การเสริมแรงพอลิเมอร์ผสมยางอะคริโลไนไตรล์-บิวทาไดอีนและพอลิไวนิลคลอไรด์ด้วยอินซิทูซิลิกา

นายธนิต ตรีพิเชฐกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมีเทคนิค ภาควิชาเคมีเทคนิค
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2545

ISBN 974-17-2115-3

REINFORCEMENT OF ACRYLONITRILE-BUTADIENE RUBBER AND POLY(VINYL CHLORIDE) BLENDS BY IN SITU SILICA

Mr. Thanit Treepichetkul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemical Technology
Department of Chemical Technology
Faculty of Science
Chulalongkorn University
Academic Year 2002
ISBN 974-17-2115-3

Thesis Title	REINFORCEMENT OF ACRYLONITRILE-BUTADIENE RUBBER AND POLY(VINYL CHLORIDE) BLENDS BY IN SITU SILICA
By	Mr.Thanit Treepichetkul
Department	Chemical Technology
Thesis Advisor	Professor Pattarapan Prasassarakich, Ph.D.
Thesis Co-advisor	Professor Shinzo Kohjiya, Ph.D.

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

…………………………………………. Dean of Faculty of Science
(Associate Professor Wanchai Phothipichitr, Ph.D.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Associate Professor Tharapong Vitidsant, Ph.D.)

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

……………………………………………….. Thesis Co-advisor
(Professor Shinzo Kohjiya, Ph.D.)

……………………………………………….. Member
(Dr. Pienpak Tasakorn, Ph.D.)

……………………………………………….. Member
(Associate Professor Somkiat Ngamprasertsith, Ph.D.)

ธนิต ตรีพิเชฐกุล : การเสริมแรงพอลิเมอร์ผสมยางอะคริโลไนไตรล์-บิวทาไดอีนและพอลิไวนิลคลอไรด์ด้วยอินซิทูซิลิกา. (REINFORCEMENT OF ACRYLONITRILE-BUTADIENE RUBBER AND POLY(VINYL CHLORIDE) BLENDS BY IN SITU SILICA) อ.ที่ปรึกษา : ศ.ดร.ภัทรพรรณ ประศาสน์สารกิจ, อ.ที่ปรึกษาร่วม : PROF. Dr. SHINZO KOHJIYA, 95 หน้า. ISBN 974-17-2115-3.

การเสริมแรงยางอะคริโลไนไตรล์-บิวทาไดอีนและพอลิไวนิลคลอไรด์กับซิลิกาด้วยวิธีโซล-เจลของสารเตตระเอทอกซีไซเลน (TEOS) และเอทิลพอลิซิลิเกต (EPS) โดยใช้เอทิลีนไดเอมีนเป็นสารเร่งปฏิกิริยา มีการเติมยางธรรมชาติทดแทนส่วนของยางอะคริโลไนไตรล์-บิวทาไดอีนในพอลิเมอร์ผสมยางอะคริโลไนไตรล์-บิวทาไดอีนกับพอลิไวนิลคลอไรด์ที่ 70/30 งานวิจัยนี้นำยางอะคริโลไนไตรล์-บิวทาไดอีนและยางธรรมชาติแช่ในสารเตตระเอทอกซีไซเลนหรือเอทิลพอลิซิลิเกตและแช่ในสารละลายของตัวเร่งปฏิกิริยา ซึ่งปฏิกิริยาโซล-เจลนั้นเริ่มต้นด้วยการผสมสารเตตระเอทอกซีไซเลนหรือเอทิลพอลิซิลิเกตกับน้ำหรือเอทานอลหรือเตตระไฮโดรฟูแลน อัตราส่วนโดยน้ำหนักของสารเตตระเอทอกซีไซเลนหรือเอทิลพอลิซิลิเกตต่อยางมีผลต่อระดับการบวมของยางจากผลของระดับการบวมและปริมาณซิลิกาที่เกิดขึ้นจากกระบวนการโซล-เจล พบว่า การใช้น้ำทั้งหมดสำหรับยางธรรมชาติ สารเตตระไฮโดรฟูแลนสำหรับยางอะคริโลไนไตรล์-บิวทาไดอีน และอัตราส่วนโดยน้ำหนักของสารเตตระเอทอกซีไซเลนหรือเอทิลพอลิซิลิเกตต่อยางที่ 10 ต่อ 1 ให้ผลดีกว่าภาวะอื่นๆ และยังพบว่าความเข้มข้นของตัวเร่งปฏิกิริยาและเวลาของการแช่มีผลน้อยต่อการเกิดซิลิกาในยาง

นอกจากนี้พบว่าอนุภาคซิลิกาเกิดจากกระบวนการโซล-เจลมีการกระจายตัวดีกว่าการกระจายตัวของอนุภาคซิลิกาทั่วไป ซึ่งซิลิกาจากกระบวนการโซล-เจลนี้ไม่มีผลยับยั้งการเกิดการเชื่อมโยงของซัลเฟอร์ นั้นคือ ซิลิกาที่ได้จะมีกลุ่มไซลานอลบนพื้นผิวน้อยกว่าซิลิกาทั่วไป ทำให้การเกิดปฏิกิริยาระหว่างซิลิกาน้อยกว่า ทำให้การกระจายตัวของซิลิกาจากกระบวนการโซล-เจลนั้นดีกว่าเมื่อเทียบกับอนุภาคซิลิกาทั่วไป และจากการทดลองพบว่าแรงที่ใช้ในการยืดพอลิเมอร์ผสมที่โมดูลัส 100 เปอร์เซ็นต์ แรงที่ใช้ในการยืดพอลิเมอร์ขาด และความยืดยาวจนขาดของพอลิเมอร์ผสมยางกับพอลิไวนิลคลอไรด์วัลคาร์ไนส์กรณีเติมซิลิกาด้วยกระบวนการโซล-เจลมีค่าต่ำกว่ากรณีการเติมผงซิลิกาด้วยวิธีการปกติ

ภาควิชา……เคมีเทคนิค……. ลายมือชื่อนิสิต…………………………………………………
สาขาวิชา……เคมีเทคนิค….. ลายมือชื่ออาจารย์ที่ปรึกษา……………………………………
ปีการศึกษา…2545………….. ลายมือชื่ออาจารย์ที่ปรึกษาร่วม………………………………

4372525423 : MAJOR CHEMICAL TECHNOLOGY
KEY WORD : POLYMER BLENDS/PVC / NITRILE RUBBER / NATURAL RUBBER BLENDS / SOL-GEL PROCESS.

THANIT TREEPICHETKUL : REINFORCEMENT OF ACRYLONITRILE-BUTADIENE RUBBER AND POLY(VINYL CHLORIDE) BLENDS BY IN SITU SILICA. THESIS ADVISOR : PROF. PATTARAPAN PRASASSARAKICH, Ph.D., THESIS COADVISOR : PROF. SHINZO KOHJIYA, Ph.D., 95 pp. ISBN 974-17-2115-3.

Acrylonitrile-butadiene rubber (NBR) and poly(vinyl chloride) (PVC) blends were reinforced with silica by sol-gel method of tetraethoxysilane (TEOS) and ethyl polysilicate (EPS) using ethylenedimine as a catalyst. Natural rubber (NR) was used to replace part of the NBR in a 70/30 NBR/PVC blend. NBR and NR were soaked in TEOS or EPS and in an aqueous solution of the catalyst. The sol-gel reaction proceeded by the mixture of TEOS or EPS with water, EtOH and THF was also related to the degree of swelling of the rubber. The amount of TEOS or EPS added and the mass ratio of TEOS or EPS to rubber was related to the degree of swelling of the rubber. From the viewpoint of the degree of swelling and silica content of sol-gel process of the NR, the method using only water at mass ratio at 10/1 (TEOS or EPS/rubber) was found to be better than other system. For NBR, the method using only THF at mass ratio of 10/1 (TEOS or EPS/rubber) was found to be better than other systems. Ethylenediamine concentration and soaking time slightly effected the silica content in the rubber.

The dispersion of the in situ silica particle was better than that of conventional silica. The in situ silica did not much inhibit the accelerated sulfur curing. Thus, it is estimated that the concentration of silanol groups on the in situ silica surface was smaller than those on the conventional silica surface. The silica-silica interaction of in situ silica seems to be weaker to result in better dispersion in the rubber matrix compared with the conventional silica. The modulus at 100% elongation, tensile strength at break and elongation at break of in situ silica-filled rubber/PVC vulcanizate were lower than those of conventional silica-filled rubber/PVC vulcanizate.

Department…Chemical Technology….   Student's signature…………………………
Field of study…Chemical Technology..   Advisor's signature…………………………
Academic year…2002…………………. Co-advisor's signature……..………………

ACKNOWLEDGEMENTS

The author wishes to express his deepest gratitude to his advisor, Professor Pattarapan Prasassarakich, his co-advisor, Professor Shinzo Kohjiya and Professor Yuko Ikeda, for their guidance, encouragement and helpful suggestion throughout this research. In addition, the author is also grateful to the members of the thesis committee for their comments and suggestions.

The author also thanks the Bayer (Thailand) Co., Ltd., TECK BEE HUNG Co., Ltd. and Silbond Co., Ltd for supplying acrylonitrile-butadiene rubber (nitrile), natural rubber and ethyl polysilicate, respectively, as well as the graduate school of Chulatongkorn University for the research financial supports. Many thanks are going to the department of Chemical Technology, the department of Chemistry, faculty of Science, Chulalongkorn University and the Rubber Research Institute of Thailand, for providing research facilities thoughout the research work.

Thanks go towards his friends and everyone whose names are not mentioned here for their suggestions, assistance, and advice concerning the experimental techniques and the encouragement during the period of this research.

Finally, and most of all, the author would like to express his deep gratitude to his family for their love, inspiration, and encouragement.

CONTENTS

page

CONTENTS (continued)

page

CONTENTS (continued)

page

LIST OF TABLES

Table page

LIST OF FIGURES

LIST OF FIGURES (continued)

Figure page

CHAPTER I

INTRODUCTION

1.1 The Purpose of the Investigation

Blending of polymers for property improvement or for economic advantage has gained considerable importance in the field of polymer science in the last decade. Miscibility of the constituent polymers is often a necessity for forming successful blends. One of the commercially important and miscible polymers blends in that of NBR and PVC. NBR acts as a permanent plasticizer for PVC in applications like wire and cable insulation, food containers, pond liners used for oil containment, etc. On the other hand, PVC improves ozone, thermal aging, and chemical resistance of NBR in applications like feed hose covers, gaskets, conveyor belt covers, pointing roll covers, etc. PVC also vastly improves abrasion resistance, tear resistance, and tensile properties. It also adds gloss and improves finish of the extruded stock and imparts flame-retardant character. NBR/PVC blends can be conveniently milled extruded and compression-molded using traditional processing equipment for natural and synthetic rubber [1]. Common rubbers such as natural rubber (NR) are not likely to be compatible with either NBR or PVC and, hence, the effect of modifying an NBR/PVC blend by any of them cannot be easily predicted [2].

Many other rubbery products are colored black, because carbon black is usually mixed in NBR/PVC products and other than carbon black, only silica is able to reinforce rubbers. The rubber/silica composite offers advantages in tear strength, abrasion resistance and the reduction in heat build-up etc. over carbon black. However, silica is usually much more expensive because of the energy-consuming complex manufacturing process, though the raw materials abound on the earth. Also, the usual silica interacts more with each other than with rubber molecules. This results in aggregation of silica particles in rubber matrix to decrease the reinforcing effect on physical properties. In order to overcome this difficulty, a coupling agent is used together with silica. The silane-coupling agent is expected to react with both silica and rubber to result in the increase of filler-to-rubber interaction. However, use of the coupling agent has complicated the processing procedure: What kind of, how much, and when to use the agent are always a big problem when designing rubbery composite. These are the reasons of preference of carbon black over silica.

Therefore, different from the conventional mechanical mixing, the in situ silica filling uses the sol-gel reaction of Tetraethoxysilane (TEOS) and Ethyl polysilicate (EPS) for production silica particles, which has been focused as a novel technique. The reaction of TEOS and EPS takes place in two steps the hydrolysis and the condensation reactions, to produce SiO_2 as shown in following equation:

$$\equiv \mathrm{Si-OR} + \mathrm{H_2O} \underset{\text{esterification}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} \equiv \mathrm{Si-OH} + \mathrm{ROH} \qquad \text{(i)}$$

$$\equiv \mathrm{Si-OR} + \mathrm{HO-Si}\equiv \underset{\text{alcoholysis}}{\overset{\text{alcohol condensation}}{\rightleftharpoons}} \equiv \mathrm{Si-O-Si}\equiv + \mathrm{ROH} \qquad \text{(ii)}$$

$$\equiv \mathrm{Si-OH} + \mathrm{HO-Si}\equiv \underset{\text{hydrolysis}}{\overset{\text{water condensation}}{\rightleftharpoons}} \equiv \mathrm{Si-O-Si}\equiv + \mathrm{H_2O} \qquad \text{(iii)}$$

This sol-gel process has been noted for the preparation of inorganic glasses at lower temperatures. In the field of rubber science, crosslinked rubbers have been subjected to this in situ filling of silica. However, in situ silica filling in vulcanizates is not industrially practical due to several reasons. For example, thickness of the samples is to be a few millimeters for swelling in TEOS and for immersing in the aqueous solution of catalyst in order to conduct the sol-gel reaction of TEOS homogeneously in the rubber matrix.

1.2 Objectives

The objectives of the research are as follows:

1. To study the appropriate conditions for the preparation of natural rubber and nitrile rubber filled with silica by sol-gel process.
2. To study the physical and mechanical properties of the silica-filled rubber/poly(vinyl chloride) blends.

1.3 Scope of the Investigation

For the preparation of the polymer compound with silica by sol-gel process, the appropriate conditions, which give the best physical and mechanical properties were studied. The investigation procedures were carried out as follows:

1. Literature survey and study the research work.
2. Design and prepare experimental procedure.
3. Prepare the silica-filled rubber by sol-gel process before curing. The appropriate conditions were determined by varying the following parameters:
    a) Dilution ratio of ethanol/distilled water/tetrahydrofuran for the tetrahydroxysilane and ethyl polysilicate solution.
    b) Mass ratio of tetrahydroxysilane or ethyl polysilicate and rubber for the tetrahydroxysilane and ethyl polysilicate solution.
    c) Catalyst concentration of the aqueous catalyst solution.
    d) Time for soaking in aqueous catalyst solution.
    e) Temperature and time of drying under a reduced pressure for the silica-filled rubber.
4. Prepare the polymer blends (poly(vinyl chloride), nitrile rubber and natural rubber) by direct mixing of the silica-filled rubber with vulcanizing agent, additives and poly(vinyl chloride).
5. Determine the physical and mechanical properties of such as tensile strength, tear resistance, viscosity, scorch time, elongation at break.
6. Study the morphology of rubber/ PVC blends.
7. Summarize the results.

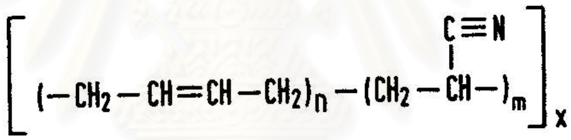
CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Acrylonitrile-butadiene Rubber (Nitrile, NBR) [1]

Acrylonitrile-butadiene rubbers (NBR) (Figure 2.1), or, simply, nitrile rubbers, are copolymers of butadiene and acrylonitrile. They are available in five grades based on the acrylonitrile (ACN) content:

1) very low nitriles: typically 18-20% ACN;
2) low nitriles: typically 28-29% ACN;
3) medium nitriles: typically 33-34% ACN;
4) high nitriles: typically 38-39% ACN;
5) very high nitriles: typically 45-48% ACN.



$$\left[(-CH_2-CH=CH-CH_2)_n-(CH_2-\overset{\overset{\displaystyle C\equiv N}{|}}{CH}-)_m \right]_x$$

Figure 2.1 Structure of acrylonitrile-butadiene rubber (NBR) [1]

Many of the vulcanizate properties are directly related to the proportion of acrylonitrile in the rubber. As the ACN content is increased, the following changes in the vulcanizate properties occur:

- resistance to petroleum-based fluids and hydrocarbon fuels increases;
- low-temperature flexibility decreases;
- rebound resilience decreases;
- compressing set deteriorates;
- gas permeability decreases;
- heat resistance improves;
- ozone resistance improves;
- abrasion resistance improves;
- tensile strength increases;

- hardness increases; and
- density increases.

In general, the high and very high nitriles are used in applications requiring good resistance to hydrocarbons of high aromatic contents (e.g., aromatic oils and gasolines).

The medium grades are used in cases where the oil is of lower aromatic content or where higher swelling of the elastomer is tolerable. The low and very low nitriles are used with liquids of low swelling effect [e.g., paraffinic oils and polyalphaolefins] or in cases where low-temperature flexibility is of greater importance than is oil resistance.

a) Compounding

Nitrile rubbers require reinforcing fillers to obtain high strength, because the unfilled vulcanizates do not crystallize on stretching. The polymer selection is an important factor in obtaining the best balance of oil resistance and low temperature flexibility.

Basically, nitrile rubber compounds contain nearly the same compounding ingredients used in Natural rubber (NR) and Stryrene-butadiene (SBR). Ester-based plasticizers are generally used in NBR compounds to improve low-temperature properties. Sulphur donor and peroxide curing systems are normally used for applications requiring good high-temperature performance and low compression set. NBR has poor compatibility with natural rubber, but it can be blended with SBR in all proportions. This reduces the overall oil resistance of the vulcanizate, but it is sometimes used also as a technique to counteract shrinkage caused by oils with low swelling power such as polyalphaolefins.

b) Vulcanizate Properties

As has been mentioned, many of the vulcanizate properties will vary depending upon the ACN content. However, it can be said that NBR vulcanizates have, in general, good physical properties over a wide hardness range. They are (like other highly unsaturated elastomers) not inherently ozone resistant. However, this property can be improved through compounding or through the use of NBR/PVC blends.

The electrical insulation properties are poor, although adequate for sheathing when oil resistance is required. Instead, conductive compounds can be obtained by using high nitriles with suitable compounding ingredients

Suitably formulated NBR compounds have low compression set, and continuous operational temperature range from –40 to +100 ^{0}C and for intermittent periods (in the absence of air) up to 120 ^{0}C.

NBR vulcanizates are resistant to a wide range of petroleum-based greases and fluids, hydrocarbon fuels, vegetable and animal oils, silicone greases and oils, organic-ester-based fluids, polyalkylene glycols, water and aqueous solutions of nonoxidizing chemicals. However, they are not resistant to phosphate ester hydraulic fluids, non petroleum-based automotive brake fluids, aromatic hydrocarbons (e.g. benzene, toluene, xylene), halogenated hydrocarbons (e.g. trichloroethylene, carbon tetrachloride), Ketones (e.g. acetone, MEK), low-molecular weight esters (e.g. ethyl acetate), strong acids and oxidizing chemicals.

c) Applications

NBR elastomers are the most widely used materials for oil- and fuel-resistant components such as seals, gaskets, diaphragms, hoses and cable jacketing.

2.2 Poly(vinyl chloride), (PVC) [2]

PVC is a thermoplastic, which can soften and melt at elevated temperatures. Thus, by the application of heat and pressure, PVC may be extruded or molded into any desired shape. Processing can be formed from 150 to 200^{0}C, depending upon the molecular weight of the resin and formulation.

PVC is uniquely responsive to functional additives, which permit the generation of rigid and flexible products, useful in novelties at low cost and in designed engineering applications. PVC is used in a wide range of applications because of its combined physical properties of:

- Compounding versatility as rigids or flexibles.
- High modulus (unplasticized).
- Ease of fabrication.
- Low flammability.
- Low cost.

Because of the compounding versatility of PVC, consequently, they can be used in many applications such as wire insulation, tube, film, sheet, footwear, toys, hose, and many other applications.

2.3 Natural Rubber (NR) [1]

The chemical name for NR is polyisoprene, which is a homopolymer of isoprene. It has the cis-1,4 configuration (Figure 2.2), which means that carbon atoms 1 and 4 are both on the same side of the double bond. (In the trans-1,4 configuration, these two carbon atoms are on opposite sides of the double bond). In addition, the polymer contains small amounts of nonrubber substances, notably fatty acids, proteins and resinous materials that function as mild accelerators and activators for vulcanization.

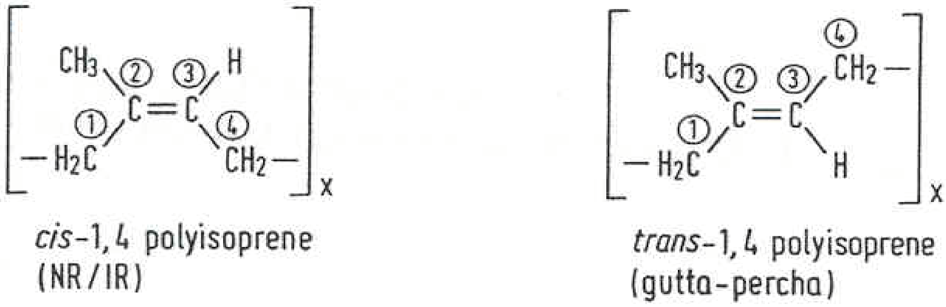


Figure 2.2 Structure of configurations of 1,4 polyisoprene [1]

NR is available in a variety of types and grades, including smoked sheet, air-dried sheet and pale crepes.

a) Compounding

NR compounds usually contain peptizers, carbon black or nonblack fillers or both, zinc oxide, fatty acids, processing aids, plasticizers, antioxidants, antiozonants, protective waxes and vulcanizing ingredients (usually sulphur, low sulphur or nonelemental sulphur vulcanizing systems; less frequently peroxides). NR can be blended with other diene rubbers such as Polyisoprene (IR), SBR and Butadiene rubber (BR).

b) Vulcanizate Properties

NR vulcanizates have high tensile strength over a wide hardness range. The high strength is due to crystallization of the polymer chains at high strains enabling NR to be used in unfilled compounds. Furthermore, NR vulcanizates have the highest resilience of all elastomers (except BR), which is responsible for very low heat buildup. Further advantages include low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear and fatigue. NR can be compounded for continuous use at 90^0C and for intermittent periods up to 100^0C. The vulcanizates remain flexible at temperatures down to -55^0C without adding plasticizers. However, they tend to crystallize readily when stored for long periods at low temperatures.

Like other unsaturated elastomers, NR vulcanizates are susceptible to attack by atmospheric ozone. However, the ozone and weather resistance can be improved by blending with a saturated rubber or by incorporating antiozonants and protective waxes in the compound. NR vulcanizates are not resistant to petroleum-based oils and fuels but they can be used with a wide range of organic and inorganic chemicals, such as nonpetroleum-based automotive brake fluids, silicone oils and greases; glycols; alcohols; water; and nonoxidizing aqueous solutions of acids, alkalis and salts.

c) Applications

NR elastomers remain the best choice for many applications that require low heat buildup, such as large tires, carcasses of passenger-car tires, vibration mounts, springs and bearings. Other products include hoses, conveyor belts, gaskets, seals, rolls, rubberized fabrics, elastic bands and pharmaceutical goods.

2.4 NBR/PVC Blends [1]

Medium and high nitriles give a homogeneous polymer phase with PVC. Some of these blends are commercially available. They usually contain 30% PVC. NBR/PVC vulcanizates have improved resistance to ozone, fire and swelling in mineral oils and hydrocarbon solvents. However, their use is restricted because of deficiencies in low-temperature flexibility and compression set resistance. Their main areas of application include hose covers, hose tubes and wire and cable covers.

It must also be pointed out that there are blends in which PVC predominates. In such blends, the rubber acts as a polymeric plasticizer for the PVC, which does not migrate and which improves properties such as cold flow and low-temperature flexibility.

2.5 Vulcanizing Ingredients [1]

As the name implies, vulcanizing ingredients are those chemicals, which are incorporated in order to insert cross-linking between the polymer chains when the compounded stock is heated to an appropriate temperature. Sulphur is the main vulcanizing agent for most crude rubbers that contain enough double bonds in their macromolecules. In order to increase the rate of vulcanization, it is necessary to add accelerators and activators. The combination of vulcanizing agent, accelerators and activators is frequently called the vulcanizing system.

Accelerators are compounding ingredients added in small amounts with a curing agent to increase the speed of vulcanization. Without accelerators, a vulcanization with sulphur usually requires several hours. By adding accelerators, the vulcanization time can be cut to minutes or seconds and in most cases the physical properties of the vulcanizates are also improved. At one time, basic oxides such as lime, litharge and magesia were widely used as accelerators. Today, accelerators are almost always organic compounds containing either nitrogen or sulphur or both. Very few accelerators, known as sulphur donors, such as tetramethylthiuram disulphide (TMD), can be used as vulcanizing agents without the addition of elemental sulphur. According to speed of action, accelerators are sometimes described as slow moderately fast, fast and ultra accelerators.

Activators are substances added in small proportions that increase the effectiveness of accelerators. The most widely used activators are zinc oxide and stearic acid.

Elemental sulphur has a cyclic structure consisting of rings composed of eight-sulphur atoms (S_8). It is generally accepted that vulcanization with elemental sulphur leads to cross-links of the type $R-S_x-R$, where R is the polymer macromolecule and x denotes the number of sulphur atoms in the cross-link. The resulting cross-links can have a monosulphide or a polysulphide structure, or both types, depending on the curing system used. However, not all the sulphur in the vulcanizing ingredient combines with the base rubber to form cross-links. Usually, a very small portion of sulphur, known as free sulphur, remains uncombined in the vulcanizate. It is extractable by acetone, whereas the combined sulphur in the cross-links cannot be removed by acetone extraction.

Conventional sulphur vulcanizing systems for soft rubber products consist of relatively high amounts of elemental sulphur (about 1-3 part per rubber (phr)) combined with a low concentration of accelerator(s). If the amount of sulphur is increased to 25-45 phr, a hard rubber, or ebonite, is formed (Figure 2.3).

