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# PREPARATION OF COMPOUNDED RUBBER FROM NATURAL RUBBER GRAFTED WITH VINYL ACETATE

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การผลิตยางรัดของในปัจจุบันใช้ยางแผ่นหรือยางแท่งเป็นวัตถุดิบ ต้องมีการย่อยและ การบดผสมสารปรับปรุงคุณภาพหลายขั้นตอน งานวิจัยนี้มุ่งเน้นพัฒนากระบวนการผลิตให้มี ต้นทุนและเวลาการผลิตลดลง โดยการใช้น้ำยางข้นผสมกับสารปรับปรุงคุณภาพโดยตรง และทำการกราฟต์ไวนิลแอซีเทตเพื่อปรับปรุงสมบัติเชิงกลให้เหมาะสม การเตรียมยางคอมพาวด์นี้จะใช้ การบดผสมด้วยเครื่องบอลมิล ยางคอมพาวด์ที่ได้จะทำการศึกษาปริมาณการเชื่อมโยงของยางและไวนิลแอซีเทตโดยการสกัดโฮโมพอลิเมอร์ด้วยเฮกเซนและเมทิลเอทิลคีโตนตามลำดับ พบว่า ปริมาณการเชื่อมโยงมีค่ามากกว่า 97 เปอร์เซ็น ศึกษาการกราฟต์ของไวนิลแอซีเทตด้วยเทคนิค เอทีอาร์ เอฟทีไออาร์ จากการศึกษาพบว่าหมู่คาร์บอนิลของไวนิลแอซีเทตปรากฏที่ตำแหน่งความยาวคลื่น 1649 ซึ่งแสดงถึงการกราฟต์ของไวนิลแอซีเทต และศึกษาสมบัติเชิงกลของยางคงรูปคือ ค่าความต้านทานแรงดึง ค่าระยะยืด ค่ามอดูลัส ค่าความแข็ง ค่าความกระดอนของยาง และสมบัติการทนความร้อน ปัจจัยที่มีผลต่อสมบัติเชิงกลที่ทำการศึกษาคือ ปริมาณของไวนิลแอซีเทต ชนิดของตัวริเริ่มปฏิกิริยา และเวลาที่ใช้ในการผสม ผลการวิจัยพบว่า สภาวะที่ให้ยางคอมพาวด์ที่มีสมบัติเชิงกลดีที่สุดคือ ยางที่กราฟต์ด้วยไวนิลแอซีเทต 4 ส่วนในยางร้อยส่วน ใช้เวลาในการผสม 1 ชั่วโมง และใช้เทอร์เทียรีบิวทิล-ไฮโดรเปอร์ออกไซด์เป็นตัวริเริ่มปฏิกิริยา ค่าสมบัติเชิงกลของยางคอมพาวด์ที่เตรียมได้ คือ ค่าความต้านทานแรงดึง 19.28 เมกกะปาสคาล ค่าระยะยืด 2326.33 เปอร์เซ็น ค่ามอดูลัส 1.223 เมกกะปาสคาล ค่าความแข็ง 42 ชอร์เอ ค่าความกระดอนของยาง 84.08 เปอร์เซ็น และนอกจากนี้ยังพบว่ามีค่าสมบัติการทนความร้อนของยางคอมพาวด์อยู่ในช่วงการใช้งานต่างๆ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต............................................
หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา.............................
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KEYWORD : RUBBER LATEX NATURAL, GRAFTING, VINYL ACETATE, RUBBER BAND.

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Rubber band production using sheet and block rubber is carried out with many stages of additive mixing. This research aims to improve the production at low cost and shorter time by using concentrated latex and, at the same time, to improve mechanical properties of rubber by grafting with vinyl acetate. Compounded rubber was prepared by ball mill and the degree of crosslink of rubber and vinyl acetate was investigated by soxhlet extraction technique to remove homopolymer using hexane and methyl ethyl ketone, respectively as solvents. It was found that the degree of crosslink was more than 97%. The grafting of vinyl acetate was studied by ATR-FTIR. From the study it was found that the carbonyl group of vinyl acetate appeared at wave number 1649 $cm^{-1}$ ,which indicated the grafting of vinyl acetate. The mechanical properties of vulcanized rubber were monitored by tensile strength, elongation at break, modulus, hardness, rebound resilience and aging properties. The effects of vinyl acetate content, types of initiator and mixing time were studied. The optimum condition of compounded rubber with the best mechanical properties were 4 phr of vinyl acetate, 1 hour of mixing time, and tert-butylhydroperoxide as an initiator. The mechanical properties of compounded rubber were 19.28 MPa tensile strength , 2326.33% elongation at break, 1.223 Mpa modulus, 42 Shore A hardness, 84.08% rebound resilience . Moreover, it was found that the aging properties of compounded rubber was in the range of various applications.

Department Petrochemistry and Polymer Science Student's signature…………………………….

Field of study Petrochemistry and Polymer Science Advisor's signature…………………………….

Academic year 2000

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# CONTENTS

# CONTENTS (continued)

# CONTENTS (continued)

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PAGE

# LIST OF TABLES

# LIST OF TABLES (continued)

# LIST OF TABLES (continued)

PAGE

# LIST OF FIGURES

FIGURE PAGE

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FIGURE PAGE

# ABBREVIATIONS

| | | |
|---|---|---|
| Ave | : | Average |
| $^{o}$C | : | Degree Celsius |
| NR | : | Natural Rubber |
| phr | : | part per hundred rubber |
| rpm | : | Rounds per minute |
| t-BuHP | : | tertiary-Byltylhydroperoxide |
| BPO | : | Benzoylperoxide |
| MBT | : | 2-Mercaptobenzothiazole |
| VAM | : | Vinyl Acetate Monomer |
| PVA | : | Poly(Vinyl Acetate) |
| MEK | : | Methyl Ethyl Ketone |
| ZnO | : | Zinc Oxide |
| hr | : | hour |
| min | : | minute |
| KN | : | Kilo Newton |
| g | : | gram |
| mm. | : | millimeter |
| ml. | : | milliliter |
| SD | : | Standard Deviation |

# CHAPTER I

# INTRODUCTION

## Statement of Problems

Natural rubber production and export in Thailand increase every year. From the data of natural rubber use and export, it was found that rubber band production used high volumes of natural rubber in the third order and exported in the fourth order when compared with all productions. Thus, it was a very interesting product to be considered as a value added rubber product [1]. However, the traditional rubber band production was carried out with many stages of additive mixing and has high production cost because sheet and block rubber were used as raw materials.

Therefore, this research aims to improve the rubber band production by preparing the compound rubber directly from rubber latex for use as the raw material. The compounded rubber was produced by directly mixing concentrated latex, which has low cost with all additives in ball mill. Furthermore, vinyl acetate monomer was grafted into the compound rubber to improve the qualities of product. The advantages of using the compounded rubber as the raw material are the reduction of processing cost and time. Moreover, the high quality of products was improved and would be suitable for exporting.

The compounded rubber from natural rubber grafted with vinyl acetate was prepared by emulsion polymerization. Many parameters, such as monomer concentration, mixing time, and type of initiator, were investigated to find the appropriate condition. Moreover, the degree of crosslink and mechanical properties was determined. Finally, the overall quality of obtained products was evaluated.

## Objectives

1. To study the appropriate conditions for the preparation of compounded rubber from natural rubber grafted with vinyl acetate.
2. To study the mechanical properties of the prepared rubber compounds.

## Scope of the investigation

For the preparation of the natural rubber compound grafted with vinyl acetate, the appropriate conditions, which give the best mechanical properties were studied. The investigation procedures were carried out as follows:

1. Literature survey and study of this research work.
2. Design and prepare experimental procedure.
3. Prepare the compounded rubber by direct mixing the concentrated latex with vulcanizing agent, additives and vinyl acetate in aqueous dispersions using a ball mill. The appropriate conditions were determined by changing the following parameters:

a) Concentration of vinyl acetate

b) Mixing time

c) Initiator types

4. Coagulate and vulcanize the rubber sheet by compression molding

5. Investigate the degree of crosslink by soxhlet extraction to remove homopolymer and study the grafting of vinyl acetate by ATR-FTIR measurement.

6. Determine the mechanical properties such as tensile strength, modulus, and elongation at break, hardness and rebound resilience following the ISO and ATM methods.

7. Summarize the results.

# CHAPTER II

# THEORY AND LITERATURE REVIEWS.

## 2.1 Natural Rubber [2]

It has been estimated that some 2000 different plant species yield polymer akin to natural rubber and that rubber of sorts have been obtained from some 500 of them. To all intents and purposes, the natural rubber of commerce is obtained from the latex of *Heavea brasiliensis*, a native of Brazil but widely grown on plantations in tropical Africa and Asia. The production of natural rubber has grown steadily since World War II. The Southeast Asian region accounted for about 80 % of the total production. Thailand was the biggest producer, followed by Indonesia and Malaysia. The world production of natural rubber is shown in Table 2.1.

### 2.1.1 Natural Rubber In Thailand [1]

The data from the Rubber Research Institute Department of Agriculture showed that in 1998, Thailand produced 2,075,950 tons of natural rubber, exported 1,839,396 tons or 88.61 % of total production, domestically used 186,379 tons and stocked 209,546 tons. The exports of rubber by type of Thailand in 1998 are shown in Table 2.2. There is no import natural rubber since 1997. The field latex is unstable to transport over the long distances and times to the consumer. So the latex is changed in many ways before shipment. There are many standard specifications in defining a range of grades of rubber in the world. The Rubber Manufacturers Association has a further set of standards for quality and packing of latex natural rubber grades as shown in Table 2.3.

**Table 2.1** World production of natural rubber in 1998

| Country | Tons (x$10^3$) |
|---|---|
| Thailand | 1,763.0 |
| Indonesia | 1,449.8 |
| Malaysia | 709.8 |
| Sri Lanka | 72.1 |
| Vietnam | 69.0 |
| Other | 368.6 |
| Total | 4,430 |

Source: Rubber Research Institute of Thailand [1] Natural Rubber in Thailand

Table 2.2 Thailand exports of rubber by type in 1998

| Types of Rubber | Tons |
|---|---|
| Smoked sheet (RSS) | 1,047,152 |
| Block rubber (STR) | 480,222 |
| Concentrated latex | 246,438 |
| Air dried sheet | 10,819 |
| Crepe rubber | 920 |
| Skim block crepe | 26,864 |
| Unsmoked Sheet | 10,404 |
| Other rubbers | 16,588 |
| Total | 1,839,396 |

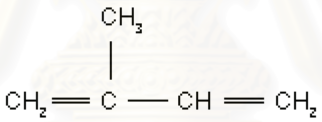
Table 2.3 International Natural Rubber Type and Grade Specification [3]

| Type | Natural Rubber | Description |
|---|---|---|
| 1 | Ribbed smoked sheet | Coagulated sheet , dried and smoked latex. Five grades available (RSS1-5) |
| 2 | White and pale crepe | Coagulated natural liquid latex milled to produce a crepe |
| 3 | Estate brown crepe | Fresh lump and other high-quality scrap generated on the plantation |
| 4 | Compo crepe | Lump, tree scrapes and smoked sheet cuttings are milled into a crepe |
| 5 | Thin brown crepe | Unsmoked sheets, wet slab , lump and other scrap from estates and small holdings |
| 6 | Thick blanket crepe | Wet slab , lump and unsmoked sheet milled to give a crepe |
| 7 | Flat bark crepe | All types of scrap natural rubber including earth scrap |
| 8 | Pure smoked blanket crepe | Milled smoked rubber derived exclusively form ribbed smoked sheets |

### 2.1.2 The Chemical Formula of Natural Rubber [2]

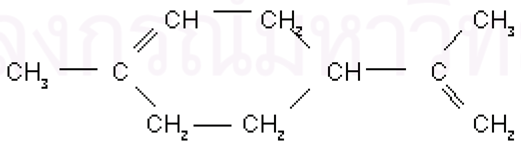
The empirical formula for the natural rubber (NR) molecule appears to have been first determined by Faraday who reported his findings in 1826. He concluded that carbon and hydrogen were the only elements present and his results correspond to the formula $C_5H_8$. Whilst this result was obtained using a product which contains associated non-rubbery material. Subsequent studies with highly purified materials have confirmed Faraday's conclusion.

Isoprene was found to have the formula $C_5H_8$, for which Tilden proposed the structure



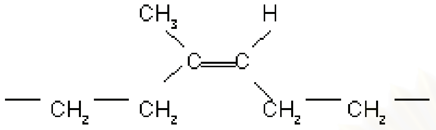
$$\mathrm{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2}$$

The structure was confirmed by synthesis of the isoprene by Euler and by others. The second fraction was separated by Himly and found to have the formula $C_{10}H_{16}$. Today this material is known as dipentene and its structure was confirmed by the synthesis of Perkin in 1904 to be :

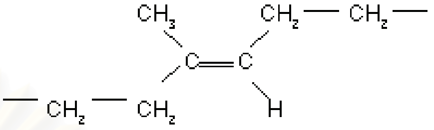


Clearly dipentene is a dimer of isoprene and latter may be converted into the former by heating at 270 °C with the process being reversed at higher temperatures.

The linear structure proposed by Pickles provided for the possibility of structural isomerism with both cis- and trans- repeating units.



**Cis-**



***trans-***

It was known at this time that the major hydrocarbon component of both gutta percha and balata (at that time important in belting, submarine cable, golf ball and container applications ) was a poly-isoprene which when reacted with bromine and ozone gave similar results to those obtained with natural rubber. It was therefore tempting to suggest that one isomer was that of gutta percha and balata and the other that of natural rubber. The early work of Staudinger suggests that the trans-isomer was natural rubber and gutta percha the cis-. However later studies of X-ray fibred diagrams of stretched rubber led Meyer and Mark to the view that natural rubber was the cis-polymer. The crystalline stretched rubber molecule is shown in Figure 2.1.

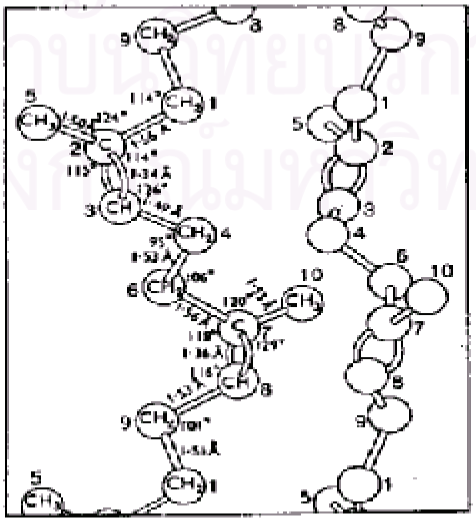


**Figure 2.1** Unit cell structure of the natural rubber molecule

The possibility that the NR molecule might contain a mixture of cis-and trans- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and be unable to crystallize in the manner of natural rubber. Infrared studies have subsequently confirmed that NR was the cis-polymer.

### 2.1.3 Composition [4]

The typical composition of natural rubber is shown in Table 2.4.

**Table 2.4** The typical composition of natural rubber

| Ingredient | Average Value (%) | Range (%) |
|---|---|---|
| Moisture | 0.5 | 0.3 - 1.0 |
| Acetone Extract | 2.5 | 1.5 - 4.5 |
| Protein | 2.5 | 2.0 - 3.0 |
| Ash | 0.3 | 0.2 – 0.5 |
| Rubber Hydrocarbon | 94.2 | - |
| Total | 100.00 | - |

### 2.1.4 Physical Properties [4]

Physical properties of natural rubber may slightly be due to the nonrubber constituents present and to degree of crytallinity. When the natural rubber is held below 10 °C, crystallization occurs, resulting in the change of density from 0.92 to about 0.95. The average molecular weight can range from 200,000 – 500,000. Some average physical properties of natural rubber are shown in Table 2.5.

**Table 2.5** Some physical properties of natural rubber

| Properties | Value |
|---|---|
| Density | 0.92 |
| Refractive index (20 °C) | 1.52 |
| Coefficient of cubical expansion | 0.00062 / °C |
| Cohesive energy density | 63.7 cal./c.c. |
| Heat of combustion | 10,700 cal./g |
| Thermal conductivity | 0.00032 cal./sec/cm$^2$/ °C |
| Dielectric constant | 2.37 |
| Power factor (1,000 cycles) | 0.15 – 0.2 |
| Volume resistivity | $10^{15}$ ohms/c.c. |
| Dielectric strength | 1,000 volts/mm$^2$ |

## 2.2 Natural Rubber Latex [5,6]

Natural rubber, on which the technology of the industry was built, is obtained by the coagulation of the milky aqueous dispersion of rubber called latex produced by the tree *Heavea brasiliensis*. Natural latex concentrates have been commercial since about 1930 and subsequently have been thoroughly exploited for the manufacture of a great variety of products. The production of dipped goods, such as gloves, balloons and teats, is the current dominant area of manufacturing using natural latex. The conversion of natural rubber latex into products is accomplished in many different ways. All of these processes share the distinctive characteristics of latex technology.

### 2.2.1 The Production of Natural Rubber Latex Concentrate [5,6]

The latex from *Heavea brasiliensis* tree has rubber content between 25-40 percent by weight. The variation is due to factors such as the type of tree, the tapping method, the soil condition and season. The latex is normally called ‘field latex’ and its average rubber content is 30 percent by weight. This material is not utilized in its original form because its high water content and susceptibility to bacteria attack. It is necessary both to preserve and concentrate it, so that the end product is stable and contains 60 percent or more of rubber. All the important processes of fabrication of latex articles begin with a latex that has a 60 percent minimum rubber content. Extensive blending of the concentrate latex ensures or consists of high quality material and international specification.

Latex concentrate is differentiated by the method of concentration and type of preservative used (shown in Table 2.6). In addition to the general purpose type of latex, there are speciality forms such as double centrifuged latex, creamed/ centrifuged latex (‘sub-stage latex’), and modified types such as prevulcanized latex. Three methods of concentration are employed, centrifugation, evaporation and creaming; centrifugation is the preferred method and accounts for 95 percent of total production.

**Table 2.6** Types of preservative system used in centrifuged NR latex concentrate [5]

| Designation | Abbreviation | Market share (%) | Preservative system (% by weight) |
|---|---|---|---|
| High or full ammonia | HA | 66 | 0.7 % ammonia |
| Low ammonia TZ | LA-TZ | 17 | 0.2% ammonia ,0.025% zinc oxide , 0.025% tetramethylthiuram disulphide |
| Low ammonia Pentachlorphenate | LA-SPP | 6 | 0.2 % ammonia , 0.2% sodium |
| Low ammonia boric Acid | LA-BA | 5 | 0.2 % ammonia<br>0.24 % boric acid |

The HA and LA-TZ type are the predominant lattices for centrifugation. Method

Fixed latex is collected form the tapping cups, and bulked. Preliminary ammoniation to about 0.05-0.2 percent is carried out to protect it from bacterial attack prior to delivery to the concentrate factory. On arrival, the latex is tested for properties such as rubber content and volatile fatty acid content. If the test results are satisfactory , the latex is put in bulking tanks . From here it is supplied to the centrifuges, where separation occurs, yielding a concentrate (60 percent or more rubber content) and a skin latex (3-6 percent rubber content). The concentrate is ammoniated using ammonia gas and treated with the rest of the preservative system, if necessary. It is kept in storage tanks for quality tests to carry out. The latex concentrate is transferred to the port installation for shipping to the consumer in bulk containers or drums. Gravitational flow is in latex factory wherever possible, otherwise air pressure pumps are employed. The production of high quality, consistent NR latex concentrates demand particular cleanliness with regard to all the vessels and pipelines used.

