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UTILIZATION OF RUBBER SCRAP POWDER IN COMPOUND FOR GOLF GRIP



Mr. Apichart Sermpnichakit

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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ผงเศษยางเป็นเศษผลิตภัณฑ์ที่ได้จากกระบวนการขัดยางหุ้มด้ามไม้กอล์ฟด้วยกระดาษทรายใน  
อุตสาหกรรมการผลิตด้ามจับไม้กอล์ฟ ผงเศษยางนี้ถือเป็นของเสียหากไม่ได้นำกลับมาใช้ใหม่  
ในลำดับแรกผงเศษยางควรจะร่อนผงเศษยางเพื่อเพิ่มประสิทธิภาพในการผสมกับสารเคมีในคอมพาวด์  
และยังเป็นการกำจัดสิ่งปลอมปนต่างๆ ขนาดอนุภาคหลังการร่อนผงเศษยางนี้มีค่าประมาณ 195  
ไมครอน คอมพาวด์ผสมระหว่างยางธรรมชาติและอีพิตีเอ็มที่เติมด้วยผงเศษยางนี้ได้ถูกเตรียมขึ้น  
ค่าความหนืดมูนีและแรงบิดสูงสุดเพิ่มขึ้นเมื่อเพิ่มปริมาณเศษยางผงในคอมพาวด์ผสม ในขณะที่ T2  
และ T90 กลับลดลง การเติมผงเศษยางในคอมพาวด์เป็นการเพิ่มเนื้อยางและสารตัวเร่งโดยสามารถ  
แพร่เข้าในคอมพาวด์ผสม เมื่อผสมผงเศษยางในคอมพาวด์ผสมมากถึง 100 ส่วนต่ออย่างหนึ่งร้อยละ  
พบว่าแรงดึงที่จุดขาดและระยะยืดจนขาดมีค่าสูงขึ้นดังนั้นผงเศษยางนี้แสดงสมบัติเป็นสารเสริมแรงใน  
คอมพาวด์ แต่ที่ระดับมากกว่า 100 ส่วนต่ออย่างหนึ่งร้อยละ ทั้งแรงดึงและระยะยืดจนขาดกลับ  
ลดลงอันเนื่องจากปริมาณ โครงร่างตาข่ายที่มากเกินไป เมื่อเปรียบเทียบสมบัติทางกายภาพของ  
คอมพาวด์ผสมระหว่างยางธรรมชาติ/อีพิตีเอ็มที่เติมผงเศษยางและแคลเซียมคาร์บอเนต พบว่า  
ผงเศษยางมีศักยภาพนำมาใช้ทดแทนแคลเซียมคาร์บอเนตได้ และยังพบอีกว่าเมื่อผสมผงเศษยาง  
ที่ระดับ 100 ส่วนต่ออย่างร้อยละ ในคอมพาวด์ด้ามจับไม้กอล์ฟให้สมบัติทางกายภาพที่ต่ำกว่า  
ยางบริสุทธิ์เล็กน้อยแต่ก็ยังอยู่ในเกณฑ์ที่ยอมรับได้ การนำเศษยางผงกลับมาใช้ใหม่นี้จึงน่าจะเป็น  
ประโยชน์อย่างมากต่ออุตสาหกรรมผลิตยางด้ามจับไม้กอล์ฟ

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Rubber Scrap Powder (RSP) is a by-product from the sanding process in golf grip manufacturing. It is waste unless salvaged for recycling purposes; first, The RSP shall be sieved to about 195  $\mu\text{m}$  for efficient blending with other rubber compound ingredients and for removal of other foreign material. The NR/EPDM blends filled with RSP were prepared. The mooney viscosity and maximum torque of the blend increased with increasing RSP amount while T2 and T90 also decreased. The RSP provides more rubber and the curatives such as accelerator can migrate. At a loading 100 phr, RSP improved the tensile strength and elongation at break properties since the RSP acts as reinforcing filler in the rubber matrix, therefore enhances the properties. But above 100 phr loading, both tensile strength and elongation at break decreased because of excessive crosslink density. The comparison of mechanical properties of RSP and  $\text{CaCO}_3$  filled NR/EPDM compound reveals the potential of using RSP as a substitute for  $\text{CaCO}_3$ . It is also found that RSP can be incorporated into the golf grip compound formulation with the very slight drop in the properties, which is still within acceptable limit even at 100 phr of RSP. This recycling RSP was shown to be very beneficial to the golf grip industry.

Field of Study... Petrochemistry and Polymer Science... Student's signature.....

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# CHAPTER I

## INTRODUCTION

The recycling of used rubber products, particularly that of automobile tires, is the most important issue for the rubber industry from the viewpoint of global environmental concerns. The recycling can save the limited resources on the earth. In the case of the rubber recycling, however, there is a problem. Polymeric materials are roughly divided into thermoplastic and thermosetting ones. Recycling of the thermoplastic polymer may be accomplished by a reverse physical treatment; that is, by heating the resin and cooling it to room temperature to obtain desired recycled products. On the other hand, thermosetting polymer materials are difficult to recycle because they have three-dimensional chemical crosslinks, and accordingly they are insoluble. The latter is the case for the vulcanized rubber. Therefore, used tires are, at the moment, used land filling or burned as fuel, mainly in cement kilns. This usage may be an effective energy conservation process and one of useful ways of used products. However, this is not an environment friendly process. The recycling of used rubbers must be a much more favorable approach to solve the waste problem and to save petroleum resources.

The golf grip mostly was made by the molding process. The surfaces between the mold sections when the mold is closed produce a parting line. If much rubber residue is allowed to build up in this area of the mold, the mold sections will not mate together completely; even under the extreme squeeze pressure of the press. The result is a noticeable "flash" at the parting line on the surface of the product. Rubber flash at the tool parting lines requires additional manufacturing processes to remove it, and quality assurance (inspection) steps to monitor the level and effectiveness of flash removal. However, scrap rubber must be handled and accounted for, all of which adds to the overall production cost. Generally, This rubber flash at the tool parting lines of golf grip product is removed by sandpaper and grinding wheel in buffing process which is part of golf grip manufacturing. Unfortunately, this process causes the non-value added material which called "Rubber Scrap Powder" or "RSP". It is essential to

eliminate this powder according to ISO14001 requirements consequences of cost reduction.

### **1.1 Problem Statements**

At present, there are about 1.5 tons of RSP every month from the factory. This waste comprises 20-30% of the total vulcanized rubber scrapped each month. It is estimated that by next year, the amount of RSP wasted will reach 2.0-2.5 tons per month because of increasing production.

### **1.2 Benefits**

This RSP can be incorporated into a virgin compound within acceptable limit to meet mechanical properties requirement of golf grip product. The main reason that uses RSP as fillers in virgin compound is to reduce cost. The RSP cost is much less than the virgin compound, thus the price reduction is generally in proportion to the level of RSP added.

### **1.3 Objectives of the Research work**

This work is to study the appropriate amount of RSP incorporated with the virgin compound, which maintains the mechanical properties of the golf grip within the acceptable limit.

### **1.4 Scope of the Research Work**

The source of RSP used in this work comes from an industry engaged in the manufacturing of natural rubber and EPDM based golf grip compound. This research will attempt to salvage the RSP back into the manufacturing process of the golf grip. The research work consists of four sections. The first section, the effect of RSP loading on mechanical properties of the NR/EPDM blend compounds was investigated. In the second section, the migration of curatives from RSP to raw rubber was studied. In the third section, the use of RSP is compared with reinforcing filler

such as carbon black (N330), silica (Ultrasil VN3) and inert filler such as calcium carbonate in the NR/EPDM blend compounds. In the last section, the effect of the RSP on the properties of a typical golf grip formulation was demonstrated. The following vulcanized rubber properties are measured in this work.

- Mooney viscosity, ML 1+4 100°C (ISO 289-1)
- Cure characteristics- MH, ML, T2 and T90
- Stress and strain (ASTM D412-98a)
- Tear strength (ISO 34)
- Abrasion loss (BS. 903 Part A9 )
- Hardness shore **A** (ASTM D2240-97)
- Specific gravity
- Crosslink density

The results are summarized and documented in this thesis.



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## CHAPTER II

### THEORY AND LITERATURE REVIEWS

In 1844, U.S. Patent number 3,633 [1] was granted to Charles Goodyear for his “Gum Elastic Composition”. In a published circular describing the sulfur vulcanization of his gum elastic composition, he stated:

- No degree of heat, without blaze, can melt it
- It resists the most powerful chemical reagents, aquafortis (nitric acid), sulfuric acid, essential and common oils, turpentine and other solvents.

Goodyear’s sulfur vulcanization of rubber fueled the industrial revolution and made possible the development of the rubber-tired automobile and much of transportation as it exists today. Since he was so successful and correct in his comments about vulcanized rubber, he also created one of the most difficult materials to recycle, as it will not melt, dissolve or lend itself to the usual methods of chemical decomposition. Interestingly, Goodyear recognized the need for methods of reuse of his spent rubber articles and in 1853 he patented the ideal of adding vulcanized rubber powders to virgin unvulcanized material, a process known as regrind blending today.

Recently, the importance of recycling waste materials has been increasing for all industries worldwide. For rubber products, the automotive and transportation industries are the biggest consumers of raw rubber. Rubber waste is usually generated during the manufacturing process of products for these industries and by disposal of post-consumer (retired) products, mainly including scrap tires. For example, in Japan, about one million tons of scrap tires are generated annually.

The oldest and simplest reclaiming method in the rubber recycling industry is called the “pan method”. The reclaimed rubber obtained by this method is far inferior in physical properties to virgin rubber, however, from the viewpoint of energy balance, material recycling of rubber waste is preferable to other recycling techniques. In spite of this, material recycles in the form of crumb rubber and reclaimed rubber accounted for only about 11% of total scrap tires in 1998. New material recycling technologies such as the microwave method and the ultrasonic method have been developed with the aim of shorter reactor times. However, here also the reclaimed

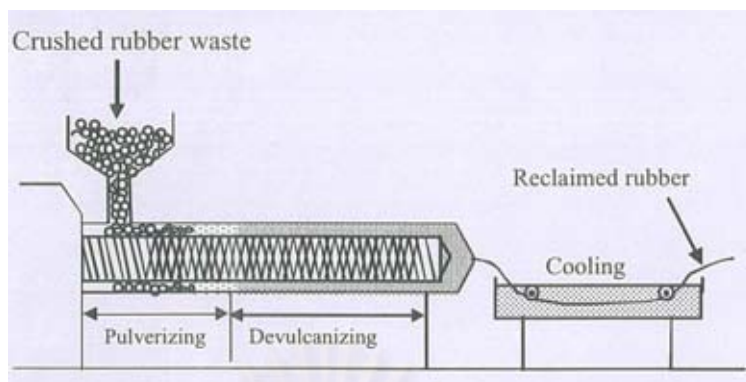


rubber from these methods are not so excellent in quality as to be widely applicable to practical rubber products.

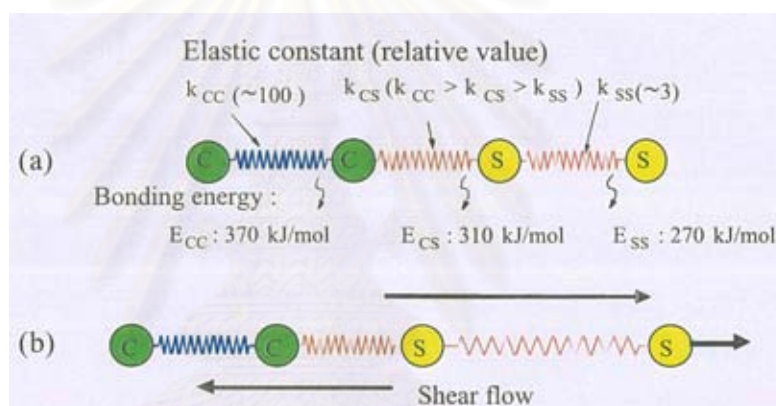
## 2.1 Principle of Producing Reclaimed Rubber [2]

Material recycling of crosslinked polymers, including rubber, is generally thought to be difficult using a simple heating procedure, because of the three-dimensional network structure restricting the material from melting. In the rubber recycling process by the conventional pan method, finely ground rubber powder mixed with oil and reagents is heated with steam in a pressure vessel at a temperature of  $\sim 200^{\circ}\text{C}$  for more than 5 hours. Moreover, usually this process has to be followed by several procedures (refining and straining) before obtaining the final reclaimed rubber. As noted above, the reclaimed rubber obtained by this method is inferior in quality to virgin rubber. This is due to the occurrence of unselective breakage of both the crosslinking points and main chain (C-C) bonds in the rubber.

In the newly developed continuous recycling process various chemical reactions corresponding to selective breakage of crosslinking points (so called, devulcanization) can be efficiently controlled by optimizing the parameters in the reactor such as shear stress, temperature, and internal pressure. The continuous recycling process for crosslinked rubber waste is performed in a modular screw type reactor as schematically shown in Fig. 2.1 The screw configuration with the modular screw elements (right-hand screw, kneading disk, etc.) is suitably designed to be applicable to a continuous recycling process. In the first pulverizing zone of this process, roughly crushed rubber material is converted into fine particle by high shear stress, and heated to the devulcanization reaction temperature quickly. The residence time is assured to be long enough to complete the devulcanization reaction under shear flow in the next devulcanizing zone. In this reaction zone, fine particles of crosslinked rubber become highly elongated by filling and shearing with the kneading disk elements, and are thus eventually plasticized.



**Figure 2.1** Schematic illustration of the reactor for the product of reclaimed rubber [2].



**Figure 2.2** Breakages of crosslinking points in high shear flow: (a) model for the network chain; (b) deformation of the network chain (particularly, S-S bonds) by shearing [2].

A basic understanding of the cleavage of crosslinking bonds under high shear stress is suggested as follows. As shown in Fig. 2.2, there appears to be only a small difference in the bond energy between C-C bonds and C-S bonds. Hence, by simple heating in a pressure vessel, cleavage of both C-C and C-S of S-S bonds may occur unselectively. This leads to the lowering of the physical properties of reclaimed rubber by the conventional method. On the other hand, with regards to the elastic constant  $k$  for these bonds (estimated approximately on the basis of the values for crystals), the  $k$ -value for the S-S bonds can be estimated to be about  $1/30^{\text{th}}$  that for the C-C bonds, as shown in Fig. 2.2(a). Generally, it is understood that the mechanical

behavior of crosslinked rubber may be mainly controlled by the entropic term in the strain energy. In contrast with this entropic deformation behavior, at extremely higher shear stresses induced by filling and kneading in the reactor, most of the rubber molecules may become fully elongated to their limited extensibility. Under these conditions, the bonds having lower elastic constant (the S-S bonds) may become more extended in comparison with bonds having higher elastic constant (the C-C bonds), in an elastic manner as shown in Fig. 2.2(b). That is, the elastic energy induced by high shearing may be particularly effective on the S-S bonds, causing the selective breakage of crosslinking points.

The use of rubber reclaim has decreased since World War II, when 32% of all rubber used was rubber reclaim. The decline is due to shortages in natural rubber supply, combined with technical, environmental and economic factors. In the intervening years, a number of inexpensive high-performance synthetic rubbers have been replacing natural rubber. Specific factor in the decline of reclaim included [3].

- Radial tires, which comprise over 80% of the market, have a lower tolerance for reclaim.
- Traditional non-tire applications, like shoe soles, floor mats, car mats, battery cases are increasingly being taken over by plastics.
- Reclaim installations have extreme difficulties meeting modern environmental and worker health and safety standards.
- The development of crumb production offers a cheaper extender for rubber compound than reclaim; the price for crumb varies from US\$ 300 to US\$ 550/ton while reclaim cost from US\$ 550 to US\$ 1200.
- The capital investment needed for economically viable installations is quite high.

## 2.2 The Production of Crumb Rubber

### 2.2.1 Ambient Grinding [4]

Dry grinding at ambient temperature is the simplest grinding process. The rubber is reduced to smaller chips and then further reduced to fine size (10 to 40 mesh). The processes usually involve the following activities: coarse crumb sizing,

ultra-fine sizing, metal separation, fiber separation, bagging, and weighing. The particle size and the distribution of particle sizes in crumb rubber produced by ambient grinding depend on the number of times crumb is recycled through the mill and the type of mill used. In general, the primary mill will reduce the large pieces of waste rubber to sizes in the range of 10 to 40 meshes. This size is considered suitable for non-dynamic applications of rubber.

As a result of the high cost of liquid nitrogen, which is used as a refrigerant in the cryogenic method, size reduction at an ambient temperature is used more often for coarse powder production.

### **2.2.2 Cryogenic Grinding [4]**

In cryogenic grinding, waste rubber is first reduced into smaller chips (about  $\frac{3}{4}$  inch long). After the tires are shredded into  $\frac{3}{4}$ -inch chips, the processor separates steel by magnetic separation and also removes the textile cord. The rubber chips are then reduced to rougher, smaller pieces by different milling devices in a series of screening and re-grinding operations to achieve the desired particle size. Data reported by Klingensmith and Baranwal [5] indicate that the costs of ambient and cryogenic grinding are comparable. Klingensmith and Baranwal [5] state that the price of liquid nitrogen, used for freezing during the cryogenic method, has come down significantly, and the ground rubber produced from this method can compete on a large scale with ambient-ground products.

The cryogenic process produces fairly smooth fracture surfaces. Little or no heat is generated in the process. This results in less degradation of the rubber. In addition, the most significant feature of this process is that almost all of the fiber or steel is liberated from the rubber, resulting in a high yield of useable product with little loss of rubber.

Table 2.2 reveals the effect of different levels of cryogenically ground crumb rubber in a rubber compound when formulated as shown in Table 2.1. Table 2.3 is provided as another example that demonstrates the effect of crumb rubber on the mechanical properties of a compound.

In addition, Table 2.4 shows ingredients for cryogenically ground butyl in the inner lining of a tire. Table 2.5 shows the effect of the cryogenically ground butyl in a tire inner liner with formulation as shown in Table 2.4. Table 2.6 shows the formulation of cryogenically ground butyl in an ethylene propylene diene monomer (EPDM) compound, and Table 2.7 shows the effect of particle size and loading for cryogenically ground EPDM on the mechanical properties of the rubber.