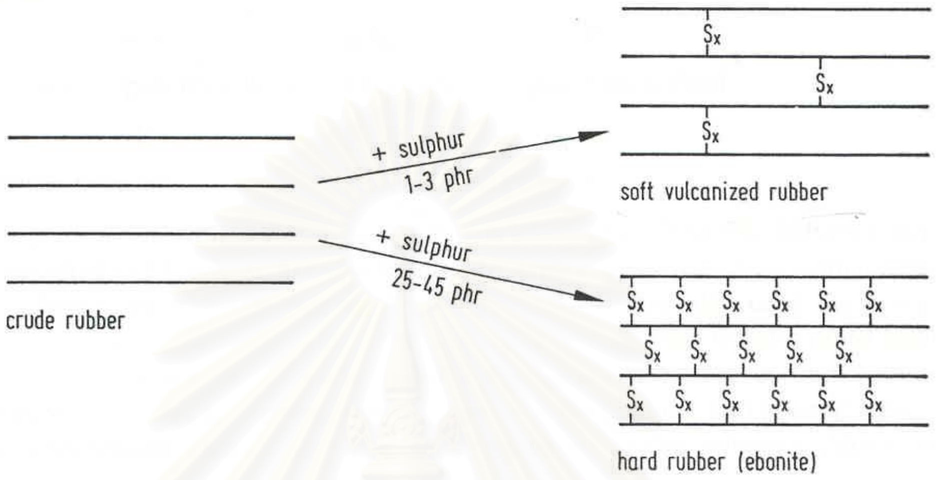


Figure 2.3 Sulphur cross-linking of highly unsaturated rubbers [1]

Low sulphur vulcanizing systems comprise a low concentration of elemental sulphur (usually 0.2-0.5 phr) and a high concentration of accelerator(s). Nonelemental sulphur vulcanizing systems consist mainly of sulphur donors that release atomic sulphur during the vulcanization. Both low sulphur and nonelemental sulphur vulcanization systems are frequently called efficient vulcanizing (EV) systems because they produce vulcanizates that resist aging at elevated temperatures, much more effectively than those cured by conventional sulphur vulcanizing systems.

It is generally accepted that the EV systems produce at optimum cure a network containing predominantly thermally stable monosulphide cross-links ($x=1$ in Figure 2.3). Once the vulcanization is complete, no sulphur is available for further cross-linking.

In contrast to EV systems, the conventional sulphur vulcanizing systems produce vulcanizates in which the combined sulphur exists predominantly in polysulphide cross-links. Such vulcanizates tend to harden excessively at elevated temperatures, possibly because sulphur is released from the polysulphide cross-links to form additional cross-links.

EV systems are much more expensive than the conventional sulphur vulcanizing systems because of the large amounts of sulphur donors used. Therefore, they are applied only when a maximum of heat resistance of the end product is required.

Saturated rubbers cannot be cross-linked by sulphur and accelerators because of the absence of double bonds in the polymer chains. They are usually vulcanized by organic peroxides, either alone or in the presence of other compounding ingredients known as co-agents or promoters. These substances, if used, are added to increase the efficiency of the organic peroxide.

Organic peroxides decompose at the vulcanization temperature and form free radicals (R•). These free radicals extract hydrogen atoms from the polymer chains (PH), forming RH and leaving polymer radicals (P•). Adjacent polymer radicals combine to form carbon to carbon cross-links (P-P). The mechanism can be illustrated as follows:

$$\underset{\text{free radical}}{R\bullet} \quad + \quad \underset{\text{polymer chain}}{PH} \quad \longrightarrow \quad \underset{\text{by-product}}{RH} \quad + \quad \underset{\text{polymer radical}}{P\bullet} \qquad (a)$$

$$\underset{\text{2 polymer radicals}}{P\bullet \quad + \quad \bullet P} \quad \longrightarrow \quad \underset{\text{cross-linked polymer}}{P\text{-}P} \qquad (b)$$

In contrast to sulphur, organic peroxides do not enter into the polymer network. Cross-links of this type are also formed by high-energy radiation using either gamma radiation or electron beams. Organic peroxides are also used for cross-linking of some unsaturated crude rubbers in applications that require good heat aging properties. Other sulphurless vulcanizing agents used for certain rubber types include, for instance, metal oxides, diamines, bisphenols and special resins. All these vulcanizing agents insert cross-linking between the polymer chains involved.

2.6 Reinforcement by Fillers [3]

The use of fillers in rubber is almost as old as the use of rubber itself. In 1939 the first reinforcing siliceous filler was introduced acalcium silicate prepared by wet precipitation from sodium silicate solution with calcium chloride. In further development of the process the calcium was leached out by hydrochloric acid to yield a reinforcing silica pigment of comparable particle size about ten year later direct precipitation of silica from sodium silicate solution has developed to a commercial process and this is a major process to day.

2.6.1 Reinforcement Concepts

The concept of reinforcement relates basically to composites built from two or more structural elements or components of different mechanical characteristics whereby the strength of one of these elements is imparted to the composite and combined with the set of favorable properties of the other component. Basically what has been done is to bond a loose network of strong, long members together by a high viscosity or solid matrix so that the members support each other.

A totally different mechanism must be responsible for the reinforcement imparted to elastomers by particulate solids which, although not actually spherical in shape, still are not sol strongly anisometric that they can be said to overlap each other over large proportions of their length. Nor are they actually so strong that they would be expected to impart additional strength to the composite. Furthermore, practically the sane flexibility as the matrix is maintained. A clear definition is required of reinforcement of vulcanized rubbers by fillers.

Therefore, the best definition is probably: *a reinforcing filler is a filler that improves the modulus and failure properties (tensile strength, tear resistance, and abrasion resistance) of the final vulcanizate.*

2.6.2 Basic Factors Influencing Elastomer Reinforcement

Figure 2.4 shows the increase of strength and energy at rupture obtained with carbon black as a function of loading. The appearance of an optimum loading indicates that there are two opposing factors in action when a reinforcing filler such as carbon black is added:

1. There is an improvement of modulus and tensile strength. This is very much dependent on the particle size of the filler; small particles have a much greater effect than coarse ones. Particle size is directly related to the reciprocal of surface are per gram of filler; thus the effect of smaller particles actually reflects their greater extent of interface between polymer and solid material.
2. The reduction in properties at higher loading is a dilution effect, general to all fillers, merely due to a diminishing volume fraction of polymer in the composite. If the volume percentage of filler becomes so high that there is not enough rubber matrix to hold the filler particles together, strength approaches zero. Before this stage of loading is reached, the compound attains a level of stiffness where it becomes brittle and, at the normal rate of testing (e.g. 50 cm per minute) such a brittle compound would show poor strength. At much lower rates of stretching the decline in strength with higher loading would be less; the height and place of the maximum in the strength vs. loading curve are rate dependent. The maximum occurs at higher loading when testing at slower rates. The place of the maximum is also dependent on the particle size of the filler.

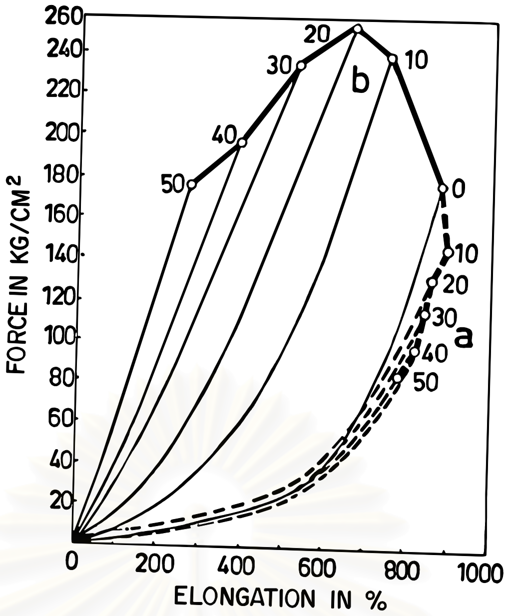


Figure 2.4 Stress-strain curves of basic compound of natural rubber with increasing volume % of (a) barytes, and (b) EPC black [3]

2.6.3 Typical Filler Characteristics

The action of particulate fillers on an elastomer is dependent on factors that can be classified as extensity, intensity, and geometrical factors. After a brief summary, they will be discussed in more detail below.

(a) The extensity factor is the total amount of surface area of filler per cm^3 of compound in contact with the elastomer.

(b) The intensity factor is the specific activity of this solid surface per cm^2 of interface, determined by the physical and chemical nature of the filler surface in relation to that of the elastomer.

(c) Geometrical factors are (1) the “structure” of the filler, determined by its void volume under standardized packing conditions, and (2) the porosity of the filler, usually a minor factor, which can be varied over a wide range with carbon blacks. Since the weight of individual spongy particles is lower than that of solid particles, the number of particles per cm^3 of compound at constant weight loading is greater.

2.6.4 Filler Characteristics and Vulcanizate Properties

Although rubber properties are interconnected and relate to the combination of all filler properties, a brief summary of the main influence of each of the four filler characteristics is given below:

1 *Smaller particle size* (larger external surface area) Results: higher tensile strength, higher hysteresis, higher abrasion resistance, higher electrical conductivity, and higher Mooney viscosity. Minor effects on extrusion shrinkage and modulus.

2 *Increase in surface activity* (physical adsorption) Results: higher modulus at the higher strains (300% up), higher abrasion resistance, higher adsorptive properties, higher ”bound rubber”, and lower hysteresis.

3 *Increase in persistent structure* (anisometry, bulkiness) Results: lower extrusion shrinkage, higher modulus at low and medium strains (up to 300%), higher Mooney viscosity, higher hysteresis, and longer incorporation time. Higher electrical conductivity and heat conductivity is found for higher structure blacks. This property is interrelated with surface activity, structure changes on fillers without surface activity (graphitised black) show the effects indicated above only rather faintly. At constant high activity, the structure effects are most pronounced.

4 *Porosity* Results: higher viscosity and higher electrical conductivity in the case of carbon blacks.

2.7. Sol-gel processing [4]

In the sol-gel process, the *precursors* (starting compounds) for preparation of a colloid consist of a metal or metalloid element surrounded by various ligands (appendages not including another metal or metalloid atom). The latter is an example of an alkoxide, the class of precursors most widely used in sol-gel research. A list of the most commonly used alkoxy ligands is presented in Table 2.1.

Table 2.1 Commonly used ligands [4]

Alkyl		Alkoxy	
methyl	$\bullet CH_3$	methoxy	$\bullet OCH_3$
ethyl	$\bullet CH_2CH_3$	ethoxy	$\bullet OCH_2CH_3$
n-propyl	$\bullet CH_2CH_2CH_3$	n-propoxy	$\bullet OCH_2CH_2CH_3$
iso-propyl	$H_3C(\bullet C)CH_3$	iso-propoxy	$H_3C(\bullet O)CHCH_3$
n-butyl	$\bullet CH_2(CH_2)_2CH_3$	n-butoxy	$\bullet O(CH_2)_3CH_3$
sec-butyl	$H_3C(\bullet C)CH_2CH_3$	sec-butoxy	$H_3C(\bullet O)CHCH_2CH_3$
iso-butyl	$\bullet CCH(CH_3)_2$	iso-butoxy	$\bullet OCH_2CH(CH_3)_2$
tert-butyl	$\bullet C(CH_3)_3$	tert-butoxy	$\bullet OC(CH_3)_3$

Metal alkoxides are members of the family of metalorganic compounds, which have an organic ligand attached to a metal or metalloid atom. The most thoroughly studied example is silicon tetraethoxide (or tetraethoxysilane, or tetraethyl orthosilicate, TEOS), $Si(OC_2H_5)_4$. Metal alkoxides are popular precursors because they react readily with water. The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the metal atom, as in the following reaction:

$$Si(OR)_4 + H_2O \rightarrow HO\text{-}Si(OR)_3 + ROH \qquad (2.1)$$

The R represents a proton or other ligand (if R is an alkyl, the •OR is an alkoxy group), and ROH is an alcohol; the bar (-) is sometimes used to indicate a chemical bond. Depending on the amount of water and catalyst present, hydrolysis may go to completion (so that all of the OR groups are replaced by OH),

$$Si(OH)_4 \quad + 4H_2O \;\rightarrow\; Si(OH)_4 \quad + \quad 4ROH \qquad (2.2)$$

or stop while the metal is only partially hydrolyzed, $Si(OR)_{4-n}(OH)_n$.

Two partially hydrolyzed molecules can link together in a condensation reaction, such as

$$(OR)_3Si\text{-}OH \;+\; HO\text{-}Si(OR)_3 \;\rightarrow\; (OR)_3Si\text{-}O\text{-}Si(OR)_3 \;+\; H_2O \qquad (2.3)$$

or

$$(OR)_3Si\text{-}OR \;+\; HO\text{-}Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH \qquad (2.4)$$

By definition, condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon containing molecules by the process of polymerization.

2.8 Hydrolysis and Condensation of Silicon Alkoxides [4]

Silicon is the most abundant metal in the earth’s crust, and evidence of silicate hydrolysis and condensation to from polysilicate gels and particles are seen in many natural systems. For, example, precious opal is composed of amorphous silica particles glued together by a lower-density silicate gel.

2.8.1 General Trends

Silicate gels are most often synthesized by hydrolyzing monomeric, tetrafunctional alkoxide precursors employing a mineral acid (e.g., HCl) or base (e.g., NH_3) as a catalyst. At the functional group level, three reactions are generally use to describe the sol-gel process:

$$\equiv Si-OR + H_2O \underset{\text{esterification}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} \equiv Si-OH + ROH \qquad (2.5)$$

$$\equiv Si-OR + HO-Si\equiv \underset{\text{alcoholysis}}{\overset{\text{alcohol condensation}}{\rightleftharpoons}} \equiv Si-O-Si\equiv + ROH \qquad (2.6)$$

$$\equiv Si-OH + HO-Si\equiv \underset{\text{hydrolysis}}{\overset{\text{water condensation}}{\rightleftharpoons}} \equiv Si-O-Si\equiv + H_2O \qquad (2.7)$$

where R is an alkyl group, C_xH_{2x+1}. Under most condition, condensation commences (Eqs. 2.6 and 2.7) before hydrolysis (Eq. 2.5) is complete. Because water and alkoxysilanes are immiscible (see, for example, Figure 2.5), a mutual solvent such as alcohol is normally used as a homogenizing agent. However, gels can be prepared from silicon alkoxide water mixtures without added solvent, since alcohol produced as the by-product of the hydrolysis reaction is sufficient to homogenize the initially phase separated system.

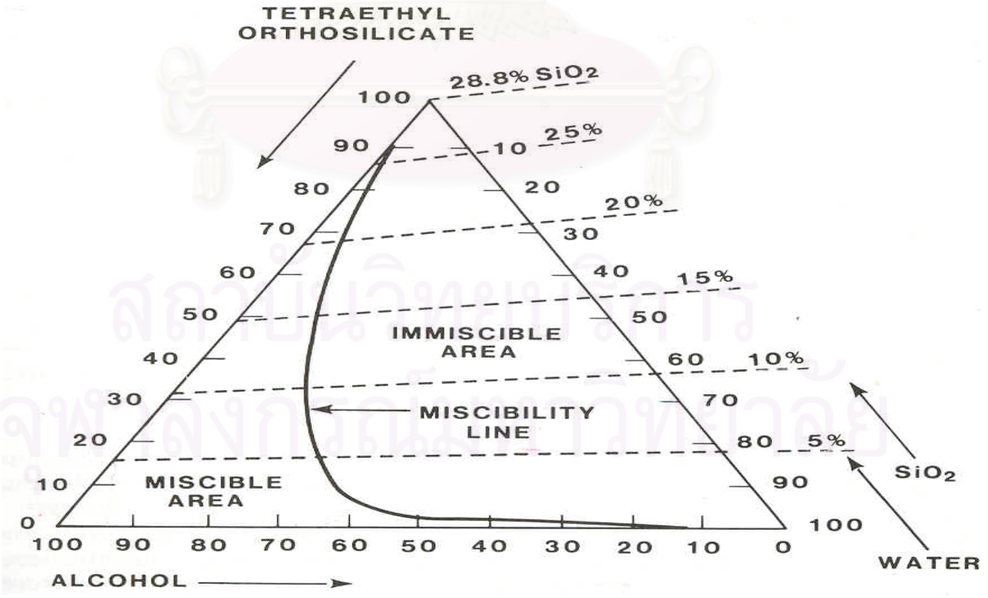


Figure 2.5 TEOS, H_2O, Synasol (95%EtOH, 5%Water) ternary-phase diagram at 25^0C. For pure ethanol the miscibility line is shifted slightly to the right [4]

2.8.2 Precursor Molecules

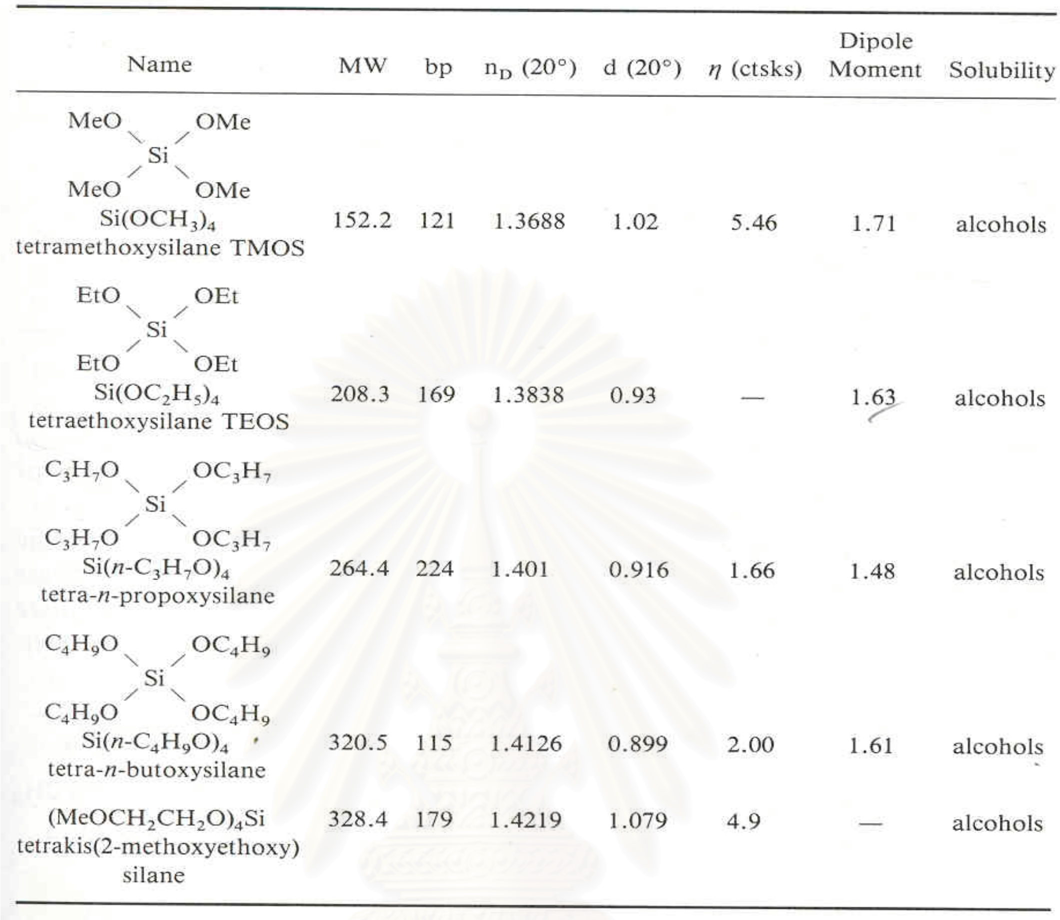
The most common tetraalkoxysilanes used in the sol-gel process are tetraethoxysilane ($Si(OC_2H_5)_4$) and tetramethoxysilane ($Si(OCH_3)_4$), which are abbreviated in the literature as TEOS and TMOS, respectively. Table 2.2 lists the formulae and properties of several tetraalkoxysilanes used in sol-gel processing.
Silicate gels have also been synthesized using oligomeric precursors. Ethyl Silicate 40 is a commercial form of ethoxypolysiloxane (ethyl polysilicate) that results when the ethanol used in the production of TEOS contains some water (industrial spirit). In practice, reaction conditions are chosen that give on ignition SiO_2 equivalent to 40wt%, which corresponds to a mixture of ethoxysiloxanes with an average of five silicon atoms per oligomer.

2.8.3 Hydrolysis

Hydrolysis occurs by the nucleophilic attack of the oxygen contained in water on the silicon atom as evidenced by the reaction of isotopically labeled water with TEOS that produces only unlabelled alcohol in both acid- and base- catalyzed systems:

$$\text{Si-OR} + \text{H}\,^{18}\text{OH} \leftrightarrow \text{Si-}\,^{18}\text{OH} + \text{ROH} \qquad (2.9)$$

Table 2.2 Physical properties of typical tetraalkoxysilanes [4]



Name	MW	bp	n_D (20°)	d (20°)	η (ctsks)	Dipole Moment	Solubility
Si(OCH$_3$)$_4$ tetramethoxysilane TMOS	152.2	121	1.3688	1.02	5.46	1.71	alcohols
Si(OC$_2$H$_5$)$_4$ tetraethoxysilane TEOS	208.3	169	1.3838	0.93	—	1.63	alcohols
Si(n-C$_3$H$_7$O)$_4$ tetra-n-propoxysilane	264.4	224	1.401	0.916	1.66	1.48	alcohols
Si(n-C$_4$H$_9$O)$_4$ tetra-n-butoxysilane	320.5	115	1.4126	0.899	2.00	1.61	alcohols
(MeOCH$_2$CH$_2$O)$_4$Si tetrakis(2-methoxyethoxy) silane	328.4	179	1.4219	1.079	4.9	—	alcohols

Hydrolysis is facilitated in the presence of homogenizing agents (alcohols, dioxane, tetrahydrofuran (THF), acetone, etc.) that are especially beneficial in promoting the hydrolysis of silanes containing bulky organic or alkoxy ligands, such as phenylphenoxysilane, which, when neat (undiluted), remains unhydrolyzed upon exposure to water vapor. It should be emphasized, however, that the addition of solvents may promote esterification or depolymerization reactions according to the reverse of Eqs. 2.5 and 2.6.

a) Effects of Catalysts

Hydrolysis is most rapid and complete when catalysts are employed. Although mineral acids or ammonia are most generally used in sol-gel processing, other known catalysts are acetic acid, KOH, amines, KF, HF, titanium alkoxides, and vanadium alkoxides and oxides. Many authors report that mineral acids are more effective catalysts than equivalent concentrations of base. However, neither the increasing acidity of silanol groups with the extent of hydrolysis and condensation (acidic silanols may neutralize basic catalysts) nor the generation of unhydrolyzed monomers via base-catalyzed alcoholic or hydrolytic depolymerization processes have generally been taken into account.

b) Steric and Inductive Effects

Steric (spatial) factors exert the greatest effect on the hydrolytic stability of organoxysilanes. Any complication of the alkoxy group retards the hydrolysis of alkoxysilanes, but the hydrolysis rate is lowered the most by branched alkoxy groups.

Substitution of alkyl groups for alkoxy groups increases the electron density on the silicon. Conversely, hydrolysis (substitution of OH for OR) or condensation (substitution of OSi for OR or OH) decreases the electron density on silicon.

Inductive effects are evident from investigations of the hydrolysis of methylethoxysilanes, $(CH_3)_x(C_2H_5O)_{4-x}Si$ where x varies from 0 to 3. Under acidic (HCl) conditions, the hydrolysis rate increases with the degree of substitution, x, of electron-providing alkyl groups, whereas under basic $(NH)_3$ conditions the reverse trend is clearly observed. The consistent acceleration and retardation of hydrolysis with increasing x under acidic and basic conditions, respectively, suggests that the hydrolysis mechanism is sensitive to inductive effects and (based on the consistent trends) is apparently unaffected by the extent of alkyl substitution. Because increased stability of the transition state will increase the reaction rate, the inductive effects are evidence for positively and negatively charged transition states or intermediates under acidic and basic conditions, respectively.

c) H_2O: Si Ratio, *r*

The hydrolysis reaction has been performed with *r* value ranging from < 1 to over 25 depending on the desired polysilicate product, for example, fibers, bulk gels, or colloidal particles. From Eq. 2.5, an increased value of *r* is expected to promote the hydrolysis reaction. Although increased values of *r* generally promote hydrolysis, when *r* is increased while maintaining a constant solvent: silicate ratio, the silicate concentration is reduced. This in turn reduces the hydrolysis and condensation rates, causing an increase in the gel time. This effect is evident in Figure 2.6 which shows gel times for acid-catalyzed TEOS systems as a function of *r* and the initial alcohol: TEOS molar ratio.

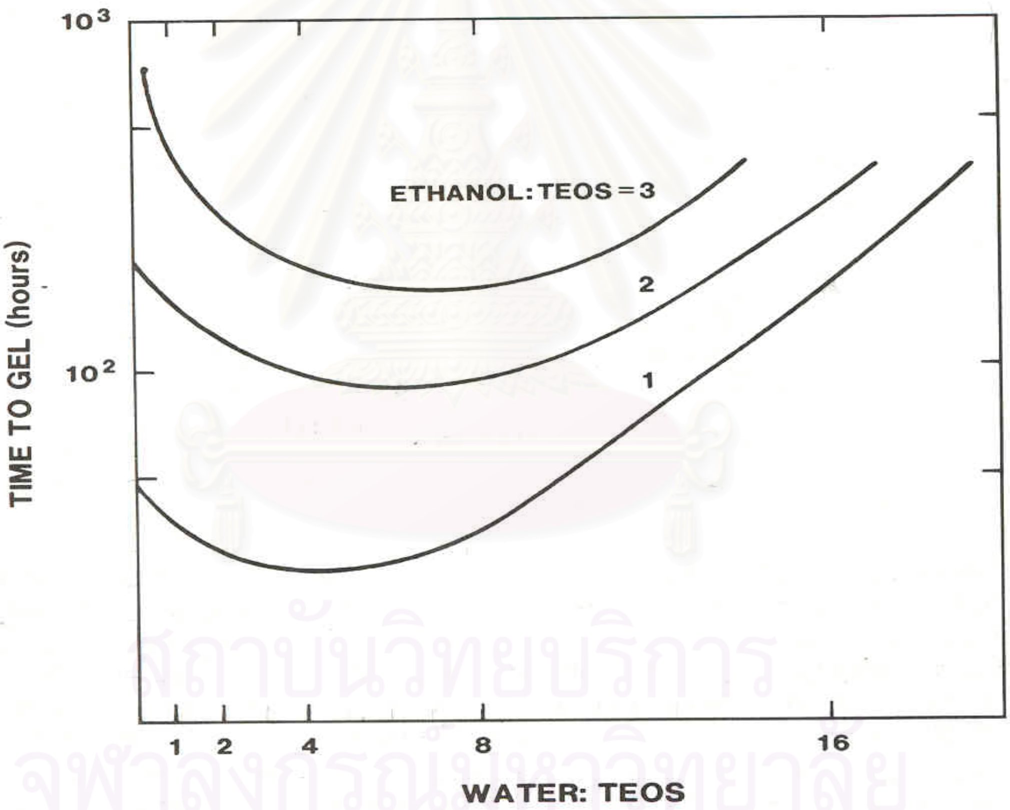


Figure 2.6 Gel times versus H_2O : TEOS ratio, r, for three ratios of EtOH to TEOS [4]

As indicated by the alcohol-water-TEOS, ternary-phase diagram shown in Figure 2.5, large values of *r* cause liquid-liquid immiscibility; however both alcohol produced as the by-product of the hydrolysis reaction and partial hydrolysis of the TEOS precursor lead to homogenization. Finally, because water is the by-product of the condensation reaction (Eq. 2.7), large values of *r* promote siloxane bond hydrolysis (the reverse of Eq. 2.7).

d) Solvent Effects

Solvents are added to prevent liquid-liquid phase separation during the initial stages of the hydrolysis reaction (Figure 2.5 shows the region of immiscibility in the TEOS-H_2O-ROH ternary system) and to control the concentrations of silicate and water that influence the gelation kinetics. More recently, the effects of solvents have been studied primarily in the context of drying control chemical additives (DCCA) used as cosolvents with alcohol in order to facilitate rapid drying of monolithic gels without cracking.

