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SILICA REINFORCEMENT OF METHYL METHACRYLATE
GRAFTED NATURAL RUBBER BY SOL-GEL PROCESS

Ms.Natchamon Watcharakul

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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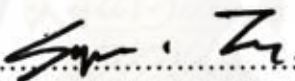Chulalongkorn University

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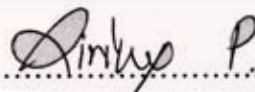Thesis Co-Advisor   Assistant Professor Sirilux Poompradub, Ph.D.

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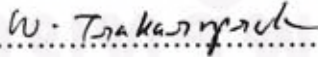
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กระบวนการ โซล-เจล (SILICA REINFORCEMENT OF METHYL METHACRYLATE
GRAFTED NATURAL RUBBER BY SOL-GEL PROCESS.) อ. ที่ปรึกษาวิทยานิพนธ์
หลัก: ศ.ดร.ภัทรพรรณ ประศาสน์สารกิจ, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.ศิริลักษณ์
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การเกิดซิลิกาอินซิทูในยางธรรมชาติกราฟต์เมทิลเมทาคริเลต โดยสังเคราะห์ผ่านปฏิกิริยา
โซลเจลของเททราเอทอกซีไซเลนโดยใช้วิธีแบบยางแห้งและแบบสารละลายน้ำยาง กราฟต์โคพอลิ
เมอไรเซชันของเมทิลเมทาคริเลตบนยางธรรมชาติทำได้โดยใช้ คิวมีนไฮโดรเปอร์ออกไซด์/เททรา
เอทิลีนเพนทามีนซึ่งเป็นตัวริเริ่มปฏิกิริยา วิเคราะห์โครงสร้างของยางกราฟต์ด้วยอินฟราเรดและ
โปรตอนสเปกโทสโคปี ศึกษาผลของความเข้มข้นของตัวเร่งปฏิกิริยา ปริมาณของเททราเอทอกซี
ไซเลน อุณหภูมิ และ เวลาต่อปริมาณซิลิกาอินซิทู สำหรับวิธีแบบยางแห้ง พบว่าปริมาณของซิลิกา
อินซิทูเพิ่มขึ้น เมื่อความเข้มข้นของตัวเร่งปฏิกิริยา ปริมาณของเททราเอทอกซีไซเลน อุณหภูมิ และ
เวลาเพิ่มขึ้น และจะได้ปริมาณซิลิกาอินซิทูในยางธรรมชาติกราฟต์สูงสุดที่ 48 phr สำหรับวิธีแบบ
สารละลายน้ำยาง พบว่าตัวแปรต่างๆมีแนวโน้มที่คล้ายกัน ยางผสมระหว่างยางธรรมชาติกราฟต์ที่มี
ซิลิกาอินซิทูกับยางธรรมชาติที่ผ่านการวัลคาไนซ์ถูกเตรียมและทดสอบสมบัติเชิงกล เปรียบเทียบ
กับยางผสมที่เติมซิลิกาเกรดเชิงการค้า สมบัติเชิงกลของยางผสมระหว่างยางธรรมชาติกราฟต์ที่มีซิ
ลิกาอินซิทูยางกับยางธรรมชาติที่ผ่านการวัลคาไนซ์สูงกว่ายางผสมระหว่างยางธรรมชาติกราฟต์กับ
ยางธรรมชาติที่เติมซิลิกาเกรดเชิงการค้า ภาพจากกล้องจุลทรรศน์แบบส่องผ่านยืนยันว่า อนุภาค
ของซิลิกาอินซิทูกระจายตัวดีในวัฏภาคของยางธรรมชาติกราฟต์ ในขณะที่เกิดการรวมตัวของ
อนุภาคซิลิกาเกรดเชิงการค้าในวัฏภาคของยางธรรมชาติกราฟต์

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อนิสิต.....................
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NATCHAMON WATCHARAKUL: SILICA REINFORCEMENT OF METHYL METHACRYLATE GRAFTED NATURAL RUBBER BY SOL-GEL PROCESS. THESIS ADVISOR: PROF.PATTARAPAN PRASASSARAKICH, Ph.D. THESIS CO-ADVISOR: ASSIST. PROF. SIRILUX POOMPRADUB, Ph.D., 79 pp.

The *in situ* generated silica in methyl methacrylate grafted natural rubber (MMA-g-NR) was synthesized through sol-gel reaction of teraethoxysilane (TEOS) using solid rubber method and latex solution method. The graft copolymerization of methyl methacrylate onto natural rubber was carried out using cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) as an initiator. The grafted NR was characterized by FT-IR and NMR analysis. The effects of catalyst concentration, TEOS content, temperature and time on *in situ* silica content were investigated. For solid rubber method, the *in situ* silica content increased with increasing the concentration of n-hexylamine, TEOS content, reaction temperature and time and the highest *in situ* silica content of 48 phr in grafted natural rubber was achieved. For latex solution method, the similar trend of these variables was observed. The *in situ* silica grafted natural rubber (GNR)/natural rubber (NR) vulcanizates were prepared and the mechanical properties were investigated and compared with commercial silica filled one. The mechanical properties of *in situ* reinforced NR/GNR vulcanizates were higher than those of commercial silica filled NR/GNR vulcanizate. The TEM micrographs confirmed that the *in situ* silica particles were well dispersed in GNR matrix while the agglomeration of commercial silica particles was formed in GNR matrix.

Field of Study:..Petrochemistry and Polymer Science..Student's Signature..Natchamon Hatcharakul

Academic Year:..............2009..............................Advisor's Signature............

Co-Advisor's Signature ..Sirilux P.

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LIST OF ABBREVIATIONS

ASTM	: American Society for Testing and Materials
CHCl$_3$	: Chloroform
DRC	: Dry rubber content
MBTS	: Mercaptobenzothiazole disulfide
MMA-g-NR	: The graft copolymer of methyl methacrylate onto natural rubber
NR	: Natural rubber
phr	: Part per hundred part
PEG	: Polyethylene glycol
SEM	: Scanning Electron Microscopy
Si	: Silica
TEM	: Transmission Electron Microscopy
TEOS	: Tetraethoxysilane
TGA	: Thermal Gravimetric Analysis
ZnO	: Zinc oxide

CHAPTER I

INTRODUCTION

1.1 Statement of Problem

Many engineering applications of natural rubber take advantage of its elasticity. Natural rubber (NR) has excellent resistance to fatigue, highly resilient, inexpensive and easy to manufacture and has a wider range of operating temperature than most other elastomers [1]. Since natural rubber is non-polar, its vulcanizates have little resistance to swelling in non-polar solvent. When in contact with mineral oils and gasoline, the volume of natural rubber increases hundred percent. Modification affects its physical properties. The most well known types of modification are oxidation, hydrogenation, halogenations and grafting. The graft copolymer of NR with vinyl monomers has gained considerable importance in modifying the properties of NR. For natural rubber, methyl methacrylate (MMA) and styrene (ST) are the most suitable monomers when polymerized to give a high level of grafting. Poly(methyl methacrylate) graft NR has been marketed since the mid 1950s under the trade name "Heveaplus", and tert-butylhydroperoxide (TBHPO) was used as the initiator [2, 3]. Graft copolymer of NR was synthesized in emulsion polymerization by various initiators and cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) was found to give the high grafting efficiiency [4, 5].

In rubber industry, besides carbon black, silica is another reinforceing filler used to impart specific properties to rubber compound. Therefore, silica is used in products where black color is not a requirement, e.g., in shoes soles which is the main application of silica. The rubber/silica composite offers advantages in tear strength, abrasion resistance and the reduction in heat build-up, etc. over carbon black [6]. However, because of presence of numerous silanol groups, the surface of precipitated silica is highly polar and hydrophilic which make it easy to agglomerate when it is dispersed in a non-polar matrix such as natural rubber. To improve the dispersibility

of silica in rubber compound, *in situ* polymerization (Sol-gel process) of TEOS in rubber was performed. Sol-gel process which brings the formation of silica enables in situ silica filling in the rubber. The reactions of TEOS take place in 2 steps, hydrolysis and condensation [7]. The sol-gel process has been developed and applied to polymers such as acrylonitrile-butadiene (NBR) [8], styrene-butadiene (SBR) [8, 9], epoxidized natural rubber (ENR) [10, 11], NR [12-15], and poly(methyl methacrylate) (PMMA) [16-18].

In this work, an attempt was made to prepare the methyl methacrylate grafted natural rubber (MMA-g-NR) using cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) as a redox initiator system. The in situ silica grafted rubber was prepared by sol-gel process via TEOS. The mechanical properties of silica reinforced grafted rubber vulcanizates were investigated.

1.2 Objectives of the Research Work

1. To synthesize the in situ silica methyl methacrylate grafted natural rubber (MMA-g-NR) by sol-gel reaction via TEOS using solid rubber and latex solution method.
2. To study the mechanical properties of in situ silica reinforced methyl methacrylate grafted rubber vulcanizates.

1.3 Scope of the Investigation

1. Literature survey and study the research work.
2. Prepare the methyl methacrylate grafted natural rubber (MMA-g-NR).
3. Characterize the chemical structure of MMA-g-NR by Fourier Transform Infrared Spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance (^{1}H NMR).
4. Prepare the *in situ* silica filled MMA-g-NR by sol-gel process via TEOS with solid rubber method. The appropriate conditions were determined by varying the following parameters:

      a) Catalyst concentration (n-hexylamine): 0.008 - 0.064 M.

      b) Reaction temperature: 40°C, 50°C and 60°C.

      c) Reaction times: 1 - 5 days.

5. Prepare the *in situ* silica filled MMA-g-NR by sol-gel process via TEOS with latex solution method. The appropriate conditions were determined by varying the following parameters:

      a) Addition method of TEOS

      b) Reaction temperature: 50°C and 60°C.

      c) Reaction times: 1 - 7 days.

      d) TEOS content: 10 - 70 phr.

6. Determine the *in situ* silica content in MMA-g-NR by Thermogravimetric Analysis (TGA).

7. Prepare the rubber blends by direct mixing of the *in situ* silica filled MMA-g-NR with vulcanizing agents, additives and NR.

8. Study the morphology of *in situ* silica reinforced MMA-g-NR vulcanizates by Transmission Electron Microscope (TEM).

9. Determine the mechanical properties of *in situ* silica reinforced MMA-g-NR.

10. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber

Natural rubber (NR) is obtained from the milky secretion (latex) of various plants, but the only important commercial source of natural rubber (sometimes called Pará rubber) is the tree *Hevea brasiliensis.* The only other plant under cultivation as a commercial rubber source is guayule (*Parthenium argentatum*). *Hevea brasiliensis* is a native of the tropical rain forest of the Amazon Basin in Brazil. Most of the world's natural rubber comes today from South East Asia, mainly Thailand, Malaysia and Indonesia [19].

Chemically, natural rubber made from *Hevea Brasiliensi* is composed about 98% of cis-1,4-polyisoprene (Figure 2.1). Rubber does not dissolve in water, alcohol or acetone. It swells and disperses in a number of organic solvents, such as toluene and benzene. The processed form of natural rubber is also commonly called "latex".
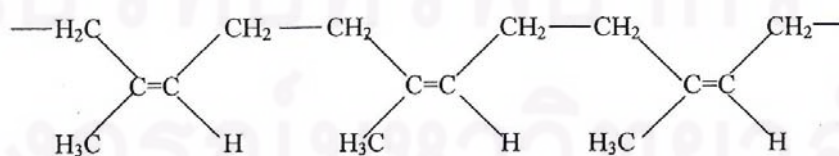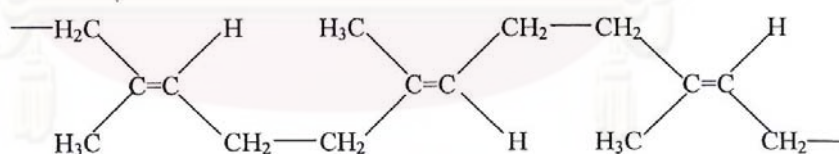
Figure 2.1 Isoprene Structure

Natural rubber latex, a milk-like liquid, comes from a layer of tiny tubes spiraling up the three beneath the outer bark. Like milk, it is an emulsion particles suspended in water. Natural latex as it comes from the tree is known as field latex. Field latex is only about 36% rubber and 4% non-rubber substances. The non-rubber components include proteins, carbohydrates, lipids and inorganic salts. Its composition varies according to the clones of rubber, age of rubber tree and tapping method. The composition of typical field latex is presented in Table 2.1.

Table 2.1 Composition of latex [20]

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

Natural rubber 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 sulfur, low sulfur or nonelemental sulfur vulcanizing systems; less frequently peroxide). NR can be blended with other diene rubbers such as Polyisoprene (IR), Styrene-butadiene rubber (SBR) and butadiene rubber (BR).

Natural rubber 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. Natural rubber 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.

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

Natural rubber 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.

2.2 Graft Copolymerization of Natural Rubber

Natural rubber has been modified in many ways since the establishment of a continuous supply of plantation rubber. Modification highly affects its physical properties. Even thermoplastic or resinous materials can be obtained by modification. The most well known types of modification are oxidation, hydrogenation, halogenations, hydrochioronation, chlorosulphonation and free radical addition or grafting [21].

In graft copolymerization, polymer side chains are formed attached to preformed macromolecules of different chemical composition [22]. The simplest case of graft copolymer can be represented by the following structure (Figure 2.2).

Figure 2.2 Graft copolymer

where a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain of graft and X is the backbone to which the graft is attached.

Graft copolymers produced by causing a post polymerization of vinyl monomers such as styrene, acrylonitrile, methyl methacrylate either independently or as a mixture of a plurality thereof to a rubber-like polymer latex have been well known.

Although graft copolymerizations are widely practiced with vinyl monomers and polymer, especially for improving compatibility, impact and low temperature properties of thermoplastics, the technology has been based more upon science. Often small proportions of actual grafting have been sufficient to give worthwhile modification of properties. If grafting does not give directly the properties desired, it may improve morphology or compatibility with specific added polymers or plasticizers that impart the desired effect. In addition, these graft copolymers have been mixed with other resins such as poly(vinyl chloride) to improve compatibility, impact and low temperature properties of thermoplastic.

Useful rubbery behavior in polymers which could be processed as thermoplastic was reported as early as 1958. There was increasing interest in the blending of rubbery and hard polymer to generate materials which had greater flexibility than many of the conventional plastics and rubber like elasticity approaching that of vulcanized rubber. In 1965, the styrene-diene block copolymers

were introduced by commercial announcement. Soon after their commercial announcement, the materials of many different types are now used in the thermoplastic rubber technology.

The Natural Rubber Research Organizations had investigated processes for grafting polymers to natural rubber using free radical chemistry. Materials were obtained which contained both plastic and rubber constituents and Heveaplus-MG, a graft copolymer of natural rubber and poly(methyl methacrylate), become commercially available. The material still has its uses, but it did not behave as a thermoplastic rubber in the currently used sense of the worlds

2.3 Emulsion Polymerization

Emulsion polymerization is a means of carrying out this process on the laboratory and industrial scales [23]. The simplest recipe for an emulsion polymerization starts with water, surfactant (soap), monomer, and initiator. The system is agitated to form an emulsion. Heating results in the production of free radicals by thermal decomposition of initiator, and free radical polymerization commences. The end result of the polymerization process is a latex comprising polymer particles, each containing many polymer chains. The polymer particles constitute a dispersed phase in continuous aqueous phase. These latex particles are typically 200 nm in diameter. They form a colloid, stabilized against coalescence by surfactant, and comprise a new phase that is formed early in the process. Thus the final result of an emulsion polymerization is a latex: a polymer colloid, with water the continuous phase. The latex can be directly (e.g. as an adhesive or surface coating), or for other applications, the polymer can be extracted.

Emulsion polymerization (including copolymerization) furnishes what in principle is a method for producing a latex and polymer with any desired morphology, composition, sequence distribution, surface end groups, molecular weight distribution, particle size distribution, particle concentration, and so on.

Ingredients and Processes

An overview of the major ingredients and processes in emulsion polymerization is now presented: a list of common monomers and where they are used in commercial products, of surfactants, and initiators.

a) Monomers: The major polymerizable component of an emulsion polymerization is a monomer that is of limited solubility in water, and that swells its polymer. The monomers used in emulsion polymerization are thus often of the vinyl type, $CH_2=CHX$. X may be C_6H_5, CN, O_2CCH_3, Cl, and CO_2R.

b) Initiators: Most initiators used in emulsion polymerization are water-soluble. A commonly used laboratory and industrial initiator is potassium persulfate ($K_2S_2O_8$, properly called potassium peroxydisulfate), or other persulfate salts such as ammonium persulfate. Persulfate produces SO_4 anion free radicals as result of bond scission; the high energy for this process is quite high, so persulfate is usually employed as the sole initiator at high temperatures ($50^{o}C$ or higher).

At lower temperature a redox system such as Fe(II) and cumene hydroperoxide, or dimethylhydroperoxide, or persulfate and metabissulfite, is often used. It is common to perform industrial emulsion polymerizations at low temperature: in the case of synthetic rubbers, this reduces the amount of branching of chains, which in turn reduces the time required to incorporate carbon black into the rubber.

