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PREPARATION OF RUBBER AND POLY(VINYL CHLORIDE)
BLENDS REINFORCED BY *IN SITU* SILICA



Miss Pattra Nasompan

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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

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

THESIS COMMITTEE

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

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

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

.....Member
(Assistant Professor Varawut Tangpasuthadol, Ph.D)

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อินซิทูซิลิกาในยางอะครีโลไนไตรล์-บิวทาไดอีน ยางธรรมชาติ และยางสไตรีน-บิวทาไดอีน
เตรียมได้ด้วยกระบวนการ โซล-เจล โดยใช้เตตราเอทอกซีไซเลน (TEOS) และเอทิลีน โพลีซิลิเกต
(EPS) แผ่นยางที่เตรียมจากน้ำยางถูกแช่ในสารละลาย TEOS และ สารละลาย EPS และ สารละลายเอ
ทิลีน ไดเอมีน ซึ่งเป็นตัวเร่งปฏิกิริยา ในงานวิจัยศึกษาผลของอัตราส่วนของน้ำและเอทานอลที่ใช้ใน
การเจือจาง ความเข้มข้นของสารละลาย TEOS และ EPS เวลาและอุณหภูมิการแช่ในสารละลาย
TEOSและ EPS ต่อระดับการบวมตัวและปริมาณซิลิกา และศึกษาผลของความเข้มข้นของตัวเร่ง
ปฏิกิริยาต่อปริมาณซิลิกา ความเข้มข้นของเอทิลีน ไดเอมีนมีผลค่อนข้างน้อยต่อปริมาณซิลิกาในยาง
พอลิเมอร์ผสมของยางอะครีโลไนไตรล์-บิวทาไดอีนอินซิทูซิลิกาและพอลิไวนิลคลอไรด์ถูกเตรียมขึ้น
และ แสดงสมบัติการเสริมแรง

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PATTRA NASOMPAN : PREPARATION OF RUBBER AND POLY(VINYL CHLORIDE) BLENDS REINFORCED BY *IN SITU* SILICA. THESIS

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In situ silica filling of acrylonitrile-butadiene rubber (NBR), natural rubber (NR) and styrene-butadiene rubber (SBR) was carried out by sol-gel process using tetraethoxysilane (TEOS) and ethylpolysilicate (EPS). The rubber film cast from latex was soaked in TEOS and EPS solution and in an aqueous solution of ethylenediamine as catalyst. The effect of the dilution ratio of ethanol/water, TEOS and EPS concentration, swelling time and temperature in TEOS and EPS solution on the degree of swelling and silica content were investigated. The effects of catalyst concentration on silica content were reported. Ethylenediamine concentration slightly affected the silica content in the rubber. The *in situ* silica filled NBR/PVC blends were prepared and exhibited the reinforcing properties.

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LIST OF ABBREVIATIONS

NBR	=	Acrylonitrile-butadiene rubber
NR	=	Natural rubber
SBR	=	Styrene-butadiene rubber
PVC	=	Poly(vinyl chloride)
TES	=	Tetraethoxysilane
EPS	=	Ethyl polysilicate
THF	=	Tetrahydrofuran
STR	=	Standard thai rubber
TSC	=	Total solid content
DRC	=	Dry rubber content
ZnO	=	Zinc oxide
MgO	=	Magnesium dioxide
MBTS	=	Mercaptobenzothiazole disulfide
TMTD	=	Tetramethyl thiuramdisulphide
Si	=	Silica
PEG	=	Polyethylene glycol
ASTM	=	American society for testing and materials
TGA	=	Thermogravimetric analysis
SEM	=	Scanning electron microscopy
DMA	=	Dynamic mechanical analysis
phr	=	Part per hundred rubber
MPa	=	Mega pascal
N/m	=	Newton per meter
mm	=	Millimeter
Avg	=	Average
W	=	Weight (s)
g	=	Gram (s)
h	=	Hour (s)
°C	=	Degree celsius

CHAPTER I

INTRODUCTION

1.1 Statement of Problems

Blending of polymers is of interest for property improvement and for economic advantage. Miscibility of the constituent polymers is often a necessity for forming successful blends. One of commercially important and miscible polymer blends is that of acrylonitrile-butadiene rubber (NBR) and poly(vinyl chloride) (PVC). NBR acts as a permanent plasticizer for PVC in applications such as wire and cable insulation, food containers, pond liners for oil containment, ect. On the other hand, PVC improves ozone, thermal aging and chemical resistance of NBR in applications as fuel hose covers, seal, diaphragm, gaskets, conveyor belt, paint roll etc. NBR/PVC blends can be conveniently milled, extruded and compressed -molded using traditional processing equipment [1].

Reinforcement is one of the most important technologies used to obtain the desired physical properties of rubber vulcanizates. Many rubbery products are colored black because carbon black is the most effective filler and other than carbon black, only silica is able to reinforce rubbers. Conventionally, filler-reinforced rubber is prepared by mechanical mixing of filler followed by compression moulding for curing. However, the incorporation of silica into rubber by normal mixing techniques causes an increase in viscosity because of the small size and large specific surface area of the filler. Silica also deactivates curing agents and accelerators, thus resulting in an insufficient cure. These problems are partially overcome or minimized by specific additives and mixing procedures. The other major difficulty is the incompatibility of inorganic silica with the organic rubber. This results in aggregation of silica particles in rubber matrix to decrease the reinforcing effect on mechanical properties.

As a method for overcoming these difficulties, the *in situ* silica filling using the sol-gel reaction of tetraethoxysilane (TEOS) and ethylpolysilicate (EPS) for production of silica particles has been focused upon. The reaction of TEOS takes place in two steps, hydrolysis and condensation, and results in SiO₂. In the field of rubber science,

crosslinked rubbers have been subjected to this *in situ* filling of silica. However, the limit of the *in situ* silica filling in the rubber vulcanizates is the thickness of rubber for swelling in TEOS and for soaking in catalyst in order to conduct the sol-gel reaction of TEOS homogeneously in the rubber matrix.

Therefore, this work aims to prepare the silica-filled rubbers by sol-gel process. The sol-gel reaction is promoted by the addition of TEOS, EPS, alcohol and water and a catalyst to the swollen rubber. The effects of ethanol/ water dilution ratio, TEOS and EPS concentration, catalyst concentration and swelling time in TEOS and EPS solution were elucidated. The *in situ* silica filled NBR/PVC blends were prepared and the mechanical properties were investigated.

1.2 Objectives

The objectives of this research are as follows :

1. To develop the dispersion of silica particle in acrylonitrile-butadiene rubber (NBR), natural rubber (NR) and styrene-butadiene rubber (SBR) by sol-gel process.
2. To study the physical and mechanical properties of the *in situ* silica filled NBR/PVC blends.
3. To study effect of using the *in situ* silica filled NR and SBR replace part of NBR in NBR/PVC blends on the physical and mechanical properties of polymer blends.

1.3 Scope of the Investigation

The stepwise investigation was carried out as follow:

1. Literature survey and study the research work.
2. Prepare the silica-filled rubbers by sol-gel process before curing. The appropriate conditions were determined by varying the following parameters :
 - a) Dilution ratio of water/ ethanol in TEOS and EPS solution.

- b) TEOS and EPS concentration.
 - c) Catalyst concentration.
 - d) Time and temperature for swelling in TEOS and EPS solution.
3. Characterize and study the morphology of the *in situ* silica filled rubbers by scanning electron microscopy (SEM).
 4. Prepare the polymer blends by direct mixing of the *in situ* silica filled rubbers with vulcanizing agents, additives and PVC.
 5. Determine the physical and mechanical properties of the *in situ* silica filled rubber/PVC blends compared with polymer blends without silica and with commercial silica.
 6. Study the thermal properties of polymer blends by dynamic mechanical analysis (DMA).
 7. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Acrylonitrile-Butadiene Rubbers (NBR) [1]

Acrylonitrile-butadiene rubbers (NBR), or, simply, nitrile rubbers are copolymers of butadiene and acrylonitrile.

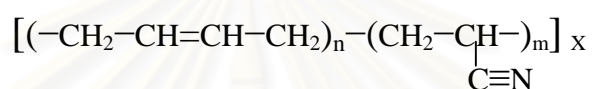


Figure 2.1 Structure of acrylonitrile-butadiene rubber

The polymerization cycle of rubbers is the same for both dry rubber and latex. In the production of latex form, it is usually to add additional stabilizing agents in the blowdown tank prior to the stripping operations which remove the excess butadiene and acrylonitrile. In the case of dry rubber production, the next step is the transfer of the latex to coagulating tanks, at which point the latex is coagulated into fine crumbs by the addition of various salts and acids. This slurry of rubber particles is then generally extracted with a caustic solution, washed, de-watered, and finally dried.

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;

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;
- compression 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, 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

As 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 NR and SBR. Ester-based plasticizers are generally used in NBR compounds to improve low-temperature properties. Sulphur donor and peroxidecuring systems are normally used for applications requiring good high-temperature performance and low compression set.

b) **Vulcanizate Properties**

As has been mentioned, many of the vulcanizate properties will very 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°C and for intermittent periods (in the absence of air) up to 120°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, nonpetroleum-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 Natural Rubber [1]

Natural rubber is a white milky fluid produced by specialised cells in a variety of plants, throughout the world, in totally unrelated families, including the *Compositae* and *Moraceae* as well as the *Euphorbiaceae*. Most of the world's natural rubber comes today from South-East Asia, mainly Thailand, Malaysia, and Indonesia.

Hevea Brasiliensis, the commercial rubber tree, is a tall tree, growing naturally up to forty metres (130 feet) and living for one hundred years or more. *Hevea Brasiliensis* requires temperatures of 20-30°C, at least 2,000 mm of rainfall per year, and high atmospheric humidity. This naturally occurring polymer is known chemically as cis-1, 4-polyisoprene (Figure 2.2)

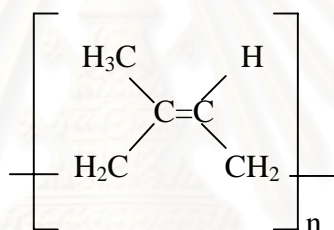


Figure 2.2 Structure of *cis*-1, 4-polyisoprene

a) Natural Rubber Latex [2]

Natural latex is produced in special vessels outside the cambium layer of the *Hevea brasiliensis* tree. The reason why the rubber tree makes rubber is still not known. One theory holds that it is a waste product of the tree. The polymer is primarily *cis*-1, 4-polyisoprene. Latex fresh from the tree is stabilized by naturally occurring proteins and phospholipids. It also contains other materials such as resins, sugars, mineral salts, and alkaloids. The protein stabilizer is very susceptible to bacterial action and would be destroyed within a few hours if ammonia were not immediately added. If latex is preserved entirely by ammonia (high ammonia latex), a portion of the ammonia is usually removed before application. The composition of typical field latex is presented in Table 2.1.

Table 2.1 Composition of latex

Constituent	% Composition
Rubber particle	36.0
Proteinaceous substance	1.5
Sugar, Lipids, Resinous substances	2.5
Water	60.0

About 10% of natural rubber is not processed into dry rubber but sold as latex. Latex concentrate is usually made by centrifugation-spinning at high speed to separate off a cream of about 60% rubber from a liquid of about 5% rubber, Latex concentrate usually made by centrifugation-spinning at high speed to separate a cream containing 60% rubber from a liquid containing 5% rubber, from which dry skim rubber is made. A small amount of ammonia is added to the latex, both on collection and before centrifugation, to prevent it from coagulation. Another concentrate made by evaporation, evaporated latex concentrated, has a higher rubber content and so slightly different properties. Finally, there is creamed latex concentrate: the field latex is mixed with a chemical, such as ammonium alginate, which makes the rubber particles rise to the top of the liquid, like cream, when left to stand for several weeks. All latex concentrate are chemically treated to prevent coagulation.

Most of the natural rubber latex is produced in Malaysia, Indonesia, and Liberia. Latex concentrate constitutes slightly more than 8% of the world natural rubber supply, and about 90% of this is centrifuge concentrated. Principal outlets for natural rubber latex are foam rubber, dipped goods, and adhesives.

b) Dry Natural Rubber

Depending on the producing country, 10-20% of the tree latex is concentrated by creaming or centrifuging, and shipped to consumer countries, where it is used as such to make finished articles, including foam for upholstery and bedding, a variety of tubing

and dipped goods, etc. The remainder is processed into dry rubber, as sheets, crepes, remills, etc.

c) 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).

d) 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°C and for intermittent periods up to 100°C. The vulcanizates remain flexible at temperatures down to -55°C without adding plasticizers. However, they tend to crystallize readily when stored for long periods at low temperatures .

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.

e) 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.

2.3 Styrene-Butadiene Rubbers (SBR) [1]

SBR are copolymers of butadiene and styrene. The regular grades contain 23% styrene. Increasing styrene content leads to a loss in resilience and a rise in the freezing point of the vulcanizates. Structure of acrylonitrile-butadiene rubber are shown in Figure 2.3.

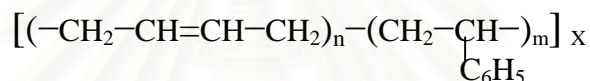


Figure 2.3 Structure of styrene-butadiene rubber

a) Compounding

In general, SBR can be compounded using the same ingredients for NR. However, SBR cures more slowly than NR and hence either more accelerator or a more active accelerator system is required than for NR.

SBR can be blended with other diene rubbers such as NR, IR and BR. Polymers containing a high proportion of styrene are widely used in blends with diene rubbers to give improved wear resistance and high hardness in conjunction with low specific gravity.

b) Vulcanizate Properties

In contrast to NR, the tensile strength of SBR gum vulcanizates (i.e., unfilled compounds) is very poor (about 10-15% of that of NR elastomers). This is because of the absence of crystallization on stretching the gum vulcanizate (section 1.7). Consequently, these rubbers do not develop high tensile strengths without the aid of

reinforcing fillers. The resilience and low-temperature behavior of SBR vulcanizates are inferior to those of NR, but heat aging characteristics are better. The vulcanizates have an operational temperature range of -50 to +100°C and they show no tendency to crystallize at low temperatures.

Like other highly unsaturated elastomers, SBR vulcanizates show poor ozone resistance, which can be improved by blending with EPDM or by incorporating antiozonants and protective waxes.

SBR vulcanizates are not resistant to petroleum-based oils and greases or hydrocarbon fuels, but they are resistant to nonpetroleum-based automotive brake fluids, silicone oils and greases; glycols; alcohols; water; and nonoxidizing aqueous solutions of acids, alkalis and salts.

c) **Applications**

SBR was produced during the Second World War as a substitute for NR. Generally speaking, SBR can be used in many applications as a replacement for NR, except in severe dynamic applications requiring low heat buildup on flexing (e.g., high-performance tires for trucks).

2.4 **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°C. 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 flexible.
- 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.

2.5 NBR/PVC Blends [1, 3]

Due to its higher polarity, poly(vinyl chloride) is compatible with most NBR grades at all blend ratios. The acrylonitrile (ACN) content of the NBR polymer influences the final properties of the NBR/PVC blend. Medium and high nitriles give a homogeneous polymer phase with PVC. In practice, nitrile rubbers with medium (34%) ACN appear to offer the best balance of properties. 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. The vulcanizates have higher tensile and tear strength. A further advantage is the good surface finish of the vulcanizates. In addition to the NBR polymer and the PVC resin, it is necessary to include PVC stabilizers, plasticizers and sometimes lubricants in the blend. Experience has shown that the metallic soap type vinyl stabilizers, when used together with an organic chelating agent, offer the best balance between cost and performance in NBR/PVC blends.

a) Vulcanization Chemicals

Cure systems for NBR/PVC are similar to those used for NBR, namely sulphur, sulphur donor and peroxides. All regular white fillers, such as silica, clays, calcium carbonate and talcs, can be used. For many NBR/PVC applications, white-filled compounds containing a small amount of carbon black for colouring and UV light protection provide a balance of properties at lower cost than compounds containing carbon black alone.

b) Compounding and Processing

Compounding principles for NBR/PVC blends are essentially the same as for NBR. Compounds can be mixed using internal mixers or open mills. NBR/PVC grades are easy to colour and have a very smooth surface.

2.6 The Compounding and Vulcanization of Rubber [1]

2.6.1 Compounding Ingredients

Rubber compounding is meant the way of making useful products from crude rubbers. It is sufficient to note here that crude rubbers are essentially noncross-linked polymers and that they are the basic component for manufacturing all elastomeric products.

The first step of rubber compounding is usually to soften the crude rubber by mechanical working. This can be done on two-roll mills or in internal mixers. In this soft condition the rubber is easily blended with a variety of compounding ingredients that are normally given in parts per weight, based on 100 parts of crude rubber (phr). A generalized rubber formula is given in Table 2.2.

Table 2.2 A generalized rubber formula

	Parts per weight
Crude rubber	100
Filler	50
Softener	5
Antioxidant	1
Stearic acid	1
Zinc oxide	5
Accelerator	1
Sulphur	2
Total	165

Each ingredient has a specific function, either in processing, vulcanization or end use of the product. The compounding ingredients may be classified according to their specific function in the following groups:

- fillers (carbon blacks and nonblack fillers);
- plasticizers or softeners (extenders, processing aids, special plasticizers);
- age resistors or antidegradants (antioxidants, antiozonants, special age resistors, protective waxes);
- vulcanizing or curing ingredients (vulcanizing agents, accelerators, activators);

a) Fillers [1, 4]

Fillers are compounding ingredients, usually in powder form, added to crude rubber in relatively large proportions (typically 50 phr). They include two major groups: carbon blacks and nonblack fillers. The nonblack fillers include, for example, clays, calcium carbonate, silicates and precipitated and fumed (anhydrous) silicas.

Fillers are added for economic or technical purposes. Some are incorporated primarily to extend and therefore make the final product less expensive and others mainly to reinforce it. By reinforcement is meant enhancement of properties such as tensile strength, tear and abrasion resistance.

The addition of silica to a compound rapidly increases the viscosity, so 50 parts is about the upper limit. Petroleum oils or resins can be chosen: however aromatic resins

are unique in giving smooth extrusions with better tensile strength and tear resistance, along with better abrasion resistance. But major reductions in viscosity are obtained only with additives that de-agglomerate the silica. Whereas there is an affinity between carbon black and nonpolar rubbers, silica is hydrophilic and incompatible. Silica-to-silica attraction is high, with the result that large aggregates are formed, impeding flow, and the mix becomes very stiff.

Another unique feature of silica compounding is the good activating effect of glycols, particularly polyethylene glycol (PEG). The activation effect shows up in significant reductions in cure time, plus higher tensile strength; compression set and heat buildup are lower [4].

b) Plasticizers

Plasticizers or softeners can be liquids, semisolids. Petroleum oils are the most widely used extenders and processing aids, depending on the amount added. A small amount (ca. 2-5 phr) as a processing aid. There are several reasons for this: these oils are effective, economical in price and, as liquids, easy to use.

c) Age Resistors

Age resistors or antidegradants are organic substances usually added in small amounts (about 1-4 phr) to retard deterioration caused by aging, thus extending the service life of the elastomeric product involved. They protect elastomers against such agents as oxygen, ozone, heat, sunlight, high energy radiation and high humidity.

d) Vulcanizing Ingredients

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. Today, accelerators are almost always organic compounds containing either nitrogen or sulphur or both. Very few accelerators, such as tetramethylthiuram disulphide.

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

- Sulphur 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.

Conventional sulphur vulcanizing systems for soft rubber products consist of relatively high amounts of elemental sulphur (about 1-3 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.

2.6.2 Mixing and Vulcanization Procedures

Rubber compounding is generally carried out on open mills or in internal mixers. An open mill consists of two adjacent, smooth, hardened-steel rolls set horizontally. They rotate in opposite directions. The back roll rotates faster than the front one in order to produce a friction or grinding action between them. Mixing is achieved by the shearing action induced in the space between the rolls, which is adjustable. The mill rolls are hollow and are equipped for internal cooling with water.