Solvents may be classified as polar or nonpolar and as protic (containing a removable or “labile” proton) or aprotic. Physical properties of some common solvents used in sol-gel processing are listed in Table 2.3. With regard to solvating power, several important characteristics of solvents are (1) polarity, (2) dipole moment, and (3) the availability of labile protons.

Table 2.3. Physical properties of typical solvents [4]

	MW	bp	ρ	n_D	ε	η	μ
Protic							
water(H_2O)	18.01	100.0	1.000	1.333	78.5	10.1	1.84
methanol(CH_3OH)	32.04	64.5	0.791	1.329	32.6	5.4	1.70
ethanol (C_2H_5OH)	46.07	78.3	0.785	1.361	24.3	10.8	1.69
2-ethoxyethanol ($C_4H_{10}O_2$)	90.12	135	0.93	1.408	-	-	2.08
formamide(CH_3ON)	45.04	193	1.129	1.448	110	33.0	3.7
Aprotic							
dimethylformamide (C_3H_7NO)	73.10	152	0.945	1.430	36.7	7.96	3.86
dioxane 1,4($C_4H_8O_2$)	88.12	102	1.034	1.422	2.21	10.87	0
tetrahydrofuran (C_4H_8O)	72.12	66	0.889	1.405	7.3	-	1.63

bp : ^{0}C. n_D : 20^0. η : millipoise.

ρ : g/cm^3 at 20^{0}C. Dielectric constant, ε : at 25^{0}C.

Dipole moment, μ : debyes.

2.8.4 Condensation

Polymerization to form siloxane bonds occurs by either an alcohol-producing condensation reaction (Eq. 2.6) or a water-producing condensation reaction (Eq. 2.7).

a) Effects of Catalysts

In sol-gel systems mineral acids, ammonia, alkali metal hydroxides, and fluoride anions are most commonly used. As discussed in the section on hydrolysis, the understanding of catalytic effects is often complicated by the increasing acidity of silanol groups with the extent of hydrolysis and polymerization, and by the effects of reverse reactions that become increasingly important with greater concentrations of water and /or base.

b) Steric and Inductive Effects

During sol-gel processing, condensation can proceed by two different reactions (Eqs. 2.6 and 2.7) that can occur between substantially different solution species (monomers, oligomers, etc.), which have undergone different extents of hydrolysis. Therefore, steric and inductive effects are not well documented for tetraalkoxides. By the researches, the condensation rate of triorganosilanols decreased with increase in the length or branching of the chain of the alkyl radical, or, if aromatic groups are present, with increase in their number. And the condensation rate increases with an increase in the number of silanols on the silicon atom (increasing silanol acidity).

c) Effects of Solvent

Solvent effects have been primarily evaluated in the context of drying control chemical additives added to facilitate the rapid drying of monolithic gels without cracking. Solvents (or additives) may be either protic or aprotic and may vary in their polarity. (See Table 2.3) Depending on the pH, either protonated or deprotonated silanols are involved in the condensation mechanism. Because protic solvents hydrogen bond to nucleophilic deprotonated silanols and aprotic solvents hydrogen bond to electrophilic protonated silanols, protic solvents retard base-catalyzed condensation and promote acid-catalyzed condensation. Aprotic solvents have the reverse effect.

2.8.5 Drying

The process of drying of a porous material can be divided into several stages. At first the body shrinks by an amount equal to the volume of liquid that evaporates, and the liquid-vapor interface remains at the exterior surface of the body. The second stage begins when the body becomes too stiff to shrink and the liquid recedes into the interior, leaving air-filled pores near the surface. Even as air invades the pores, a continuous liquid film supports flow to the exterior, so evaporation continues to occur from the surface of the body. Eventually, the liquid becomes isolated into pockets and diffusion of the vapor to the outside.

2.9 Literature Review

K. E. George, et al. [5] studied on NBR/PVC blends. Studies conducted on butadiene-acrylonitrile copolymer (NBR)/poly(vinyl chloride)(PVC) blends at different brabender temperatures indicate that an optimum temperature exists for the formation of a particular blend. The mechanical properties of the blends confirm this observation. PVC stabilizer based on magnesium oxide, zinc oxide, and stearic acid was found to be very useful in NBR/PVC blends.

K. E. George, et al. [6] studied modification of butadiene-acrylonitrile rubber/poly(vinyl chloride)blend using natural rubber, styrene-butadiene rubber and polybutadiene rubber. The natural, styrene-butadiene and polybutadiene rubber were used to replace part of the butadiene acrylonitrile rubber in a 70/30 butadiene-acrylonitrile rubber/poly(vinyl chloride) blend. Such replacement up to 15% of the total weight of the blend improved the mechanical properties, while decreasing the cost of the blend. Styrene-butadiene rubber could replace butadiene-acrylonitrile rubber up to 30% of the total weight of the blend without deterioration in the mechanical properties.

S.-H. Zhu, et al. [7] studied mechanical properties of PVC/SBR blends compatibilized by acrylonitrile-butadiene rubber and covulcanization. The mechanical properties of poly(vinyl chloride) (PVC)/ styrene-butadiene rubber (SBR) blends compatibilized by acrylonitrile-butadiene rubber (NBR). A sulphur curing system was employed to crosslink the rubber of the blends. In the case of the blends without any curing agents, an increase in NBR content did not improve the tensile strength and elongation-at-break. However, a significant improvement in the mechanical properties was observed when NBR was added as a compatibilizer and the blend was vulcanized. In the PVC/NBR/SBR (50/10/40) blends the tensile strength and elongation-at break increased with an increase in sulphur concentration. This improvement was attributed to covulcanization between NBR and SBR. The fracture toughness of PVC/NBR/SBR (50/10/40) blends was characterized by the critical strain energy release rate, G_c. In the case of the PVC/NBR-2a/SBR (50/10/40) blend, an increase in sulphur concentration resulted in a dramatic increase in G_c. However, the G_c value of PVC/NBR-40/SBR (50/10/40) blends decreased with an increase in sulphur concentration owing to the brittle behavior of one of the blend components the PVC/NBR-40 (50/10) phase.

Y. Ikeda, and S. Kohjiya [8] studied in situ formed silica particles in rubber vulcanizate by the sol-gel method. In situ silica filling of butadiene rubber (BR) was carried out by the sol-gel process using tetraethoxysilane (TEOS). BR was sulphur-cured, and the resultant crosslinked BR was subjected to soaking in TEOS at 30^0C for 48 h. The swollen vulcanizates were kept in the aqueous solution of n-butylamine at 30^0C for 24 h, followed by standing at 50^0C for 72 h to conduct the in situ sol-gel reaction of TEOS. The resultant vulcanizates contained silica particles, which were prepared by the in situ filling technique. They were subjected to tensile and dynamic mechanical measurement, differential scanning calorimetry and transmission electron microscopic observation. The in situ formed silica was dispersed homogeneously in the rubber matrix. The size of in situ silica was influenced by the crosslinking density, probably because it was formed in the crosslinked rubber networks. Compared to the conventional silica-filled BR vulcanizate, which was prepared by mechanical mixing of the silica particles, the new vulcanizates with the in situ formed silica showed better mechanical properties.

H. Tanahashi, et al. [9] studied reinforcement of acrylonitrile-butadiene rubber by silica generated in situ. In situ silica reinforcement was applied to the acrylonitrile-butadiene rubber (NBR) vulcanizates. The amount of in situ silica introduced in the NBR vulcanizates was limited due to the high polarity of NBR. The presence of γ-mercaptopropyltrimethoxysilane (γ-MPS) in the NBR vulcanizate increased the conversion of TEOS in the sol-gel reaction and resulted in the higher amount of in situ silica compared to the system without γ-MPS. The obtained silica was very fine and dispersed very homogeneously. In situ sol-gel reaction of TEOS in the NBR vulcanizates mixed with a conventional silica (VN-3) was also carried out. The reinforcement efficiency in this system increased with the increase of the amount of mechanically mixed conventional silica. Interestingly, the hysteresis loss decreased by the in situ filling of silica.

S. Kohjiya, and Y. Ikeda [10] studied reinforcement of natural rubber by silica generated in situ. The new method to produce in situ silica in natural rubber (NR) matrix was developed for a NR/silica composite material, and the good reinforcement effect of the silica was observed on the NR vulcanizate. The silica was generated by the sol-gel reaction of tetraethoxysilane before crosslinking, which gave a homogeneous dispersion of in situ-generated silica particles in the NR matrix. This method is expected to be an industrially practical technique. It is estimated that the concentration of silanol groups on the silica surface were smaller than those on the conventional silica surface. Therefore, the silica-silica interaction of in situ silica seems to be weaker than that of silica-rubber to result in better dispersion compared with the conventional silica. The results suggest that NR which is a renewable resource and in situ silica composite has much potential as a “green” material and a useful system for studying the reinforcement mechanism of inorganic filler onto NR.

S. Kohjiya, and Y. Ikeda [11] studied reinforcement of general-purpose grade rubbers by silica generated in situ. The use of the sol-gel process on general-purpose grade rubbers is reviewed in the absence or presence of silane coupling agents. The sol-gel reactions of tetraethoxysilane (TEOS) in epoxidized natural rubber (ENR), styrene-butadiene rubber (SBR) or butadiene rubber (BR) vulcanizates produced silica generated in situ. This silica was found to be a good reinforcing agent by investigating tensile and dynamic mechanical properties and morphology observation by transmission electron microscopy (TEM). The amount of silica formed was limited by the degree of swelling of the rubber vulcanizate by TEOS, which was the precursor of the silica. However, the dispersion of silica generated in situ was better than conventionally added silica due to its formation in place. Also, it was noted that the diameter distribution of in situ silica was monodispersed. Silane coupling agents, such as mercaptosilane, aminosilane, and bis(3-triethoxysilylpropyl) tetrasulphide, were compounded in the vulcanizates and their effects on silica generated in situ were evaluated. Their effects were significant. The dispersion of the silica in the rubbery matrix became better and the particle size became smaller and monodispersed, as observed by TEM, which improved mechanical properties.

Y. Ikeda, et al. [12] studied reinforcement of styrene-butadiene rubber vulcanizate by in situ silica prepared by the sol-gel reaction of tetraethoxysilane. In situ silica reinforcement of styrene-butadiene rubber (SBR) has been achieved by a sol-gel process using tetraethoxysilane (TEOS). SBR was sulphur-cured and the sol-gel reaction of TEOS was carried out in TEOS or in a TEOS-tetrahydrofuran (THF) mixture. The in situ silica was filled homogeneously in the rubber matrix and the size of the in situ silica was influenced by the cross-linking density of the SBR vulcanizate. n-Butylamine was effective for the method using TEOS only, whereas both hydrochloric acid and n-butylamine worked as catalysts under the experimental conditions using THF for the in situ polymerization of TEOS in the SBR vulcanizate. From the viewpoint of the reinforcement of in situ silica and the size stability of the SBR vulcanizate, the method using only TEOS was found to be better than the mixture system. This conclusion was based on the results of tensile tests, dynamic mechanical measurements, optical and transmission electron microscopies.

Y. Ikeda, et al. [13] studied effect of catalyst on in situ silica reinforcement of styrene-butadiene rubber vulcanizate by the sol-gel reaction of tetraethoxysilane. In situ silica reinforcement of styrene-butadiene rubber (SBR) vulcanizate has been achieved by a sol-gel reaction of tetraethoxysilane (TEOS) using n-butylamine as a catalyst. SBR was vulcanized with sulphur and soaked in TEOS and in an aqueous solution of the catalyst. When hydrochloric acid was used as a catalyst for the sol-gel reaction, silica particles were not introduced into the SBR matrix in this study. The increase of the dynamic modulus and tensile strength at break was considered to be due to the interaction between the rubber and the in situ silica filler in the SBR vulcanizate.

Y. Kazumasa, et al. [14] studied silica reinforcement of synthetic diene rubbers by sol-gel process in the latex. Styrene-butadiene rubber (SBR) and nitrile rubber (NBR) were reinforced with silica by the sol-gel method of tetraethoxysilane (TEOS) in latex. The sol-gel reaction proceeded in the mixture of latex, TEOS, water, and a catalyst. The compound that involved silica was crosslinked with the curing agent at 150^0C. The amount of TEOS added and the molar ratio of TEOS to water ([H_2O]/ [TEOS]) in the mixture were related the silica content in the compounds, particle size, and reinforcing behavior of silica. The paticle size and reinforcing behavior of the silica were greatly in fluenced by the amount of TEOS and [H_2O]/[TEOS]. The diameter of the dispersed silica particles in cured rubbers was controlled by the amount of TEOS and [H_2O]/[TEOS], which were smaller than 100 nm. By the dispersion of the fine silica in the nanometer-order level, the tensile strength of the compound was drastically improved. The tensile strength of SBR was over 30 MPa, and of NBR, over 25 MPa. Compounds with a high tensile strength had a high bound rubber fraction and a very strong interaction of the fine silica with rubber.

CHAPTER III

APPARATUS AND EXPERIMENTAL

3.1 Chemicals

1.	Acrylonitrile-butadiene rubber (NBR)	:Bayer (Thailand) Co., Ltd.
	Bound Acrylonitrile (%)	32.4
	Mooney viscosity ML(1+4), 100^{0}C	31
	Volatiles content (%)	0.26
	Ash content	0.61
2.	Natural rubber (NR, STR5L)	:TECK BEE HANG Co., Ltd.
	Dirt, retained on 46 aperture (%Wt)	0.009
	Ash (%Wt)	0.24
	Volatile matter (%Wt)	0.20
	Nitrogen (%Wt)	0.30
3.	Poly(vinyl chloride) (PVC)	:Thai Plastic&Chemical Co., Ltd.
	K-value	58
	Bulk density	0.54
	% Volatile matter	0.50
	Polymerization degree(P)	720
4.	Tetraethoxysilane (TEOS)	:Fluka
5.	Ethyl polysilicate (EPS)	:Silbond Co., Ltd.
6.	Ethylenediamine	:Fluka
7.	Ethanol (AR grade)	:Fluka
8.	Tetrahydrofuran (AR grade)	:Fluka
9.	Zinc oxide (white seal)	:Unithaioxide Co., Ltd.
10.	Stearic acid	:Imperial (Thailand)Co., Ltd.
11.	Magnesium dioxide	:Unithaioxide Co., Ltd.
12.	N-cyclohexyl-2-benzothiazyl sulphenamide (CBS)	:Flexsys Co., Ltd.
13.	Tetramethyl thiuramdisulphide (TMTD)	:Flexsys Co., Ltd.
14.	Sulphur	:Loxley Public Co., Ltd.
15.	Silica (Hi-Sil®255-S)	:PPG Siam Silica Co., Ltd.

pH (5% Suspension)	6.9
Moisture (as packed) (%)	5.5
Na_2SO_4 (%)	1.17
Bulk density (g/cm^3)	0.250
Surface area (m^2/g)	177

3.2 Apparatus

1. Two-roll mill: diameter 8×20 inches.
2. Compression molding machine: 30×30 cm and 150 kg/cm^2.
3. Compression air sample cutter.
4. Capillary rheometer.
5. Mooney viscometer.
6. Rheometer (moving die type).
7. Tensile testing machine.
8. Scanning electron microscopy.

3.3 Procedure

3.3.1 Preparation of the Silica-Filled Rubber Compound by the Sol-Gel Method

a) The Effect of Dilution Ratio of Ethanol/Distilled water/Tetrahydrofuran and TEOS and EPS/Rubber Mass Ratio on NR and NBR Swelling

5 g of NR and NBR was subjected to the tight milling to prepare the sheet of ca. 1.5 and 7 mm thickness, respectively. The NR and NBR sheet were immersed in 50 ml of TEOS and EPS solution (see Table 3.1, 3.2) at room temperature for 24 h. Then, the swollen sample was weighed and the degree of swelling in solution was calculated. The amounts of TEOS and EPS were ten time the mass of the rubber sample. The degree of swelling was calculated from equation 3.1.

$$\text{Degree of swelling in TEOS or EPS (\%)} = 100[(M_1-M_2)/M_2] \qquad (3.1)$$

where M_1 was the mass of sample after swelling and M_2 was the mass of sample before swelling.

b) The Temperature and Time of Drying

5 g of NR and NBR was subjected to the tight milling to prepare the sheet of ca. 1.5 and 7 mm thickness, respectively. The NR and NBR sheet were immersed in 50 ml of TEOS and EPS solution (from section 3.3.1a) at room temperature for 24 h and soaked in 50 ml of ethylenediamine aqueous solution at 40^0C for 24 h. Then, the samples were placed in air for 24 h and dried at 40, 50, 60, 70^0C under a reduced pressure until ready to weigh the sample. The amount of ethylenediamine concentration used was 5% of TEOS and EPS concentrations.

Table 3.1 Formulation of sol-gel process in NR case

Experiment	EtOH/H_2O(v/v)	TEOS/Rubber (w/w)	EPS/Rubber (w/w)
1	H_2O 100%	5/1	5/1
2	1/3.4	10/1	10/1
3	1/1.2	30/1	30/1
4	1/0.5	50/1	50/1
5	EtOH 100%	-	-

Table 3.2 Formulation of sol-gel process in NBR case

Experiment	EtOH/H_2O (v/v)	EtOH/H_2O/THF (v/v)	TEOS/Rubber (w/w)	EPS/Rubber (w/w)
1	H_2O 100%	THF 100%	5/1	5/1
2	1/3.4	1/3.4/3.4	10/1	10/1
3	1/1.2	1/3.4/1.2	30/1	30/1
4	1/0.5	1/3.4/0.5	50/1	50/1
5	EtOH 100%	1/3.4/0	-	-

c) The Effect of Catalyst Concentration and Soaking Time

20 g of NR and NBR was subjected to the tight milling to prepare the sheet of ca. 1.5 and 7 mm thickness, respectively. The NR and NBR sheet were immersed in 200 ml of TEOS and EPS solution (from section 3.3.1a) at room temperature for 24 h and soaked in 200 ml of ethylenediamine aqueous solution at 40^0C for 24 h. Then, the samples were placed in air for 24 h and dried under a reduced pressure (from section 3.3.1b) The amount of ethylenediamine concentration used was 1-5 % of TEOS or EPS concentration. Then, thermogravimetric analysis (TGA) was employed to calculate the silica content (%) and conversion (%). The silica content (%) and conversion (%) was calculated from equation 3.2-3.3.

$$\text{Silica content (\%)} = 100(M_3/M_4) \tag{3.2}$$

$$\text{Conversion of TEOS and EPS (\%)} = 100(M_3/M_5) \tag{3.3}$$

where M_3 was the mass of silica in the sample and M_4 was the mass of the sample. M_4 was the mass of in situ generated silica in the sample, which was estimated by the results of TGA. M_5 was the imaginary mass of silica in the sample assuming quantitative conversion of TEOS or EPS into silica by the sol-gel reaction, which calculated from the mass of TEOS or EPS in the swollen sample.

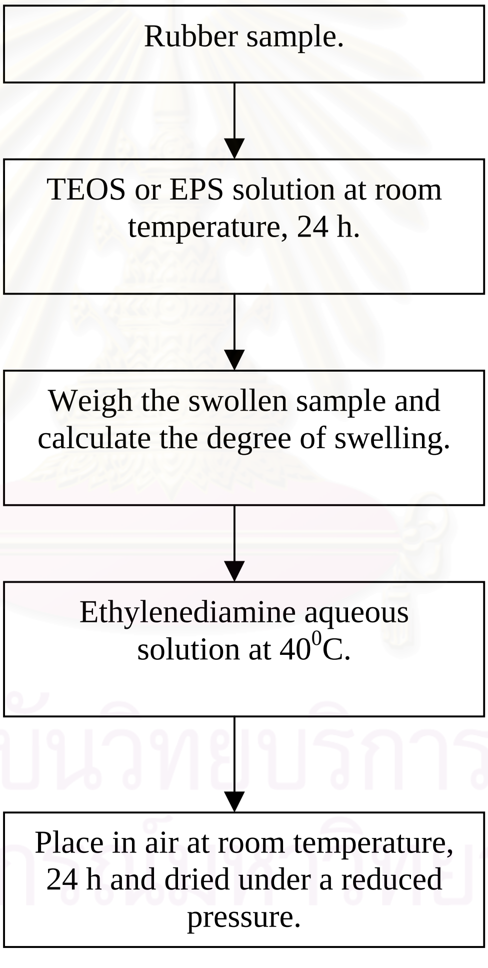


Figure 3.1 The overall schematic silica-filled rubber compound by the sol-gel method

3.3.2 Preparation of Polymer NBR/PVC/NR Blend

First, the roll of two-roll mill was heated to 160^{0}C for NBR/PVC blend, 70^{0}C for NBR/PVC/NR blend and maintained at this temperature.

a) NBR/PVC Blend

Steps of polymer blending is as follows:

at 0 min: The NBR was transferred to two-roll mill.
at 3 min: The PVC and stabilizers were added.
at 13 min: The polymer blend sheet of ca. 1 mm thickness was removed and placed at room temperature.

b) NBR/PVC/NR Vulcanizate (Recipe 1,4 and 5)

Steps of polymers compounding are as follows:

at 0 min: The NBR/PVC (from section 3.3.2a) (Recipe 1,4) and NR (Recipe 5) was transferred to two-roll mill.
at 3 min: The silica powder was added. (Recipe 4)
The ZnO and stearic acid. (Recipe 1)
at 5 min: The NBR/PVC (from section 3.3.2a) was transferred to two-roll mill.(Recipe 5)
The TMTD and CBS were added. (Recipe 1)
at 7 min: The sulphur was added. (Recipe 1)
at 8 min: The ZnO and stearic acid were added. (Recipe 4)
at 10 min: The TMTD and CBS were added. (Recipe 4)
at 12 min: The sulphur was added. (Recipe 4)
The NBR/PVC vulcanizate (Recipe 1) was removed and placed at room temperature.
at 15 min: The silica powder was added. (Recipe 5)

at 17 min: The silica-filled NBR/PVC vulcanizate (Recipe 4) was removed and placed at room temperature.

at 20 min: The ZnO and stearic acid were added. (Recipe 5)

at 22 min: The TMTD and CBS were added. (Recipe 5)

at 24 min: The sulphur was added. (Recipe 5)

at 29 min: The silica-filled NBR/PVC/NR vulcanizate (Recipe 5) was removed and placed at room temperature.

c) The In Situ Silica-Filled NBR/PVC/NR Vulcanizate (Recipe 2,3,6 and 7)

NR and NBR was subjected to the tight milling to prepare the sheet of ca. 1.5 and 7 mm thickness, respectively. The NR and NBR sheet were immersed in 300 ml of TEOS and EPS solution (used TEOS and EPS solution from recipe 2 and 3 in case of recipe 6 and 7) at room temperature for 48 h and soaked in 300 ml of ethylenediamine aqueous solution at 40^0C for 48 h. Then, the samples were placed in air for 24 h and dried under a reduced pressure at 40^0C, 60^0C for 48 h, respectively. The amount of TEOS and EPS were seven time the mass of the rubber sample and amount of ethylenediamine concentration used was 5% of TEOS and EPS concentrations. Then, thermogravimetric analysis (TGA) was employed to calculate the silica content (%) and conversion (%).

The roll of two-roll mill was heated to 70^0C and maintained at this temperature. Steps of polymer compounding (a) are as follows:

at 0 min: The in situ silica-filled NBR (Recipe 2,3) and NR (Recipe 6,7) was transferred to two-roll mill.

at 3 min: The PVC and stabilizers were added. (Recipe 2,3)

at 5 min: The in situ silica-filled NBR was transferred to two-roll mill.(Recipe 6,7)

at 8 min: The ZnO and stearic acid were added. (Recipe 2,3)
The PVC and stabilizers were added. (Recipe 6,7)

at 10 min: The TMTD and CBS were added. (Recipe 2,3)

at 11 min: The ZnO and stearic acid was added. (Recipe 6,7)

at 12 min: The sulphur was added. (Recipe 2,3) at 13 min: The TMTD and CBS were added. (Recipe 6,7)

at 15 min: The sulphur was added. (Recipe 6,7)

at 17 min: The in situ silica-filled NBR/PVC vulcanizate (Recipe 2,3) was removed and placed at room temperature.

at 20 min: The in situ silica-filled NBR/PVC/NR vulcanizate (Recipe 6,7) was removed and placed at room temperature.