Finally, it is possible to employ an organic-phase initiator such as AIBN (azobisisobutyronitrile) in an emulsion polymerization. Oil-soluble initiator can be employed under special circumstances in emulsion polymerization: e.g. in the preparation of large-particle size monodisperse polystyrene latexes, using AIBN and water-soluble initiator in seed emulsion polymerization. Oil-soluble initiators also find use in dispersion polymerizations.

c) Surfactants: Surfactant is used to impart colloidal stability to latex particles, which are the loci of polymerization. There are three basic types of

surfactant: (i.) electrostatic stabilizers such as anionic or cationic soaps, which prevent coagulation by electrostatic repulsion arising from the charges located on the particle surfaces and their associated electric double layer. (ii.) Polymeric stabilizer such as partially hydrolyzed poly(vinyl acetate), which stabilizers *inter alia* through the entropic repulsion caused by trying to pack two chains in the same space, and (iii.) electrostatic stabilizer displays the characteristics of both surfactant types (i.) and (ii.). Some commoner laboratory anionic surfactants are sodium dodecyl sulfate (SDS).

d) Other Ingredients: It is often to add a modifier in commercial emulsion polymerization: chain transfer agents to control molecular weight. Buffers are another usual additive, their role being control pH. This prevents hydrolysis of surfactants and may also be necessary to ensure reasonable initiator efficiency. Electrolytes may be added. Usually with the aim of including particle size monodispersity; since electrolytes may also have the determental effect of promoting particle coagulation, caution needs to be exercised in using them. It is also common to add a chaser, which is means of reducing residual monomer at the end of the polymerization process (typically a chaser might comprise a shot of redox initiator added late in the batch).

2.4 Polymer Blends [24]

The term polymer blend is use in two ways. First, it involves all multicomponent polymer materials composed primarily of two or more polymers. Second, it is used specifically to describe combinations of two or more polymers that are not bonded chemically to each other. Important combinations of two or more polymers bonded together include graft copolymers, block copolymers, and interpenetrating polymer networks (IPNs).

The blending of polymers has become an important industrial technique that is an economic and versatile way to produce materials having a wide range of properties. Their enhanced, especially adapted property profiles provide advantages to the processor and end user such as extra ease of processing, better low temperature impact performances, higher strength, higher or lower gloss, reduced flammability, and higher transparency, often in combination with a lower price.

2.5 Vulcanization [25]

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. Sulfur is the main vulcanizing agent for most crude rubbers that contain enough double bonds in their macromolecules. In order to increase the rate of vulcanizing, it is necessary to add accelerators and activators. The combination of vulcanizing agent, accelerators and activators is frequently called the vulcanizing system.

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

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

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

by acetone, whereas the combined sulfur in the cross-links cannot be removed by acetone extraction.

Conventional sulfur vulcanizing systems for soft rubber products consist of relatively high amounts of elemental sulfur (about 1-3 part per rubber (phr)) combined with a low concentration of accelerators. If the amount of sulfur is increased to 25-45 phr, a hard rubber, or ebonite is formed. (See Figure 2.3)
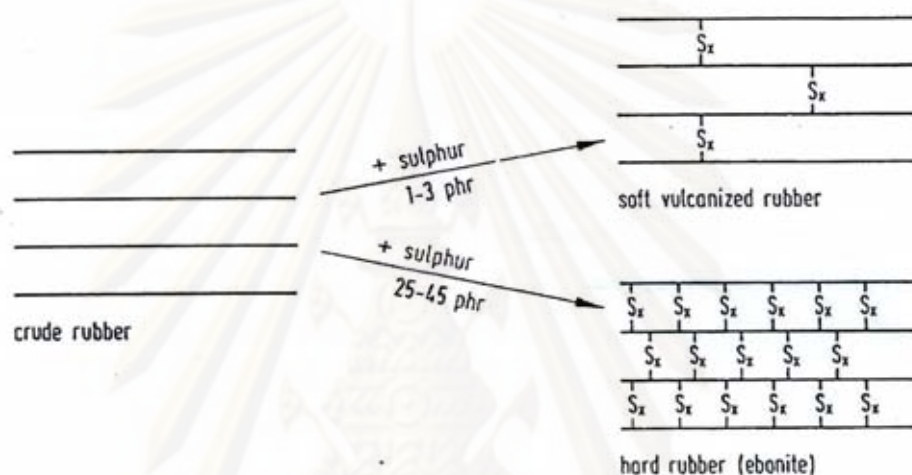
Figure 2.3 Sulfur cross-linking of highly unsaturated rubbers [25]

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

It is generally accepted that the EV system produce at optimum cure a network containing prednominantly stable monosulphide cross-links. Once the vulcanization is complete, no sulphur is available for further cross-linking.

In contrast to EV systems, the conventional sulfur vulcanizing systems produce vulcanizates in which the combined sulfur exists predominantly in polysulphide cross-links. Such vulcanizate tend to harden excessively at elevated

temperatures, possibly because sulfur is released from the polysulphide cross-links to form additional cross-inks.

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

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

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

2.6 Filler for Rubbers

Filler may be of two types, reinforcing and non-reinforcing. Common reinforcing fillers are silica and carbon black. The latters are the most widely used in automotive tires to improve wear characteristics such as abrasion resistance. Non-reinforcing fillers, such as calcium carbonate, may provide color or opacity or may merely lower the price of final product [26].

2.6.1 Reinforcement Concepts

The concept of reinforcement relates basically to composites built from two or more structural elements or components of different mechanical characteristics where by 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 the other component. Basically what has been done is to bond a loose network of strong, long members together by a high viscosity or solid matrix so that the members support each other.

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

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

2.6.2 Basic Factors Influencing Elastomer Reinforcement

1. There is an improvement of modulus and tensile strength. This is very much dependent on the particle size of the filler; small particles have a much greater effect than coarse ones. Particle size is directly related to the reciprocal of surface are per gram of filler; thus the effect of smaller particles actually reflects their greater extant 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 diminish volume fraction of polymer in the composite. If the volume percentage of filler becomes so high that there is not enough rubber matrix to hold the filler particles together, strength

approaches zero. Before this stage of loading is reached, the compound attains a level of stiffness where it becomes brittle and, at the normal rate of testing (e.g. 50 cm per minute) such a brittle compound would show poor strength. At much lower rates of stretching, the decline in strength with higher loading would be less; the height and place of the maximum in the strength vs. loading curve are rate dependent. The maximum occurs at higher loading when testing at slower rates. The place of the maximum is also dependent on the particle size of the filler.

2.6.3 Typical Filler Characteristics

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

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

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

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

2.6.4 Filler Properties [27]

The characteristics that filler will impart to rubber compound are article size, surface area, structure and surface activity.

a) Particle size: If the size of filler particle greatly exceeds the polymer inter-chain distance, it introduces an area of localized stress. This can contribute to the rupture of elastomer chain on flexing or stretching. Fillers with particle size greater than 10,000 nm (10 µm) are therefore avoided because they can reduce performance rather than reinforcement. Fillers with particle sizes between 1,000 – 10,000 nm (1 – 10 µm) are used primarily as diluents and usually have no significant effect on rubber properties. Semi-reinforced fillers, which range from 100 – 1,000 nm (0.1 – 1 µm) improve strength and modulus properties. The truly reinforcing fillers, which range from 10 – 100 nm (0.01 – 0.1 µm), significantly improve rubber properties.

Carbon blacks and precipitated silica are available in various particle sizes that range from semi-reinforcing to highly reinforcing. They generally exist as structural agglomerates or aggregates rather than individual spherical particles.

b) Surface Area: Filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Filler that has a high surface area has more contact area available and therefore has a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surface area available for contacting the rubber than spherical particles with an equivalent average particle diameter. Particles of carbon black or precipitated silica are generally spherical, but their aggregates are anisometric and are considerably smaller than the particles of clay, which have planar-shaped particle. Surface area for rubber-grade carbon blacks vary from 6 - 250 m^2/g. Most reinforcing precipitated silica varies from 125 - 200 m^2/g and typical hard clay ranges vary from 20 - 25 m^2/g.

c) Structure: The shape of an individual particle of reinforcing filler is less important than the filler's effective shape once dispersed in an elastomer. The carbon black and precipitated inorganic used for reinforcement have generally round primary particles but function as anisometric (needle-like) aggregates.

d) Surface Activity: Filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm^2 of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to nonpolar elastomers; polar fillers work best in polar elastomers. Beyond this general chemical compatibility is the potential for reaction between the elastomer and active sites in the filler surfaces.

2.7 Silica [28]

Addition of silica to a rubber compound offers a number of advantages such as improvement in tear strength, reduction in heat build up and increase a compound adhesion in products such as tires. Two fundamental properties of silica influence its use in rubber compound: ultimate particle size and extent of hydration. Other physical properties such as pH, chemical composition and oil absorption are of secondary importance.

Silica, when compared to carbon blacks of the same particle size does not provide the same level of reinforcement. Nevertheless the deficiency of silica largely disappears when coupling agents are used with silica [29].

The chemistry of silica is described as follows:

1. Silica is amorphous, consists of silicon and oxygen arranged in a tetrahedral structure of a three-dimensional lattice. Particle size range from 1 to 30 nm and surface area from 20 to 300 m^2/g. There is no long-range crystal order, only short-range ordered domains in a random arrangement with neighboring domains.

2.   Silanol types fall into three categories: isolated, geminal (two hydroxyl groups on the same silicon atom) and vicinal (two hydroxyl groups on adjacent silicon atoms) as illustrated in Figure 2.4.

3.   Surface silanol concentration (silanol groups, Si-OH) influences the degree of surface hydration and acidity. The interaction between rubber and filler is affected by these sites. Also a high level of hydration can adversely affect final compound physical properties.
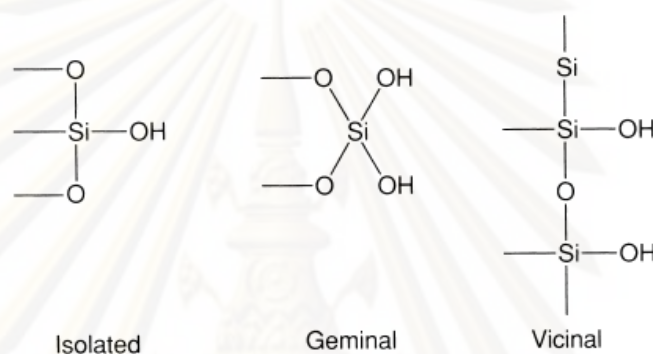
Figure 2.4 Typical silanol groups on silica [30]

The manufacturing siliica has various steps. In the first step (precipitation), the raw materials consisting of water glass (sodium silicate solution) and a mineral acid (normally sulfuric acid is used) are dosed into a stirred vessel containing water. IN many cases, once a defined pH value has been set, the components are fed continuously to the reactor, this process taking place simultaneously over a certain time interval. Another possibility is to first supply a particular quantity of water glass and initially dose just the sulfuric acid. Normally, this is followed by a second stage in which water glass and sulfuric acid are added simultaneously under defined reaction conditions. During the reaction time, primary particles are first formed in the reactor; later these particles react with each other, accompanied by dehydration, to form aggregate. Within the aggregates, the primary particles are linked together via siloxane bonds. During this process, the aggregates are deposited to form larger units, or agglomerates. In these agglomerates the aggregates are held together by hydrogen bonding or van der Waals interactions that are considerably weaker than siloxane bonds, as shown in Figure 2.5.
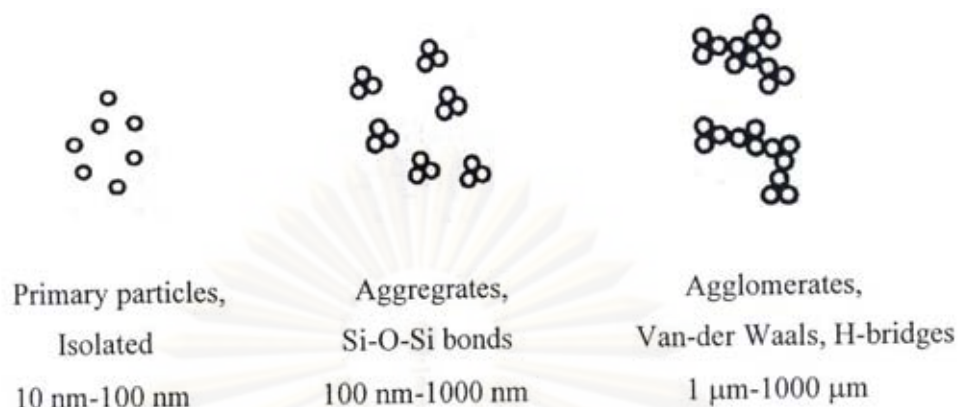
Figure 2.5 Sketechs of primary particle, aggregates and agglomerate occurring in silica [29].

2.8 Sol-Gel Process [7]

The sol-gel process involves the hydrolysis of a reactive, multifunctional inorganic monomer. A reaction is the acid- or base-catalyzed hydrolysis of tetraethoxysilane (TEOS) in Scheme 2.1. This compound can be hydrolyzed in solution to silicic acid [$Si(OH)_4$], a monomer that will condense rapidly to a cross-linked matrix and ultimately to silica

Hydrolysis:

$$-\underset{|}{\overset{|}{Si}}-OC_2H_5 \quad + \quad H_2O \quad \rightleftharpoons \quad -\underset{|}{\overset{|}{Si}}-OH \quad + \quad C_2H_5OH \qquad (2.1)$$

Alcohol Condensation:

$$-\underset{|}{\overset{|}{Si}}-OC_2H_5 \quad + \quad HO-\underset{|}{\overset{|}{Si}}- \quad \rightleftharpoons \quad -\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- \quad + \quad C_2H_5OH \qquad (2.2)$$

Water Condensation:

$$-\underset{|}{\overset{|}{Si}}-OH \quad + \quad HO-\underset{|}{\overset{|}{Si}}- \quad \rightleftharpoons \quad -\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- \quad + \quad H_2O \qquad (2.3)$$

Over all reaction:

$$Si(OC_2H_5)_4 \quad + \quad 2H_2O \quad \rightleftharpoons \quad SiO_2 \quad + \quad 4C_2H_5OH \qquad \textbf{(2.4)}$$
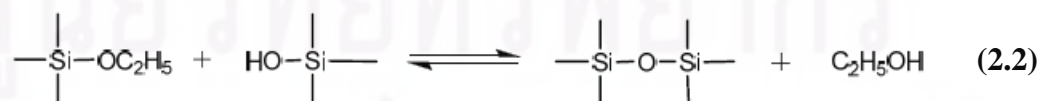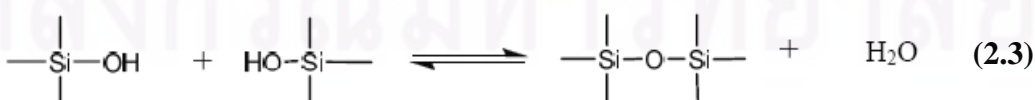
Scheme 2.1 Hydrolysis and condensation reactions of TEOS to form silica

In pratice, the hydrolysis is carried out in ethanol solvent under controlled conditions that allow the solution (sol) to form a formable loosely cross-linked matrix (gel). This, after molding into a prescribed shape, is heated to remove the remaining water and alcohol and convert the matrix to a heavily cross-linked ceramic with a composition similar to that of silica. The method is also applicable to the alkoxides of titanium, aluminum, and many other elements. The main drawback of this process is that a considerable concentraction of volume occurs during the final condensation steps.

Parameters which influence the sol-gel process are follows:

a) Types of Precursor: The stability and reactivity of the silicon alkoxides are influenced by a steric factor. Bulky ligands slow down the hydrolysis:

Reactivity: $Si(OMe)_4 > Si(OEt)_4 > Si(OnPr)_4 > Si(OiPr)_4$

Me= methyl , Et = ethyl , nPr =n-propyl , iPr= iso-propyl

b) The Ratio between Alkoxide and Water (RW): The reaction states that a water ratio of RW = 2 (OR/H$_2$O), OR=Alkoside groups, is need to convert everything to SiO$_2$. A water ratio of RW=1 leads to complete hydrolysis but no condensation. Increasing the water content (i.e. lower RW) will reduce condensation and reducing the water content increases the condensation.

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH \qquad \textbf{(2.5)}$$

        c) Types of Catalyst: The dependence of the reaction rate with pH is different for acid and base catalyzed systems as shown in Figure 2.6. The polymerization process is divided into three approximate pH domains: <pH 2, pH 2-7, and pH>7. The pH 2 appears as a boundary, since the point of zero charge (PZC), where the surface charge is zero, and the isoelectric point (IEP), where the electric mobility of the silica particles is zero, both are in the range pH 1-3. The pH 7 appears as a boundary because both the silica solubility and dissolution rates are maximized at or above pH 7 and because the silica particles are appreciably ionzed above pH 7 so that particle growth occurs without aggregation or gelation.
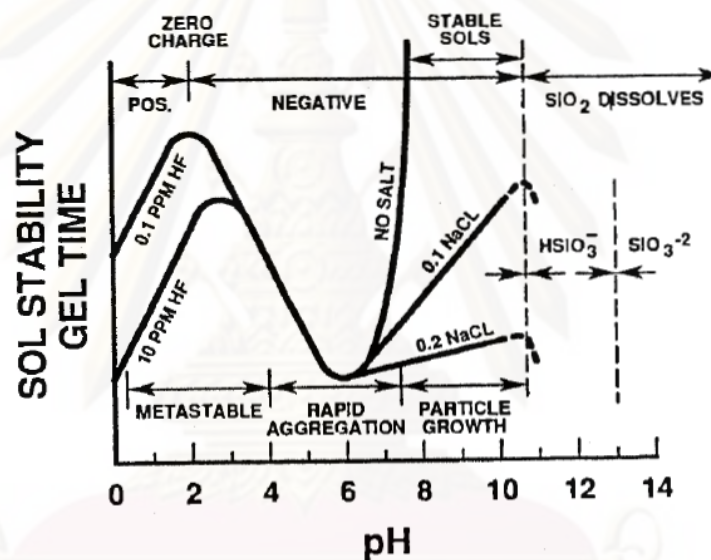
Figure 2.6 Effect of pH in the colloidal Silica- water system [30]

        d) Types of Solvent: The polarity, dipolar moment, viscosity, and protolytic/non protolytic properties are important for the reactions taking place. Polar solvents stabilize polar gels by hydrogen bonding. Non-polar solvents are better for systems which are not completely hydrolyzed. Solvents may be either protic or aprotic and may vary in their proarity. Depending of the pH, either protonated or deprotonated silanol are involved in the condensation mechanism. Because in protic solvents, hydrogen bond of nuclepphilic deprotonated silanols group and aprotic solvents retard base-catalyzed condensation and promote acid catalyzed condensation. Aprotic solvents have the reverse effect.