The mixing process on an open mill involves masticating or breaking down the crude rubber until an even and smooth band is formed around the front roll. When the crude rubber becomes soft and plastic, the fillers and other ingredients are added and worked in, following a definite time, temperature range and sequence schedule. During the mixing operation, cutting and blending is carried out in order to obtain a thorough and uniform dispersion of the ingredients in the rubber mix.

2.7 Reinforcement by Fillers [2]

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 a calcium 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 today.

2.7.1 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 so 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 same 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 of the final vulcanizate.

2.7.2 Basic Factors Influencing Elastomer Reinforcement

The appearance of an optimum loading indicates that there two opposing factors in action when a reinforcing filler such as carbon black 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 area 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 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.

2.7.3 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.

2.8 Sol-Gel Processing [5]

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 most thoroughly studied example is silicon tetraethoxide (or tetraethoxysilane, or tetraethyl orthosilicate, TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$. Metal alkoxides are popular precursors because they react readily with water. The reaction is called hydrolysis, because a hydroxylion becomes attached to the metal atom, 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). Two partially hydrolyzed molecules can link together in a condensation reaction. 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. Therefore, The reaction of TEOS takes place in two steps, hydrolysis and condensation, and results in SiO_2 as shown in Figure 2.4.

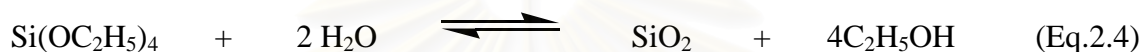
Hydrolysis**Condensation****Overall reaction**

Figure 2.4. The sol-gel reaction of TEOS.

2.8.1 Hydrolysis and Condensation of Silicon Alkoxides

Silicon is the most abundant metal in the earth's crust, and evidence of silicate hydrolysis and condensation to form polysilicate gels and particles are seen in many natural systems. Silicate gels are most often synthesized by hydrolyzing monomeric, tetrafunctional alkoxide precursors employing a mineral acid or base as a catalyst.

The *hydrolysis reaction* (Eq. 2.1) replaces alkoxide groups (OR) with hydroxyl groups (OH). Subsequent *condensation reactions* involving the silanol groups produce siloxane bonds (Si-O-Si) plus the by-products alcohol (ROH) (Eq. 2.2) or water (Eq. 2.3). Under most conditions, condensation commences (Eqs. 2.2 and 2.3) before hydrolysis (Eq. 2.1) is complete. Because water and alkoxysilanes are immiscible, 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. It should be noted that alcohol is not simply a solvent. As indicated by the reverse of Eq. 2.1 and 2.2, it can participate in *esterification* or *alcoholysis* reactions.

2.8.2 Precursor Molecules

The most common tetraalkoxysilanes used in the sol-gel process are tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and tetramethoxysilane ($\text{Si}(\text{OCH}_3)_4$), which are abbreviated in the literature as TEOS and TMOS, respectively. 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 40 wt%, which corresponds to a mixture of ethoxysiloxanes with an average of five silicon atoms per oligomer.

2.8.3 Sol-Gel Process in Polymers

Recently, a sol-gel process of TEOS was applied to prepare silica for reinforcing many types of rubbers; e.g. synthetic rubber [9, 10, 11, 13, 14] and natural rubber [12]. The thin sheet rubbers were swollen in TEOS, followed by soaking in catalyst to follow the sol-gel reaction of TEOS. Then the samples were subjected to heating after removal from the catalyst solution. The drying of the samples was conducted for several day. The *in situ* silica-filled rubbers were obtained.

2.9 Literature Review

K.E. George, et al. [6] studied on NBR/PVC blend. The studies were conducted on NBR/PVC blends at different brabender temperatures. An optimum temperature existed for the formation of a particular blend. The mechanical properties of the blends confirm this observation. PVC stabilizers based on magnesium oxide, zinc oxide, and stearic acid were found to be very useful in NBR/PVC blends

K.E. George, et al. [7] studied the modification of NBR/PVC blend using natural rubber, styrene-butadiene rubber and polybutadiene rubber. The natural rubber, styrene-butadiene rubber and polybutadiene were used to replace part of the NBR in a 70/30

NBR/PVC blend. Such replacement up to 15% of the total weight of the blend improved the mechanical properties, while reducing the cost of the blend. SBR could replace NBR up to 30% of the total weight of the blend without deterioration in the mechanical properties.

S.H. Zhu, et al. [8] studied the mechanical properties of PVC/SBR blends compatibilized by NBR and covulcanization. A sulphur curing system was employed to crosslink the rubber of the blend. In the case of the blend 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) blend the tensile strength and elongation-at break increased with an increase in sulphur concentration. This improvement was attributed to covulcanization between NBR and SBR.

Y. Ikeda, and S.Kohjya [9] studied the *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 resulting crosslinked BR was subjected to soaking in TEOS at 30° C for 48 h. The swollen vulcanizates were kept in an aqueous solution of n-butylamine at 30°C for 24 h, followed by standing at 50°C for 72 h to conduct the *in situ* sol-gel reaction of TEOS. The resulting 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

Y. Ikeda, et al. [10] studied the reinforcement of styrene-butadiene rubber vulcanizate by *in situ* silica prepared by the sol-gel reaction of TEOS. *In situ* silica reinforcement of SBR has been achieved by a sol-gel process using 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 on the results of tensile tests, dynamic mechanical measurements, optical and transmission electron microscopies.

H. Tanahashi, et al. [11] studied the reinforcement of acrylonitrile-butadiene rubber by silica generated *in situ*. *In situ* silica reinforcement was applied to the 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 [12] studied the reinforcement of natural rubber by silica generated *in situ*. The new method to produce *in situ* silica in 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 rubber 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 [13] studied the reinforcement of general-purpose grade rubber 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 TEOS in epoxidized natural rubber (ENR), SBR or 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. Silica coupling agents, such as mercaptosilane, aminosilane, and bis(3-trithoxysilylpropyl) 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 particle size became smaller and monodispersed, as observed by TEM, which improved mechanical properties.

Y. Kazumasa, et al. [14] studied the silica reinforcement of synthetic diene rubbers by sol-gel process in the latex. SBR and NBR were reinforced with silica by the sol-gel method of 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°C. The amount of TEOS added and 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 particle size and reinforcing

behavior of the silica were greatly influenced 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.



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CHAPTER III

APPARATUS AND EXPERIMENTAL

3.1 Chemicals

1. Acrylonitrile-butadiene rubber latex and solid rubber (34% ACN) : Bayer (Thailand) Co, Ltd. and Pan Innovation Co, Ltd.
2. Natural rubber latex, high ammonia and solid rubber, STR5L : Thai Rubber Latex Corporation (Thailand) Public Co, Ltd. and Teck Bee Hang Co, Ltd.
3. Styrene-butadiene rubber latex and solid rubber : HCMC Co, Ltd. Pan Innovation Co, Ltd.
4. Poly(vinyl chloride) : Thai Plastic & Chemical Co, Ltd.
5. Tetraethylorthosilicate : Fluka
6. Ethyl polysilicate : Silbond Co, Ltd.
7. Ethanol, AR grade : Fluka
8. Tetrahydrofuran, AR grade : Fluka
9. Ethylenediamine : Fluka
10. Zinc oxide, white seal : Unithaioxide Co, Ltd.
11. Stearic acid : Imperial (Thailand)Co, Ltd.
12. Magnesium dioxide : Unithaioxide Co, Ltd.
13. Mercaptobenzothiazole disulfide : Flexsys Co, Ltd.
14. Tetramethyl thiuramdisulphide : Flexsys Co, Ltd.
15. Sulphur : Loxley Public Co, Ltd.
16. Wingstay L (Antioxidant) : Goodyear Co, Ltd.
17. Silica, Hi-Sil[®] 255-S (particle size is 0.22-2.17 μ m from SEM) : PPG Siam Silica Co, Ltd.
18. Polyethylene glycol : Pan Innovation Co, Ltd.
19. Petroleum oil : Loxley Public Co, Ltd.

3.2 Apparatus

1. Oven : WTB Binder, Model ED-115i
2. Vacuum Oven : Binder, Model VD-23
3. Furnace : CARBOLITE, Model ELF
4. Two-roll mill : Model R 11-3-FF
5. Compression molding machine : Model V 75h-18-BPX, Serial 9593
6. Compression air sample cutter : Model SDAP-100-N Intro Enterprise Co, Ltd.
7. Mooney viscometer : Visc. Tech.
8. Rheometer, moving die type : Rheotech[®] Techpro
9. Tensile testing machine : Instron Corporation Series IX Automated Materials Testing
10. Tear testing machine : LLOYD Instruments LS 500
11. Hardness testing machine : Durometer Hardness System (Shore A), Model 716
12. Thermogravimetric Analyzer : Shimadzu TGA-50
13. Scanning Electron Microscope : JEOL, Model JSM-6400
14. Dynamic Mechanical Analyzer : GABO, Model EPLEXOR QC 25

3.3 Procedure

3.3.1 Preparation of the Silica-filled Rubbers by Sol-Gel Method

The appropriate condition for preparation of the *in situ* silica filled rubbers were determined by varying of the following parameters:

- a) Effect of dilution ratio of water/ ethanol in TEOS and EPS solution
: 1/0, 3/1, 1/1, 1/3 and 0/1 in 25%w/w of TEOS and EPS solution
- b) TEOS and EPS concentration: 25-100%w/w
- c) Catalyst concentration: 3-15%w/w
- d) Time and temperature for swelling in TEOS and EPS solution
: 24-120 h at room temperature and 40°C for TEOS and 40°C for EPS

The concentrated natural rubber latex (DRC 60%, TSC 61.5%), NBR latex (TSC 42%) and SBR latex (TSC 67%) were cast at 70°C for 18 h to form a film of ca. 0.75 mm thickness for use in the experiments.

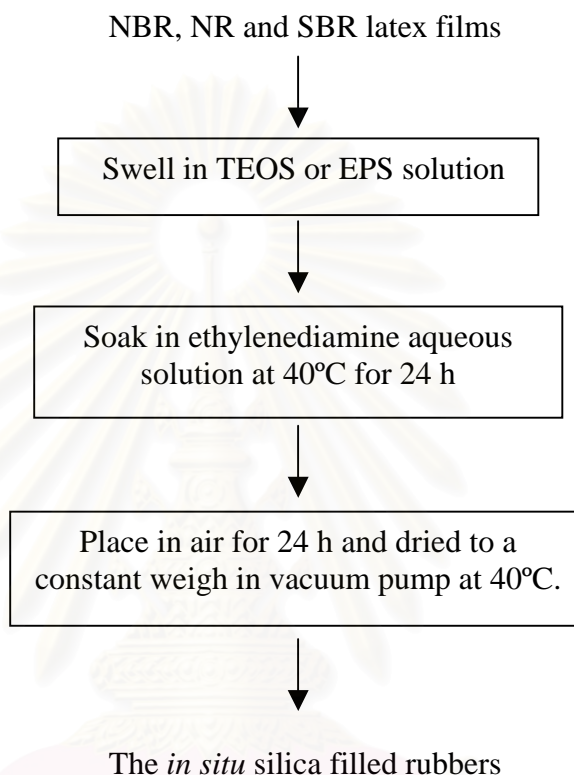
Two g of NBR, NR and SBR latex films were immersed in 30 g of TEOS and EPS solution (H₂O/EtOH) at room temperature for TEOS and 40°C for EPS for 48 h and soaked in 60 g of 3%wt ethylenediamine aqueous solution at 40°C for 24 h. Then, the samples were placed in air for 24 h and dried to a constant weight in vacuum pump at 40°C. The amount of TEOS, EPS, ethanol, water and catalyst, time and temperature for swelling was varied. The silica content of the *in situ* silica-filled rubber sample was determined by 2 methods: one is thermogravimetric analysis (Shimadzu TGA-50) the other is heating in furnace at 900°C. The degree of swelling (%) and the silica content (%) were calculated from Eq. 3.1 and 3.2, respectively.

$$\text{Degree of swelling (\%)} = 100[(W_1 - W_2)/W_2] \quad (3.1)$$

$$\text{Silica content (\%)} = 100(W_3/W_4) \quad (3.2)$$

Where W_1 is the weight of sample after swelling in TEOS or EPS, W_2 is the weight of sample before swelling, W_3 is the weight of silica in the sample and W_4 is the weight of

sample. The overall schematic diagram for the preparation of *in situ* silica filled rubbers by a sol-gel method is shown in scheme 3.1.



Scheme 3.1 The overall schematic diagram for the preparation of *in situ* silica filled rubbers by sol-gel method

3.3.2 Determination of the Degree of Swelling and the Silica Content

a) Degree of Swelling of TEOS or EPS [9]

The degree of swelling of sample was followed by swelling in TEOS or EPS solution. The degree of swelling in solution was calculated using Eq. 3.1.

b) Determination of the Silica Content: 2 Methods

A sample was prepared by passing 10 times between the rolls of a two-roll mill. The roll temperature was maintained at 50°C. Approximately 2 g of the thin sheet was dried for 1 h in the oven at 100°C. The dried sheet was kept in a desiccator until ready to weigh the samples. The silica content of the *in situ* silica filled rubber sample can be determined by 2 methods as follows:

Method 1. Thermogravimetric Analysis (ASTM D5805)

Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50. A dried sample (ca 20 mg) was placed in a platinum pan and heated under air to 900°C at a temperature increase of 20°C/min. The silica content of rubber was determined from the results of TGA by Eq. 3.2.

Method 2. Heating in Furnace

A piece of the *in situ* silica filled rubber (ca 50 mg) was placed in a crucible and heated under air to 900°C in a furnace for 3 h. The silica contents of rubber was calculated from the weight of remaining ash by Eq. 3.2.

3.3.3 Scanning Electron Microscopy (SEM) Study

The morphology of the samples was observed by scanning electron microscopy (SEM). The samples were frozen in liquid nitrogen and broken. The obtained cross sections were subjected to SEM using an instrument (S-4100 instrument of Hitachi Ltd.). The accelerating voltage was 15 kV.

3.3.4 Preparation of the Rubber/PVC Blends

The in situ silica filled rubbers and the vulcanizing chemicals were mixed on a two-roll mill. For comparison purposes, NBR/PVC, NBR/NR/PVC and NBR/SBR/PVC blends filled with commercial silica and the unfilled NBR/PVC blends were also prepared by the conventional mixing technique. The vulcanized rubber/PVC sheets were cured at 150°C under pressure in the compression mold. The composition of rubber/PVC blends without silica, with commercial silica and *in situ* silica (TEOS) is shown in Table 3.1. The chemicals used in the preparation of rubber/PVC blends are shown in Table 3.2. The overall schematic diagram of the preparation of silica filled rubber/PVC blends is shown in scheme 3.2. Detailed blending procedure is as follows:

a) NBR/PVC Compound

The mixing roll temperature of two-roll mill was kept constant at 150°C. The NBR or the *in situ* silica filled NBR was fed to the two-roll mill for 2 min and then blended with PVC and stabilizers (composition in Table 3.1) for 7 min until the polymer compound was homogeneous. The polymer blend sheet was removed and placed at room temperature.

b) Vulcanized Rubber/PVC

The mixing roll temperature of two-roll mill was kept constant at 70°C. The NBR/PVC compound or the in situ silica filled NBR/PVC compound was fed to the two-roll mill for 3 min and then blended with NR or SBR or in situ silica filled NR or in situ silica filled SBR. Then, compounding ingredients (Table 3.2) were added slowly to the rubber. The mixing proceeded until homogeneous compound was obtained. The sheet was cut from the roll and placed on the clean place. The sample sheet was vulcanized by curing at 150°C under pressure of 150 kg/cm² in the compression mold for a prescribed time. The vulcanized rubber/PVC sheet of ca. 2 mm thickness was obtained.

Table 3.1 Composition of rubber/PVC* blends.

Code	Compound rubber	Rubber/PVC Ratio (by weight)	Si (phr)**
R1	NBR/ PVC	70/ 30	0
R2	NBR/ PVC/ Si	70/ 30	40
R3	NBR/ PVC/ NR/ Si	55/ 30/ 15	40
R4	NBR/ PVC/ SBR/ Si	55/ 30/ 15	40
R5	NBR/ PVC/ <i>In situ</i> Si	70/ 30	40
R6	NBR/ PVC/ NR / <i>In situ</i> Si	55/ 30/ 15	38.5
R7	NBR/ PVC/ SBR/ <i>In situ</i> Si	55/ 30/ 15	39

1) Si = Commercial silica powder.

2) *In situ* Si = *in situ* silica by the sol-gel method of TEOS.

3) * = Stabilizer of PVC: MgO 4, ZnO 4 and stearic acid 3 part per hundred of PVC

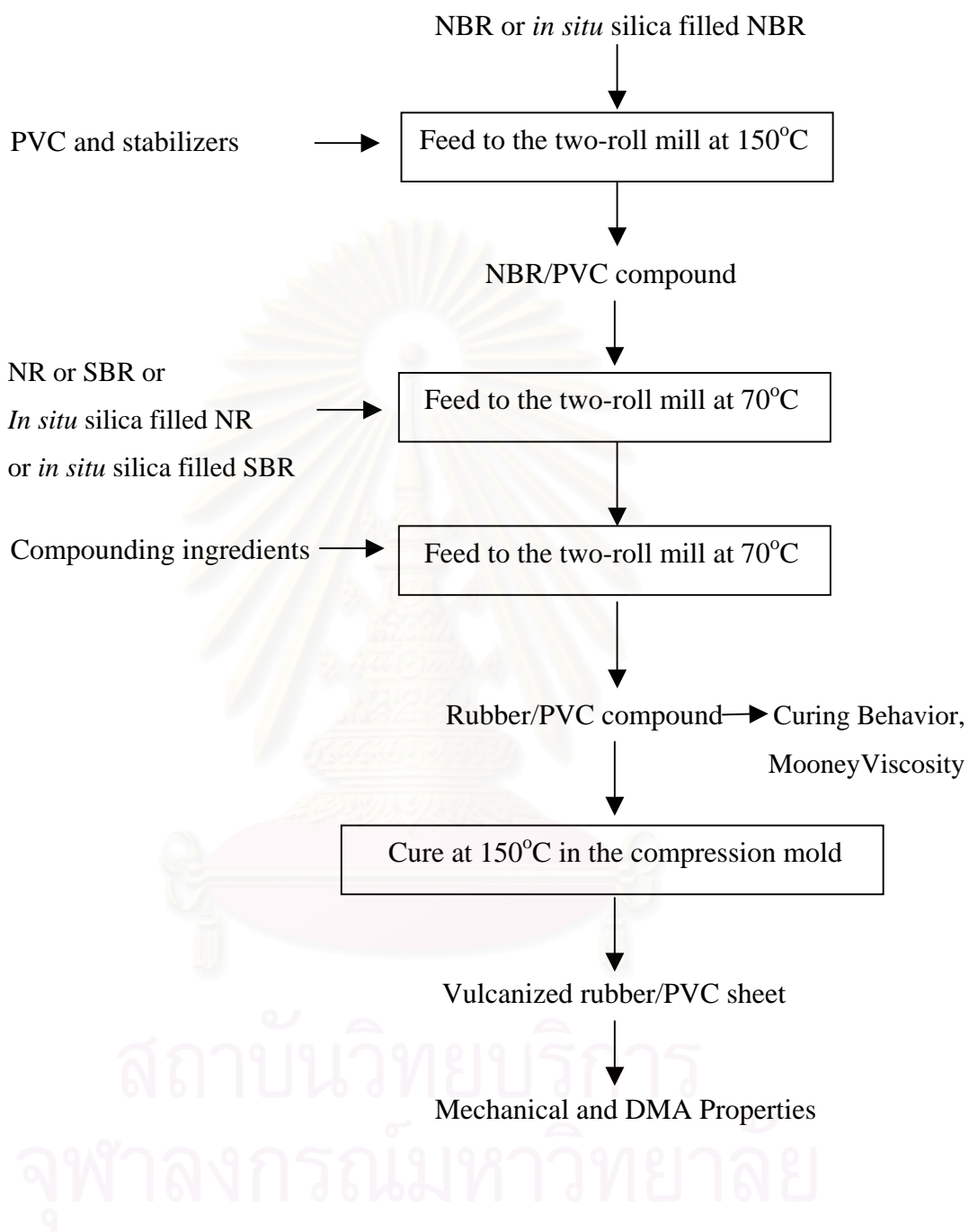
4) ** = Part per hundred of rubber (g in 100 g rubber).