### 2.2.2 Composition [2]

The composition of the Heavea latex varies between quite wide limits, but the following may be considered as a typical composition.

| | |
|---|---|
| Total solid content | 36 % (including a dry rubber content |
| Proteinous substance | 33 %) |
| Resinous substance | 1-1.5 % |
| Ash | 1-2.5 % |
| Sugar | less than 1 |

Water 1

60

The non- rubber components and not only have a biological function, but also influence both the methods of coagulation to form dry rubber and also the techniques of latex technology.

## 2.3 Compounded Rubber [6]

Compounded rubber has many unique characteristics not found in other materials, such as dampening properties, high elasticity, and abrasion resistance. The good properties of compounded rubber are dependent on many parameters such as the following:

### 2.3.1 The Design of Latex Compounds [4,6]

Compounding transforms raw natural rubber into a range of materials suitable for applications. The objective of compounding are a) to facilitate processing and fabrication, b) to ensure a rapid throughput with minimal reject rate, c) to achieve the required balance in vulcanizate properties, and d) to provide durability, all at the lowest possible cost. Other important consideration is product specifications in mixing, storage capacity, increasing significance, health and safety. Compounding also involves compromise because an ingredient added to maximize one property may detract from another.

In general, most latex compounds require three classes of additives:

1) Stabilizers to ensure adequate processing stability;

2) Vulcanizing agent to effect crosslinking of the rubber;

3) Protective agent to ensure adequate service life.

In addition some compounds , depending on the natural process or the end use, may require gelling agents, foaming agent, thickeners, flameproofing agent, pigment, fillers, extender, and tackifying resins.

### 1) Stabilization [4]

The materials used as stabilizers for latex compounds are the most important additives. Unless the compound has sufficient stability to withstand the processing condition no products will be made. Natural latex already contains its own stabilizing material, proteins and soaps, and in a few cases these may be sufficient. In most instances, the stability of the compound must be increased by the further addition of chemicals. The fatty acid soaps commonly used as stabilizers are the potassium, and sodium or ammonium salts of fatty acid having from 8 to 18 carbon atoms. Not all of these soaps are equally suitable. Among the saturated soaps those having 8-12 carbon atoms are the most effective, whereas of the unsaturated soap those with 18 carbon atoms, such as oleic, ricinoleic and linoleic are the best. The effectiveness of the soaps is probably related to their solubility.

### 2) Vulcanization System [8]

Vulcanization describes the process which physically, soft compounded rubber converts materials into high- quality engineering products. The vulcanizing system constitutes the fourth component in an elastomeric formulation and function by inserting crosslinks between adjacent polymer chains in the compound. A normal vulcanization system in compound consists of three components: 1) activators, 2) vulcanizing agent, and 3) accelerators

#### a) Activators [8]

The vulcanization activator system consisting of zinc oxide and stearic acid. Stearic acid and zinc oxide level of 2.0 and 5.0 phr, respectively, are accepted throughout the rubber industry as being adequate for achievement of optimum compound physical properties when combination our with a wide range of accelerator classes and types are also accelerator - to - sulfur ratios. Zinc oxide is selected over the other oxides because its electronegativity is in the range of 1.6 to 1.8 and optimum vulcanizate properties will be obtained. Zinc atoms increase the contribution of the polar canonical form and non – toxic use. Stearic acid is selected because it can reduce vulcanization activation energy more than the other fatty acid when it is increased. Stearic acid / zinc oxide activated compounds show higher crosslink densities, aging and tear resistance when compared with the other fatty acid.

### b) Vulcanizing agents [4,8]

Three vulcanizing agents find extensive use in the rubber industry: sulfur, insoluble sulfur and peroxide. Rhombic sulfur is the most common form of sulfur used in the rubber industry. Sulfur is soluble in natural rubber at levels up to 2.0 phr. above this concentration, insoluble sulfur must be used to prevent migration of sulfur to the compound surface, i.e. sulfur bloom . The modulus and hardness of vulcanizate increase with increasing sulfur content assuming that the added sulfur is utilized in crosslinks.

### c) Accelerators [8]

Accelerators increase both the rate of sulfur crosslinking in rubber compound and crosslink density. Secondary accelerators, when added to primary accelerator, increase the rate of vulcanization and degree of crosslink. These are a combination of the individual components. Accelerators can be classified by rate of vulcanization and chemical classification. Fast accelerators are thiazole and sulfurnamides. A medium - rate system is diphenylguanidine. A slow accelerator is thiocarbanilide. Most accelerators fall into one of eight groups, e.g. aldehydeamines, sulfurnamides, thioureas, dithiocarbamates, guanidines, thiuaurams, thiazoles and xanthates.

### 3) Protective Agents [4,9]

Protective agents, such as antioxidants or antiozonants, may require inlatex formulations, depending on the nature of the product and survival condition envisaged. The earlier antioxidants used to help natural rubber life prolongation were based on various aromatic amine and phenol, and even today such materials are still used. It is usual to use quantities of the order of 1 part to 100 parts of rubber, but the amount obviously must and does depend on the service requirement of the product and the actual basic formulation of the rubber. Some antioxidants are specific to the type of protection which they impart, and can be used to improve ozone, oxygen and heat resistance.

### 2.3.2 Mixing Techniques . [6,4]

In general, the thermoplastic elastomer can be compounded in mill or Banbury mixing equipment, Farrel continuous mixing equipment, injection molders, and extruders. The most common technique used to produce dispersions for latex compounding is ball milling. Ball mills consist of porcelain or rubber- lined steel cylinders containing a charge of balls or pebbles. It takes from 2 –72 hours to get a good dispersion depending on the size of the mill and the material being ground. There are five main types of ingredients in normal rubber mix which should be added in correct order as the following:

1) Stabilizing agents;
2) Sulfur, accelerators, antioxidants;
3) Pigments, fillers;
4) Zinc oxide;
5) Thickener solution

This order of addition should not be regarded as unchangeable, but it is the best for most formulations.

## 2.4 Vinyl Acetate [8,9,10,11]

Vinyl acetate was first reported in 1912 in patent describing the preparation of ethylidine diacetate from acetylene and acetic acid. Industrial interest in vinyl acetate and poly( vinyl acetate ) develop of vinyl acetate monomer were produced worldwide.

### 2.4.1 Physical Properties [8]

Vinyl acetate is a colorless, flammable liquid with an intially pleasant odor that quickly becomes sharp and irritating. Physical properties are shown in Table 2.7. Vinyl acetate is completely miscible with organic liquids but not with water. At 20 $^{o}$C, a saturated solution of vinyl acetate in water contains 2.0 –2.4 % by weight vinyl acetate, while a saturated solution of water in vinyl acetate contains 0.9-1.0 % water. At 50 $^{o}$C, the solubility of vinyl acetate in water is 0.1 % higher than at 20 $^{o}$C, but the solubility of water in vinyl acetate doubles to 2 %. Vinyl acetate is soluble in a dilute (2.0 wt%)solution of sodium dodecyl sulfate to the extent of 4.0 wt% at 30 °C. Azeotropes containing vinyl acetate are given in Table 2.8.

**Table 2.7** Properties and Characteristics of Vinyl Acetate [9]

| | |
|---|---|
| Flash point | |
| Tag closed cup (ASTM D 56) | -8 °C |
| Tag open cup (ASTM D 1310) | -4 °C |
| Autoignition temperature | 426.9 °C |
| Boiling point at 760 mm Hg | 72.7 °C |
| Vapor pressure | |
| At 60 °C | 487.4 mm Hg |
| At 40 °C | 222.1 mm Hg |
| At 20 °C | 89.1 mm Hg |
| Critical temperature | 246 °C |
| Critical pressure | 574.0 psia |
| Specific gravity (20/20 °C) | 0.934 |
| Vapor density (Air = 1.00) | 2.97 |
| Viscosity at 20 °C | 0.43 cps |
| Freezing point | -92.8 °C |
| Heat of polymerization | 21.3 Kcal / mole |
| Specific heat at 20 °C (liquid) | 0.46 cal/gram °C |
| Refractive index, $n^{20}_{D}$ | 1.3953 |
| Surface tension (° C) | 23.6 dynes /cm |

**Table 2.8** Vinyl acetate Azeotropes [10]

| Second compound | Azeotropic Boiling point, °C | Vinyl acetate, wt% |
|---|---|---|
| Water | 66.0 | 92.7 |
| Methanol | 58.9 | 63.4 |
| 2 Propanol | 70.8 | 77.6 |
| Cyclohexane | 67.4 | 61.3 |
| Heptane | 72.0 | 83.5 |

The infrared vinyl acetate is show in Figure 2.2 [10]

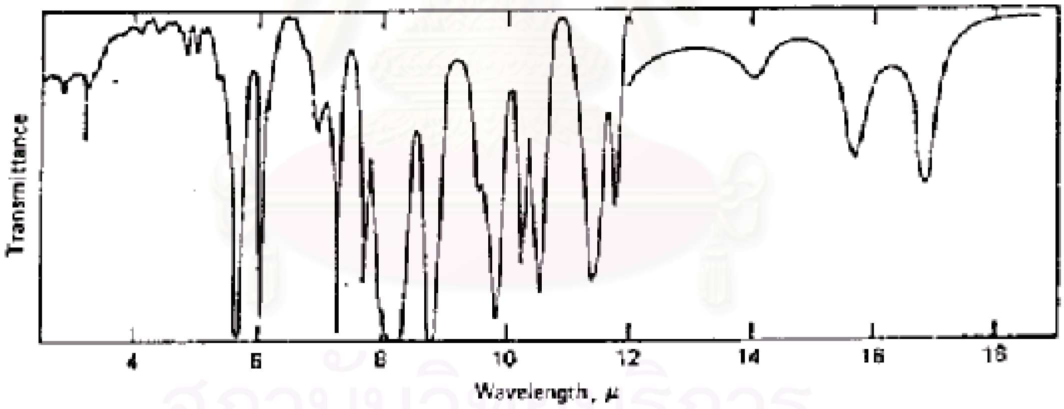
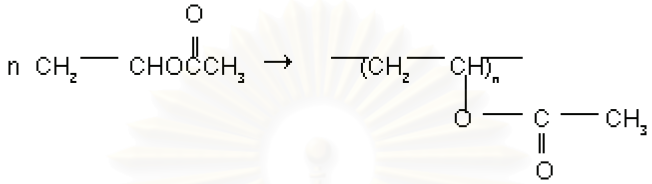


**Figure 2.2** The infrared spectrum of vinyl acetate

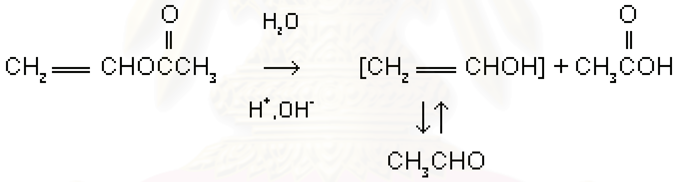
### 2.4.2 Chemical Properties [8]

The most important chemical reaction of vinyl acetate is free-radical polymerization. The reaction is shown in an equation as follows:



$$n\ CH_2-CHO\overset{O}{\overset{\|}{C}}CH_3 \rightarrow -(CH_2-\underset{O-\underset{\underset{O}{\|}}{C}-CH_3}{\underset{|}{CH}})_n-$$

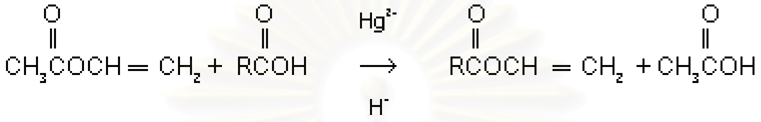
Other chemical reactions of vinyl acetate are those common to an ester and compound containing a double bond. Acidic and basic catalysts, forming acetic acid, hydrolyze vinyl acetate. The expected alcohol, i.e., vinyl alcohol, instantaneously forms acetaldehyde by tautomeric rearrangement ;



$$CH_2{=}CHO\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[H^+,OH^-]{H_2O} [\underset{\underset{CH_3CHO}{\downarrow\uparrow}}{CH_2{=}CHOH}] + CH_3\overset{O}{\overset{\|}{C}}OH$$

Chemical reactions involving the addition of a reagent to the double bond are known. Chlorine or bromine adds readily giving the 1,2 –dihaloethyl acetate. Hydrogen chlorine or hydrogen bromide adds readily and quantitatively at low temperatures, yielding the 1 – haloethyl acetate. The dry ozonide of vinyl acetate is explosive.

Vinyl acetate can be used to prepare other vinyl esters by transfer of its vinyl group to another organic acid; a mercuric salt is necessary as catalyst. (18,19) Numerous vinyl carboxylates have been prepared by this method.



$$CH_3\overset{\overset{O}{\|}}{C}OCH=CH_2+R\overset{\overset{O}{\|}}{C}OH \xrightarrow[H^-]{Hg^{2-}} R\overset{\overset{O}{\|}}{C}OCH=CH_2+CH_3\overset{\overset{O}{\|}}{C}OH$$

Acetic acid adds to the double bond with acid catalysis giving ethylidene diacetate, $CH_3CH(OCCH_3)_2$. Oxidation of vinyl acetate with palladium acetate at 60 $^{o}$ C produces 1,4-diacetoxy-1,3-btuadiene and significant amounts of 1,1,4-triacetoxy-2-butene, 1,1,4,4-tetraacetoxybutane, and 1-acetoxy-1,3-butadiene. By use of diiodometane with azinc-copper catalyst, a methylene group is added to vinyl acetate, yielding cyclopropyl acetate. Polyhaloalkanes, eg, $CCl_4$ and $CCl_3Br$, react with vinyl acetate by free-radical mechanism to yield 1: 1 adduct or telomers having the fragments of the polyhalomethane as end groups. Numerous other molecules, that participate similarly in free-radical chain reactions, add across the double bond or are active in telomerization (qv) with vinyl acetate. Vinyl acetate undergoes the oxo-reaction forming acetoxypropionaldeydes. Thiols add across the double bond with Lewis acid catalysis and by a free-radical-catalyzed reaction to form thioacetates. Similar additions are known for ammonia, amines, silanes and metal carbonyl. Vinyl acetate also serves as a weak dienophile in Diels-Alder reactions, generally requiring forcing conditions.

### 2.4.3 Analytical and Test Methods [8,11]

Gas Chromatography is an excellent method for simultaneous determination of vinyl acetate and its volatile impurity. The other methods used for quality testing are shown in Table 2.9.

**Table 2.9** Test methods for quality testing of vinyl acetate [12].

| Substance | Method |
|---|---|
| Carbonyl groups | - Titration of the hydrochloric acid formed after conversion to the oxime using hydroxylamine hydrochloride solution |
| Water content | - Titration with Karl-fischer solution |
| Acid content | - Neutral to litmus or direct titration in methanol solution with standard caustic |
| Peroxide | - Test with potassium iodine solution |
| Polymer content | - Mixtures with petroleum ether must not produce turbidity or precipitation of solids |
| Polymerization test | - Carried out differently by individual producers; the time taken for the on set of polymerization following the addition of defined quantity of dibenzoyl peroxide and warming to a defined temperature |
| Inhibitors (p-hydroquinone and diphylamine ) | - Standard titration technique or spectrophotometerically in UV region after evaporation of vinyl acetate |
| Aldehydes | - Addition of excess sodium bisulfate Followed by titration with standard iodine solution |

## 2.5 Graft Copolymer from Natural Rubber [5]

Grafted natural rubber, starting in 1941, performed considerable work on chemically attaching polymerizable polymers, such as styrene, acrylonitrile, acrylic esters, etc., to natural rubber. These have been called grafted rubbers. *Heveaplus* is the name for a family of graft rubber, wherein methyl methacrylate monomer has been polymerized in natural rubber latex. *Heveaplus* materials are self- reinforcing, and can be added to natural or synthetic rubbers to confer high hardness and impact strength to nonblack compounds. The other improved properties such as increasing in modulus, improvement in tear strength, and good retention of tensile strength were obtained by adding some additives such as polyvinyl acetate or polystyrene [chapter 3, 90 ].

Natural rubber can be transformed into thermoplastic rubber which are in ways similar to some of the synthetic copolymer thermoplastic rubber of commercial importance. The process makes use of specialized chemistry to attach preformed chains of glassy polymer to the NR backbone and requires some degree of control over the molecular weight of the glassy polymer and the frequency of attachment to the NR backbone. In comparison with nonblock copolymers with carefully controlled molecular weight distribution, the graft copolymers must always have a less than ideal structure for formation of an efficient three-dimensional network, and this is particularly so when, as is normally the case, there is no specific control over the spacing of graft sites along the backbone chain. The technological properties of the natural rubber graft copolymer reflect this fundamental difference to some extent. This, combined with economic constraints, has so far prevented the commercial development of the materials. The process does, however, have some versatility and, within the constraints imposed by the synthetic chemistry of the prepolymers and the requirement of some double bond unsaturation in the backbone chain, it has provided access to an interesting range of experimental graft copolymers.

## 2.6 The Rubber Band Production [12]

Rubber band production was started in 1955 for supporting the domestic demand with poor quality. In 1971 the rubber was exported, the high technology was used to develop the qualities of the products. Now Thailand is a bigger exporter in the world.

Rubber bands can be separated into two types : crepe rubber bands and compound rubber bands. The raw materials for the producing are shown in Table 2.10 .

**Table 2.10** The ingredients of rubber band production [13,14]

| Ingredient | Type |
|---|---|
| 1. Block rubber or aired dry sheet | TTR 5L |
| 2. Vulcanizing agent | Sulfur |
| 3. Accelerator | Ammonium thiocarbonate and MBT |
| 4. Activator | Zinc oxide |
| 5. Fatty acid | Stearic acid |
| 6. Filler | Calcium carbonate |
| 7. Plasticizer and softener | Processing oil |
| 8. Peptizing agent | Disulfide |
| 9. Color | - |

The stages of the rubber band production are described as follows : [13,14,15]

1. Masticate the block or sheet rubber in two-roll mill. Fill the chemical ingredients and mix to the homogeneous. Further mix the compounded rubber with Sulfur.
2. Extrude the rubber compound from the two-roll mill. The thickness and width of rubber are 0.25 and 1 inch , respectively.
3. Insert the compounded rubber to the extruder and extrude them covering the aluminum or stainless steel rod. The rubber pipe is obtained.
4. Vulcanize the rubber pipe in the steam pot at 140 °C for 15 mins.
5. Flow the talcum through the rubber pipe to prevent the sticking.
6. Strip the rubber from aluminum rod and wash.
7. Cut with cutting machine.
8. Dry at 40 °C for 4 - 5 mins.
9. Collect, select and pack.

## 2.7 Literature Review

B. Laongsri, [16 ] studied the preparation of premixed natural rubber product containing carbon black ready to be used. The appropriate formulations were obtained. The compounded rubber sheets were prepared by direct mixing the concentrated latex with the additives. Ball mill mixer was used to prepare the aqueous dispersion of the additives at appropriate time. The ingredient were changed to obtain the good properties of the products. The effects of surfactant, carbon black, vulcanizing system and mixing type were studied. The carbon black dispersion was assessed and the mechanical properties were determined following the ISO and ASTM methods. From the study it was found that, the formulation of compounded sheet that gives the best properties was :

| | |
|---|---|
| - Rubber latex | 100 parts by dry weight |
| - Carbon black type N330 | 25 phr |
| - Sulfur | 2 phr |
| - Zinc oxide | 5 phr |
| -Stearic acid | 2 phr |
| - 2-Mercaptobenzothiazole | 1 phr |
| - Tergitol NP10 | 3 phr |

The best properties that obtained were consisted of 16.49 MPa tensile strength, 1538 % elongation, 8.23 MPa modulus, 60.4 shore A hardness, 57.15 KN/m tear strength , and 250 % solvent swelling. The dispersion rating of carbon black was 5.0.

