การใช้กากกาแฟเป็นสารตัวเติมในยางธรรมชาติ

นายเศรษฐณัชย์ เตี้ยบัวแก้ว

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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USE OF COFFEE RESIDUE AS FILLER IN NATURAL RUBBER

Mr. Setthanat Tiabuakaew

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Applied Polymer Science and Textile Technology
Department of Materials Science
Faculty of Science
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Thesis Title	USE OF COFFEE RESIDUE AS FILLER IN NATURAL RUBBER
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เศรษฐณัชย์ เตี้ยบัวแก้ว : การใช้กากกาแฟเป็นสารตัวเติมในยางธรรมชาติ (USE OF COFFEE RESIDUE AS FILLER IN NATURAL RUBBER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.กนกทิพย์บุญเกิด, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.ธนากร วาสนาเพียรพงศ์, 144 หน้า.

วัตถุประสงค์ของงานวิจัยนี้เพื่อศึกษาความเป็นไปได้ในการใช้กากกาแฟเป็นสารตัวเติมในยางธรรมชาติ สารตัวเติมชนิดต่างๆ ที่เตรียมได้จากกากกาแฟประกอบด้วยอนุภาคกากกาแฟ อนุภาคกากกาแฟดัดแปรพื้นผิวด้วย Si69 ถ่าน และถ่านกัมมันต์ ผลจากการวิเคราะห์ด้วยเครื่องวัดขนาดอนุภาคด้วยเลเซอร์พบว่าขนาดอนุภาคของถ่านและถ่านกัมมันต์มีขนาดใกล้เคียงกันและมีขนาดเล็กกว่าขนาดอนุภาคของอนุภาคกากกาแฟครึ่งหนึ่ง อย่างไรก็ตามพื้นที่ผิวของถ่านและถ่านกัมมันต์ที่เตรียมที่อุณหภูมิ 700 และ 800 องศาเซลเซียสมีค่าสูงกว่าอนุภาคกากกาแฟเพียงเล็กน้อยเท่านั้น แต่พื้นที่ผิวของถ่านกัมมันต์ที่เตรียมที่อุณหภูมิ 600 องศาเซลเซียสมีค่าสูงกว่าสารตัวเติมชนิดอื่นมาก ค่าพีเอชของถ่านและถ่านกัมมันต์ที่เตรียมได้มีค่าใกล้เคียงกันและมีค่าสูงกว่าค่าพีเอชของอนุภาคกากกาแฟ เมื่อเปรียบเทียบประสิทธิภาพการเสริมแรงของสารตัวเติมที่เตรียมได้จากกากกาแฟ พบว่าอนุภาคกากกาแฟมีประสิทธิภาพการเสริมแรงต่ำที่สุดเนื่องจากมีขนาดอนุภาคที่ใหญ่ที่สุดและมีความเป็นกรดซึ่งขัดขวางกระบวนการคงรูปของยางทำให้ปริมาณการเชื่อมขวางของยางคงรูปน้อยลง การดัดแปรพื้นผิวกากกาแฟด้วย Si69 ช่วยเพิ่มความสามารถในการเสริมแรงของอนุภาคกากกาแฟได้ อย่างไรก็ตามประสิทธิภาพการเสริมแรงของอนุภาคกากกาแฟดัดแปรพื้นผิวด้วย Si69 ยังคงต่ำเมื่อเทียบกับถ่านและถ่านกัมมันต์ ผลของการเติมถ่านและถ่านกัมมันต์ในยางธรรมชาติพบว่า ลักษณะการคงรูป ความหนืดมูนนี และสมบัติเชิงกลของยางธรรมชาติมีแนวโน้วไปในทิศทางเดียวกัน เมื่อเปรียบเทียบประสิทธิภาพการเสริมแรงของสารตัวเติมชนิดต่างๆ ที่เตรียมได้จากกากกาแฟพบว่า ถ่านมีประสิทธิภาพการเสริมแรงสูงสุดโดยทำให้ยางธรรมชาติมีค่าความต้านแรงดึง ความต้านแรงฉีกขาด โมดูลัสและความแข็งสูงที่สุด ปริมาณการเติมถ่านที่เหมาะสมที่ทำให้ยางธรรมชาติมีความต้านแรงดึงและความต้านแรงฉีกขาดสูงสุดคือที่ปริมาณ 10 และ 20 ส่วนในยางธรรมชาติ 100 ส่วนตามลำดับ นอกจากนี้ทำการเปรียบเทียบลักษณะการคงรูป ความหนืดมูนนี และสมบัติเชิงกลของยางธรรมชาติที่เติมถ่านซึ่งเป็นสารตัวเติมที่เตรียมได้จากกากกาแฟที่มีประสิทธิภาพการเสริมแรงสูงที่สุดกับยางธรรมชาติที่เติมสารตัวเติมเชิงการค้าได้แก่ เขม่าดำเกรดเสริมแรง (N330) เขม่าดำเกรดกึ่งเสริมแรง (N774) และแคลเซียมคาร์บอเนต แม้ว่าลักษณะการคงรูปและความหนืดมูนนีของยางธรรมชาติที่เติมถ่านมีค่าใกล้เคียงกับยางธรรมชาติที่เติม N774 แต่ความสามารถในการเพิ่มสมบัติเชิงกลของยางธรรมชาติที่เติมถ่านก็ยังมีค่าน้อยกว่ายางธรรมชาติที่เติมทั้ง N330 และ N774 นอกจากนี้ยังพบว่ายางธรรมชาติที่เติมถ่านมีสมบัติเชิงกลสูงกว่ายางธรรมชาติที่เติมแคลเซียมคาร์บอเนตแต่ไม่ส่งผลต่อค่าความต้านแรงดึงของยางธรรมชาติ จากผลการทดลองข้างต้นพบว่า ถ่านที่เตรียมได้จากกากกาแฟด้วยกระบวนการคาร์บอไนเซชันสามารถนำมาใช้เป็นสารตัวเติมเฉื่อยสำหรับยางธรรมชาติได้

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต

สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

##5272224723: MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY

KEYWORDS : COFFEE RESIDUE / FILLER / NATURAL RUBBER

SETTHANAT TIABUAKAEW : USE OF COFFEE RESIDUE AS FILLER IN NATURAL RUBBER. ADVISOR: KANOKTIP BOONKERD, Ph.D. CO-ADVISOR: ASST. PROF. THANAKORN WASANAPIARNPONG, D.Eng., 144 pp.

The objective of this research is to study the possibility of the use of coffee residue as filler in natural rubber. The various forms of filler were prepared from coffee residue including coffee residue particle (CRP), Si69 treated CRP, char, and activated carbon. The result from a laser particle size analyzer indicated that the particle size of char and activate carbon were comparable and nearly half of that of CRP. However, the BET surface area of char and two activated carbons prepared at 700 and 800°C were only slightly higher than that of CRP. Interestingly, the activated carbon prepared at 600°C had tremendously higher BET surface area than the others. The pH value of char and all activated carbons were also comparable and higher than that of CRP. Among various forms of filler prepared from coffee residue, it was found that CRP showed the lowest reinforcing efficacy. It was not only its largest particle size but also its acidity nature inhibiting curing process, thus giving the vulcanizates with lower crosslink density. The modifying CRP surface by Si69 enhanced the reinforcing ability of CRP. But its reinforcing ability was still low when comparing with the other two forms (char and activated carbon). The presence of char and all three different activate carbons showed nearly similar trend on the cure characteristics, Mooney viscosity, and mechanical properties but different in degree. Importantly, it was observed that amongst fillers prepared from coffee residue, char had highest reinforcing efficacy. This was evident by highest tensile and tear strength, modulus and hardness. The optimum loading for tensile and tear strength is observed at 10 and 20 phr, respectively. Then, the effect of char, highest reinforcing filler from coffee residue, on the cure characteristics, Mooney viscosity, and mechanical properties was compared with the commercial fillers including reinforcing CB (N330), semi-reinforcing CB (N774), and inert calcium carbonate. Char showed similar effect on the cure characteristics and Mooney viscosity as did N774. But the ability to enhance mechanical properties of char was much lower than that of CB both N330 and N774. With the exception of tensile strength, char gave mechanical properties more or less better than $CaCO_3$. Therefore, coffee residue that was turned into char by carbonization can be used as inert filler for natural rubber.

Department: Materials Science Student's Signature
Field of Study: Applied Polymer Science and Textile Technology Advisor's Signature
Academic Year: 2011 Co-advisor's Signature

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CHAPTER 1
INTRODUCTION

Fillers have been widely used in the rubber industry for two main purposes which are improvement mechanical properties of vulcanized rubber and reduction in material costs. Commonly, fillers can be classified into three broad groups, i.e., non-reinforcing filler, semi-reinforcing filler, and reinforcing filler [1]. Among commercial fillers, carbon black and silica are the most important reinforcing fillers in the rubber industry because these fillers extensively improve the mechanical properties: tensile strength, tear strength and abrasion resistance, of the final vulcanized rubber. However, some applications are greatest concern about cost of the end products. The use of non- reinforcing filler or semi-reinforcing filler, for example, calcium carbonate, clay and talc are recommended. The non-reinforcing filler and semi-reinforcing filler may just slightly or may not improve the mechanical properties of vulcanizates but added to reduce the overall production cost.

Nowadays, many rubber researches have been interested in using the wastes, residues, or by-products as filler for natural rubber, for example limestone dust [1], rice husk [2], cuttlebone [3], lime kiln dust [4], and newsprint paper fiber [5], etc. The advantages of these fillers are low cost, abundance, easy availability, and renewable material. In addition, the use of these as fillers can reduce the environmental problems.

Coffee residue is agricultural waste after extraction process in coffee industry. It consists of most hemicelluloses and fiber components. In Thailand, the expansion of coffee industry leads to large quantities of coffee waste that are disposed by burning as a fuel or using as an animal feed or fertilizer [6]. One possible way, to reduce the amount of this waste or increase the value of this waste is to use it as filler in the rubber compound.

Thus, this research is interested in studying the possibility of the use of coffee residue and its modified products including Si69 treated coffee residue particle, char and activated carbon as fillers for natural rubber. And in order to know their influence on cure characteristic and reinforcing level, the study was carried out by comparing the cure characteristic and physical properties of natural rubber compounds filled with coffee residue or modified coffee residues with those of natural compounds filled with reinforcing carbon black N330, semi-reinforcing carbon black N774, and inert calcium carbonate.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

Natural rubber (NR) can be derived from the milky latex of various trees, but the main commercial source of natural rubber is the tree *Hevea brasiliensis*. The chemical structure of NR is a polyterpene. It consists of 1,4-isoprene molecules linked into loosely twisted chains. The monomer units along the backbone of the carbon chains are in a *cis* arrangement almost 100% as shown in Figure 2.1. The average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution [7]. In the polyisoprene of NR, there is one double bond for each isoprene unit. These double bonds and the α-methylene groups are reactive groups for vulcanization reactions with sulfur. The double bonds can, however, also enter into additional reactions with oxygen or ozone, thus leading to the degradation of the rubber. NR has a density of 0.93 g/cm^3 at 20 °C [8]. Its glass transition temperature (Tg) is about -70 °C [9]. For commercial, in addition to latex form, it is also available in the dry rubber form including ribbed smoked sheet, air-dried sheet and pale crepes, etc.

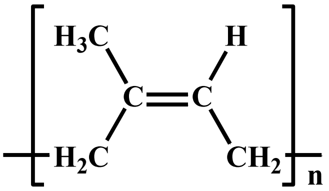


Figure 2.1 cis-1,4-polyisoprene repeating unit

2.1.1 Properties of NR

Elasticity is the most important property of NR [10]. When stretched, it expands and pulls back its original state, when released. Because of its highly regular structure, NR crystallizes at low temperature and upon straining which is called low temperature crystallization and strain induced crystallization, respectively [4-16]. Strain crystallizability imparts outstanding high green strength and good crack growth resistance [12,14]. However, NR has poor resistance to oils, sunlight, ozone, solvent and limited thermal capability. Generally, raw NR becomes sticky when hot and brittle when cold. The vulcanization process modifies raw NR so that these changes will not occur. This reaction converts the plastic and viscous nature of raw NR into the elastic. In the typical vulcanization process, sulfur and certain other substances are added to raw NR and the mixture is then heated. The molecules of NR are crosslinked together into a three-dimensional network as shown in Figure 2.2. NR vulcanizates will have high tensile strength with a high rebound elasticity and its mechanical properties now are less sensitive to temperature. Its hardness, abrasion resistance and tear strength and also oxidation resistance is higher when compared to those of raw rubber.

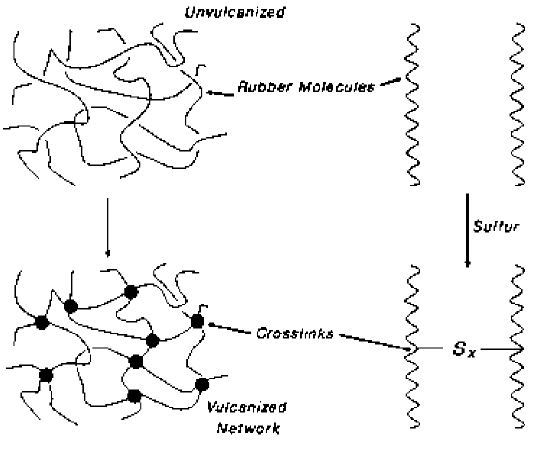


Figure 2.2 Sulfide network formation [17]

2.1.2 Applications of NR

NR is a very versatile raw material. It is mainly used as solid rubber, and to a lesser extent, as latex. NR is an indispensable material for many industrial and household applications especially, for heavy-duty tires and quake-absorbing structures [11-14]. NR is preferred also for medical products such as surgical gloves and condoms, because of its softness, extensibility, and the ability to form a very thin film having the complicated shape without any pinholes [12,13]. Other applications include toys, balls, rafts, elastic bandages, adhesives, paints, hoses, conveyor belts, and a multitude of other products. In addition to this, NR can be blended with many polymers to be used for many applications [18-20].

2.2 Fillers

Generally, NR does not require the use of fillers to obtain high tensile strength. However, the use of fillers is necessary, in order to achieve the level and range of properties that are required for technical reasons. Fillers have been widely used in the rubber industry for two main purposes which are improvement mechanical properties of vulcanized rubber and reduction in material costs. Commonly, fillers can be classified into three broad groups, i.e., non-reinforcing filler, semi-reinforcing filler and reinforcing filler. In some cases, they are divided into black and non-black type [1,21].

2.2.1 Factors Affecting Filler Reinforcement

2.2.1.1 Particle Size and Surface Area

Particle size is directly related to the reciprocal of surface area per gram of filler. The smaller particles have larger surface area to interact with the rubber. In Figure 2.3, the limit of the particle size of fillers that can reinforce the rubber should be smaller than 10^3 nm. In case of commercial fillers, carbon black (some carbon black grades) and precipitated silica are the most important reinforcing fillers due to the small particle size. Other larger fillers such as clay and calcium carbonate ($CaCO_3$) are used mainly as diluents fillers because of unable reinforcing rubber [7,22-24].

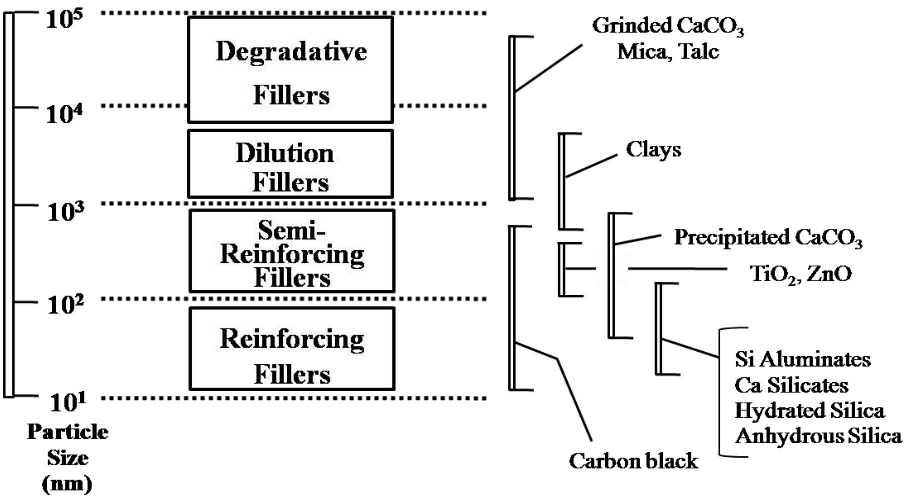


Figure 2.3 Classification of filler according to average particle size [24]

2.2.1.2 Specific Activity of Filler Surface

Filler can have chemically or adsorptively bound functional groups on its surface. The formed bonds cause, an increased deformation stiffness, because of less mobility of the polymer chains. For example, carbon black surface consists of phenolic, hydroxyl, quinine, carboxyl, lactone, and free radicals [24-26] which can react chemically with rubber molecules. However, the filler-rubber interaction is affected by the reactivity of the rubber also.

2.2.1.3 Structure of Filler

Many fillers, among them especially carbon black, during the manufacture the primary particles fuse to form aggregates which are not even destroyed by mechanical influences. The shape and degree of aggregate branching is referred to as structure as shown in Figure 2.4. The filler with high structure has large void volume within its structure in which rubber molecules may become occluded. The occluded rubber-filler microcomposite then effectively becomes the reinforcing entity. Generally, reinforcement is increased by high structure and strong bonding between filler and rubber [7,21].

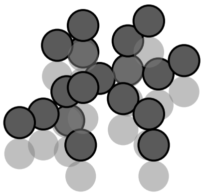


Figure 2.4 Schematic of carbon black aggregate consisting of fused primary particles [9]

2.2.1.4 Filler Content

The reduction in properties at higher loading is a dilution effect, general to all fillers, merely due to a diminishing volume fraction of polymer in the composite. If the volume percentage of filler becomes so high that there is not enough rubber matrix to hold the filler particles together, strength approaches zero.

2.2.1.5 pH Value

The pH value does not affect directly on degree of reinforcing. However, it can give important clues for the vulcanization behavior and the possible adsorption of accelerator by the filler; this can upset the vulcanization process and result in poor properties of the vulcanizate.

2.2.2 Carbon Black

Carbon black (CB) is an amorphous carbon of quasi-graphitic structure. Most of the CB produced is used in mainly rubber products, although an important secondary application is in printing inks [8]. CB is prepared either by incomplete combustion of hydrocarbons or by thermal cracking [26]. There are different chemical groups on the surface of carbon black. Such are phenolic, hydroxyl, quinine, carboxyl and lactone groups. The average primary particle size of CB ranges from about 10 to 500 nanometers [27]. During the initial CB formation stage, the primary structures are fused together building up three-dimensional branched clusters called aggregates as shown in Figure 2.5. These aggregates are not even destroyed by mechanical influences. The degree of aggregate branching is referred as structure. High structure has large void volume within its structure in which rubber molecules may become occluded. The occluded rubber-filler microcomposite then effectively becomes the reinforcing entity. Generally, reinforcement is increased by high structure and strong bonding between filler and rubber. Furthermore, these aggregates can link together to form agglomerates via van der Waals interaction.

According to the manufacturing process, CB are classified into main three types by which are furnace black, channel black and thermal black. Furnace black is today the most important of them. The furnace blacks are produced from liquid aromatic feedstock. Basically, the feedstock is preheated and burned in a reaction zone with insufficient air supply. Reaction to form finely divided carbon is completed within milliseconds and the hot smoke stream is quenched with water. Furnace black has low oxygen contents and its surface is neutral or alkaline.

Thermal black is generally produced from oil or natural gas by cracking in absence of oxygen at a hot refractory surface. The process produces unoxidized blacks of relatively small specific surface area. Channel blacks are more acidic than the other carbon blacks. They therefore cause a more or less strong effect on vulcanization. The channel black is produced from natural gas by burning in small burner with a sooty diffusion flame. The carbon then is collected on a cooled iron channel.

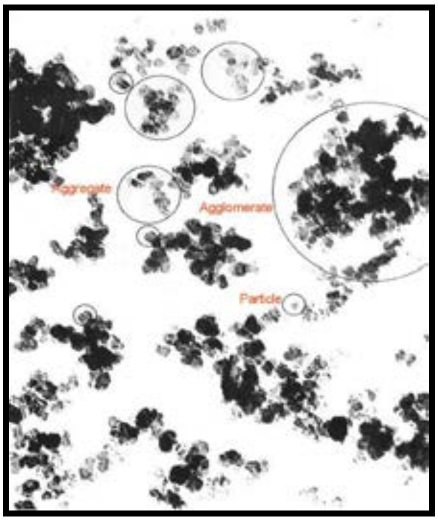


Figure 2.5 Carbon black morphology [27]

The American Society of Testing Materials (ASTM) has established a CB classification system based essentially on particle size and degree of surface oxidation with the intention of replacing an earlier letter-type nomenclature. The N series comprises “normal-curing” furnace and thermal blacks while the S series represents “slow curing” channel blacks and deliberately oxidized furnace blacks. The first number of a three-digit suffix identifies particle size as shown in Table 2.1. The remaining two digits are assigned arbitrarily.

Table 2.1 ASTM first digit versus particle size [26,28]

First digit	Range of ASTM numbers	Nominal number average particle diameter (nm)	Specific surface area m^2/g
0	000-099	1-10	>155
1	100-199	11-19	125-155
2	200-299	20-25	110-140
3	300-399	26-30	70-90
4	400-499	31-39	43-69
5	500-599	40-48	36-52
6	600-699	49-60	26-42
7	700-799	61-100	17-33
8	800-899	101-200	-
9	900-999	201-500	-

The CB used in rubber industry can be categorized into three grades such are reinforcing, semi-reinforcing and non-reinforcing grades as shown in Table 2.2.

Table 2.2 Main categories of CB for the rubber industry

Reinforcement level	Suitable grades
Reinforcement grades	N100 to N300
Semi-reinforcement grades	N550 to N700
Non-reinforcement grades	N880 to N990

The properties of NR vulcanizate filled with CB relate to the characteristics of each CB grade including particle size, surface area, structure and surface activity. Figure 2.6 illustrates the general trends for the effect of CB loading on the properties of CB filled NR vulcanizates. As CB level increases there are increases in modulus, heat buildup, tear strength, abrasion resistance, hardness, and, in tire, an increase in rolling resistance and wet skid properties. Tensile strength, compound processability and abrasion resistance go through an optimum after which these properties deteriorate.

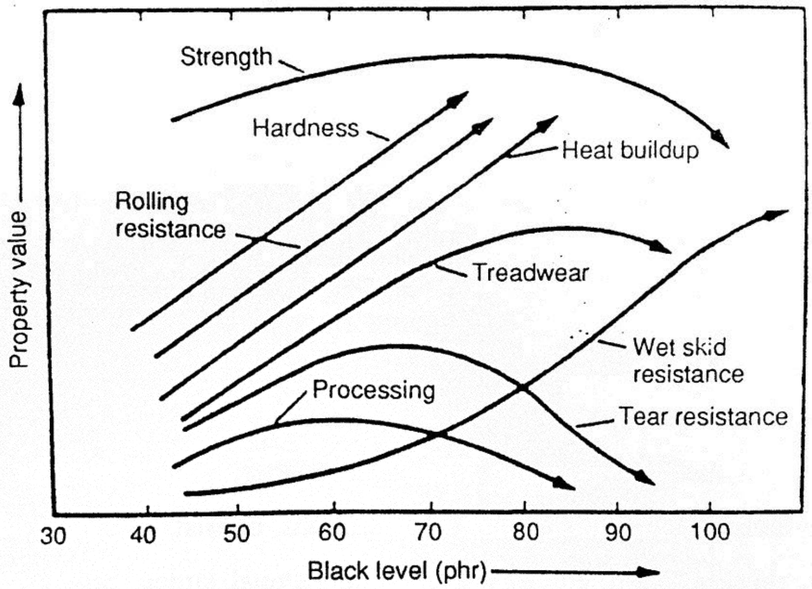


Figure 2.6 Effect of CB level on compound properties [26]

2.2.3 Calcium Carbonate

Calcium carbonate ($CaCO_3$) is the most important filler for plastics and it is also wildly used in rubber and paints [29,30]. Natural calcium carbonate is produced from chalk, limestone, marble, or calcite. Generally, commercial calcium carbonate can be divided into two forms [1,28,31]. One is natural ground calcium carbonate (GCC) used as a diluent to reduce compound cost. The particle diameter is relatively large, ranging from 1 to 5 μm, and bulk density is low. GCC generally could be mixed easily into rubber. Good dispersion is obtained even at very high loading, up to 200 phr, without significant increase in compound viscosity. Although GCC reduces cost, the magnitude of the practically important volume cost reduction is limited because of the high specific gravity. The other form is precipitated calcium carbonate (PCC). PCC is obtained as a by-product during the manufacture of Na_2CO_3 by the ammonia process or during the manufacture of NaOH by the sodalime process or recarbonation from limestone as shown in Figure 2.7.

(a) $$NH_3 + H_2O + CO_2 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + H_2O + CO_2$$

$CaCO_3$ is used in this process as follows:

$$CaCO_3 + \text{heat} \rightarrow CO_2 + CaO \xrightarrow{H_2O} Ca(OH)_2$$

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + 2H_2O + CaCl_2 \xrightarrow{CO_2} H_2O + 2NH_4Cl + CaCO_3$$

(b) $$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

(c) $$CaCO_3 + \text{heat} \rightarrow CO_2 + CaO \xrightarrow{H_2O} Ca(OH)_2 \xrightarrow{CO_2} CaCO_3$$

Figure 2.7 Schematic of the manufacture of precipitated calcium carbonate by (a) Na_2CO_3 (b) NaOH (c) limestone [30]

PCC products are of high purity, with a very fine. The particle size of PCC is below 0.1 µm, thus being used as a reinforcing filler for rubber compounds. However, it is a higher cost process and more energy intensive than that involved in GCC production.

The most important applications of calcium carbonate by the rubber industry are in electrical wire and cable insulation where the low moisture content and natural insulating properties make it a preferred filler; in the production of articles where low cost and smooth surface appearance are desired, such as footwear; and in extruded hoses and automotive sealing part. Typical calcium carbonate levels in rubber compounds range from 20 to 300 phr [21].

2.2.4 Fillers from Wastes/Residues/By-products for NR

There are many wastes, residues or by-products from several industries which cause environmental problems and health hazards. One way to solve these problems is to use them as fillers in rubber due to their low cost, abundance and renewable source. Nowadays, the rubber researcher has interested to use the wastes, residues or by-products as filler in rubber as shown in the following references.

Sae-oui et al. [1] studied the possibility of using limestone dust waste (LDW) which is generated from the explosions during the mining of limestone to obtain raw materials for cement manufacturing as a filler in NR. LDW is mainly composed of $CaCO_3$ (98.90 wt%). Other oxides are also observed in LDW such as MgO, SiO_2 and Al_2O_3. The reinforcing efficiency of LDW was compared with commercial types of $CaCO_3$ such as precipitated $CaCO_3$ (PCC) and nano- precipitated $CaCO_3$ (NPCC). The results revealed that the LDW does not give reinforcement to the NR due to its low specific surface area. When added to NR, LDW causes a slight increase in compound viscosity together with deterioration of tensile strength, tear strength, and abrasion resistance. Among the three fillers studied, the degree of reinforcement could be placed in the following order: NPCC > PCC > LDW. The main reason for this was due to the decreasing of specific surface area.

