink density, ν_r is a volume fraction of the rubber network in the swollen gel, V_0 is a molar volume of the swelling solvent and χ is equal to 0.393 and used as the rubber-solvent interaction parameter [62].

3.3.6 Scanning Electron Microscopy (SEM).

The samples were frozen in liquid nitrogen and fractured by using pliers. A cross-section of each sample was then measured by a scanning electron microscope JSM-6480LV (JEOL, Japan) at the voltage of 15 kV after coating with gold.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Properties of Devulcanized Rubber Using the Mechano-Chemical Process.

Table 4.1 shows the formulation and properties of NR vulcanizate and devulcanized rubber obtained by the mechano-chemical devulcanization using thiosalicylic acid as the devulcanizing agent (sample D1-D7), compared with reference NV. The amount of process oil except the case of NV, was kept constant at 8 phr. In this study, the degree of devulcanization, which implies the cleavage of intermolecular bonds of the three dimensional network, was determined by the sol-gel fraction of devulcanized rubber. High sol fraction indicates that the three dimensional network in NR vulcanizate is efficiently destroyed, resulting in the decrease of crosslink density.

Table 4.1 Formulations in the unit of phr[a] and properties of NR vulcanizate and devulcanized rubber by thiosalicylic acid.

Sample code	Thiosalicylic acid (phr[a])	Devulcanizing time[b] (min)	Devulcanizing temperature (^{o}C)	Sol fraction (%)	Gel fraction (%)	Crosslink density (mol/g) (× 10^4)
NV	-	-	-	1±0	99±0	1.47±0.02
D1	1	095	120	22±1	78±1	0.56±0.01
D2	1	090	140	26±1	74±1	0.54±0.00
D3	1	24	140	29±1	71±1	0.47±0.01
D4	1	48	140	33±0	67±0	0.39±0.01
D5	1	72	140	33±1	67±1	0.39±0.00
D6	0.5	48	140	29±1	71±1	0.50±0.01
D7	2	48	140	35±1	65±1	0.37±0.01

[a] Part by weight per hundred part of rubber [b] At ambient temperature

In order to investigate the efficiency of thiosalicylic acid as devulcanizing agent, NR vulcanizates were mixed with 1 phr of thiosalicylic acid at various devulcanizing temperature and times. Considering different devulcanizing temperature (D1-D2), it was found that the sol fraction was increased with increasing devulcanizing temperature to 140°C. The high sol fraction indicated that the three dimensional network in NR vulcanizate was well destroyed, resulting in the decrease of crosslinking density as summarized in Table 4.1.

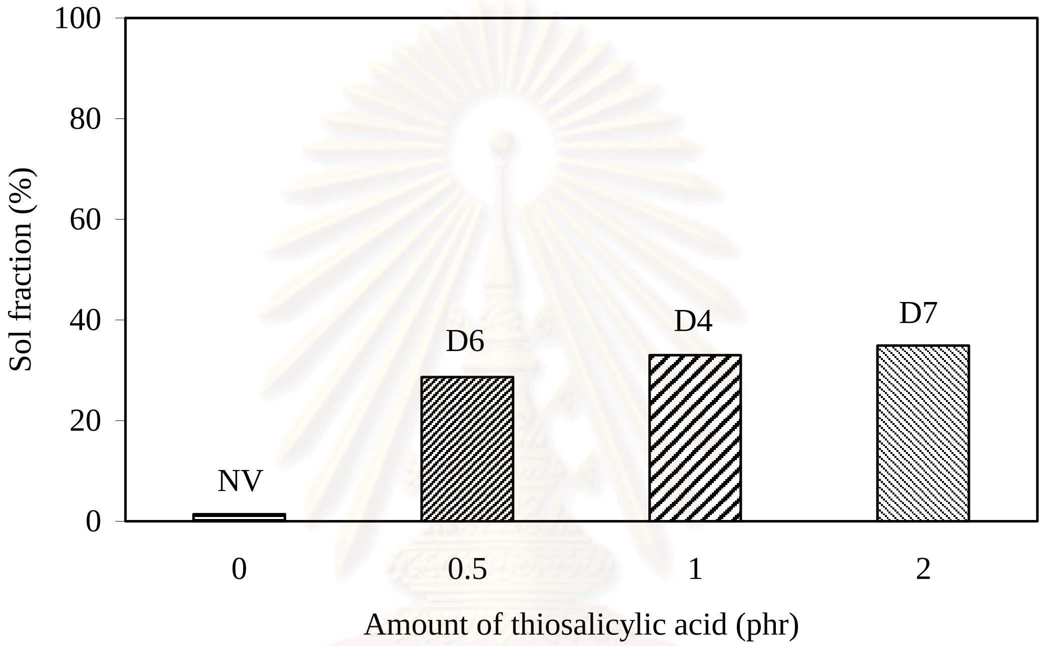


Figure 4.1 The sol fraction of revulcanized rubber at various amount of thiosalicylic acid.

According to the sol and gel fractions of sample D2-D5, the results indicated that the sol fraction of devulcanized rubber was gradually increased with increasing devulcanizing time, while the gel fraction was decreased because of the longer the devulcanizing time and the higher the degree of devulcanization. The sol-gel fraction seemed to be constant when the devulcanizing time reached 48 h. Accordingly, the shortest time to provide the high sol fraction, hence low crosslink density; of devulcanized rubber was 48 hr.

Samples D6, D4 and D7 were prepared to investigate the effect of amount of thiosalicylic acid on the properties of devulcanized rubber, including percentage of sol fraction and crosslink density as shown in Figures 4.1 and 4.2, respectively. The amount of thiosalicylic acid was varied from 0 to 2.0 phr. The amount of process oil, devulcanizing time and devulcanizing temperature were kept constant. While the sol fraction of devulcanized rubber was increased with increasing amount of thiosalicylic acid, its crosslink density of devulcanized samples was significantly decreased compared with that of NR vulcanizate. However, the sol fraction of D4 and D7 was almost comparable. Thus, the optimal condition for mechano-chemical process of NR vulcanizate in this study was found to be the use of 1 phr thiosalicylic acid at 140 °C for 48 h.

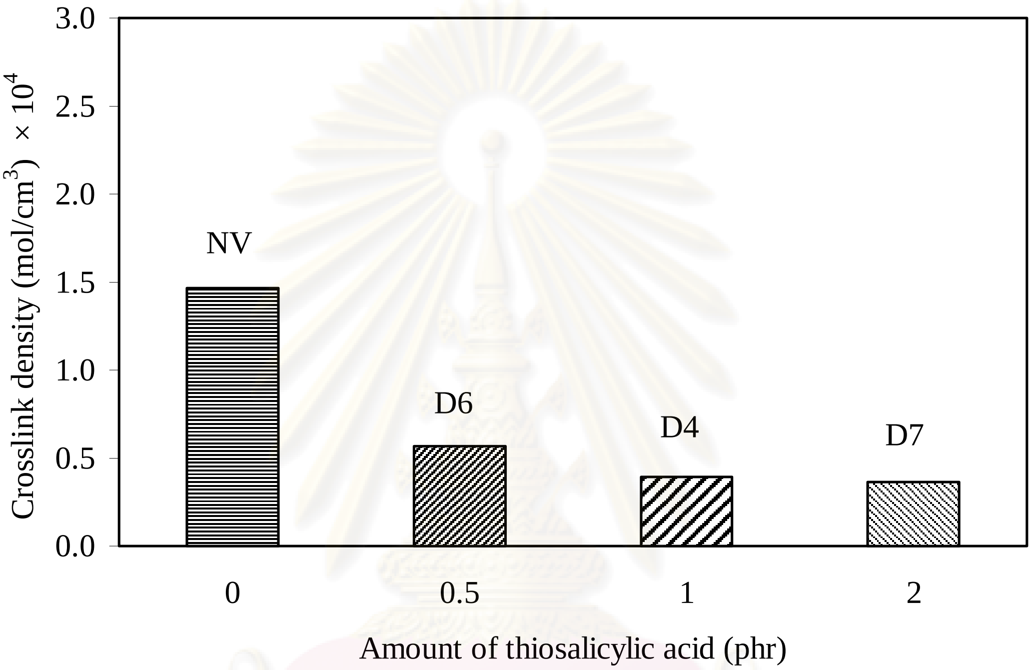


Figure 4.2 The crosslink density of revulcanized rubber at various amount of thiosalicylic acid.