**Table 2.1** Cryogenically ground rubber (20 Mesh) in an SBR 1502 compound [4]

Formulation Ingredient	Level
SBR 1502	100.0
Zinc oxide	5.0
Stearic acid	1.0
TMQ	2.0
N660 carbon black	90.0
Aromatic oil	50.0
Sulfur	2.0
MBTS	1.0
TMTD	0.5

**Table 2.2** Properties of compound with 17, 33 and 50 percent crumb addition [4]

Properties	Control	17% Crumb	33% Crumb	50% Crumb
Mooney viscosity	40	61	91	111
Rheometer max. torque	59	57	33	34
T90, min.	2.5	2.4	1.8	2.0
Tensile strength (psi)	1,470	1,150	870	560
Ultimate elongation %	330	330	300	27

**Table 2.3** Test results of soft tread grade compounds containing 5 percent by weight of crumb rubber [4]

Properties	A	B	C
Tensile strength (psi)	2,950	2,210	2,080
Elongation %	820	750	740
100% modulus (psi)	106	105	106
Hardness shore A	52	52	53
Die C tear (psi)	253	240	243

A = control (soft tread grade compound)

B = control + 5% by weight of crumb rubber from tread

C = control + 5% by weight of crumb rubber from whole tire

**Table 2.4** Cryogenically ground butyl in the inner liner [4]

Formulation Ingredient	Level
Butyl HT-1068	80.0
RSS #1	20.0
N-650	65.0
Mineral rubber	4.0
Durez 29095	4.0
Stearic acid	2.0

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**Table 2.5** Cryogenically ground butyl at various levels [4]

Properties	Control	5%	10%	15%
Masterbatch, phr	188	178.6	169.2	159.8
Cryo ground butyl	---	9.4	18.8	26.2
Cure time, T90, min.	47.5	46.3	47.0	46.5
Cure rate, lbf. In./min.	0.59	0.58	0.55	0.56
Tensile strength (psi)	1,410	1,350	1,290	1,280
300% modulus (psi)	1,120	1,040	1,000	950

**Table 2.6** Cryogenically ground butyl in EPDM compound [4]

Formulation Ingredient	Level
EPDM	100.0
N-650	70.0
N-774	130.0
Paraffinic oil	130.0
Zinc oxide	5.0
Low MW PE	5.0
Stearic acid	1.0
Antioxidant	1.0
Sulfur	1.25
Sulfads	0.8
Methyl tuads	0.8
Ethyl tellurac	0.8
Altax	1.0

**Table 2.7** Cryogenically ground butyl at 10 percent and 20 percent levels [4]

Properties	Control	40 Mesh	60 Mesh	80 Mesh	100 Mesh
Cryogenically ground rubber at 10% levels					
Tensile strength (psi)	1,410	1,290	1,430	1,470	1,440
Ultimate elongation, %	410	330	340	400	380
300% modulus (psi)	1,180	1,220	1,230	1,230	1,220
100% modulus (psi)	535	490	530	490	480
Hardness (psi)	73	70	70	70	71
Die C tear (psi)	193	175	173	171	172
Cryogenically ground rubber at 20% levels					
Tensile strength (psi)	1,410	1,230	1,360	1,460	1,410
Ultimate elongation, %	410	320	390	390	390
300% modulus (psi)	1,180	1,220	1,300	1,200	1,160
100% modulus (psi)	535	450	500	460	460
Hardness (psi)	73	72	70	69	68
Die C tear (psi)	193	178	163	165	181

### 2.2.3 Water Solution Grinding [4]

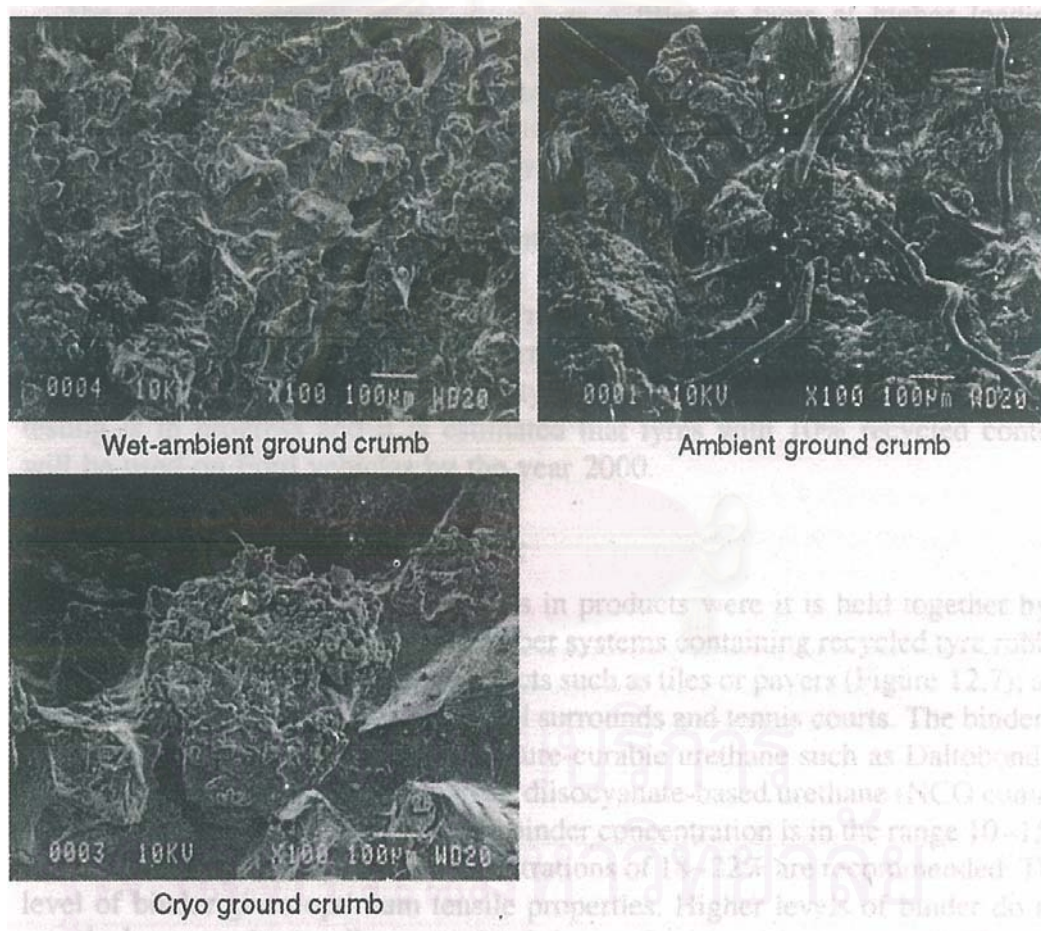
Wet grinding involves feeding coarse ground rubber into water, followed by grinding between closely spaced wheels (similar to flour mills). The material is finely ground, and sizes ranging from 60 to 120 mesh are commonly made and used. It is reported that particle sizes as small as 500 mesh can be produced using this method. Due to its uniformity and cleanliness, these products are used in many tire compounds.

Rouse, as compiled by Khait et al. [6], reported the development of high-surface area-fine rubber powder of 80 mesh by wet grinding. These rubber powders are highly resilient and can be used in many component parts of the tire as reinforcing fillers and processing aids. It is reported that rubber powder from 80 mesh tires behaved more like a reinforcing carbon black than an inert filler, due to the enhanced surface morphology of the rubber particles.



### 2.3 Quality of Crumb Rubber [7]

The main properties of recycled crumb rubber that determine its quality are its particle size distribution (PSD) and level of fiber contamination. Often crumb with a specific particle size i.e. 20 mesh and a narrow PSD is preferred. The presence of fiber and steel is undesirable and should be as low as possible. New ASTM specifications call for the metal content to be below 0.1% and the fiber content to be below 0.5%. Since “peel” and “buffing” are by-products of the retreading industry, there is little contamination problem with these.



**Figure 2.3** Micrographs of wet-ambient ground crumb, ambient ground crumb and cryogenically ground crumb [7].

Note, the ambient ground crumb shows ductile fibril features while the cryogenically ground crumb is more cubic with smooth faces.

## 2.4 Ground Rubber Crumb in Filler Applications [7]

This technology involves grinding rubber articles into crumb and then reusing it as particular filler in lower-performance rubber articles and as a toughening agent in asphalt. Up to 60% of the original weight of a tire can be recovered as a powder known as ground tires (GRT)

Many rubber manufacturers currently carry out primary recycling on a small scale by adding in-house ground rubber scrap to fresh compounds. This can be done at loadings of up to 10 wt%. However, beyond this, the physical properties of the rubber end product begin to deteriorate since the rubber crumb acts primarily as inert filler.

Historically, untreated ground rubber crumb when added to virgin rubber products gave increased viscosity and decreased tensile strength, and these factors led to its predominant use in non-technical applications such as flooring, mats and footwear. These poor properties can be attributed to the fact that a discrete vulcanized rubber particle in a matrix of unvulcanized rubber does not bond to the compound when the mix is vulcanized. Other properties such as rebound, resilience and flex fatigue resistance also suffer as a result of the lack of adhesion across the crumb/matrix interface. Thus, untreated rubber crumb is mainly use as a low-loading filler or extender in applications where a modest reduction in properties is acceptable. Smaller particle size crumbs do allow greater loading levels but at greater expense due to the increased granulation involved. The smallest particle size of crumb rubber commercially available at present is 75  $\mu\text{m}$ .

The addition of rubber crumb, even at low concentrations, to virgin rubber, generally results in decrease in physical properties. For instance, it has been shown that the addition of 10% rubber crumb (425-600  $\mu\text{m}$ ) to a virgin compound, led to a 15% reduction in tensile strength. Phadke [7] attributed the poor properties of virgin rubber – rubber crumb vulcanizes, to poor adhesion and the relatively large crumb particle size.

It was also found that the addition of ground rubber crumb to virgin SBR compounds led to decreased maximum rheometer torque and increased tendency to “scorch”. These effects were attributed to migration of the curatives from the matrix to the rubber particles. The migration of sulfur into the ground vulcanized rubber particles triggers the release of bound accelerator fragments from the rubber crumb and these diffuse into matrix, speeding vulcanization.

A French company, Roll-Gum, recycle three million used tire per year into rubber castors, using a process which shreds tires, removes the metal and fiber and grinds the contaminant free rubber to give an ultra-fine powder. The rubber powder is then revulcanized and molded into castors.

An application for rubber crumb that is growing in popularity, especially in Canada, is anti-fatigue, anti-static floor matting. Such mats can be used to provide a comfortable surface in the workplace where they decrease fatigue and aches caused by prolonged standing. Anti-fatigue mats based on 100% recycled rubber are 25 times softer than concrete and provide a non-skid surface. Such fatigue mats are manufactured by Les entreprises Reveco Inc., (Montreal, Quebec, Canada).

## **2.5 Factors Affecting Both the Costs and Benefits of Increasing the Recycled content in New Tires [4]**

A number of crumb rubber production technologies are available on the market. While effort is underway to develop a sound technology that is cost-competitive, none has been accepted in the tire industry for wide use in new tire production.

There is an increasing need for fine waste tire rubber powder of 80 mesh and finer, in order to create parts with smoother surfaces. Finer powders also improve the physical properties of rubber compounds and allow for faster mixing times when rubber powder is used as a partial substitute for virgin rubber. Few techniques, however, have been found that can produce fine tire rubber powder economically.

In order to substantially increase the use of crumb rubber in new tires, several factors must be considered

- Reliable source of crumb rubber with consistent physical characteristics such as size, shape, and surface texture. Equally significant is the consistency in the chemical composition of the ground rubber.

- Waste tire recycling involves tire collection, transportation, and processing of waste tires to produce new high performance, raw materials, blend treatment and separation technology. The logistics of collecting and transporting waste tires to processing plants—or transporting processed rubber to tire manufacturing plants—in a timely manner is considered one of the cost determinants.

- Maintaining consistency in crumb rubbers for use in new tires has been difficult primarily because of the many compounds used in tires.

- The processing methods must be consistent in the way the crumb rubber is produced. The same is true for the mixing of ingredients and tire building. The performance characteristics of the crumb rubber compounds must be equivalent to the virgin compounds they are replacing.

- Economic incentives need to be in place, particularly in the development of new technology, to produce high-quality crumb rubber. High-value products that are competitive in pricing and performance must be derived as a raw material from the waste tires.

- The low price of virgin rubber sets upper limit on the price of recycled rubber.

- At the present time, the price of tires with recycled content appears to be comparable or slightly higher to that of tires made from virgin compounds.

In the effort to regenerate carbon black from waste tires, Mondal et al. [4] concluded the following:

- Regenerated carbon blacks have higher surface area, due to the increase in surface roughness, compared to virgin carbon blacks.

- The structure of regenerated carbon blacks remains almost the same as that of virgin carbon black.

- Compounds containing regenerated carbon blacks have a lower cure rate, comparable dispersion, lower hardness, and lower modulus when compared to the virgin carbon blacks.

- The tensile strength of compounds containing regenerated carbon black is comparable to that of the virgin carbon black.

- Compounds containing regenerated carbon black give more scorch safety, higher optimum cure time, higher tear strength, higher heat build-up and higher elongation at break compared to that of respective virgin black.

- Compounds containing regenerated carbon black give better aging properties, compared to that of virgin black.

The above outlined factors need to be considered in designing a feasible approach to increase the recycled content in new tires. Most of the ongoing research is focused on addressing the technical feasibility at a development level and does not address the commercialization aspect of the methods and processes developed.

Ford and Michelin estimated that recycling waste tires back into new tires (with the use of recycled rubber at a rate of 10 percent) could cut the number of tires going into the landfills by approximately 33 million tires annually, or 12 percent of the approximately 281 million waste tires generated in 2001. (Annual waste tire generated is assumed as approximately one tire per capita). On this basis, approximately 34 million waste tires are generated in the State of California alone (approximately 12 percent of the total waste tire generated in the U.S. per year).

Chandra and Pillai [3] concluded that in addition to the physical properties that impact the performance of tires with increased recycled content, the savings are “not significant enough” to merit the effort of introducing recycled materials into tire formulations in larger volumes.

## **2.6 Literature Reviews**

Jacob et al. [8] studied the utilization of powdered EPDM scrap in EPDM compound. The rubber powder was factory scraps from an industry engaged in the manufacturing of EPDM based window seal compound. Processability, curing characteristics and vulcanizate properties of EPDM compounds containing ground waste EPDM (W-EPDM) have been studied. Ground waste was prepared from factory scraps, using a mechanical grinder with silicon carbide abrasive wheel rotating at 2950 rpm. The particle size shows a range between 2 and 50  $\mu\text{m}$  with an average size of 10  $\mu\text{m}$ . Particle surface seems to be rough and convoluted and mild oxidation during the abrasion enhances the aggregation of particles. Mooney scorch time and the maximum rheometric torque of the EPDM compound decrease gradually with increasing W-EPDM content. Migration of curatives between the virgin rubber and waste rubber phases is believed to be the reason for the variation in the curing behavior. The processability of the EPDM compound shows improvement on addition

of W-EPDM (that is, both die swell and extrudate distortion are less). The vulcanizate properties of the W-EPDM –filled EPDM compounds reveal the reinforcing nature of the ultrafine W-EPDM particles. Comparison of W-EPDM with an inert filler like precipitated  $\text{CaCO}_3$  in an EPDM compound reveals the potential of W-EPDM as a cheap filler in EPDM compounds. It is also found that W-EPDM can be incorporated into the window seal compound formulation and the drop in properties even at 100 phr of W-EPDM is within acceptable limit, thus providing a scope for on-site recycling of EPDM.

Naskar et al. [9] studied the characterization of ground rubber tire and effect on natural rubber compound. Ground rubber tire (GRT) particles of different size were characterized and effect of these particles in a natural rubber (NR) compound was studied. It is found that the smaller particles contain less polymer, but have higher amounts of fillers and metals with respect to polymer. NR compound containing smaller GRT particle shows better physical properties, but poorer aging characteristics.

Ghosh et al. [10] studied the recycling of silicone rubber waste : effect of ground silicone rubber vulcanizate powder on the properties of silicone rubber. The silicone rubber vulcanizate powder (SVP) obtained from silicone rubber by mechanical grinding exists in a highly aggregated state. The particle size distribution of SVP is broad, ranging from 2  $\mu\text{m}$  to 110  $\mu\text{m}$  with an average particle size of 33  $\mu\text{m}$ . X-ray Photoelectron Spectroscopy (XPS) and Infrared (IR) Spectroscopy studies show that there is no chemical change on the rubber surface following mechanical grinding of the heat-aged (200°C/10 days) silicone rubber vulcanizate. Addition of SVP in silicone increased the Mooney viscosity, Mooney scorch time, shear viscosity and activation energy for viscous flow. Measurement of curing characteristics reveals that incorporation of SVP into the virgin silicone rubber causes an increase in minimum torque, but marginal decrease in maximum torque and rate constant of curing. However, the activation energy of curing shows an increasing trend with increasing loading of SVP. Expectedly, incorporation of SVP does not alter the glass-rubber transition and cold crystallization temperatures of silicone rubber, as observed in the dynamic mechanical spectra. It is further observed that on incorporation of even

a high loading of SVP (i.e, 60 phr), the tensile and tear strength of the silicone rubber are decreased by only 20%, and modulus dropped by 15%, while the hardness, tension set and hysteresis loss undergo marginal change and compression stress-relaxation is not significantly changed. Atomic Force Microscopy studies reveal that incorporation of SVP into silicone rubber does not cause significant changes in the surface morphology.

Ghosh et al. [11] studied the effect of ground fluororubber vulcanizate powder (FVP) on the properties of fluororubber compound. FVP obtained from fluororubber based on tetrafluoroethylene/propylene/vinylidene fluoride terpolymer by mechanical grinding exists in a highly aggregated chain-like structure. X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy studies show that there are no chemical changes on the rubber surface following mechanical grinding of the fluororubber vulcanizate after heat ageing at 200°C for 10 days. The incorporation of FVP as a filler in the fluororubber compound results in a marginal increase of Mooney viscosity, Mooney scorch time and shear viscosity. While tensile strength, modulus and hardness marginally increase on addition of FVP into the fluororubber compound, tear strength decreases. Rheometric studies show that FVP alone is susceptible to further crosslinking in the presence of a curing agent. Dynamic mechanical spectra reveal that the glass to rubber transition temperature shifts higher by the addition of FVP into the fluororubber compound. Atomic force microscopy (AFM) images show uniform dispersion of FVP particles into the rubber matrix.

Gibala et al. [12] investigated the cure and mechanical behavior of rubber compound containing ground vulcanizates. Mooney viscosities and thixotropic behavior were determined for SBR melts containing carbon black and/or ground vulcanizate particles. A composition containing ambiently ground rubber has a higher viscosity than one with crygenically ground rubber. This is attributed to occlusion of continuum rubber within the sponge-like, ambiently ground rubber; occlusion is not possible with the smooth, cryo-ground particles. Viscosity was independent of particle size. On an equal phr (weight) basis, the addition N330 carbon black and cryo-ground rubber augment Mooney viscosity to a similar extent. While the Guth-Gold Equation is approximately applicable to black-filled melts, samples containing ground rubber are a much better fit by the simple Einstein Equation. Ground rubber addition has

only a minor influence of thixotropy, in contrast to carbon black, which greatly increases thixotropy.

