ผลของคาร์บอนแบล็คต่อสภาพนำไฟฟ้าของยางนีโอพรีน

นางสาวหนึ่งฤทัย ปะระใจ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2550

EFFECTS OF CARBON BLACK ON CONDUCTIVITY OF NEOPRENE RUBBER

Ms.Nuengruthai Parajai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2007

Thesis Title EFFECTS OF CARBON BLACK ON CONDUCTIVITY OF NEOPRENE RUBBER
By Miss Nuengruthai Parajai
Field of study Petrochemistry and Polymer Science
Thesis Advisor Professor Pattarapan Prasassarakich, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

S. Hannongbua .... Dean of the Faculty of Science
(Professor Supot Hannongbua, Ph.D.)

THESIS COMMITTEE

.... Chairman
(Associate Professor Mongkol Sukwattanasinitt, Ph.D.)

.... Thesis Advisor
(Professor Pattarapan Prasassarakich, Ph.D.)

Vp. Hoven .... Member
(Assistant Professor Voravee Hoven, Ph.D.)

Sirilux P. .... Member
(Sirilux Poompradub, Ph.D.)

หนึ่งฤทัย ประระใจ : ผลของคาร์บอนแบล็คต่อการนำไฟฟ้าของยางนีโอพรีน (EFFECTS OF CARBON BLACK ON CONDUCTIVITY OF NEOPRENE RUBBER) อ.ที่ปรึกษา: ศ.ดร. ภัทรพรรณ ประศาสน์สารกิจ, 67 หน้า.

งานวิจัยนี้ได้ศึกษาปัจจัยของปริมาณและชนิดคาร์บอนแบล็คต่อการนำไฟฟ้าของยางนีโอพรีนและสมบัติทางกายภาพของยางวัลคาไนซ์การเสื่อมสภาพที่อุณหภูมิ125°C พบว่ายางคอมปาวด์เติมคาร์บอนแบล็คมีการนำไฟฟ้าเพิ่มขึ้นเมื่อปริมาณของคาร์บอนแบล็คเพิ่มขึ้นและคาร์บอนแบล็คที่มีโครงสร้างสูง (ค่า DBP สูง), พื้นที่ผิวต่ำ (ค่า BET ต่ำ) และมีค่า critical volume fraction (ϕ_c) ต่ำเมื่อเติมลงในยางปริมาณต่ำจะทำให้ยางมีค่าการนำไฟฟ้าที่สูงความหนืดของยางต่อ การไหลในแม่พิมพ์ต่ำรวมถึงเวลาในการบ่มเร่งยาวขึ้นซึ่งจะเหมาะสมต่อกระบวนการขึ้นรูปที่ดีและง่ายต่อการผลิตและพบว่าคาร์บอนแบล็ค CCB7055 จะให้ค่าดังกล่าวที่ดีที่สุดโดยจุดเปลี่ยนแปลงอย่างชัดเจนของค่าการนำไฟฟ้าจะอยู่ในช่วงคาร์บอนแบล็คปริมาณที่ 20-35phr จากนั้นวิเคราะห์คุณสมบัติทางกายภาพต่อการเสื่อมสภาพที่อุณหภูมิ 125°C ของตัวอย่างยางที่มีคาร์บอนแบล็คชนิด CB7055 เป็นสารเติมแต่งที่ปริมาณ 20 และ 30 phr พบว่า ค่าความหนาแน่น, ค่าความแข็ง, ค่าความทนต่อแรงดึง และค่าการนำไฟฟ้าของยางตัวอย่างจะสูงขึ้นในช่วงแรกและจะเริ่มต่ำลง ณ วันที่ 30-35 ผลเช่นนี้อาจเนื่องจากยางสูญเสียพอลิเมอร์เมทริกซ์ทำให้อนุภาคของคาร์บอนแบล็คอยู่ชิดติดกันมากขึ้นยางตัวอย่างที่มีสารตัวเติมมากจะส่งผลให้การเสื่อมสภาพเกิดขึ้นได้เร็วกว่ายางที่มีสารตัวเติมน้อย สำหรับผลดังกล่าวสามารถใช้ประโยชน์ในอุตสาหกรรมยางที่ต้องการยางที่สามารถนำไฟฟ้าได้ และทำนายระยะเวลาการเสื่อมสภาพของยางได้อีกด้วย

สาขาวิชา.. ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต....หนึ่งฤทัย ประระใจ....

ปีการศึกษา.. ....2550.......................... ลายมือชื่ออาจารย์ที่ปรึกษา..........

4773430023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: NEOPRENE RUBBER / ELECTRICAL CONDUCTIVITY

NUENGRUTHAI PARAJAI: EFFECTS OF CARBON BLACK ON CONDUCTIVITY OF NEOPRENE RUBBER. THESIS ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, Ph.D., 67 pp.

In this study, effect of carbon black type and content to the electrical property and physical properties of Neoprene rubber as well as aging time at 125°C were studied. High conductivity, low viscosity and long aging time were achieved in the rubber compound containing carbon black with high structure (high DPE), low surface area (low BET) and low critical volume fraction, ϕ_c even though small amount was added to the rubber compound. These properties of rubber compounds are advantageous for the molding and processing. The rubber compound with CCB0075CB shows the optimum value of conductivity. The change in conductivity of the rubber compound was obviously observed when carbon black content was in the range of 20 to 35 phr. Physical property after aging at 125°C of the rubber compounds filled with CCB0075 at 20 and 30 phr was studied. The density, hardness, tensile strength and conductivity of the rubber compound increased with aging time until day 30-35th and constancy afterward. The result is due to the lost of small volatile molecule from polymer matrix and the carbon black particles are more close to each other. The rubber compound filled with high carbon black loading could be degraded easier than that filled with low loading. The result in this study can be useful in the production of conductive rubber as well as the prediction of their degradation.

Field of Study...Petrochemistry and polymer science.. Student's signature P. Nuengruthai

Academic year... ....2007.................. Advisor's signature..........

ACKNOWLEDGEMENTS

The author would like to express the grateful appreciation to her advisor, Professor Pattarapan Prasassarakich, Ph.D. for providing valuable advice, encouragement and assistance throughout the course of this research. In addition, the author also wishes to express deep appreciation to Associate Professor Mongkol Sukwattanasinitt, Ph.D., Assistant Professor Voravee Hoven, Ph.D. and Dr. Sirilux Poompradub, Ph.D., serving as the chairman and members of his thesis committee, respectively, for their valuable suggestions and comments.

The author also wishes to express her appreciation to Pacific Rubber Works Co.,ltd. and PRW (Research & Development), for their support with processing machine, testing equipment and materials. Finally, the author wishes to express deep gratitude to his parents for their understanding and encouragement. Without all of them, she would not have withstood many difficulties that encountered.

CONTENTS

PAGE

PAGE

LIST OF TABLES

TABLES **PAGE**

LIST OF FIGURES

FIGURES **PAGE**

FIGURES **PAGE**

LIST OF ABBREVIATIONS

^{0}C	:	Degree Celsius
g	:	gram
kg	:	Kilogram
mg	:	Milligram
MW	:	Molecular Weight
µm	:	Micrometer
%wt	:	Percent by weight
avg	:	Average
nm	:	Nanometer
phr	:	Part per hundred rubber
ASTM	:	The American Society for Testing and Material
MBTS	:	Dibenzothiazole disulphide
ETU-80	:	Ethylene thiourea
TMQ	:	2, 2, 4-Trimethyl-1, 2-dihydroquinoline
hr	:	Hour

CHAPTER I

INTRODUCTION

1.1 The Statement of problem

Elastomers are normally good insulators with relatively high electrical resistivity, the nonpolar (nonoil-resistant) elastomers being better than the polar (oil-resistant) ones. However, the electrical properties of rubber compounds are more dependent on the compounding ingredients than on the basic rubber.

Extensive research work on material having important electronic properties of semiconductors and metals and with attractive properties (i.g. light weight, good mechanical properties and corrosion resistance) and processing advantages of polymers has culminated in the development of electrically conducting polymer blends which are needed for replacing conductors. Some of potential application includes batteries, belts, hoses, footwear, transducers, switches, photocells, and circuit boards, heating elements, dissipation of electrostatic discharge from rubber and plastic parts and for electromagnetic shielding devices.

Electrically conducting polymer blends can be broadly classified into (a) intrinsically and (b) extrinsically conducting polymer blends. Extrinsically conductive filler is the best-known method of making polymer electrically conductive. Several kinds of fillers are available; for example, carbon black, carbon fiber, metal powder, metal fiber and metal coated fiber.

Carbon black powder is the most widely used conductive fillers in commercial products due to its low cost, lightweight and ability to form network. Therefore, rubber finished parts are lighter in weight, easier to handle, and less costly to ship. Additionally, fabrication of the part is usually easier and less expensive. However, using carbon black as an additive to achieve electrical conductivity usually requires a concentration so high that it will increase the viscosity and decrease the mechanical properties of the polymer.

So, the present work reports the results of study relating to assessment of some physical and mechanical properties and aging behavior, a percolation threshold and electrical conducting character of types carbon black filled vulcanize based on compounds from neoprene rubber. The main objective of the work relates to ascertaining how the properties vary with variation in the extent of loading of carbon black filler.

1.2 Objectives

The objectives of this work are as follows:

1. To study the conductivity of carbon black filled neoprene rubber.
2. To study the thermal oxidation aging of carbon black filled neoprene rubber.

1.3 Scope of the Research Work

The neoprene rubber compound was prepared at various loading levels of fillers and different carbon black types. The physical and mechanical properties, aging behavior, a percolation threshold and electrical conducting characteristic were investigated.

The experimental procedures were carried out as follows:

1. Literature survey and study the research work.
2. To prepare the neoprene rubber filled with carbon black at 0-70 phr. Banbury mixer was used to mix compounds.
3. To study the mooney viscosity and mooney scorch characteristics of chloroprene rubber compounds using mooney tester
4. To prepare the vulcanizates by compression molding at temperature of 160^0C, cure time of 10 minutes and pressure of 120 kg/cm^2.
5. To investigate the mechanical properties and the electrical conductivity of rubber compounds.

6. To investigate the thermal oxidation aging of rubber compounds for 60 days and compares the mechanical properties and the electrical conductivity with unaging samples.
7. To summarize the results.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

Elastomers are normally good insulators with relatively high electrical resistivity, the nonpolar (nonoil-resistant) elastormers being better than the polar (oil-resistant) ones. However, the electrical properties of rubber compounds are more dependent on the compounding ingredients than on the basic rubber [1]. Extensive research work on material having important electronic properties of semiconductors and metals and with attractive properties (i.g. light weight, good mechanical properties and corrosion resistance) and processing advantages of polymers has culminated in the development of electrically conducting polymer blends which are needed for replacing conductors. Some of potential application includes batteries, belts, hoses, footwear, transducers, switches, photocells, and circuit boards, heating elements, dissipation of electrostatic discharge from rubber and plastic parts and for electromagnetic shielding devices [2].

It is not possible to make a clear-cut distinction between insulating, antistatic and conducting elastomer. Generally, elastomers having resistances below 10^4 ohms are considered conductive; between 10^4 and 10^8 ohms, antistatic; and above this, insulating. The upper limit is usually about 10^{16} ohms (See Figure 2.1).

Electrically conducting polymer blends can be broadly classified into (a) intrinsically and (b) extrinsically conducting polymer blends.

Extrinsically conductive filler is the best-known method of making polymer electrically conductive. Several kinds of fillers are available; for example, carbon black, carbon fiber, metal powder, metal fiber and metal coated fiber.

Carbon black (CB) powder is the most widely used conductive fillers in commercial products due to its low cost, lightweight and ability to form network. Therefore, rubber finished parts are lighter in weight, easier to handle, and less costly to ship. Additionally, fabrication of the part is usually easier and less expensive. However, using CB as an additive to achieve electrical conductivity usually requires a concentration so high that it will increase the viscosity and decrease the mechanical properties of the polymer [3].

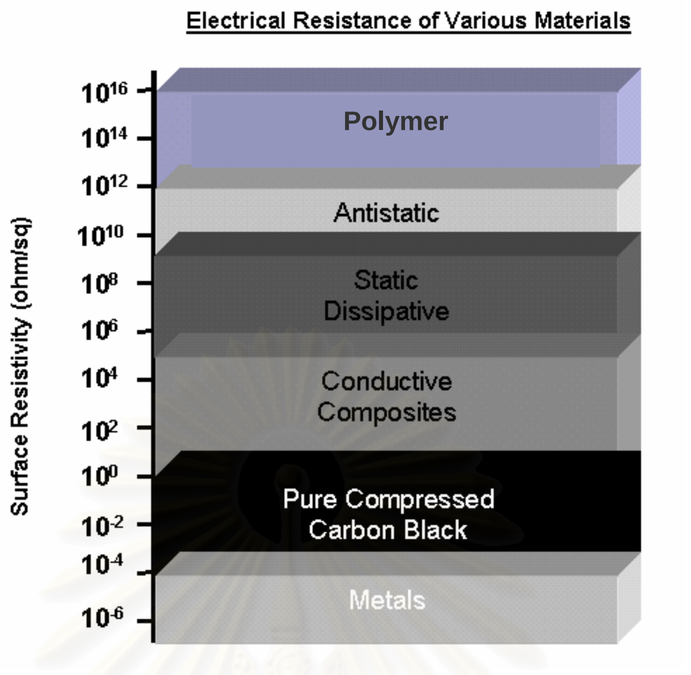
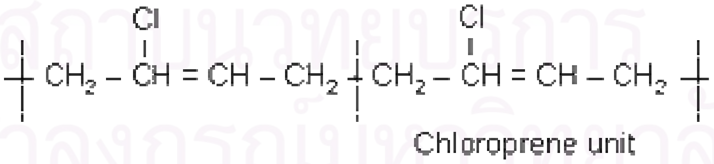


Figure 2.1 Classification of materials based on surface resistivity (Ohm/Square) [3]

2.1 Neoprene Rubber (CR) [5]

Neoprene rubber (CR), introduced by Du Pont in the USA in 1931, is the first rubber of high performance engineering polymers. Polychloroprene is a chloro-2-butadiene homopolymer and its structure is derived from isoprene by substitution of a chlorine atom for a methyl group. Its chemical structure is:



$$\left[CH_2 - \overset{\overset{Cl}{|}}{CH} = CH - CH_2 \right]\left[CH_2 - \overset{\overset{Cl}{|}}{CH} = CH - CH_2 \right]$$

Figure 2.2 Chemical structure of neoprene rubber [5].

The special features of its molecular architecture are:

(a) As a halogenated elastomer, CR has a much higher fire resistance than non-halogenated elastomer like SBR and NR.

(b) Its polarity leads to good solubility in aromatic, chlorinated, and polar solvents for solvent-based adhesives. Owing to its permanent $Cl^{\delta-} - C^{\delta+}$ dipole, its resistance to non-polar, paraffinic, and naphthenic solvents is good. By copolymerizing chloroprene with a polyfunctional monomer, polychloroprene gels are obtained and these have improved processability in calendaring and extrusion due to low nerve.

(c) The deactivation of double bonds by the chlorine atom gives CR an increased resistance to ageing (ozone and oxygen). However, the rate of vulcanization, using combinations of sulphur and organic accelerators, is slow. As a result of carbon-carbon unsaturation, Cl is co-curable with other types of elastomers. In the presence of metallic oxides, the allylic atoms of (1-2) and (3-4) configurations make possible thiourea-induced vulcanization leading to mono-sulphidic links.

(d) CR contains a high proportions of trans 1,4 structure (about 85%) and has a marked tendency to crystallization owing to this stereo-regular structure.

The polymer, being synthetic, can be produced having different properties. Polychloroprene molecular structure is determined largely by polymerization temperature and modifying agents (sulphur and mercaptans) used during the polymerization. Chloroprene is emulsion polymerized with conventional free-radical initiators and with either sulphur or a chain transfer modified (G type) chloroprenes; the reagent which is commonly used is thiuram sulphate, which is added as an aqueous solution of an emulsion of an emulsion in xylene. As the polymerization temperature is increased from 10 to 80 ^{o}C, 1-4trans structure decreases while 1-4 cis increases. The alkaline latex after 8 hour is acidified to pH 5.5-5.8 by addition of 10 % acetic acid, in order to arrest the peptising action of thiuram disulphide, and to prepare the latex for coagulation as a film on freeze rolls which are maintained at -15^{o}C. The film is stripped from the roll and dried, “roped”, cut, and bagged.

A number of commercial varieties are available, both as solid polymers and as lattices. The general purpose polychloroprene are divided into two type-sulphur modified (G type) and mercaptan modified (W type)-with various levels of viscosity and crystallization tendency, as shown in Table 2.1

Table 2.1 Type of polychloroprene rubber [5]

Sulphur modified (G types)	Mercaptan modified (W types)
Peptizable, having good building tack.	Non-peptizable.
Curable with metal oxides only	
Vulcanizates have higher resilience and tear strength than W types	Vulcanizates have better resistance to heat and compression set than the G type
Poorer thermal resistance than W types	
Grades: GN: General purpose	W: General purpose
GW: Heat resistant	WHC: High viscosity
GRT: Flex, tack, and low temperature properties	WRT: Best low temperature properties

There are other grades also available. Some of them are copolymerized with small amounts of styrene to reduce the crystallization tendency of unvulcanized polychloroprene, with modifiers (other than sulphur) which do not breakdown on milling. Other grades are suitable for adhesive applications.

Polychloroprene rubbers are used in wire and cable industry, adhesives, sundries and sponge, in mechanical goods such as hose, belting and automotive part. Excellent adhesives suitable for a number of applications in footwear, furniture, automobile, and other industries are also made from polychloroprene rubber. CR latex products are characterized by high modulus, high tensile, strength, high tear strength, and good electrical properties. There are various grades suitable for the manufacture of gloves, balloons, rubber protective clothing, and as binders for abrasives, etc.

