วัลคาไนเซชันและสมบัติของยางไนไทรล์ไฮโดรจิเนต/ยางไนไทรล์เบลนด์

นางสาวญาณินี ศรีสุวรรณ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2549

VULCANIZATION AND PROPERTIES OF HYDROGENATED NITRILE RUBBER/NITRILE RUBBER BLENDS

Miss Yaninee Srisuwan

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 2006

Thesis Title VULCANIZATION AND PROPERTIES OF HYDROGENATED NITRILE RUBBER/NITRILE RUBBER BLENDS
By Miss Yaninee Srisuwan
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

……………………………………………Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

THESIS COMMITTEE

……………………………………………Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

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

……………………………………………Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

……………………………………………Member
(Napida Hinchiranan, Ph.D.)

ญาณินี ศรีสุวรรณ : **วัลคาไนเซชันและสมบัติของยางไนไทรล์ไฮโดรจิเนต/ยางไนไทรล์เบลนด์** (VULCANIZATION AND PROPERTIES OF HYDROGENATED NITRILE RUBBER/NITRILE RUBBER BLENDS). อ.ที่ปรึกษา : ศ.ดร. ภัทรพรรณ ประศาสน์สารกิจ, 133 หน้า.

ยางไนไทรล์ไฮโดรจิเนต/ยางไนไทรล์เบลนด์เตรียมโดยเครื่องบดผสมสองลูกกลิ้งที่สัดส่วนเท่ากับ 100/0, 90/10, 80/20 และ 70/30 โดยศึกษาผลของชนิดคาร์บอนแบล็ก ได้แก่ GPF N-660 และ SRF N-774 (50 phr) ด้วยระบบวัลคาไนซ์ต่างๆ คือ ระบบปกติ ระบบอีวีและเปอร์ออกไซด์ ผลการศึกษา พบว่า ลักษณะการวัลคาไนซ์ของยางไนไทรล์ไฮโดรจิเนต/ยางไนไทรล์เบลนด์ที่สัดส่วน 20 และ30 เปอร์เซ็นต์ยางไนไทรล์ที่วัลคาไนซ์ด้วยระบบเปอร์ออกไซด์มีค่าทอร์คสูงสุดและยางที่วัลคาไนซ์ด้วยระบบอีวีมีค่าต่ำที่สุด คอมปาวด์ที่วัลคาไนซ์ด้วยระบบเปอร์ออกไซด์มีค่า 100% โมดูลัสและความทนแรงดึงสูงกว่าระบบซัลเฟอร์ แต่ระยะยืดมีค่าต่ำและคอมปาวด์ที่เติมคาร์บอนแบล็กชนิด GPF N-660 ให้สมบัติเชิงกลดีกว่า SRF N-774 ส่วนสมบัติด้านความทนต่อความร้อน โอโซนและน้ำมันของยางเบลนด์มีค่าลดลงเมื่อปริมาณยางไนไทรล์เพิ่มขึ้น และระบบเปอร์ออกไซด์มีความเสถียรต่อความร้อนดีกว่าระบบซัลเฟอร์ ระบบเปอร์ออกไซด์มีราคาคอมปาวด์ถูกที่สุดและสมบัติเชิงกลดีที่สุด

สาขาวิชา... ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต....Yaminee Srisuwan....
ปีการศึกษา..............2549................ .ลายมือชื่ออาจารย์ที่ปรึกษา..........................

4873404823 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD : HNBR / NBR / BLEND

YANINEE SRISUWAN : VULCANIZATION AND PROPERTIES OF HYDROGENATED NITRILE RUBBER/NITRILE RUBBER BLENDS. THESIS ADVISOR : PROF. PATTARAPAN PRASASSARAKICH, Ph.D., 133 pp.

The HNBR/NBR blends were prepared at ratios of 100/0, 90/10, 80/20 and 70/30 (wt%). The compounds by using a two-roll mixing mill at various ratios filled with two types of carbon black loading, GPF N-660 and SRF N-774 (fixed at 50 phr) were cured by three vulcanization systems: conventional vulcanization, efficient vulcanization and peroxide vulcanization. From the cure characteristics, the HNBR/NBR blends at 20 and 30%NBR cured by peroxide system exhibited maximum torque and the blends cured by EV system showed the lowest. The HNBR/NBR blends cured by peroxide system also exhibited the higher 100%modulus and tensile strength with lower elongation at break than that cured by sulfur system. The N-660 filled vulcanizate exhibited the better mechanical properties than filled N-774 vulcanizate. Thermal aging, ozone and oil resistance properties of HNBR/NBR blends decreased with increasing the NBR content. The HNBR/NBR blends cured by peroxide system showed the better heat stability than that cured by sulfur system. The cost of the HNBR/NBR blend using peroxide curing systems which have the superior mechanical properties showed the lowest cost of compound.

Field of Study..Petrochemistry and polymer science.. Student's signature....Yaninee Srisuwan....

Academic year............2006.................. 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 Supawan Tantayanon, Ph.D., Associate Professor Wimonrat Trakarnpruk, Ph.D. and Napida Hinchiranan, Ph.D., serving as the chairman and members of her thesis committee, respectively, for their valuable suggestions and comments.

The author also wishes to express her appreciation to Inoac Tokai (Thailand) Co., Ltd. for their support with processing machine, testing equipment and materials. Finally, the author wishes to express deep gratitude to her parents and brothers for their understanding and encouragement. Without all of them, she would not have withstood many difficulties that encountered.

CONTENTS

PAGE

PAGE

PAGE

PAGE

LIST OF TABLES

TABLES **PAGE**

TABLES **PAGE**

TABLES **PAGE**

TABLES **PAGE**

LIST OF FIGURES

FIGURES **PAGE**

FIGURES **PAGE**

FIGURES **PAGE**

FIGURES **PAGE**

LIST OF ABBREVIATIONS

^{O}C	Degree Celsius
g	gram
kg	Kilogram
mg	Milligram
MW	Molecular Weight
μm	Micrometer
%wt	Percent by weight
Med	Median
nm	Nanometer
phr	Part per hundred rubber
pphm	Part per hundred million
TMTD	Tetramethylthiuram disulfide
MBTS	2, 2'-Dithiobisbenzothiazole
TAIC	Triallyl isocyanate
ASTM	The American Society for Testing and Material
JIS	Japanese Industrial Standard
DMTA	Dynamic Mechanical Thermcal Analysis
CV	Conventional Vulcanization
SEV	Semi-efficient Vulcanization
EV	Efficient Vulcanization
h	Hour

CHAPTER I

INTRODUCTION

1.1 The Statement of Problem

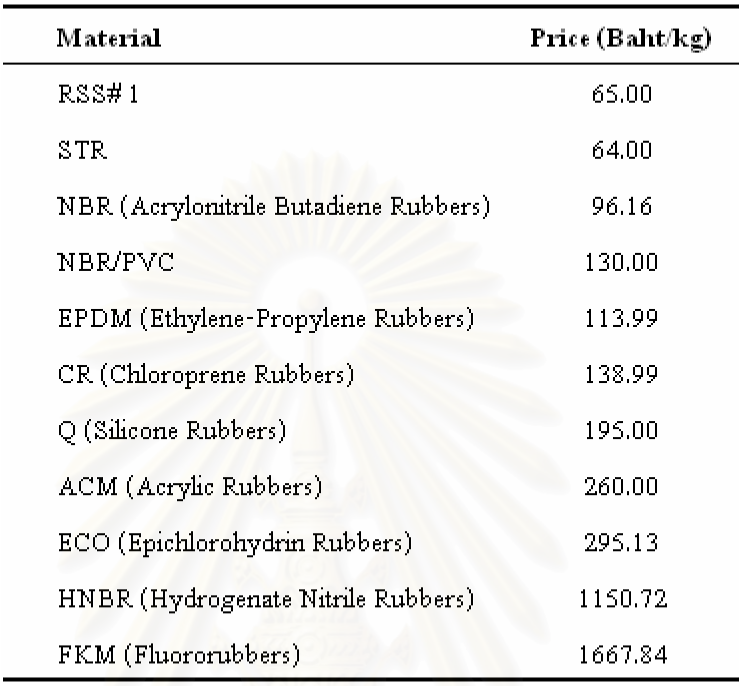
In recent years Thailand is often referred as the "Detroit of Asia". Automobile, motorbike, auto and motorcycle spare parts and items for the after sale auto market are made by numerous factories throughout Thailand. In fact, the Auto Industry is the number one manufacturing industry in Thailand in terms of value, followed by Hard Disk Drive manufacture. Increasingly the Thai government's policy of early promotion of the Auto Industry and then recent acceleration of trade preferences under the Asia Free Trade Area (AFTA), FTAs with Australia, India and pending FTA's with China and the U.S. are creating even more favorable conditions in which the economies of scale and efficiencies of the Thai Auto and parts industry are magnifying Thailand's advantages in this area. The automotive industry is one of the major routes taken by developing countries on their way to becoming industrialized. This is mainly because it paves the way for a large number of related and connecting industries. Thailand is no exception. Automobiles and parts industries in Thailand were expanded continuously. The year 2003, the new vehicle sales locally has enlarged 30.25%, reaching 533,176 units. The pick-up 1 ton remains the core of market sharing. The export vehicle sales in 2003 were grown 29.56%, getting 235,122 units. The export value was 102,207.92 million baht. The three main exporters are Mitsubishi (export vehicles 66,991 units), Mazda (export vehicles 5,214 units) and Honda (export vehicles 37,769 units). In 2003, the auto production was expanded 26.86% compared with the year 2002, to 742,062 units and export motorcycles roughly were 600,000 units, increased 3.36% or 105 billoin baht [1].

In tradition polymer material selection, designers consider part performance requirements in narrowing down, or pruning, a set of candidate materials. Typical issues include material cost, stiffness, creep, impact and fatigue resistance, dimensional stability, service temperature, chemical and UV resistance, hardness or abrasion resistance, regulation compatibility, flow characteristics, and surface finish.

Quantitative pruning of candidate materials occurs on several levels. For instance, aesthetic, regulation, and service environment requirements can immediately eliminate certain materials. In addition, detailed structural and process analyses, mechanical, thermal, cost and processing properties requirements will narrow the search even further. For critical applications, or for part requirement for which no adequate predictive models may exist (e.g., long term creep, or abrasion resistance), engineers must often resort to prototype and testing to arrive at a final material choice [2].

In the search on material behavior required for various applications, the process ability of two or more polymer mixtures has been much interesting. A major feature of two polymer mixtures is the dependence of the resulting properties on various characteristics of components: structure, blending ratio, morphology, purity and stabilization along with the prevalent conditions. However, blend stability determines the success during both production and end-use. The objective of the blending of different polymers, it is possible to bring the properties of the individual components to a single material. This technique has helped to develop many materials, to be better and cheaper in market. Table 1.1 shows the examples of elastomer cost in tradition.

Table 1.1 Elastomer cost in 2006-2007 [3].



Material	Price (Baht/kg)
RSS# 1	65.00
STR	64.00
NBR (Acrylonitrile Butadiene Rubbers)	96.16
NBR/PVC	130.00
EPDM (Ethylene-Propylene Rubbers)	113.99
CR (Chloroprene Rubbers)	138.99
Q (Silicone Rubbers)	195.00
ACM (Acrylic Rubbers)	260.00
ECO (Epichlorohydrin Rubbers)	295.13
HNBR (Hydrogenate Nitrile Rubbers)	1150.72
FKM (Fluororubbers)	1667.84

1.2 Objective of the Research Work

The objective of this work is to study the effect of carbon black type and vulcanization system on physical and mechanical properties of Hydrogenated Nitrile Rubber/Nitrile Rubber (HNBR/NBR) blends.

1.3 Scope of the Reseach Work

The HNBR/NBR blends were prepared at ratios of 100/0, 90/10, 80/20 and 70/30 (wt%). The effect of two types of carbon black at 50 phr and different vulcanization systems on properties of rubber blends were investigated.

The experimental procedures were carried out as follows:

1. Literature survey and study the previous research works.
2. Prepare the HNBR/NBR compounds by using a two-roll mixing mill at various ratios filled with two types of carbon black loading, GPF N-660 and SRF N-774 (fixed at 50 phr) and with different vulcanization systems: conventional vulcanization, efficient vulcanization and peroxide vulcanization.
3. Study the cure characteristics of HNBR/NBR blends using moving die rheometer (MDR2000) to find the optimum curing time.
4. Prepare the vulcanizates by compression molding at 170°C and 120 kg/cm^2.
5. Investigate the mechanical properties such as tensile properties, hardness and compression set of the vulcanizates.
6. Investigate the thermal aging properties and ozone resistance of the vulcanizates.
7. Investigate the oil resistance properties and the crosslinking density of the vulcanizates.
8. Investigate the thermal properties using Dynamic Mechanical Thermal Analysis (DMTA) technique.
9. Investigate the morphological properties using Scanning Electron Microscope (SEM) technique.
10. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Elastomers [4]

Elastomers are long polymer chains above their glass transition temperature. Elastomers are usually lightly crosslinked and are easily deformed. The term elastomer is often used interchangeably with the term rubber, and is preferred when referring to vulcanizates. Elastomer comes from two terms, elastic (describing the ability of a material to return to its original shape when a load is removed) and mer (from polymer, in which poly means many and mer means parts). Each link of the chain is the "-mer" or basic unit that is usually made of carbon, hydrogen, oxygen and/or silicon. To make the chain, many links or "-mers" are hooked or polymerized together. They are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. At ambient temperatures rubbers are thus relatively soft and deformable. Their primary uses are for seals, adhesives and molded flexible parts.

Elastomers are usually thermosets (requiring vulcanization) but may also be thermoplastic (see thermoplastic elastomer). The long polymer chains cross-link during curing. The molecular structure of elastomers can be imagined as a 'spaghetti and meatball' structure, with the meatballs signifying cross-links. The elasticity is derived from the ability of the long chains to reconfigure themselves to distribute an applied stress. The covalent cross-linkages ensure that the elastomer will return to its original configuration when the stress is removed. As a result of this extreme flexibility, elastomers can reversibly extend from 5-700%, depending on the specific material. Without the cross-linkages or with short, uneasily reconfigured chains, the applied stress would result in a permanent deformation as shown in Figure 2.1.

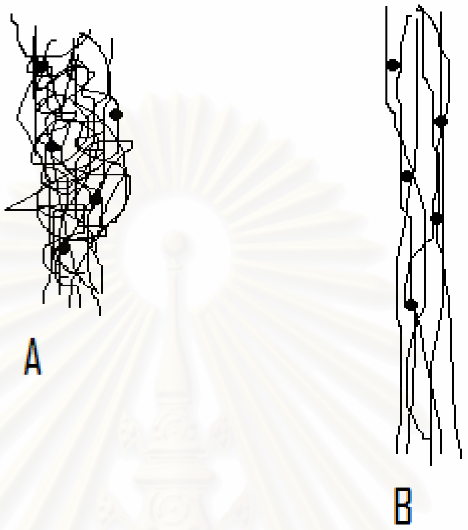


Figure 2.1 A) is a schematic drawing of an unstressed polymer. The dots represent cross-links. B) is the same polymer under stress. When the stress is removed, it will return to the A configuration [4].

Temperature effects are also present in the demonstrated elasticity of a polymer. Elastomers that have cooled to a glassy or crystalline phase will have less mobile chains and consequentially less elasticity than those manipulated at temperatures higher than the glass transition temperature of the polymer.

Unsaturated rubbers that can be cured by sulfur vulcanization: Natural Rubber (NR), Polyisoprene (IR), Butyl rubber (copolymer of isobutylene and isoprene, IIR), Halogenated butyl rubbers (Chloro Butyl Rubber: CIIR; Bromo Butyl Rubber: BIIR), Polybutadiene (BR), Styrene-butadiene Rubber (copolymer of polystyrene and polybutadiene, SBR), Nitrile Rubber (copolymer of polybutadiene and acrylonitrile-NBR), also called buna N rubbers, Hydrogenated Nitrile Rubbers (HNBR) Therban and Zetpol, Chloroprene Rubber (CR), polychloroprene, Neoprene, Baypren etc.

Saturated Rubbers that cannot be cured by sulfur vulcanization: EPM (ethylene propylene rubber, a copolymer of polyethylene and polypropylene) and EPDM rubber (ethylene propylene diene rubber, a terpolymer of polyethylene, polypropylene and a diene-component), Epichlorohydrin rubber (ECO), Polyacrylic rubber (ACM, ABR), Silicone rubber (SI, Q, VMQ), Fluorosilicone Rubber (FVMQ) Fluoroelastomers (FKM, FPM) Viton, Tecnoflon, Fluorel and Dai-El, Perfluoroelastomers (FFKM), Tetrafluoro ethylene/propylene rubbers (FEPM), Chlorosulfonated Polyethylene (CSM), (Hypalon), Ethylene-vinyl acetate (EVA) .

2.2 Polymer Blends [5]

Sometimes user wants a material that has the some of the properties of one polymer, and some of the properties from another. Instead of going back into the lab and trying to synthesize a brand new polymer with all the desired properties, the mixing of two polymers together to form a blend will hopefully have some properties of both. In general, a miscible blend of two polymers is going to have properties somewhere between those of the two unblended polymers. Take for example the glass transition temperature, or T_g for short. If user take polymer A and blend it with polymer B, the T_g will depend on the ratio of polymer A to polymer B in the blend. This can see in the Figure 2.2.

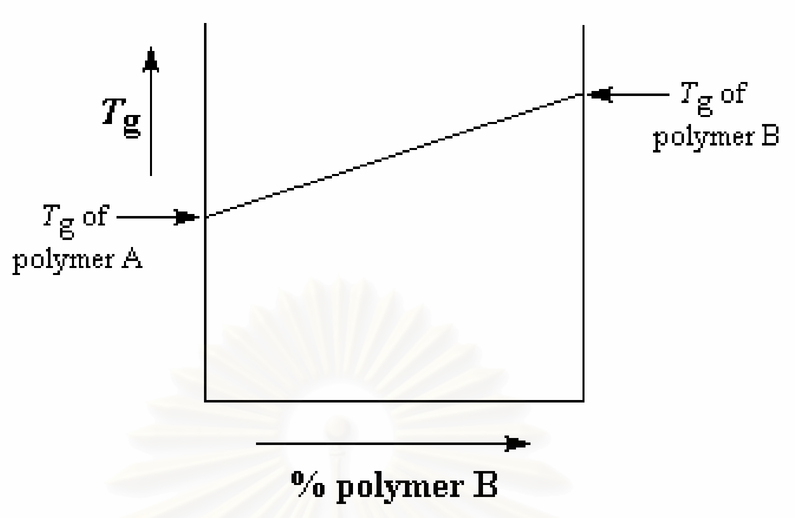


Figure 2.2 Glass transition temperatures, polymer A and blend it with polymer B [5].

If polymer B has a higher T_g than polymer A, the T_g of the blend is going to increase as the relative amount of polymer B in the blend increases. The increase is generally linear, like you see in the graph. But the plot isn't perfectly linear. Sometimes if the two polymers bind more strongly to each other than to themselves, the T_g will be higher than expected, because the stronger binding lowers chain mobility.

The shape is made by the two phases and the arrangement of the two phases morphology. The biggest one can do to affect the morphology of an immiscible blend is to by controlling the relative amounts of the two polymers. For trying to make an immiscible blend from two polymers (polymer A and polymer B), If the blend has the more of polymer A than polymer B, polymer B separates into little spherical globs. The spheres of polymer B will be separated from each other of polymer A, as shown in the Figure 2.3. In such a case, polymer A is the major component and polymer B is the minor component.

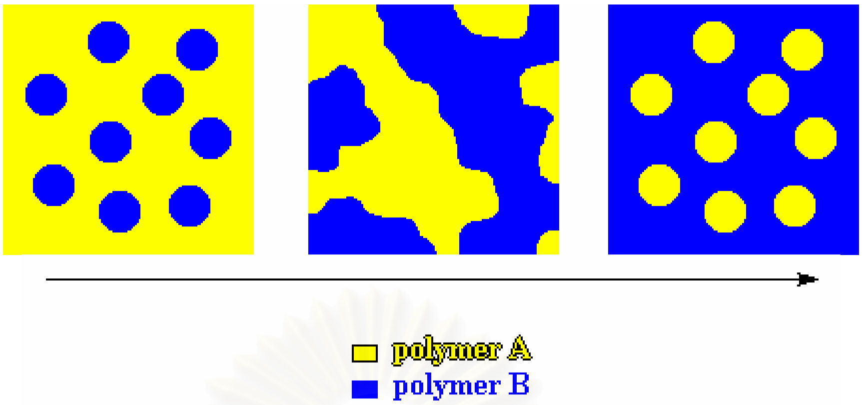


Figure 2.3 Relative amount of polymer B in the immiscible blend [5].

But if the higher content of polymer B is added into the immiscible blend, that spheres will get bigger and then they become jointed together as a continuous phase. The immiscible blend now looks like the middle picture above. It might help to think of a block of Colby-jack cheese. The domains of polymer B are now jointed together, but so are the domains of polymer A. When this happens, say that the polymer A phase and the polymer B phase are co-continuous.

2.2.1 Blending Methods [6]

From the practical point of view, the first consideration must be the available methods for elastomer blending. These are encompass latex blending, solution blending, combinations of these methods, conventional mechanical and mechanochemical mixing methods, and powder mixing in special cases.

1) Latex : Since the coagulation of mixture of lattices may be a random process which is entirely dependent upon soap concentration, latex blending offers the possibility of finer-scale dispersions rather than solution blending.

2) Solution : The solution blending of incompatible polymers is hindered to some extent by the high mobility of the solution prior to recovery, which permits a relatively gross separation of the polymers into their constituent phases. Such blends may be macroheterogeneous rather than microheterogeneous.

3) Solution and Latex : A number of processes have been developed for preparation of elastomer blends from combinations of polymer solutions and lattices. Claimed advantages of the processes are simplification of the polymer recovery procedures, and products with better dispersion of fillers than that would be obtained from a mechanical mixture of dry rubbers.

4) Mechanical : It has been recognized that, while two polymers may be virtually mutually insoluble, blends may be produced which are macroscopically homogeneous and have useful properties provided by sufficiently mechanical mixing to get the high viscosity to prevent the gross phase separation. Such blends are termed microheterogeneous. The high shearing forces required to blend high molecular weight elastomers are such that mechanical blending is confined to open roll mills, internal mixers, and extruders. With regard to open roll mills, attention has been called to the desirability of similar polymer viscosities (at the mixing temperature) for ease of dispersion.

5) Mechanochemical : Under certain conditions, the mechanical working of a mixture of polymers can lead to interpolymerization. For example, when the tendency of the polymeric radicals produced by mechanical rupture is to recombine rather than to disproportionate, block copolymer formation may be favored.

6) Powder Rubbers : The use of powdered rubbers is increasing and the possibility of blending a powdered rubber with a solid rubber by conventional mixing techniques is obvious. Blending of two rubbers-both in powdered form is also possible.

2.3 Acrylonitrile-Butadiene Rubbers (NBR) [7]

NBR is produced by emulsion polymerization system. The water, emulsifier/soap, monomers (butadiene and acrylonitrile), radical generating activator, and other ingredients are introduced into the polymerization vessels. The emulsion process yields a polymer latex that is coagulated using various materials (e.g. calcium chloride, aluminum sulfate) to form crumb rubber that is dried and compressed into bales. Figure 2.4 shows the chemical structure of NBR, indicating the three possible isomeric structures for the butadiene segments.

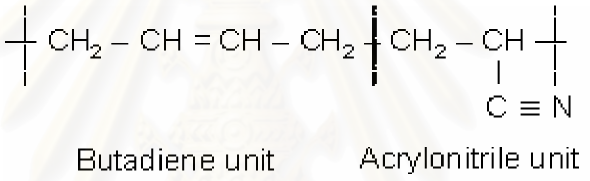


Figure 2.4 Structures NBR [7].

Some specialty of products are packaged in the crumb form. Most NBR manufacturers make at least 20 conventional elastomer variations, with one global manufacturer now offering more than 100 grades from which to choose. NBR producers vary polymerization temperatures to make "hot" and "cold" polymers. Acrylonitrile (ACN) and butadiene (BD) ratios are varied for specific oil and fuel resistance and low temperature requirements. Special NBR polymers which contain a third monomer (e.g. divinyl benzene, methacrylic acid) are also offered. Some NBR elastomers are hydrogenated to reduce the chemical reactivity of the polymer backbone, significantly improving heat resistance. Each modification contributes uniquely different properties. Figure 2.5 shows the typical NBR manufacturing process

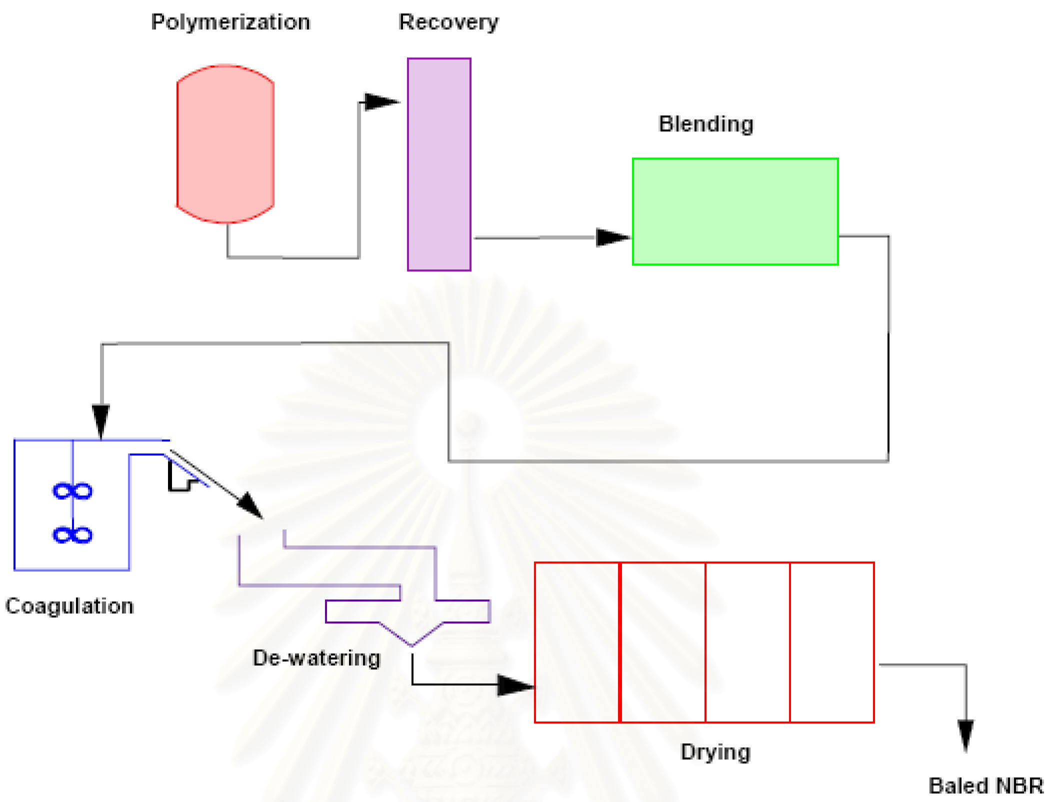


Figure 2.5 NBR manufacturing process [7].

2.3.1 Properties and Applications of NBR

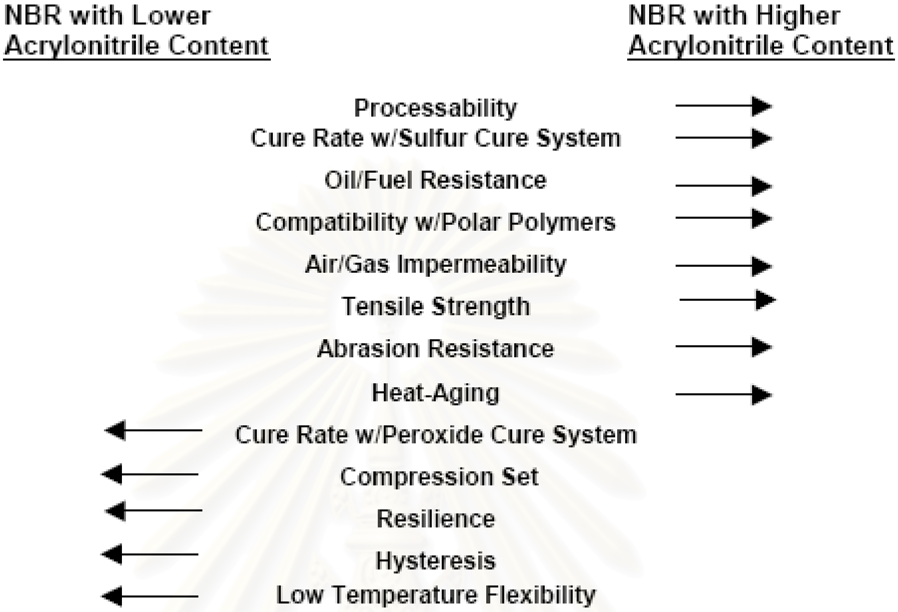
NBR is commonly considered to the workhorse of the industrial and automotive rubber products industries. NBR is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene. By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder can use NBR in a wide variety of application areas requiring oil, fuel, and chemical resistance. In the automotive area, NBR is used in fuel and oil handling hoses, seals and grommets, and water handling applications. With a temperature range of –40°C to +125°C, NBR materials can withstand all including the most severe automotive applications. On the industrial side, NBR is used in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications. Worldwide consumption of NBR is expected to reach 368,000 metric tons annually by the year 2005.

Like most unsaturated thermoset elastomers, NBR requires formulating with added ingredients, and further processing to make useful articles. Additional ingredients typically include reinforcement fillers, plasticizers, protectants, and vulcanization packages. Processes include mixing, pre-forming to required shape, application to substrates, extrusion, and vulcanization to make the finished rubber article. Mixing and processing are typically performed on open mills, internal mixers, extruders, and calenders. Finished products are found in the marketplace as injection or transfer molded products (seals and grommets), extruded hose or tubing, calendered sheet goods (floor mats and industrial belting), or various sponge articles.

2.3.2 Acrylonitrile (ACN) Content

The ACN content is one of two primary criteria defining each specific NBR grade. The ACN level, by reason of polarity, determines several basic properties, such as oil and solvent resistance, low-temperature flexibility/glass transition temperature, and abrasion resistance. Higher ACN content provides the improvement of solvent, oil and abrasion resistance along with higher glass transition temperature. Table 2.1 summarizes most of the common properties of conventional NBR polymers. The direction of the arrows signifies an increase/improvement in the values.

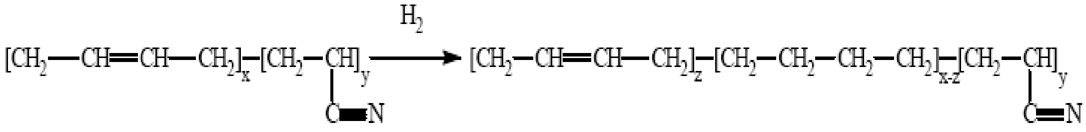
Table 2.1 NBR properties – relationship to acrylonitrile content [7].



NBR with Lower Acrylonitrile Content		NBR with Higher Acrylonitrile Content
	Processability	→
	Cure Rate w/Sulfur Cure System	→
	Oil/Fuel Resistance	→
	Compatibility w/Polar Polymers	→
	Air/Gas Impermeability	→
	Tensile Strength	→
	Abrasion Resistance	→
	Heat-Aging	→
←	Cure Rate w/Peroxide Cure System	
←	Compression Set	
←	Resilience	
←	Hysteresis	
←	Low Temperature Flexibility	

2.4 Hydrogenated Nitrile Butadiene Rubbers (HNBR) [8]

The basic structure of an HNBR elastomer is provided in Figure 2.6. As outlined below, the process begins with the production of an emulsion-polymerized NBR. This polymer is then dissolved in an appropriate solvent. After the dissolution process is complete, the addition of hydrogen gas, in conjunction with a precious metal catalyst at a designated temperature and pressure, brings about a selective hydrogenation to produce a “highly saturated nitrile” (HSN) polymer. Even today, HNBR is still sometimes referred to as “HSN”.



$$[CH_2-CH=CH-CH_2]_x-[CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}}]_y \xrightarrow{H_2} [CH_2-CH=CH-CH_2]_z-[CH_2-CH_2-CH_2-CH_2]_{x-z}-[CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}}]_y$$

Figure 2.6 The basic structure of an HNBR [8].

The solvent and catalyst are then recovered and the remaining crumb is dried. The dried product is then baled and packaged. This process is outlined in Figure 2.7 below.

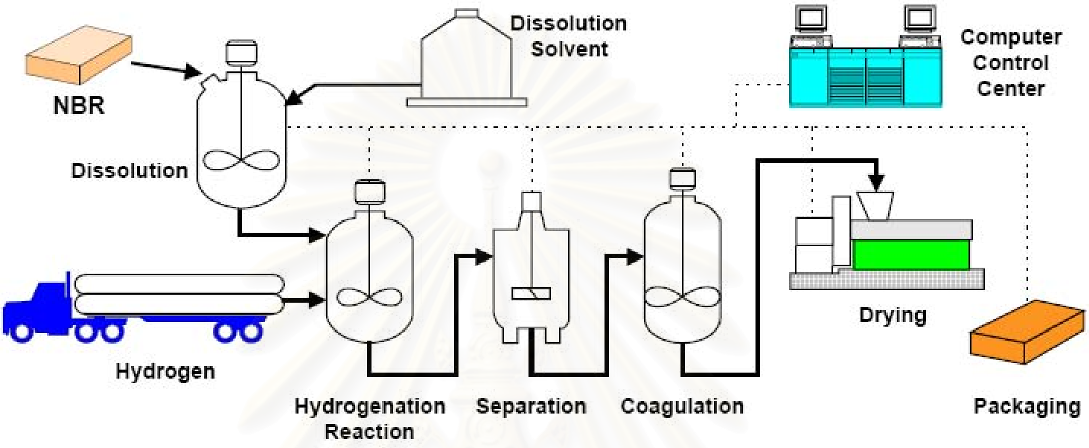


Figure 2.7 HNBR production process [8].

2.4.1 Properties and Applications of HNBR

Compounding techniques allow for HNBR to be used over a broad temperature range, -40°C to 165°C, with minimal degradation over long periods of time. For low-temperature performance, low ACN grades should be used; high-temperature performance can be obtained by using highly saturated HNBR grades with white fillers. As a group, HNBR elastomers have excellent resistance to common automotive fluids (e.g., engine oil, coolant, fuel, etc.) and many industrial chemicals. Like NBR, fluid and chemical resistance improves as the ACN content is increased. The unique properties attributed to HNBR have resulted in wide adoption of HNBR in automotive, industrial, and assorted, performance-demanding applications. On a volume basis, the automotive market is the largest consumer, using HNBR for a host of dynamic and static seals, hoses, and belts. HNBR has also been widely employed in industrial sealing for oil field exploration and processing, as well as rolls for steel and paper mills.

There are a wide variety of acrylonitrile (ACN) content polymers available in the HNBR market today. They range from approximately 17 to 50% ACN. The ACN content not only controls fluid resistance but also impacts the low-temperature performance. If the ACN content of the polymer is increased, the volume swell of the associated compound will decrease while the low-temperature flexibility will become poorer. Alternatively, if one decreases the ACN level of the polymer, the associated compound will have higher volume swell and improved low-temperature flexibility.

