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MODIFICATION OF STYRENE GRAFTED NATURAL RUBBER BY TETRAETHOXYSILANE

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ยางธรรมชาติกราฟต์สไตรีนเตรียมได้ด้วยปฏิกิริยาพอลิเมอไรเซชันแบบอิมัลชัน โดยใช้คิวมีนไฮโดรเปอร์ออกไซด์และเททระเอทิลีนเพนทามีนเป็นตัวริเริ่มปฏิกิริยาแบบรีดอกซ์ การสังเคราะห์อินซิทูซิลิกาให้เกิดขึ้นในยางธรรมชาติกราฟต์สไตรีนทำได้ด้วยปฏิกิริยาโซลเจลของเททระเอทอกซีไซเลนโดยใช้วิธีแบบยางแห้งและแบบสารละลายน้ำยาง ศึกษาผลของภาวะของปฏิกิริยา สำหรับวิธีแบบยางแห้ง ศึกษาผลของความเข้มข้นของตัวเร่งปฏิกิริยา อุณหภูมิ และ เวลาที่มีต่อปริมาณอินซิทูซิลิกา ปริมาณของอินซิทูซิลิกาเพิ่มขึ้น เมื่อความเข้มข้นของตัวเร่งปฏิกิริยาและเวลาเพิ่มขึ้น ในขณะที่อุณหภูมิไม่ส่งผล ได้ปริมาณอินซิทูซิลิกาสูงสุดที่ 50 ส่วนเมื่อเทียบกับยาง 100 ส่วน สำหรับวิธีแบบสารละลายน้ำยาง ศึกษาผลของปริมาณเททระเอทอกซีไซเลน อุณหภูมิ ลำดับในการเติมเททระเอทอกซีไซเลน และ เวลา ปริมาณของอินซิทูซิลิกาเพิ่มขึ้น เมื่อปริมาณของเททระเอทอกซีไซเลน และเวลาเพิ่มขึ้น ในขณะที่อุณหภูมิไม่ส่งผล ได้ปริมาณอินซิทูซิลิกาสูงสุดที่ 24 ส่วนเมื่อเทียบกับยาง 100 ส่วนเมื่อเติมเททระเอทอกซีไซเลนหลังจากปฏิกิริยาการกราฟต์สิ้นสุดแล้ว นอกจากนี้ศึกษาและเปรียบเทียบผลของซิลิกาเกรดการค้าและอินซิทูซิลิกาที่มีต่อสมบัติเชิงกลของยางกราฟต์ที่ผ่านการวัลคาไนซ์แล้ว ยางกราฟต์ที่ผ่านการวัลคาไนซ์แล้วที่มีอินซิทูซิลิกามีสมบัติเชิงกลสูงกว่ายางกราฟต์ที่ผ่านการวัลคาไนซ์แล้วที่มีซิลิกาเกรดการค้า ภาพจากกล้องจุลทรรศน์แบบส่องผ่านระบุว่า อนุภาคของอินซิทูซิลิกากระจายตัวดีในวัฏภาคของยาง ในขณะที่อนุภาคของซิลิกาเกรดการค้าเกิดการรวมตัวกันในวัฏภาคของยาง

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507 22784 23: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
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TORPONG SITTIPHAN: MODIFICATION OF STYRENE GRAFTED NATURAL RUBBER BY TETRAETHOXYSILANE PROCESS. THESIS ADVISOR: ASST. PROF. SIRILUX POOMPRADUB, Ph.D., 84 pp.

Styrene graft natural rubber (ST-g-NR) was prepared via an emulsion polymerization with redox system of cumene hydroperoxide (CHPO)/ tetraethylene pentamine (TEPA) as initiators. *In situ* silica filling of ST-g-NR was carried out by using sol-gel reaction of tetraethoxysilane (TEOS) with solid rubber and latex solution method. The effects of reaction condition were studied. For solid rubber method, the effects of catalyst concentration, reaction temperature and reaction time on the *in situ* silica content were investigated. The *in situ* silica content increased with the increase of catalyst concentration and reaction time, while the reaction temperature was not affected. The maximum *in situ* silica content about 50 phr was obtained. For latex solution method, TEOS content, reaction temperature, addition time of TEOS and reaction time were investigated. The *in situ* silica content increased with the increase of TEOS content and reaction time, while the reaction temperature was not affected. The maximum *in situ* silica content about 24 phr was achieved when TEOS added after graft copolymerization finished. Moreover, the effects of the conventional silica and *in situ* silica on the mechanical properties of GNR vulcanizate were also investigated and compared. The mechanical properties of *in situ* silica filled GNR vulcanizate were higher than those of commercial silica filled GNR vulcanizate. The TEM micrographs indicated that the *in situ* silica particles were well dispersed in the rubber matrix while the commercial silica particles were agglomerated in the rubber matrix.