2.2 Carbon Blacks

Carbon black is material that has found widespread use in number of application. It consists mainly of element of carbon, and it is the form of spherical particles that have been fused together to form aggregates that are typically around 30-100 mm in size. Elastomers have been filled with carbon black in order to improve their electrical conductivity for use in conductive compounds. Carbon black comes in several different forms, depending on the feedstock and the process used to produce the material. The most common process for the production of carbon black is the thermal oxidation process. Approximately 98 % of the carbon black consume annually is produced from this method [3].

Carbon black can also be formed from another process that creates a material that is better suited for electrical applications. This highly electrically conductive type of Columbian Ultra Carbon Black (Conductex ®7055 Ultra), is developed furnace carbons that are of the highest purity available, excellent dispersion, superior surface smoothness etc [4].

2.2.1 Basic Information on Carbon Black [3]

Production: CB results from incomplete combustion or thermal cracking of a hydrocarbon raw material (Figure 2.3). Nowadays almost all carbon black is manufactured by the oil furnace process: a highly aromatic feedstock is partially burned by atomization into a hot flame made of natural gas and preheated air, the reactor temperature reaching more than 1500 ^{o}C. At the process end, powder (fluffy) or palletized carbon black is collected. The oil furnace process permits efficient control of end product physical and chemical properties.

$$C_xH_y + O_2 \xrightarrow{\text{Heat}} C + CH_4 + CO + H_2 + CO_2 + H_2O$$

Figure 2.3 Partial oxidation of aromatic hydrocarbons[3].

Form: Carbon black is a particulate form of industrial carbon which exhibits a “quasi-graphitic” microstructure (Figure 2.4). The manufacturing process leaves various forms of oxygenated groups on carbon black layer planes: mainly phenolic, quinolic and carboxyl chemisorbed complexes. During the nucleation process, three to four layers form crystallites, which combine to form primary particles which continue to grow into aggregates. Agglomerates are a dense collection of aggregates formed due to the small distances between them and the strong van der waals forces present. CB dispersion into a polymer matrix will require the breaking of these links. An aggregate is individable and represents the carbon black "base unit", although a carbon black is often characterized by its primary particle size.

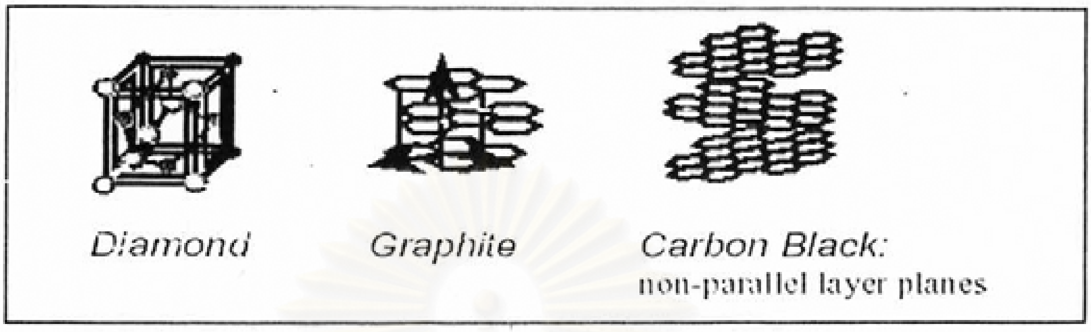


Figure 2.4 Carbon black "quasi-graphitic" microstructure compared to the two regular crystalline forms of carbon (diamond and graphite) [3].

2.2.2 Fundamental Properties of Conductive Carbon Black

Particle Size: Electron microscopy shows carbon black to be composed of clusters of spherical primary particles, called aggregate or primary aggregates (see Figure 2.5).

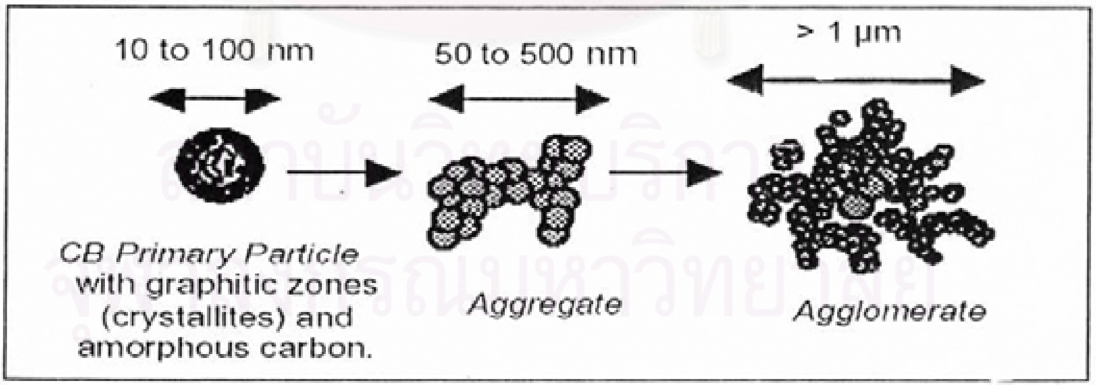


Figure 2.5 CB primary particle fuse together in the reactor and form aggregate and agglomerates [3].

Though the primary particles appear to be fused together, the average diameter of the primary particles, other factors being constant, determines the relative size of the aggregate. Thus blocks of finer primary particle size will have smaller aggregates determining their behavior when dispersed in plastic, assuming that other properties are constant. The smaller the aggregates of carbon black composing the given weight, the more aggregates will be distributed throughout the fixed-volume matrix and, consequently; the smaller will be the interaggregate distances or gaps. This translates to increasing ease of electron transfer from aggregate on its path through the matrix. In short, the finer the prime particles, consequently the smaller the aggregates, the lower will be the level of electrical resistivity when dispersed in plastics.

Structure: Structure is complex property that refers to the morphology of the aggregate. It not only expresses the number of prime particles composing the aggregate, but it indicates the manner in which they are fused together.

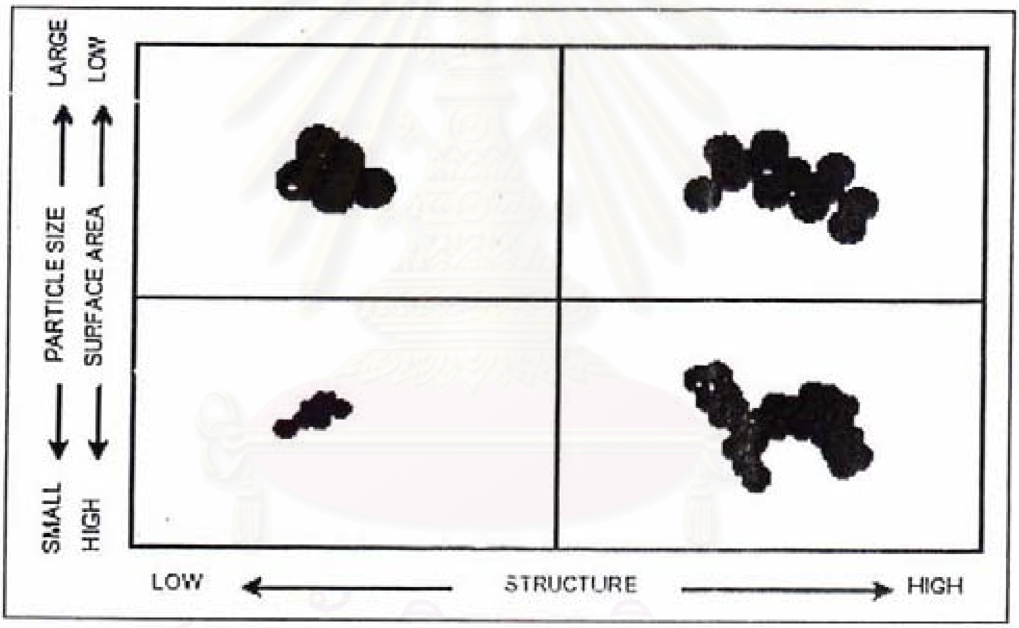


Figure 2.6 Visualisation of carbon black particle size/surface area and structure [3].

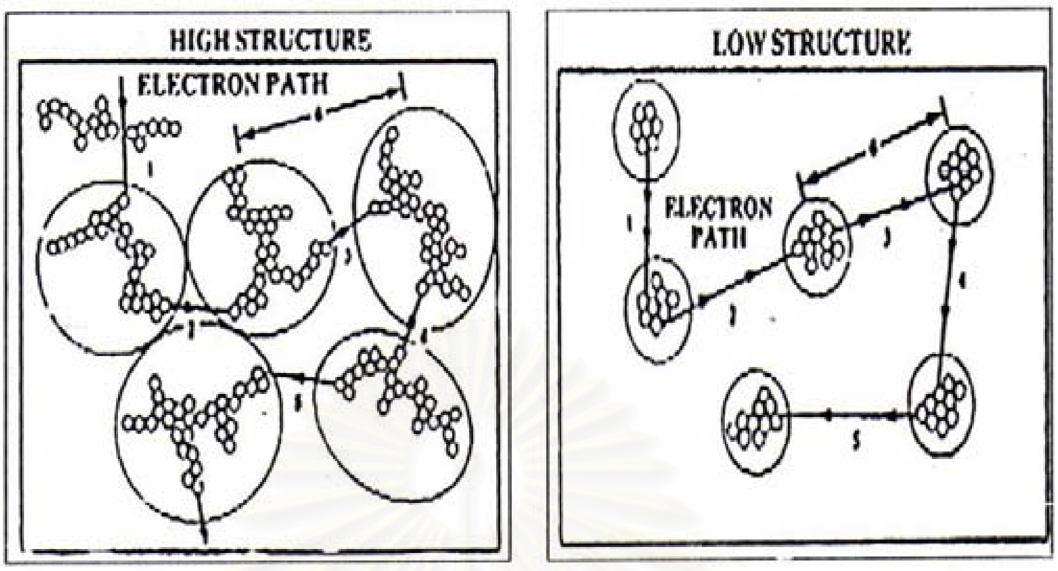


Figure 2.7 The creation of electron path of high structure CB and low structure CB [3].

Figure 2.6 illustrates how higher structure carbon black are characterized by aggregates composed of many primary particles with considerable branching and chaining. Lower-structure carbon black, on the other hand, are compact and contain fewer primary particles. Thus the effect of structure on the resistivity of dispersed carbon black is two fold. It contributes to aggregate size as discussed above, and it determines the relative anisometry, or shape irregularity, of the aggregate. The latter effect is, by far, the more important with regard to electrical resistivity.

Figure 2.7 illustrates how higher structure carbon black create more electron path. This translates to decreasing resistivity with increasing structure when dispersed in polymer. Which the simulates aggregates of very high structure black-top, show gaps (1 to 5) to be considerably smaller than those of a very low structure black (bottom) even at comparable average interaggregate distance (d), as measured center to center. This translates to greater ease of electrons bridging those gaps or, i.e., higher structure increases electron path, thereby increasing conductivity.

Porosity: Depending on the condition of manufacture, a carbon black can have a more or less porous surface. This porosity results from oxidative etching of the surface wherever sufficient oxygen is available at elevated temperatures during manufacture. The fixed volume matrix, as porosity increases, apparent density decreases, so that there are more aggregates per fixed weight of carbon black. This creates an effect, analogous to that of decreasing aggregate size discussed previously, that results in smaller interaggregate gaps. Thus as porosity increases, the resistivity of the black, when dispersed in rubber, decreases, assuming that other properties remain constant.

Surface Chemistry: All carbon black acquire chemisorbed oxygen complexes on their surfaces during the manufacturing process and, in some cases, this is enhanced by chemical oxidation called after treatment. The chemisorbed complexes comprise what is referred to, in the industry, as volatiles content. It is measured and expressed as the percent weigh loss of the pre-dried black when heated to 950 ^{o}C. The complexes are of four types: phenolic, lactonic, carboxylic, or quinonic. Volatile content tends to act as an insulator of particles/aggregates so that more energy is needed for electrons to jump from aggregate to aggregate. Thus increasing volatile content means increasing resistivity when dispersed in rubber assuming that other properties are constant.

The important point is that the conductivity of carbon black-rubber compounds, regardless of the mechanism, has been shown to be affected by loading levels and key carbon black properties that operate by varying interaggregate gap widths. Electrical conductivity of carbon black filled compounds is controlled by gap between carbon aggregates and aggregate distribution. To achieve acceptable conductivity, aggregation of carbon black must form network-like structure with the gap between aggregates in the range of 1.5-10 nm throughout polymeric matrix. Network-like structure formed can be in percolation or reticulated/segregated structures which is continuous conducting paths formed at the lowest filler concentration, called critical filler concentration or percolation threshold ($Ø_c$).

2.2.3 Percolation theory [6]

The arrangement of aggregates and gaps (see Figure 2.8) and the effect of this arrangement on conductivity have been treated by percolation theory.

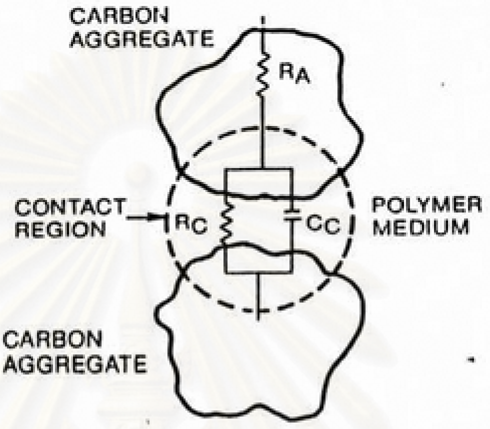


Figure 2.8 Equivalent resistor-capacitor circuit in the contact region of carbon black aggregates [6].

A statistical treatment which has been applied to many processes such as diffusion and heat transfer and which is similar to some familiar processes in polymer chemistry such as chain branching and gelation. If we add conducting particle such as carbon black aggregates to a matrix one at a time, the particles will at first be isolated, then isolated clusters will be formed, and finally a though-going path will arise. (The term “through-going path” is used here to refer to a continuous network of conductive particles in close enough contact to permit flow of current from one and of the specimen to the opposite and, but not necessarily with negligible interparticle resistance, as in the “throughgoing chains” of the previous section.) This point (the percolation threshold) occurs when the mean number of contacts per particle exceeds a certain critical value. At this point, conduction is possible but is limited by the number of throughgoing paths. Further addition of particles joins many clusters together and so forms many more throughgoing paths, leading to rapid rise in conductivity. This of course is what is observed experimentally (Figure 2.9).

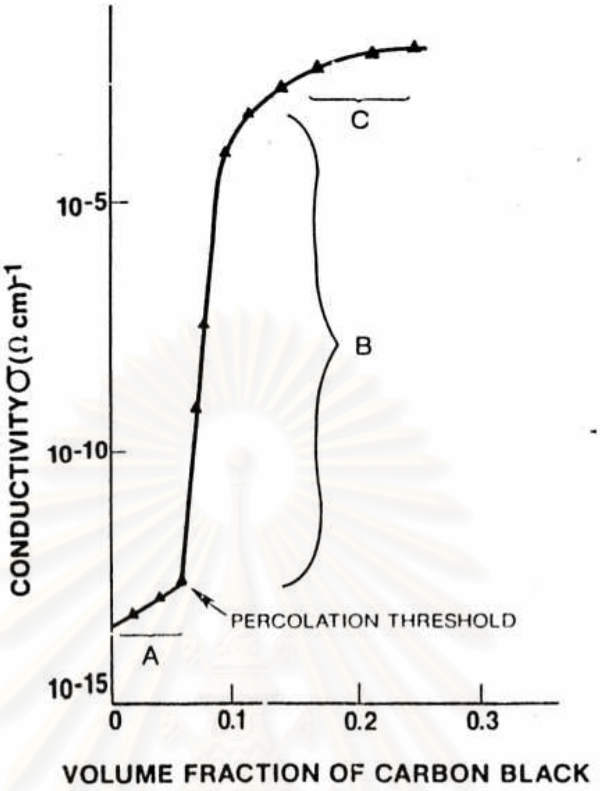


Figure 2.9 DC conductivity of composites of NR with carbon black (Corax® L, a conductive black). After Bellamy et al 33, with regions added as indicated: A, insulating; B, percolation; C, limiting high conductivity [6].

In the percolation theory as developed by Kirkpatrick, a composite is regarded as a lattice of conductive "sites" joined by resistive "bonds" i.e., the sites have zero resistivity, and the bonds have finite resistivity; while in the absence of a bond, adjacent sites are separated by a medium of infinite resistivity. By Monte Carlo techniques one can calculate the conductivity of the lattice if either bonds or sites are removed at random. Removal of a site is equivalent to removal of C strongly correlated bonds (i.e., the bonds are all grouped around the same site); one can also (mathematically) removes sites with any desired degree of corrrelation5. On a simple cubic lattice, the bond treatment gives $\rho_{c,b} = 0.25$, while the site treatment gives $\rho_{c,s} = 0.31$.

Above the percolation threshold, these treatments predict a power law dependence of conduction on the concentration above the threshold:

$$\sigma = \sigma^0 (\rho - \rho_c)^b , \qquad (2.1)$$

where ρ is the probability that a site or bond is present (depending on which treatment is used) and ρ_c is the critical or threshold probability. The exponent *b* of Equation (2.1) has been calculated as 1.6, or more recently as 1.95.