2.9 Literature Survey

Graft Copolymerization of MMA onto NR

Merkel *et al*. [3] studied on the process parameters and their effect on grafting reactions in core/shell latexes. The grafting of methyl methacrylate (MMA) onto polybutadiene (PB) was carried out at 50°C. Grafting MMA onto PB increased with increasing specific surface area of the seed latex while the molecular weight of the acetone-soluble graft copolymer decreased. Increasing the ratio of polymer and methyl methacylate monomer decreased the proportion of graft copolymer, supporting the theory that the periphery of the latex particle is the site of the grafting reaction. The influence of the initiator flux reflected the dependence of the concentration of free radicals on the grafting reaction and on the termination reaction.

Kochthongrasamee *et al*. [4] studied the effect of redox initiator on graft copolymerization of methyl methacrylate onto natural rubber. The effects of cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA), *tert*-butyl hydroperoxide (TBHPO)/TEPA, and potassium persulfate ($K_2S_2O_8$)/sodium thiosulfate ($Na_2S_2O_3$) redox initiator on grafting properties were investigated. CHPO dissolved very well in the oil phase and TBHPO dissolved moderately in oil phase, and $K_2S_2O_8$) / ($Na_2S_2O_3$) initiation was water-soluble. Each could interact with TEPA in the aqueous phase. The grafted poly(methyl methacrylate) stayed on the surface of rubber particles. CHPO/TEPA was found to give a higher grafting efficiency. Percentages of grafting of MMA on NR latex initiated by CHPO/TEPA was 84.4 %. CHPO/TEPA was thus a better redox system for grafting of MMA monomer on natural rubber latex.

Oommen and Thomas [31] studied the interfacial activity of natural rubber-g-poly (methyl methacrylate) in incompatible natural rubber/poly(methyl methacrylate) blends. The blend of natural rubber and poly(methyl methacrylate) (NR/PMMA) has been made compatible by the addition of grafted natural rubber (NR-g-PMMA). NR-g-PMMA was prepared by using a redox initiator consisting of cumene peroxide (CHPO) and tetraethylene pentamine (TEPA). The reaction was performed at room

temperature for about 24 hr. NR and PMMA (60/40) were blended in toluene. Addition of copolymer led to reduce the size of dispersed PMMA. The mechanical properties of blends are improved by the addition of grafted natural rubber.

Nakason *et al.* [33] studied on rheological, thermal and curing properties of natural rubber-*g*-poly(methyl methacrylate). The graft copolymers of NR and PMMA with the bipolar redox iniator system used various percentages of molar ratio of NR/MMA. It was found that the mooney viscosity, shear stress and shear viscosity of the NR-g-PMMA increased with an increase in the molar ratio of NR/MMA used in the graft copolymerization. The tensile strength of the NR-g-PMMA gum vulcanizate increased with an increase in molar ratios of NR/MMA whereas the elongation at break decresed. The tensile strength of grafted rubber the molar ratio of NR/MMA at 60/40 was 20 MPa.

In situ Silica Reinforced Rubber by Sol-gel Process

Kohjiya and Ikeda [6] studied the reinforcement of natural rubber by silica generated in situ. 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 was expected to be an industrially practical technique. It was 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 seemed to be weaker than that of silica-rubber to result in better dispersion compared with the conventional silica. The results suggested that NR which was a renewable resource and in situ silica composite had much potential as a "green" material and a useful system for studying the reinforcement mechanism of inorganic filler onto NR.

Yoshikai *et al.* [8] studied on the silica reinforcement of synthetic diene rubbers by sol–gel process in the latex. Styrene-butadiene rubber (SBR) and nitrile rubber (NBR) were reinforced with silica by sol-gel process of TEOS in the latex. It was found that the amount of TEOS added and molar ratio of TEOS to water

([H2O]/[TEOS]) in the mixture were related the silica content in the compounds, particle size, and reinforcing behavior of silica. The diameter of dispersed silica particle in cured rubbers was controlled by the amount of TEOS and [H_2O]/[TEOS], which were smaller than 100 nm. The tensile strength of SBR was over 30 MPa, and of NBR, over 25 MPa.

Ikeda *et al*. [9] studied the effect of catalyst on in situ silica reinforcement of styrene–butadiene rubber (SBR) vulcanizate by the sol–gel reaction of TEOS and n-butylamine was used as the catalyst. SBR was vulcanized with sulfur and soaked in TEOS and in an aqueous solution of the catalyst. When hydrochloric acid was used as a catalyst for the sol–gel reaction, silica particles were not introduced into the SBR matrix. The silica particles formed in the SBR vulcanizate were dispersed homogeneously in the matrix. The increase of the dynamic modulus and tensile strength at break was considered to be due to the interaction between the rubber and the in situ silica filler in the SBR vulcanizate.

Hashim *et al*. [10] studied on the silica reinforcement of epoxidized natural rubber by sol-gel method. The epoxidized natural rubber (ENR) was reinforced by sol-gel process of TEOS. The rubber was first procured with 3-aminoprolytriethoxysilane (APS). The sheet of rubber vulcanizate was swollen in TEOS and n-butylamine aqeous solution as catalyst. Hydrolysis and condensation of the TEOS resulted in the formation of silica particle in the rubber network yielding silica-contained vulcanizates. Silica content as high as 28% and TEOS-to-silica conversion of over 60% were observed. The sol-gel technique could be employed to prepare high-modulus vulcanizates with tensile strength comparable to or better than the one prepared by the conventional method.

Bandyopadhyay *et al.* [11] studied the effect of reactants on the structure and the properties of epoxidised natural rubber (ENR)/silica hybrid nanocomposites. The sol-gel reaction was conducted at a constant concentration of tetraethoxysilane (45 wt% with respect to the rubber), used as the precursor for silica under a constant pH of 1.5. Infrared spectroscopic studies and the ash content data indicated the maximum

silica generation in tetrahydrofuran compared to chloroform and carbon tetrachloride, which are less polar and had low affinity towards water than the former. The silica particles prepared from tetrahydrofuran were scattered within the rubber matrix with an average dimension of 100 nm, as evident from the transmission electron microscopic study. The nanocomposite prepared with 1:2 tetraethoxysilane to water mole ratio in tetrahydrofuran under room temperature showed the highest tensile strength and 100% tensile modulus, probably due to better polymer-filler interaction, in the uncrosslinked state and after crosslinking.

Ikeda and Kohjiya [12] studied on the *in situ* formed silica particles in rubber vulcanizate by the sol-gel method. Butadiene rubber (BR) was sulfur cured and the vulcanizate was soaked in TEOS at 30°C for 48 h. The swollen vulcanizates were kept in an aqueous solution of n-butyamine 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 *in situ* formed silica was dispersed homogeneously in the rubber matrix by transmission electron microscopic observation.. 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.

Ikeda *et al*. [13] studied on the nano-structural observation of in situ silica in natural rubber matrix by three dimensional transmission electron microscopy. The dispersion of particulate nano-fillers has been assumed to be one of the most important determining factors of physical properties of the composites. The three dimensional (3D) observation of nano-structure of particulate silica in natural rubber (NR) was reported by using a 3D transmission electron microscope (3D-TEM), which was a TEM combined with electron tomography to reconstruct 3D structural images. Here, in situ silica generated in NR matrix and a conventional silica (VN-3) mechanically mixed into NR were, without any staining of the samples, subjected to elucidation of their structural characteristics such as particle size, volume fraction and aspect ratio in NR matrix at nanometer scale. 3D-TEM/electron tomography enabled

to evaluate the density of in situ silica in NR matrix. The same samples were also subjected to atomic force microscopy (AFM) measurements to suggest a difference in the nano-filler/rubber interface area between the two samples. Since the dispersion of nano-filler in the amorphous matrix significantly controled the properties of nano-composites, 3D-TEM/electron tomography together with AFM was expected to play a most important role in revealing nanometer level 3D structure of soft materials.

Poompradub *et al.* [14] studied on the natural rubber/in situ silica nanocomposite of a high silica content. By using n-hexylamine as a catalyst of sol-gel reaction of TEOS in uncured natural rubber matrix, spherical silica particles of ca. 46 nm were homogeneously generated in situ at a high content, i.e., 71 phr. The mechanical properties of this soft nanocomposite were very unique comparing with those of conventional silica filled one. Especially, hysteresis loss and permanent set of the former were much lower than those of the latter.

Ikeda *et al.* [15] studied the effect of reaction conditions on *in situ* silica generation of high content in natural rubber and n-hexylamine was used as the catalyst. The mechanical properties of conventional silica composites were studied comparing with the *in situ* silica composites. The dispersion of the silica in the rubbery matrix was more homogeneous than that of commercial silica dispersed by a conventional mechanical mixing. The uses of *n*-hexylamine as the catalyst in sol-gel reaction generated high *in situ* silica content of 80 phr.

Tangpasuthadol *et al.* [32] studied on the silica-reinforced natural rubber prepared by the sol–gel process of ethoxysilanes in rubber latex. The NR composite was prepared by as precursor to generate silica particles inside the rubber. The results showed that the conversion of TEOS to silica were ranging from 90% to 97%, the silica particles size was between 100 and 500 nm in diameter, determined by SEM. The 0.7% ammonia content present in the commercial-grade concentrated latex was sufficient for the conversion reaction of TEOS to silica. A composite having silica as high as 19% was prepared. It was also found that the composite containing *in situ*

silica had a shorter cure time and higher tensile modulus than the composite prepared by conventional mixing with silica powder.

Chaichua *et al.* [34] studied on the *in situ* silica reinforcement of natural rubber by sol–gel process via rubber solution. The effect of the in situ silica content on the curing, mechanical, dynamic mechanical and thermal properties of the composite vulcanizate materials was investigated in comparison to that with a commercial silica preparation. It was found that the Mooney viscosity of the in situ silica filled NR vulcanizates showed a lower value compared with that of the commercial filled ones. The mechanical properties of the in situ silica composite materials, i.e., the moduli and compression set, were improved compared with the commercial silica filler NR vulcanizates.

CHAPTER III

EXPERIMENTALS

3.1 Chemicals

1. High ammonia NR latex (solids content of 60%)   : Thai Rubber Latex Corp.
   Co., LTD.

3. Methyl methacrylate (A.R grade)   : Merck

3. Sodiumdodecyl sulfate (A.R grade)   : Ajax Finchem

4. Potassium hydroxide (A.R grade)   : Ajax Finchem

5. Oleic acid (A.R grade)   : Panreac

6. Cumene hydroperoxide (A.R grade)   : Merck

7. Tetraethylene pentamine (A.R grade)   : Merck

8. Sodium hydroxide (A.R grade)   : Ajax Finchem

9. n-hexylamine (A.R grade)   : Sigma - Aldrich

10. Tetraethoxysilane (A.R grade)   : Fluka

11. Light petroleum ether (AR grade)   : Lab scan Analytical
    Sciences

12. Acetone (AR grade)   : Merck

13. Active zinc oxide (Commercial grade)   : Pan Innovation Ltd.

14. Stearic acid (Commercial grade)   : Imperial Industrial
    Chemicals Co. Ltd.

15. Polyethylene glycols (Commercial grade)   : Pan Innovation Ltd.

16. Mercaptobenzothiazole disulfide   : Pan Innovation Ltd.
    (Commercial grade)

17. Silica (Hisil-255)   : PPG-Siam Silica Co., Ltd.

3.2 Equipments

1. 4-Necked round bottom reactor, 500 cm^3 capacity
2. Condenser
3. Nitrogen tube
4. Soxhlet extraction apparatus
5. Other general laboratory glassware
6. Fourier-Transform Infrared Spectrometer : Thermo 470 FT-IR
                      Spectroscopy
7. Nuclear Magnetic Resonance Spectrometer : Bruker ACF
                      400 MHz
8. Universal testing machine : LLOYD Instrument LR
                      10K
9. Tear testing machine : Hounsfield H10KS
10. Hardness : Rockwell Hardness Tester
                      4150 AR
11. Abrasion Tester : DIN 53516 (ZWICK)
12. Transmission Electron Microscopy : JEOL JEM-2010
13. Scanning Magnetic Resonance Microscopy : JEOL model JSM-6400

3.3 Procedure

3.3.1 Purification of Methyl Methacrylate Monomer

The methyl methacrylate monomer contained a trace amount of hydroquinone as inhibitor. The inhibitor was removed by washing with 10% NaOH solution. Then, methyl methacrylate was washed with distilled water until neutral, dried with anhydrous Na_2SO_4, and passed through an activated aluminum oxide column to remove the residual inhibitor. The purified methyl methacrylate was stored in the refrigerator [35].

3.3.2 Preparation of Grafted Natural Rubber

The natural rubber latex (50 g, 60% DRC) was charged to a round-bottom reactor (Figure 3.1) along with 100 mL of deionized water. Potassium hydroxide solution at 1 wt % based on dry rubber content (phr) was added as a buffer, and sodium dodecylsulfate (1 phr) as an emulsifier was then added while stirring. The mixture was deoxygenated by passing through the nitrogen gas bubbles for approximately 15 min at room temperature. The stabilizer, oleic acid (10 phr), was added after 15 min of stirring. The MMA monomer was then added continuously while stirring for 30 min to allow the latex particles to swell. The mixture was heated up to 50°C and the initiator (CHPO) was then added. After 15 min of mixing, the amine activator (10 wt % aqueous solution of TEPA) was added. The bipolar redox initiating system was employed at a CHPO:TEPA ratio of 1:1 (based on 1 phr). The reaction was then allowed to proceed for 8 h under continuous stirring to complete the polymerization. The final graft natural rubber was coagulated by using ethanol. The experimental procedure is summarized in Figure 3.2. The standard recipe used for graft copolymerization is shown in Table 3.1.

Table 3.1 Recipe for the preparation of MMA-g-NR

Materials	Quantities (g)
Natural rubber (60% DRC)	50
Water	100
Stabilizer (oleic acid)	3
Buffer (potassium hydroxide)	0.3
Surfactant (sodium dodecyl sulfate)	0.3
Redox initiator (CHPO : TEPA = 1:1)	0.15
Methyl methacrylate monomer	30
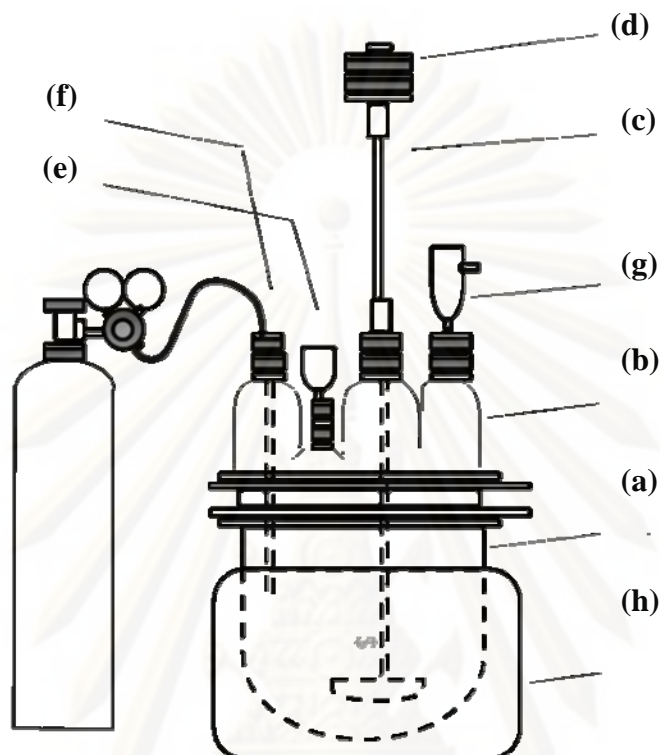
Figure 3.1 Apparatus for emulsion graft polymerization of methyl methacrylate onto
natural rubber latex

(a) reaction kettle bottom   (e) condenser

(b) reaction kettle top   (f) nitrogen-inlet tube

(c) stainless steel stirrer   (g) sampling tube

(d) motor   (h) water bath

3.3.3 Sol-gel Reaction of MMA-g-NR Using Solid Rubber Method

The solid MMA-g-NR was prepared into thin sheets of ca. 1 mm thickness on a two-roll mill and the sheets were immersed in TEOS at 40 °C for 1 h and then room temperature for 24 h in a container. After that, the swollen sheets were immersed in aqueous solution of n-hexylamine as catalyst. The catalyst solution varied at 0.008 M and 0.064 M for 1-5 days. Finally, the rubber sheets were dried under vacuum at 40°C. The preparation procedure is shown in Figure 3.2.

3.3.4 Sol-gel Reaction of MMA-g-NR Using Latex Solution Method

The MMA-g-NR was reinforced with silica by sol-gel process of TEOS in latex. The MMA-g-NR latex was prepared by graft copolymerization (section 3.3.2) and then TEOS was added in the grafted rubber latex at $50^{O}C$-$60^{o}C$ for 1-7 days. The effects of parameters such as the sequential addition of TEOS, reaction temperature, time and TEOS content were investigated. The preparation procedure is shown in Figure 3.2.