Field of Study:..Petrochemistry and Polymer Science..Student's Signature..Torpong..Sittiphan
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LIST OF ABBREVIATIONS

ASTM : American Society for Testing and Materials
°C : Degree Celsius
CHPO : Cumene hydroperoxide
DRC : Dry rubber content
h : Hour
mm : Millimeter
MBTS : Mercaptobenzothiazole disulfide
nm : Nanometer
NR : Natural rubber
phr : Part per hundred part of rubber
PEG : Polyethylene glycol
SEM : Scanning Electron Microscopy
ST-g-NR : Styrene grafted natural rubber
TEM : Transmission Electron Microscopy
TEOS : Tetraethoxysilane
TEPA : Tetraethylene pentamine
TGA : Thermal Gravimetric Analysis

CHAPTER I

INTRODUCTION

1.1 Introduction

NR is obtained in the form of latex, which are exudation from the Hevea brasiliensis tree. It is the only agriculture product among rubbers. NR has good properties, i.e., high resilience, tear strength and elongation. The use of NR is widespread, ranging from household to industrial product. Most industrial and engineering products contain rubber phase in multiphase materials to improved impact strength. However, it has some limitation, i.e., low compatibility when mixed with high polarity rubber, synthetic rubber or plastic, resulting in poor mechanical properties. To improve compatibility, the modification of NR by grafting with vinyl monomers is interesting method to suppress this problem [1-4]. Vinyl monomer such as methyl methacrylate (MMA) or styrene (ST) is usually use for grafting onto the NR backbone. Graft copolymers are synthesized by an emulsion polymerization process. A redox-initiating system used for grafting monomer onto NR in almost commercial processes [5-9]. The modified NR can be used as the compatibilizer, impact modifier, toughening polymer, adhesives and coatings fields.

Moreover, in many applications, the strength of materials is one of important factors. Recently, silica powder is an alternative and it has been increasingly used for rubber reinforcement. Silica is used for modifying some properties of NR, i.e., reduced heat buildup, high tear strength, high tensile strength and high abrasion resistance. However, a problem of the conventional silica reinforced rubber is highly aggregated due to filler-to-filler interaction, resulting in lower dispersion in rubbery matrix. It is the incompatibility between the hydrophobic NR and hydrophilic silica, resulting in poor mechanical properties. For improving the reinforcement effect, *in situ* silica generated in rubber matrix by sol-gel processes is focused as one of the preparation methods for nanocomposites of silica particle and polymers. This method is starting precursor which undergoes various forms of hydrolysis and polycondensation reaction. Typical precursors are metal alkoxides and metal chlorides. The sol-gel process brings the well dispersion of silica filling in the rubbery matrix [10-17].

In this study, the modification of ST grafted NR (ST-g-NR) by using *in situ* sol-gel reaction of tetraethoxysilane (TEOS) by 2 methods, i.e., solid rubber method and latex solution method was focused. In the case of latex solution method, the effects of reaction time, reaction temperature, TEOS content and addition time of TEOS were investigated. In the case of solid rubber method, the effects of reaction time, reaction temperature and catalyst concentration were investigated. Moreover, the effect of commercial silica and *in situ* silica on mechanical properties of modified ST-g-NR was also investigated.

1.2 Objectives

1. To find the optimum condition for modify the graft copolymer, ST-g-NR by TEOS by sol – gel reaction in latex solution and solid rubber method.
2. To investigate and compare the effect of commercial silica and *in situ* silica on mechanical properties of modified ST-g-NR.