The "structure" or bulkiness of the carbon black aggregates would be expected to play a role similar to that of loading, since aggregates of higher structure occupy, in effect, a higher volume of the composite. The effect of structure on the percolation threshold was investigated by Janzen, who emphasized the number of contacts which a particle makes with its neighbors, $\bar{c}$ rather than the probability of bond or site occupancy. The critical mean contact number $\bar{c}_{crit}$ is equal to $\rho_c C$, where *C* is the coordination number—i.e., the maximum number of contacts which a particle (or aggregate) could have. Janzen took $c_{\ crit}$ as 1.5, based on Monte Carlo calculation. (This same number has also been found by Gurland both experimentally and by percolation theory). From an assumed simple function relation of the number of contacts $(\bar{c})$ at a given volume,

$$\bar{c}\,\alpha\phi/(1-\phi) \tag{2.2}$$

He derived the equation

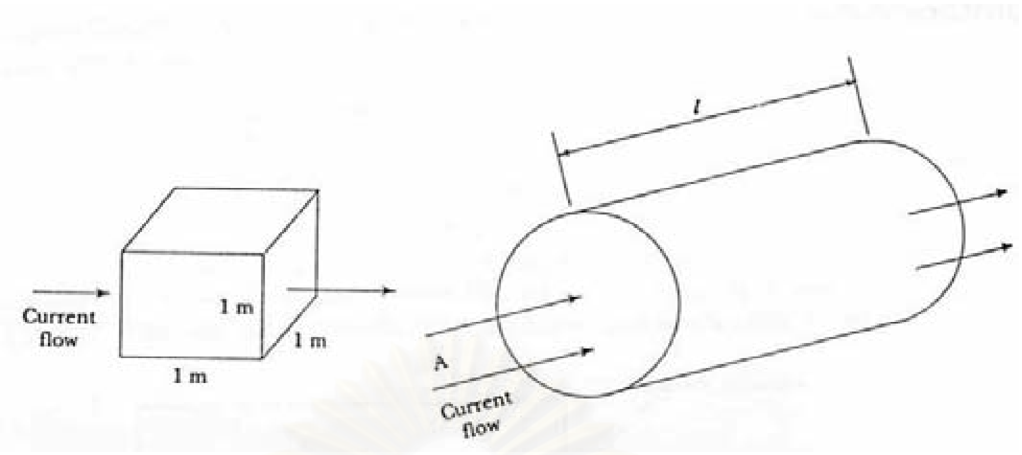
$$\phi_{crit} = \left[1+(C/\bar{c}_{crit})\rho\upsilon\right]^{-1} \tag{2.3}$$

where ρ is the density of carbon black and v is the compressed dibutyl phthalate absorption number (CDBP) [i.e., the dibutyl phthalate absorption number (DBPA) after precrushing] in cm3/g.For various reasons he took C=6 ,leading to

$$\phi_{crit} = \left[1+4\rho\upsilon\right]^{-1} \tag{2.4}$$

2.3 Measurement of resistivity [5]

Resistivity tests are important for the classification of anti-static and conductive rubber. 'Volume resistivity' is defined as the electrical resistance between opposite faces of unit cube of material (Figure.2.10)



Figture 2.10 Volume resistivity [5].

$$R = \frac{\rho A}{l} \tag{2.5}$$

where ρ is the electrical resistivity which is expressed in Ωm.

Separate methods are employed for anti-static, conducting and insulating compounds. The method give below is suitable for materials with a volume resistivity higher than 10^{9} Ωm. The test specimen is a flat sheet 1-3.2 mm thick, to the surface of which special circular contact electrodes are applied (Figure.2.11).

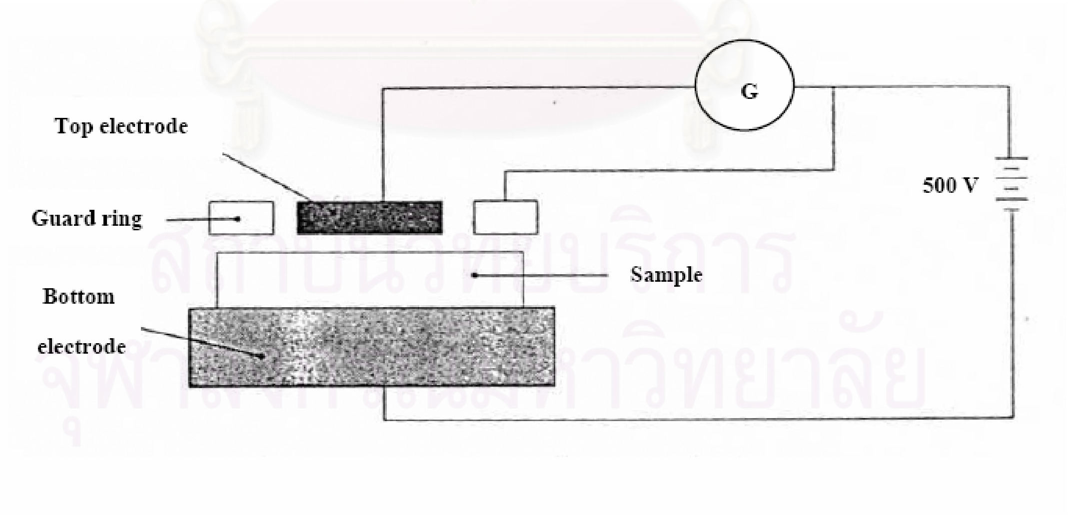


Figure 2.11 Measurement of volume resistivity of insulators [5].

The assembly must ensure good contact between electrode and the material under test. The thin circular electrodes are covered by metal backing plate so that connections can be made between the electrode assembly and the measuring circuit. A potential difference of 500 v D.C. is applied between the inner/upper electrode and the lower electrode, for 1 min. The current flowing between these two electrodes is measured directly and the volume resistivity is calculated as follows:

$$\rho_\upsilon = \left(\frac{500}{\mathrm{I}}\right) \times \left(\frac{\pi d^2}{4}\right) \times \frac{1}{t} \tag{2.6}$$

where ρ_υ is volume resistivity of the sample, *d* diameter of the top electrode, *t* sample thickness and *I* current flowing in amps.

ISO 1853 method for measurement of volume resistivity of specially prepared vulcanized rubber sample is given below. The schematic diagram of test circuit is given in Figure 2.12. This method is suitable for anti-static and conducting rubbers.

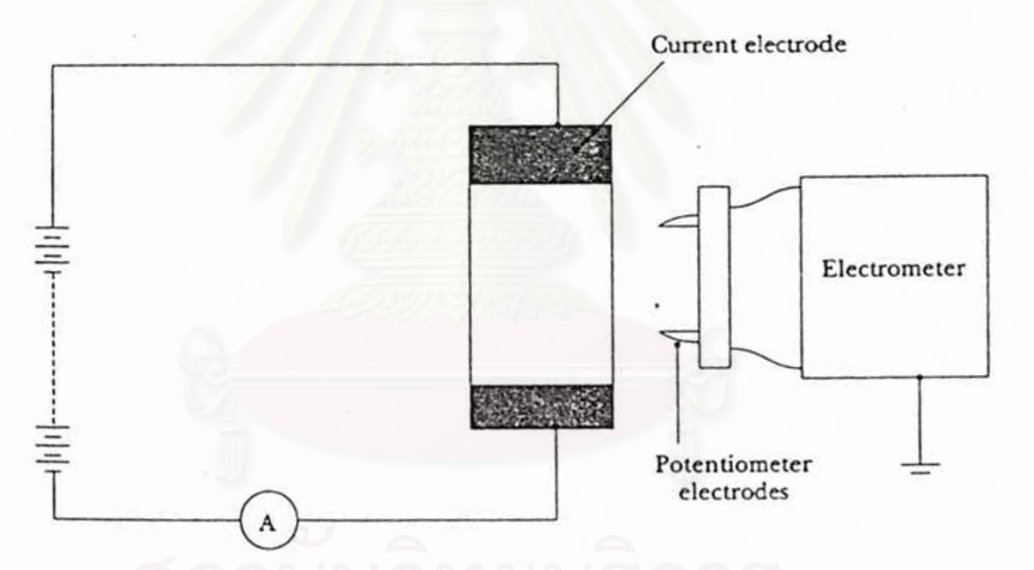


Figure 2.12 ISO 1853 method for the determination of volume resistivity of antistatic and conducting rubbers [5].

The test piece is a strip 10-150 mm wide, of vulcanized rubber 70-150 mm long and 2.4-6.3 mm thick which is clamped to the current electrodes at the ends. Direct current, which will cause a dissipation of power less 1 W within the test piece, is used together with an ammeter in the circuit. An electrometer -- a high input resistance valve voltmeter in which valve is used as a null detector – is used to measure voltage at the terminals. The steady resistance between the potentiometric electrodes is determined after 1 min. of current flow. The volume resistivity is calculated as follows:

$$\text{Resistivity } \Omega_m = \frac{\text{average resistance in x cross-sectional area in m}^2}{\text{Distance between potentiometric contacts in meters}} \qquad (2.7)$$

2.4 Literature review

Y. Sun et al. [7] studied the electrical approach to monitor the thermal oxidation aging of carbon black filled ethylene propylene rubber. This work were (1) to establish the correlation between changes in the electrical conductivity (resistivity) and the mechanical properties during thermal oxidation oven aging at 125 ^{o}C and (2) to show the feasibility of using the resistivity change as a non-destructive monitor method of the aging process. It was found that the decrease of resistivity was mainly due to increasing CB volume fraction caused by thermal degradation, and high CB loading had slower degradation due to the antioxidant effect of carbon black. These results indicate that electrical resistivity measurements could be used as a potential non-destructive and in situmeasurement for cable condition monitoring.

P. Ghosh and A. Chakrabari [8] studied the effect of the extra conducting carbon black as filler on some selected physical and mechanical properties, aging behavior and DC electrical conducting character of vulcanizates of ethylene-propylene diene monomer (EPDM). Increasing carbon black loading caused a monotonic increase in density and hardness and in tensile strength with a leveling off trend for carbon black filler loading >40 phr. Elongation at break of the initial EPDM vulcanizates, however, passed through a maximum corresponding to 20 phr carbon black loading; the position of the maximum shifts to 30 phr carbon black loading on aging of the vulcanizates at 135^{o}C for 7 days. The percolation concentration ranged over 15-30 phr of conducting carbon black loading. Trends of voltage (V) developed with increase in the current (I) applied at different temperatures. Beyond the critical current (I_C), the developed voltage became practically insensitive to large enhancements in the applied current; the filled vulcanizates, thus, exhibit non-ohmic character for $I > I_C$: An attempt was made to analyze and interpret the observed effects. Electromagnetic interference (EMI) shielding effectiveness (SE) was increased with increasing the carbon black loading.

I. Novak et al. [9] studied the correlation between percolation concentrations and elongation at break in filled electroconductive epoxy-based adhesives with electroconductive carbon black, graphite or with silver-coated basalt particles or fibres. Percolation concentrations were estimated to be 14 vol% for epoxy/carbon black composites, 22 vol% for epoxy/graphite composites, and 28–29 vol% for both epoxy/silver-coated particles and epoxy/silver-coated fibres. Electrical conductivity increased in the order of fillers: silver-coated fibres>silver-coated particles>graphite at the comparable concentrations of the filler. In the case of carbon black, the maximum concentration of the filler only 18 vol% was found due to insufficient dispergation and high agglomeration of aggregates. The decrease of elongation at break with an increase in filler content was observed in all cases. A good correlation between phenomenological model and experimental data for all investigated systems was also observed.

M. H. Ali, A. Hashem [10] studied the concentration and temperature dependence of the electrical conductivity of the non-crystallisable chloroprene rubber CR (WRT) mixed with high abrasion furnace (HAF) carbon black. It was found that the concentration dependence of satisfied the scaling law of percolation clusters within the range of $P_c < P < 0.43$. The percolation threshold was 0.17, the effective coordination number (Z) was 8.2 and β, which accounts for the cluster size, is 9. The correlation between β and Z was found to be $\beta \sim Z + 1$. The filling factor of HAF carbon black is found to be 0.70. The particles of HAF carbon black were arranged in both spheres, random close packing and rods, uniaxial simple cubic with the same ratio inside the rubber matrix. The temperature dependence of σ below the percolation threshold was thermally activated while above the percolation threshold, it is a metal-like behaviour. This behaviour was attributed to the break-down of the extended carbon clusters with temperature.

M. H. Ali, A.Hashem [11] studied the concentration and temperature dependence of the electrical conductivity (σ) of the crystallisable chloroprene rubber CR (Butaclor 41H) mixed with fast extrusion furnace (FAF) carbon black. It was found that the percolation concept holds true for these composites where σ shows a nearly sharp increase when the mass fraction of FEF carbon black in the mixture exceeds 20 %. The estimated values of the filling factor (f) and the occupation number (Z) were found to be 0.82 and 8.2 respectively. The scaling law of the percolation clusters [$\sigma = \sigma (P - P_c)^{\beta}$] was valid within the rang $P_c < P < 0.34$ and the estimated value of β is 6.8. The temperature dependence of σ is thermally activated below and at the percolation threshold with the same activation energy. The decrease in σ with temperature followed by a subsequent increase above certain temperature was attributed to the phase transition of CR (41H) and the change in the size of carbon black clusters from infinite to finite with temperature. In the highly loaded compounds the temperature dependence of σ is controlled by the beak-down and re-formation of carbon clusters with temperature.

G. M. Nasr [12] studied the effect of vulcanization conditions (time, pressure and mould thickness) on the electrical conductivity u of a 60 furnace carbon black (FAF)/Styrene Butadiene Rubber (SBR) sample. It was found that the mechanism of conduction is highly affected by the different vulcanization conditions. The minimum conductivity value $\sigma_{\min}$ of this compound increased with both time and pressure of vulcanization. On the other hand, it decreases with the mould thickness. The interspacing distance between carbon black particles and/or aggregates was calculated as a junction of the time of vulcanization. The minimum conductivity value is nearly washed out with increasing mould thickness and decreasing time of vulcanization. The optimum vulcanization conditions for manifesting the existence of a minimum conductivity value of 60 furnace carbon black (FAF)/Styrene Butadiene Rubber (SBR) composite were : time of vulcanization >20 min, mould pressure >20 kg/cm^2 and mould thickness <5 mm.

N. Dishovsky et al. [13] studied the effect of Bi-containing superconducting ceramic ($Bi_2Pb_{0.35}$ Sr_2Ca_2 Cu_3O_{10}) on the volume resistivity of butyl rubber composites. The volume resistivity decreased with increase in superconductor concentration, applied pressure and temperature. A change from non-linear to linear behavior was observed with increasing superconductor concentration in volume resistivity–applied pressure and volume resistivity–temperature dependencies and in temperature hysteresis. Composites containing 30–35 phr of superconductor had good stability and reproducibility of volume resistivity and provided a wide range of relationships between the applied force and the volume resistivity. The material exhibited almost linear reduction in the resistivity value as a gradually increased pressing force is applied. The volume resistivity changed very slowly with temperature and the hysteresis loop is smaller. From the electrical characteristics viewpoint they were the most suitable for pressure sensitive sensor applications but some additional investigations on their aging resistance are needed. The effects observed were discussed from the viewpoint of ionic and electronic mechanisms of electrical conductivity in rubber-based composites.

F. El-Tantawy [14] studied Joule heating treatments of conductive butyl rubber (IIR) /ceramic superconductor $((\mathrm{Bi,Pb})_2\mathrm{Sr}_2\mathrm{Ca}_2\mathrm{Cu}_3\mathrm{O}_z)$ composites. Electrical conductivity characteristics, stability and reproducibility at various processing conditions of IIR with different concentrations of superconductor were measured. Also, the conduction mechanism of electrical conductivity was discussed. Specific heat and the amount of heat transferred by radiation and convection were calculated via the proposed model and calorimetry as a function of superconductor content. It was found that superconductor accelerated the driving force during the sintering process and the characteristic time constant during sintering decreased while the sintering factor, the apparent cross-linking density, hardness and volume fraction of rubber increases as the content of superconductor increases. In addition, it was proved that the superconductor and Joule heating effect improve the electrical and thermal properties of IIR.

F. El-Tantawy [15] studied the ethylene–propylene-diene monomer (EPDM)/ loaded with 50 phr HAF carbon black and different concentrations of TiC composites as thermistors, with new double negative and positive temperature coefficients of conductivity (NTCC/PTCC). The DC conductivity probe during the curing process was related to the curing kinetics; the onset of crosslinking during the curing period depends on TiC content. The characteristic time constant (τ) during the curing process decreased with an increase in TiC, which implied that TiC acted as a catalyst, reduces the curing time, and accelerated the driving force during the curing process.

The electrical properties of EPDM composites were strongly affected by TiC content, and exhibit hopping conductivity and P-type semiconductor behavior. The dielectric constant increased linearly with temperature, without any remarkable change in behavior. TiC improved the thermal stability and microstructure core of the rubber matrix i.e. gave more difference in the sample temperature for the same power. It is worth mentioning that the availability of raw materials, the low cost of the product and the easy processability of this composite makes this work a significant contribution in the field of energy science and technology.

F. El-Tantawy and F.S. Deghaidy [16] studied the effect of iron oxide on vulcanization kinetics and electrical conductance of butyl rubber composites. The rate and degree of crosslinking were evaluated as a function of Fe_2O_3 concentration. It was found that the characteristic time constant during vulcanization decreased as the Fe_2O_3 concentration increased. The energy of activation of the crosslinking reaction increased with iron oxide content. An abrupt decrease in electrical conductance appeared after a characteristic time of swelling. A modified model was suggested to calculate the separation distance in the conductive rubber matrix. The effect of microwave irradiation on electrical conductance and separation between conductive aggregate of butyl rubber (IIR) composites was also studied. Fe_2O_3 inhibited the degradation of IIR composites and microwave irradiation enhances the texturing microstructure of rubber matrix.

CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

Table 3.1 Rubber and chemicals used in this study

Chemicals		**Commercial name**	**Supplier**
Chloroprene WRT	Rubber	Chloroprene WRT	Sunny World Chemicals Co., Ltd.
Carbon black	Filler	Conductex®7055	Columbian Chemicals
	Filler	N-220 (ISAF)	TCB Co., Ltd
	Filler	N-234 (ISAE-HS)	TCB Co., Ltd
	Filler	N-330 (HAF)	TCB Co., Ltd
	Filler	N-339 (HAF-HS)	TCB Co., Ltd
Calcium Light Carbonate	Filler	Calcium Light	Sand and Soil Industry Co., Ltd.
Aromatic Oil	Processing	Aromatic Oil	Lucky Union Company Limited
TMQ	Antioxidant	TMQ	Multichemicals
ZnO(W)	Activator	ZnO White Seal	CMC Trading Co.,ltd
Stearic acid	Activator	Stearic acid	Imperial Industrial Chemicals
MBTS	Accelerator	Perkacit MBTS	Flexsys Antwerp Belgium
ETU-80	Accelerator	Mixland ETU 80	MLPC International
MgO#150	Vulcanizing agent	Magnesium Oxide Starmag 150	Konoshima Chemical Co.,Ltd

3.2 Instruments

1) Banbury mixer : Ho-Shuenn Industrial District,Tainan,Taiwan
2) Two roll mill mixer: Shenyang Rubber And Plastics Machinery Factory,China
3) Mooney viscometer: Gotech, Taiwan
4) Tensile machine : Lloyd Instruments, England
5) Hardness Tester : Affri, Italy
6) Specific Gravity Tester : AND, Japan
7) Hot Air Oven : Gotech, Taiwan
8) Volume resistivity testing : Agilent4339B

3.3 Procedure

Neoprene rubber WRT (100 phr) was masticated for 10 min by Banbury mixer. Then activator additives such as MgO (4 phr), stearic acid (1 phr), TMQ (3 phr) and fillers (0-70phr), Aromatic oil (25 phr) were added. The compound was mixed with accelerators and zinc oxide. The cure time of sheet was determined by using moving die rheometer (MDR2000). The rubber compounds were then pressed into the preheated mold of compression molding at temperature of 160 ^{0}C, cure time for 10 min and pressure at 120 kg/cm^2.

After pressing, the rubber sheet of the specified size (Table 3.2) was transferred to an air cooled press for 5 min. The sheet was cut into the standard specimens according to the ASTM test method. The rubber sheets filled with fillers were prepared in the same manner. The summarized procedure for preparation of compound is shown in Figure 3.1. The compositions of compound formulation are shown in Table 3.3.

Table 3.2 Mould Dimensions

Properties	Mould dimension (length x width x thickness, mm.)
Tensile	160 x 160 x 2
Hardness	ø29 x 12.5 (cylinder)
Volume resistivity testing	150 x 150 x 2

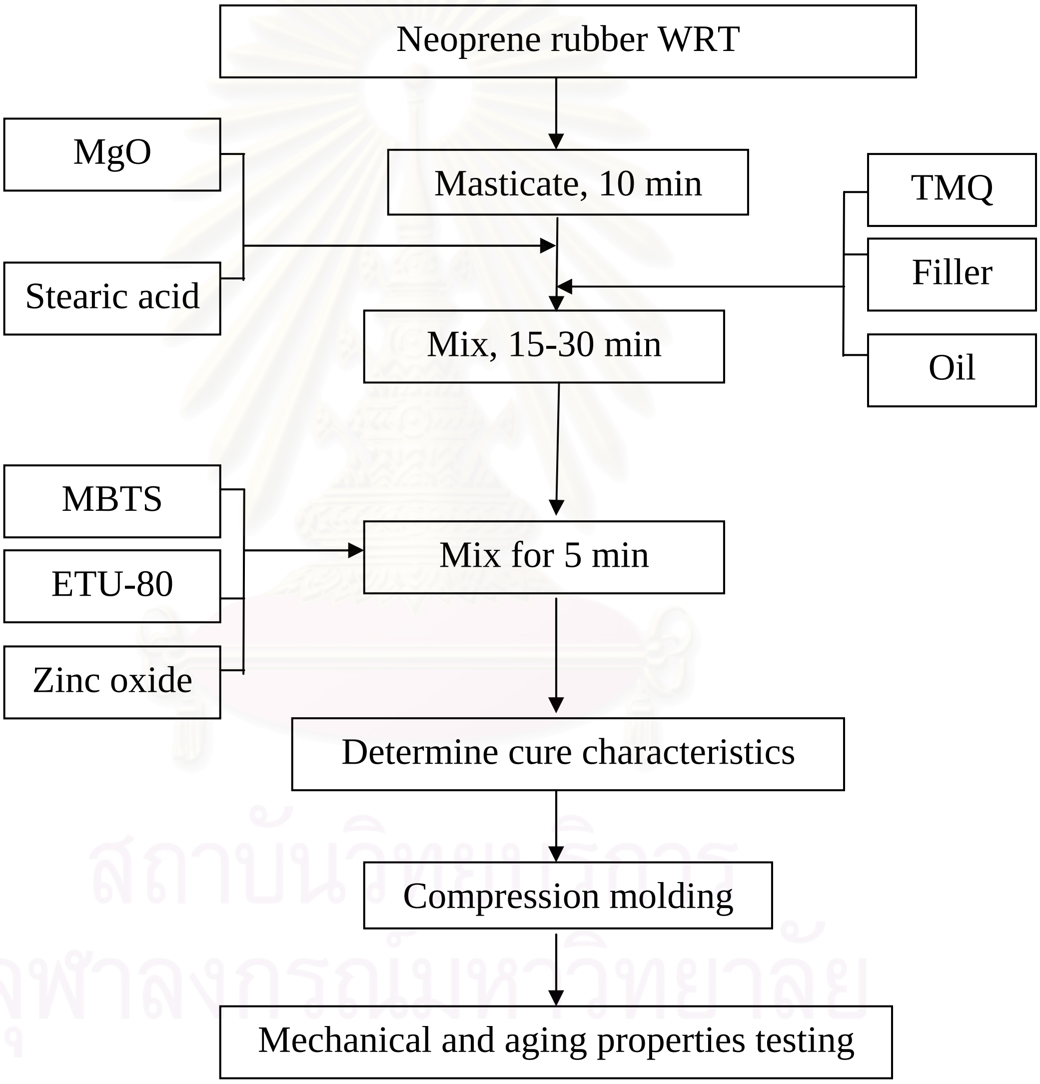


Figure 3.1 The overall schematic experiment process.

3.4 Formulation of the Compounds in the Experiment

In this experiment, the formulations are presented in Tables 3.3 and 3.4

Table 3.3 Compound ingredients.

Ingredients	Composition, phr (part per hundred rubber)
CR WRT	100
Carbon black	0-70
Aromatic oil	25
TMQ*	2
Stearic acid	1
Zinc oxide	3
MgO	3
MBTS**	1
ETU-80***	2

* TMQ = 2, 2, 4-Trimethyl-1, 2-dihydroquinoline

** MBTS = Dibenzothiazole disulphide

*** ETU-80 = Ethylene thiourea

Table 3.4 Formulation of rubber compounds with various carbon black types.

Ingredient	CR/CB70 - 10	CR/CB70 - 20	CR/CB70 - 30	CR/CB70 - 40	CR/CB70 - 50	CR/CB70 - 60	CR/CB70 - 70
CCB 7055	10	20	30	40	50	60	70

Ingredient	CR/N22-10	CR/N22-20	CR/N22-30	CR/N22-40	CR/N22-50	CR/N22-60	CR/N22-70
N220	10	20	30	40	50	60	70

Ingredient	CR/N23-10	CR/N23-20	CR/N23-30	CR/N23-40	CR/N23-50	CR/N23-60	CR/N23-70
N234	10	20	30	40	50	60	70

Ingredient	CR/N33-10	CR/N33-20	CR/N33-30	CR/N33-40	CR/N33-50	CR/N33-60	CR/N33-70
N330	10	20	30	40	50	60	70

Ingredient	CR/N39-10	CR/N39-20	CR/N39-30	CR/N39-40	CR/N39-50	CR/N39-60	CR/N39-70
N339	10	20	30	40	50	60	70

3.5 Testing

3.5.1 Testing of unvulcanized samples

3.5.1.1 Mooney viscosity

The compound (before vulcanization) was cut into cylinder shape, diameter 5.5 cm about 25 g. It was then preheated at 100^{o}C for 1 minute after the platens were closed before measuring its Mooney viscosity by using a Mooney viscometer. The rheological property was studied after rotating the disc for 4 minute with speed 1 s^{-1} at 100^{o}C by large rotor in accordance with ASTM D1646 as shown in Figure 3.2. The Mooney viscosity was then determined and expressed as ML1+4 (100^{o}C)

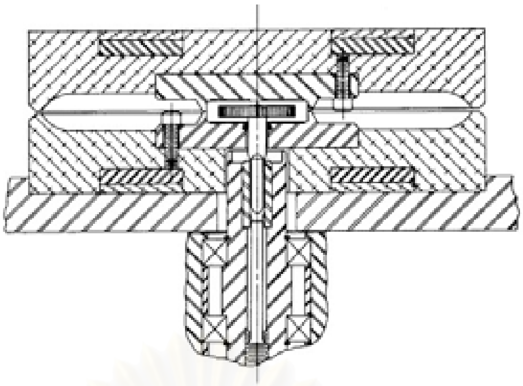


Figure 3.2 Die and rotor of Mooney viscometer

3.5.1.2 Mooney Scorch time

The mooney viscometer has been used to measure scorch since the 1930s. It was the first instrument method used to measure scorch of mixed stock. Usually, the Mooney viscometer is set at a temperature higher than 100^{o}C, such as 121^{o}C or 135^{o}C, for example. From a practical viewpoint, some rubber technologists consider the best scorch test temperature which is selected when the compound routinely reaches scorch within 10 to 20 minutes. However, other rubber technologists agree that the temperature for the moony scorch test should be close to the normal temperature of the factory process.

Mooney scorch is generally reported for a large rotor as the time required for the viscosity to rise five Mooney units above the minimum viscosity (referred to t_5). However, when the small rotor is used, the scorch time is reported as the time required for viscosity to rise three Mooney units above the minimum (referred to t_3). It should be noted that the Mooney rotor is unheated, which means that mooney scorch values are not true isothermal measurements.

3.5.2 Tensile Properties

Tensile strength, tensile modulus and elongation at break of specimen were measured in a universal testing machine. Dumbbell specimens were required according to ASTM D 412-00 (Figure 3.3). The specimens were placed in the grips at a specified grip separation and pulled until failure. Three specimens were required for each measurement. The test speed was 500 mm/min for measuring strength and elongation.

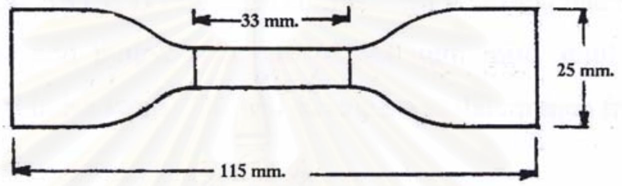


Figure 3.3 Dumbbell shape specimen for tensile property testing.

The tensile strength and % elongation at break were determined from Eq.3.1 and 3.2.

$$\text{Tensile strength (MPa)} = \frac{\text{Force at rupture (N)}}{\text{Cross-section area (m}^2\text{)}} \qquad (3.1)$$

$$\text{\%Elongation at break (\%)} = \frac{\text{(Length at rupture-original length) x100}}{\text{Original length}} \qquad (3.2)$$

3.5.3 Hardness Measurement

The test specimen is at least 3 mm in thickness. The lateral dimensions of the specimen are sufficient to permit measurements at least 12 mm from any edge. The specimen is flat and parallel over a sufficient area to permit the pressure foot to contact the specimen.

The specimen was placed on a hard and horizontal surface. The pressure was held on a vertical position with the point of the indenter at least 12 mm from any edge of the specimen. The pressure was applied to the specimen. After the pressure foot was in firm contact with the specimen, the scale reading was taken within 30 s. One measurement was made in 3 samples and the average of these measurements was used as hardness value.

3.5.4 Determination of Specific Gravity

The vulcanized rubber specific gravity was determined by using Electronic Densimeter, Auto-Specific Gravity Tester adopted from Archimedes' principle. The determination of (relative) density value was based on the density of water at 4 ^{0}C: 1g/cm per electronic densimeter instruction manual.

3.5.5 Volume Resistivity Measurement

The Volume electrical conductivity of adhesives was measured according to ASTM D-257 as shown in Figure 3.4. Three-electrode electrometer arrangement was used for the DC measurement of the resistivity. The voltage level varied in the range 0.1-500 V.

In general, volume resistivity is defined as the resistivity per unit volume.

$$\rho_{\upsilon} = \frac{Area}{t} R_{\upsilon} \times \frac{1}{10} \tag{3.3}$$

where,

ρ_{υ} Volume resistivity $\left[\Omega - cm\right]$

$Area$	Effective area [mm^2]
t	Thickness of the sample [mm]
R_υ	Measured volume resistance $[\Omega]$

When the 16008B Resistivity Cell is used, the above equation becomes:

$$\rho_\upsilon = \frac{\pi\left(D_1 + \frac{B(D_2 - D_1)}{2}\right)}{4t} \times R_\upsilon \times \frac{1}{10} \tag{3.4}$$

where,

D_1	Main electrode diameter [mm]
D_2	Guard electrode diameter [mm]
B	Effective area coefficient

B is the fraction of the gap width to be added to the diameter of the circular electrodes or to the dimensions of rectangular or cylindrical electrodes. The value is usually specified by the standard that you use. (For example: 1 for ASTM D 257; 0 for JIS K6911).

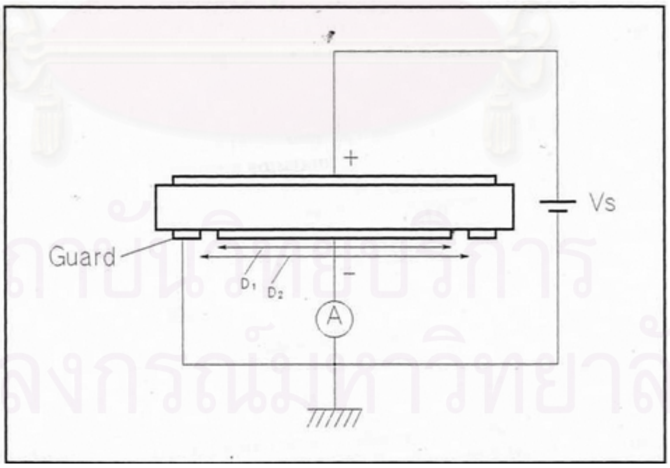


Figure 3.4 Volume resistivity.

CHAPTER IV

RESULTS AND DISCUSSIONS

To perform an intensive study on the development of conductive Neoprene rubber (CR) compounds with carbon black (CB), the effects of types and loadings of carbon black, Mooney viscosity, Mooney Scorch time and mechanical properties before and after aging of all composites were investigated. Details of investigation are presented below.

4.1 Characteristics of rubber and filler

4.1.1 Electrical property of polymers

Generally, elastomers having resistances below 10^4 Ω are considered conductive; between 10^4 and 10^8 Ω, antistatic; and above this, insulating. The upper limit is usually about 10^{16} Ω. For experimental, Neoprene rubber is antistatic polymer, thus, volume resistivity measured is in the order of 10^{11} Ω.cm. (see Figure 4.5)

4.1.2 Physical properties of carbon black

Table 4.1 shows the physical properties of various carbon black types including CCB7055, N234, N339, N220 and N330. The characteristics of carbon black, i.e., porosity, surface area, apparent bulk density, surface chemistry and particle size strongly affect the equilibrium electrical properties. The specific area was determined by nitrogen absorption capacity on surface area of carbon black using the Brunauer Emment Teller (BET) procedure. Typically, carbon black with small particle size has larger surface area (per unit weight) than the large particle carbon black. Structure of carbon black is measured by di-butyl-phthalate (DBP) oil absorption (ml/100g) that is the amount of DBP absorbed on 100 g of carbon black at fixed torque value, measured by ASTM D-2414. Carbon black structure is void volumes of the aggregates and used to describe how well the carbon black particles fused together to form aggregates. A low structure carbon black (low DBP) is from a few carbon black particles fused to form aggregates while a high structure otherwise. Therefore, the high structure is defined from many primary particles with considerable numbers of branching and chaining. Diameters of carbon black particle are determined by Transmission Electron Microscopy (TEM) using ASTM D-3849. As seen in Table 4.1, CB7055 shows the lowest surface area based on the lowest BET value. On the other hand, CC7055 also shows the highest structure due to the highest DBP value. This can be explained that the CCB7055 developed from furnace carbon black with chemical modification surface (see Figure 4.1 (b)) has lowest surface area, highest structure and longest branching. The surface of other types of carbon black are not modified (see Figure 4.1 (a)), thus all commercial carbon black except CCB7055 possess the higher surface area but lower structure compared with CCB7055.

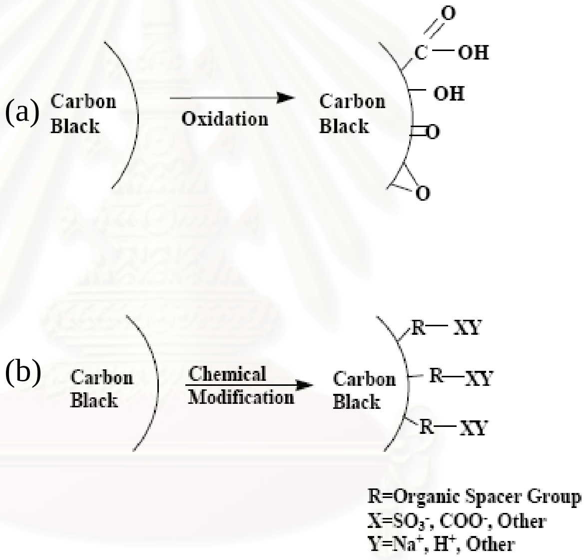


Figure 4.1 Developed furnace carbon black (a) before (b) after modification [29].