2.5 Vulcanization [9]

Vulcanization is a process that converts a viscous entanglement of long chain molecules into a three-dimensional elastic network by chemically joining (crosslinking) these molecules at various points along the chain in Figure 2.8.

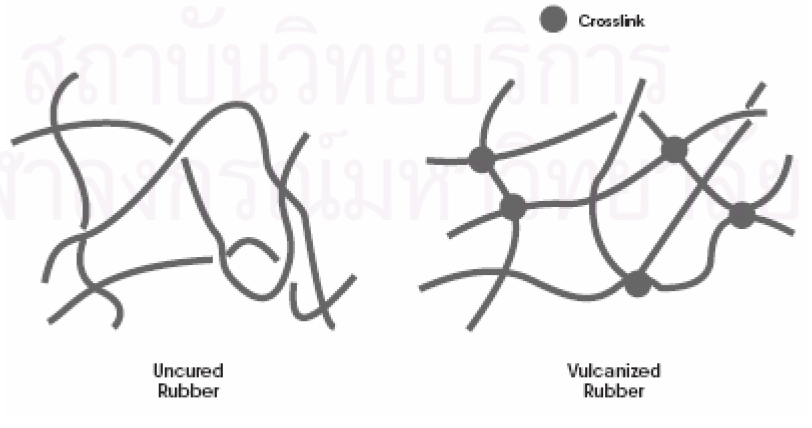


Figure 2.8 The crosslinking a three-dimensional elastic network [9].

Crosslinking or curing, i.e., forming covalent, hydrogen or other bonds between polymer molecules, is a technique used very widely to alter polymer properties. The first commercial method of crosslinking has been attributed to Charles Goodyear in 1839. His process, heating rubber with sulfur, was first successfully used in Springfield, Massachuseets, in 1841. Thomas Hancock used essentially the same process about year later in England. Heating natural rubber with sulfur resulted in improved physical properties. However, the vulcanization time was still too long (> 5 h) and the vulcanizate suffered from disadvantages, e.g., aging properties.

Since these early days, the process and the resulting vulcanized articles have been greatly improved. In addition to natural rubber, many synthetic rubbers have been introduced over the years, Furthermore, many substances other than sulfur have been introduced as components of curing (vulcanization) systems.

The accelerated sulfur vulcanization of gerneral purpose diene rubbers (e.g., natural rubber (NR), styrene butadiene rubber (SBR), and butadiene rubber (BR)) in the presence of organic accelerators and other rubbers, which are vulcanized by closely related technology (e.g., ethylene-propylene-diene terpolymer (EPDM) rubber, butyl rubber (IIR), halobutyl rubber (XIIR), nitrile rubber (NBR)) comprises more than 90% of all vulcanizations.

There are many types of vulcanization systems. Deciding which system is optimal for a given application depends on the required curing conditions, the elastomer or elastomer blend employed, and the desired physical properties of the final vulcanizate. The most widely used systems are accelerated sulfur vulcanization, curing with phenolic resins or similar compounds, using metal oxides for crosslink formation, and vulcanization with peroxides and coagents. Both sulfur vulcanization and most resin curing systems require unsaturated polymers for effective reactions. The use of metal oxides is only compatible with polymers containing halides allylic to pendant vinyl groups. Peroxides, however, are capable of vulcanizing most polymer types, including unsaturated and saturated elastomers, fluoroelastomers, and silicones. The use of coagents synergistically with peroxides helps expand the utility of this vulcanization process.

The vulcanization behavior is important to the processor, who has to know how long and at what temperature scorching occurs and vulcanization is complete. A rubber compound is transformed from a viscous to an elastic material during vulcanization so that the mechanical properties such as hardness, tensile strength, damping, modulus etc. change. Monitoring one or several of these data permits the evaluation of the degree of vulcanization as a function of time and temperature. A typical rheometer trace is shown in Figure 2.9. This procedure is the most reliable but the most complicated one as well.

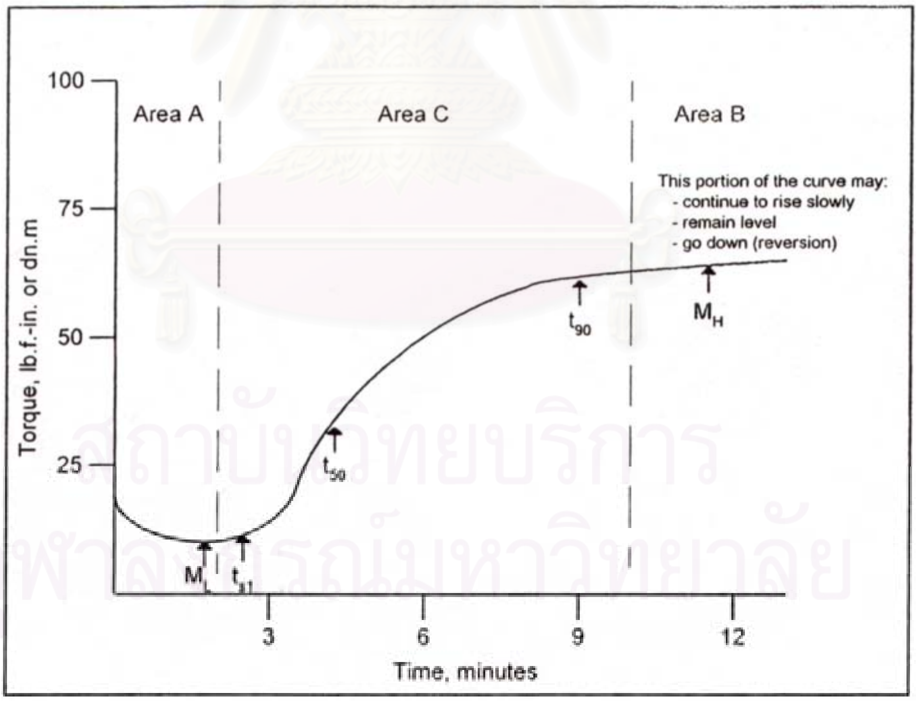


Figure 2.9 Typical rheometer trace [9].

The measurements which can be made from this trace and the terms used to describe them are:

Area A : This gives an indication of compound viscosity.

Area B : This indicates the rate of cure of the compound.

Area C : This indicates the state of cure of the vulcanizate.

M_L, Minimum torque : A measure of the viscosity of the uncured compound.

M_H, Maximum torque : A measure of cure state. With some compounds, maximum torque can be related to vulcanizate modulus and hardness.

ts_1: Time for torque to increase 1 dn.m (0.1 N.m) or 1 lbf-in above M_L- a measure of scorch time or processing safety. Some laboratories use ts_2 instead of ts_1.

t_{50}, t_{90} : Time to reach 50% or 90% of maximum torque development, calculated as time to 0.5 M_H or 0.9 M_H - a measure of cure rate or an estimate of cure time at the test temperature. The shorter the time, the faster the cure rate.

2.5.1 Sulfur-Based Vulcanization [9]

Over the years three special types of cure systems have been develop. They are:

- Conventional vulcanization (CV) systems,
- Efficient vulcanization (EV) systems and
- Semi-efficient vulcanization (SEV) systems.

EV systems are those where a low leval of sulfur and a correspondingly high level of accelerator or sulfurless curing are employed in vulcanization for which an extremely high heat and reversion resistance is required. In the conventional curing systems, the sulfur dosage is high and correspondingly the accelerator level is low. The CV systems provides better flex and dynamic properties but worse thermal and reversion resistance. For optimum levels of mechanical and dynamic properties of vulcanizates with intermediate heat, reversion, flex and dynamic properties, the so-called SEV systems with an intermediate level of accelerator and sulfur are employed. The levels of accelerator and sulfur in CV, SEV and EV system are shown in Table 2.2

Table 2.2 CV, SEV and EV vulcanization systems [9].

Type	Sulfur (S, phr)	Accelerator (A, phr)	A/S ratio
CV	2.0-3.5	1.2-0.4	0.1-0.6
SEV	1.0-1.7	2.4-1.2	0.7-2.5
EV	0.4-0.8	5.0-2.0	2.5-12

Many studies have documented both the advantages (increase age resistance), and the disadvantages (impaired fatigue resistance) of EV and SEV systems. The worse fatigue resistance correlates to lower amounts of polysulfidic crosslinks in the network. The CV systems provide higher amounts of poly- and disulfidic crosslinks and higher proportions of sulfidic and non-sulfidic modifications. This combination provides high flex fatigue resistance but at the expense of heat and reversion resistance. A schematic representation of crosslinks formed in sulfur vulcanization is shown in Figure 2.10.

(a) (b)

Figure 2.10 Schematic representation of sulfur crosslinks formed during vulcanization using (a) mono- and disulfidic crosslinks, (b) and polysulfidic crosslink [9].

The vulcanizate structures and propertiess for CV, SEV and EV systems are shown in Table 2.3.

Table 2.3 Vulcanizate structures and properties [9].

Features	**Systems**		
	CV	**SEV**	**EV**
Poly- and disulfidic crosslink (%)	95	50	20
Monosulfidic crosslinks (%)	5	50	80
Cyclic sulfide (conc.)	High	Medium	Low
Non-sulfidic (conc.)	High	Medium	Low
Reversion resistance	Low	Medium	High
Heat aging resistance	Low	Medium	High
Fatigue resistance	High	Medium	Low
Heat build up	High	Medium	Low
Tear resistance	High	Medium	Low
Compression set (%)	High	Medium	Low

2.5.2 Non-Sulfur Vulcanization

Elastomer with chemically saturated backbones cannot be crosslink with sulfur and so require alternate curing agents. The most widely used are the peroxides, which are also used with unsaturated elastomers. Metal oxides or difunctional compounds are used in special cases.

2.5.2.1 Peroxide Vulcanization [9]

Crosslinking with peroxides has been known since 1915 when Ostromyslenski disclosed that natural rubber could be transformed in a crosslinked state with dibenzoyl peroxide. However, little interest in peroxide crosslinking evolved until the development of fully saturated ethylene-propylene copolymers in the early 1970s.

The use of peroxides for the crosslinking of elastomer is limited to those that are stable during storage, safe to handle during processing. On the other hand, the peroxides are decomposed sufficiently fast at cure temperatures. In order to meet these requirements, peroxides containing tertiary carbon atoms are most suitable, whilst peroxy groups bonded to primary and secondary carbon atoms are less stable. Organic peroxides that are suitable for crosslinking elastomers are shown in Figure 2.11. Peroxides containing more than one peroxy groups are also suitable (Figure 2.12).

A further limitation with regard to the suitability of peroxides concerns the efficiency of crosslinking. Higher efficiencies are observed for those peroxides that form one of the radicals shown in Figure 2.13 during hemolytic decomposition.

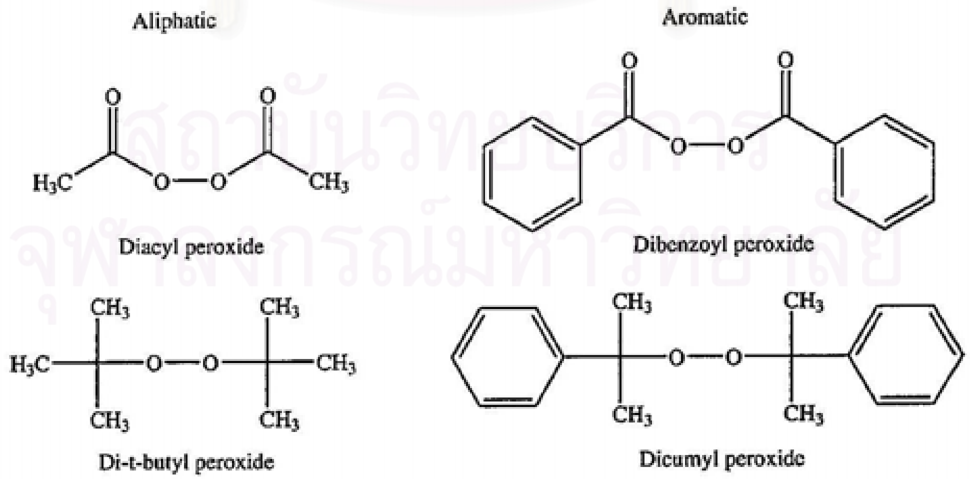
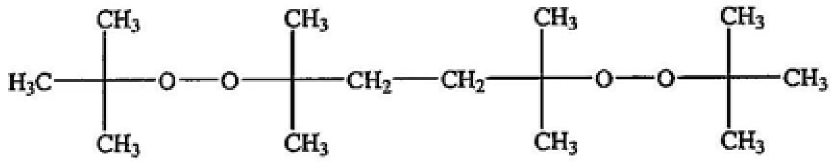
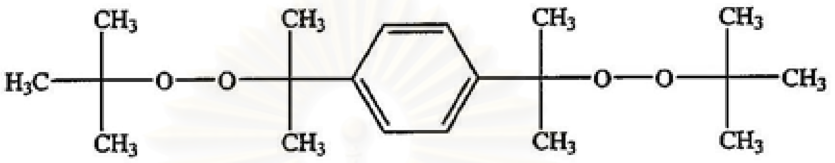


Figure 2.11 Organic peroxides for crosslink elastomers [9].

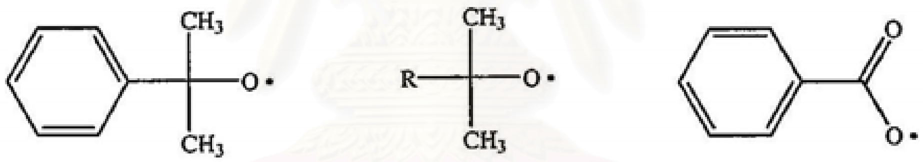


2,5-Bis(tert-butylperoxy)-2,5 dimethyl hexane



1,4-Bis(tert-butylperoxy isopropyl) benzene

Figure 2.12 Peroxides containing more than one peroxide group [9].



Cumyloxy radical Alkyloxy radical Acyloxy radical

Phenyl radical Methyl radical

Figure 2.13 Radicals formed during the hemolytic cleavage of peroxides that are most effective in producing crosslink [9].

Networks formed from peroxide vulcanization typically possess good heat-ageing stability and low compression set. These qualities are a direct manifestation of the chemical composition of the covalent crosslinks formed. Synergistic use of multifunctional coagents can improve upon these properties by increasing the crosslink density of the network and by altering the crosslink composition. Greater adhesion to polar substrates and a better balance of heat-aged and dynamic properties result from a judicious choice of coagent. There are many functional compounds that have been used as coagents for peroxide cure. The final properties of the formed network will depend on the reactivity and structure of the coagent. Understanding these structure-property relationships will allow for more informed coagent selection [10].

The present article will review the use of peroxides to cure elastomer systems, and introduce the concept of improving vulcanizate performance by proper coagent selection through an understanding of structure-property relationships. Many commercially available coagent types will be discussed, along with relevant application data supporting their use.

The choice of peroxide type to employ in a given system typically depends on the desired cure temperature and cure rate, as well as the microstructure of the elastomer. Peroxides with faster cure rates, such as the diacyl peroxides and peroxyesters, are inherently less stable and exhibit faster half-life times or reduced ten-hour half life temperatures. More stable peroxides include the dialkyl and dicumyl types. However, peroxide stability is sacrificed for reactivity. For example, only the more highly reactive radical products of diacyl peroxides are suitable for the vulcanization of silicone elastomers. However, dialkyl peroxides are favored for unsaturated polymers, as they exhibit more discriminating reactivity in these allylic-hydrogen rich elastomer systems. The variety of peroxide structures available commercially allows for the fine-tuning of reactivity toward a given elastomer, and provides for the selection of radicals that balance effective crosslink formation with deleterious side reactions. Figure 2.14 provides a mechanistic scheme for peroxide vulcanization, describing both the desirable reactions which lead to effective crosslink formation and those competing reactions which detract from productive use of radicals [10].

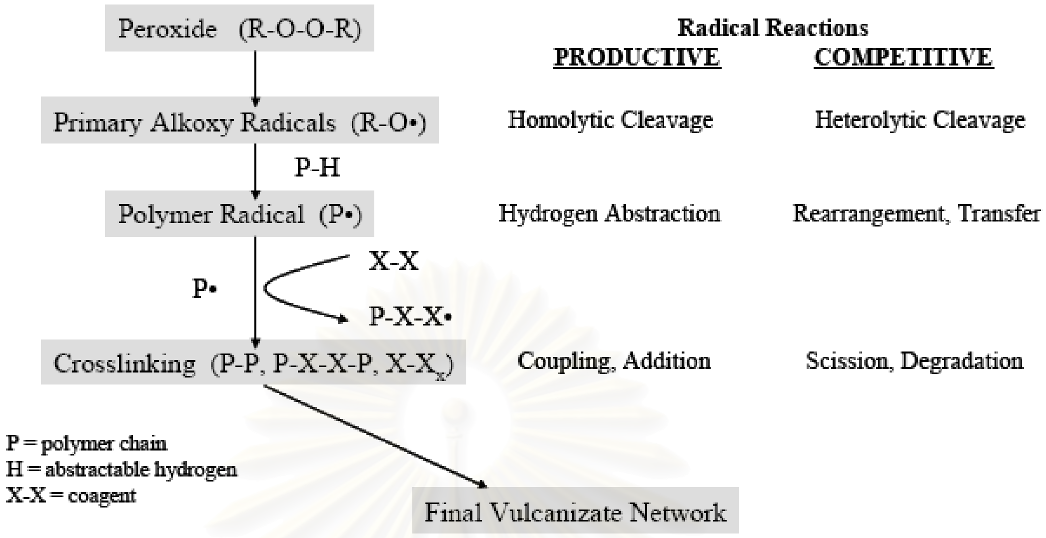


Figure 2.14 Scheme for peroxide vulcanization [10].

Of course the desired reaction pathways for a polymer radical (P•) are crosslink formation either through coupling with another polymer radical or addition reactions through in-chain or pendant double bonds (unsaturated elastomers). The competitive reactions include polymer scission or other degradation reactions. The balance between productive and non-productive competing reactions depends on many factors, including the elastomer microstructure, the presence of hydrogen donors in the formulation (fatty acids, oils, anti-oxidants, etc.) and the ubiquitous presence of dissolved oxygen. Unfortunately, many of the destructive reactions are kinetically favored, and typically only the very high concentration of reactive sites on the polymer backbone allows for effective crosslink formation to occur at all.

The quality of crosslink formed when coagents are employed can exhibit great influence on the dynamic and fatigue properties of the composite. The bridging structure of the coagent is often the member which will carry the load under network deformation. Covalent carbon-carbon linkage formed (Figure 2.15) have high dissociation energies and produce vulcanizates of high strength and heat-aging resistance but poor flex fatigue and tear strength. The latter properties rely on internal energy dissipation mechanisms to reduce stresses and delay rupture. Crosslinks that rupture and reform can dissipate energy and reduce local stresses to provide improved properties. It has recently been discovered that certain peroxide coagents based on zinc salts of acrylic and methacrylic acid provide improvements in applications where heat resistance is required under dynamic strains.

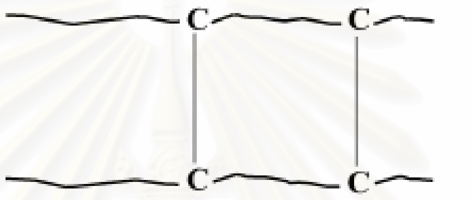


Figure 2.15 Schematic representation of crosslink formed using peroxide system [10].

2.5.3 Influence of Crosslink Type and Density [11]

Crosslink density or crosslink concentration of a network is described by Funke in terms of:

Mean molecular weight (Mc): Average mass of a polymer chain which connects two adjacent crosslinks.

Crosslink density: Moles of crosslinked basic units per weight unit of the crosslinked polymer.

Degree of crosslinking: Moles of crosslinked basic units per total moles of basic units.

Crosslinking index: Crosslinked basic units per primary (linear) macromolecules.

Figure 2.16 summarizes the dependence of various tensile and dynamic properties on the crosslink density. Increasing the crosslink density increases compound modulus and hardness, while elongation and permanent set are decreased. Properties associated with bond rupture energies are dependent on both the number of crosslinks and the hysteresis of the network. As hysteresis generally decreases with an increase in the rosslink density, properties such as tear strength and fatigue to failure often display local maxima, typically at different crosslink densities. Table 2.4 outlines the bond dissociation energies of various crosslinks.

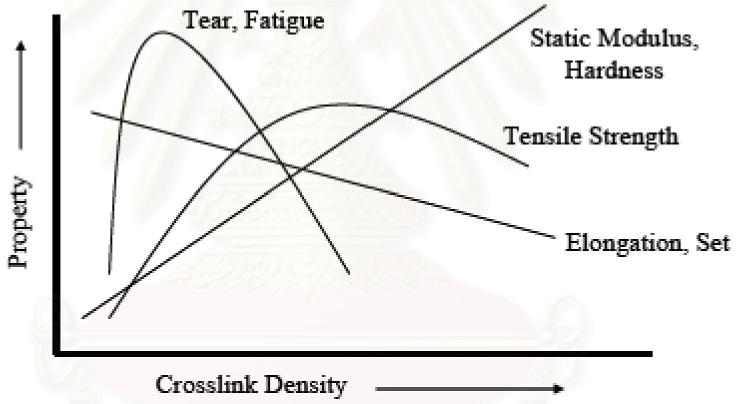


Figure 2.16 Vulcanizate properties as a function of crosslink density [11].

Table 2.4 Bond dissociation energies of typical crosslinks [11].

Bond Type	Dissociation Energy (kJ/mol)
C-C	335
C-S-C	314
C-S-S-S-C	230
C-S_x-C	147
C-O-Zn^{2+}-O-C	293

2.6 Carbon Black [12],[13]

Carbon black is a black powder or granular substance made by burning hydrocarbons in a limited supply of air. This produces a black smoke containing extremely small carbon black particles which can be separated from the combustion gases to form a fluffy powder of intense blackness. Carbon black is used mostly as a reinforcing agent for rubbers. The largest use of carbon black is in the manufacture of automotive tires. It is also used to color printing ink, painting, paper, and plastics.

Carbon black is produced by the reaction of a hydrocarbon fuel such as oil or gas with a limited supply of combustion air at temperatures of 1320°C to 1540°C (2400°F to 2800°F). The unburned carbon is collected as an extremely fine black fluffy particle, 10 to 500 nanometers (nm) in diameter. The principal uses of carbon black are as a reinforcing agent in rubber compounds (especially tires) and as a black pigment in printing inks, surface coatings, paper, and plastics.

There are five processes currently used to make carbon black:

Furnace black process: aromatic oils (based on crude oil) are burned in a reactor, producing carbon black and tailgas. After cooling, the carbon black is separated from the tailgas, densified, and processed into pellets of varying grades/sizes. This process is the most widely used in the U.S, comprising over 95% of all domestic carbon black production.

In the oil furnace process, an aromatic liquid hydrocarbon feedstock is heated and injected continuously into the combustion zone of a natural gas-fired furnace, where it is decomposed to form carbon black. Primary quench water cools the gases to 500°C (1000°F) to stop the cracking. The exhaust gases entraining the carbon particles are further cooled to about 230°C (450°F) by passage through heat exchangers and direct water sprays. The black is then separated from the gas stream, usually by a fabric filter. A cyclone for primary collection and particle agglomeration may precede the filter. A single collection system often serves several manifolded furnaces.

The recovered carbon black is finished to a marketable product by pulverizing and wet palletizing to increase bulk density. Water from the wet pelletizer is driven off in a gas-fired rotary dryer. Oil or process gas can be used. From 35 to 70 percent of the dryer combustion gas is charged directly to the interior of the dryer, and the remainder acts as an indirect heat source for the dryer. The dried pellets are then conveyed to bulk storage. Process yields range from 35 to 65 percent, depending on the feed composition and the grade of black produced. Furnace designs and operating conditions determine the particle size and the other physical and chemical properties of the black. Generally, yields are highest for large particle blacks and lowest for small particle blacks.

Thermal black process: The thermal process is a cyclic operation in which natural gas is thermally decomposed (cracked) into carbon particles, hydrogen, and a mixture of other organics. Two furnaces are used in normal operation. The first cracks natural gas and makes carbon black and hydrogen. The effluent gas from the first reactor is cooled by water sprays to about 125°C (250°F), and the black is collected in a fabric filter. The filtered gas (90 percent hydrogen, 6 percent methane, and 4 percent higher hydrocarbons) is used as a fuel to heat a second reactor. When the first reactor becomes too cool to crack the natural gas feed, the positions of the reactors are reversed, and the second reactor is used to crack the gas while the first is heated. Normally, the excess hydrogen content is produced to make the thermal black process (self-sustaining), and the surplus hydrogen is used to fire boilers that supply process steam and electric power.

Acetylene black process: similar to the thermal black process, except that acetylene is the raw material used, and the carbon black is not processed into pellets.

Lampblack process: one of the oldest carbon black processes. An aromatic oil (based on coal tar) is heated in a flat cast-iron pan to produce carbon black.

Two major processes presently used in the United States to manufacture the carbon black are the oil furnace process and the thermal process. The oil furnace process accounts for about 90 percent of production and about 10 percent for the thermal process. Two others, the lamp process for production of lamp black and the cracking of acetylene to produce acetylene black, are each used at 1 plant in the U. S. However, these are small-volume specialty black operations that constitute less than 1 percent of total production in this country. The gas furnace process is being phased out, and the last channel black plant in the U. S. was closed in 1976.

2.6.1 ASTM Nomenclature [14]

The ASTM nomenclature system for carbon black, ASTM D1765, is detailed in Figure 2.17. It is composed of a letter followed by three numbers. The letter in the nomenclature system indicates the effect of the carbon black on the cure rate of a typical rubber compound. “N” is used for the vast majority of rubber-grade carbon blacks, indicating “normal” cure rate. Carbon blacks are made with the “oil furnace” process fit this category. The letter “S” indicates a slow cure rate and is typically used for carbon blacks that have a high concentration of oxygen-containing groups and are therefore acidic in nature. Channel-process carbon blacks, or after-treated carbon blacks, are an example. An acidic surface inhibits the amine-based accelerator systems typically used in rubber compounds.

The first number is inversely related to the average nitrogen surface area and directly related to the particle size; hence, a low number means a high surface area. The range of surface area (from 0 to 150 m^2/g of carbon black) has been grouped into 10 categories, as shown in Figure 2.17. Note that there are ASTM-recommended target values for iodine adsorption and DBP, with “typical” values given for other characteristics.

The third and fourth characters in the ASTM system are numbers arbitrarily assigned by carbon black manufacturer that has successfully petitioned for an ASTM number. The latest ASTM list has 42 classified grades.

Position	Designation			
1st digit	N = Normal cure rate S = Slow cure rate (channel grades, modified furnace w/reduced cure rate)			
2nd digit	Particle Size Group (nanometers) now Surface area group			
	Group	**Typical Na SA (m^2/g)**	**Typical Particle Size**	**Former Identification**
	0	> 150	1-10	-
	1	121-150	11-19	SAF
	2	100-120	20-25	ISAF
	3	10-99	26-30	HAF (EPC, MPC)
	4	50-69	31-39	FF
	5	40-49	40-48	FEF
	6	33-39	49-60	GPF
	7	21-32	61-100	SRF
	8	11-20	101-200	FT
	9	0-10	291-500	MT
3rd & 4th digits	Assigned arbitrarily by ASTM D24, indicating differences within group (Structure level, modulus level, or any physico-chemical property)			

Figure 2.17 ASTM nomenclatures for rubber grade carbon blacks [14].

2.7 Compound Cost Calculations [15]

Compound cost is not just the simple calculation of the cost per pound or kilogram of material. It must also take into account whether the application is volume-based or weight-based. The case of volume-based applications includes the concept of cost-volume relationship and calculations.

Compound cost calculations require three parameters:

1) The amount of each ingredient
2) The cost of each ingredient
3) The specific gravity of each ingredient

The equivalent formulae can be used simply by substituting kg-vol for lb-vol in cost/lb-vol calculations. Cost can be any monetary unit as long as it remains the same for all calculations.

2.7.1 Reducing Compound Cost

1) High-Structure Carbon Blacks

The use of higher structure carbon blacks with increasing the oil content to maintain 300%modulus levels decreases the cost/lb and cost/lb-vol by taking advantage of these carbon blacks' ability to increase modulus. Subsequently, the addition of oil reduces the modulus to the original level. However, other properties that may be important to the product's performance may be compromised.

2) White Compounds

In compounds where high levels of titanium dioxide are used for maximum whiteness, it may be possible to substitute light colors clays, light colored treated clays, calcium carbonate, and optical whiteners, among others, for some of pigments. The selection and quantities of the substitutes will depend on several factors including the required whiteness level, physical properties (tensile, modulus and hardness), grindability, and fatigue resistance among others.

3) Antioxidants/Antiozonants

Antioxidant/antiozonants are another class of materials that can significantly impact the cost. There are numerous examples of synergy between two or more ingredients that are not only more effective than a single ingredient, but also reduce cost as well. One example which might work is substituting 4 phr of 6PPD [N-phenyl-N'(1,3-dimethylbutyl)-p-phenylene-diamine] with 2.5 phr of 6PPD, 2 phr of TMQ (polymerized 1,2-dihydro-2,2,4-trimethylquinoline), and 1 phr of wax.

4) Polymer Substitution

Polymers are often the largest constituent of a recipe, providing an opportunity for reducing compound costs, including lb-vol. costs. There are three major areas of polymer substitutions. First, high specific gravity polymers or high cost polymers can be replaced. Second, non-oil-extended polymers can be replaced by oil-extended types. Third, free carbon black/oil mixed compounds can be changed to carbon black/oil masterbatches.

5) High Cost/High Specific Gravity Polymers

Replacing chloroprene with NBR eliminates not only a high specific gravity material, but a higher cost one. Both the cost/lb and the cost/lb-vol. are reduced.

6) Clear and Oil-Extended Polymer Replacements

The replacement of clear polymers with oil-extended grades usually permits the use of higher loadings and oil content.

7) Carbon Black/Oil Masterbatches Replacing Free Mix Compounds

The use of carbon black/oil masterbatches can replace free black mixed compound. Because the black/oil masterbatch compound can be mixed in one step, this first stage is completely eliminated. Due to the savings in mixing cost, there is the consideration of increased mixing capacity. By eliminating the first longer mixing stage, two additional final or one stage mix can be accomplished, effectively increasing output by three times. This may be particularly important if the factory has limited mixing capacity.

These are just a few examples of the substitutions and manipulations that can lead to saving the costs and increase in extrusion efficiencies. Suppliers are usually very willing to assist compounders to find more cost effective solutions. Whenever making substitutions, whether of your own design or those suggested by a supplier, it should be made sure to thoroughly test the resultant product to verify that unexpected. The detrimental attributes have not been introduced.

2.8 Literature Reviews

Rahiman *et al*. [16] studied the cure characteristic and mechanical properties of styrene-butadiene rubber/acrylonitrile butadiene rubber (SBR/NBR). Blends of SBR/NBR were prepared at ratios of 0/100, 20/80, 40/60, 60/40, 80/80, and 100/0. Sulfur, dicumyl peroxide (DCP) and a combination of sulfur and DCP were used as vulcanizing agents. Blends prepared by using sulfur as the vulcanizing agent showed comparatively better mechanical properties. Tensile and tear strengths showed synergism for the blends containing 60%SBR. The morphology of the blends was examined to correlate with observations on mechanical properties by using an optical microscope with reference to the effects of blend ratio. A relatively co-continuous morphology was observed for 60:40 SBR/NBR composition.

Botros and Nour [17] studied the preparation and characterization of IIR/NBR vulcanizates. Blends of butyl rubber (IIR) with nitrile rubber (NBR) were prepared on a laboratory open mill. Cure behaviour of the blends, physico-mechanical properties and ageing and oil resistance properties of the vulcanizates were determined. For electric insulation application, dielectric contant, dielectric loss and tanδ were measured. The results indicated that the vulcanizates of IIR/NBR blends of the ratios (70:30), (30:70) and (20:80), showed the superior thermal stability upon ageing, compared to individual rubbers and other blend compositions. Blending of IIR with NBR (main component) improved the swelling behaviour of NBR in brake fluid and toluene. However, blending of NBR with IIR (main component) improved the swelling resistance of IIR in motor oil and gasoline. Thus, the results obtained reveal effective improvement in thermal and oil resistance upon blending.

Hayashi *et al*. [18] studied the low-temperature properties of hydrogenated nitrile rubber. The Tg and low-temperature flexibility as measured by the TR-test and Gehman Torsional Stiffness test of HNBR showed the different behaviors for the various degrees of hydrogenation and acrylonitrile contents. Conversely, the brittle temperature of HNBR became lower with an increase in the degree of hydrogenation. The Tg of NBR before hydrogenation was decided in relation to its acrylonitrile content. Normally, the Tg of NBR decreased during the progress of hydrogenation. The Tg of NBR was within a wide range of -15 to -60°C. But this range was narrowed between -15 and -40°C with the progress of the hydrogenation reaction. When the acrylonitrile content was low, the Tg of HNBR became higher than that of NBR.

Ibnelwaleed *et al*. [19] studied the miscibility and mechanical properties of HNBR/NBR blends. Pure samples and blends of 10%, 30%, 50%, 70%, and 90% HNBR (w/w) were conditioned in a Haake Polydrive blender with Cam-type internal rotors. For the 50/50 HNBR/NBR blend, the SEM micrographs suggest a uniform elongated structure. The thermal analysis showed the presence of two glass transitions, representing the pure components, at all blend ratios, suggesting the absence of segmental miscibility of the blends. The small-strain mechanical properties such as tensile modulus and yield stress followed linear additivity. However, HNBR and HNBR-rich blends were observed to strain harden at a rate higher than that of NBR. Induced crystallization of HNBR was suggested to be the reason for the strain hardening.

Sandland *et al*. [20] studied the peroxide cured HNBR/methacrylate blends with improved low temperature performance. The ZSC4195 and HNBR4300 materials were selected due to their unique balance of properties and extremely wide operating temperature range. Four typical recipes of both straight HNBR and ZSD/HNBR blends were used to demonstrate the mechanical properties across a range of hardness values. The results reported and discussed with an HNBR/zinc dimethacrylate blend. It is possible to produce elastomer compounds capable of yielding very high tensile and tear strength values coupled with high elongation. These advantages are particularly evident at high hardness levels. When the HNBR component was of the fully-saturated terpolymer variety, these properties achieved in conjunction with excellent low temperature and heat resistance.

Thormer *et al*. [21] studied the effect of crosslinking system on processing behavior and performance profile of HNBR. It has been found that the substitution of zinc peroxide for zinc oxide and magnesium oxide in sulfur systems improved the performance profile of the vulcanizates. Thus, in comparison with standard EV systems, EV system modified with zinc peroxide gave more favorable (lower) compound viscosity, similar or longer scorch times, higher modulus, lower compression set, improved ozone resistance, considerably better hot air resistance, and improved resistance to dynamic stresses. As compared with the use of peroxides, the modified system gave the higher tensile strength, considerably greater elongation at break, higher rebound resistance, substantially higher tear strength and better wear resistance at elevated temperatures.