Y.E. Fang , X. B. Lu , S.Z. Wang , X. Zhao and F. Fang [17 ] studied the grafting of vinyl acetate onto ethylene – co – propylene rubber (EPR; which has excellent chemical stability and mechanical properties ) by simultaneous radiation grafting technique, to obtain new material with desired properties. The EPR membrane was prepared by dissolving it in benzene and the initial membrane weight, $W_o$ was measured. The membrane was immersed in grafting solution. The grafted membrane was extracted and the graft membrane weight, $W_g$ was determined. The degree of grafting was calculated using the following equation:

$$\text{Degree of grafting (\%)} = ( W_g - W_o ) / W_o \times 100$$

From the study it was found that, the degree of grafting increased with the increasing dose rate of irradiation. At higher dose rates, short grafting branches were formed. At lower dose rates vinyl acetate diffused into the EPR membrane, and longer grafting branches were formed. The degree of grafting depended on monomer concentration and temperature. At the low monomer concentration and low temperature the degree of grafting increased rapidly. However, at higher condition, the degree of grafting decreased. From the spectrum of grafted EPR, the new absorption of ester carboxyl group appears at 1720 $cm^{-1}$. The result proves that vinyl acetate is grafted onto EPR membrane. The tensile strength increases and elongation at break decreases in the region of low grafting percentage ( $\cong$ 10 %).

M.Patri, A.b. Samui, and P.C.Deb [18] studied sequential interpenetrating polymer network based on Nitrile rubber and poly ( vinyl acetate ). The cross-linked NBR was swollen in vinyl acetate monomer containing benzoyl peroxide ( BPO ) as an initiator and tetraethylene glycol dimethacrylate [TEGDM] as a cross-linker. The swelling time and concentration of BPO and TEGDM was varied. The PVA content in the IPNS increased on increasing the concentration of BPO and TEGDM concentrations. On increasing the PVA content in the IPNs, the tensile strength increased because of the increase in stiffness of the compound. The IPNs also showed better solvent resistance properties than those of NBR.

J. Schellenberg and B. Hamann [19] studied the graft polymerization of styrene and acrylonitrile onto polybutadiene in the presence of vinyl acetate. The grafted products were formed in emulsion polymerization by substituting part of the monomers by vinyl acetate. The composition of the graft product was determined by elementary analysis of the nitrogen or oxygen content. The ungrafted polymers of styrene, acrylonitrile and vinyl acetate were separated by acetone extraction and precipitation by ethanol. The acrylonitrile content in the polymer increases with rising vinyl acetate quantity in the monomer mixture and in the polymer, in case of styrene substitution, the styrene content decreased. In case of acrylonitrile substitution, the acrylonitrile quantity decreases while the characteristics of this polymer were improved.

A.B. Moustafa, A.A. Abd, E. Hakim, and G.A.Mohamed [20] studied the some parameters affecting the emulsifier-free emulsion polymerization of vinyl acetate. The development of a redox pair initiation system which consists of potassium persulfate –potassium metabisulfate, was studied to obtain a stable emulsion of high conversion at low temperature in the absence of an emulsifier. Also the effect of some organic substances on the rate of polymerization was obtained. The results show that the conversion percentage and the initial rate of polymerization increased with increasing initiator concentration, temperature, and acetone percentage in the medium. Increasing the percentage of $TiO_2$ and $CaCO_3$ in the medium decreases the initial rate of polymerization as well as the maximum conversion.

A.B.Moustafa, A.A. Hakim, S.M. Sayyah, and G.A. Mohamed [21] studied the emulsifier –free emulsion polymerization of vinyl acetate whih was carried out in the absence or in the presence of some electrolytes such as sodium chloride, calcium chloride, aluminum chloride, sodium sulphate and ammonium phosphate using potassium persuphate-sodium bisulphite as a redox initiation system. The viscosity average molecular weight of the polymers obtained was determined. It was found that the presence of electrolyte in the polymerization reaction conditions for either cationic electrolyte ( NaCl, $CaCl_2$, $AlCl_3$ ) or anionic radical electrolyte ( $Na_2SO_4$ and $(NH_4)_3PO_4$) in the polymerization of vinyl acetate monomer caused a decrease in the conversion percentage and the initial rate of polymerization. But it increased the viscosity average molecular weight obtained.

T.F. Mckenna, A.Villanueva [22 ] studied the kinetic constants for the solution polymerization of vinyl acetate in different solvents (toluene and ethyl acetate) and with different initiators (azo-bis-isobutyronitrile : AIBN and benzoyl peroxide: BPO). The rate of change of conversion seems to be a function of the initial concentration of the monomer in solution and of the type of solvent used. The kinetic constant values obtained with AIBN and BPO at the same monomer concentration in the same solvent show only very small variations. The values obtained with BPO were slightly lower than those with AIBN. The use of toluene had a very strong effect on the rate of polymerization. The variation in the value of kinetic constant as a function of monomer concentration in ethyl acetate is significantly more marked than for toluene. However, it has also been shown that the value of kinetic constants depends on the ratio of monomer to solvent in the system at fixed initiator concentrations for both toluene and ethyl acetate.

S.X. Zheng, J.Y. Huang , J. Li, and Q.P. Guo [23] studied the phase behavior and properties of poly(methyl methacrylate), poly(vinyl acetate) blends prepared via in situ polymerization. The polymer blends were prepared by radical –initiated polymerization of MMA in the presence of PVAc. Differentialing by scanning calorimetry and dynamic mechanical analysis were employed to investigate the miscibility and phase behavior of the blend. The MMA / PVAc blends of in situ polymerization were found to be phase separated and exhibited a two – phase structure, although some chain transferring reactions between the components occurred. The phase separation resulted from the solvent effect of MMA. The solubility analysis indicated that some inclusion of PVAc increased the gel content. The thermogravimetric analysis study indicated that the inclusion of small amouth of PVAc gives rise to a marked stabilization effect on the thermal stability. The PMMA / PVAc blend exhibited increased notched impact properties.

# CHAPTER III

# EXPERIMENTAL

## 3.1 Chemicals

1. Natural rubber latex : Thai Rubber Latex Corporation
2. Zinc oxide (ZnO) : Ajax Chemicals
3. Stearic acid : Ajax Chemicals
4. Sulfur : Ajax Chemicals
5. 2-Mercaptobenzothiazole (MBT) : Fluka
6. Tergitol NP 10 : Union Carbide
7. Tert-butylhydroperoxide : Fluka
8. Benzoylperoxide : Merck
9. Formic acid : Fluka
10. Ammonim hydroxide : Fluka
11. Vinyl Acetate Monomer : Merck
12. Hexane : Merck
13. Methyl Ethyl Ketone : Merck

## 3.2 Instruments and Apparatus

1. Ball mill
2. Soxhlet Apparatus
3. Compression Molding : Lab Tech, Engineering
4. Rebound Resilience Tripsometer : Wallace, RRIT Institute of Thailand
5. Rheometer : Gribite Rheocheck OD 2000
6. Universal testing machine : Instron Corporation Series IX, Rubber Research Institute of Thailand
7. Hardness testing machine : Zwich, Rubber Research Institute of Thailand
8. ATR FT-IR Spectrometer : Bruker Vector 33 FT-IR spectrometer

## 3.3 Procedures

### 3.3.1 Preparation of Compounded Rubber Grafted with Vinyl Acetate

All compounding ingredients were used without further purification . The aqueous dispersion of additives such as vulcanizing agent ( sulfur ), accelerator (2-mereaptobenzothiazole), accelerator activator (ZnO and stearic acid), surfactant (tergitol NP 10) and water, was prepared by ball mill for 3 hours. The rate of ball mill was 130 rpm. Then, the concentrated natural rubber latex, vinyl acetate emulsion and initiator were added and mixed at various mixing times. These parameters were varied, e.g. The concentration of vinyl acetate, the mixing time and types of initiator were varied. The compounded rubber latex was coagulated with 5 % by volume formic acid. The compounded sheet was washed with water and compressed in the mold. The sheet was dried at room temperature.

The appropriate condition was investigated by varying the parameter as follows.

### 3.3.1.1 Effect of Vinyl Acetate Monomer Concentration

The dispersive emulsion of vinyl acetate used for grafting was prepared by mixing vinyl acetate with warm water (60 °C) and the initiator. The mixture was stirred for 0.5 hr., adjusted to the suitable pH by adding 2 ml. of concentrated ammonium hydroxide ($NH_4OH$). Then vinyl acetate was used by changing the concentration of 0,2,4,6,8, 10, 15 and 20 phr. The formulation of compounded rubber is shown in Table 3.1.

Table 3.1 Compounded rubber formulation

| Ingredient | Quantity of mix (phr) |
|---|---|
| Natural Rubber Latex | 100 parts by dry weight |
| Vulcanizing system: | |
| Sulfur | 2 |
| ZnO | 5 |
| Stearic acid | 2 |
| MBT | 1 |
| Surfactant system: | |
| Tergitol NP 10 | 0.5 |
| Water | 85 |

### 3.3.1.2 Effect of Mixing Time

The appropriate mixing time, which affected the degree of polymerization, was studied by varying the time to 0.5, 1.0, 1.5 and 2.0 hours. The formulations of compounded rubber were the same as in Table 3.1.

### 3.3.1.3 Effect of Initiator Types

The effects of the initiator types on the degree of polymerization was studied by varying the initiator system to tert-butylhydroperoxide (tert-BuHP ) and benzoyl peroxide (BPO). The initiator concentration was dependent on the various monomer concentrations (1 % monomer). The formulation of compounded rubber were the same as in Table 3.1.

All of the various parameters, which were investigated are shown in Table 3.2.

**Table 3.2** The various parameter investigated in polymerization process

| Parameter | Unit | Quantity |
|---|---|---|
| Vinyl acetate concentration | Phr | 2 , 4 , 6 , 8 , 10 , 15 , 20 |
| Mixing time | Hours | 0.5 , 1.0 , 1.5 , 2.0 |
| Initiator types<br>- Tert –butylhydroperoxide<br>- Benzoylperoxide | %VAM | 1 |

### 3.3.2 Determination of Selected Vulcanization Characteristics of Vulcanizable Rubber Compounds.

The vulcanization characteristics of vulcanizable rubber compounds were determined by using the Gribitre Rheocheck OD 2000 cure meter. This method was used for research and development testing of raw-rubber compound in an evaluation formulation, and for evaluating various raw materials used in preparing vulcanizable rubber compounds. The time required to obtain a cure was a function of the characteristics of rubber compound and of the test temperature.

| | | | |
|---|---|---|---|
| Test condition : | Temperature | 150 | °C |
| | Testing time | 15 | Min |
| | Rotational amplitude | 3 | ° |

### 3.3.3 Preparation of Vulcanized Sheet ( ASTM D 3182 )

The vulcanized sheet was prepared by the compression molding. The mold was closed; held and preheated at curing temperature (150 °C) and tested for 20 min. before the unvulcanized piece was inserted . The press was opened, then the uncured piece was inserted into the mold and closed. The mold was held on the cavity areas under a pressure of 120 kg / cm$^2$ (1700 psi). After the required curing time, the press was opened and the vulcanized sheet was removed from the mold . This sheet was cooled on water-cooling metal surface for 10 to 15 min. Before preparing and testing , the vulcanized sheet was conditioned at 23 ± 2 °C for at least 16 hours.

## 3.4 Characterization

### 3.4.1 Determination of the Degree of Crosslink by Soxhlet Extraction Technique

The soxhlet apparatus was used to determine the degree of crosslink of rubber and VAM. The apparatus was set as shown in Figure 3.1. The rubber sheet was cut to 3 x 3 mm and dried at 80 °C for 8 hours. 2 g of rubber pieces were weighed and put into the soxhlet and extracted with hexane for 8 hours. After that, the rubber pieces were removed and dried at 80 °C for 8 hours, and cooled to room temperature in a desiccator. The degree of crosslink was calculated as shown in Appendix A.

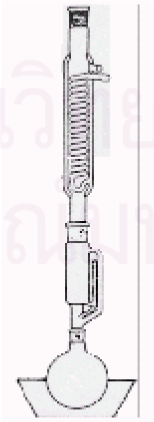


**Figure 3.1** Soxhlet Apparatus

### 3.4.2 Determination of Spectrum of Compounded Rubber by ATR–FTIR Spectroscopy

The spectrum of compounded rubber was determined by using ATR-FTIR spectroscopy technique. The rubber sheet was cut to the required dimensions. The spectrum of carbonyl group was especially investigated to confirm the grafting between natural rubber and vinyl acetate. The simple optical and geometric arrangements of ATR- FTIR measurement is shown in Figure 3.2.

**Figure 3.2** ATR-FTIR

### 3.5 Mechanical Testing

Mechanical properties of the vulcanized rubber were investigated by following the ISO and the ASTM test methods as follows :

### 3.5.1 Tensile Stress – Strain Properties (ISO 37)

The properties of vulcanized rubber, which were determined by this method, are the tensile strength, the elongation at break and the stress at a given elongation (modulus).

The dimension of the test specimen in this experiment is type 2 as shown in

Figure 3.3 and Table 3.3.

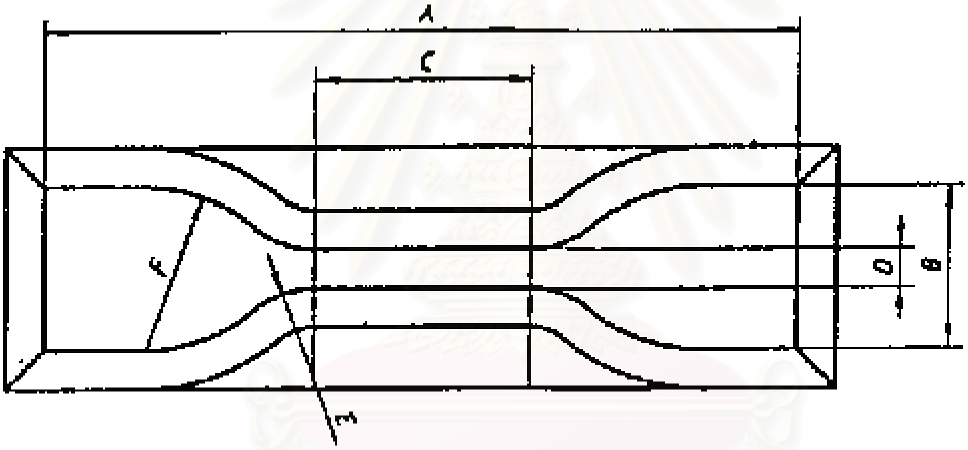


**Figure 3.3** Schematic of tensile test specimen

**Table 3.3** The dimension of tensile test specimen

| Dimension | Type (mm) |
|---|---|
| A. Overall length (minimum) | 75 |
| B. Width | 12.5 ± 1.0 |
| C. Length of narrow portion | 25.0 ±1.0 |
| D. Width of narrow portion | 4.0 ±0.1 |
| E. Transition radius outside | 8.0 ±0.5 |
| F. Transition radius inside | 12.5 ± 1.0 |

The tensile testing condition

| | | |
|---|---|---|
| Temperature | 25 | $^{o}$C |
| Humidity | 60 | % |
| Test length of dumb – bells | 20±0.5 | mm |
| Cross head speed | 500 | mm / min |
| Full scale load range | 5.0 | KN |

### 3.5.2 Hardness Properties (ASTM D 2240)

In this experiment, the type A- Durometer was used for investigating the hardness of vulcanized sheets. The shape of the indenter is shown in Figure 3.4.

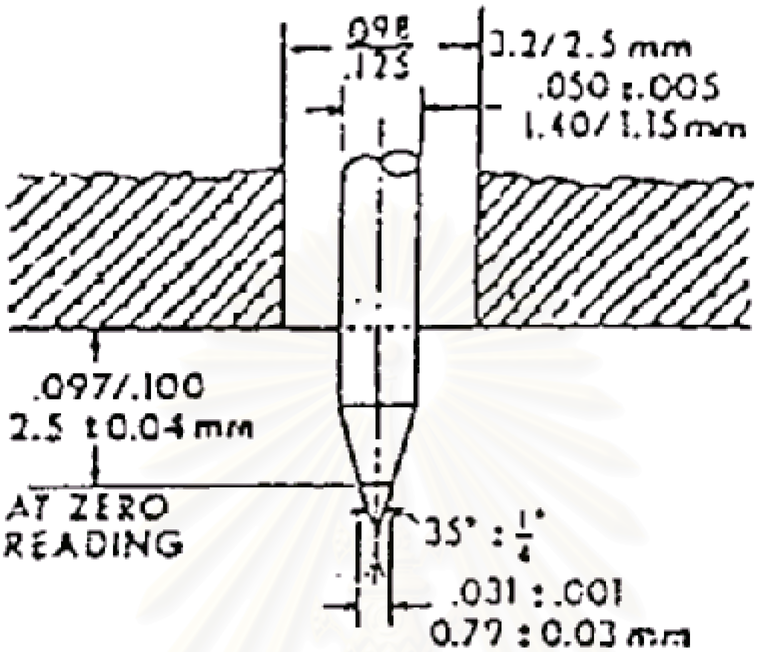


**Figure 3.4** Indentor of type A-Durometer

The test specimen was of at least 6 min. in thickness unless it was known that the results were equivalent to the 6 min valves that were obtained with a thinner specimen. The specimen was composed of plied pieces to the necessary thickness. For the type A-Durometer, the thickness of specimens was at least 3 mm and measurements should not be made closer than 6 mm to any edge. The surfaces of specimen were flat and parallel over a sufficient area to permit the presser foot to contact the specimen. The lateral dimensions of the specimen were measured at least 12 mm from any edge. The conditions in this testing are shown as follows:

| | | |
|---|---|---|
| Temperature | 25 | $^{o}$C |
| Relative humidity | 50 | % |
| Number of pieces plied | 2 | pieces |

The test result for hardness was the medium of five individual hardness reading to obtain a reliable average and standard deviation.

### 3.5.3 Rebound Resilience Properties (ASTM D 1054-91)

The test specimens with thickness of 12.5 ± 0.5 mm and a diameter of 41 ± 12 mm were used to test the rebound resilience. The specimens were performed no earlier than 16 hours and no later than four weeks after vulcanization. The samples shall be stored at a temperature of 23 ± 2 °C for at least 3 hours for testing. The test is generally performed at a temperature of 23 ± 2 °C. The schematic representation of a testing device is shown in Figure 3.5.

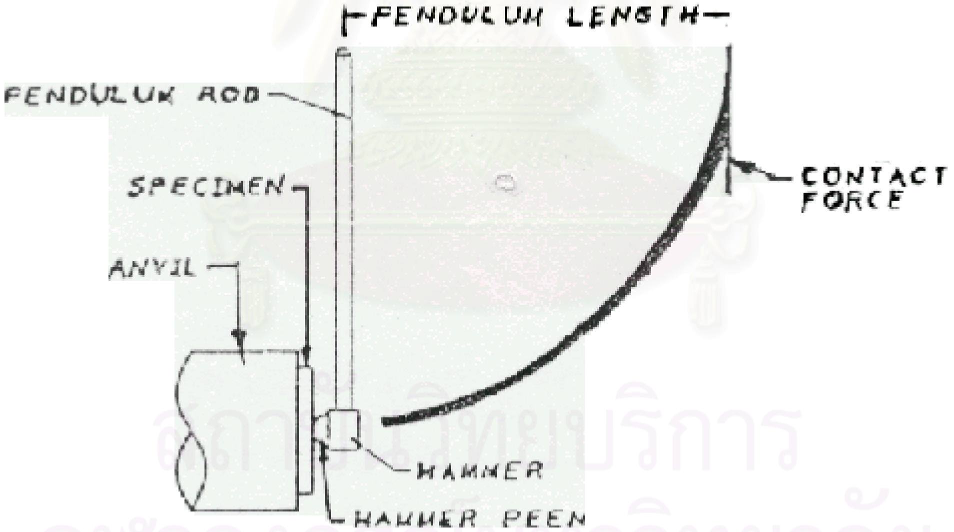


**Figure 3.5** Schematic Representation of a testing device

Procedure : After the specimen has been placed on the anvil in the holder and the thermal conditioning set, the pendulum is allowed to fall six times from the horizontal position (45 °C) onto the same place on the specimen and caught each time before it strikes the sample once more.