Table 4.1 Physical properties of carbon black

Properties	CCB 7055	N220 (ISAF-HM)	N234 (ISAF-HS)	N330 (GPF)	N339 (HAF-HS)
BET Nitrigen Surface Area(m^2/g)	55	114	119	78	91
DBP Absorption (CC/100g)	170	112	125	102	120
Iodine (mg/g)	65	121	120	82	90
Pour Density (kg/m^3)	241	355	319	380	345
Particle Size (nm)	42.0	22.2	24.7	26.7	27.9
Ash loading(%Max)	0.03	0.25	0.26	0.22	0.24

4.2 Rheological and cure time properties of rubber compounds.

4.2.1 Mooney viscosity

The mooney value (M) is one of the indicators that used to explain the processability. In this experiment, the mooney viscosities of the rubber compounds with various carbon black types and loadings were investigated. The results are shown in the Table 4.2 and Figure 4.2. The Mooney value (M) of the rubber compounds increased with increasing filler loadings for all carbon black types. It can be explained that when the loadings of carbon black increased, interactions between the carbon black and the polymer matrix are also increased. The model of interaction between carbon black particle and rubber as well as rubber-rubber interaction is show in figure 4.3. More functional groups (the volatiles are; carboxylic acids, phenols, epoxides, ketones), more interaction between polymer chains related to BET and DBP values (Table 4.1). As can be seen, mooney viscosity was affected by carbon black structure. Therefore, the large aggregate of carbon black with higher porosity (higher surface area) and long branches are more susceptibly broken into individual aggregates which provide the larger surface area. Based on very high in BET and DBP values of N234 or N220, their filled compounds was processed with more difficulty than the compounds filled with CCB7055, N330 or N339.

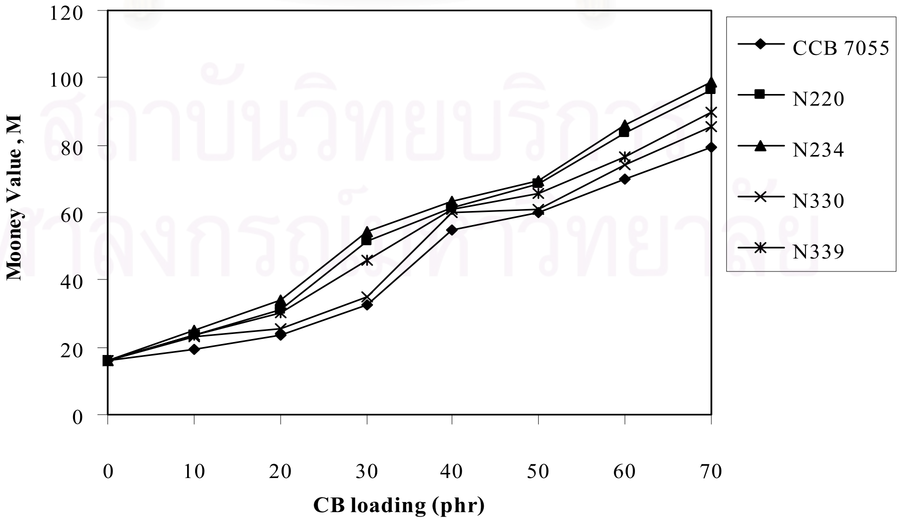


Figure 4.2 Effect of carbon black types and loading on mooney viscosity.

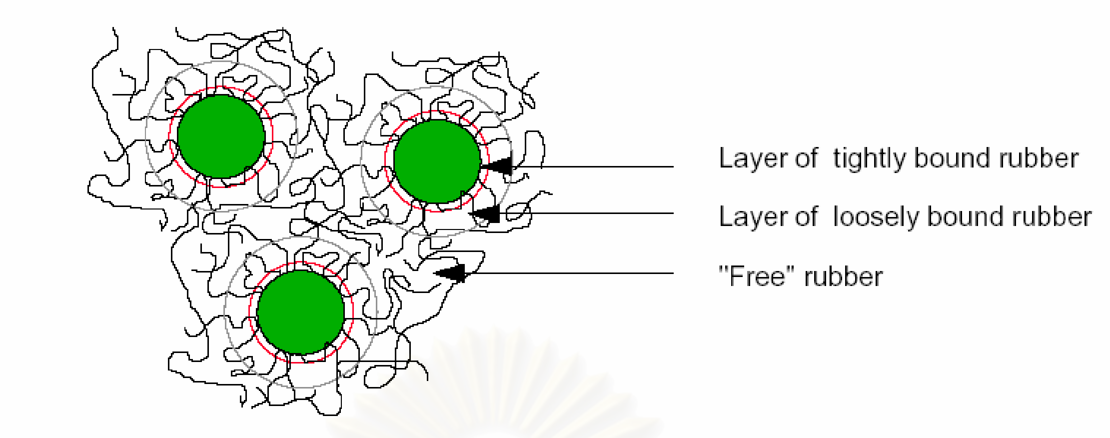


Figure 4.3 Model of bound rubber with the two regions of different mobility. The carbon black particles have been drawn as single primary particles for convenience [30].

4.2.2 Mooney scorch time

The effect of carbon black types and loading on the vulcanization time of rubbers was measured as the mooney scorch (T_5). This parameter corresponds to the time that rubber used in cross linking or molding. Therefore, very short T_5 is not appropriate for processing because rubber with short T_5 will be became hard before molding finished. Table 4.2 and Figure 4.4 show the T_5 of the rubber compounds at various carbon black types and loadings.

It can be seen that the T_5 decreased with increase in filler loading for all carbon black types. The lowest T_5 value (4.1) is found for CR compound containing carbon black type N234. The T_5 values for all other compounds were not different. It can be noted that the crosslinking of polymer chains in CR compound containing CB type N234 occurred faster than the compounds filled with other type of carbon black. It can be explained that carbon black type N234 has the highest structure and surface area. The same result was found in other types of rubber compound. In this study, it can be concluded that CR compound filled with carbon black type N234 is not recommended to be commercial product.

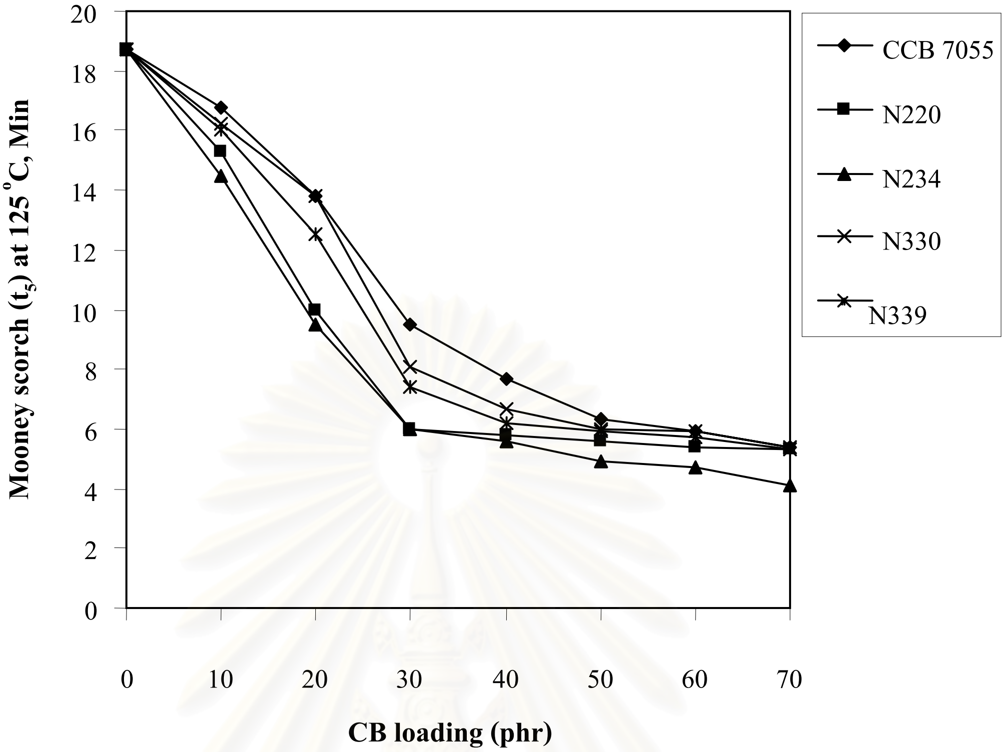


Figure 4.4 Effect of carbon black types and loadings on mooney scorch time.

Table 4.2 Effect of carbon black types on rheological and cure time properties

Properties	**CR/CB 70-10**	**CR/CB 70-20**	**CR/CB 70-30**	**CR/CB 70-40**	**CR/CB 70-50**	**CR/CB 70-60**	**CR/CB 70-70**
Mooney ML(1+4) at 100^{o}C	19.4	23.5	32.5	54.9	59.8	69.9	79.2
Mooney Scorch time(t_5) at 125^{o}C, min	16.8	13.8	9.5	7.7	6.3	5.9	5.4

Properties	**CR/N22-10**	**CR/N22-20**	**CR/N22-30**	**CR/N22-40**	**CR/N22-50**	**CR/N22-60**	**CR/N22-70**
Mooney ML(1+4) at 100^{o}C	23.70	31.00	51.60	61.30	68.50	83.60	96.40
Mooney Scorch time(t_5) at 125^{o}C, min	15.3	10.0	6.0	5.8	5.6	5.4	5.3

Properties	**CR/N23-10**	**CR/N23-20**	**CR/N23-30**	**CR/N23-40**	**CR/N23-50**	**CR/N23-60**	**CR/N23-70**
Mooney ML(1+4) at 100^{o}C	24.9	34.2	54.1	63.3	69.6	85.8	98.7
Mooney Scorch time(t_5) at 125^{o}C, min	14.5	9.5	6.0	5.6	4.9	4.7	4.1

Properties	**CR/N33-10**	**CR/N33-20**	**CR/N33-30**	**CR/N33-40**	**CR/N33-50**	**CR/N33-60**	**CR/N33-70**
Mooney ML(1+4) at 100^{o}C	23.1	52.3	35.0	59.8	61.0	74.3	85.4
Mooney Scorch time(t_5) at 125^{o}C, min	16.2	13.8	8.1	6.7	6.0	5.9	5.4

Properties	**CR/N39-10**	**CR/N39-20**	**CR/N39-30**	**CR/N39-40**	**CR/N39-50**	**CR/N39-60**	**CR/N39-70**
Mooney ML(1+4) at 100^{o}C	23.5	30.2	45.6	60.8	65.5	76.7	89.6
Mooney Scorch time(t_5) at 125^{o}C, min	16.0	12.5	7.4	6.2	5.9	5.7	5.3

4.3 Properties of rubber vulcanizates

The properties of neoprene rubber with different carbon black types (CCB7055, N220, N234, N330, N339) at various loading (0, 10, 20, 30, 40, 50, 60, 70 phr) were investigated. The results of specific gravity, tensile strength, elongation at break, hardness, electrical conductivity are presented in Table 4.3.

Table 4.3 Effect of carbon black types on mechanical properties of CR blends

Properties	**CR/CB70 - 10**	**CR/CB70 - 20**	**CR/CB70 - 30**	**CR/CB70 - 40**	**CR/CB70 - 50**	**CR/CB70 - 60**	**CR/CB70 - 70**
Specific gravity, g/cm^3	1.355	1.375	1.392	1.412	1.428	1.444	1.456
T.S, MPa	15.75	15.96	16.03	15.57	14.96	14.88	14.28
E.B, %	903	782	599	493	410	358	299
Hardness, Shor A	36	42	48	54	59	65	71
Resistivity, Ohm.cm	4.32E+11	5.84E+10	3.63E+06	7.23E+03	1.62E+02	1.10E+02	1.10E+02

Properties	**CR/N22-10**	**CR/N22-20**	**CR/N22-30**	**CR/N22-40**	**CR/N22-50**	**CR/N22-60**	**CR/N22-70**
Specific gravity, g/cm^3	1.351	1.372	1.391	1.411	1.427	1.445	1.455
T.S, MPa	16.24	17.03	17.32	17.25	16.22	15.78	14.99
E.B, %	833	696	617	488	385	325	285
Hardness, Shor A	38	46	53	61	68	76	84
Resistivity, Ohm.cm	7.75E+11	4.48E+11	7.55E+09	1.42E+07	9.86E+04	4.86E+03	4.86E+02

Properties	**CR/N23-10**	**CR/N23-20**	**CR/N23-30**	**CR/N23-40**	**CR/N23-50**	**CR/N23-60**	**CR/N23-70**
Specific gravity, g/cm^3	1.356	1.376	1.391	1.410	1.430	1.444	1.454
T.S, MPa	16.34	18.41	19.76	19.47	18.86	18.65	17.87
E.B, %	1082	992	893	739	670	550	470
Hardness, Shor A	39	47	54	62	70	78	86
Resistivity, Ohm.cm	6.53E+11	2.36E+11	1.84E+08	9.82E+04	1.71E+03	3.70E+02	1.71E+02

Properties	**CR/N33-10**	**CR/N33-20**	**CR/N33-30**	**CR/N33-40**	**CR/N33-50**	**CR/N33-60**	**CR/N33-70**
Specific gravity, g/cm^3	1.353	1.374	1.393	1.414	1.429	1.442	1.453
T.S, MPa	15.45	15.65	15.74	15.56	14.95	14.22	13.13
E.B, %	836	691	614	523	409	339	289
Hardness, Shor A	37	43	50	57	64	70	77
Resistivity, Ohm.cm	7.69E+11	6.44E+11	1.11E+10	9.17E+07	4.66E+05	1.26E+04	1.26E+03

Properties	**CR/N39-10**	**CR/N39-20**	**CR/N39-30**	**CR/N39-40**	**CR/N39-50**	**CR/N39-60**	**CR/N39-70**
Specific gravity, g/cm^3	1.352	1.376	1.395	1.414	1.430	1.441	1.455
T.S, MPa	16.24	17.43	17.63	17.55	16.76	16.15	15.61
E.B, %	824	691	614	523	409	339	289
Hardness, Shor A	38	44	51	58	63	71	78
Resistivity, Ohm.cm	5.85E+11	3.12E+11	5.77E+09	1.99E+06	2.07E+04	5.07E+02	3.07E+02

4.3.1 Specific gravity

Specific gravity of each compound can be determined experimentally and calculated based on the formulation of compound so called ‘Specific gravity from theory’ (Appendix B, Table B-1). All specific gravity values of various rubber compounds containing different carbon black types are presented in Table 4.3. It can be seen that experimental specific gravity values of all rubber compounds increased with increasing of carbon black loadings. In addition, specific gravity values of rubber compounds filled with different carbon black types were not significantly different.

Experimental specific gravity values were lower than that of the theoretical specific gravity values for all rubber compounds. This phenomenon can be described by the amount of micro voids found in rubber compound after adding carbon black. The carbon black with high porosity and structure could not be completely filled or occluded by the elastomer chain segment in the rubber compound.

4.3.2 Tensile properties

The mechanical property of rubber compound filled with different carbon black types and loading is presented in Table 4.3 and Figure 4.5. It was found that the rubber compounds filled with carbon black types N234 and N330 exhibited the highest and lowest tensile strength, respectively.

The maximum tensile strength was observed for carbon black with loading for all rubber compound 30 %. The tensile strength of rubber compound was slightly decreased at carbon at loading above 40 %. Typically, the tensile strength is dependent on structure and surface area of carbon black. The higher in the structure and surface area introduce higher tensile strength of rubber compound. Thus, the tensile strength values of rubber compounds increased in the following order: N234 > N339 > N220 > CCB7055 > N330. In addition, the tensile strength of rubber compounds containing N330 and CCB7055 at 70 % loading was lower than that of unfilled rubber compound (0%). The plot of % elongation versus carbon black loading for neoprene rubber vulcanized is show in Figure 4.6. It can be seen that the % elongation decreased with an increase in filler loading for all carbon black types due to the enhanced physical stiffening effect of carbon black loading.

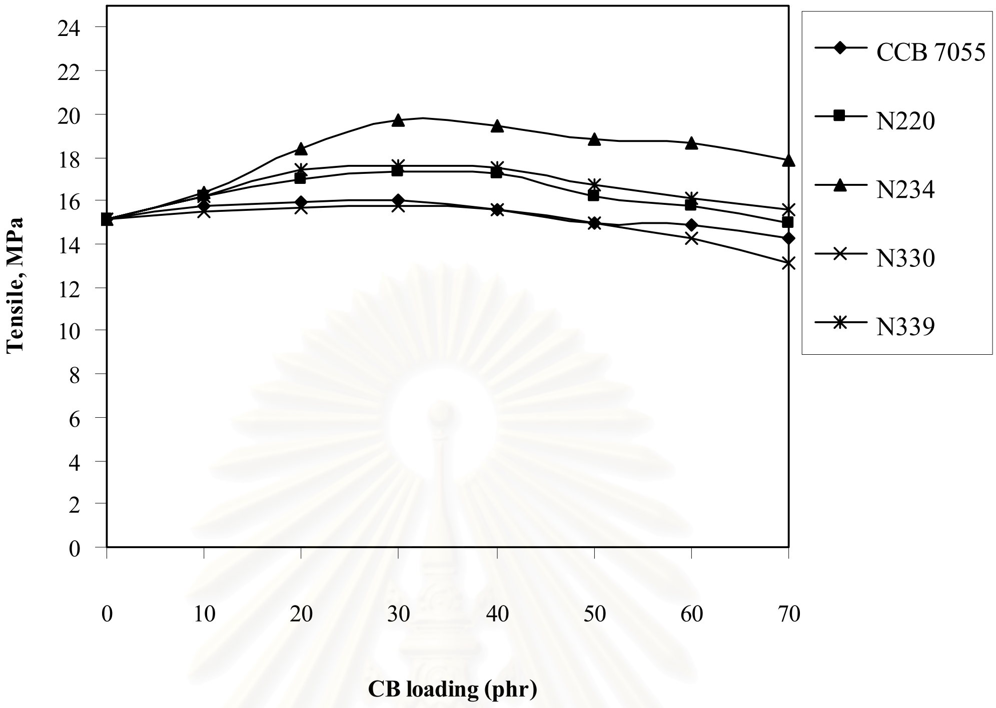


Figure 4.5 Effect of carbon black types and loading on tensile strength.