Jana *et al.* reported that the use of disulfide families as a devulcanizing agent for NR vulcanizate gave a good efficiency of sulfide bond cleavage [23, 24]. Additionally, Campbell reported that the the thiol/amine agent was found to be the most effective one among several devulcanizing agents such as dimethyl sulfoxide, di-*n*-propyl sulfoxide and methyl iodide. The thiol–amine combination gave a complex in which the sulfur atom had enhanced nucleophilic properties, and was capable of cleaving organic trisulfides and higher polysulfides [50, 51]. For the comparison purpose, the degree of devulcanization of NR vulcanizate by using diphenyl disulfide or thiosalicylic acid/*n*-butylamine as devulcanizing agent was thus examined as seen in Table 4.2. It is clearly seen that the sol fraction and crosslink density of thiosalicylic acid (D4) and diphenyl disulfide (D8) showed the similar values. The sol fraction of devulcanized rubber in with devulcanizing agent (D4 and D8) was higher than that of devulcanized rubber with thiosalicylic acid/*n*-butylamine (D9) as the devulcanizing agent and without the devulcanizing agent (D10). Occasionally, the thiosalicylic acid by using with *n*-butylamine was not an appropriate devulcanizing agent for this study. It may be because thiol/amine agent was not specific with *n*-butylamine in this system [37]. According to these results, the thiosalicylic acid can be used as the devulcanizating agent for NR vulcanizate and its efficiency for devulcanization was comparable with that of widely used diphenyl disulfide.

Table 4.2 Formulations in the unit of phr[a] and properties of NR vulcanizate and devulcanized rubber by various types of devulcanizing agents**.**

Sample code	NV	D4	D8	D9	D10
NR vulcanizate	100	100	100	100	100
Thiosalicylic acid	-	1	-	-	-
Diphenyl disulfide	-	-	1	-	-
Thiosalicylic acid/*n*-butylamine	-	-	-	1	-
Without the devulcanizing agent	-	-	-	-	-
Process oil	-	8	8	8	8
Devulcanizing time[b] (min)	-	48	48	48	48
Devulcanizing temperature[c] (°C)	-	140	140	140	140
Sol fraction (%)	1±0	33±1	33±1	28±1	22±1
Gel fraction (%)	99±0	67±1	67±1	72±1	78±1
Crosslink density × 10^4 (mol/cm^3)	1.47±0.02	0.39±0.01	0.41±0.02	0.43±0.02	0.57±0.02

[a] Part by weight per hundred part of rubber [b] At ambient temperature

[c] Time 30 min

4.2 Properties of Revulcanized Rubber Obtained by Using Thiosalicylic Acid as Devulcanizing Agent

4.2.1 Effect of Devulcanized Rubber Content on the Curing Properties

The devulcanized rubber obtained from section 4.1 was revulcanized with the virgin rubber at various proportions together with the curing reagents as listed in Table

4.3. The cure behaviors of the resulting revulcanized rubber are elucidated in Figure 4.3. Three regions of cure behaviors were clearly observed for all samples. The first region was the scorch time or the induction period. The torque initially dropped due to the increase of temperature, and remained low before the crosslink formation. The scorch time was slightly decreased with the increase of devulcanized rubber contents. The reason for decrease in scorch time is evident. According to De et al. [63], the devulcanized rubber contained active cross-linking gel, resulting in reduction of scorch time. Jana et al. [23] reported that the *n*-cyclohexyl-2-benzothiazyl sulfenamide (CBS) first decomposed to amine and dibenzothiazole disulfide. The dibenzothiazole disulfides then dissociated to form mercaptobenzothiazoles (MBT), which was only responsible for cross-linking. For this reason, sulfenamide is a delayed action accelerator. Thus, MBT diffusion into the matrix would reduce the scorch time. It is likely that the accelerator migrated from ground rubber to the matrix when the ground rubber was accelerator/sulfur cured and that species reduced the scorch time [64].

Table 4.3 Formulations in the unit of phr[a] and curing properties of revulcanized rubber with various devulcanized rubber contents

Sample code	NV	R1	R2	R3	R4	R5	R6	R7
NR	100	95	90	85	80	60	40	20
D4[b]	-	5	10	15	20	40	60	80
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Sulfur	3	3	3	3	3	3	3	3
CBS[c]	1	1	1	1	1	1	1	1
Scorch time (min)	6.0	3.3	2.4	2.0	2.0	1.3	1.1	1.1
Optimum cure time (min)	10.2	7.2	6.1	5.3	5.2	4.6	5.0	5.1
Maximum torque (dNm)	8.61	8.86	8.80	8.74	8.50	8.47	8.32	7.69

[a] Part by weight per hundred part of rubber [b] Devulcanized rubber prepared by using thiosalicylic acid 1 phr [c] *n*-Cyclohexyl-2-benzothiazyl sulfenamide

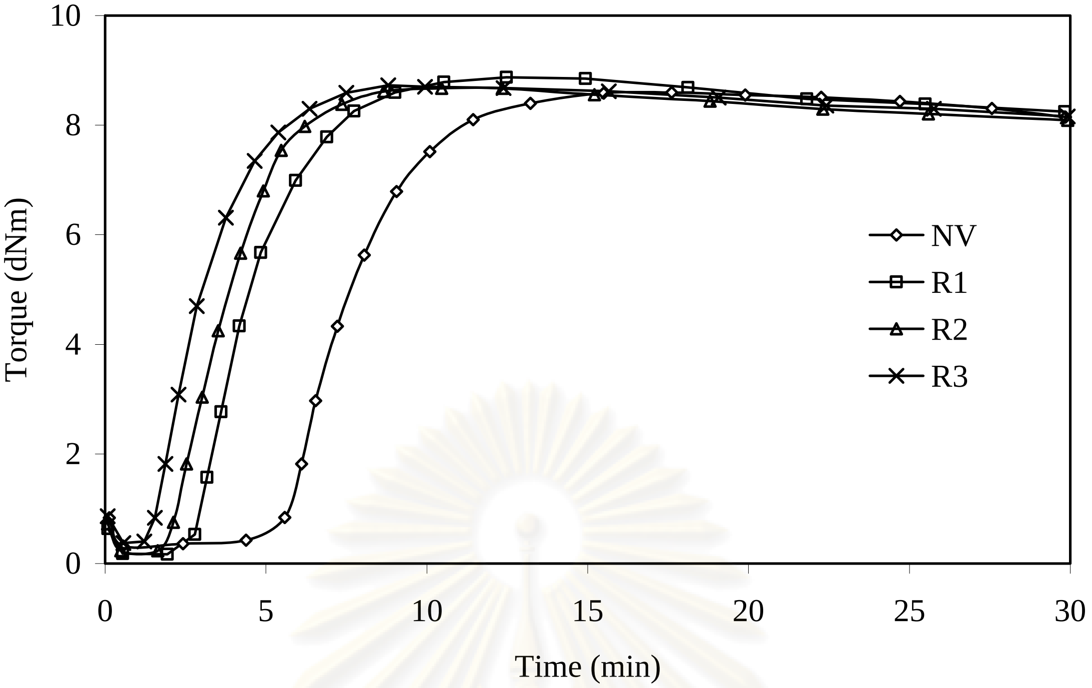


Figure 4.3 Cure behaviors of NR vulcanizate (NV) and revulcanized rubber.

In the second region of the curves, the torque rapidly increased due to the curing reaction during which the network structure was developed. The cure rate, obtained from the slope of cure curve, also increased with the increase of devulcanized rubber content. In the last region when the equilibrium was reached, a slight decrease of torque was observed in all samples which were assumed to be attributed to the slow degradation of polysulfide bonds or so-called “reversion” [1].

However, the torques at the equilibrium of those three revulcanized samples showed the comparable values with that of NR vulcanizate. These results indicate that the mechanical properties for the three samples should be comparable with those of NR vulcanizate.