Bandyopadhyay *et al.* [22] studied the influence of surface oxidation of carbon black on its interaction with nitrile rubber (NBR) and carboxylated nitrile rubber (XNBR). The interactions were studied by measurements of bound rubber, physical and dynamic mechanical properties of the vulcanizates including Monsanto rheometric studies on the rubber-filler mixes. Compared with NBR, XNBR showed a higher degree of interaction with the filler. The oxidation of the filler surface increased the extent of the rubber-filler bonding, which involved the weak hydrogen bonding and Van der Waal's forces. In the case of XNBR, the additional chemical bonding occured between the –COOH groups of the rubber and the reactive groups on the filler surface. Results of solvent swelling studies revealed that the percentage of weight loss on swelling in chloroform decreased the incorporation of filler. The reduction was more pronounced in the oxidized grade of carbon black in both XNBR and NBR. It is also observed that the percentage weight loss on swelling of XNBR vulcanizates was less than that of NBR vulcanizates.

Nanoj *et al.* [23] studied the thermally induced crosslinking in blends of poly(vinyl chloride) (PVC) and HNBR. The progressive rise in torque with curing time of the PVC-HNBR blends was the result of gradual formation of a network structure. Since the neat polymers (PVC and HNBR) showed only marginal or no rise in torque, it can be presumed that the thermovulcanization of the individual components in the blend did not occur. The rheograph of a 50/50 blend of PVC and cis-1, 4-polybuytadiene rubber (BR), also showed no rise in torque even after 120 min. This indicates that the crosslinking reaction took place through the acrylonitrile group in HNBR. Again, the presence of a PVC stabilizer like tribasic lead sulfate (TBLS) inhibited the crosslinking reaction, as seen from the absence of torque rise in the case of the blend containing the PVC stabilizer. This indicates that the active sites in PVC for its crosslinking with HNBR were generated during its thermal degradation. Further showed the effect of blend ratio on the extent of crosslinking. The 75/25 of PVC/HNBR blend showed the highest torque rise in a span of 120 min, as compared to 50/50 and 25/75 of PVC/HNBR blends. This can be explained on the basis of the availability of the functional groups in the component polymers for the chemical interaction.

Dunn *et al.* [24] studied the compounding NBR for high temperature applications. It was found that NBR compound showed the excellent retention of physical properties after aging at 135°C for 168 h. This required the use of silica fillers, magnesium oxide, etherthioether plasticizer, selected antioxidants, and an optimized sulfur/sulfur donor cure system. The presence of even 10 phr of N-550 black markedly reduces aging resistance. The system 1.0 phr of CBS, 1.5 phr of TMTD, 2.5 pht of OTOS, and 0.4 phr of sulfur imparted the excellent resistance to air aging. Resistance to air aging after exposure to ASTM Oil #3 was enhanced by the presence of 1.0 part diaryl-p-phenylenediamine at the expense of air aging resistance in absence of oil. Compression set in sulfur vulcanizates was lowest for black filled compounds in optimized low sulfur/sulfur donor systems. Although silica filled vulcanizates had compression set values approximately twice as large as corresponding black filled vulcanizates, they exhibited the comparable retention of sealing force in air. Silanes generally reduce compression set and improve sealing force retention in silica filled vulcanizates. Silica filled compounds optimized for physical property retention on air aging are not necessarily the best for sealing force retention in air aging. The system 1.0 phr of MBTS, 3.0 phr of OTOS, 1.0 phr of TMTD, 0.25 phr of sulfur with 4.0 parts of polysulfidic silane (SI69) imparted the excellent retention of physical properties after air aging at 125°C and excellent retention of sealing force after exposure to ASTM Oil #3 and air.

Ferrari *et al.* [25] studied the enhanced performance properties of compounds based on hydrogenated carboxylated acrylonitrile butadiene terpolymer (HXNBR). The article was undertaken to investigate the effect of the type of carbon black on the physical properties and abrasion resistance of rubber compounds. The hardness of all compounds was kept constant at 70 durometer shore A by changing the carbon black loading for each carbon black type. Accordingly, the N-110 and N-300 carbon black series were expected to give the better abrasion resistance compared to N-774 and N-990. All the carbon blacks, except for N-990 (thermal) and N-472 (conductive), were designated as furnace blacks. The effect of carbon black type on compound scorch (t_5) measured at 125°C remained greater than 30 minutes for all compounds; however, the scorch safety at 135°C decreased with decreasing the surface area and structure.

Giurginca and Zaharescu [2] investigated the changed in sol fraction simultaneously with the determination of sulfur and chlorine contents. The kinetic depiction of structural modifications occurring in HNBR/CSPE (CSPE, Carom CSM type contained 33.6% chlorine, 1.3% sulfur and 1.4% molar unsaturation) blends during oxidative degradation was investigated on the basis of the mechanical approach for thermal and radiation aging. The behavior of HNBR/CSPE blends during thermal degradation and radiochemical processing emphasized some relevant aspects. The activation energy involved in thermal degradation of HNBR/CSPE blends was higher than similar values displayed by the components. It suggested a higher chemical and radiation stability in comparison with individual polymers. Radiation exposure induced the "self-crosslinking" and this treatment was applied to the studied materials for the improvement of their lifetime.

CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

Table 3.1 Rubber and chemicals used in this study.

Chemicals	**Function**	**Commercial name**	**Supplier**
HNBR	Elastomer	ZETPOL 1020	Zeon Corporation
NBR	Elastomer	JSR N-220S	JSR
Carbon black	Filler	GPF N-660	Thai Carbon Product Co.,Ltd.
Carbon black	Filler	SRF N-774	Thai Carbon Product Co.,Ltd.
ZnO	Activator	ZnO White Seal	P.T. Indo Lysaght
Stearic acid	Activator	Stearic acid	Imperial Industrial Chemicals
TMTD	Accelerator	Perkacit TMTD	Flexsys Antwerp Belgium
MBTS	Accelerator	Perkacit MBTS	Flexsys Rubber Chemical Ltd.
Sulfur	Vulcanizing agent	CURAGENT-OS	Chemmin Corporation Ltd.
Peroxide	Vulcanizing agent	Elastoperse DCP-60	Polymer Innovation Co.,Ltd.
Co-agent	Co-agent	TAIC M-60	Nippon Kasei Chemical Co.,Ltd.
IRM 903 oil	ASTM Oil# 3	SUNOCO	Japan Sun Oil Company Ltd.
Diesel engine oil	Engine oil	PTT Dynamic Turbo	PTT
Toluene	Solvent	Toluene	Fisher Scientific UK Limited.
Isooctane	Cleaning solvent	Isooctane	Ajax Finechem

3.2 Instruments

Table 3.2 Instruments used in this study.

Instruments	Manufacturer
Two roll mill mixer	Yi Tzung Precision Machinery, Taiwan
Rheometer	Alpha Technology, USA
Compression machine	Hong Yow Thai, Thailand
Autograph tensile testing machine	AGS-J Series, Shimadzu, Japan
Wallace micro hardness tester	H12 Models, Cogenix, England
Geer oven	45UL-P Model, Toyoseiki, Japan
Ozone weather tester	OMS-LE, Suga, Japan
Electronic densimeter	EW-200SG, Alfa Mirage, German
Digital microscope	VHX-100K, Keyence, Japan
Line of balance	AL Model, Mettler Toledo, USA
Test tube aging tester	No.273, Toyoseiki, Japan
Dynamic mechanical tester	DMA 242C, Netzsch, German
Scanning microscope	JSM-6400, Jeol, Japan

3.3 Procedure

3.3.1 Compounding and Cure Assessment

The rubbers utilized in this study were HNBR and NBR. Blends of HNBR/NBR were prepared at ratios of 100/0, 90/10, 80/20, and 70/30 (wt%). The two types of carbon black loading (General purpose furnace; GPF N-660 and Semi reinforcing furnace; SRF N-774) were fixed at 50 phr with three types of vulcanization systems (CV, EV, and peroxide). The formulations of the blends are given in Tables 3.3-3.5. The rubbers were masticated for 5 min and then activator additives such as zinc oxide (5 phr), stearic acid (1 phr) and filler (50 phr) were added. The rubber compound was mixed by cut-and-fold technique on the two-roll mill for 10 min until the surface of compound was smooth. The compound was mixed with accelerators (co-agent) and vulcanizing agents. The sheet of rubber compound was kept at room temperature (25°C) for 24 h before cure assessment using Monsanto Moving Die Rheometer (MDR2000) at 170°C to determine the cure characteristics according to ASTM D2084-200.

3.3.2 Vulcanization Process

Rubber sheets of approximately 4 mm of thickness were vulcanized in an electrical hydraulic compression mold preheated at 170°C for 30 min and then followed by compressing at 120 kgf/cm^2 of pressure for the respective cure time (tc_{90}) obtained from the MDR2000 tests.

The summarized procedure for preparation of HNBR/NBR compound and experimental process are shown in Figure 3.1.

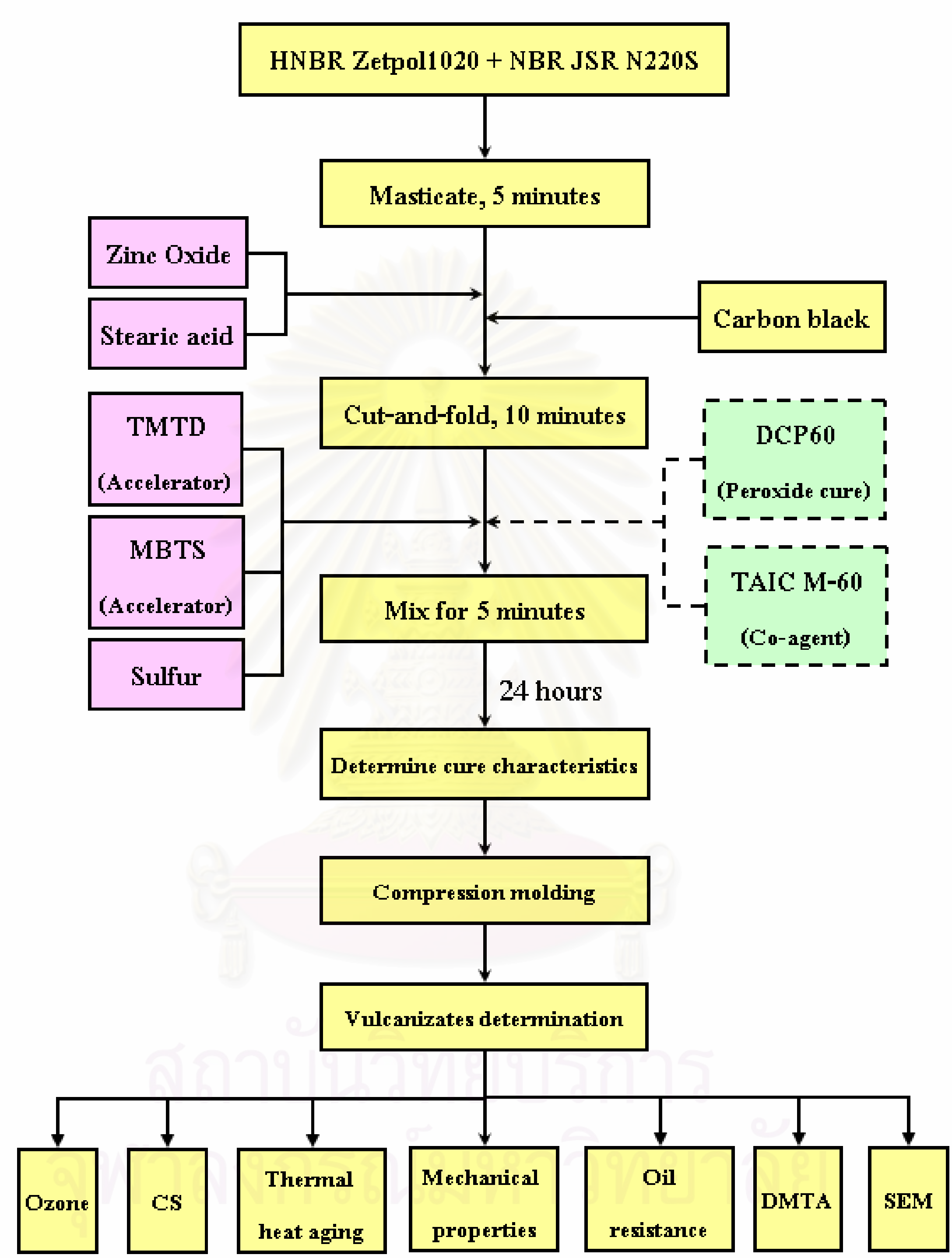


Figure 3.1 The overall schematic experimental process.

3.4 Formulation of the Compounds in the Experiments

In this experiment, the formulations were used as shown in Tables 3.3-3.5.

Table 3.3 Formulation for conventional vulcanization (CV) system.

Ingredient	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
ZETPOL 1020	100	90	80	70	100	90	80	70
JSR N-220S	0	10	20	30	0	10	20	30
GPF N-660	50	50	50	50	-	-	-	-
SRF N-774	-	-	-	-	50	50	50	50
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBTS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	2	2	2	2	2	2	2	2

Table 3.4 Formulation for efficient vulcanization (EV) system.

Ingredient	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
ZETPOL 1020	100	90	80	70	100	90	80	70
JSR N-220S	0	10	20	30	0	10	20	30
GPF N-660	50	50	50	50	-	-	-	-
SRF N-774	-	-	-	-	50	50	50	50
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1
TMTD	2	2	2	2	2	2	2	2
MBTS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Table 3.5 Formulation for peroxide vulcanization system.

Ingredient	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
ZETPOL 1020	100	90	80	70	100	90	80	70
JSR N-220S	0	10	20	30	0	10	20	30
GPF N-660	50	50	50	50	-	-	-	-
SRF N-774	-	-	-	-	50	50	50	50
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1
DCP60	7	7	7	7	7	7	7	7
TAIC M-60	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

3.5 Testing

3.5.1 Determination of Cure Characteristics

A Monsanto moving die rheometer, MDR2000 model, was used to obtain the torque-time curve at 170°C with 1 amplitude.

- M_L- Minimum torque, lbf-in.
- M_H-Highest torque, lbf-in attained during specified period of time when plateau or maximum torque is obtained.
- Scorch time (ts_2) in minute is the time taken for a two unit rise above the minimum torque.
- Cure time (tc_{90}) in minute is the time taken for attaining 90% of the maximum torque.

3.5.2 Tensile Properties

Tensile tests were carried out using Autograph tensile testing machine AGS-J Series. Test was done according to ASTM D412-98a, Method A, at a crosshead speed of 500 mm/min. Dumbbell specimens were cut from molded sheet with a die cutter (Die C) (Figure 3.2). Five specimens were used in each case to obtain the median and standard deviation values. The tensile strength (T.S), stress at 100% elongation (M_{100}) and elongation at break (E.B) were recorded directly from the digital displays at the end of each test. The stress at 100% elongation (M_{100}), tensile strength and % elongation at break were determined from Eq.3.1-3.3.

$$100\%\text{Modulus (MPa)} = F_{(100)} / A \tag{3.1}$$

where:

$F_{(100)}$ = Force at specified elongation, N

A = Cross-sectional area of unstrained specimen, mm^2

$$\text{Tensile strength (MPa)} = F_{(BE)} / A \tag{3.2}$$

where:

$F_{(BE)}$ = The force magnitude at rupture, N

A = Cross-sectional area of unstrained specimen, mm^2

%Elongation = $100\,[L\text{-}L_O] / L_O$ (3.3)

where:

L = Observed distance between bench marks on the extended specimen

L_O = Original distance between bench marks (use same units for L and L_O)

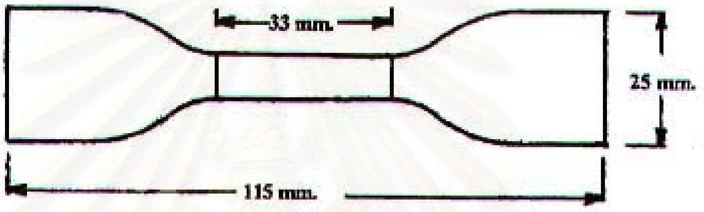


Figure 3.2 Dumbbell (Die C) shape specimen for tensile property testing.

3.5.3 Hardness Measurement

The test was conducted following ASTM D2240-97 using a micro hardness tester with an automatic electrical balance, model H12. The thickness of test specimen was at least 2 mm. The sufficient lateral dimensions of the specimens to permit for this measurement were at least 12 mm from any edge. The specimens were 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 indention at least 12 mm from any edge of the specimen. The pressure was applied to the specimen. After the pressure foot was in form to contact with the specimen, the hardness value was read. Every specimen was tested in 5 replications. The median and standard variations of hardness values were presented.

3.5.4 Compression Set

Compression set testing is used to determine the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress. The test was conducted according to ASTM D395-03 Method B to measure the somewhat permanent deformation of the specimen after it has been exposed to compressive stress for a set period of time. This test is particularly useful for applications in which elastomers would be in a constant pressure/release state.

The thickness of the original specimen was measured. The specimen was then placed between spacer in the compression device. The specimen was compressed to 25% of its original height using the spacers to accurately measure the compression. Within 2 h of assembly, the compression device was placed in an oven at a 125°C for 22 h. At the end of the test period, the device was taken from the oven. The specimen was then removed from the device and allowed to cool for 30 min before measuring the final thickness.

The specimen was prepared as the cylindrical disk with 12.5±0.5 mm of thickness and 29.0±0.5 mm of diameter. The compression set was calculated as a percentage of the original thickness from Eq.3.4.

$$CS,\% = \frac{t_o - t_i}{t_o - t_n} \times 100 \tag{3.4}$$

where:

CS = Compression set as a percentage of the original thickness, %

t_o = Original thickness of the specimen, mm

t_i = Final thickness of the specimen, mm

t_n = Thickness of the spacer bars used, 9.75 mm

3.5.5 Thermal Aging Properties

The effect of thermal aging on the mechanical properties of the blends was investigated. The representative samples of the blends were aged in a hot air aging oven with air circulating at 125°C for 168 h. The test was conducted according to ASTM D573. Dumbbell specimens were cut from molded sheet with a die cutter (Die C).

At the termination of the aging interval, specimens were removed from the oven and cooled at room temperature on a flat surface for 24 h before determination of the tensile properties according to ASTM D412-98. The thermal aging properties were calculated as a percentage of the original properties from Eq.3.5.

$$P = \frac{A - O}{O} \times 100 \tag{3.5}$$

where:

P = change in property, %

O = Original value

A = Value after aging

3.5.6 Ozone Resistance Properties

The static ozone testing was performed according to JIS K 6301-1995. The condition were 50 parts per hundred million (pphm) ozone concentrate at 40°C under 20%strain for 72 h. The rectangular specimens with 60x10x2 mm of dimension were stretched to 20%strain on a test rack for 24 h before placed in the ozone chamber. After weathering the test pieces continuously for the prescribed time, the specimens were taken out from the ozone chamber. The rate of cracks would be observed and recorded according to Table 3.6 and Figure 3.3. Photographs were taken using a digital microscope VHX-100K Keyence with magnification 10X.

Table 3.6 Observed rate of cracks [26].

Number of cracks	Size and depth of cracks
A : a small number of cracks	1 : That which can not be seen with the marked eyes but can be confirmed with 10 times magnifying glass
B : a large number of crack	2 : That which can be confirmed with the naked eyes
C : numberless crack	3 : That which is deep and comparatively large (under 1 mm)
	4 : That which is deep and large (1 mm or over to and excl. 3 mm)
	5 : That which is 3 mm or more or about to sever

Remarks

1. To record the state of deterioration, the number of cracks, the largeness and depth of cracks shall be collectively denoted. Example: A-4
2. To express especially the cracks occurred at the edge portion, mark e shall be used. Example: eA-4

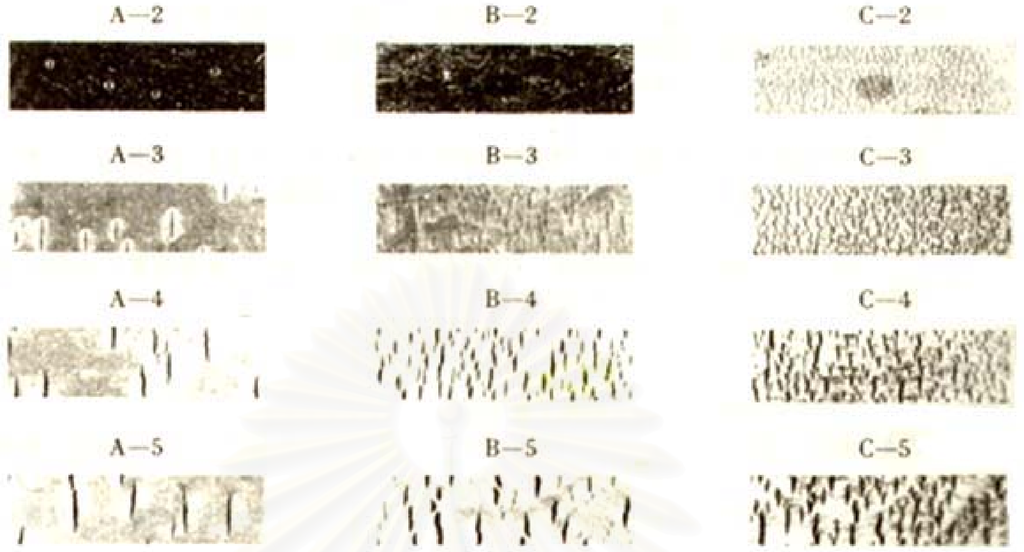


Figure 3.3 Example recorded rate of cracks [26].

3.5.7 Measurement of Swelling Behaviour

The test was conducted according to ASTM D471-98. For determination of the tensile strength, ultimate elongation, and hardness, three specimens was cut as dumbbell using Die C following ASTM D412, and then their thickness was measured. The test specimens with 20x20x2 mm of dimension were weighed in air (W_1) and in water (W_2) using an electrical balance to determine their volume change after immerging in 100 ml of IRM 903 oil (ASTM #3 oil) at 125°C for 70 h. The test specimens were removed from the test tubes and then cooled to room temperature by transferring them to cool clean portion of the test liquid for 30 min. The specimens were quickly dipped in the isooctane at room temperature and lightly wiped by tissue paper to remove the excess oil from their surface. Immediately, bench marks were applied. The tensile and hardness properties were determined according to ASTM D412 and D2240-97, respectively. The test specimens were weighed in air (W_3) and in water (W_4) to determine the change of volume. The measurement was replicated in method using an engine oil. The change of tensile properties, hardness, and their volume was calculated from Eq.3.6-3.8.

$$\Delta P,\% = \frac{P_i - P_o}{P_o} \times 100 \tag{3.6}$$

where:

ΔP = Change in properties (tensile properties) after immersion, %

P_o = Original property before immersion,

P_i = Property after immersion.

$$\Delta H = H_i - H_o \tag{3.7}$$

where:

ΔH = Hardness change after immersion, units,

H_o = Original hardness before immersion, units and

H_i = Hardness after immersion, units.

$$\text{Change in volume, \%} \quad = \frac{(W_3 - W_4) - (W_1 - W_2)}{W_1 - W_2} \times 100 \tag{3.8}$$

where:

W_1 = Initial weight of specimen in air, g

W_2 = Initial weight of specimen in water, g

W_3 = Weight of specimen in air after immersion, g

W_4 = Weight of specimen in water after immersion, g

3.5.8 Determination of Specific Gravity

The specific gravity of vulcanized rubbers was determined by using Electronic Densimeter (Auto-Specific Gravity tester, model EW-200SG). The determination of (relative) density value was based on the density of water at 4°C:1g/cm per electronic densimeter instruction manual.

3.5.9 Determination of Crosslink Density

Specimens with approximately 20 mm. of diameter and 2.5 mm. of thickness were allowed to swell in toluene. The density of each specimen was determined according to section 3.5.8. Specimen was then placed in a vital containing toluene. The vital was always covered to prevent the evaporation. Periodically, over a period of 24 hours, the specimens were removed from the toluene, blotted dry on a paper towel, and then weighed quickly and accurately. The swelling index, which is defined as the grams of solvent per gram of rubber hydrocarbon, was calculated according to the Flory-Huggins Theory (Appendix D).

3.5.10 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) of the specimens in rectangular shape with dimensions of 13x6x2 mm. was investigated using a dynamic mechanical analyzer, model DMA 242C, Netzsch, Germany. The range of testing temperature was -80 to 50°C with 3.0°C/min of heating rate under nitrogen atmosphere. The tension mode was applied at 1 Hz of constant frequency and 1 μm of amplitude. The storage modulus (E'), loss modulus (E'') and the mechanical loss factor ($\tan\delta = E''/E'$) were determined.

3.5.11 Scanning Electron Microscopy (SEM)

The morphology of blends was studied using a JEOL model JSM-6400 scanning electron microscope operated at 15 kV. The specimens were fractured after freezing in liquid nitrogen and put in the vapor of osmium tetroxide (OsO_4) over a 2.0% aqueous solution. After staining for 4 h, the specimens were dried in a desiccator for 48 h, and taken a treatment of gold evaporation before observation.

3.6 Compound Cost Calculations

The cost/kg was calculated as following Eq.3.9.

$$Compond\ \cos t/kg. = \sum \frac{weight(phr)_i \times \cos t/kg._i}{\sum weight(phr)_i} \qquad (3.9)$$

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Cure Characteristic

The rheometric characteristics of the various blends are shown in Tables 4.1-4.3 and Figures 4.1-4.2. The minimum torque, M_L was slightly affected by varying NBR content and different curing systems, as shown in Figure 4.1(a)-(b). The maximum torque in the rheograph is measurement of cross-link density in the rubber. For three curing systems, the maximum torque (M_H) of EV system was lower than CV and peroxide systems because of lower crosslink density. When 20 and 30%NBR in the blends with various cross-linking systems were compared, it was found that the peroxide system exhibited maximum torque, and the EV system, the lowest, as shown in Figure 4.1(c)-(d). This is due to the fact that peroxide can cure both HNBR and NBR phases uniformly. Moreover, the rigid carbon-carbon structure in the peroxide curing system offers the more resistance to rheometric torque [16].

The scorch time (ts_2) as [Figure 4.1(e)-(f)] and cure time (tc_{90}) [Figure 4.2(a)-(b)] were slightly affected by varying the NBR content for the various blend compositions. Among the various vulcanizing modes for given blend, the scorch safety was highest for the sulfur system and lowest for the peroxide cure system. For sulfur system, scorch time of CV system was shorter than that of EV system because the amount of TMTD (sulfur donor) in EV system was higher than CV system, thus the partial replacement of sulfur by sulfur donor was able to increase the scorch time [27]. However, the peroxide system showed the lowest scorch time because the rate of cross-linking was directly proportional to the decomposition rate of the peroxide;

therefore, any delayed action before cure was not present, which led to problems of scorching [28].

For the sulfur cure systems, cure time of EV system was slightly longer than that of CV system because sulfur-less and high accelerator content led to the more effective use of sulfur to produce the shorter sulfur linkage as well as to reduce the amount of unused sulfur for crosslinking. During vulcanization with TMTD, no free sulfur was formed. This can be demonstrated by using non-blackening of a silver mirror. However, this material gave a relatively rapid start of vulcanization with a flat flow time/cure time relation [29]. The effect of carbon black type on cure characteristic was also similar.

Table 4.1 Effect of blend ratios and carbon black types on cure characteristics of HNBR/NBR blends using CV system.

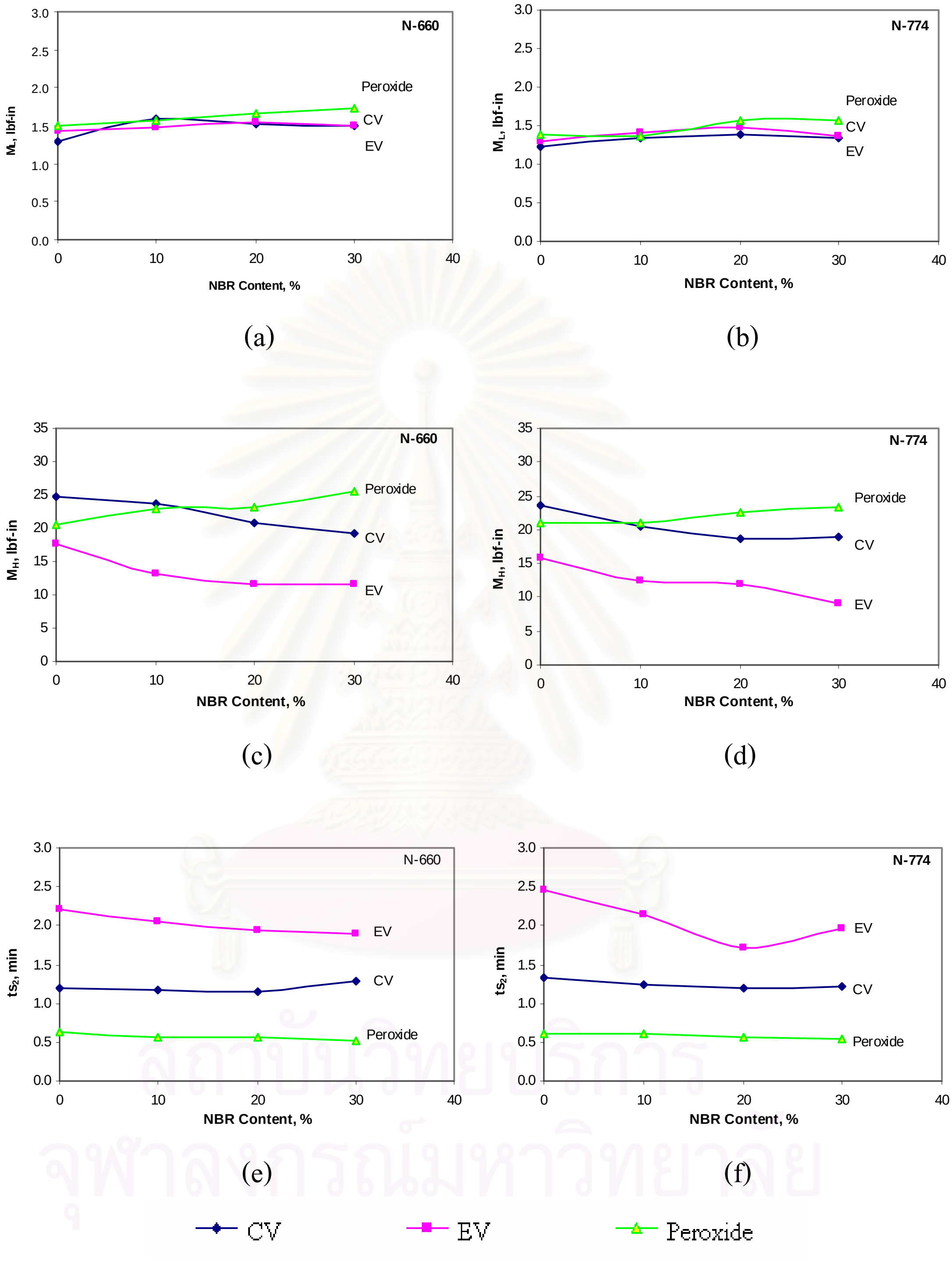
Properties	**C0-660**	**C10-660**	**C20-660**	**C30-660**	**C0-774**	**C10-774**	**C20-774**	**C30-774**
M_L, lbf-in	1.29	1.59	1.52	1.51	1.22	1.34	1.38	1.35
M_H, lbf-in	24.69	23.64	20.72	19.16	23.61	20.54	18.62	18.89
ts_2, min	1.20	1.17	1.16	1.28	1.32	1.23	1.20	1.22
tc_{90}, min	4.94	4.26	3.93	3.86	5.31	4.69	4.29	3.95

Table 4.2 Effect of blend ratios and carbon black types on cure characteristics of HNBR/NBR blends using EV system.

Properties	**E0-660**	**E10-660**	**E20-660**	**E30-660**	**E0-774**	**E10-774**	**E20-774**	**E30-774**
M_L, lbf-in	1.42	1.48	1.54	1.51	1.29	1.4	1.47	1.36
M_H, lbf-in	17.64	13.12	11.67	11.54	15.89	12.37	11.83	8.95
ts_2, min	2.20	2.05	1.95	1.89	2.45	2.15	1.71	1.97
tc_{90}, min	5.12	4.92	4.92	4.89	5.37	5.17	4.49	4.58

Table 4.3 Effect of blend ratios and carbon black types on cure characteristics of HNBR/NBR blends using peroxide curing system.

Properties	**P0-660**	**P10-660**	**P20-660**	**P30-660**	**P0-774**	**P10-774**	**P20-774**	**P30-774**
M_L, lbf-in	1.49	1.56	1.67	1.74	1.38	1.37	1.56	1.56
M_H, lbf-in	20.54	23.01	23.22	25.43	21.1	20.9	22.62	23.37
ts_2, min	0.63	0.56	0.56	0.52	0.61	0.60	0.56	0.54
tc_{90}, min	5.10	4.93	4.93	4.86	5.10	5.05	4.97	4.91



(a)

(b)

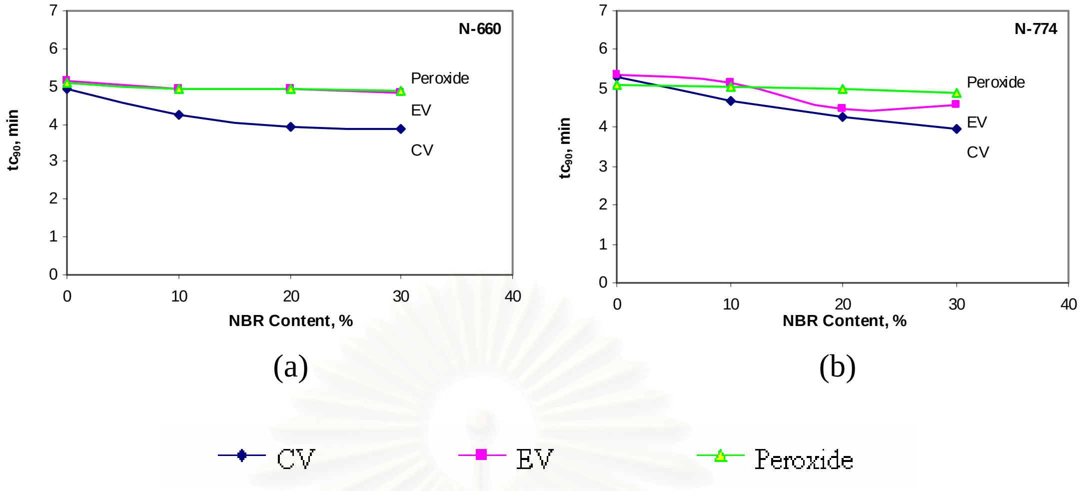
(c)

(d)

(e)

(f)

Figure 4.1 Effect of blend ratios and vulcanization systems on; (a) minimum torque, M_L for N-660, (b) minimum torque, M_L for N-774, (c) maximum torque, M_H for N-660, (d) maximum torque, M_H for N-774, (e) scorch time, ts$_2$ for N-660 and (f) scorch time, ts$_2$ for N-660 filled vulcanizates.



(a) (b)

Figure 4.2 Effect of blend ratios and vulcanization systems on cure time, tc_{90} for; (a) carbon black N-660 and (b) carbon black N-774 filled vulcanizates.