Sae-oui et al. [2] also studied the curing and mechanical properties of NR vulcanizates filled with rice husk ash (RHA) and then compared the degree of reinforcement of RHA and other commercial fillers such as talcum, china clay, $CaCO_3$, Silica, and CB. RHA is a by-product obtained from the electric power plant by using rice husk as a power source. The ash mainly consists of amorphous silica and the residual carbon black. RHA contains about 49-98 % of silica. The residual carbon cannot be completely eliminated because it is apparently trapped within the amorphous silica structure or completely coated with silica so that its removal by thermal processes is difficult. In this study, two grades of RHA (low-and high-carbon contents) were used as filler in NR. The ashes were milled for 2 h and sieved on a 200-mesh sieve. The mean agglomerate particle sizes of all fillers are not significantly different, even though silica is found to have the largest agglomerate size because of its highly reactive surface chemistry (hydroxyl and silanol groups). However, there is the lack of hydroxyl or silanol groups on the surface of both RHAs. The BET surface area of both RHAs is considerably lower than that of highly reinforcing fillers (e.g., CB and silica) but comparable to that of inert fillers such as talcum, china clay, and $CaCO_3$. When incorporated in to NR, the ash, regardless of its carbon contents, imparts the compound with low viscosity and faster vulcanization. Because their surface area and surface activity are very low, relatively comparable to those of the other inert fillers, resulting in poor mechanical properties of filled vulcanizates. Moreover, there is no improvement in mechanical properties of the both RHAs-filled vulcanizates when added of silane-coupling agent.

Poompradub et al. [3] prepared the filler for NR in peroxide vulcanization from cuttlebone obtained from waste stock at commercial processor. The cuttlebone was crushed and sieved using a mesh sieve of 25 μm. Cuttlebone was composed of $CaCO_3$ of 92% and an organic part of 8%. Commercial $CaCO_3$ filler without any surface treatment was used as a reference. The BET surface area of both of cuttlebone particles and commercial $CaCO_3$ was not significantly different, even though the cuttlebone was found to have the larger particle size than commercial $CaCO_3$ about 6 times. The results revealed that at 40 phr of filler, the cuttlebone filled NR sample showed more tensile strength than the commercial $CaCO_3$ filled NR sample. In addition, the good tensile strength property of NR filled with cuttlebone particles was explained by the interaction between the organic part of cuttlebone which was supported by SEM observation.

Arayapranee et al. [4] compared the mechanical properties of lime kiln dust (LKD) filled NR vulcanizates at various loadings from 0 to 60 phr with those of commercial fillers filled NR vulcanizate including stearic acid coated $CaCO_3$, ground $CaCO_3$, silica, and CB. LKD is a byproduct obtained from kraft chemical recovery systems by conversion of $CaCO_3$ back into calcium oxide for reuse in the causticizing process, It is mainly composed of $CaCO_3$. The results revealed that the mechanical properties of NR filled with LKD were lower than those of NR filled with coated $CaCO_3$, ground $CaCO_3$ silica, or CB. This was due to the aggregation of LKD, causing the dispersion of the filler in the rubber matrix become inhomogeneous, and hence weakened the interaction between the filler and the rubber.

Nashar et al. [5] compared the properties of NR products consisting of both of untreated newsprint paper fiber waste and newsprint paper fiber waste treated with sodium silicate and magnesium chloride with those of the NR product consisting of silica. The treatment of fiber waste improved the water resistance by approximately 47% with respect to untreated newsprint fibers. The incorporation of treated newsprint paper fiber waste into NR showed better scorch safety. The mechanical properties (stress at yield, stress at rupture, strain at yield, and strain at rupture) of all types of filler increased with the addition of 20 phr filler and then decreased with increasing filler loading. At 20 phr of filler loading, the mechanical properties of the treated waste newsprint filled NR was comparable to that of the silica filled one.

Osabohien et al. [32] studied cure characteristic and physic-mechanical properties of NR filled with the cherry seed shells (CSS) which are agro-wastes in Nigeria in comparison with CB filler (N330). The particle size of the CSS and CB are in range 15-212 nm and 30-32 nm, respectively. The results showed the scorch and cure time were generally increased in the case of the CSS filled NR compounds, while they were decreased in the case of CB filled NR compounds. This observation may be attributed to the metals or their oxides present in the CSS filler that can cause the retardation of the accelerator activity. The achieved optimum tensile strength of the both of filler filled NR vulcanizates was at 40 phr. However, at the similar filler loading, the CB filled NR vulcanizates gave the higher tensile strength, modulus, hardness and abrasion resistance. The CSS filled NR vulcanizates showed higher elongation at break and showed higher Dunlop resilience at all filler loadings.

Sombatsompop et al. [33] studied the effect of fly ash (FA) particles on the mechanical properties of NR. Fly ash is a waste from coal-fired power plant. It consists of silica similar to the precipitated silica (Psi) but with the lower content of silica than Psi which is about 46.25% silica by weight of the total FA. The average particle size of FA used in this study was 50-100 µm. The silica contents used in this study ranged from 0 to 75 phr. In general, the bound rubber content can be used to directly indicate the filler-rubber interaction. The result revealed that the bound rubber of the Psi filled NR increased at silica contents between 30 and 75 phr. The increase in bound rubber content indicated some interaction between NR and Psi. However, there was no interaction between NR and FA because the bound rubber of the FA filled NR was not increased at all FA contents. The mechanical properties of FA filled vulcanizates were similar to those of PSi filled vulcanizates at silica contents of 0-30 phr. Above these concentration, the properties of the PSi filled vulcanizates still improved, whereas those of the FA filled vulcanizates remained the same due to there was no rubber-filler interaction between NR and FA.

2.3 Coffee Residue

2.3.1 Coffee Breeds

Coffee (*Coffea* sp.) is one of the most important agricultural commodities in the world. There are about more than 500 genera and over 6,000 species of coffee plants in the world. The two most commercially important types of coffee plant are Arabica (coffea arabica) and Robusta (coffea canephora) [34-38].

Arabica coffee is the more popular coffee in the world, it holds about 70-75 percent of the world's coffee production and consumption. The Arabica plant is a large bush which is grown at 600 to 2000 meter above sea level, and has a lower yield and less caffeine content (0.8 to 1.4%). It is widely recognised to be superior to Robusta. Because Arabica plant is delicate it is harder to grow and its beans are more expensive. It can be drunk as a pure Arabica or used as the base for coffee blends with Robusta. Arabica has a delicate taste and is used to add acidity and body to the finished brew.

Robusta coffee is a popular coffee but not as frequently used as Arabica coffee. It still plays a big part in the contribution to the coffee industry as it takes up about 25-

30 percent of the world's coffee production and consumption. The Robusta plant is a small tree or a small bush which is grown from sea level to 700 meter above. It has a high yield and high caffeine content (1.7 to 4.0%). As the Robusta plant is stronger than the Arabica plant, it is easier and cheaper to grow. But this does not mean that a blend of coffee containing Robusta beans is lower quality than pure Arabica, therefore coffee blends are designed to bring out the best balance of different flavours. Robusta has a strong flavour and is usually used as a filler in instant coffee and popular commercial blends.

2.3.2 Coffee Bean Botany

The coffee fruit (also called berry or cherry) consists of a smooth, tough outer skin or pericarp, usually green in unripe fruits but that turns red-violet or deep red when ripe (even yellow or orange in particular genotypes). The pericarp covers the soft yellowish, fibrous and sweet pulp or outer mesocarp. This is followed by a translucent, colorless, thin, viscous and highly hydrated layer of mucilage (also called the pectin layer). Then, there is a thin endocarp yellowish in color, also called parchment. Finally, the silverskin covers each hemisphere of the coffee bean (endosperm). Constitution of the coffee bean is depicted in Figure 2.8.

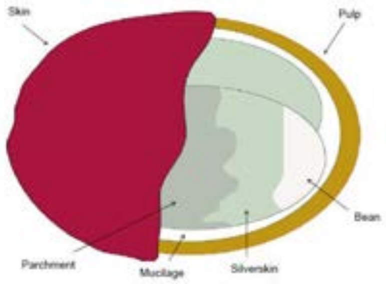


Figure 2.8 Layers in a coffee fruit [36]

2.3.3 Coffee Residue

Generally, there are three main steps for coffee processing; roasting, grinding and extraction. Coffee residue is the waste obtained after the extraction process of raw coffee bean in the coffee industry. The extraction process provides 2 parts of coffee compositions including coffee residue and coffee liquor. In roasting process, the roast coffee beans have both parts of soluble and insoluble substances as shown in Table 2.3. There are 27-35 percent of soluble substance and 65-73 percent of insoluble substance. The insoluble substance is the main component of coffee residue. There are 50 percent of hemi-celluloses and fiber is the main composition of coffee residue as reported in Table 2.4. The ash composition of coffee residue is shown in Table 2.5

Table 2.3 Chemical composition of soluble and insoluble substances of roast coffee [39]

Chemical compositions	**Percent**	
	Soluble	**Insoluble**
1. Carbohydrates (53%)		
Reducing sugar	1-2	-
Caramelized sugar	10-17	7-0
Hemi-cellulose (hydrolizable)	1	14
Fiber (Holo-cellulose and Lignin:non-hydrolizable)	-	22
2. Oils	-	15
3. Proteins	1-2	11
4. Ash (Oxide)	3	1
5. Acid, non-volatile		
Chlorogenic	4.5	-
Cafeic	0.5	-
Quinic	0.5	-
Oxalic, Malic, Citric, Tartaric	1.0	-
Volatile acids	0.35	-
6. Thiganelline	1.0	-
7. Caffeine (Arabicas 1.0%, Robustas 2.0%)	1.2	-
8. Phenolics	2.0	-
9. Volatile		
Carbon dioxide	Trace	2.0
Essence of aroma and flavor	0.04	-
Total	27-35	65-73

Table 2.4 Chemical compositions of coffee residue [39]

Chemical compositions	wt.%
1. Carbohydrates (60%)	
Caramelization sugar	10
Hemi-cellulose	20
Fiber (Holo-cellulose and Lignin)	30
2. Oils (and fatty acids)	18
3. Proteins (amino acid and complex)	15
4. Ash (Oxide)	1
5. Volatile	
Carbon dioxide	3
6. Thiganelline, Caffeine, Phenolics etc.	3

Table 2.5 Ash composition of coffee residue [39]

Mineral oxide	wt.%
K_2O	33.65
P_2O_5	32.05
CaO	9.62
MgO	9.62
Fe_2O_3	1.92
Na_2O	0.32
SiO_2	3.21
SO_3	9.61

2.3.4 Coffee Residue in Thailand

The Office of Agricultural Economics of Thailand had been reported the amount of coffee production in 2006-2008 as shown in Table 2.6. It was found that a lot of coffee beans were used in domestic consumption and the number tends to increase. The high demand coffee bean in domestic consumption leads to high amount coffee residue. Generally, there are coffee residue waste produced from coffee industry with

40 to 60 % of coffee bean production depending on the processing mode of coffee industry [39]. As can be seen in Table 2.6, up to 2008, amount around 29,000 tons of coffee residue waste were generated from coffee industry and became a matter of environmental problem.

Table 2.6 Coffee production and coffee residue in Thailand in year 2006-2008 [40]

Year	Production (Tons)	Exportation (Tons)	Domestic consumption (Tons)	Coffee residue (Tons)
2006	47,000	26,044	20,956	8,382-12,574
2007	56,000	11,239	44,761	17,904-26,857
2008	50,000	1,662	48,338	19,335-29,003

2.4 Activated Carbon (AC)

2.4.1 Definition of AC

There are several definitions for AC as follows;

American Society for Testing and Material (ASTM) defines AC as a family of carbonaceous substances manufactured by processes that develop adsorptive properties [41].

Bansal and Goyal defines AC as a term that includes a wide range of amorphous carbonaceous materials that exhibit a high degree of porosity and extended interparticulate surface area [42].

Ioannidou and Zabaniotou defines AC as carbons of highly microporous form with both high internal surface area and porosity [43].

The substances suggested in the literature as suitable raw materials for preparing AC can be classified into three groups [44] i.e. cellulose from plant (coconut shell, sawdust, wood), coal (lignite, peat) and materials from animal (bones). These are carbonaceous solid precursors with a high carbon content and low level of inorganic compounds.

AC are artificial materials characterized by the high internal surface area and well-developed pore structure, which provides it with many useful properties. Therefore, AC has been employed in a wide number of applications on an industrial scale, including technologies for the purification of gases; the removal of organic pollutants from water (i.e., purification of drinking water and hazardous compound from waste water); a catalyst or a catalyst support in the catalytic processes and electrode materials in electrochemical devices and processes over the last few decades [45-48]. Moreover, it is also used in the removal of color from various syrups and pharmaceutical products, in the air pollution control from industrials and automobile exhausts and in the purification of many chemical, pharmaceutical, and food product [42].

2.4.2 Structure of AC

AC has a microcrystalline structure. On the X-ray studies, it was shown the amorphous carbon of AC consists of flat plates in which the carbon atoms are arranged in a hexagonal lattice. The structure of AC consists of elementary microcrystallines of graphite but these microcrystallines are stacked upon another layer of graphite in random orientation and space between the adjacent layers provides micropore. AC with a random arrangement of microcrystalline and with a strong cross-linking between them has well-developed porous structure. It has relatively low density and low degree of graphitization.

AC is a highly porous material with an internal surface area of about 500-2500 m^2/g [49]. The porous structure is perhaps the main physical property that characterizes AC. AC is formed by pores of different sizes. According to International Union of Pure and Applied Chemistry (IUPAC), the size of pore can be classified into three major groups of pore [50-52].

- Micropores with breadths less than 2 nm (20 Å)
- Mesopores with breadths between 2 and 50 nm (20-500 Å)
- Macropores with breadths greater than 50 nm (500 Å)

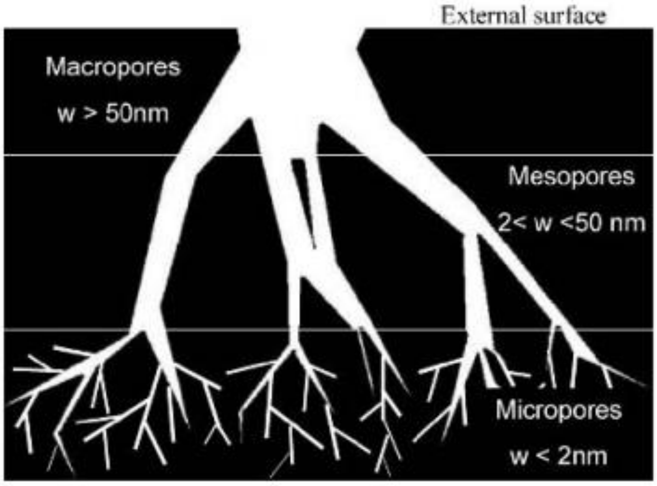


Figure 2.9 Schematic representation of the pore network of a carbon adsorbent [53]

The properties of the final product will be different, depending on the nature of the raw material used and activation technique used in their production. Any cheap material, with a high carbon content and low level of inorganic compounds, can be used as a raw material for the production of activated carbon.

2.4.3 Activated Carbon Manufacture

In principle, the manufacture for preparing the AC can be divided into two main steps; carbonization and activation.

2.4.3.1 Carbonization

The primary stage in the preparation of AC involves carbonization of the raw material. During carbonization, most of the non-carbon elements such as oxygen, hydrogen, nitrogen, and sulfur are eliminated as volatile gaseous products by the pyrolysis decomposition of the source raw material. Generally, carbonization temperature range between 400 and 850 °C, and sometimes reaches 1000 °C in an inert atmosphere [42,45,47]. The residual elementary carbon atoms group themselves into stacks of aromatic sheets cross-linked in a random manner. The mutual arrangement of these aromatic sheets is irregular and, therefore, leaves free interstices between the sheet, which may become filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. These interstices give rise to pores that make AC excellent adsorbents. The char product after carbonization does not have high adsorption capacity because of its less developed pore structure. The pore structure is further enhanced during the activation process when the spaces between the aromatic sheets are cleared of various carbonaceous compounds and disorganized carbon.

2.4.3.2 Activation

The activation process converts the carbonized char into a form that contains the largest possible number of randomly distributed pore of various shapes and sizes, giving a product with an extended and extremely high surface area. Generally, the temperature for activation of carbonized product ranges between 600 and 900 °C [45,47].

Basically, in the process of manufacturing AC there are two methods of activation, physical and chemical.

- Physical Activation

Physical or thermal activation involves the carbonization of a carbonaceous precursor followed by activation of the resulting char in the presence of some mild oxidizing gases such as carbon dioxide or steam. The porous structure is created due to the elimination of volatile matter during the carbonization step and the carbon on the char is removed by reaction with oxidizing gases during the activation step.

- Chemical Activation

In the chemical activation process the two steps are carried out simultaneously, with the precursor is first impregnated with chemical activating agents, as dehydrating agents and oxidants, which degrades the cellulosic material. The most commonly used activating agents are phosphoric acid, zinc chloride and sulfuric acid. After the impregnation, the impregnated material is then heated in an inert atmosphere or absence oxygen. By dehydration and oxidation reactions of chemical, the pores are developed.

In physical activation, elimination of a large amount of internal carbon mass is necessary to obtain a well developed carbon structure, whereas in the chemical activation process all the chemical agents used are dehydrating agents that influence pyrolytic decomposition and inhibit formation of tar, thus enhancing the yield of carbon. The temperatures and time used in chemical activation are also lower and shorter than that used in the physical activation process, and therefore the development of a porous structure is better in the case of the chemical process [54-56]. However, chemical activation involves a complex recovery and recycle of the activating agent, which generates liquid discharge that demands effluent treatment [48].

CHAPTER 3
EXPERIMENTAL

3.1 Conceptual Framework

This research has been investigated the possibility of using coffee residue, the agricultural waste after extraction process, as a filler for natural rubber. The study was carried out by comparing the properties of the NR filled with various formed fillers prepared from coffee residue with those of the NR filled with carbon black and calcium carbonate. The overview procedure of this work is described in Figure 3.1.

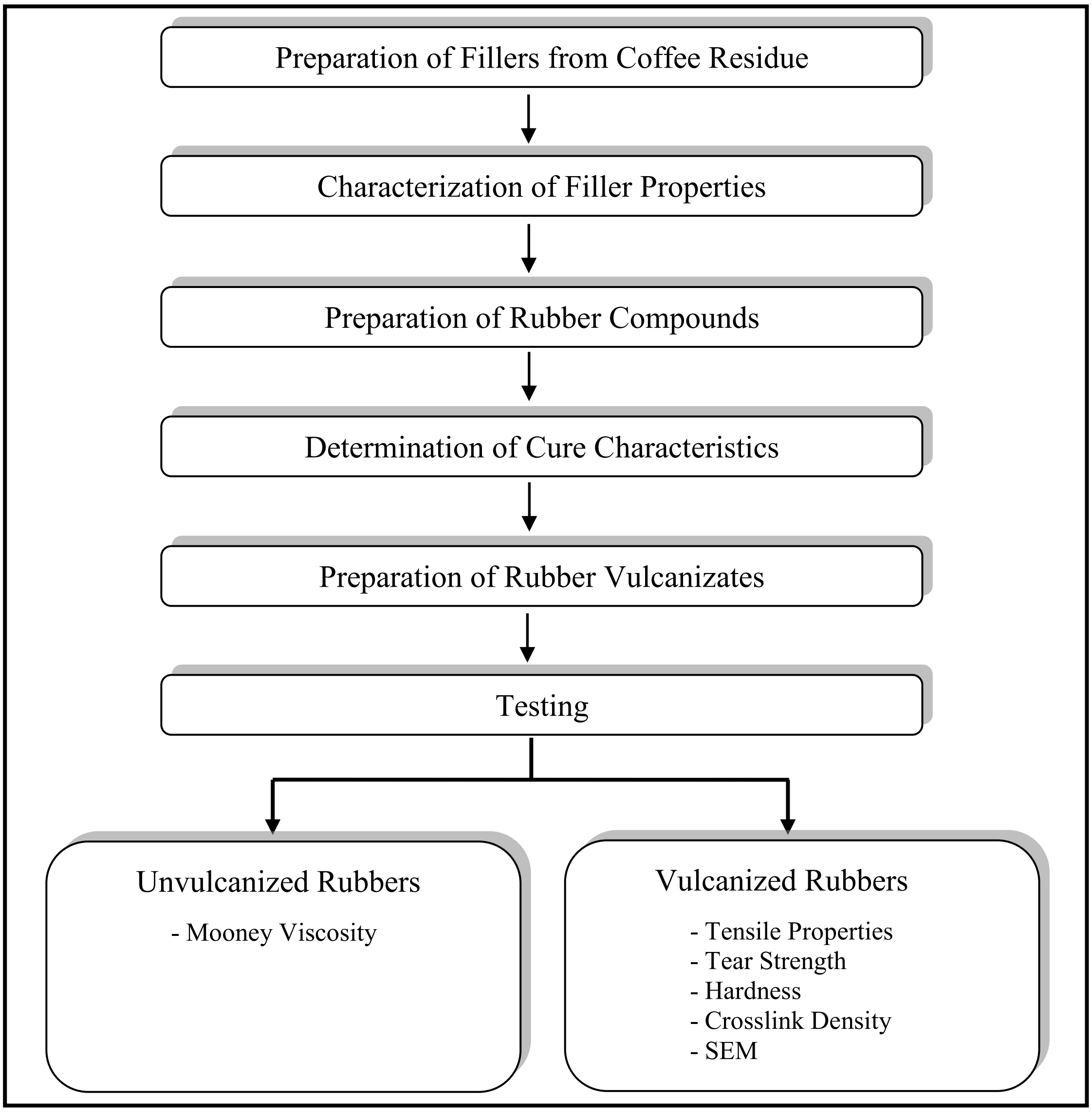


Figure 3.1 Flow diagram of experimental procedure

3.2 Materials and Chemical Agents

Materials and chemical agents along with their function used in the present study are listed in Table 3.1.

Table 3.1 Materials and chemical agents

Materials/Chemical Agents (function)	Trade Name/ Grade	Manufacturer
Natural rubber (NR) (matrix)	RSS 3	Sakdaroongreungkij Co. Ltd., Thailand
Coffee residue (filler)	Arabica/Robusta	True coffee company
Carbon black (CB) (filler)	N330	Sakdaroongreungkij Co. Ltd., Thailand
	N774	Sakdaroongreungkij Co. Ltd., Thailand
Calcium carbonate (filler)	Commercial	C.P. Chemical Industry Co. Ltd., Thailand
Zinc oxide (ZnO) (cure activator)	Commercial	Sakdaroongreungkij Co. Ltd., Thailand
Stearic acid (cure activator)	Commercial	Sakdaroongreungkij Co. Ltd., Thailand
N-tert-butyl-2-benzothiazolesulfenamide (TBBS) (cure accelerator)	Commercial	Sakdaroongreungkij Co. Ltd., Thailand
N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine (6PPD) (antidegradant)	Commercial	Sakdaroongreungkij Co. Ltd., Thailand
Sulfur (vulcanizing agent)	Commercial	Sakdaroongreungkij Co. Ltd., Thailand
Toluene (solvent for swelling rubber)	AR grade	RCI Labscan Limited

3.3 Instruments

The instruments used in the present study are shown in Table 3.2.

Table 3.2 The list of instruments used in the present study

Instruments	Model	Manufacture
Internal Mixer	MX500-D75L90	Chareontut Co., Ltd., Thailand
Laboratory Two-Roll Mill	LRM-S-110	Labtech Engineering, Thailand
Compression Molding Machine	LP-S-50	Labtech Engineering, Thailand
Moving Die Rheometer	TECH PRO A022S	CG Engineering Co., Ltd., USA
Universal Testing Machine	5843	Instron, USA
Fourier Transform Infrared Spectrometer	Nicolet 6700	Thermo Scientific, USA
Laser Particle Size Analyzer	Mastersizer 2000	Malvern Instrument Ltd., UK
Scanning Electron Microscope	JSM-6480LV	JEOL Ltd., Japan
BET Surface Area Analyzer	SA 3100	Beckman Coulter, lnc, USA
Gas Pycnometer	Ultrapycnometer 1000	Quantachrome, USA
Thermogravimetric analyzer	TGA/SDTA851^{e}	Mettler Toledo, Greifensee, Switzerland

3.4 Preparation of Fillers from Coffee Residue

In this work, to use as a filler, the coffee residue was prepared into 3 different forms based on different preparing methods as follows.

3.4.1 Coffee Residue Particle (CRP)

The coffee residue was crushed by a wet ball mill for an hour and dried. Then the pre-crushed coffee residue was ground by a vibratory mill and sieved to a controlled size of below 100 mesh.

3.4.2 Si69 Treated of Coffee Residue Particle

Bis-(3-triethoxysilylpropyl) tetrasulfide designated as Si69 was used as a surface treated reagent. Its chemical structure is shown in Figure 3.2. The 2 grams of Si69 was added into 100 ml of ethanol, and then stirred for 30 minutes. About 100 grams of coffee residue particle was then added into the solution for 15 minutes stirring, in order to ensure a uniform distribution of the Si69 on the coffee residue particle surface. The treated coffee residue particle was then dried at 100°C for 12 hrs in an oven until a constant weight was achieved [57].

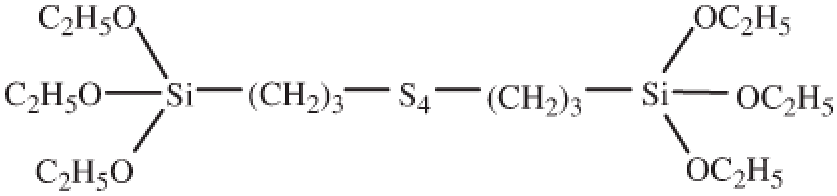


Figure 3.2 Chemical structure of Si69

3.4.3 Carbonized Coffee Residue

The coffee residue was carbonized for an hour under N_2 condition at 400°C. The product from carbonization was called as char. Then, it was crushed by a jet mill and sieved to a controlled size of below 100 mesh.

3.4.4 Activated Carbon

The char was activated with CO_2 for an hour at 600, 700, and 800 °C. The prepared activated carbon was designated as AC600, AC700, and AC800 respectively. After that, it was crushed by a jet mill and sieved to a controlled size of below 100 mesh.

Figure 3.3 shows all forms of fillers prepared from coffee residue in this work along with their preparing method.