4.2.2 Effect of Devulcanized Rubber Content on the Mechanical Properties

Figure 4.4 illustrates the modulus at 100% and 200% elongation, hence M_{100} and M_{200}, for all revulcanized samples. M_{100} and M_{200} were gradually increased with increasing devulcanized rubber contents (R1-R7) and their values of revulcanized samples were higher than those of the NR vulcanizate when the ratio of virgin rubber to D4 was more than 85/15. The higher moduli of the devulcanized rubber may be due to the higher crosslink density of the revulcanized rubber, arising out of the gel present in devulcanized rubber, which is also corroborated by crosslinking value data. As crosslink density increased with increasing devulcanized rubber content in the rubber matrix as seen in Table 4.4, chain mobility was decreased and more loads was required for high elongation. This result is consistent with that described by Cavalieri et al. [65].

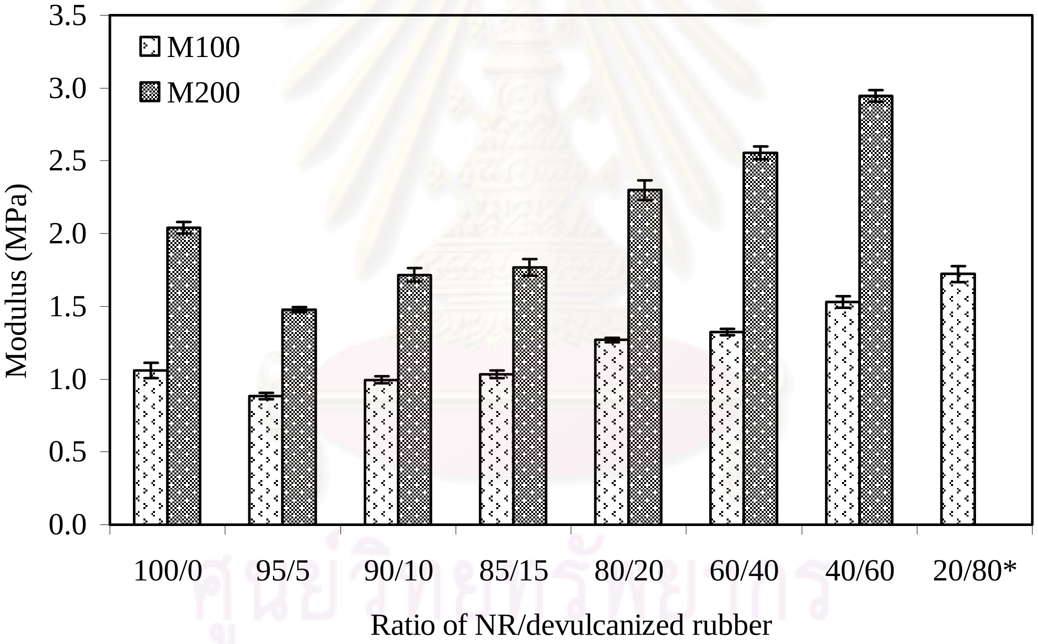


Figure 4.4 Modulus as a function of devulcanized rubber.

* elongation at break was stopped before M_{200}

Table 4.4 Formulation of revulcanized rubber by using various of devulcanized rubber content and properties of NR vulcanizate and revulcanized rubber.

Sample code	Virgin Rubber (phr[a])	Devulcanized rubber (phr[a])	Thiosalicylic acid (phr[a])	Hardness (Shore A)	Crosslink density (mol/g) ($\times 10^4$)	Gel fraction (%)
NV	100	-	-	45±1	1.47±0.02	99±0
R1	95	5	1	46±1	1.93±0.04	97±0
R2	90	10	1	46±1	2.00±0.00	96±1
R3	85	15	1	47±1	2.13±0.02	96±1
R4	80	20	1	48±1	2.20±0.04	96±1
R5	60	40	1	48±1	2.80±0.04	94±1
R6	40	60	1	50±1	3.52±0.06	93±1
R7	20	80	1	51±1	4.02±0.08	92±1

[a] Part by weight per hundred part of rubber.

The tensile strength (T_B) and percentage of elongation at breaks (E_B) of the revulcanized rubber are shown in Figures 4.5 and 4.6, respectively. It is evident that both the T_B and E_B decreased with the increase of devulcanized rubber contents. The significant change of T_B and E_B was obtained when virgin NR to devulcanized rubber ratio was equal 80/20. However, T_B values of the revulcanized rubber based on the proportion of virgin rubber to devulcanized rubber as 95/5, 90/10 and 85/15 were slightly smaller than those of the NR vulcanizate. The decrease of T_B may be mainly being caused by the low-molecular-weight component and by the polymer structural changes that occurred during the devulcanization process [16]. It is noteworthy that the improvement of E_B by 5–10% is obtained at the devulcanized rubber content of 5–15 phr.

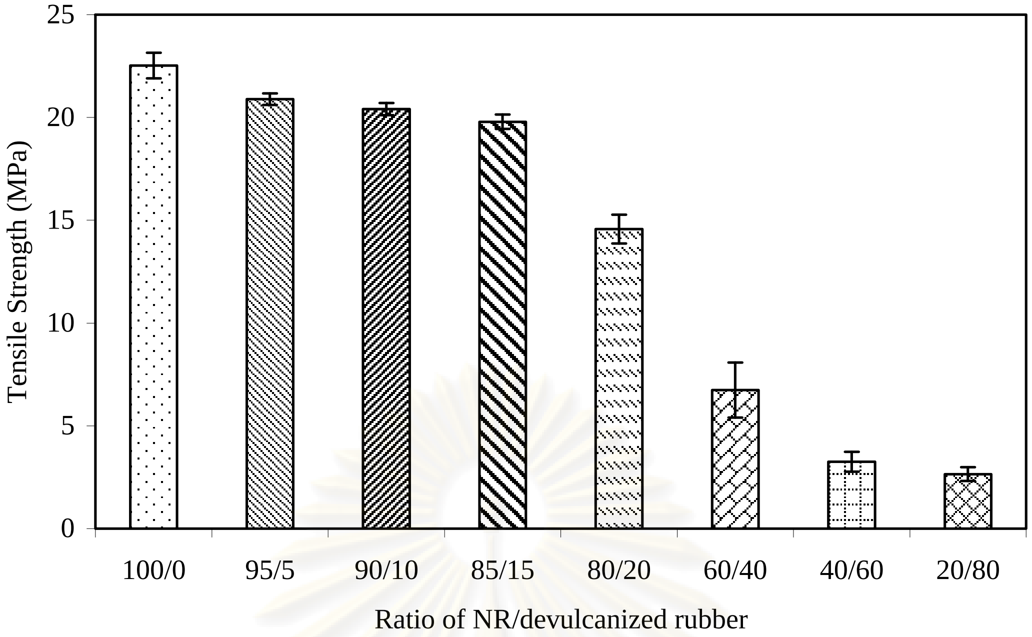


Figure 4.5 Tensile strength as a function of devulcanized rubber contents.