Table 3.2 Compounding recipes for rubber (phr).

Chemical of rubber	R1	R2	R3	R4	R5	R6	R7
Sulfur	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Commercial silica	-	40	40	40	-	-	-
Polyethylene glycol (PEG)	-	2	2	2	-	-	-
Petroleum oil	-	3	3	3	-	-	-
Wingstay L	1	1	1	1	1	1	1
MBTS ^a	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD ^b	1	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5

^a Mercaptobenzothiazole disulfide

^b Tetramethylthiuramdisulfide



Scheme 3.2 The overall schematic diagram of the preparation of silica filled rubber/PVC blends.

3.3.5 Material Characterization of the Rubber/PVC Blends

a) Cure Behavior (ASTM D2705)

This test method measured the cure time of rubber. The moving die type Rheometer (Rheotech[®] Techpro) was used for determining vulcanizing behavior of NBR/PVC compound. Test specimen size was 1.5 cm x 1.5 cm x 5 mm. The test temperature was 30 min at 150°C.

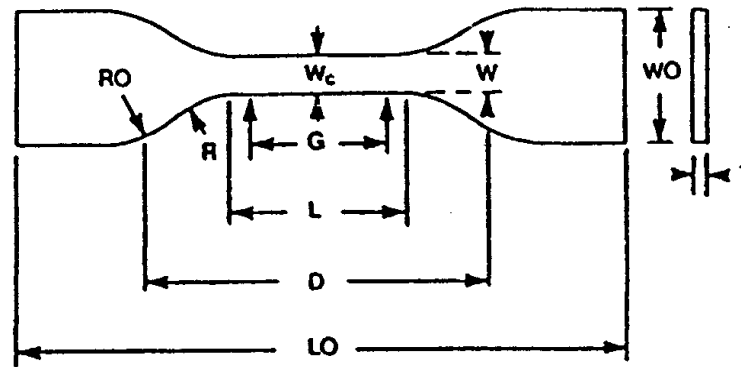
b) Mooney Viscosity (ASTM D1646)

A Mooney viscometer measures the effect of temperature and time on the viscosity of rubber. The test specimen consists of two pieces which completely fill the test chamber. The rotor was continuously rotated at 2 rpm in one direction for a specified time. The resistance to this rotation offered by the rubber was measured in arbitrary torque units as the Mooney viscosity (MV). The temperature for viscosity determination was 100°C. The sample was allowed to warm up for one minute. The motor was then started and reading taken at 4 min.

c) Tensile Properties (ASTM D412)

Tensile strength, elongation and modulus were determined. The vulcanized rubber was stamped with a compressed air sample cutter into a dumbbell shape (Type IV) as illustrated in Figure. 3.1. The gage length was 2.50 cm and the thickness of specimen was 2 mm. The testing was performed on a tensile testing machine. An average of 3 specimens was considered as representative value. The test condition was as follows:

Temperature	25°C
Humidity	60%
Sample rate	10.00 pts/sec.
Crosshead speed	500 mm/min.



TYPE IV

W : 6 mm WO : 19 mm G : 25 mm R : 14 mm T : 4 mm or under
 L : 33 mm LO : 115 mm D : 65 mm RO : 25 mm

Figure 3.1 A schematic of the specimen for tensile test

d) Tear Properties (ASTM D624)

Dimension and shape of specimen was cut to die C as illustrated in Figure 3.2. The cutting edges of specimens was kept sharp and cut to free of all nicks to avoid leaving ragged edges. It is important that the apex of 90° angle was sharpened to provide a sharp corner. The sample thickness was 2.0 mm. An average of 3 specimens was considered as representative value. The tear testing condition was as follows:

Temperature	25°C
Humidity	50%
Crosshead	500 mm/min
Full scale load range	500 N

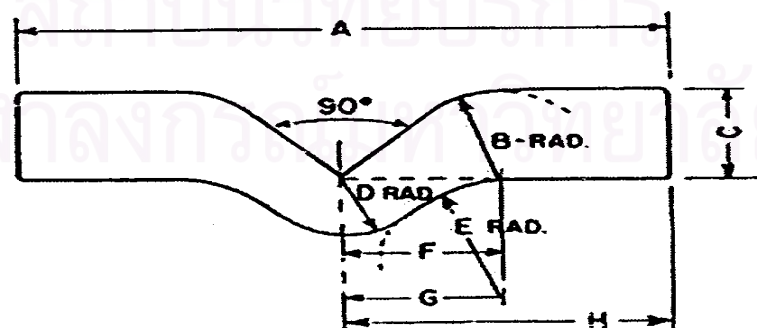


Figure 3.2 A schematic of the specimen for tear test (Die C)

e) **Hardness (ASTM D2240)**

The test specimen was at least 6 mm in thickness. In this experiment, the test specimen was composed of plied pieces to obtain the necessary thickness. Type A Durometer was used to measure the hardness. The specimen was placed on a hard and horizontal surface. The presser was held on a vertical position with the point of the indenter at least 12 mm from any edge of the specimen. The presser was applied to the specimen. After the presser foot was in firm contact with the specimen, the scale reading was taken within 30 s. Measurements were made at five different points distributed over the specimen. The median of these measurement was used as the hardness value. The condition of testing was as follows:

Temperature	25°C
Relative Humidity	50%
Number of pieces plied	3 pieces

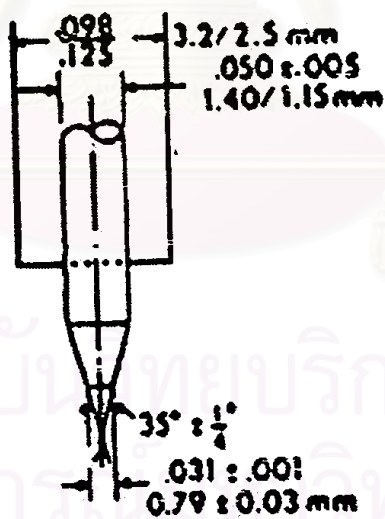


Figure 3.3 A schematic of indenter or type a durometer

f) Dynamic Mechanical Properties

The dynamic mechanical properties of vulcanized rubber/PVC blends were measured on a dynamic mechanical analyzer (GABO model EPLEXOR QC 25) with a liquid nitrogen cooling system. The tension mode was used to characterize the unfilled and silica filled rubber/PVC blends in a temperature range of -70 to 90 °C at heating rate of 2 °C/min and frequency of 10 Hz.



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CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of Dilution Ratio of Water/ Ethanol in TEOS and EPS Solution

The effects of dilution ratio of water/ ethanol in TEOS and EPS solution on the degree of swelling and silica content of rubbers are shown in Table 4.1. The silica contents were determined by TGA and heating in furnace. The parameters of sol-gel process are as follows:

- amount of TEOS and EPS solution : 15 times of rubber mass
- concentration of TEOS and EPS solution : 25% w/w
- swelling time in TEOS and EPS solution : 48 h
- swelling temperature in TEOS solution : room temperature (33°C)
- swelling temperature in EPS solution : 40°C
- amount of ethylenediamine solution : 30 time of rubber mass
- aqueous ethylenediamine concentration : 3% w/w
- soaking time and temperature in catalyst : 24 h, 40°C

For NBR, the degree of swelling and silica content increased with increasing amount of ethanol but decreased when 100% ethanol was used as the solvent. It can be noted that in the hydrolysis reaction, a mutual solvent such as alcohol is sufficient to homogenize the initial phase separated system of water and TEOS to form silanol groups. The results indicate that an increasing ethanol content resulted in an increasing silanol group which diffuses well in NBR. However, if 100% ethanol was used as the solvent in solution, the silanol from hydrolysis reaction was not generated yet, the result that the diffusion of solution into NBR was decreased. Therefore, a high polarity of

NBR and the appropriate amount of ethanol are responsible for the high swelling degree of the NBR in TEOS and EPS. The amount of silica-incorporated in rubbers is primarily defined by the degree of swelling, which is the only limiting factor in the sol-gel reaction. Therefore, the use of polar solvent such as ethanol is advantageous for the polar rubber e.g. NBR.

For NR and SBR, the degree of swelling and silica content decreased with increasing ethanol content. The results indicate that increasing ethanol content causes the increasing silanol group which hardly diffuses in NR and SBR due to the non polar structure of rubber.

However, the degree of swelling and silica content in EPS solution slightly increased compared with TEOS solution. This can be explained by 1) EPS is partially soluble in water with phase separation, 2) the EPS have poly- structures and the chain sizes of EPS are larger than that of TEOS. Thus, the degree of swelling and silica content of rubber in EPS solution is lower than in TEOS solution.

For NR and SBR, the appropriate solvent in TEOS and EPS solution which gave the highest degree of swelling and silica content was water. In these conditions, the degree of swelling and silica content of NR were 147.4 ± 0.25 and 9.5 ± 0.02 (ca. Si 10.4 ± 0.03 phr) for TEOS, 53.2 ± 0.65 and 4.2 ± 0.05 (ca. Si 4.4 ± 0.04 phr) for EPS. The degree of swelling and silica content of SBR were 196.2 ± 0.35 and 12 ± 0.05 (ca. Si 13.6 ± 0.07 phr) for TEOS, 55.0 ± 0.30 and 10.1 ± 0.15 (ca. Si 11.2 ± 0.37 phr) for EPS. For NBR, the appropriate dilution ratio of solvent in TEOS and EPS solution which gave the high degree of swelling and silica content was found to be H₂O/EtOH at ratio of 1/3. In these conditions, the degree of swelling and silica content of NBR were 229.9 ± 0.55 and 20.5 ± 0.08 (ca. Si 25 ± 0.15 phr) for TEOS, 200 ± 0.75 and 11.5 ± 0.18 (ca. Si 12.9 ± 0.22 phr) for EPS.

Table 4.1 Effect of dilution ratio of water/ ethanol in TEOS and EPS solution on the degree of swelling and the silica content of rubber.

Rubber	Water/ Ethanol (%w/w)	TEOS solution		EPS solution	
		Degree of swelling	Silica content	Degree of swelling	Silica content
		(%)	(%)	(%)	(%)
NR	1/0	147.4 ± 0.25	9.5 ± 0.02	53.2 ± 0.65	4.2 ± 0.05
	3/1	137.4 ± 0.50	5.2 ± 0.08	48.3 ± 0.50	3.9 ± 0.13
	1/1	98.5 ± 0.65	3.5 ± 0.10	48.0 ± 0.50	3.2 ± 0.10
	1/3	50.5 ± 0.60	2.7 ± 0.10	44.1 ± 0.55	3.0 ± 0.08
	0/1	23.2 ± 0.60	1.7 ± 0.05	30.0 ± 0.45	2.8 ± 0.08
SBR	1/0	196.2 ± 0.35	12.0 ± 0.05	55.0 ± 0.30	10.1 ± 0.15
	3/1	200.0 ± 0.78	9.7 ± 0.10	50.9 ± 0.25	7.8 ± 0.10
	1/1	154.6 ± 0.30	9.1 ± 0.10	46.3 ± 0.75	7.2 ± 0.05
	1/3	145.0 ± 0.35	7.0 ± 0.30	50.0 ± 1.00	7.0 ± 0.08
	0/1	120.3 ± 0.65	5.0 ± 0.15	38.0 ± 0.85	5.0 ± 0.13
NBR	1/0	51.0 ± 0.50	7.0 ± 0.10	104.7 ± 0.35	1.4 ± 0.10
	3/1	210.6 ± 0.50	15.5 ± 0.15	120.8 ± 0.60	2.3 ± 0.13
	1/1	230.5 ± 0.80	16.8 ± 0.08	149.3 ± 0.25	5.0 ± 0.25
	1/3	229.9 ± 0.55	20.5 ± 0.08	200.0 ± 0.75	11.5 ± 0.18
	0/1	90.0 ± 0.90	3.0 ± 0.10	40.5 ± 0.70	4.1 ± 0.20

Swelling: TEOS concentration = 25% w/w

EPS concentration = 25% w/w

Swelling condition in TEOS solution = 33°C, 48 h Swelling condition in EPS solution = 40°C, 48 h

Soaking in catalyst: Ethylenediamine concentration = 3% w/w , Soaking condition = 40°C, 24 h

4.2 Effect of TEOS and EPS Concentration

The effects of TEOS and EPS concentration on the degree of swelling and silica content of rubbers are shown in Table 4.2. The silica contents were determined by heating in furnace. The parameters of sol-gel process are as follows:

- amount of TEOS and EPS solution : 15 times of rubber mass
- solvent in TEOS and EPS solution
for NR and SBR : water
- dilution ratio of solvent in TEOS and EPS
solution for NBR : H₂O/EtOH =1/3
- swelling time in TEOS and EPS solution : 48 h
- swelling temperature in TEOS solution : room temperature (33°C)
- swelling temperature in EPS solution : 40°C
- amount of ethylenediamine solution : 30 time of rubber mass
- aqueous ethylenediamine concentration : 3% w/w
- soaking time and temperature in catalyst : 24 h, 40°C

For NR and SBR, the degree of swelling and silica content increased with the increasing amount of TEOS and slightly increased with increasing EPS content. The reason is that, the TEOS and EPS can diffuse well (compatible) into NR and SBR due to the non polar structure of TEOS, EPS and rubbers. For NBR, the degree of swelling and silica content decreased with increasing concentration of TEOS and EPS. The reason is that, TEOS and EPS poorly diffuse in NBR due to the polar property of NBR and non polar property of TEOS and EPS. This also confirmed the important role of ethanol as the solvent that could help the diffusion of TEOS and EPS into the NBR sheet.

For NR and SBR, the appropriate concentration of TEOS and EPS solution was found to be 100%w/w. In these conditions, the degree of swelling and silica content of NR was 246.0 ± 0.55 and 20.4 ± 0.08 (ca. Si 25.6 ± 0.10 phr) for TEOS, 21.1 ± 0.45 and 6.5 ± 0.10 (ca. Si 6.9 ± 0.11 phr) for EPS. The degree of swelling and silica content of SBR was 192.2 ± 0.30 and 18 ± 0.10 (ca. Si 21.9 ± 0.15 phr) for TEOS, 32.4 ± 0.30

and 13.5 ± 0.30 (ca. Si 15.6 ± 0.50 phr) for EPS. For NBR, the appropriate concentration of TEOS and EPS solution was found to be 50% w/w. In these conditions, the degree of swelling and silica content of NBR was 151.6 ± 0.65 and 24.3 ± 0.20 (ca. Si 31.6 ± 0.70 phr) for TEOS, 142.0 ± 0.85 and 14.8 ± 0.45 (ca. Si 17.3 ± 0.60 phr) for EPS

Table 4.2 Effect of TEOS and EPS concentration on the degree of swelling and the silica content of rubber.

Rubber	TEOS, EPS concentration (% w/w)	TEOS solution		EPS solution	
		Degree of swelling (%)	Silica content (%)	Degree of swelling (%)	Silica content (%)
NR	100	246.0 ± 0.55	20.4 ± 0.08	21.1 ± 0.45	6.5 ± 0.10
	75	236.0 ± 0.50	18.0 ± 0.05	55.0 ± 1.00	5.5 ± 0.08
	50	230.8 ± 0.65	13.2 ± 0.10	54.2 ± 0.80	5.0 ± 0.20
	25	147.4 ± 0.25	9.5 ± 0.02	53.2 ± 0.65	4.2 ± 0.05
SBR	100	192.2 ± 0.30	18.0 ± 0.10	32.4 ± 0.30	13.5 ± 0.30
	75	200.0 ± 0.60	15.0 ± 0.18	55.8 ± 0.65	11.8 ± 0.25
	50	226.1 ± 0.75	12.3 ± 0.11	52.3 ± 0.70	11.0 ± 0.50
	25	196.2 ± 0.35	12.0 ± 0.05	55.0 ± 0.30	10.1 ± 0.15
NBR	100	21.1 ± 0.65	7.4 ± 0.19	17.4 ± 0.40	1.8 ± 0.11
	75	72.6 ± 0.40	16.7 ± 0.10	50.0 ± 0.75	6.3 ± 0.09
	50	151.6 ± 0.65	24.3 ± 0.20	142.0 ± 0.85	14.8 ± 0.45
	25	229.9 ± 0.55	20.5 ± 0.08	200.0 ± 0.75	11.4 ± 0.18

Swelling: TEOS in H₂O for NR and SBR

EPS in H₂O for NR and SBR

Swelling: TEOS in H₂O/EtOH for NBR=1/3

EPS in H₂O/EtOH for NBR =1/3

Swelling condition in TEOS solution = 33°C, 48 h

Swelling condition in EPS solution = 40°C, 48 h

Soaking in catalyst: Ethylenediamine concentration = 3% w/w , Soaking condition = 40°C, 24 h

4.3 Effect of Catalyst Concentration

The effect of aqueous ethylenediamine concentration on silica content of rubbers are shown in Figure 4.1. The silica contents were determined by heating in furnace. The parameters of sol-gel process are as follows:

- amount of TEOS and EPS solution : 15 times of rubber mass
- concentration of TEOS and EPS solution
for NR and SBR : 100%, 75% w/w
- concentration of TEOS and EPS solution
for NBR : 50%, 25% w/w
- solvent in TEOS and EPS solution
for NR and SBR : water
- dilution ratio of solvent in TEOS and EPS
solution for NBR : H₂O/EtOH =1/3
- swelling time in TEOS and EPS solution : 48 h
- swelling temperature in TEOS solution : room temperature (33°C)
- swelling temperature in EPS solution : 40°C
- amount of ethylenediamine solution : 30 time of rubber mass
- soaking time and temperature in catalyst : 24 h, 40°C

The appropriate aqueous ethylenediamine concentrations for NR, SBR and NBR were found to be 3% w/w. For NR and SBR swelling in TEOS and EPS concentration at 100% w/w, the silica content was higher than at 75% w/w. For NBR, the silica content in TEOS and EPS concentration at 50% w/w was higher than at 25% w/w. The silica content was slightly changed with increasing catalyst concentration. It can be noted that, catalyst concentration slightly affect that the silica content in rubber. The silica content of NR, SBR and NBR was about 17.1 ± 1.9 , 17.5 ± 0.8 and 23.9 ± 0.9 , respectively for TEOS and 5.8 ± 0.5 , 12.4 ± 0.6 and 13.2 ± 0.9 , respectively for EPS (catalyst concentration range of 3 to 15% w/w).