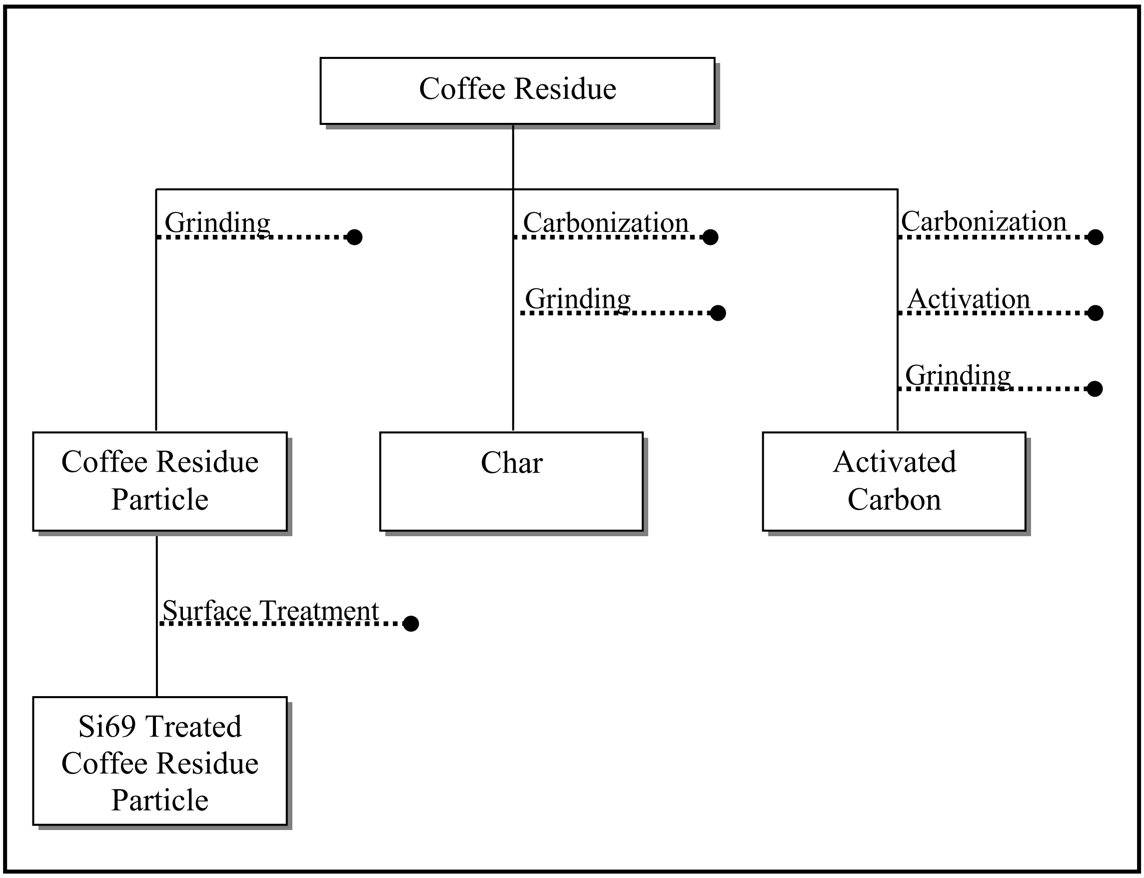


Figure 3.3 Fillers from coffee residue

3.5 Characterization of Filler Properties

3.5.1 Thermal Properties

Decomposition temperature of the coffee residue was determined using thermogravimetric analyzer model TGA/SDTA 851^{e}. Approximately 10 mg of coffee residue was heated from 50-800 °C at heating rate of 20 °C/min under nitrogen atmosphere. The onset and endset temperature of degradation were reported.

3.5.2 Particle Size

The average particle size of filler was determined using laser light scattering analyzer model Mastersizer 2000 with a Hydro 2000 MU as dispersion unit as shown in Figure 3.4. Noted that before measurement, the filler particle was ultrasonicated for 10 minutes.

Figure 3.4 Mastersizer 2000 laser light scattering analyzer

3.5.3 Surface Area

The surface area of the fillers was determined by the Brunauer-Emmett-Teller (BET) method using a BET surface area analyzer model SA 3100. The BET surface area of filler was measured by N_2 adsorption at 77 ^{o}K.

3.5.4 Surface Functional Group

The specific activity of filler surface was studied using Fourier Transform Infrared spectrometer (FTIR) model Nicolet 6700 as shown in Figure 3.5. The samples were mixed with dry potassium bromide (KBr) with weight ratio of 1:100 were scanned and recorded from 4000 to 400 cm^{-1}. For each measurement, 64 scans were taken at a resolution of 4 cm^{-1}.

Figure 3.5 NICOLET 6700 Fourier Transform Infrared spectrometer

3.5.5 pH Value

The pH value was determined by the procedure described in ASTM D1512. The 5 grams of filler were added into a stainless steel beaker containing 50 cm^3 of boiling distilled water. About 2 to 3 drops of acetone were added to facilitate wetting of the sample. The beaker was covered with a watch glass and boiled for 15 minutes. Then let the mixture cool down to room temperature. The pH of media representing the pH of filler was measured using pH meter as shown in Figure 3.6.

Figure 3.6 pH meter

3.5.6 True Density

The true density of the fillers was measured by a gas pycnometer model Ultrapycnometer 1000. The porous of the filler was displaced by the helium gas to measure the volume of a sample. Then, the volume of the sample is translated into the absolute density, as the weight of the sample is known.

3.5.7 Morphology

The morphology of fillers was studied by a Scanning Electron Microscope (SEM) model JSM-6480LV. The filler particles for SEM study were coated with gold before examination to prevent electrostatic charging on the surface of filler.

3.6 Formulation of Rubber Compounds

The formulation of rubber compounds used for studying the effect of filler on the physical properties of rubber vulcanizates is given in Table 3.3. The filler loading was varied from 10 to 50 phr with increment of 10 phr.

Table 3.3 Formulations of rubber compounds

Materials	Parts by hundred (phr)
RSS 3	100
Fillers	0,10, 20, 30, 40 and 50
ZnO	5
Stearic acid	2
6PPD	3
TBBS	1.2
Sulfur	1.5

3.7 Mixing Procedure

The mixing was divided into two steps in order to avoid rubber to be scorched. Rubber compounds were prepared in a laboratory-size internal mixer as shown in Figure 3.7 with a fill factor of 0.7 at a temperature of 50°C and a rotor speed of 50 rpm.

Figure 3.7 CHAREONTUT MX500-D75L90 internal mixer

The steps of mixing in the internal mixer are presented in Table 3.4. In first step, the rubber was masticated for 1 minute. All ingredients, except the curatives, were mixed with rubber until 7 minutes. Then the mixed rubber compound was dumped and then kept at the room temperature until its temperature was equilibrated with the room temperature before carrying out to the second mixing step.

The second step, the mixed rubber compound was loaded into the internal mixer. After masticating for one minute, the curatives were added and continuously mixed for 4 minutes. Then the compound was dumped and sheeted off with a two-roll mill as shown in Figure 3.8. The rubber compound sheet was kept at least 24 hours at the room temperature before the characterization step.

Figure 3.8 Labtech LRM-S-110 two-roll mill

Table 3.4 The steps of mixing in the internal mixer

Step I

Step	Procedure	Time (min)
1	Load rubber	0
2	Add ZnO, Stearic acid, $\frac{1}{2}$ filler	1-2
3	Add 6PPD, $\frac{1}{2}$ filler	2-3
4	Dump	7

Step II

Step	Procedure	Time (min)
1	Load mixed rubber compound	0
2	Add sulfur and TBBS	1-5
3	Dump	5

3.8 Determination of Cure Characteristics

The cure characteristics of rubber compounds were determined using a Moving Die Rheometer (MDR) as shown in Figure 3.9 in according with ASTM D5289-95.

Figure 3.9 TECH PRO A022S moving die rheometer

The uncured rubber was placed between the heated parallel plates under oscillating force. About 5 gram of uncured rubber was tested at 160°C for 30 minutes. For each compound, three tests were carried out. The increase in torque was determined as a function of time. The scorch time (t_s2) and optimum cure time (t_c90) were obtained from the time when torque increases 2 units above minimum torque (M_L) and 90% of the maximum torque (M_H) of cure curve, respectively. The general characteristic of cure curve of rubber compound is illustrated in Figure 3.10. The rate of curing time is measured by the cure rate index (CRI) which can be calculated as following equation.

$$\mathrm{CRI} = \frac{100}{t_c90 - t_s2} \tag{3.1}$$

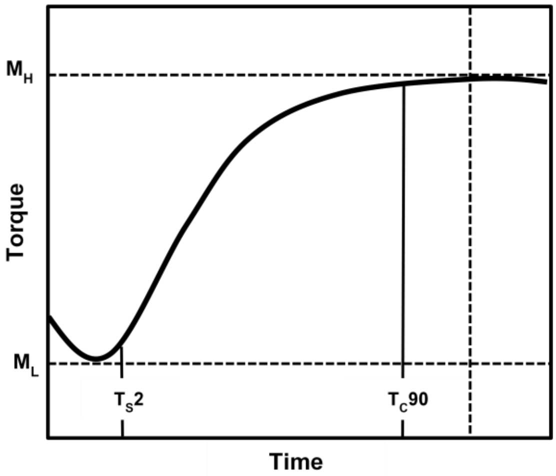


Figure 3.10 Cure curve of rubber compound

3.9 Preparation of Rubber Vulcanizates

The rubber vulcanizates with 2 mm thickness were prepared with a compression molding machine as shown in Figure 3.11. The rubber compounds were compressed according to their respective cure time (t_c90) at 160°C under pressure 50 bar. After compression, rubber vulcanizate~~s~~ sheet were left at the room temperature for 24 hours before testing.

Figure 3.11 Labtech LP-S-50 compression molding machine

3.10 Testing

3.10.1 Properties of Unvulcanized Rubbers

3.10.1.1 Mooney Viscosity

The viscosity of rubber compounds was determined using a Mooney viscometer in according to ISO 289-1. Mooney viscosity is defined as a torque on instrument's rotating spindle with heated rotor, imposed by rubber compound enclosing and overflowing the spindle. Torque to rotate rotor representing the Mooney viscosity is measured and given as Mooney-units.

3.10.2 Testing of Vulcanized Rubbers

3.10.2.1 Tensile Properties

Tensile properties of rubber vulcanizates were measured according to ISO 37 using an Instron universal testing machine model 5843 at a crosshead speed of 500 mm/min with load of 1 kN. The rubber vulcanizates sheets were cut by a type II die into the dumb-bell specimens with the dimension as shown in Figure 3.12. The 100% and 300% modulus, tensile strength and elongation at break were determined. At least five specimens were tested and the average value was reported.

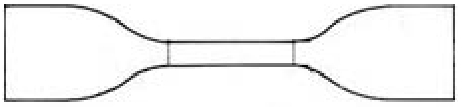


Figure 3.12 Dimension of tensile specimen

The tensile properties were calculated as following:

1. 100% modulus = stress at 100% elongation
2. 300% modulus = stress at 300% elongation
3. Tensile strength (TS) = stress at break

when Stress = $\frac{F}{A}$ (3.2)

where F = observed force (N)

A = cross-sectional area of unstrained specimen (mm^2)

4. Percent elongation at break (EB)

$$EB = \left[\frac{-}{\qquad}\right] \quad (3.3)$$

where L = observed distance between grip of extended specimen

L_0 = original distance between the extensometer

3.10.2.2 Tear Strength

Tear strength of rubber vulcanizates was measured according to ISO 34 using an Instron universal testing machine model 5843 at a crosshead speed of 500 mm/min with load of 1kN. The rubber vulcanizates were cut by a type C die into the crescent shape specimen having dimension as shown in Figure 3.13. At least five specimens were tested and the average value was reported. The tear strength can be calculated from maximum force required to tear a specified test into two parts per unit of thickness according to equation 3.4.

$$\text{Tear strength (N/mm)} = \frac{F}{d} \quad (3.4)$$

where F = the maximum force (N)

d = the thickness of the specimen (mm)

Figure 3.13 Dimension of tear specimen

3.10.2.3 Hardness

The hardness was determined according to ASTM D2240 using durometer hardness system Shore A. The surface of the specimen was flat and parallel over an area to permit the presser foot to contact the specimen. The thickness of specimen about 6 mm was tested. The hardness reported here was averaged from 3 measurements.

3.10.2.4 Crosslink Density

The crosslink density was determined using the swelling test. Toluene was used as the liquid medium. The rubber vulcanizates were cut into small pieces, weighing approximately 0.2 gram and immersed in 50 ml of toluene. The samples were kept in a dark for 7 days at the room temperature. After that the swollen samples were taken out. The sample were bottled with a paper and then transferred quickly to the weighing bottle to determine the weight. The swollen samples were dried to constant weight at room temperature. The weight of dried sample was measured. At least three samples for each compound were measured. The crosslink density (n_{swell}) was calculated using the Flory-Rehner equation [57] as shown in equation 3.6.

$$\ln(\quad v_r) \quad {}_r \quad {}_r \qquad {}^t \; {}_{swell} \quad {}_r \quad \frac{r}{f} \tag{3.6}$$

when $$V_r \quad \frac{\left[\frac{\quad_d}{_d}\quad\frac{\quad_f}{_t}\right]}{\left[\frac{\quad_d}{_d}\quad\frac{\quad_f}{_t}\right]\left[\frac{\quad_s\quad_d}{_t}\right]}$$

where W_d = weight of dried sample (g)

W_f = weight of filler in sample (g)

W_s = weight of swollen sample (g)

$_d$ = density of rubber (g/cm^3)

$_f$ = density of filler

$_t$ = density of toluene (0.862 g/cm^3)

V_r = volume fraction of rubber in the swollen gel

V_t = molar fraction of toluene (106.2 cm^3/mol)

χ = rubber-solvent interaction parameter (0.39 for NR-toluene)

f = function of crosslink with sulfur vulcanization (4)

$_{swell}$ = number of moles of crosslink per unit volume (mol/cm^3)

3.10.2.5 Morphology

The morphology of NR vulcanizates was studied by a Scanning Electron Microscope (SEM) model JSM-6480LV. The broken samples of the fatigue tensile test were cut and sticked on the stub using double-sided tape. Then the samples were coated with gold before examination.

CHAPTER 4

RESULTS AND DISCUSSION

The results and discussion of this research was divided into 4 parts. The first part presented the characteristics of all fillers used in this study. Then, to determine the possibility of using coffee residue as filler, the properties of NR vulcanizates filled with various fillers prepared from coffee residue were shown in the second part. The next part concerned about the effect of the presence of silane coupling agent on the properties of NR vulcanizates filled with coffee residue particle. Finally, to determine the reinforcing efficacy of coffee residue, the properties of NR vulcanizates filled with the highest reinforcing efficient filler prepared from coffee residue were compared with those of NR vulcanizates filled with commercial fillers including both reinforcing and non-reinforcing ones.

4.1 Characterization of Fillers

4.1.1 Thermal Properties of the Coffee Residue

The thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of coffee residue are presented in Figure 4.1. The onset of decomposition temperature of the coffee residue started around 276°C, while the final decomposition temperature was around 382°C. As seen in Figure 4.1(b), the coffee residue showed four decomposition steps. In common, the initial weight loss is found in the range from 50 to 120°C due to the loss of the moisture from biomass materials [58]. According to the explanation given by Kirubakaran et al. [59], the second decomposition step ranging from 215 to 330°C presented a significant weight loss of hemicelluloses. The third and forth step found in the range of 330-370°C and 370-500°C is corresponding to the decomposition of cellulose and lignin, respectively. Upon increasing temperature up to 800°C, the amount of residue char was nearly constant at approximately 20%.

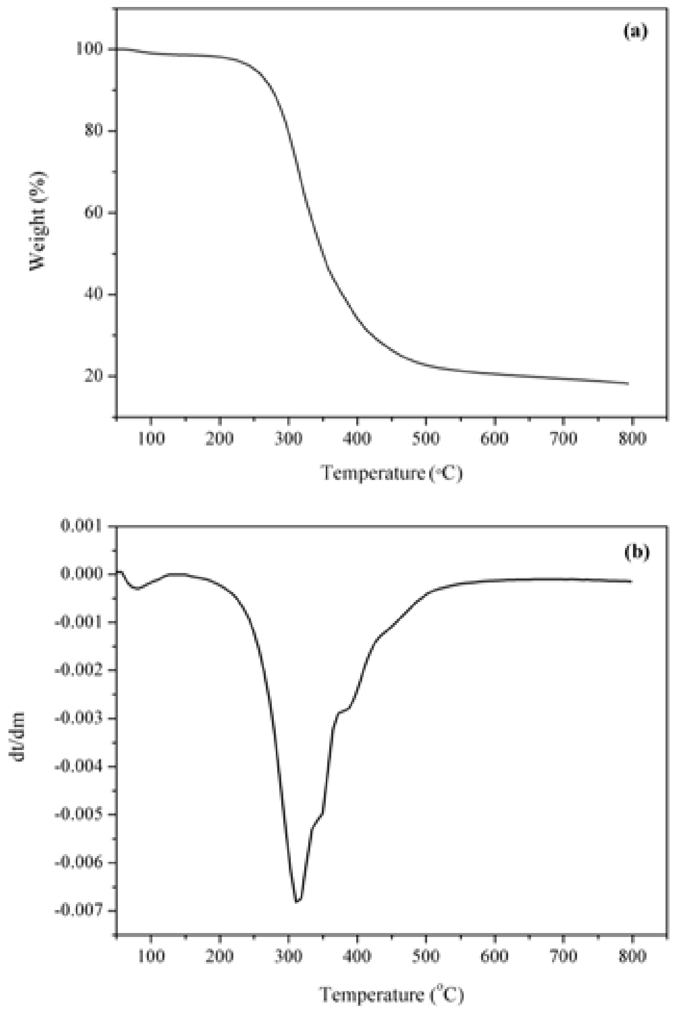


Figure 4.1 (a) TGA and (b) DTG thermograms of coffee residue

4.1.2 Physical Properties of the Fillers

The physical properties of fillers used in this study are given in Table 4.1. As can be seen, the mean particle size of coffee residue particle (CRP) was larger than that of other fillers. It is well-known that the particle size is inversely proportional to the surface area. Because of the mean particle size of CRP, thereby its BET surface area was the lowest. The mean particle size of char, AC600, AC700, and AC800 was not significantly different. However, their mean particle size was larger than that of $CaCO_3$ and both carbon blacks (N330 and N774). The BET surface area of char was higher than CPR. This may be attributed to the pyrolysis process which removes the moisture and the volatile contents of biomass [43]. Among the three ACs prepared here, the BET surface area could be placed in the following reducing order: AC600, AC700, and then AC800. In general, the higher activation temperature will result in the formation of the AC with the greater surface area. And this is because increasing temperature causes more volatile component to be removed and also more carbon component to burned off due to carbon-CO_2 reaction as demonstrated by the result from Zhang et al. [60] and Yang et al. [61]. However, in this study, the controversy result was observed. The surface area of ACs prepared from coffee residue tended to reduce when the activation temperature was increased. This might be due to the alkali metal oxides in ash of coffee residue. Applying activation temperature more than 600 °C not only burns off the organic component but do melt the alkali metal oxide also. Thus, the decrease of BET surface area of AC700 and AC800 was due to the shielding of the ACs pore with the molten alkali metal oxide.

From Table 4.1, it was also found that the pH value of CRP was considerable lower than that of other fillers. As known very well in the rubber technology that the acidity of the filler can retard the sulfur cure process. Therefore, the addition of CRP into the NR compound may affect the cure process more or less. This will be mentioned again in the following part. The pH value of the other fillers shifts toward neutral or slight alkalinity.

Table 4.1 Physical properties of the fillers

Filler	**Mean particle size (µm)**	**BET surface area (m^2/g)**	**pH**	**Density (g/cm^3)**
CRP	24.46	1.51	4.58	1.28
Char	10.04	4.04	7.85	1.24
AC600	9.31	201.42	9.23	1.46
AC700	10.42	9.11	7.97	1.29
AC800	10.59	3.17	8.46	1.25
$CaCO_3$	6.43	2.75	9.35	2.70
N776	2.39	38.24	8.13	1.77
N330	2.27	93.10	7.35	1.77

4.1.3 Chemical Properties of the Fillers

The surface chemistry of fillers was evaluated by FTIR. Figure 4.2 showed the FTIR spectra of the Coffee residue particle (CRP), char, and activated carbon (AC600, AC700, and AC800), respectively. There are four characteristic bands of the coffee residue were clearly observed. The first band locating at 3716-3022 cm^{-1} could be assigned to the hydroxyl group (O-H). The second one at 2977-2838 cm^{-1} was assigned to the $C\text{-}H_n$ stretching vibration. The next one at 1775-1722 cm^{-1} was assigned to C=O stretching vibration. The last one at 1632 cm^{-1} was assigned to aromatic C=C stretching vibration. The FT-IR bands for functional group of cellulose, hemicelluloses, and lignin were summarized in Table 4.2. These four characteristic bands indicated the functional group of hemicelluloses, cellulose, and lignin in the coffee residue. For spectra of char and ACs, they were different from that of CRP. Many bands disappear, exhibiting the vaporization of organic matters after thermal treatment. The peak of hydroxyl group of char and ACs was involved in water absorption because it was narrower than that of CRP. The peak at 2977-3838 cm^{-1} almost disappeared in the char and ACs. This result indicated the hydrogen element was removed to a large extent [62]. The peak between 1600 and 1500 cm^{-1}could be attributed to aromatic C=C ring stretching [63]. Finally, the band at 1016 $cm^{-1}$was assigned to the C-O stretching vibration.

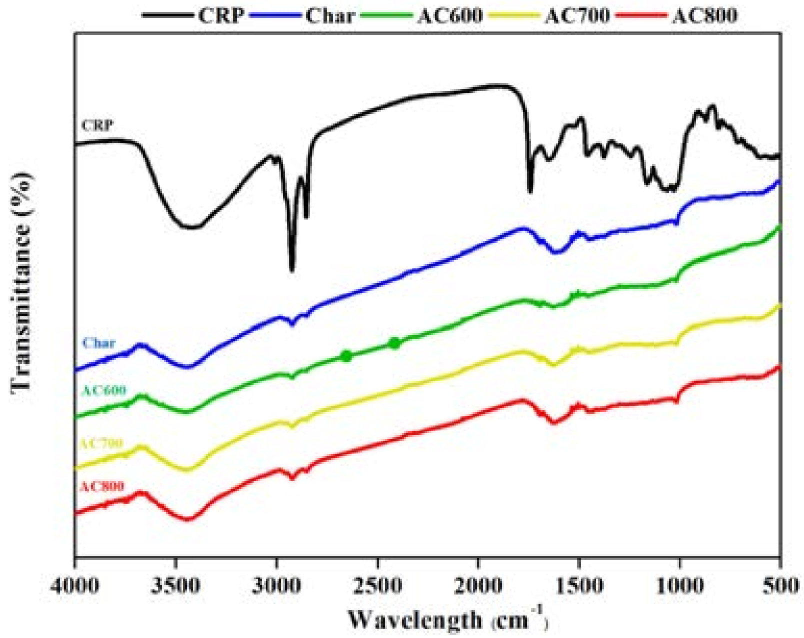


Figure 4.2 FTIR spectra of different fillers prepared from coffee residue

Table 4.2 The FTIR bands for functional groups of cellulose, hemicelluloses, and lignin [64,65]

Fiber component	Wavenumber (cm^{-1})	Functional group	Compounds
Cellulose	4000-2995	OH	Acid, methanol
	2970-2860	$C-H_n$	Alkyl, aliphatic
	1640	Fiber-OH	Adsorbed water
	1270-1232	C-O-C	Aryl-alkyl ether
	1170-1082	C-O-C	Pyranose ring skeleton
	1108	OH	C-OH
Hemicellulose	4000-2995	OH	Acid, methanol
	2970-2860	$C-H_n$	Alkyl, aliphatic
	1765-1715	C=O	Ketone and carbonyl
	1108	OH	C-OH
Lignin	4000-2995	OH	Acid, methanol
	2890	H-C-H	Alkyl, aliphatic
	1730-1700		Aromatic
	1632	C=C	Benzene stretching ring
	1613, 1450	C=C	Aromatic skeleton mode
	1430	$O-CH_3$	Methoxyl- $O-CH_3$
	1270-1232	C-O-C	Aryl-alkyl ether
	1215	C-O	Phenol
	1108	OH	C-OH
	900-700	CH	Aromatic hydrogen

4.1.4 Morphology of the Fillers

The SEM pictures of all fillers used here are compared in Figure 4.3. Even though prepared with different thermal processes, it clearly showed that the particle shape of all fillers prepared coffee residue were nearly similar with the non-uniform shapes. Some of them were the sharp-edged particulates. It was noted that their shape was similar to that of $CaCO_3$. The shape of both carbon blacks (N330 and N774) was extremely different from that of all fillers prepared coffee residue and $CaCO_3$. Mainly, the particle of carbon black looked like spherical. As mentioned in the Chapter 2, these spheres called as primary particles are fused together via covalent bond during production.

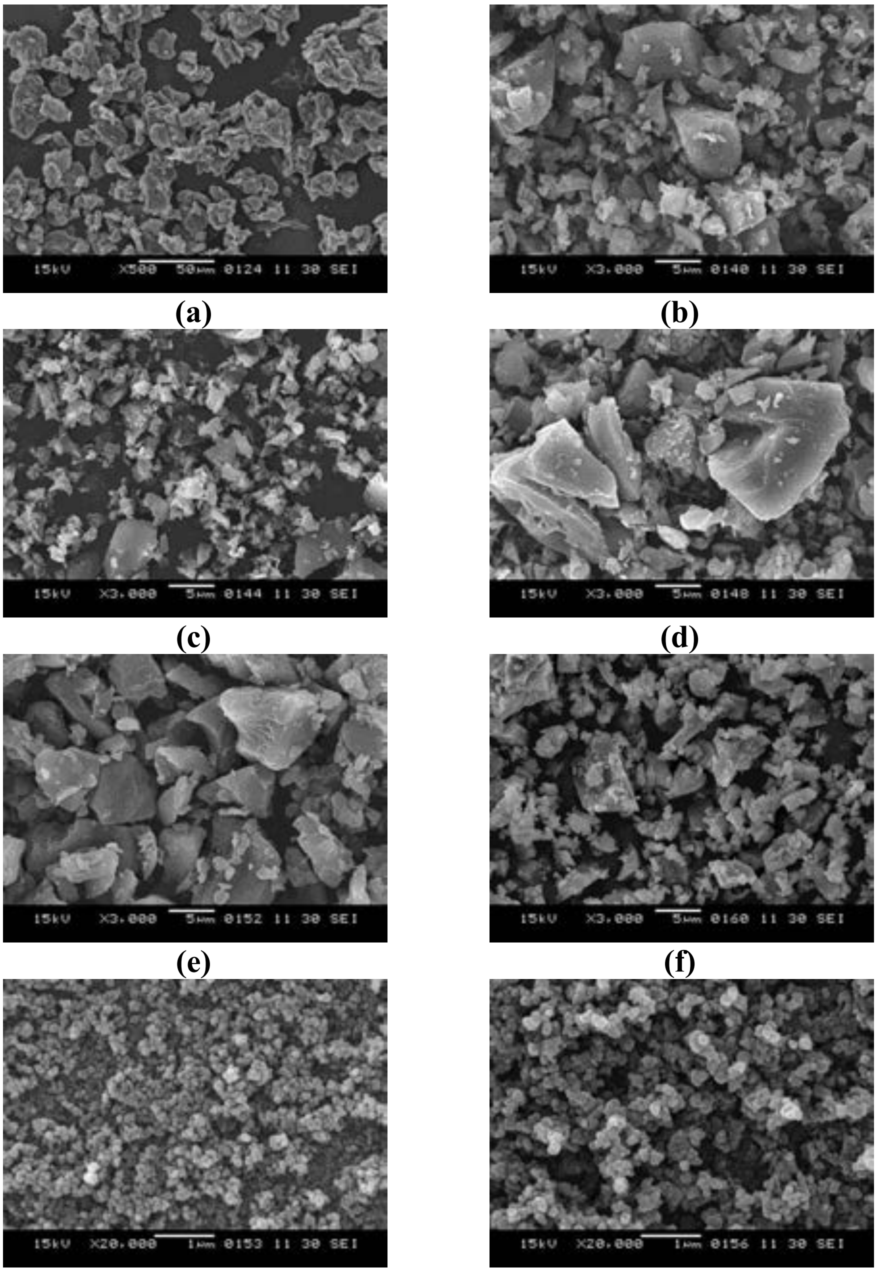


Figure 4.3 SEM micrographs of (a) CRP at 500x magnification, (b) char, (c) AC600, (d) AC700, (e) AC800 and (f) $CaCO_3$ at 3000x magnification, (g) N330 and (h) N776 at 20,000x magnification

4.2 Properties of the NR Vulcanizates Filled with Different Fillers Prepared from Coffee Residue

In this part, the effects of fillers prepared from coffee residue on the properties of NR vulcanizates including Mooney viscosity, cure characteristics, mechanical properties, and crosslink density are shown here. The amount of filler was varied from 0 to 50 with the increment of 10 phr.