Gibala et al. [13] investigated the cure and mechanical behavior of rubber compounds containing ground vulcanizates. A black-filled styrene-butadiene rubber (SBR) vulcanizate was ambiently ground, then used as an additive to the original, uncured compound. Sheets of the resulting composite (matrix/ground rubber particulate) were cured, and tensile and trouser tear strength were determined. The composite had reduced tensile strength, but enhanced tear strength relative to the original vulcanizate. The contrasting behavior is attributed to the effects of sulfur migration into the particulate rubber and differences in the responses of a tensile and a tear testpiece to discontinuities. In brief, the ground rubber acts as a stress-raising flaw in tensile testing, while promoting crack tip blunting and stick-slip behavior in trouser testing.

Grigoryeva et al. [14] studied the ground tire rubber (GTR) reclamation for virgin rubber/reclaimed GTR (re)vulcanizates. Thermochemically partially devulcanized ground tire rubber (GTR) was revulcanized in compositions with different virgin rubbers. Two different devulcanizing grounds (mixture of softeners) with and without processing oil have been used for GTR treatment. As virgin rubbers methylstyrene/butadiene (SBR), Isoprene(IR) and butadiene (BR) rubbers or their combinations were selected. They were cured by using sulfur, tetramethyl thiuram disulfide (TMTD) or peroxide based vulcanizing systems. The rubber/GTR (re)vulcanizates with the GTR content from 20 to 80 wt% have been prepared and studied. Vulcanization by sulfur system was found as preferable for IR/GTR formulations. The best properties for BR/GTR and SBR/GTR vulcanizates were reached with the vulcanization system based on TMTD. The co-curing in the interphase between the GTR particles and the surrounding rubber matrix improves the mechanical properties of (re)vulcanizates obtained. The reclaimed GTR studied has been used successfully in standard formulations for tires instead of the part of virgin rubbers.

Gibala et al. [15] investigated the tensile behavior of an SBR vulcanizate containing a single rubber particle. The effect of a single, embedded rubber particle



on the tensile strength of an SBR vulcanizate has been determined. For a given size, a particle taken from an ambient grind resulted in higher strength compared to a sample containing a particle prepared by hand-cutting with a blade. In the former case, fracture initiated within the particles, strength decreased with increased particle size.

Myhre et al. [16] studied the modification of crumb rubber to enhance properties of products made from recycle rubber. The process for devulcanization of the crumb involves stirring the crumb with plasticizers and a chemical that can promote scission of the sulfur-sulfur crosslinks. A catalyst is employed. The process is exothermic and requires cooling to prevent polymer degradation. The devulcanized crumb, referred to in this paper as “DVR” can be milled and compounded with conventional curatives and cured in ten minutes at 142°C to give a re-bonded rubber vulcanizate with moderate properties. Typical physical properties are tensile strength of 8 MPa., elongation of 225%, and tear strength of 270 N/cm. For the DVR/30%-NR blended with natural rubber, some good physical properties are obtained. A 70%-DVR/30%-NR blend exhibits tensile strength of 17 MPa, elongation of 425% and tear strength of 515 N/cm. Some low cost DVR/NR compounds can be prepared with the addition of carbon black, mineral fillers and extenders. Preliminary studies indicated that the property balance can be improved and optimized by selection of the appropriate cure systems, method of mixing, and by matching the properties in the different phases.

Tripathy et al. [17] studied the preparation of the rubber plasticizers from degraded/devulcanized scrap rubber : a method of recycling waste rubber. Seeking a solution to the problem of disposing scrap tires, they attempted to depolymerize or degrade vulcanized rubber scrap such that the resulting pseudo-liquid material could be used as an extender/plasticizer in virgin rubber compounds. As degraded natural rubber (DNR) and degraded styrene-butadiene rubber (DSBR) are polymeric in nature (confirmed from gel-permeation chromatography (GPC) and differential scanning calorimetry (DSC) results), they can be unique substitutes for typical rubber plasticizers (oil). DNR-loaded samples have shown better mechanical property retention after aging and a lower extractable content in actone than the respective oil-plasticized samples. Solvent swelling in toluene and 100% modulus values indicate that DNR-added rubber vulcanizates undergo a phase adhesion between the rubber

matrix and the degraded polymer, as well as incurring extra reinforcement due to particulate carbon black present in the degraded rubber.

Verbruggen et al [18] studied the mechanisms involved in the recycling of NR and EPDM. The thermochemical recycling of natural rubber (NR) and ethylene-propylene-diene rubber (EPDM) vulcanizates with disulfides was studied. NR sulfur vulcanizates were completely plasticized when heated with diphenyldisulfide at 200°C. It could be concluded that both main chain scission and crosslink scission caused the network breakdown. NR peroxide vulcanizates were less reactive towards disulfide at 200°C, and only reacted through main chain scission. For EPDM, a temperature range of 200-275°C was studied. In the presence of diphenyldisulfide at 200°C there was almost no devulcanization of EPDM sulfur vulcanizates, and at 225 and 250°C, there was only slightly more devulcanization. A decrease in crosslink density of 90% was found when  $2 \times 10^{-4}$  mol diphenyldisulfide/cm<sup>3</sup> vulcanizate was added and the EPDM sulfur vulcanizates were heated to 275°C. EPDM peroxide vulcanizates showed a decrease in crosslink density of ca. 40% under the same conditions. The lower reactivity of EPDM towards disulfide compared with NR is the result of higher crosslink densities, The presence of a higher percentage of more stable monosulfidic crosslinks and the fact that EPDM is less apt to main chain scission relative to NR.

Morin et al. [1] investigated a novel method to recycle scrap tires: High-Pressure High-Temperature Sintering (HPHTS). HPHTS was a novel recycling technique that makes it possible to recycle vulcanized rubber powders made from waste rubber (namely scrap tires) through only the application of heat and pressure. A brief look into the mechanism of sintering was presented along with information about the influence of molding variables, such as time, temperature, pressure and rubber particle sizes on the mechanical properties of the produced parts. One of the most interesting observations was that powders of every crosslinked elastomer attempted to sinter together via this technique, including silicone rubber (SI), sulfur cured NR, EPDM, styrene-butadiene rubber (SBR), peroxide cured butadiene rubber (BR), and fluoroelastomers (FKN). Early work on sintered rubber made from commercially available rubber powder had a modulus of 1 to 2 MPa, strength of 4 to 7 MPa and an elongation at break of 150-250%. Recently, in-house ground samples of

SBR have had sintered values over 9.5 MPa strength and 275% elongation, or greater than 60% retention of the original properties. Many of these mechanical properties are comparable with industrially manufactured rubbers, and it is believed that recycled rubbers produced via HPHTS offer the potential to replace virgin rubber in numerous applications.

Hon et al. [19] studied the De-Link recycling system: A revolutionary process for devulcanization of post-consumer and factory waste rubber. Sulfur vulcanization has generally been viewed as an irreversible process. Past attempts to recycle rubber products focused on mechanical size reduction to vulcanized crumbs and partial depolymerization to reclaimed rubber with relatively low physical properties. The De-Link system uses the De-Link chemical reactant to open up sulfur crosslinks in vulcanized rubber at low temperatures with little breakup of the main polymer chains. The resulting devulcanized DE-VULC rubber compounds have high physical properties with broad applications in rubber product manufacturing. The process can be used for the effective recovery of sulfur-vulcanized natural rubber, SBR, BR, NBR, Butyl, EPDM, etc. The rubber molecules of the DE-VULC rubber can be re-linked in a new manufacturing process without the addition of compounding ingredients.

Romine et al. [20] studied the microbial processing of waste tire rubber. Microorganisms exhibiting biological activity towards sulfur were evaluated for use in producing surface-modified Ground Tire Rubber (GTR) that exhibits the improved compounding characteristics with virgin rubber stocks. Combining waste tire material with virgin rubber is an attractive recycling option that has the potential of producing a wide variety of lower cost products. Finely ground waste tire rubber (74-micron particle diameter) was processed in the presence of strains of *Thiobacillus*, *Rhodococcus*, and *Sulfolobus*. The surface chemistry of the microbially treated GTR was characterized by infrared spectroscopy (FT-IR) and X-ray Analysis of Near Edge Surfaces (XANES). FT-IR and XANES data revealed that sulfur in the GTR was oxidized, which agrees with the proposed “4S” biodegradation model. Ion chromatography was used to characterize spent process media and showed that bound sulfur was released as sulfate ions when the bioreaction was allowed to run to completion, corroborating the proposed degradative pathway. Physical properties

were determined on rubber samples compounded with various loadings of the surface-modified GTR. Results showed significant increase in modulus of elasticity for compounds containing up to 15% GTR processed with S. acidocaldaius.

Naskar et al. [21] studied the surface chlorination of ground rubber tire and its characterization. Ground Rubber Tire (GRT) powders were chlorinated by trichloroisocyanuric acid (TCLCA). GRT powders of different chlorination levels were characterized by X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDAX), Attenuated Total Reflection Infrared (ATR-IR) spectroscopy, thermal, dielectric, and stress-strain properties of molded GRT specimens. Surface energy of the powders was estimated. Dynamic mechanical thermal analysis of molded GRT specimen reveals a biphasic structure. Plasticized poly(vinyl chloride) PVC compound, when blended with chlorinated GRT, shows improved physical properties in comparison to non-chlorinated GRT.

Ghose et al [22] studied the improvement of the properties of polyurethane rubber that has been devulcanized using the coaxial ultrasonic reactor. After devulcanization of the cured rubber under varying gap sizes and amplitudes, blends of the devulcanized and virgin rubber at different ratios were prepared. Rheological and mechanical properties, hardness as well as gel fraction and crosslink density of the vulcanized blends have been investigated. Results show that compared to the vulcanizates of the devulcanized samples, the vulcanizates of blends show a remarkable improvement in properties, which are sometimes comparable to or even better than the virgin vulcanizate. Blends have also been prepared using different proportions of ground samples and virgin rubber, and a comparison of properties between these blends and the blends of the devulcanized rubber has been carried out. The results show that compared to the ground samples, the blends of the devulcanized sample are easier to mix and exhibit enhanced and more uniform properties.

Yun et al. [23] studied the recycling of roofing membrane rubber by Ultrasonic Devulcanization. The recycling of vulcanizates based on EPDM roofing membrane rubber using a new ultrasonic devulcanization reactor with a grooved barrel was carried out. This reactor provided continuous devulcanization at an output as high as 2.52 g/s. Die pressure and ultrasonic powder consumption were measured

as a function of processing conditions. The mechanical properties of virgin vulcanized and revulcanized roofing membranes were measured. Tensile strength of the revulcanized rubber was found to be similar to that of the virgin vulcanizate. Gel fraction, crosslink density, and dynamic properties of the virgin vulcanizate, the ultrasonically devulcanized rubber, and the reculcanized rubber were determined. Also, dynamic properties and the cure behavior of the virgin compound and of the devulcanized roofing membrane were investigated. All these properties were found to be dependent on processing conditions during devulcanization. The thermal stability of the virgin compound, virgin vulcanizate, and devulcanized and revulcanized rubbers were studied by means of TGA. It was found that the thermal stability of all the vulcanizates in air and nitrogen environment was a function of processing condition.

Kojima et al. [24] studied the devulcanization of sulfur-cured isoprene rubber in supercritical carbon dioxide. A new devulcanization process that utilizes supercritical CO<sub>2</sub> (ScCO<sub>2</sub>) along with devulcanizing reagents was studied. Unfilled polyisoprene rubber samples (vulcanizates) with different crosslink distributions were prepared by controlling the cure time and the curatives. Each of the vulcanizates was subjected to the Soxhlet extraction using azeotropic acetone/chloroform to remove residual curatives. The devulcanization was performed at various temperatures (140-200°C) in the presence of ScCO<sub>2</sub> 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 was 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<sub>2</sub> pressure. In the supercritical fluid state of CO<sub>2</sub>, the vulcanizate was more efficiently devulcanized than in an ordinary gaseous state of CO<sub>2</sub>. 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 ScCO<sub>2</sub>.

Bilgili et al. [25] studied the effects of the pulverization process on the physical, chemical and thermal properties of the Solid State Shear Extrusion (SSSE) produced

rubber particle. Vulcanized natural rubber was pulverized using a single screw extruder in a non-cryogenic SSSE process where rubber granulates were subjected to high compressive and shear stresses. The produced particles had diameters ranging from 40 to 1700  $\mu\text{m}$ . Reprocessing of the produced powder resulted in a narrow particle size distribution. Considerable heat generated in the extruder due to friction caused surface oxidation of the fine rubber particles and, in turn, initiation of agglomeration of a portion of the produced particles. Physical, chemical and thermal analyses were performed on the produced rubber particle and the rubber granulates to determine the effects of the pulverization process. The produced particles had irregular shape with rough surfaces. The external surfaces of the particle were porous, but no microporosity was detected by nitrogen BET analysis. Swelling and extraction experiments showed that both the crosslink and gel fraction of the particles were lower than those of the rubber granulates. The reprocessing of the produced particles caused further reduction in the crosslink density and the gel fraction. A correlation was established between the crosslink density and the gel fraction. Thermal analysis revealed similar behavior of all particles and granulates in a nitrogen environment, but there was considerable thermo-oxidative degradation of the fine particles in air. The chemical analysis indicated that some of the bonds were broken.

Anandhan et al. [26] studied the preparation of the novel thermoplastic elastomers based on acrylonitrile-butadiene-strene terpolymer (ABS) from waste computer equipment and nitrile rubber. ABS is one of the engineering plastic most frequently used as outer castings for computer equipment such as monitors, keyboards and other similar components. In an attempt to recycle, blends of scrap computer plastics (SCP) based on ABS with nitrile rubber (NBR) were prepared and mechanical properties and morphology were studied. Effect of dynamic vulcanization on the properties of 60/40, 70/30 and 80/20 NBR/SCP blends was assessed. These blends show the thermoplastic elastomeric behavior. Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) studies show that the dynamically vulcanized NBR particles are dispersed in the ABS matrix. The thermoplastic elastomeric blends show excellent swelling resistance in IRM#93 oil.

Mousa et al. [27] studied the influence of hygrothermally decomposed polyester-urethane on cure characteristics and viscoelastic behaviour of

styrene/butadiene rubber. Hygrothermally decomposed polyester-urethane (HD PUR) was mixed at concentrations up to 20 phr with a styrene/butadiene rubber (SBR), using an efficient vulcanisation system. Changes in the cure behaviour were followed by vulcanometry, plate-plate rheometry, and differential scanning calorimetry. It was found that the degree of crosslinking was increased by the incorporation of HD PUR, which acts as an accelerator in SBR stocks. Increasing crosslinking resulted in higher stiffness and strength and was accompanied by a reduction in elongation at break and swelling index.

Tipanna et al. [28] studied the preparation of the composites of waste, ground rubber particles and poly(vinyl chloride). Composites of poly(vinyl chloride) (PVC) were prepared with waste, finely ground printing rollers of nitrile rubber over a wide range of composition (up to 90% by weight of rubber component), through melt blending. The effect of different amounts of waste rubber on the tensile strength, % elongation, hardness, and flex crack resistance was studied. There was a considerable increase in the impact properties of PVC. Flex crack resistance was also significantly improved as the specimen did not crack even after 150,000 cycles for all composition containing more than 40% waste rubber. The waste also imparted a plasticizing effect to PVC. The improvement in these properties could be due to interaction between PVC and the acrylonitrile part of nitrile rubber.

Amit et al. [28] investigated the thermoplastic elastomeric composition based on ground tire. Ground rubber tire (GRT) is a particulate vulcanizate consisting mainly of rubber hydrocarbon and fillers. Rubber hydrocarbon of GRT (RGRT) has been used as a partial substitute for EPDM rubber in a dynamically vulcanized EPDM / acrylic modified HDPE (A-HDPE) blend. The blends with higher rubber content show poor processability and physical properties, while the compositions with higher plastic content behave like toughened plastics. However, the 60:40 rubber/plastic blend was found to behave as a thermoplastic elastomer, and it was observed that 50% of EPDM can be replaced by RGRT without deterioration in properties.

Lin et al [29] studied the preparation of the thermoplastic elastomer and rubber-toughened plastics from recycled rubber and plastics. An experimental investigation has been conducted to evaluate the use of recycled rubbers in blends for

the development of new thermoplastic elastomers (TPE) and rubber-toughened plastics. The recycled rubber were obtained from various commercial sources and including representatives from the EPDM, SBR, and NR/SBR blend families, as well as a range of particle sizes. A series of five different virgin polypropylenes (PP) were used as the plastic phase, representing a range of molecular weights and suppliers. Blend were prepared in a Haake Buechler batch mixer over a broad range of condituent fractions. Compatibilization and reactive blending techniques were used to improve the quality of the scrap rubber/plastic blends with respect to both mechanical and rheological properties. Results indicate that these blending techniques are required to obtain acceptable mechanical strength in the resultant materials. Additional parameters that significantly enhanced properties included elevating the blending temperature, reducing rubber particle size, and increasing PP molecular weight. This later conclusion was attributed to a lower degree of crystallinity in the PP phase that contributes to better blending between the phases.



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## CHAPTER III

### EXPERIMENT

#### 3.1 Raw Materials

**Table 3.1** Rubbers and chemicals used in this work

Material	Trade name	Function	Supplier
NR	STR5L	Polymer	Thai Hua Rubber
EPDM	Keltan5508	Polymer	DSM Elastomers Asia
Carbon black	THAIBLACK N330 (HAF)	Filler	Kij Paiboon Chemical
Silica	Ultrasil VN3 GR	Filler	United Silica (Siam)
CaCO <sub>3</sub>	Hicoat-410	Filler	Sand and Soil Industry
Zinc oxide	Zinc oxide Active	Activator	Hsien and Industrial
Stearic acid	Stearic acid 101	Activator	P.T. Cisadane Raya Chemicals
Tetramethylthiuram monosulfide	TMTM	Accelerator	FLEXSYS
Dibenzothiazyl disulfide	MBTS	Accelerator	COSAN
Sulfur	Sulfur Powder	Curing agent	Utids Enterprise

#### 3.2 Instruments

1. Two-roll mill, HF-2RM, Taiwan.
2. Compression Machine, HCV 100D Taiwan.
3. Oscillating Disc Rheometer, PT-100.
4. Electronic Densimeter, MD-200S Japan.
5. Durometer: Teclock, GS-719N.
6. Tensile Testing Machine: Gotech, GT-7010-CD Taiwan.

7. Mooney Viscometer, TECHPRO-VIS TECH type 123103.
8. Universal Testing Machine, LLOYD K.
9. Abrasion Tester, Wallance
10. Particle Size Analyzer, Mastersizer S,
11. Thermogravimetry, Mettler Toledo TGA/SDTA 851
12. Scanning Electron Micoscope (SEM), JEOL JSM 5800

### **3.3 Experiment Procedure**

#### **3.3.1 Preparation of RSP**

The RSP was obtained from buffing process in golf grip manufacture products, using a mechanical grinder with sand paper and abrasive wheel. A shaker sieve was used to eliminate some dirt from RSP before incorporation into the virgin compound. The particle size distributions of the sieved RSP were measured.