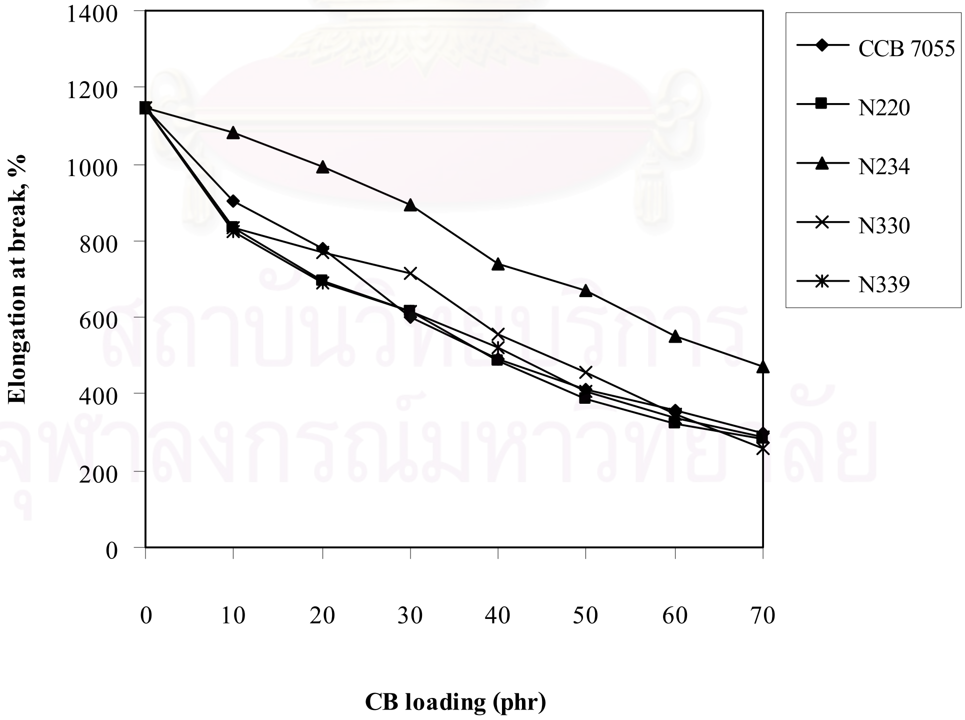


Figure 4.6 Effect of carbon black types and loading on elongation at break.

4.3.3 Hardness

Hardness is typically measured as resistance to surface indentation under specific condition, so the force is supplied as a point of compression rather than an area of tension. In general, hardness of rubber compound increased with increase in crosslink density and reinforcement of the filler. The hardness of the various rubber compounds with varying of carbon black types and loading are shown in Table 4.3 and Figure 4.7.

The hardness of all rubber compounds was in increased order with increasing filler loadings for all carbon black types. And the rubber compound containing carbon black types CCB7055 and N234 had the lowest and highest hardness values, respectively. Thus, it can be explained that the highest structure and surface area of carbon black type N234 affected the hardness of the rubber compounds.

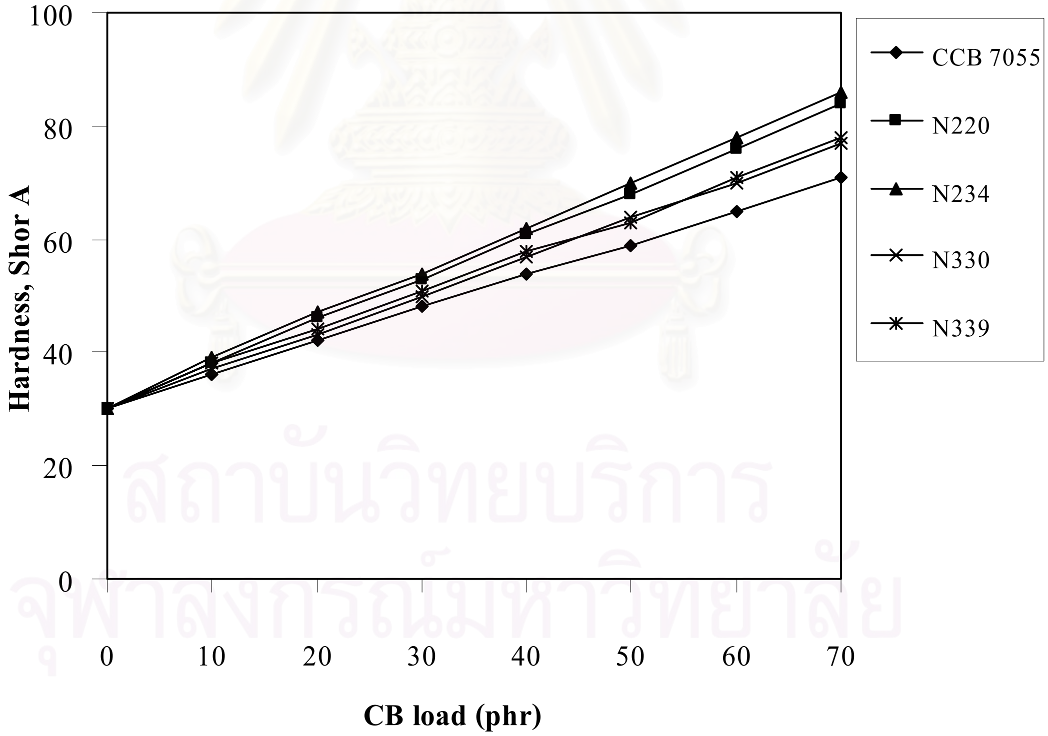


Figure 4.7 Effect of carbon black types and loading on hardness.

4.3.4 Electrical conductivity

Based on the widely use of carbon black as an additive to increase the electrical property of insulating polymers. Figure 4.8 shows resistor-capacity circuit to determine electrical property of rubber compound. The electrical resistivity of rubber compounds with different carbon black types and loadings are determined and the results are presented in Table 4.4 and Figure 4.9. It can be seen that the resistivities of rubber compounds decreased with increasing carbon black loadings. The highest and lowest resistivities were achieved in rubber compounds containing carbon black types N330 and CCB7055, respectively. As the carbon black loading was increased, the resistivities of all rubber compounds with 10 – 20 phr carbon black were not different. When a critical loading was reached (20 phr), the resistivity decreased rapidly (or conductivity increase rapidly) with increasing carbon black loading (see Figure 4.9).

A sharp transition of the conductivity (σ) value was observed over carbon black loading range in of 20 and 35 phr called the percolation region. At low CB loading (≤ 15 phr), the carbon black particles in the elastomer matrix were widely separated. Large gap-widths between the conducting CB particles existed as physical barriers to flow of electrons throughout the elastomer matrix (see Figure 4.9).

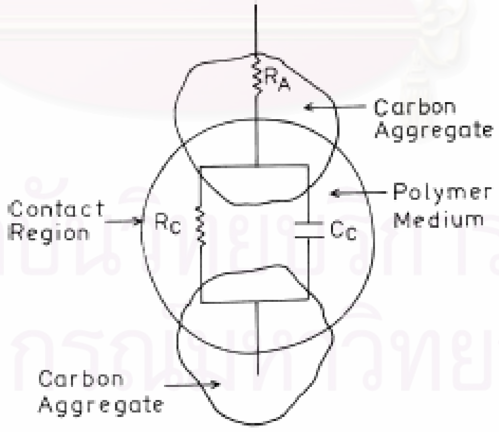


Figure 4.8 Equivalent resistor-capacitor circuits in the contact region of carbon black filler aggregates in an elastomer compound [6].

Thus, rubber compound with low carbon black loading had low electrical conductivity. Over the percolation zone (20-35phr), as the carbon black loading increased, the barrier or hindrance to electron mobility dropped sharply. This caused a sharp rise in the electrical conductivity with enhancement in carbon black loading over the percolation zone. For further increase in carbon black filler loading, the increase in conductivity value decreased gradually above the quantity in a range of 50 to 70 phr over. The high carbon black loading contributed to progressive narrowing or elimination of the gap widths, thus facilitating much improved electrical conduction. It can be concluded that conductivity of the rubber compound depends on both type and loading of the carbon black. The carbon black with high porosity (structure) such as CBB 7055 enhances the conductivity of the rubber. Conductivity of all rubber compounds seems to be constant at 50-70% loading of carbon black.

It is interesting to investigate the effect of carbon black structure on the percolation threshold by determining the number of CB particles contact to its neighbours. The equation relating the critical volume to the fraction of carbon black ϕ_c and the structure of carbon black is proposed as follows:

$$\phi_{crit} = \left[1 + 4\rho\upsilon\right]^{-1} \tag{2.3}$$

where ρ is the density of carbon black and υ is the compressed dibutyl phthalate absorption number (CDBP) (i.e., the dibutyl phthalate absorption number (DBPA) after precrushing) in cm^3/g. Equation (2.3) describes a simple relation between ϕ_c and the apparent change in morphology of carbon black particles, υ.

Table 4.4 shows the CDBP values of all commercial carbon blacks used in this work. The corresponding ϕ_c for all rubber compounds based on CDBP values were computed from equation 2.3. Because of highest conductivity and lowest mooney viscosity, rubber compound with CCB7055 shows the highest ϕ_c while N330 show the lowest. The ϕ_c values for all rubber compounds increased in the following order: N330 > N220 > N339 > N234 > CCB7055.

Table 4.4 Effect of structure on percolation threshold

Carbon black	CDBP, (cm^3/100 g)	ϕ_{crit} (volume fraction)
CCB 7055	170	0.074
N220	112	0.108
N234	125	0.098
N330	102	0.132
N339	120	0.101

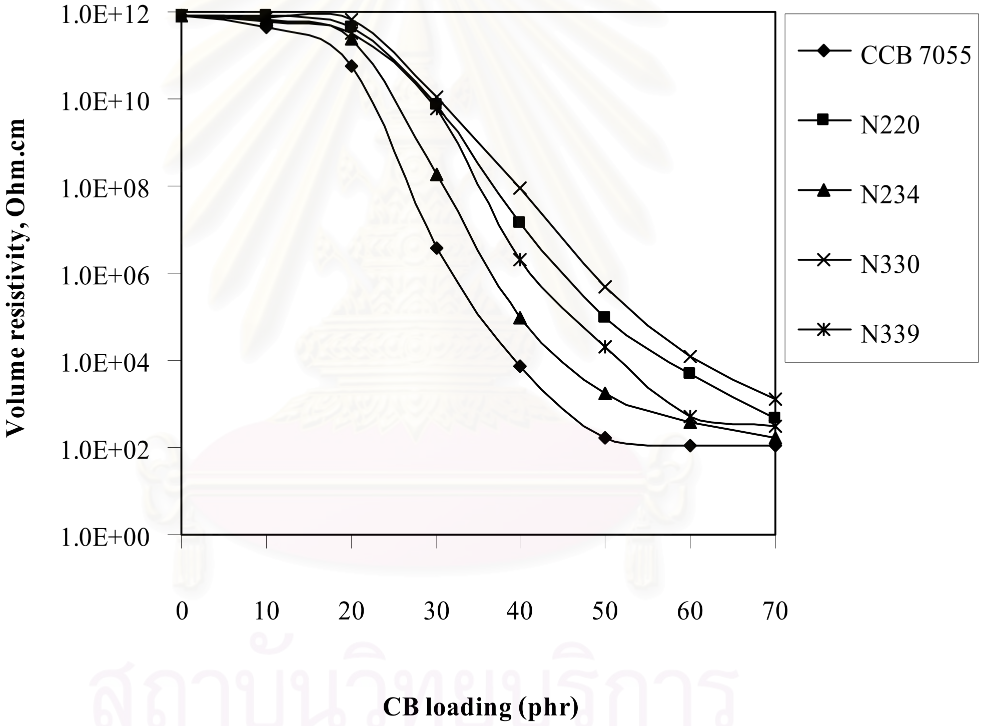


Figure 4.9 Effect of carbon black types and loading on volume resistivity.

4.4 Effect of thermal oxidation aging

The thermal resistance of the rubber vulcanizates is considered as an essential requirement for the long service life of the products. Based on the optimal properties (i.e. high conductivity, low Mooney viscosity at low loading) required, the rubber containing carbon black type CCB7055 was chosen for further study of thermal oxidation aging. The aging of 20 and 30 phr of carbon black filled CR compound was investigation.

The time dependent Hardness (Shore A) and Specific gravity were determined every 5 days for total 60 days aging. The Shore A and Specific gravity for the rubber compound are presented in Table 4.5. From Figure 4.11, Figure 4.12 the Shore A increased with aging time and reached maximum at day 30th then decreased with time for all carbon black loading. The specific gravity of rubber filled with CCB7055 increased with aging time and reached maximum at day 35th then decreased with time.

Figures 4.13, 4.14 and 4.15 show tensile strength, elongation and electrical resistivity at room temperature of the rubbers, respectively. Tensile strength, elongation of the rubber compound decreased continuously with aging time (see Figure 4.13, Figure 4.14). Electrical resistivity (Figure 4.15) of the rubber compound decreased with aging time and above day 30th, not significantly changed.

The stability of the rubber compound after aging is dependent on the stability of chain scission and crosslinking. Oxidation plays an important role in rubber degradation. Thermal oxidation leads to both of crosslinking and scission processes, as well as generation of oxidation products such as ketones, aldehydes, acids, peroxides and alcohols and gaseous products. The increase in specific gravity (density) could be due to the following causes, firstly, the crosslinking of polymer matrix (see Figure 4.15), secondly, the incorporation of higher density oxidation products along the polymer chain and third, the weight loss (gaseous products) of polymeric material that based on density change. Thus, the carbon black particles were easily contacted to each other. The conductivity as well as specific gravity of the rubber compound increased with aging time. This can be explained that during aging, the smaller molecules was released from the rubber phase, then the carbon black particles were more close to each other. In addition, the highly loading of carbon black affected to the electrical property. It can be seen that 30 phr carbon black filled rubber compounds had lower resistivity than 20 phr carbon black filled CR compound.

Table 4.5 Effect of carbon black 20, 30 ratios on percent properties changes of CR blends after thermal aging at 125° C

Properties	Aging @125°Cx 5 days		Aging @125°Cx 10 days		Aging @125°Cx 15 days	
	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30
Specific gravity, g/cm^3	1.380	1.398	1.380	1.398	1.387	1.399
Specific gravity, %	0.36	0.43	0.36	0.43	0.87	0.50
T.S., Mpa	15.53	14.57	15.53	14.57	14.70	13.79
T.S change, %	-2.73	-9.10	-2.73	-9.10	-7.90	-13.97
E.B, %	750	550	750	550	680	379
E.B. Change, %	-4.08	-8.26	-4.08	-8.26	-13.01	-36.72
Hardness, Short A	43	49	43	49	46	52
Hardness change, %	2.38	2.08	2.38	2.08	9.52	8.33
Resistivity, Ohm.cm	9.17E+09	2.17E+06	9.17E+09	2.17E+06	8.84E+09	9.85E+05
Resistivity, %	-84.30	-40.22	-84.30	-40.22	-84.86	-72.86

Properties	Aging @125°Cx 20 days		Aging @125°Cx 25 days		Aging @125°Cx 30 days	
	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30
Specific gravity, g/cm^3	1.390	1.410	1.392	1.442	1.394	1.492
Specific gravity, %	1.09	1.29	1.24	3.59	1.38	7.18
T.S., Mpa	13.60	12.96	12.53	11.94	12.20	8.55
T.S change, %	-14.79	-19.15	-21.47	-25.49	-23.57	46.69
E.B, %	617	258	550	195	384	99
E.B. Change, %	-21.04	-56.94	-29.67	-67.44	-50.81	-83.44
Hardness, Short A	47	53	48	55	49	55
Hardness change, %	11.90	10.42	14.29	14.58	16.67	14.58
Resistivity, Ohm.cm	9.52E+08	8.52E+04	7.87E+08	4.87E+04	9.54E+07	3.54E+02
Resistivity, %	-98.36	-97.65	-98.65	-98.65	-99.83	-99.99

Table 4.5 Effect of carbon black 20, 30 ratios on percent properties changes of CR blends after thermal aging at 125 °C (continue)

Properties	**Aging @125°Cx 35 days**		**Aging @125°Cx 40 days**		**Aging @125°Cx 45 days**	
	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30
Specific gravity, g/cm^3	1.475	1.501	1.479	1.532	1.483	1.539
Specific gravity, %	7.27	7.83	7.56	10.06	7.85	10.56
T.S., Mpa	8.73	8.07	7.52	6.86	6.98	5.86
T.S change, %	-45.28	-49.64	-52.88	-57.21	-56.27	-63.47
E.B, %	179	85	151	84	125	77
E.B. Change, %	-77.07	-85.78	-80.63	-85.94	-84.00	-87.11
Hardness, Short A	51	54	50	53	49	52
Hardness change, %	21.43	12.50	19.05	10.42	16.67	8.33
Resistivity, Ohm.cm	5.91E+04	3.54E+02	4.41E+03	3.11E+02	3.34E+02	2.75E+02
Resistivity, %	-99.99	-99.99	-99.99	-99.99	-99.99	-99.99