4.2.1 Mooney Viscosity of the NR Compounds Filled with Different Fillers Prepared from Coffee Residue

The Mooney viscosities of NR compounds are shown in Figure 4.4. It is obviously seen that incorporation of fillers such as char, AC600, AC700, and AC800 into the NR compounds led to the increase of Mooney viscosity. The reasons for the increase of viscosity may be due to the reduction of the mobility of the rubber molecular chain and also the rubber-filler interaction. In addition to, the increment of Mooney viscosity greatly increased with increasing filler loading. This may also be mathematically explained in the term of hydrodynamic volume effect. The more filler, the more hydrodynamic volume, thus resulting in having less mobility [66,67]. Therefore, the rubber compounds with higher filler loading shows higher viscosity. Moreover, it was also observed that the influence of char, AC600, AC700, and AC800 on Mooney viscosity of the NR compounds was comparable. On the other hand, the NR compounds filled with CRP showed lower Mooney viscosity than that of gum NR compounds and also essentially non dependency on the amount of CRP compared with the other fillers. The decrease of Mooney viscosity with the presence of CRP might be due to some natural organic components of CRP acting as processing aid. One possible reason for this might be due to the low surface area of CRP. As mentioned earlier, the rubber-filler interaction is one possible reason for the increase of viscosity. Due to its low surface area, the rubber-CRP interaction may be too low to cause the increase of viscosity. However, the lower Mooney viscosity of the CRP filled NR compounds indicated that this compound can be processed more easily than the NR compounds filled with other fillers.

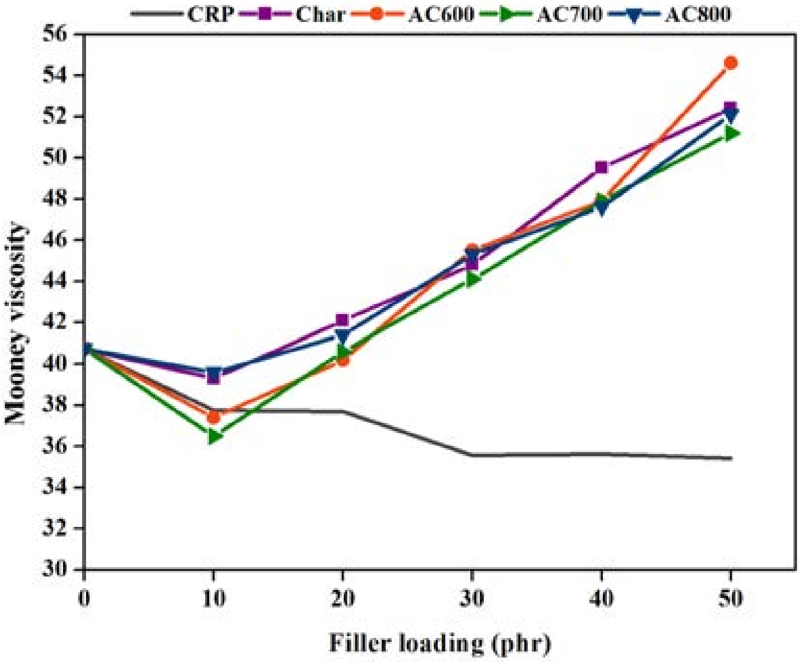


Figure 4.4 Mooney viscosity of the NR compounds filled with different fillers prepared from coffee residue

4.2.2 Cure Characteristics of the NR Compounds Filled with Different Fillers Prepared from Coffee Residue

Cure characteristics including scorch time, cure time, and cure rate index of the NR compounds filled with various fillers prepared from coffee residue as a function of loading are shown in Figures 4.5-4.7, respectively.

It can be seen that the addition of all fillers but CRP significantly decreased the scorch time and cure time. This might be due to their slightly alkalinity value that can facilitate the sulfur vulcanization. The decrease of scorch time markedly increased with increasing of filler loading. On the other hand, the decrease of cure time was independent of filler loading. Amongst them, AC600 and AC700 had comparable and highest effect on the decrease of the scorch time and cure time, though AC600 had the highest pH value. In turn, char showed lowest effect on the decrease of the scorch time and cure time. This might be because its pH was lowest. Although the presence of CRP also reduced the scorch time, its effect was obviously small compared with that of char and activated carbons prepared from coffee residue. Its influence on the cure time was also negligible. This might be due to its pH value toward to the acidity.

The cure rate index of the NR compounds filled with all fillers decreased significantly when the filler loading was increased. The effect of filler type on the cure rate index was not clearly observed.

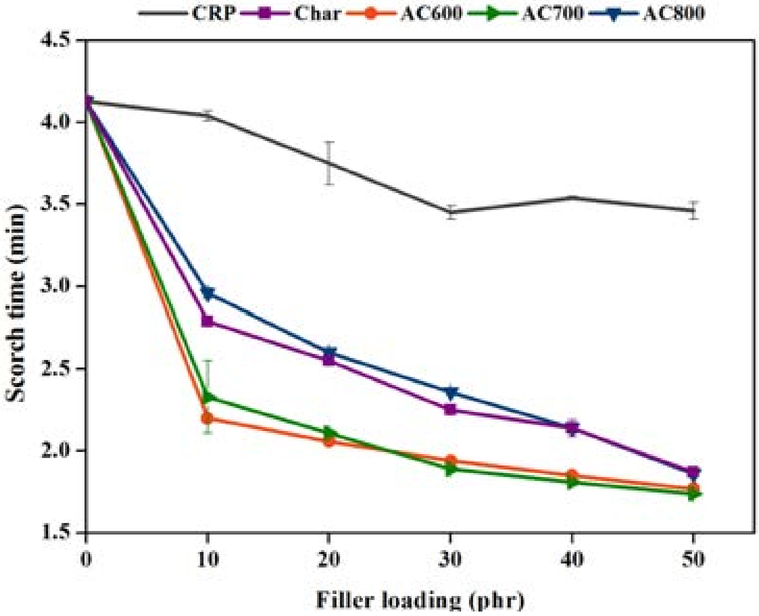


Figure 4.5 Scorch time of the NR compounds filled with different fillers prepared from coffee residue

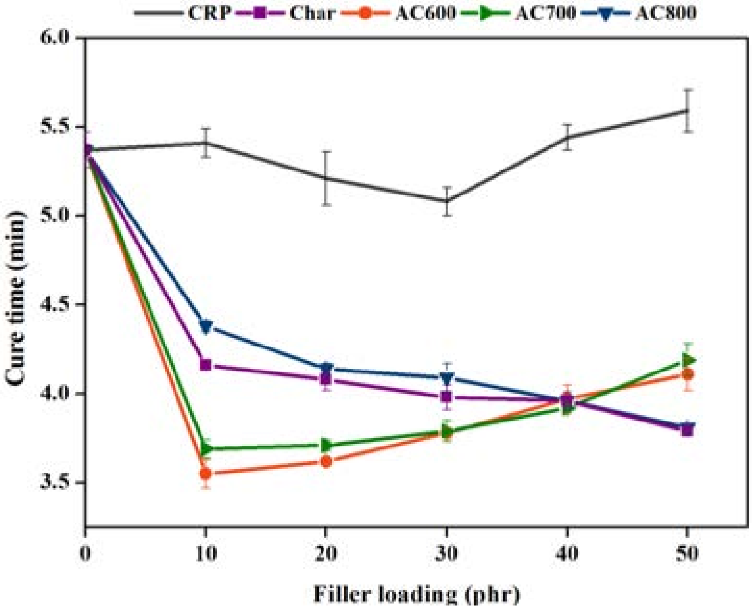


Figure 4.6 Cure time of the NR compounds filled with different fillers prepared from coffee residue

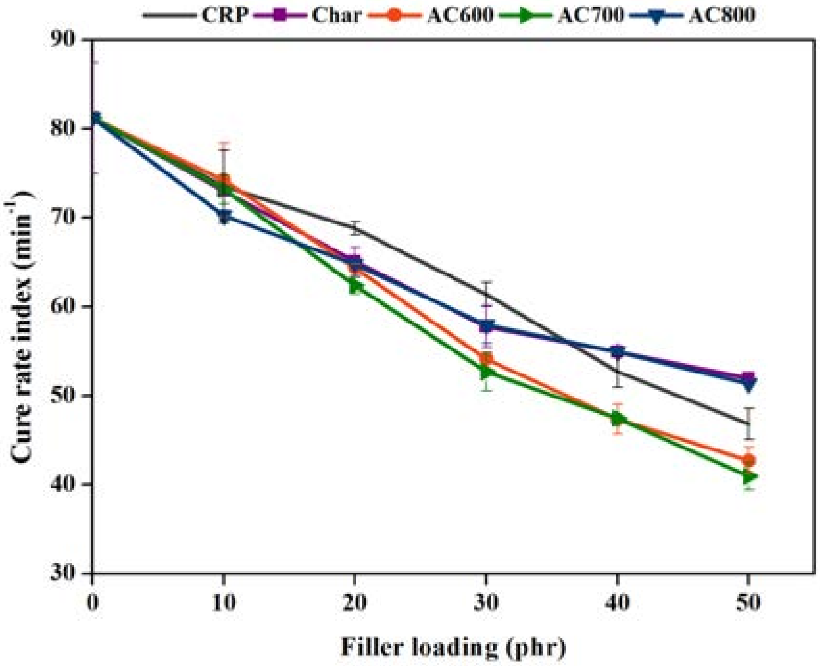


Figure 4.7 Cure rate index of the NR compounds filled with different fillers prepared from coffee residue

4.2.3 Mechanical Properties of the NR Vulcanizates Filled with Different Fillers Prepared from Coffee Residue

4.2.3.1 Tensile Properties

The tensile properties of filled NR vulcanizates including 100% modulus, 300% modulus, tensile strength, and elongation at break are presented in Figures 4.8-4.11. As can be seen, the addition of fillers resulted in a continuous increase in both 100% and 300% modulus of the filled NR vulcanizates. These results indicated that the addition of fillers improved stiffness of the filled NR vulcanizates. The CRP-filled NR vulcanizates showed the lowest both 100% and 300% modulus. This was owing to the aggregation of CRP causing the poor dispersion of the filler in the rubber, and this likely weakened the modulus of CRP-filled NR vulcanizates. At low filler loading, the influence of filler type on the modulus was not observed. However, at higher loadings (20 phr or more), char seemed to have the highest impact on the increase of modulus.

From Figure 4.10, it was seen that AC600 and AC 700 showed the same influence on the tensile strength in which no matter how much they were added into the NR vulcanizates, the presence of AC600 and AC700 reduced the tensile strength of the NR vulcanizates. The decrease of the tensile strength due to AC600 and AC700 increased with increasing their loadings. At the lowest filler loading, 10 phr, the tensile strength of the NR vulcanizates filled with CRP, AC800, and char was higher than that of the unfilled NR vucanizates. A further increase in the filler loading resulted in the decrease of tensile strength. For CRP and AC800, the loading giving tensile strength lower than that of the unfilled NR vulcanizates was 20 phr. But in the case char, the loading showing tensile strength lower than that of the unfilled NR vulcanizates was 30 phr. For all filler loadings, char gave the NR vulcanizates with highest tensile strength.

For all fillers, the elongation at break of the filled NR vulcanizates as shown in Figure 4.11 reduced with increasing filler loading. The higher quantity of filler in the rubber matrix, the more the flow of rubber chain was blocked and restricted. Therefore, the NR rubber vulcanizates broke at lower elongation. Above 30 phr, the elongation at break of the NR vulcanizates filled with CRP was higher than that of the NR vulcanizate filled with char, AC800, AC700, and AC600 on the respective order. Below 20 phr, the NR vulcanizates filled with CRP, char, and AC800 showed nearly the same elongation at break and higher than the ones filled AC600 and AC700.

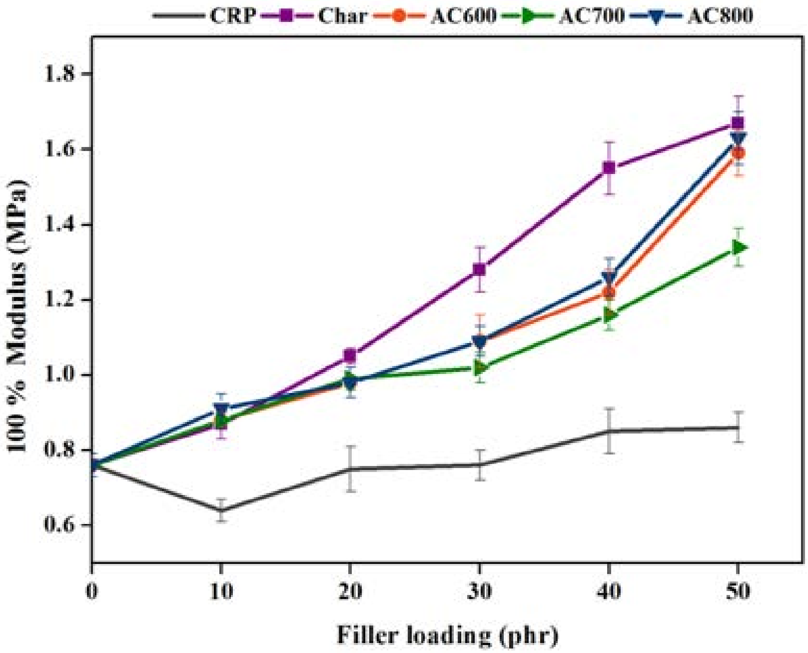


Figure 4.8 100% Modulus of the NR vulcanizates filled with different fillers prepared from coffee residue

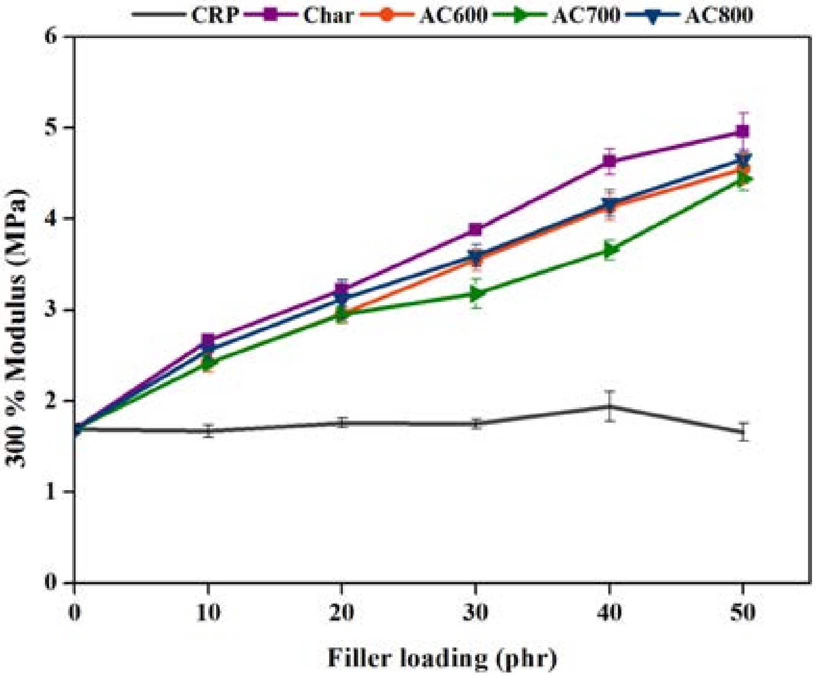


Figure 4.9 300% Modulus of the NR vulcanizates filled with different fillers prepared from coffee residue

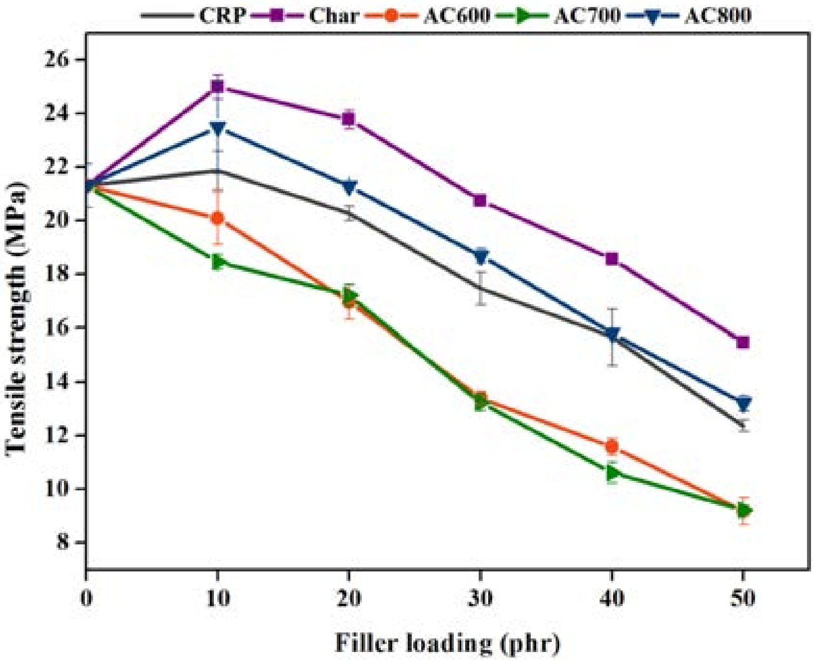


Figure 4.10 Tensile strength of the NR vulcanizates filled with different fillers prepared from coffee residue

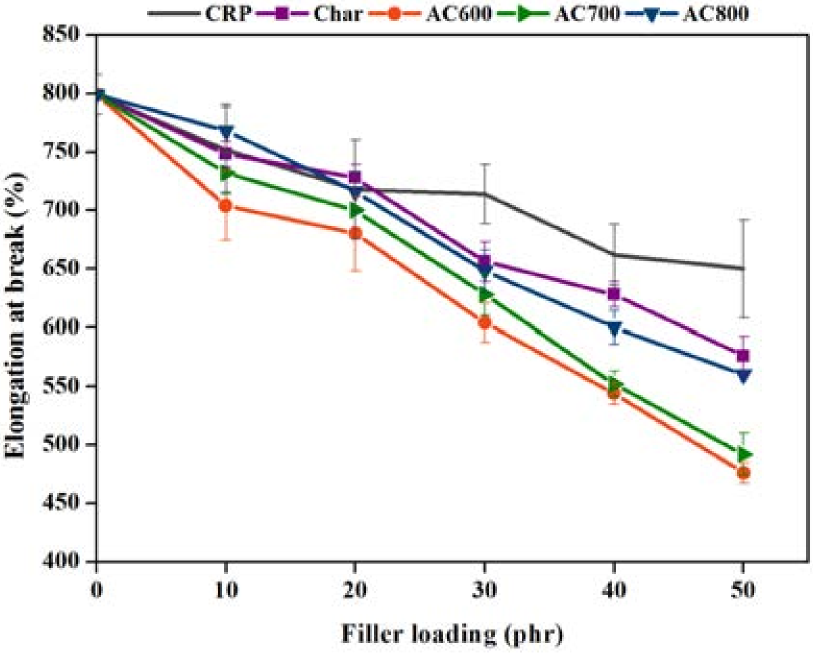


Figure 4.11 Elongation of the NR vulcanizates filled with different fillers prepared from coffee residue

4.2.3.2 Tear Strength

The effects of filler type and loading on the tear strength of the filled NR vulcanizates are presented in Figure 4.12. As can be seen, the CRP-filled NR vulcanizates had no effect on the improvement of tear strength at all. Moreover, it worsened the tear strength at all filler loadings. For other fillers, the tear strength was first increased and then decreased with the further increasing of filler loading. All fillers except char showed the optimum loading for tear strength at 10 phr like the tensile strength. In the case of char, the optimum loading was observed at 20 phr. It was useful to note that the NR vulcanizates filled with char at various loadings from 10 to 50 phr showed the higher tear strength than did the unfilled NR vulcanizates. Regardless at 10 phr, char had the highest efficiency to enhance the tear strength for the NR vulcanizates.

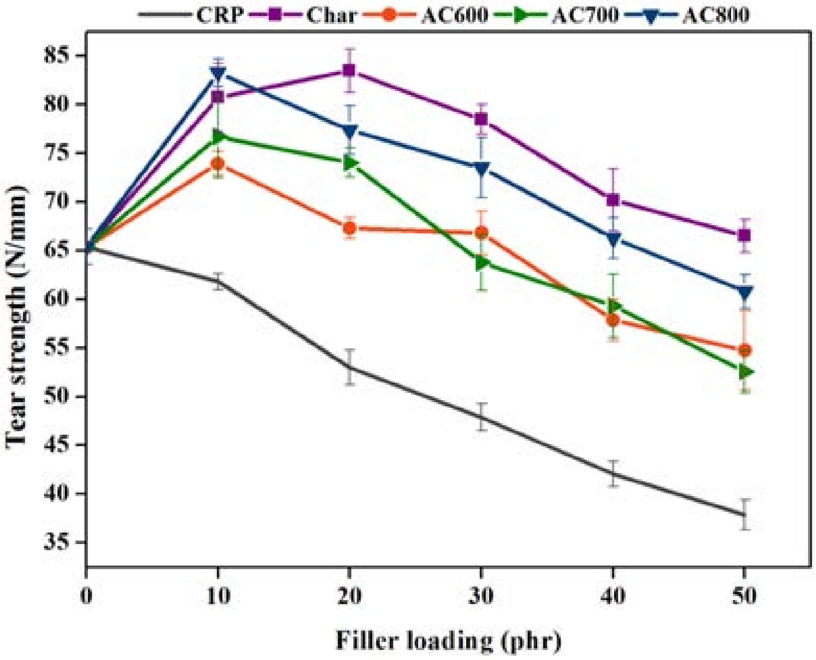


Figure 4.12 Tear strength of the NR vulcanizates filled with different fillers prepared from coffee residue

4.2.3.3 Hardness

Figure 4.13 shows the effect of both filler type and filler loading on the hardness of the NR vulcanizates. It was clearly shown that all filler types prepared from coffee residue comparably affected on the increase of the hardness. However, it was observed that at high loadings (40 and 50 phr), AC700 seemed to have lowest efficiency to enhance the hardness. The hardness of the NR vulcanizates increased with increasing filler loading. This result could explain on the fact that the addition of more filler into the rubber matrix reduces the elasticity of the rubber chains, thus leading to the more rigid rubber.

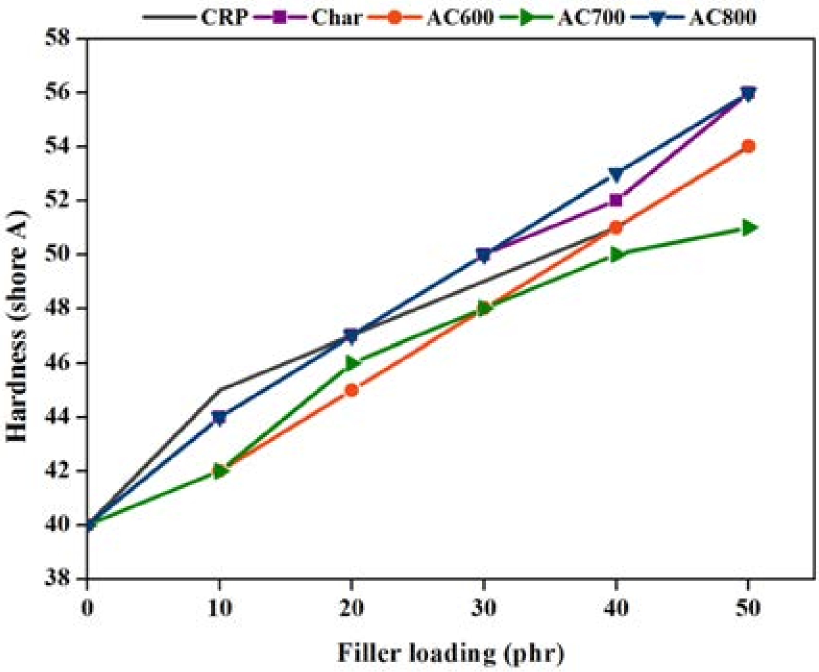


Figure 4.13 Hardness of the NR vulcanizates filled with different fillers prepared from coffee residue

4.2.4 Crosslink Density of the NR Vulcanizates Filled with Different Fillers Prepared from Coffee Residue

Figure 4.14 shows the crosslink density of the filled NR vulcanizates. The results indicated that the presence of CRP reduced the crosslink density of the NR vulcanizates. Moreover, the decrease of the crosslink density causing by CRP increased with increasing CRP loading. This was due to its acidity which not only can retard the sulfur cure as seen in the precious part but also can reduce the crosslink mechanism. In the other cases, the crosslink density of NR vulcanizates filled with char, AC600, AC700, and AC800 increased consistently with increasing filler loadings. At any filler loading, AC600 and AC700 showed comparably influence on the increase of crosslink density of the NR vulcanizates. And their influence on the increase of crosslink density slightly increased with increasing filler loading. Meanwhile, the presence of char and AC800 gave the NR vulcanizates with comparable and highest crosslink density. Moreover, their influence on the increase of crosslink density was much more dependent of the increase of filler loading compared with that of AC600 and AC700. The influence of filler type and loading on the crosslink density was comparable to those on the cure characteristics. Although the relationship between the physical properties of fillers and their influence on the cure characteristics could not be clearly explained here, it was found that filler facilitating most cure reaction seemed to give the NR vulcanizates with highest crosslink density.