4.2 Mechanical Properties

The mechanical properties of the rubber compound filled with different carbon black types (GPF-N660 and SRF-N774) at various NBR contents (0, 10, 20 and 30%w/w) using various vulcanization systems (CV, EV and peroxide) were investigated. The 100%modulus (M_{100}), tensile strength (T.S), elongation at break (E.B), hardness and compression set (C.S) of rubber compound are presented in Tables 4.4- 4.6.

4.2.1 Tensile Properties

The mechanical properties in term of tensile properties of HNBR/NBR blends are shown in Figure 4.3.

Table 4.4 Effect of blend ratios and carbon black types on mechanical properties of HNBR/NBR blends using CV system.

Properties	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
M_{100}, MPa	5.54	6.06	5.86	5.96	4.90	5.25	4.92	5.44
T.S, MPa	21.78	20.51	18.41	18.72	18.66	19.51	18.76	17.68
E.B, %	406	359	346	345	304	378	384	315
Hardness, IRHD	75	75	73	73	73	71	71	70
C.S @125^{O}Cx72h, %	70.75	68.91	68.83	66.77	82.76	81.88	78.83	76.19

Table 4.5 Effect of blend ratios and carbon black types on mechanical properties of HNBR/NBR blends using EV system.

Properties	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
M_{100}, MPa	4.19	4.13	3.74	3.94	3.75	3.83	3.97	4.20
T.S., MPa	19.43	17.47	16.74	16.39	18.10	17.60	16.02	15.95
E.B, %	488	507	484	472	439	516	418	407
Hardness, IRHD	72	71	70	69	70	67	67	68
C.S @125^{O}Cx72h, %	52.30	51.84	51.54	48.84	56.19	52.00	51.48	48.38

Table 4.6 Effect of blend ratios and carbon black types on mechanical properties of HNBR/NBR blends using peroxide system.

Properties	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
M_{100}, MPa	8.57	8.99	9.75	10.53	6.63	8.13	8.61	8.70
T.S., MPa	25.61	22.96	23.85	23.45	23.13	22.83	21.92	21.48
E.B, %	233	196	205	184	225	196	196	188
Hardness, IRHD	76	76	74	75	73	72	72	74
C.S @125^{O}Cx72h, %	14.42	13.64	12.97	12.54	31.27	25.15	25.00	16.29

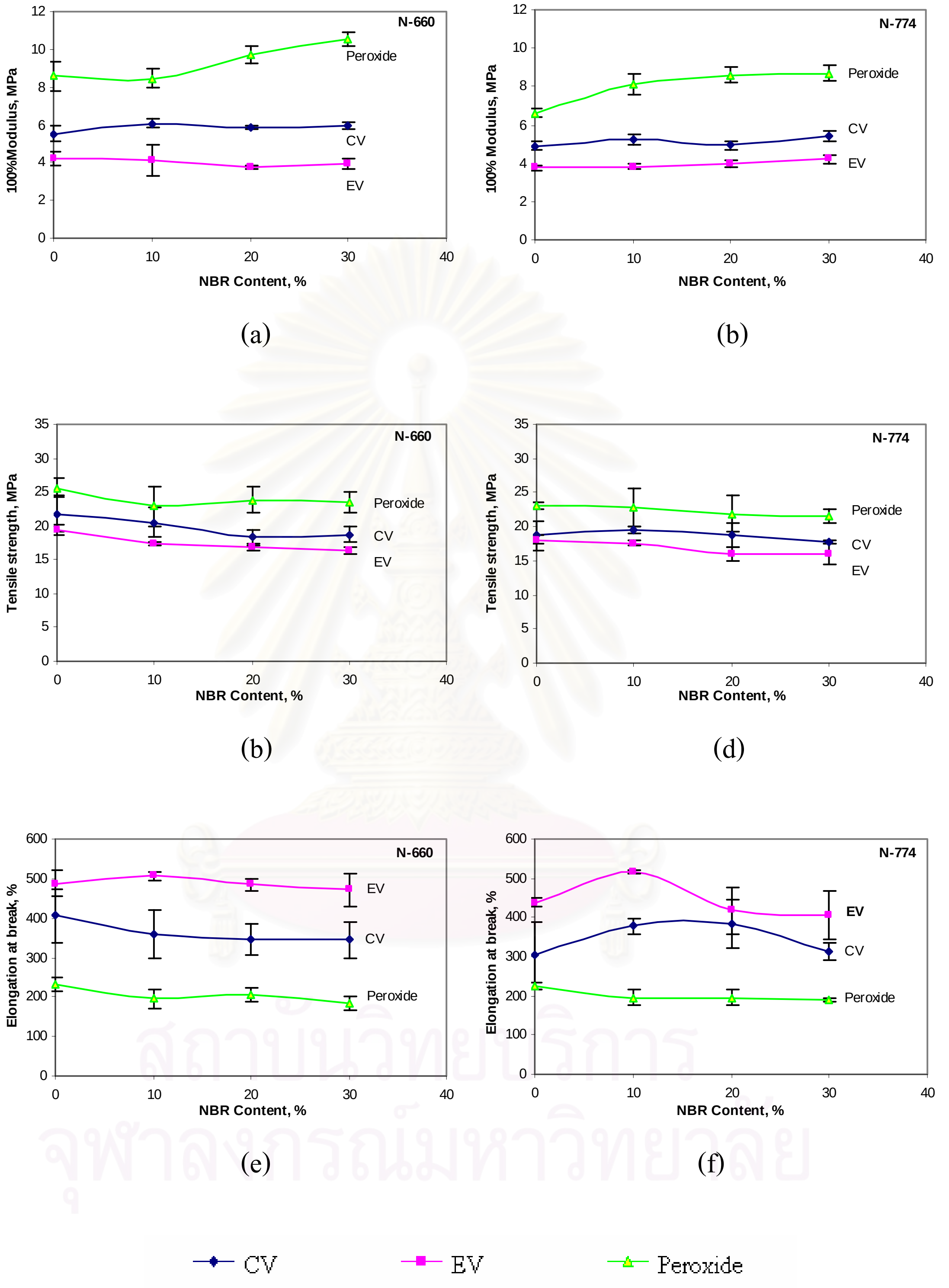


Figure 4.3 Effect of blend ratios and vulcanization systems on; (a) M_{100} for N-660, (b) M_{100} for N-774, (c) T.S for N-660, (d) T.S for N-774, (e) E.B for N-660 and (f) E.B for N-774 filled vulcanizates.

From Figure 4.3(a)-(b), the blends using various different curing systems are compared. It was found that the 100%modulus of blend obtained from peroxide system increased with increasing NBR content because the peroxide system gave the maximum torque and crosslink density. This is due to the fact that peroxide could cure both HNBR and NBR phases uniformly and the carbon-carbon structure in the peroxide system is rigid. However, the 100%modulus of blend using CV system was higher than that of blend using EV system because of higher crosslink density.

The tensile strength [Figure 4.3(c)-(d)] and elongation at break [Figure 4.3(e)-(f)] decreased with an increase in the percentage of NBR in the blend. This can be explained by Treloar's theory that the HNBR is more highly saturated, thus the rotation of the polyethylene chain in certain random linkage becomes more difficult than with butadiene unit having double bonds in the same random linkages. For simplicity, only the carbon skeleton of the chains is shown in Figure 4.4. The spheres are just optical guidelines. The remaining double bond in the lower chain effectively prevents any close alignment with the other chains. The ethylene units enable the polymer structure to exhibit strain-induced crystallization, which creates the significantly enhanced mechanical properties over NBR [30].

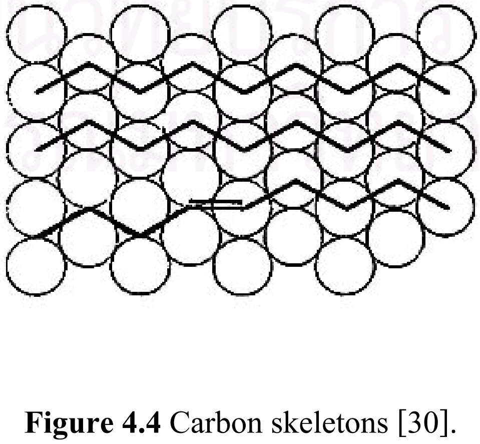


Figure 4.4 Carbon skeletons [30].

For the effect of curing systems, the HNBR/NBR blends using the peroxide curing system also exhibited highest tensile strength and poorer elongation at break than those using the sulfur curing systems. It can be explained that the peroxide curing system produced a rubber network consisting of more stable C-C linkages between the rubber molecules; while the sulfur-cured system generated weaker and less stable S-S and C-S linkages. This resulted in higher tensile strength of peroxide cured blends [31]. For the sulfur curing systems; the tensile strength of blends using CV system was higher than those using EV system but elongation was opposite because the longer crosslinks (polysulfidic linkage) promote the better tensile strength.

For effect of carbon black type, it was found that the tensile strength and 100%modulus of N-660 filled compound was higher than N-774 filled compound because the higher surface area (the smaller particle size of N-660) gave the higher tensile strength. Therefore, it is recognized that the increase in component of surface free energy of the carbon black surfaces is important for improving the degree of adhesion between the carbon blacks and the HNBR or NBR. The interaction between NBR or HNBR and the carbon black surface is believed to be due to the hydrogen bonding or Van der Waal's forces and the extent of interaction increases when the oxygen content on the filler surface increases [22]. A schematic representation of the interaction between the nitrile rubbers and carbon black is shown in Figure 4.5.

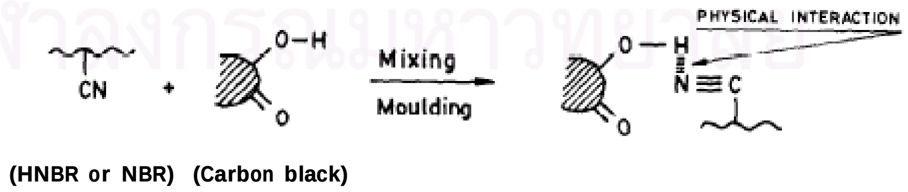
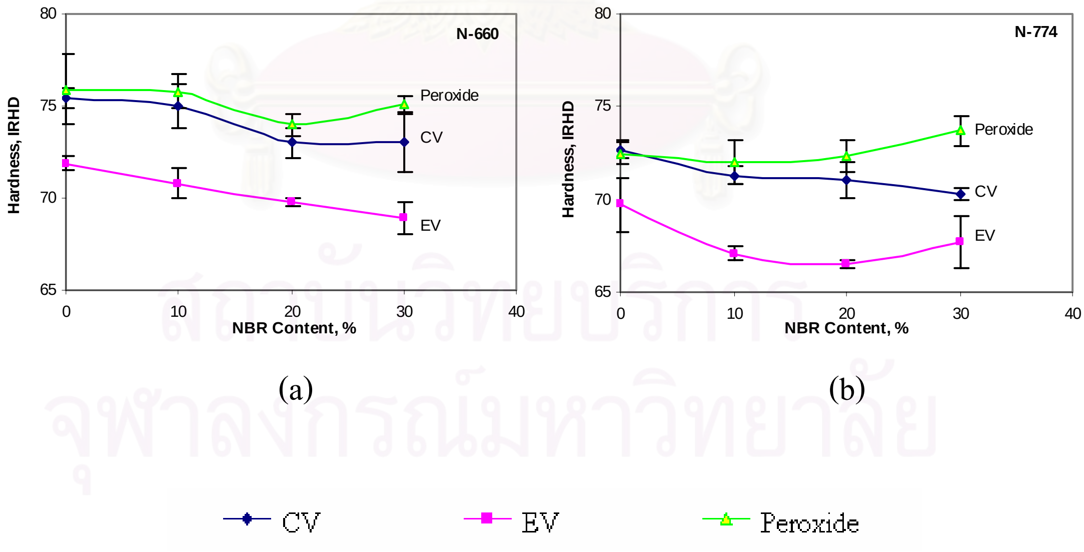


Figure 4.5 Probable mechanism of bonding in HNBR or NBR with carbon black system [22].

4.2.2 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. The effect of curing system and carbon black type on hardness of rubber vulcanizates are shown in Figure 4.6. It can be seen that the hardness of vulcanizates obtained from peroxide system was higher than that from CV and EV systems because HNBR/NBR blend using peroxide system exhibits maximum torque and crosslink density, thus the hardness increased analogous to the stress value with increasing crosslink density until it reached the hard rubber (ebonite) stage [29]. The hardness of N-660 filled compound was higher than that of N-744 filled compound because the higher surface area (smaller particle size of N-660) resulted in a compound with high hardness.

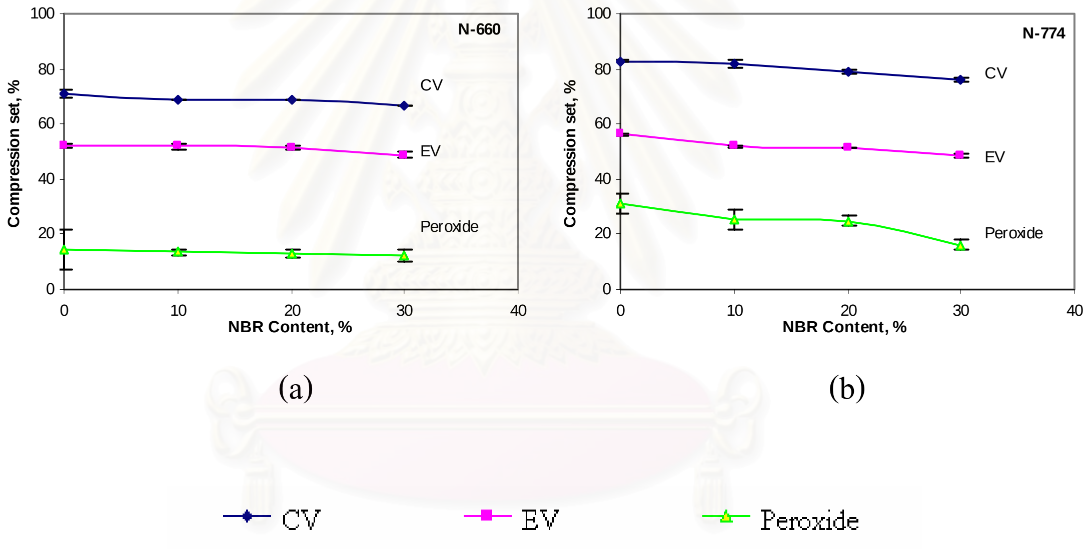


(a) (b)

Figure 4.6 Effect of blend ratios and vulcanization systems on hardness for; (a) carbon black N-660 and (b) carbon black N-774 filled vulcanizates.

4.2.3 Compression set

Figure 4.7 shows the compression set performance at 125°C for 22 h. It can be seen that the compression set of HNBR/NBR blends decreased with increasing the NBR content. It can be explained that HNBR has higher saturation, so the rotation of the polyethylene chain in certain random linkage becomes more difficult than that of butadiene unit having double bonds in the same random linkages. Consequently, HNBR has the higher degree of compactness of the chains network.



(a) (b)

Figure 4.7 Effect of blend ratios and vulcanization systems on compression set for: (a) carbon black N-660 and (b) carbon black N-774 filled vulcanizates.

The rubber compound vulcanized by CV system exhibited the much higher compression set than that by EV and peroxide systems because the longer crosslinks (S_x) of CV cured blends cause the higher free mobility of the chain segments. The vulcanizates with peroxide system have the lowest compression set among the three curing systems because the vulcanizates with high bond strength crosslinks (C-C bonds) are superior than those with lower bond strength ($C-S_x-C$ bonds). This is the reason why the vulcanizates with shorter crosslinks (semi-EV, EV and peroxide systems) have generally better heat stability than those with polysulfidic crosslinks (CV system). Therefore, the higher bond strength of shorter crosslinks is important for the high temperature compression set and the heat stability of the vulcanizates (low values of x in $C-S_x-C$ generally give better permanent set values) [29]. Thus, EV and peroxide systems generally have lower compression set values, especially at elevated temperatures.

For the effect of carbon black types, the compression set was slightly affected by carbon black type for the various blend compositions.

4.3 Thermal Aging Properties

The thermal resistance of the rubber vulcanizates is considered as an essential requirement for the long service life of products. The percentages of change in 100%modulus, tensile strength, elongation at break and hardness as a result of aging at 125°C for 168 h are present in Tables 4.7-4.9 and Figures 4.8-4.9. It can be seen that after aging the change in hardness and tensile properties increased with increasing the concentration of NBR in the blends. The static heat resistance of HNBR elastomers is dependent on the level of saturation within a given polymer. As the level of saturation increases, the static heat resistance is improved [32].

The results indicated that after aging the change in hardness and tensile properties of vulcanizates obtained from peroxide system was lower than that from EV and CV system. Vulcanizates with high bond strength crosslinks (C-C bonds) are superior than those with lower bond strength (C-S_x-C bonds). This is the reason why vulcanizates with shorter crosslinks (semi-EV, EV and peroxide systems) generally have better heat stability than those with polysulfidic crosslinks (CV system). Therefore, the sulfur/accelerator ratio is especially important for the thermal stability of the vulcanizates. A temperature stability is not achieved by either the proper adjustment of the sulfur dose or the addition of antidegradants. The vulcanization with low sulfur content also has a beneficial effect on the tendency to reversion. Moreover, momo- and disulfide crosslinks are more stable (less prone to scission) than polysulfide links. Thus, the thermal and aging characteristics are improved. The thermal decomposition of peroxide produces the oxy radicals, which abstract a hydrogen from the elastomer to generate the polymer radicals to form the more thermally stable carbon-carbon crosslinks.

Table 4.7 Effect of blend ratios and carbon black types on percent properties change of HNBR/NBR blends (CV) after thermal aging at 125°C for 168 h.

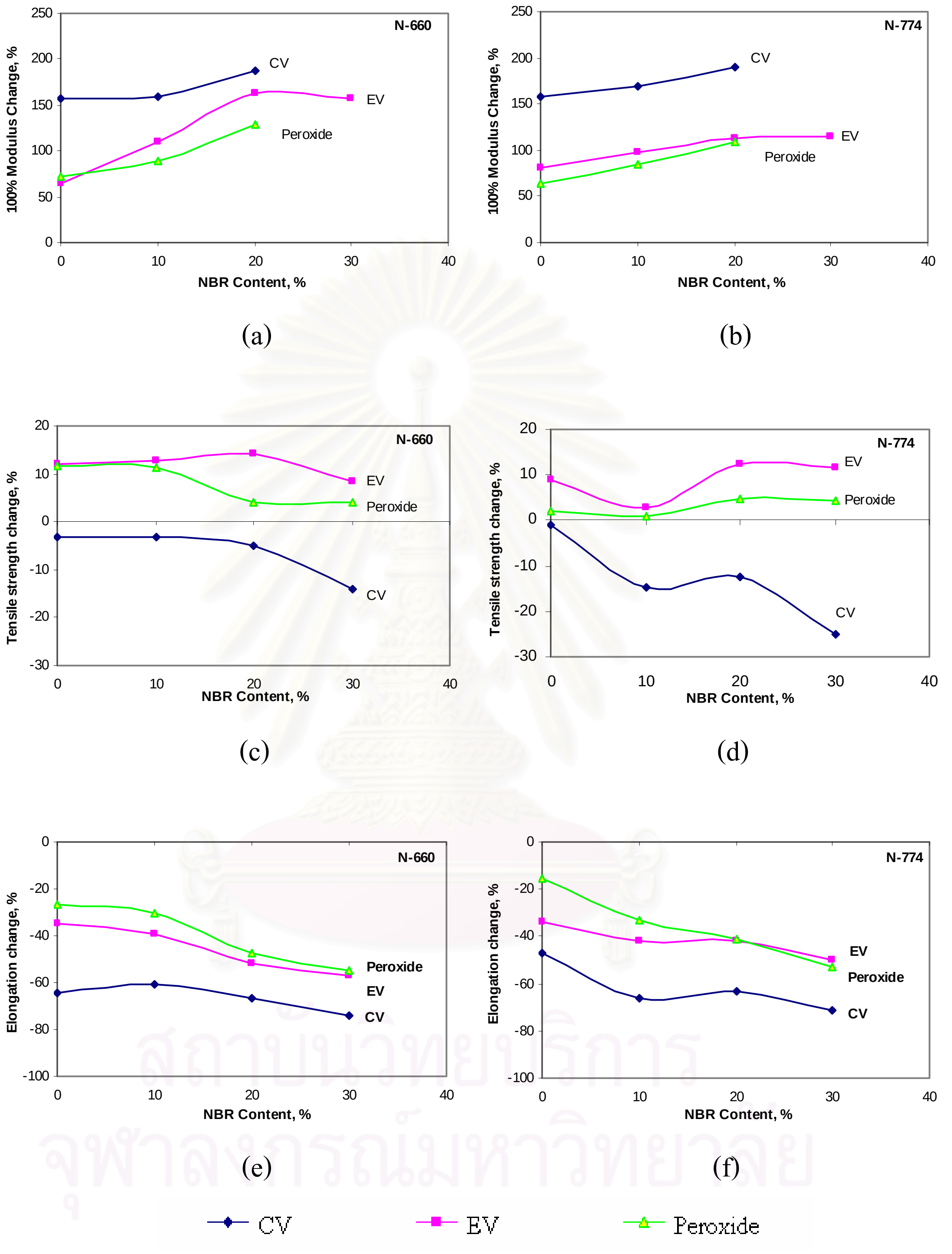
Properties	**C0-660**	**C10-660**	**C20-660**	**C30-660**	**C0-774**	**C10-774**	**C20-774**	**C30-774**
M_{100} change, %	157	159	188	-	157	169	190	-
T.S change, %	-3	-3	-5	-14	-1	-15	-12	-25
E.B, %	-64	-61	-67	-74	-47	-66	-64	-71
Hardness change, Hs.	9	16	22	22	9	18	18	22

Table 4.8 Effect of blend ratios and carbon black types on percent properties change of HNBR/NBR blends (EV) after thermal aging at 125°C for 168 h.

Properties	**E0-660**	**E10-660**	**E20-660**	**E30-660**	**E0-774**	**E10-774**	**E20-774**	**E30-774**
M_{100} change, %	64	110	163	158	81	98	112	114
T.S change, %	12	13	14	8	9	3	12	12
E.B, %	-35	-39	-52	-57	-33	-42	-42	-50
Hardness change, Hs.	6	11	13	18	3	11	11	10

Table 4.9 Effect of blend ratios and carbon black types on percent properties change of HNBR/NBR blends (peroxide) after thermal aging at 125°C for 168 h.

Properties	**P0-660**	**P10-660**	**P20-660**	**P30-660**	**P0-774**	**P10-774**	**P20-774**	**P30-774**
M_{100} change, %	72	79	128	-	64	84	109	-
T.S change, %	12	11	4	4	2	1	5	4
E.B, %	-27	-31	-47	-55	-16	-33	-41	-53
Hardness change, Hs.	2	9	13	17	6	11	16	16

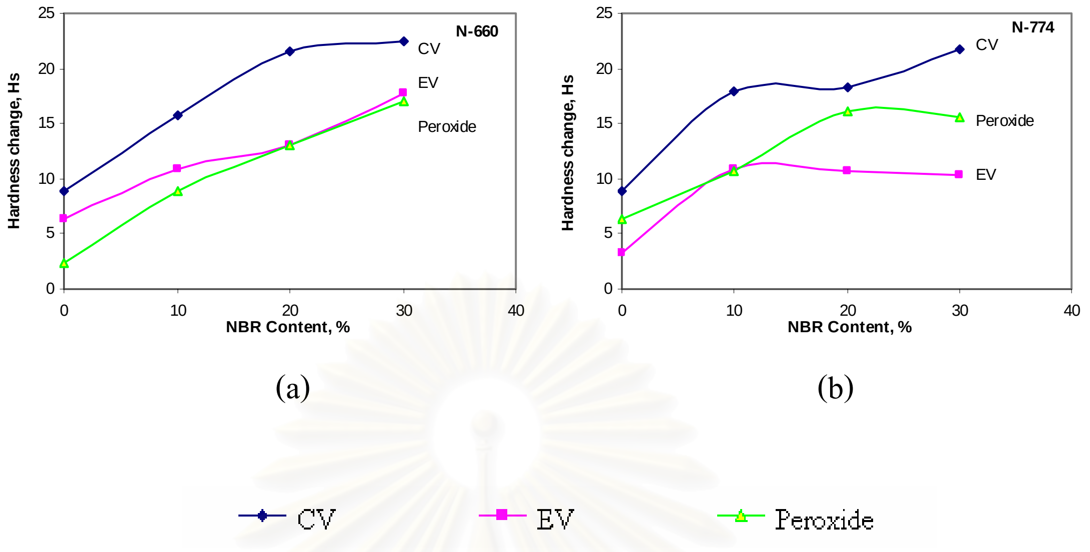


(a) (b)

(c) (d)

(e) (f)

Figure 4.8 Effect of blend ratios types and vulcanization systems on percent change after thermal aging (a) M_{100} for N-660, (b) M_{100} for N-774, (c) T.S for N-660, (d) T.S for N-774, (e) E.B for N-660 and (f) E.B for N-774 filled vulcanizates.



(a) (b)

Figure 4.9 Effect of blend ratios and vulcanization systems on percent change in hardness after thermal aging (a) carbon black N-660 and (b) carbon black N-774 filled vulcanizates.

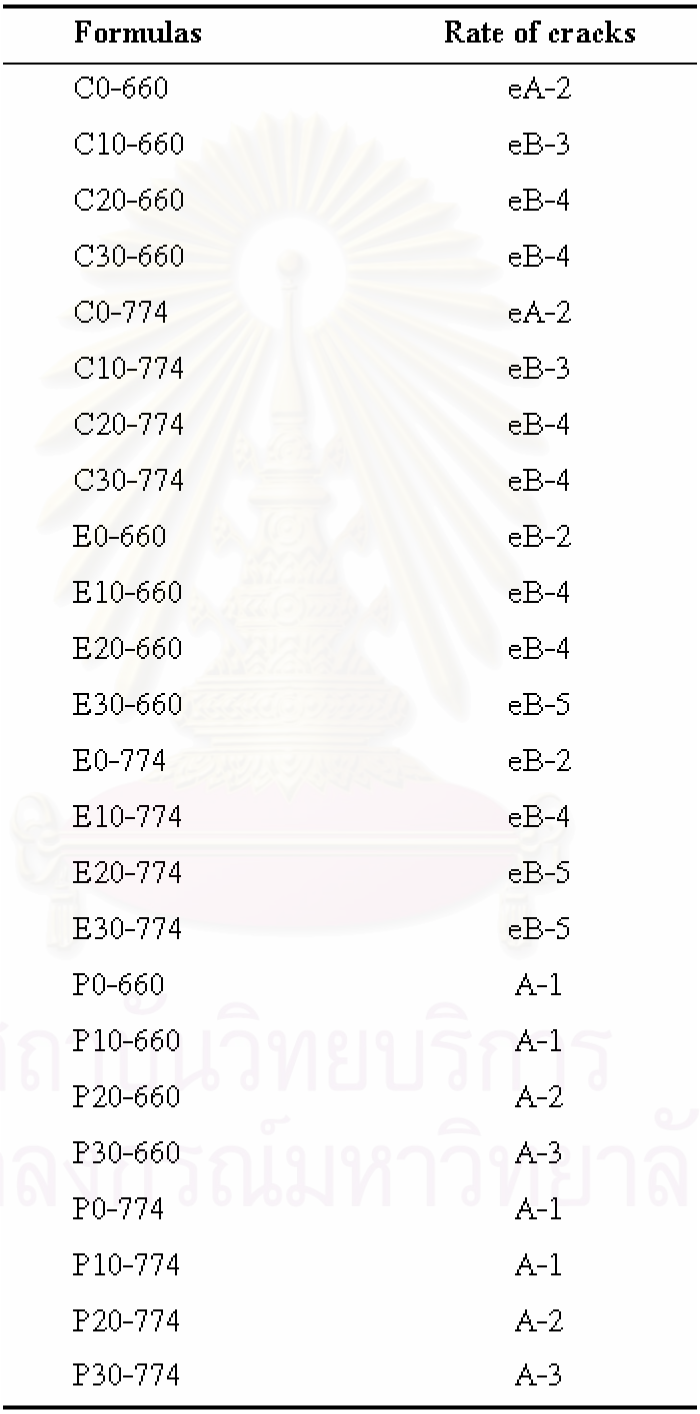
4.4 Ozone Resistance

Ozone aging studies under static conditions were performed according to JIS K 6301-1995. The HNBR/NBR blends are exposed to 50 pphm of ozone concentration for 72 h at 40°C. Table 4.10 presents the rate of cracks of carbon black filled vulcanizates. Figures 4.10-4.12 show photographs of the ozone-cracked samples of HNBR/NBR blends cured by using CV, EV and peroxide systems. Figures 4.10(a)-4.12(d) show the ozone cracked surface of N-660 filled vulcanizates. Figures 4.10(e)-4.12(h) indicate the ozone cracked surface of N-774 filled vulcanizates. It can be seen that the severe cracks were developed on the surface of vulcanizates without any antioxidants. The surface of pure HNBR vulcanizates showed the less cracking [Figures 4.10(a)/(e), 4.11(a)/(e), and 4.12(a)/(e)], while the deeper cracks were observed for samples containing 10-30%NBR content. It can be explained that the saturated backbone of HNBR network formation could prevent the initiation and propagation of ozone cracks on the surface, this results in a superior ozone resistance of HNBR vulcanizates.

Figures 4.10-4.12 show the ozone-cracked surface of HNBR/NBR blends using various curing systems. The photographs clearly show that the blends cured with peroxide system have the less number of cracks; while, the surfaces of samples cured by EV system show the deeper and larger crack than those cured by CV system. Despite having lower modulus values, the sulfur cured samples have remarkably less resistance to ozone than the peroxide cured samples [21].

The ozone-cracked surface of HNBR/NBR was slightly affected by carbon black type for the various blend compositions. Because ozone effected are surface-based. Ozone attack, on the other hand, happens only to stress vulcanizate of unsaturated polymers [28].

Table 4.10 Effect of blend ratios, carbon black types and vulcanization systems on ozone cracking of HNBR/NBR blends.



Formulas	Rate of cracks
C0-660	eA-2
C10-660	eB-3
C20-660	eB-4
C30-660	eB-4
C0-774	eA-2
C10-774	eB-3
C20-774	eB-4
C30-774	eB-4
E0-660	eB-2
E10-660	eB-4
E20-660	eB-4
E30-660	eB-5
E0-774	eB-2
E10-774	eB-4
E20-774	eB-5
E30-774	eB-5
P0-660	A-1
P10-660	A-1
P20-660	A-2
P30-660	A-3
P0-774	A-1
P10-774	A-1
P20-774	A-2
P30-774	A-3