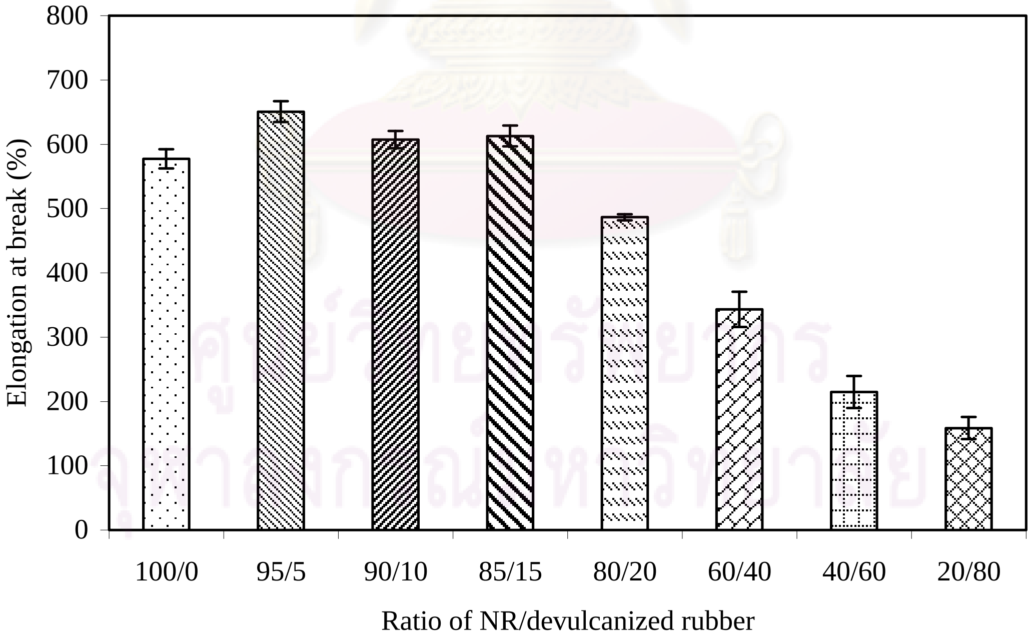
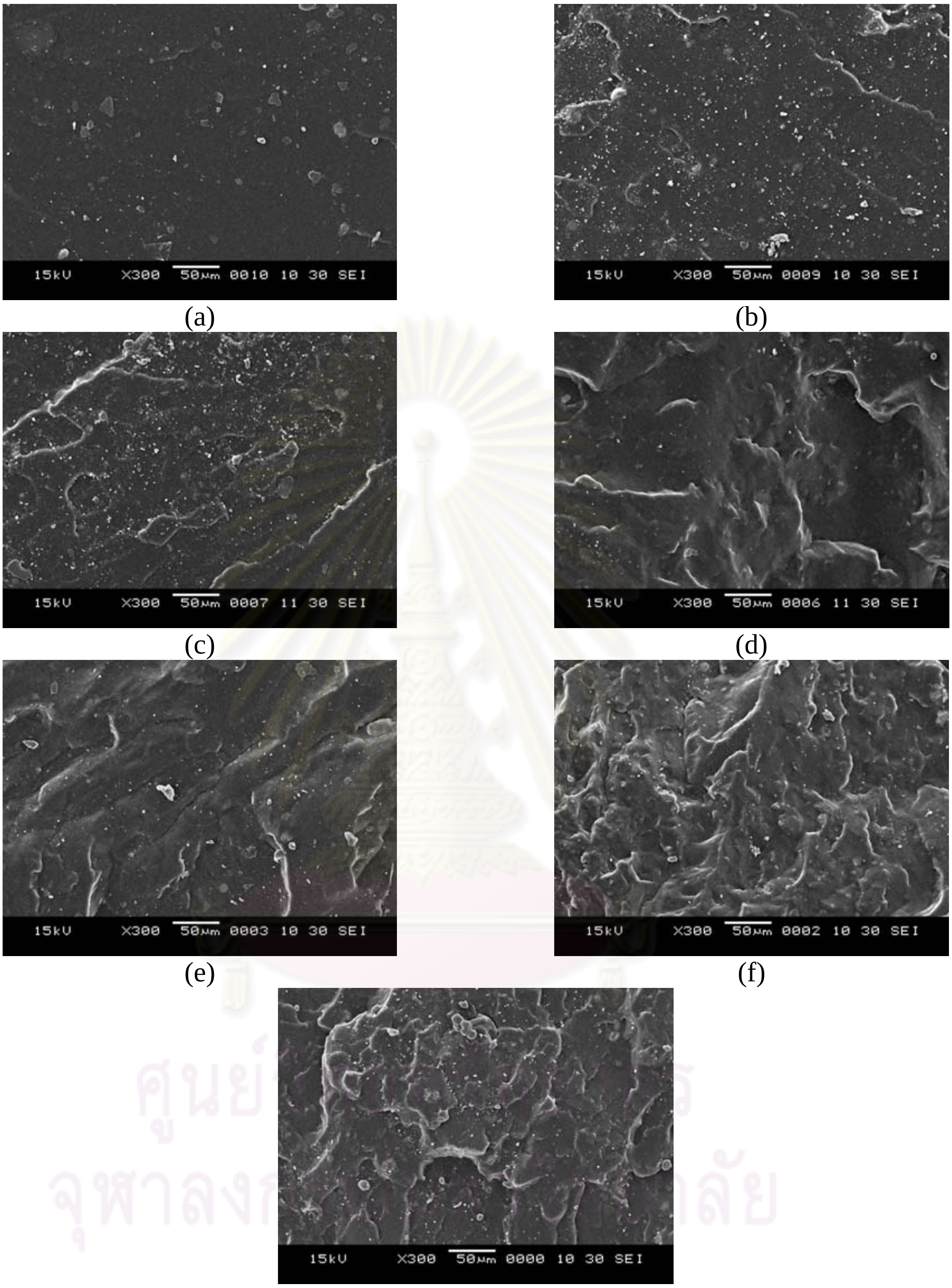


Figure 4.6 Percentage of elongation at break as a function of devulcanized rubber contents.

Another factor which is also responsible for the decrease in T_B value is that the devulcanized rubber contains crosslinked gel. When devulcanized rubber was blended with NR, much gel remains as such without dispersing as a continuous matrix with virgin rubber. Such gel remains present as weak sites for stress transmission to its surrounding (continuous matrix) resulting in a lower tensile stress. Table 4.4 represents the hardness, crosslink density, and gel fraction values of NR vulcanizate and revulcanized rubber. It is clearly that the hardness and crosslink density increased with increasing devulcanized rubber contents. It is because the higher amount of devulcanized rubber incorporated into rubber compounds vulcanizates made the sample stiffer and the devulcanized rubber contains the active cross-linking gel [63]. Gel fraction slightly decreased with increasing devulcanized rubber contents.

4.2.3 Effect of Devulcanized Rubber Content on the Morphology

Figure 4.7 shows the SEM photographs of the NR vulcanizate and revulcanized rubber samples. The number of crack paths in different directions increased with the increase of the proportion of devulcanized rubber content. It is also evident that the NR/devulcanized rubber vulcanizate prepared at 3 ratios (95/5, 90/10 and 85/15) had approximate homogeneity with the NR vulcanizate. This result confirms that at the lower content of the devulcanized rubber (5–15 phr), the higher compatibility between virgin NR and devulcanized rubber was obtained, resulting in the improvement of mechanical properties of the resulting revulcanized rubber. Accordingly, the devulcanized rubber prepared by using thiosalicylic acid can serve for a practical use with the combination of virgin rubber.



(a) (b) (c) (d) (e) (f) (g)

Figure 4.7 SEM photographs of the (a) NR vulcanizate, (b) R1 (NR/D4=95/5), (c) R2 (NR/D4=90/10), (d) R3 (NR/D4=85/15), (e) R4 (NR/D4=80/20), (f) R5 (NR/D4=60/40), and (g) R7 (NR/D4=20/80).

4.3 Properties of Revulcanized Rubber Obtained by Using Various Types of Devulcanizing Agents

4.3.1 Effect of Types of Devulcanizing Agents on the Mechanical Properties

In this study, three types of devulcanizing agents were applied to devulcanize NR vulcanizate. The condition for devulcanization was the use of incubating temperature at 140^{o}C for 48 h in the presence of devulcanizing agent at 1 phr. Formulations of revulcanized rubber obtained by using various types of devulcanizing agents in the unit of phr and properties of NR vulcanizate and revulcanized rubber are shown in Table 4.5. It was clearly that the M_{100} and M_{200} values of revulcanized rubbers by mixing with a devulcanizing agent showed the similar values. However, the M_{100} and M_{200} of revulcanized rubbers by using the devulcanized rubber in the absence of devulcanizing agent (PO) were lower than those of the revulcanized rubbers using the devulcanized rubber with the devulcanizing agent. Additionally, the M_{100} and M_{200} values depended on the devulcanized rubber content as described in the section 4.2.2 and they are related to the crosslink density as seen in Table 4.6.

The comparison of the T_B and E_B of revulcanized rubber are shown in Figures 4.8 and 4.9. The T_B of revulcanized rubber decreased by 5−10% by mixing the devulcanized rubber in the presence of thiosalicylic acid (R_1-R_3) or diphenyl disulfide (R_8-R_{10}) and decreased by 20−25% when in the presence of thiosalicylic acid/*n*-butylamine (R_8-R_{10}) at the devulcanized rubber content of 5−15 phr and E_B was improved by 5−10% when in presence of thiosalicylic acid and increased by 0−5% by mixing the devulcanized rubber in the presence of diphenyl disulfide or thiosalicylic acid/*n*-butylamine. However, T_B and E_B were not improved when the revulcanized rubber was prepared by the devulcanized rubber in the absence of devulcanizing agent (PO).