#### **3.3.2 Characterizations of the RSP**

The RSP was characterized as follows:

- a) Particle Size Analysis: The RSP particle size was measured by using “mastersizer S” to measure the dimensions of the particles.
- b) Thermogravimetry (TGA): 50 mg of RSP was heated at 40 °C/min in nitrogen atmosphere up to 600 °C and then in oxygen atmosphere up to 850 °C in a Mettler Toledo TGA/SDTA 851.

#### **3.3.3 Formulations**

The formulation of NR/EPDM blends with different RSP loading as filler are given in Table 3.2. For the study of migration of curatives from RSP to virgin compound, the formulations of NR/EPDM blends with 100 phr RSP and without RSP are presented in Tables 3.3 and 3.4. The compounds with and without 100 phr of RSP and different curative combinations were prepared. In order to understand the effect of curing migration, the curing characteristics were compared with those of corresponding compounds without RSP compound (Table 3.4) but with the same

curative combinations and dosages. Since calcium carbonate is often used in combination with other fillers such as carbon black (N330) and silica (Ultrasil VN3). These fillers were commonly used in the factory. The formulations for this part of study are given in Table 3.5. In order to study for the possible blend, RSP was incorporated in typical golf grip compound and its effect on the properties were determined. The formulations used are given in Table 3.6 where G compound is a golf grip formulation and GB100 compound is the same as G but contains 100 phr of RSP.

**Table 3.2** Formulations used of rubber compound with RSP loadings (in phr)

Ingredient	RB0	RB50	RB100	RB200	RB300
STR5L	60	60	60	60	60
EPDM5508	40	40	40	40	40
RSP	0	50	100	200	300
ZnO	5	5	5	5	5
Stearic acid	1	1	1	1	1
MBTS	1	1	1	1	1
TMTM	0.5	0.5	0.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5	1.5

**Table 3.3** Formulations used for the study of the curative migration with RSP (in phr)

Ingredient	B100	RB100a	RB100b	RB100c	RB100d	RB100e	RB100
STR5L	-	60	60	60	60	60	60
EPDM5508	-	40	40	40	40	40	40
RSP	100	100	100	100	100	100	100
ZnO	-	-	-	-	5.0	5.0	5.0
Stearic acid	-	-	-	-	1.0	1.0	1.0
MBTS	-	-	-	1.0	-	1.0	1.0
TMTM	-	-	-	0.5	-	0.5	0.5
Sulfur	-	-	1.5	1.5	1.5	-	1.5

a: without curative agent

b: sulfur 1.5 phr

c: MBTS 1.0; TMTM 0.5; sulfur 1.5 phr

d: ZnO 5.0; Stearic acid 1.0; Sulfur 1.5 phr

e: ZnO 5.0; Stearic acid ; MBTS 1.0; TMTM 0.5 phr



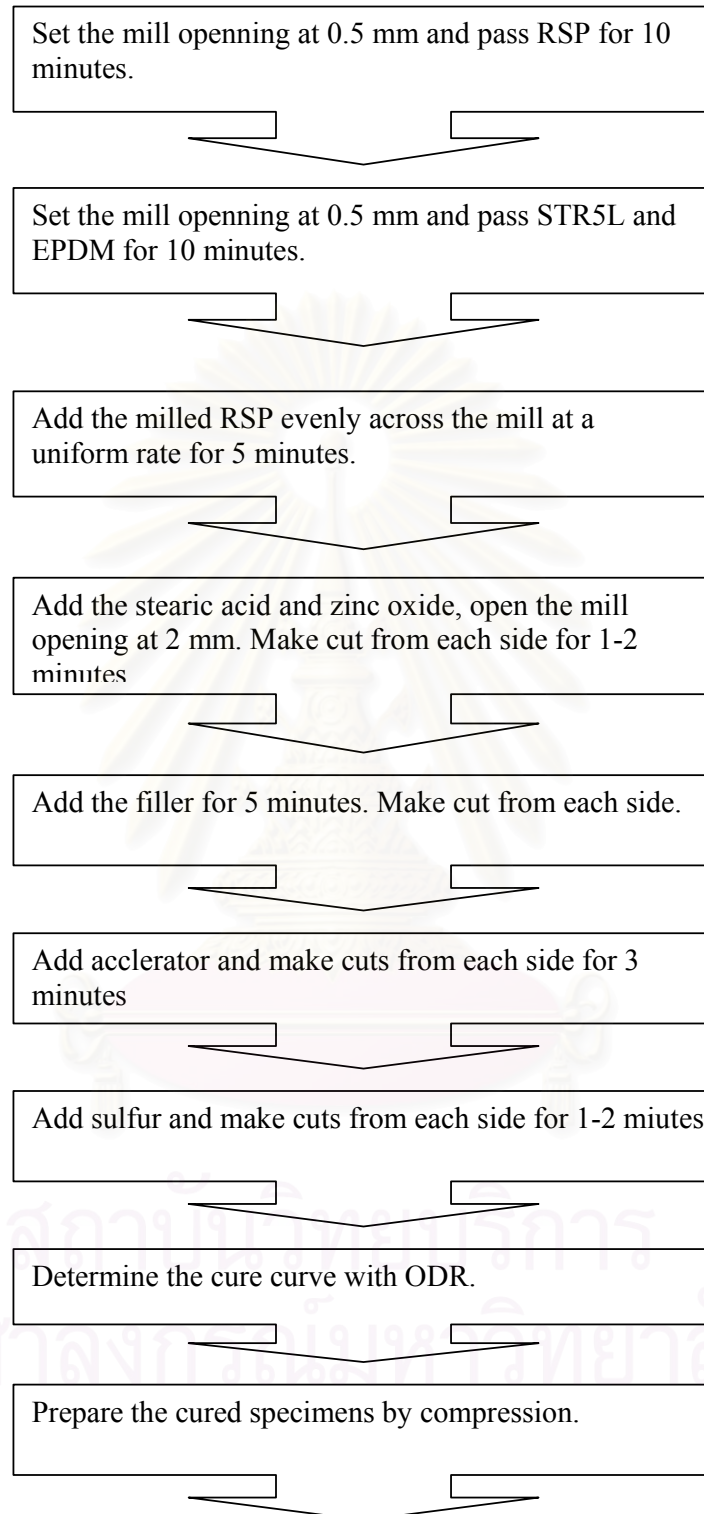
**Table 3.6** Formulations for incorporating RSP into virgin compound for golf grip (in phr)

Ingredient	G	GB100
STR5L	60-70	60-70
EPDM 5508	25-30	25-30
N330	10-20	10-20
RSP	-	100
Ultrasil VN3	20-30	20-30
HICOAT 410	5-10	5-10
White Oil	10-15	10-15
ZnO	3-5	3-5
Stearic Acid	1-3	1-3
MBTS	0.5-1	0.5-1
DPG	0.5-1	0.5-1
Sulfur	1.5-2.0	1.5-2.0

#### 3.3.4 Mixing

The compounds were prepared by two-roll mill, HF-2RM, Taiwan with size 8 inches in diameter and 18 inches in length at room temperature. The mixing was carried out according to Fig. 3.1.

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**Figure 3.1** The schematic diagram for rubber compound preparation.

### 3.3.5 Molding

The vulcanization was performed by using a compression molding press (HCV 100D) at 160°C and by applying a pressure of 14 MPa. The curing time corresponded to the time required to achieve 90% of maximum torque on the cure curve. Vulcanized sheets with dimension of 127 x 127 x 2 mm<sup>3</sup> were obtained and used for mechanical testing. Vulcanized cylindrical sample of rubber, 30 mm in diameter and 7 mm in thickness were prepared for hardness test.

## 3.4 Testing

### 3.4.1 Determination of Mooney Viscosity

Mooney viscosity of the compound, ML (1+4), was determined by using Mooney viscometer (TECHPRO-VIS TECH) at 100°C according to ISO289-1.

### 3.4.2 Determination of Cure Characteristics

A Monsanto oscillating disc rheometer, PT-100 model, was used to obtain the torque-time curve at temperature 170°C with 1° amplitude. The torque requirement plotted versus time (Fig. 3.2)

- $M_L$  – Minimum torque, lb<sub>f</sub> \*in
- $M_H$  – Highest torque, lb<sub>f</sub> \*in attained during specified period of time when no plateau or maximum torque is obtained.
- Cure time (T<sub>90</sub>) in minute is the time taken for attaining 90% of the maximum torque.
- Scorch time (T<sub>2</sub>) in minute is the time taken for a two-unit rise above the minimum.

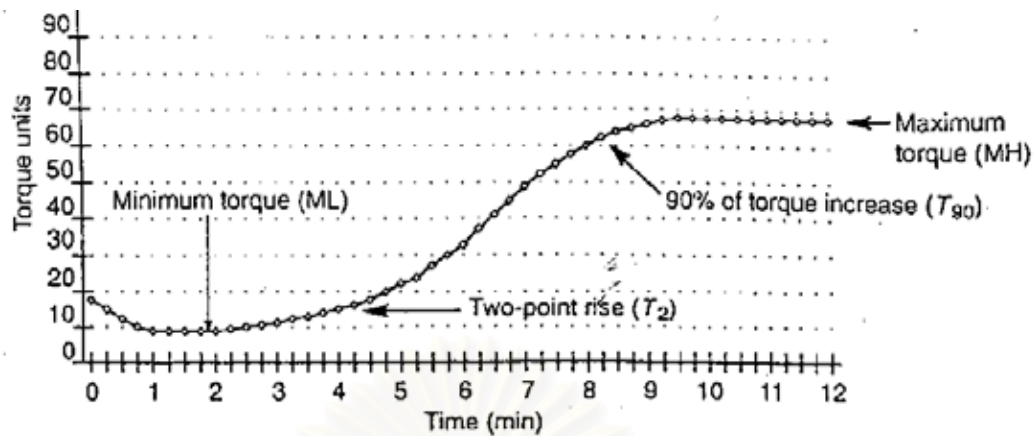


Figure 3.2 A typical rheometer chart [30].

### 3.4.3 Determination of Mechanical Properties

Dumbbells and angle specimens were punched out from the vulcanized sheets. Stress and strain test was performed by using the tensile testing Machine, Gotech, GT-7010-CD, according to ASTM D 412-98a at a crosshead speed of 500 mm/min.

Tear strength was determined by using a universal testing machine, LLOYD K with the crosshead speed of 500 mm/min according to ISO 34 and angle specimens were used.

Hardness was determined by using a durometer, GS-719N and Shore A according to ASTM D2240-97. The samples were placed in a shore A Durometer type, and the hardness of rubber was measured at 23°C.

Abrasion, Akron was determined in an abrasion tester, Wallance according to BS 903 Part A9 and expressed as abrasion loss, which is the volume in cm<sup>3</sup> abraded from test sample per 1000 cycles.

### 3.4.4 Determination of Specific Gravity

The vulcanized rubber specific gravity was determined by using Electronic Densimeter, MD-200S adopted from Archimedes' principle. The determination of (relative) density value was based on the density of water at 4°C: 1 g/cm<sup>3</sup> per electronic densimeter MD-200S instruction manual [31].



### 3.4.5 Determination of Crosslink Density [32]

Specimen of approximately 15 mm in diameter and 2.5 mm in thickness were allowed to swell in toluene. The density of each specimen was determined according to section 3.4.4. Specimen was then placed in a vial containing toluene. The vial was always kept covered to prevent evaporation. Periodically, over a period of 1-3 days, the specimens were removed from the toluene, blotted dry on a paper towel, and then weighed quickly and accurately. The swelling index, which is defined as the grams of solvent per gram of rubber hydrocarbon, is calculated according to the Flory-Huggins Theory.

### 3.4.6 SEM studies of the Fractured Surface

Morphology of tensile fracture surfaces was examined by using the Scanning Electron Microscope (JEOL JSM 5800). The fracture surfaces were coated with gold.

## CHAPTER IV

### RESULTS AND DISCUSSIONS

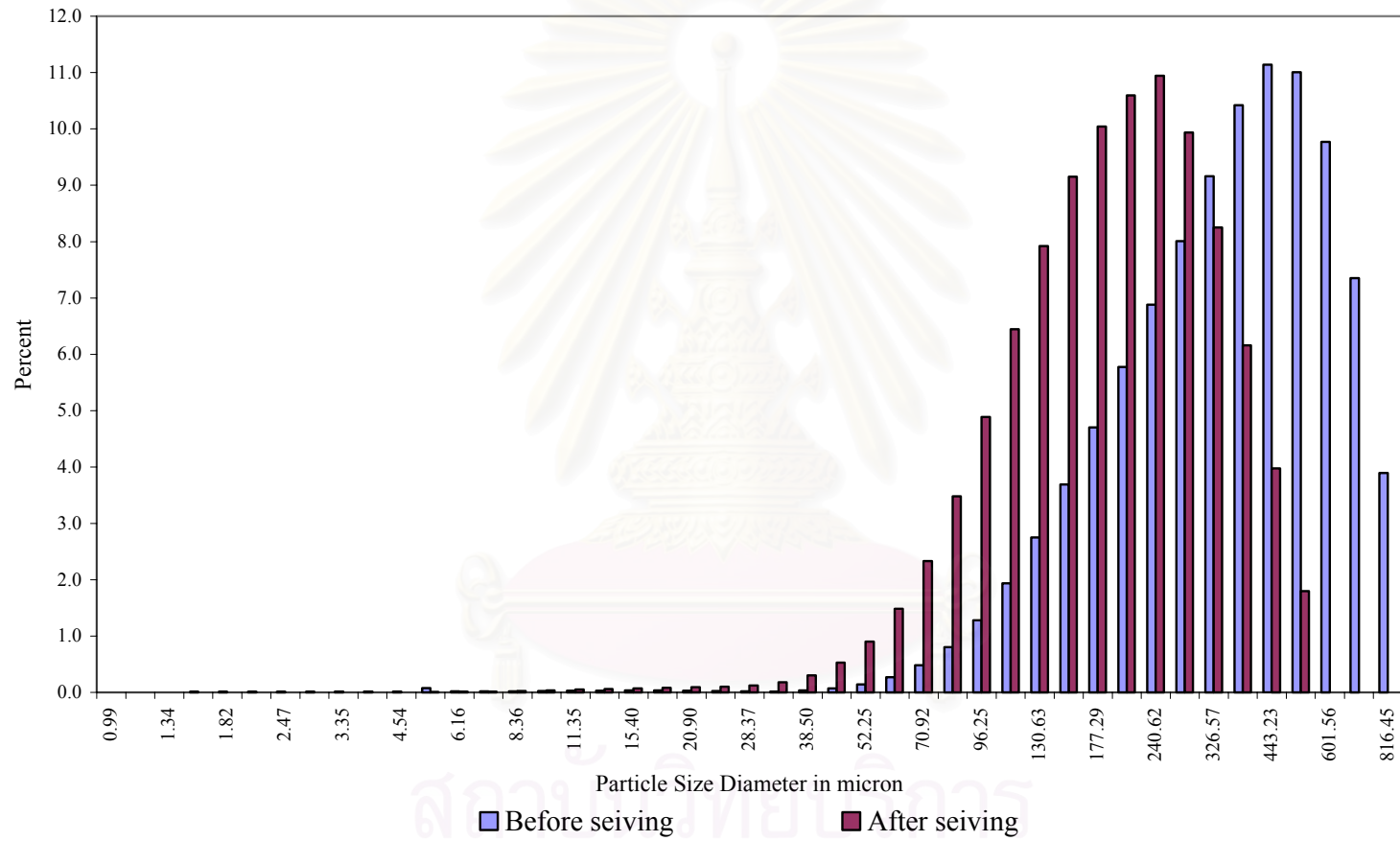
#### 4.1 Characterization of RSP

The result of Mastersizer S analysis shows that average particle size of the rubber powder, RSP, is  $\sim 371.57 \mu\text{m}$  and  $\sim 195.52 \mu\text{m}$  before and after sieving respectively. The histograms of particle size distribution of RSP is shown in Fig. 4.1.

Composition of RSP from thermogravimetric analysis (TGA) is shown in Table 4.1 and Fig. 4.2. It was found that up to  $150^\circ\text{C}$  there was no weight loss. In  $\text{N}_2$  atmosphere, the rubber started to decompose and the weight reduced until all rubber was totally decomposed. At  $600^\circ\text{C}$ , the chamber was changed with oxygen. Carbon black started to burn in an oxygen atmosphere and produce  $\text{CO}_2$  at  $\sim 625^\circ\text{C}$ . The weight loss due to oxidation gave the carbon black content and the residual weight represented the noncombustible matter or ash, including inorganic fillers, inorganic pigments or metal oxides [33].

**Table 4.1** Composition of RSP from TGA

Composition	Weight, %
Polymer	72.18
Carbon black	5.95
Ash	21.87



**Figure 4.1** Particle size distributions of rubber powder, RSP.

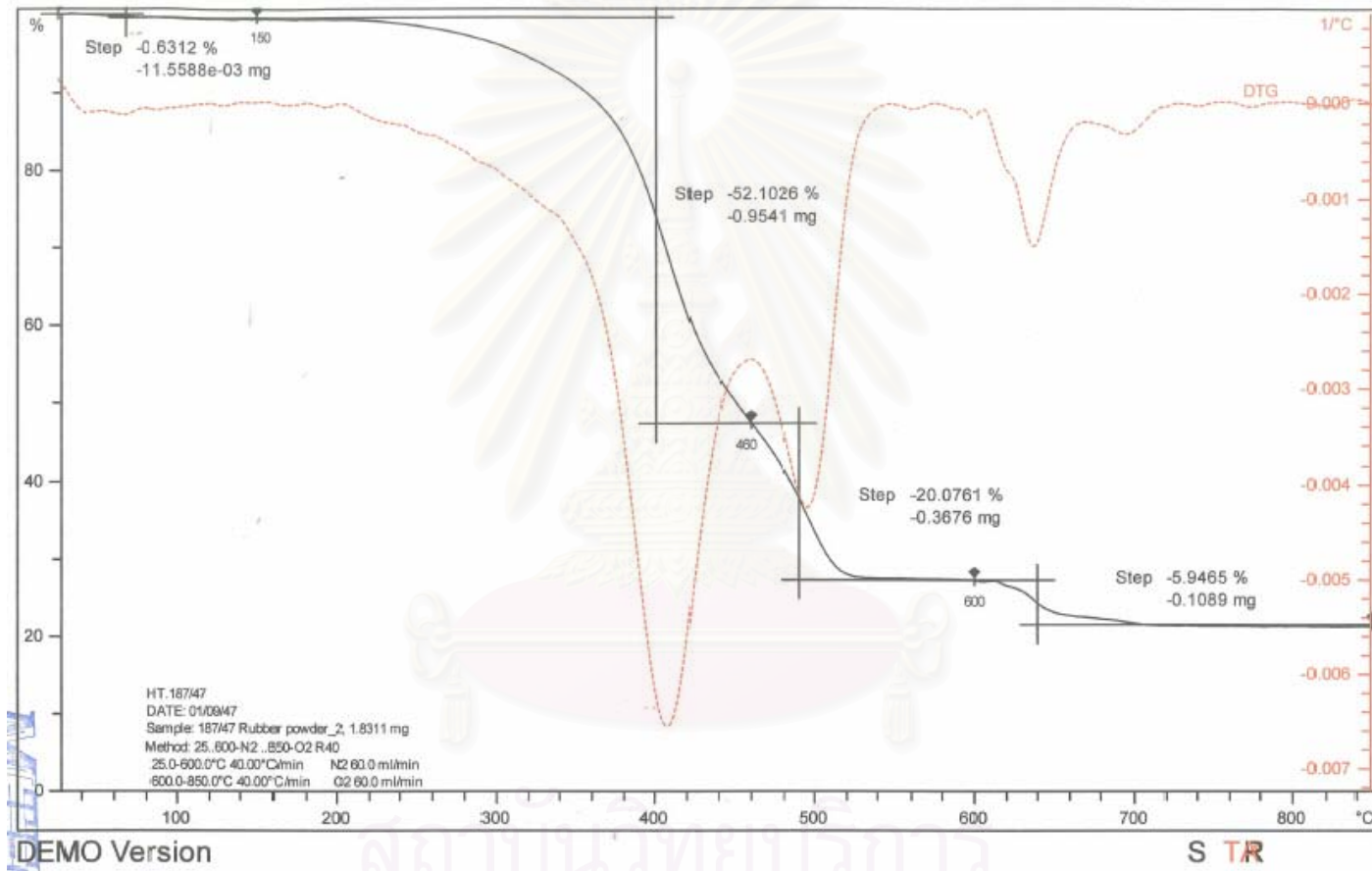


Figure 4.2 TGA thermogram of RSP.