Table 3.3 Recipe for the polymer blend

Plasticizer	**Parts per hundred (phr) parts of PVC**
MgO	4.0
ZnO	4.0
Stearic acid	3.0

Rubber and chemical	**Recipe in phr of Rubber compound**								
	1 NBR/PVC	**2** NBR^a/PVC	**3** NBR^b/PVC	**4** NBR/PVC/Si	**4’** NBR/PVC/Si	**5** NBR/PVC/NR/Si	**5’** NBR/PVC/NR/Si	**6** NBR^a/PVC/NR^a	**7** NBR^b/PVC/NR^b
NBR	70	70^a	70^b	70	70	60	60	60^a	60^b
PVC	30	30	30	30	30	30	30	30	30
NR	-	-	-	-	-	10	10	10^a	10^b
ZnO	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Steric acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Silica powder	-	-	-	20	7	20	7	-	-

Subscript a : in situ silica-filled rubber of TEOS.

b : in situ silica-filled rubber of Ethyl polysilicate.

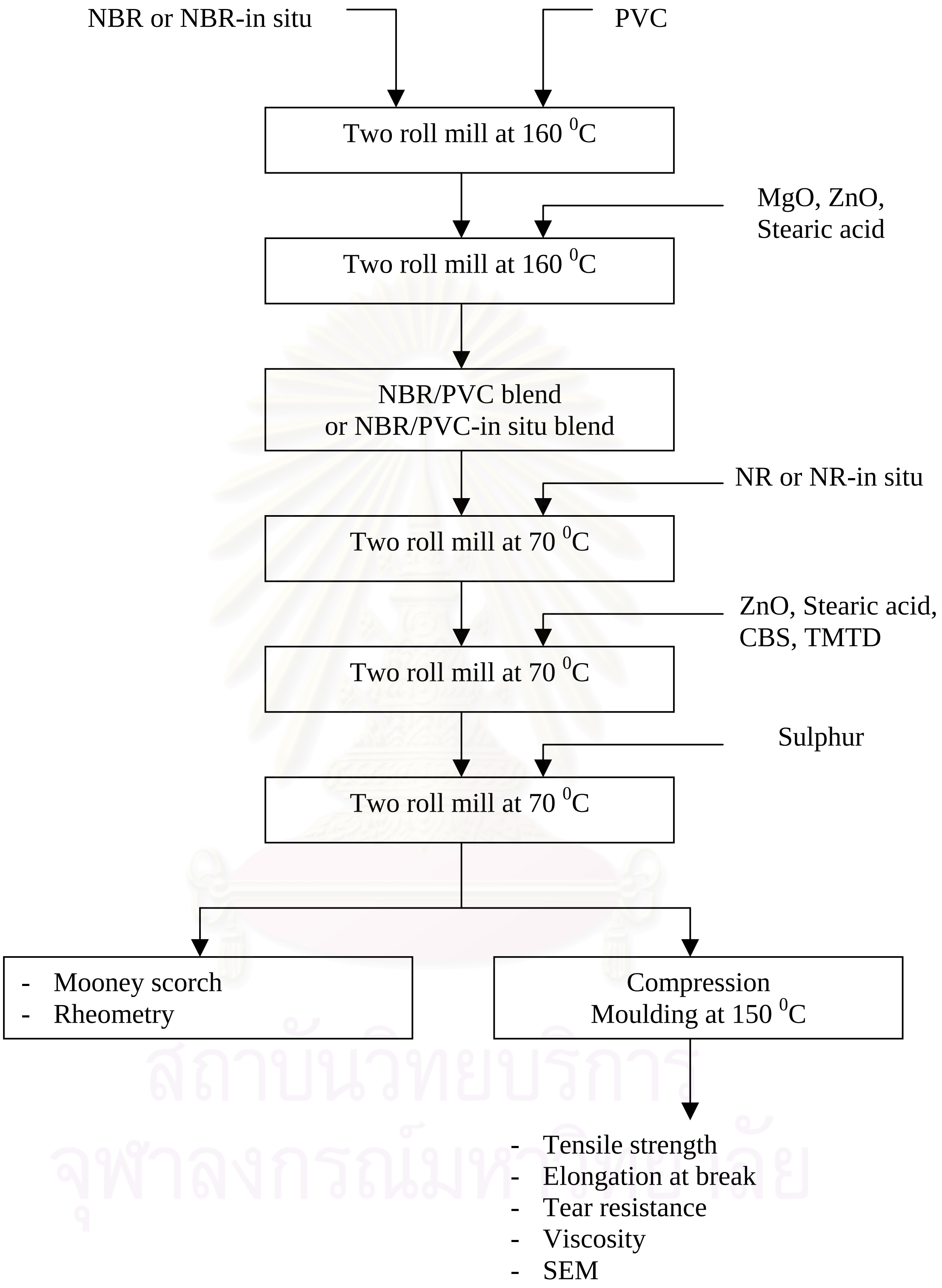


Figure 3.2 The overall schematic diagram of preparation of silica-filled polymer blends vulcanizate

3.4 Material Characterization of the Rubber with and without Silica [1]

3.4.1 Thermogravimetry (ASTM D5805) [1]

Thermogravimetric analysis (TGA) was carried out by using a NETZSCH STA 409C. A sample was prepared by blending 20 g of dried sample by passing it 10 times between the rolls of a laboratory mill. The roll temperature was maintained at 50± 5^0C and a distance between the rolls of 0.5 ± 0.13 mm. Approximately 2 g of the blended thinly sheeted material was dried for 1 h in the oven at 100 ± 5^0C. The dried sheet was kept in a desiccator until ready to weigh the samples. A dried sample (ca. 20 mg) was placed in a platinum pan and heated under air to 900^0C at a temperature increase of 20 ^{0}C/min. The silica contents of polymer vulcanizates were determined from the results of TGA by Equation (3.2). The conversion of TEOS and EPS into silica by the sol-gel reaction was evaluated by using equation (3.3).

3.4.2 Degree of Swelling of TEOS or EPS [9]

The degree of swelling of the sample was followed by soaking in TEOS or Ethyl polysilicate. The degree of swelling in solution was calculated using equation (3.1).

3.4.3 Scanning Electron Microscopy [2]

The samples were prepared by freeze cutting in liquid nitrogen. The obtained cross section was subjected to the scanning electron microscopy (SEM) using a S-4100 instrument of Hitachi Ltd. The accelerating voltage was 15 kV.

3.4.4 Mechanical Tests [2]

a) Tensile Test (ASTM D412) [2]

Specimen was Die C as illustrated in Figure 3.3. The crashed speed of universal testing machine at 100 mm/min was used. The test condition was at 27±2^{0}C. An average of five specimens was considered as representative value. The gage length was 2.50 cm and the thickness of specimen was 2 mm.

$$\text{Tensile stress} = F/A \tag{3.4}$$

F = Tensile force (N)

A = Cross section area (m^2)

Tensile at break = N/m^2(Pascal) or MPa(1 MPa = 10^6Pascal)

Tensile at break is tensile stress at which the specimen ruptures

$$\text{Modulus at 100\% elongation} = F_1/A \tag{3.5}$$

$$\text{Modulus at 300\% elongation} = F_3/A \tag{3.6}$$

F_1 = Tensile force at 100% elongation (N)

F_3 = Tensile force at 300% elongation (N)

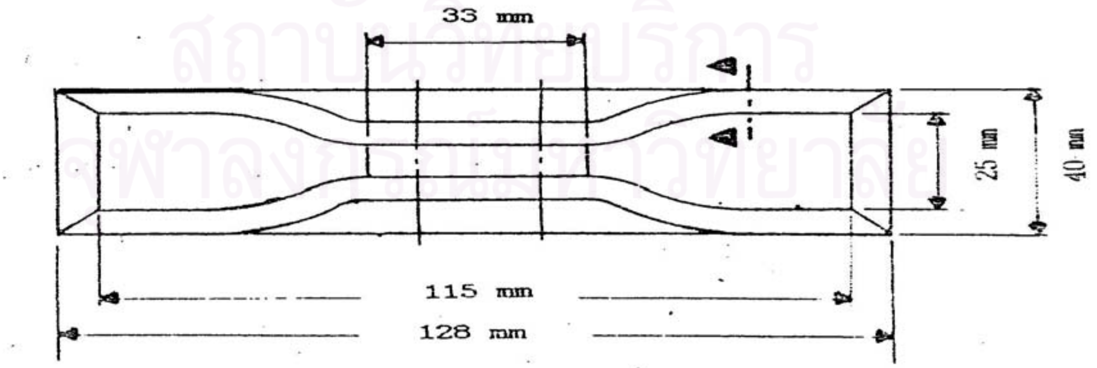


Figure 3.3 Tensile specimen Die C [1]

b) Tear Test (ASTM D624) [1]

Dimension and shape of specimen was die C cut followed to Figure 3.4. A crushed speed of the universal testing machine at 500 ± 50 mm/min was used. The test temperature was at 27 ± 2^0C. An average of five specimens was considered as representative value. The thickness of specimen was 2 mm.

Calculation to tear resistance is as follows:

$$T_s = F/d \qquad (3.7)$$

T_s = Tear resistance (kN/m or N/mm)
F = Force (N)
d = Specimen thickness (mm)

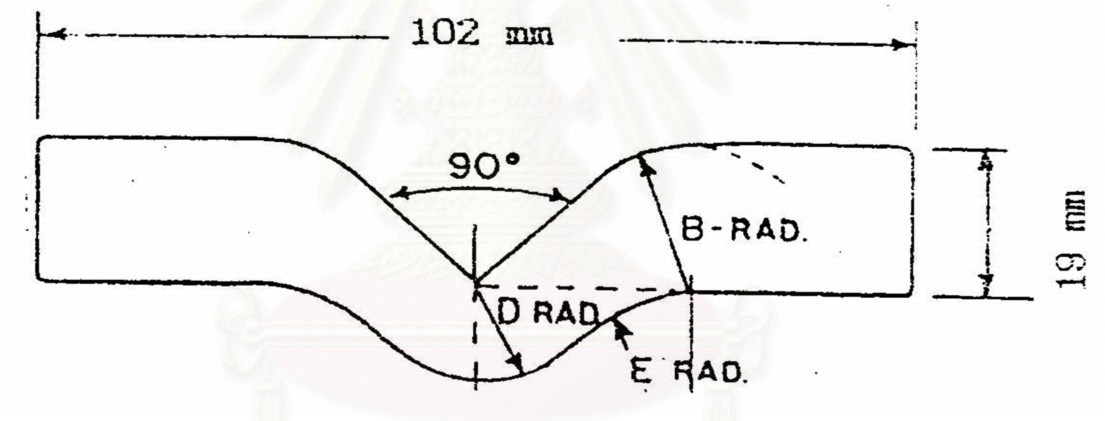


Figure 3.4 Tear specimen Die C [1]

c) Rheometer (ASTM D2705) [2]

This test method measured the cure time of rubber vulcanizated. Test specimen size was1.5 cm×1.5 cm × 5 mm. The test temperature was 30 min at 150^0C.

d) Scorch Time [2]

The scorch time was measured when the torque curve increased from the minimum torque in two units (such as 2 lb.-in). Test specimen size was 20 g, 6 cm diameter and 5 mm thickness. The test temperature was 121 ^{0}C.

e) Capillary Rheometer (ASTM D5099) [3]

These test methods cover the use of a capillary rheometer for the measurement of the flow properties of thermoplastic elastomers, unvulcanized rubber and rubber compounds. The viscosity of rubber compounds was measured on a Capillary rheometer (Figure 3.5) at 100 ^{0}C.

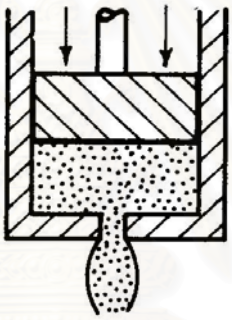


Figure 3.5 Capillary rheometer [3]

CHAPTER IV

RESULTS & DISCUSSION

The in situ silica filling using the sol-gel reaction of tetraethoxysilane (TEOS) or Ethyl polysilicate (EPS) has been focused as a novel technique to reinforce the rubber vulcanizate. The reaction of TEOS or EPS takes place in two steps, the hydrolysis and the condensation reaction, to produce SiO_2. This sol-gel process has been noted for the preparation of inorganic glasses at lower temperature [13]. The sol-gel system of TEOS and EPS was used to initiate the silica-filled in situ rubber. The effects of dilution ratio of initiator, mass ratio of TEOS/rubber or EPS/rubber, drying temperature, catalyst concentration, time for soaking in catalyst on sol-gel process were investigated.

4.1 The Effect of TEOS/Rubber and EPS/Rubber Mass Ratio

The effects of TEOS/rubber and EPS/rubber mass ratios on degree of swelling are shown in Figure 4.1a-b and Table 4.1. The parameters of sol-gel process are as follows:

- weight of rubber : 5 g
- dilution ratio of TEOS solution in NR case (v/v), TEOS:H_2O = 1:(2.7-36) : H_2O 100%
- dilution ratio of TEOS solution in NBR case (v/v) TEOS:(EtOH/H_2O) = 1:(2.7-36) : EtOH/H_2O (1/3.4)
- dilution ratio of EPS solution in NR case (v/v) EPS:H_2O = 1:(3.2-40) : H_2O 100%
- dilution ratio of EPS solution in NR case (v/v) EPS:EtOH = 1:(3.2-40) : EtOH 100%
- volume of TEOS and EPS : 50 ml
- time for soaking in TEOS and EPS solution : 1 day
- temperature for soaking in TEOS and EPS solution : room temperature

Degree of swelling is illustrated in Figure 4.1a-b and Table 4.1. For NR, The degree of swelling in TEOS increased with increasing amount of TEOS. This can be explained that, the TEOS can diffuse well (compatible) into NR due to the non-polar structure of TEOS and NR. However, the degree of swelling in EPS slightly increased with increasing amount of EPS. This can be explained that, 1) EPS is partially soluble in water with phase separation, 2) the EPS have mono-, di-, tri- and polymer structure and the chain sizes of EPS are larger than that of TEOS. Thus, the degree of swelling of NR in EPS is lower than in TEOS.

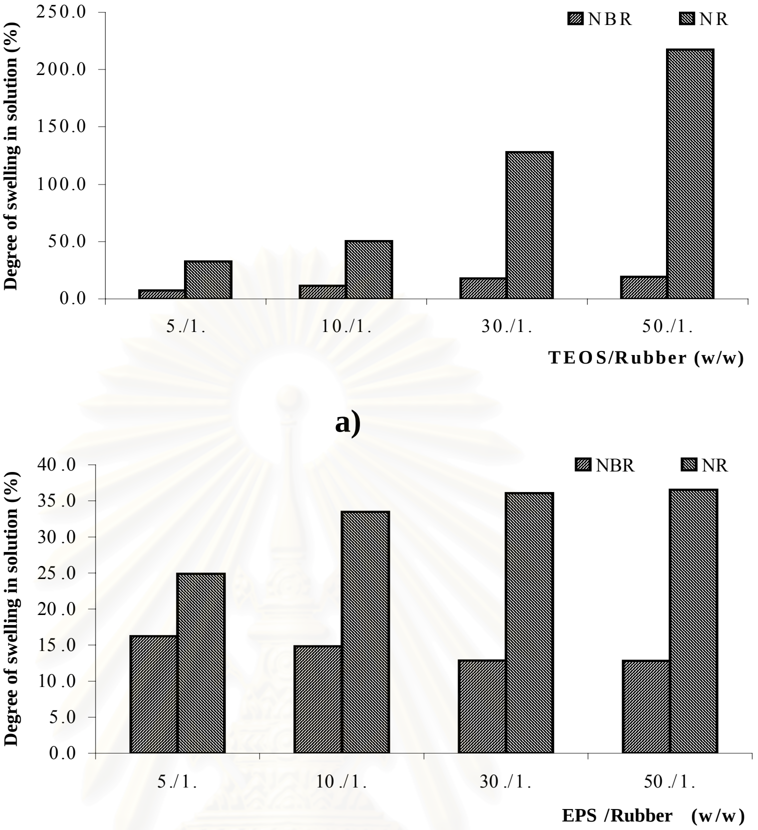
For NBR, the degree of swelling slightly increased with increasing amount of TEOS and EPS. The reason is that, TEOS and EPS poorly diffuse in NBR and the NBR is polar rubber but TEOS and EPS are nonpolar solvents.

For NR, the appropriate TEOS/rubber and EPS/rubber mass ratio are found to be 10/1 for TEOS and EPS. At this condition, the degree of swelling of NR for TEOS and EPS are 50.4 and 33.5, respectively. The high degree of swelling of NR in TEOS is found to be at mass ratio of 50/1 but at mass ratio greater than 10/1, the silica did not well disperse on rubber surface.

For NBR, the appropriate of TEOS/rubber and EPS/rubber mass ratio are found to be 10/1 for TEOS and EPS. At this condition, the degree of swelling of NBR for TEOS and EPS are 11.2 and 14.8, respectively.

Table 4.1 Effect of mass ratio of solvent/rubber on degree of swelling

Solvent/Rubber	**Solvent/Rubber Ratio (w/w)**	**Degree of swelling in solution (%)**	
		NR	**NBR**
TEOS/Rubber	5/1	32.4	7.5
	10/1	50.4	11.2
	30/1	128.0	18.0
	50/1	217.2	19.4
EPS/Rubber	5/1	24.9	16.2
	10/1	33.5	14.8
	30/1	36.1	12.9
	50/1	36.6	12.8



a)

b)

Figure 4.1 Effect of mass ratio of a) TEOS/Rubber b) EPS/Rubber on degree of swelling

4.2 The Effect of Dilution Ratio of Ethanol/Distilled water/Tetrahydrofuran

The effects of dilution ratio of ethanol/distilled water/tetrahydrofuran on degree of swelling in solution (TEOS or EPS) are shown in Figure 4.2a-c and Table 4.2. The parameters of sol-gel process are as follows:

- weight of rubber : 5 g
- amount of TEOS and EPS per rubber (w/w) : 10/1
- volume of TEOS and EPS : 50 ml
- time for soaking in TEOS and EPS solution : 1 day
- temperature for soaking in TEOS and EPS solution : room temperature

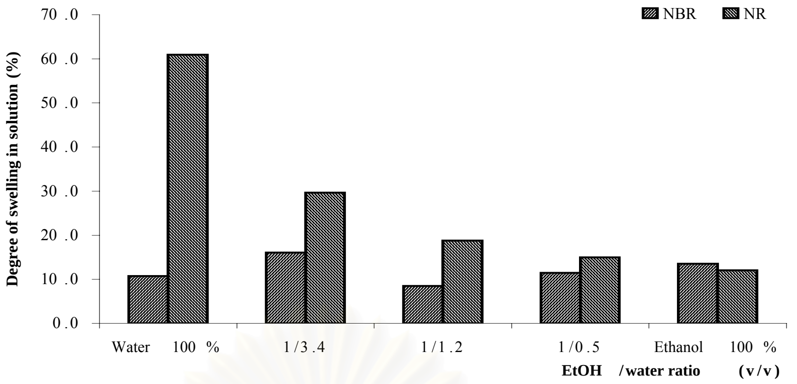
Degree of swelling is illustrated in Figure 4.2a-c and Table 4.2. For NR, the degree of swelling decreased with increasing ethanol content. This can be explained that in the hydrolysis reaction, the TEOS is completely soluble in distilled water with no phase separation and flocculation. But EPS is partially soluble in distilled water with phase separation. Therefore, the distilled water can generate $Si(OH)_4$ species which are formed on rubber surface for both TEOS and EPS.

For NBR, the degree of swelling increased with increasing amount of THF. The results indicate that swelling of NBR in THF is high because of the high diffusion of TEOS and EPS into the rubber networks. The degree of swelling of NBR was very high (ca. 227 and 282 %) when compared with that of NR (ca. 70 and 32 %). The important factor, which determine the degree of swelling of the NBR is the solubility of NBR in solution. Therefore, the high polarity of NBR and THF are responsible for the high swelling of the NBR in TEOS and EPS. The amount of silica-incorporated in the NR and NBR is primarily determined by the degree of swelling in TEOS and EPS, which is only limiting factor in the present sol-gel reaction. Therefore, the use of polar solvent such as tetrahydrofuran is the advantage for polar rubber e.g. NBR.

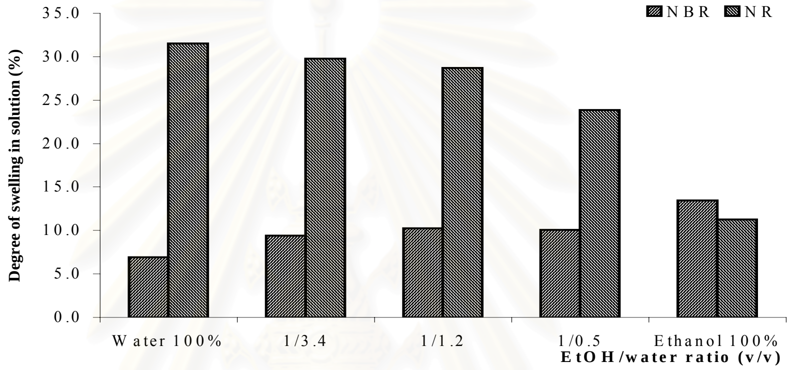
For NR, the appropriate dilution ratios of TEOS and EPS which give the high degree of swelling are found to be the distilled water (100 %). At this condition, the degree of swelling of NR for TEOS and EPS are 70 and 31.5, respectively. For NBR, the appropriate dilution ratios of TEOS and EPS are found to be the THF (100%). At this condition, the degree of swelling of NBR for TEOS and EPS are 227 and 282.2, respectively.

Table 4.2 Degree of swelling in TEOS or EPS at different diluted ratio

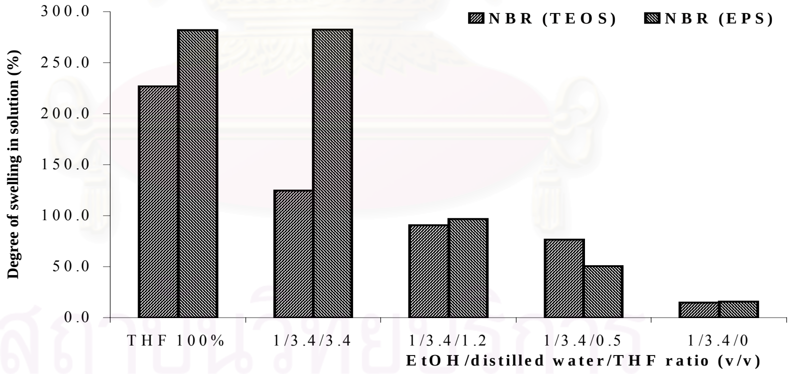
EtOH/H_2O/THF (v/v)	**Degree of swelling in TEOS of NR (%)**	**Degree of swelling in EPS of NR (%)**	**Degree of swelling in TEOS of NBR (%)**	**Degree of swelling in EPS of NBR (%)**
H_2O 100%	70.0	31.5	10.8	6.9
1/3.4/0	29.7	29.8	16.1	9.4
1/1.2/0	18.8	28.7	8.5	10.2
1/0.5/0	15.0	23.9	11.4	10.1
EtOH 100%	12.0	11.2	13.5	13.5
THF 100%	-	-	227.0	282.2
1/3.4/3.4	-	-	124.7	282.6
1/3.4/1.2	-	-	90.4	96.7
1/3.4/0.5	-	-	76.4	50.4
1/3.4/0	-	-	14.7	15.6



a)



b)



c)

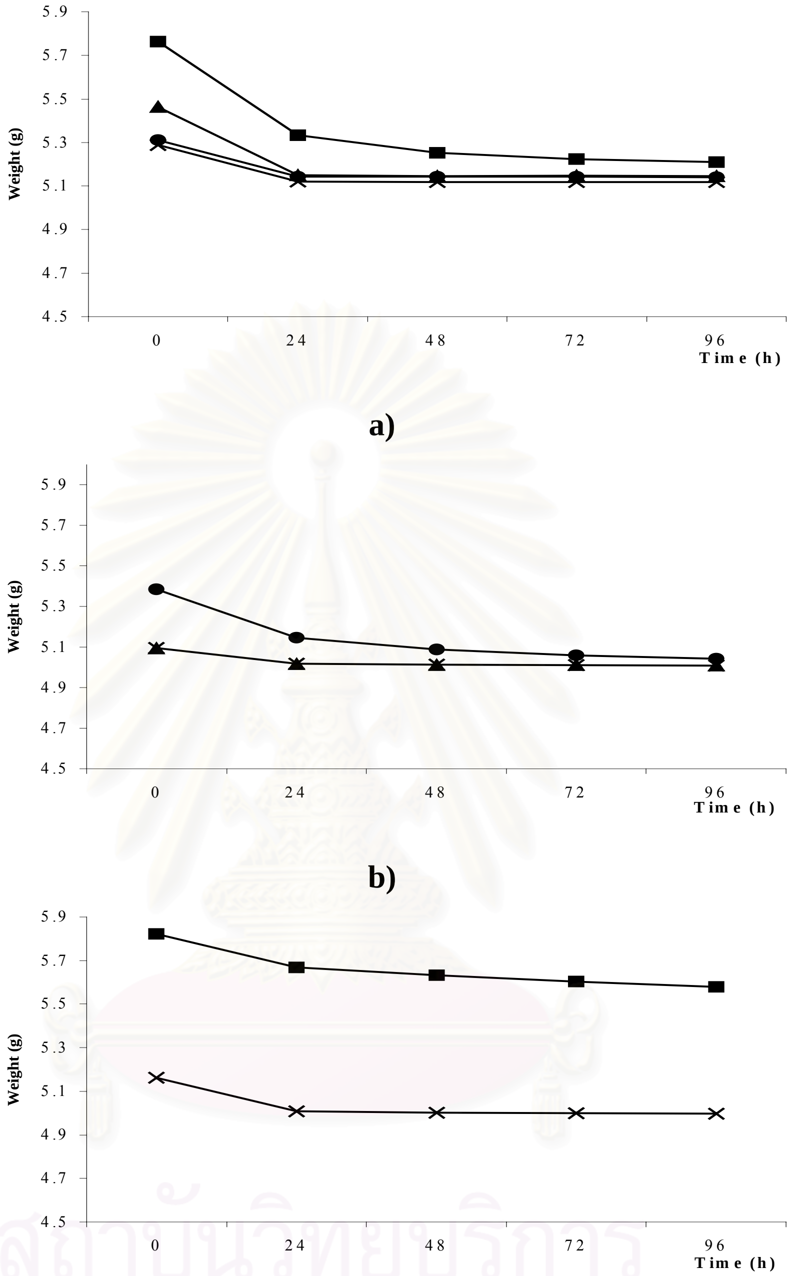
Figure 4.2 Effect of ethanol/distilled water/ THF ratio (v/v) on degree of swelling of a) NBR and NR in TEOS, b) NBR and NR in EPS and c) NBR in TEOS and EPS

4.3 The Effect of Temperature and Time of Drying

The effect of temperature and time of drying of the rubbers are shown in Figure 4.3a-c. The parameters of sol-gel process are as follows:

- weight of rubber : 5 g
- amount of TEOS and EPS per rubber (w/w) : 10/1
- dilution ratio of TEOS solution in NR case (v/v) : H_2O 100%
- dilution ratio of TEOS solution in NBR case (v/v) : EtOH/H_2O (1/3.4)
- dilution ratio of EPS solution in NR case (v/v) : H_2O 100%
- dilution ratio of EPS solution in NR case (v/v) : EtOH 100%
- volume of TEOS and EPS : 50 ml
- time for soaking in TEOS and EPS solution : 1 day
- temperature for soaking in TEOS and EPS solution : room temperature
- catalyst concentration (per TEOS or EPS concentration) : 5%
- volume of catalyst : 50 ml
- temperature and time for soaking in catalyst : 40^0C, 24h

The weight of rubber as a function of time at various temperatures (40-70^0C) are illustrated in Figure 4.3a-c. For NR and NBR, the appropriate temperature and time are found to be at 40^0C, 48 h and 60^0C, 48 h, respectively. It can be noted that, the high temperature and short time can cause the gel break of sol-gel process. Therefore, the slow drying rate is employed for the control of rubber weight. Finally, the constant rubber weight refers that the solvent is completely removed from rubber sample.



a)

b)

c)

Figure 4.3 Temperature and time of reduced vacuum drying of a) NR in TEOS b) NBR in TEOS and c) NR and NBR in EPS: (■) 40^{0}C; (•) 50^{0}C; (×) 60^{0}C; and (▲) 70^{0}C

4.4 Effect of Soaking Time in Catalyst

The effect of soaking time in catalyst on silica content and conversion of TEOS and EPS are shown in Table 4.3. The parameters of sol-gel process are as follows:

- weight of rubber : 20 g
- amount of TEOS and EPS per rubber (w/w) : 10/1
- dilution ratio of TEOS solution in NR case (v/v) : H_2O 100%
- dilution ratio of TEOS solution in NBR case (v/v) : THF 100%
- dilution ratio of EPS solution in NR case (v/v) : H_2O 100%
- dilution ratio of EPS solution in NR case (v/v) : THF 100%
- volume of TEOS and EPS : 200 ml
- time for soaking in TEOS and EPS solution : 1 day
- temperature for soaking in TEOS and EPS solution : room temperature
- catalyst concentration (per TEOS or EPS concentration) : 5%
- volume of catalyst : 200 ml
- temperature and time for soaking in catalyst : 40^0C

Silica content and conversion are illustrated in Table. 4.3. For NR, the appropriate time for soaking in catalyst is found to be 24 h for TEOS and EPS. It can be noted that, time does not affect silica content and conversion because the hydrolysis and condensation reaction can reach equilibrium in 24 h.