Properties	**Aging @125°Cx 50 days**		**Aging @125°Cx 55 days**		**Aging @125°Cx 60 days**	
	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30	CR/CB70-20	CR/CB70-30
Specific gravity, g/cm^3	1.486	1.551	1.491	1.592	1.493	1.601
Specific gravity, %	8.07	11.42	8.44	14.37	8.58	15.01
T.S., Mpa	5.75	3.73	4.26	3.35	3.11	3.01
T.S change, %	-64.00	-76.71	-73.31	-79.10	-80.49	-81.20
E.B, %	120	68	91	64	75.89	56.23
E.B. Change, %	-84.67	-88.63	-88.30	-89.28	-90.29	-90.62
Hardness, Short A	47	51	46	50	45	49
Hardness change, %	11.90	6.25	9.52	4.17	7.14	2.08
Resistivity, Ohm.cm	2.96E+02	1.37E+02	2.84E+02	1.19E+02	1.84E+02	1.08E+02
Resistivity, %	-99.99	-99.99	-99.99	-99.99	-99.99	-99.99

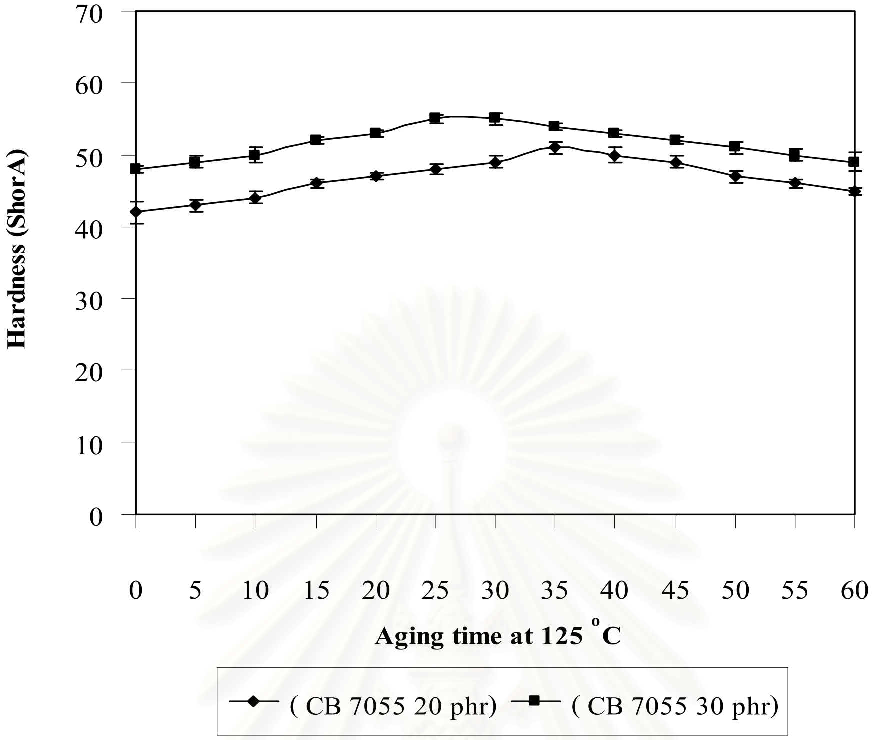


Figure 4.10 Effect of thermal aging on hardness of rubber compound.

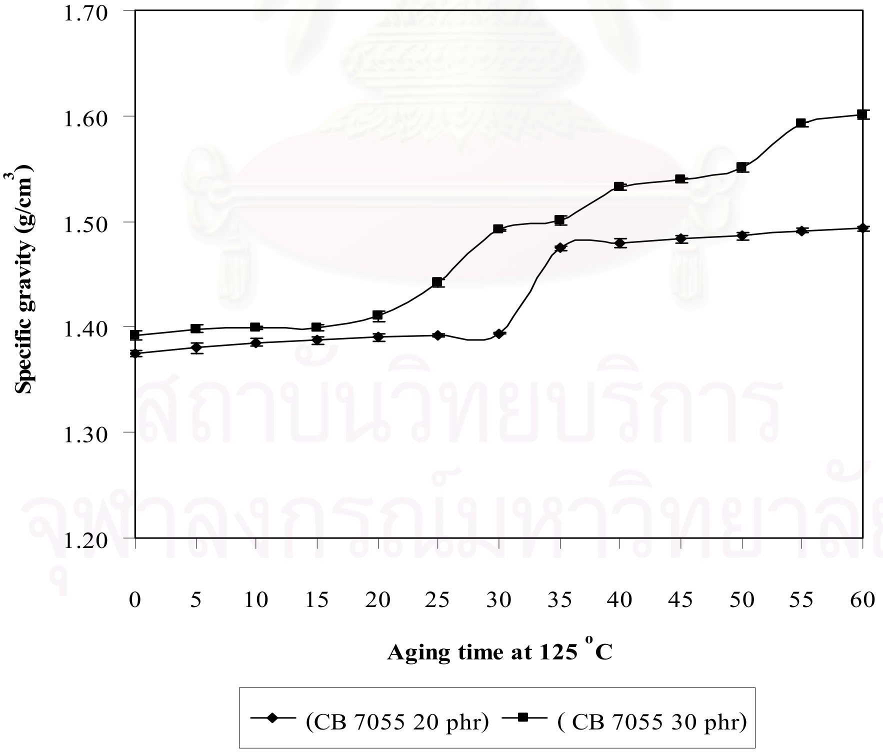


Figure 4.11 Effect of thermal aging on specific gravity of rubber compound.

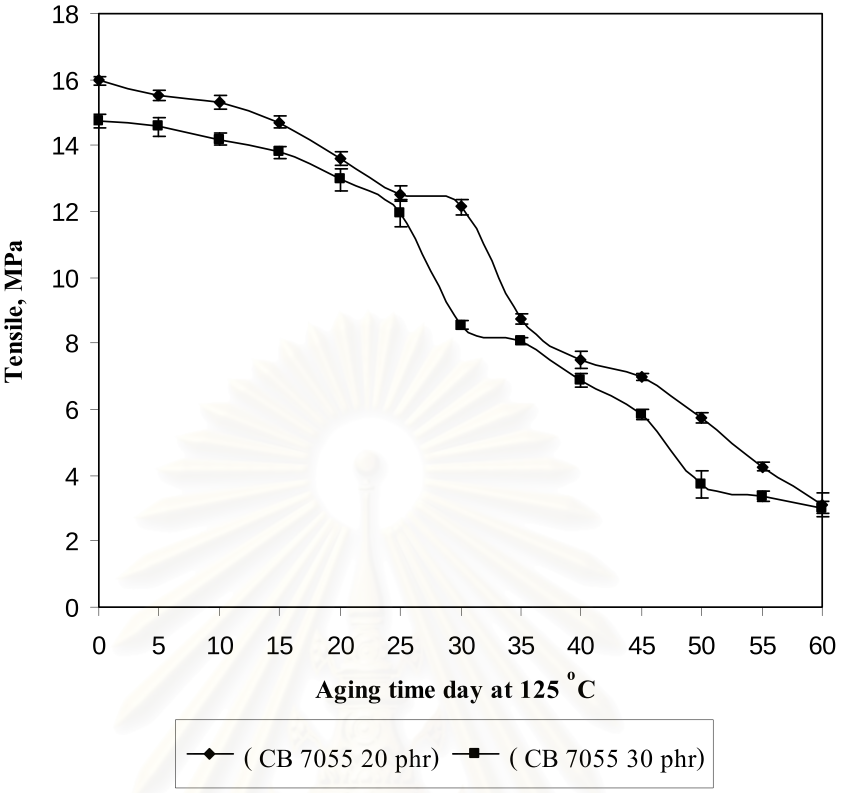


Figure 4.12 Effect of thermal aging on tensile strength of rubber compound.

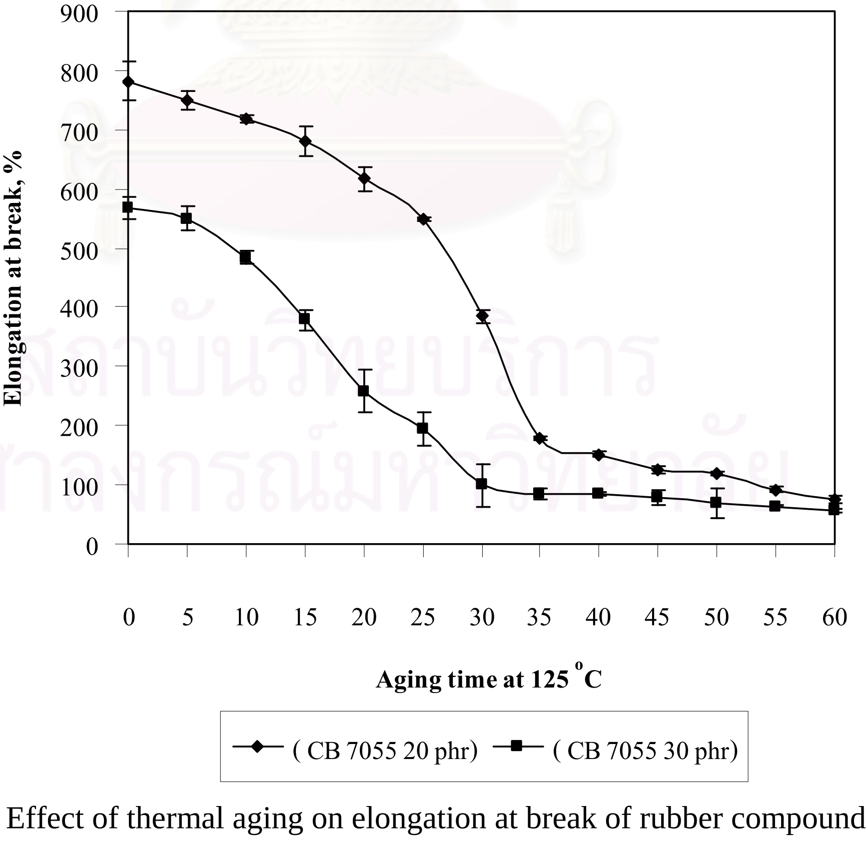


Figure 4.13 Effect of thermal aging on elongation at break of rubber compound.

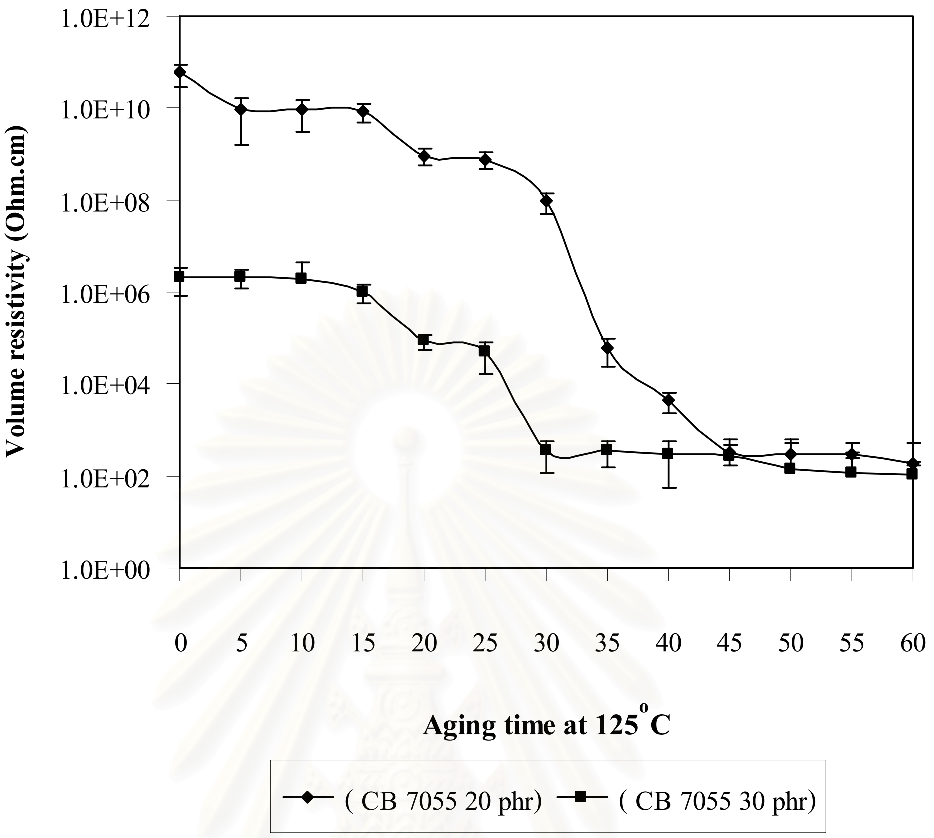
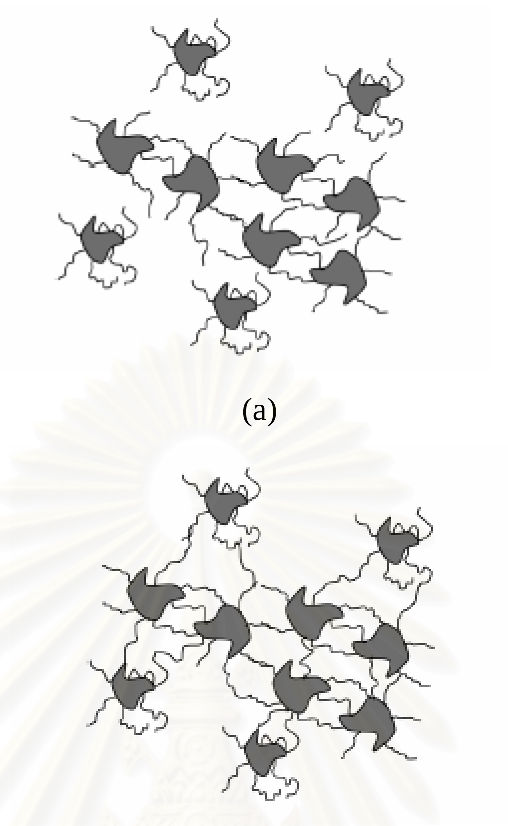


Figure 4.14 Effect of thermal aging on resistivity of rubber compound.



(a)

(b)

Figure 4.15 Schematic representation of bridging flocculation and its evolution during thermal aging. (a) before aging and (b) after aging [33].

CHAPTER V

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The effects of carbon black types on mechanical and electrical properties of Neoprene rubber were studied. In this work, the Neoprene rubbers filled with various carbon black types were prepared. The cure characteristics, mechanical and electrical properties of various rubber compounds were determined and can therefore be summarized as follows:

1. Carbon black with high structure, high DPE, low critical volume fraction (predicted by using Jansen theory) and low surface area could enhance the conductivity of the rubber compound.
2. Rubber compound containing carbon black with high structure (high DBP and surface area) was easy to be processed with short period of time required. Therefore, the rubber compound with low Mooney viscosity and high Scorch time can therefore be easily cured in molding process.
3. Percolation threshold range of the rubber compounds were in the range of 20 to 35 phr based on Janzen theory.
4. For the thermal oxidation aging tensile strength, elongation, % and volume resistivity of the rubber compounds are decreased slowly with aging time but sharply after day 30-35th.
5. For the thermal oxidation aging hardness and specific gravity value of the rubber compound are increased with aging time and above day 30-35th, decreased with time.
6. Therefore rubber with high carbon black loading was deteriorated faster than that with lose carbon black loading.

5.2 Future work

- To study on electrical property of the rubber compound with conductive and non-conductive carbon black.
- To study on the blend containing two types of rubber with varying carbon black types.
- To explore other additives which are cheaper than conductive carbon black and study the mixing ability and stability of the rubber compound.

REFERENCES

[1.] Khairi Nagdi. Rubber as an Engineering Material: Guideline of Users. New York: Hanser Publ, (1993).

[2.] Indra K. Varma. Extrinsically conducting polymer blends. Metals Materials And Processes 9, (1997).

[3.] Weawkamol Leelapornpisit. Conductivity improvement of carbon black filled polypropylene(PP)/polystyrene(PS) blend by controlling morphology. Thailand :Mahidol University, (2004).

[4.] Columbian Chemicals Company, Properties of Columbian Ultra Carbon Black :www.columbianchemical.com, (2007).

[5.] Tata McGraw. Rubber Engineering. New York: Hill Publishing Company Limited, (1988).

[6.] Avrom I. Medalia. Electrical conduction in carbon black composites. Rubber Chemistry And Technilogy 59 ,(1985).

[7.] Yangyang Sun, Shijian Luo, Ken Watkins, C.P. Wong. Electrical approach to monitor the thermal oxidation aging of carbon black filled ethylene propylene rubber . Polymer Degradation and Stability 86 (2004): 209-215.

[8.] Premamoy Ghosh, Amit Chakrabarti. Conducting carbon black filled EPDM vulcanizates: assessment of dependence of physical and mechanical properties and conducting character on variation of filler loading. European Polymer Journal 36 (2000): 1043-1054.

[9.] Igor Novak , Igor Krupa, Ivan Chodak.Analysis of correlation between percolation concentration and elongation at break in filled electroconductive epoxy-based adhesives. European Polymer Journal 39 (2003): 585-592.

[10.] M.H. Ali, A. Abo-Hashem.Precolation concept and the electrical conductivity of carbon black-polymer composites 2 : Non-crystallisable chloroprene rubber mixed with HAF carbon black. Journal of Materials Processing Technology 68(1997): 163-167.

[11.] M.H. Ali, A. Abo-Hashem.Precolation concept and the electrical conductivity of carbon black-polymer composites 3 : Crystallisable chloroprene rubber mixed with FAF carbon black. Journal of Materials Processing Technology 68(1997): 168-171.

[12.] G.M. Nasr.Vulcanization Conditions: How They Affect the Electrical Conductivity of SBR Loaded with the Percolation Concentration of FEF-Black. Polymer Testing 15(1996): 585-591.

[13.] N.C. Das, D. Khastgir, T.K. Chaki, A. Chakraborty. Electromagnetic interference shielding effectiveness of carbon black and carbon fibre filled EVA and NR based composites Composites Part A 31 (2000): 1069-1081.