From these observations, thiosalicylic acid plays an important role not only to devulcanize the NR vulcanizate but also to revulcanized rubber. As mentioned above, the hardness and crosslink density increased with increasing the devulcanized rubber content. The gel fraction for all samples after the revulcaization showed the similar values as the gel fraction of NR vulcanizate as seen in Table 4.6.

Table 4.5 Formulations of revulcanized rubber obtained by using various types of devulcanizing agents and properties of NR vulcanizate and revulcanized rubber

Sample code	Virgin Rubber (phr[a])	Devulcanized rubber (phr[a])	Devulcanizing agent	M_{100}[b] (MPa)	M_{200}[c] (MPa)
NV	100	-	-	1.14±0.05	2.02±0.04
R1	95	5	Thiosalicylic acid[2] (TS)	0.88±0.02	1.48±0.02
R2	90	10		0.99±0.02	1.72±0.05
R3	85	15		1.03±0.03	1.77 ±0.06
R8	95	5	Diphenyl disulfide[2] (DD)	1.02±0.02	1.69 ±0.03
R9	90	10		1.07±0.02	1.93±0.03
R10	85	15		1.11±0.03	1.96±0.07
R11	95	5	Thiosalicylic acid/ *n*-butylamine[2] (TS_BU)	1.05±0.04	1.67±0.03
R12	90	10		1.13±0.03	1.97±0.07
R13	85	15		1.12±0.03	2.07±0.06
R14	95	5	Without the devulcanizing agent[b] (PO)	0.69±0.03	1.17±0.04
R15	90	10		0.83±0.04	1.38±0.04
R16	85	15		0.81±0.05	1.39±0.08

[a] Part by weight per hundred part of rubber [b] by using 1 phr

[c] M_{100} and M_{200} mean the stress at 100% and 200% elongation, respectively

Table 4.6 Formulations of revulcanized rubber of various types of devulcanized agent and properties of NR vulcanizate and revulcanized rubber

Sample code	Virgin Rubber (phr[a])	Devulcanized rubber (phr[a])	Devulcanizing agent	Hardness (Shore A)	Crosslink density (mol/g) $(\times 10^4)$	Gel fraction (%)
NV	100	-	-	45±1	1.47±0.02	99±0
R1	95	5	Thiosalicylic acid[2]	46±1	1.93±0.04	97±0
R2	90	10		46±1	2.00±0.00	96±1
R3	85	15		47±1	2.13±0.02	96±1
R8	95	5	Diphenyl disulfide[2]	46±1	1.97±0.02	97±1
R9	90	10		46±1	2.02±0.03	97±1
R10	85	15		47±1	2.13±0.03	96±1
R11	95	5	Thiosalicylic acid/ *n*-butylamine[b]	46±1	1.99±0.03	97±1
R12	90	10		47±1	2.05±0.04	97±1
R13	85	15		47±1	2.15±0.03	96±1
R14	95	5	Without the devulcanizing agent[b]	46±1	1.92±0.03	97±0
R15	90	10		46±1	1.94±0.06	97±0
R16	85	15		47±1	2.04±0.03	96±1

[a] Part by weight per hundred part of rubber [b] 1 phr

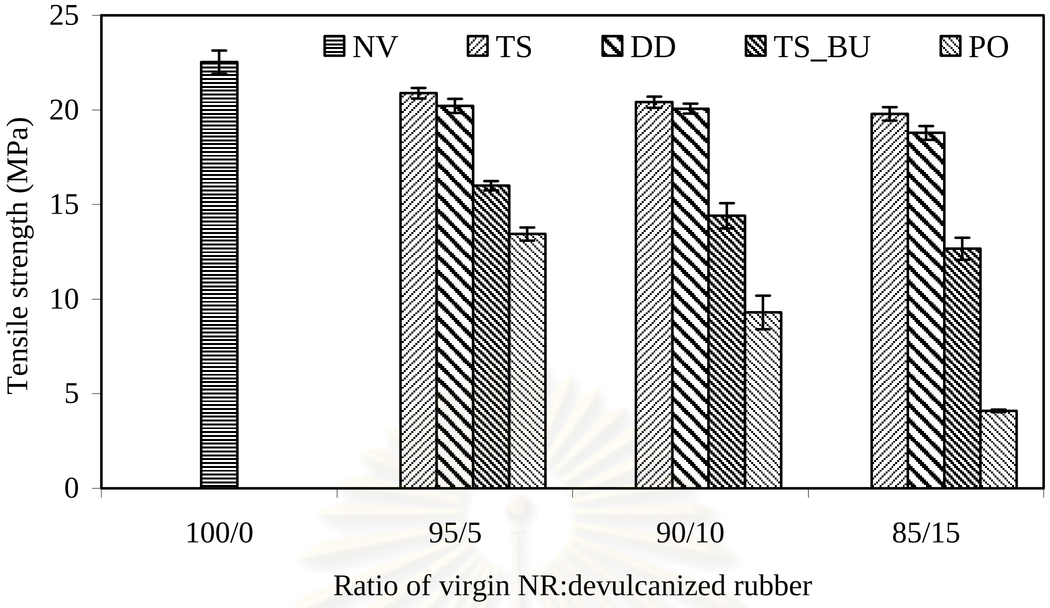


Figure 4.8 Tensile strength as a function of devulcanizing agents.

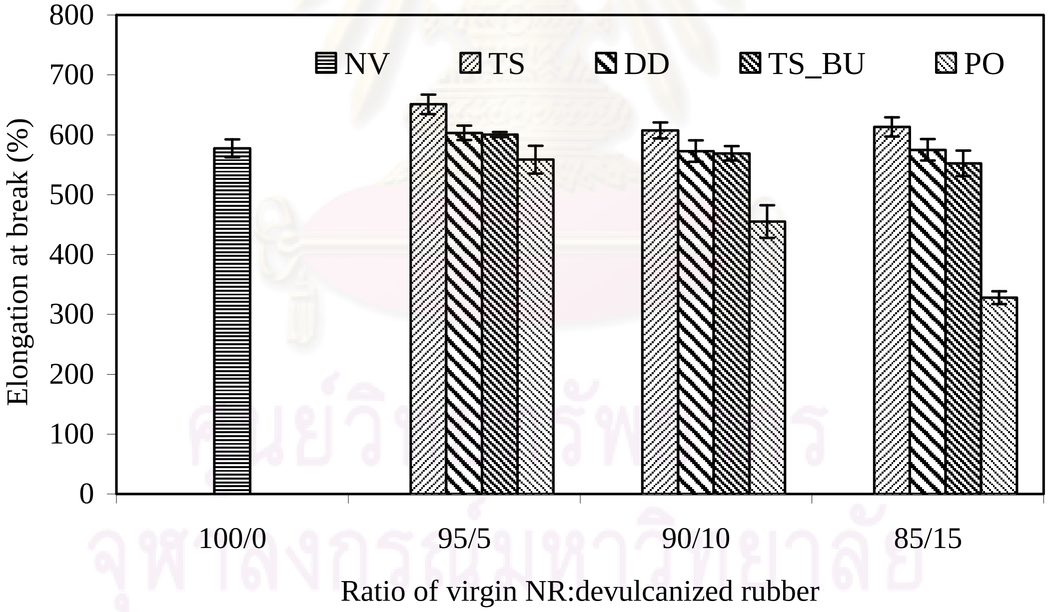
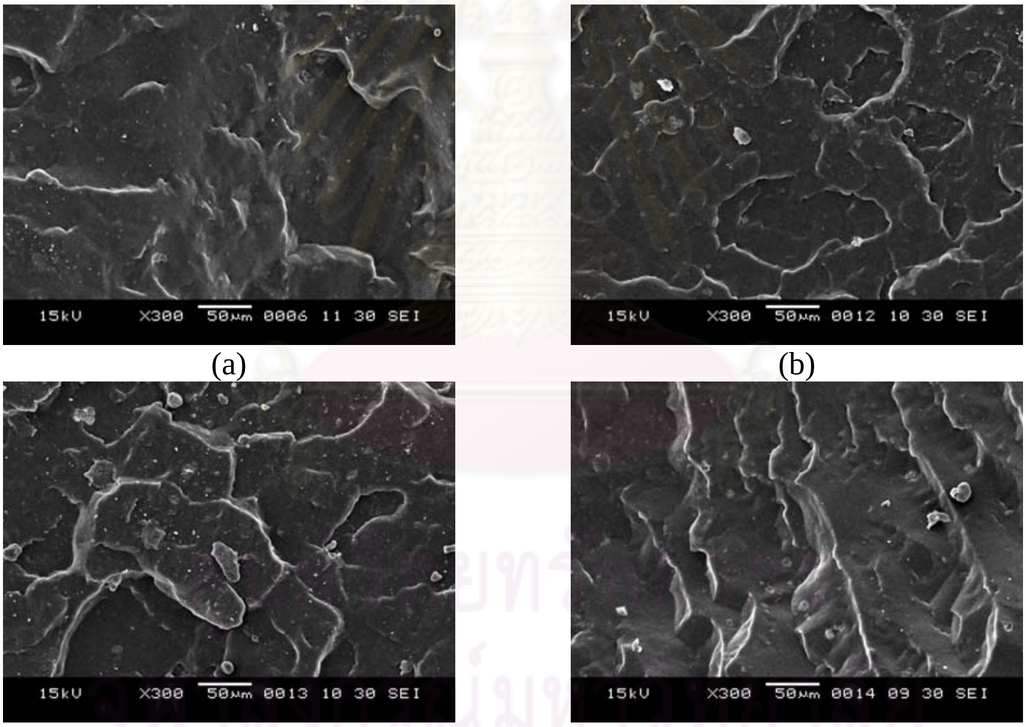