The first of these three blows constitutes the mechanical conditioning of the specimen. There rebound resilience is read on the fourth, fifth and sixth strokes. The median of the three readings is recorded.

### 3.5.4 Aging properties (ISO 188)

The compounded rubber is subjected to controlled deteriorating influence for definite periods, after appropriate properties are measured and compared with the corresponding properties of the unaged rubber. It is recommended that the tensile strength, breaking elongation, and hardness be measured.

In this experiment the air-oven was used. The testing pieces were placed in the oven after it had been preheated at the operating temperature. The testing pieces shall be stational free from strain, freely exposed to air on all sides and not posed to light. The temperature and periods which used in this research were 70 ± 1 °C and 168 hours. When the heating period is complete, remove the testing pieces from the oven and condition them for not less than 16 hours and not more than 6 days in the strain free condition.

The testing results of the unaged and the aged test pieces shall be reported together with the percent change of the value of the property measured as calculated in Appendix A.

# CHAPTER IV

# RESULTS AND DISCUSSION

In this research, the compounded rubber from natural rubber grafted with vinyl acetate was prepared by directly mixing the concentrated latex with the additives and emulsion of vinyl acetate in a ball mill. The parameter variation, which consists of vinyl acetate monomer concentration, mixing time, and types of initiator, were studied. Then the vulcanized sheet products were used to determine the degree of crosslink by soxhlet extraction technique. ATR FT–IR spectroscopy was used to prove the grafting of vinyl acetate onto the rubber. The mechanical properties were investigated to find the optimum condition of the preparing compounded rubber.

## 4.1 Preparation of Compounded Rubber Grafted with Vinyl Acetate

In this study, the formulation of compounded rubber consists of natural rubber latex 100 parts by dry weight, sulfur 2 phr as the vulcanizing agent, 2-mercaptobenzothiazole (MBT) 1 phr as the accelerator, zinc oxide (ZnO) 5 phr as the accelerator activator, and stearic acid 2 phr as the fatty acid. The effects of vinyl acetate monomer concentration, mixing time, and types of initiator on the degree of crosslink of compounded rubber were evaluated. The appropriate conditions were studied to yield high degrees of crosslink . The degree of crosslink was obtained by using soxhlet extraction technique. The calculation is shown in Appendix A.

### 4.1.1 Effect of Vinyl Acetate Concentrations on The Degree of Crosslink

The vinyl acetate monomer concentration was varied at 2, 4, 6, 8, 10, 15, and 20 phr for investigating the effect of vinyl acetate concentrations on the degree of crosslink . The monomer emulsion was prepared by mixing a required monomer with warm water, surfactant (Tergitol NP 10), and initiator. The pH was adjusted by using ammonium hydroxide. All ingredients were stirred for 0.5 hour at room temperature. The details are shown in Table 4.1 and Figure 4.1.

The fixed parameters were obtained as following :

- Initiator system : Tert-butylhydroperoxide
- Mixing time : 1 hour

In Figure 4.1, it was found that when the concentration of the monomer was increased, the degree of crosslink also increased. The degree of crosslink rapidly reached a maximum at 4 % of monomer concentration. Beyond 4 %, the degree of crosslink slightly increased. With a higher monomer concentration, the large amount of homopolymers of vinyl acetate was formed in the solution. At first, the gel effect enhanced the rate of polymerization, thus depleting further the monomer available for NR crosslink. The grafting system became very viscous due to gel formation. The gel was presented to inhibit the diffusion of unreacted monomer to the grafting chains. The optimum monomer concentration of 4% was found. This condition resulted in a high degree of crosslink at minimum concentration.

**Table 4.1** Effect of vinyl acetate monomer concentration on the degree of crosslink

Initiator system : tert- butylhydroperoxide, mixing time : 1 hour

| Vinyl acetate monomer concentration (%) | Degree of crosslink (%) |
|---|---|
| 2 | 97.84 |
| 4 | 98.79 |
| 6 | 98.75 |
| 8 | 98.81 |
| 10 | 98.78 |
| 15 | 98.83 |
| 20 | 99.15 |

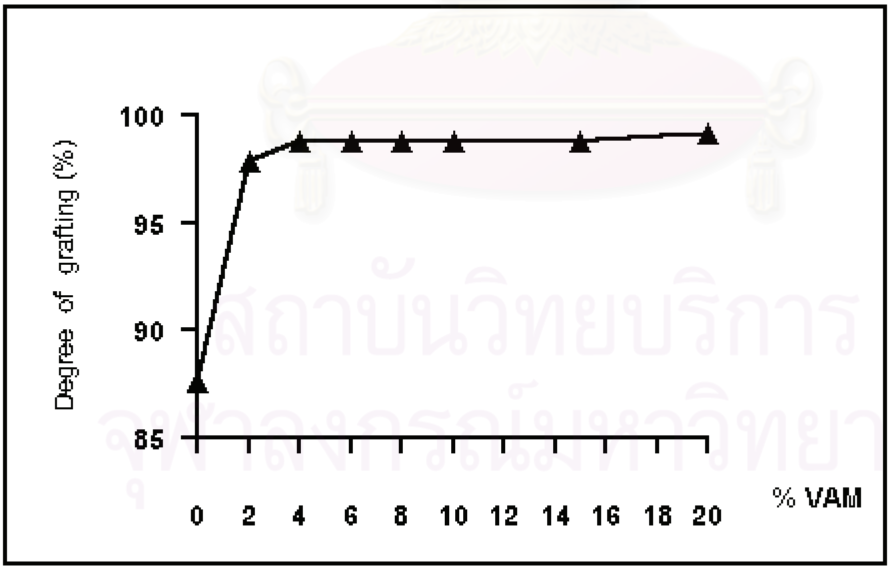


**Figure 4.1** Effect of vinyl acetate monomer concentration on the degree of crosslink

**4.1.2 Effect of Mixing Time on the Degree of Crosslink**

The effect of mixing time on the degree of crosslink was investigated by varying the time to 2,4,6,8,10,15, and 20 hours . The effect of mixing time is shown in Table 4.2 and Figure 4.2. The fixed parameters were obtained as the following shown :

- Vinyl acetate monomer concentration : 4 phr
- Initiator system : tert-butylhydroperoxide

From Figure 4.2, it was indicated that the degree of crosslink - mixing time curve for grafting vinyl acetate onto NR initially increased with increasing mixing time and reached the highest value at 1 hour . However, 1 hour over the degree of crosslink tended to decrease. On short mixing time, the converted heat from shearing action was low. The diffusion of monomer onto the polymer matrix and the mobility of the chain segment were improved at low temperature, thus causing an increase in the initial crosslink. However, on the longer mixing time, the higher heat was obtained. The more homopolymer gel of vinyl acetate was obtained. These viscous gels hindered a monomer diffusion toward the grafting chain and decrease the degree of crosslink. The suitable mixing time, 1 hour, was used.

**Table 4.2** Effect of mixing time on the degree of crosslink

Vinyl acetate monomer concentration : 4 phr, initiator system : tert-butylhydroperoxide

| Mixing time (hour) | Degree of crosslink (%) |
|---|---|
| 0.5 | 97.35 |
| 1.0 | 98.79 |
| 1.5 | 98.44 |
| 2.0 | 98.38 |

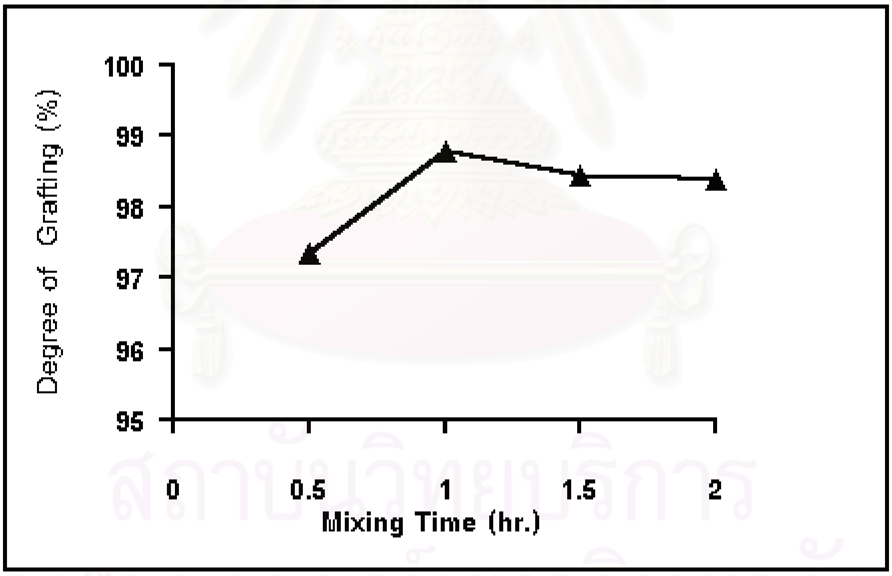


**Figure 4.2** Effect of mixing time on the degree of crosslink

### 4.1.3 Effect of Type of Initiator on The Degree of Crosslink

The effect of initiator type on the degree of crosslink was studied by varying the types of initiator. Tret- butylhydroperoxide and benzoyl peroxide were used in this experiment. The employed amount of initiator was 1 % of monomer. The details are shown in Table 4.3 and Figure 4.3. The fixed conditions were obtained as follows :

- vinyl acetate monomer : 4 phr
concentration : 0.5,1.0,1.5, and 2.0
- mixing time hour

From Figure 4.3, it was found that the crosslink curve of tert-butylhydroperoxide initiator system was similar to the curve of benzoyl peroxide initiator system. The degree of crosslink initially was increased slightly and then kept constant. The obtained degree of crosslink from tert- butylhydroperoxide initiator system showed a higher value than the system of benzoyl peroxide. Tert-buylhydroperoxide had a smaller structure than benzoyl peroxide, so it could be provided more radical sites and good mobilization. The long branches were formed during the reaction, resulting in a larger degree of crosslink.

**Table 4.3** Effect of type of initiator on the degree of crosslink

Vinyl acetate monomer concentration : 4 phr, mixing time : 0.5,1.0,1.5,and 2.0 hour

| Mixing time (hour) | Degree of crosslink (%) | |
|---|---|---|
| | Tert- BuHP | BPO |
| 0.5 | 97.35 | 96.81 |
| 1.0 | 98.79 | 97.32 |
| 1.5 | 98.84 | 97.40 |
| 2.0 | 98.98 | 97.45 |

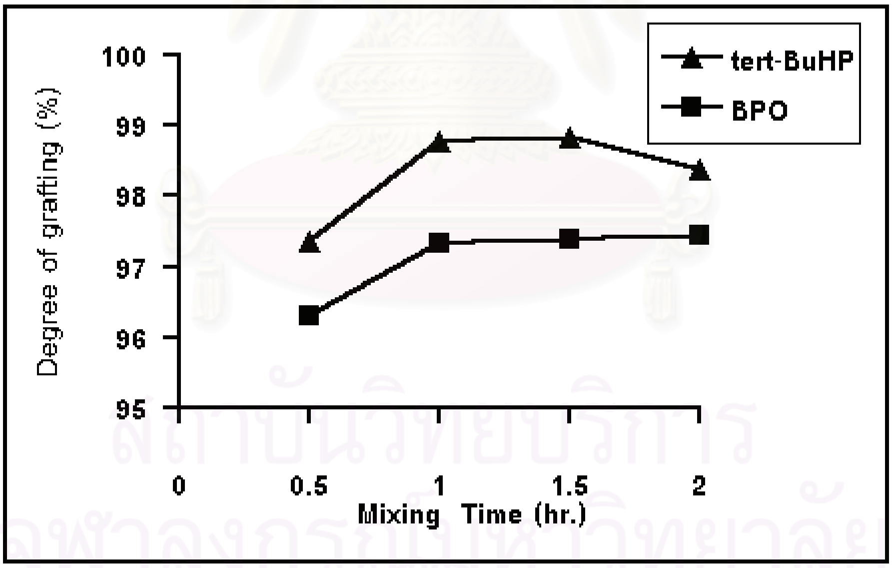


**Figure 4.3** Effect of type of initiator on the degree of crosslink

## 4.2 Selected Vulcanization Characteristics of Vulcanizable Rubber Compounds

The compounded sheet obtained from the coagulation procedure were prepared to the vulcanized sheet used for studying the mechanical properties. The curing time of this compounded sheet was determined by using a rheometer. The test conditions were as follows :

| | | |
|---|---|---|
| Temperature | : | 150 $^{o}$C |
| Testing time | : | 15 min |
| Rotational amplitude | : | 3 $^{o}$ |

In the rubber production , the lease times were required to reduce the cost of production. The curing curve of this study is presented in Appendix B.

From Figure B1 and the rheometer data , the required curing time was 6.83 min. For this compound, the approximate curing time was 10 min because the curing time curve was nearly constant at 30.82 dNm after 90 % of curing time. It means that the mechanical properties were changed a little after 90 % of curing time.

## 4.3 Characterization

### 4.3.1 Determination of the Degree of Crosslink by Soxhlet Extraction [23]

The degree of crosslink of the natural rubber and vinyl acetate was determined by soxhlet extraction technique. The homopolymer of natural rubber was removed by using hexane as a solvent for extraction. Methyl ethyl ketone (MEK) was used to remove the non-grafted vinyl acetate. The differentce between the initial weight and the weight after extraction was a non-grafted homopolymer which was removed. The different value was divided by the initial weight and multiplied with 100 to obtained the degree of crosslink. The details are shown in Figure 4.4, and the calculations are presented in Appendix A.

From Figure 4.4, it was found that the compounded rubber gave a high degree of crosslink at 4 % vinyl acetate monomer, although increasing the monomer concentration caused an increase in the degree of crosslink. The mixing time showed a little effect to the degree of crosslink. The use of tert-butylhydroperoxde as initiator resulted in the higher degree of crosslink than using benzoyl peroxide because tert- butylhydroperoxde provided more radical sites and good mobility to give long grafting branches.

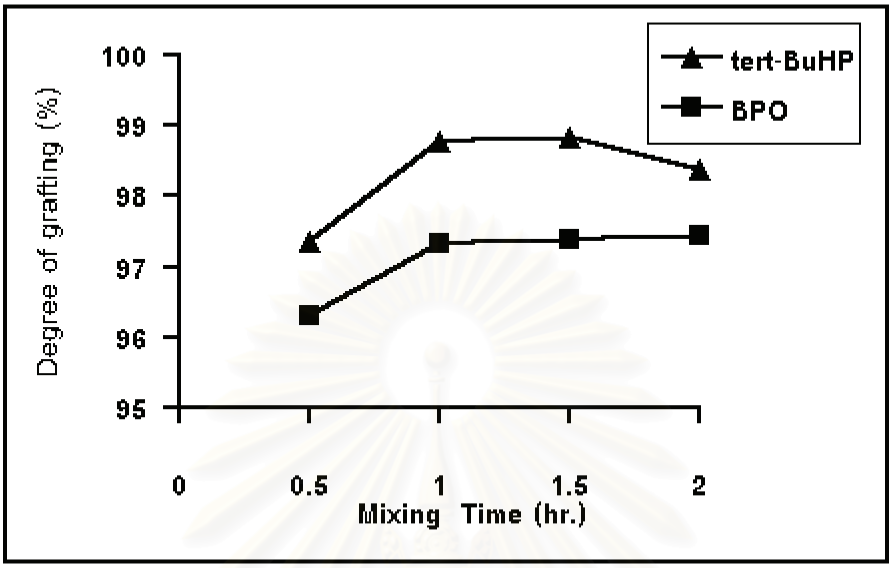


Figure 4.4 The degree of crosslink determined by Soxhlet extraction technique

4.3.2 Determination of Spectrum of Compounded Rubber by ATR FT-IR Spectroscopy

The carbonyl group of compounded rubber was determined by using ATR FT-IR spectrometer. The absorption peak of carbonyl group was used to confirm the grafting between the natural rubber and vinyl acetate. The compounded rubber was extracted homopolymer before a non-grafted determination was performed. The carbonyl group was suggested to bring about the real grafting. The spectrum of compounded rubber is sh own in Appendix C.

From Figures C1 and C2, it was found that the ATR spectrum of compounded rubber grafted with vinyl acetate showed the new absorption peak at 1649 $cm^{-1}$ (ester carbonyl group). The result proved that vinyl acetate was grafted onto natural rubber. The result was used to confirm the degree of crosslink by soxhlet extraction, although the spectras from ATR FT-IR spectroscopy were not the data for quantitative analysis.

## 4.4 Mechanical Properties of Compounded Rubber [24]

Mechanical properties of compounded rubber were investigated to evaluate the value of tensile properties (tensile strength, elongation at break, and modulus), hardness, rebound resilience, and aging properties. The details of all data and calculation are presented in Appendix A.

### 4.4.1 Tensile Properties

#### 4.4.1.1 Tensile Strength

The result of tensile strength of all the compounded sheet are presented in Table 4.4, and the effects of monomer concentration, mixing time, and initiator type on the tensile strength are shown in Figures 4.5 and 4.6

From the results, it was found that the optimum conditions which yield the highest tensile strength, were 4 % vinyl acetate monomer concentration, 1 hour of mixing time and using tert-butylhydroperoxide as the initiator. The tensile strength initially increased with increasing monomer concentration and mixing time, while over 4 % monomer concentration and 1 hour of mixing time the tensile strength tended to decrease.

The trensile strength did not increase continuously with the number of crosslink. Instead it increased initially, then decreased as the crosslink density was increased further beyond optimum level. The increasing of tensile strength of natural rubber gum vulcanizate resulted from the ability of the elastomer to crystallize on extension. Noncrystallizing rubber was poorer in strength than the crystallizing ones. It was found that when the monomer concentration increased, crystallization increased. It would cause a increase in tensile strength.