## 4.2 Effect of RSP Loading in Compound

### 4.2.1 Mooney Viscosity and Cure Characteristics

The cure characteristics of RSP were examined. The formulas of rubber compound at various RSP loading are previously summarized in the Table 3.1. Mooney viscosity and cure characteristics of compounds are presented in Table 4.2

Mooney viscosity, ML (1+4) 100°C of the compounds increased with increasing RSP loading., shown in Fig. 4.2. Jacob et al. [8] and Ghosh et al. [10] reported that Mooney viscosity increased exponentially with increase in rubber powder according to Eqs. 4.1 and 4.2, respectively. In this work, the experimental data can be fitted by Eq. 4.3.

$$M_f = M_g (1.00 + 0.70c + 0.85c^2) \quad (4.1)$$

$$M_f = M_g (1.00 + 1.27c + 4.91c^2) \quad (4.2)$$

$$M_f = M_g (1.00 + 1.04c + 6.97c^2) \quad (4.3)$$

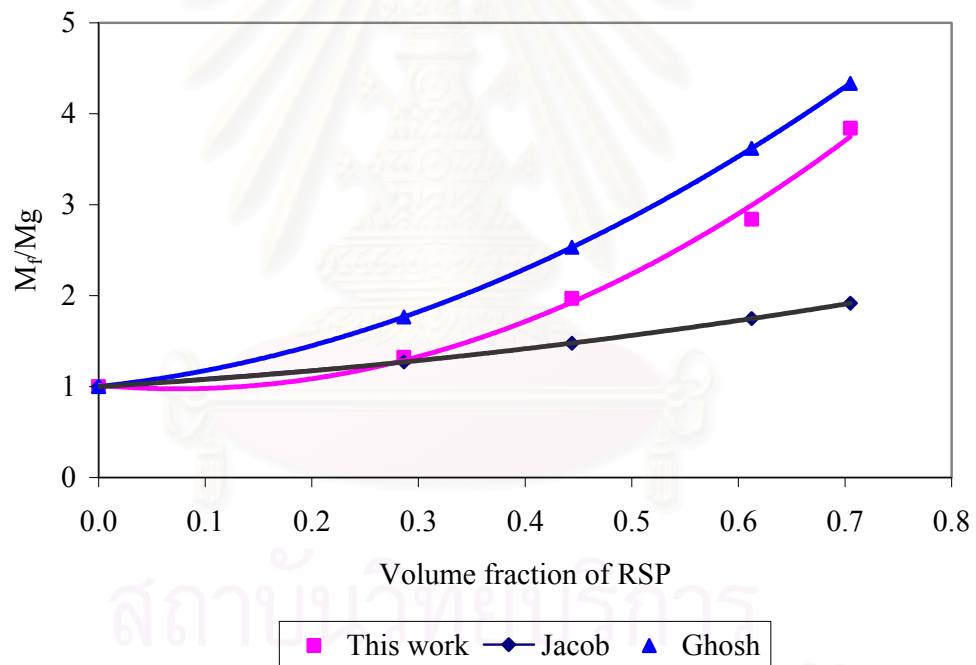
$M_f$  is the Mooney viscosity of the powder-filled compound;  $M_g$  is the Mooney viscosity of gum rubber and  $c$  is volume fraction of RSP.

In all cases, the minimum torque values (ML) continuously increased as similar to Mooney viscosity. Maximum torque (MH) decreased with increasing RSP loading. The increase in torque (MH-ML) continuously decreases with increasing amount of RSP, indicating lowering of degree of crosslink. The scorch time, T2 and optimum cure time, T90 of the rubber compounds decreased as RSP was added. The decrease in T2 and T90 (Figs. 4.4 and 4.5) could be due to the curative migration effect. It could be noted that RSP contained some amount of accelerator; activator and curing agent (sulfur) remain. The migration effect of RSP would be studied in the next section (Sec.4.3) and it demonstrated that migration of the accelerators would cause the decrease in the scorch time and optimum cure time.

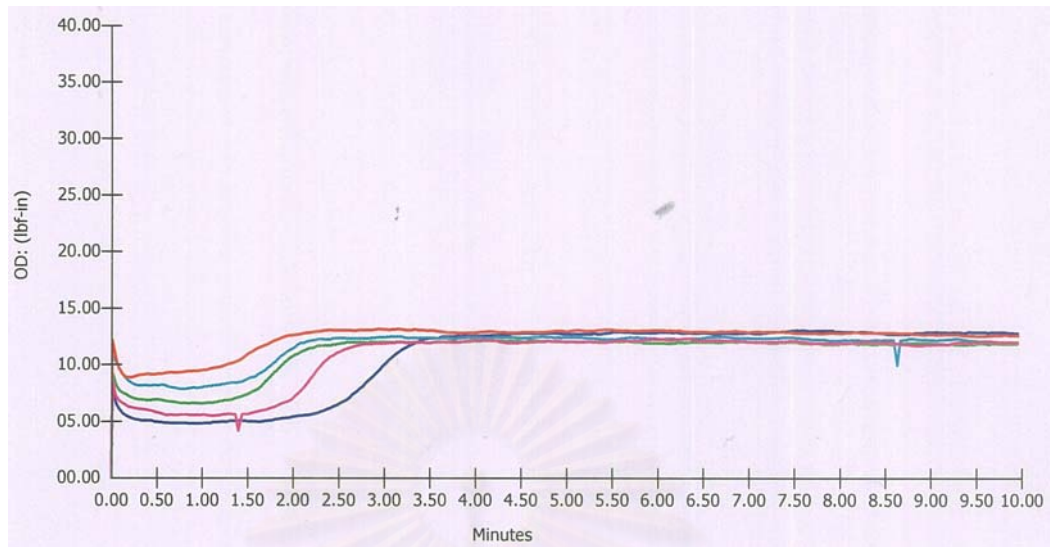
**Table 4.2** Mooney viscosity and cure characteristics of the rubber compounds with various RSP loading.

Properties	RB0	RB50	RB100	RB200	RB300
ML(1+4) 100°C	18.50	24.44	36.44	52.55	71.07
ML, lb*in	4.80	5.62	6.61	7.88	8.93
MH, lb*in	13.11	12.34	12.19	12.55	13.16
MH-ML, lb*in	8.31	6.72	5.58	4.67	4.23
Scorch time, T2, min	2.57	2.08	1.71	1.75	1.51
Optimum cure time, T90, min	3.44	2.70	2.27	2.17	2.11

Sample code in Table 3.2

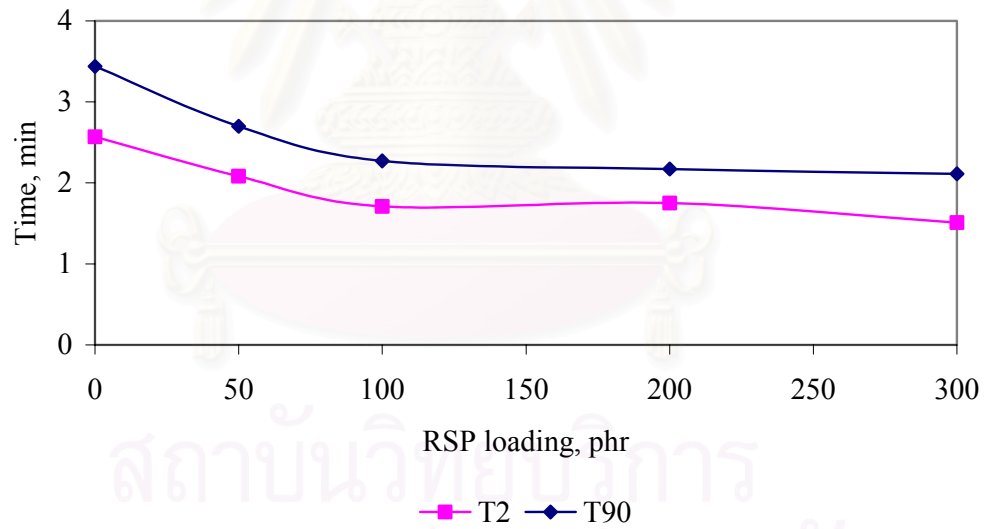


**Figure 4.3** Effect of RSP loading on relative  $M_f/M_g$ .



**Figure 4.4** Cure curves of the compounds at various RSP loading.

(— RB0, — RB50, — RB100, — RB200, — RB300)



**Figure 4.5** Effect of RSP loading on T2 and T90.

## 4.2.2 Mechanical Properties of Vulcanized Rubber

The mechanical properties of the unfilled and RSP-filled compound are summarized in Table 4.3. The addition of RSP into virgin compound (RB0) increased tensile strength and elongation at break because of residual of carbon black particles in RSP (see Table 4.2). From Fig. 4.6 the tensile strength and elongation at break increase until a maximum when increasing RSP loading to 100 phr. At more than 100 phr of RSP, these two values, however, decreased.

From Fig. 4.6c, tear strength increased and reached maximum at RSP load of 50 phr. And then decreased. The hardness slightly decreased with increasing RSP loading (Fig. 4.6 d).

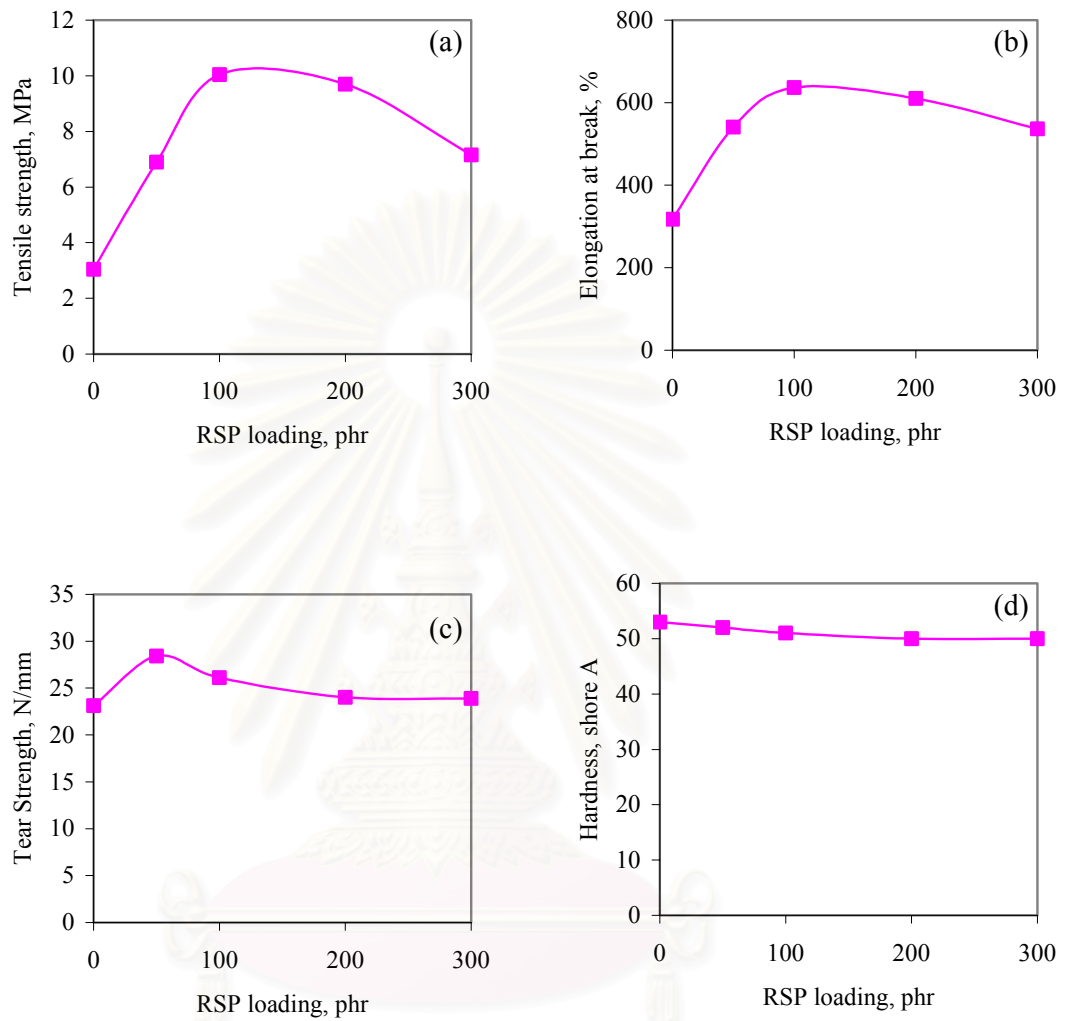
Fig. 4.7 shows the relationship of tensile strength and crosslink density. As crosslinking is increased further the gel point is eventually reached, and a three dimensional network is formed. Some chains may not be attached to the network (soluble sol phase), but the whole composition will no longer dissolve in a solvent, a gel cannot be fractured without breaking chemical bonds. Thus, strength is higher at the gel point, since chemical bond must be ruptured to create fracture surface. However, strength does not increase indefinitely with more crosslinking. When an external force deforms an elastomer, part of the in out energy is stored elastically in the chains and is available as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into heat and, in this manner, is made unavailable to break chains. At high crosslink level, chain motions become restricted, and the “tight” network is incapable of dissipating much energy [33].

Fig. 4.8 shows that tear strength increased with increasing crosslink density. Hamed et al. [34] reported that the mechanical behavior such as, tear and tensile strength of an elastomer depends strongly on crosslink density pass through a maximum as crosslink is increased.

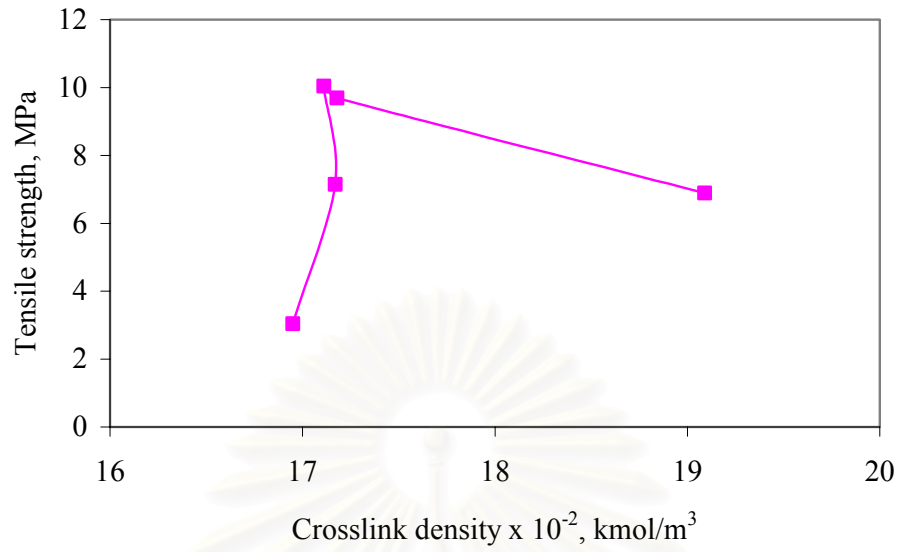
The Abrasion loss of compounds increased with increasing RSP (Fig. 4.9) and the specific gravity marginally increased with the incorporation of RSP (Table 4.3). The increase in abrasion loss may be due to large particle size of the RSP [35]. In the earlier work, Jacob [8] reported that the abrasion loss of the samples increased progressively with increasing amount of powdered EPDM scrap. The interplay of the reinforcing effect, crosslinking effect and the possible lubricating effect from the large



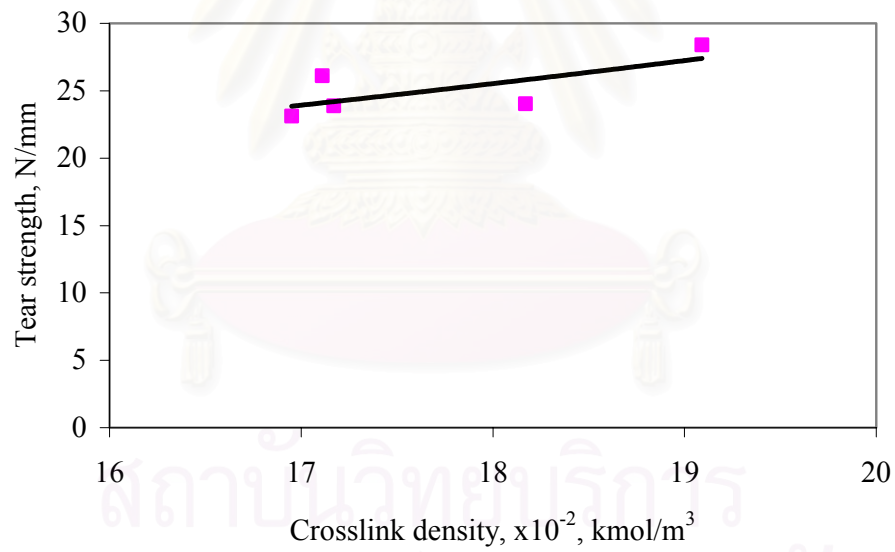
amount of plasticizers migrating from the RSP in the compound might contribute to the were mechanism, which is not clearly understood.