*50 pphm of ozone concentration at 40°C for 72h under 20%strained

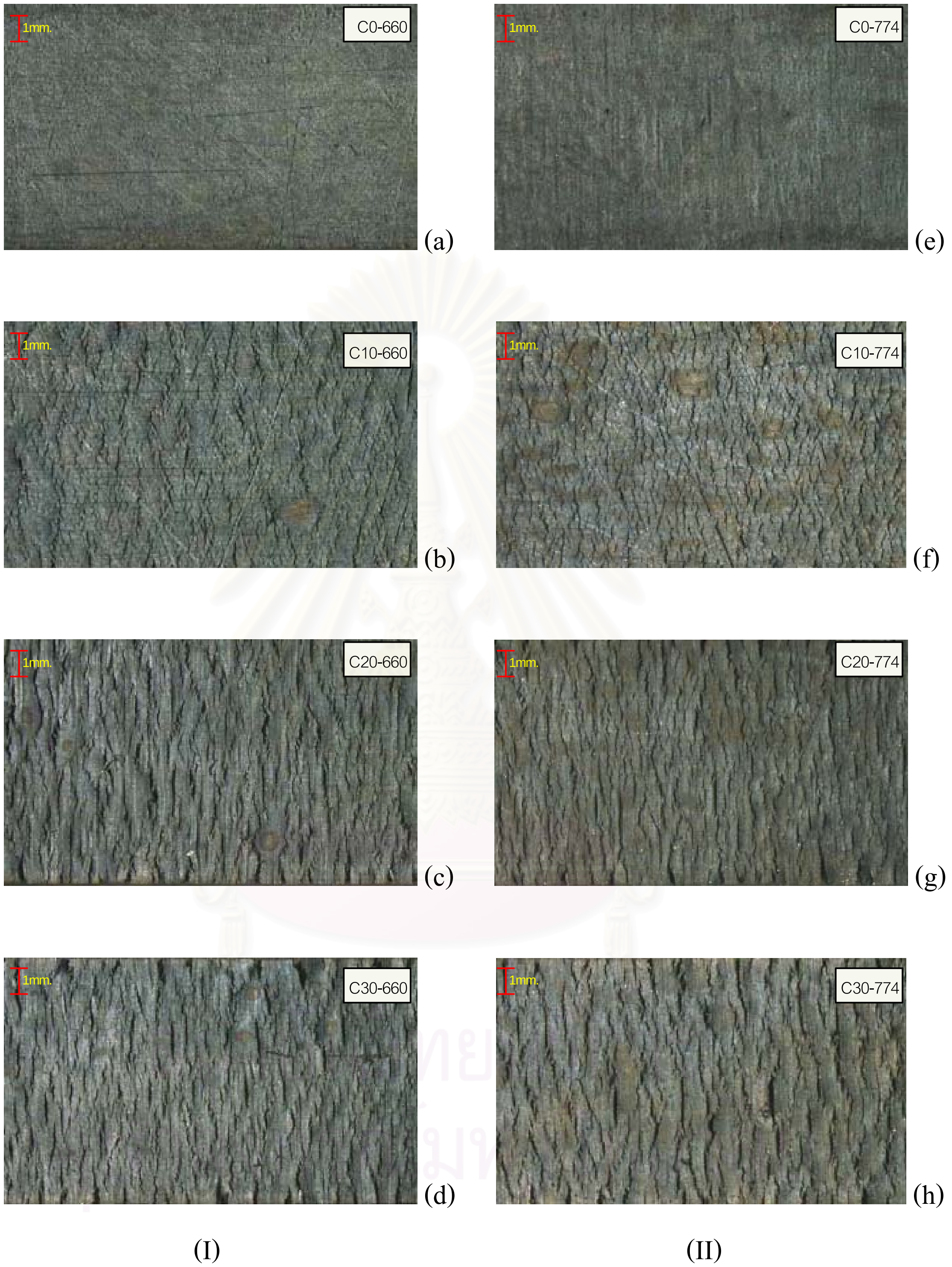
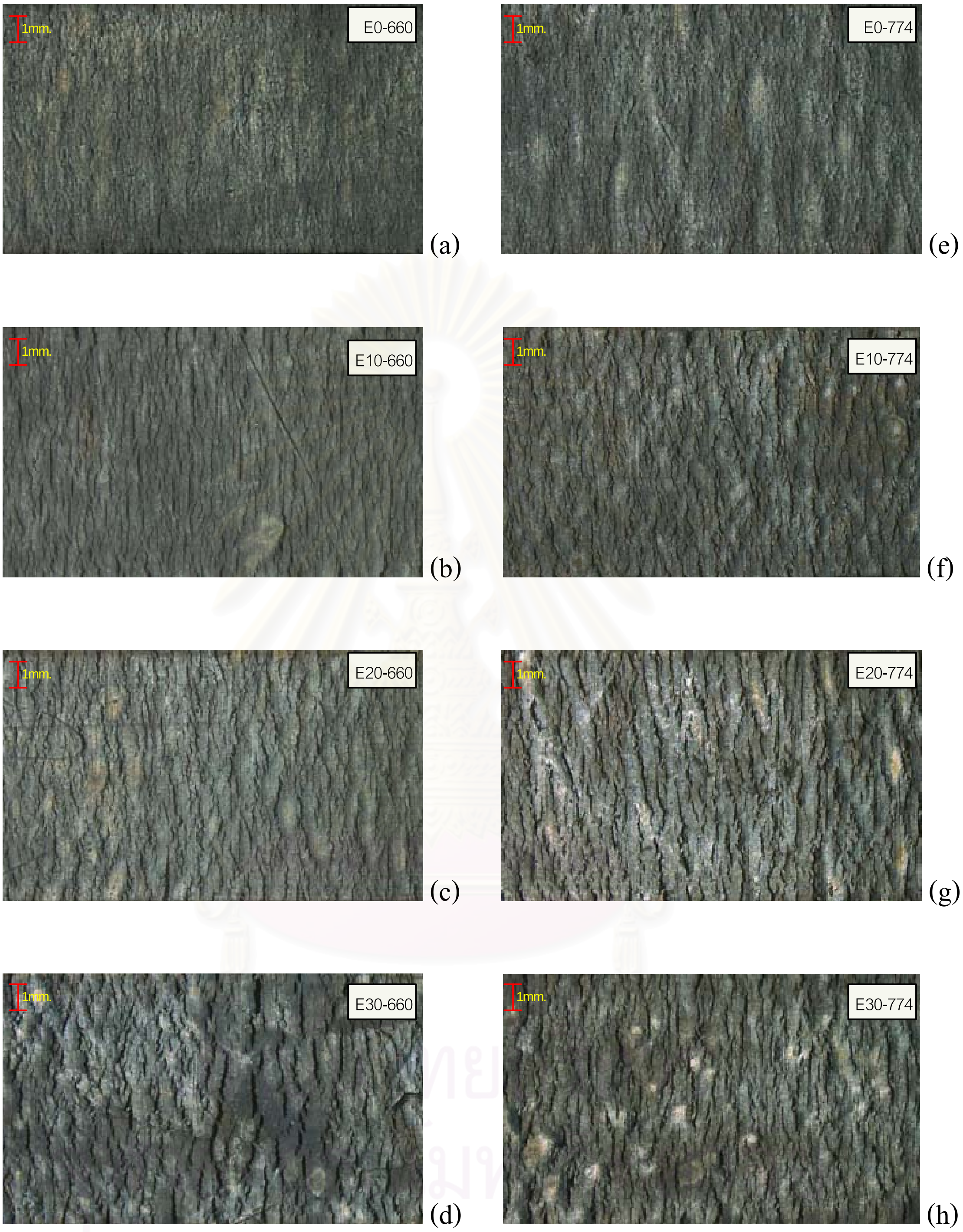
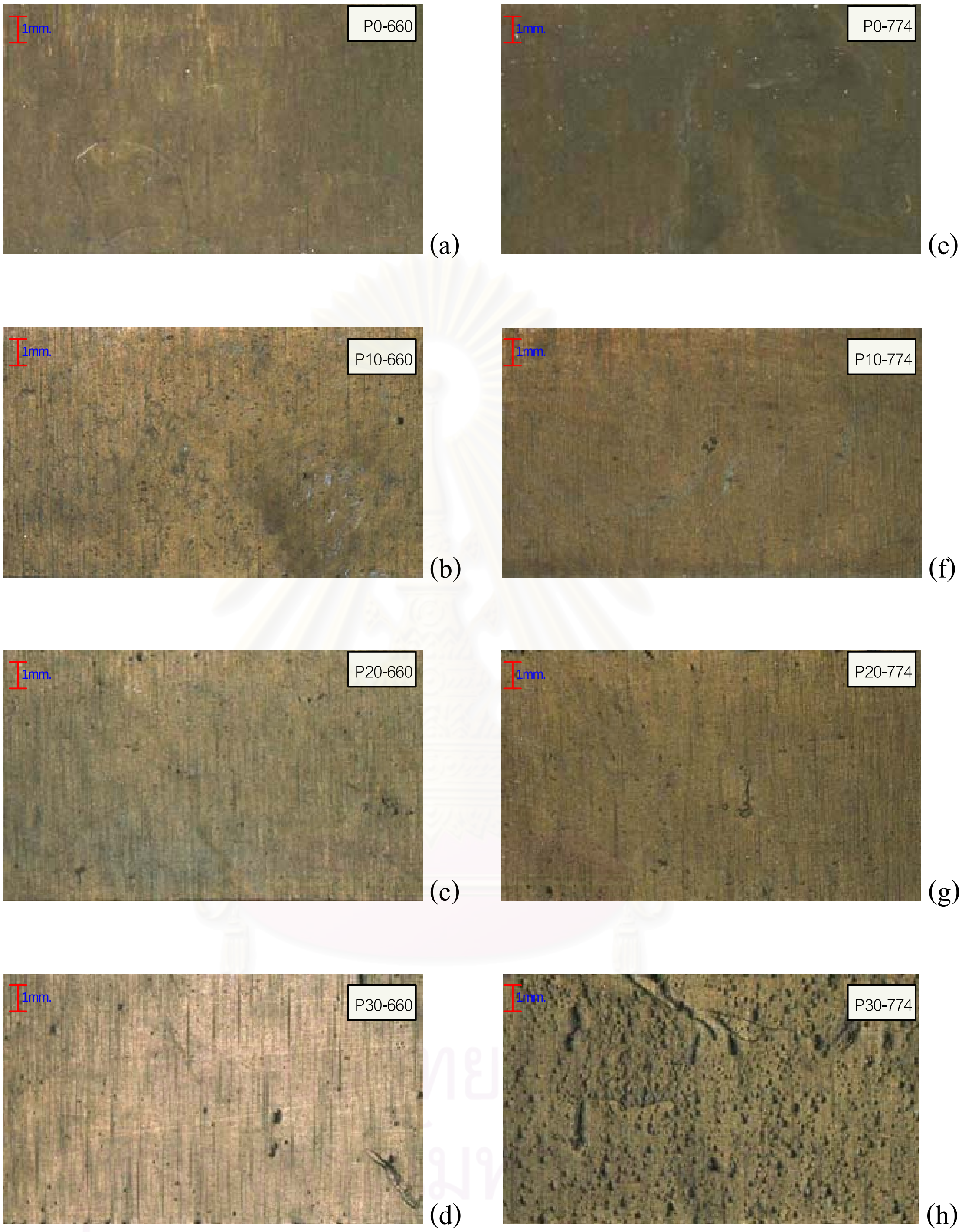


Figure 4.10 (I) Ozone cracked surface of N-660 filled vulcanizates cured by CV system: (a) pure HNBR, (b) 10%NBR, (c) 20%NBR and (d) 30%NBR. (II) ozone cracked surface of N-774 filled vulcanizates cured by CV system: (e) pure HNBR, (f) 10%NBR, (g) 20%NBR and (h) 30%NBR.



(I) (II)

Figure 4.11 (I) Ozone cracked surface of N-660 filled vulcanizates cured by EV system: (a) pure HNBR, (b) 10%NBR, (c) 20%NBR and (d) 30%NBR. (II) ozone cracked surface of N-774 filled vulcanizates cured by EV system: (e) pure HNBR, (f) 10%NBR, (g) 20%NBR and (h) 30%NBR.



(a) (e)

(b) (f)

(c) (g)

(d) (h)

(I) (II)

Figure 4.12 (I) Ozone cracked surface of N-660 filled vulcanizates cured by peroxide system: (a) pure HNBR, (b) 10%NBR, (c) 20%NBR and (d) 30%NBR. (II) ozone cracked surface of N-774 filled vulcanizates cured by peroxide system: (e) pure HNBR, (f) 10%NBR, (g) 20%NBR and (h) 30%NBR.

4.5 Swelling

Swelling measurements in the presence of IRM 903 oil and engine oil were applied to HNBR and NBR vulcanizates and their blends. The percentage of change in tensile properties, hardness, and volume after immersed in oil at 125°C for 70 h are presented in Tables 4.11-4.13 and Figures 4.13-4.15. The swelling resistance of pure HNBR in IRM 903 and engine oil was lower than that of HNBR/NBR vulcanizates due to the saturated structure of hydrogenated nitrile rubber (HNBR) [33]. From Figures 4.13-4.15, it can be seen that after immersion in IRM 903 oil, the change in tensile strength, elongation at break, hardness and volume of vulcanizates obtained from peroxide system was lowest, but the change in 100%modulus was highest. For the samples after immersion in engine oil, the change in 100%modulus, tensile strength, elongation at break, and volume of vulcanizates obtained from peroxide cure was also lowest. The vulcanizates cured by peroxide had maximum crosslink density (maximum torque from Table 4.3) therefore; a small amount of oil was absorbed. In addition, it was found that the carbon black type did not affect the oil resistance of the blends.

Table 4.11 Effect of blend ratios and carbon black types on percent change of properties of HNBR/NBR blends cured by CV system after immersion in oils at 125°C for 70 h.

Properties	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
IRM903 @125°C x 70h								
M_{100} change, %	2	4	1	11	9	1	15	15
T.S change, %	-1	-13	-5	-19	0	-20	-12	-7
E.B, %	-27	-34	-20	-40	-11	-35	-39	-30
Hardness change, Hs.	-3	-8	-11	-11	-7	-6	-9	-6
Volume change, %	10.8	12.6	12.0	9.2	10.1	10.6	10.1	9.2
Engine oil @125°C x 70h								
M_{100} change, %	27	34	30	30	30	43	50	37
T.S change, %	-9	-3	-7	-8	-9	-1	-14	-9
E.B, %	-44	-35	-43	-39	-29	-38	-48	-36
Hardness change, Hs.	-2	-2	-6	-2	-5	-1	-1	0
Volume change, %	5.4	5.2	6.9	5.2	5.0	4.3	4.5	4.0

Table 4.12 Effect of blend ratios and carbon black types on percent change of properties of HNBR/NBR blends cured by EV system after immersion in oils at 125°C for 70 h.

Properties	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
IRM903 @125°C x 70h								
M_{100} change, %	11	3	7	4	10	1	0	1
T.S change, %	26	12	4	2	17	2	6	2
E.B, %	-9	-15	-17	-18	-17	-36	-15	-12
Hardness change, Hs.	-4	-4	-5	-4	-4	-3	-1	-4
Volume change, %	7.4	7.3	7.3	7.3	7.2	8.4	7.1	6.3
Engine oil @125°C x 70h								
M_{100} change, %	28	35	40	24	30	35	23	23
T.S change, %	15	7	12	8	11	10	13	8
E.B, %	-32	-35	-29	-32	-30	-34	-14	-25
Hardness change, Hs.	2	1	3	1	2	3	3	0
Volume change, %	1.5	1.6	1.6	1.6	1.5	1.6	1.8	1.6

Table 4.13 Effect of blend ratios and carbon black types on percent change of properties of HNBR/NBR blends cured by peroxide system after immersion in oils at 125°C for 70 h.

Properties	**P0-660**	**P10-660**	**P20-660**	**P30-660**	**P0-774**	**P10-774**	**P20-774**	**P30-774**
IRM903 @125°C x 70h								
M_{100} change, %	12	15	13	16	2	5	10	12
T.S change, %	5	1	5	7	7	1	4	4
E.B, %	-1	-14	-10	-6	-2	-6	-1	-8
Hardness change, Hs.	-6	-4	-1	-1	-5	-2	-1	-2
Volume change, %	7.2	6.3	5.9	7.2	6.7	5.9	6.6	5.2
Engine oil @125°C x 70h								
M_{100} change, %	2	23	26	32	21	22	23	23
T.S change, %	3	2	9	10	7	3	0	2
E.B, %	-1	-8	-8	-7	-1	-7	-13	-19
Hardness change, Hs.	-1	2	3	4	0	3	4	1
Volume change, %	-0.1	-0.1	-0.1	-0.2	-0.1	-0.5	-0.1	-0.1

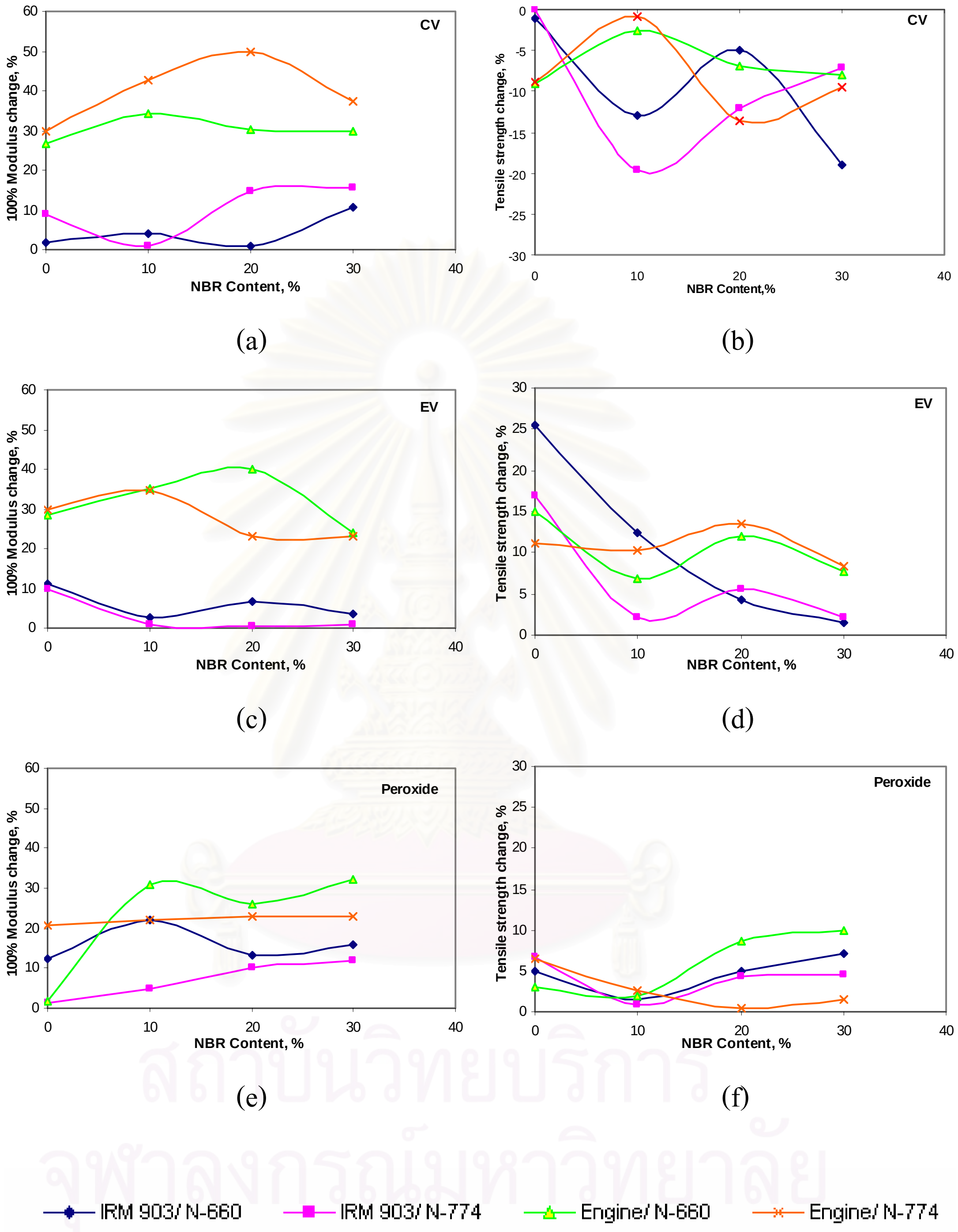
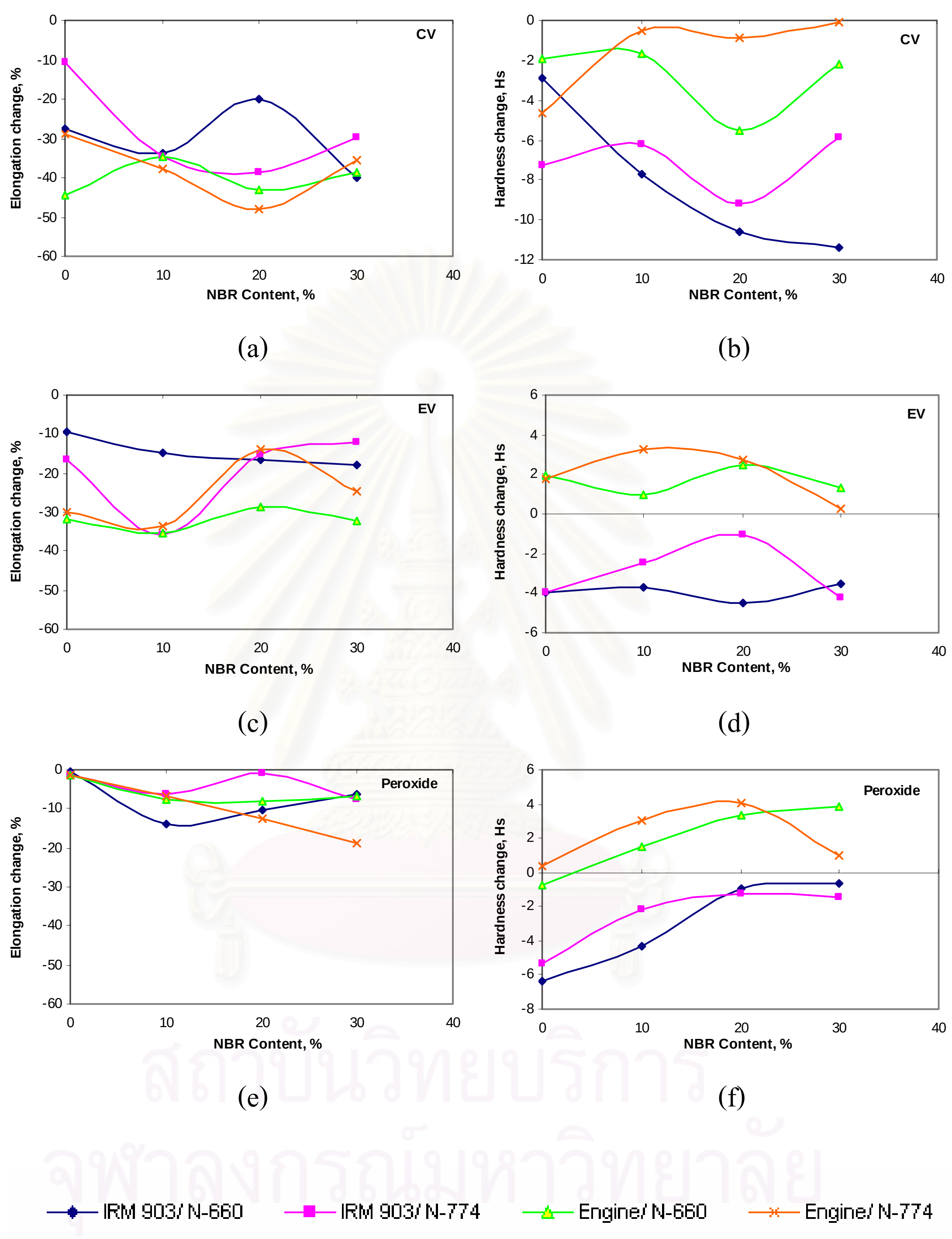


Figure 4.13 Effect of blend ratios and carbon black types on percent change of M_{100} and T.S of HNBR/NBR blends: (a)/(b) CV, (c)/(d) EV and (e)/(f) peroxide systems after immersion in IRM 903 and engine oils.

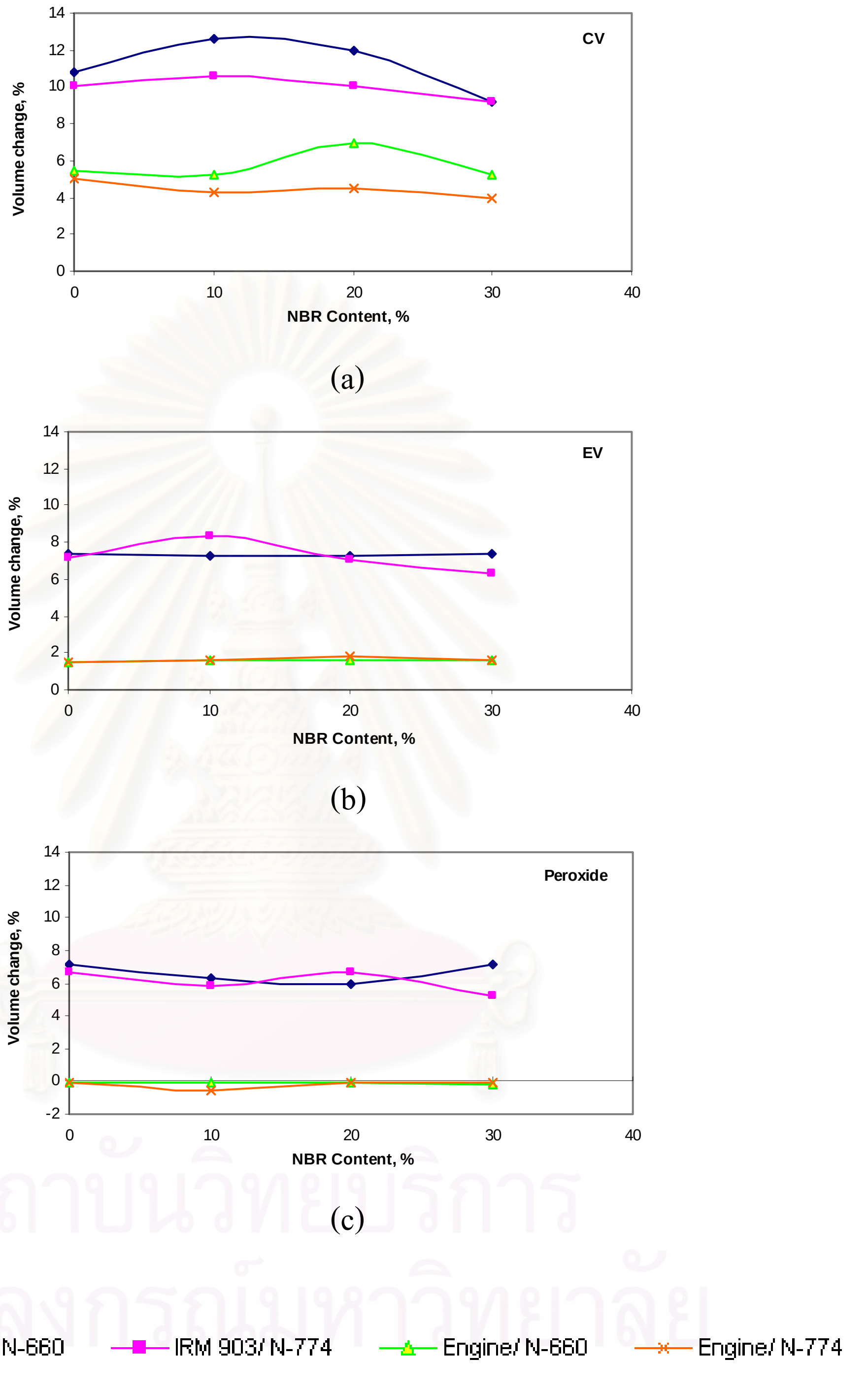


(a) (b)

(c) (d)

(e) (f)

Figure 4.14 Effect of blend ratios and carbon black types on percent change of E.B and hardness of HNBR/NBR blends: (a)/(b) CV, (c)/(d) EV and (e)/(f) peroxide systems after immersion in IRM 903 and engine oils.



(a)

(b)

(c)

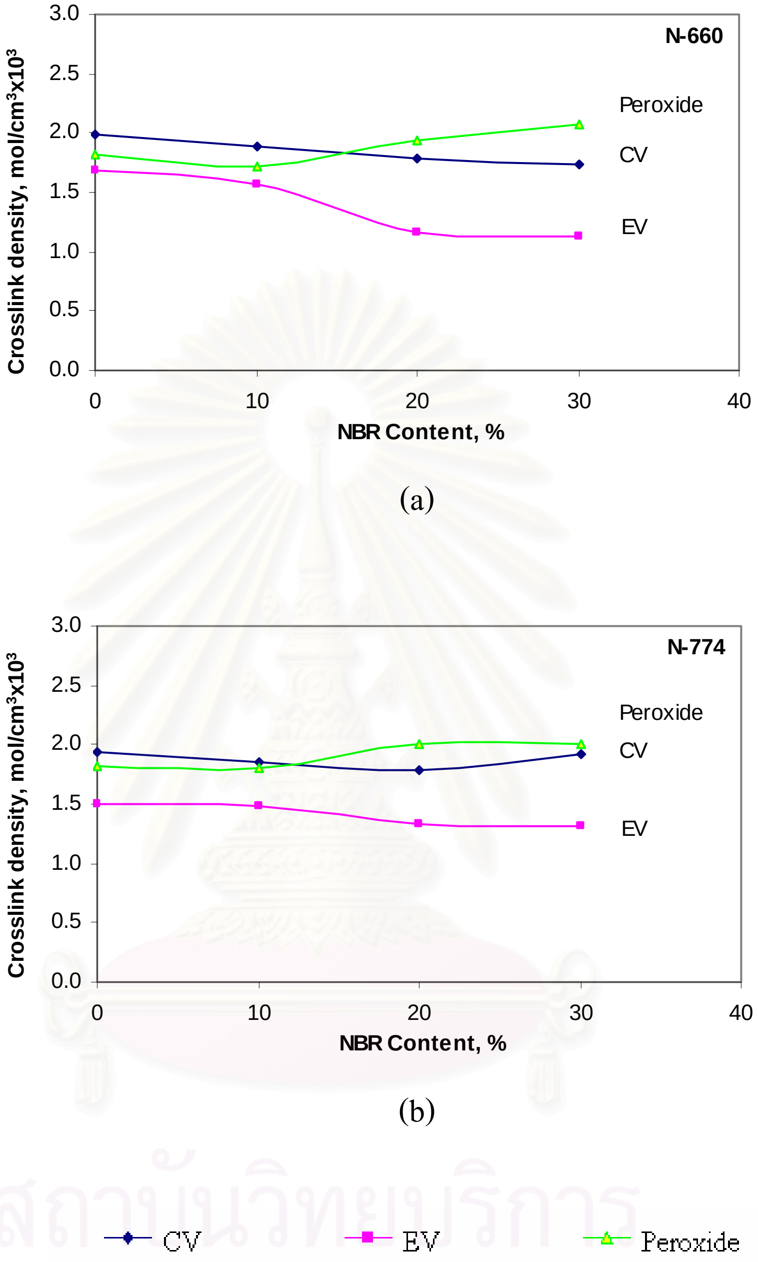
Figure 4.15 Effect of blend ratios and carbon black types on percent change of volume of HNBR/NBR blends: (a) CV, (b) EV and (c) peroxide systems after immersion in IRM 903 and engine oils.

4.6 Crosslink density

The total crosslink density of the vulcanizates determined by using the toluene swelling method developed by Flory-Huggins are presented in Table 4.14 and Figure 4.16. When the blends with 20 and 30%NBR contents was cured by three vulcanizing systems, the HNBR/NBR blends cured by the peroxide system showed the highest crosslink density. The HNBR/NBR blends cured with EV system exhibited the lowest for all blend ratios. This is due to the fact that the peroxide could cure both HNBR and NBR phases uniformly. For pure HNBR and the blend with 10%NBR cured by CV systems, the degree of crosslinking was substantially higher than those cured by peroxide and EV systems. Due to the formation of more interfacial regions between filler and rubber matrix; consequently, the crosslink density increased. Since the crosslink density increased, the molecular movement of the rubber chains was limited and it resulted in the difficulty for the penetration of toluene through the rubber. Therefore, the swelling percentage of HNBR/NBR blend cured by CV system was lower.

Table 4.14 Effect of blend ratios and carbon black types on crosslink density.

Carbon black type	NBR Content (%)	Crosslink density (mol/cm^3 x10^3)		
		CV	EV	Peroxide
N-660	0	1.99	1.69	1.82
	10	1.89	1.57	1.72
	20	1.78	1.16	1.94
	30	1.73	1.13	2.07
N-774	0	1.94	1.50	1.82
	10	1.85	1.48	1.80
	20	1.79	1.34	2.01
	30	1.93	1.32	2.01



(a)

(b)

Figure 4.16 Effect of blend ratios and vulcanization systems on crosslink density of HNBR/NBR vulcanizate filled with (a) carbon black N-660 and (b) carbon black N-774.

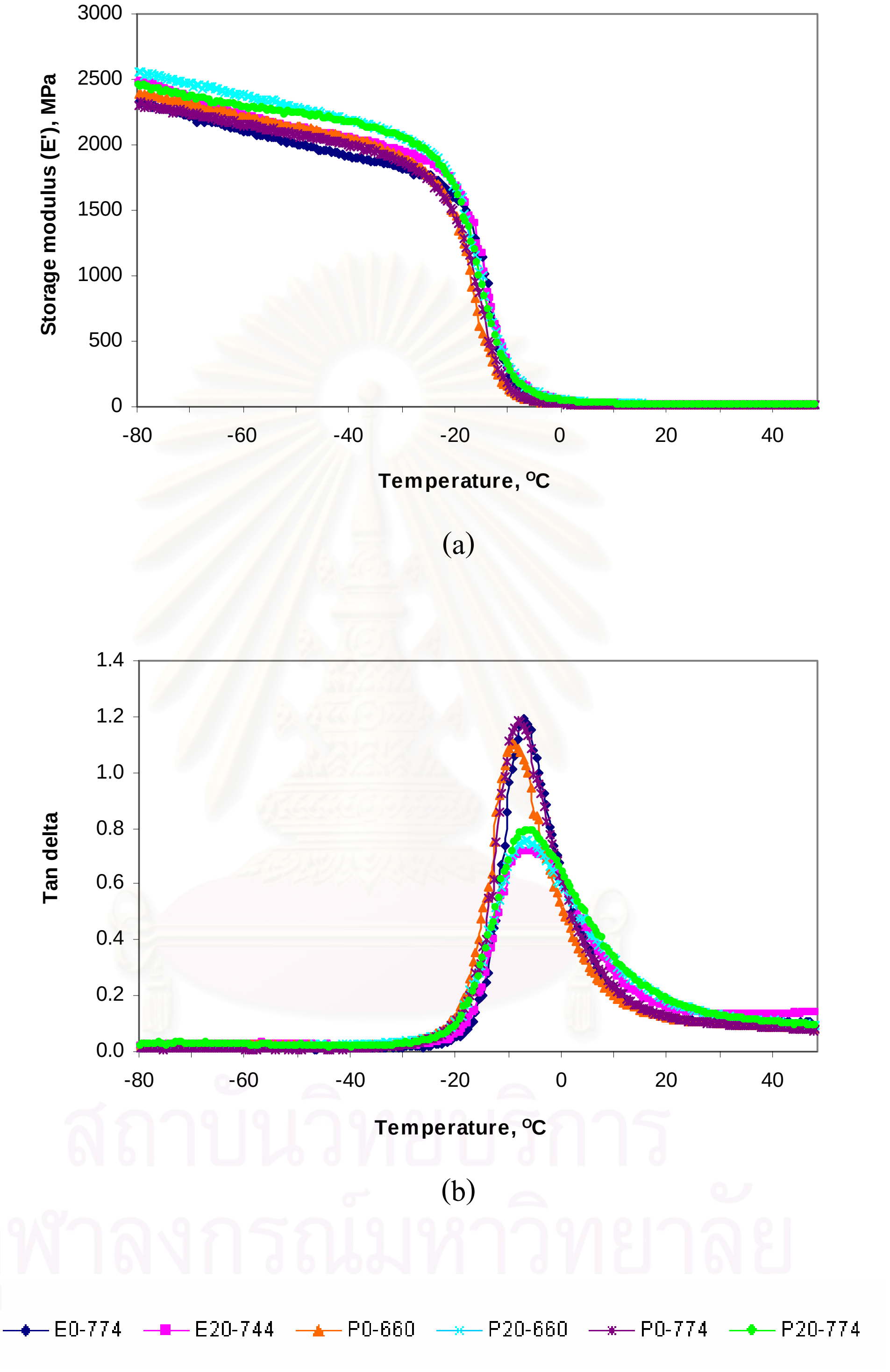
4.7 Dynamic Mechanical Thermal Properties

The dynamic mechanical thermal properties (DMTA) were investigated by using DMA 242C, Netzsch machine with tension mode in the range of temperature from -80 to 50°C with a heating rate of 3.0°C/min at frequency of 1.0 Hz. The results are summarized in Table 4.15 and Figure 4.17. From Figure 4.17(a)-(b), tanδ of HNBR/NBR blend (80/20) was lower than that of pure HNBR vulcanizates. Conversely, the storage moduli of HNBR/NBR (80/20) sample was higher. It can be explained that the rotation of the polyethylene chains in certain random linkages of HNBR becomes more difficult than with butadiene units having double bonds in the same random linkages. Therefore, the HNBR/NBR blends are more flexible.

Compared with EV and peroxide vulcanizing system, the HNBR/NBR blends cured by the peroxide system had the higher storage moduli as shown in Figure 4.17(a). Nonetheless, the tanδ of blend cured by this system was lower than that of EV system as shown in Figure 4.17(b). This reveals that the rigid C-C structure in the peroxide system offers the higher modulus and crosslinking density. For the effect of the two types of carbon black on storage moduli and the loss tangents of HNBR/NBR vulcanizates, it was found that the incorporation of carbon black caused the change in the dynamic mechanical properties of the rubbers. At the same blend ratio, tanδ N-660 filled blends was lower than that of N-774 filled blends while, storage modulus (E') of N-660 filled blends was higher. Because the structure of HNBR and NBR affects modulus, it plays a role in hysteresis tests that are conducted with either a constant stress or constant strain mode of deformation. For under constant strain testing, a higher modulus of compound reaches a higher stress level. It has a larger area under the stress/strain curves, and more work is done on it. The compound absorbs more energy (gets hotter in a heat build up test, for example) than a compound with the same tanδ but lower modulus. Conversely, a compound with a higher modulus has the less deformation under constant stress conditions. Thus, the less work is done on it [14].

Table 4.15 Value of *T*g, tanδ at *T*g, storage modulus and loss modulus of vulcanizates.