**Table 4.4** The tensile strength of compounded rubber (MPa)

| % VAM | 0.5 hr. | | 1.0 hr. | | 1.5 hr. | | 2.0 hr. | |
|---|---|---|---|---|---|---|---|---|
| | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO |
| 0 | 8.42 | 8.42 | 8.50 | 8.50 | 9.73 | 9.73 | 9.15 | 9.15 |
| 2 | 12.53 | 11.15 | 14.78 | 9.00 | 15.47 | 10.53 | 13.46 | 11.51 |
| 4 | 16.93 | 14.23 | 19.28 | 18.18 | 19.16 | 15.65 | 17.57 | 13.29 |
| 6 | 14.54 | 13.08 | 17.98 | 15.5 | 17.46 | 14.29 | 15.48 | 12.66 |
| 8 | 13.42 | 11.14 | 14.05 | 6.98 | 14.61 | 9.99 | 14.03 | 8.38 |
| 10 | 11.41 | 9.98 | 10.46 | 6.07 | 12.04 | 8.40 | 13.32 | 7.20 |
| 15 | 8.7 | 8.08 | 9.19 | 4.11 | 9.73 | 5.10 | 11.28 | 6.64 |
| 20 | 5.69 | 5.53 | 6.95 | 4.06 | 5.33 | 4.75 | 9.32 | 5.26 |

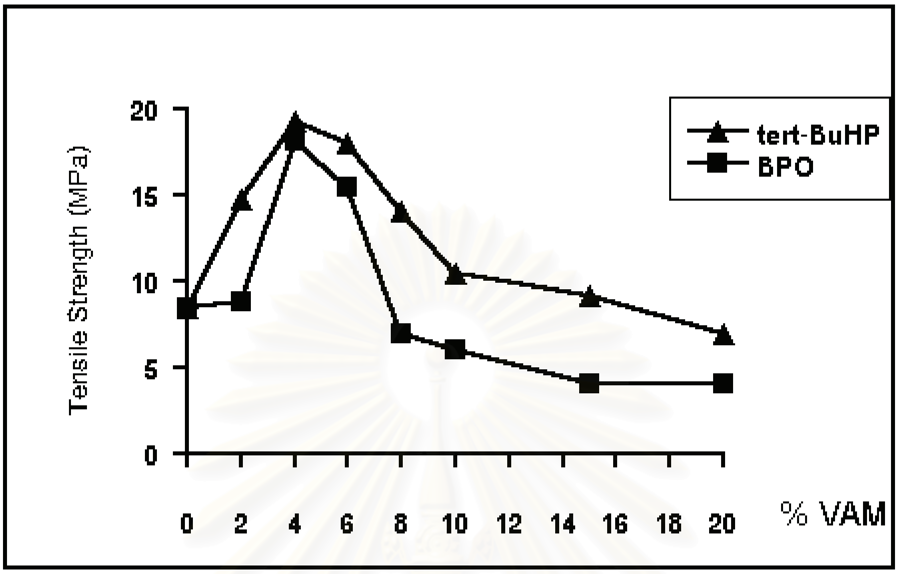


Figure 4.5 Effects of monomer concentration and type of initiator on the tensile strength

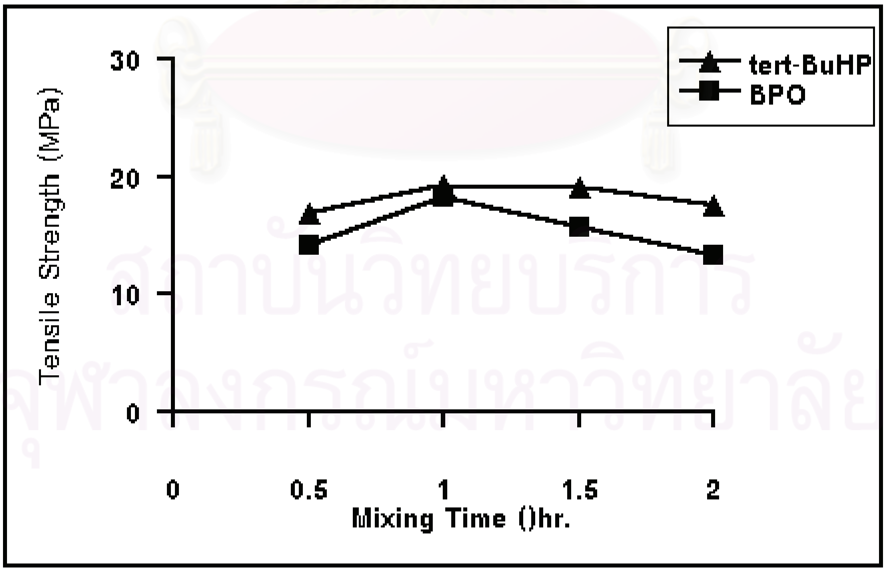


Figure 4.6 Effects of mixing time and type of initiator on the tensile strength

### 4.4.1.2 Modulus

The results of the modulus of all the compounded sheet are presented in Table 4.5, and the effects of monomer concentration, mixing time, and type of initiator on the modulus are shown in Figures 4.7 and 4.8.

From the results, it was found that the optimum conditions which yield the lowest modulus, were 4 % vinyl acetate monomer concentration, 1 hour of mixing time and using tert-butylhydroperoxide as the initiator. The modulus initially decreased with increasing monomer concentration and mixing time, while over 4 % monomer concentration and 1 hour of mixing time the modulus tended to increases. The modulus ,the minimum stress at the given elongation of products, was low due to the high value of tensile strength and elongation. At the optimum condition, the products had the lowest modulus while he highest tensile strength and elongation were observed.

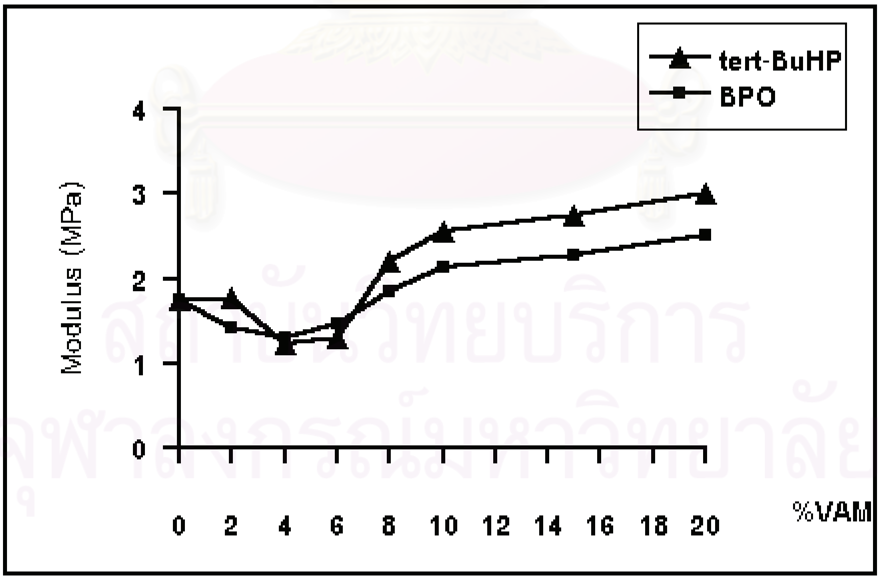


**Figure 4.7** Effects of monomer concentration and type of initiator on the modulus

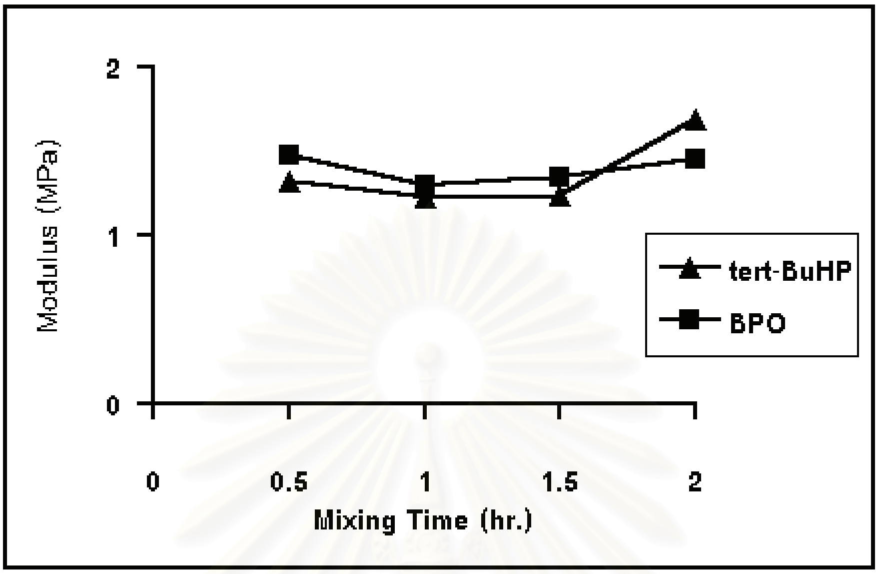


**Figure 4.8** Effects of mixing time, and type of initiator on the modulus

**Table 4.5** The modulus of compounded rubber (MPa)

| % VAM | 0.5 hr. | | 1.0 hr. | | 1.5 hr. | | 2.0 hr. | |
|---|---|---|---|---|---|---|---|---|
| | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO |
| 0 | 2.104 | 2.104 | 1.749 | 1.749 | 1.976 | 1.976 | 1.991 | 1.991 |
| 2 | 1.823 | 1.769 | 1.773 | 1.411 | 1.855 | 1.651 | 1.910 | 1.938 |
| 4 | 1.324 | 1.473 | 1.223 | 1.303 | 1.242 | 1.341 | 1.686 | 1.448 |
| 6 | 1.479 | 1.751 | 1.311 | 1.465 | 1.336 | 1.680 | 1.771 | 1.827 |
| 8 | 1.532 | 1.882 | 2.191 | 1.846 | 2.108 | 1.843 | 1.855 | 1.971 |
| 10 | 1.700 | 2.315 | 2.559 | 2.141 | 2.124 | 2.133 | 2.510 | 2.372 |
| 15 | 1.987 | 2.611 | 2.743 | 2.267 | 2.820 | 2.527 | 2.715 | 2.577 |
| 20 | 3.133 | 2.938 | 3.007 | 2.517 | 2.938 | 2.709 | 2.851 | 2.754 |

### 4.4.1.3 Elongation At Break

The elongation at break of all the compounded sheets is presented in Table 4.6, and the effects of monomer concentration, mixing time, and type of initiator on the elongation at break are shown in Figure 4.9 and 4.10

From the results, it was found that the optimum conditions which yielded the highest elongation at break, were 4 % vinyl acetate monomer concentration, 1 hour of mixing time and using tert-butylhydroperoxide as the initiator. The elongation at break initially was increaseed with increasing monomer concentration and mixing time, while over 4 % monomer concentration and 1 hour of mixing time the elongation at break tended to decreased because the crystallization of the product increased.

**Table 4.6** The elongation at break of compound rubber (%)

| % VAM | 0.5 hr. | | 1.0 hr. | | 1.5 hr. | | 2.0 hr. | |
|---|---|---|---|---|---|---|---|---|
| | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO |
| 0 | 1707.00 | 1707.00 | 1813.00 | 1813.0 | 1755.00 | 1755.00 | 1173.00 | 1173.00 |
| 2 | 1504.00 | 1059.00 | 1907.00 | 0 | 1863.20 | 1662.86 | 821.90 | 671.46 |
| 4 | 2114.33 | 1778.75 | 2326.33 | 1608.2 | 2266.33 | 2223.66 | 1210.00 | 1176.46 |
| 6 | 1673.17 | 1285.00 | 1868.67 | 3 | 2190.67 | 1628.00 | 861.33 | 1100.00 |
| 8 | 915.70 | 1180.00 | 1203.00 | 2193.0 | 1845.00 | 807.42 | 802.9 | 658.60 |
| 10 | 702.9 | 796.10 | 757.3 | 01649. | 1272.00 | 683060 | 673.5 | 505.00 |
| 15 | 704.60 | 495.10 | 725.7 | 73582. | 738.80 | 677.48 | 635.8 | 497.00 |
| 20 | 619.3 | 433.80 | 630.8 | 55 | 701.5 | 529.00 | 571.8 | 345.40 |
| | | | | 541.4 | | | | |
| | | | | 534.7 | | | | |
| | | | | 318.1 | | | | |

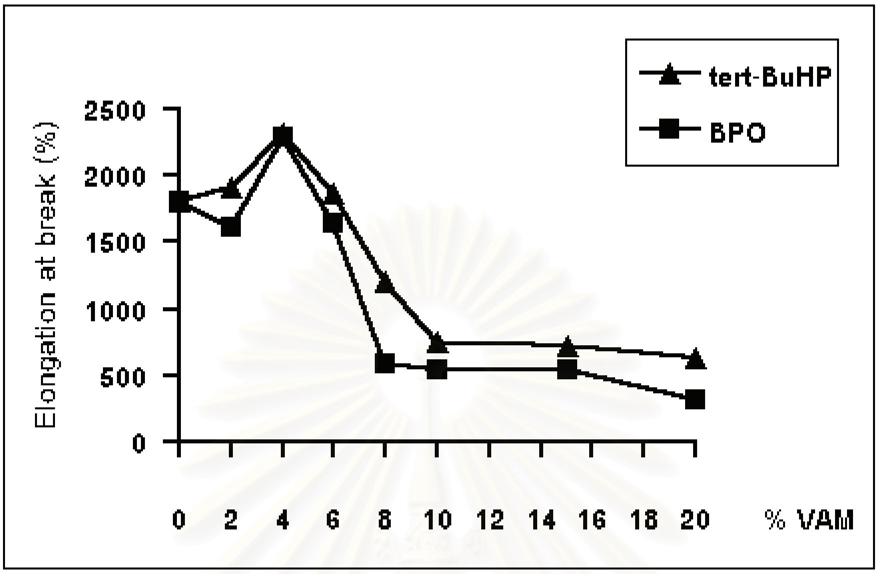


Figure 4.9 Effects of monomer concentration and type of initiator on elongation at break

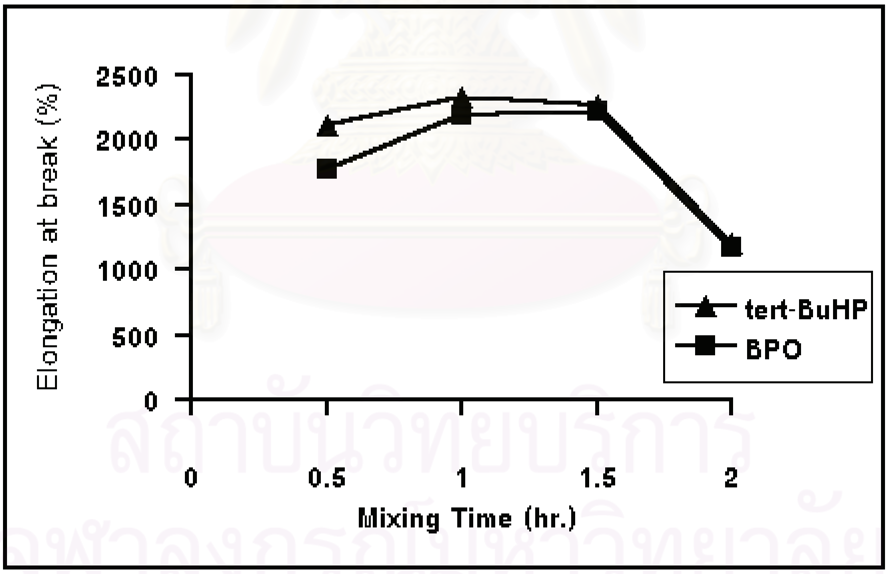


Figure 4.10 Effects of mixing time and type of initiator on elongation at break

### 4.4.2 Hardness

The results of elongation at break of all the compounded sheet are presented in Table 4.7, and the effects of monomer concentration, mixing time, and type of initiator on the elongation at break are shown in Figures 4.11 and 4.12.

From the results, it was found that the optimum conditions, which yield the highest hardness, were 4 % vinyl acetate monomer concentration, 1 hour of mixing time and using tert-butylhydroperoxide as the initiator. The hardness initially was increased with increasing monomer concentration and mixing time, until the material become ebonite. The more complex network, the shorter molecular segment enhancing a tighter network, which causes increased hardness. After surpassing the optimum condition, the hardness slightly decreased.

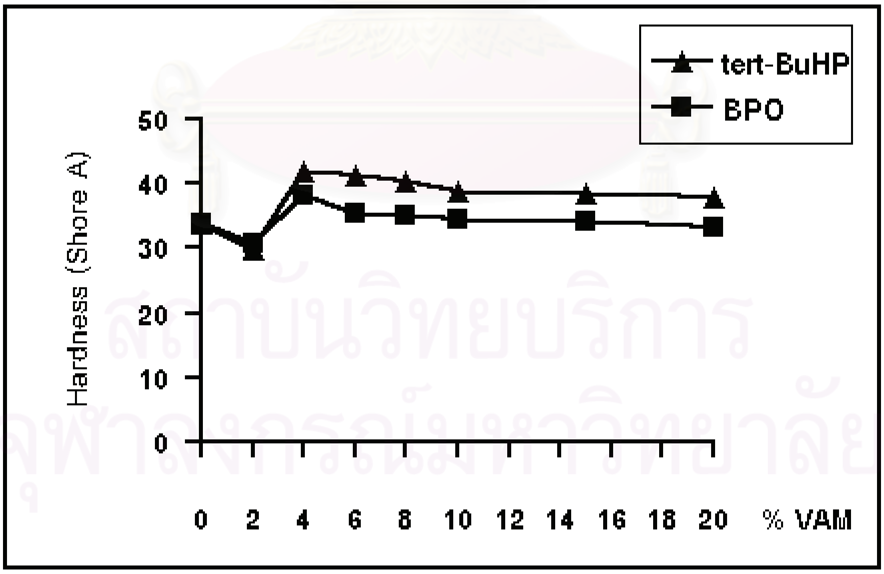


Figure 4.11 Effects of monomer concentration and type of initiator on the hardness

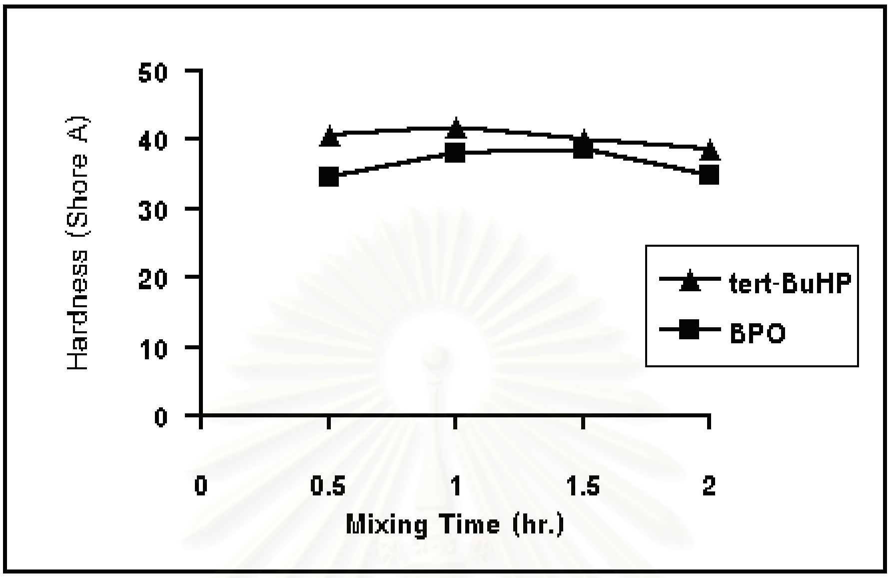


Figure 4.12 Effects of mixing time and type of initiator on the hardness

| Table 4.7 The hardness of compounded rubber (Shore A) | 0.5 hr. | | 1.0 hr. | | 1.5 hr. | | 2.0 hr. | |
|---|---|---|---|---|---|---|---|---|
| % VAM | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO |
| 0 | 28.1 | 28.1 | 34.0 | 34.0 | 33.5 | 33.5 | 29.4 | 29.4 |
| 2 | 31.7 | 30.4 | 29.8 | 30.8 | 31.4 | 34.9 | 35.3 | 30.3 |
| 4 | 40.7 | 34.7 | 42.0 | 38.1 | 40.1 | 38.8 | 38.6 | 35.0 |
| 6 | 38.6 | 34.6 | 41.2 | 35.4 | 39.2 | 36.8 | 38.5 | 34.9 |
| 8 | 35.1 | 32.6 | 40.3 | 35.0 | 38.4 | 36.9 | 38.0 | 34.2 |
| 10 | 34.2 | 30.5 | 38.9 | 34.4 | 37.0 | 35.5 | 37.9 | 34.2 |
| 15 | 34.0 | 30.4 | 38.5 | 34.1 | 36.3 | 34.8 | 37.6 | 34.0 |
| 20 | 33.9 | 29.4 | 37.9 | 33.2 | 36.3 | 34.4 | 37.5 | 32.2 |

### 4.4.3 Rebound Resilience

The result of rebound resilience of all the compounded sheets is presented In Table 4.6, and the effects of monomer concentration, mixing time, and type of initiator on the rebound resilience are shown in Figures 4.9 and 4.10.