For NBR, the appropriate time for soaking in catalyst is found to be 24 h for TEOS and EPS. It can be noted that, time does not affect silica content and conversion for TEOS and affect slightly for EPS.

Table 4.3 Effect of time for soaking in catalyst on silica content and conversion of rubber.

Rubber	Solvent	Time for soaking (day)	Silica content (%)	Conversion (%)
NR	TEOS	4	13.9	22.69
		6	13.3	22.49
	Ethyl polysilicate	4	9.3	72.84
		6	7.9	61.41
NBR	TEOS	1	4.7	6.35
		6	3.1	6.26
	Ethyl polysilicate	1	7.3	7.19
		6	9.2	12.45

4.5 Effect of Aqueous Ethylenediamine Concentration

The effect of aqueous ethylenediamine concentration on silica content and conversion of TEOS and EPS are shown in Figure 4.4a-b and Table 4.4. The parameters of sol-gel process are as follows:

- weight of rubber : 20 g
- amount of TEOS and EPS per rubber (w/w) : 10/1
- dilution ratio of TEOS solution in NR case (v/v) : H_2O 100%
- dilution ratio of TEOS solution in NBR case (v/v) : THF 100%
- dilution ratio of EPS solution in NR case (v/v) : H_2O 100%
- dilution ratio of EPS solution in NR case (v/v) : THF 100%
- volume of TEOS and EPS : 200 ml
- time for soaking in TEOS and EPS solution : 1 day
- temperature for soaking in TEOS and EPS solution : room temperature
- volume of catalyst : 200 ml
- temperature and time for soaking in catalyst : 40^0C, 24h

In this study, the ethylenediamine is used as catalyst for sol-gel process. Silica content and conversion are illustrated in Figure 4.4a-b and Table 4.4. For NR, the appropriate aqueous ethylenediamine concentration for TEOS and EPS are found to be 3 and 1%, respectively. At this condition, the silica content for TEOS and EPS are 14.2 and 4.7 %, respectively.

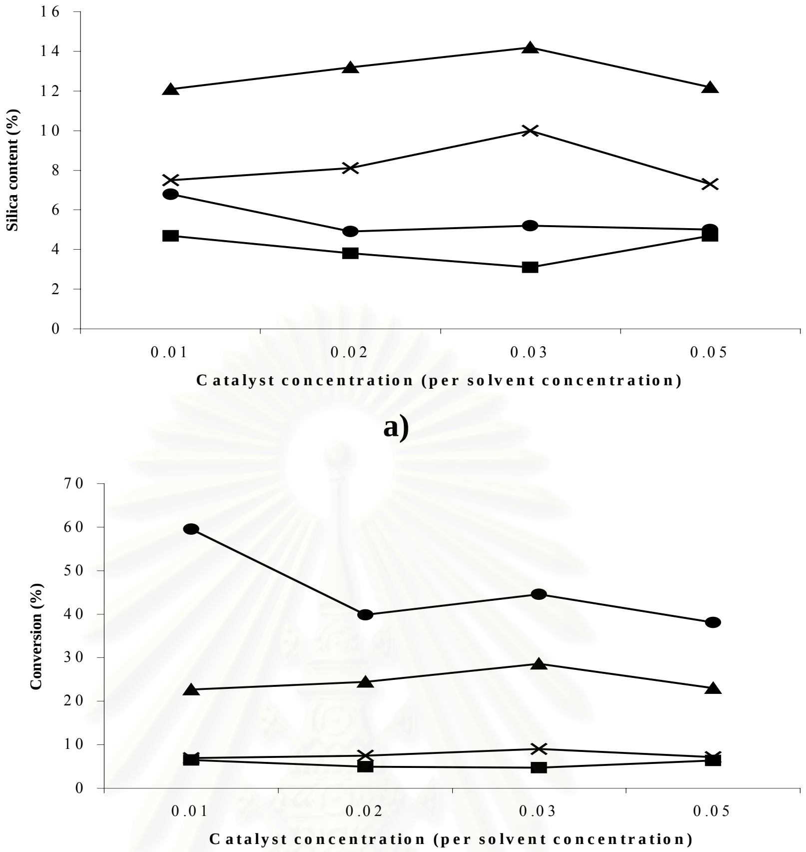
For NBR, the appropriate aqueous ethylenediamine concentration for TEOS and EPS are found to be 1 and 3%, respectively. At this condition, the silica content for TEOS and EPS are 6.8 and 10.0 %, respectively.

For NR, silica content and conversion in TEOS slightly increase with increasing catalyst concentration. For EPS, silica content and conversion slightly decrease with increasing catalyst concentration. It can be noted that, the catalyst concentration has small effect on silica content.

For NR, the conversion in EPS (59.49%) is higher than that of TEOS (28.64%). It can be noted that, the effect of catalyst concentration on silica content in EPS more pronounced than in TEOS. This can be explained that, the swelling of NR in TEOS is very high which proceed by TEOS and solvent (distilled water). But for EPS, solvent does not affect on swelling of NR. From equation 3.3, M_5 is the imaginary mass of silica in the sample assuming quantitative conversion of TEOS or EPS into silica by the sol-gel reaction, which calculated from the mass of TEOS or EPS in the swollen sample. Thus, M_5 increased with increasing mass of swollen sample.

Table 4.4 Effect of catalyst concentration on silica content and conversion of NR and NBR

Rubber	Catalyst concentration (per TEOS concentration)	Silica content (%) (TEOS)	Conversion of TEOS (%)
NR	0.01	12.1	22.66
	0.02	13.2	24.48
	0.03	14.2	28.64
	0.05	12.2	22.96
NBR	0.01	4.7	6.52
	0.02	3.8	4.97
	0.03	3.1	4.72
	0.05	4.7	6.35
Rubber	**Catalyst concentration (per EPS concentration)**	**Silica content (%) (EPS)**	**Conversion of EPS (%)**
NR	0.01	6.8	59.49
	0.02	4.9	39.79
	0.03	5.2	44.53
	0.05	5.0	38.12
NBR	0.01	7.5	6.95
	0.02	8.1	7.53
	0.03	10.0	8.98
	0.05	7.3	7.19



a)

b)

Figure 4.4 Effect of catalyst concentration on a) silica content b) conversion: (▲) NR (TEOS); (•) NR (EPS); (■) NBR (TEOS); and (×) NBR (EPS)

4.6 Oscillating Disk Rheograph of Polymer Blend

Figure 4.5 shows the oscillating disk rheograph of unfilled and filled compounded polymer for different techniques of silica filling. The oscillating disk rheometer test can determine the scorch time, cure time (or vulcanization time) and cure rate by plotting the torque curve versus time. The scorch time was measured when the torque curve increased from the minimum torque in two units (such as 2 lb-in). The temperature was 121ºC.

Table 4.5 shows the scorch time of unfilled and filled compounded polymer blend. The scorch time is an induction period before the start of crosslinking reaction by sulphur. The scorch time of in situ polymer blends is short (2.8-3.5 minutes), which implies the minimum deactivation (due to adsorption) of crosslinking agents by in situ silica. The scorch time of polymer blends with conventional silica powder is long (11.1-11.8 minutes).

Table 4.5 The scorch time of compounded rubbers

Recipe	Compounded rubber	Ratio (phr)	Scorch time (minutes)
1	NBR/PVC	70/30	3.6
2	NBR/PVC/TEOS	70/30/0.97*	3.5
3	NBR/PVC/EPS	70/30/3.15*	2.9
4	NBR/PVC/Si	70/30/13.98*	11.8
5	NBR/PVC/NR/Si	60/30/10/13.69*	11.1
6	NBR/PVC/NR/TEOS	60/30/10/0.40*	2.8
7	NBR/PVC/NR/EPS	60/30/10/2.54*	3.4

Note: 1) Codes of TEOS and EPS are in situ silica by sol-gel reaction. Code of Si is conventional silica powder.

2) * Determined by Thermogravmetric Analysis (TGA)

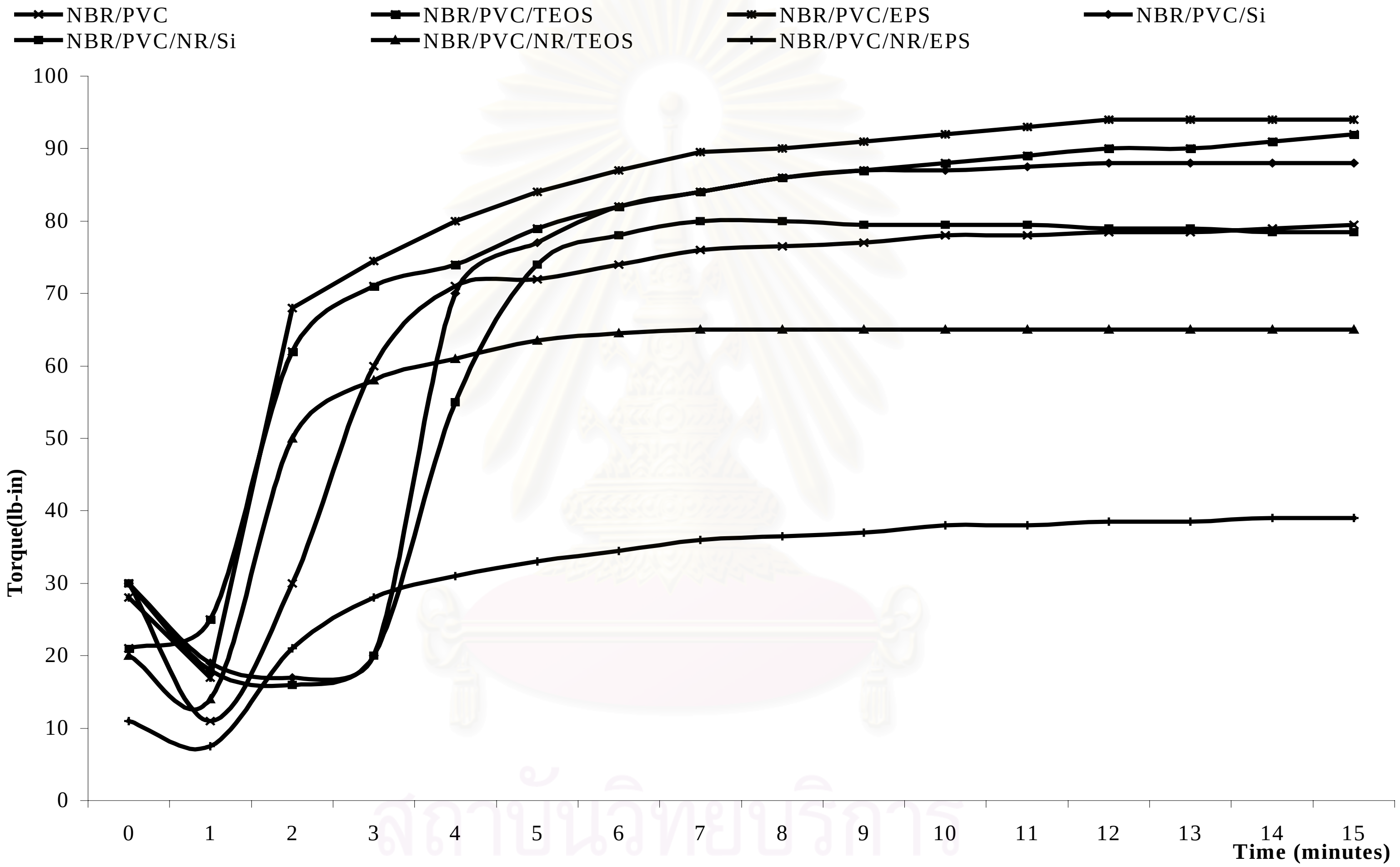


Figure 4.5 The rheograph of unfilled polymer blend and filled polymer blend for different techniques of silica filling

4.7 Viscosity of Rubber/PVC Blend

Table.4.6 shows the viscosity of unfilled and filled rubber/PVC blends for different techniques of silica filling. The viscosity at 100^0C of rubber/PVC-in situ was slightly lower than that of rubber/PVC-mix (silica powder), which is favorable to rubber/PVC-in situ for the processing. It is known that the filling of conventional silica powder to rubbers brings about the significant increase of viscosity that is attributed to the formation of pseudo-network structure due to the aggregation of conventional silica. Therefore, the results of viscosity qualitatively suggest that the degree of aggregation to in situ silica was less than conventional silica. Namely, the interaction between the in situ silica particles seems to be smaller than that between the conventional silica particles at 100^0C.

Table 4.6 Viscosity of compound rubber unvulcanizate by capillary rheometer

Recipe	Compound rubber	Viscosity (Pa.s)	Silica content (%)
1	NBR/PVC	1.8×10^4	0
3	NBR/PVC/EPS	3.0×10^6	3.15
4	NBR/PVC/Si	3.1×10^6	13.98

4.8 Mechanical Properties of Rubber/PVC vulcanizates

Effects of rubber/PVC vulcanizates compositions and silica filling technique upon the mechanical properties were examined. The moduli at 100%, 200%, and 300% elongation (M_{100}, M_{200}, and M_{300}, respectively), tensile strength at break (T_B), tear resistance, elongation at break (E_B) and silica content (%) are summarized in Table 4.7 and Figure 4.6-4.7. For rubber/PVC-in situ-V (vulcanizate) (recipe 2,3,6 and 7), the tensile strength at break and elongation at break of the rubber/PVC-in situ-V were lower than that of NBR/PVC-V (control sample). The moduli at 100% and 200 % of NBR/PVC-in situ-V (recipe 2,3) are higher than that of NBR/PVC-V (recipe 1).

Here, the comparison of reinforcement of the in situ silica filling and conventional silica powder in rubber/PVC vulcanizates can not be made because the silica contents are not equal. Moreover, THF was chosen as the solvent for the swelling of the NBR. But the THF may affect the mechanical properties of NBR. Therefore, the mechanical properties of rubber/PVC-in situ-V were lower than those of rubber/PVC-V and rubber/PVC-mix-V.

Table 4.7 Mechanical properties of rubber/PVC blend

Sample code	**Recipe 1**	**Recipe 2**	**Recipe 3**	**Recipe 4**	**Recipe 4’**	**Recipe 5**	**Recipe 5’**	**Recipe 6**	**Recipe 7**
M_{100},MPa	3.35	3.75	4.09	4.24	-	4.12	-	2.86	3.46
M_{200},MPa	6.21	-	8.70	7.24	-	7.44	-	6.17	6.89
M_{300},MPa	10.31	-	-	10.81	-	11.52	-	9.84	-
T_B, MPa	10.45	9.20	8.44	14.44	9.94	14.44	10.75	9.92	7.99
E_B, %	289.20	261.50	241.33	399.56	434.48	362.19	450.12	317.25	254.04
Tear,N/mm	42.12	37.14	37.12	52.95	-	50.52	-	33.89	32.27
Silica content (%)	0	0.97*	3.15*	13.98*	5.10*	13.69*	5.23*	0.40*	2.54*

Note: Recipe 1 : NBR/PVC-V
Recipe 2 : NBR/PVC/Si (TEOS)-V
Recipe 3 : NBR/PVC/Si (EPS)-V
Recipe 4 : NBR/PVC/Si-V
Recipe 4’ : NBR/PVC/Si-V
Recipe 5 : NBR/PVC/NR/Si-V
Recipe 5’ : NBR/PVC/NR/Si-V
Recipe 6 : NBR/PVC/NR/Si (TEOS)-V
Recipe 7 : NBR/PVC/NR/Si (EPS)-V

* Determined by Thermogravmetric Analysis (TGA)

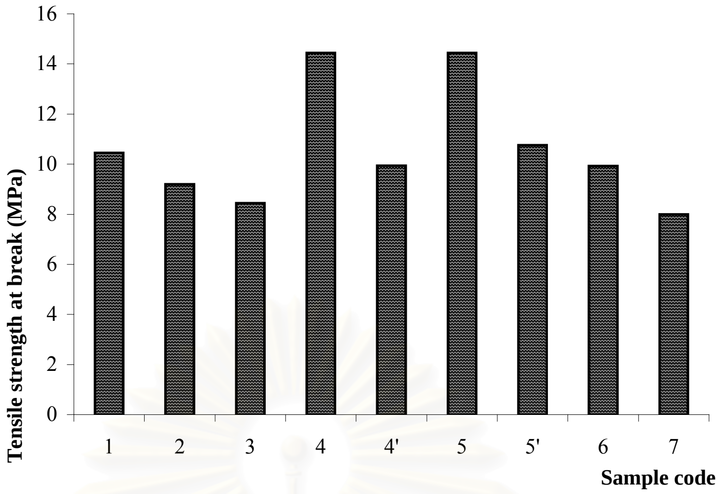


Figure 4.6 Tensile strength at break (T_B) of rubber/PVC vulcanizate

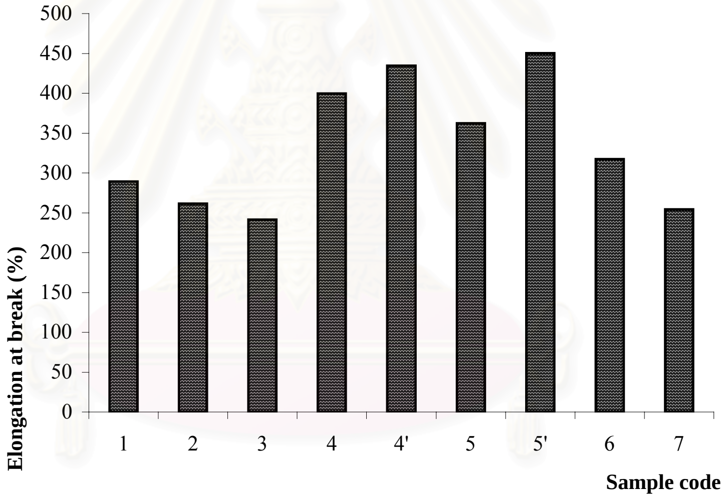
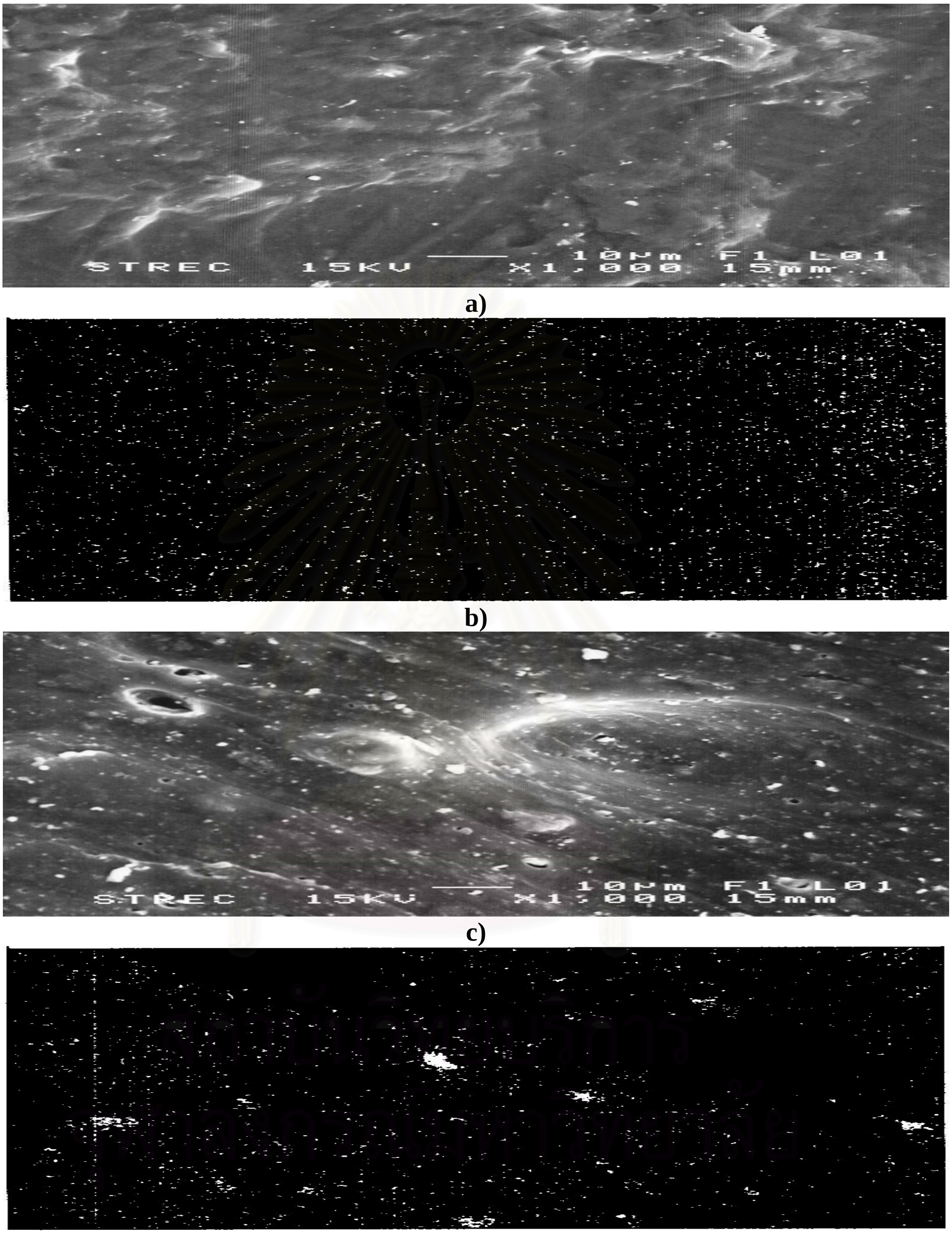


Figure 4.7 Elongation at break (E_B) of rubber/PVC vulcanizate

4.9 Morphology of the Rubber/PVC Vulcanizates

The results of SEM observations for rubber/PVC-V, rubber/PVC-mix-V and rubber/PVC-in situ-V are shown in Figure 4.8a-h. It is clear that the in situ silica particles dispersed more homogeneously in the rubber/PVC-in situ-V (recipe 2,3) (Figure 4.8d, 4.8f) than the conventional silica particles in the rubber/PVC-mix-V (recipe 4) (Figure 4.8h). The inter-particle interaction among in situ silica particles was found to be smaller than that among the silica particles in rubber/PVC-mix-V. The well-dispersed in situ silica in the rubber/PVC blend is ascribed to the lower concentration of silanol group on the surface of in situ silica particles compared to the rubber/PVC-mix-V, which was speculated in the results of sulphur curing of the rubber/PVC compounds. As described in the previous section, the crosslinking reaction of rubber/PVC compounds with in situ silica was faster than that of rubber/PVC compounds with the conventional silica, which is in accord with the results revealed by SEM. From the results of SEM the characteristics of rubber/PVC-in situ-V was evidenced. The better reinforcement effect of in situ silica was attributed to the more homogeneous dispersion of in situ silica particles in the rubber/PVC matrix and the higher wettability at room temperature between the in situ silica particles and rubber/PVC molecules than evidenced with the system of conventional silica.