Figure 4.9 Percentage of elongation at break as a function of devulcanizing agents.

4.3.2 Effect of Devulcanizing Agents Types on the Morphology

SEM photographs of the rubber samples revulcanized by using various types of devulcanizing agents are shown in Figure 4.10. It is evident that the rubber revulcnaized by using thiosalicylic acid or diphenyl disulfide as devulcanizing agent exhibited the smooth fractured surface. The rubber revulcanized by using thiosalicylic acid/*n*-butylamine as devulcanizing agent or without the devulcanizing agent had the number of crack paths in different directions, making the revulcanized rubber vulnerable under mechanical stress. Therefore, conditions using thiosalicylic acid/*n*-butylamine and that without the devulcanizing agent were unsuitable for this devulcanization process. This result confirms that the rubber revulcanized by using thiosalicylic acid or diphenyl disulfide encouraged the compatibility between virgin NR and devulcanized rubber, which is also corresponding to the results in terms of T_B and E_B.



(a) (b)

(c) (d)

Figure 4.10 SEM photographs of rubber revulcanized at ratio NR/devulcanized rubber (85/15) in the presence of various devulcanizing agent: (a) thiosalicylic acid, (b) diphenyl disulfide, (c) thiosalicylic acid/n-butylamine, and (d) without the devulcanizing agent.

4.3.3 Effect of Devulcanizing Agents Types on the Thermal Properties at Ratio NR/devulcanized Rubber (85/15)

Figure 4.11 shows the thermal degradation characteristics of NR vulcanizates and revulcanized rubber. Degradation temperature and %weight loss values were summarized in Table 4.7. The thermal degradation of devulcanized rubber in inert gas atmosphere occurred in three temperature regions. The weight loss of the rubber sample at first low intensity stage is mainly related to thermal decomposition of vulcanization crosslinks (sulfur links), decomposition of links formed by zinc oxide, stearic acid, and partial breakage of rubber backbone. Intensive thermal depolymerization process occurred at the second stage with maximum rate of weight loss at 379.8 ^{o}C. The weight loss slows down at third stage. Above 700 ^{o}C, sample weight became constant. When compared thermal stability of NR vulcanizate with that of revulcanized rubber (NR blend with devulcanized rubber in a ratio of 85/15) by using various devulcanizing agents, the thermograph of revulcanized rubber of all samples showed the comparable values with that of the NR vulcanizate because the thermal stability depend on crosslink density [63]. In this case, the results illustrated that the crosslink density of the vulcanized rubber gave approximate value. Therefore, the thermal stability had the same tendency. However, the rubber revulcanized in the absence of devulcanizing agent exhibited slightly higher more residual weight than other samples.

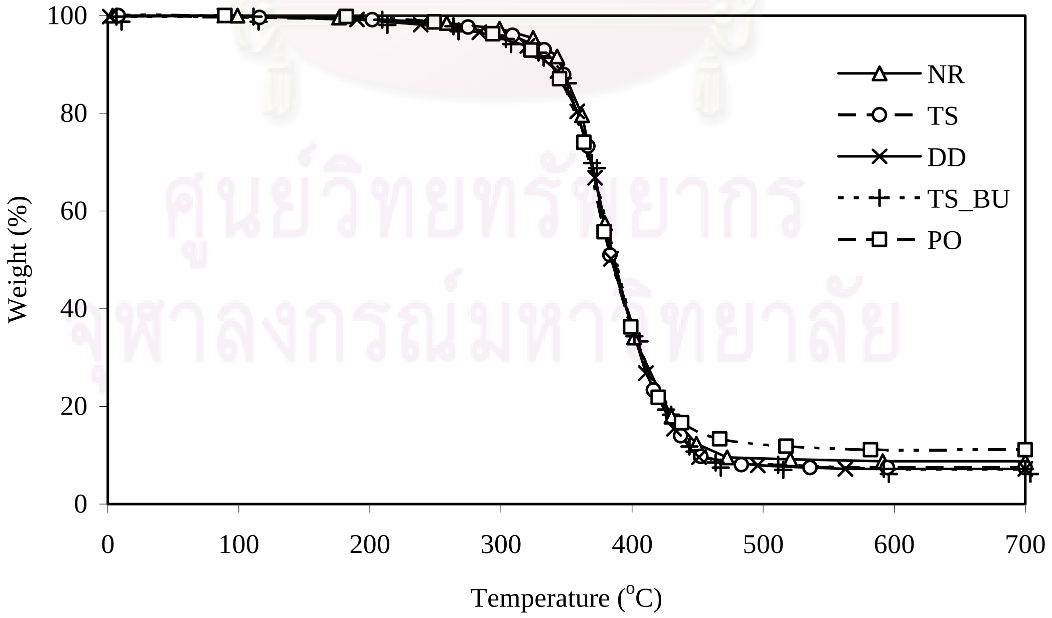


Figure 4.11 Thermogravimetric analysis of virgin NR/devulcanized rubber vulcanizates when various types of devulcanizing agents were employed.

Table 4.7 Degradation temperature and %weight loss of virgin NR/devulcanized rubber vulcanizates when various types of devulcanizing agents were employed.

Sample code	Degradation temperature (^oC)			%Weight loss	%Residue
	Start	Peak	End		
NR	312.44	375.20	472.53	90.68	9.32
TS	308.13	375.79	475.54	90.73	9.27
DD	306.64	374.45	474.95	90.70	9.30
TS_BU	309.97	376.44	473.64	90.52	9.48
PO	304.54	379.83	469.99	86.67	13.33

4.4 Effect of Thiosalicylic Acid on the Vulcanization System

As mentioned in the section 4.2.2, T_B of the revulcanized rubber was similar to that of NR vulcanizate and E_B of revulcanized rubber by using the devulcanized rubber in the presence of thiosalicylic acid was improved by 5−10% at the devulcanized rubber content 5−15 phr. Thus, in this section, the revulcanized rubber was prepared in 3 ratios, of including 95/5, 90/10 and 85/15. The effect of thiosalicylic acid on the vulcanization system was studied. Three types of the vulcanization system used to study are as follows: conventional vulcanization (CV), semi-efficiency vulcanization (Semi-EV) and efficiency vulcanization (EV). According to the result in the section 4.3.1, we can conclude that the suitable condition for devulcanization NR vulcanizate in the CV system is the use of 1 phr thiosalicylic acid and mixed at 140^{o}C for 48 h. Thus, at the same condition we would like to know whether thiosalicylic acid can be applied for devulcanization NR vulcanizate in the Semi-EV and EV whether or not. The formulations for rubber compounding and the mechanical properties of revulcanized rubber were summarized in Table 4.8.