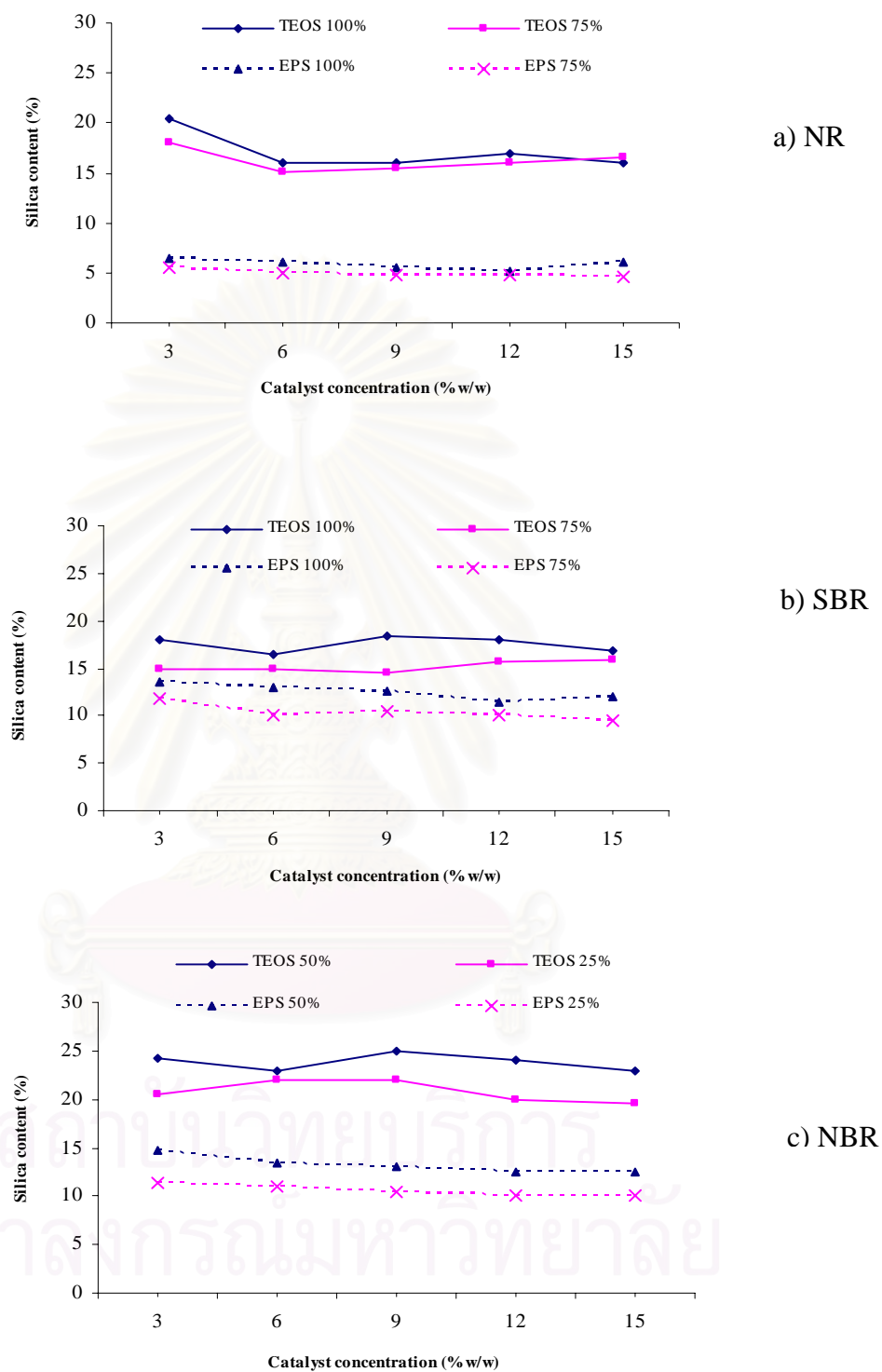


Figure 4.1 Effect of catalyst concentration on the silica content of rubbers at concentration of TEOS and EPS solution for NR and SBR: 100%, 75% w/w and concentration of TEOS and EPS solution for NBR: 50%, 25% w/w

4.4 Effect of Swelling Time and Temperature in TEOS and EPS Solution

The effect of the swelling time and Temperature in TEOS and EPS solution on degree of swelling of rubbers are shown in Figure 4.2 and the silica content of rubbers in Figure 4.3. The silica contents were determined by heating in furnace. The parameters of sol-gel process are as follows:

- amount of TEOS and EPS solution : 15 times of rubber mass
- concentration of TEOS and EPS solution
for NR and SBR : 100% w/w
- concentration of TEOS and EPS solution for NBR : 50% w/w
- dilution ratio of solvent in TEOS and EPS
solution for NBR : H₂O/EtOH =1/3
- swelling temperature in EPS solution : 40°C
- amount of ethylenediamine solution : 30 time of rubber mass
- aqueous ethylenediamine concentration : 3% w/w
- soaking time and temperature in catalyst : 24 h, 40°C

The degree of swelling and silica content increased with the increasing soaking time and temperature for NBR and SBR. For NR, the degree of swelling and silica content slightly increased with increasing the swelling time and increased with increasing swelling temperature in TEOS and EPS solution. At 40°C, the maximum silica content of NR (25.0%), SBR (40.8%) and NBR (50.5%) could be achieved at a swelling time of 72, 96 and 120 h, respectively for TEOS (Figure 4.3). However, the *in situ* silica rubber with a silica content of more than 40% exhibited a hard property of rubber. It can be noted that at 40°C, the swelling time could be shortened due to the high diffusion rate of TEOS into rubber.

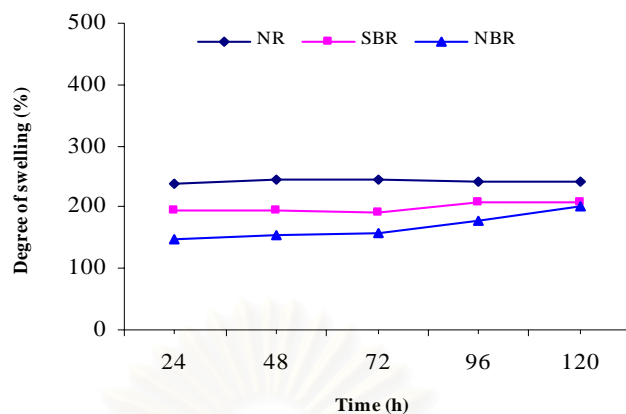
The appropriate time and temperature for soaking in precursor solution of NR, SBR and NBR are found to be 72, 24 and 24 h at 40°C for TEOS. In these conditions, the silica content of NR, SBR and NBR was 25.0, 26.1 and 28.6 % (ca. Si 33, 35, 40 phr), respectively. Judging from the rate of increase of silica content against temperature and time in Figure 4.3, it should be noted that the diffusion rate of TEOS

depends on rubber structure in the order of: NR > SBR > NBR, but the formed silica content is in the order of: NBR > SBR > NR because silica is hydrophilic and less compatible with non polar rubber than polar rubber.

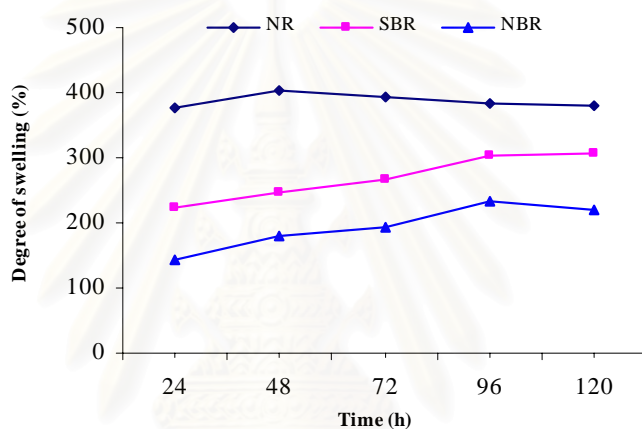
Thus, swelling time and temperature affect the sol-gel reaction. For EPS, the effect of the swelling time and temperature in EPS solution are similar to the TEOS solution and the silica content of NR, SBR and NBR was reported to be 7.4, 26.0, 26.5% respectively at a swelling time of 120 h at 40°C.



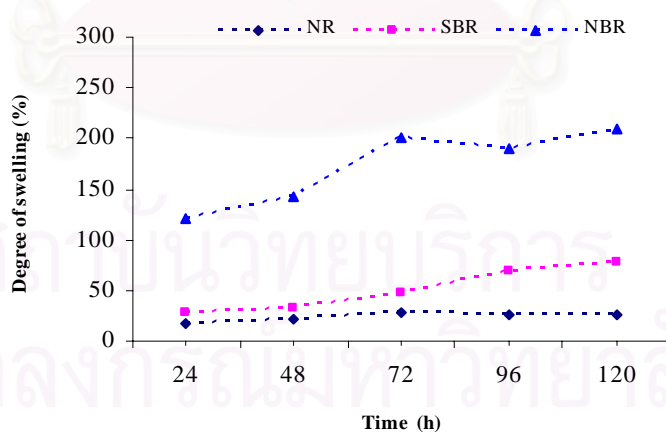
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a) TEOS at rt.

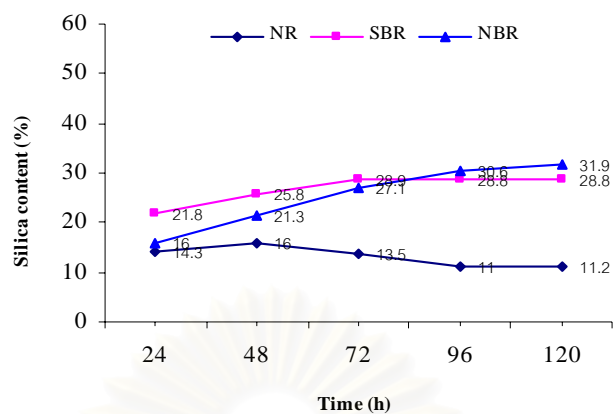


b) TEOS at 40°C

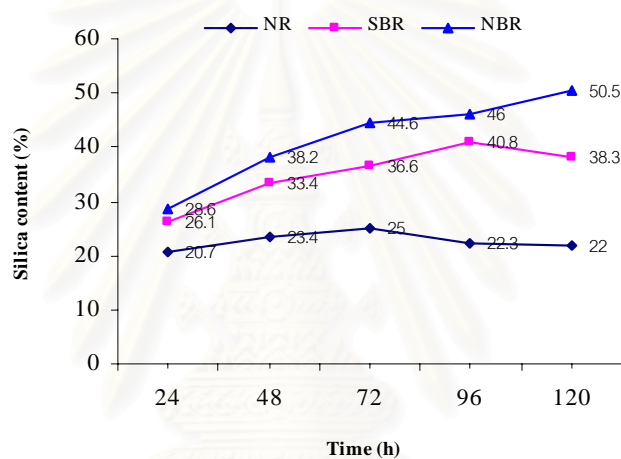


c) EPS at 40°C

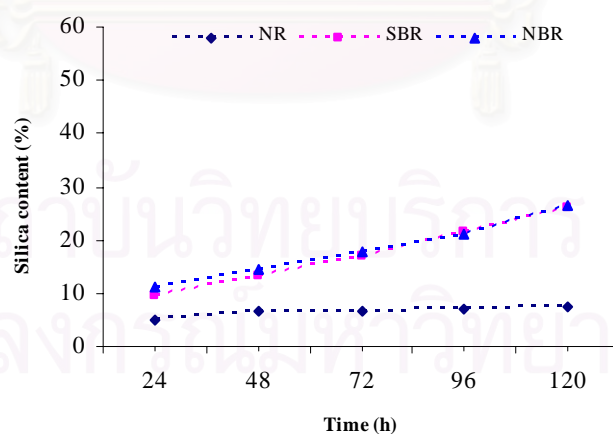
Figure 4.2 Effect of swelling time and temperature in TEOS and EPS solution on degree of swelling of rubbers. Degree of swelling a) TEOS at rt (28°C), b) TEOS at 40°C and c) EPS at 40°C. For NR and SBR, TEOS concentration = 100% w/w. For NBR, TEOS concentration = 50% w/w (H₂O:EtOH = 1:3), ethylenediamine concentration = 3% w/w, soaking time and temperature in catalyst = 24 h, 40°C



a) TEOS at rt.



b) TEOS at 40°C



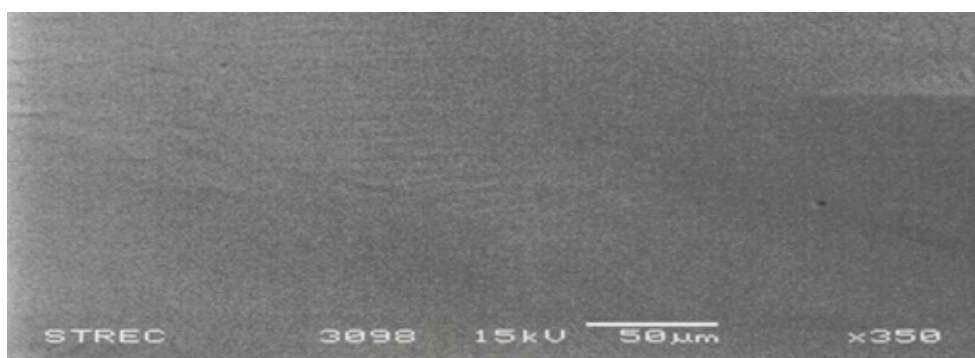
c) EPS at 40°C

Figure 4.3 Effect of swelling time and temperature in TEOS and EPS solution on silica content of rubbers. a) TEOS at rt (28°C), b) TEOS at 40°C and c) EPS at 40°C. For NR and SBR, TEOS concentration = 100%w/w. For NBR, TEOS concentration = 50%w/w (H₂O:EtOH = 1:3), ethylenediamine concentration = 3% w/w, soaking time and temperature in catalyst = 24h, 40°C

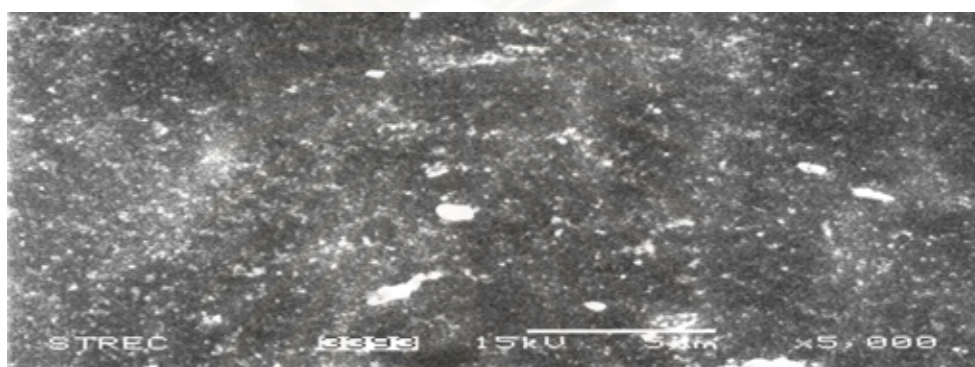
4.5 Morphology of *In situ* Silica in Rubbers

The results of SEM observations for NBR, NR and SBR are shown in Figure 4.4. It can be seen that the *in situ* silica particles dispersed more homogeneously than the conventional silica particles in the rubber. The inter-particle interaction among *in situ* silica particles from TEOS was found to be smaller than that among the commercial silica particles and *in situ* silica particles from EPS because the chain sizes of EPS are larger than that of TEOS. Thus, the size of *in situ* silica particles from EPS was larger than the size of silica particles from TEOS. From the results of SEM, the morphology of the *in situ* silica from TEOS in NBR is considered as bringing excellent reinforcement to the NBR/PVC vulcanizate. Because the reinforcement effect of *in situ* silica can be enhanced by the more homogeneous dispersion of *in situ* silica particles in the NBR matrix and the higher wettability between the *in situ* silica particles and NBR molecules than evidenced with the system of conventional silica.

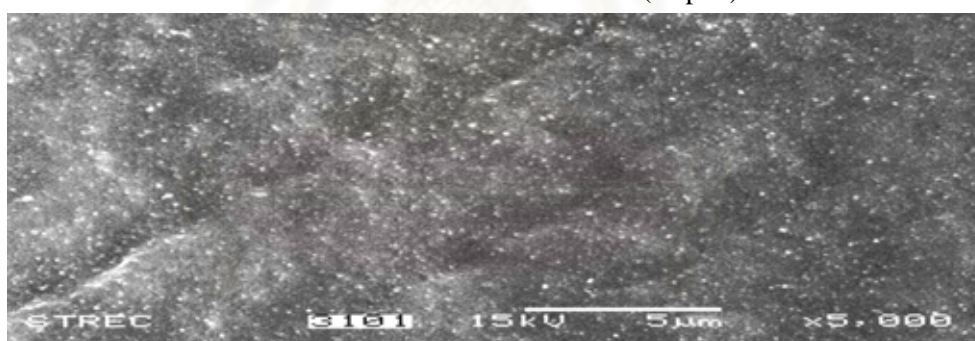


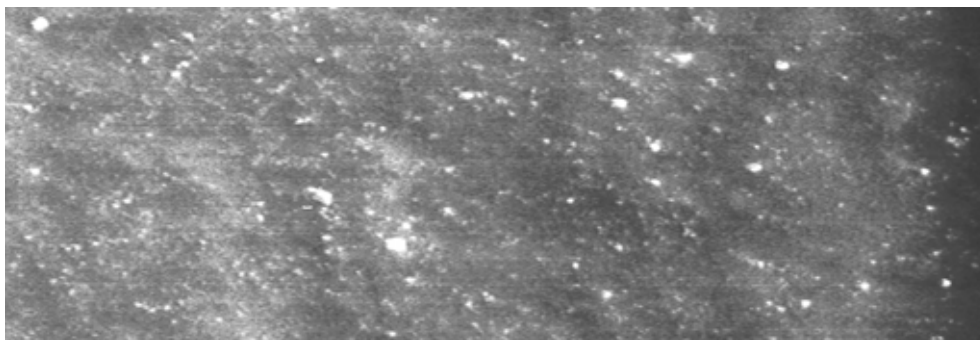


NBR without silica

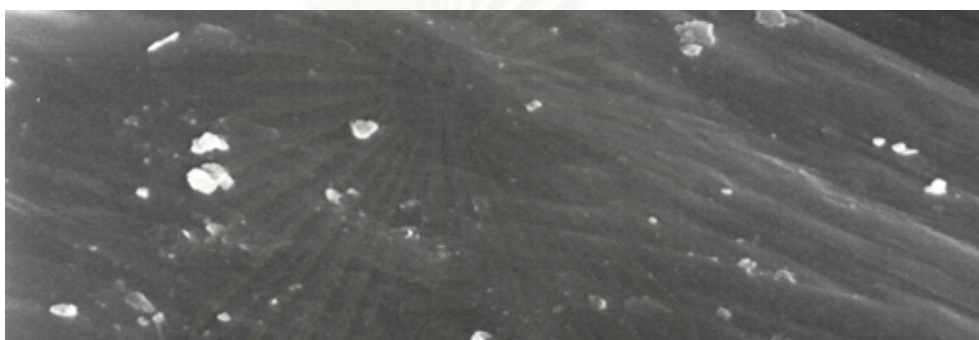


NBR with conventional silica (40 phr)

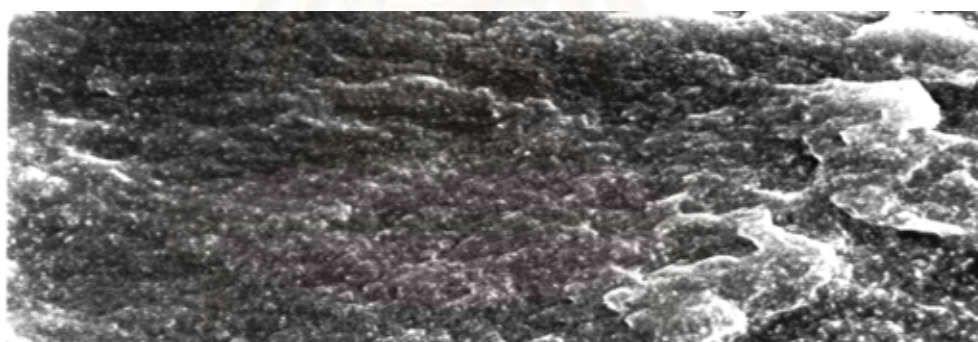
NBR with *in situ* silica from TEOS (40 phr)NBR with *in situ* silica from E PS (35 phr)**Figure 4.4** SEM photographs of NBR, NR and SBR with silica



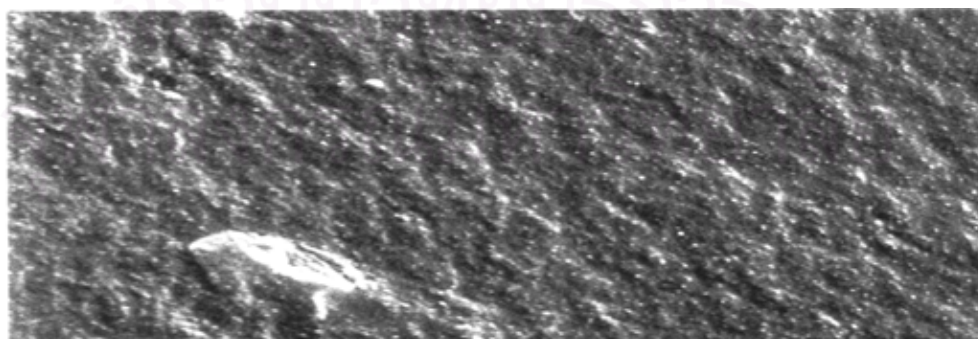
NR with *in situ* silica from TEOS (33 phr)



NR with *in situ* silica from EPS (8 phr)



SBR with *in situ* silica from TEOS (35 phr)



SBR with *in situ* silica from EPS (35 phr)

Figure 4.4 (Continued)

4.6 Mooney Viscosity and Cure Behavior of Rubber/PVC Blends

The Mooney viscosity and cure time of rubber/PVC blends are summarized in Table 4.3. The cure curves of silica filled rubber/PVC compound is shown in Figure 4.5. Mooney viscosity and cure time of rubber/PVC/ *in situ* Si (R5, R6 and R 7) were slightly higher than rubber/PVC/Si (recipe R2, R3 and R4). The addition of silica powder causes the increase in viscosity and cure time because the silanol groups on silica surface can generate silica-to-silica attraction. Therefore, the large aggregates are formed and this leads to the increase in viscosity. The silanol group also deactivates the curing agents and accelerators, this results in an insufficient cure. From Table 4.3, Mooney viscosity and cure time of rubber/PVC/Si without oil and PEG (R2') was highest. So petroleum oils was chosen for reducing the viscosity and PEG was also mixed in the polymer compound with conventional silica in order to reduce the cure time [4]. Therefore, oil and PEG were used in the rubber/PVC/Si compound (R2, R3 and R4).