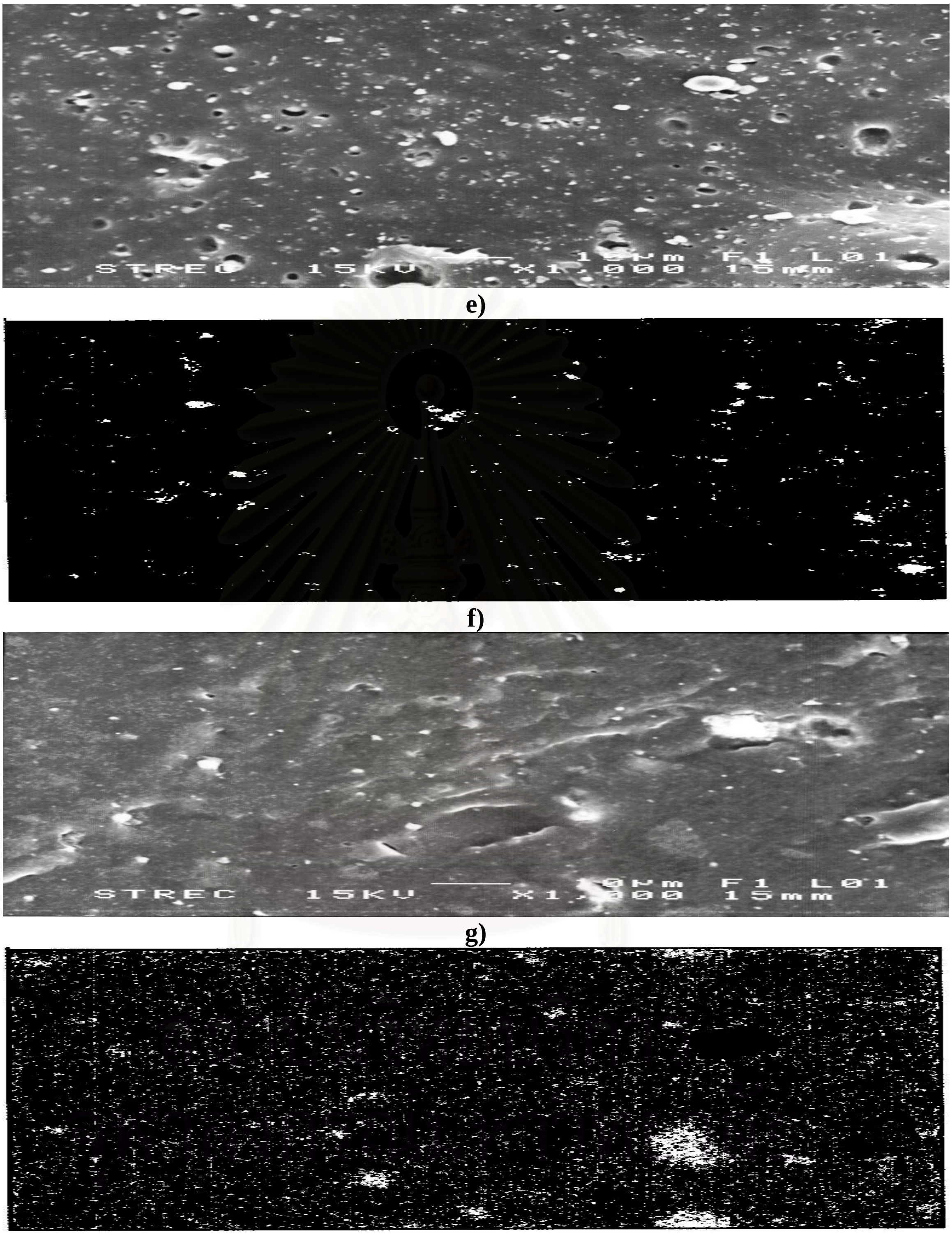
a)

b)

c)

d)

Figure. 4.8 SEM photograph and SEM mapping of polymer vulcanizate (a-b) without silica, (c-d) with silica from TEOS, (e-f) with silica from EPS, (g-h) with conventional silica. (×1000, Magnification)



e)

f)

g)

h)

Figure. 4.8 SEM photograph and SEM mapping of polymer vulcanizate (a-b) without silica, (c-d) with silica from TEOS, (e-f) with silica from EPS, (g-h) with conventional silica. (×1000, Magnification) (continued)

CHAPTER V

CONCLUSION

Nitrile rubber and PVC compound was blended in a two-roll mill and mixed with silica and vulcanization system. The reinforcement systems can be divided into four recipes; the first recipe (NBR/PVC) without silica, the second recipe (NBR/PVC/TEOS, NBR/PVC/NR/TEOS) with silica-in situ from Tetraethoxysilane (TEOS), the third (NBR/PVC/EPS, NBR/PVC/NR/EPS) with silica-in situ from Ethyl polysilicate (EPS) and the fourth (NBR/PVC/Si, NBR/PVC/NR/Si) with conventional silica powder.

Effects of sol-gel conditions on degree of swelling and silica content of NBR and NR were studied. The effect of silica content and the partial substitution of NBR with NR on mechanical properties of NBR/PVC blend was examined. The results led to the following conclusion:

1. For varying TEOS/rubber and EPS/rubber mass ratio, the degree of swelling of NR increased with increasing TEOS and slightly increased with increasing EPS content. For NBR, the degree of swelling slightly increased with increasing TEOS and EPS content.
2. For various dilution ratios of ethanol/distilled water/tetrahydrofuran, the degree of swelling of NR in TEOS or EPS solution decreased with increasing ethanol content. For NBR, the degree of swelling increased with increasing THF content.
3. For varying temperature and time of drying, the appropriate temperature and time of drying for NR and NBR was found to be 40^0C, 48 h and 60^0C, 48 h, respectively.

4. The aqueous ethylenediamine concentration affected the silica content and conversion of TEOS and EPS. For NR , silica content and conversion in TEOS slightly increased with catalyst concentration and slightly decreased with increasing catalyst concentration for EPS. For NBR, the catalyst concentration does not affect the silica content and conversion of TEOS and EPS.
5. For various soaking time in aqueous catalyst solution (TEOS and EPS), the appropriate time is found to be 24 h for NR and NBR.
6. For NR, the appropriate conditions of sol-gel process for TEOS are found to be at TEOS:H_2O = 1:17 (v/v)(water 100%) at mass ratio of TEOS/rubber (10/1 w/w), catalyst concentration of 3%[TEOS], soaking time of 24 h. This condition yield the degree of swelling of 70%, silica content and conversion of 14.2 and 28.64%, respectively.
7. For NBR, the appropriate condition of sol-gel process for EPS are found to be at EPS:THF = 1/20 (v/v)(THF 100%) at mass ratio of EPS/rubber (10/1 w/w), catalyst concentration of 1%[EPS], soaking time of 24 h. This condition yield the degree of swelling of 282.2% (EPS), silica content and conversion of 10 and 8.98%, respectively.
8. For unfilled and filled compounded polymer blend, the scorch time of in situ polymer blends is the shortest which implies the minimum deactivation (due to adsorption) of crosslinking agents by in situ silica.
9. Viscosity at 100^0C of rubber/PVC-in situ silica was slightly lower than that of rubber/PVC-mix. Therefore, the degree of aggregation of in situ silica was less than that of conventional silica. Namely, the interaction between the in situ silica particles seems to be smaller than that between the conventional silica particles at 100^0C.
10. From mechanical properties of rubber/PVC blends, the rubber/PVC-in situ-V showed the higher moduli at 100% or 200% than those of rubber/PVC-V.
11. From the morphology of the polymer vulcanizates, the in situ silica particles dispersed more homogeneously in the rubber/PVC blend than the conventional silica particles in the rubber/PVC-mix-V.

Suggestions for future works

In the field of silica reinforcing of rubber and polymer blend, it should be studied further in the following aspects:

1. Effect of catalyst concentration with wide concentration range.
2. Effect of temperature and time of soaking in solution on degree of swelling and in-situ silica content.

REFERENCES

1. K. Nagdi. Rubber as an Engineering Material: guideline for uses. New York : Hanser Publ., 1993.
2. Paiboon Tepumnoysuk. Physical properties of PVC/Nitrile rubber blends, Petro-Polymer (Inter-Program) Thesis, 7-8, 1992.
3. Maurice Morton, Rubber Technology, 2nd ed., pp. 51-84, 1973.
4. C. J. Brinker and G. W. Schere, Sol-gel science: The physics and chemistry of sol-gel processing. San Diego : Academic Press, 1990.
5. K. E. George, R. Joseph, and D. J. Francis. Studies on NBR/PVC blends. J. Applied Polymer Science. Vol. 32(1986) : 2867-2873.
6. K. E. George, R. Joseph, D. J. Francis, and K. T. Thomas. Modification of butadiene-acrylonitrile rubber/poly(vinyl chloride) blend using natural rubber, styrene-butadiene rubber, and polybutadiene rubber. Polymer Engineering and Science. Vol. 27(15)(1987) : 1137-1140.
7. S.-H. Zhu, C.-M. Chan, S. C. Wong, and Y.-W. Mai. Mechanical properties of PVC/SBR blends compatibilized by acrylonitrile-butadiene rubber and covulcanization. Polymer Engineering and Science. Vol. 39(10)(1999) : 1998-2006.
8. Y. Ikeda, and S. Kohjiya. In situ formed silica particles in rubber vulcanizate by the sol-gel method. Polymer. Vol. 38(17)(1997) : 4417-4423.
9. H. Tanahashi, S. Osanai, M. Shigekuni, K. Murakami, Y. Ikeda, and S. Kohjiya. Reinforcement of acrylonitrile-butadiene rubber by silica generated in situ. Rubber Chemistry and Technology. Vol. 71(1)(1998) : 38-52.
10. S. Kohjiya, and Y. Ikeda. Reinforcement of natural rubber by silica generated in situ. Proc. Japan Acad. Vol. 76(B)(2000) : 29-34.
11. S. Kohjiya, and Y. Ikeda. Reinforcement of general-purpose grade rubbers by silica generated in situ. Rubber Chemistry and Technology. Vol. 73(3)(2000) : 534-549.

12. Y. Ikeda, A. Tanaka and S. Kohjiya. Reinforcement of styrene-butadiene rubber vulcanizate by in situ silica prepared by the sol-gel reaction of tetraethoxysilane. J. Mater. Chem. Vol. 7(8)(1997) : 1497-1503.
13. Y. Ikeda, A. Tanaka and S. Kohjiya. Effect of catalyst on in situ reinforcement of stryrene-butadiene rubber vulcanizate by the sol-gel reaction of tetraethoxysilane. J. Mater. Chem. Vol. 7(3)(1997) : 455-458.
14. K. Yoshikai, T. Ohsaki and M. Furukawa. Silica reinforcement of synthetic diene rubbers by sol-gel process in the latex. J. Applied Polymer Science. Vol.85 (2002) : 2053-2063.

APPENDIX

APPENDIX A

CALCULATION

A1. Preparation TEOS and Ethyl Polysilicate Solution

The amount of TEOS and Ethyl polysilicate was ten time the mass of the rubber sample. Exp. 10 g of rubbers =► 100 g of TEOS and Ethyl polysilicate

The concentration of TEOS and Ethyl polysilicate was evaluated by using equation (A1),

$$C = W/Mw \qquad \text{(A1)}$$

C = TEOS or Ethyl polysilicate concentration.
W = weight of TEOS or Ethyl polysilicate.
Mw = molecular weight of TEOS or Ethyl polysilicate.

The volume of TEOS and Ethyl polysilicate stock was evaluated by using equation (A2),

$$V = C \times V_1/C_1 \qquad \text{(A2)}$$

V = Volume of TEOS or Ethyl polysilicate stock.
C = TEOS or Ethyl polysilicate concentration.
C_1 = TEOS or Ethyl polysilicate stock concentration.
V_1 = Volume of TEOS or Ethyl polysilicate solution at preparation.

A2. Preparation Ethylenediamine Aqueous Solution.

The concentration of Ethylenediamine aqueous solution at 1-5 % TEOS or Ethyl polysilicate concentration was evaluated by using equation (A3),

$$E = \text{Constant} \times C \qquad \text{(A3)}$$

E = Ethylenediamine concentration.
C = TEOS or Ethyl polysilicate concentration.
Constant = 0.01 or 0.02 or 0.03 or 0.05.

The volume of Ethylenediamine stock was evaluated by using equation (A4),

$$V_2 = E \times V_3 / C_2 \qquad \text{(A4)}$$

V_2 = Volume of Ethylenediamine stock.
E = Ethylenediamine concentration.
C_2 = Ethylenediamine stock concentration.
V_3 = Volume of Ethylenediamine solution at preparation.

APPENDIX B

TGA graph of rubber at different catalyst concentration

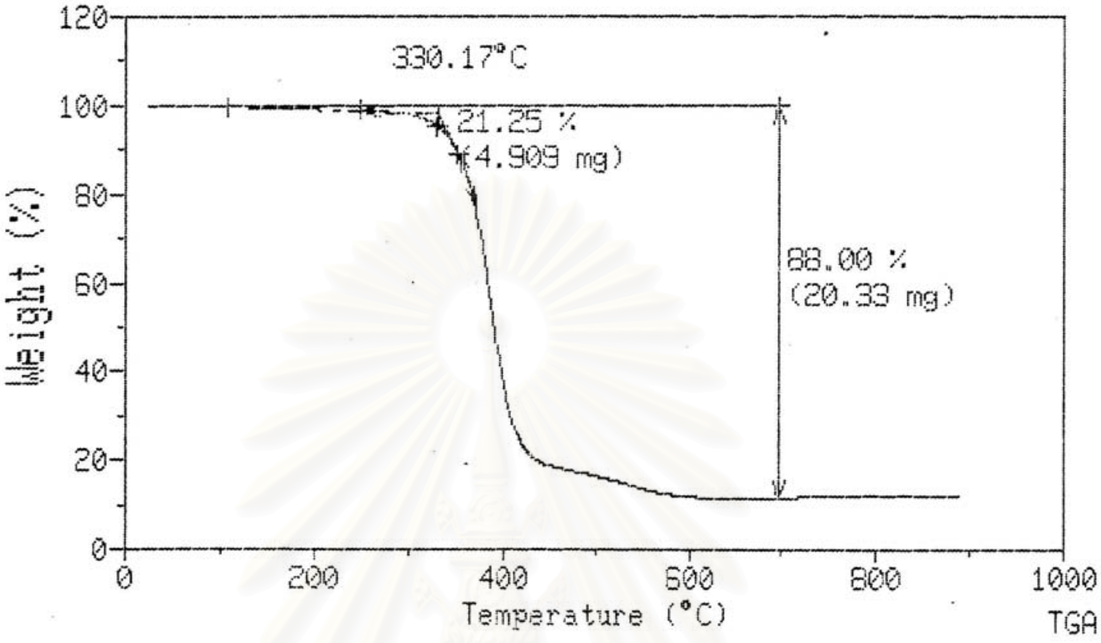


Figure B1: TGA graph of NR in catalyst at concentration of 0.01 per TEOS.

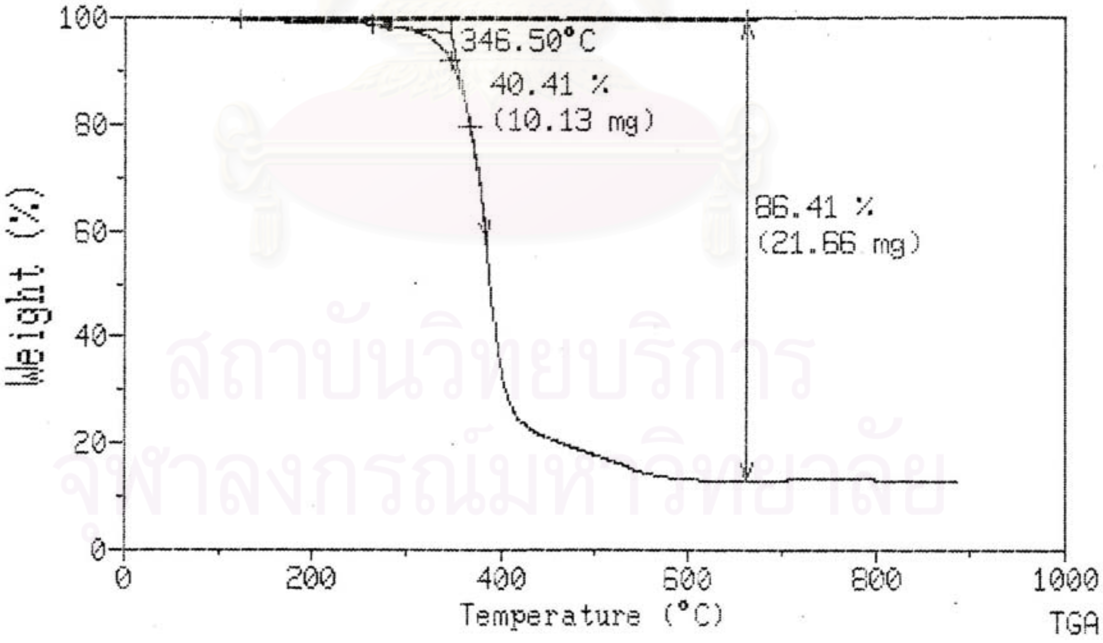


Figure B2: TGA graph of NR in catalyst at concentration of 0.02 per TEOS.

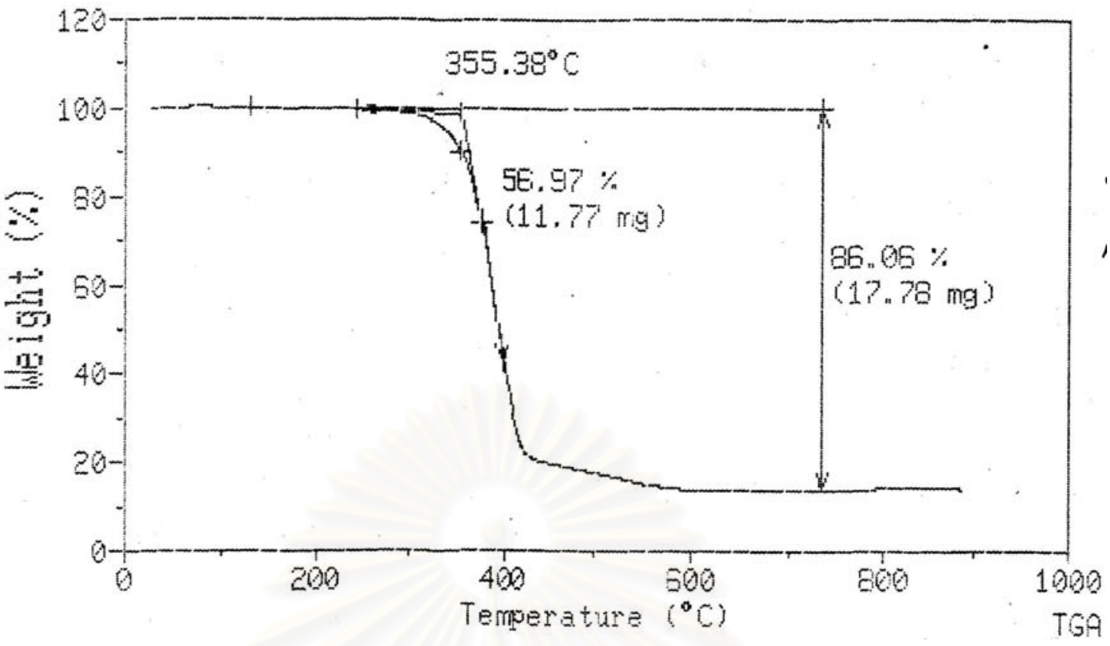


Figure B3: TGA graph of NR in catalyst at concentration of 0.03 per TEOS.

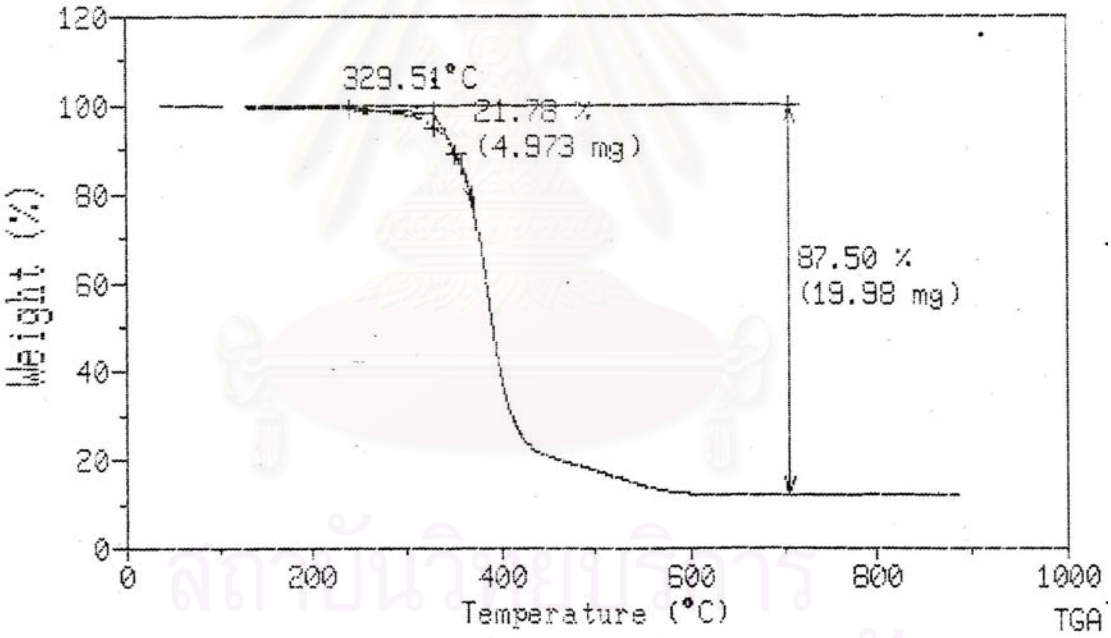


Figure B4: TGA graph of NR in catalyst at concentration of 0.05 per TEOS.

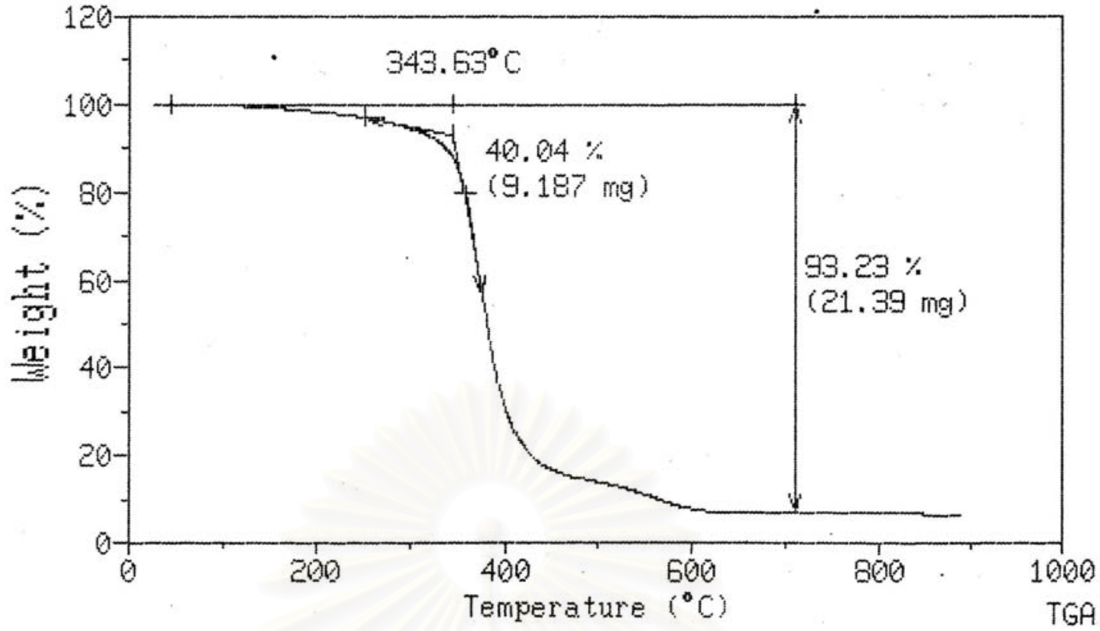


Figure B5: TGA graph of NR in catalyst at concentration of 0.01 per EPS.

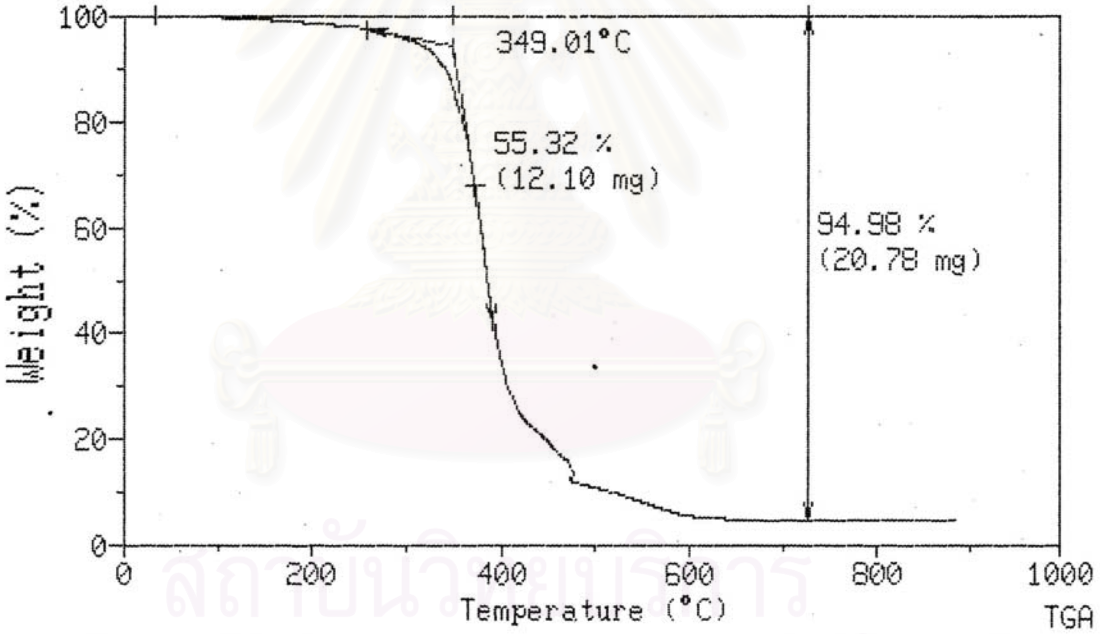


Figure B6: TGA graph of NR in catalyst at concentration of 0.02 per EPS.