From the results, it was suggested that the optimum conditions, which yielded the highest rebound resilience were 4 % vinyl acetate monomer concentration, 1 hour of mixing time and using tert-butylhydroperoxide as the initiator. However, for other conditions, the rebound resilience was also higher than 75 %. The rebound resilience increased with increasing monomer concentration and mixing time. Beyond the optimum condition, the rebound resilience decreased. The resilience was dependent on the vulcanizate structure. It was extented to some improvement for a degree of grafting. The evaluated temperature and the distribution of crosslink were important for rebound resilience.

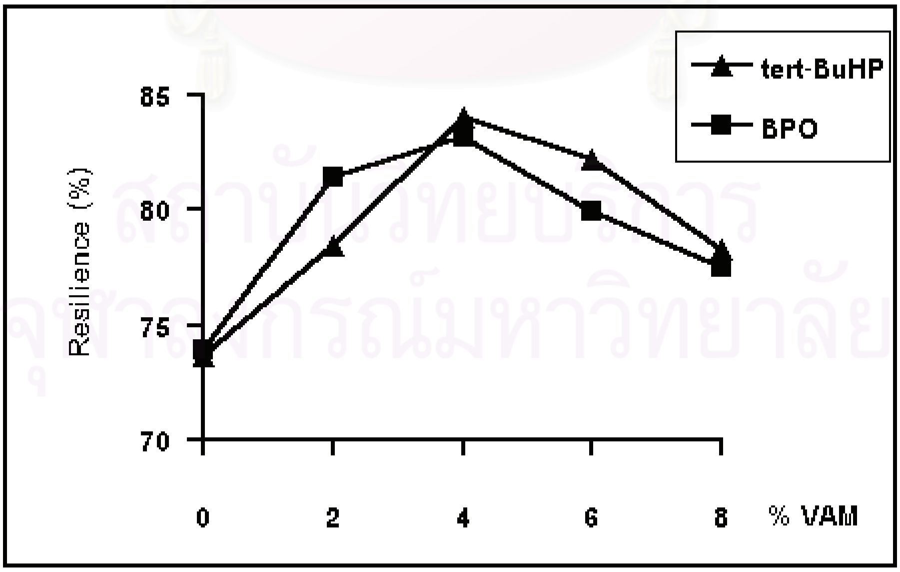


**Figure 4.13** Effects of monomer concentration and type of initiator on the rebound resilience

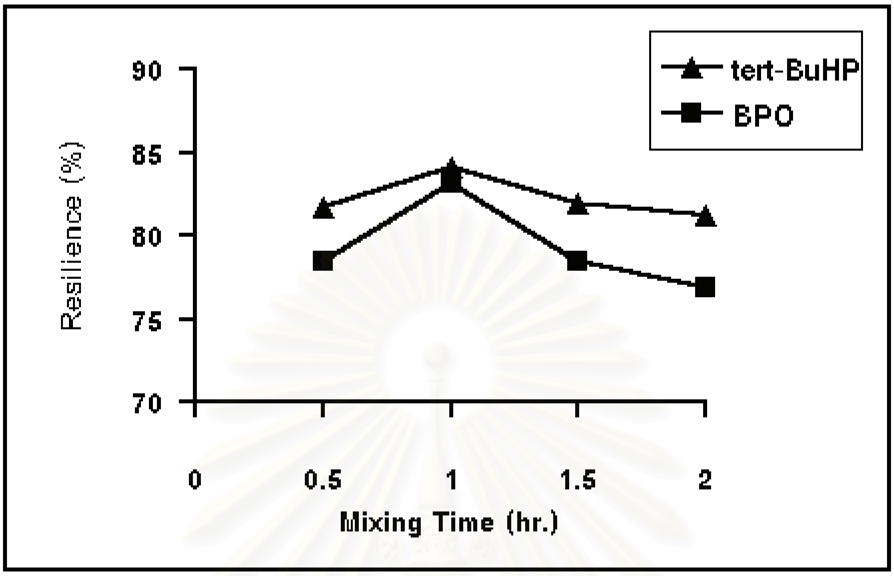


**Figure 4.14** Effects of mixing time and type of initiator on the rebound resilience

**Table 4.8** The rebound resilience of compounded rubber (%)

| % VAM | 0.5 hr. | | 1.0 hr. | | 1.5 hr. | | 2.0 hr. | |
|---|---|---|---|---|---|---|---|---|
| | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO | Tert-BuHP | BPO |
| 0 | 71.67 | 71.67 | 73.96 | 73.96 | 73.02 | 73.02 | 71.65 | 71.65 |
| 2 | 75.32 | 76.06 | 78.42 | 81.41 | 80.86 | 78.88 | 77.04 | 75.21 |
| 4 | 81.65 | 78.49 | 84.08 | 83.15 | 81.89 | 78.38 | 81.15 | 76.82 |
| 6 | 80.39 | 78.41 | 82.21 | 79.97 | 79.07 | 77.25 | 78.96 | 76.04 |
| 8 | 79.68 | 77.53 | 78.29 | 77.47 | 76.07 | 75.96 | 77.61 | 75.96 |

### 4.4.4 Aging Properties

The under or overcrosslink vulcanizates showed poor aging properties. Resistance of aging was the best in the zone of optimum vulcanization. Aging of vulcanizate could reduce the strength properties. The results of the aging test were expressed as the percentage of change in each physical property (tensile strength or ultimate elongation). The calculation is shown in Appendix A.

#### 4.4.4.1 Tensile strength

The percentage of changing of tensile strength at the optimum condition is shown in Table 4.9 and Figure 4.13.

**Table 4.9** The percentage of changing of tensile strength

| % VAM | % Change |
|---|---|
| 0 | 28.76 ± 0.40 |
| 2 | 25.72 ± 0.70 |
| 4 | 28.42 ± 0.08 |
| 6 | 33.00 ± 1.28 |

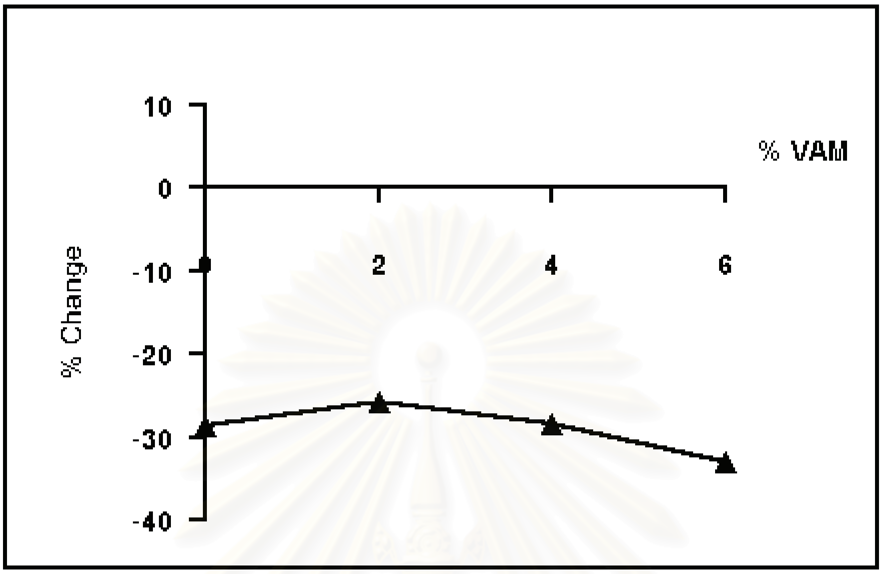


Figure 4.15 The percentage of changing of tensile strength

From Table 4.9 and Figure 4.15, it was found that the percentage of change of tensile strength increased with increasing monomer concentration. The degree of grafting decreased when the products stayed at the testing temperature for a longer time, so the tensile strength decreased.

### 4.4.4.2 Elongation at break

The percentage of changing of elongation at break on the optimum condition is shown in Table 4.10 and Figure 4.16.

**Table 4.10** The percentage of changing of elongation at break

| % VAM | % Change |
|---|---|
| 0 | 52.69 ± 0.91 |
| 2 | 27.68 ± 1.74 |
| 4 | 23.89 ± 0.29 |
| 6 | 22.64 ± 0.38 |

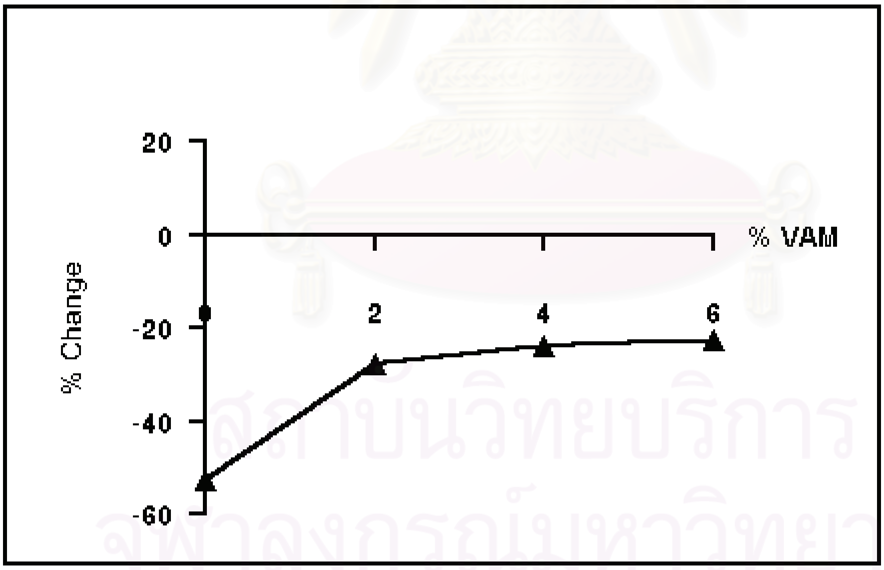


**Figure 4.16** The percentage of changing of elongation at break

From Table 4.10 and Figure 4.16, it was suggested that the percentage of changing of elongation at break decreased with increasing monomer concentration. The degree of grafting decreased when the products stayed at the testing temperature for a longer time, so the elongation at break decreased.

### 4.4.4.3 Hardness

The difference value of hardness at the optimum condition is shown in Table 4.11 and Figure 4.17.

**Table 4.11** The difference value of hardness

| % VAM | Difference Value |
|---|---|
| 0 | 1.70 ± 0.30 |
| 2 | 3.05 ± 0.85 |
| 4 | 4.65 ± 0.15 |
| 6 | 4.40 ± 0.30 |

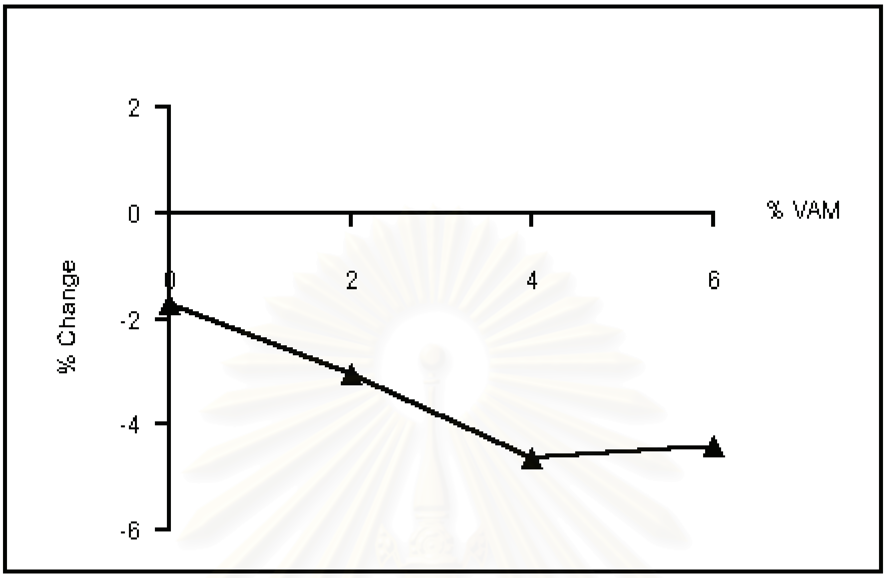


Figure 4.17 The difference values of hardness

From Table 4.11 and Figure 4.17, it was found that the difference value of hardness increased with increasing monomer concentration. The degree of grafting decreased when the products stayed at the testing temperature for a long time, so the hardness decreased.

## 4.5 Comparison

### 4.5.1 Comparison of the Properties of Compounded Rubber from this Work with the Work of B. Laonbgsri.

The work of B.Laongsri was summarized in Literature review [16]. The preparation of the compounded rubber that used in this experiment had the same formulations and conditions, as his work except carbon black was not used. Moreover, vinyl acetate was added to improve the properties. Some mechanical properties were compared with the work of B. Laongsri as shown in Table 4.12.

**Table 4.12** The comparison of some mechanical properties with the work of B. Laongsri

| Properties | B. Laongsri | This work |
|---|---|---|
| Tensile properties | | |
| - Tensile strength (MPa) | 16.49 | 19.28 |
| - Elongation at break (%) | 1538 | 2326.33 |
| - Modulus 300 % (Mpa) | 8.23 | 1.223 |
| Hardness (Shore A) | 60.4 | 42 |

From Table 4.12, the tensile strength and elongation at break that obtained by this work higher than the work of B. Laongsri, but the modulus and hardness lower than his work because carbon black was not filled in this work.

### 4.5.2 Comparison of Some Properties of Compounded Rubber from this work with the other works.

The other works [17,18] that grafted vinyl acetate onto the rubber like this work, although they used the difference conditions and formulations. Some mechanical properties of the other works were compared with this work as shown in Table 4.13.

**Table 4.13** The comparison of some mechanical properties with the other works.

| Properties | Y.E. Fang et. al. | M. Patri et. al. | This work |
|---|---|---|---|
| % VAM | 4 | 5 | 4 |
| Tensile strength (MPa) | 1.8 | 13.7 | 19.20 |
| Elongation (%) | 3525 | 171 | 2326.33 |

From Table 4.13, the tensile strength and elongation at break that obtained by this work higher than the work of Y.E.Fang and M.Patri except the elongation of Y.E.Fang et. al. work higher than this work because their work used EPR (ethylene-co-propylene rubber), which has excellent mechanical properties.

### 4.5.3 Comparison of the Properties of Compounded Rubber from this Work with Thailand Industrial Standard

The properties of the compounded rubber that were obtained were compared with the standard properties of rubber band are presented in Table 4.14.

**Table 4.14** The comparison of some mechanical properties with Thailand Industrial Standard

| Properties | Standard values | Obtained values |
|---|---|---|
| Tensile properties | | |
| - Tensile strength (MPa) | 14.7 | 19.28 |
| - Elongation at break (%) | >700 | 2326.33 |
| - Modulus 300 % (Mpa) | <1.37 | 1.223 |
| Hardness (Shore A) | * | 42 |
| Rebound resilience (%) | * | 84.08 |
| Aging Properties | | |
| - Changing of tensile strength (%) | < 25 | 28.42 |
| - Changing of elongation at break (%) | < 25 | 23.89 |
| - Difference value of hardness | * | 4.65 |

* The properties were not studied

From Table 4.12, the tensile strength and elongation at break which were obtained were higher than the standard value and the modulus also in the range of standard recommendation . For aging properties, the percentage of change of tensile strength was lower than the standard recommendation. A heat resistant agent must be added to the product for improving the aging properties. The elongation at break was in the optimum range.

# CHAPTER V

# CONCLUSION

## 5.1 Conclusion

### 5.1.1 The Preparation of Compounded Rubber Grafted with Vinyl Acetate

The compounded sheets of natural rubber grafted with vinyl acetate were prepared by directly mixing the concentrated latex with the additive and the emulsion of the monomer. The optimum condition of grafted rubber was found and the grafted products were characterized.

In this work, the appropriate conditions for preparing the grafted rubber were 4 % vinyl acetate monomer concentration, 1.0 hour of mixing time, and using tert-butylhydroperoxide as the initiator. The degree of crosslink that was obtained was 98.79%, which initially increases with increasing monomer concentration and mixing time. Beyond the optimum monomer concentration and mixing time, the degree of crosslink slightly increased and decreased, respectively, due to the gel formation of monomer. ATR FT-IR confirmed that vinyl acetate was grafted onto the rubber. The carbonyl absorption peak appears at 1649 $cm^{-1}$.

### 5.1.2 The Mechanical Properties of Compounded Rubber

At the optimum condition, the best mechanical properties of the compounded rubber were obtained as shown in Table 5.1.

**Table 5.1** The mechanical properties of compounded rubber

| 4<br>Mechanical properties | Values |
|---|---|
| Properties | |
| Tensile strength (MPa) | 19.28 |
| Modulus (MPa) | 1.223 |
| Elongation at break (%) | 2326.33 |
| Hardness (Shore A) | 42.0 |
| Rebound resilience (%) | 84.08 |
| Aging properties | |
| Change of tensile strength (%) | 28.42 |
| Change of elongation at break (%) | 23.89 |
| Difference value of hardness | 4.65 |

This product has potential to be used for rubber band production because it has many advantages as the following :

1. The preparation is convenient because it uses simple instruments and works at mild condition.

2. It can reduce processing cost because concentrated latex, which was used was cheaper than the sheet and block rubber which used in rubber band production.

3. It can reduce production time because it is made from direct mixing all ingredients into concentrated latex.

4. The compounded rubber, which was obtained, has good properties that are suitable for rubber band producing, and the products can be competitive in the world market.

## 5.2 Suggestions

1. Investigation should be carried out on the other parameters such as monomer type, mixing type or temperature for polymerization, on the preparation compounded rubber.

2. Studying the other applications which are suitable for the compounded rubber such as rubber for automobile, conveyer belt or elastic.