Although oil and PEG were not used in *in situ* silica filled rubber/PVC (R5, R6 and R7) but the mooney viscosity and cure time of *in situ* silica filled rubber/PVC were not much different from rubber/PVC/Si (R2, R3 and R4). This implies that the amount of silanol group of the *in situ* generated silica was less than that of the conventional silica surface which agrees with the results revealed by SEM. Namely, the inter-particle interaction among *in situ* silica particles was found to be less than that among the commercial silica particles. Therefore, the results of viscosity and cure time also suggest that the degree of aggregation of *in situ* silica was less than that of conventional silica.

Table 4.3 The mooney viscosity and cure time of rubber/PVC blends

Sample	Mooney Viscosity	Cure Time (min)	Si (phr)
R1	66	7.5	0
R2' (non PEG, oil)	83	17	40
R2	53.9	3.6	40
R3	48.2	3.5	40
R4	50.0	4.3	40
R5	60.0	4.5	40
R6	50.0	3.8	38.5
R7	54.1	4.3	39

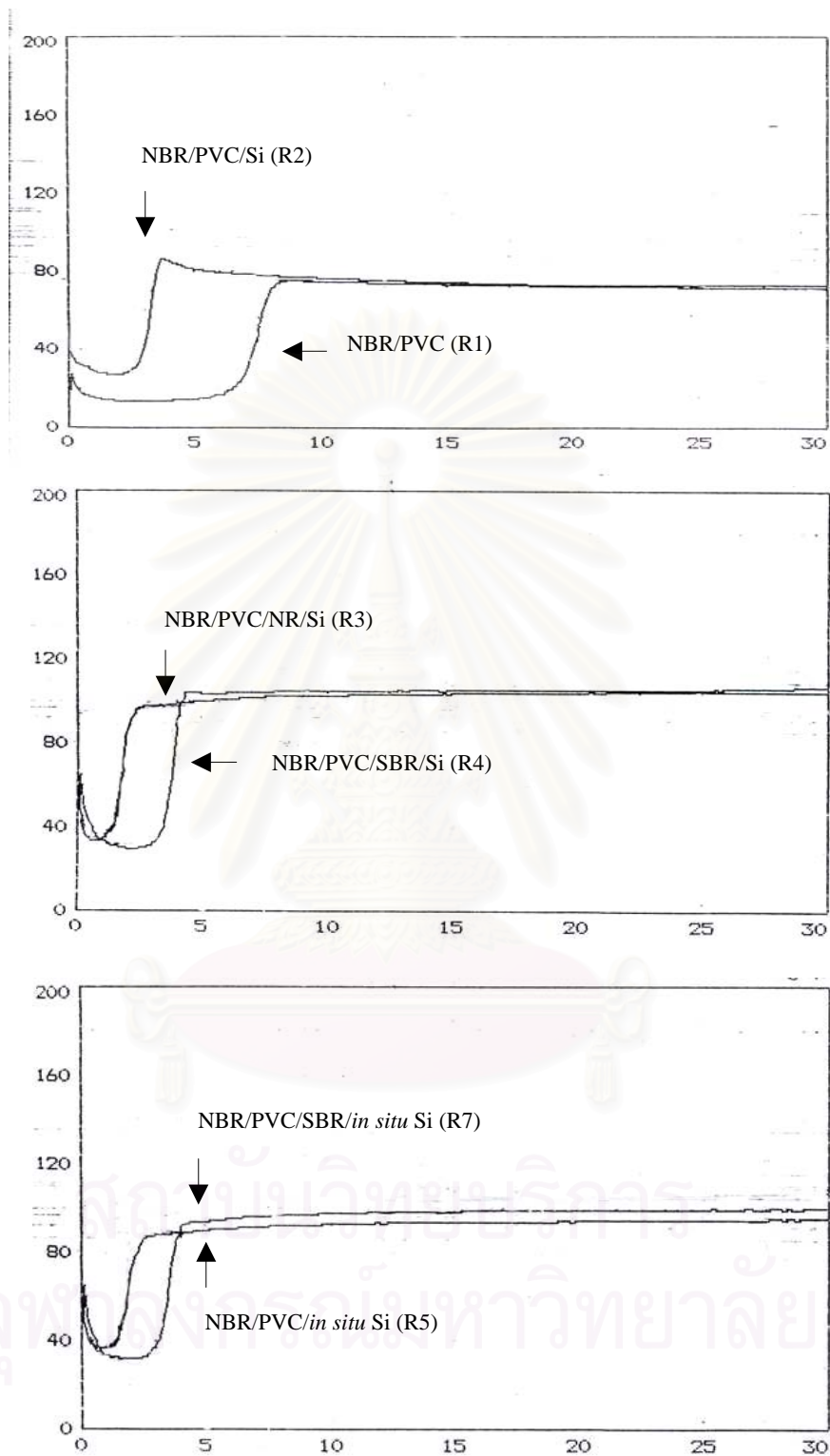


Figure 4.5 Cure curves of silica filled rubber/PVC compound

4.7 Mechanical Properties of Rubber/PVC Blends

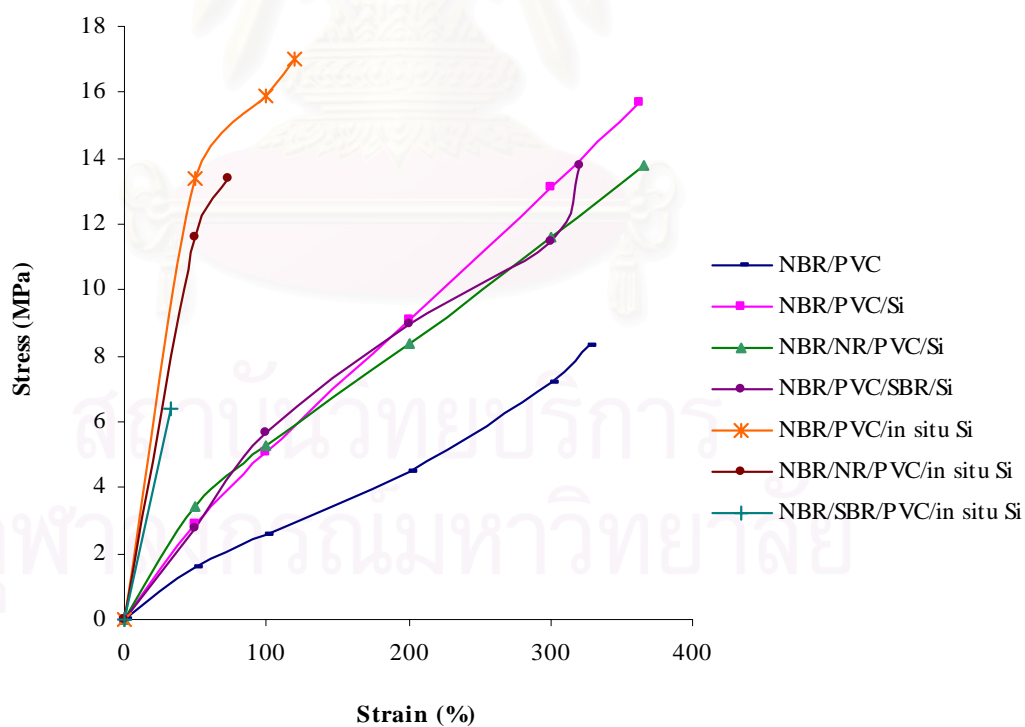
Effects of rubber/PVC vulcanizates compositions and silica filling technique upon the mechanical properties were examined. The moduli at 50%, 100%, 200% and 300% elongation (M_{50} , M_{100} , M_{200} and M_{300} , respectively), tensile strength at break (T_B), elongation at break (E_B), tear resistance and hardness are summarized in Table 4.4. The stress-strain curves of rubber/PVC blends are shown in Figure 4.6.

The tensile strength of NBR/PVC/*in situ* Si (R5 and R6) was not much different from that of NBR/PVC/Si (R2, R3 and R4). However, the moduli at 50% of rubber/PVC/*in situ* Si (R5 and R6) was higher than that of rubber/PVC/Si (R2, R3 and R4). The hardness of rubber/PVC/*in situ* Si (R5, R6 and R7) was higher than that of rubber/PVC/Si (R2, R3 and R4), while the elongation at break was much lower. This can be explained by the fact that, the *in situ* silica generated from TEOS exhibited a small particle size which dispersed more homogeneously than the conventional silica in rubber, resulting in the hard and tough properties of blends. Therefore, rubber/PVC/*in situ* Si exhibited high modulus, high tensile strength and less elongation.

In this work, natural rubber or SBR was used to replace some portion of the NBR in the polymer blend. The mechanical properties of NBR/NR/PVC/Si (R3 and R6) were not much different from those from NBR/PVC/Silica (R2 and R5). Therefore, natural rubber can replace NBR in the NBR/PVC blend for economic advantage. For SBR, the tensile strength and elongation at break of NBR/SBR/PVC/*in situ* Si (recipe 7) was the lowest. One reason is that the miscibility of the constituent polymers is often a necessity for forming successful blends, NBR/NR/PVC/*in situ* Si blends can be more miscible than NBR/SBR/PVC/*in situ* Si blends. The other reason is that the mechanical properties of NR are better than SBR.

Table 4.4 Mechanical properties of rubber/PVC blends.

Properties	R1	R2	R3	R4	R5	R6	R7
M_{50} , MPa	1.6	2.9	3.4	2.8	13.4	11.6	-
M_{100} , MPa	2.6	5.1	5.3	5.7	15.9	-	-
M_{200} , MPa	4.5	9.1	8.4	9.8	-	-	-
M_{300} , MPa	7.2	13.1	11.6	11.9	-	-	-
Tensile strength, MPa	8.3	15.7	13.8	13.8	17.0	13.4	6.4
Elongation at break, %	327.0	362.6	365.8	319.5	120.0	73.3	33.3
Tear, N/m	37.9	61.3	51.7	52.6	58.0	35.3	19.4
Hardness	63.9	79.0	82.0	81.5	90.3	90.4	89.9

**Figure 4.6** Stress-strain curves of rubber/PVC blends

4.8 Dynamic Mechanical Properties

The results of dynamic mechanical measurements are given in Figure 4.6 and Table 4.5. From Figure 4.6 (a), the E' of samples decreased in the order: NBR/PVC/*in situ* Si (R5) > NBR/PVC/Si (R2) > NBR/PVC (R1). From Figure 4.7 (b), the $\tan \delta$ peak, which is attributed to glass transition temperature (T_g) of NBR/PVC/*in situ* Si was shifted from 10 °C to a higher temperature of 29.1 °C and its peak height was decreased compared to that of NBR/PVC/Si and NBR/PVC. Generally, the T_g of the rubber is shifted to high temperature region and the height of $\tan \delta$ peak becomes lower by adding a filler when the interaction between the rubber and filler is becomes sufficiently strong [12]. This result suggests the presence of the interaction between the rubber and silica particles. This implied that the small particle size of *in situ* silica which dispersed more homogeneously gives the better interaction between the rubber and silica and this results in motion of chains molecule more difficult. Therefore, the storage modulus of rubber/PVC *in situ* Si was higher and $\tan \delta$ was lower than NBR/PVC/Si and NBR/PVC blends. These results from DMA are in good agreement with those of the tensile test. The *in situ* silica particles, which were generated by the sol-gel method of TEOS, show the reinforcement effect on the NBR/PVC blends.

In addition, DMA was used to investigate the miscibility of various polymer system. For an immiscible blend, the $\tan \delta$ curve shows the presence of two damping peaks corresponding to the T_g of individual polymers. For miscible blend, the curve shows only a single peak between the transition temperatures of the component polymers [15]. From Figure 4.6 (b), the $\tan \delta$ curves of all samples show only a single peak between the transition temperatures of the component polymers (T_g of NBR and PVC are -20 °C and 80 °C, respectively [16]), this indicated that the NBR/PVC blends were miscible.

Table 4.5 Glass transition temperature (T_g) and $\tan \delta$ of NBR/PVC blends

Sample	Maximum $\tan \delta$	T_g (°C)
NBR/PVC	0.8976	10.1
NBR/PVC/Si	0.6005	10.0
NBR/PVC/ <i>in situ</i> Si	0.5225	29.1

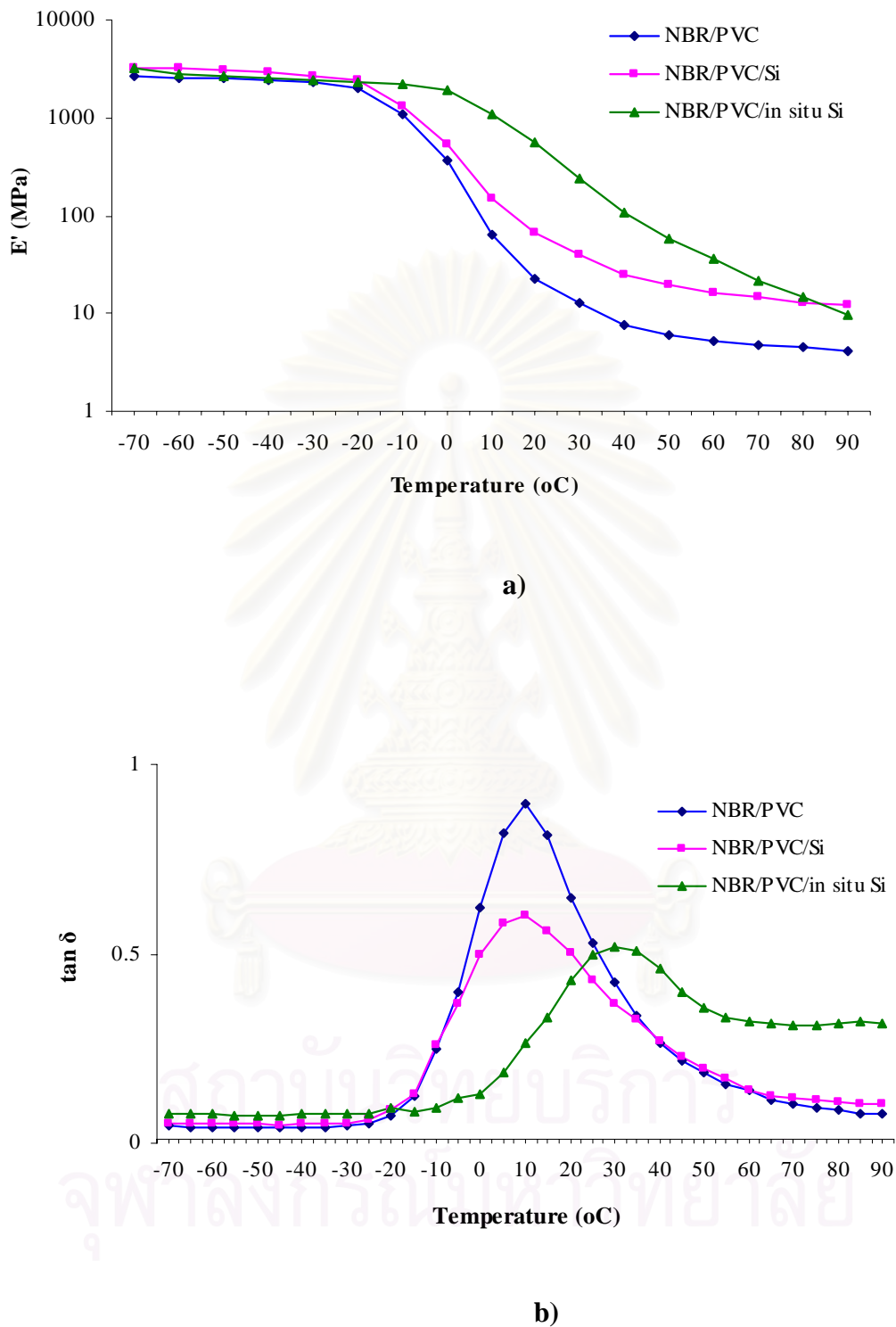


Figure 4.7 Temperature dependence of E' (a) and $\tan \delta$ (b) for NBR/PVC without and with commercial silica and with *in situ* silica

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

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

1. For various dilution ratios of water/ethanol in TEOS and EPS solution, the degree of swelling and silica content of NR and SBR in TEOS or EPS solution decreased with increasing ethanol content. For NBR, the degree of swelling and silica content increased with increasing ethanol content.

2. For varying TEOS and EPS concentrations, the degree of swelling and silica content of NR and SBR increased with increasing TEOS and slightly increased with increasing EPS content. For NBR, the degree of swelling and silica content decreased with increasing TEOS and EPS concentrate.

3. The silica content of NR, SBR and NBR in TEOS and EPS slightly changed with increasing ethylenediamine concentration. It can be noted that, the catalyst concentration slightly affected the silica content in rubber.

4. The degree of swelling and silica content of SBR and NBR increased with increasing the swelling time and temperature. For NR, the degree of swelling and silica content slightly increased with increasing the swelling time and temperature.

5. For NR, the appropriate condition of sol-gel process was found to be at TEOS and EPS concentration of 100% w/w, catalyst concentration of 3% w/w, swelling

time of 72 h (TEOS) and 120 h (EPS) at 40°C. This condition yielded the degree of swelling and silica content of 393.7% and 25.0% (ca. Si 33 phr) for TEOS and degree of swelling of 23.4% and silica content of 7.4% (ca. Si 8 phr) for EPS.