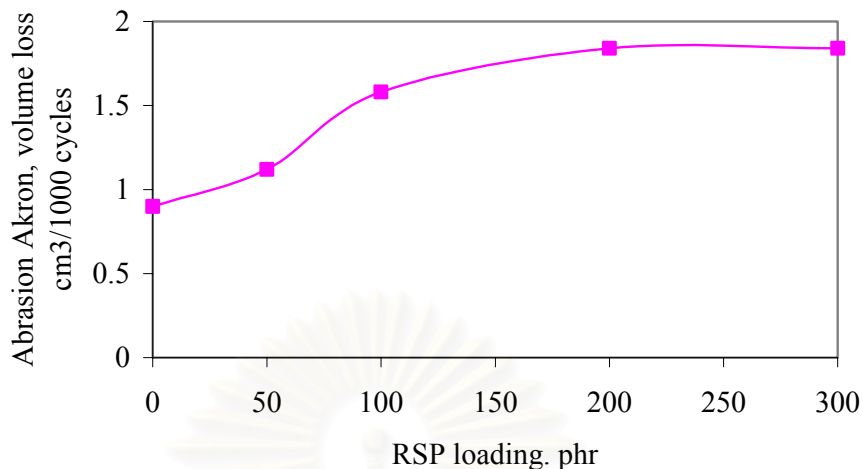
**Figure 4.6** Effect of RSP loading on (a) Tensile strength (b) Elongation at break (c) Tear Strength (d) Hardness.



**Figure 4.7** Plot of tensile strength versus crosslink density.



**Figure 4.8** Plot of tear strength versus crosslink density.



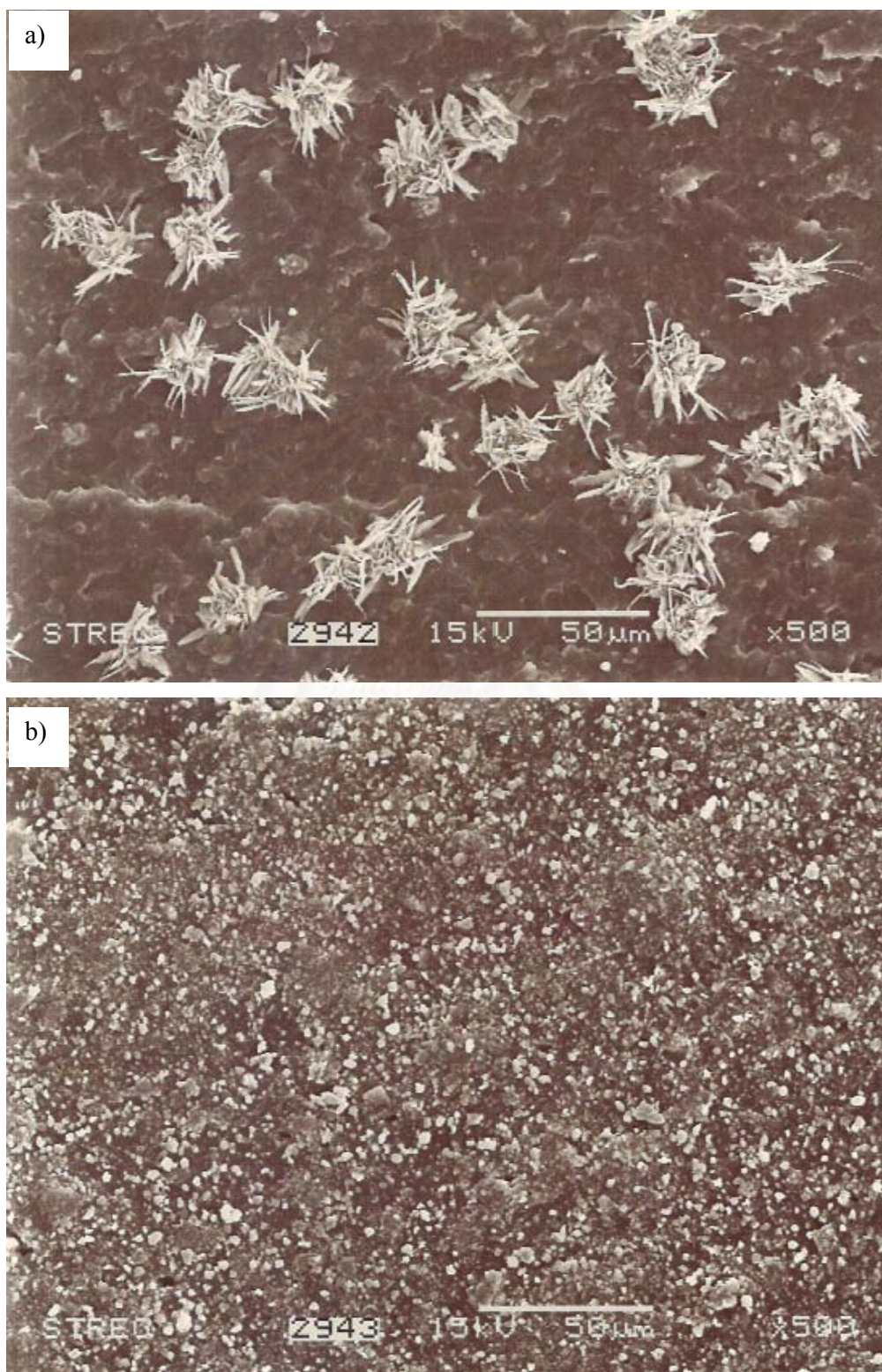
**Figure 4.9** Effect of RSP loading on Abrasion Akron, Volume loss.

**Table 4.3** Mechanical properties of the compounds with various RSP loading.

Properties	RB0	RB50	RB100	RB200	RB300
Tensile strength, MPa	3.04	6.89	10.04	9.69	7.15
Elongation at break, %	317.50	540.83	636.67	610.00	536.67
Modulus at 100%, MPa	1.13	1.08	1.01	1.01	1.06
Modulus at 300%, MPa	2.61	2.21	2.09	2.80	2.33
Tear strength, N/mm	23.11	28.41	26.12	24.03	23.88
Abrasion, Akron, volume loss cm <sup>3</sup> /1000 cycles	0.90	1.12	1.58	1.84	1.84
Hardness, shore A	53	52	51	50	50
Specific gravity	0.945	0.984	1.003	1.023	1.039
Crosslink Density, x 10 <sup>-2</sup> kmol/m <sup>3</sup>	16.95	19.09	17.11	18.17	17.17

#### 4.2.3 Morphology

From Fig. 4.10a, the tensile fracture surface of the gum vulcanizate (RB0) shows the nonhomogeneous characteristic of low strength and less elongation. Fig. 4.10b shows the fracture surface of 100 phr RSP filled vulcanizates, is similar to that of black-filled compounds. Jacob [8] reported the fracture surface of W-EPDM filled vulcanizates show similarity to that of black-filled compound.



**Figure 4.10** SEM photographs of fracture surface: a) RB0 b) RB100.

### 4.3 Curative Migration of RSP

#### 4.3.1 Mooney Viscosity and Cure Characteristics

From Tables 4.4 and 4.5, the Mooney Viscosity of RSP-filled compound (RB100b) is higher than that without RSP for same compounds. According to Eq. 4.3, Mooney viscosity increased due to the addition of RSP.

The cure characteristics of these compounds are also summarized in Tables 4.4 and 4.5. The cure curves of RB100a and B100 (Fig. 4.11a) show that even without additional curative, the crosslinking can take place in RB100a. The presence of unreacted curative in RSP compound was confirmed by the re-curing of the powder itself in the absence of fresh curatives. Thus, the high rheometric torque value of RB100a could be due to the migration of curatives from RSP to virgin rubber.

For the addition of sulfur to this rubber compound (RB100b) shows an increase in the increase in torque (MH-ML). From Fig. 4.11b, the cure curve of RB100b compound with the gum compound (Rb) shows the migration of accelerator and activator from RSP to rubber blend, resulting in the completion of crosslinking process. It was also reported that addition of fresh sulfur into a compound containing vulcanized rubber particles enhances the release of accelerators from the waste rubber, which migrates to the fresh rubber [8].

From Fig. 4.11c for compound RB100c and Rc, containing no activator, RB100c was shorter cure time than that of Rc and also the higher MH. This is due to the fact that RSP contains considerable amount of unreacted activators, which take part in the curing of rubber compound.

Moreover, the cure curves of RB100d and Rd (Fig. 4.12a) containing no accelerator further confirm the migration of accelerator from RSP to gum rubber. Thus, the cure time, T90 of RB100d was shorter than that of Rd.

The cure curves of RB100e and Re, absence of sulfur (Fig. 4.12b), show that the cure time (T90) and MH of RB100e is higher than that of Re. This can be explained that the migration of residue sulfur in RSP to gum rubber took place. Some investigators have reported several commonly used curatives such as sulfur; sulfenamide accelerators and sulfur donors could diffuse quite readily across a rubber-to-rubber interface [36].

Thus, the increase in curing rate as well as the extent of curing by the addition of RSP to gum rubber in all the compositions confirm the migration of curatives from RSP.

**Table 4.4** Mooney viscosity and curing characteristics of 100 phr of RSP filled compounds for the study on curative migration.

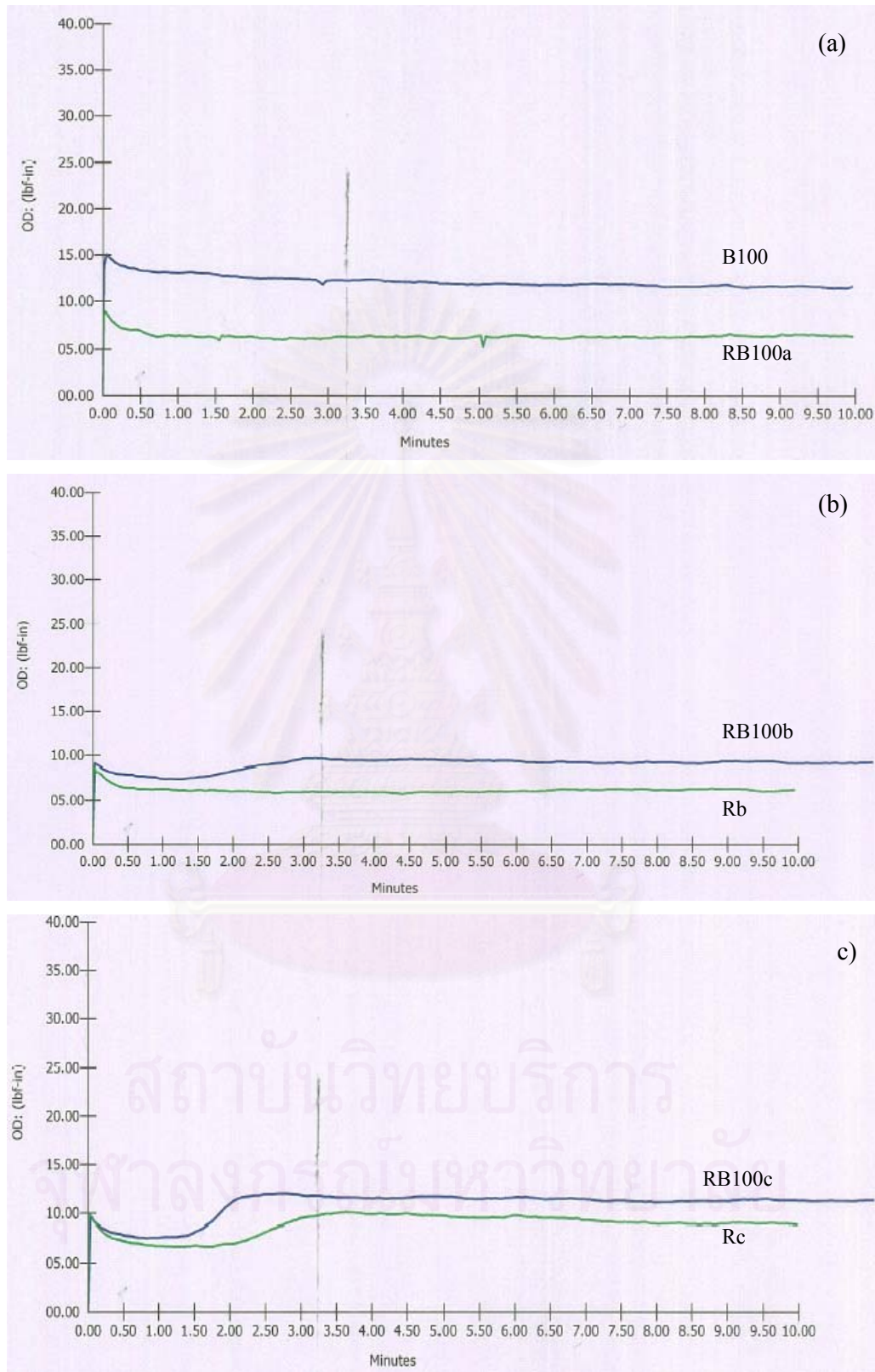
Properties	B100	RB100a	RB100b	RB100c	RB100d	RB100e	RB100
ML(1+4) 100°C	122.39	41.69	62.88	64.94	66.76	69.19	36.44
ML, lb*in	11.85	5.27	7.41	7.59	7.57	7.72	6.61
MH, lb*in	12.38	6.61	9.66	12.02	10.80	10.73	12.19
MH-ML, lb*in	0.53	1.34	2.25	4.43	3.23	3.01	5.58
Scorch time, T2, min	> 10.0	>10.0	2.85	1.81	2.06	3.55	1.71
Optimum cure time, T90, min	3.36	5.42	2.87	2.15	2.72	5.85	2.27

a: without curative agent  
b: sulfur 1.5 phr  
c: MBTS 1.0; TMTM 0.5; sulfur 1.5 phr  
d: ZnO 5.0; Stearic acid 1.0; Sulfur 1.5 phr  
e: ZnO 5.0; Stearic acid ; MBTS 1.0; TMTM 0.5 phr

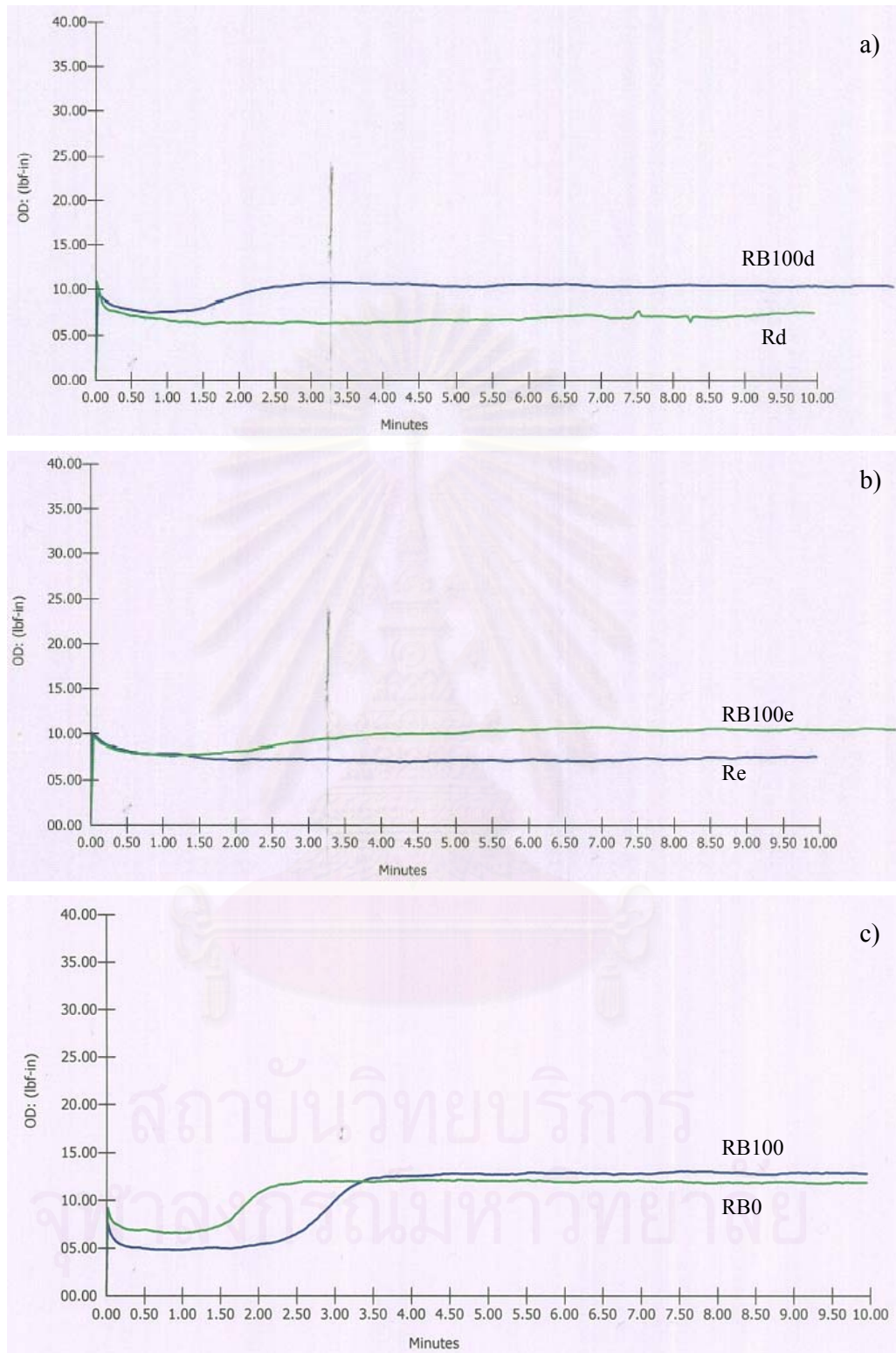
**Table 4.5** Mooney viscosity and curing characteristics of unfilled compounds for curative migration.