NR Latex + Water

→ Stir at RT for 10 min

KOH

→ Slowly drop and stir at RT

Sodiumdodecyl sulfate

→ Slowly drop and stir at RT

Oleic acid

→ Slowly drop and stir
under N_2 atmosphere for 30 min

MMA monomer, CHPO

→ Stir and increase temperature
to 50°C for 30 min

TEPA

→ Reaction time = 8 hr

MMA-g-NR Latex

Coagulate by ethanol

MMA-g-NR solid   MMA-g-NR latex

2-Roll Mill

MMA-g-NR sheet   Add TEOS (10-70 phr)

→ Slowly drop
and stir at 50°C

Immerse in TEOS   in situ silica MMA-g-NR
at 40°C and 30°C   (Latex solution method)

Immerse in n-hexylamine solution

in situ silica MMA-g-NR
(Rubber solid method)

Figure 3.2 Preparation of in situ silica MMA-g-NR by using solid rubber and

latex solution method

3.4 Determination of Conversion and Grafting Properties

a) Conversion of Graft Copolymerization

The conversion of graft copolymerization was determined by the percentage increase of rubber weight. The conversion was calculated by the following equation.

$$\text{Conversion (\%)} = \frac{\text{Total weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \qquad (3.1)$$

b) Percentage Grafted Natural Rubber and Grafting Efficiency

The amount of grafted natural rubber, free natural rubber and free homopolymer in the product could be determined by soxhlet extraction. The free natural rubber was extracted by light petroleum ether (60-80°C) for 24 h. The residue was dried to constant weight in an oven at 40°C under vacuum for 24 h. To remove free homopolymer, the residue was extracted in a acetone just as described when petroleum ether was used. The weight difference between the initial sample and extracted samples is the measurement of free natural rubber, free homopolymers, grafted natural rubber, and grafting efficiency. All calculations were made by the following equations.

$$\text{Free Natural Rubber (\%)} = \frac{\text{Total weight of free natural rubber}}{\text{Total weight of the gross polymer}} \times 100 \qquad (3.2)$$

$$\text{Free Homopolymer (\%)} = \frac{\text{Total weight of free homopolymer}}{\text{Total weight of the gross polymer}} \times 100 \qquad (3.3)$$

$$\text{Grafted Natural Rubber (\%)} = \frac{\text{Total weight of graft copolymer}}{\text{Total weight of the gross polymer}} \times 100 \qquad (3.4)$$

$$\text{Grafting Efficiency (\%)} = \frac{\text{Total weight of monomers grafted}}{\text{Total weight of the monomers polymerized}} \times 100 \qquad (3.5)$$

3.5 Characterization of Grafted Natural Rubber Product

After the soxhlet extraction, the grafted natural rubber (MMA-g-NR) was characterized by fourier-transform infrared spectroscopy (FT-IR) and Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR).

The grafted NR was dissolved in chloroform and casted on a KBr cell. FTIR spectrum of the grafted NR was determined in range of 400-4000 cm^{-1} with 32 scans at resolution of 4 cm^{-1}.

The grafted NR was dissolved in D-chloroform. NMR spectra were taken by a Varain NMR spectrometer operating at a proton resonance frequency of 400 MHz.

3.6 Determination of *In situ* Silica Content in MMA-g-NR.

Thermogravimetric analysis was performed on TG/DTA Perkin–Elmer to determine in situ silica generated in MMA-g-NR. MMA-g-NR sample (ca.10 mg) was placed in a platinum pan and heated under air at room temperature up to 1000°C using the heating rate of 10°C/min. Silica content and the conversion of TEOS to silica were calculated by using equation 1 and 2, respectively [11].

$$\text{Silica content (phr)} = 100 \text{ x } (W_1/W_2) \tag{3.6}$$

where W_1 is the weight of remaining ash, W_2 is the composite weight.

$$\text{Conversion (\%)} = 100 \text{ x } (W_3/W_4) \tag{3.7}$$

where W_3 is the amount of in situ generated silica in the sample, obtained from eq. (1) and W_4 is the theoretical amount of silica being generated assuming quantitative conversion of TEOS to silica by

$$Si(OC_2H_5)_4 + 2H_2O \rightleftharpoons SiO_2 + 4C_2H_5OH \tag{3.8}$$
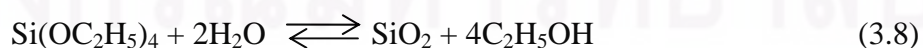
3.7 Preparation of Natural Rubber /Grafted Natural Rubber Blends

The rubber compound was prepared by using a two-roll mill. The NR was fed to the two-roll mill and then blended with grafted natural rubber until the surface of blend was smooth. The compositions of grafted natural rubber/NR blends are presented in Tables 3.2. Then additives (Table 3.2) such as zinc oxide, stearic acid, mercaptobenzothiazole disulfide and sulfur were added. The cure time of the sheet was determined by using rheometer. The rubber compound sheets were then pressed in a preheated mold of compression molding at $150^{o}C$ and pressure of 150 kg/cm^2 for a prescribed time.

Table 3.2 Formulations for rubber compounding in parts by weight per hundred parts of rubber

Ingredients	NR	NR/GNR	NR/GNR-Si9C	NR/GNR-Si9L	NR/GNR-Si9S	NR/GNR-Si20S
NR	100	50	50	50	50	50
MMA-g-NR	-	50	50	-	-	-
In situ filled MMA-g-NR	-	-	-	59 (Si 18 phr)	59 (Si 18 phr)	70 (Si 40 phr)
Silica[a]	-	-	9	-	-	-
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
MBTS[b]	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	3	3	3	3	3	3
PEG[b]	-	-	0.4	0.4	0.4	0.8

[a]Commercial silica

[b]Mercabtobenzothiazole disulfide

3.8 Morphological Study

The dispersion and particle size of the filler in NR vulcanizates were studied by using Transmission Electron Microscopy (TEM). Ultra thin films of the vulcanized rubber sample were prepared using a microtome (Boeckeler Instrument, Inc.) in liquid nitrogen. The rubber thin films were placed on a copper grid, which was coated by carbon. The observation was then carried out on a transmission electron microscopy (JEOL JEM-2010 instrument, Hitachi Co. Ltd.). The accelerating voltage was 200 kV.

The scanning electron microscopy (SEM) was used to investigate the fracture surface of the NR grafted natural rubber blend from the tensile properties test. Samples were mounted on a SEM stub using a double-side tape and the fracture specimens were coated with gold. The scanning electron microscopy (JEOL model JSM-6400) was operated at 15 kV.

3.9 The Swelling Study

The vulcanized rubber sample was cut to 20 x 20 x 2 mm sized pieces and weighed prior to swelling in toluene until it reached equilibrium (within 72 h.) at room temperature. The percentage of swelling was calculated using the following equation,

$$\% \text{ Swelling } \frac{m_1 - m_0}{m_0} \times 100 \tag{1}$$

Where m_0 is the mass of specimen before immersion (g)

m_1 is the mass of specimen before immersion (g)

3.10 Mechanical Testing

a) Tensile Testing

Tensile properties of the samples were measured at 25°C and humidity of 60% according to ASTM D412. The specimens were cut from a 2.0 mm thick sheet into dumbbell-shaped test pieces (Type IV) as illustrated in Figure 3.3. The testing was performed on a Universal testing machine (LLOYD LR 10K) with a crosshead speed of 500 mm/min. and a load cell of 5 kN. Values reported for each sample were based on an average of six measurements [36].
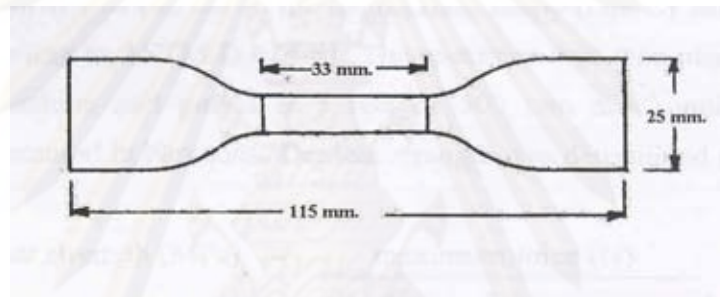
Figure 3.3 Dumbbell shaped test piece for tensile testing

b) Tear Strength

The tear properties were measured by using a Hounsfield H10KS testing machine according to ASTM D624-02. The specimens were cut using die C (Figure 3.4) and the thickness of each specimen at the notch was measured using a micrometer. The gauge length was 70 mm and the crosshead speed was 500 mm/min. The values reported for each sample were averaged from three specimens.
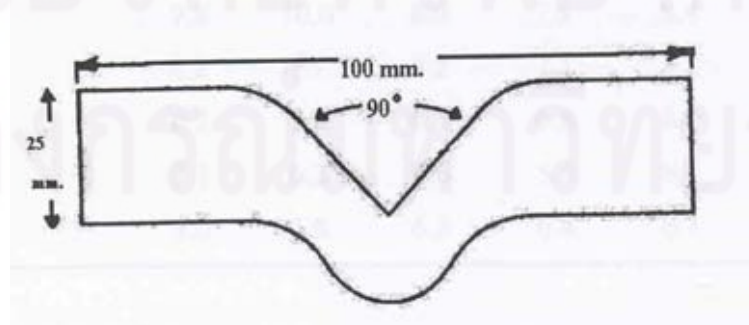
Figure 3.4 Tear testing specimen (ASTM D624 Die C)

c) Hardness

The hardness of the samples were measured according to ASTM D2240 using a Shore- type-A Lever Loader (REX GAUGE 2000 & OS-2 Stand). The test specimen was at least 3 mm in thickness. The specimen was placed on a hard and horizontal surface. The presser was held on a vertical position with the point of the indentor 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. One measurement was made at five different points distributed over the specimen and the median of these measurements was used as the hardness value.

d) Abrasion Resistance [ISO 4649]

Abrasion resistance of the samples were measured by using Happen Abrasion according to DIN 53516 (ZWICK) at room temperature. The cylindrical shape of samples used was 16 mm in diameter and had a minimum thickness of 6 mm. Abrasion tests use an abradant to be applied to the surface of a rubber sample. Tested compounds are usually compared with a "volume loss" basis which is calculated from the weight loss and density of the compound. The rubber test piece with a holder traverses a rotating cyclinder covered with the specified abradant paper. By allowing the sample holder to move the test piece across the drum as it rotates, there is less chance of rubber buildup on the abradant paper [37].

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Graft Copolymerization of MMA onto NR latex

The graft copolymer of methyl methacrylate onto natural rubber was prepared by emulsion polymerization with redox system of cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) as initiator at 50°C for 8 h. The grafting efficiency was determined by analyzing the amount of graft copolymer and homopolymer formed during the graft copolymerization. The percentages of monomer conversion, graft copolymer, free homopolymer and grafting efficiency (GE) are presented in Table 4.1. The graft copolymer product was extracted by petroleum ether and acetone. The weight difference between the initial sample and extracted sample was used to calculate the percentage of free NR, free homopolymer, graft NR and grafting efficiency.

Table 4.1 Grafting properties of MMA-g- NR

Grafting Properties	MMA-g-NR
Grafting Efficiency	39.2
Free NR	19.6
Free Homopolymer	28.7
Grafted NR	51.7

FT-IR spectra of NR and MMA-g-NR samples are shown in Figure 4.1. For NR, the characteristic transmission peaks were found at 2958, 1442, 1371 and 837 cm^{-1} corresponding to the stretching vibration of aliphatic =C-H, C-H bending of CH$_2$, C-H bending of CH$_3$ and C=C bending vibration, respectively. For grafted NR, the peaks at 837 and 1216 cm^{-1} correspond to C=C and C–C stretching, respectively and the peak at 1371 cm^{-1} corresponds to C–H stretching of natural rubber structure. The evidence of MMA in the graft copolymer was observed at 1728 cm^{-1} for C=O stretching and 1142 cm^{-1} for –C-O- of the ester functional groups of MMA.
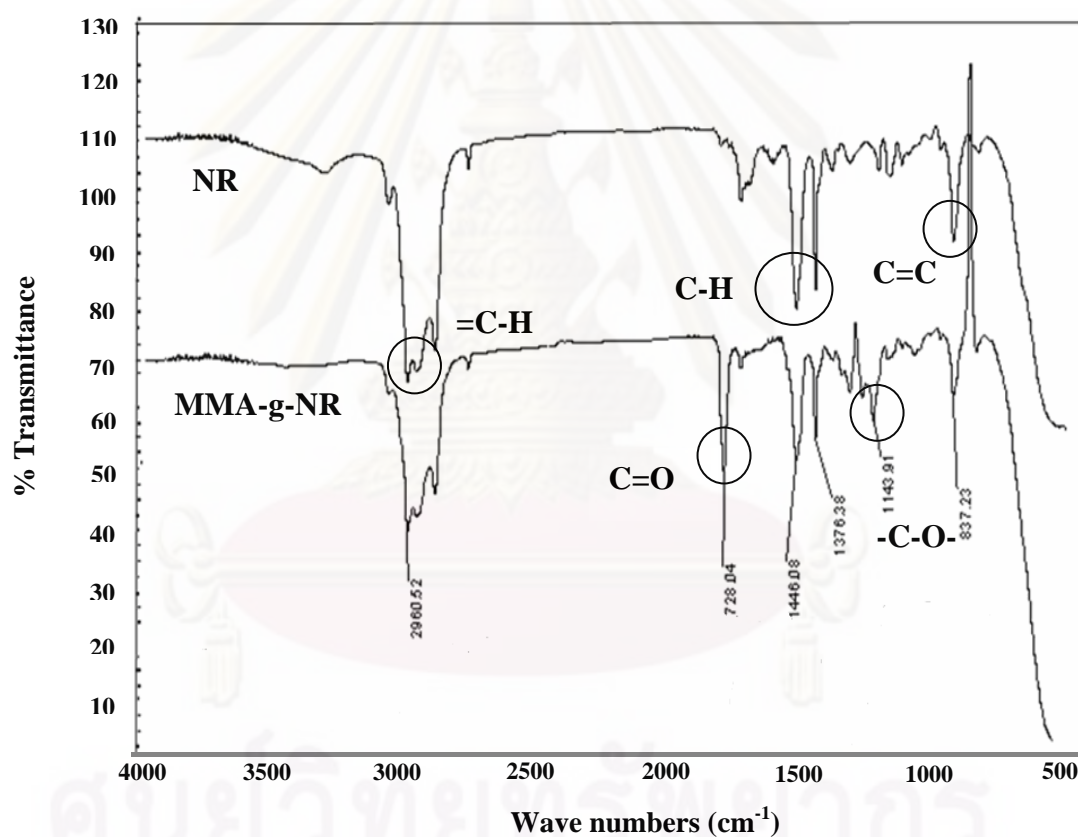
Figure 4.1 FTIR spectra of MMA-g-NR

^{1}H NMR spectrum of MMA-g-NR is shown in Figure 4.2. The grafted NR was dissolved in D-chloroform. The peaks at 1.67, 2.01 and 5.12 ppm correspond to the natural rubber structure. The signal at 3.69 ppm corresponds to the methoxy group of methyl methacrylate. These results from FTIR and ^{1}H NMR indicate that methyl methacrylate was grafted onto natural rubber.
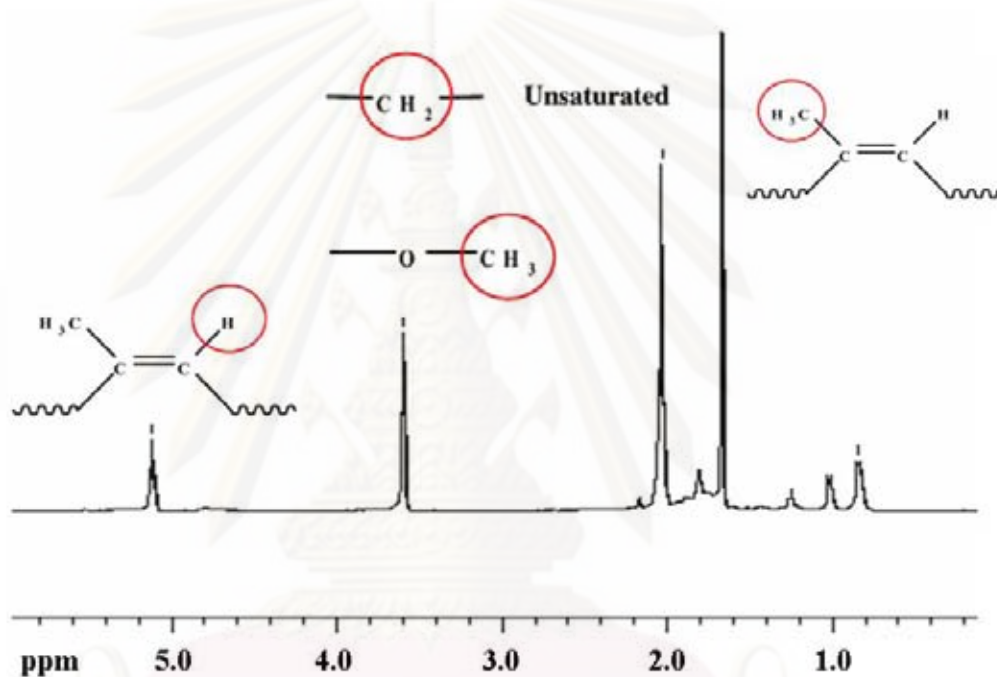
Figure 4.2 ^{1}H NMR spectrum of MMA-g-NR

4.2 Sol-gel Reaction of Grafted Rubber Using Solid Rubber Method

The graft copolymer was modified by TEOS using solid rubber method. In order to find the suitable condition of sol – gel reaction and to obtain the amount of in situ silica generated, MMA-g-NR sheets prepared by using a two-roll mill were immersed in TEOS at 40 °C for 1 h and then room temperature for 24 h in a container. After that, the swollen sheets were immersed in aqueous solution of n-hexylamine. The silica content in grafted rubber was determined by Thermogravimetric Analysis (TGA). The effects of catalyst concentration and temperature on amount of in situ silica were investigated.

4.2.1 Swelling Degree of Grafted Rubber

The swelling times used for immersing the grafted rubber in TEOS at 40°C and room temperature were varied to determine the suitable swelling degree. The MMA-g-NR sheets of 1.5 mm x 1.5 mm x 1 mm were prepared. The rubber sheets were immersed in TEOS at various times in range of 1 – 24 h at 40°C and room temperature (30°C). Table 4.2 presents the optimum time to achieve maximum degree of swelling of grafted rubber in TEOS at 40°C and room temperature. Figure 4.3 also shows the effect of temperature and immersing time on swelling degree of grafted rubber in TEOS.

For immersion at 40°C, the swelling degree of MMA-g-NR was sharply increased to 120% swelling degree in the first hour. The significant change of swelling degree of graft copolymer in TEOS at 40°C with time during 1-24 h was not observed due to the limiting diffusion and the final swelling degree of MMA-g-NR was about 139% at 24 h.