6. For SBR, the appropriate condition of sol-gel process was found to be at TEOS and EPS concentration of 100% w/w, catalyst concentration of 3% w/w, swelling time of 24 h (TEOS) and 120 h (EPS) at 40°C. This condition yielded the degree of swelling of 221.8% and silica content of 26.1% (ca. Si 35 phr) for TEOS and degree of swelling of 65.8% and silica content of 26.0% (ca. Si 35 phr) for EPS.

7. For NBR, the appropriate condition of sol-gel process was found to be at TEOS and EPS concentration of 50% w/w, H₂O:EtOH ratio of 1:3, catalyst concentration of 3% w/w, swelling time of 24 h (TEOS) and 120 h (EPS) at 40°C. This condition gave the degree of swelling of 146.6% and silica content of 28.6% (ca. Si 40 phr) for TEOS and degree of swelling of 209% and silica content of 26.5% (ca. Si 35 phr) for EPS.

8. From the morphology of rubbers, the *in situ* silica particles dispersed more homogeneously than the conventional silica particles in the rubber. The inter-particle interaction among *in situ* silica particles from TEOS was found to be smaller than that among the commercial silica particles and *in situ* silica particles from EPS. This implies that the amount of silanol group on the *in situ* generated silica was smaller than that the conventional silica surface. Therefore, the mooney viscosity and cure time of *in situ* silica filled rubber/PVC blends were not much different from rubber/PVC/Si blends, although oil and PEG were not used in *in situ* silica filled rubber/PVC blends.

9. The results of mechanical properties and DMA indicated that the *in situ* silica particles, which were generated by the sol-gel method of TEOS, exhibited the reinforcement effect on the NBR/PVC blends. The hardness, modulus and tensile strength of rubber/PVC/ *in situ* Si blends were higher than these of rubber/PVC/Si blends.

5.2 Suggestions for Future Works

- To modify NBR/PVC blends by using the *in situ* silica filled other rubber, e.g. butadiene rubber to replace part of NBR in NBR/PVC blends.
- To use the *in situ* silica filled NR or SBR blended with the other thermoplastic, e.g. polyethylene, polypropylene for developing the reinforcement of polymer blends.

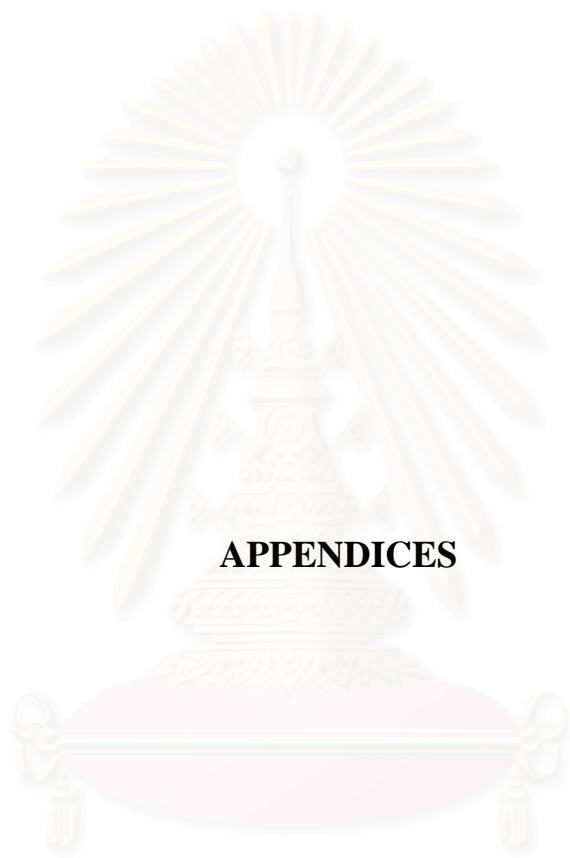


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APPENDICES

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APPENDIX A

CALCULATION

A.1 Preparation of Latex Film

Latex film was prepared by casting in the mould. Mass of latex film was calculated by using Eq. A.1. Latex content for preparation of film was calculated by using Eq. A.2.

$$M/D = A \times h \quad (A.1)$$

$$M = L \times \% \text{ TSC} \quad (A.2)$$

M	=	mass of latex film (g)
D	=	density of rubber (g/cm ³)
A	=	area of mould (cm ²)
h	=	thickness of rubber (cm)
L	=	latex content (g)
TSC	=	total solid content (%)

A.2 Preparation of TEOS and EPS Concentration (%w/w)

The amount of TEOS and EPS solution was 15 times of the mass of rubber sample. For the swelling experiment, 10 g of rubbers required 150 g of TEOS and EPS solution. The concentration of TEOS and EPS solution was evaluated by using Eq. A.3. Weight of solvent was evaluated from $W_2 - W_1$. Water/EtOH ratio was evaluated by using Eq. A.4.

$$C = (W_1 / W_2) \times 100 \quad (\text{A.3})$$

$$\text{H}_2\text{O}/ \text{EtOH ratio} = W_3 / W_4 \quad (\text{A.4})$$

$$W_3 = (W_2 - W_1) \times \text{ratio of H}_2\text{O}/\text{solvent} \quad (\text{A.5})$$

$$W_4 = (W_2 - W_1) - W_3 \quad (\text{A.6})$$

C = concentration of TEOS and EPS solution (%w/w)

W_1 = weight of TEOS and EPS in solution

W_2 = weight of TEOS and EPS solution (Exp. 150 g)

$W_2 - W_1$ = weight of solvent in solution

W_3 = weight of water

W_4 = weight of EtOH

A.3 Preparation of Ethylenediamine Aqueous Solution Concentration (%w/w)

The amount of ethylenediamine aqueous solution was 30 times of the weight of rubber sample. For the soaking in catalyst experiment, 10 g of rubbers required 300 g of ethylenediamine aqueous solution. The concentration of ethylenediamine aqueous solution was evaluated by using Eq. A.7.

$$C = (W_5 / W_6) \times 100 \quad (\text{A.7})$$

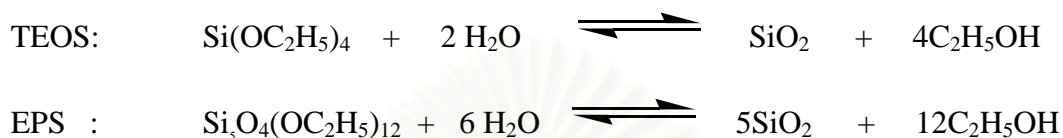
C = concentration of ethylenediamine aqueous solution (%w/w)

W_5 = weight of ethylenediamine in solution

W_6 = weight of ethylenediamine aqueous solution (Exp. 300 g)

A.4 Determination of the Conversion (%)

From the sol-gel reaction, conversion of TEOS and EPS was calculated by using Eq. A.8.



$$\text{Conversion of TEOS and EPS (\%)} = (W_7/W_8) \times 100 \quad (\text{A.8})$$

W_7 = weight of *in situ* generated silica in the sample estimated from Eq. 3.1 (Section 3.3.1)

W_8 = imaginary weight of silica in the sample assuming quantitative conversion of TEOS and EPS into silica by the sol-gel reaction, which calculated from the weight of TEOS and EPS in the swollen sample.

A.5 Determination of the Silica Content (phr)

The silica content in part per hundred (g in 100 g rubber) was evaluated by using Eq. A.9.

$$\text{Silica content (phr)} = (W_7/W_9) \times 100 \quad (\text{A.9})$$

W_7 = weight of *in situ* generated silica in the sample estimated from Eq. 3.1 (Section 3.3.1)

W_9 = weight of the initial rubber sample

APPENDIX B

Table B.1 Effect of Dilution Ratio of Water/ Ethanol in TEOS and EPS solution

Rubber	Water/ Ethanol (% w/w)	TEOS solution			EPS solution				
		Degree of swelling (%)	Silica content (%)	Conversion (%)	Silica content (phr)	Degree of swelling (%)	Silica content (%)	Conversion (%)	Silica content (phr)
NR	1/0	147.4 ± 0.25	9.5 ± 0.02	24.7 ± 0.02	10.4 ± 0.03	53.2 ± 0.65	4.2 ± 0.05	20.4 ± 0.03	4.4 ± 0.04
	3/1	137.4 ± 0.50	5.2 ± 0.08	13.8 ± 0.16	5.5 ± 0.09	48.3 ± 0.50	3.9 ± 0.13	20.8 ± 0.48	4.0 ± 0.10
	1/1	98.5 ± 0.65	3.5 ± 0.10	12.7 ± 0.30	3.6 ± 0.10	48.0 ± 0.50	3.2 ± 0.10	17.1 ± 0.37	3.3 ± 0.10
	1/3	50.5 ± 0.60	2.7 ± 0.10	19.0 ± 0.50	2.8 ± 0.10	44.1 ± 0.55	3.0 ± 0.08	17.4 ± 1.71	3.1 ± 0.10
	0/1	23.2 ± 0.60	1.7 ± 0.05	25.8 ± 0.03	1.7 ± 0.05	30.0 ± 0.45	2.8 ± 0.08	23.8 ± 0.31	2.9 ± 0.07
SBR	1/0	196.2 ± 0.35	12.0 ± 0.05	24.1 ± 0.07	13.6 ± 0.07	55.0 ± 0.30	10.1 ± 0.15	50.6 ± 1.04	11.2 ± 0.37
	3/1	200.0 ± 0.78	9.7 ± 0.10	18.6 ± 0.14	10.7 ± 0.12	50.9 ± 0.25	7.8 ± 0.10	41.1 ± 0.37	8.5 ± 0.12
	1/1	154.6 ± 0.30	9.1 ± 0.10	22.4 ± 0.03	10.0 ± 0.12	46.3 ± 0.75	7.2 ± 0.05	41.5 ± 0.36	7.8 ± 0.07
	1/3	145.0 ± 0.35	7.0 ± 0.30	18.0 ± 0.79	7.5 ± 0.35	50.0 ± 1.00	7.0 ± 0.08	37.3 ± 0.32	7.5 ± 0.10
	0/1	120.3 ± 0.65	5.0 ± 0.15	15.2 ± 0.40	5.3 ± 0.17	38.0 ± 0.85	5.0 ± 0.13	34.3 ± 0.13	5.3 ± 0.14
NBR	1/0	51.0 ± 0.50	7.0 ± 0.10	51.2 ± 0.24	7.5 ± 0.12	104.7 ± 0.35	1.4 ± 0.10	3.4 ± 0.23	1.4 ± 0.10
	3/1	210.6 ± 0.50	15.5 ± 0.15	30.2 ± 0.25	18.3 ± 0.21	120.8 ± 0.60	2.3 ± 0.13	4.8 ± 0.25	2.4 ± 0.13
	1/1	230.5 ± 0.80	16.8 ± 0.08	30.3 ± 0.10	20.2 ± 0.10	149.3 ± 0.25	5.0 ± 0.25	8.7 ± 0.42	5.3 ± 0.30
	1/3	229.9 ± 0.55	20.5 ± 0.08	38.8 ± 0.10	25.0 ± 0.15	200.0 ± 0.75	11.5 ± 0.18	16.1 ± 0.22	12.9 ± 0.22
	0/1	90.0 ± 0.90	3.0 ± 0.10	12.1 ± 0.30	3.09 ± 0.10	40.5 ± 0.70	4.1 ± 0.20	26.1 ± 0.90	4.3 ± 0.22

Table B.2 Effect of TEOS and EPS concentration

Rubber	TEOS, EPS concentration (%w/w)	TEOS solution			EPS solution				
		Degree of swelling (%)	Silica content (%)	Conversion (%)	Silica content (phr)	Degree of swelling (%)	Silica content (%)	Conversion (%)	Silica content (phr)
NR	100	246.0 ± 0.55	20.4 ± 0.08	36.1 ± 0.15	25.6 ± 0.10	21.1 ± 0.45	6.5 ± 0.10	81.6 ± 0.45	6.8 ± 0.11
	75	236.0 ± 0.50	18.0 ± 0.05	32.2 ± 0.08	21.9 ± 0.10	55.0 ± 1.00	5.5 ± 0.08	26.2 ± 0.09	5.8 ± 0.10
	50	230.8 ± 0.65	13.2 ± 0.10	22.8 ± 0.14	15.2 ± 0.12	54.2 ± 0.80	5.0 ± 0.20	24.0 ± 0.65	5.3 ± 0.10
	25	147.4 ± 0.25	9.5 ± 0.02	24.7 ± 0.02	10.5 ± 0.03	53.2 ± 0.65	4.2 ± 0.05	20.4 ± 0.03	4.4 ± 0.04
SBR	100	192.2 ± 0.30	18.0 ± 0.10	39.6 ± 0.20	21.9 ± 0.15	32.4 ± 0.30	13.5 ± 0.30	97.1 ± 2.10	15.6 ± 0.50
	75	200.0 ± 0.60	15.0 ± 0.18	30.6 ± 0.35	17.6 ± 0.25	55.8 ± 0.65	11.8 ± 0.25	59.4 ± 1.25	13.4 ± 0.30
	50	226.1 ± 0.75	12.3 ± 0.11	21.5 ± 0.19	14.0 ± 0.15	52.3 ± 0.70	11.0 ± 0.50	58.5 ± 2.20	12.4 ± 0.65
	25	196.2 ± 0.35	12.0 ± 0.05	24.1 ± 0.07	13.6 ± 0.07	55.0 ± 0.30	10.1 ± 0.15	50.6 ± 1.04	11.2 ± 0.37
NBR	100	21.1 ± 0.65	7.4 ± 0.19	97.0 ± 1.50	7.9 ± 0.10	17.4 ± 0.40	1.8 ± 0.11	26.1 ± 1.00	1.8 ± 0.13
	75	72.6 ± 0.40	16.7 ± 0.10	89.4 ± 0.50	20.0 ± 0.30	50.0 ± 0.75	6.3 ± 0.09	33.3 ± 0.05	6.7 ± 0.10
	50	151.6 ± 0.65	24.3 ± 0.20	70.3 ± 1.20	31.6 ± 0.70	142.0 ± 0.85	14.8 ± 0.45	30.3 ± 0.90	17.3 ± 0.60
	25	229.9 ± 0.55	20.5 ± 0.08	38.8 ± 0.10	25.7 ± 0.15	200.0 ± 0.75	11.4 ± 0.18	16.1 ± 0.22	12.9 ± 0.22

Table B.3 Effect of Catalyst concentration

Precursor	Catalyst concentration (% w/w)	NR				SBR				NBR			
		TEOS, EPS 100% wt.		TEOS, EPS 75% wt.		TEOS, EPS 100% wt.		TEOS, EPS 75% wt.		TEOS, EPS 50% wt.		TEOS, EPS 25% wt.	
		Silica content (%)	Conversion (%)	Silica content (%)	Conversion (%)	Silica content (%)	Conversion (%)	Silica content (%)	Conversion (%)	Silica content (%)	Conversion (%)	Silica content (%)	Conversion (%)
TEOS	3	20.4	36.1	18.0	32.3	18.0	39.6	15.0	30.6	24.3	70.3	20.5	38.8
	6	16.0	33.0	15.1	28.1	16.4	37.2	15.0	31.0	20.0	68.0	22.0	39.8
	9	16.0	32.0	15.4	28.7	18.3	39.9	14.5	28.7	25.0	72.0	22.0	39.9
	12	17.1	34.6	16.0	29.7	18.0	39.5	15.0	30.6	24.0	69.5	20.0	36.5
	15	16.0	32.7	16.5	29.9	16.9	39.3	15.1	30.4	23.0	70.0	19.5	36.3
EPS	3	6.5	81.6	5.5	26.2	13.5	97.1	11.8	59.4	14.8	30.3	11.4	16.1
	6	6.0	78.3	4.9	24.1	12.9	92.0	10.0	56.7	13.5	28.9	11.0	15.3
	9	5.5	72.0	4.8	23.8	12.6	92.0	10.5	55.4	13.0	28.0	10.5	15.0
	12	5.2	69.0	4.8	23.8	11.5	87.9	10.0	54.2	12.4	26.9	10.0	14.5
	15	6.0	78.1	4.6	24.0	12.0	89.0	9.5	53.8	12.5	27.0	10.0	14.3

Table B. 4 Effect of Soaking Time and temperature in TEOS, EPS solution.

Precursor	Time (day)	Temperature (°C)	NR			SBR			NBR		
			Silica content (%)	Conversion (%)	Silica content (phr)	Silica content (%)	Conversion (%)	Silica content (phr)	Silica content (%)	Conversion (%)	Silica content (phr)
TEOS	1	Rt.	14.3	24.4	16.6	21.8	49.0	27.0	16.0	45.0	19.0
		40	20.7	24.1	26.0	26.1	55.0	35.0	28.6	79.8	40.0
	2	Rt.	16.0	26.9	19.0	25.8	58.2	34.8	21.3	66.0	27.1
		40	23.4	26.3	30.5	33.4	69.0	50.2	38.2	82.5	61.8
	3	Rt.	13.5	22.2	15.6	28.8	70.1	40.6	27.1	80.5	37.2
		40	25.0	29.3	33.3	36.6	75.0	57.7	44.6	80.0	80.5
	4	Rt.	11.0	17.6	12.4	28.8	67.5	40.0	30.6	84.5	44.1
		40	22.3	26.1	28.7	40.8	79.0	68.0	46.0	85.7	85.0
	5	Rt.	11.2	18.0	12.6	28.8	67.5	40.0	31.9	83.4	46.8
		40	22.0	25.7	28.2	38.3	70.0	62.0	50.5	90.1	99.9
EPS	1	40	Silica content (%)	Conversion (%)	Silica content (phr)	Silica content (%)	Conversion (%)	Silica content (phr)	Silica content (%)	Conversion (%)	Silica content (phr)
			5.0	72.4	5.3	9.5	89.0	10.0	11.3	26.3	12.7
	2	40	6.5	81.5	7.0	13.2	97.1	15.6	14.8	30.3	17.4
			6.8	66.9	7.3	16.9	89.1	20.3	18.0	27.2	22.0
	4	40	7.0	70.3	7.5	21.5	95.0	27.4	21.0	34.8	26.6
			7.4	74.0	8.0	26.0	91.2	35.0	26.5	42.7	36.0

APPENDIX C

Table C.1 Tensile strength of rubber/PVC blends

	R1	R2	R3	R4	R5	R6	R7
Tensile strength (MPa)	8.44	15.84	14.30	14.20	17.24	13.37	6.46
	7.99	15.05	13.48	13.90	16.00	13.64	6.44
	8.32	16.20	13.50	13.40	16.30	13.11	6.30
Mean	8.25	15.70	13.76	13.83	16.51	13.37	6.40
Standard deviation	0.19	0.48	0.38	0.33	0.52	0.22	0.07

Table C.2 Elongation at break of rubber/PVC blends

	R1	R2	R3	R4	R5	R6	R7
Elongation at break (%)	310.0	360.5	338.7	315.5	115.3	76.0	34.7
	338.0	393.0	361.3	318.2	120.0	69.9	31.4
	333.0	334.4	397.3	324.8	124.8	74.0	33.8
Mean	327.0	362.6	365.8	319.5	120.0	73.3	33.3
Standard deviation	12.1	23.9	4.6	3.9	3.8	3.8	1.4