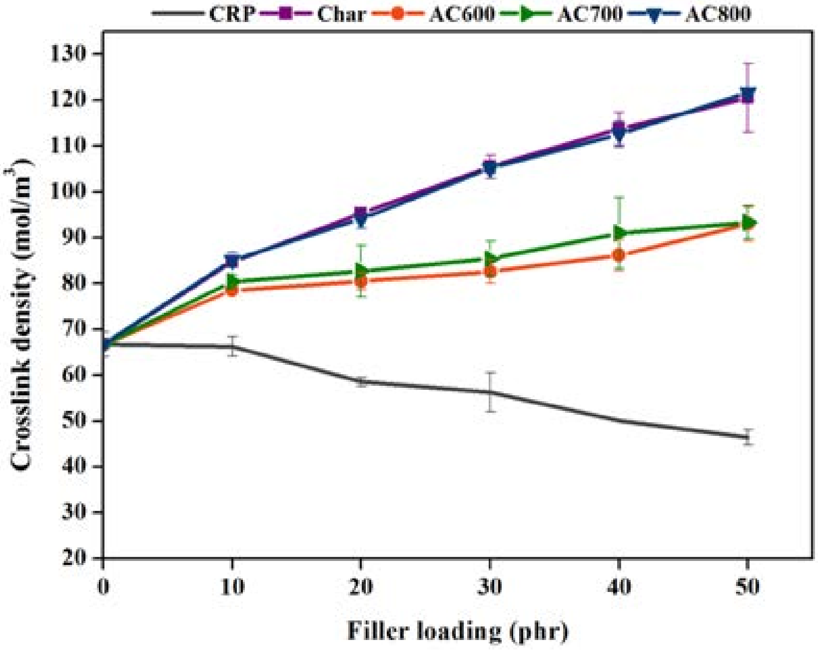
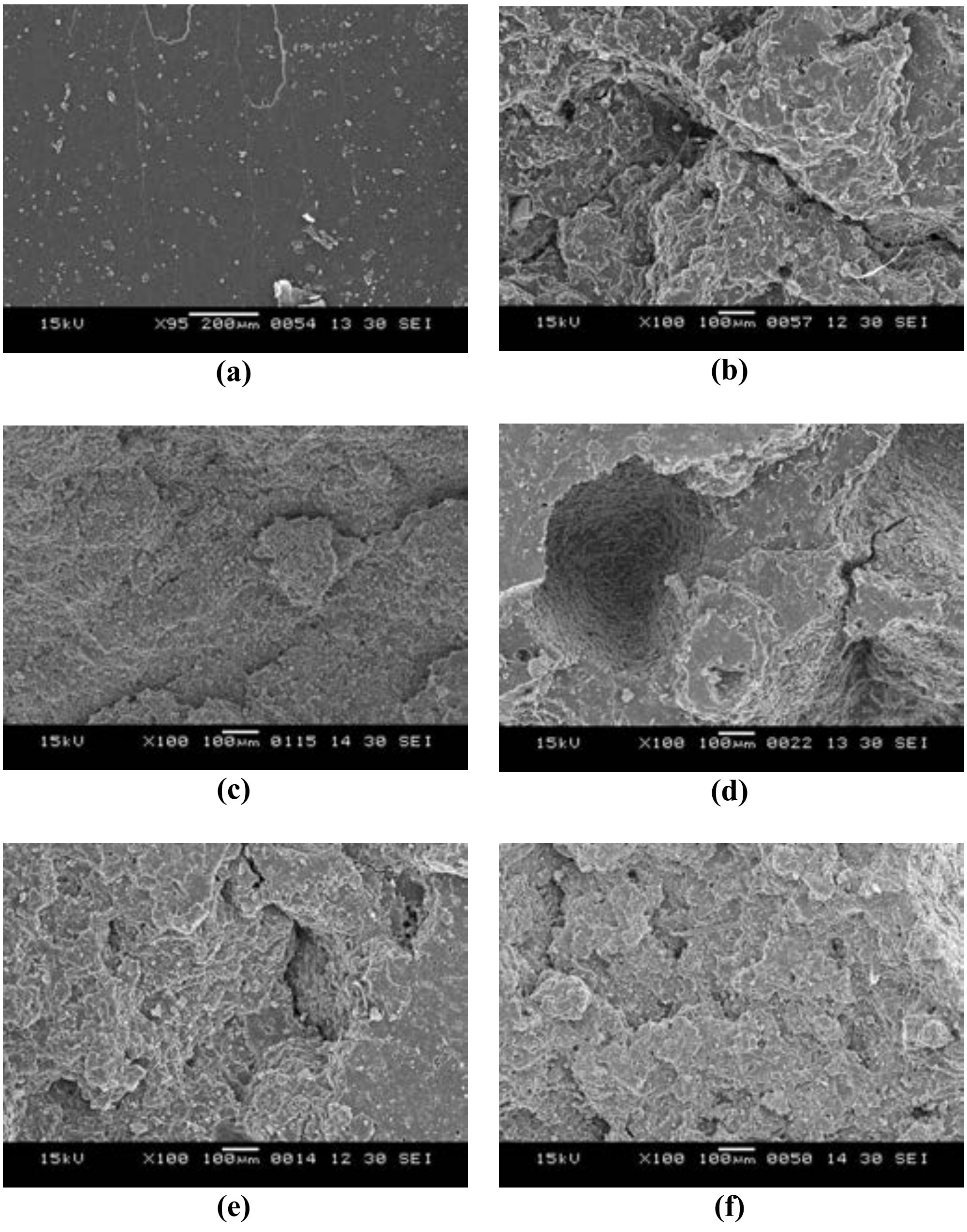


Figure 4.14 Crosslink density of the NR vulcanizates filled with different fillers prepared from coffee residue

4.2.5 Morphology of the NR Vulcanizates Filled with Different Fillers Prepared from Coffee Residue



(a) (b)

(c) (d)

(e) (f)

Figure 4.15 SEM micrographs of the NR vulcanizates filled with (a) 0 phr, (b) 10 phr CRP, (c) 10 phr char, (d) 10 phr AC600, (e) 10 phr AC700, and (f) 10 phr AC800 at 100x magnification

The SEM micrographs taken from the tensile fractured specimen of the unfilled and filled NR vulcanizates at filler loading of 10 phr are presented in Figure 4.15. As can be seen, the surface of unfilled NR vulcanizates was smoother than the filled NR vulcanizates. The SEM micrographs of the CRP, AC600, and AC700 filled NR vulcanizates showed the detachment of filler from the rubber matrix. These results indicated that the adhesion between them and rubber matrix was poor. However, the SEM micrographs of char and AC800 showed more homogeneous phase dispersion and better interaction. And this result was accompanied with their higher tensile strength.

Various types of filler including CRP, char, and activated carbons were prepared from coffee residue. The main reason was to vary the reinforcing efficacy. Although it was expected that the filler with the largest surface area (AC600) will show the highest ability to enhance the mechanical properties of the NR vulcanizates, it did not. In fact, the result here showed that char had the greatest reinforcing efficacy. The possible reason might be due to the difference in crosslink density varying with the filler type. The crosslink density is also one of possible factors influencing on the properties of rubber vulcanizates. As seen in topic 4.2.4, for all filler loadings, the char and AC800 gave the NR vulcanizates with comparable and highest the crosslink density. Interesting, next to char, the highest reinforcing efficient filler was AC 800.

4.3 The Effect of Silane Coupling Agent on the Properties of Coffee Residue Particle Filled NR Vulcanizates

Ismail et al. [68] studied effect of silane coupling agent Si69 on the reinforcing efficacy of cellulose fiber when using as filler for natural rubber vulcanizates. It was found that the NR vulcanizates filled with the Si69 treated cellulose fiber had much higher strength than the ones filled with the untreated cellulose fiber. Figure 4.16 showed the proposed reaction between alkoxyl groups of Si69 and hydroxyl groups of cellulose fiber and then between the Si69 treated cellulose fiber and natural rubber [69]. Basically, it can be clearly seen that the increase of reinforcing capability of cellulose fiber by Si69 was owing to the enhancement of rubber-filler interaction. As mentioned earlier in the Chapter 2, coffee residue is consisted mainly of hemicelluloses and cellulose. The mechanism between Si69 and CRP may also follow what has been depicted in Figure 4.16. Therefore, it was expected that the coffee residue particle (CRP) treated with Si69 may give the NR vulcanizates with better mechanical properties more or less compared with the untreated CRP.

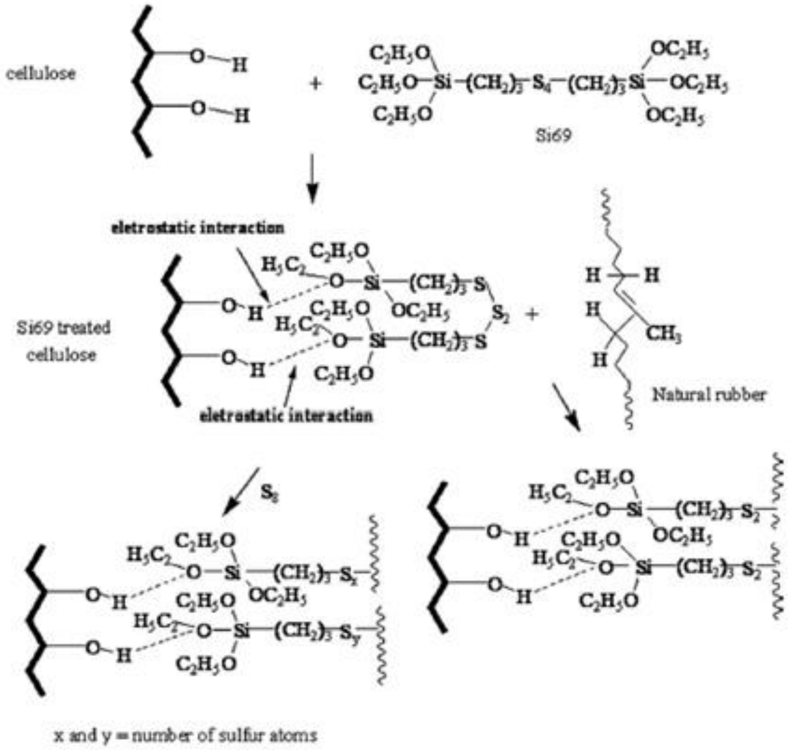


Figure 4.16 Schematic presentation proposed for the reaction between Si69 and the cellulose fiber [69]

4.3.1 Effect of Si69 on Mooney Viscosity of CRP Filled NR Compounds

Figure 4.17 reveals Mooney viscosity of the NR compounds filled with untreated CRP and Si69 treated CRP. It was found that at the lowest loading (10 phr), both fillers showed the same effect on Mooney viscosity of NR compounds which was the reduction of Mooney viscosity compared with the unfilled NR compounds. However, at the higher filler loading, the opposite influence was now observed. As mentioned in the previous part, the decrease of Mooney viscosity with the presence of CRP might be due to some natural organic components of CRP acting as processing aid. Therefore, the more, the lower Mooney viscosity. On the other hand, Mooney viscosity of the Si69 treated CRP filled NR compounds increased with increasing the Si69 treated CRP loadings. This might be because Si69 increased the rubber-filler interaction, thus reducing the mobility of the rubber chain. Therefore, Mooney viscosity of the Si69 treated CRP filled NR compounds now tended to increasing with the filler loadings.

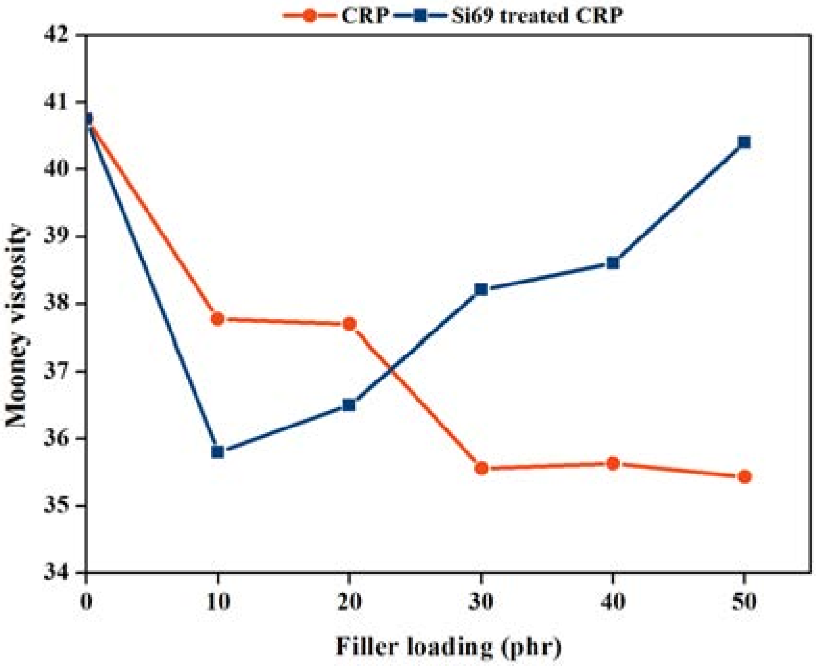


Figure 4.17 Mooney viscosity of the NR compounds filled with CRP and Si69 treated CRP

4.3.2 Effect of Si69 on Cure Characteristics of CRP Filled NR Compounds

The scorch time, cure time, and cure rate index of the NR compounds filled with untreated and Si69 treated CRP are shown in Figures 4.18- 4.20, respectively. With respect to the filler loading, both untreated and Si69 treated CRP showed the similar influence on the cure characteristics of the NR vulcanizates. The scorch time and cure rate index decreased with increasing filler loading. The cure time passed through minimum with increasing filler loading. When considering the effect of Si69 on the cure characteristics of the CRP filled NR vulcanizates, it was found that Si69 accelerated the cure process by decreasing both scorch time and cure time. The comparable behavior was also observed by Ismail et al. when the other natural resource fillers including bamboo fiber [68], kenaf fiber [70], and rattan [71] were treated with Si69 for using as filler for the NR compounds. The Si69 consists of the sulfidic linkage within the molecule which can involve in the sulfur cure. Therefore, the enhancement of cure properties in term of lowering scorch time and cure time by adding Si69 was due to the increasing of sulfur content in the compounds. However, the cure rate indexes of both untreated and Si69 treated CRP were nearly comparable as shown in Figure 4.20.

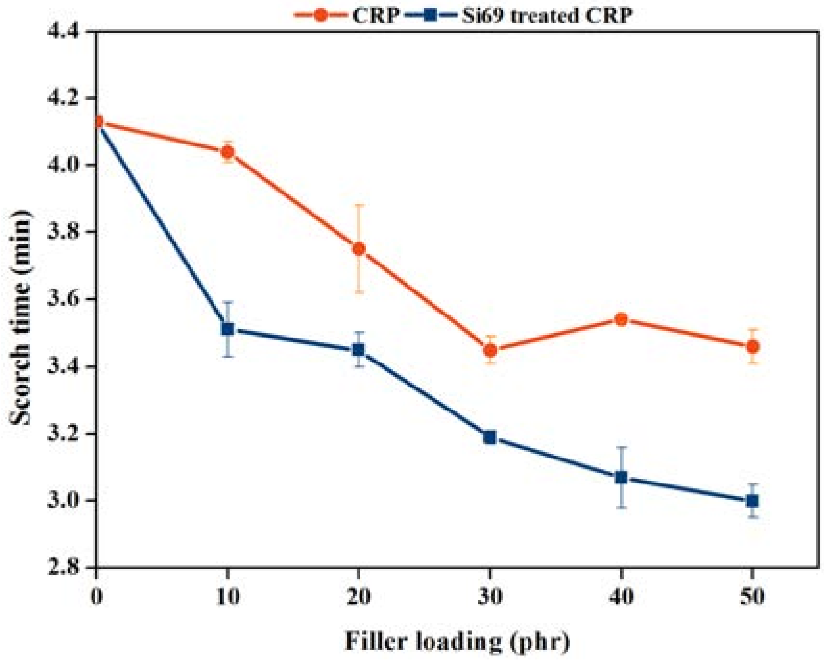


Figure 4.18 Scorch time of the NR compounds filled with CRP and Si69 treated CRP

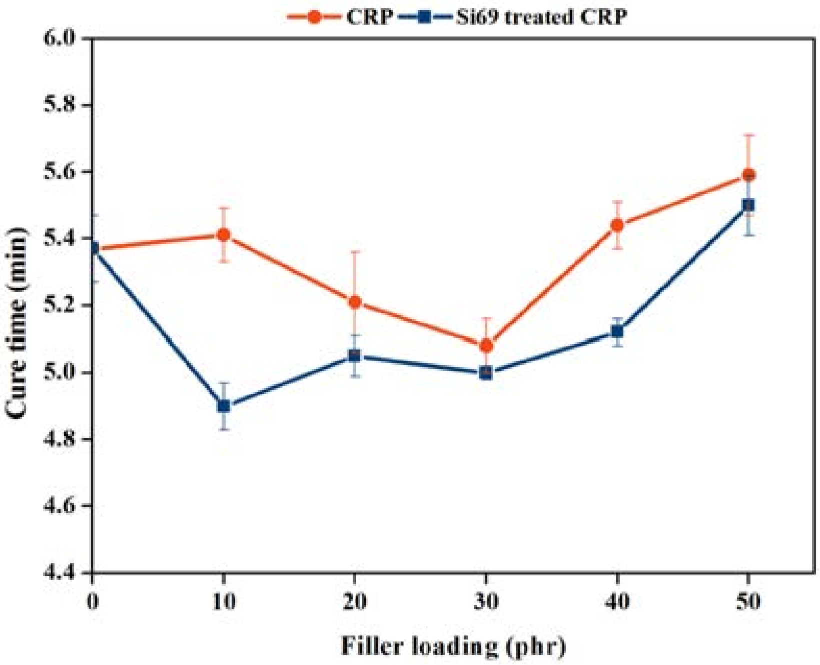


Figure 4.19 Cure time of the NR compounds filled with CRP and Si69 treated CRP

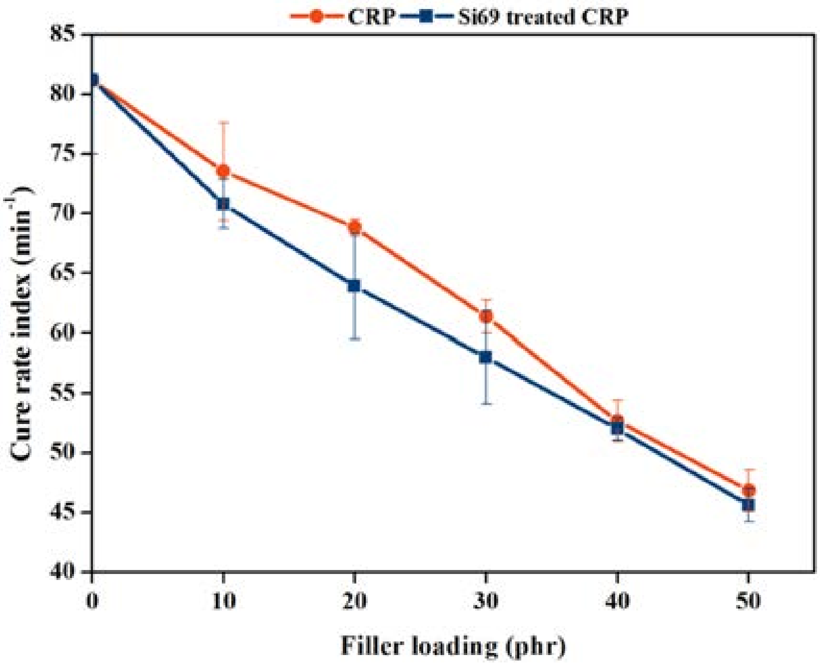


Figure 4.20 Cure rate index of the NR compounds filled with CRP and Si69 treated CRP

4.3.3 Effect of Si69 on Mechanical Properties of CRP Filled NR Vulcanizates

4.3.3.1 Tensile Properties

The effect of Si69 on tensile properties of the NR vulcanizates is shown Figures 4.21-4.24. It can be seen in Figures 4.21-4.22 that regardless of filler loading, the 100% and 300% moduli of the NR vulcanizates filled with Si69 treated CRP were higher than those of the NR vulcanizates filled with untreated CRP. This might be attributed to both the improvement in the bonding between rubber matrix and CRP and the more curing level in the presence of Si69. The chemical bonds were formed between hydroxyl groups of celluloses and hemicelluloses in CRP and alkoxyl groups of Si69. On the other side of Si69, the C-S linkages can act as sulfur donor to form crosslink with NR as shown in Figure 4.16.

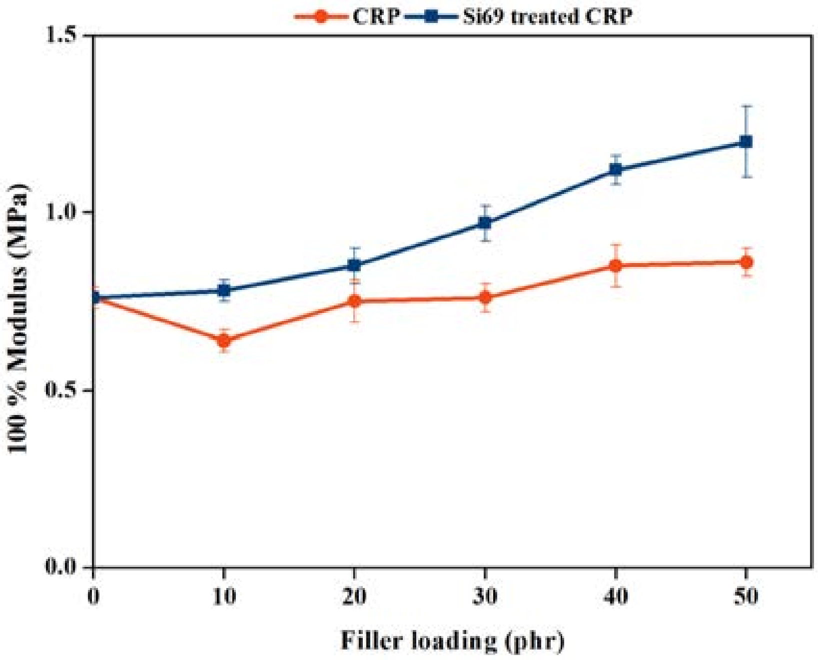


Figure 4.21 100% modulus of the NR vulcanizates filled with CRP and Si69 treated CRP

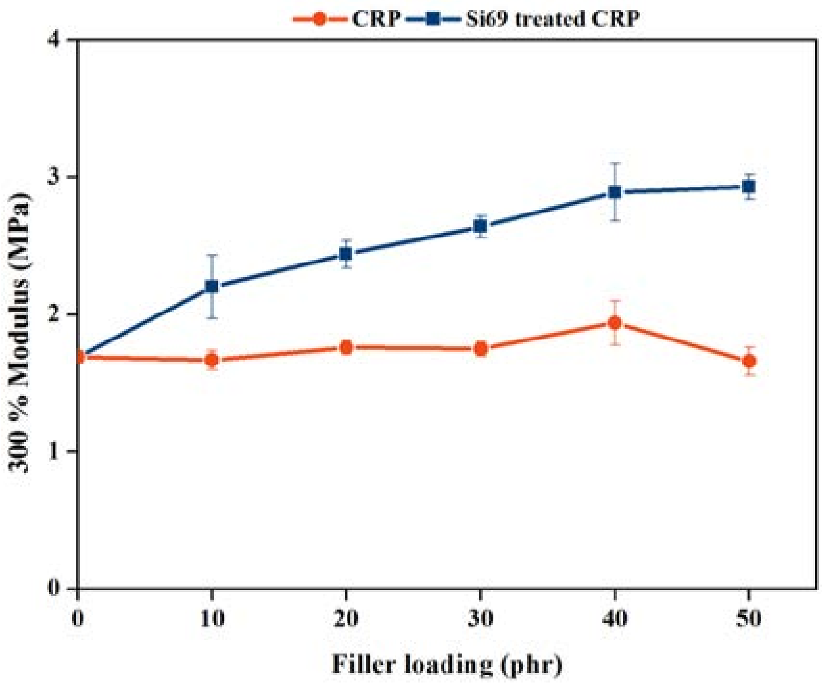


Figure 4.22 300% modulus of the NR vulcanizates filled with CRP and Si69 treated CRP

Tensile strength and elongation at break of the CRP filled NR vulcanizates with and without Si69 are shown in Figures 4.23 and 4.24, respectively. As can be seen, at all filler loadings except 40-50 phr, the tensile strengths of the NR vulcanizates filled with the treated Si69 CRP were higher than those of the ones filled with the untreated CRP. The lower tensile strength of the CRP filled NR vulcanizates was owing to poor adhesion and incompatibility between CRP and rubber matrix. The modification of the CRP surface with Si69 improved the interfacial adhesion between CRP and rubber matrix, thus giving the NR vulcanizates with higher strength. However, at higher filler loading, the benefit of Si69 surface treatment was not observed. Both untreated and Si69 treated CRP gave the NR vulcanizates nearly the same tensile strength. This may be due to the poor dispersion of filler at high loading. Interestingly, at any filler loading, the elongation at break of the Si69 treated CRP filled NR vulcanizates was higher than that of the CRP filled NR vulcanizates. In general, the increase of filler-rubber interaction will reduce elongation at break of the vulcanizates. The reason for this is attributed to the restriction of the rubber chain on to the filler surface. In addition, Si69 also enhances the cure level of the vulcanizates.

This will also reduce the elongation at break of the vulcanizates. The effect of Si69 on the increase of elongation at break could not be clearly explained here.