Properties	Rb	Rc	Rd	Re	RB0
ML (1+4) 100°C	23.19	30.50	31.00	33.75	18.50
ML, lb*in	5.81	6.69	6.33	7.04	4.80
MH, lb*in	6.35	10.13	7.65	7.64	13.11
MH-ML, lb*in	0.54	3.44	1.32	0.6	8.31
Scorch time, T2, min	>10.0	2.68	>10.0	>10.0	2.57
Optimum cure time, T90, min	7.40	3.24	7.49	9.46	3.44

b: sulfur 1.5 phr  
c: MBTS 1.0; TMTM 0.5; sulfur 1.5 phr  
d: ZnO 5.0; Stearic acid 1.0; Sulfur 1.5 phr  
e: ZnO 5.0; Stearic acid ; MBTS 1.0; TMTM 0.5 phr



**Figure 4.11** Cure curves of RSP-filled compounds a) B100 and RB100a, b) RB100b and Rb, c) RB100c and Rc.



**Figure 4.12** Cure curves of RSP filled compounds. A) RB100d and Rd, b) RB100e and Re, and c) RB100 and RB0.



## 4.4 Comparison between RSP and Other Fillers

### 4.4.1 Cure Characteristics

The cure characteristics of filler filled compounds are presented in Table 4.6. The increase in torque of N330-filled compound (RN100) is very high because of the high of corsslink density whereas that of the RSP-filled compound (RB100) is low. The increase in torque of  $\text{CaCO}_3$ -filled compound (RC100) is higher than that of RB100 (Fig. 4.13a) because of the lower extent of crosslink density of RB100 (see Table 4.7). The increase in torque during vulcanizations proportional to the number of crosslink formed per unit volume of rubber [37]. The optimum cure time, T90 of RB100 is lower than RC100 because of curative migration of RSP to virgin compound, but is higher than RN100. Le Bras [37] demonstrated that carboxyl, phenolic, quinone, and other functional groups on the carbon black surface react with the polymer and provided evidence that chemical crosslinks exist between these materials in vulcanizates.

The carbon black contains carboxyl, lactone quinone and other organic function groups, which promote a high affinity of rubber to filler. This, together with the high surface area of the carbon black, means that there will be intimate elastomer-carbon black contact. The carbon black also has a limited number of chemically active sites, which arise from broken carbon-carbon bonds as a consequence of the methods used to manufacture the carbon black. The close contact of elastomer and carbon black will allow these active sites to chemically react with elastomer chains. The carbon black particles effectively become a crosslink. The non-carbon black fillers generally offer less affinity and less surface activity toward the common elastomers [37].

Cure curve of blend of filler binary system blend in Fig. 4.13b showed that the increase in torque of N330 and  $\text{CaCO}_3$  filled blend (RNC100) is higher than that of N330 and RSP (RNB100) because of higher crosslink density of RNC100. Optimum cure time, T90 of RNC100 is lower than RNB100. The decrease in T90 with the addition of N330 and  $\text{CaCO}_3$  suggests the dependency of scorch on the previous heat history of the sample.

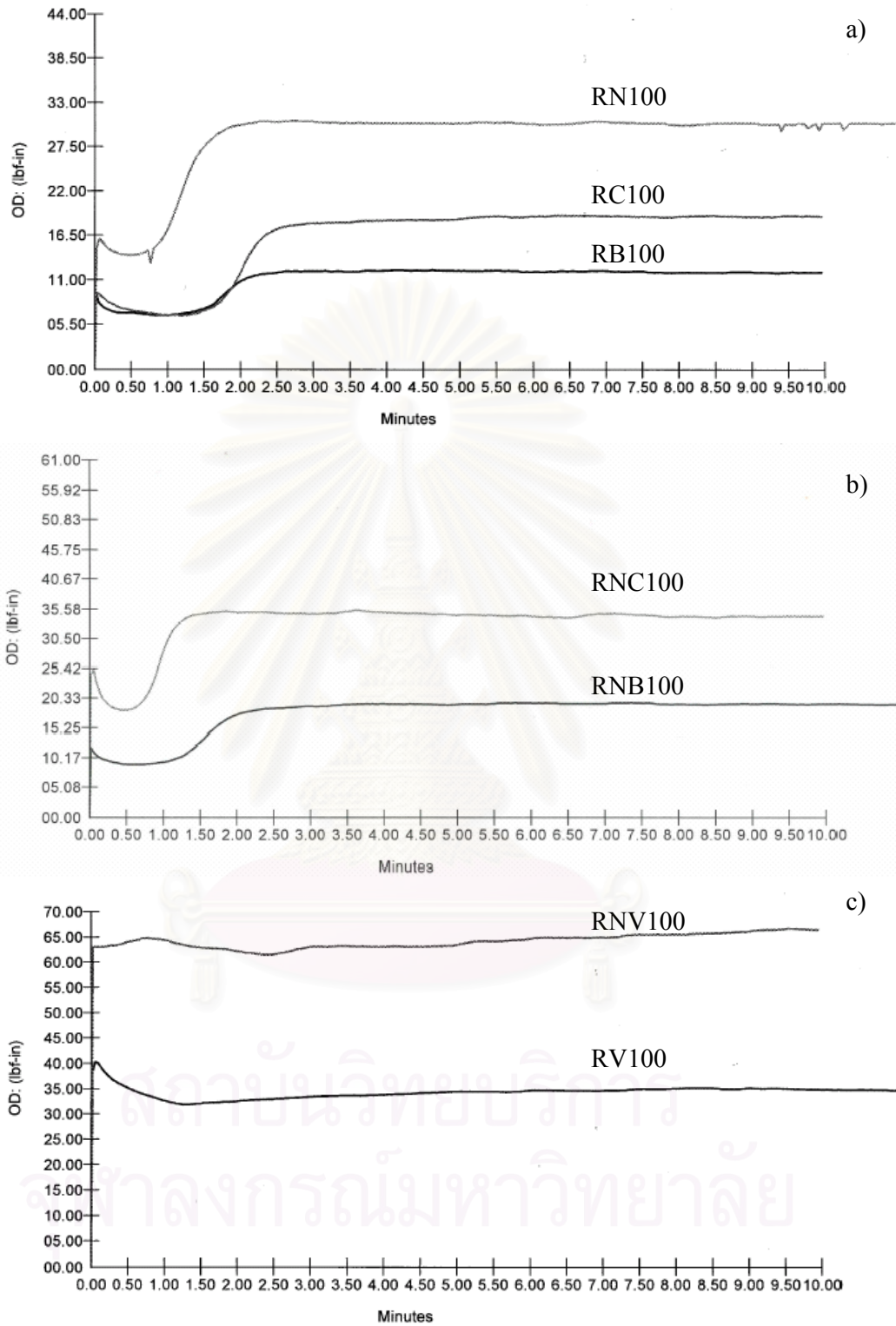
Cure curves of silica filled and silica incorporated RSP (Fig. 4.13c) show high cure time because both silica and silicates have surface silica ( $\text{SiO}_2$ ) groups, which are

hydrolyzed to silanols (-SiOH). These silanol groups behave as acids (-SiO-H<sup>+</sup>) and chemically active. The higher surface area fillers have more silanols available and are thus more reactive. Silanols show similarities to carboxylic acid groups in their reactions with amines, alcohols, and metal ions. While water adsorbed on the surface of filler particles will reduce silanol reactivity, hot compounding volatilized some of this, leaving a reactive surface. Some of the reactions with silanols can have a significant effect on the properties of the rubber compound, especially where the chemical involved is an important part of the cure system. Most of the accelerators used in sulfur cure system contain an amine group. Strong adsorption or reaction with filler particles can decrease the amount of accelerator available for vulcanization reactions. This can give slower cure rates and a reduce state of cure. Similar effects can result from the reaction of zinc ion with filler particles [38]. While the slab was taken out the mold, it cracked. For this reason, the mechanical properties of RV100 and RNV100 could not be measured.

**Table 4.6** Curing characteristics of the compounds containing N330, RSP and CaCO<sub>3</sub>.

Properties	One-filled system				Binary-filled system		
	RN100	RB100	RC100	RV100	RNB100	RNC100	RNV100
ML, lb*in	14.40	6.61	6.56	31.87	9.02	18.28	63.20
MH, lb*in	30.70	12.19	18.96	35.18	19.50	35.40	66.68
MH-ML, lb*in	16.30	5.58	12.40	3.31	10.48	17.12	3.48
Scorch time, T2, min	0.95	1.71	1.76	4.16	1.34	0.75	7.28
Optimum cure time, T90, min	1.69	2.27	2.73	7.38	2.43	1.27	9.12

B = RSP; N = Carbon Black; C = CaCO<sub>3</sub>; V = Ultrasil VN



**Figure 4.13** Cure curves of a) RN100, RB100 and RC100 compound. B) RNB100 and RNC100 compound. C) RV100, RNV100 compound.

#### 4.4.2 Mechanical Properties of vulcanized Rubber

Mechanical properties of the compounds are presented in Table 4.7. As expected, the addition of RSP improved the tensile strength of the compound. The results show that tensile strength of RB100 is significantly higher than that of RC100 because of residue of carbon black in RSP, but both are lower than that of RN100. When comparing between RB100 and RC100. The results also indicate that RSP yielded significantly higher reinforcement than CaCO<sub>3</sub>. For tear strength, the similar trend was observed.

Table 4.7 also shows the effect of RSP and binary filler system on mechanical properties of vulcanizates. The moduli, tensile strength, tear strength and abrasion loss of RNB100 (Carbon black and RSP) is found to be higher than those of RNC100 (Carbon black and CaCO<sub>3</sub>). This increasing in mechanical properties can be due to the fine carbon black particle present in RSP, providing reinforcement. Accordingly, it can be recommended that RSP can be partially or fully replaced CaCO<sub>3</sub> in some applications such as golf grip rubber.

**Table 4.7** Mechanical properties of compound containing N330, RSP and CaCO<sub>3</sub>.

Properties	One-filler system			Binary filler system	
	RN100	RB100	RC100	RNB100	RNC100
Tensile strength, MPa	11.22	10.04	4.28	13.76	8.91
Elongation at break, %	140.00	620.00	407.50	432.50	97.50
Modulus at 100%, MPa	8.32	1.01	1.79	2.81	8.01
Modulus at 300%, MPa	0.00	2.09	2.72	8.86	0.00
Tear strength, N/mm	41.45	26.12	21.22	43.16	29.18
Abrasion, Akron, Volume loss cm <sup>3</sup> /1000 cycles	0.76	1.12	1.72	0.74	0.80
Hardness, shore A	89	51	67	71	92
Specific gravity	1.214	1.003	1.343	1.105	1.430
Crosslink density, x 10 <sup>-2</sup> kmol/m <sup>3</sup>	35.36	17.11	28.70	27.01	86.38

B = RSP; N = Carbon Black; C = CaCO<sub>3</sub>; V = Ultrasil VN3

## 4.5 Proposed On-site Recycling of RSP for Golf Grip Rubber

### 4.5.1 Mooney Viscosity and Cure Characteristics

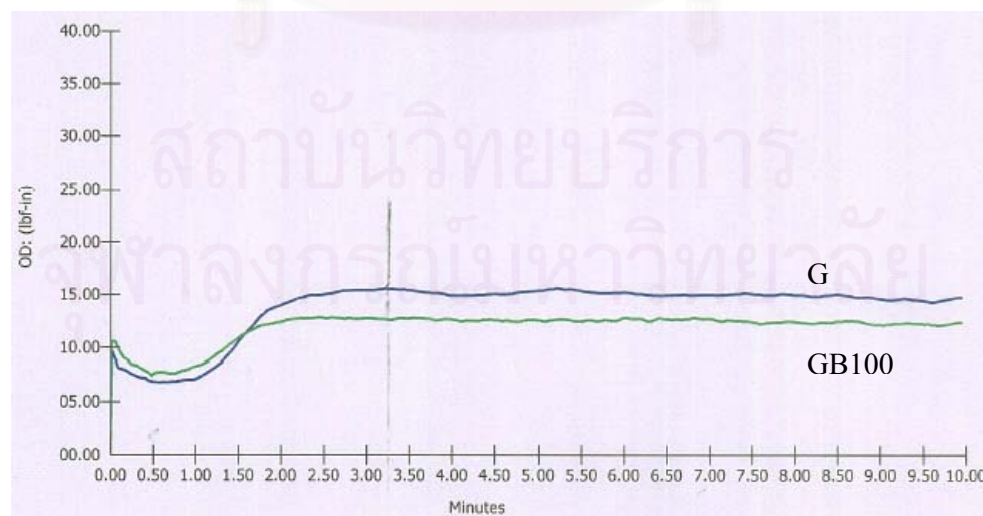
The addition of RSP in golf grip compound (GB100) increases the Mooney viscosity according to equation 4.1, From Fig. 4.14, GB100 is less MH-ML than GB100 because of the lower crosslink density in GB100 (see Table 4.9) and the optimum cure time, T90 also decrease. This can be explained by migration curative which curative in RSP diffuses in virgin compound.

**Table 4.8** Mooney viscosity and cure characteristics for G and GB100 compound.

Properties	G	GB100
ML (1+4) 100°C	35.88	58.38
ML, lb*in	6.81	7.74
MH, lb*in	15.61	12.88
MH-ML, lb*in	8.80	5.14
Scorch time, T2, min	1.32	1.31
Optimum cure time, T90, min	2.25	1.95

G = Virgin Golf Grip Compound.

GB100 = RSP filled Golf Grip Compound.



**Figure 4.14** Cure curves of G and GB100 compounds.

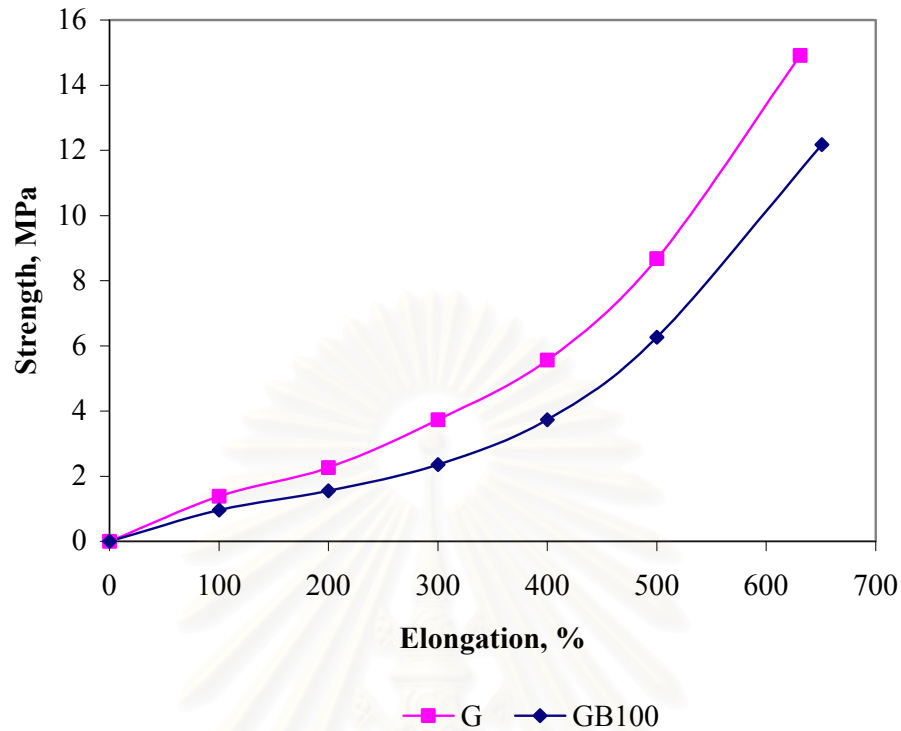
#### 4.5.2 Mechanical Properties of Golf Grip Rubber

A comparison has been made between RSP filled and virgin golf grip rubbers. The mechanical properties of virgin rubber and RSP filled rubber are presented in Table 4.9 and the stress-strain curves are shown in Fig. 4.15. It is observed that the modulus, tensile strength, elongation at break, tear strength and hardness slightly decrease with the addition of 100 phr RSP in golf grip compound. The slight decrease in mechanical properties of RSP-filled compound can be due to the lower extent of crosslink density than virgin compound. However, a slight drop in tensile strength, hardness and modulus is also observed and may be compensated by the addition of carbon black as reported by earlier workers [8]. In addition, Table 4.9 also shows the comparison of RSP filled rubber with the industrial formulation specifications. It can be seen that only specific gravity of RSP filled rubber is slightly higher than the specification and it is not critical for golf grip application. In conclusion, recycling RSP may be economically beneficial to the golf grip industry.

**Table 4.9** Mechanical properties of G and GB100 compounds.

Properties	Industrial formulation	G	GB100
Tensile strength, MPa	9.81 min	14.19	12.11
Elongation at break, %	600 min	630.83	655.83
Modulus at 100%, MPa	-	1.38	1.04
Modulus at 300%, MPa	-	3.73	2.66
Tear strength, N/mm	-	35.59	34.49
Abrasion, Akron, volume loss cm <sup>3</sup> /1000 cycles	-	0.62	1.00
Hardness, shore A	50 +/- 3	53	50
Specific gravity	1.067 +/- 0.02	1.076	1.089
Crosslink density, x 10 <sup>-2</sup> kmol/m <sup>3</sup>	-	17.53	15.12

G = Virgin Golf Grip Compound.  
GB100 = RSP filled Golf Grip compound.



**Figure 4.15** Strength and elongation curve of G and GB compound.

### 4.5.3 Cost comparison

Material cost comparison of both formulations in lab scale is presented in Table 4.10 and this is based on the 50 bahts per kilogram of G formula material compound and 5 bahts per kilogram of sieving cost. Consequently, the virgin compound is more expensive than RSP filled compound by a factor of 1.56. The major cost savings are ~35.8% in the golf grip product based on this experimental blend.

**Table 4.10** Material cost analysis of G and Gb100 compound.

Compound	Weight (kg)	Material Cost (Baht)	Sieving Cost (Baht)	Total Material Cost (Baht)
<b>G</b>				
- Golf Grip Compound	1.0	50.0	-	50.0
<b>GB100</b>				
- Golf Grip Compound	0.602	30.1	-	30.1
- RSP	0.398	-	2.0	2.0

G = Virgin Golf Grip Compound.

GB100 = RSP filled Golf Grip compound.

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## CHAPTER V

### CONCLUSIONS AND FURTHER WORK

#### 5.1 Conclusions

This work was attempted to salvage the RSP back into the manufacturing process of the golf grip. The work was to prepare RSP and blended with golf grip virgin compound. The mechanical properties were investigated.

1. The RSP obtained by the grinding technique in golf grip manufacture was sieved. It was found that average particle size was approximately 195.52  $\mu\text{m}$ .

2. The blends at all RSP loading show higher mechanical properties compared to virgin rubber. Therefore, the RSP acts as reinforcing filler in the blends of virgin rubber.

3. Addition of RSP to a virgin compound caused the decrease in curing rate because of the migration of curative in RSP.

4. The mechanical properties of the compounds filled with RSP and  $\text{CaCO}_3$  reveal the potential of RSP used as a substitute for  $\text{CaCO}_3$  in NR/EPDM compounds.

5. The RSP can be incorporated into the golf grip compound formulation with a slight drop in the properties even at 100 phr of RSP. However, it is within acceptable limit, which is proved to be beneficial to the golf grip industry.

#### 5.2 Further Work

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

- The characterizations of RSP such as particle sizes and composition should be made to improve the mechanical properties of compound.
- This RSP can utilize in other products such as tire, automotive rubber part etc.