Table C.3 Moduli at 50%, 100%, 200% and 300% elongation of rubber/PVC blends

	R1				R2				R3				R4				R5				R6				R7							
	M ₅₀	M ₁₀₀	M ₂₀₀	M ₃₀₀	M ₅₀	M ₁₀₀	M ₂₀₀	M ₃₀₀	M ₅₀	M ₁₀₀	M ₂₀₀	M ₃₀₀	M ₅₀	M ₁₀₀	M ₂₀₀	M ₃₀₀	M ₅₀	M ₁₀₀	M ₂₀₀	M ₃₀₀	M ₅₀	M ₁₀₀	M ₂₀₀	M ₃₀₀	M ₅₀	M ₁₀₀	M ₂₀₀	M ₃₀₀				
Moduli (MPa)	1.69	2.66	4.59	7.25	2.90	5.10	9.14	13.14	3.60	5.57	8.70	11.90	2.94	5.95	10.0	12.50	13.70	15.95	-	-	11.40	-	-	-	-	-	-	-	-	-	-	-
	1.55	2.57	4.40	7.10	2.78	5.06	8.98	12.45	3.40	5.30	8.55	11.75	2.78	5.71	9.88	12.00	13.55	15.90	-	-	12.00	-	-	-	-	-	-	-	-	-	-	-
	1.60	2.60	4.51	7.23	2.95	5.13	9.19	13.70	3.33	5.00	8.05	11.20	2.63	5.58	9.65	11.30	12.95	15.88	-	-	11.50	-	-	-	-	-	-	-	-	-	-	-
Mean	1.61	2.61	4.50	7.19	2.88	5.10	9.10	13.09	3.44	5.29	8.43	11.61	2.79	5.74	9.84	11.93	13.40	15.91	-	-	11.63	-	-	-	-	-	-	-	-	-	-	-
Standar deviation	0.06	0.04	0.08	0.07	0.07	0.03	0.09	0.5	0.11	0.23	0.28	0.30	0.13	0.15	0.15	0.49	0.32	0.03	-	-	0.26	-	-	-	-	-	-	-	-	-	-	-

Table C.4 Tear strength of rubber/PVC blends

	R1	R2	R3	R4	R5	R6	R7
Tear strength (N/mm)	40.70	60.70	51.00	53.93	58.22	34.44	18.10
	37.60	60.10	51.30	52.45	57.58	35.30	20.77
	35.36	63.05	52.90	51.33	58.19	36.26	19.35
Mean	37.89	61.28	51.73	52.57	58.00	35.30	19.41
Standard deviation	2.19	1.27	0.83	1.06	0.74	0.74	1.09

Table C.5 Hardness of rubber/PVC blends

	R1	R2	R3	R4	R5	R6	R7
Hardness	63.8	79.0	82.2	82.0	90.7	90.4	90.0
	64.2	79.0	82.0	81.6	90.0	90.5	89.9
	63.6	79.0	81.9	81.0	90.1	90.3	89.9
Mean	63.9	79.0	82.0	81.5	90.3	90.4	89.9
Standard deviation	0.25	0.00	0.12	0.31	0.31	0.08	0.05

APPENDIX D

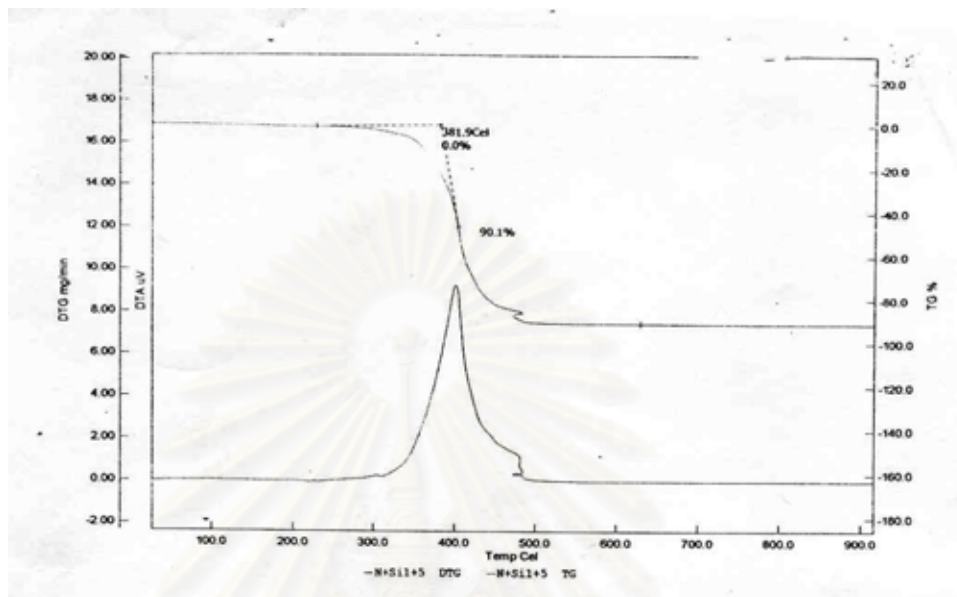


Figure D.1 TGA graph of NR in TEOS 25% wt($H_2O/EtOH=1/0$)

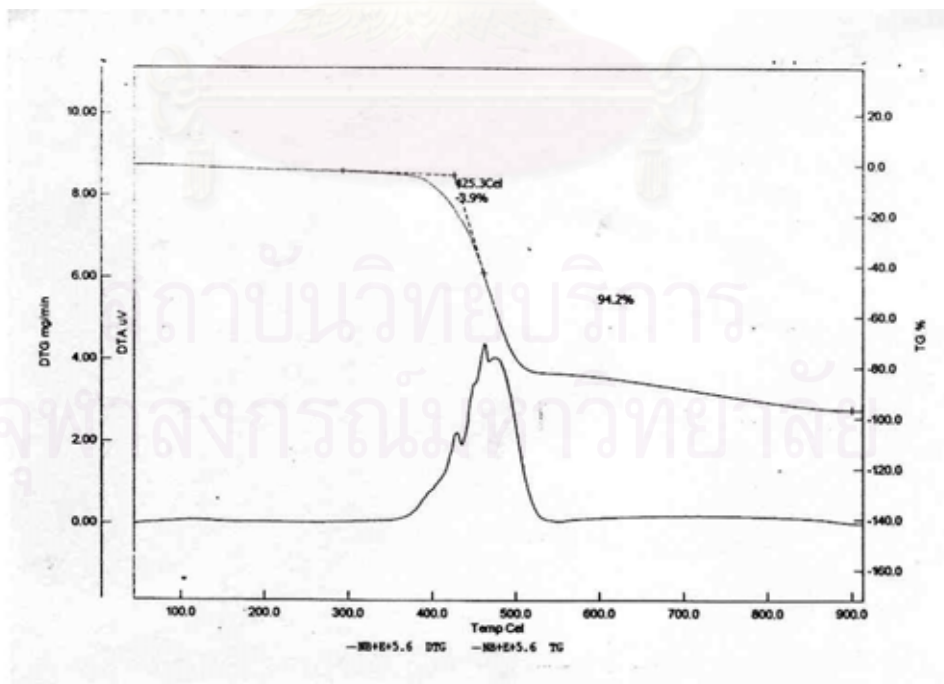


Figure D.2 TGA graph of NR in TEOS 25% wt. ($H_2O/EtOH=3/1$)

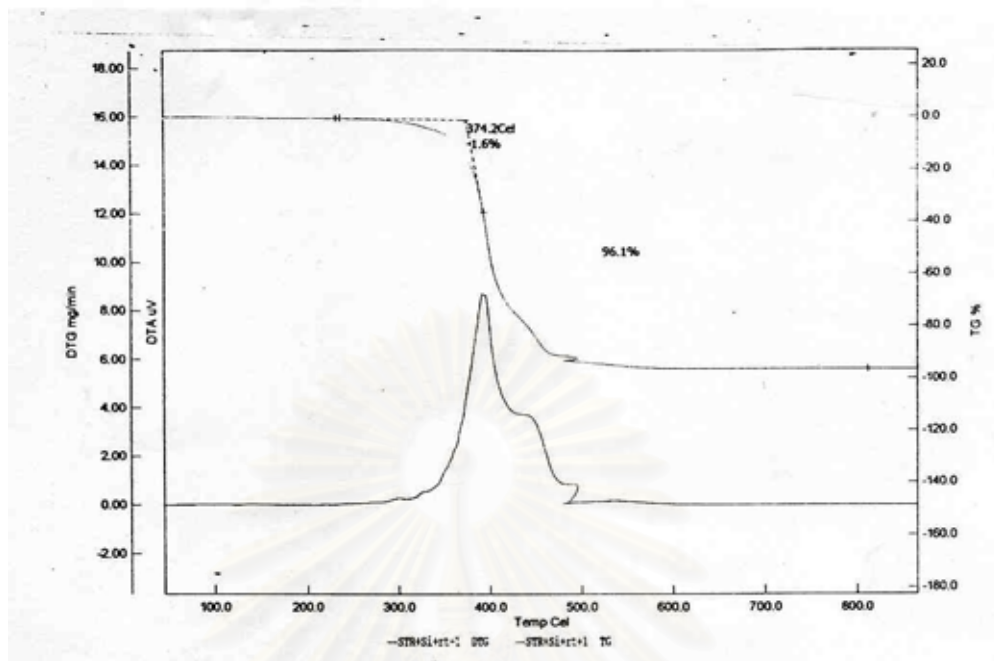


Figure D.3 TGA graph of NR in TEOS 25% wt. ($H_2O/EtOH=1/1$)

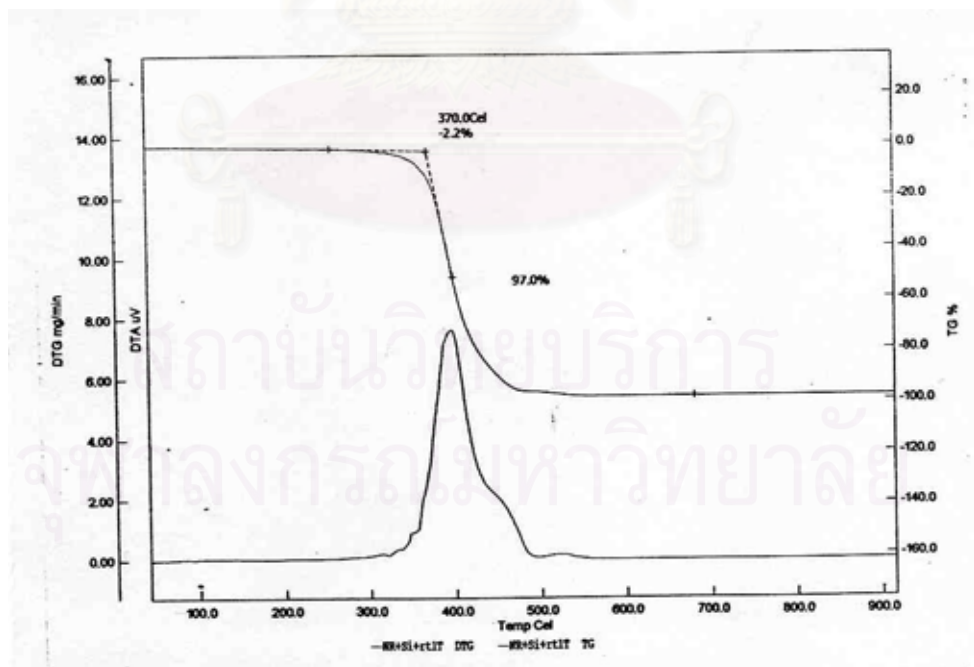


Figure D.4 TGA graph of NR in TEOS 25% wt. ($H_2O/EtOH=1/3$)

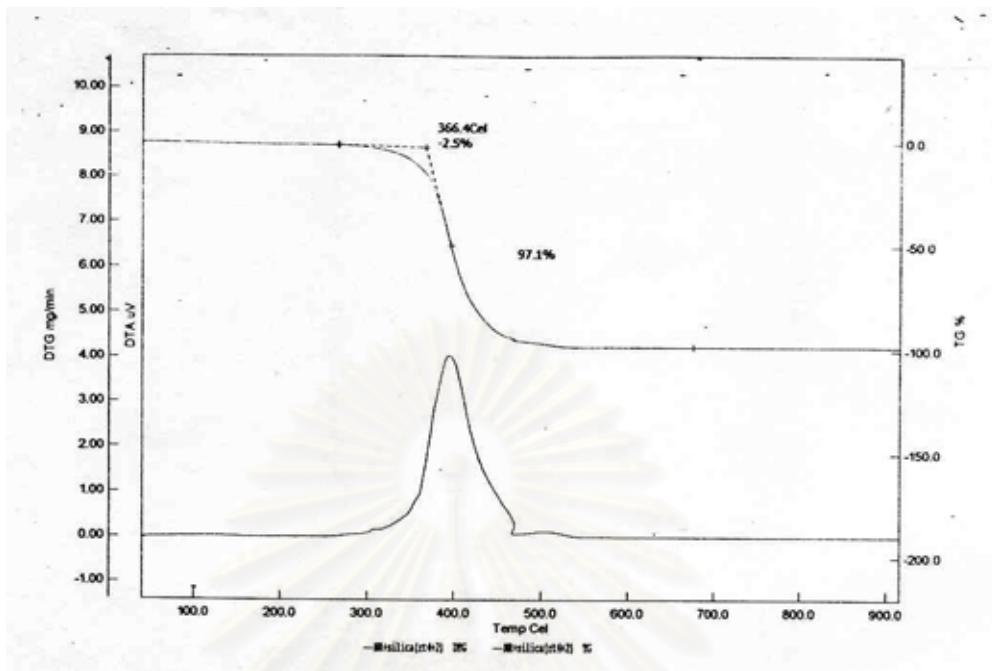


Figure D.5 TGA graph of NR in TEOS 25% wt. (H₂O/EtOH=0/1)

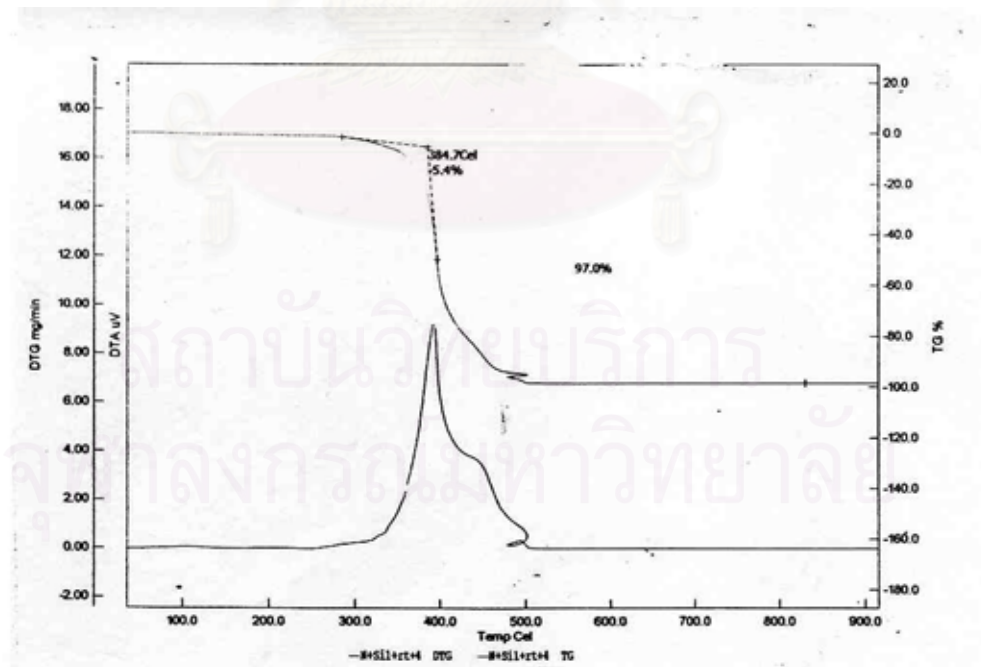


Figure D.6 TGA graph of NR in EPS 25% wt. (H₂O/EtOH=0/1)

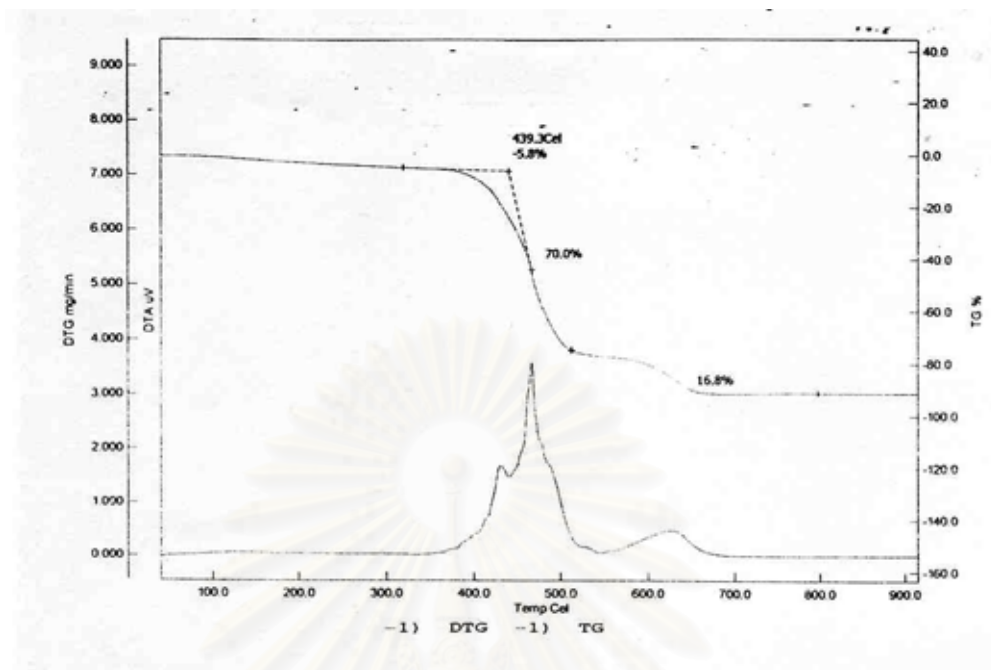


Figure D.7 TGA graph of SBR in TEOS 25% wt. ($H_2O/EtOH=1/0$)

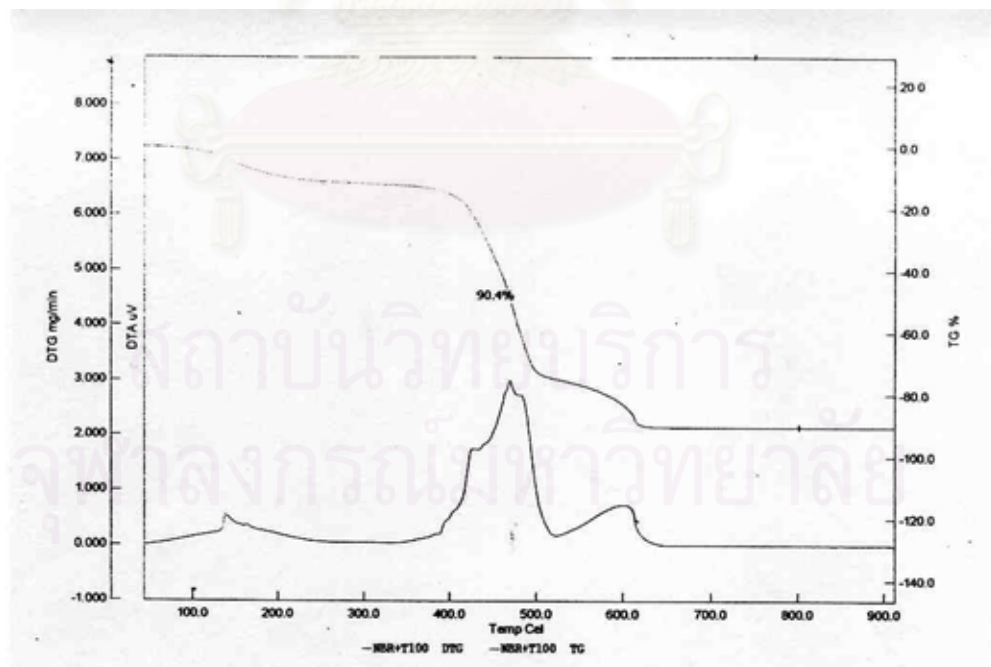


Figure D.8 TGA graph of SBR in TEOS 25% wt. ($H_2O/EtOH=1/1$)