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# APPENDICES

# APPENDIX A

The degree of crosslink was calculated using the following equation :

$$\text{Degree of crosslink (\%)} = \frac{(W_1 - W_o)}{W_o} \times 100$$

Where $W_o$ is the weight before

extracting

$W_1$ is the weight after

extracting

The test results of the unaged and the aged test pieces shall be reported together with the percent change of the property measured as calculation. from the formula :

$$\text{\% Change} = \frac{X_a - X_o}{X_o} \times 100$$

Where $X_o$ is the value of property

before aging

$X_a$ is the value of property

before aging

The change in hardness shall be expressed as difference calculated from the formula

$$X_a - X_o$$

**Table A.1** Effect of monomer concentration , mixing time , and type of initiators on the degree of crosslink

| Mixing time (hour) | % VAM | Degree of Crosslink (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No.1 | No.2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 0.5 | 0 | 85.88 | 84.82 | 85.35 | 0.53 | 85.88 | 84.82 | 85.35 | 0.53 |
| | 2 | 96.25 | 96.35 | 96.30 | 0.05 | 93.15 | 94.59 | 93.87 | 0.72 |
| | 4 | 97.99 | 96.71 | 97.35 | 0.64 | 96.46 | 96.16 | 96.31 | 0.15 |
| | 6 | 99.43 | 98.35 | 98.89 | 0.54 | 95.81 | 97.74 | 96.77 | 0.96 |
| | 8 | 98.57 | 98.29 | 98.43 | 0.14 | 97.48 | 97.74 | 97.61 | 0.13 |
| | 10 | 98.6 | 98.34 | 98.47 | 0.13 | 96.61 | 98.17 | 97.39 | 0.78 |
| | 15 | 98.91 | 98.17 | 98.54 | 0.37 | 96.26 | 98.52 | 97.39 | 1.13 |
| | 20 | 98.86 | 98.40 | 98.63 | 0.23 | 96.22 | 98.68 | 97.45 | .<br>1.23 |
| 1.0 | 0 | 85.08 | 90.22 | 87.65 | 2.57 | 85.08 | 90.22 | 87.65 | 2.57 |
| | 2 | 99.10 | 96.58 | 97.84 | 1.26 | 95.95 | 92.81 | 94.38 | 1.57 |
| | 4 | 98.94 | 98.64 | 98.79 | 0.15 | 99.04 | 95.60 | 97.32 | 1.72 |
| | 6 | 99.17 | 98.33 | 98.75 | 0.42 | 97.57 | 97.35 | 97.46 | 0.11 |
| | 8 | 99.03 | 98.59 | 98.81 | 0.22 | 96.56 | 98.48 | 97.52 | 0.96 |
| | 10 | 98.79 | 98.77 | 98.78 | 0.01 | 97.06 | 98.40 | 97.73 | 0.67 |
| | 15 | 98.96 | 98.70 | 98.83 | 0.13 | 97.74 | 98.54 | 98.14 | 0.40 |
| | 20 | 99.33 | 98.97 | 99.15 | 0.18 | 97.66 | 98.78 | 98.22 | 0.56 |

**Table A. 1** Continued

| Mixing time (hour) | % VAM | Degree of Crosslink (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No.1 | No.2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 1.5 | 0 | 85.99 | 89.47 | 87.73 | 174 | 85.99 | 89.47 | 87.73 | 1.74 |
| | 2 | 98.81 | 97.63 | 98.22 | 0.59 | 97.38 | 92.38 | 94.88 | 2.50 |
| | 4 | 98.66 | 98.22 | 98.84 | 0.22 | 98.36 | 96.44 | 97.40 | 0.96 |
| | 6 | 99.03 | 98.55 | 98.79 | 0.24 | 98.15 | 96.93 | 97.54 | 0.61 |
| | 8 | 98.87 | 98.85 | 98.86 | 0.01 | 97.91 | 97.35 | 97.63 | 0.28 |
| | 10 | 98.59 | 98.07 | 98.83 | 0.26 | 97.98 | 97.60 | 97.79 | 0.19 |
| | 15 | 99.65 | 98.29 | 98.97 | 0.68 | 98.84 | 97.72 | 98.28 | 0.56 |
| | 20 | 99.30 | 99.12 | 99.21 | 0.09 | 98.64 | 98.04 | 98.34 | 0.30 |
| 2.0 | 0 | 88.90 | 86.82 | 87.86 | 1.04 | 88.90 | 86.82 | 87.86 | 1.04 |
| | 2 | 98.42 | 98.14 | 98.28 | 0.14 | 97.86 | 92.54 | 95.20 | 2.66 |
| | 4 | 99.57 | 98.39 | 98.98 | 0.59 | 98.73 | 96.17 | 97.45 | 1.28 |
| | 6 | 98.56 | 98.96 | 98.76 | 0.20 | 97.53 | 97.85 | 97.69 | 0.16 |
| | 8 | 99.05 | 98.63 | 98.84 | 0.21 | 97.88 | 97.66 | 97.77 | 0.11 |
| | 10 | 98.86 | 98.88 | 98.87 | 0.01 | 96.98 | 98.70 | 97.84 | 0.86 |
| | 15 | 98.83 | 99.07 | 98.95 | 0.12 | 97.91 | 98.81 | 98.36 | 0.45 |
| | 20 | 98.96 | 99.22 | 99.09 | 0.13 | 98.58 | 98.26 | 98.42 | 0.16 |

**Table A.2** The statistic of tensile strength

| % VAM | Mixing Time (Hour) | Tensile Strength (Mpa) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 0 | 0.5 | 8.26 | 8.58 | 8.42 | 0.16 | 8.26 | 8.58 | 8.42 | 0.16 |
| | 1 | 8.43 | 8.57 | 8.50 | 0.07 | 9.43 | 8.57 | 9.00 | 0.43 |
| | 1.5 | 9.27 | 10.19 | 9.73 | 0.46 | 9.27 | 10.19 | 9.73 | 0.46 |
| | 2.0 | 8.97 | 9.33 | 9.16 | 0.18 | 8.99 | 9.33 | 9.16 | 0.17 |
| 2 | 0.5 | 11.98 | 13.08 | 12.53 | 0.55 | 10.82 | 11.48 | 11.15 | 0.33 |
| | 1 | 14.31 | 15.25 | 14.78 | 0.47 | 9.00 | 8.70 | 8.85 | 0.15 |
| | 1.5 | 15.14 | 15.80 | 15.47 | 0.33 | 10.68 | 10.38 | 10.53 | 0.15 |
| | 2.0 | 14.20 | 12.72 | 13.46 | 0.74 | 10.77 | 12.25 | 11.51 | 0.74 |
| 4 | 0.5 | 16.54 | 17.32 | 16.93 | 0.39 | 14.03 | 14.43 | 14.23 | 0.20 |
| | 1 | 18.79 | 19.77 | 19.28 | 0.49 | 17.89 | 18.27 | 18.08 | 0.19 |
| | 1.5 | 19.24 | 19.08 | 19.16 | 0.08 | 15.93 | 15.37 | 15.65 | 0.28 |
| | 2.0 | 18.18 | 16.96 | 17.57 | 0.16 | 13.18 | 13.40 | 13.29 | 0.11 |

**Table A.2** continued

| % VAM | Mixing Time (Hour) | Tensile Strength (Mpa) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 6 | 0.5 | 14.37 | 14.71 | 14.54 | 0.17 | 12.75 | 13.41 | 13.08 | 0.33 |
| | 1 | 17.04 | 18.92 | 17.98 | 0.94 | 15.67 | 15.33 | 15.50 | 0.17 |
| | 1.5 | 18.00 | 16.92 | 17.46 | 0.54 | 15.21 | 13.37 | 14.29 | 0.92 |
| | 2.0 | 14.90 | 16.06 | 15.48 | 0.58 | 12.58 | 12.74 | 12.66 | 0.08 |
| 8 | 0.5 | 13.01 | 13.83 | 13.42 | 0.41 | 10.76 | 11.52 | 11.14 | 0.38 |
| | 1 | 15.23 | 12.87 | 14.05 | 1.18 | 6.84 | 7.12 | 6.98 | 0.14 |
| | 1.5 | 14.80 | 14.42 | 14.61 | 0.19 | 9.20 | 10.78 | 9.99 | 0.79 |
| | 2.0 | 13.69 | 14.37 | 14.03 | 0.34 | 8.33 | 8.43 | 8.38 | 0.05 |
| 10 | 0.5 | 12.12 | 10.70 | 11.41 | 0.71 | 10.38 | 9.58 | 9.98 | 0.40 |
| | 1 | 10.59 | 10.33 | 10.46 | 0.13 | 5.92 | 6.22 | 6.07 | 0.15 |
| | 1.5 | 12.64 | 11.44 | 12.04 | 0.60 | 8.83 | 7.97 | 8.40 | 0.43 |
| | 2.0 | 14.24 | 12.40 | 13.32 | 0.92 | 7.45 | 6.95 | 7.20 | 0.25 |

**Table A.2** continued

| % VAM | Mixing Time (Hour) | Tensile Strength (Mpa) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 15 | 0.5 | 8.53 | 8.87 | 8.70 | 0.17 | 7.89 | 8.27 | 8.08 | 0.19 |
| | 1 | 8.76 | 9.62 | 9.19 | 0.43 | 3.92 | 4.30 | 4.11 | 0.19 |
| | 1.5 | 10.14 | 9.32 | 9.73 | 0.41 | 4.68 | 5.52 | 5.10 | 0.42 |
| | 2.0 | 12.87 | 9.69 | 11.28 | 1.59 | 6.30 | 6.98 | 6.64 | 0.34 |
| 20 | 0.5 | 5.25 | 6.15 | 5.69 | 0.45 | 5.38 | 5.68 | 5.53 | 0.15 |
| | 1 | 7.27 | 6.63 | 6.95 | 0.32 | 3.79 | 4.33 | 4.06 | 0.27 |
| | 1.5 | 5.30 | 5.36 | 5.33 | 0.03 | 5.94 | 3.56 | 4.75 | 1.19 |
| | 2.0 | 8.88 | 9.76 | 9.32 | 0.44 | 4.83 | 5.69 | 5.26 | 0.43 |

**Table A.3** The statistic of modulus

| % VAM | Mixing Time (Hour) | Modulus (MPa) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 0 | 0.5 | 2.236 | 1.972 | 2.104 | 0.132 | 2.236 | 1.972 | 2.104 | 0.132 |
| | 1 | 1.724 | 1.774 | 1.749 | 0.025 | 1.724 | 1.774 | 1.749 | 0.025 |
| | 1.5 | 1.934 | 2.018 | 1.976 | 0.047 | 1.934 | 2.018 | 1.976 | 0.042 |
| | 2.0 | 1.968 | 2.014 | 1.991 | 0.023 | 1.968 | 2.014 | 1.991 | 0.023 |
| 2 | 0.5 | 1.851 | 1.795 | 1.823 | 0.028 | 1.753 | 1.785 | 1.769 | 0.016 |
| | 1 | 1.728 | 1.818 | 1.773 | 0.045 | 1.387 | 1.435 | 1.411 | 0.024 |
| | 1.5 | 1.804 | 1.906 | 1.855 | 0.051 | 1.603 | 1.699 | 1.651 | 0.048 |
| | 2.0 | 1.872 | 1.930 | 1.910 | 0.027 | 1.920 | 1.956 | 1.938 | 0.018 |
| 4 | 0.5 | 1.298 | 1.350 | 1.324 | 0.026 | 1.431 | 1.515 | 1.473 | 0.042 |
| | 1 | 1.256 | 1.190 | 1.223 | 0.033 | 1.124 | 1.082 | 1.103 | 0.022 |
| | 1.5 | 1.204 | 1.280 | 1.242 | 0.038 | 1.311 | 1.371 | 1.341 | 0.030 |
| | 2.0 | 1.700 | 1.672 | 1.686 | 0.014 | 1.281 | 1.215 | 1.248 | 0.033 |

Table A.3 continued

| % VAM | Mixing Time (Hour) | Modulus (Mpa) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 6 | 0.5 | 1.386 | 1.572 | 1.479 | 0.093 | 1.743 | 1.759 | 1.751 | 0.008 |
| | 1 | 1.279 | 1.343 | 1.311 | 0.032 | 1.435 | 1.495 | 1.465 | 0.030 |
| | 1.5 | 1.314 | 1.358 | 1.336 | 0.022 | 1.667 | 1.693 | 1.680 | 0.013 |
| | 2.0 | 1.753 | 1.789 | 1.771 | 0.018 | 1.834 | 1.820 | 1.827 | 0.007 |
| 8 | 0.5 | 1.499 | 1.565 | 1.532 | 0.033 | 1.874 | 1.890 | 1.882 | 0.008 |
| | 1 | 2.202 | 2.180 | 2.191 | 0.011 | 1.856 | 1.836 | 1.846 | 0.010 |
| | 1.5 | 2.097 | 2.119 | 2.108 | 0.011 | 1.877 | 1.809 | 1.843 | 0.034 |
| | 2.0 | 1.832 | 1.878 | 1.855 | 0.023 | 1.946 | 1.996 | 1.971 | 0.025 |
| 10 | 0.5 | 1.681 | 1.719 | 1.700 | 0.019 | 2.277 | 2.353 | 2.315 | 0.038 |
| | 1 | 2.570 | 2.548 | 2.559 | 0.011 | 2.158 | 2.124 | 2.141 | 0.017 |
| | 1.5 | 2.097 | 2.151 | 2.124 | 0.027 | 2.140 | 2.126 | 2.133 | 0.007 |
| | 2.0 | 2.493 | 2.527 | 2.510 | 0.017 | 2.355 | 2.389 | 2.372 | 0.017 |

Table A.3 continued

| % VAM | Mixing Time (Hour) | Modulus (Mpa) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 15 | 0.5 | 1.920 | 2.054 | 1.987 | 0.067 | 2.572 | 2.650 | 2.611 | 0.039 |
| | 1 | 2.710 | 2.776 | 2.743 | 0.033 | 2.303 | 2.231 | 2.267 | 0.036 |
| | 1.5 | 2.835 | 2.805 | 2.820 | 0.015 | 2.489 | 2.565 | 2.527 | 0.038 |
| | 2.0 | 2.740 | 2.690 | 2.715 | 0.025 | 2.563 | 2.591 | 2.577 | 0.014 |
| 20 | 0.5 | 3.106 | 3.160 | 3.133 | 0.027 | 2.945 | 2.931 | 2.938 | 0.077 |
| | 1 | 2.982 | 3.032 | 3.007 | 0.025 | 2.534 | 2.500 | 2.517 | 0.017 |
| | 1.5 | 2.913 | 2.963 | 2.938 | 0.025 | 2.682 | 2.736 | 2.709 | 0.027 |
| | 2.0 | 2.906 | 2.796 | 2.851 | 0.055 | 2.684 | 2.824 | 2.754 | 0.070 |

**Table A.4** The statistic of elongation at break

| % VAM | Mixing Time (Hour) | Elongation at break (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 0 | 0.5 | 1756.21 | 1657.79 | 1707.00 | 49.2 | 1756.21 | 1657.79 | 1707.00 | 49.2 |
| | 1 | 1784.00 | 1842.00 | 1813.00 | 29.0 | 1784.00 | 1842.00 | 1813.00 | 29.0 |
| | 1.5 | 1801.00 | 1709.00 | 1755.00 | 46.0 | 1801.00 | 1709.00 | 1755.00 | 46.0 |
| | 2.0 | 1210.33 | 1135.67 | 1173.00 | 37.3 | 1210.33 | 1135.67 | 1173.00 | 37.3 |
| 2 | 0.5 | 1522.00 | 1486.00 | 1504.00 | 18.0 | 1101.00 | 1017.00 | 1059.00 | 42.0 |
| | 1 | 1878.20 | 193508 | 1907.00 | 28.8 | 1539.77 | 1676.69 | 1608.23 | 68.4 |
| | 1.5 | 1840.40 | 0 | 1863.20 | 22.8 | 1656.41 | 1669.31 | 1662.86 | 6.4 |
| | 2.0 | 845.50 | 1886.00 | 821.90 | 23.6 | 666.33 | 676.59 | 671.46 | 5.1 |
| | | | 798.30 | | | | | | |
| 4 | 0.5 | 1782.25 | 1775.25 | 1778.75 | 3.5 | 2094.66 | 2134.00 | 2114.33 | 19.6 |
| | 1 | 2270.00 | 2382.66 | 2326.33 | 56.3 | 2311.00 | 2275.00 | 2293.00 | 18.0 |
| | 1.5 | 2337.00 | 2195.66 | 2266.33 | 40.6 | 2255.33 | 2191.99 | 2223.66 | 31.6 |
| | 2.0 | 1268.00 | 1152.00 | 1210.00 | 58.0 | 1217.53 | 1135.39 | 1176.46 | 41.0 |

Table A.4 continued

| % VAM | Mixing Time (Hour) | Elongation at break (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 6 | 0.5 | 1602.39 | 1743.95 | 1673.17 | 70.7 | 1224.00 | 1346.00 | 1285.00 | 61.0 |
| | 1 | 1915.30 | 1822.04 | 1868.67 | 46.6 | 1693.20 | 1606.26 | 1649.73 | 43.4 |
| | 1.5 | 2220.00 | 2161.34 | 2190.67 | 29.3 | 1659.00 | 1597.00 | 1628.00 | 31.0 |
| | 2.0 | 795.17 | 927.49 | 861.33 | 66.1 | 998.12 | 1201.88 | 1100.00 | 83.1 |
| 8 | 0.5 | 934.80 | 896.60 | 915.70 | 19.1 | 1231.00 | 1129.00 | 1180.00 | 57.0 |
| | 1 | 1247.00 | 1159.00 | 1203.00 | 4.4 | 561.43 | 603.57 | 582.50 | 21.0 |
| | 1.5 | 1788.00 | 1902.00 | 1845.00 | 5.7 | 822.36 | 792.48 | 807.42 | 14.9 |
| | 2.0 | 784.20 | 821.60 | 802.90 | 18.7 | 673.00 | 644.20 | 658.60 | 14.4 |
| 10 | 0.5 | 731.80 | 674.00 | 702.90 | 28.9 | 770.00 | 822.20 | 796.10 | 26.1 |
| | 1 | 735.50 | 779.10 | 757.30 | 21.8 | 524.00 | 558.80 | 541.40 | 17.4 |
| | 1.5 | 1304.00 | 1240.00 | 1272.00 | 32.0 | 698.30 | 668.90 | 683.60 | 14.7 |
| | 2.0 | 703.00 | 644.00 | 673.50 | 29.5 | 493.00 | 517.00 | 505.00 | 12.0 |

**Table A.4** continued

| % VAM | Mixing Time (Hour) | Elongation at break (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 15 | 0.5 | 719.00 | 690.20 | 704.60 | 14.40 | 464.80 | 525.40 | 495.10 | 30.30 |
| | 1 | 684.12 | 767.28 | 725.70 | 41.58 | 556.41 | 530.99 | 543.70 | 12.71 |
| | 1.5 | 729.30 | 748.30 | 738.80 | 9.50 | 680.00 | 674.96 | 677.48 | 2.52 |
| | 2.0 | 674.90 | 596.70 | 635.80 | 39.50 | 471.00 | 523.00 | 497.00 | 26.00 |
| 20 | 0.5 | 632.00 | 606.60 | 619.30 | 12.70 | 458.20 | 409.40 | 433.80 | 24.40 |
| | 1 | 671.00 | 590.60 | 630.80 | 40.20 | 296.84 | 339.56 | 318.10 | 21.46 |
| | 1.5 | 738.50 | 664.50 | 701.50 | 37.00 | 544.00 | 514.00 | 529.00 | 15.00 |
| | 2.0 | 563.33 | 580.27 | 571.80 | 8.47 | 457.80 | 413.00 | 435.00 | 22.00 |

**Table A.5** The statistic of hardness

| % VAM | Mixing Time (Hour) | Hardness (Shore A) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | ve. | SD | No. 1 | No. 2 | Ave. | SD |
| 0 | 0.5 | 27.8 | 28.4 | 28.1 | 0.30 | 27.8 | 28.4 | 28.1 | 0.30 |
| | 1 | 33.0 | 35.0 | 34 | 1.00 | 33.0 | 35.0 | 34.0 | 1.00 |
| | 1.5 | 32.8 | 34.2 | 33.6 | 0.60 | 32.8 | 34.2 | 33.6 | 0.70 |
| | 2.0 | 28.9 | 29.9 | 29.4 | 0.50 | 28.9 | 29.9 | 29.4 | 0.50 |
| 2 | 0.5 | 31.2 | 32.2 | 31.7 | 0.50 | 29.8 | 31.0 | 30.4 | 0.60 |
| | 1 | 30.1 | 29.5 | 29.8 | 0.30 | 30.5 | 31.1 | 30.8 | 0.30 |
| | 1.5 | 30.8 | 32.0 | 31.4 | 0.60 | 32.7 | 31.7 | 34.9 | 3.20 |
| | 2.0 | 35.9 | 34.7 | 35.3 | 0.60 | 29.5 | 31.1 | 30.3 | 0.80 |
| 4 | 0.5 | 41.3 | 40.1 | 40.7 | 0.60 | 35.3 | 34.1 | 34.7 | 0.60 |
| | 1 | 42.5 | 41.5 | 42.0 | 0.50 | 37.9 | 38.3 | 38.1 | 0.20 |
| | 1.5 | 40.6 | 39.6 | 40.1 | 0.50 | 39.0 | 38.6 | 38.8 | 0.20 |
| | 2.0 | 38.2 | 39.0 | 39.6 | 0.60 | 36.1 | 33.9 | 35.0 | 1.10 |