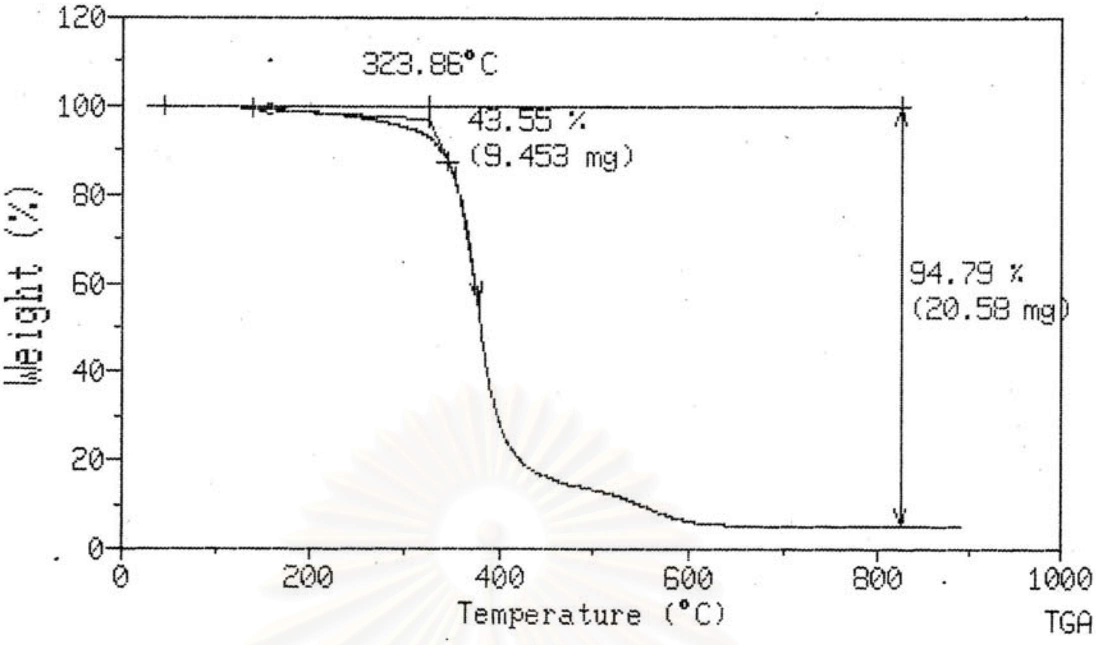


Figure B7: TGA graph of NR in catalyst at concentration of 0.03 per EPS.

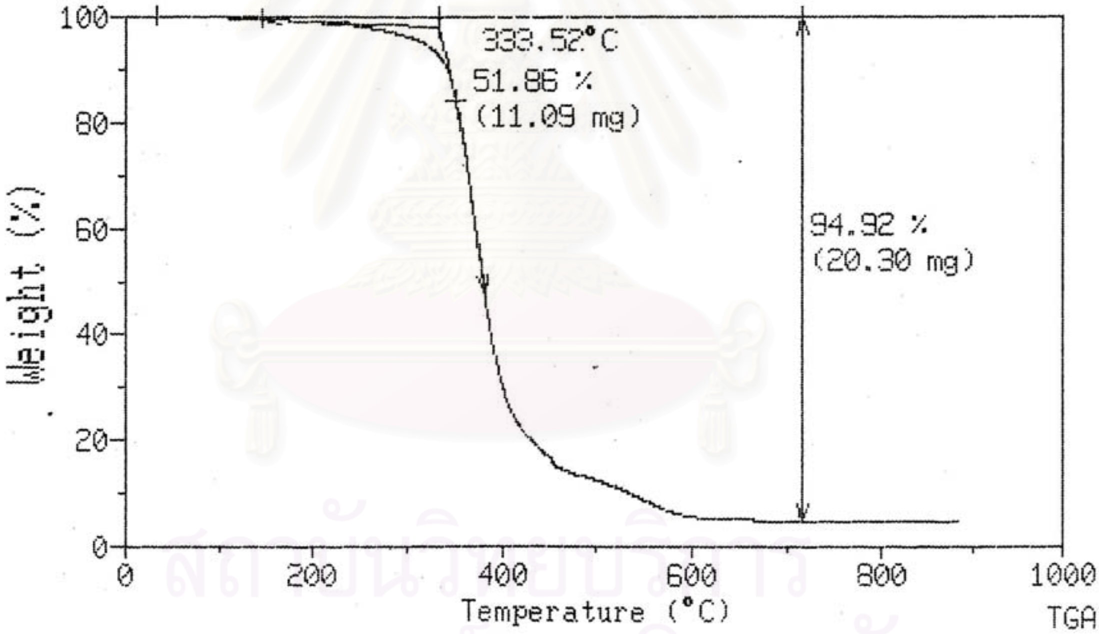


Figure B8: TGA graph of NR in catalyst at concentration of 0.05 per EPS.

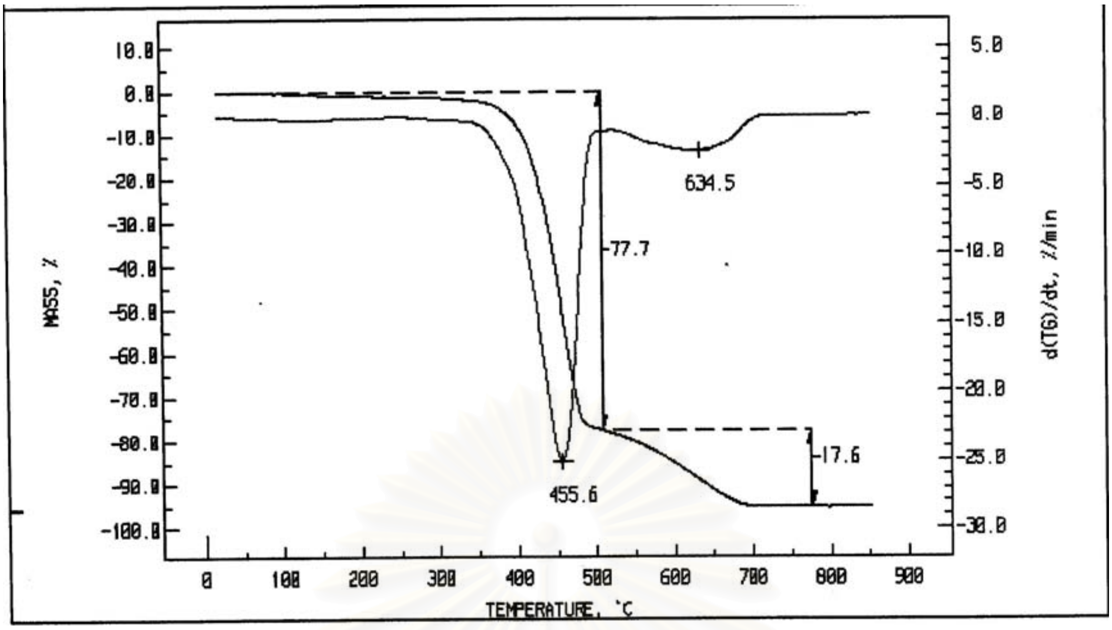


Figure B9: TGA graph of NBR in catalyst at concentration of 0.01 per TEOS.

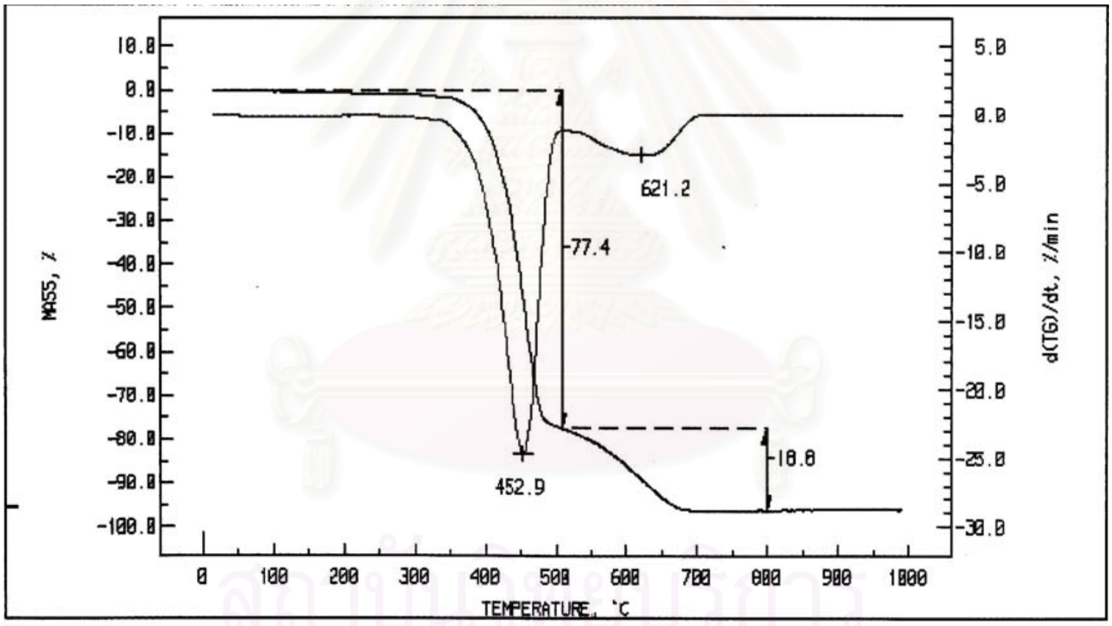


Figure B10: TGA graph of NBR in catalyst at concentration of 0.02 per TEOS.

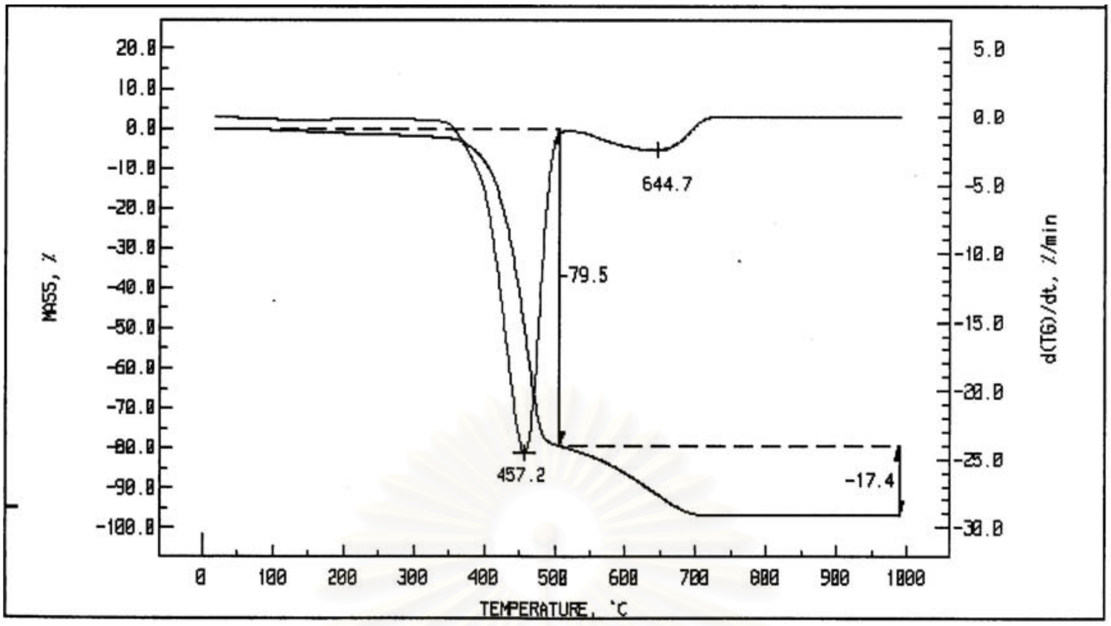


Figure B11: TGA graph of NBR in catalyst at concentration of 0.03 per TEOS.

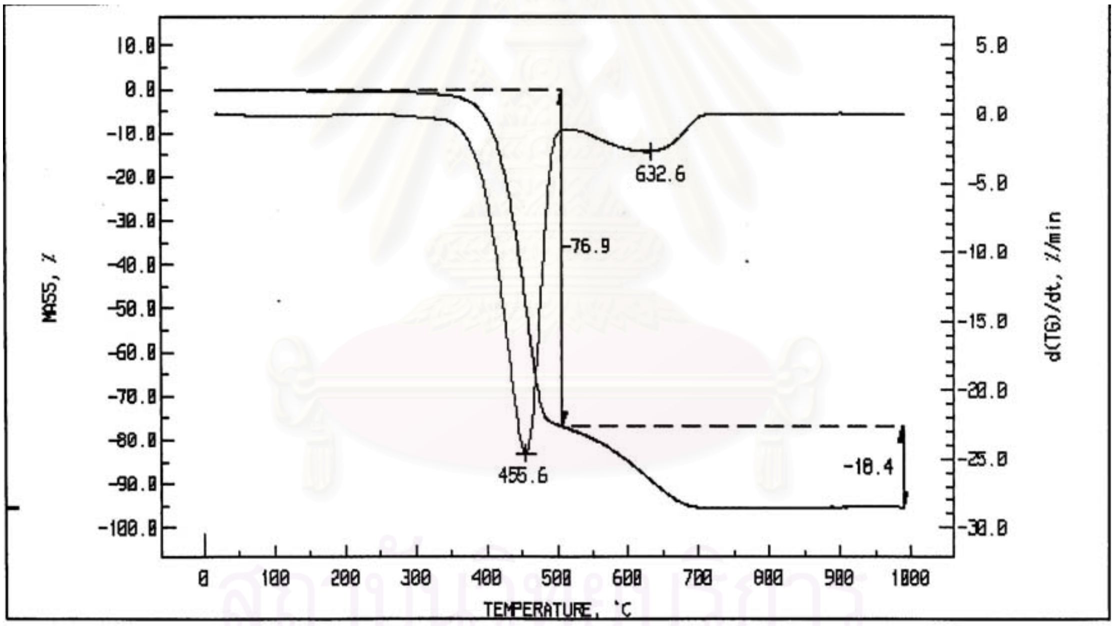


Figure B12: TGA graph of NBR in catalyst at concentration of 0.05 per TEOS.

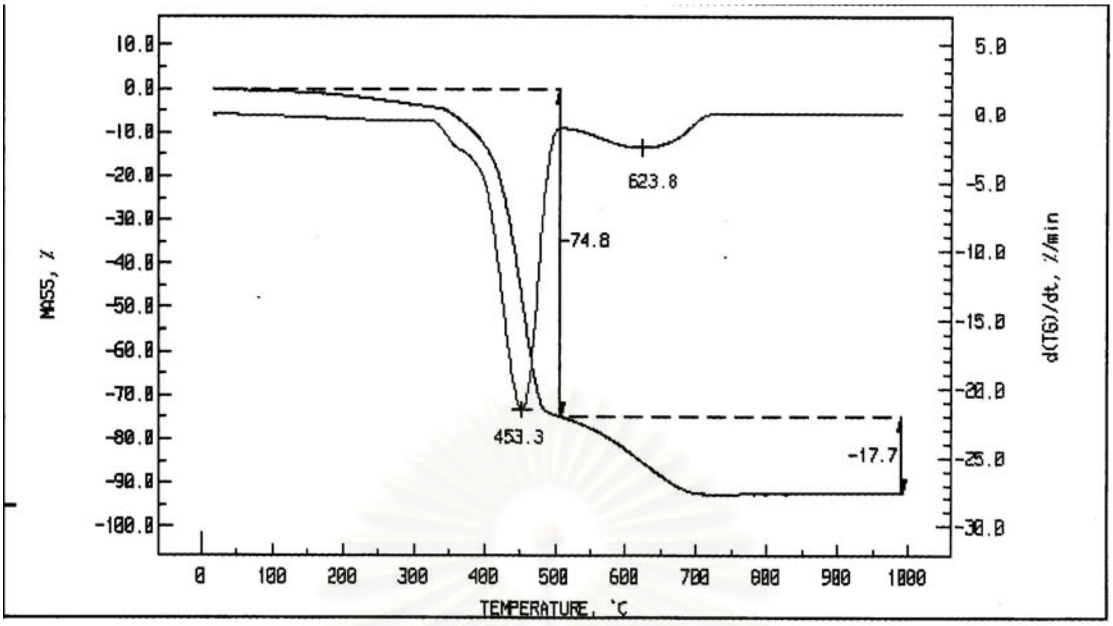


Figure B13: TGA graph of NBR in catalyst at concentration of 0.01 per EPS.

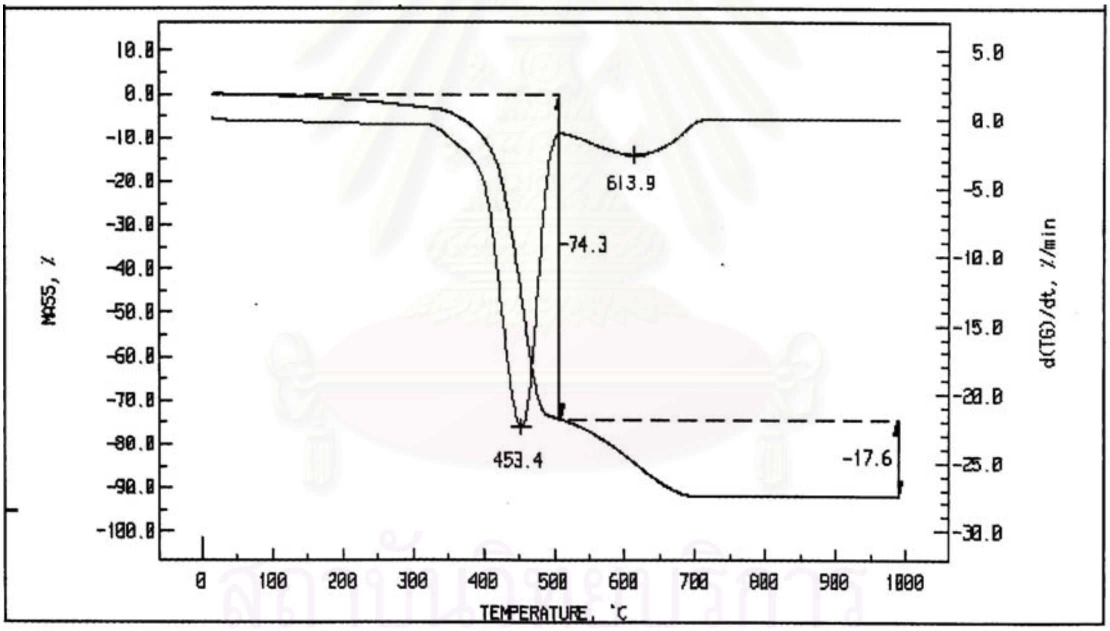


Figure B14: TGA graph of NBR in catalyst at concentration of 0.02 per EPS.

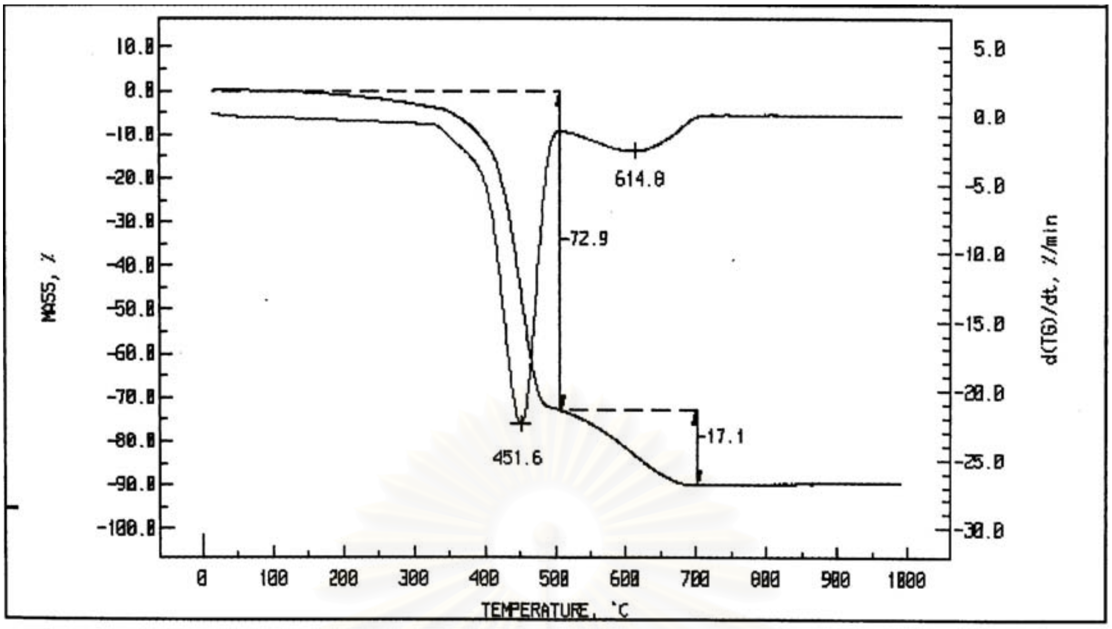


Figure B15: TGA graph of NBR in catalyst at concentration of 0.03 per EPS.

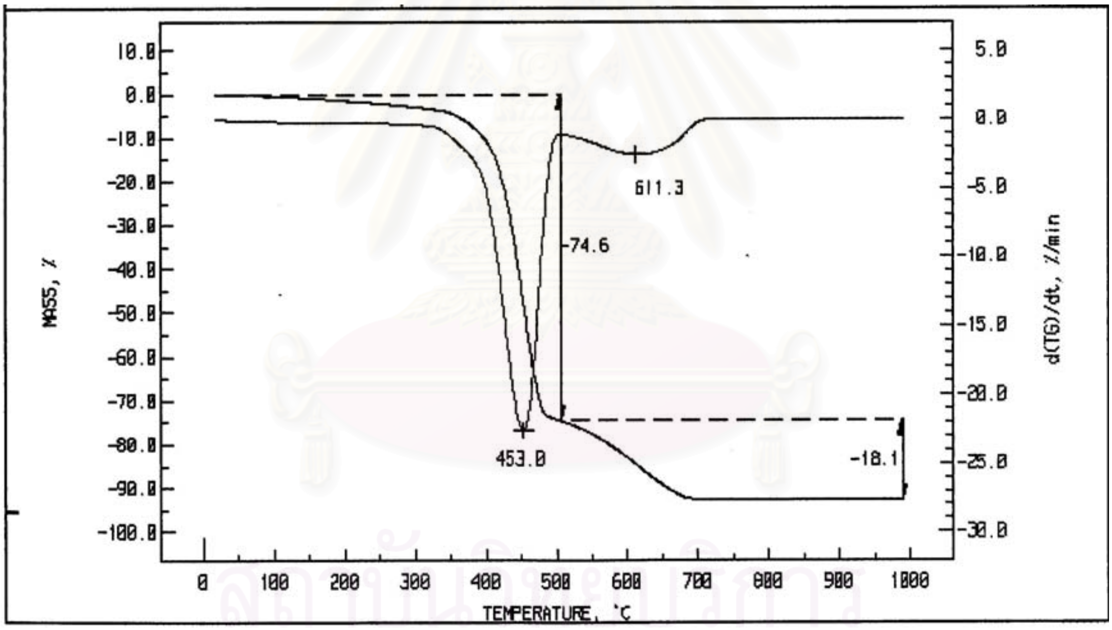


Figure B16: TGA graph of NBR in catalyst at concentration of 0.05 per EPS.

APPENDIX C

TGA graph of rubber at different soaking time in catalyst.