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## APPENDICES

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**Appendix A****Table A.1** Particle Size Distribution Analysis of sieved RSP.

Size_Low ( $\mu\text{m}$ )	Size_High ( $\mu\text{m}$ )	Average Size ( $\mu\text{m}$ )	Percent			
			Sample No.			Average
			1	2	3	
1.44	1.68	1.56	0.01	0.01	0.01	0.01
1.68	1.95	1.82	0.01	0.01	0.01	0.01
1.95	2.28	2.12	0.01	0.01	0.01	0.01
2.28	2.65	2.47	0.01	0.01	0.01	0.01
2.65	3.09	2.87	0.01	0.01	0.01	0.01
3.09	3.60	3.35	0.01	0.01	0.02	0.01
3.60	4.19	3.90	0.01	0.01	0.02	0.01
4.19	4.88	4.54	0.01	0.02	0.02	0.02
4.88	5.69	5.29	0.01	0.02	0.2	0.08
5.69	6.63	6.16	0.02	0.02	0.02	0.02
6.63	7.72	7.18	0.02	0.02	0.02	0.02
7.72	9.00	8.36	0.02	0.02	0.02	0.02
9.00	10.48	9.74	0.02	0.03	0.03	0.03
10.48	12.21	11.35	0.03	0.03	0.03	0.03
12.21	14.22	13.22	0.03	0.03	0.03	0.03
14.22	16.57	15.40	0.03	0.03	0.04	0.03
16.57	19.31	17.94	0.03	0.03	0.04	0.03
19.31	22.49	20.90	0.03	0.03	0.03	0.03
22.49	26.20	24.35	0.02	0.03	0.03	0.03
26.2	30.53	28.37	0.02	0.02	0.02	0.02
30.53	35.56	33.05	0.02	0.02	0.01	0.02
35.56	41.43	38.50	0.04	0.04	0.02	0.03
41.43	48.27	44.85	0.08	0.09	0.04	0.07
48.27	56.23	52.25	0.16	0.17	0.10	0.14
56.23	65.51	60.87	0.29	0.31	0.22	0.27
65.51	76.32	70.92	0.50	0.53	0.42	0.48
76.32	88.91	82.62	0.81	0.86	0.75	0.81
88.91	103.58	96.25	1.27	1.34	1.24	1.28
103.58	120.67	112.13	1.90	1.97	1.94	1.94
120.67	140.58	130.63	2.67	2.75	2.83	2.75
140.58	163.77	152.18	3.53	3.66	3.88	3.69
163.77	190.80	177.29	4.45	4.65	5.01	4.70
190.8	222.28	206.54	5.42	5.70	6.20	5.77
222.28	258.95	240.62	6.45	6.79	7.41	6.88
258.95	301.68	280.32	7.53	7.92	8.57	8.01
301.68	351.46	326.57	8.67	9.11	9.7	9.16
351.46	409.45	380.46	9.97	10.45	10.85	10.42
409.45	477.01	443.23	11.21	11.13	11.08	11.14
477.01	555.71	516.36	11.42	11.08	10.52	11.01
555.71	647.41	601.56	10.48	9.86	8.97	9.77
647.41	754.23	700.82	8.22	7.36	6.48	7.35
754.23	878.67	816.45	4.52	3.83	3.33	3.89

**Table A.2** Particle Size Distribution Analysis of RSP.

Size_Low ( $\mu\text{m}$ )	Size_High ( $\mu\text{m}$ )	Average Size ( $\mu\text{m}$ )	Percent			Average
			Sample No.			
			1	2	3	
4.88	5.69	5.29	0.00	0.01	0.01	0.01
5.69	6.63	6.16	0.01	0.01	0.01	0.01
6.63	7.72	7.18	0.01	0.02	0.02	0.02
7.72	9.00	8.36	0.02	0.02	0.03	0.02
9.00	10.48	9.74	0.03	0.03	0.04	0.03
10.48	12.21	11.35	0.05	0.05	0.06	0.05
12.21	14.22	13.22	0.06	0.06	0.07	0.06
14.22	16.57	15.40	0.07	0.07	0.08	0.07
16.57	19.31	17.94	0.08	0.08	0.09	0.08
19.31	22.49	20.90	0.09	0.09	0.10	0.09
22.49	26.2	24.35	0.09	0.10	0.11	0.10
26.2	30.53	28.37	0.11	0.13	0.13	0.12
30.53	35.56	33.05	0.15	0.19	0.20	0.18
35.56	41.43	38.50	0.26	0.31	0.33	0.30
41.43	48.27	44.85	0.47	0.54	0.57	0.53
48.27	56.23	52.25	0.83	0.92	0.96	0.90
56.23	65.51	60.87	1.39	1.50	1.57	1.49
65.51	76.32	70.92	2.21	2.34	2.45	2.33
76.32	88.91	82.62	3.35	3.46	3.62	3.48
88.91	103.58	96.25	4.76	4.85	5.06	4.89
103.58	120.67	112.13	6.33	6.38	6.62	6.44
120.67	140.58	130.63	7.83	7.85	8.09	7.92
140.58	163.77	152.18	9.11	9.09	9.26	9.15
163.77	190.80	177.29	10.06	10.00	10.07	10.04
190.80	222.28	206.54	10.67	10.59	10.53	10.60
222.28	258.95	240.62	11.08	10.99	10.77	10.95
258.95	301.68	280.32	10.11	10.02	9.67	9.93
301.68	351.46	326.57	8.44	8.35	7.96	8.25
351.46	409.45	380.46	6.33	6.23	5.92	6.16
409.45	477.01	443.23	4.10	3.99	3.84	3.98
477.01	555.71	516.36	1.88	1.76	1.76	1.80
555.71	647.41	601.56	0.00	0.00	0.00	0.00

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**Table A.3** 100% Modulus of compound according to ASTM D412-98a.

Sample	Strength@100% (MPa)						Average
	1	2	3	4	5	6	
RB0	1.19	1.21	1.19	1.04	1.11	1.04	1.13
RB50	1.10	1.12	1.06	1.05	1.06	1.05	1.08
RB100	0.97	1.03	1.02	0.97	1.07	0.99	1.01
RB200	1.05	1.07	1.01	0.92	1.01	1.00	1.01
RB300	1.06	1.09	1.15	0.95	1.12	0.98	1.06
RB100b	0.83	0.80	0.78	0.71	0.69	0.74	0.76
RB100c	1.09	1.01	1.03	0.99	1.02	1.02	1.02
RB100d	0.85	0.86	0.87	0.92	0.89	0.91	0.88
RB100e	0.85	0.87	0.88	0.82	0.84	0.86	0.85
RN100	5.51	9.29	8.57	8.73	8.95	8.84	8.32
RC100	1.79	1.76	1.81	1.77	1.82	1.80	1.79
RNB100	2.69	2.95	2.69	2.88	2.87	2.79	2.81
RNC100	7.95	8.11	8.14	8.01	8.14	7.70	8.01
G	1.37	1.20	1.24	1.60	1.46	1.42	1.38
GB100	1.07	1.04	1.02	0.75	0.84	1.05	0.96

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**Table A.4** 300% Modulus of compound according to ASTM D412-98a.

Sample	Strength@300% (MPa)						Average
	1	2	3	4	5	6	
RB0	2.74	2.85	2.71	2.31	2.49	2.53	2.61
RB50	2.17	2.32	2.27	2.18	2.09	2.22	2.21
RB100	2.25	2.07	2.26	1.95	1.93	2.10	2.09
RB200	2.42	2.51	2.30	3.37	3.17	3.02	2.80
RB300	2.38	2.43	2.50	2.28	2.21	2.18	2.33
RB100b	1.37	1.43	1.52	1.27	1.24	1.27	1.35
RB100c	2.11	2.12	2.30	2.12	2.14	2.18	2.16
RB100d	1.87	1.71	1.80	1.76	1.82	1.82	1.80
RB100e	1.56	1.71	1.58	1.71	1.74	1.80	1.68
RN100	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RC100	2.71	2.76	2.78	2.63	2.69	2.72	2.72
RNB100	8.93	8.86	9.04	9.05	8.76	8.51	8.86
RNC100	0.00	0.00	0.00	0.00	0.00	0.00	0.00
G	3.57	3.60	3.41	3.99	4.01	3.81	3.73
GB100	2.65	2.62	2.70	1.71	2.09	2.39	2.36

**Table A.5** Tensile strength of compound according to ASTM D412-98a.

Sample	Tensile Strength (MPa)						Average
	Sample No.						
	1	2	3	4	5	6	
RB0	2.74	3.36	3.34	2.84	2.80	3.16	3.04
RB50	6.77	7.59	9.97	6.77	5.46	4.78	6.89
RB100	10.39	10.28	11.38	11.06	9.17	7.99	10.04
RB200	9.51	9.02	11.00	9.02	11.30	8.31	9.69
RB300	6.05	8.38	6.95	7.19	8.96	5.34	7.15
RB100b	6.10	6.17	5.34	5.16	4.94	5.66	5.56
RB100c	12.09	11.84	11.67	11.28	11.61	11.88	11.73
RB100d	10.86	10.40	11.39	10.67	10.85	11.04	10.87
RB100e	9.51	9.77	8.98	9.56	8.17	8.77	9.13
RN100	9.65	11.22	12.01	11.39	12.29	10.79	11.22
RC100	4.58	4.05	3.70	4.24	3.79	5.33	4.28
RNB100	14.30	13.46	13.55	12.73	14.69	13.86	13.76
RNC100	8.50	9.15	9.45	8.34	8.81	9.21	8.91
G	15.56	17.18	16.42	14.25	13.10	12.97	14.91
GB100	13.10	12.29	11.60	11.76	11.95	12.37	12.18

**Table A.6** Elongation at break of compound according to ASTM D412-98a.

Sample	Elongation at break (%)						Average
	1	2	3	4	5	6	
RB0	275	315	335	325	325	330	317.5
RB50	550	545	585	575	515	475	540.8
RB100	590	650	625	680	600	675	636.7
RB200	585	560	565	570	690	690	610.0
RB300	510	545	510	550	630	475	536.7
RB100b	650	660	645	640	650	705	658.3
RB100c	690	670	620	650	670	670	661.7
RB100d	685	710	745	705	720	735	716.7
RB100e	685	665	655	660	595	625	647.5
RN100	170	135	155	125	140	115	140.0
RC100	420	400	385	410	385	445	407.5
RNB100	460	415	430	385	470	435	432.5
RNC100	110	100	105	85	90	95	97.5
G	640	700	685	640	607.5	747.5	670.0
GB100	635	640	595	645	690	699.5	650.8

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**Table A.7** Tear strength of compound according to ISO 34.

Sample	Tear Strength (N/mm)						Average
	1	2	3	4	5	6	
RB0	26.88	16.46	15.54	28.90	24.73	26.12	23.11
RB50	26.69	26.69	27.36	29.33	30.79	29.61	28.41
RB100	26.65	27.46	25.70	24.73	26.25	25.91	26.12
RB200	23.35	24.45	23.85	24.81	24.43	23.28	24.03
RB300	23.47	23.08	23.00	23.58	25.72	24.41	23.88
RN100	43.40	43.85	42.33	39.50	38.18	41.45	41.45
RC100	22.43	18.86	22.17	21.96	23.09	18.81	21.22
RNB100	43.07	41.34	42.08	45.04	42.32	45.12	43.16
RNC100	29.62	27.27	29.66	31.59	26.20	30.74	29.18
G	34.38	36.66	35.41	36.75	36.66	33.67	35.59
GB100	36.96	31.23	28.68	31.67	33.03	45.39	34.49

**Table A.8** Abrasion, Akron (volume loss) of compound according to BS.903 Part A9.

Sample	Abrasion, arkron (volume loss, cm <sup>3</sup> /1000 cycles)		Average
	Sample No.		
	1	2	
RB0	0.80	0.82	0.81
RB50	1.00	1.04	1.02
RB100	1.12	1.12	1.12
RB200	1.16	2.00	1.58
RB300	1.84	1.84	1.84
RN100	0.76	0.76	0.76
RC100	1.68	1.76	1.72
RNB100	0.76	0.72	0.74
RNC100	0.80	0.80	0.80
G	0.62	0.62	0.62
GB100	1.04	0.96	1.00

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**Table A.9** Hardness (shore A) of compound according to ASTM D2240-97.

Sample	Hardness (shore A)		Average
	Sample No.		
	1	2	
RB0	53	53	53.0
RB50	52	51	51.5
RB100	51	51	51.0
RB200	50	50	50.0
RB300	51	48	49.5
RB100b	44	44	44.0
RB100c	50	51	50.5
RB100d	48	46	47.0
RB100e	45	45	45.0
RN100	88	89	88.5
RC100	67	67	67.0
RNB100	71	71	71.0
RNC100	93	90	91.5
G	53	53	53.0
GB100	50	49	49.5

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**Table A.10** Specific gravity of compound.

Sample	Specific Gravity		Average
	Sample No.		
	1	2	
RB0	0.939	0.950	0.945
RB50	0.980	0.987	0.984
RB100	1.006	0.999	1.003
RB200	1.024	1.022	1.023
RB300	1.038	1.039	1.039
RB100b	0.981	0.981	0.981
RB100c	0.991	0.989	0.990
RB100d	1.008	1.010	1.009
RB100e	1.003	1.003	1.003
RN100	1.215	1.213	1.214
RC100	1.343	1.342	1.343
RNB100	1.104	1.105	1.105
RNC100	1.426	1.434	1.430
G	1.074	1.078	1.076
GB100	1.086	1.091	1.089

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**Table A.11** Original and swollen polymer weight according to section 3.4.5.

Sample	Original polymer weight (g)			Swollen polymer weight (g)		
	Sample No.			Sample No.		
	1	2	Average	1	2	Average
RB0	0.38	0.37	0.375	1.65	1.61	1.630
RB50	0.39	0.39	0.390	1.54	1.59	1.565
RB100	0.39	0.41	0.400	1.61	1.70	1.655
RB200	0.43	0.43	0.430	1.71	1.71	1.710
RB300	0.44	0.44	0.440	1.75	1.79	1.770
RN100	0.50	0.50	0.500	1.35	1.39	1.370
RC100	0.49	0.49	0.490	1.35	1.36	1.355
RNB100	0.44	0.43	0.435	1.42	1.38	1.400
RNC100	0.62	0.64	0.630	1.17	1.21	1.190
G	0.44	0.44	0.440	1.75	1.67	1.710
GB100	0.44	0.44	0.440	1.81	1.79	1.800

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**Appendix B****Table B.1** Material Specification of Natural Rubber.

Properties	Test Result
Dirt	0.010
Ash	0.21
Volatile matter	0.38
Nitrogen	0.35
Color	4.0
Initial Wallace Plasticity (Po)	35.3
Plasticity Retention Index (PRI)	82.4
Mooney Viscosity (ML (1+4) 100°C)	60.8

**Table B.2** Material Specification of Keltan 5508.

Properties	Test Result
Mooney Viscosity, ML (1+4) 125°C	54.5
Volatiles, % wt	0.23
Ethylene, % wt	69.70
ENB, % wt	4.63

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**Table B.3** Material Specification of Thai Black-N330 (HAF) (Carbon Black).

Properties	Test Result
Iodine No., mg/g	81.1
DBP, cc/100g	103.00
24M4 DBP, cc/100g	84.5
Tint Strength, %IRB#3	104.1
Heating Loss, % Max	0.5
Ash Content, %Max	0.21
Pour Density, Kg/m <sup>3</sup>	368.8
Fine Content, %Max	4.0
P. Hardness, g	16.2
Sieve Residue #325, % Max	0.0105
Sieve Residue #35, % Max	0.0000

**Table B.4** Material Specification of Ultrasil VN3 GR.

Properties	Test Result
Specific Surface Area (Aremeter), m <sup>2</sup> /g	172
Electrical Conductivity, 4% in water, $\mu$ S/cm	738
Loss on drying, 2 h at 105°C, %	5.0
pH values, 5% in water	6.5
Sieve Analysis > 300 $\mu$ m (Ro-Tap), %	96.6
Sieve Analysis < 75 $\mu$ m (Ro-Tap), %	1.9

**Table B.5** Material Specification of HiCoat 410.

Properties	Test Result
Average Particle Size (d=50), $\mu\text{m}$	1.86
Specific Surface Area, $\text{cm}^2/\text{g}$	12,856
Residue on 325 mesh, %	0.000
DOP absorption, g/100g	19.20
Moisture Content, %	0.11
Whiteness (Powder)	93.57
Whiteness (Paste)	68.51



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### Appendix C

The crosslink density of RB100 was calculated according to Flory-Huggins Theory [32]. Swelling can be determined gravimetrically, by weighing the polymer sample before the experiment ( $w_0$ ) and subtracting this value from the solvent swollen polymer weight ( $w_s$ ) as in Eq. B.1

$$V_{equil} = \frac{w_0}{\rho_2} + \frac{w_s - w_0}{\rho_1} \quad (B.1)$$

and

$$V_{2m} = \frac{w_0}{V_{equil} \times \rho_2} \quad (B.2)$$

where

$\rho_2$	=	polymer density	=	1.003 g/cm <sup>3</sup> (TableA9)
$\rho_1$	=	solvent density (toluene)	=	0.860 g/cm <sup>3</sup>
$w_0$	=	Original polymer weight	=	0.40 g
$w_s$	=	swollen polymer weight	=	1.655 g

$$V_{equil} = \frac{0.400}{1.003} + \frac{1.655 - 0.400}{0.860} = 1.858$$

Substituting  $V_{equil} = 1.80$  in Eq. B.2

$$V_{2m} = \frac{0.400}{1.858 \times 1.003} = 0.215$$

The molecular weight per crosslink unit,  $M_c$  is calculated using Eq. B.3

$$M_c = \frac{V_1 \rho_2 \left( V_{2m}^{1/3} - \frac{V_{2m}}{2} \right)}{-[\ln(1 - V_{2m}) + V_{2m} + \chi_1 V_{2m}^2]} \quad (B.3)$$

where  $V_1$  is molar volume of solvent and  $\chi_1$  is polymer-solvent interaction parameter.

In chemistry, the molar volume of a substance is the volume of one mole of that substance. It can be computed as the substance's atomic or molecular weight, divided by its density.

Hence,

$$V_1 = 107.10 \text{ cm}^3/\text{mol}$$

Substituting the known value  $V_1$ ,  $\rho_2$ ,  $V_{2m}$  and  $\chi_1 = 0.39$  [32] for rubber/toluene in Eq. B.3

$$M_c = 5862.442 \text{ g/mol}$$

Thus, the crosslink density of RB100 is,

$$\begin{aligned} n_c &= \frac{\rho_2}{5862.442} \\ &= 0.1711 \text{ mol/cm}^3 \\ &= 17.11 \times 10^{-2} \text{ kmol/m}^3 \end{aligned}$$

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## VITAE

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