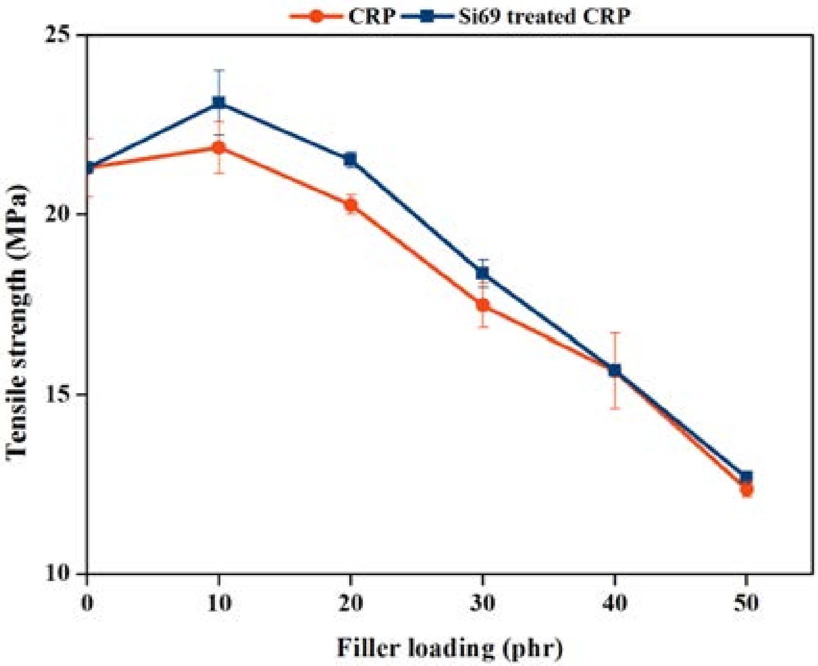


Figure 4.23 Tensile strength of the NR vulcanizates filled with CRP and Si69 treated CRP

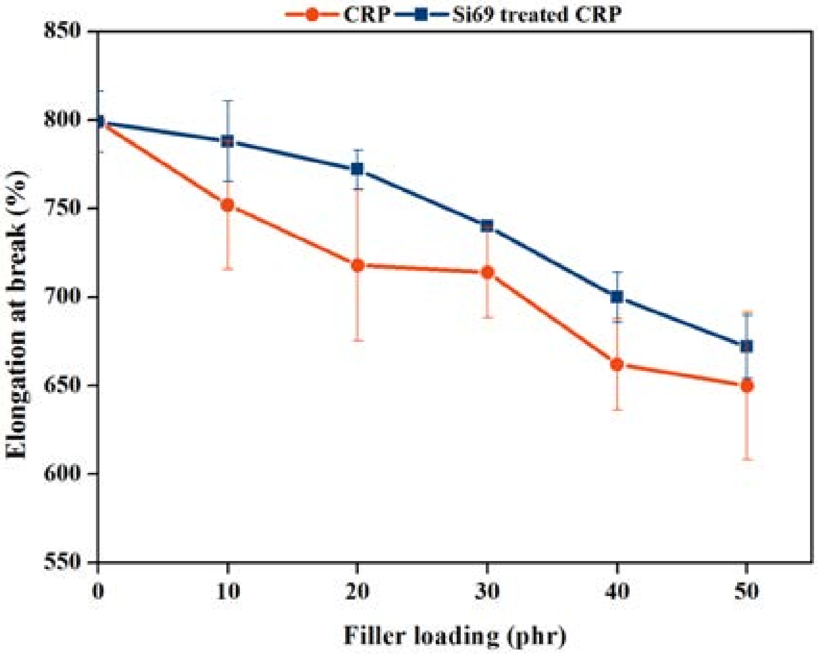


Figure 4.24 Elongation at break of the NR vulcanizates filled with CRP and Si69 treated CRP

4.3.3.2 Tear Strength

Figure 4.25 clearly showed that the presence of Si69 increased tear strength of the NR vulcanizates filled with CRP at any filler loading. The change in tear strength could be discussed on term of continuity of rubber phases by the presence of Si69 [57]. The NR vulcanizates filled with Si69 treated CRP produced more continuous phases causing by the chemical bonding between CRP and rubber matrix.

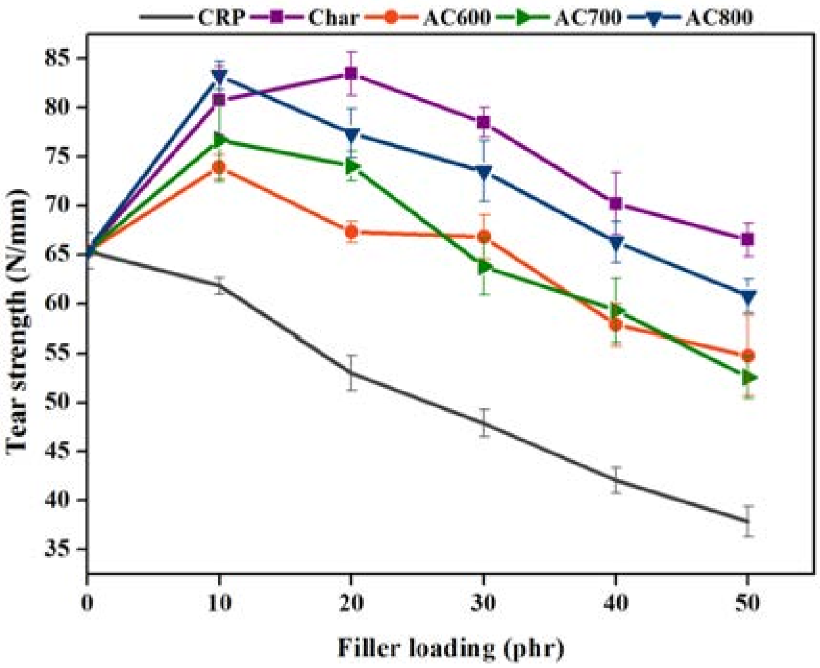


Figure 4.25 Tear strength of the NR vulcanizates filled with CRP and Si69 treated CRP

4.3.3.3 Hardness

The effect of Si69 on the hardness is presented in Figure 4.26. The results showed that the hardness of the NR vulcanizates filled with untreated CRP was lower than the corresponding NR vulcanizates filled with Si69 treated CRP. This might be because the presence of Si69 reduced elasticity of rubber chain and increased curing level, resulting in increasing of rigidity of the NR vulcanizates.

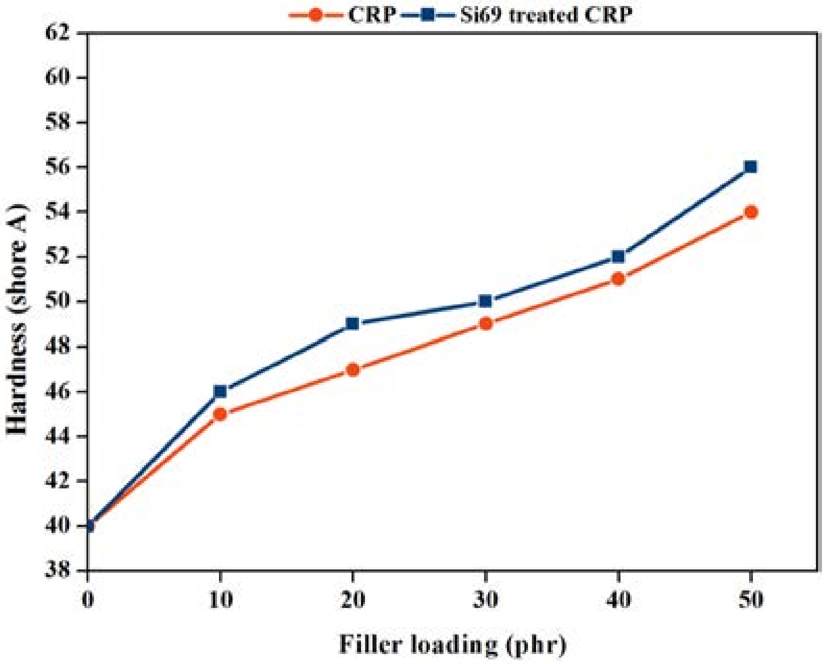


Figure 4.26 Hardness of the NR vulcanizates filled with CRP and Si69 treated CRP

4.3.4 Effect of Si69 on Crosslink Density of CRP Filled NR Vulcanizates

The effect of Si69 on the crosslink density of the NR vulcanizates was shown in Figure 4.27. It was observed that the incorporation of the untreated CRP into the NR compounds reduced the crosslink density. The decrease of the crosslink density increased with increasing CRP loading. This is due to the acidity of CRP as mentioned earlier. However, after treated Si69, the opposite behavior was observed. First, the crosslink density now increased with increasing the CRP loading. Second, at any CRP loading, the crosslink density of the NR vulcanizates filled with Si69 treated CRP was higher than that of the corresponding one filled with untreated CRP. Thongsang et al. [57] reported that the increase in crosslink density by Si69 was caused by two crosslink reactions, one reaction from NR-sulfur-NR and the other reaction from C-S linkages between rubber and Si69. Krysztafkiewicz et al. [72] reported that the addition of silane coupling agent increases the amount of sulfur linked to rubber. Therefore, the vulcanizates with higher crosslink level were obtained.

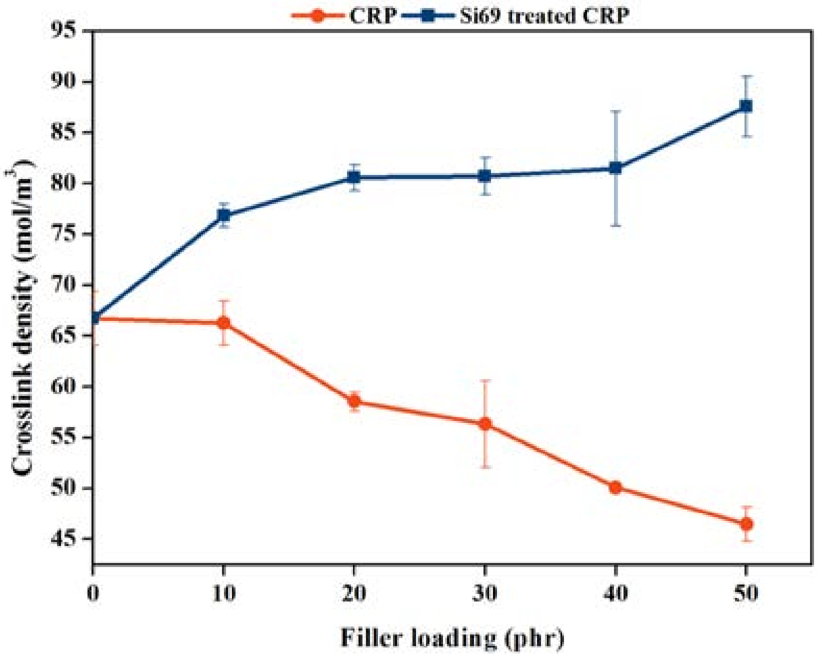
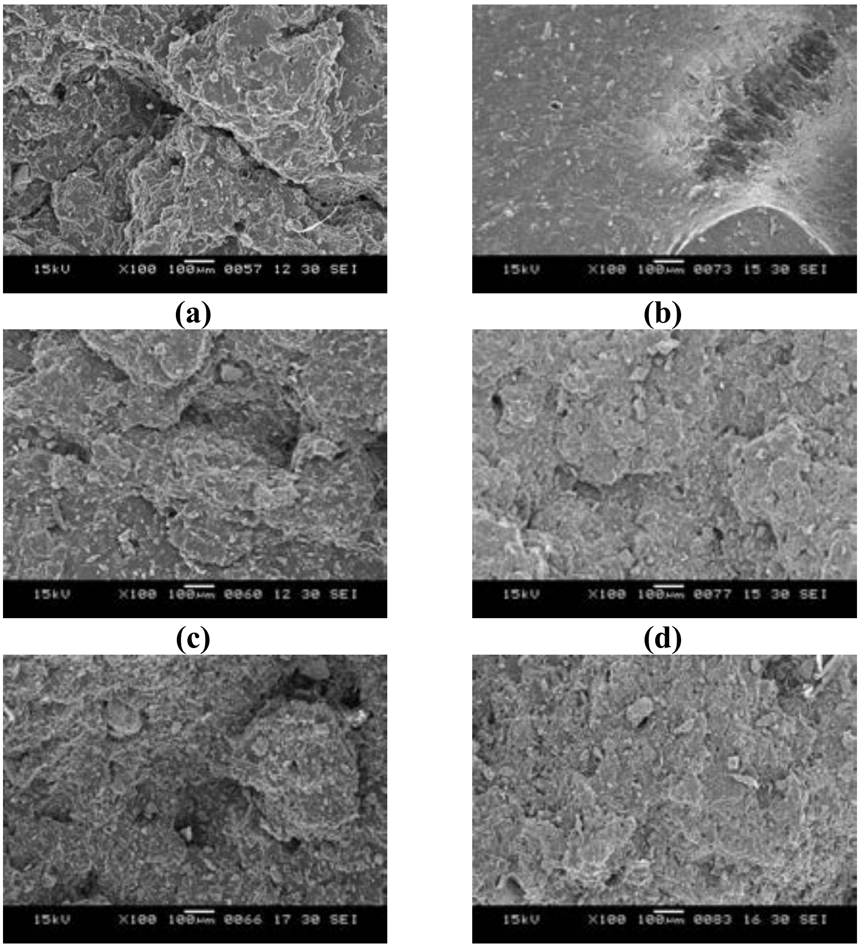


Figure 4.27 Crosslink density of the NR vulcanizates filled with CRP and Si69 treated CRP

4.3.5 Morphology of NR Vulcanizates Filled with CRP and Si69 Treated CRP

The SEM micrographs of tensile fractured surface of NR vulcanizates, in the presence and absence of Si69 are shown in Figure 4.28. As can be seen, the SEM micrographs of the NR vulcanizates filled with Si69 treated CRP presented more homogeneous surface than those filled untreated CRP. The homogeneous and smooth surface indicated that the use of the Si69 as a coupling agent promoted better adhesion between CRP and rubber matrix. These SEM micrographs were in good agreement with the improvement in the physical properties of NR vulcanizates in the presence of Si69.



(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 4.28 SEM micrographs of the natural rubber reinforced with (a) 10 phr untreated CRP, (b) 10 phr treated CRP, (c) 20 phr untreated CRP, (d) 20 phr treated CRP, (e) 40 phr untreated CRP, and (f) 40 phr treated CRP at 100x magnification

4.4 Comparison of the Properties of the NR Vulcanizates Filled with Commercial Fillers and Filler Prepared from Coffee Residue

To study the possibility of the use of filler prepared from coffee residue as filler for NR compound, the properties of the NR compound filled with char, the highest reinforcing efficient filler prepared from the coffee residue were compared with those of the NR compound filled with commercial fillers including CB (reinforcing N330 and semi-reinforcing N774 grade) and $CaCO_3$ (inert filler).

4.4.1 Comparison of Mooney Viscosity of the NR Compounds Filled with Commercial Fillers and Char Prepared from Coffee Residue

In general, Mooney viscosity is a parameter indicating the processability of the rubber compound. The rubber compound with high Mooney viscosity will be difficult to process and vice versa. The effect of the filler type and loading on Mooney viscosity of the filled NR compounds is shown in Figure 4.29. Regardless of filler type, Mooney viscosity increased with increasing filler loading. It can be seen that N330 showed much pronounced effect on the increment of Mooney viscosity. It is due to its highest surface, thus causing the highest mobility restriction of the rubber molecular chain. The effect of char on the Mooney viscosity of the NR compounds was very similar to that of N774. Their effect on the increase in Mooney viscosity was lower than N330 but higher than $CaCO_3$. The presence of $CaCO_3$ did not increase Mooney viscosity of the NR compound much even at the high loading.

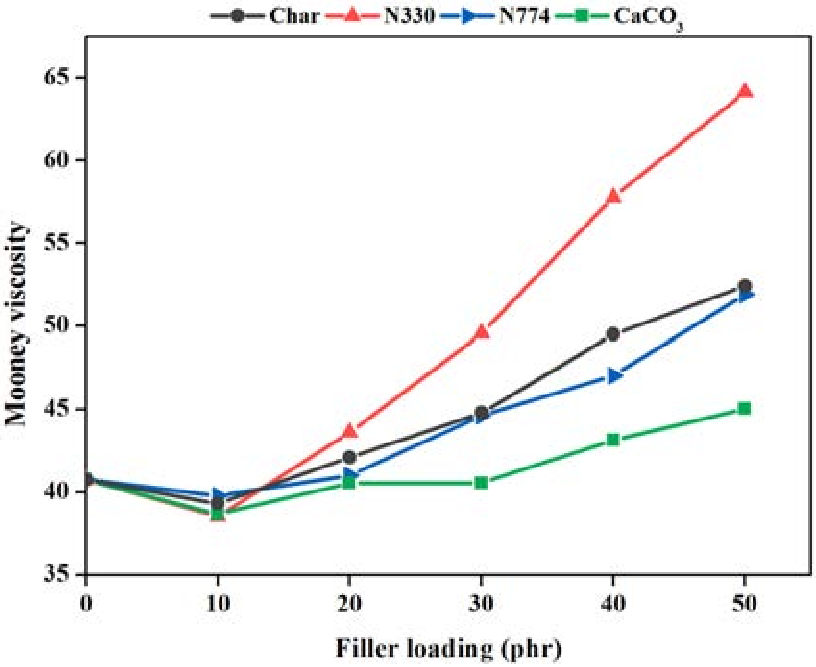


Figure 4.29 Comparison of Mooney viscosity of the NR compounds filled with commercial fillers and char prepared from coffee residue

4.4.2 Comparison of Cure Characteristics of the NR Compounds Filled with Commercial Fillers and Char Prepared from Coffee Residue

Cure characteristics including scorch time, cure time, and cure rate index of the filled NR compounds as a function of filler loading are shown in Figures 4.30-4.32, respectively. It was observed for all types of filler studied in this part, the presence of filler enhanced the processability in term of reduction in the scorch time and cure time. The cycle of the production got shorter. N330 had the highest effect on the reduction in scorch time and cure time. Moreover, its effect on the reduction in these two parameters was directly proportional to its loading. Char showed almost comparable effect on the reduction in scorch time and cure time with N774. And its effect was higher than that of $CaCO_3$. However, its effect on the reduction in cure time was not strongly dependent of loading.

The cure rate index of the NR compounds filled with all commercial fillers decreased slightly when the filler loading was increased. However, the NR compounds filled with char showed markedly decreased in the cure rate index with increasing char loading.

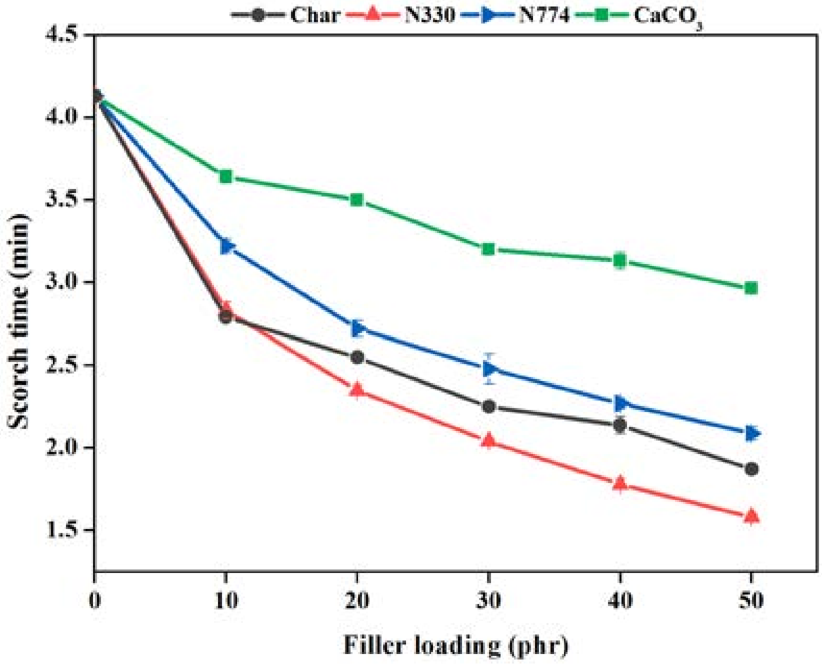


Figure 4.30 Comparison of scorch time of the NR compounds filled with commercial fillers and char prepared from coffee residue

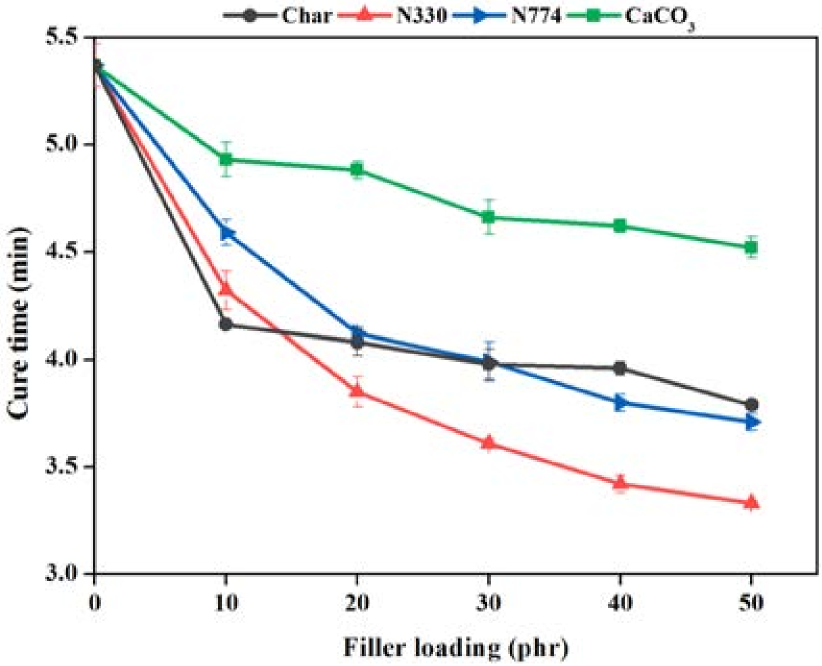


Figure 4.31 Comparison of cure time of the NR compounds filled with commercial fillers and char prepared from coffee residue

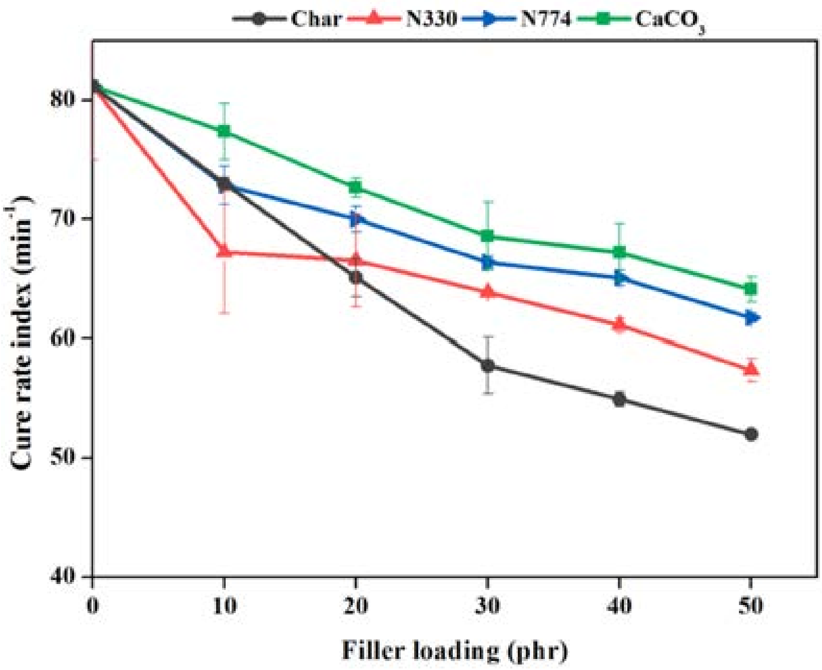


Figure 4.32 Comparison of Cure rate index of the NR compounds filled with commercial fillers and char prepared from coffee residue

4.4.3 Comparison of Mechanical Properties of the NR Vulcanizates Filled with Commercial Fillers and Char Prepared from Coffee Residue

4.4.3.1 Tensile Properties

The 100% modulus, 300% modulus, tensile strength, and elongation at break of filled NR vulcanizates are presented in Figures 4.33-4.36. It appeared that the addition of fillers resulted in a continuous increase in both 100% modulus and 300% modulus of the NR vulcanizates as a function of filler laoding. At all filler loadings, the NR vulcanizates filled with N330 showed the highest 100% and 300 % modulus, whereas the lowest both 100% and 300% modulus was found in the NR vulcanizates filled with $CaCO_3$. The 100% modulus of NR vulcanizates filled with char was comparable to that of the NR vulcanizates filled with N774. However, the NR vulcanizates filled with N774 had higher 300% modulus than the NR vulcanizates filled with char.

It can be seen in Figure 4.35 that tensile strength of the NR vulcanizates filled with char at every loading was lower than that of the NR vulcanizates filled with N330, N774 and $CaCO_3$. So its effect on the tensile strength was poorer than that of the inert filler like $CaCO_3$. The addition of char from 10 to 20 phr could increase the tensile strength of the NR vulcanizates, at which the optimum loading was at 10 phr. For loading of 10 to 50 phr, the addition of N330, N774, and $CaCO_3$ gave tensile strength of the NR vulcanizates higher than that of the unfilled NR vulcanizate, at which the optimum loading was at 20 phr. For all filler loadings, the NR vulcanizates filled N330 showed the highest tensile strength because of its high surface area.

Figure 4.36 present the elongation at break of the filled NR vulcanizates. It can be seen that all fillers exhibited similar tended at which the elongation at break of the filled NR vulcanizates reduced with increasing filler loading. The effect of char on the elongation at break was not much different from that of the commercial fillers used here.