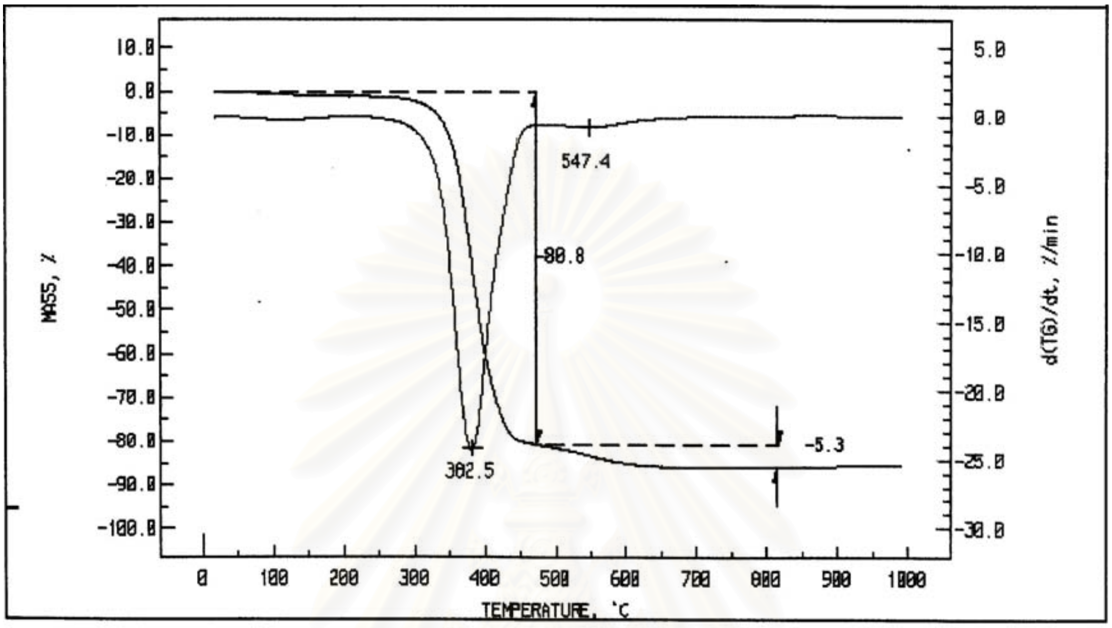


Figure C1: TGA graph for 4 days in catalyst of NR (TEOS)

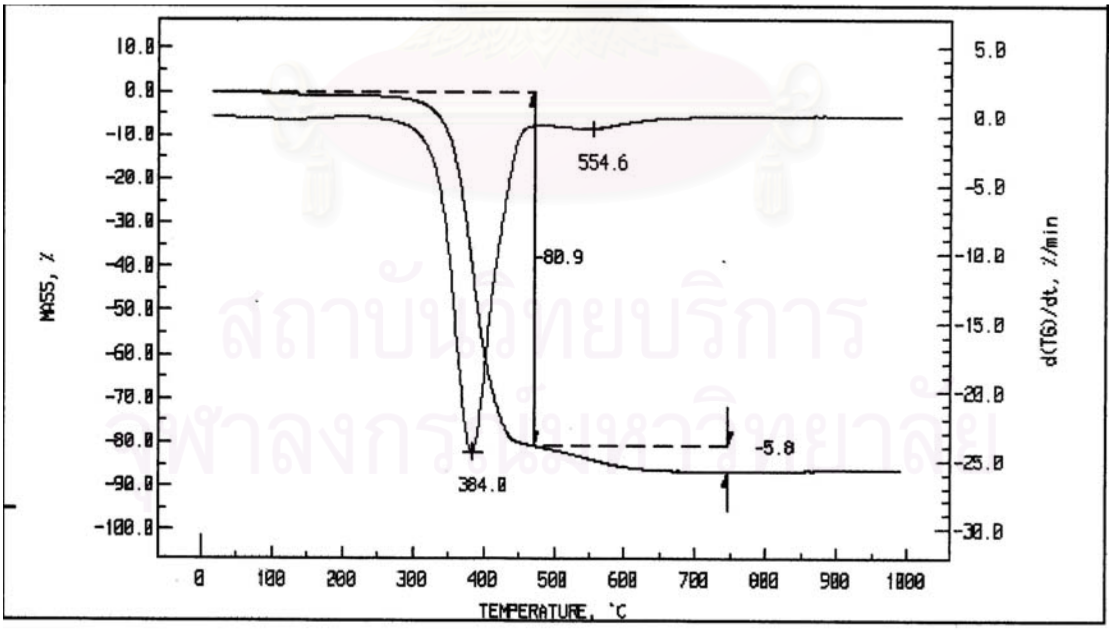


Figure C2: TGA graph for 6 days in catalyst of NR (TEOS)

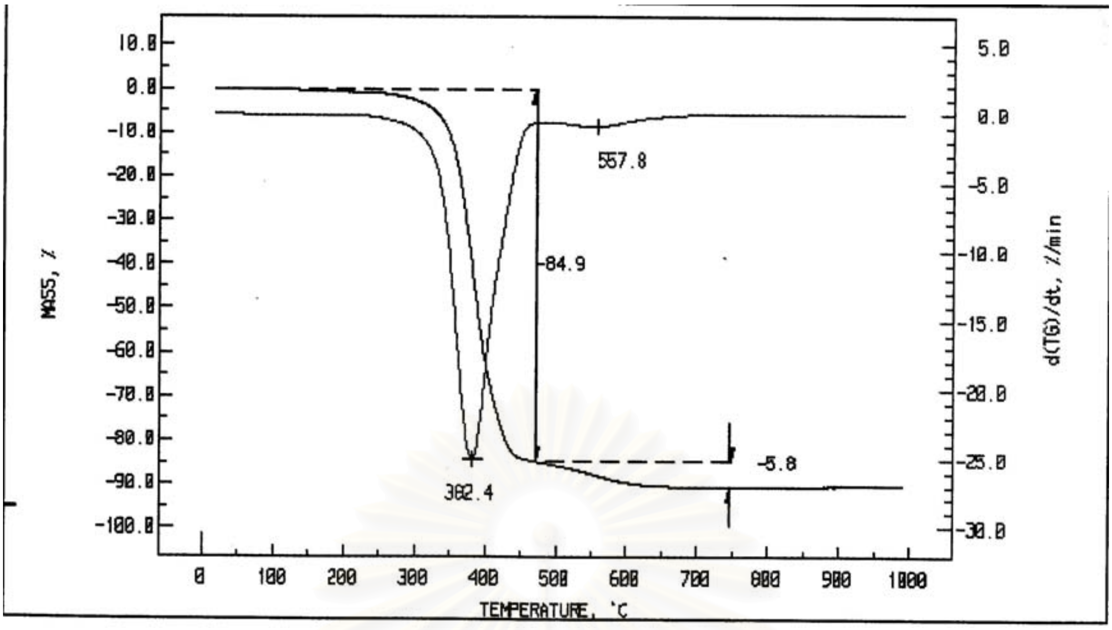


Figure C3: TGA graph for 4 days in catalyst of NR (Ethyl polysilicate)

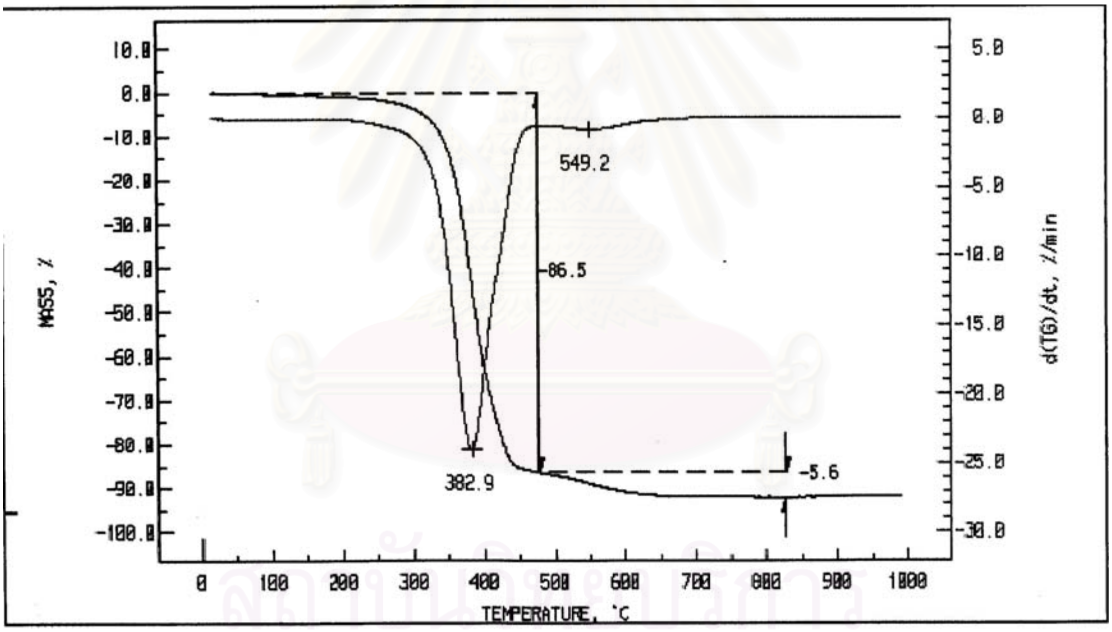


Figure C4: TGA graph for 6 days in catalyst of NR (Ethyl polysilicate)

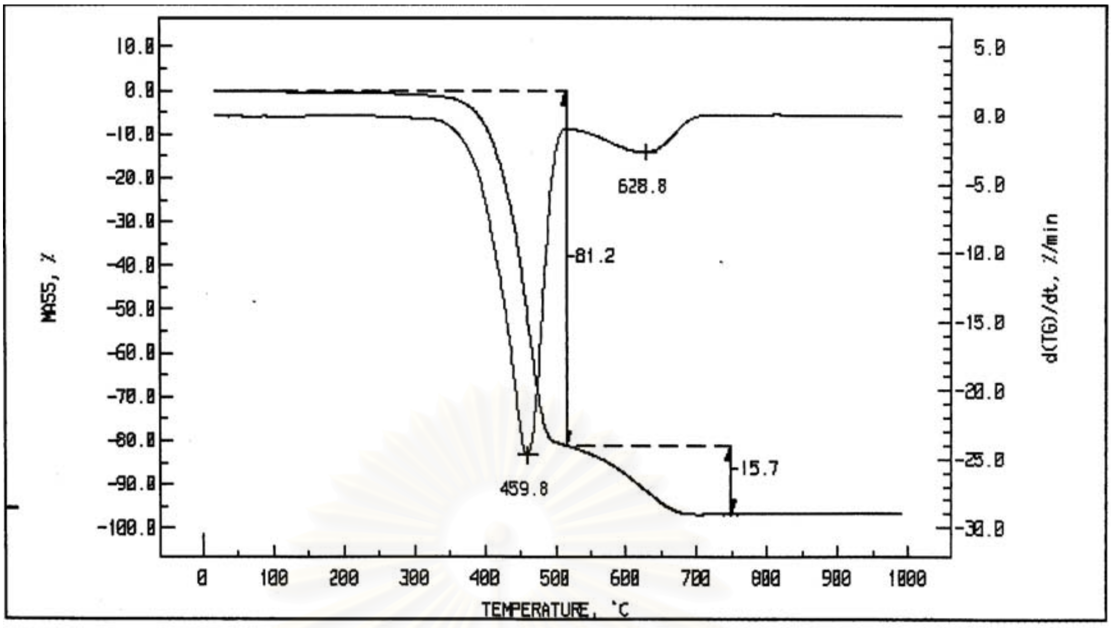


Figure C5: TGA graph for 6 days in catalyst of NBR (TEOS)

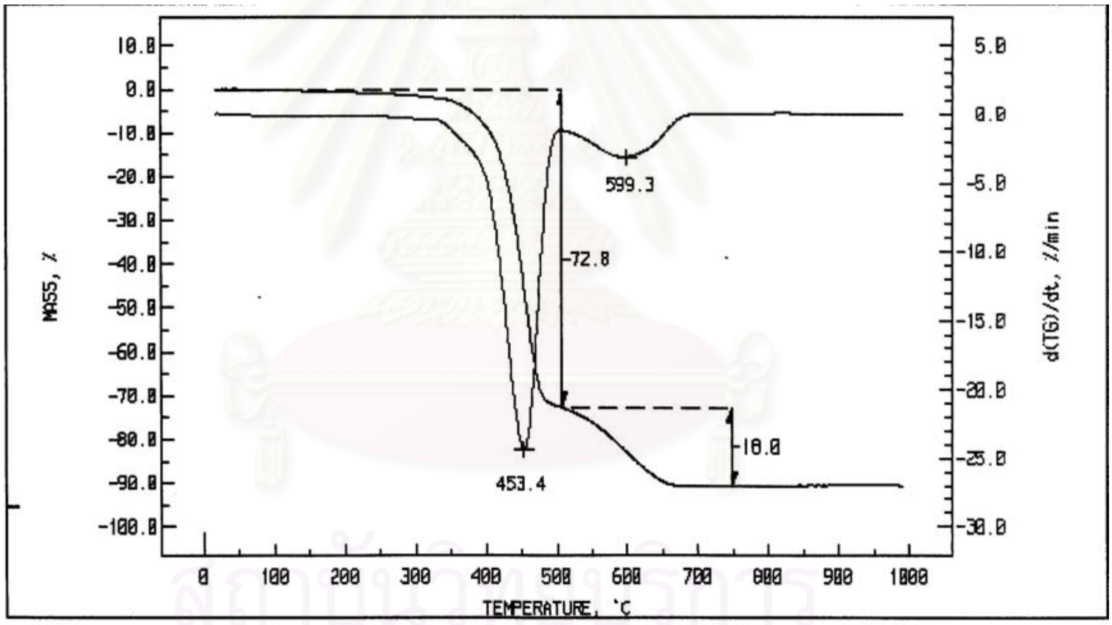


Figure C6: TGA graph for 6 days in catalyst of NBR (Ethyl polysilicate)

APPENDIX D

Mechanical properties of rubber/PVC vulcanizates

Table D1. Tensile strength of rubber/PVC vulcanizates

Mechanical property	NBR/PVC	NBR/PVC/Si (TEOS)	NBR/PVC/Si (EPS)	NBR/PVC/Si	NBR/PVC/Si’	NBR/PVC/NR/Si	NBR/PVC/NR/Si’	NBR/PVC/NR/Si (TEOS)	NBR/PVC/NR/Si (EPS)
	70/30	70/30/0.97	70/30/3.15	70/30/13.98	70/30/5.10	60/30/10/13.96	60/30/10/5.23	60/30/10/0.40	60/30/10/2.54
Tensile strength (MPa)	11.63	9.34	7.71	14.87	-	14.58	-	10.24	8.19
	10.40	9.54	8.23	13.84	10.62	13.96	10.62	10.13	7.97
	9.32	8.72	9.38	14.60	9.26	14.78	10.88	9.37	7.81
Average	10.45	9.20	8.44	14.44	9.94	14.44	10.75	9.92	7.99

Table D2. Elongation at break of rubber/PVC vulcanizates

Mechanical property	NBR/PVC	NBR/PVC/Si (TEOS)	NBR/PVC/Si (EPS)	NBR/PVC/Si	NBR/PVC/Si’	NBR/PVC/NR/Si	NBR/PVC/NR/Si’	NBR/PVC/NR/Si (TEOS)	NBR/PVC/NR/Si (EPS)
	70/30	70/30/0.97	70/30/3.15	70/30/13.98	70/30/5.10	60/30/10/13.96	60/30/10/5.23	60/30/10/0.40	60/30/10/2.54
Elongation at break (MPa)	207.25	260.40	233.30	434.07	-	341.67	-	324.54	298.86
	369.22	281.04	236.65	401.93	498.03	346.87	471.84	321.92	238.65
	291.12	243.07	254.05	362.68	370.93	398.05	428.41	305.28	224.60
Average	289.20	261.50	241.33	399.56	434.48	362.19	450.12	317.25	254.04

Table D3. Tear strength of rubber/PVC vulcanizates

Mechanical property	NBR/PVC	NBR/PVC/Si (TEOS)	NBR/PVC/Si (EPS)	NBR/PVC/Si	NBR/PVC/Si’	NBR/PVC/NR/Si	NBR/PVC/NR/Si’	NBR/PVC/NR/Si (TEOS)	NBR/PVC/NR/Si (EPS)
	70/30	70/30/0.97	70/30/3.15	70/30/13.98	70/30/5.10	60/30/10/13.96	60/30/10/5.23	60/30/10/0.40	60/30/10/2.54
Tear strength (N/mm)	38.27	38.24	37.68	50.88	-	51.66	-	33.90	32.36
	41.54	37.16	37.73	56.27	-	53.55	-	32.88	33.15
	45.07	40.43	37.61	52.72	-	49.11	-	36.23	33.18
	40.72	39.69	35.53	55.02	-	49.49	-	34.43	33.03
	44.45	34.75	38.15	51.28	-	50.01	-	33.83	30.74
	42.68	32.57	36.56	51.54	-	49.33	-	32.07	31.19
Average	42.12	37.14	37.12	52.95	-	50.52	-	33.89	32.27
SD	2.51	3.01	0.98	2.21	-	1.74	-	1.42	1.07

Table D4. Moduli at 100, 200 and 300 % elongation of rubber/PVC vulcanizates

Mechanical property	NBR/PVC			NBR/PVC/Si (TEOS)			NBR/PVC/Si (EPS)			NBR/PVC/Si			NBR/PVC/Si’			NBR/PVC/NR/ Si			NBR/PVC/NR/ Si’			NBR/PVC/NR/ Si (TEOS)			NBR/PVC/NR/ Si (EPS)		
	70/30			70/30/0.97			70/30/3.15			70/30/13.98			70/30/5.10			60/30/10/13.96			60/30/10/5.23			60/30/10/0.40			60/30/10/2.54		
	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}	M_{100}	M_{200}	M_{300}
Moduli (MPa)	3.3	6.2	10.4	3.5	7.2	-	4.3	9.2	-	4.5	7.6	11.3	-	-	-	4.6	8.4	13.0	-	-	-	3.0	6.5	10.1	3.2	6.4	9.5
	3.3	6.2	10.3	3.8	8.1	-	3.8	8.4	-	4.2	7.0	10.4	-	-	-	4.1	7.4	11.4	-	-	-	2.9	6.3	10.1	3.5	6.9	-
	3.1	5.6	9.1	3.7	7.8	-	4.1	8.4	-	4.2	7.2	10.9	-	-	-	3.9	7.1	11.0	-	-	-	3.1	6.6	10.1	3.5	7.1	-
	3.5	6.6	11.1	4.5	-	-	4.3	9.2	-	4.1	7.1	10.3	-	-	-	3.9	6.9	10.6	-	-	-	2.8	6.0	9.69	3.4	6.8	-
	3.5	6.5	10.9	3.5	7.4	-	3.9	8.3	-	3.9	6.8	10.2	-	-	-	3.9	7.1	11.0	-	-	-	2.9	6.3	10.1	3.7	7.5	-
	3.4	6.1	10.2	3.6	7.2	-	4.1	8.8	-	4.5	7.8	11.7	-	-	-	4.3	7.8	12.2	-	-	-	2.5	5.4	9.0	3.4	6.6	-
Average	3.4	6.2	10.3	3.8	-	-	4.1	8.7	-	4.2	7.2	10.8	-	-	-	4.1	7.4	11.5	-	-	-	2.9	6.2	9.8	3.5	6.9	-
SD	0.1	0.4	0.7	0.4	-	-	0.2	0.4	-	0.2	0.4	0.62	-	-	-	0.3	0.6	0.9	-	-	-	0.2	0.5	0.5	0.2	0.4	-

APPENDIX E

Mechanical properties of rubber/PVC vulcanizates

Table E1. Effect of dilution ratio of Ethanol/distilled water on NBR swelling

EtOH/H_2O (v/v)	M_2 (g)	TEOS or EPS (g)	TEOS or EPS (mol)	TEOS or EPS (ml)	EtOH (ml)	H_2O (ml)	M_1 (g)	Degree of swelling (%)	Average
H_2O	5.02	50.2	0.24	2.68	0	47.31	5.55	10.58	10.75
H_2O	5.03	50.3	0.24	2.68	0	47.31	5.57	10.91	
1/3.4	5.01	50.0	0.24	2.68	10.80	36.50	5.85	16.20	16.08
1/3.4	5.05	50.5	0.24	2.68	10.80	36.50	5.85	15.95	
1/1.2	5.02	50.2	0.24	2.68	21.44	25.88	5.45	8.75	8.49
1/1.2	5.02	50.2	0.24	2.68	21.44	25.88	5.42	8.22	
1/0.5	5.04	50.4	0.24	2.68	32.40	14.90	5.62	11.40	11.44
1/0.5	5.01	50.0	0.24	2.68	32.28	15.03	5.61	11.47	
EtOH	5.03	50.3	0.24	2.68	47.31	0	5.67	12.94	13.53
EtOH	5.03	50.3	0.24	2.68	47.31	0	5.74	14.12	
H_2O	5.03	50.3	0.07	2.38	0	47.62	5.37	6.82	6.94
H_2O	5.02	50.2	0.07	2.38	0	47.63	5.38	7.05	
1/3.4	5.01	50.1	0.07	2.38	9.46	38.17	5.38	7.42	9.38
1/3.4	5.01	50.1	0.07	2.38	9.48	38.15	5.58	11.33	
1/1.2	5.01	50.1	0.07	2.38	18.96	28.67	5.50	9.62	10.23
1/1.2	5.02	50.2	0.07	2.38	18.96	28.67	5.56	10.83	
1/0.5	5.02	50.2	0.07	2.38	28.48	19.15	5.59	11.33	10.09
1/0.5	5.02	50.2	0.07	2.38	28.48	19.15	5.46	8.85	
EtOH	5.03	50.3	0.07	2.38	47.62	0	5.74	14.03	13.45
EtOH	5.02	50.2	0.07	2.38	47.63	0	5.66	12.86	

Table E2. Effect of dilution ratio of Ethanol/distilled water on NR swelling

$EtOH/H_2O$ (v/v)	M_2 (g)	TEOS or EPS (g)	TEOS or EPS (mol)	TEOS or EPS (ml)	EtOH (ml)	H_2O (ml)	M_1 (g)	Degree of swelling (%)	Average
H_2O	5.07	50.7	0.24	2.71	0	47.29	8.24	62.72	60.95
H_2O	5.05	50.5	0.24	2.70	0	47.30	8.04	59.17	
1/3.4	5.03	50.3	0.24	2.69	10.76	36.55	6.58	30.90	29.67
1/3.4	5.04	50.4	0.24	2.70	10.81	36.49	6.47	28.44	
1/1.2	5.02	50.2	0.24	2.69	21.53	25.78	5.82	15.96	18.745
1/1.2	5.02	50.2	0.24	2.69	21.53	25.78	6.10	21.53	
1/0.5	5.05	50.5	0.24	2.71	32.56	14.73	5.85	15.75	14.98
1/0.5	5.04	50.4	0.24	2.70	32.42	14.87	5.75	14.20	
EtOH	5.02	50.2	0.24	2.69	47.31	0	5.63	12.25	12.04
EtOH	5.01	50.1	0.24	2.69	47.31	0	5.61	11.82	
H_2O	5.05	50.5	0.07	2.38	0	47.61	6.70	32.63	31.54
H_2O	5.05	50.5	0.07	2.38	0	47.61	6.59	30.44	
1/3.4	5.03	50.3	0.07	2.38	9.52	38.10	6.57	30.43	29.75
1/3.4	5.03	50.3	0.07	2.38	9.51	38.12	6.50	29.07	
1/1.2	5.04	50.4	0.07	2.38	19.07	28.54	6.62	31.21	28.71
1/1.2	5.05	50.5	0.07	2.38	19.10	28.52	6.37	26.12	
1/0.5	5.04	50.4	0.07	2.38	28.56	19.06	6.20	23.02	23.88
1/0.5	5.04	50.4	0.07	2.38	28.56	19.06	6.28	24.74	
EtOH	5.04	50.4	0.07	2.38	47.62	0	5.70	13.09	11.25
EtOH	5.04	50.4	0.07	2.38	47.62	0	5.51	9.40	

Table E3. Effect of dilution ratio of Ethanol/distilled water/THF on NBR swelling

EtOH/H_2O/ THF (v/v)	M_2 (g)	TEOS or EPS (g)	TEOS or EPS (mol)	TEOS or EPS (ml)	EtOH (ml)	H_2O (ml)	THF (ml)	M_1 (g)	Degree of swelling (%)
THF	5.01	50.14	0.24	2.68	-	-	47.31	16.40	227.02
1/3.4/3.4	5.02	50.20	0.24	2.68	2.44	8.31	36.56	11.28	124.69
1/3.4/1.2	5.02	50.22	0.24	2.68	4.89	16.62	25.81	9.56	90.35
1/3.4/0.5	5.01	50.12	0.24	2.68	7.17	24.37	15.77	8.84	76.35
1/3.4/0	5.00	50.03	0.24	2.68	10.75	36.57	-	5.74	14.71
THF	5.03	50.31	0.07	2.40	-	-	47.61	19.23	282.17
1/3.4/3.4	5.02	50.19	0.07	2.40	10.83	-	36.82	19.20	282.55
1/3.4/1.2	5.03	50.26	0.07	2.40	21.64	-	25.97	9.89	96.67
1/3.4/0.5	5.02	50.24	0.07	2.40	31.74	-	15.87	7.56	50.43
1/3.4/0	5.02	50.16	0.07	2.40	47.64	-	-	5.80	15.62

Table E4. Effect of TEOS and EPS/rubber mass ratio on NBR swelling

TEOS/Rubber (w/w)	M_2 (g)	TEOS or EPS (g)	TEOS or EPS (mol)	TEOS or EPS (ml)	M_1 (g)	Degree of swelling (%)	Average
5/1	5.05	25.2	0.12	1.35	5.44	7.85	7.46
5/1	5.04	25.2	0.12	1.35	5.40	7.06	
10/1	5.01	50.1	0.24	2.68	5.47	9.34	11.22
10/1	5.02	50.2	0.24	2.68	5.68	13.10	
30/1	5.01	150.3	0.72	8.06	6.08	21.21	18.01
30/1	5.01	150.4	0.72	8.06	5.76	14.80	
50/1	5.04	251.8	1.21	13.50	6.20	23.63	19.43
50/1	5.04	252.0	1.21	13.51	5.81	15.22	
5/1	5.01	25.0	0.03	1.19	5.87	17.10	16.22
5/1	5.02	25.1	0.03	1.19	5.79	15.33	
10/1	5.02	50.2	0.07	2.37	5.79	15.35	14.81
10/1	5.03	50.3	0.07	2.38	5.75	14.27	
30/1	5.03	150.8	0.20	7.13	5.68	13.06	12.85
30/1	5.02	150.6	0.20	7.12	5.66	12.64	
50/1	5.02	251.0	0.34	11.86	5.68	13.13	12.80
50/1	5.02	250.8	0.34	11.85	5.64	12.47	

Table E5. Effect of TEOS and EPS/rubber mass ratio on NR swelling

TEOS/Rubber (w/w)	M_2 (g)	TEOS or EPS (g)	TEOS or EPS (mol)	TEOS or EPS (ml)	M_1 (g)	Degree of swelling (%)	Average
5/1	5.04	25.2	0.12	1.35	6.75	33.77	32.40
5/1	5.04	25.2	0.12	1.35	6.60	31.03	
10/1	5.01	50.1	0.24	2.68	7.55	50.74	50.37
10/1	5.01	50.1	0.24	2.68	7.51	49.99	
30/1	5.02	150.5	0.72	8.07	11.63	131.77	128.01
30/1	5.01	150.4	0.72	8.06	11.25	124.24	
50/1	5.03	251.6	1.21	13.48	16.00	218.01	217.22
50/1	5.04	251.8	1.21	13.50	15.94	216.43	
5/1	5.01	25.0	0.03	1.19	6.27	25.13	24.89
5/1	5.02	25.0	0.03	1.19	6.25	24.65	
10/1	5.05	50.5	0.07	2.39	6.82	34.98	33.49
10/1	5.04	50.4	0.07	2.39	6.65	32.00	
30/1	5.02	150.7	0.20	7.12	6.79	35.14	36.09
30/1	5.03	150.8	0.20	7.13	6.89	37.03	
50/1	5.02	251.1	0.34	11.86	6.86	36.62	36.55
50/1	5.02	250.9	0.34	11.86	6.85	36.48	

Note : M_1 was the mass of sample after swelling and M_2 was the mass of sample before sweling.

VITA

Mr. Thanit Treepichetkul was born on April 15, 1977 in Nakhon si thammarat, Thailand. He received his Bachelor’s degree of Science in Chemistry, from the Faculty of Science, Prince of Songkla University in 1999. He has pursued Master Degree in Chemical Technology, Faculty of Science, Graduate School, and Chulalongkorn University since 2000 and finished his study in 2002.