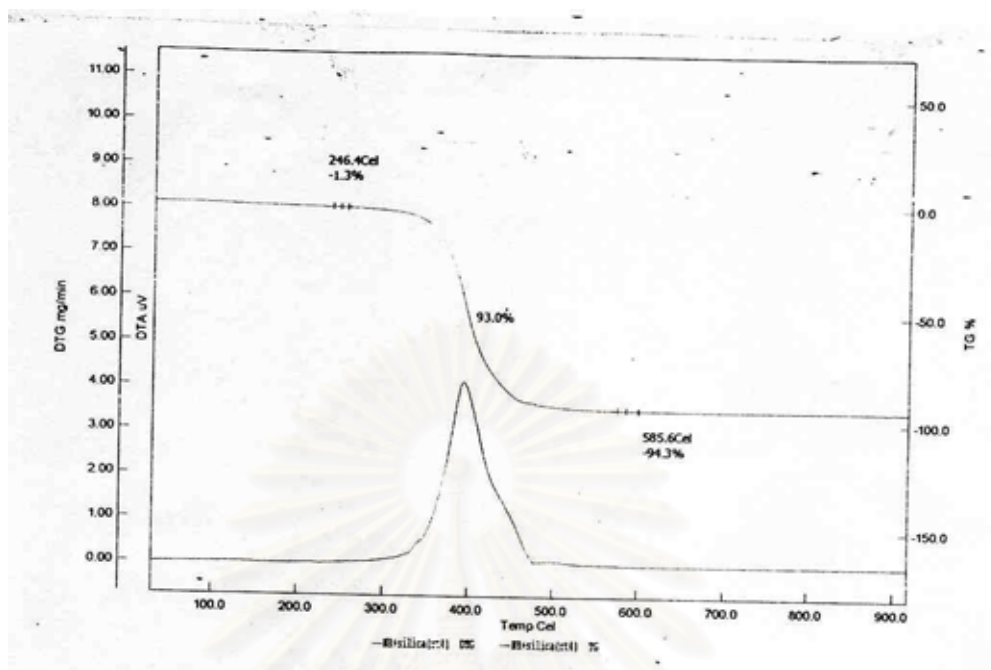


Figure D.9 TGA graph of SBR in TEOS 25% wt. ($H_2O/EtOH=1/3$)

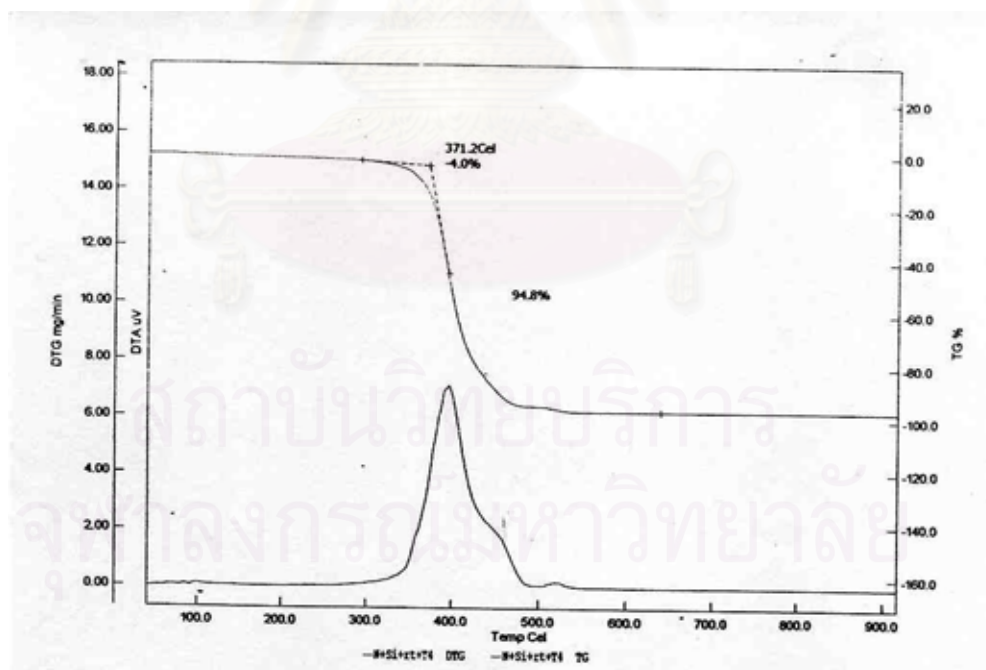


Figure D.10 TGA graph of SBR in TEOS 25% wt. ($H_2O/EtOH=0/1$)

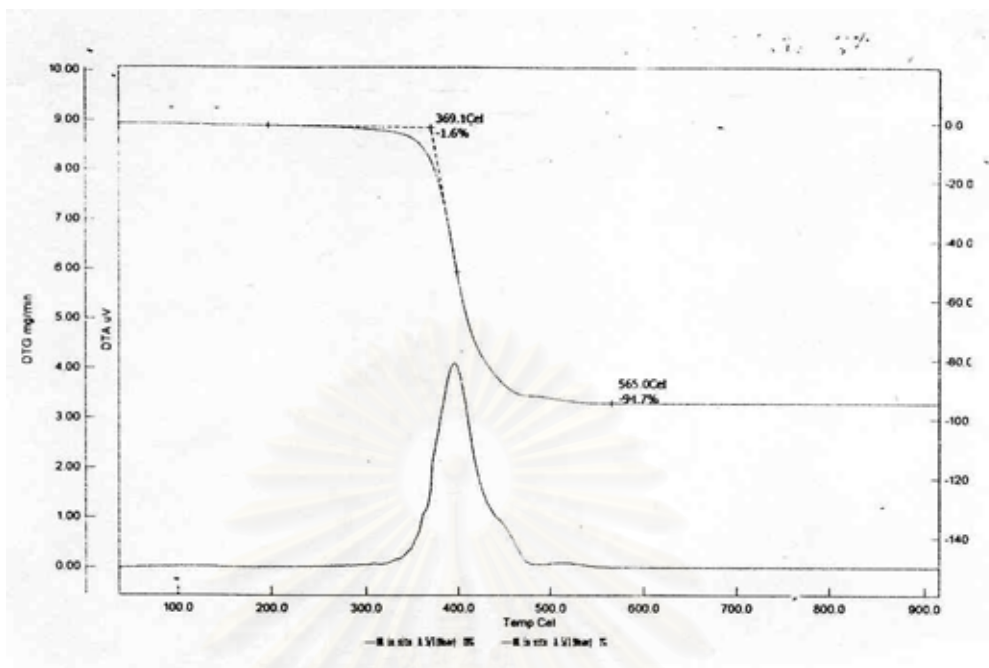


Figure D.11 TGA graph of SBR in EPS 25% wt. ($H_2O/EtOH=0/1$)

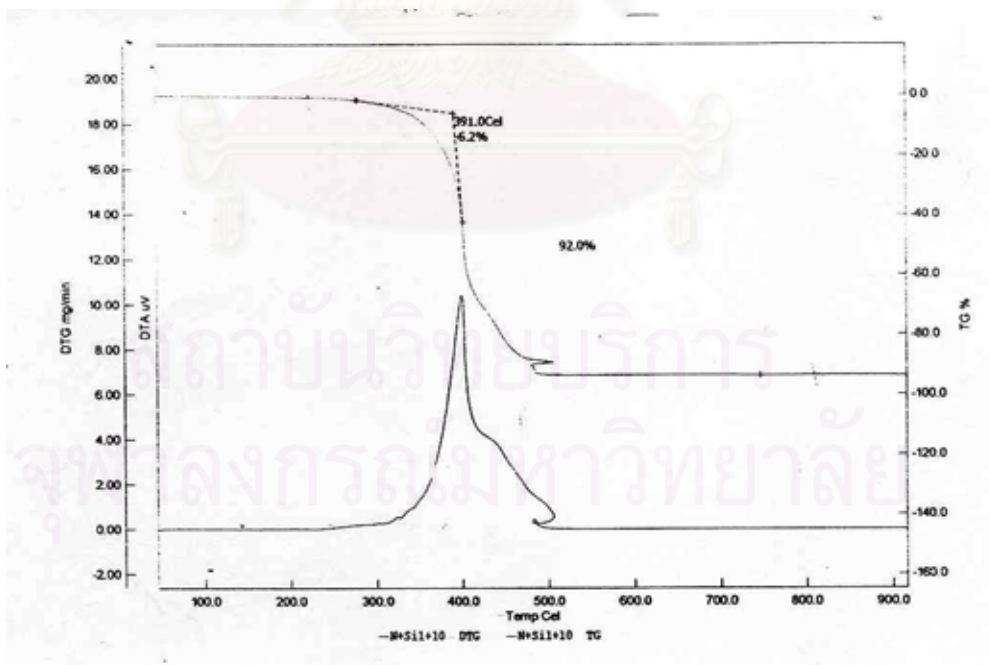


Figure D.12 TGA graph of NBR in TEOS 25% wt. ($H_2O/EtOH=1/0$)

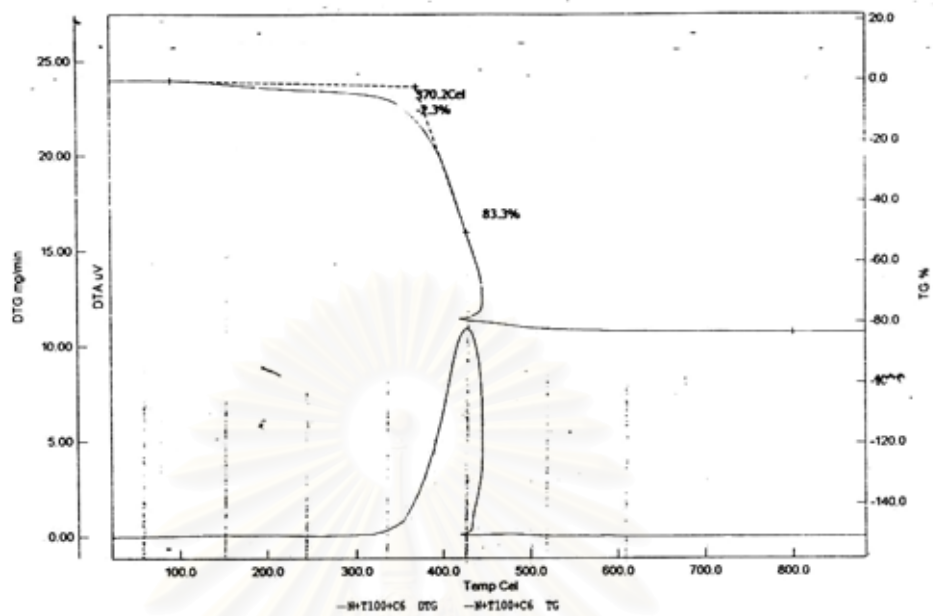


Figure D.13 TGA graph of NBR in TEOS 25% wt. (H₂O/EtOH=3/1)

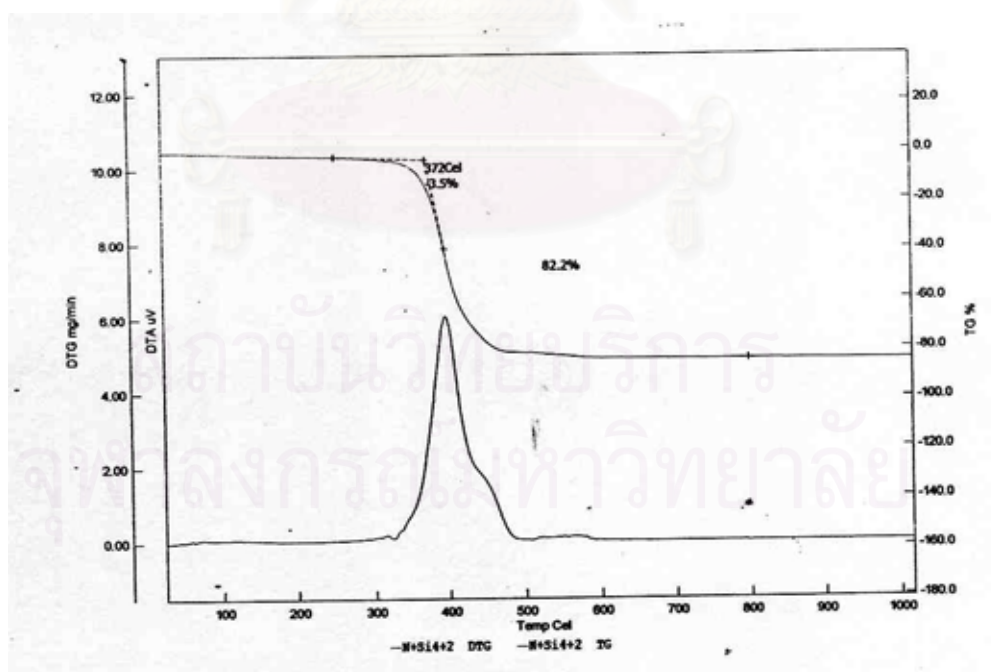


Figure D.14 TGA graph of NBR in TEOS 25% wt. (H₂O/EtOH=1/1)

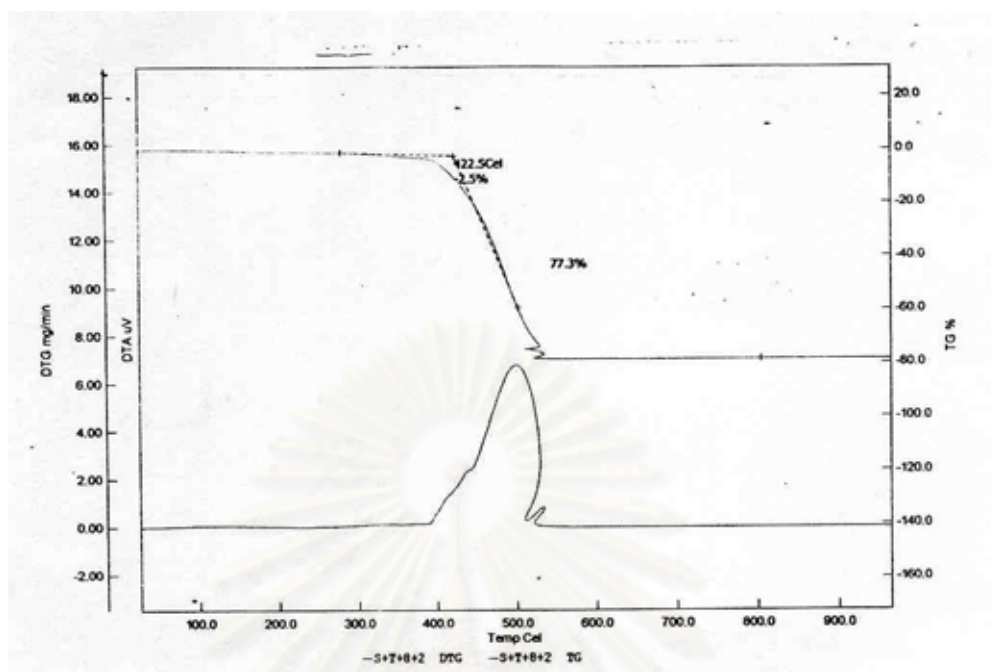


Figure D.15 TGA graph of NBR in TEOS 25% wt. ($H_2O/EtOH=1/3$)

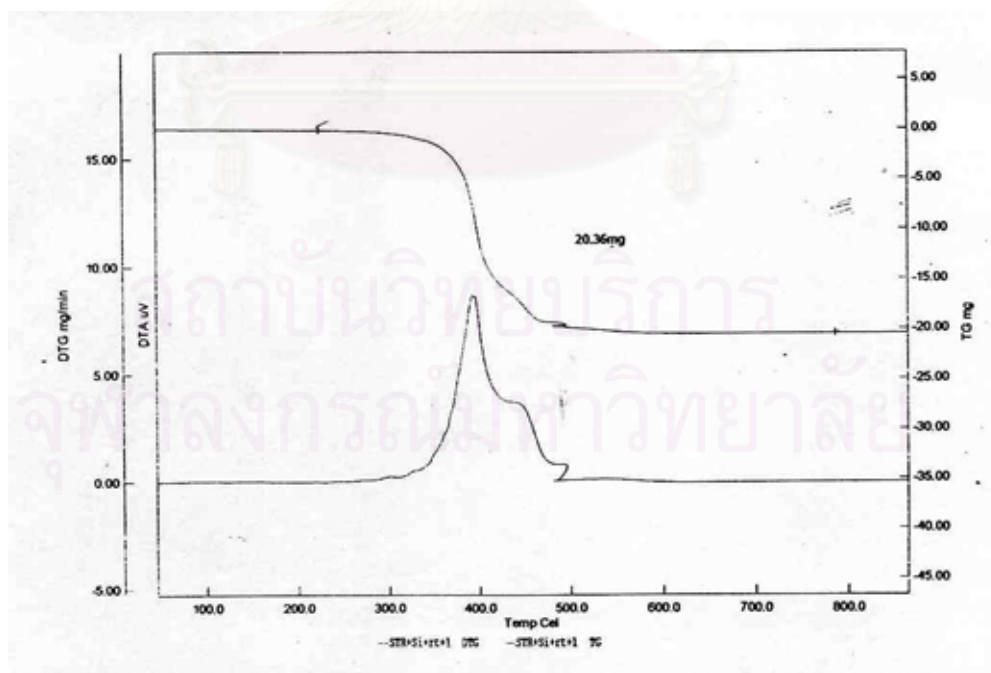


Figure D.16 TGA graph of NBR in TEOS 25% wt. ($H_2O/EtOH=0/1$)

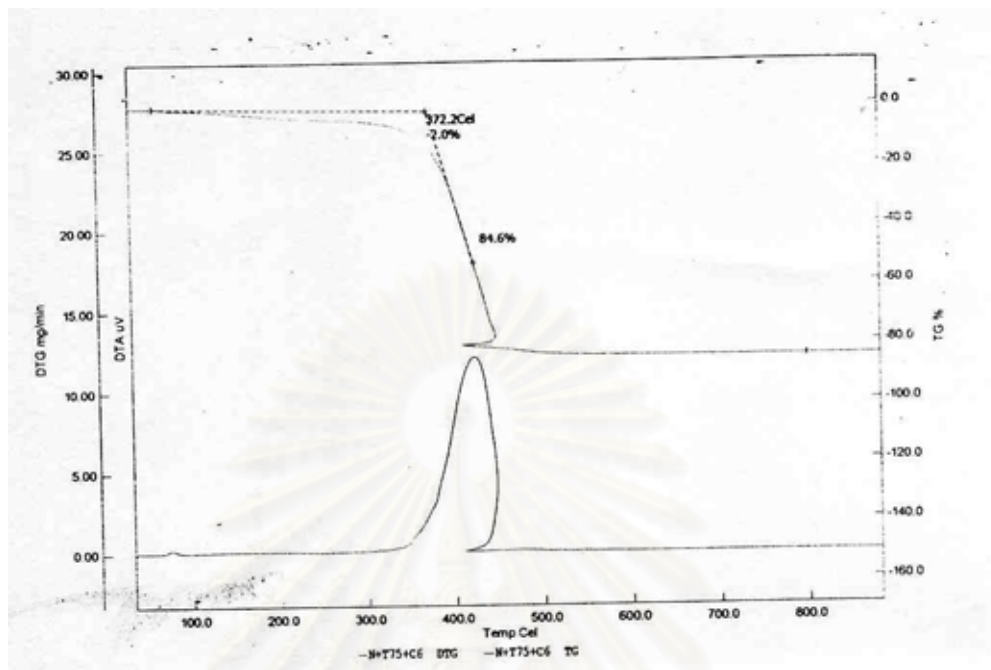


Figure D.17 TGA graph of NBR in EPS 25%wt. ($H_2O/EtOH=1/3$)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

VITAE

Miss Pattra nasompan was born on December 12, 1978 in Kalasin, Thailand. She received her Bachelor's degree in Chemistry, from the Faculty of Science, Khon Kaen University in 2001. She has pursued Master's degree in Petrochemistry and Polymer Science, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University science 2002 and finished her study in Academic Year 2004.



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