From Figure 4.3, for swelling at 30°C, the swelling degree of MMA-g-NR was gradually increased with increasing immersing time and nearly constant after 24 h due to the swelling saturation, the optimum condition for immersion of MMA-g-NR in TEOS with 150% swelling degree was at 30°C and 24 h.

Thus, in order to keep the short time for the sol – gel process, the optimum condition for immersion of graft copolymer in TEOS with 180% swelling degree was at 40°C for 1 h and 30°C for 24 h.

Table 4.2 Swelling degree (%) of MMA-g-NR in TEOS

Time (h)	Degree of swelling (%)	
	40°C	30°C
1	123	61
2	123	68
4	124	82
8	125	99
12	126	122
16	129	137
20	131	146
24	139	149
28	-	151
32		152
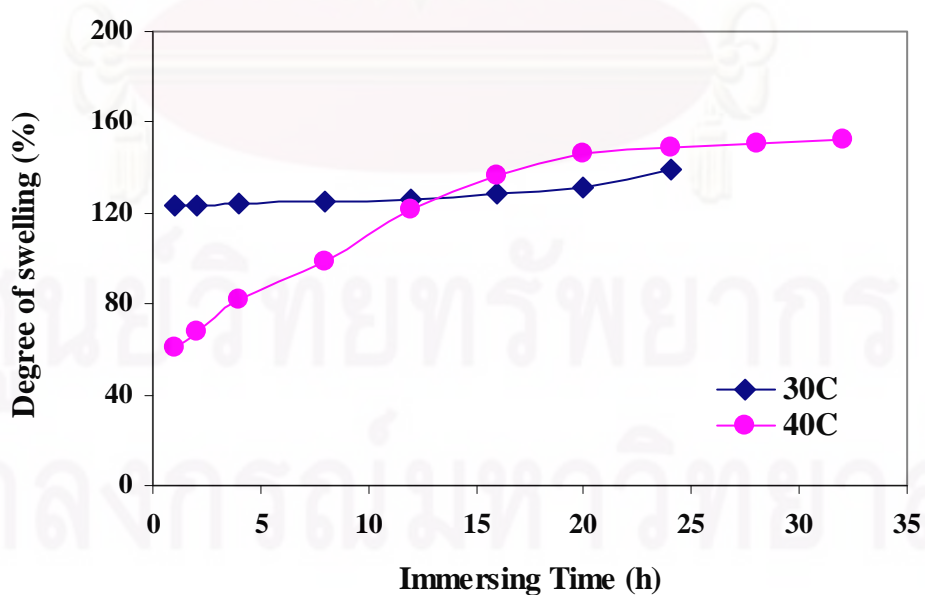
Figure 4.3 Swelling degree of MMA-g-NR in TEOS at 40^{0}C and 30^{0}C

4.2.2 Effect of Catalyst Concentration

From the result of swelling of grafted rubber in TEOS, the optimum condition of 40°C for 1 h and then at 30°C for 24 h was chosen, and the swelling degree of MMA-g-NR was 180%. The swollen MMA-g-NR sheet was immersed in aqueous solution of n-hexylamine as catalyst at 50°C and the concentration of n-hexylamine was varied from 0.008 M to 0.064 M. Table 4.3 and Figure 4.4 show the effect of catalyst concentration on the amount of *in situ* generated silica in MMA-g-NR. For reaction time of 5 days, the *in situ* silica content in the rubber matrix and % conversion increased with increasing the catalyst concentration. The catalyst (n-hexylamine), the amino group catalyzed to promote the sol–gel reaction of TEOS to generate in situ silica particles. At 0.064 M n-hexylamine, the high amount of *in situ* silica in the rubber matrix was achieved as high as 48.7 phr and % conversion was about 94.8%. The primary alkylamines with long hydrocarbon segments are estimated to form reverse micelles like a surfactant in the TEOS-swollen NR matrix [38, 39] as shown in Figure 4.4 The similar result was earlier reported by Ikeda *et al.* [15] on the *in situ* silica generation in NR, that the *in situ* silica content increased with increasing catalyst concentration.
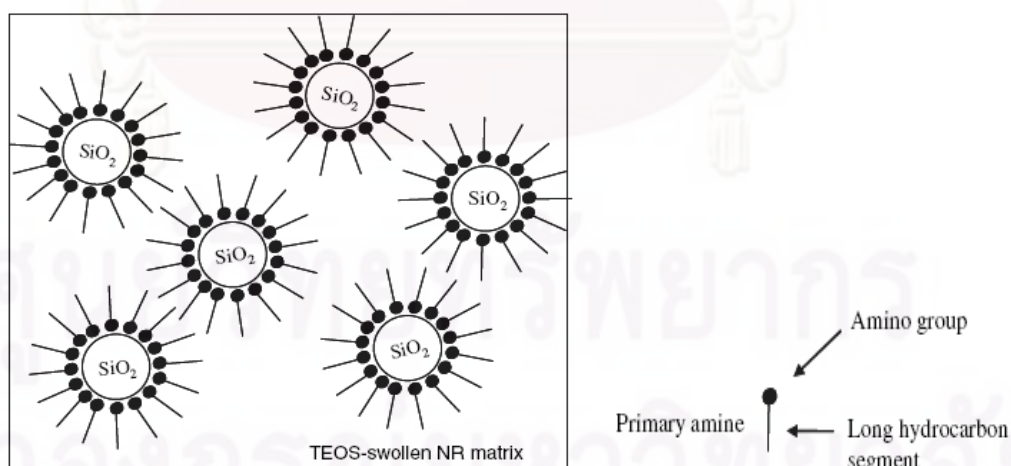
Figure 4.4 Speculated formation of *in situ* silica in TEOS-swollen NR matrix by

primary alkylamine with long hydrocarbon segment [15].

Table 4.3 Effect of catalyst concentration on sol-gel reaction by using solid rubber
method at 50°C

Catalyst concentration (mol/l)	Time (day)	Silica content (phr)	Conversion (%)
0.008	1	27.4	68.5
	2	31.1	75.3
	3	35.2	82.8
	4	34.3	81.6
	5	35.6	83.0
0.064	1	32.1	76.4
	2	34.7	82.3
	3	38.3	88.6
	4	37.7	86.7
	5	38.4	88.9
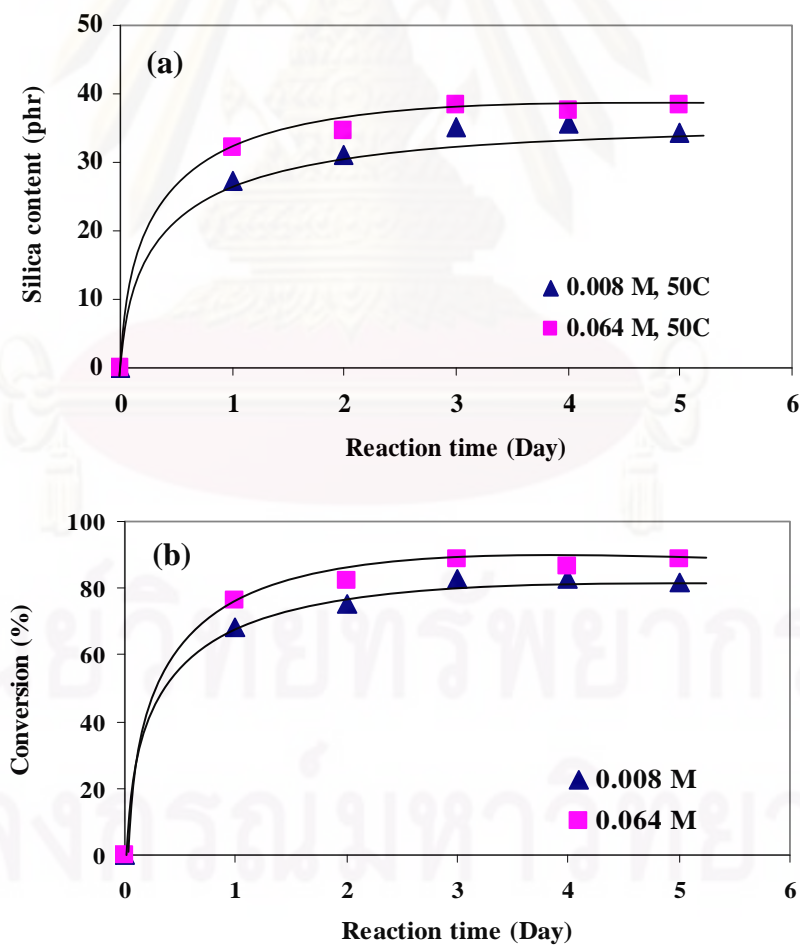
Figure 4.5 Effect of catalyst concentration on sol-gel reaction by using solid rubber
method at 50°C: (a) silica content and (b) conversion

4.2.3 Effect of Reaction Temperature and Time

The reaction temperature is the one of important parameters to generate *in situ* silica because the temperature controls the sol-gel reaction rate. The swollen MMA-g-NR sheet was immersed in aqueous solution of n-hexylamine as catalyst at reaction temperature of 50°C and 60°C. Table 4.4 and Figure 4.6 show the effect of temperature of sol-gel reaction on the amount of *in situ* silica in MMA-g-NR and % conversion at reaction time of 5 days. For reaction at 40°C and 50°C the *in situ* silica content was increased with increasing immersing time reached the maximum value at 3 days and remained constant above 3 days. For reaction at 60°C, the silica content increased with time reached the maximum value at 2 days and remained constant. This result indicated that the silica contents in matrix increased with increasing reaction temperature. According to Arrhenius Equation, the reaction proceeds at high rate at the higher temperature. The optimum condition was at 60°C and 5 days and the high silica content of 48 phr and conversion of 94% was achieved.

Table 4.4 Effect of reaction temperature and time on sol-gel reaction by using solid rubber method

Temperature (^{0}C)	Time (day)	Silica content (phr)	Conversion (%)
40	1	24.4	68.4
	2	29.8	75.7
	3	34.5	81.2
	4	33.2	83.0
	5	33.6	85.6
50	1	32.1	76.4
	2	34.7	82.3
	3	38.3	88.6
	4	37.7	87.7
	5	36.4	87.3
60	1	41.3	87.2
	2	46.4	92.7
	3	47.2	93.5
	4	47.2	93.5
	5	48.7	94.3

Condition: 0.064 M of n-hexylamine concentration

Figure 4.6 Effect of reaction temperature and time on sol-gel process by using solid
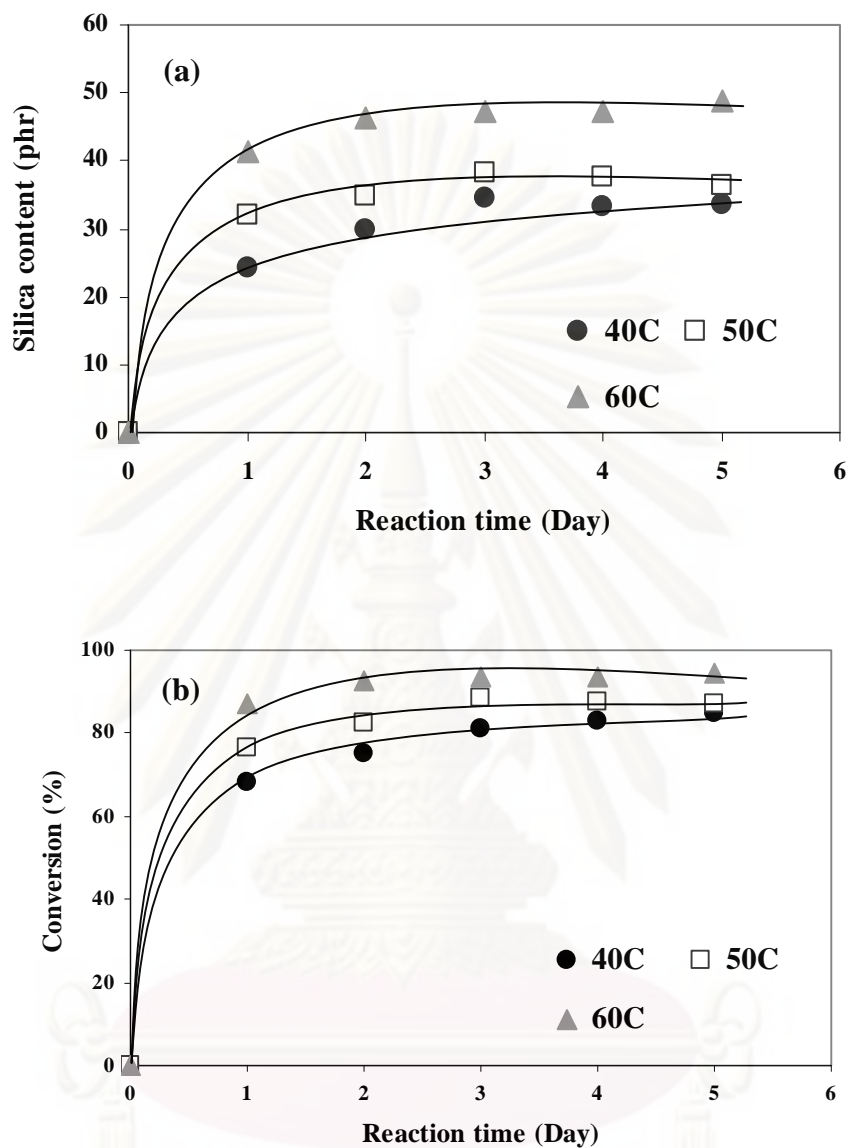rubber method at 0.064 M of n-hexylamine concentration: (a) silica
content and (b) conversion

4.3 Sol-Gel Reaction of Grafted Rubber Using Latex Solution Method

In this section, the in situ silica reinforced NR-g-MMA was prepared by sol-gel process via TEOS using latex solution method. The MMA-g-NR latex was prepared by graft copolymerization and then TEOS was added. The grafted rubber latex with TEOS was heated and stirred at various times (1 - 5 days). The effect of TEOS content, addition method of TEOS, reaction temperature and reaction time on amount of in situ silica were investigated**.**

4.3.1 TEOS Addition During Graft Copolymerization: Effect of Reaction Temperature and Time

In the section, the TEOS was added during graft copolymerization. Table 4.5 and Figure 4.7 show the effect of reaction temperature on the amount of *in situ* generated silica in MMA-g-NR and % conversion for adding TEOS amount of 10 and 20 phr. For 10 phr TEOS addition, the *in situ* silica content was the same for both temperature, 50°C and 60°C. For TEOS addition of 20 phr, the increasing reaction temperature gave slight effect on in situ generated silica content in MMA-g-NR. At

Table 4.5 Effect of reaction temperature and time on sol-gel reaction by using latex solution method

TEOS (phr)	Time (day)	Silica content (phr)		Conversion (%)	
		50^{0}C	60^{0}C	50^{0}C	60^{0}C
10	8 h	1.9	1.8	67.4	63.7
	1	2.0	2.0	70.1	70.5
	2	2.2	2.4	75.5	83.7
	3	2.3	2.5	80.7	86.4
	4	2.4	2.6	84.8	89.2
	5	2.5	2.6	88.2	90.2
20	8 h	4.0	4.1	70.1	71.8
	1	4.3	4.5	74.5	78.0
	2	4.4	4.9	76.3	85.5
	3	4.6	5.0	80.2	87.3
	4	4.8	C	83.7	C
	5	5.1	C	88.4	C

Condition: 0.064 M of n-hexylamine concentration

C = Coagulation

temperature of 50^0C and 60^0C, *in situ* silica content was increased with increasing reaction time and approached constant value after 3 days. However, latex was coagulated after 3 days when 20 phr TEOS was added at 60^oC.
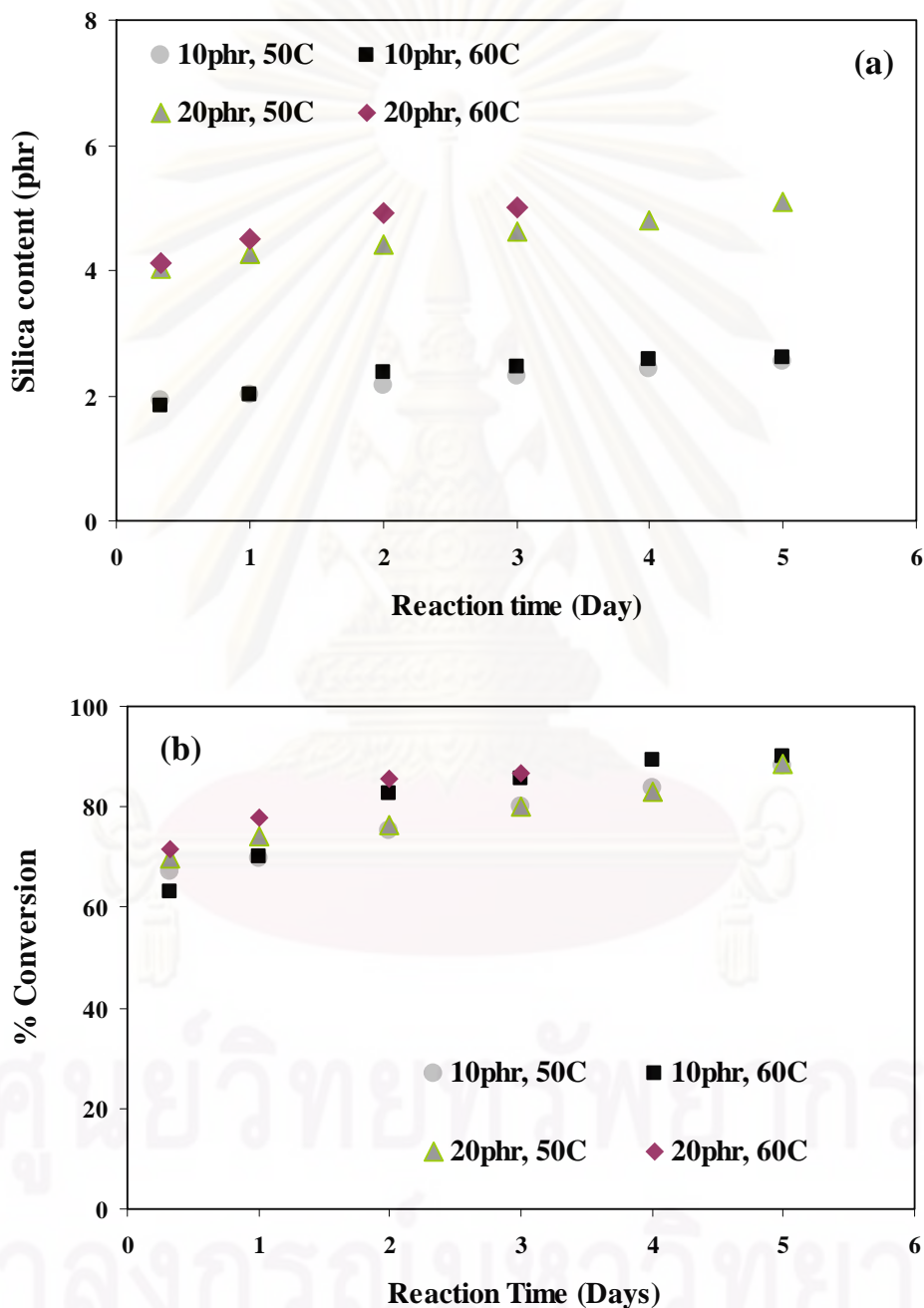

Figure 4.7 Effect of reaction temperature and time on sol-gel reaction by using latex solution method: (a) silica content and (b) conversion

4.3.2 TEOS Addition During and After Graft Copolymerization

Comparison of two addition methods of TEOS in sol-gel reaction was studied. Method A: TEOS was added during graft copolymerization reaction and Method B: TEOS was added after graft copolymerization. The percentages of grafted NR, free NR and free homopolymer of *in situ* of MMA-g-NR from both methods are presented in Figure 4.8. The percentages of graft NR from method A, TEOS addition during graft copolymerization (39.3%) was less than that from method B (51.9%), TEOS addition after graft copolymerization. However, the percentages of free NR and free homopolymer from method A were higher than that of method B. It is believed that the silica particles in MMA-g-NR latex could retarded or inhibited the grafting reaction between MMA monomer and NR chain. Additionally, the latex solution of method A was coagulated when TEOS was added more than 20 phr. For the method B, TEOS could be loaded up to 70 phr which was higher than method A.