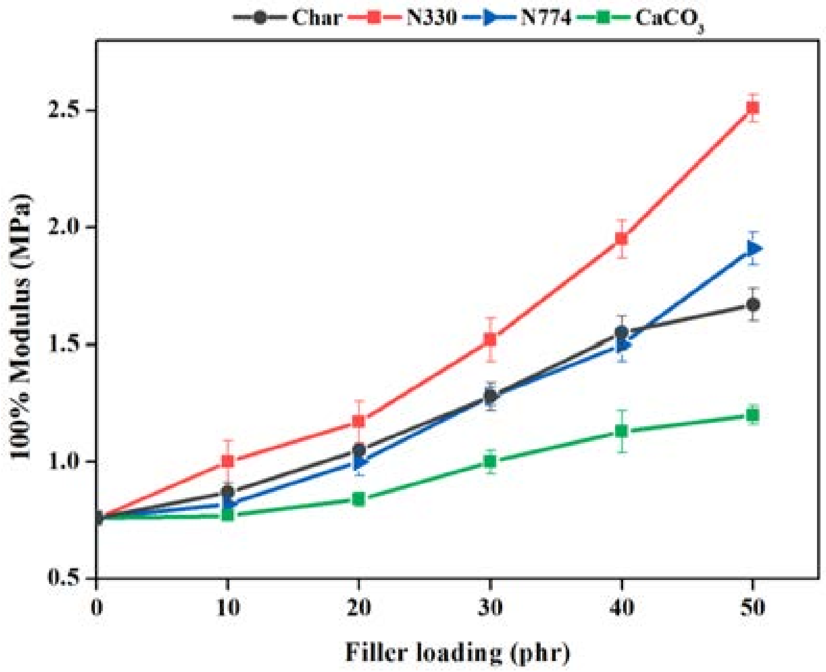


Figure 4.33 Comparison of 100% modulus of the NR culcanizates filled with commercial fillers and char prepared from coffee residue

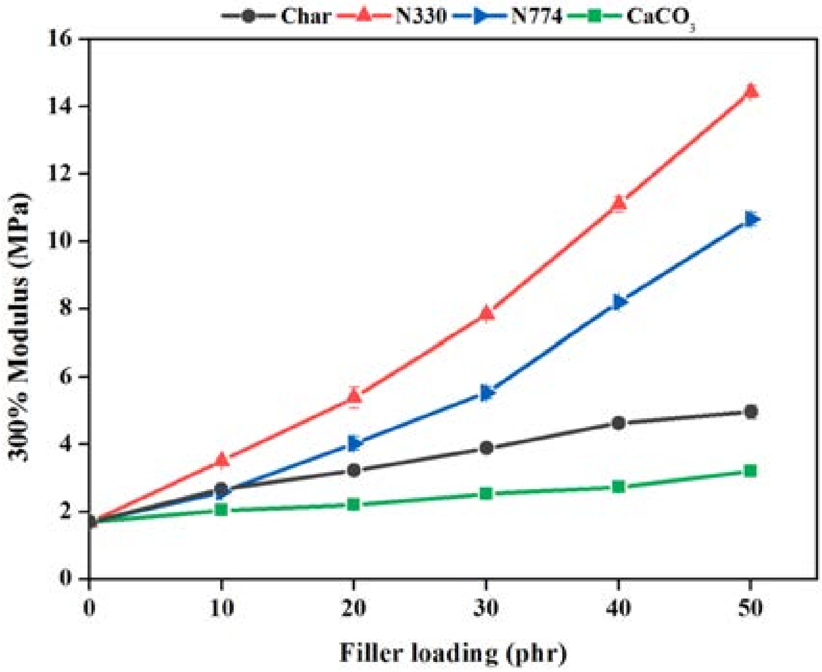


Figure 4.34 Comparison of 300% modulus of the NR vulcanizates filled with commercial fillers and char prepared from coffee residue

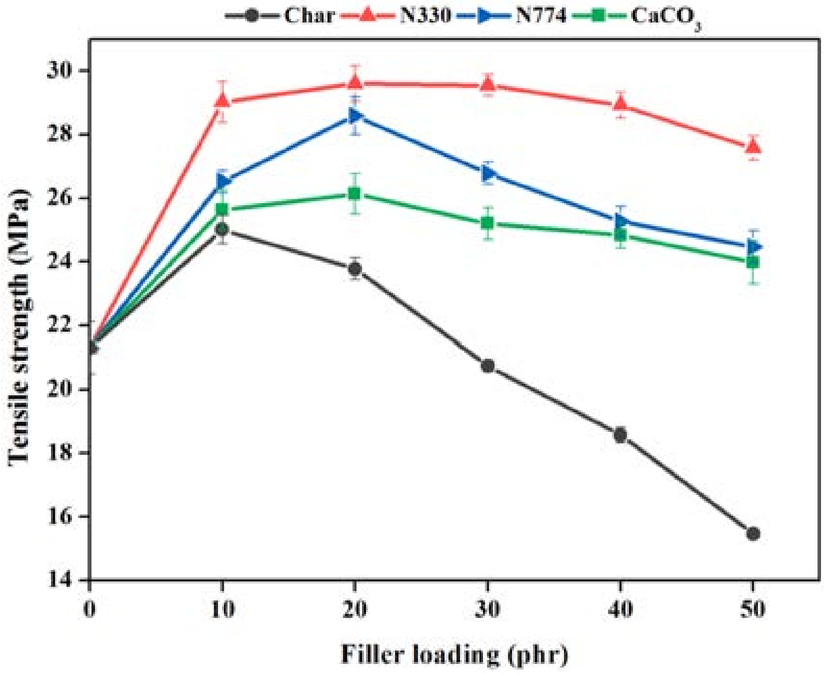


Figure 4.35 Comparison of tensile strength of the NR vulcanizates filled with commercial fillers and char prepared from coffee residue

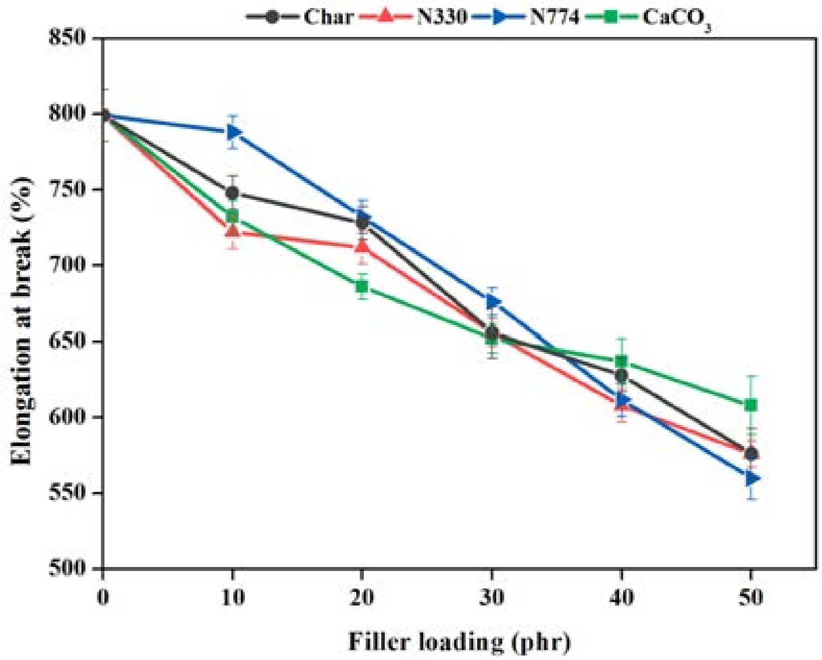


Figure 4.36 Comparison of elongation at break of the NR vulcanizates filled with commercial fillers and char prepared from coffee residue

4.4.3.2 Tear Strength

It can be seen in Figure 4.37 that the addition of CB (both N330 and N774) from 10 to 50 phr significantly enhanced the tear strength of the NR vulcanizates. The tear strength increased with increasing CB loading up to 40 and then decreased at 50 phr. The NR vulcanizates filled with N330 showed higher efficiency on the improvement of tear property than NR vulcanizates filled with N774. It was observed that the tear strength of the NR vulcanizates filled with char and $CaCO_3$ was not much different at various filler loadings. However, the addition of char showed slightly higher tear strength than $CaCO_3$ at loading of 10-30 phr.

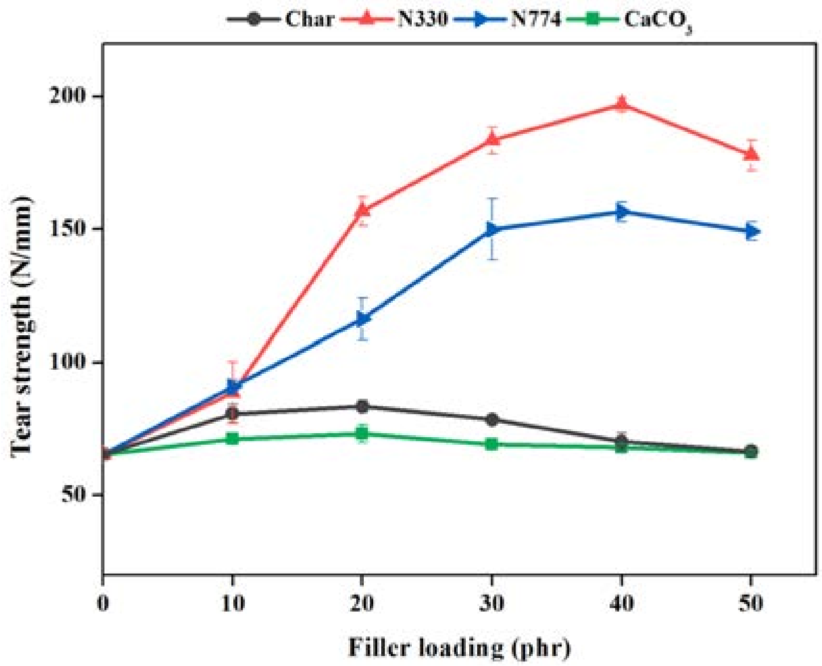


Figure 4.37 Comparison of tear strength of the NR vulcanizates filled with commercial fillers and char prepared from coffee residue

4.4.3.3 Hardness

The hardness of the filled NR vulcanizates is shown in Figure 4.38. It was observed that the hardness of the filled NR vulcanizates increased with increasing filler loading, regardless of filler type. At a similar filler loading, the N330 filled NR vulcanizates had the highest hardness, followed by the NR vulcanizates filled with N774, char, and $CaCO_3$. Even the ability to enhance the hardness properties of char was much lower than that of both CB, in turn its was much higher than $CaCO_3$.

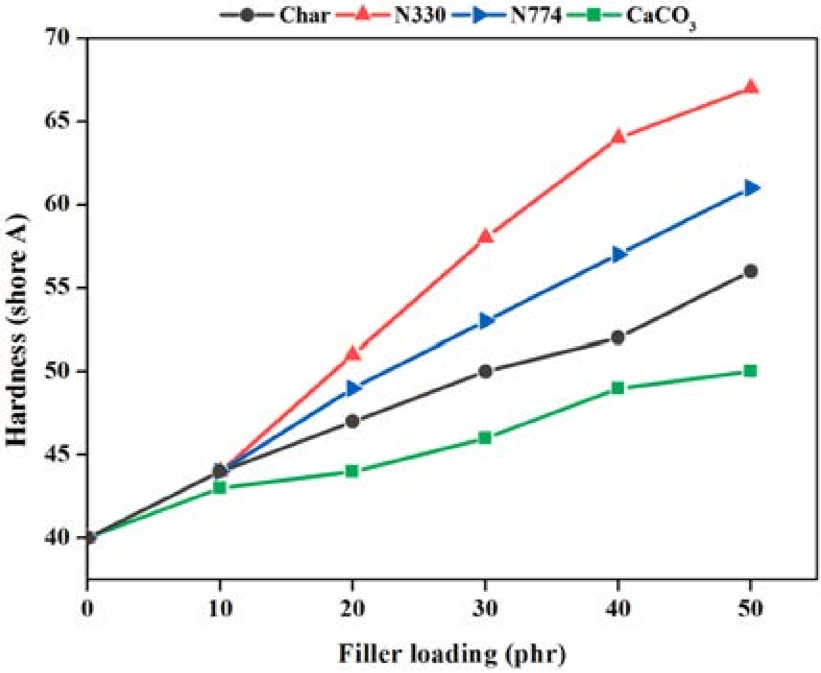


Figure 4.38 Comparison of hardness of the NR vulcanizates filled with commercial fillers and char prepared from coffee residue

4.4.4 Comparison of Crosslink Density of the NR Vulcanizates Filled with Commercial Fillers and Char Prepared from Coffee Residue

The crosslink density of the filled NR vulcanizates is illustrated in Figure 4.39. As can be seen, for all fillers, the rising in crosslink density was observed with increasing filler loading. Both N330 and N774 at various loadings from 10 to 40 phr showed comparable influence on the increase of crosslink density of the NR vulcanizates but at 50 phr, N330 gave higher crosslink density than N774. Meanwhile, the crosslink density of the NR vulcanizates filled with char and $CaCO_3$ was lower than that of the NR vulcanizates filled CB (both grades). At 10 to 30 phr, the crosslink density of the NR vulcanizates filled with char was comparable to the NR vulcanizates filled with $CaCO_3$. However, it was observed that at higher loading, char seemed to have lowest crosslink density.

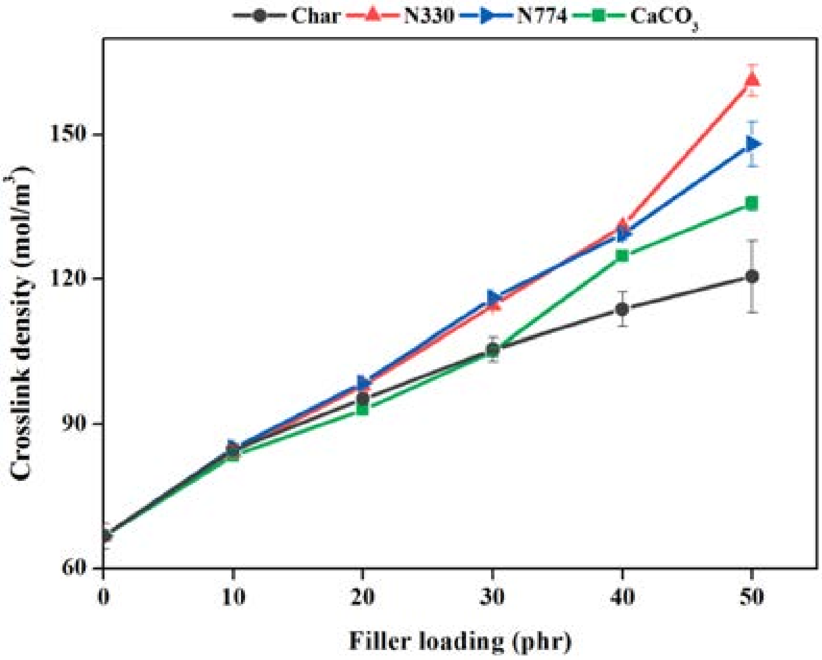
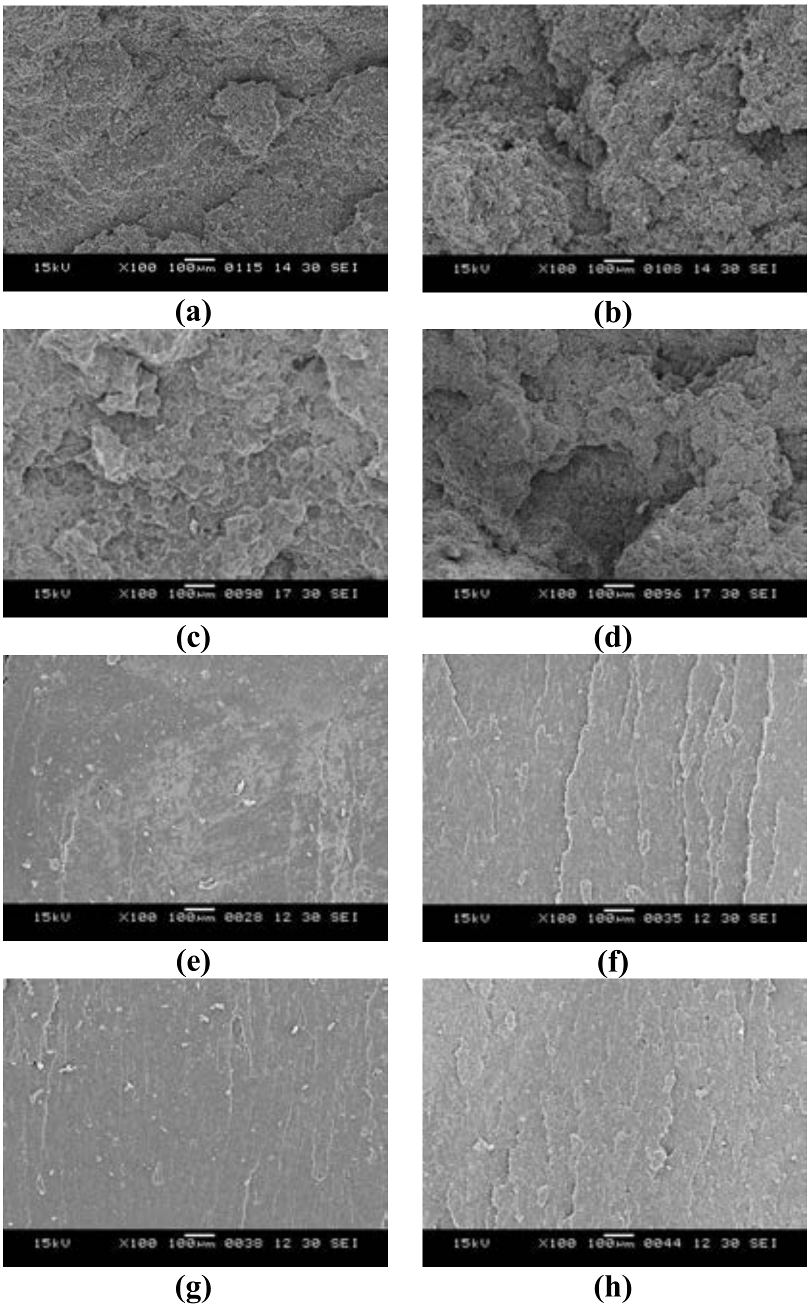


Figure 4.39 Comparison of crosslink density of the NR vulcanizates filled with commercial fillers and char prepared from coffee residue

4.4.5 Morphology of the NR Vulcanizates Filled with Commercial Fillers and Char Prepared from Coffee Residue

Figure 4.40 represents the SEM micrographs taken from the tensile fractured specimen of the NR vulcanizates filled with char, $CaCO_3$, N330, and N774 at 10 and 40 filler loading. The fractured surfaces of the NR vulcanizates filled with char at both filler loadings were similar to those of the NR vulcanizates filled with $CaCO_3$. It was seen that their surface was not smooth when compared to those of the NR vulcanizates filled with N330 and N774. Furthermore, in the case of char and $CaCO_3$, the bumpier surfaces were observed at high filler loading indicating poorer adhesion while in the case of both CB nearly similar surface was observed even at high loading. This can be used to explain why at high filler loading, char and $CaCO_3$ significantly cause the reduction of strength than both CB.



(a) **(b)**

(c) **(d)**

(e) **(f)**

(g) **(h)**

Figure 4.40 SEM micrographs of NR vulcanizates filled with (a) 10 phr char, (b) 40 phr char, (c) 10 phr $CaCO_3$, (d) 40 phr $CaCO_3$, (e) 10 phr N330, (f) 40 phr N330, (g) 10 phr N774, and (h) 40 phr N774 at 100x magnification

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This work was attempted to study the possibility of the use of coffee residue as filler for natural rubber (NR). Therefore, various forms of filler were prepared from coffee residue including coffee residue particle (CRP), char and activated carbons (AC600, AC700, and AC800: number indicates activation temperature). The difference amongst these fillers were the particle size, BET surface area, pH value. The influence of these fillers on the cure characteristics, Mooney viscosity, and mechanical properties was first compared. The effect of silane coupling, Si-69, on the reinforcing efficiency of the CRP was also investigated here. Later, the cure characteristics, Mooney viscosity, and mechanical properties of the NR compound filled with the highest reinforcing efficient filler (with respect of highest tensile and tear strength and hardness) prepared from coffee residue were compared to those of the NR compounds filled with commercial fillers including reinforcing CB (N330), semi-reinforcing CB (N774), and inert $CaCO_3$. The reinforcing level of the highest reinforcing efficient filler prepared from coffee residue was ranked with respect to that of commercials. From the results, it can be summarized as follows.

5.1.1 Properties of the NR Vulcanizates Filled with Different Fillers Prepared from Coffee Residue

1. Compared with the Mooney viscosity of the unfilled NR compound, the incorporation of char, AC600, AC700, and AC800 led to the increase of Mooney viscosity, while CRP cause the reduction of Mooney viscosity.

2. The addition of all fillers but CRP significantly decreased the scorch time and cure time. In contrast, the addition of CRP did not effect on the cure characteristics of the NR compounds significantly. This might be due to its pH value toward to the acidic which could retard the cure process.

3. Amongst different fillers prepared from coffee residue, it was found that char had the highest reinforcing efficacy in term of giving highest tensile and tear strength

and hardness. However, it showed the optimal loading at 10 and 20 phr for tensile and tear strength, respectively. On the other hand, the CRP had the lowest reinforcing efficacy. This was explainable by its largest particle size.

4. It was useful to note here that the benefit of the large BET surface area of AC600 on reinforcing efficacy was not observed at all. In fact, this filler had lower ability to enhance the mechanical properties than char having much lower BET surface area.

5.1.2 The Effect of Silane Coupling Agent on the Properties of CRP Filled NR Vulcanizates

1. After treated with CRP with Si-69, the Mooney viscosity of the filled NR compounds tended to increase and was directly dependent of filler loading while without the addition of CRP had no effect on the Mooney viscosity.

2. The presence of Si69 accelerated the cure process by decreasing the scorch time and cure time of the CRP filled NR compounds.

3. The presence of Si-69 enhanced the mechanical properties of the CRP filled NR vulcanizates. This might be due to the increasing in both interaction between CRP and rubber matrix and curing stage evident by the higher crosslink density.

5.1.3 Comparison of the Properties of the NR Vulcanizates Filled with Commercial Fillers and the Highest Reinforcing Efficient Filler Prepared from Coffee Residue

1. From the first part, char was found to be the highest reinforcing efficient filler prepared from coffee residue. Therefore, its effect on the properties of the NR compounds was compared to those of the commercial fillers.

2. The Mooney viscosity of the char filled NR compounds gave considerable higher than that of the $CaCO_3$ filled NR compounds. Comparing with both CB, it was found that the Mooney viscosity of the char filled NR compounds was comparable to N774 but much lower than N330.

3. The cure properties of the char filled NR compounds showed similar tend to other commercial fillers.

4. The char filled NR vulcanizates showed lower tensile strength than both CB and $CaCO_3$ filled NR vulcanizates but gave higher tear strength and hardness than $CaCO_3$ filled NR vulcanizates.

5. From this present study, for economic purpose and environment concern, char could be used as inert filler for NR.

5.2 Recommendations

As the results, the recommendation can be given as follows:

1. Since char showed the highest reinforcing efficiency, the further reduction its particle size might be able to enhance its reinforcing efficiency.

2. Among the three ACs prepared here, the BET surface area decreased with increasing activation temperature. This result was contradicted to the theory. Thus, effect of activation temperature on the BET surface area of AC prepared from coffee residue should be further investigated.

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APPENDICES

APPENDIX A

CURE CHARACTERISTICS OF NR COMPOUNDS

Table A-1 Cure characteristic of gum NR compounds

Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
1	4.13	5.3	85.47
2	4.13	5.48	74.07
3	4.13	5.32	84.03
Mean	4.13	5.37	81.19
SD	0.00	0.10	6.21

Table A-2 Cure characteristic of CRP filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	4.03	5.48	68.97
	2	4.08	5.42	74.63
	3	4.02	5.32	76.92
	Mean	4.04	5.41	73.51
	SD	0.03	0.08	4.10
20	1	3.90	5.37	68.03
	2	3.71	5.16	68.97
	3	3.65	5.09	69.44
	Mean	3.75	5.21	68.81
	SD	0.13	0.15	0.72
30	1	3.40	5.00	62.50
	2	3.48	5.15	59.88
	3	3.47	5.09	61.73
	Mean	3.45	5.08	61.37
	SD	0.04	0.08	1.35
40	1	3.53	5.41	53.19
	2	3.55	5.52	50.76
	3	3.55	5.40	54.05
	Mean	3.54	5.44	52.67
	SD	0.01	0.07	1.71
50	1	3.49	5.59	47.62
	2	3.48	5.71	44.84
	3	3.40	5.48	48.08
	Mean	3.46	5.59	46.85
	SD	0.05	0.12	1.75

Table A-3 Cure characteristic of Si69 treated CRP filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	3.29	4.89	62.50
	2	3.3	4.97	59.88
	3	3.32	4.83	66.23
	Mean	3.30	4.90	62.87
	SD	0.02	0.07	3.19
20	1	3.41	5.01	62.50
	2	3.48	5.11	61.35
	3	3.39	5.02	61.35
	Mean	3.43	5.05	61.73
	SD	0.05	0.06	0.66
30	1	3.19	4.99	55.56
	2	3.18	5	54.95
	3	3.21	5.02	55.25
	Mean	3.19	5.00	55.25
	SD	0.02	0.02	0.31
40	1	3	5.1	47.62
	2	3.17	5.17	50.00
	3	3.04	5.09	48.78
	Mean	3.07	5.12	48.80
	SD	0.09	0.04	1.19
50	1	3.01	5.4	41.84
	2	2.95	5.53	38.76
	3	3.04	5.57	39.53
	Mean	3.00	5.50	40.04
	SD	0.05	0.09	1.60

Table A-4 Cure characteristic of char filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	2.81	4.17	73.53
	2	2.77	4.14	72.99
	3	2.80	4.18	72.46
	Mean	2.79	4.16	73.00
	SD	0.02	0.02	0.53
20	1	2.57	4.15	63.29
	2	2.52	4.04	65.79
	3	2.55	4.06	66.23
	Mean	2.55	4.08	65.10
	SD	0.03	0.06	1.58
30	1	2.26	3.92	60.24
	2	2.26	4.06	55.56
	3	2.23	3.97	57.47
	Mean	2.25	3.98	57.76
	SD	0.02	0.07	2.36
40	1	2.12	3.94	54.95
	2	2.10	3.94	54.35
	3	2.19	3.99	55.56
	Mean	2.14	3.96	54.95
	SD	0.05	0.03	0.60
50	1	1.87	3.79	52.08
	2	1.88	3.81	51.81
	3	1.86	3.78	52.08
	Mean	1.87	3.79	51.99
	SD	0.01	0.02	0.16

Table A-5 Cure characteristic of AC600 filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	2.20	3.64	69.44
	2	2.20	3.51	76.34
	3	2.20	3.50	76.92
	Mean	2.20	3.55	74.23
	SD	0.00	0.08	4.16
20	1	2.04	3.60	64.10
	2	2.08	3.64	64.10
	3	2.07	3.61	64.94
	Mean	2.06	3.62	64.38
	SD	0.02	0.02	0.48
30	1	1.94	3.80	53.76
	2	1.92	3.75	54.64
	3	1.95	3.80	54.05
	Mean	1.94	3.78	54.15
	SD	0.02	0.03	0.45
40	1	1.86	4.06	45.45
	2	1.85	3.93	48.08
	3	1.85	3.91	48.54
	Mean	1.85	3.97	47.36
	SD	0.01	0.08	1.67
50	1	1.78	4.22	40.98
	2	1.76	4.06	43.48
	3	1.77	4.06	43.67
	Mean	1.77	4.11	42.71
	SD	0.01	0.09	1.50

Table A-6 Cure characteristic of AC700 filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	2.32	3.66	74.63
	2	2.35	3.75	71.43
	3	2.31	3.67	73.53
	Mean	2.33	3.69	73.19
	SD	0.02	0.05	1.63
20	1	2.12	3.75	61.35
	2	2.10	3.69	62.89
	3	2.10	3.69	62.89
	Mean	2.11	3.71	62.38
	SD	0.01	0.03	0.89
30	1	1.87	3.86	50.25
	2	1.90	3.74	54.35
	3	1.90	3.77	53.48
	Mean	1.89	3.79	52.69
	SD	0.02	0.06	2.16
40	1	1.81	3.93	47.17
	2	1.81	3.90	47.85
	3	1.81	3.92	47.39
	Mean	1.81	3.92	47.47
	SD	0.00	0.02	0.34
50	1	1.74	4.08	42.74
	2	1.74	4.24	40.00
	3	1.75	4.24	40.16
	Mean	1.74	4.19	40.97
	SD	0.01	0.09	1.53