In the case of CV system, M_{100} and M_{200} of rubber revulcanized by using the devulcanized rubber in the presence of thiosalicylic acid and without devulcanizing agent were gradually increased with increasing devulcanized rubber contents. The T_B of revulcanized rubber was decreased by 5−10% and the E_B was improved by 5−10% by mixing the devulcanized rubber in the presence of thiosalicylic acid (TS1-TS3). T_B and E_B were not improved when the revulcanized rubber was prepared without the use of devulcanizing agent (PO1-PO3).

Table 4.8 Formulations of revulcanized rubber under various vulcanization system and mechanical properties of NR vulcanizate and revulcanized rubber.

Sample code	NR[b] (phr[a])	DR[c] (phr[a])	M_{100}[d] (MPa)	M_{200}[d] (MPa)	T_B[e] (MPa)	E_B[f] (%)
CV system						
NV1	100	-	1.14±0.05	2.02±0.04	22.5±0.6	577±15
TS1	95	5	0.88±0.02	1.48±0.02	20.9±0.3	651±16
TS2	90	10	0.99±0.02	1.72±0.05	20.4±0.3	607±13
TS3	85	15	1.03±0.03	1.77 ±0.06	19.8±0.4	613±16
PO1	95	5	0.69±0.03	1.17±0.04	13.4±0.4	558±23
PO2	90	10	0.83±0.04	1.38±0.04	9.3±0.9	455±27
PO3	85	15	0.81±0.05	1.39±0.08	4.1±0.1	328±11
Semi-EV system						
NV2	100	-	1.13±0.04	2.00±0.09	22.7±1.1	539±11
TS4	95	5	0.86±0.06	1.40±0.03	17.0±0.5	593±20
TS5	90	10	0.80±0.04	1.34±0.02	16.2±0.3	585±20
TS6	85	15	0.81±0.01	1.32±0.03	15.6±0.6	552±36
PO4	95	5	0.76±0.05	1.26±0.04	14.4±1.2	579±32
PO5	90	10	0.74±0.05	1.27±0.06	13.3±0.4	555±24
PO6	85	15	0.80±0.06	1.29±0.01	10.6±0.5	529±24
EV system						
NV3	100	-	0.86±0.01	1.38±0.02	23.9±1.5	696±32
TS7	95	5	0.96±0.05	1.58±0.02	22.6±0.3	625±16
TS8	90	10	0.94±0.02	1.55±0.04	20.9±0.4	609±8
TS9	85	15	0.98±0.06	1.64±0.12	19.5±1.4	580±19
PO7	95	5	0.73±0.01	1.22±0.04	14.6±0.5	628±11
PO8	90	10	0.83±0.05	1.37±0.06	14.3±0.2	573±3
PO9	85	15	0.82±0.02	1.45±0.11	13.9±0.1	538±33

[a] Part by weight per hundred part of rubber. [b] Virgin NR. [c] Devulcanized rubber.

[d] M_{100} and M_{200} mean the stress at 100% and 200% elongation, respectively.

[e] T_B means the tensile strength. [f] E_B means the elongation at break

M_{100} and M_{200} in Semi-EV system showed the similar tendency as in CV system. T_B was decreased by 25−30% when the revulcanized rubber was prepared from the devulcanized rubber in the presence of thiosalicylic acid (TS4-TS6) and decreased by 35−55% when no devulcanizing agent (PO4-PO6). E_B of revulcanized rubber increased in 5−10% by mixing the devulcanized rubber in the presence of thiosalicylic acid or without of devulcanizing agent.

Finally, in EV system, M_{100} and M_{200} showed the similar tendency as CV and Semi-EV system. T_B values of rubber obtained by using thiosalicylic acid (TS7-TS9) and without devulcanizing agent (PO7-PO9) were decreased by 5−20% and 35−40%, respectively. E_B was declined by 10−15% in the presence of thiosalicylic acid and 10−25% in the absence of devulcanizing agent.

It was found that mechanical properties of rubber revulcanized in presence of thiosalicylic acid were better than rubber revulcanized in the absence of devulcanizing agent. This may be due to the fact that in the presence of thiosalicylic acid the devulcanization reaction was enhanced as a result of revulcanization steps. The curatives were well mixed and easily dispersed with devulcanized rubber. It was also evident that in CV system the thiosalicylic acid led to better mechanical properties in revulcanized rubber than the other system.

The crosslink density of NR vulcanizate and the revulcanized rubber are shown in Table 4.9. It was observed that the crosslink density of revulcanized rubber was increased in the presence of thiosalicylic acid in the devulcanization step. The crosslink density was increased in with the presence of the devulcanizing agent and the devulcanized rubber content. The hardness of revulcanized rubber was increased with increasing the devulcanized rubber content as the cross-link density of revulcanized rubber was increased. Gel fraction was slightly decreased with increasing the devulcanized rubber content as mention in the section 4.2.2. Similar results were observed in case of semi EV and EV system.

Table 4.9 Formulations of revulcanized rubber under various vulcanization system and properties of NR vulcanizate and revulcanized rubber.

Sample code	NR[b] (phr[a])	DR[c] (phr[a])	Hardness (Shore A)	Crosslink density (mol/g) ($\times 10^4$)	Gel fraction (%)
CV system					
NV1	100	-	45±1	1.47±0.02	99±0
TS1	95	5	46±1	1.93±0.04	97±0
TS2	90	10	46±1	2.00±0.00	96±1
TS3	85	15	47±1	2.13±0.02	96±1
PO1	95	5	46±1	1.92±0.03	97±0
PO2	90	10	46±1	1.94±0.06	97±0
PO3	85	15	47±1	2.04±0.03	96±1
Semi-EV system					
NV2	100	-	46±1	1.54±0.02	99±0
TS4	95	5	47±1	1.87±0.02	97±0
TS5	90	10	48±1	1.89±0.02	97±1
TS6	85	15	48±1	1.91±0.01	97±1
PO4	95	5	47±1	1.85±0.02	97±0
PO5	90	10	47±1	1.87±0.02	96±1
PO6	85	15	48±1	1.90±0.01	96±1
EV system					
NV3	100	-	38±1	1.60±0.03	99±0
TS7	95	5	40±1	1.97±0.01	97±0
TS8	90	10	41±1	2.05±0.02	97±1
TS9	85	15	41±1	2.12±0.00	97±1
PO7	95	5	40±1	1.96±0.01	97±0
PO8	90	10	40±1	2.02±0.03	96±1
PO9	85	15	41±1	2.09±0.01	96±1

[a] Part by weight per hundred part of rubber [b] Virgin NR [c] Devulcanized rubber

4.5 Devulcanization of a Truck Tire Vulcanizate

A devulcanization of a truck tire vulcanizate was investigated toward the practical application. Truck tire vulcanizate was devulcanized under the same conditions employed in the study on the devulcanization of NV. The sol fraction of the truck tire devulcanized by thiosalicylic acid was significantly increased, while the crosslink density was decreased compared with the case where in a devulcanizing agent is absent is shown in Table 4.10.

Table 4.10 Formulation of devulcanized truck tire**.**

Sample code	Without devulcanizing agent	Thiosalicylic acid
Truck tire rubber	100	100
Thiosalicylic acid	-	1
Process oil	-	8
Devulcanization time (min)	-	48
Devulcanization temperature (^oC)	-	140
Sol fraction (%)	9±1	30±1
Gel fraction (%)	91±1	70±1
Crosslink density (mol/g) (× 10^4)	1.33±0.04	0.53±0.01

These results indicate that thiosalicylic acid can also be utilized to destroy the three dimensional network in the truck tire. The revulcanized truck tire was then prepared by mixing NR with the devulcanized truck tire. Thus, in this section, the revulcanized rubber was prepared in 3 ratios, of including 95/5, 90/10 and 85/15. T_B and E_B of the truck tire obtained from the revulcanization using the thiosalicylic are illustrated in Figures 4.12, 4.13. The T_B of the revulcanized truck tire at the same virgin NR to devulcanized rubber ratio in the presence of thiosalicylic acid was improved by 20–30%. The similar tendency was also observed at virgin NR to devulcanized rubber ratio of 90/10 and 85/15. In the similar manner E_B was found to be improved by 5-10%. It is most likely that the devulcanized rubber can serve for practical application with the combination of the virgin rubber.