Table 4.6 and Figure 4.9 show the amount of *in situ* silica content and % conversion in modified MMA-g-NR for TEOS addition (20 phr) during and after graft copolymerization at 50°C. It was found that the amount of *in situ* silica content was increased with increasing reaction time and approached constant value after 3 days. The addition method of TEOS did not affect the *in situ* content and % conversion. The optimum condition was at 50°C for TEOS addition (20 phr) after graft copolymerization and the maximum *in situ* silica content of 5.5 phr was achieved.
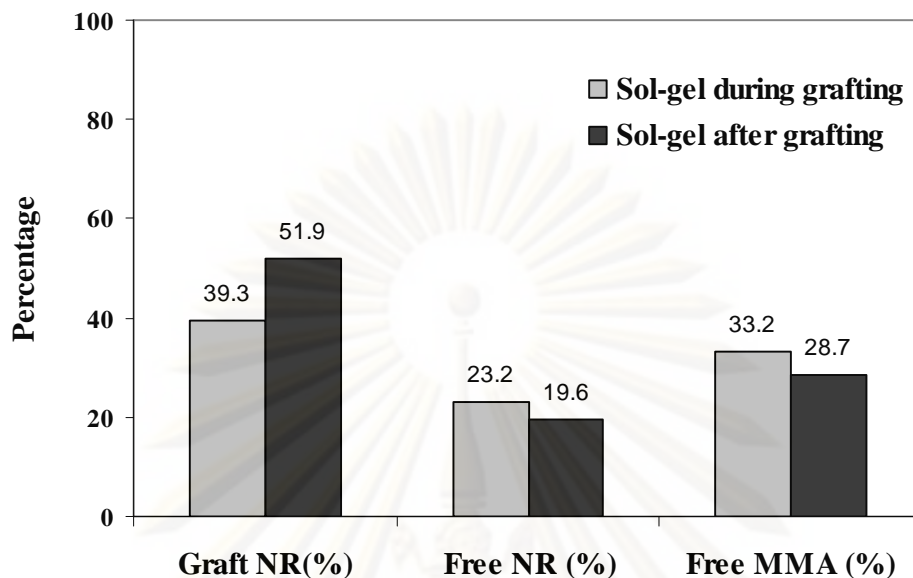
Figure 4.8 Effect of addition method of TEOS (20 phr) on grafting properties
of *in situ* silica filled MMA-g-NR

Table 4.6 Effect of addition method of TEOS (20 phr) on sol-gel reaction by using
latex solution method

Addition method of TEOS	Temperature (^{0}C)	Time (day)	Silica content (phr)	Conversion (%)
During graft copolymerization	50	1	4.3	74.5
		2	4.4	76.3
		3	4.6	80.2
		4	4.8	83.7
		5	5.1	88.4
During graft copolymerization	60	1	4.5	78.0
		2	4.9	85.5
		3	5.0	87.3
After graft copolymerization	50	1	2.2	37.1
		2	3.1	54.3
		3	3.6	63.4
		4	3.8	67.6
		5	5.3	91.9
		6	5.4	93.2
		7	5.5	93.2

Figure 4.9 Effect of addition method of TEOS (20 phr) on sol-gel reaction by using latex solution method: (a) silica content and (b) conversion

4.3.3 Effect of TEOS Content

The method of TEOS addition after graft copolymerization was applied for sol-gel reaction at 50°C for 7 days. Table 4.8 and Figure 4.10 show the effect of TEOS amount on the *in situ* generated silica content and %conversion. The amount of TEOS was varied from 10 phr to 70 phr. It was found that MMA-g-NR latex was coagulated when TEOS higher than 70 phr was added. However, the in situ silica content was increased with increasing TEOS amount (10 to 70 phr). TEOS could undergo hydrolysis and condensation to form silica and reached 90 % conversion. The optimum condition was at TEOS amout of 70 phr and temperature of 50°C and the maximum in situ silica content of 17.9 phr was achieved.

From Figure 4.10, the silica conversion was also increased with time and approached the 89-90 % for all TEOS concentration (10-70 phr). The high TEOS concentration gave higher rate of conversion than the low TEOS in the 1-2 days due to the high diffusion rate. During 2-7 days, the amount of TEOS (10-70 phr) did not significantly affect the conversion. Therefore, the TEOS molecule could completely produce the silica particles in MMA-g-NR matrix according to the hydrolysis and condensation reaction [32].

Table 4.7 Effect of TEOS content on sol-gel reaction by using latex solution method
at 50°C

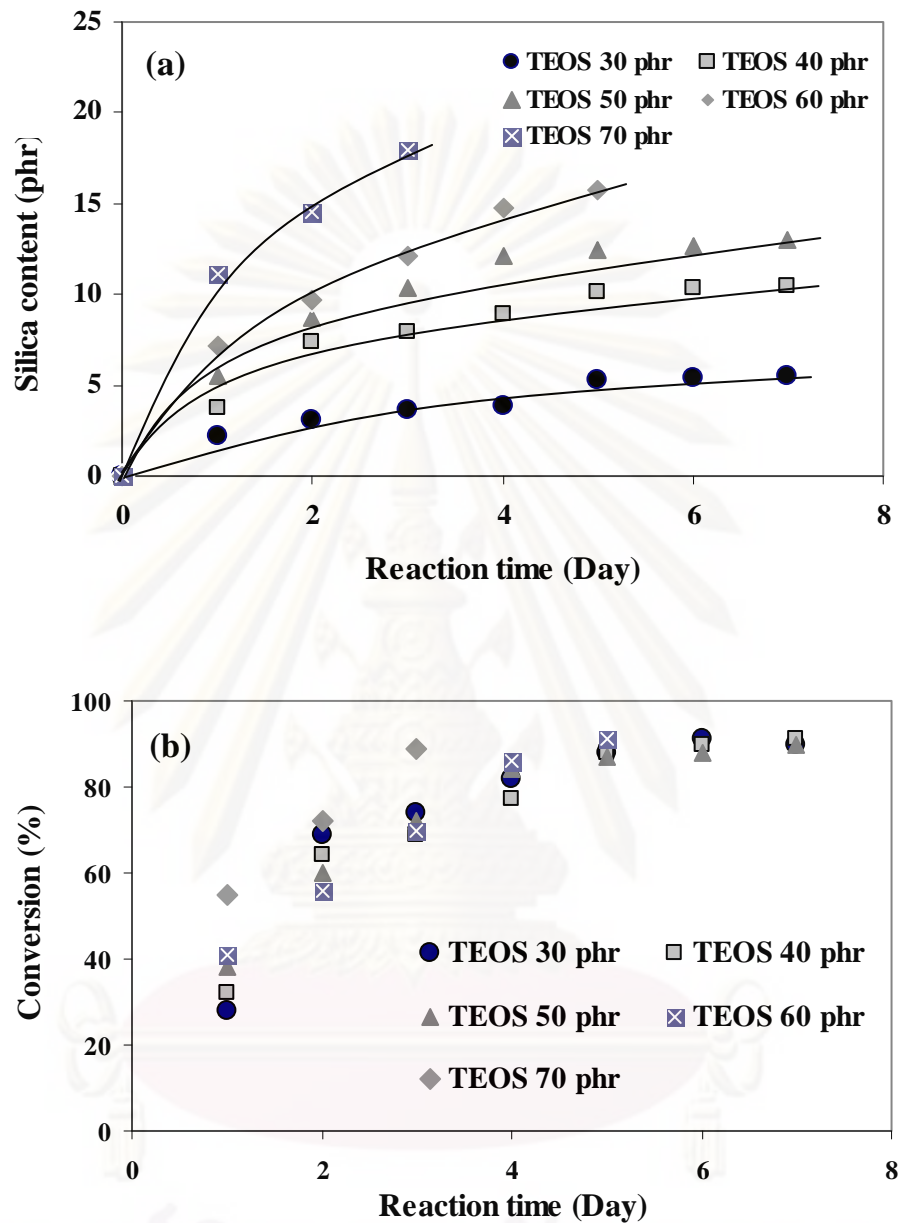| TEOS content (phr)	Time (day)	Silica content (phr)	Conversion (%)
20	1	2.2	37.1
	2	3.1	54.3
	3	3.6	63.4
	4	3.8	67.6
	5	5.3	91.9
	6	5.4	93.2
	7	5.5	93.2
30	1	2.5	28.3
	2	5.9	69.5
	3	6.4	74.6
	4	7.1	82.2
	5	7.6	88.3
	6	7.9	91.5
	7	7.8	90.5
40	1	3.7	32.4
	2	7.4	64.7
	3	7.9	69.1
	4	8.9	77.0
	5	10.1	88.3
	6	10.3	90.2
	7	10.5	91.2
50	1	5.5	38.4
	2	8.7	60.7
	3	10.4	72.4
	4	12.1	84.9
	5	12.5	87.4
	6	12.7	88.5
	7	13.0	90.1
60	1	7.2	41.5
	2	9.7	56.6
	3	12.1	70.8
	4	14.8	86.1
	5	15.7	91.1
70	1	11.1	55.2
	2	14.5	72.8
	3	17.9	89.3

Figure 4.10 Effect of TEOS content on sol-gel reaction by using latex solution
method at 50°C: (a) silica content and (b) conversion

4.4 Morphology of NR/GNR Vulcanizates

The morphology of NR/GNR vulcanizate was characterized by Transmission Electron Microscopy (TEM). The surface morphology of *in situ silica* MMA-g-NR prepared by sol-gel process using latex solution and solid rubber method are shown in Figure 4.12. It is well known that the surface of precipitated silica is highly polar and hydrophilic because of the presence of numerous silanol groups, so the silica particles agglomerate easily [40]. From Figure 4.12(a), the commercial silica particles in NR/GNR-Si9C vulcanizate were aggregated to form agglomeration structure. On the other hand, the *in situ* silica particles in NR/GNR-Si9L vulcanizate were dispersed more homogeneously in the NR matrix as shown in Figure 4.12(b). This implies that the agglomeration structure of *in situ* silica particles NR/GNR-Si9L vulcanizate was smaller than that of the commercial silica particles. From Figure 4.12(c) shows that the dispersion of silica particles in NR/GNR-Si9S (solid rubber method) was similar to NR/GNR-Si9L (latex solution method). Hence, the morphology of *in situ* silica MMA-g-NR prepared by using solid rubber method and latex solution method were not different. For high *in situ* silica loading (20 phr) (Figure 4.12(d)), the silica particles agglomeration was more than that of *in situ* silica (9 phr) NR/GNR vulcanizate. The approach model of *in situ* silica generated in MMA-g-NR is shown in Figure 4.11.
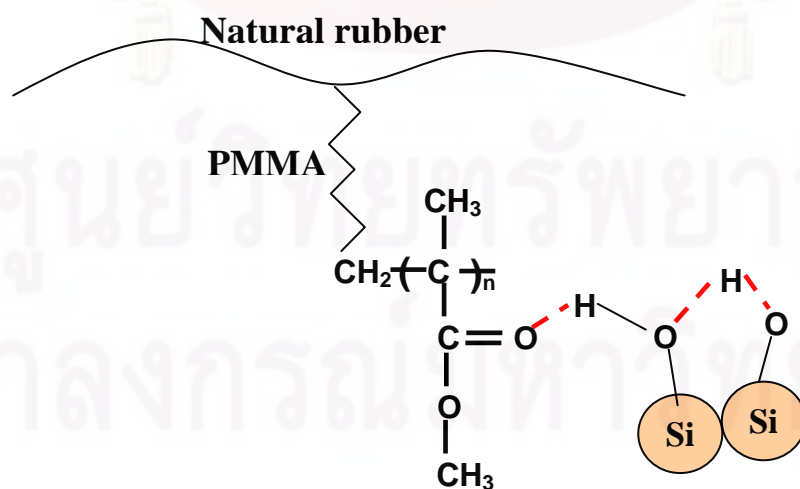
Figure 4.11 Silica particles dispersed in MMA-g-NR

a) NR/GNR-Si9C

b) NR/GNR-Si9L

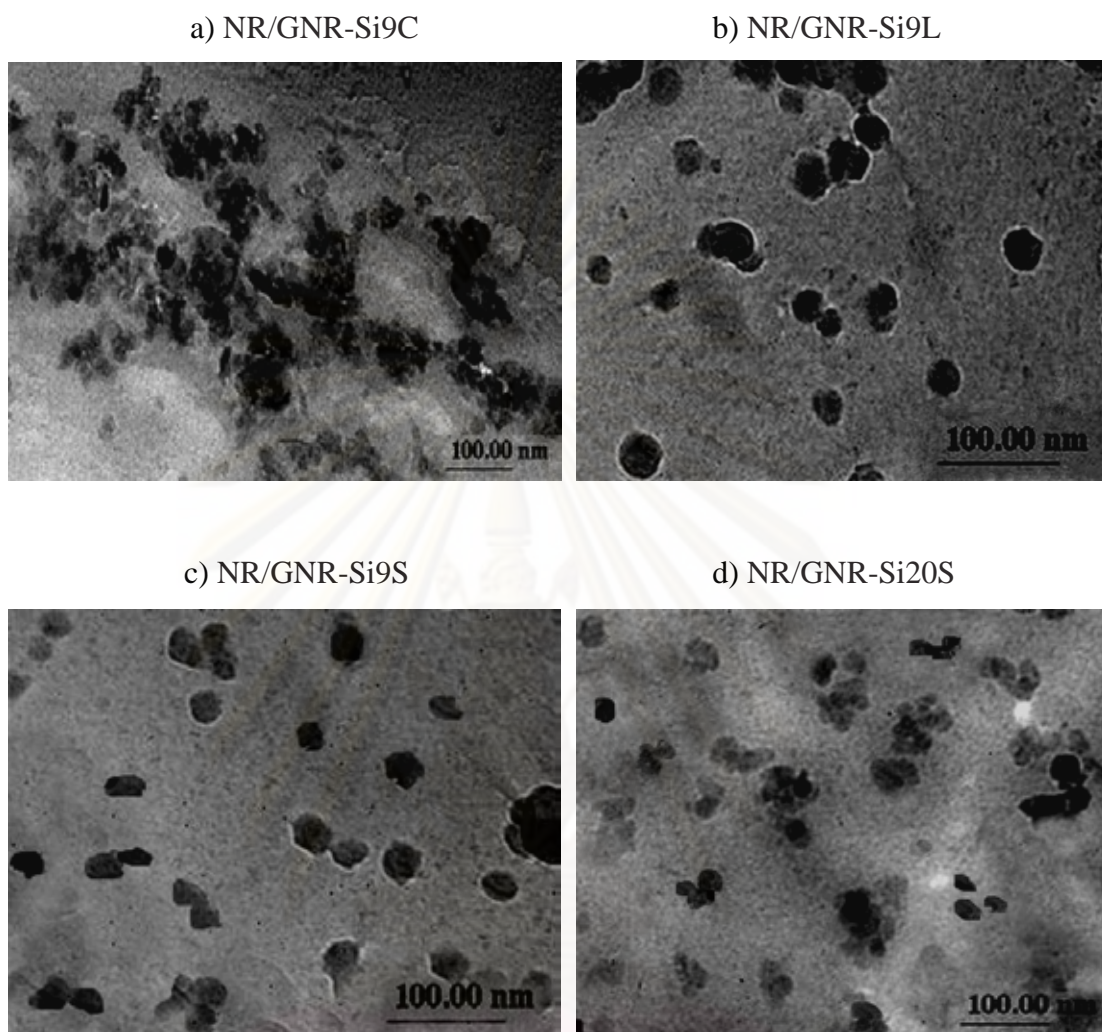c) NR/GNR-Si9S

d) NR/GNR-Si20S

Figure 4.12 TEM photogragphs of NR/GNR vulcanizates: a) commercial silica of 9
phr, b) *in situ* silica 9 phr (latex solution method), c) *in situ* silica 9 phr
(solid rubber method) and d) *in situ* silica 20 phr (solid rubber method)

4.5 Cure Characteristics of *in situ* silica MMA-g-NR

The cure characteristics of NR/GNR blend and NR/*in situ* silica GNR blend are presented in Table 4.8. The cure time of NR/GNR blend was higher than that of NR due to the higher level of polar functional groups of the NR-*g*-PMMA. In the compounding procedure, the same accelerator amount was used to prepare the NR-*g*-PMMA compounds. Some CBS amount was probably absorbed by the polar functional groups of the graft copolymer due to the similar polarities. The accelerator could not be performed at this accelerator amount accelerating the vulcanization. Hence, a longer time was needed to perform the crosslinking to reach the optimum curing characteristics [33]. The curing time of NR/GNR blends increased with increasing *in situ* silica contents due to the surface properties of *in situ* silica. Generally, the surface of silica particles contains the silanol groups, as acidic and highly reactive agent. The silanol groups could react with the curing agents, i.e., accelerator or activator as basic and reactive agent, and reduced the efficiency of curing agent leading to an increase in curing time [41]. The curing time of NR/*in situ* silica GNR blends (NR/GNR-Si9S and NR/GNR-Si9L) were lower than that of NR/commercial silica GNR blend (NR/GNR-Si9C).