**Table A.5** continued

| % VAM | Mixing Time (Hour) | Hardness (Shore A) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 6 | 0.5 | 38.2 | 39.0 | 38.6 | 0.40 | 35.1 | 34.1 | 34.6 | 0.50 |
| | 1 | 40.6 | 41.8 | 41.2 | 0.60 | 34.8 | 36.0 | 35.4 | 0.60 |
| | 1.5 | 40.1 | 38.3 | 39.2 | 0.90 | 37.2 | 36.4 | 36.8 | 0.40 |
| | 2.0 | 38.4 | 38.6 | 38.5 | 0.10 | 34.2 | 35.6 | 34.9 | 0.70 |
| 8 | 0.5 | 34.8 | 35.4 | 35.1 | 0.30 | 31.7 | 33.5 | 32.6 | 0.90 |
| | 1 | 40.5 | 40.1 | 40.3 | 0.20 | 36.0 | 34.0 | 35.0 | 1.00 |
| | 1.5 | 37.6 | 39.6 | 38.4 | 1.20 | 37.2 | 36.5 | 36.9 | 0.40 |
| | 2.0 | 38.4 | 37.6 | 38.0 | 0.40 | 33.9 | 34.5 | 34.2 | 0.30 |
| 10 | 0.5 | 34.6 | 33.8 | 34.2 | 0.40 | 29.7 | 31.3 | 30.5 | 0.80 |
| | 1 | 39.0 | 38.8 | 38.9 | 0.10 | 34.2 | 34.6 | 34.4 | 0.20 |
| | 1.5 | 36.0 | 38.0 | 37.0 | 1.00 | 34.9 | 36.1 | 35.5 | 0.60 |
| | 2.0 | 37.8 | 38.5 | 37.9 | 0.60 | 35.0 | 33.4 | 34.2 | 0.80 |

**Table A.5** continued

| % VAM | Mixing Time (Hour) | Hardness (Shore A) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 15 | 0.5 | 33.5 | 34.5 | 34.0 | 0.50 | 30.8 | 30.0 | 30.4 | 0.40 |
| | 1 | 37.4 | 39.6 | 38.5 | 1.10 | 35.8 | 32.4 | 34.1 | 1.70 |
| | 1.5 | 34.3 | 38.3 | 36.3 | 2.00 | 35.2 | 34.4 | 34.8 | 0.40 |
| | 2.0 | 36.9 | 38.3 | 37.6 | 0.70 | 33.0 | 35.0 | 34.0 | 1.00 |
| 20 | 0.5 | 33.6 | 34.2 | 33.9 | 0.30 | 29.2 | 29.6 | 29.4 | 0.20 |
| | 1 | 37.5 | 38.3 | 37.9 | 0.40 | 33.2 | 33.4 | 33.3 | 0.10 |
| | 1.5 | 36.4 | 36.2 | 36.3 | 0.10 | 30.9 | 32.1 | 31.5 | 0.60 |
| | 2.0 | 37.7 | 37.3 | 37.5 | 0.20 | 32.6 | 31.8 | 32.2 | 0.40 |

**Table A.6** The statistic of rebound resilience

| % VAM | Mixing Time (Hour) | Rebound resilieece (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 0 | 0.5 | 70.04 | 73.30 | 71.67 | 1.63 | 70.04 | 73.30 | 71.67 | 1.63 |
| | 1 | 73.18 | 74.74 | 73.96 | 0.78 | 73.18 | 74.74 | 73.96 | 0.78 |
| | 1.5 | 72.99 | 73.05 | 73.02 | 0.03 | 72.99 | 73.05 | 73.02 | 0.03 |
| | 2.0 | 71.83 | 71.47 | 71.65 | 0.18 | 71.83 | 71.47 | 71.65 | 0.18 |
| 2 | 0.5 | 74.78 | 75.86 | 75.32 | 0.54 | 76.40 | 75.72 | 76.06 | 0.34 |
| | 1 | 78.32 | 78.52 | 78.42 | 0.10 | 81.25 | 81.57 | 81.41 | 0.16 |
| | 1.5 | 80.54 | 81.18 | 80.86 | 0.32 | 78.35 | 79.41 | 78.88 | 0.53 |
| | 2.0 | 76.83 | 77.25 | 77.04 | 0.21 | 75.33 | 75.09 | 75.71 | 0.62 |
| 4 | 0.5 | 81.43 | 81.87 | 81.65 | 0.22 | 78.16 | 78.37 | 78.49 | 0.12 |
| | 1 | 83.82 | 84.34 | 84.08 | 0.26 | 83.30 | 83.00 | 83.15 | 0.15 |
| | 1.5 | . | 82.21 | 81.99 | 0.22 | 78.51 | 78.25 | 78.38 | 0.13 |
| | 2.0 | 81.77 | 81.38 | 81.15 | 0.23 | 76.70 | 76.94 | 76.82 | 0.12 |
| | | 80.92 | | | | | | | |

**Table A.6** continued

| % VAM | Mixing Time (Hour) | Rebound resilieece (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Tert- butylhydroperoxide | | | | Benzoylperoxide | | | |
| | | No. 1 | No. 2 | Ave. | SD | No. 1 | No. 2 | Ave. | SD |
| 6 | 0.5 | 80.14 | 80.64 | 80.39 | 0.25 | 78.32 | 78.50 | 78.41 | 0.09 |
| | 1 | 83.03 | 82.59 | 82.81 | 0.22 | 79.55 | 80.39 | 79.97 | 0.42 |
| | 1.5 | 78.80 | 79.34 | 79.07 | 0.27 | 77.34 | 77.16 | 77.25 | 0.09 |
| | 2.0 | 78.81 | 79.11 | 78.96 | 0.15 | 76.20 | 75.88 | 76.04 | 0.16 |
| 8 | 0.5 | 79.53 | 79.83 | 79.68 | 0.15 | 77.62 | 77.44 | 77.53 | 0.09 |
| | 1 | 77.88 | 78.70 | 78.29 | 0.41 | 77.42 | 77.52 | 77.47 | 0.05 |
| | 1.5 | 76.35 | 75.79 | 76.07 | 0.28 | 75.68 | 76.24 | 75.96 | 0.28 |
| | 2.0 | 78.11 | 77.11 | 77.61 | 0.50 | 76.26 | 75.66 | 75.96 | 0.30 |

**Table A.7** The percent change of tensile strength

| % VAM | No. | Tensile Strength (MPa) | | % Change | Average |
|---|---|---|---|---|---|
| | | Unaged | Aged | | |
| 0 | 1 | 8.50 | 6.09 | -28.35 | -28.76 ± 0.40 |
| | 2 | 7.93 | 5.61 | -29.16 | |
| 2 | 1 | 14.78 | 11.08 | -25.01 | -25.72 ± 0.70 |
| | 2 | 13.65 | 10.04 | -26.42 | |
| 4 | 1 | 19.8 | 13.78 | -28.50 | -28.42 ± 0.08 |
| | 2 | 18.20 | 13.04 | -28.34 | |
| 6 | 1 | 17.98 | 11.82 | -34.28 | -33.00 ± 1.28 |
| | 2 | 16.38 | 11.18 | -31.72 | |

**Table A.8** The percent change of elongation at break

| % VAM | No. | Elongation (%) | | % Change | Average |
|---|---|---|---|---|---|
| | | Unaged | Aged | | |
| 0 | 1 | 1813.00 | 874.00 | -51.79 | -52.69 ± 0.91 |
| | 2 | 1789.00 | 829.92 | -53.60 | |
| 2 | 1 | 1907.00 | 1412.18 | -25.94 | -27.68 ± 1.74 |
| | 2 | 1966.00 | 1387.41 | -29.42 | |
| 4 | 1 | 2326.33 | 1763.40 | -24.19 | -23.89 ± 0.29 |
| | 2 | 2199.00 | 1680.00 | -23.60 | |
| 6 | 1 | 1868.67 | 1438.21 | -23.03 | -22.64 ± 0.38 |
| | 2 | 2026.00 | 1575.30 | -22.26 | |

**Table A.9** The difference value of hardness

| % VAM | No. | Hardness (Shore A) | | Difference | Average |
|---|---|---|---|---|---|
| | | Unaged | Aged | | |
| 0 | 1 | 34.0 | 32.0 | 2.0 | 1.70 ± 0.30 |
| | 2 | 32.0 | 30.6 | 1.4 | |
| 2 | 1 | 29.8 | 27.6 | 2.2 | 3.05 ± 0.85 |
| | 2 | 30.3 | 26.4 | 3.9 | |
| 4 | 1 | 42.0 | 37.2 | 4.8 | 4.65 ± 0.15 |
| | 2 | 41.8 | 37.3 | 4.5 | |
| 6 | 1 | 41.2 | 36.5 | 4.7 | 4.40 ± 0.30 |
| | 2 | 40.1 | 36.0 | 4.1 | |

# APPENDIX B

The rheometer data of compounded rubber and compounded rubber grafted with vinyl acetate

Test condition : Temperature 150 °C
Testing time 15 min
Rotational amplitude 3 °

The rheometer data and curing curve of the products that were used to determine the appropriate curing time are shown in Tables B.1 , B.2 and Figures B.1,B.2.

**Table B.1** The rheometer data of compounded rubber

| Rheometer Data | Results |
|---|---|
| $M_L$ - Minimum Torque | 15.20 |
| $M_H$ - Maximum torque | 23.82 |
| ts1 - Scorch Time | 1.63 |
| ts2 - Scorch Time | 1.96 |
| tc10 - Time Torque 10 | 1.54 |
| tc50 - Time Torque 50 | 2.75 |
| tc90 - Time Torque 90 | 4.79 |

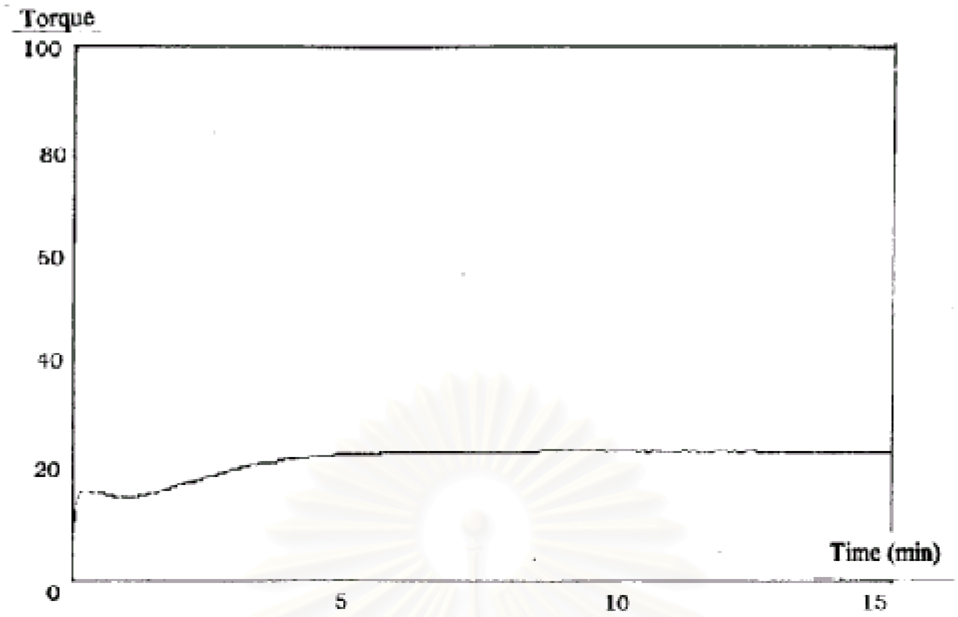
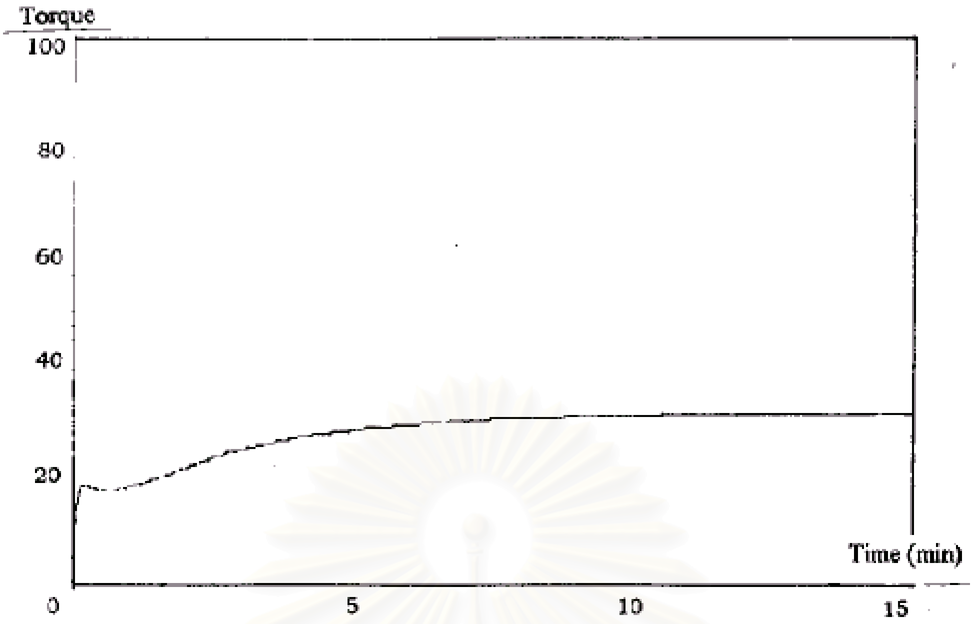


Figure B.1 Curing curve of compounded rubber

**Table B.2** The rheometer data of compounded rubber grafted with vinyl acetate

| Rheometer Data | Results |
|---|---|
| $M_L$ - Minimum Torque | 17.25 |
| $M_H$ - Maximum torque | 30.82 |
| ts1 - Scorch Time | 1.23 |
| ts2 - Scorch Time | 1.54 |
| tc10 - Time Torque 10 | 1.35 |
| tc50 - Time Torque 50 | 2.94 |
| tc90 - Time Torque 90 | 6.83 |



**FigureB.2** Curing curve of compounded rubber grafted with vinyl acetate

# APPENDIX C

ATR Spectra of compounded rubber and compounded rubber grafted with vinyl acetate are shown in Figures C.1 and C.2 , respectively .

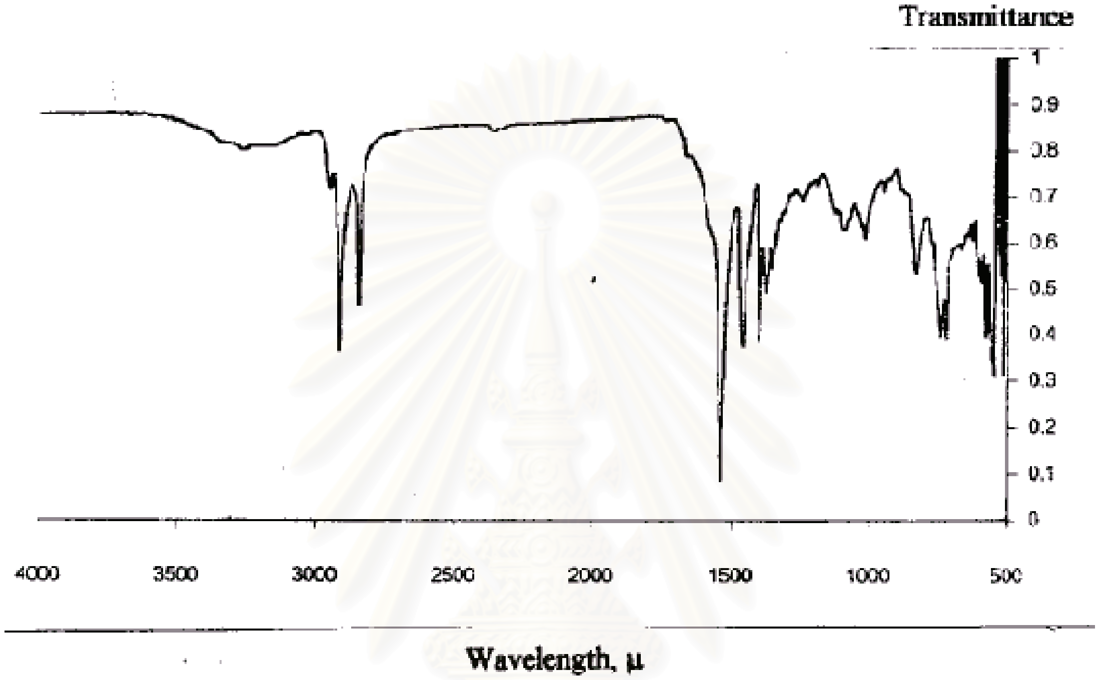


Figure C.1 ATR spectrum of compounded rubber

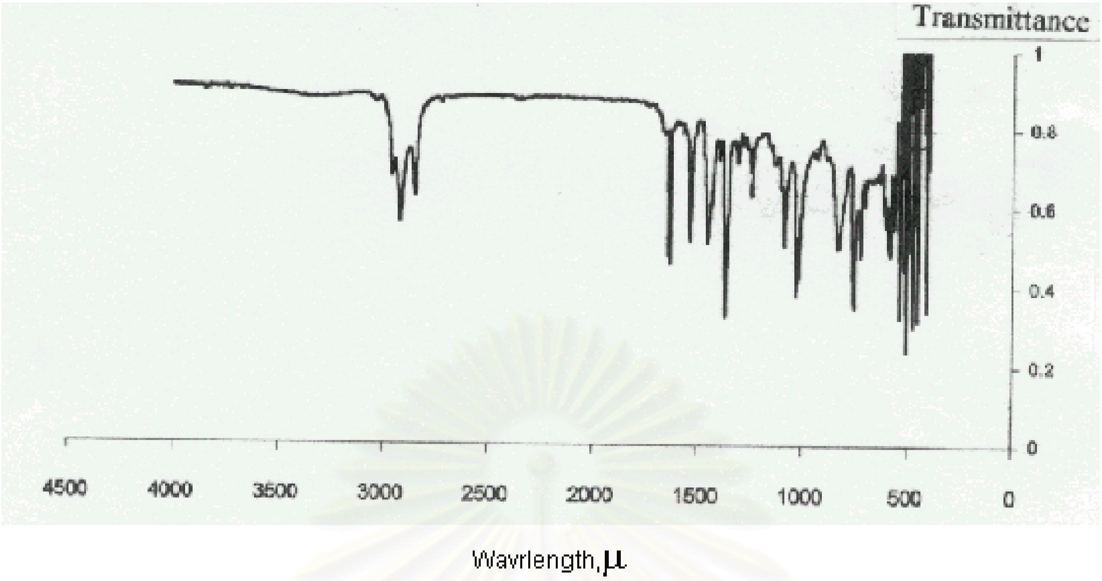


**Figure C.2** ATR spectrum of compounded rubber grafted compounded rubber with vinyl acetate

# VITA

Miss Thitinat Srisuwan was born on September 19, 1975 in Chumporn, Thailand. She received her associate professor. Bachelor Degree of Science in industrial chemistry, King Mongkut 's Institute of Technology North Bangkok in 1998. She continued her Master study in the Program of Petrochemistry and Polymer Science, Faculty of science, Chulalongkorn University and completed in 2001.