Compound	*T* g (^{o}C)	tan δ at *T* g	E' (MPa)	E" (MPa)
E0-774	-7.6	1.19	1555	291
E20-774	-6.4	0.72	1681	307
P0-660	-9.2	1.12	1663	295
P20-660	-7.3	0.76	1807	321
P0-774	-8.4	1.19	1611	283
P20-774	-6.6	0.79	1826	310



(a)

(b)

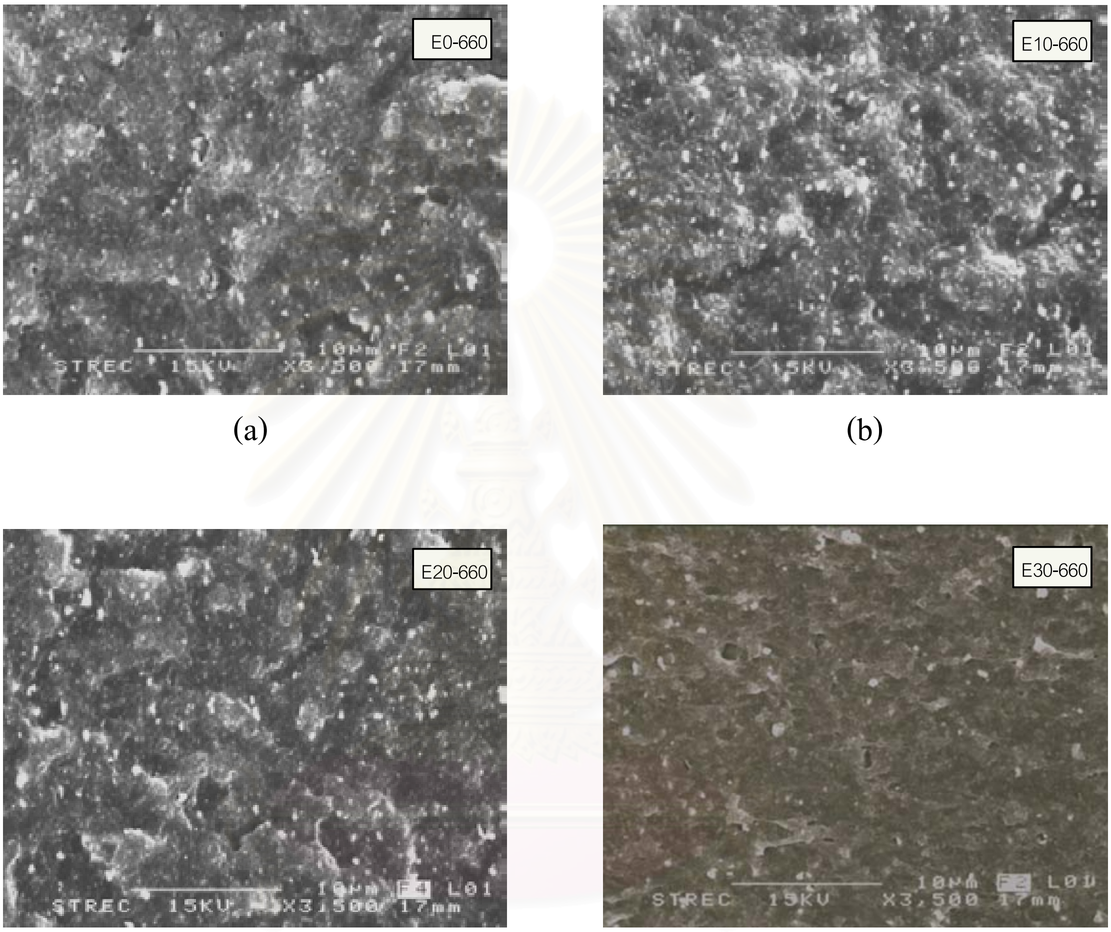
Figure 4.17 Dynamic mechanical thermal properties of HNBR/NBR blends: (a) storage modulus and (b) tanδ.

4.8 Morphology of the Blends

After staining with osmium tetroxide on the fracture surface of sample, the rubber phases in HNBR/NBR blends could be identified as dark area in the SEM micrograph because their double bonds had combined with osmium tetroxide and endowed them a higher scattering capacity to electrons. Figures 4.18(a)-(d) show the observed morphology of the N-660 filled blends cured by EV system. Figures 4.19(a)-(d) show the observed morphology of the N-774 filled blends cured by EV system Figures 4.20(a)-(d) show the observed morphology of the N-660 filled blends cured by peroxide system. Figures 4.21(a)-(d) show the observed morphology of the N-774 filled blends cured by peroxide system.

Compared the SEM micrograph of the sample of HNBR/NBR blends with 0-30%NBR content, the intensity of the black color of the discrete phase increased while the intensity of the gray color decreased with increasing NBR content. The increase in the intensity of the black color of the discrete phase was resulted by the increase in the concentration of the unsaturated double bonds of the polymer blends. Evidently, as the NBR content increased, not only the interaction between the polar nature of HNBR and NBR molecules was occurred but the interaction between NBR or HNBR with carbon black was also presented. It is due to the fact that the surface of carbon black was important for improving the degree of adhesion between the carbon blacks and the HNBR or NBR as shown in Figure 4.5.

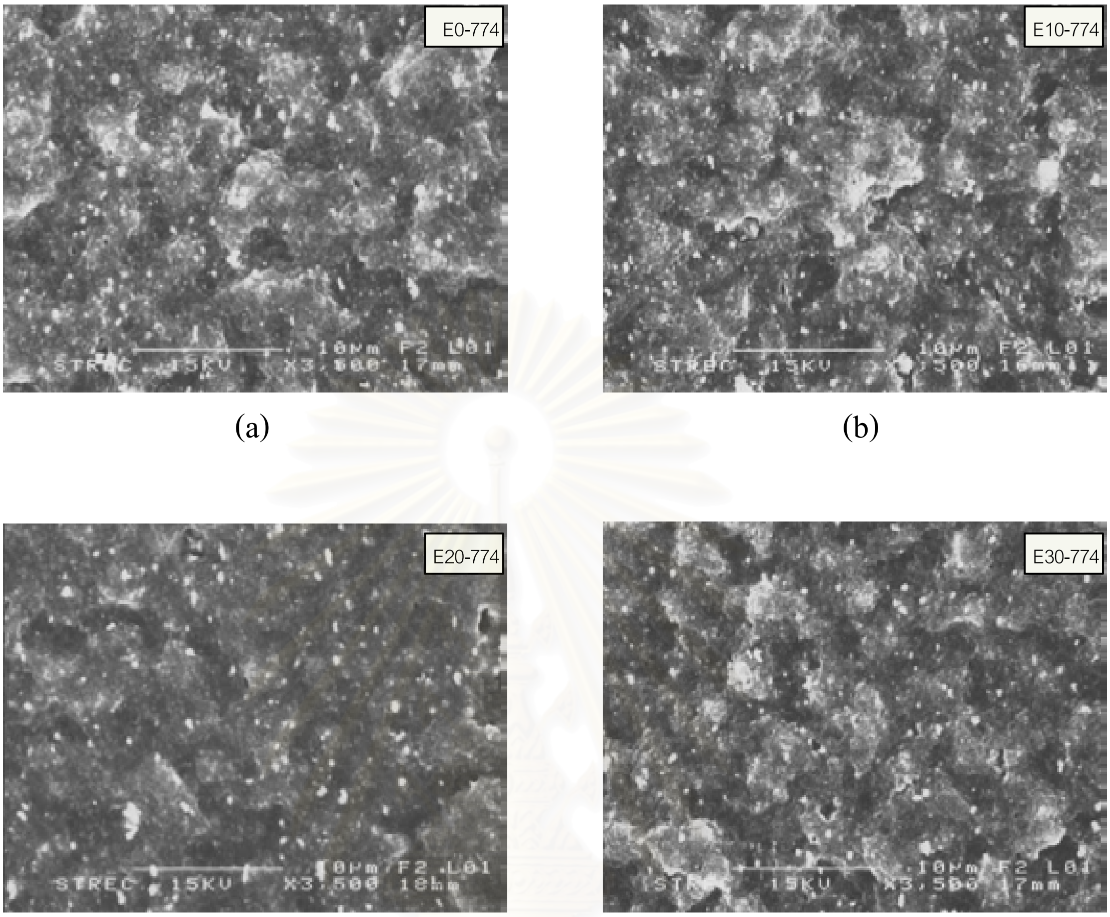
From Figures 4.18-4.21, the morphology of HNBR/NBR blends vulcanized by using EV curing system shows the larger dispersed HNBR domain than the sample vulcanized by peroxide curing system. For peroxide curing system, the dispersed domain was fine and uniform; thus, the crosslinking was also more effective. The morphology of N-660 filled HNBR/NBR blends was similar to that of N-774 filled HNBR/NBR blends except for the size distribution of the rubber-rich domain.



(a) (b)

(c) (d)

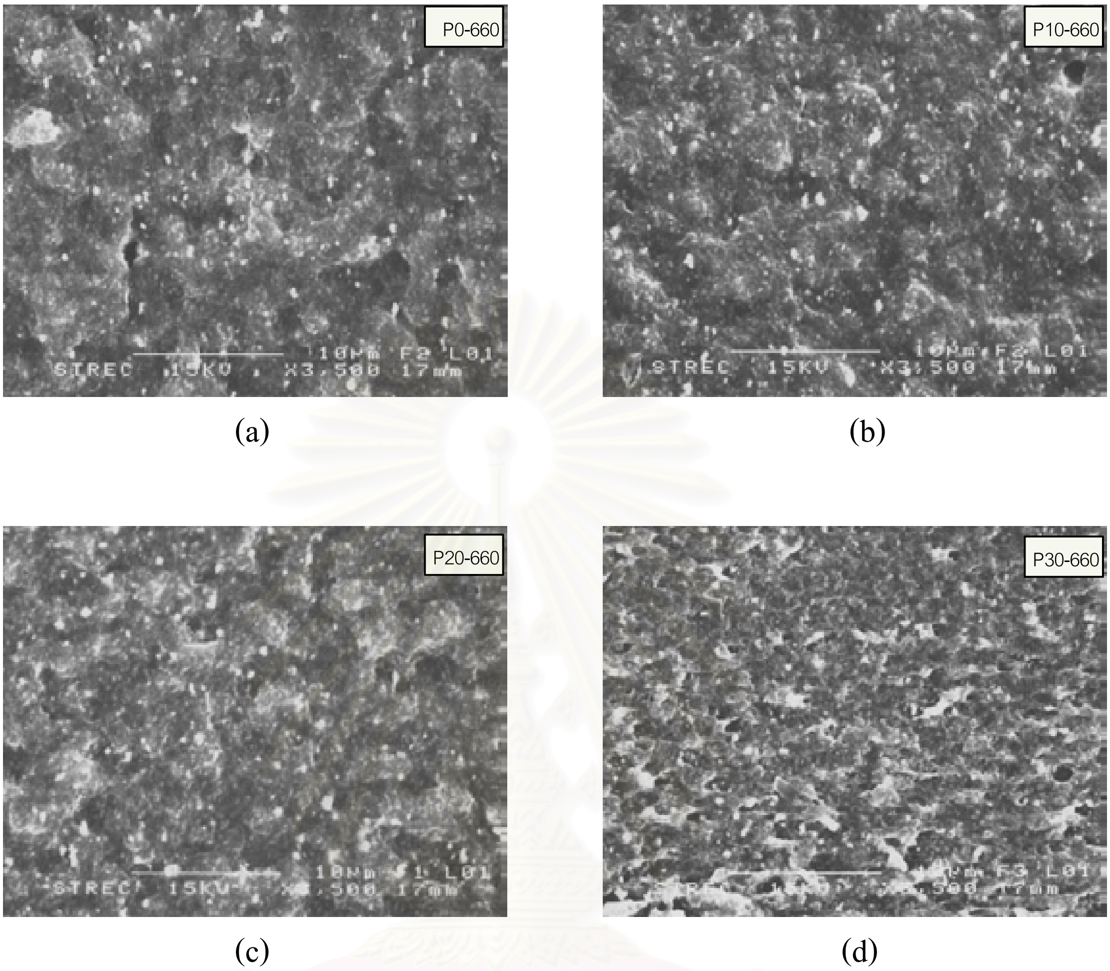
Figure 4.18 SEM micrographs of the fracture surface of N-660 filled HNBR/NBR blends cured by EV system: (a) pure HNBR, (b) 10%NBR, (c) 20%NBR and (d) 30%NBR.



(a) (b)

(c) (d)

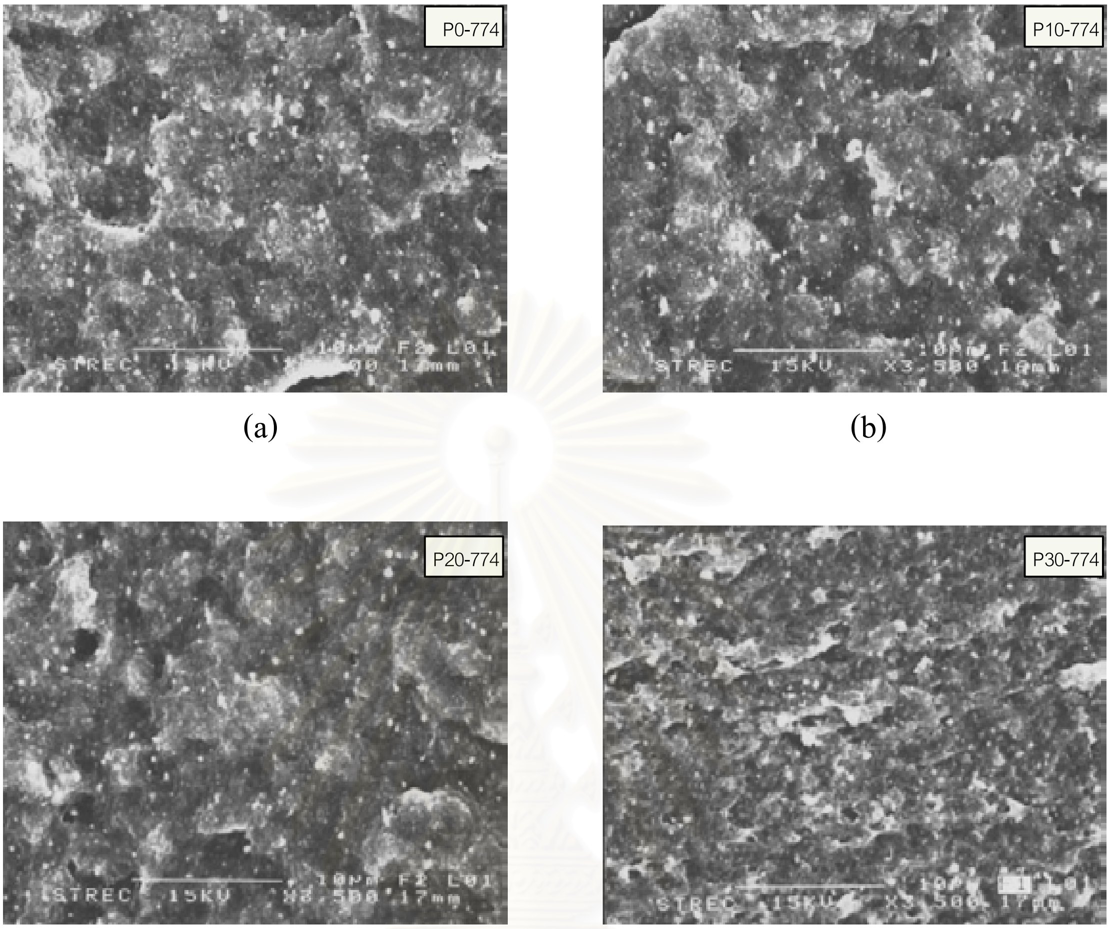
Figure 4.19 SEM micrographs of the fracture surface of N-774 filled HNBR/NBR blends cured by EV system: (a) pure HNBR, (b) 10%NBR, (c) 20%NBR and (d) 30%NBR.



(a) (b)

(c) (d)

Figure 4.20 SEM micrographs of the fracture surface of N-660 filled HNBR/NBR blends cured by peroxide system: (a) pure HNBR, (b) 10%NBR, (c) 20%NBR and (d) 30%NBR.



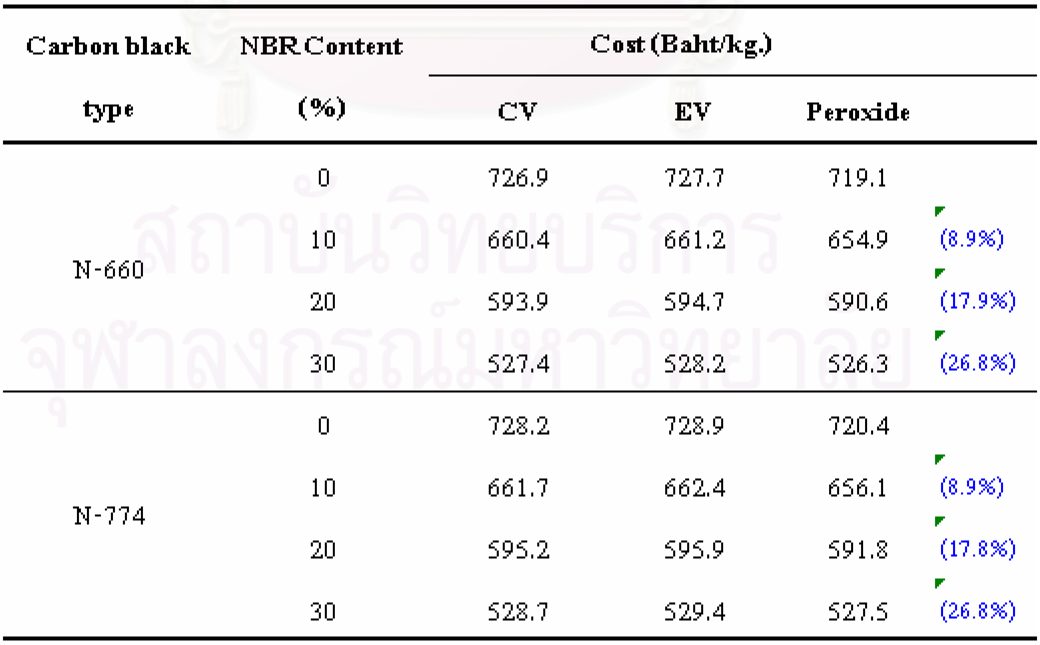
(a) (b) (c) (d)

Figure 4.21 SEM micrographs of the fracture surface of N-774 filled HNBR/NBR blends cured by peroxide system: (a) pure HNBR, (b) 10%NBR, (c) 20%NBR and (d) 30%NBR.

4.9 Compound Cost

Compound cost is the simple calculation of the cost per kilogram of material. It must also take into account whether the application is weight-basis. These compounds are used for illustration of the cost effect of substitution of polymers and are not intended to describe real world compounds. The cure systems and properties will be different. The costs of rubber compounds are presented in Table 4.16. The compound cost decreased with increasing NBR content. The peroxide cured rubber compound had the lowest cost while the cost of the compounds cured by CV and EV systems were similar. The cost of compounds filled with different the carbon black types, were a little or not different.

Table 4.16 Compound cost calculation of HNBR/NBR blends at difference blend ratios and carbon black types.



Carbon black type	NBR Content (%)	Cost (Baht/kg.)			
		CV	EV	Peroxide	
N-660	0	726.9	727.7	719.1	
	10	660.4	661.2	654.9	(8.9%)
	20	593.9	594.7	590.6	(17.9%)
	30	527.4	528.2	526.3	(26.8%)
N-774	0	728.2	728.9	720.4	
	10	661.7	662.4	656.1	(8.9%)
	20	595.2	595.9	591.8	(17.8%)
	30	528.7	529.4	527.5	(26.8%)

Remark: ( ) = % Cost Reduction

CHAPTER V

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The effects of vulcanization systems and carbon black types on properties of HNBR/NBR blends were studied. In this work, the HNBR/NBR blends filled with GPF N-660 and SRF N-774 using various vulcanization systems: CV, EV and peroxide were prepared. The properties of various rubber compounds were investigated and compared as follows:

1. The cure characteristics of HNBR/NBR at 20, 30% NBR in the blends using peroxide system exhibited maximum torque and the blends using EV system showed the lowest. This is due to the fact that peroxide could cure both HNBR and NBR phase uniformly. The carbon black type did not affect the cure characteristics.
2. The tensile strength and elongation at break of HNBR/NBR blend decreased with an increase in the percentage of NBR in the blend, but 100%modulus increased because the HNBR structure exhibited strain-induced crystallization; while NBR chain was more flexible. The blends cured by peroxide system also exhibited the higher 100%modulus and tensile strength with lower elongation at break than that cured by sulfur system. The N-660 filled vulcanizates exhibited the better mechanical properties than N-774 filled vulcanizates because of the higher surface area of N-660.

3. The thermal aging, ozone and oil resistance properties of HNBR/NBR blends decreased with increasing the concentration of NBR in the blends. The HNBR/NBR blend cured by peroxide system showed the better heat stability than that cured by sulfur system.
4. The tanδ of the sample decreased; while its storage modulus increased with increasing NBR content in blends. The sample vulcanized by peroxide system had higher storage modulus and lower tanδ compared to that vulcanized by EV system. The compound filled with N-660 had lower tanδ than that filled with N-774; while its storage modulus of compound filled with N-660 was higher.
5. SEM micrographs of HNBR/NBR blend showed the presence of the dispersed particles with smaller size and the amount increased with the increasing of HNBR content. The morphology of the blend cured by EV system showed the larger size of the dispersed HNBR domain compared with the sample vulcanized by peroxide system.
6. The compound cost calculations were proposed and the HNBR/NBR blends cured by peroxide systems which had the superior properties showed the lowest cost.

5.2 Future work

The recommended further study the effect of the various filler types such as silica, calcium carbonate and clay on the properties of HNBR/NBR blends.

REFERANCES

1. Thailand Automotive Institute, Thailand Continues to Grow as the Detroit of Asia [online]. 2004. Available from www.business-in-asia.com/auto_industry.html [2006, June 22]

2. Giurginca, M., and Zaharescu, T. Thermal and Radiation Behaviour of HNBR and CSPE Blends. Polymer 41 (2000): 7583-7587.

3. Infochems.com. Structure Unit and Each Function of Zetpol. Zeon Corporation[Online]. 2002-2004. Available from: http://www.inforubber.com/product/NBR/zetpol.asp[2006, June 22]

4. Wikipedia, Elastomer[Online]. 2006. Available from http://en.wikipedia.org/wiki/elastomer[2007, January 6]

5. Fayt, R., Hadjiandreou, P. and Teyssie, P., J. Polym. Sci. Polym. Chem. Ed., 1985, pp. 23, 337.

6. Corish, P. J. Science and Technology of Rubber; Elastomer Blends. Academic Press, Inc., 1987, pp. 489-495.

7. Semon, W. L., Acrylonitrile Butadiene Rubber[online]. 2002. Available from www.iisrp.com/webpolymers/07nbr.pdf[2006, June 22]

8. Mackey, D. and Jorgensen, A. H., Hydrogenated Nitrile Butadiene Rubber[online]. 2001. Available from www.iisrp.com/webpolymers/03hnbr.pdf[2006, June 22]

9. Datta, R. N. Rubber Curing Systems. Rapra Review Reports, Expert overviews covering the sciecnce and technology of rubber and plastics. United Kingdom 12 (2002): 3-28.

10. Henning, S. H. and Costin, R. Fundamentals of Curing Elastomers with Peroxides and Coagents. Presented at the Spring 167th Technical Meeting of the Rubber Division, American Chemical Society 2005.

11. Daniel, L. and Hertz, JR. Theory & Practice of Vulcanization. Elastomeric. USA, 1984.

12. Crump, E. L. Economic Impact Analysis for the Proposed Carbon Black Manufacturing NESHAP[online]. [2007, January 6]

13. Serth, R. W. and Hughes, T. W. Source Assessment: Carbon Black Manufacture, EPA-600/2-77-107k, U. S. Environmental Protection Agency, Cincinnati, OH, October 1977.

14. Laube, S. and Wang, M. J. Rubber Technology, Compounding with Carbon Black and Oil. Munich: Hanser Publishers, 2001, pp. 301-302, 313-314.

15. Long, J. M. Rubber Technology; Rubber Compound Economics. Munich: Hanser Publishers, 2001, pp. 75-80.

16. Rahiman, K. H., Unnikrishnan, G., Sujith, A. and Radhakrishnan, C.K. Cure Characteristics and Mechanical Properties of Styrene-Butadiene Rubber/Acrylonitrile Butadiene Rubber. Materials Letters 59 (2005): 633-639.

17. Botros, S. H., and Abdel-Nour, K. N. Preparation and characterization of butyl/NBR vulcanizates. Polymer Degradation and Stability 62 (1998): 479-485.

18. Hayashi, S., Sakakida, H., Oyama, M. and Nakagawa, T. Low-temperature Properties of Hydrogenated Nitrile Rubber. Rubber Chemistry and Technology 64 (1990): 534-544.

19. Ibnelwaleed, A. H., Rehan, A.C.and Basel, F.A.S. Study of the Miscibility and Mechanical Properties of NBR/HNBR Blends. Polymer Engineering and Science 44 (2004): 2346-2351.

20. Sandland, N., Ito, S., Oyama, M. and Files, E. Peroxide Cured HNBR/Methacrylate Blends with Improved Low Temperature Performance. Rubber World 232 (2005): 40-46.

21. Thormer, J., Mirza, J., Sventivanyi, Z., Obrecht, W. and Rohde, E. Crosslinking System Effect on Processing Behavior and Performance Profile of HNBR. Rubber World 198 (1989): 25-30.

22. Bandyopadhyay, S., De, P. P., Tripathy, D. K., De, S. K. Influence of Surface Oxidation of Carbon Black on Its Interaction with Nitrile Rubbers. Polymer 37 (1996): 353-357.

23. Manoj, N. R., De, S. K. and De, P. P. Thermally Induced Crosslink in Blends of Poly(vinyl chloride) and Hydrogenated Acrylonitrile-Butadiene Rubber. Rubber Chemistry and Technology 66 (1993): 550-558.

24. Dunn, J. R. and Ontario, S. Compounding NBR for High Temperature Applications. Rubber World 192 (1984): 16-27.

25. Ferrari, L. Pazur, R. J. and Ezio, C. HXNBR for Oil Well Specialties and Roll Applications. Rubber World 230 (2004): 39-43.

26. Japanese Industrial Standard. K6301. Resistance to Ozone Cracking Test. 1995, pp.54-57.

27. Brydson, J. A. Rubber Materials and Their Compounds. London: Elsevier Science Publishers, 1988, pp. 362.

28. Ciullo , P. A. The Rubber Formulary. New York: Noyes Publications/William Andrew Publishing, 1999, pp. 25,66.

29. Hofmann, W. Rubber Technology Handbook. Munich Vienna New York: Hanser Publishers, 1989, pp. 224,227, 230,247.

30. Jones, M. and Files, E. Low Temperature HNBR Technology. Rubber World 231 (2005): 39-46.

31. Nakason, C., Wannavili, P. and Kaesaman, A. Effect of Vulcanization System on Properties of Thermoplastic Vulcanizates based on Epoxidized Natural Rubber/Polypropylene Blends. Polymer Testing 25 (2006): 34-41.

32. Wood, M. E. Rubber Technology; Hydrogenated Nitrile Butadiene Elastomers. Munich: Hanser Publishers, 2001, pp. 201-202.

33. Shen, K. K. and Schultz, D. R. Rubber Technology; Flame Retardants. Munich: Hanser Publishers, 2001, pp. 500-501.

34. Hepburn, C. Rubber Compounding Ingredients Need, Theory and Innovation part I. (n.p.): Rapa Technology, 1981.

35. Arroyo, M., Lopez-Manchado, M.A. and Herrero, B. Organo-montmorillonite as Substitute of Carbon Black in Natural Rubber Compounds. Polymer 44(2003): 2447-2453.

APPENDICES

APPENDIX A

Table A-1 Elastomer properties.

Grade	Characteristic		
	Bound ACN (%)	**Iodine Value (g/100g)**	**Mooney viscosity [ML(1+4) 100°C]**
JSR N-220S (NBR)	41±2	-	55±5
ZETPOL 1020 (HNBR)	44.2±2	25	78±5

Table A-2 Carbon black properties.

Characteristic	Unit	GPF N-660	SRF N-774
Iodine No.	mg/g	36±9	28±7
DBP No.	ml/100g	90±9	72±7
Ash content	(%)	1.0 max.	0.7 max.
pH value	-	7.0±2.0	7.0±2.0
Heat loss	(%)	2.0 max.	2.0 max.
Particle size	nm	49~60	61~100
Sieve residue#45	(%)	0.03 max.	0.04 max.
Sieve residue#500	(%)	0.001 max.	0.001 max.

Table A-3 IRM 903 oil properties.

Characteristic	**Properties**
Ingredients	100%Petroleum hydrocarbon
Boiling point	Wide range
Flash point	> 163 °C
S.G.	0.920
Vapor pressure	< 0.03 Pa (at 25 °C)
Vapor density	> 10 (AIR=1)
Solubility in water	Insoluble
% Volatiles by vol.	Negligible
Evaporation rate	Negligible
Appearance	Clear pale yellow liquid
Odor	Slight odor

Table A-4 Semi-synthetic diesel engine oil properties.

Characteristic	**Properties**
Ingredient	SAE 15W-40 (API-CF4)
Viscosity @100 °C	14.8 cSt
Viscosity index	143
Cold-crack simulator @ -20 °C	6,190 cP
Total base number	10.7 mgKOH/g
Pour point	-27 °C
Appearance	Dark green liquid

APPENDIX B

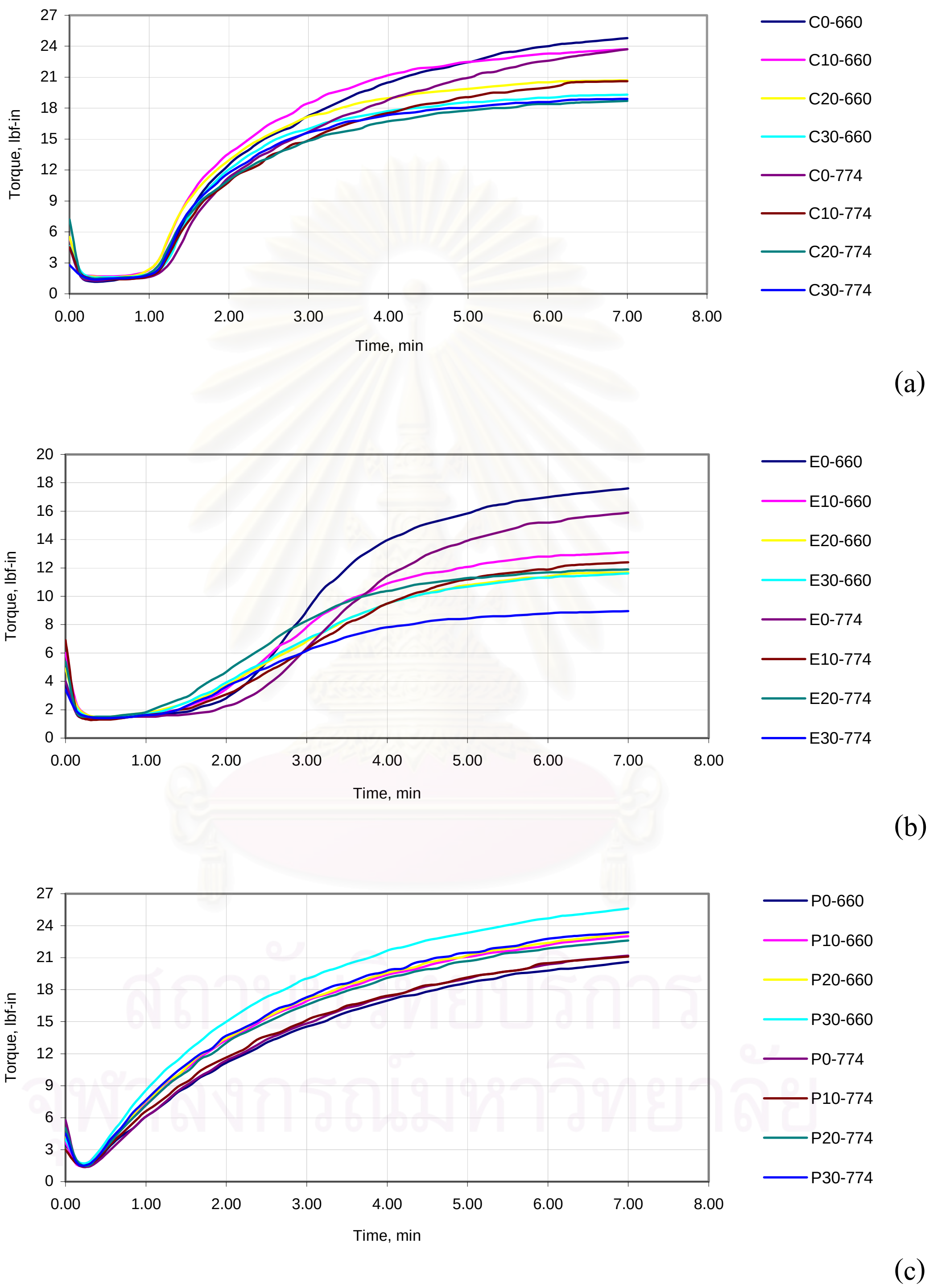


Figure B-1 Cure curves of rubber compounds with different blend ratios and carbon black types for; (a) CV, (b) EV and (c) peroxide vulcanization system.

APPENDIX C

Table C-1 100%Modulus of vulcanizates with CV system according to ASTM D412.

Original

No.	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
1	5.49	6.06	5.86	6.08	4.90	5.63	4.82	5.71
2	5.52	6.03	5.86	5.96	4.74	5.25	5.09	5.53
3	6.37	5.58	6.08	5.98	5.23	5.62	4.92	5.06
4	5.63	6.08	5.99	5.85	4.74	5.08	5.43	5.24
5	5.54	6.12	5.80	5.69	4.90	5.12	4.83	5.44
Med.	5.54	6.06	5.86	5.96	4.90	5.25	4.92	5.44
SD.	0.37	0.22	0.11	0.15	0.20	0.27	0.25	0.25

Aging @125^{O}Cx168h

No.	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
1	12.30	16.53	0.00	0	12.60	14.15	12.42	0
2	14.25	15.58	15.66	0	11.95	14.64	14.29	0
3	15.44	16.31	16.91	0	12.64	14.45	14.50	0
4	15.29	15.70	17.52	0	13.31	13.50	14.85	0
5	13.75	14.91	17.03	0	12.48	13.47	12.42	15.12
Med.	14.25	15.70	16.91	0	12.60	14.15	14.29	0
SD.	1.28	0.64	7.54	0	0.49	0.54	1.18	6.76
%change	157	159	188	-	157	169	190	-

IRM 903 oil @125^{O}Cx70h

No.	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
1	6.08	6.33	6.87	6.62	4.41	5.29	5.65	6.59
2	5.55	5.36	5.92	6.59	5.52	5.20	4.92	5.75
3	5.65	6.32	5.82	6.00	5.33	5.48	5.95	6.28
Med.	5.65	6.32	5.92	6.59	5.33	5.29	5.65	6.28
SD.	0.28	0.56	0.58	0.35	0.59	0.14	0.53	0.43
%change	2	4	1	11	9	1	15	15

Engine oil @125^{O}Cx70h

No.	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
1	6.88	8.57	7.64	7.16	5.42	7.50	7.38	6.85
2	7.02	8.15	7.01	7.73	6.75	8.06	7.43	7.88
3	7.21	7.83	7.89	7.80	6.35	6.98	7.28	7.46
Med.	7.02	8.15	7.64	7.73	6.35	7.50	7.38	7.46
SD.	0.17	0.37	0.45	0.35	0.68	0.54	0.08	0.52
%change	27	34	30	30	30	43	50	37

Table C-2 100%Modulus of vulcanizates with EV system according to ASTM D412.