Table A-7 Cure characteristics of AC800 filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	2.98	4.41	69.93
	2	2.93	4.36	69.93
	3	2.96	4.37	70.92
	Mean	2.96	4.38	70.26
	SD	0.03	0.03	0.57
20	1	2.56	4.11	64.52
	2	2.61	4.15	64.94
	3	2.62	4.16	64.94
	Mean	2.60	4.14	64.80
	SD	0.03	0.03	0.24
30	1	2.38	4.18	55.56
	2	2.36	4.05	59.17
	3	2.34	4.03	59.17
	Mean	2.36	4.09	57.97
	SD	0.02	0.08	2.09
40	1	2.17	4.00	54.64
	2	2.14	3.97	54.64
	3	2.11	3.91	55.56
	Mean	2.14	3.96	54.95
	SD	0.03	0.05	0.53
50	1	1.87	3.81	51.55
	2	1.84	3.79	51.28
	3	1.88	3.83	51.28
	Mean	1.86	3.81	51.37
	SD	0.02	0.02	0.15

Table A-8 Cure characteristics of N330 filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	2.81	4.43	61.73
	2	2.89	4.28	71.94
	3	2.8	4.27	68.03
	Mean	2.83	4.33	67.23
	SD	0.05	0.09	5.15
20	1	2.32	3.93	62.11
	2	2.37	3.81	69.44
	3	2.35	3.82	68.03
	Mean	2.35	3.85	66.53
	SD	0.03	0.07	3.89
30	1	2.03	3.6	63.69
	2	2.06	3.63	63.69
	3	2.03	3.59	64.10
	Mean	2.04	3.61	63.83
	SD	0.02	0.02	0.24
40	1	1.82	3.46	60.98
	2	1.76	3.38	61.73
	3	1.77	3.42	60.61
	Mean	1.78	3.42	61.10
	SD	0.03	0.04	0.57
50	1	1.57	3.33	56.82
	2	1.57	3.33	56.82
	3	1.61	3.32	58.48
	Mean	1.58	3.33	57.37
	SD	0.02	0.01	0.96

Table A-9 Cure characteristics of N774 filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	3.18	4.52	74.63
	2	3.21	4.61	71.43
	3	3.26	4.64	72.46
	Mean	3.22	4.59	72.84
	SD	0.04	0.06	1.63
20	1	2.68	4.08	71.43
	2	2.72	4.13	70.92
	3	2.77	4.14	72.99
	Mean	2.72	4.12	71.78
	SD	0.05	0.03	1.08
30	1	2.38	3.88	66.67
	2	2.53	4.05	65.79
	3	2.53	4.03	66.67
	Mean	2.48	3.99	66.37
	SD	0.09	0.09	0.51
40	1	2.27	3.82	64.52
	2	2.29	3.83	64.94
	3	2.24	3.76	65.79
	Mean	2.27	3.80	65.08
	SD	0.03	0.04	0.65
50	1	2.12	3.75	61.35
	2	2.05	3.67	61.73
	3	2.11	3.72	62.11
	Mean	2.09	3.71	61.73
	SD	0.04	0.04	0.38

Table A-10 Cure characteristics of $CaCO_3$ filled NR compounds

Loading	Sample	t_s2 (min)	t_c90 (min)	CRI (min^{-1})
10	1	3.65	4.92	78.74
	2	3.59	4.86	78.74
	3	3.67	5.01	74.63
	Mean	3.64	4.93	77.37
	SD	0.04	0.08	2.37
20	1	3.51	4.9	71.94
	2	3.47	4.83	73.53
	3	3.52	4.9	72.46
	Mean	3.50	4.88	72.65
	SD	0.03	0.04	0.81
30	1	3.22	4.75	65.36
	2	3.2	4.64	69.44
	3	3.18	4.59	70.92
	Mean	3.20	4.66	68.58
	SD	0.02	0.08	2.88
40	1	3.12	4.65	65.36
	2	3.18	4.61	69.93
	3	3.08	4.59	66.23
	Mean	3.13	4.62	67.17
	SD	0.05	0.03	2.43
50	1	2.92	4.47	64.52
	2	2.98	4.57	62.89
	3	2.98	4.52	64.94
	Mean	2.96	4.52	64.11
	SD	0.03	0.05	1.08

APPENDIX B

TENSILE PROPERTIES OF NR VULCANIZATES

Table B-1 Tensile properties of gum NR vulcanizates

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.7505	1.165	1.742	21.5	740
2	0.7586	1.164	1.663	21.22	700
3	0.7516	1.203	1.641	20.39	716
4	0.7181	1.176	1.696	20.84	740
5	0.8144	1.167	1.71	22.55	728
Mean	0.76	1.18	1.69	21.30	725
SD	0.03	0.02	0.04	0.81	17.06

Table B-2 Tensile properties of CRP filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.63	1.09	1.63	21.33	720
2	0.60	1.01	1.59	21.20	708
3	0.68	1.14	1.69	22.85	780
4	0.63	1.16	1.71	22.36	768
5	0.68	1.27	1.76	21.62	788
Mean	0.64	1.13	1.67	21.87	752.80
SD	0.03	0.10	0.07	0.71	32.54

Table B-3 Tensile properties of CRP filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.81	1.31	1.81	20.50	708
2	0.76	1.32	1.69	19.82	732
3	0.68	1.29	1.78	20.47	704
4	0.78	1.25	1.78	20.33	780
5	0.70	1.25	1.73	20.25	664
Mean	0.75	1.29	1.76	20.27	717.60
SD	0.06	0.03	0.05	0.27	42.58

Table B-4 Tensile properties of CRP filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.79	1.26	1.77	17.71	740
2	0.73	1.20	1.80	16.59	672
3	0.72	1.25	1.67	17.44	720
4	0.78	1.31	1.77	18.27	712
5	0.81	1.33	1.74	17.36	724
Mean	0.76	1.27	1.75	17.47	713.60
SD	0.04	0.05	0.05	0.61	25.39

Table B-5 Tensile properties of CRP filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.79	1.31	1.87	14.54	640
2	0.84	1.45	2.21	15.01	632
3	0.86	1.40	1.87	17.06	696
4	0.81	1.34	1.81	15.29	672
5	0.94	1.42	1.95	16.41	668
Mean	0.85	1.38	1.94	15.66	661.60
SD	0.06	0.06	0.16	1.04	25.86

Table B-6 Tensile properties of CRP filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.80	1.12	1.63	12.38	680
2	0.86	1.29	1.77	12.05	588
3	0.84	1.21	1.64	12.38	680
4	0.89	1.29	1.69	12.64	676
5	0.90	1.25	1.71	12.38	624
Mean	0.86	1.23	1.69	12.37	649.60
SD	0.04	0.07	0.06	0.21	41.82

Table B-7 Tensile properties of Si69 treated CRP filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.81	1.34	1.95	22.96	780
2	0.79	1.43	2.16	22.58	820
3	0.78	1.41	2.14	22.69	760
4	0.74	1.42	2.15	22.61	800
5	0.80	1.55	2.59	24.7	780
Mean	0.78	1.43	2.20	23.11	788.00
SD	0.03	0.08	0.23	0.90	22.80

Table B-8 Tensile properties of Si69 treated CRP filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.80	1.55	2.40	21.31	780
2	0.93	1.66	2.60	21.72	780
3	0.84	1.60	2.48	21.52	760
4	0.86	1.60	2.38	21.78	780
5	0.82	1.55	2.34	21.30	760
Mean	0.85	1.59	2.44	21.53	772.00
SD	0.05	0.05	0.10	0.22	10.95

Table B-9 Tensile properties of Si69 treated CRP filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.04	1.755	2.7	18.61	740
2	0.9874	1.69	2.702	18.26	740
3	0.9137	1.764	2.503	17.77	740
4	0.9262	1.654	2.618	18.34	740
5	0.9937	1.786	2.653	18.81	740
Mean	0.97	1.73	2.64	18.36	740.00
SD	0.05	0.06	0.08	0.39	0.00

Table B-10 Tensile properties of Si69 treated CRP filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.14	2.07	3.04	15.76	680
2	1.11	1.99	3.13	15.83	720
3	1.17	1.90	2.90	15.71	700
4	1.09	1.78	2.58	15.56	700
5	1.08	1.89	2.80	15.52	700
Mean	1.12	1.93	2.89	15.68	700.00
SD	0.04	0.11	0.21	0.13	14.14

Table B-11 Tensile properties of Si69 treated CRP filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.21	2.07	2.92	12.63	660
2	1.26	2.00	3.03	12.63	700
3	1.22	2.12	2.99	12.72	660
4	1.28	2.01	2.90	12.80	660
5	1.03	1.88	2.79	12.65	680
Mean	1.20	2.02	2.93	12.69	672.00
SD	0.10	0.09	0.09	0.07	17.89

Table B-12 Tensile properties of char filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.85	1.53	2.76	25.47	740
2	0.87	1.63	2.66	25.42	760
3	0.91	1.72	2.66	24.96	760
4	0.90	1.62	2.60	24.72	740
5	0.82	1.64	2.66	24.41	740
Mean	0.87	1.63	2.67	25.00	748.00
SD	0.04	0.07	0.06	0.45	10.95

Table B-13 Tensile properties of char filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.08	2.04	3.26	23.95	720
2	1.05	2.09	3.06	23.28	720
3	1.05	2.07	3.31	23.83	740
4	1.05	2.10	3.30	23.62	720
5	1.01	2.04	3.18	24.18	740
Mean	1.05	2.07	3.22	23.77	728.00
SD	0.02	0.03	0.10	0.34	10.95

Table B-14 Tensile properties of char filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.23	2.41	3.79	20.47	660
2	1.30	2.58	3.85	20.72	660
3	1.36	2.64	3.90	20.93	640
4	1.21	2.52	3.90	20.84	680
5	1.32	2.66	3.96	20.72	640
Mean	1.28	2.56	3.88	20.74	656.00
SD	0.06	0.10	0.06	0.17	16.73

Table B-15 Tensile properties of char filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.61	2.94	4.48	18.19	640
2	1.54	3.10	4.72	18.82	620
3	1.44	3.01	4.63	18.63	620
4	1.54	2.91	4.50	18.65	640
5	1.61	3.19	4.81	18.56	620
Mean	1.55	3.03	4.63	18.57	628.00
SD	0.07	0.12	0.14	0.23	10.95

Table B-16 Tensile properties of char filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.74	3.39	4.96	15.37	560
2	1.62	3.43	5.17	15.55	580
3	1.61	3.25	4.97	15.31	560
4	1.76	3.48	5.06	15.50	580
5	1.63	3.17	4.63	15.56	600
Mean	1.67	3.34	4.96	15.46	576.00
SD	0.07	0.13	0.20	0.11	16.73

Table B-17 Tensile properties of AC600 filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.89	1.58	2.55	20.80	720
2	0.86	1.56	2.41	20.90	700
3	0.85	1.49	2.35	20.39	740
4	0.87	1.49	2.33	19.88	700
5	0.91	1.54	2.49	18.49	660
Mean	0.88	1.53	2.42	20.09	704.00
SD	0.02	0.04	0.10	0.98	29.66

Table B-18 Tensile properties of AC600 filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.98	1.85	3.03	17.79	660
2	0.97	1.84	2.90	16.64	720
3	0.93	1.78	2.94	16.41	680
4	1.03	1.83	2.87	17.51	700
5	0.98	1.98	3.06	16.49	640
Mean	0.98	1.86	2.96	16.97	680.00
SD	0.04	0.07	0.08	0.64	31.62

Table B-19 Tensile properties of AC600 filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.19	2.40	3.71	13.21	580
2	1.05	2.09	3.52	13.49	600
3	1.07	2.15	3.41	13.55	620
4	1.02	2.10	3.62	13.67	600
5	1.13	2.22	3.51	13.13	620
Mean	1.09	2.19	3.55	13.41	604.00
SD	0.07	0.13	0.12	0.23	16.73

Table B-20 Tensile properties of AC600 filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.28	2.63	4.12	11.58	560
2	1.24	2.46	4.28	11.71	540
3	1.21	2.48	4.13	11.36	540
4	1.12	2.60	4.23	12.02	540
5	1.27	2.57	3.90	11.22	540
Mean	1.22	2.55	4.13	11.58	544.00
SD	0.06	0.07	0.15	0.31	8.94

Table B-21 Tensile properties of AC600 filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.508	3.185	4.617	8.63	480
2	1.592	2.925	4.317	9.78	480
3	1.681	2.922	4.481	9.54	480
4	1.581	3.097	4.76	8.69	460
5	1.574	2.988	4.554	9.3	480
Mean	1.59	3.02	4.55	9.19	476.00
SD	0.06	0.11	0.16	0.51	8.94

Table B-22 Tensile properties of AC700 filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.89	1.60	2.44	18.31	740
2	0.88	1.51	2.44	18.84	740
3	0.85	1.63	2.41	18.16	700
4	0.92	1.57	2.40	18.36	740
5	0.88	1.57	2.41	18.61	740
Mean	0.88	1.58	2.42	18.46	732.00
SD	0.02	0.04	0.02	0.27	17.89

Table B-23 Tensile properties of AC700 filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.98	1.83	2.96	17.19	700
2	0.96	1.89	2.83	16.82	700
3	1.00	1.91	2.97	17.19	700
4	1.04	1.99	2.90	17.90	700
5	1.00	1.94	3.08	16.94	700
Mean	0.99	1.91	2.95	17.21	700.00
SD	0.03	0.06	0.09	0.42	0.00

Table B-24 Tensile properties of AC700 filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.04	2.03	3.31	13.10	620
2	0.95	1.95	2.97	13.08	660
3	1.02	2.10	3.17	13.74	620
4	1.06	1.95	3.08	13.07	620
5	1.03	2.16	3.35	13.19	620
Mean	1.02	2.04	3.18	13.24	628.00
SD	0.04	0.09	0.16	0.29	17.89

Table B-25 Tensile properties of AC700 filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.22	2.33	3.68	10.41	560
2	1.12	2.28	3.62	10.96	560
3	1.14	2.27	3.79	10.27	540
4	1.16	2.33	3.51	10.34	540
5	1.17	2.48	3.71	11.14	560
Mean	1.16	2.34	3.66	10.62	552.00
SD	0.04	0.08	0.11	0.40	10.95

Table B-26 Tensile properties of AC700 filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.32	2.56	4.24	9.06	520
2	1.27	2.47	4.35	9.03	480
3	1.32	2.71	4.58	9.27	480
4	1.39	2.66	4.34	9.37	500
5	1.39	2.77	4.48	9.41	480
Mean	1.34	2.63	4.40	9.23	492.00
SD	0.05	0.12	0.13	0.17	17.89

Table B-27 Tensile properties of AC800 filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.90	1.69	2.52	25.06	800
2	0.97	1.67	2.39	24.87	780
3	0.90	1.72	2.59	23.42	760
4	0.89	1.70	2.68	23.26	760
5	0.88	1.68	2.64	20.78	740
Mean	0.91	1.69	2.56	23.48	768.00
SD	0.04	0.02	0.11	1.72	22.80

Table B-28 Tensile properties of AC800 filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.01	2.28	3.39	21.49	700
2	1.00	1.91	3.09	21.28	720
3	1.03	1.95	2.93	21.27	720
4	0.95	1.96	3.29	21.19	740
5	0.94	1.96	2.91	21.15	700
Mean	0.98	2.01	3.12	21.28	716.00
SD	0.04	0.15	0.21	0.13	16.73

Table B-29 Tensile properties of AC800 filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.16	2.29	3.50	18.86	660
2	1.09	2.20	3.56	18.26	620
3	1.05	2.00	3.48	18.85	640
4	1.11	2.35	3.74	18.83	660
5	1.07	2.31	3.71	18.65	660
Mean	1.09	2.23	3.60	18.69	648.00
SD	0.04	0.14	0.12	0.26	17.89

Table B-30 Tensile properties of AC800 filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.24	2.53	4.02	15.80	600
2	1.21	2.68	4.00	15.83	600
3	1.21	2.67	4.20	15.87	620
4	1.31	2.85	4.32	15.80	580
5	1.30	2.77	4.30	15.75	600
Mean	1.26	2.70	4.17	15.81	600.00
SD	0.05	0.12	0.15	0.04	14.14

Table B-31 Tensile properties of AC800 filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.56	3.19	4.65	13.03	560
2	1.58	3.22	4.69	13.66	560
3	1.74	3.38	4.69	13.07	560
4	1.61	3.24	4.72	13.33	560
5	1.64	3.06	4.54	12.98	560
Mean	1.63	3.22	4.66	13.21	560.00
SD	0.07	0.11	0.07	0.28	0.00

Table B-32 Tensile properties of N330 filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.85	1.72	3.59	28.06	800
2	1.02	1.93	3.51	28.95	780
3	0.98	1.80	3.43	29.60	800
4	1.09	1.95	3.44	29.60	780
5	1.05	2.04	3.59	28.87	780
Mean	1.00	1.89	3.51	29.02	788.00
SD	0.09	0.13	0.08	0.64	10.95

Table B-33 Tensile properties of N330 filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.23	2.45	5.02	30.30	740
2	1.28	2.71	5.66	29.16	740
3	1.11	2.56	5.10	29.77	720
4	1.07	2.88	5.73	29.89	720
5	1.16	2.48	5.37	28.91	740
Mean	1.17	2.62	5.38	29.61	732.00
SD	0.09	0.18	0.32	0.56	10.95

Table B-34 Tensile properties of N330 filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.49	3.70	7.95	29.44	680
2	1.65	3.75	7.92	29.72	680
3	1.44	3.89	7.82	29.56	680
4	1.46	3.34	7.82	29.06	660
5	1.58	3.68	7.62	29.98	680
Mean	1.52	3.67	7.83	29.55	676.00
SD	0.09	0.20	0.13	0.34	8.94

Table B-35 Tensile properties of N330 filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	2.01	5.18	11.14	28.46	600
2	2.04	5.93	10.89	28.69	620
3	1.97	6.11	11.22	29.22	600
4	1.90	5.44	11.39	28.82	620
5	1.85	5.64	10.86	29.47	620
Mean	1.95	5.66	11.10	28.93	612.00
SD	0.08	0.37	0.22	0.41	10.95

Table B-36 Tensile properties of N330 filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	2.47	8.28	14.16	27.40	540
2	2.49	7.46	14.54	27.03	560
3	2.52	7.82	14.57	27.59	560
4	2.47	7.24	14.55	27.81	560
5	2.62	8.43	14.40	28.00	580
Mean	2.51	7.84	14.44	27.57	560.00
SD	0.06	0.51	0.17	0.38	14.14

Table B-37 Tensile properties of N774 filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.85	1.53	2.60	26.87	800
2	0.86	1.52	2.50	26.30	780
3	0.79	1.45	2.72	26.92	800
4	0.82	1.58	2.53	26.36	780
5	0.80	1.55	2.59	26.17	780
Mean	0.82	1.53	2.59	26.52	788.00
SD	0.03	0.05	0.09	0.35	10.95

Table B-38 Tensile properties of N774 filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.09	1.96	3.82	29.43	740
2	0.97	2.06	3.88	28.67	740
3	0.95	1.81	3.96	28.65	720
4	0.98	1.94	4.22	28.44	720
5	1.04	2.28	4.29	27.78	740
Mean	1.00	2.01	4.03	28.59	732.00
SD	0.06	0.18	0.21	0.59	10.95

Table B-39 Tensile properties of N774 filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.262	2.881	5.327	26.66	680
2	1.32	3.16	5.699	26.37	680
3	1.307	2.626	5.678	27.15	680
4	1.268	2.775	5.346	27.13	660
5	1.224	2.737	5.617	26.58	680
Mean	1.28	2.84	5.53	26.78	676.00
SD	0.04	0.20	0.18	0.35	8.94

Table B-40 Tensile properties of N774 filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.49	3.73	8.23	26.24	600
2	1.59	4.28	8.12	24.86	620
3	1.52	3.94	8.13	24.82	600
4	1.52	3.57	8.36	25.10	620
5	1.40	3.73	8.17	25.31	620
Mean	1.50	3.85	8.20	25.27	612.00
SD	0.07	0.27	0.10	0.58	10.95

Table B-41 Tensile properties of N774 filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.93	4.74	10.74	24.88	540
2	1.82	5.11	10.50	24.98	560
3	1.88	4.51	10.40	23.82	560
4	2.01	5.07	10.81	24.05	560
5	1.91	5.81	10.86	24.64	580
Mean	1.91	5.05	10.66	24.47	560.00
SD	0.07	0.49	0.20	0.51	14.14

Table B-42 Tensile properties of $CaCO_3$ filled NR vulcanizates with 10 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.77	1.42	1.99	26.13	740
2	0.78	1.41	2.04	24.58	720
3	0.77	1.47	2.05	26.11	720
4	0.80	1.38	2.08	25.57	740
5	0.75	1.34	2.03	25.76	740
Mean	0.77	1.40	2.04	25.63	732.00
SD	0.02	0.05	0.03	0.63	10.95

Table B-43 Tensile properties of $CaCO_3$ filled NR vulcanizates with 20 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.88	1.42	2.12	26.11	684
2	0.83	1.50	2.14	25.47	700
3	0.82	1.44	2.27	26.63	680
4	0.86	1.46	2.30	25.55	680
5	0.84	1.44	2.15	26.91	684
Mean	0.84	1.45	2.20	26.13	685.60
SD	0.03	0.03	0.08	0.64	8.29

Table B-44 Tensile properties of $CaCO_3$ filled NR vulcanizates with 30 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	0.93	1.76	2.49	24.75	660
2	0.98	1.56	2.62	25.68	644
3	1.05	1.77	2.46	25.44	656
4	0.98	1.71	2.52	25.56	660
5	1.04	1.68	2.56	24.58	640
Mean	1.00	1.70	2.53	25.20	652.00
SD	0.05	0.08	0.06	0.50	9.38

Table B-45 Tensile properties of $CaCO_3$ filled NR vulcanizates with 40 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.05	1.85	2.71	24.57	632
2	1.06	1.85	2.61	25.50	636
3	1.10	1.83	2.73	24.78	628
4	1.25	1.94	2.75	24.46	664
5	1.18	1.97	2.78	24.86	628
Mean	1.13	1.89	2.72	24.83	637.60
SD	0.09	0.07	0.06	0.41	15.13

Table B-46 Tensile properties of $CaCO_3$ filled NR vulcanizates with 50 phr

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	% Elongation
1	1.15	2.20	3.13	23.14	620
2	1.19	2.18	3.11	24.22	588
3	1.18	2.11	3.13	24.44	588
4	1.21	2.19	3.35	24.69	628
5	1.25	2.30	3.29	23.38	620
Mean	1.20	2.19	3.20	23.97	608.80
SD	0.04	0.07	0.11	0.68	19.27

APPENDIX C

TEAR STRENGTH OF NR VULCANIZATES

Table C-1 Tear strength of gum NR vulcanizates

Sample	TEAR STRENGTH
1	67.81
2	64.99
3	63.58
4	66.70
5	63.82
Mean	65.38
SD	1.84

Table C-2 Tear strength of CRP filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	62.56	54.97	48.74	43.56	35.83
2	61.07	52.82	47.80	41.79	38.59
3	62.60	52.34	48.53	41.22	36.79
4	60.83	50.48	48.86	40.50	38.43
5	62.11	54.41	45.57	43.16	39.66
Mean	61.83	53.00	47.90	42.05	37.86
SD	0.83	1.78	1.37	1.29	1.53

Table C-3 Tear strength of Si69 treated CRP filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	68.1	63.08	58.55	56.26	54.55
2	73.98	64.23	65.11	52.79	51.91
3	76.03	64.24	60.52	55.45	54.09
4	68.73	66.33	61.36	54.83	51.29
5	66.41	65.51	63.86	52.77	50.31
Mean	70.65	64.68	61.88	54.42	52.43
SD	4.13	1.26	2.6	1.58	1.82

Table C-4 Tear strength of char filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	76.47	81.57	77.94	71.29	64.90
2	82.84	81.88	80.22	71.83	65.04
3	80.00	87.03	76.23	74.57	68.48
4	78.91	84.21	79.04	67.89	66.00
5	85.42	82.69	79.04	65.44	68.11
Mean	80.73	83.48	78.49	70.20	66.51
SD	3.48	2.23	1.50	3.57	1.69

Table C-5 Tear strength of AC600 filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	73.9	68.89	64.98	57.79	56.92
2	73.04	67.8	68.29	57.15	48.19
3	74.53	66.08	69.63	54.96	55.72
4	75.63	66.79	66.98	60.76	58.78
5	72.53	67.03	64.23	58.65	54.21
Mean	73.93	67.32	66.82	57.86	54.76
SD	1.23	1.07	2.25	2.12	4.04

Table C-6 Tear strength of AC700 filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	74.53	73.27	59.76	58.61	52.06
2	72.5	73.77	62.5	57.32	56.03
3	74.14	72.1	64.44	59.03	50.41
4	80.32	75.48	67.46	64.88	51.45
5	82.17	75.6	64.82	56.74	52.92
Mean	76.73	74.044	63.80	59.316	52.574
SD	4.24	1.49	2.87	3.25	2.14

Table C-7 Tear strength of AC800 filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	85.02	78.57	70.37	65.18	59.39
2	83.23	76.45	70.37	65.76	62.35
3	83.87	73.37	75.35	64.23	62.16
4	81.13	79.14	77.28	66.53	61.52
5	83.11	79.27	74.17	69.73	58.52
Mean	83.27	77.36	73.51	66.29	60.79
SD	1.42	2.50	3.07	2.10	1.73

Table C-8 Tear strength of N330 filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	77.52	158.83	187.49	198.65	176.95
2	86.52	152.90	179.81	198.50	173.33
3	85.97	156.87	190.24	195.95	187.33
4	108.25	150.29	181.38	192.88	178.26
5	84.96	164.61	178.62	198.65	173.39
Mean	88.64	156.70	183.51	196.93	177.85
SD	11.55	5.54	5.08	2.54	5.73

Table C-9 Tear strength of N774 filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	93.55	119.07	142.17	160.09	152.53
2	87.58	119.07	154.64	160.12	148.10
3	89.11	107.77	144.52	153.83	152.10
4	92.73	126.17	168.12	156.82	149.40
5	91.27	108.38	140.04	151.72	143.90
Mean	90.85	116.09	149.90	156.52	149.21
SD	2.49	7.87	11.62	3.74	3.49

Table C-10 Tear strength of $CaCO_3$ filled NR vulcanizates

Sample	10 phr	20 phr	30phr	40 phr	50 phr
1	71.75	70.92	67.54	66.1	65.82
2	72.28	70.77	67.74	68.99	65.94
3	70.44	70.65	72.77	67.95	65.94
4	70.88	75.67	68.7	68.95	65.26
5	70.2	77.73	69.01	67.65	67.58
Mean	71.11	73.15	69.15	67.93	66.11
SD	0.88	3.32	2.12	1.18	0.87

BIOGRAPHY

Mr. Setthanat Tiabuakaew was born in Bangkok, Thailand on April 30, 1987. He received the Degree of the Bachelor of Science, majoring in Materials Science, Chulalongkorn University in 2009. Then, he continued his post graduate study in Applied Polymer Science and Textile Technology, Faculty of Science, Department of Materials Science, Chulalongkorn University and ultimately completed the Degree of the Master of Science in Applied Polymer Science and Textile Technology in May 2012.