[14.] F. El-Tantawy. Joule heating treatments of conductive butyl rubber/ceramic superconductor composites: a new way for improving the stability and reproducibility. European Polymer Journal 37 (2001): 565-574.

[15.] F. El-Tantawy. New double negative and positive temperature coefficients of conductive EPDM rubber TiC ceramic composites. European Polymer Journal 38 (2002): 567-577.

[16.] F. El-Tantawy, FS Deghaidy. Effect of iron oxide on vulcanization kinetics and electrical conductance of butyl rubber composites. Polymer International 49 (2000): 1371-1376.

[17.] E.M. Abdel-Bary. Some Factors Affecting the Electrical Properties of Carbon-Black-Loaded Butyl Rubber during Vulcanization. Polymer International 30 (1993): 371-374.

[18.] K.P. Sau,T.K. Chaki and D.Khastgir. The change in conductivity of a rubber-carbon black composite subjected to different modes of pre-strain. Composites Part A 29A (1998): 363-370.

[19.] N.C. Das, D. Khastgir, T.K. Chaki, A. Chakraborty. Electromagnetic interference shielding effectiveness of carbon black and carbon fibre filled EVA and NR based composites. Composites Part A 31 (2000): 1069-1081.

[20.] A.E. Job, F.A. Oliveira, N. Alves, J.A.Giacometti ,L.H.C. Mattoso. Conductive composites of natural rubber and carbon black for pressure sensors. Synthetic Metals 135-136 (2003): 99-100.

[21.] Yue Sun, Eli Ruckenstein. Poly(3-methythiophene)-rubber conductive composite prepared via an inverted emulsion pathway. Synthetic Metals 74 (1995): 145-150.

[22.] M.M. Badawy, G.M. Nasr. Effect of Molding Pressure on the Electrical Conductivity of Conductive NBR/PVC Composites.Polymer Testing 16(1997): 155-164.

[23.] Brydson, J.A. Rubber Materials and Their Compounds. New York: Elsevier Science Publishers, (1988), 147-165, pp.

[24.] Hofmann, W. Rubber Technology Handbook. Munich Vienna New York: Hanser Publishers, (1989), 430-432, pp.

[25.] Dick, J.S. Compounding and Testing for Performance. Rubber Technology. Munich: Hanser Publishers, 2001, 386, pp..

[26.] Barlow, F.W. Rubber Compounding. Principle, Material and Technique. New York: Marcel Dekker, (1998), 97-98, pp.

[27.] Ica Manas-Zloczower, Zehev Tadmor. Mixing and compounding of polymer The USA and Canada: Hanser/Gardner Publication, (1988).

[28.] Bing R. Hsieh, Yen Wei. Semiconducting Polymers Applications, Properties, and Synthesis. American : Library of Congress Cataloging-in-Publication Data, (1999).

[29.] Cabot Corporation, Coatings Business Unit, Chemical Modification of Carbon Black for Improve: www.google.com, (2007).

[30.] Martin Bellander, High Pressure Vulcanization Crosslinking of Diene Rubber Without Vulcanization Agents: www.google.com, (2007).

[31.] Timcal Ltd., Carbon additives for polymer compounds from www.timal.com, 2004.

[32.] Gustavo A.Schwart, Silivina Cerveny. Thermal aging of carbon black filled rubber compounds. I. Experiment evidence for bridging flocculation. Polymer 44 (2003): 7229-7240.

APPENDICES

APPENDIX A

Table A-1 Specification of Carbon black

Properties	CCB 7055	N220 (ISAF-HM)	N234 (ISAF-HS)	N330 (GPF)	N339 (HAF-HS)
BET Nitrigen Surface Area(m^2/g)	55	114	119	78	91
DBP Absorption (CC/100g)	170	112	125	102	120
Iodine (mg/g)	65	121	120	82	90
Pour Density (kg/m^3)	241	355	319	380	345
Particle Size (nm)	42.0	22.2	24.7	26.7	27.9
Ash content(%Max)	0.03	0.25	0.26	0.22	0.24

Table A-2 Specification of neoprene WRT (lot no. 07B0611024)

Item	Unit	Guarantee	Result
Volatile	%	$\leq$ 1.3	0.4
Mooney Viscosity ML1+4@100		42.0~51.0	47.0
Form		Chip	Chip
Color		Deep Cream	Deep Cream
Contamination		None	None
Judgment			Pass

APPENDIX B

Table B-1 Specific gravity calculation of rubber compound

Materials	Weight; W (g)	Density; d (g/cm^3)	Volume (=W/d)
CR WRT	100.00	1.25	80.00
Carbon black	10.00	1.85	5.41
$CaCO_3$	20.00	2.65	7.55
Aromatic Oil	25.00	1.00	24.98
TMQ	2.00	1.04	1.93
Stearic acid	1.00	0.85	1.18
MgO#150	4.00	3.20	1.25
MBTS	2.00	1.54	1.29
ETU-80	1.00	1.27	0.79
ZnO(w)	5.00	5.57	0.89
Total	170.00		125.27

Density = Total weight / Total volume
= 170.00/125.27
= 1.355 (g/cm^3)

Specific gravity = 1.357

APPENDIX C

Table C-1 The Mooney viscosity of CR/CB

Carbon Black Type	phr	Mooney viscosity			
		Sample no.			Medium
		1	2	3	
CCB7055	10	19.4	19.0	20.5	19.4
	20	23.2	24.0	23.5	23.5
	30	32.5	32.0	32.6	32.5
	40	54.9	54.8	55.1	54.9
	50	59.8	59.8	59.8	59.8
	60	69.9	70.3	69.7	69.9
	70	79.2	75.4	79.6	79.2
N220	10	23.1	23.7	23.9	23.7
	20	30.3	31.0	31.9	31.0
	30	50.0	51.6	52.6	51.6
	40	59.8	61.3	61.8	61.3
	50	69.1	68.5	67.5	68.5
	60	84.3	83.6	76.8	83.6
	70	95.4	96.4	98.6	96.4
N234	10	24.9	25.1	24.5	24.9
	20	34.2	35.3	34.2	34.2
	30	54.1	55.1	45.6	54.1
	40	63.3	63.8	62.8	63.3
	50	69.6	71.0	65.5	69.6
	60	85.8	84.3	86.7	85.8
	70	98.7	95.4	99.6	98.7
N330	10	22.5	23.1	24.1	23.1
	20	24.2	25.3	26.4	25.3
	30	45.6	45.0	44.9	45.0
	40	60.8	59.8	58.8	59.8
	50	61.5	61.0	61.0	61.0
	60	75.7	74.3	72.4	74.3
	70	84.6	85.4	85.5	85.4
N339	10	23.8	23.1	23.5	23.5
	20	30.2	29.3	31.3	30.2
	30	45.6	45.6	45.6	45.6
	40	61.1	60.8	59.8	60.8
	50	65.0	65.5	66.1	65.5
	60	76.8	76.7	75.3	76.7
	70	90.0	89.6	89.4	89.6

Table C-2 The Mooney Scorch time of CR/CB

Carbon Black Type	phr	Mooney Scorch Time,t_5(min)			
		Sample no.			Medium
		1	2	3	
CCB7055	10	16.5	16.8	16.9	16.8
	20	13.8	13.3	14.0	13.8
	30	9.0	9.6	9.5	9.5
	40	7.7	7.1	7.9	7.7
	50	6.6	6.3	6.4	6.3
	60	5.9	6.0	5.8	5.9
	70	5.1	5.4	5.3	5.4
N220	10	15.3	16.0	14.5	15.3
	20	9.8	10.0	10.0	10.0
	30	6.0	5.9	6.2	6.0
	40	5.6	5.8	5.7	5.8
	50	5.6	5.0	6.0	5.6
	60	5.2	5.5	5.4	5.4
	70	5.3	5.6	5.1	5.3
N234	10	14.5	16.1	13.0	14.5
	20	10.1	9.6	9.5	9.5
	30	6.0	6.6	5.5	6.0
	40	5.0	5.6	5.7	5.6
	50	4.9	5.0	4.8	4.9
	60	5.1	4.6	4.7	4.7
	70	4.1	5.0	3.9	4.1
N330	10	16.5	16.2	16.1	16.2
	20	14.0	13.7	13.8	13.8
	30	8.1	9.0	7.9	8.1
	40	6.8	6.7	6.6	6.7
	50	6.0	5.8	6.1	6.0
	60	5.5	5.8	5.9	5.9
	70	5.5	5.4	5.3	5.4
N339	10	16.0	16.0	17.1	16.0
	20	12.4	12.5	12.5	12.5
	30	6.9	7.5	7.4	7.4
	40	6.3	6.2	6.1	6.2
	50	6.5	7.0	6.4	6.5
	60	5.7	5.6	5.1	5.7
	70	5.2	5.3	6.5	5.3

Table C-3 The SG of CR/CB vulcanizates

Carbon Black Type	phr	Specific Gravity, g/cm^3			
		Sample no.			Medium
		1	2	3	
CCB7055	10	1.365	1.355	1.346	1.355
	20	1.373	1.375	1.376	1.375
	30	1.394	1.392	1.391	1.392
	40	1.442	1.412	1.410	1.412
	50	1.425	1.428	1.429	1.428
	60	1.434	1.444	1.454	1.444
	70	1.476	1.456	1.455	1.456
N220	10	1.351	1.345	1.354	1.351
	20	1.372	1.371	1.376	1.372
	30	1.391	1.395	1.390	1.391
	40	1.411	1.415	1.410	1.411
	50	1.427	1.429	1.426	1.427
	60	1.445	1.451	1.443	1.445
	70	1.445	1.435	1.496	1.445
N234	10	1.356	1.355	1.356	1.356
	20	1.376	1.376	1.376	1.376
	30	1.391	1.397	1.391	1.391
	40	1.410	1.410	1.410	1.410
	50	1.430	1.436	1.430	1.430
	60	1.444	1.443	1.444	1.444
	70	1.454	1.466	1.454	1.454
N330	10	1.358	1.353	1.352	1.353
	20	1.356	1.374	1.375	1.374
	30	1.385	1.393	1.394	1.393
	40	1.415	1.414	1.412	1.414
	50	1.432	1.429	1.422	1.429
	60	1.445	1.442	1.441	1.442
	70	1.456	1.453	1.452	1.453
N339	10	1.352	1.353	1.350	1.352
	20	1.376	1.379	1.363	1.376
	30	1.395	1.397	1.391	1.395
	40	1.414	1.415	1.412	1.414
	50	1.430	1.436	1.430	1.430
	60	1.441	1.443	1.440	1.441
	70	1.455	1.469	1.448	1.455

Table C-4 The Hardness, ShorA of CR/CB vulcanizates

Carbon Black Type	phr	Hardness, Shor A			
		Sample no.			Medium
		1	2	3	
CCB7055	10	35	36	36	36
	20	42	41	43	42
	30	48	48	47	48
	40	53	55	54	54
	50	59	60	59	59
	60	65	64	65	65
	70	71	70	71	71
N220	10	38	39	37	38
	20	45	46	47	46
	30	53	54	53	53
	40	60	61	62	61
	50	68	69	67	68
	60	75	76	76	76
	70	84	85	84	84
N234	10	40	39	39	39
	20	47	46	48	47
	30	54	54	55	54
	40	61	63	62	62
	50	69	70	71	70
	60	78	79	77	78
	70	85	86	86	86
N330	10	37	36	38	37
	20	42	43	43	43
	30	50	50	50	50
	40	56	57	58	57
	50	64	63	64	64
	60	69	70	71	70
	70	77	76	77	77
N339	10	39	38	38	38
	20	44	45	43	44
	30	50	51	52	51
	40	59	57	58	58
	50	62	63	64	63
	60	71	70	71	71
	70	77	78	79	78

Table C-5 The tensile strength of CR/CB vulcanizates

Carbon Black Type	phr	Tensile strength, MPa			
		Sample no.			Medium
		1	2	3	
CCB7055	10	15.60	15.75	15.84	15.75
	20	15.97	15.89	15.96	15.96
	30	16.03	16.03	16.11	16.03
	40	15.57	15.67	15.37	15.57
	50	14.92	15.37	14.96	14.96
	60	14.73	14.88	14.98	14.88
	70	14.13	14.28	14.58	14.28
N220	10	16.24	17.77	15.76	16.24
	20	17.89	17.03	16.72	17.03
	30	16.80	17.71	17.32	17.32
	40	17.92	17.25	17.13	17.25
	50	16.22	16.65	15.58	16.22
	60	15.95	15.78	15.54	15.78
	70	15.95	14.78	14.99	14.99
N234	10	16.34	16.03	16.45	16.34
	20	18.99	18.24	18.41	18.41
	30	20.00	19.76	18.41	19.76
	40	19.47	19.76	19.36	19.47
	50	19.47	18.86	18.31	18.86
	60	18.95	18.56	18.65	18.65
	70	17.27	17.87	18.55	17.87
N330	10	15.14	15.45	15.55	15.45
	20	15.50	15.65	15.74	15.65
	30	15.68	15.82	15.74	15.74
	40	15.14	15.56	16.04	15.56
	50	15.56	14.26	14.95	14.95
	60	14.27	14.22	14.15	14.22
	70	12.99	13.19	13.13	13.13
N339	10	16.21	16.04	16.35	16.21
	20	17.22	17.43	17.82	17.43
	30	17.94	17.10	17.63	17.63
	40	17.35	17.55	17.63	17.55
	50	16.76	16.04	16.89	16.76
	60	16.19	16.15	16.04	16.15
	70	15.30	15.98	15.61	15.61

Table C-6 The elongation at break, % of CR/CB vulcanizates

Carbon Black Type	phr	Elongation at break, %			Medium
		Sample no.			
		1	2	3	
CCB7055	10	903	1081	903	903
	20	782	833	739	782
	30	599	617	488	599
	40	493	398	590	493
	50	410	399	617	410
	60	358	315	395	358
	70	299	287	325	299
N220	10	833	736	996	833
	20	696	749	550	696
	30	617	600	739	617
	40	488	389	650	488
	50	385	346	393	385
	60	325	470	279	325
	70	285	299	266	285
N234	10	1181	1082	953	1082
	20	779	992	993	992
	30	686	893	997	893
	40	666	739	798	739
	50	893	670	570	670
	60	659	550	458	550
	70	356	470	694	470
N330	10	836	726	1006	836
	20	767	646	850	767
	30	713	560	799	713
	40	557	395	750	557
	50	458	356	593	458
	60	349	570	290	349
	70	256	400	216	256
N339	10	824	913	731	824
	20	691	682	893	691
	30	614	559	697	614
	40	523	494	698	523
	50	409	410	399	409
	60	339	330	455	339
	70	289	296	287	289

Table C-7 The volume resistivity of CR/CB vulcanizates

Carbon Black Type	phr	Volume Resistivity, Ohm.cm			
		Sample no.			Medium
		1	2	3	
CCB7055	10	4.58E+11	4.32E+11	4.32E+11	4.32E+11
	20	5.84E+10	6.44E+11	1.11E+10	5.84E+10
	30	4.66E+08	3.64E+06	3.63E+06	3.63E+06
	40	7.23E+03	9.23E+03	4.87E+03	7.23E+03
	50	1.51E+02	1.61E+02	1.62E+02	1.62E+02
	60	1.10E+02	1.10E+02	1.08E+02	1.10E+02
	70	1.04E+02	1.04E+02	1.10E+02	1.07E+02
N220	10	7.75E+11	5.54E+11	8.77E+11	7.75E+11
	20	6.58E+11	4.47E+11	4.48E+11	4.48E+11
	30	7.55E+09	1.41E+10	9.57E+07	7.55E+09
	40	1.42E+07	1.40E+07	1.44E+07	1.42E+07
	50	1.95E+06	9.86E+04	1.41E+03	9.86E+04
	60	4.86E+03	4.85E+03	4.86E+03	4.86E+03
	70	1.73E+02	4.86E+02	1.81E+03	4.86E+02
N234	10	5.94E+11	9.76E+11	6.53E+11	6.53E+11
	20	5.84E+10	2.36E+11	2.37E+11	2.36E+11
	30	7.95E+09	2.95E+06	1.84E+08	1.84E+08
	40	1.95E+05	9.81E+04	9.82E+04	9.82E+04
	50	1.71E+03	1.74E+03	3.70E+02	1.71E+03
	60	1.36E+04	3.70E+02	3.71E+02	3.70E+02
	70	1.74E+02	1.04E+02	1.71E+02	1.71E+02
N330	10	9.76E+11	7.68E+11	7.69E+11	7.69E+11
	20	6.44E+11	2.36E+11	6.43E+11	6.44E+11
	30	6.55E+09	4.32E+10	1.11E+10	1.11E+10
	40	6.85E+09	9.16E+07	9.17E+07	9.17E+07
	50	4.66E+05	2.75E+06	9.91E+04	4.66E+05
	60	1.30E+04	1.26E+04	1.25E+04	1.26E+04
	70	1.27E+03	1.94E+02	1.26E+03	1.26E+03
N339	10	5.85E+11	5.86E+11	6.44E+11	5.85E+11
	20	3.12E+11	3.11E+11	3.02E+10	3.12E+11
	30	4.32E+10	5.77E+09	5.78E+09	5.77E+09
	40	1.99E+06	1.98E+06	1.16E+06	1.99E+06
	50	2.07E+04	4.46E+05	2.06E+04	2.07E+04
	60	5.07E+02	5.07E+02	5.05E+03	5.07E+02
	70	3.07E+02	3.08E+02	3.01E+02	3.07E+02

VITAE

Ms. Nuengruthai Parajai was born on January 1, 1981, in Uttaradit, Thailand. In 2003, she received B.E in Chemical education, Faculty of Education, Srinakharinwirot University. In 2008, she obtained M.Sc in Petrochemistry and Polymer Science from Department of Chemistry, Faculty of Science, Chulalongkorn University.