Original

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	4.47	4.13	3.86	3.94	3.75	3.88	3.97	4.26
2	4.19	4.29	3.74	4.18	3.98	3.97	3.73	3.81
3	4.32	4.19	3.73	4.21	3.94	3.83	3.81	4.37
4	3.96	2.28	3.65	3.60	3.67	3.67	4.20	4.05
5	3.57	3.93	3.79	3.77	3.73	3.67	4.12	4.20
Med.	4.19	4.13	3.74	3.94	3.75	3.83	3.97	4.20
SD.	0.35	0.84	0.08	0.26	0.14	0.13	0.20	0.22

Aging @125^{O}Cx168h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	7.80	7.91	9.80	10.18	6.45	7.60	7.92	9.33
2	7.69	8.86	9.97	10.17	7.26	8.12	8.41	8.68
3	6.86	8.25	9.68	9.67	6.48	7.28	8.63	9.22
4	6.65	8.83	10.08	10.43	6.79	7.79	8.89	8.93
5	6.79	8.69	9.83	9.70	6.87	7.38	7.71	8.97
Med.	6.86	8.69	9.83	10.17	6.79	7.60	8.41	8.97
SD.	0.54	0.41	0.16	0.33	0.33	0.33	0.49	0.26
%change	64	110	163	158	81	98	112	114

IRM 903 oil @125^{O}Cx70h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	4.66	3.87	4.11	3.73	3.91	3.95	3.98	4.12
2	4.64	4.43	3.99	4.08	4.28	3.87	3.98	4.24
3	4.93	4.24	2.40	4.21	4.11	3.81	3.97	4.23
Med.	4.66	4.24	3.99	4.08	4.11	3.87	3.98	4.23
SD.	0.16	0.29	0.96	0.25	0.19	0.07	0.01	0.07
%change	11	3	7	4	10	1	0	1

Engine oil @125^{O}Cx70h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	5.31	5.82	5.23	5.36	5.13	4.68	5.90	4.92
2	6.48	5.58	5.53	4.89	4.85	5.23	4.89	5.82
3	5.38	5.26	4.88	4.85	4.86	5.16	4.82	5.17
Med.	5.38	5.58	5.23	4.89	4.86	5.16	4.89	5.17
SD.	0.65	0.28	0.32	0.28	0.16	0.30	0.60	0.46
%change	28	35	40	24	30	35	23	23

Table C-3 100%Modulus of vulcanizates with peroxide system according to ASTM D412-98a.

Original

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	8.74	8.34	9.75	10.25	6.81	8.34	8.63	8.78
2	8.69	8.99	9.80	10.41	6.63	8.46	7.84	8.20
3	8.57	8.41	8.74	10.53	7.07	8.13	8.91	9.05
4	7.25	8.47	9.81	11.20	6.61	7.58	8.61	8.19
5	7.23	9.43	9.50	10.78	6.59	7.26	8.11	8.70
Med.	8.57	8.47	9.75	10.53	6.63	8.13	8.61	8.70
SD.	0.79	0.47	0.45	0.37	0.21	0.51	0.43	0.38

Aging @125^{O}Cx168h

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	16.27	16.66	20.24	0	11.35	14.25	18.82	0
2	14.29	16.50	22.21	0	10.99	15.96	16.86	0
3	14.30	15.66	22.90	22.65	10.25	15.25	17.98	0
4	14.71	16.08	18.51	0	10.84	14.98	17.11	19.30
5	14.80	15.91	23.73	0	10.89	14.80	17.98	0
Med.	14.71	16.08	22.21	0	10.89	14.98	17.98	0
SD.	0.82	0.41	2.12	10.13	0.40	0.63	0.78	8.63
%change	72	90	128	-	64	84	109	-

IRM 903 oil @125^{O}Cx70h

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	9.62	10.35	11.04	12.20	6.41	8.51	9.50	9.75
2	9.68	10.99	11.98	12.89	6.77	7.86	10.19	9.55
3	8.61	10.07	9.97	11.26	6.73	9.07	8.89	10.74
Med.	9.62	10.35	11.04	12.20	6.73	8.51	9.50	9.75
SD.	0.60	0.47	1.00	0.82	0.20	0.61	0.65	0.64
%change	12	22	13	16	2	5	10	12

Engine oil @125^{O}Cx70h

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	8.73	11.07	12.47	13.84	8.01	9.18	11.23	10.61
2	8.46	10.32	11.51	13.91	8.69	10.07	10.60	10.70
3	9.58	11.44	12.29	14.16	7.12	9.90	10.56	12.23
Med.	8.73	11.07	12.29	13.91	8.01	9.90	10.60	10.70
SD.	0.59	0.57	0.51	0.17	0.79	0.47	0.37	0.91
%change	2	31	26	32	21	22	23	23

Table C-4 Tensile strength of vulcanizates with CV system according to ASTM D412.

Original

No.	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
1	16.18	16.03	19.72	19.81	17.34	19.23	17.32	17.84
2	20.26	20.51	18.95	16.90	20.52	19.19	18.76	17.26
3	22.91	21.39	18.41	18.09	18.66	19.59	20.35	17.68
4	22.28	20.52	17.16	18.98	15.17	19.51	19.46	17.35
5	21.78	20.05	17.66	18.72	19.77	20.48	15.67	17.76
Med.	21.78	20.51	18.41	18.72	18.66	19.51	18.76	17.68
SD.	2.70	2.11	1.01	1	2.12	0.52	1.85	0.26

Aging @125^{O}Cx168h

1	18.31	21.31	17.06	14.13	19.63	16.65	12.44	12.74
2	23.51	17.07	21.54	16.22	18.47	15.49	16.42	14.43
3	21.12	20.59	17.45	16.99	18.76	15.19	17.92	13.28
4	22.37	22.21	17.52	16.08	18.33	17.89	17.51	10.15
5	18.25	19.22	18.65	15.09	16.58	17.02	12.42	15.12
Med.	21.12	20.59	17.52	16.08	18.47	16.65	16.42	13.28
SD.	2.38	2.01	1.83	1.11	1.11	1.11	2.71	1.92
%change	-3	0	-5	-14	-1	-15	-12	-25

IRM 903 oil @125^{O}Cx70h

1	21.54	17.68	17.50	17.33	20.37	13.46	15.99	16.44
2	21.02	19.55	17.48	15.15	18.57	15.70	18.61	15.56
3	24.28	17.84	18.82	14.94	18.65	18.55	16.50	16.80
Med.	21.54	17.84	17.50	15.15	18.65	15.70	16.50	16.44
SD.	1.75	1.04	0.77	1.32	1.02	2.55	1.39	0.64
%change	-1	-13	-5	-19	0	-20	-12	-7

Engine oil @125^{O}Cx70h

1	18.34	19.98	17.13	17.21	18.20	19.34	16.22	16.01
2	19.81	18.50	15.82	18.32	16.27	19.93	17.00	14.78
3	21.69	20.59	18.98	16.74	17.01	17.78	16.08	16.34
Med.	19.81	19.98	17.13	17.21	17.01	19.34	16.22	16.01
SD.	1.68	1.08	1.59	0.81	0.97	1.11	0.50	0.82
%change	-9	-3	-7	-8	-9	-1	-14	-9

Table C-5 Tensile strength of vulcanizates with EV system according to ASTM D412.

Original

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	20.55	17.74	17.09	16.25	17.53	17.83	15.03	15.40
2	19.43	17.47	16.57	16.60	17.73	17.92	16.67	15.95
3	20.64	17.61	17.08	17.45	18.27	17.60	16.02	17.16
4	18.95	17.34	16.54	15.96	19.29	17.41	17.17	17.31
5	19.27	17.13	16.74	16.39	18.10	17.12	14.66	13.56
Med.	19.43	17.47	16.74	16.39	18.10	17.60	16.02	15.95
SD.	0.77	0.23	0.27	0.57	0.68	0.33	1.06	1.53

Aging @125^{O}Cx168h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	22.16	19.68	19.14	18.54	19.74	17.92	19.27	17.16
2	19.10	21.05	18.31	17.74	20.94	18.09	17.46	16.97
3	21.95	16.26	19.05	17.48	19.81	17.28	17.99	18.31
4	21.78	19.49	19.34	17.99	18.75	18.80	15.43	17.78
5	20.61	20.32	20.36	17.35	17.37	19.25	18.61	17.79
Med.	21.78	19.68	19.14	17.74	19.74	18.09	17.99	17.78
SD.	1.28	1.84	0.74	0.47	1.34	0.77	1.47	0.54
%change	12	13	14	8	9	3	12	12

IRM 903 oil @125^{O}Cx70h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	25.03	19.00	17.46	16.64	23.16	17.97	16.79	16.31
2	24.39	19.62	17.44	16.52	19.74	17.31	16.90	16.51
3	23.72	19.95	16.18	17.61	21.15	17.96	18.40	15.58
Med.	24.39	19.62	17.44	16.64	21.15	17.96	16.90	16.31
SD.	0.66	0.48	0.73	0.60	1.72	0.38	0.90	0.49
%change	26	12	4	2	17	2	6	2

Engine oil @125^{O}Cx70h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	21.08	20.50	18.93	17.66	21.65	18.11	18.45	16.05
2	22.73	18.15	18.75	17.64	19.80	20.19	14.45	17.27
3	22.37	18.66	17.43	17.51	20.11	19.40	18.17	18.06
Med.	22.37	18.66	18.75	17.64	20.11	19.40	18.17	17.27
SD.	0.87	1.24	0.82	0.08	0.99	1.05	2.24	1.01
%change	15	7	12	8	11	10	13	8

Table C-6 Tensile strength of vulcanizates with peroxide system according to ASTM D412-98a.

Original

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	25.61	23.33	25.28	24.42	23.58	17.68	24.76	21.48
2	24.34	19.04	21.80	23.45	23.89	23.13	17.28	19.91
3	28.03	17.44	23.85	21.39	23.13	22.54	22.91	21.67
4	25.20	22.96	26.09	25.72	22.49	22.83	21.92	19.78
5	26.89	24.17	21.76	23.32	22.80	24.89	21.81	21.90
Med.	25.61	22.96	23.85	23.94	23.13	22.83	21.92	21.48
SD.	1.45	2.96	1.98	1.59	0.57	2.70	2.76	1.02

Aging @125^{O}Cx168h

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	27.16	27.25	24.85	25.06	24.30	23.07	24.98	22.23
2	26.68	25.56	23.27	8.03	24.38	23.31	18.39	23.62
3	31.61	23.83	24.64	22.65	20.51	23.99	21.73	24.95
4	28.57	22.12	25.15	27.19	23.61	21.34	22.93	21.78
5	28.96	25.53	25.31	24.40	22.58	21.51	23.70	22.37
Med.	28.57	25.53	24.85	24.40	23.61	23.07	22.93	22.37
SD.	1.93	1.95	0.81	7.68	1.60	1.16	2.51	1.29
%change	12	11	4	2	2	1	5	4

IRM 903 oil @125^{O}Cx70h

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	19.84	23.30	25.01	26.82	24.65	22.16	22.85	24.86
2	28.00	22.96	25.52	23.33	26.07	23.04	26.13	21.72
3	26.90	23.37	21.47	25.10	22.45	24.87	22.14	22.44
Med.	26.90	23.30	25.01	25.10	24.65	23.04	22.85	22.44
SD.	4.42	0.22	2.21	1.75	1.83	1.38	2.13	1.64
%change	5	1	5	5	7	1	4	4

Engine oil @125^{O}Cx70h

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	28.16	23.39	25.78	25.73	24.56	11.61	23.46	22.24
2	24.64	26.52	25.93	26.95	27.08	23.40	21.23	19.78
3	26.38	21.06	26.20	25.77	24.63	24.27	22.03	21.82
Med.	26.38	23.39	25.93	25.77	24.63	23.40	22.03	21.82
SD.	1.76	2.74	0.22	0.69	1.43	7.07	1.13	1.31
%change	3	2	9	8	7	3	0	2

Table C-7 Elongation at break of vulcanizates with CV system according to ASTM D412-98a.

Original

No.	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
1	256	251	386	411	304	381	306	315
2	406	359	383	293	401	420	384	300
3	416	413	346	301	225	371	417	357
4	405	378	296	346	255	378	402	330
5	413	340	322	345	418	370	281	306
Med.	406	359	346	345	304	378	384	315
SD.	68.97	60.88	38.85	46.95	86.11	20.83	60.75	22.88
Aging @125^{o}Cx168h								
1	117	143	97	84	165	150	117	84
2	159	121	141	93	177	127	151	93
3	145	138	116	89	161	121	141	90
4	158	166	116	95	143	145	140	61
5	121	140	124	72	143	129	114	107
Med.	145	140	116	89	161	129	140	90
SD.	19.9	16.0	15.9	9.3	14.9	12.7	16.5	16.6
%change	-64	-61	-67	-74	-47	-66	-64	-71
IRM 903 oil @125^{O}Cx70h								
1	295	237	289	216	286	214	228	215
2	268	279	246	194	267	247	261	227
3	340	231	276	207	271	265	235	221
Med.	295	237	276	207	271	247	235	221
SD.	36.3	26.0	22.4	11.5	10.4	25.7	17.4	5.7
%change	-27	-34	-20	-40	-11	-35	-39	-30
Engine oil @125^{O}Cx70h								
1	216	234	197	211	235	253	199	215
2	225	233	195	224	196	235	203	179
3	257	244	227	196	216	212	198	202
Med.	225	234	197	211	216	235	199	202
SD.	21.6	6.2	18.0	13.8	19.4	20.5	2.3	18.3
%change	-44	-35	-43	-39	-29	-38	-48	-36

Table C-8 Elongation at break of vulcanizates with EV system according to ASTM D412-98a.

Original

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	490	519	467	472	439	524	369	345
2	479	505	482	477	423	514	465	407
3	488	507	489	501	451	511	418	458
4	413	512	507	420	451	521	494	423
5	494	488	484	405	431	516	354	305
Med.	488	507	484	474	439	518	418	407
SD.	33.75	11.43	14.68	40.77	12.31	5.45	60.28	61.61
Aging @125^{o}Cx168h								
1	319	312	226	214	292	260	238	200
2	253	307	209	211	302	280	222	210
3	335	212	247	200	294	299	241	203
4	326	255	234	194	257	298	283	192
5	297	309	263	201	230	298	243	203
Med.	319	307	234	201	292	298	241	203
SD.	32.6	44.2	20.6	8.3	30.2	17.0	22.4	6.3
%change	-35	-39	-52	-58	-33	-42	-42	-50
IRM 903 oil @125^{O}Cx70h								
1	457	432	404	388	410	329	333	274
2	443	375	421	370	330	330	354	357
3	394	459	320	403	366	342	402	367
Med.	443	432	404	388	366	330	354	357
SD.	32.8	42.8	53.9	16.4	40.2	7.0	35.1	51.0
%change	-9	-15	-17	-18	-17	-36	-15	-12
Engine oil @125^{O}Cx70h								
1	304	381	336	314	359	342	360	274
2	333	310	368	320	306	361	246	324
3	334	329	346	356	301	331	387	307
Med.	333	329	346	320	306	342	360	307
SD.	16.8	36.7	16.3	22.7	31.9	14.9	75.0	25.2
%change	-32	-35	-29	-33	-30	-34	-14	-25

Table C-9 Elongation at break of vulcanizates with peroxide system according to ASTM D412-98a.

Original

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	206	219	205	183	224	162	220	191
2	198	167	180	185	247	194	167	188
3	233	165	208	158	233	202	197	183
4	237	203	211	203	224	196	189	188
5	239	196	177	184	225	223	196	196
Med.	233	196	205	184	225	196	196	188
SD.	19.0	23.5	16.5	15.9	10.2	21.8	18.7	5.0
Aging @125°Cx168h								
1	155	138	132	92	191	132	135	96
2	170	114	103	81	196	131	115	86
3	144	144	108	101	173	130	105	89
4	172	110	109	78	189	130	118	105
5	174	136	110	83	178	144	108	87
Med.	170	136	109	83	189	131	115	89
SD.	12.9	15.3	11.2	9.4	9.5	5.8	11.7	8.2
%change	-27	-31	-47	-55	-16	-33	-41	-53
IRM 903 oil @125°Cx70h								
1	203	174	188	173	225	172	200	174
2	231	169	184	162	221	184	194	174
3	263	151	179	192	220	207	188	18
Med.	231	169	184	173	221	184	194	174
SD.	29.9	11.9	4.9	15.6	2.9	18.2	6.0	90.3
%change	-1	-14	-10	-6	-2	-6	-1	-8
Engine oil @125°Cx70h								
1	240	181	179	171	215	123	176	162
2	230	213	188	172	221	183	171	144
3	217	155	191	174	231	199	167	153
Med.	230	181	188	172	221	183	171	153
SD.	11.8	29.1	6.2	1.4	8.2	40.3	4.6	8.7
%change	-1	-8	-8	-7	-1	-7	-13	-19

Table C-10 Hardness of vulcanizates with CV system according to ASTM D2240-97.

Original

No.	C0-660	C10-660	C20-660	C30-660	C0-774	C10-774	C20-774	C30-774
1	76	76	74	75	73	71	71	71
2	75	75	72	72	73	72	70	70
3	75	75	73	73	74	71	72	70
Med.	75	75	73	73	73	71	71	70
SD.	0.56	0.70	0.81	1.59	0.49	0.49	0.97	0.31

Aging @125^{O}Cx168h

1	84	91	95	89	75	90	89	91
2	79	90	91	98	82	84	88	92
3	85	91	88	95	78	82	89	96
4	85	91	95	94	82	89	90	81
5	84	91	97	98	82	90	91	98
Med.	84	91	95	95	82	89	89	92
SD.	2.42	0.35	3.69	3.59	3.00	3.81	1.06	6.50
%change	9	16	22	22	9	18	18	22

IRM 903 oil @125^{O}Cx70h

1	73	67	74	57	65	67	47	61
2	67	64	58	62	67	65	62	71
3	73	67	62	62	64	63	63	64
Med.	73	67	62	62	65	65	62	64
SD.	3.16	1.76	7.99	2.57	1.75	2.10	8.94	4.81
%change	-3	-8	-11	-11	-7	-6	-9	-6

Engine oil @125^{O}Cx70h

1	75	74	68	71	67	81	70	70
2	74	69	67	73	68	71	70	70
3	72	73	75	69	75	70	73	72
Med.	74	73	68	71	68	71	70	70
SD.	1.47	2.59	4.62	1.81	4.01	6.15	1.59	1.40
%change	-2	-2	-6	-2	-5	-1	-1	0

Table C-11 Hardness of vulcanizates with EV system according to ASTM D2240-97.

Original

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	72	70	70	69	70	67	67	68
2	72	71	70	68	67	67	67	65
3	71	71	69	69	70	67	66	68
Med.	72	71	70	69	70	67	67	68
SD.	0.35	0.85	0.23	0.87	1.42	0.38	0.25	1.36

Aging @125$^{\mathrm{O}}$Cx168h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	77	80	83	88	74	78	78	78
2	78	82	77	87	73	78	78	79
3	78	85	83	87	73	79	77	78
4	80	82	81	76	73	78	77	8
5	79	81	90	80	75	80	76	77
Med.	78	82	83	87	73	78	77	78
SD.	0.94	2.01	4.79	5.21	0.93	0.91	0.85	31.08
%change	6	11	13	18	3	11	11	10

IRM 903 oil @125$^{\mathrm{O}}$Cx70h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	68	67	67	65	66	64	78	64
2	65	66	64	66	65	67	63	64
3	68	67	65	65	66	65	65	63
Med.	68	67	65	65	66	65	65	64
SD.	1.66	0.99	1.40	0.51	0.25	1.89	8.06	0.45
%change	-4	-4	-5	-4	-4	-3	-1	-4

Engine oil @125$^{\mathrm{O}}$Cx70h

No.	E0-660	E10-660	E20-660	E30-660	E0-774	E10-774	E20-774	E30-774
1	74	71	73	69	70	72	69	67
2	71	72	70	70	72	70	69	68
3	74	75	72	70	72	70	69	69
Med.	74	72	72	70	72	70	69	68
SD.	1.51	1.93	1.39	0.53	0.78	1.13	0.23	0.81
%change	2	1	3	1	2	3	3	0

Table C-12 Hardness of vulcanizates with Peroxide system according to ASTM D2240-97.

Original

No.	P0-660	P10-660	P20-660	P30-660	P0-774	P10-774	P20-774	P30-774
1	76	76	74	75	73	73	71	74
2	76	77	74	76	72	72	73	74
3	73	75	75	75	73	71	72	73
Med.	76	76	74	75	73	72	72	74
SD.	1.88	0.92	0.58	0.40	0.57	1.21	0.87	0.79
Aging @125$^{\mathrm{O}}$Cx168h								
1	78	85	86	93	79	80	89	89
2	78	84	87	92	79	85	88	88
3	78	85	85	93	79	84	89	89
4	81	86	89	88	73	83	88	92
5	76	82	90	91	68	81	88	90
Med.	78	85	87	92	79	83	88	89
SD.	1.56	1.69	1.82	1.97	5.17	2.03	0.71	1.36
%change	2	9	13	17	6	11	16	16
IRM 903 oil @125$^{\mathrm{O}}$Cx70h								
1	69	72	72	75	68	70	71	72
2	70	72	73	74	66	70	71	72
3	70	71	74	75	67	71	71	72
Med.	70	72	73	75	67	70	71	72
SD.	0.58	0.15	0.60	0.36	0.75	0.58	0.21	0.31
%change	-6	-4	-1	-1	-5	-2	-1	-2
Engine oil @125$^{\mathrm{O}}$Cx70h								
1	75	77	77	79	73	74	76	76
2	75	78	78	79	73	75	75	75
3	75	77	77	78	73	75	77	74
Med.	75	77	77	79	73	75	76	75
SD.	0.21	0.40	0.23	0.57	0.21	0.75	0.74	0.98
%change	-1	2	3	4	0	3	4	1

Table C-13 Compression set of vulcanizates according to ASTM D395-03.

Fomulae	t_o (mm)			t_1 (mm)			Compression set, %				
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Med.**	**SD.**
C0-660	12.88	12.93	12.93	10.69	10.68	10.62	69.97	70.75	72.64	70.75	1.37
C10-660	12.83	12.88	12.87	10.71	10.72	10.72	68.83	69.01	68.91	68.91	0.09
C20-660	12.90	12.83	12.83	10.72	10.71	10.72	69.21	68.83	68.51	68.83	0.35
C30-660	12.83	12.88	12.91	10.78	10.79	10.80	66.56	66.77	66.77	66.77	0.12
C0-774	12.97	12.94	12.92	10.29	10.30	10.30	83.23	82.76	82.65	82.76	0.31
C10-774	12.84	12.91	12.84	10.38	10.30	10.31	79.61	82.59	81.88	81.88	1.56
C20-774	12.82	12.86	12.83	10.40	10.44	10.40	78.83	77.81	78.90	78.83	0.61
C30-774	12.81	12.90	12.90	10.48	10.50	10.45	76.14	76.19	77.78	76.19	0.93
E0-660	12.79	12.81	12.81	11.20	11.22	11.17	52.30	51.96	53.59	52.30	0.86
E10-660	12.76	12.78	12.74	11.21	11.16	11.19	51.50	53.47	51.84	51.84	1.05
E20-660	12.99	12.87	12.86	11.32	11.31	11.25	51.54	50.00	51.77	51.54	0.96
E30-660	12.81	12.84	12.78	11.36	11.32	11.30	47.39	49.19	48.84	48.84	0.96
E0-774	12.74	12.74	12.74	11.07	11.06	11.06	55.85	56.19	56.19	56.19	0.19
E10-744	12.80	12.85	12.75	11.23	11.23	11.19	51.48	52.26	52.00	52.00	0.40
E20-774	12.81	12.80	12.83	11.24	11.23	11.23	51.31	51.48	51.95	51.48	0.33
E30-774	12.89	12.91	12.83	11.36	11.42	11.34	48.73	47.15	48.38	48.38	0.83

Table C-13 (Continue)

Fomulae	**t_o (mm)**			**t_1 (mm)**			**Compression set, %**				
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Med.**	**SD.**
P0-660	12.87	12.90	12.87	12.58	12.14	12.42	9.29	24.13	14.42	14.42	7.53
P10-660	13.05	12.97	13.07	12.60	12.55	12.56	13.64	13.04	15.36	13.64	1.20
P20-660	12.92	12.91	12.90	12.52	12.50	12.43	12.62	12.97	14.92	12.97	1.24
P30-660	13.02	13.08	12.95	12.61	12.58	12.61	12.54	15.02	10.63	12.54	2.20
P0-774	12.90	12.98	12.98	12.10	11.97	11.97	25.40	31.27	31.27	31.27	3.39
P10-774	13.00	13.05	13.00	12.00	12.22	12.22	30.77	25.15	24.00	25.15	3.62
P20-774	12.88	12.91	12.87	12.17	12.09	12.09	22.68	25.95	25.00	25.00	1.68
P30-774	12.97	12.94	12.88	12.49	12.37	12.37	14.91	17.87	16.29	16.29	1.48

*Thickness of spacer bar 9.75 mm

Table C-14 Change in volume of vulcanizates after immersed in IRM 903 oil at 125°C for 70 h according to ASTM D471-98.

Formulae	Original weight in air, g			Original weight in water, g			Swollen weight in air, g			Swollen weight in water, g			Volume change, %				
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	Med.	SD.
C0-660	1.120	1.134	1.139	0.165	0.169	0.167	1.211	1.214	1.231	0.153	0.158	0.154	10.785	9.430	10.802	10.785	0.787
C10-660	1.280	1.282	1.270	0.195	0.194	0.193	1.400	1.402	1.388	0.178	0.177	0.176	12.627	12.592	12.535	12.592	0.046
C20-660	1.108	1.111	1.173	0.170	0.169	0.181	1.215	1.211	1.277	0.154	0.156	0.167	13.113	11.996	11.895	11.996	0.676
C30-660	1.070	1.075	1.045	0.163	0.161	0.156	1.147	1.151	1.118	0.153	0.153	0.149	9.592	9.190	8.999	9.190	0.303
C0-774	1.179	1.164	1.150	0.176	0.173	0.168	1.270	1.249	1.232	0.160	0.158	0.154	10.668	10.091	9.776	10.091	0.452
C10-774	1.168	1.165	1.151	0.174	0.174	0.172	1.261	1.257	1.241	0.163	0.161	0.158	10.463	10.595	10.623	10.595	0.086
C20-774	1.418	1.405	1.420	0.221	0.216	0.220	1.529	1.515	1.530	0.208	0.206	0.209	10.359	10.093	10.083	10.093	0.157
C30-774	1.145	1.151	1.157	0.174	0.175	0.176	1.226	1.232	1.239	0.165	0.168	0.168	9.269	9.016	9.174	9.174	0.128
E0-660	1.106	1.135	1.121	0.162	0.165	0.163	1.162	1.192	1.178	0.148	0.152	0.149	7.415	7.216	7.411	7.411	0.114
E10-660	1.077	1.079	1.094	0.157	0.158	0.162	1.133	1.150	1.149	0.147	0.146	0.149	7.174	9.012	7.296	7.296	1.028
E20-660	1.064	1.058	1.088	0.160	0.160	0.165	1.119	1.109	1.141	0.149	0.146	0.150	7.301	7.238	7.367	7.301	0.064
E30-660	1.115	1.118	1.102	0.166	0.165	0.163	1.172	1.174	1.158	0.152	0.153	0.150	7.482	7.135	7.348	7.348	0.175
E0-774	1.105	1.119	1.102	0.159	0.160	0.159	1.162	1.175	1.156	0.150	0.147	0.144	6.977	7.195	7.317	7.195	0.172
E10-774	1.152	1.084	1.076	0.171	0.160	0.158	1.210	1.153	1.141	0.161	0.147	0.146	6.932	8.874	8.388	8.388	1.011
E20-774	1.131	1.126	1.120	0.169	0.168	0.168	1.188	1.182	1.177	0.158	0.158	0.152	7.069	6.889	7.668	7.069	0.408
E30-774	1.057	1.033	1.107	0.159	0.154	0.166	1.110	1.086	1.163	0.155	0.152	0.162	6.347	6.257	6.376	6.347	0.062

Table C-14 (Continue)

Formulae	Original weight in air, g			Original weight in water, g			Swollen weight in air, g			Swollen weight in water, g			Volume change, %				
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Med.**	**SD.**
P0-660	1.337	1.385	1.243	0.194	0.203	0.180	1.420	1.307	1.404	0.195	0.171	0.187	7.174	-3.892	14.487	7.174	9.253
P10-660	1.141	1.121	1.120	0.167	0.163	0.164	1.174	1.174	1.195	0.156	0.156	0.159	4.475	6.263	8.368	6.263	1.949
P20-660	1.106	1.102	1.082	0.164	0.166	0.163	1.156	1.133	1.156	0.158	0.155	0.158	5.945	4.487	8.596	5.945	2.083
P30-660	1.183	1.147	1.164	0.177	0.171	0.174	1.197	1.215	1.234	0.165	0.169	0.171	2.584	7.172	7.374	7.172	2.709
P0-774	1.087	1.162	1.212	0.153	0.163	0.173	1.223	1.234	1.146	0.160	0.168	0.147	13.812	6.707	-3.850	6.707	8.887
P10-774	1.405	1.384	1.305	0.210	0.206	0.194	1.470	1.449	1.367	0.205	0.203	0.190	5.858	5.772	5.941	5.858	0.084
P20-774	1.163	1.232	1.153	0.170	0.184	0.170	1.290	1.203	1.217	0.180	0.167	0.169	11.782	-1.145	6.612	6.612	6.507
P30-774	1.132	1.099	1.147	0.169	0.164	0.170	1.183	1.149	1.198	0.169	0.165	0.172	5.296	5.241	5.015	5.241	0.149

Table C-15 Change in volume of vulcanizates after immersed in engine oil at 125°C for 70 h according to ASTM D471-98.

Formulae	Original weight in air, g			Original weight in water, g			Swollen weight in air, g			Swollen weight in water, g			Volume change, %				
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	Med.	SD.
C0-660	1.147	1.127	1.093	0.173	0.167	0.162	1.181	1.166	1.134	0.157	0.154	0.146	5.133	5.417	6.122	5.417	0.509
C10-660	1.280	1.105	1.108	0.195	0.167	0.168	1.318	1.144	1.146	0.186	0.154	0.157	4.332	5.544	5.213	5.213	0.626
C20-660	1.170	1.081	1.078	0.184	0.168	0.166	1.221	1.129	1.123	0.167	0.152	0.153	6.897	7.010	6.360	6.897	0.347
C30-660	1.058	1.127	1.138	0.162	0.174	0.174	1.099	1.166	1.177	0.150	0.163	0.164	5.915	5.247	5.083	5.247	0.441
C0-774	1.262	1.180	1.242	0.188	0.175	0.184	1.304	1.222	1.285	0.179	0.165	0.174	4.749	5.174	5.009	5.009	0.215
C10-774	1.133	1.154	1.102	0.171	0.177	0.167	1.166	1.186	1.133	0.164	0.167	0.157	4.158	4.299	4.385	4.299	0.115
C20-774	1.262	1.221	1.268	0.196	0.189	0.197	1.300	1.260	1.306	0.188	0.179	0.187	4.315	4.748	4.482	4.482	0.218
C30-774	1.109	1.085	1.151	0.173	0.166	0.179	1.134	1.112	1.179	0.161	0.158	0.168	3.953	3.808	4.012	3.953	0.105
E0-660	1.155	1.104	1.133	0.170	0.164	0.165	1.157	1.106	1.136	0.158	0.149	0.153	1.421	1.809	1.550	1.550	0.197
E10-660	1.111	1.072	1.084	0.156	0.159	0.160	1.116	1.076	1.089	0.154	0.148	0.147	0.733	1.643	1.948	1.643	0.632
E20-660	1.043	1.054	1.091	0.157	0.158	0.165	1.046	1.057	1.093	0.145	0.147	0.154	1.693	1.562	1.404	1.562	0.145
E30-660	1.116	1.127	1.092	0.167	0.170	0.165	1.118	1.128	1.095	0.154	0.159	0.153	1.581	1.254	1.618	1.581	0.200
E0-774	1.097	1.112	1.123	0.159	0.161	0.161	1.097	1.116	1.127	0.146	0.149	0.151	1.386	1.682	1.455	1.455	0.155
E10-774	1.063	1.156	1.059	0.156	0.173	0.155	1.065	1.157	1.060	0.143	0.158	0.143	1.654	1.628	1.438	1.628	0.118
E20-774	1.093	1.107	1.096	0.164	0.167	0.167	1.095	1.110	1.099	0.155	0.153	0.150	1.184	1.809	2.153	1.809	0.491
E30-774	1.025	1.099	1.018	0.153	0.164	0.151	1.025	1.101	1.019	0.139	0.151	0.138	1.606	1.604	1.615	1.606	0.006

Table C-15 (Continue)

Formulae	Original weight in air, g			Original weight in water, g			Swollen weight in air, g			Swollen weight in water, g			Volume change, %				
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	Med.	SD.
P0-660	1.345	1.236	1.365	0.196	0.179	0.172	1.347	1.234	1.363	0.197	0.178	0.173	0.087	-0.095	-0.251	-0.095	0.169
P10-660	1.134	1.264	1.244	0.165	0.182	0.181	1.133	1.263	1.242	0.163	0.184	0.18	0.103	-0.277	-0.094	-0.094	0.190
P20-660	1.123	1.118	1.195	0.166	0.165	0.177	1.122	1.117	1.198	0.166	0.166	0.178	-0.104	-0.210	0.196	-0.104	0.211
P30-660	1.17	1.25	1.232	0.173	0.188	0.183	1.168	1.248	1.228	0.173	0.187	0.182	-0.201	-0.094	-0.286	-0.201	0.096
P0-774	1.182	1.068	1.203	0.166	0.147	0.171	1.185	1.07	1.205	0.17	0.153	0.173	-0.098	-0.434	0.000	-0.098	0.228
P10-774	1.337	1.362	1.353	0.199	0.203	0.2	1.335	1.361	1.352	0.202	0.208	0.206	-0.439	-0.518	-0.607	-0.518	0.084
P20-774	1.223	1.208	1.206	0.182	0.178	0.182	1.221	1.206	1.205	0.181	0.177	0.176	-0.096	-0.097	0.488	-0.096	0.338
P30-774	1.121	1.162	1.074	0.166	0.174	0.16	1.119	1.159	1.073	0.165	0.172	0.157	-0.105	-0.101	0.219	-0.101	0.186

Table C-16 Specific gravity of vulcanizates for crosslink density calculation.

	NBR-CB							
	0-660	**10-660**	**20-660**	**30-660**	**0-774**	**10-774**	**20-774**	**30-774**
CV1	1.19	1.20	1.19	1.19	1.20	1.20	1.20	1.20
CV2	1.19	1.19	1.20	1.20	1.19	1.19	1.20	12.10
CV3	1.19	1.19	1.20	1.20	1.19	1.19	1.20	1.20
Med.	1.19	1.19	1.20	1.20	1.19	1.19	1.20	1.20
SD.	0.00	0.01	0.01	0.01	0.01	0.01	0.00	6.29
EV1	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.20
EV2	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19
EV3	1.20	1.20	1.20	1.19	1.20	1.20	1.20	1.19
Med.	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19
SD.	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01
P1	1.18	1.18	1.18	1.18	1.18	1.18	1.18	1.18
P2	1.19	1.18	1.18	1.18	1.18	1.18	1.18	1.18
P3	1.18	1.19	1.18	1.18	1.19	1.18	1.18	1.18
Med.	1.18	1.18	1.18	1.18	1.18	1.18	1.18	1.18
SD.	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00

Table C-17 Original weight of vulcanizates for crosslink density calculation.