Table 4.8 Cure time of NR/GNR blends at 150°C

NR vulcanizes	Cure Time (min)
NR	7.2
NR/GNR	7.9
NR/GNR-Si9C	10.1
NR/GNR-Si9L	8.8
NR/GNR-Si9S	9.0
NR/GNR-Si20S	11.1

4.6 Mechanical Properties NR/GNR Vulcanizates

The NR/GNR and NR/*in situ* silica GNR vulcanizates were prepared and the mechanical properties, the tensile strength (T.S.), elongation at break, 300% modulus (M_{300}), tear resistance, hardness and abrasion resistance are summarized in Table 4.10

From Figure 4.13, comparing the tensile properties of NR and NR/GNR vulcanizates, it was found that 300% modulus and tensile strength of NR/GNR vulcanizate were higher than that of NR due to the increasing hard segment PMMA molecule in NR chain [42]. The elongation at break of NR/GNR vulcanizate was lower than that of NR. The increasing chain stiffness of PMMA in NR was the reason for a decreasing of elongation at break.

For the NR/GNR blends filled with commercial silica (NR/GNR-Si9C), tensile properties were lower than that of the NR/*in situ* silica GNR vulcanizate, NR/GNR-Si9S and NR/GNR-Si9L. It was due to the fact that the *in situ* silica generated by using solid rubber and latex solution method seemed to be dispersed homogenously throughout the rubber matrix which contributed effectively to the reinforcement [37]. This is also confirmed by the TEM micrograph of NR/GNR-Si9S and NR/GNR-Si9L (Figure 4.11(b and c)). Therefore, the 300% modulus and tensile strength increased with increasing *in situ* silica contents because the stress applied from an external force to the composite was transferred to the filler (which were the load-bearing element) through the filler-matrix interface [43, 44]. However, the tensile properties of NR/GNR-Si9S and NR/GNR-Si9L vulcanizates were the same.

The hardness of NR/GNR vulcanizates are shown in Table 4.10. The hardness of NR/GNR vulcanizate was higher than NR. The hardness increased with increasing *in situ* silica content in NR/GNR vulcanizate. And the hardness of NR/*in situ* silica GNR vulcanizate was even higher than that of commercial silica NR/GNR vulcanizate.

From Table 4.10 and Figure 4.14, the tear strength of NR/GNR vulcanizate was higher than that of NR vulcanizate due to the increase in hard segment of PMMA in NR chain of grafted rubber. The NR/GNR-Si20S exhibited the highest tear strength. The tear strength of NR/GNR-Si9L and NR/GNR-Si9S were higher than that of NR/GNR-Si9C. To reduce the size of agglomeration of silica particles, a good

bonding between the silica particles and to network was formed to reduce a load transfer between them [45].

  The abrasion resistance was measured from the volume loss of the compound after applying the external force. The abrasion volume loss of NR/GNR filled with *in situ* silica is shown in Table 4.10 and Figure 4.15. The abrasion resistance of NR/ *in situ* silica GNR vulcanizate was higher than that of NR/GNR filled with commercial silica (NR/GNR-Si9). The commercial silica was not well dispersed in the matrix with high agglomeration from TEM micrograph (Figure 4.12(a)), thus the reinforcement in the vulcanizate was reduced compared with silica reinforcement by sol-gel process.

Table 4.9 Mechanical properties of NR/GNR vulcanizates

| Mechanical properties	NR	NR/GNR	NR/GNR -Si9C	NR/GNR -Si9L	NR/GNR -Si9S	NR/GNR -Si20S
Tensile strength (MPa)	18.4 (0.42)	21.5 (0.44)	23.5 (0.47)	24.6 (0.41)	24.2 (0.41)	27.6 (0.46)
Elongation at break (%)	819.7 (34.63)	694.7 (31.78)	496.8 (18.21)	540.3 (52.48)	524.4 (40.63)	457.8 (47.20)
300% modulus (MPa)	1.8 (0.11)	8.9 (0.28)	10.4 (0.22)	11.2 (0.27)	10.9 (0.49)	13.4 (0.38)
Tear strength (N/mm)	26.4 (0.69)	44.1 (1.30)	47.4 (0.63)	49.9 (0.58)	49.4 (0.49)	54.4 (2.11)
Hardness	40.0 (0.58)	64.0 (0.00)	69.3 (0.58)	70.0 (0.00)	70.0 (0.00)	74.7 (0.58)
Abrasion loss (mm^3)	46.4 (13.00)	43.4 (5.00)	38.9 (9.00)	35.3 (2.00)	35.6 (6.00)	31.5 (10.00)
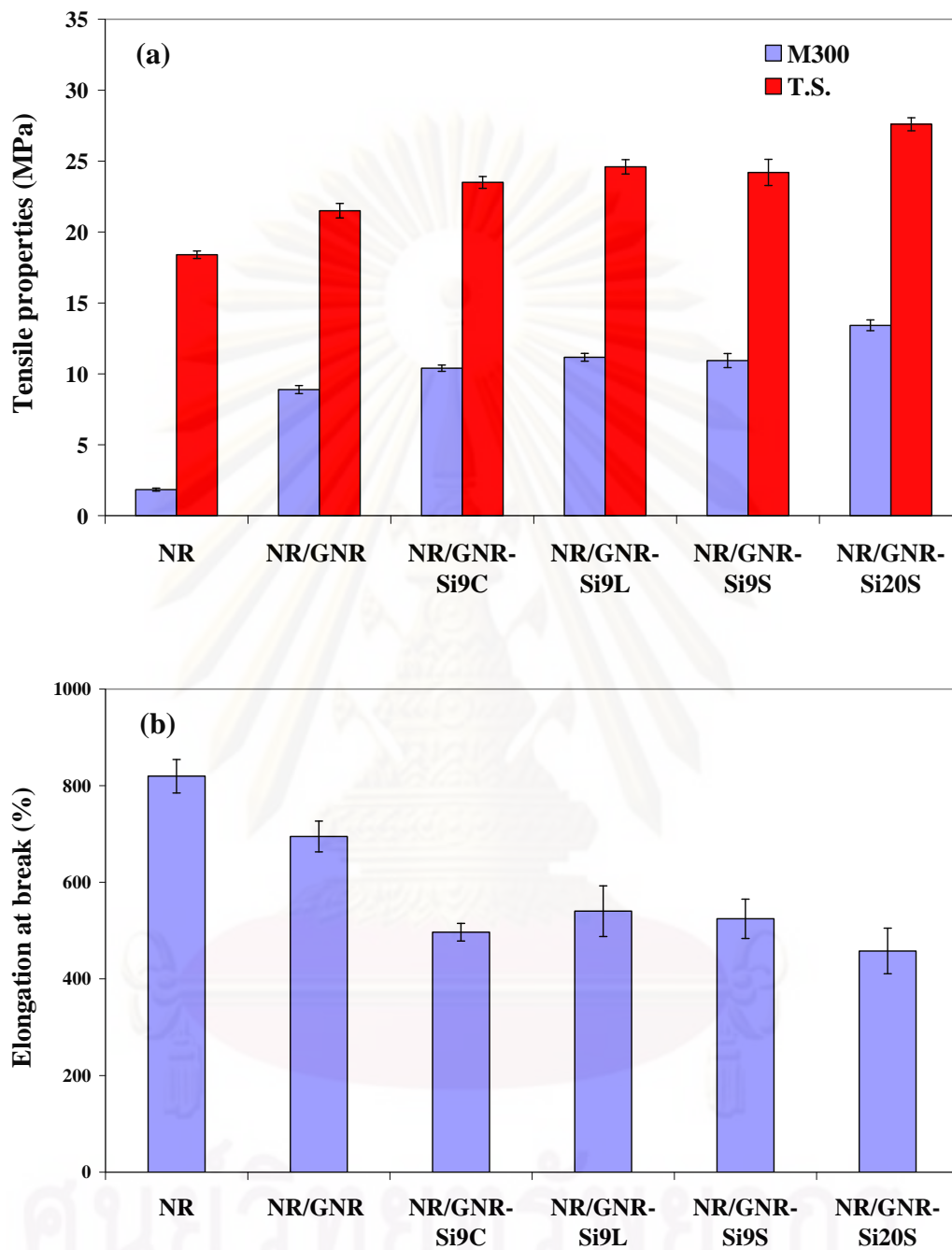
Figure 4.13 Tensile properties of NR/GNR vulcanizates: a) Tensile strength and
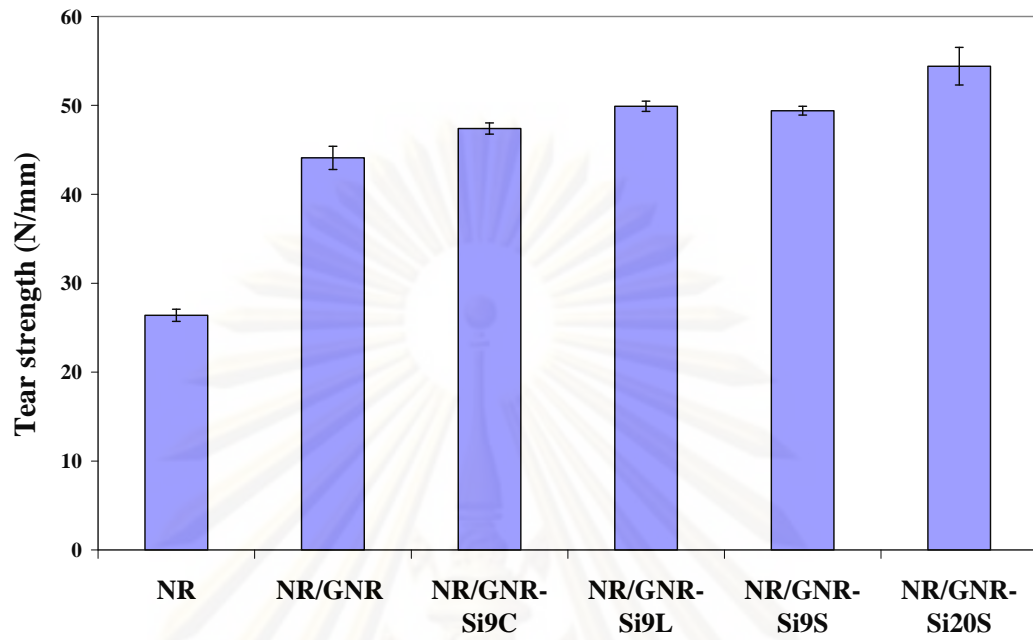300% modulus and b) Elongation at break

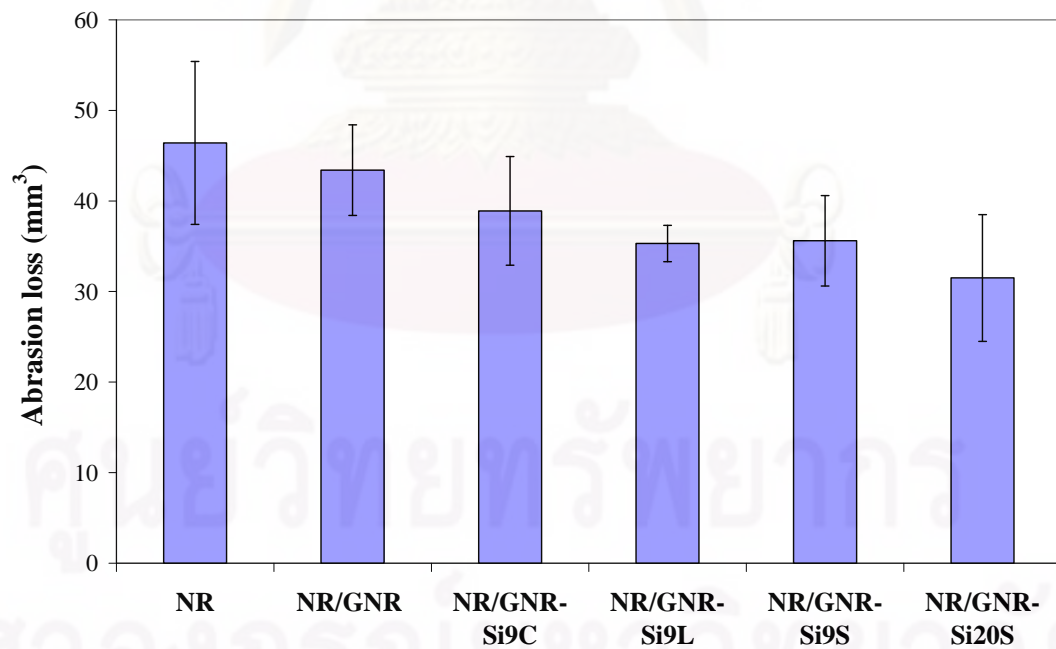**Figure 4.14** Tear strength of NR/GNR vulcanizates

Figure 4.15 Abrasion resistance of NR/GNR vulcanizates

CHAPTER V

CONCLUSION AND FUTURE DIRECTION

5.1 Conclusion

The *in situ* silica reinforced methyl methacrylate grafted natural rubber (MMA-g-NR) was prepared by a sol-gel reaction of teraethoxysilane (TEOS) using solid rubber method and latex solution method. The graft copolymerization of methyl methacrylate onto natural rubber was carried out using cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) as an initiator. The effects of parameters, catalyst concentration, TEOS content, TEOS addition method, reaction temperature and time on the amount of in situ generated silica in MMA-g-NR were investigated. The *in situ* grafted natural rubber/natural rubber vulcanizate were prepared, and mechanical properties of NR/GNR vulcanizate were also investigated in comparison with commercial silica filled one.

The structure of grafted NR was confirmed by FT-IR and NMR analysis. The *in situ* silica reinforced MMA-g-NR was prepared by sol-gel process via TEOS using solid rubber method with *n*-hexylamine as a catalyst. It was found that the *in situ* silica content increased with increasing the concentration of n-hexylamine, TEOS content, reaction temperature and time. For latex solution method, the in situ silica content increased with increasing TEOS content, reaction temperature and time. The percentages of graft NR of *in situ* MMA-g-NR for TEOS addition during graft copolymerization less than that of MMA-g-NR for TEOS addition after graft copolymerization.

The optimum condition of sol-gel process using solid rubber method with *n*-hexylamine as catalyst was at the n-hexylamine concentration of 0.064 M and temperature of 60°C and the high silica content of 48 phr was achieved. The conversion reached almost 95% conversion after 3 days. For sol-gel process using

latex solution method, the optimum condition was at TEOS amount of 70 phr and 50°C resulting the high silica content of 18 phr.

The mechanical properties of NR/*in situ* silica GNR vulcanizates were higher than that of commercial silica filled one. The mechanical properties were increased with increasing the *in situ* silica content in NR/GNR vulcanizates. It found the sol-gel process could be employed to prepare high-modulus vulcanizates with higher tensile strength, tear strength and abrasion resistance than the one prepared by the conventional mixing method. The TEM micrographs confirmed that the in situ silica particles were well dispersed in GNR matrix while the agglomeration of commercial silica particles was formed in GNR matrix.

5.2 Future Direction

1) Explore the surfactant for increasing TEOS addition in the sol-gel reaction using latex solution method with the aim to maximize the in situ silica content.

2) Study in more detail on the effect of reaction parameters such as the percentage of graft NR, monomer types, and silica precursor types on *in situ* silica content and the mechanical properties of vulcanizates.

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APPENDICES

APPENDIX A

CALCULATION

A.1 Calculation of swelling degree

$$Degree\ of\ swelling\ (\%) = \frac{Weight\ of\ NR\ sheet\ after\ swell - Weight\ of\ NR\ sheet\ before\ swell}{Weight\ of\ NR\ sheet\ before\ swell} \times 100$$

Degree of swelling(%)= $\frac{56.70 - 24.46}{24.4}$ x 100 = 131.80 %

A.2 Calculation of amount of TEOS

$$Amount\ of\ TEOS = Weight\ of\ NR\ sheet\ after\ swell - Weight\ of\ NR\ sheet\ before\ swell$$

Amount of TEOS = 56.70 – 24.46 = 32.34 g

A.3 Calculation of amount of water

Amount of water (15 times of amount of TEOS)

Amount of water = 15 x 32.24 = 483.60 mL

A.4 Calculation of amount of n-hexylamine

Amount of n-hexylamine (MW of n-Hexylamine = 101.19)

Concentration of n-hexylamine used in this study was 0.064 mol/l

Water 1000 mL n-hexylamine 0.064 mol

Water 483.60 mL n-hexylamine = $\frac{0.064 \times 483.60}{1000}$ mol

= 0.0309 mol = 3.13 g.