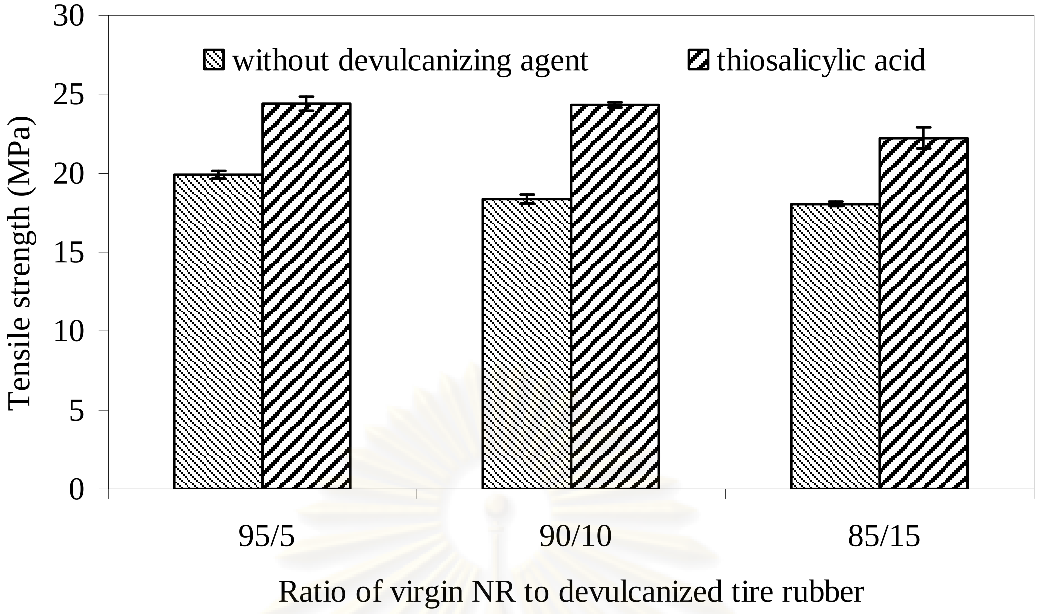


Figure 4.12 Tensile strength as a function of devulcanized truck tire.

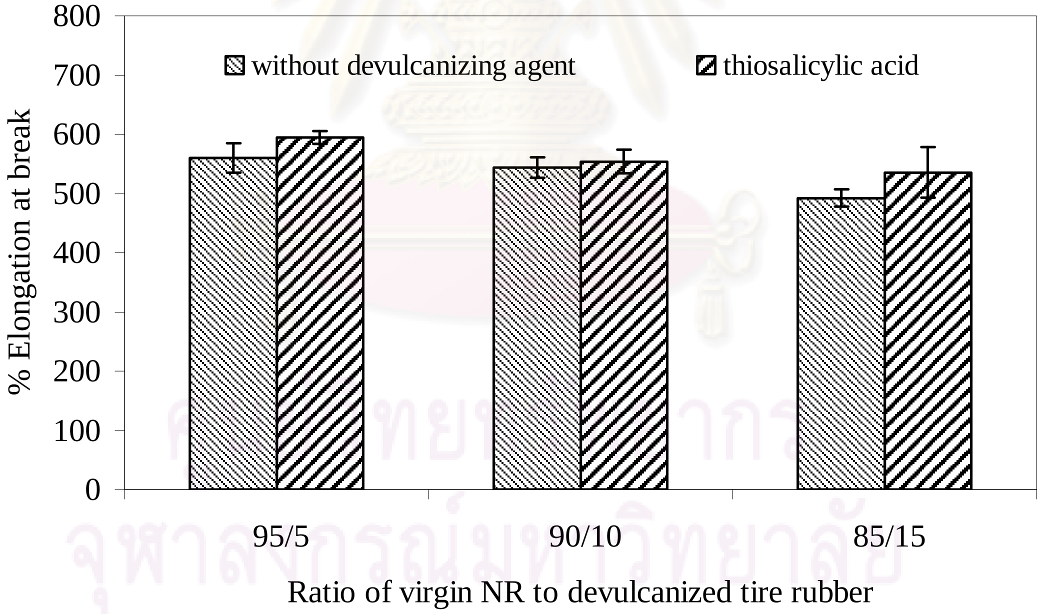


Figure 4.13 Percentage of elongation at break as a function of devulcanized truck tire.

CHAPTER V
CONCLUSION AND FUTURE DIRECTION

5.1 Conclusion

NR vulcanizate was subjected to devulcanize by using mechano-chemical process in the presence of thiosalicylic acid as devulcanizing agent. The optimum condition for mechano-chemical process of NR vulcanizate for CV system was the use of 1 phr thiosalicylic acid performed at 140^{o}C for 48 h. The sol fraction of devulcanized rubber was significantly decreased compared with the NR vulcanizate. The efficiency of thiosalicylic acid was comparable with that of the widely used diphenyl disulfide and better than that of thiosalicylic acid/*n*-butylamine. The revulcanized rubber obtained from this process showed satisfactory mechanical properties. Up to 5−10% improvement of elongation at breaks was obtained at the devulcanized rubber content 5−15 phr. It is due to high compatibility between virgin NR and the devulcanized rubber, which was observed by SEM. The devulcanization method suggested in this study is expected to have good processibility and can serve a practical use in rubber industry.

5.2 Future Direction

Further improvement on mechanical properties of devulcanized rubber will be made on the following aspects.

- The characterization of particle sizes of scrap rubber and composition should be made to improve the mechanical properties of compound because particle sizes have affected to surface area for reaction between rubber and devulcanizing agent together with energy input.
- This devulcanized rubber can use in other products such as automotive rubber part etc.

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APPENDIX

Sol-Gel Determination

Sol and gel fractions were taken as the indication of degree of devulcanization and calculated by using equations (A.1) and (A.2)

$$\text{Sol fraction (\%)} = \frac{(W_0 - W_1)}{W_0} \times 100 \tag{A.1}$$

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction (\%)} \tag{A.2}$$

where W_0 and W_1 is the dry sample mass before and after swelling, respectively.

Substituting equation (A.1 and A.2) by

W_0 = 0.2015 g, W_1 = 0.1950 g

$$\text{Sol fraction (\%)} = \frac{(0.2015 - 0.1950)}{0.2015} \times 100$$

$$\text{Sol fraction (\%)} = 3.23$$

So $$\text{Gel fraction (\%)} = 100 - 3.23$$

$$\text{Gel fraction (\%)} = 96.77$$

Determination of Crosslink Density

The crosslink density of the rubber vulcanizate was determined using the Flory–Rehner equation as follows:

$$\nu = \frac{-[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2]}{V_0[\nu_r^{\frac{1}{3}} - (\nu_r/2)]} \tag{A.3}$$

where ν is the crosslink density, ν_r is a volume fraction of the rubber network in the swollen gel, V_0 is a molar volume of the swelling solvent and χ is equal to 0.379 and used as the rubber-solvent interaction parameter [62].

The volume fraction of a rubber network in the swollen phase is calculated from equilibrium swelling data as:

$$\nu_r = \frac{\left(\frac{W_2}{d_2}\right)}{\left(\frac{W_1}{d_1}\right)+\left(\frac{W_2}{d_2}\right)} \tag{A.4}$$

where W_1 is the weight fraction of solvent, d_1 is the density of the solvent, W_2 is the weight fraction of the polymer in the swollen specimen, and d_2 is the density of the polymer.

Substituting equation (A.3 and A.4) by

W_D = 0.9015 g, W_S = 2.3234 g, W_F = 0.1265 g, ρ_D = 0.9688 g/cm^3, ρ_S = 0.867 g/cm^3.

$$V_r = \frac{\left[\frac{0.9015-0.1265}{0.867}\right]}{\left[\left(\frac{0.9015+0.1265}{0.9688}\right)+\left(\frac{2.3234}{0.867}\right)\right]}$$

$$V_r = 0.2542$$

Substituting equation (A.3) by V_1 = 106.3, χ_1= 0.393

$$\nu_e = \frac{-\left[\ln(1-0.2542)+0.2542+(0.393\times 0.2542^2\right]}{\left[106.3\left(.02542^{\frac{1}{3}}-\frac{0.2542}{2}\right)\right]}$$

$$\nu_e = 2.55\times 10^{-4}$$

Crosslink density of revulcanized rubber is 2.55×10^{-4} mol/cm^3.

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