	NBR-CB							
	0-660	**10-660**	**20-660**	**30-660**	**0-774**	**10-774**	**20-774**	**30-774**
CV1	1.091	1.135	1.129	1.153	1.182	1.153	1.118	1.219
CV2	1.091	1.117	1.134	1.151	1.191	1.147	1.135	1.204
CV3	1.096	1.120	1.112	1.125	1.185	1.145	1.142	1.195
Med.	1.091	1.120	1.129	1.151	1.185	1.147	1.135	1.204
SD.	0.003	0.010	0.012	0.016	0.005	0.004	0.012	0.012
EV1	1.106	1.077	1.064	1.115	1.105	1.152	1.131	1.057
EV2	1.115	1.079	1.058	1.118	1.119	1.084	1.126	1.033
EV3	1.121	1.094	1.088	1.102	1.102	1.076	1.12	1.107
Med.	1.115	1.079	1.064	1.115	1.105	1.084	1.126	1.057
SD.	0.008	0.009	0.016	0.009	0.009	0.042	0.006	0.038
P1	1.337	1.151	1.129	1.183	1.087	1.327	1.183	1.162
P2	1.385	1.154	1.123	1.167	1.062	1.284	1.232	1.099
P3	1.243	1.148	1.182	1.194	1.112	1.325	1.152	1.187
Med.	1.337	1.151	1.129	1.183	1.087	1.325	1.183	1.162
SD.	0.072	0.003	0.032	0.014	0.025	0.024	0.040	0.045

Table C-18 Swollen weight of vulcanizates for crosslink density calculation.

	NBR-CB							
	0-660	**10-660**	**20-660**	**30-660**	**0-774**	**10-774**	**20-774**	**30-774**
CV1	1.794	1.914	1.931	1.966	1.957	1.955	1.910	2.020
CV2	1.785	1.866	1.902	1.955	1.968	1.920	1.918	1.988
CV3	1.798	1.855	1.866	1.903	1.960	1.916	1.885	1.986
Med.	1.794	1.866	1.902	1.955	1.960	1.920	1.910	1.988
SD.	0.007	0.031	0.033	0.034	0.006	0.021	0.017	0.019
EV1	1.886	1.892	2.051	2.144	1.968	1.925	2.104	1.937
EV2	1.957	1.885	2.007	2.134	1.951	1.926	2.040	1.940
EV3	1.911	1.884	2.024	2.069	1.955	1.902	2.057	1.904
Med.	1.911	1.885	2.024	2.134	1.955	1.925	2.057	1.937
SD.	0.036	0.004	0.022	0.041	0.009	0.014	0.033	0.020
P1	2.252	1.970	1.875	1.932	1.833	2.233	1.932	1.934
P2	2.256	1.952	1.864	1.965	1.834	2.242	1.956	1.911
P3	2.271	2.041	1.916	1.912	1.789	2.253	1.946	1.862
Med.	2.256	1.970	1.875	1.932	1.833	2.242	1.946	1.911
SD.	0.010	0.047	0.027	0.027	0.026	0.010	0.012	0.037

Table C-19 Summary properties of HNBR/NBR blends at various blend ratios.

Properties	**C0-660**	**C10-660**	**C20-660**	**C30-660**	**C0-774**	**C10-774**	**C20-774**	**C30-774**	**E0-660**	**E10-660**	**E20-660**	**E30-660**	**E0-774**	**E10-774**	**E20-774**	**E30-774**	**P0-660**	**P10-660**	**P20-660**	**P30-660**	**P0-774**	**P10-774**	**P20-774**	**P30-774**
Cure characteristic @125°C																								
M_L, lbf-in	1.29	1.59	1.52	1.51	1.22	1.34	1.38	1.35	1.42	1.48	1.54	1.51	1.29	1.4	1.47	1.36	1.49	1.56	1.67	1.74	1.38	1.37	1.56	1.56
M_H, lbf-in	24.69	23.64	20.72	19.16	23.61	20.54	18.62	18.89	17.64	13.12	11.67	11.54	15.89	12.37	11.83	8.95	20.54	23.01	23.22	25.43	21.1	20.9	22.62	23.37
ts_2, min	1.20	1.17	1.16	1.28	1.32	1.23	1.20	1.22	2.20	2.05	1.95	1.89	2.45	2.15	1.71	1.97	0.63	0.56	0.56	0.52	0.61	0.60	0.56	0.54
tc_{90}, min	4.94	4.26	3.93	3.86	5.31	4.69	4.29	3.95	5.12	4.92	4.92	4.89	5.37	5.17	4.49	4.58	5.1	4.93	4.93	4.86	5.1	5.05	4.97	4.91
Original properties																								
100%M, MPa	5.54	6.06	5.86	5.96	4.90	5.25	4.92	5.44	4.19	4.13	3.74	3.94	3.75	3.83	3.97	4.20	8.57	8.99	9.75	10.53	6.63	8.13	8.61	8.70
T.S., MPa	21.78	20.51	18.41	18.72	18.66	19.51	18.76	17.68	19.43	17.47	16.74	16.39	18.10	17.60	16.02	15.95	25.61	22.96	23.85	23.45	23.13	22.83	21.92	21.48
E.B., %	406	359	346	345	304	378	384	315	488	507	484	472	439	516	418	407	233	196	205	184	225	196	196	188
Hardness, IRHD	75	75	73	73	73	71	71	70	72	71	70	69	70	67	67	68	76	76	74	75	73	72	72	74
CS @125°Cx72h, %	70.75	68.91	68.83	66.77	82.76	81.88	78.83	76.19	52.30	51.84	51.54	48.84	56.19	52.00	51.48	48.38	14.42	13.64	12.97	12.54	31.27	25.15	25.00	16.29
Aging @125°Cx168hr.																								
100%M Change, %	157	159	188	-	157	169	190	-	64	110	163	158	81	98	112	114	72	79	128	-	64	84	109	-
T.S. Change, %	-3	-3	-5	-14	-1	-15	-12	-25	12	13	14	8	9	3	12	12	12	11	4	4	2	1	5	4
E.B. Change, %	-64	-61	-67	-74	-47	-66	-64	-71	-35	-39	-52	-57	-33	-42	-42	-50	-27	-31	-47	-55	-16	-33	-41	-53
Hardness change, pts.	9	16	22	22	9	18	18	22	6	11	13	18	3	11	11	10	2	9	13	17	6	11	16	16
IRM903 @125°C, 70hr.																								
100%M Change, %	2	4	1	11	9	1	15	15	11	3	7	4	10	1	0	1	12	15	13	16	2	5	10	12
T.S. Change, %	-1	-13	-5	-19	0	-20	-12	-7	26	12	4	2	17	2	6	2	5	1	5	7	7	1	4	4
E.B. Change, %	-27	-34	-20	-40	-11	-35	-39	-30	-9	-15	-17	-18	-17	-36	-15	-12	-1	-14	-10	-6	-2	-6	-1	-8
Hardness change, pts.	-3	-8	-11	-11	-7	-6	-9	-6	-4	-4	-5	-4	-4	-3	-1	-4	-6	-4	-1	-1	-5	-2	-1	-2
Volume Change, %	10.8	12.6	12.0	9.2	10.1	10.6	10.1	9.2	7.4	7.3	7.3	7.3	7.2	8.4	7.1	6.3	7.2	6.3	5.9	7.2	6.7	5.9	6.6	5.2
Engine oil @125°Cx70hr.																								
100%M Change, %	27	34	30	30	30	43	50	37	28	35	40	24	30	35	23	23	2	23	26	32	21	22	23	23
T.S. Change, %	-9	-3	-7	-8	-9	-1	-14	-9	15	7	12	8	11	10	13	8	3	2	9	10	7	3	0	2
E.B. Change, %	-44	-35	-43	-39	-29	-38	-48	-36	-32	-35	-29	-32	-30	-34	-14	-25	-1	-8	-8	-7	-1	-7	-13	-19
Hardness change, pts.	-2	-2	-6	-2	-5	-1	-1	0	2	1	3	1	2	3	3	0	-1	2	3	4	0	3	4	1
Volume Change, %	5.4	5.2	6.9	5.2	5.0	4.3	4.5	4.0	1.5	1.6	1.6	1.6	1.5	1.6	1.8	1.6	-0.1	-0.1	-0.1	-0.2	-0.1	-0.5	-0.1	-0.1
X-link density, mol/cm^{3}x10^3	1.19	1.87	1.78	1.73	1.94	1.85	1.79	1.93	1.69	1.57	1.16	1.13	1.50	1.48	1.34	1.32	1.82	1.72	1.94	2.07	1.82	1.80	2.01	2.01
Compound cost, Baht/kg.	726.9	660.4	593.9	527.4	728.2	661.7	595.2	528.7	727.7	661.2	594.7	528.2	728.9	662.4	595.9	529.4	719.1	654.9	590.6	526.3	720.4	656.1	591.8	527.5

APPENDIX D

The crosslink density of HNBR/NBR blends was calculated according to Flory-Huggins Theory [34]. Swelling can be determined gravimetrically by weighting the polymer sample before the experiment (W_o) and then subtracting this value from the solvent swollen polymer weight (W_s) as shown in Eq.D-1.

$$V_{equil} = \frac{W_o}{\rho_2} + \frac{W_s - W_o}{\rho_1} \qquad \text{(D-1)}$$

and

$$V_{2m} = \frac{W_o}{V_{equil} \times \rho_2} \qquad \text{(D-2)}$$

Where:

ρ_1 = solvent density (toluene) = 0.870 g/cm^2 (COA)

ρ_2 = polymer density = 1.19 g/cm^2 (Table C-16)

W_o = original polymer weight = 1.091 g (Table C-17)

W_s = swollen polymer weight = 1.794 g (Table C-18)

$$V_{equil} = \frac{1.091}{1.19} + \frac{1.794 - 1.091}{0.870} = 1.725$$

Substituing V_{equil} = 1.725 in Eq.D-2

$$V_{2m} = \frac{1.091}{1.725 \times 1.19} = 0.532$$

The molecular weight per crosslink unit, M_c is calculated using Eq.D-3.

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

where V_1 is molar volume of solvent and χ_1 is polymer-solvent interaction parameter.

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

Hence,

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

Substituting the know value V_1 , ρ_2 , V_{2m} and χ_1 = 0.393 [35] for rubber/toluene in Eq.D-3.

$$M_c = 559.449 \text{ g/mol}$$

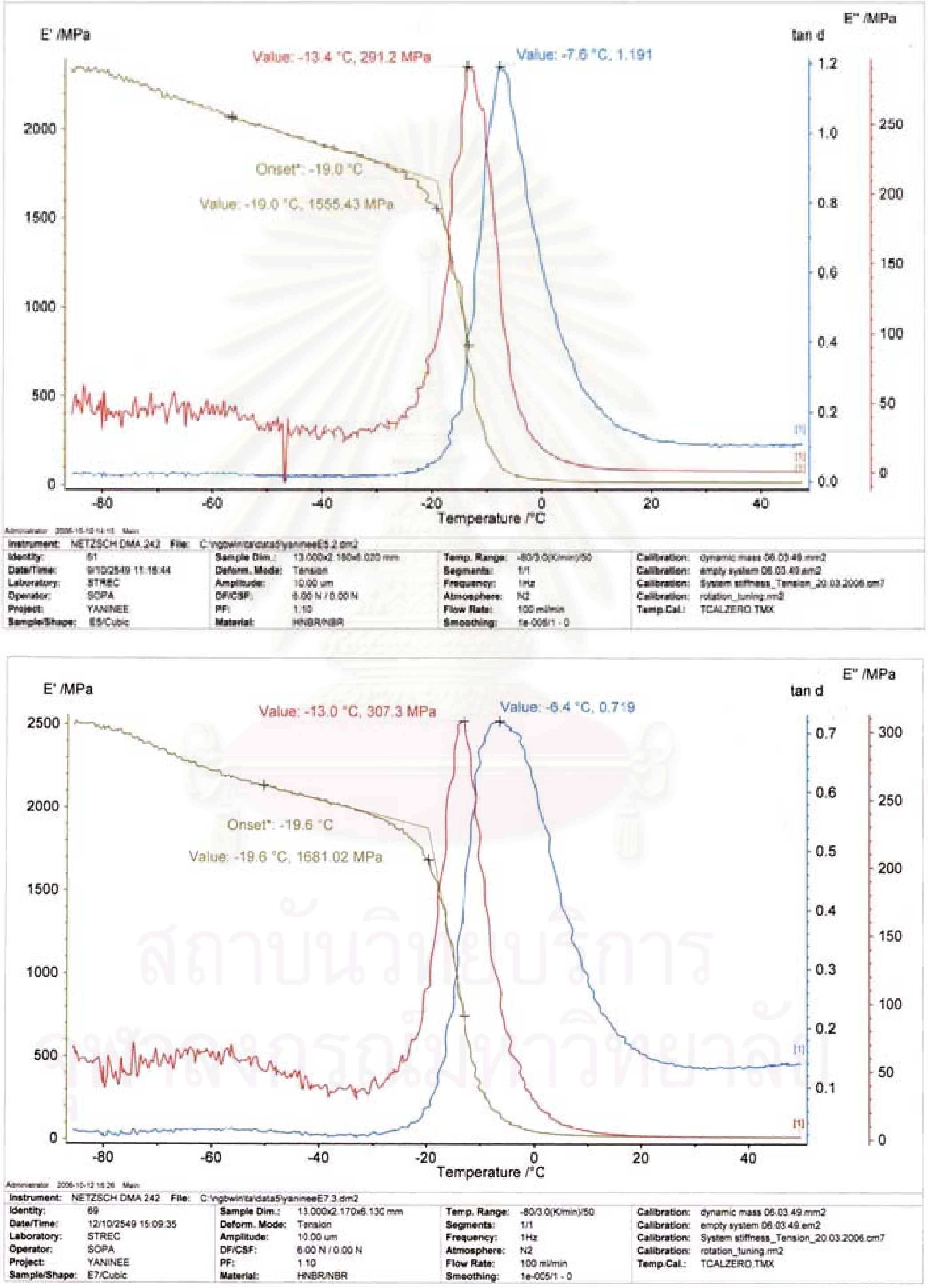
Thus, the crosslink density of HNBR/NBR compound is,

$$n_c = \frac{\rho_2}{M_c}$$

$$n_c = \frac{1.19}{559.449}$$

$$n_c = 1.985 \times 10^{-3}\ mol/cm^3$$

APPENDIX E



Administrator 2006-10-12 14:15 Main

Instrument: NETZSCH DMA 242 File: C:\ngbwin\ta\data5\yanineeE5.2.dm2

Identity: 61
Date/Time: 9/10/2549 11:15:44
Laboratory: STREC
Operator: SOPA
Project: YANINEE
Sample/Shape: E5/Cubic

Sample Dim.: 13.000x2.180x6.020 mm
Deform. Mode: Tension
Amplitude: 10.00 um
DF/CSF: 6.00 N / 0.00 N
PF: 1.10
Material: HNBR/NBR

Temp. Range: -80/3.0(K/min)/50
Segments: 1/1
Frequency: 1Hz
Atmosphere: N2
Flow Rate: 100 ml/min
Smoothing: 1e-006/1 - 0

Calibration: dynamic mass 06.03.49.mm2
Calibration: empty system 06.03.49.em2
Calibration: System stiffness_Tension_20.03.2006.cm7
Calibration: rotation_tuning.rm2
Temp.Cal.: TCALZERO.TMX

(a)

Administrator 2006-10-12 16:26 Main

Instrument: NETZSCH DMA 242 File: C:\ngbwin\ta\data5\yanineeE7.3.dm2

Identity: 69
Date/Time: 12/10/2549 15:09:35
Laboratory: STREC
Operator: SOPA
Project: YANINEE
Sample/Shape: E7/Cubic

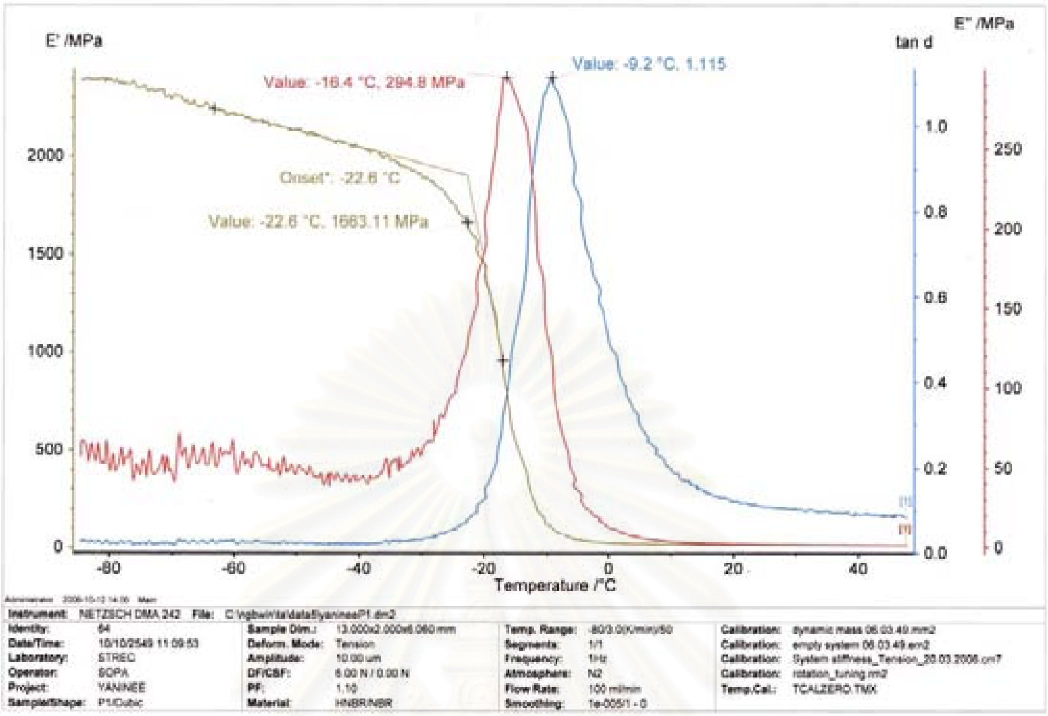
Sample Dim.: 13.000x2.170x6.130 mm
Deform. Mode: Tension
Amplitude: 10.00 um
DF/CSF: 6.00 N / 0.00 N
PF: 1.10
Material: HNBR/NBR

Temp. Range: -80/3.0(K/min)/50
Segments: 1/1
Frequency: 1Hz
Atmosphere: N2
Flow Rate: 100 ml/min
Smoothing: 1e-005/1 - 0

Calibration: dynamic mass 06.03.49.mm2
Calibration: empty system 06.03.49.em2
Calibration: System stiffness_Tension_20.03.2006.cm7
Calibration: rotation_tuning.rm2
Temp.Cal.: TCALZERO.TMX

(b)

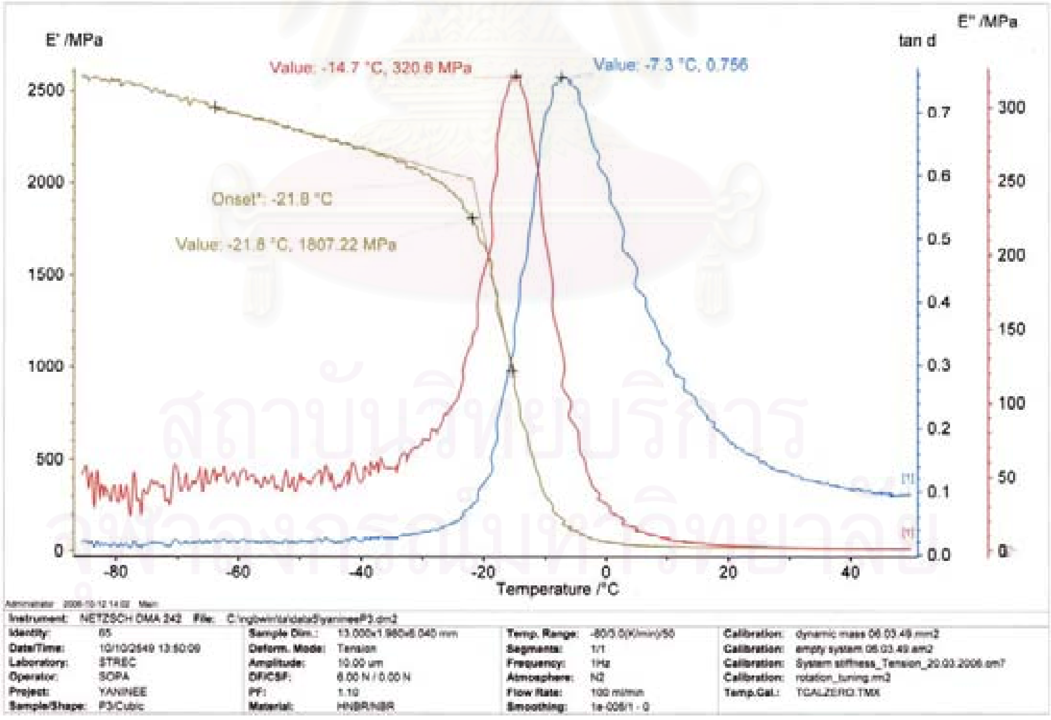
Figure E-1 DMTA thermograms of rubber compounds; (a) E0-774, (b) E20-774, (c) P0-660, (d) P20-660, (e) P0-774 and (f) P20-774.



Instrument: NETZSCH DMA 242 File: C:\ngbwin\ta\data5\yaninee\P1.dm2

Identity:	64	**Sample Dim.:**	13.000x2.000x6.060 mm	**Temp. Range:**	-80/3.0(K/min)/50	**Calibration:**	dynamic mass 06.03.49.mm2
Date/Time:	10/10/2549 11:09:53	**Deform. Mode:**	Tension	**Segments:**	1/1	**Calibration:**	empty system 06.03.49.em2
Laboratory:	STREC	**Amplitude:**	10.00 um	**Frequency:**	1Hz	**Calibration:**	System stiffness_Tension_20.03.2006.cm7
Operator:	SOPA	**DF/CSF:**	6.00 N / 0.00 N	**Atmosphere:**	N2	**Calibration:**	rotation_tuning.rm2
Project:	YANINEE	**PF:**	1.10	**Flow Rate:**	100 ml/min	**Temp.Cal.:**	TCALZERO.TMX
Sample/Shape:	P1/Cubic	**Material:**	HNBR/NBR	**Smoothing:**	1e-005/1 - 0		

(c)

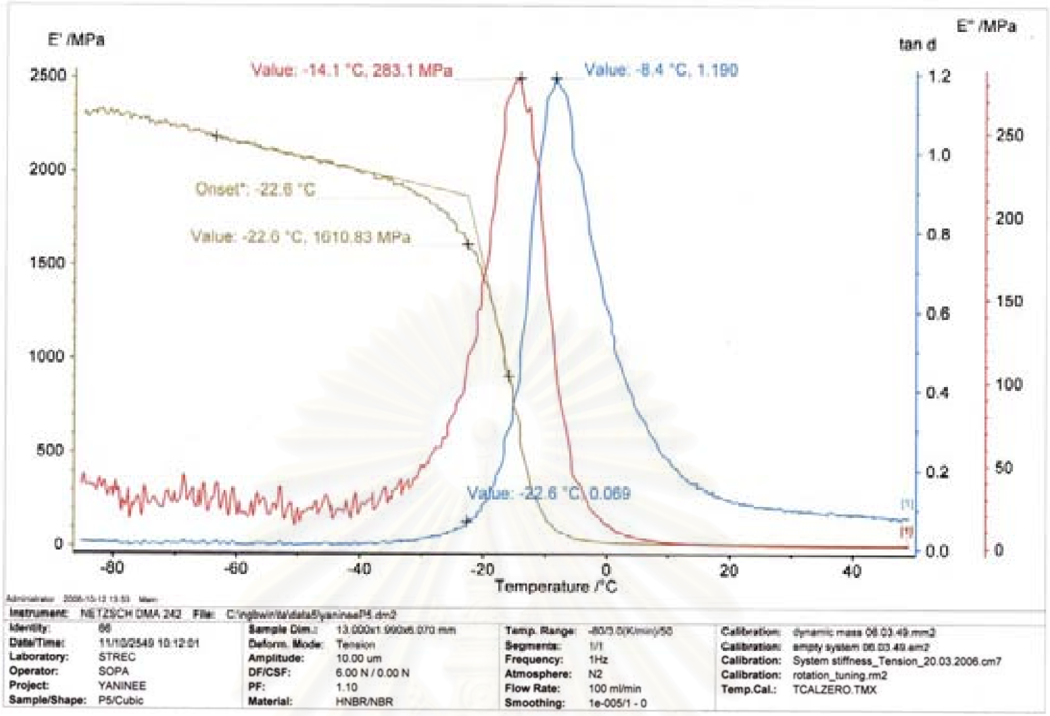


Instrument: NETZSCH DMA 242 File: C:\ngbwin\ta\data5\yaninee\P3.dm2

Identity:	65	**Sample Dim.:**	13.000x1.980x6.040 mm	**Temp. Range:**	-80/3.0(K/min)/50	**Calibration:**	dynamic mass 06.03.49.mm2
Date/Time:	10/10/2549 13:50:09	**Deform. Mode:**	Tension	**Segments:**	1/1	**Calibration:**	empty system 06.03.49.em2
Laboratory:	STREC	**Amplitude:**	10.00 um	**Frequency:**	1Hz	**Calibration:**	System stiffness_Tension_20.03.2006.cm7
Operator:	SOPA	**DF/CSF:**	6.00 N / 0.00 N	**Atmosphere:**	N2	**Calibration:**	rotation_tuning.rm2
Project:	YANINEE	**PF:**	1.10	**Flow Rate:**	100 ml/min	**Temp.Cal.:**	TCALZERO.TMX
Sample/Shape:	P3/Cubic	**Material:**	HNBR/NBR	**Smoothing:**	1e-005/1 - 0		

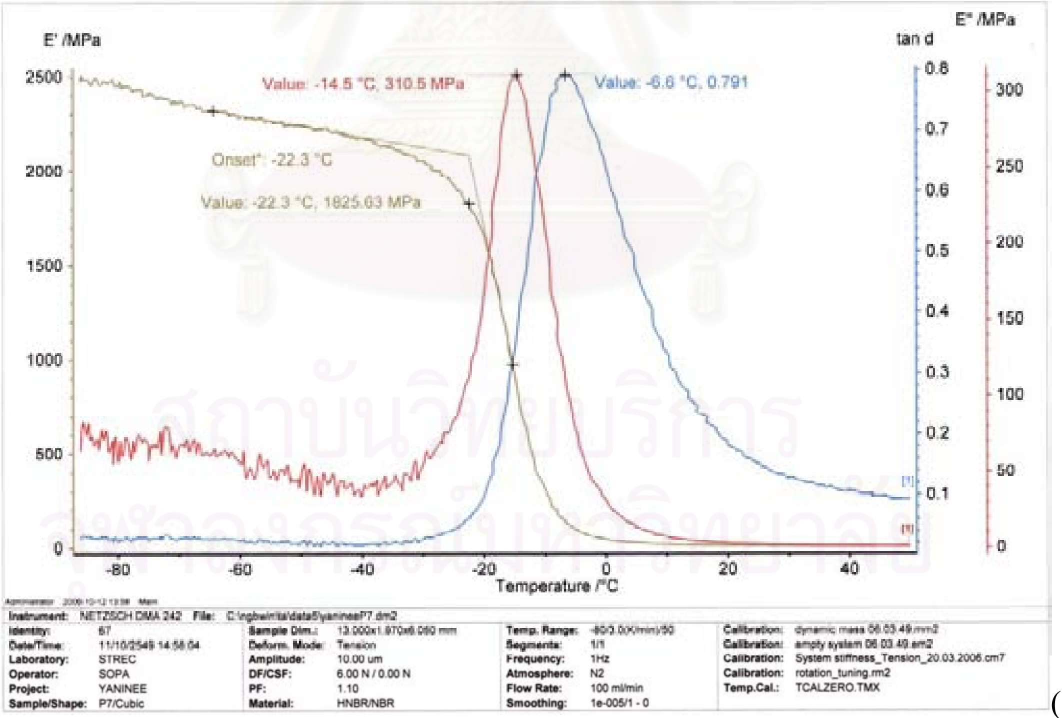
(d)

Figure E-1 (Continue)



Administrator 2006-10-12 13:53 Main
Instrument: NETZSCH DMA 242 File: C:\ngbwin\ta\data5\yanineeP5.dm2
Identity: 66
Date/Time: 11/10/2549 10:12:01
Laboratory: STREC
Operator: SOPA
Project: YANINEE
Sample/Shape: P5/Cubic
Sample Dim.: 13.000x1.990x6.070 mm
Deform. Mode: Tension
Amplitude: 10.00 um
DF/CSF: 6.00 N / 0.00 N
PF: 1.10
Material: HNBR/NBR
Temp. Range: -80/3.0(K/min)/50
Segments: 1/1
Frequency: 1Hz
Atmosphere: N2
Flow Rate: 100 ml/min
Smoothing: 1e-005/1 - 0
Calibration: dynamic mass 06.03.49.mm2
Calibration: empty system 06.03.49.em2
Calibration: System stiffness_Tension_20.03.2006.cm7
Calibration: rotation_tuning.rm2
Temp.Cal.: TCALZERO.TMX

(e)



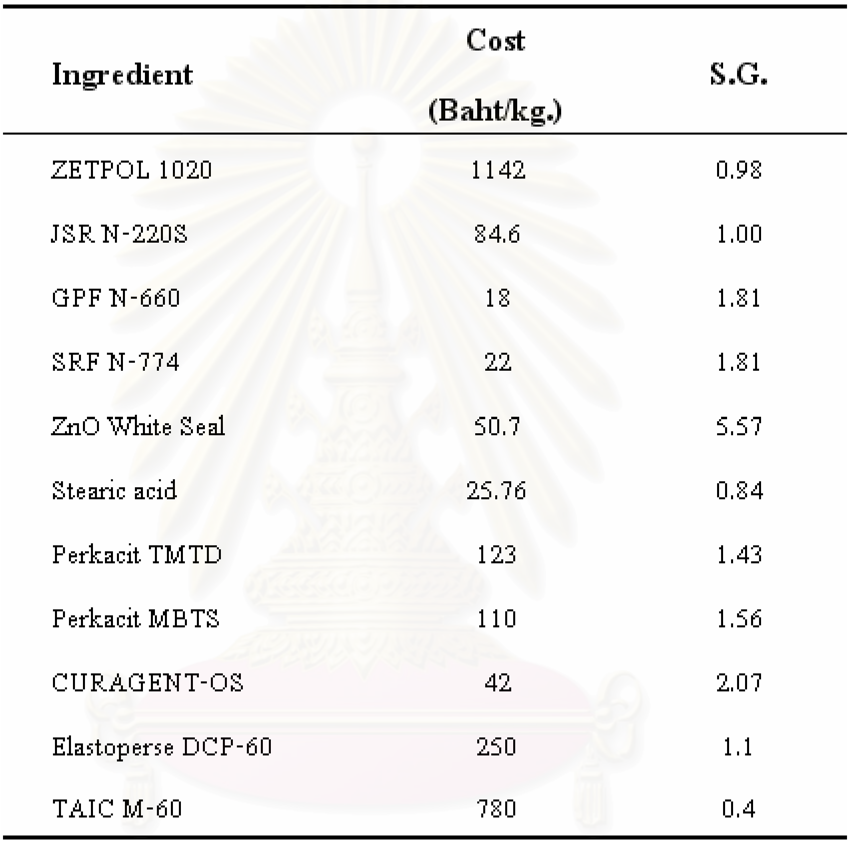
Administrator 2006-10-12 13:58 Main
Instrument: NETZSCH DMA 242 File: C:\ngbwin\ta\data5\yanineeP7.dm2
Identity: 67
Date/Time: 11/10/2549 14:58:04
Laboratory: STREC
Operator: SOPA
Project: YANINEE
Sample/Shape: P7/Cubic
Sample Dim.: 13.000x1.970x6.060 mm
Deform. Mode: Tension
Amplitude: 10.00 um
DF/CSF: 6.00 N / 0.00 N
PF: 1.10
Material: HNBR/NBR
Temp. Range: -80/3.0(K/min)/50
Segments: 1/1
Frequency: 1Hz
Atmosphere: N2
Flow Rate: 100 ml/min
Smoothing: 1e-005/1 - 0
Calibration: dynamic mass 06.03.49.mm2
Calibration: empty system 06.03.49.em2
Calibration: System stiffness_Tension_20.03.2006.cm7
Calibration: rotation_tuning.rm2
Temp.Cal.: TCALZERO.TMX

(f)

Figure E-1 (Continue)

APPENDIX F

Table F-1 Cost and specific gravity of ingredient.



Ingredient	Cost (Baht/kg.)	S.G.
ZETPOL 1020	1142	0.98
JSR N-220S	84.6	1.00
GPF N-660	18	1.81
SRF N-774	22	1.81
ZnO White Seal	50.7	5.57
Stearic acid	25.76	0.84
Perkacit TMTD	123	1.43
Perkacit MBTS	110	1.56
CURAGENT-OS	42	2.07
Elastoperse DCP-60	250	1.1
TAIC M-60	780	0.4

Examination methods of determining the compound cost and densities. For an example, a rubber compound such as Model Compound C10-660, which includes the costs and densities as list in Table F-2.

Table F-2 Compound cost calculation.

Ingredient	Weight (phr)	Cost (Baht/kg.)	Weight x Cost (phrxBaht/kg.)	S.G.	V (phr)/S.G.
ZETPOL 1020	90.00	1142.00	102780.00	0.98	91.84
JSR N-220	10.00	84.60	846.00	1.00	10.00
GPF N-660	50.00	18.00	900.00	1.81	27.62
ZnO	5.00	50.70	253.50	5.57	0.90
STEARIC ACID	1.00	25.76	25.76	0.84	1.19
Sulfur	2.00	42.00	84.00	2.07	0.97
TMTD	0.50	123.00	61.50	1.43	0.35
MBTS	0.50	110.00	55.00	1.56	0.32
Total	159.00		105005.76		133.19
Compound cost	**660.41**	Baht/kg.			
Compound S.G.	**1.19**				

Specific gravity is calculated as follow Eq. F-1.

$$Compond\ \cos t / kg. = \sum \frac{weight(phr)_i \times \cos t / kg._i}{\sum weight(phr)_i} \qquad \text{(F-1)}$$

$$= \frac{105005.76}{159.00}$$

$$= 660.41 \text{ Baht/kg.}$$

Specific gravity is calculated as follow Eq. F-2.

$$Compound\ specific\ gravity = \frac{\sum\left(\frac{weight(phr)_i}{S.G._i}\right)}{\sum weight(phr)_i} \tag{F-2}$$

$$= \frac{159.00}{133.19}$$

$$= 1.19$$

VITAE

Miss Yaninee Srisuwan was born on September 23, 1981, in Suratthani, Thailand. She received her Bachelor’s degree in Rubber Technology, from the Faculty of Science and Technology, Prince of Songkla University in 2004. She has pursued Master’s Degree in Petrochemistry and Polymer Science, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University science 2005 and finished her study in 2007.