APPENDIX B

Table B.1 Grafting Properties of MMA-g-NR

EXP.	Conv. (%)	Sample (g)	NR (g)	MMA (g)	Free NR (g)	Free MMA (g)	Graft NR (g)	Free NR (%)	Free MMA (%)	Graft NR (%)	GE (%)
GNR1	66.7	2.820	1.433	1.387	0.551	0.811	1.458	19.6	28.7	51.7	39.2
GNR2	64.8	2.149	1.092	1.057	0.348	0.714	1.087	16.2	33.2	50.6	37.4
GNR3	61.2	2.009	1.058	0.753	0.355	0.536	1.118	17.7	26.7	55.7	29.9
GNR4	72.1	2.765	1.405	1.360	0.510	0.800	1.455	18.4	28.9	52.6	41.2
GNR5	75.6	3.132	1.592	1.540	0.612	0.950	1.570	19.5	30.3	50.1	42.5

$$\% \ Graft \ efficiency = \frac{Total \ weight \ of \ monomer \ grafted}{Total \ weight \ of \ monomer \ polymerized} \ x \ 100$$

$$= \frac{0.811 - 1.387}{1.387} \ x \ 100 = 39.2 \ \%$$

$$\% \ Free \ NR = \frac{Total \ weight \ of \ free \ NR}{Total \ weight \ of \ polymer} \ x \ 100$$

$$= \frac{0.551}{2.820} \ x \ 100 = 19.6 \ \%$$

$$\% \ Free \ monomer = \frac{Total \ weight \ of \ free \ monomer}{Total \ weight \ of \ polymer} \ x \ 100$$

$$= \frac{0.811}{2.820} \ x \ 100 = 28.7 \ \%$$

$$\% \ Grafted \ NR = \frac{Total \ weight \ of \ grafted \ NR}{Total \ weight \ of \ polymer} \ x \ 100$$

$$= \frac{1.458}{2.820} \ x \ 100 = 19.6 \ \%$$

APPENDIX C
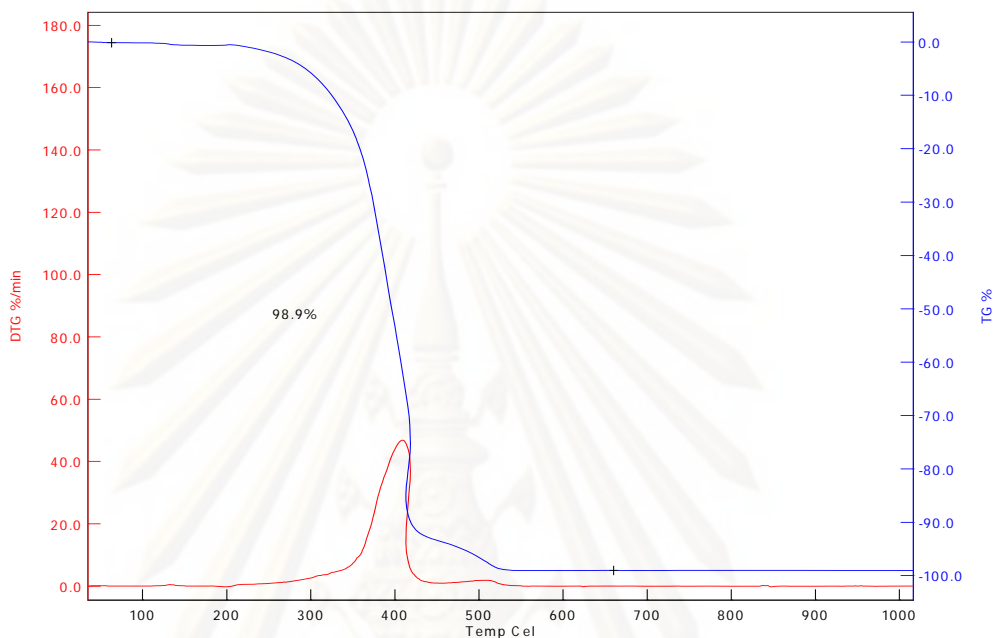
Figure C.1 Thermogram of MMA-g-NR
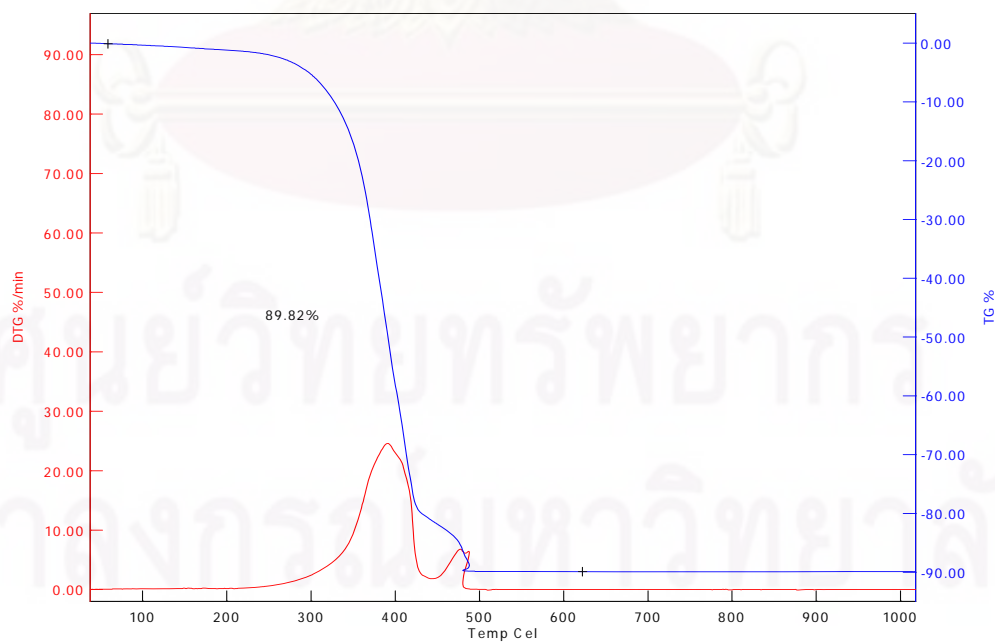
Figure C.2 Thermogram of MMA-g-NR with *in situ* silica 18 phr
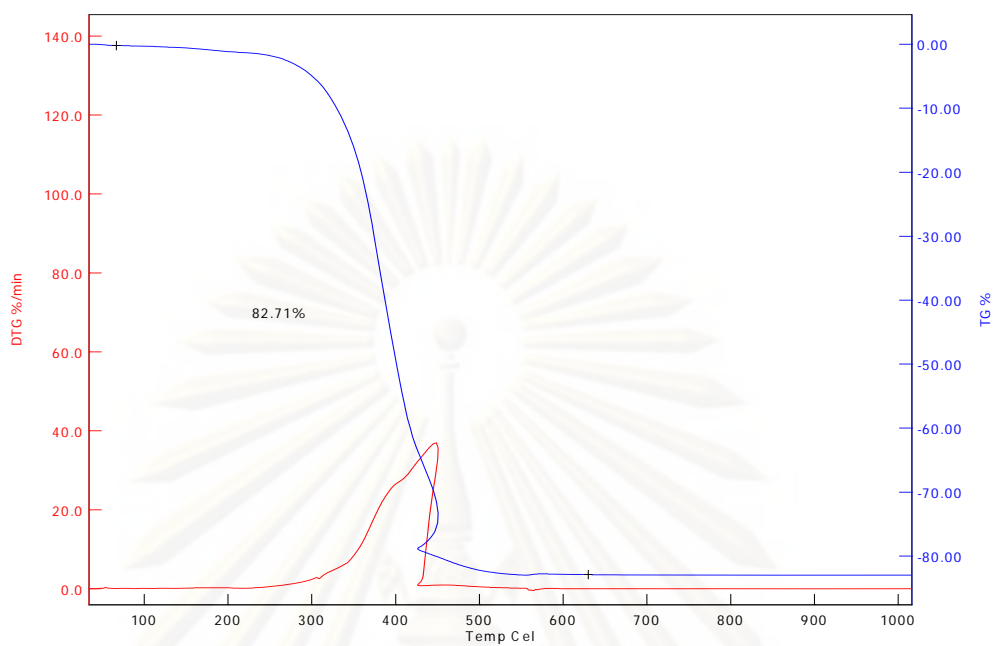
using latex solution method

Figure C.3 Thermogram of MMA-g-NR with *in situ* silica 18 phr
using solid rubber method

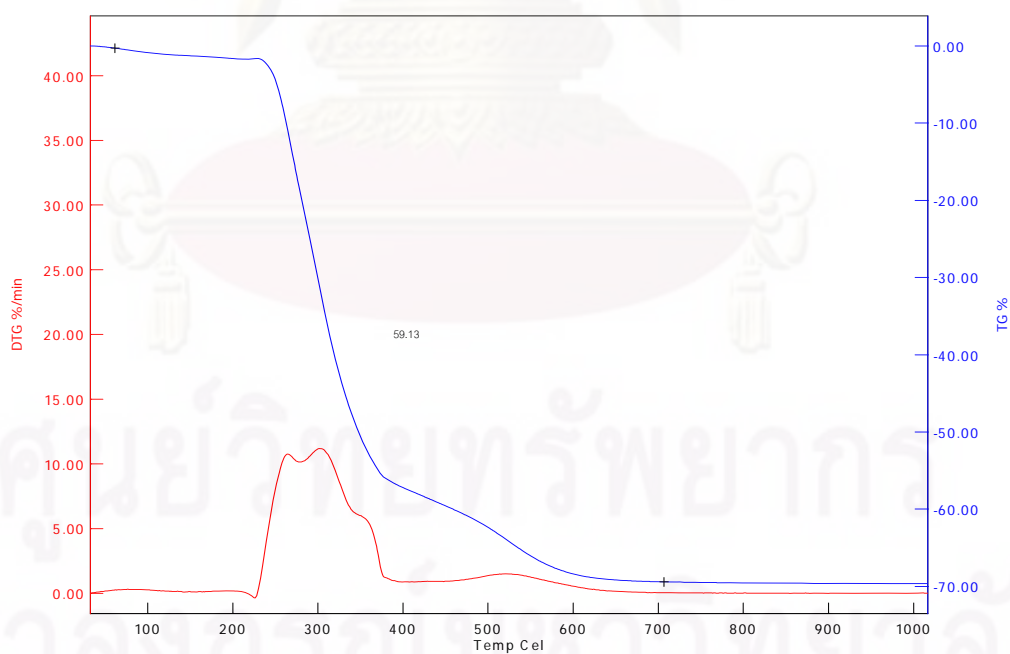**Figure C.4** Thermogram of MMA-g-NR with *in situ* silica 20 phr
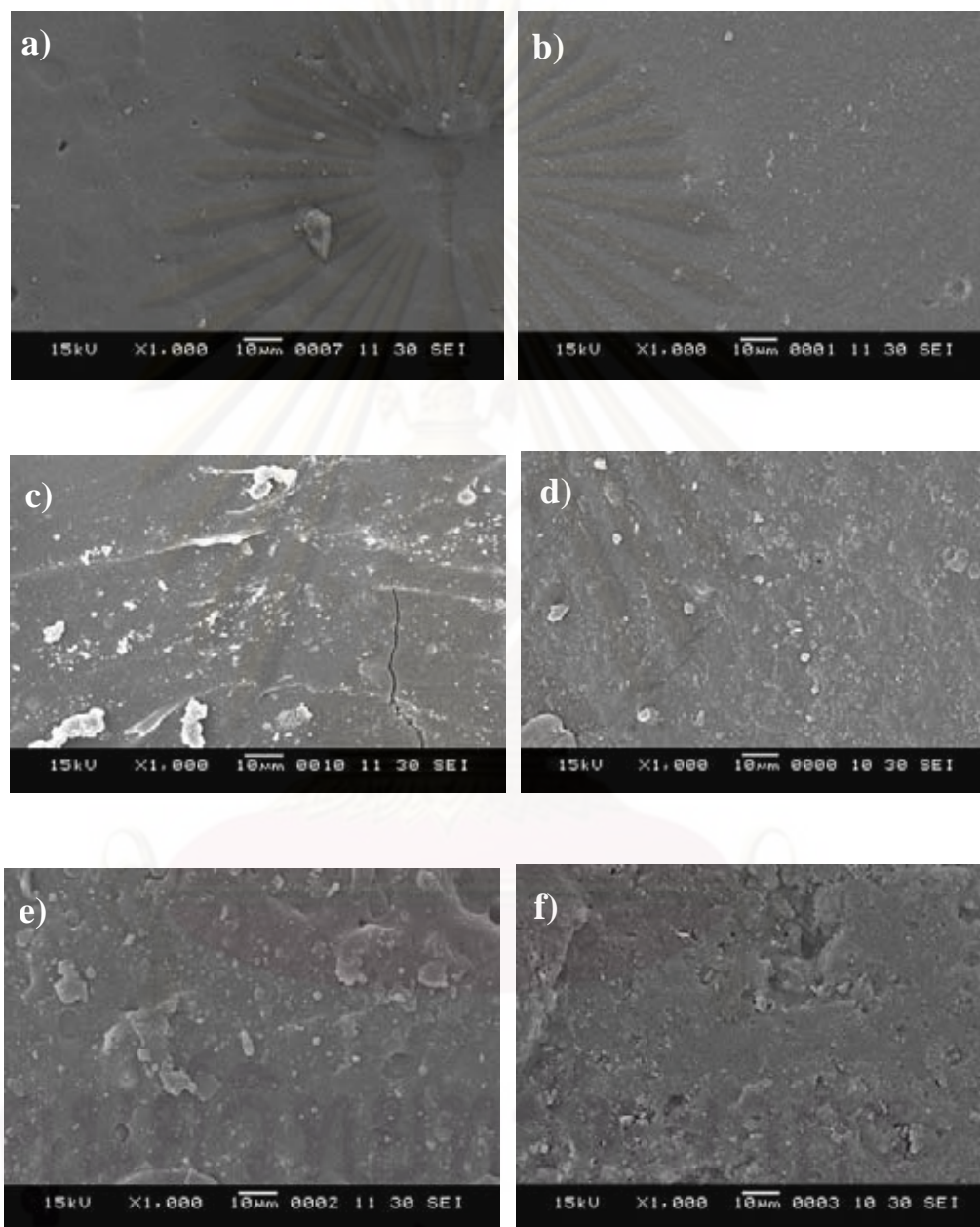using solid rubber method

APPENDIX D

Figure D.1 SEM micrograph of NR/GNR vulcanizates: a) NR, b) NR/GNR,
c) NR/GNR-Si9C, d) NR/GNR-Si9L, e) NR/GNR-Si9S and
f) NR/GNR-Si20S

Table D.1 Swelling degree (%) of NR/GNR vulcanizates

Sample	Degree of swelling (%)
NR	347.7±12.58
NR/GNR	318.8±6.22
NR/GNR-Si9C	285.7±11.61
NR/GNR-Si9L	267.±8.65
NR/GNR-Si9S	273±7.28
NR/GNR-Si20S	244±8.34

Table D.2 Tensile strength of NR/GNR vulcanizates

	NR	NR/GNR	NR/GNR-Si9C	NR/GNR-Si9L	NR/GNR-Si9S	NR/GNR-Si20S
	18.77	21.28	23.11	24.42	24.45	27.93
Tensile strength (Mpa)	18.48	22.00	23.39	25.08	23.76	27.86
	17.95	21.22	24.02	24.32	24.49	26.98
mean	18.40	21.50	23.50	24.61	24.23	27.59
Standard deviation	0.42	0.44	0.47	0.41	0.41	0.46

Table D.3 Elongation at break of NR/GNR vulcanizated

	NR	NR/GNR	NR/GNR-Si9C	NR/GNR-Si9L	NR/GNR-Si9S	NR/GNR-Si20S
Elongation at break (%)	792.93	724.69	497.70	598.69	488.58	410.43
	858.78	661.39	514.50	525.01	516.13	457.99
	807.26	697.93	478.11	497.12	568.56	504.82
mean	819.66	694.67	496.77	540.27	524.42	457.75
Standard deviation	34.63	31.78	18.21	52.48	40.63	47.20

Table D.4 300% modulus of NR/GNR vulcanizates

	NR	NR/GNR	NR/GNR-Si9C	NR/GNR-Si9L	NR/GNR-Si9S	NR/GNR-Si20S
300% Modulus (Mpa)	1.94	9.17	10.50	11.17	10.73	13.58
	1.73	8.60	10.15	11.44	11.50	12.98
	1.85	8.89	10.56	10.90	10.58	13.69
mean	1.84	8.89	10.40	11.17	10.94	13.42
Standard deviation	0.11	0.28	0.22	0.27	0.49	0.38

Table D.5 Hardness of NR/GNR vulcanizates

	NR	NR/GNR blend	NR/GNR-Si9C	NR/GNR-Si9L	NR/GNR-Si9S	NR/GNR-Si20S
	39.00	64.00	69.00	70.00	70.00	74.00
Hardness	40.00	64.00	70.00	70.00	70.00	75.00
	40.00	64.00	69.00	70.00	70.00	75.00
mean	40.00	64.00	69.33	70.00	70.00	74.67
Standard deviation	0.58	0.00	0.58	0.00	0.00	0.58

Table D.6 Tear strength and Abrasion resistance of NR/GNR vulcanizates

Mechanical properties	NR	NR/GNR	NR/GNR-Si9C	NR/GNR-Si9L	NR/GNR-Si9S	NR/GNR-Si20S
Tear strength (N/mm)	26.4±0.69	44.1±1.30	47.4±0.63	49.9±0.58	49.4±0.49	54.4±2.11
Abrasion loss (mm3)	46.4±13	43.4±5	38.9±9	35.3±2	35.6±6	31.5±10

VITAE

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Presentations at the national conference

2009 Silica reinforcement of methyl methacrylate grafted natural rubber by sol-gel process, October 15-17, 2009, Burapha University, Thailand.