1.3 Scope of the Investigation

1. Literature survey.
2. Synthesis of ST-g-NR.
3. Characterize the chemical structure of ST-g-NR by Fourier Transform Infrared Spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance (^{1}H NMR).
4. Generate the *in situ* silica in ST-g-NR matrix via sol-gel technique with solid rubber method by varying parameters as follows:
    a) Catalyst concentration of the n-hexylamine solution for sol-gel reaction: 0.008 - 0.064 M.
    b) Reaction temperature of sol-gel reaction: 40°C and 50°C.
    c) Reaction times of sol-gel reaction 1 - 5 days.
5. Generate the *in situ* silica in ST-g-NR matrix via sol-gel technique with latex solution method by varying parameters as follows:
    a) Amount of TEOS: 20 - 80 phr.
    b) Reaction temperature of sol-gel reaction: 50°C and 60°C.

    c) Addition time of TEOS: before and after graft copolymerization reaction.
    d) Reaction times of sol-gel reaction 1 - 15 days.

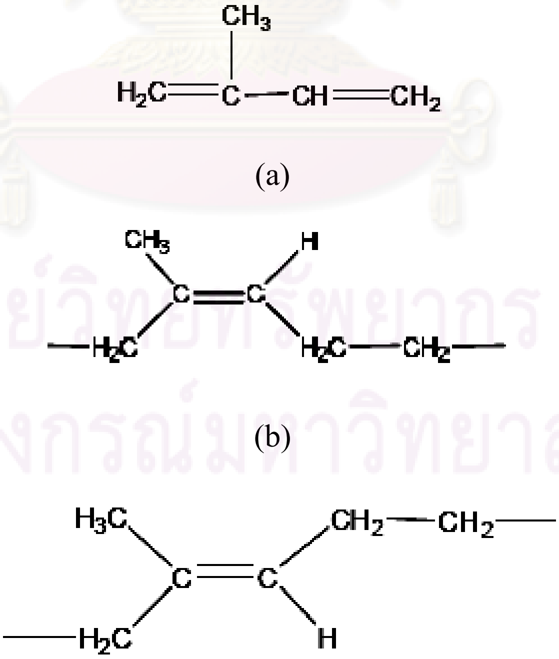
6. Determine the *in situ* silica content filled ST-g-NR matrix by Thermogravimetric Analysis (TGA).
7. Prepare the rubber compounding using mechanical mixing.
8. Study the mechanical properties of modified ST-g-NR vulcanizates: tensile strength, tear strength, hardness, and abrasion resistance.
9. Study the morphology of modified ST-g-NR vulcanizate by using Transmission Electron Microscope (TEM).
10. Compare the mechanical and morphology of modified ST-g-NR vulcanizates with commercial silica filled ST-g-NR vulcanizates.
11. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber

NR is a processed plant product which is obtained through coagulating the latex or milky sap produced by certain plants, particularly the Brazilian rubber-tree (*Hevea Brasiliensis*). *Heavea Brasiliensis* requires temperatures of 20-30°C, at least 2,000 mm of rainfall per year, and high atmospheric humidity [18]. To harvest rubber, a small cut is made in the bark and milky-substance call latex flows out. Today, 85% of the world's NR from the Far East (Malaysia, Indonesia, Thailand, Sri Lanka and India) [19]. The fundamental structure of NR was firstly found to have the formula C_5H_8, so-called isoprene, for which Tilden proposed the structure as shown in Figure 2.1 (a). The linear structures of isoprene were proposed by Pickles, providing for the structure isomerism with both *cis*- and *trans*- repeating units as shown in Figures 2.1 (b) and (c), respectively [20].



(a)

(b)

(c)

Figure 2.1 Structure of polyisoprene (a) Isoprene structure (b) Cis-repeating units and (c) Trans-repeating units**.**

2.1.1 Physical Properties

Physical properties of NR may vary slightly due to the non-rubber constituents present and to the degree of crystallinity. When NR is held below 10 ˚C, crystallization occurs, resulting in a change of density from 0.92 to about 0.95 [19]. Listed in Table 2.1 are some average physical properties.

Table 2.1 Physical properties of NR

Properties	value
Density	0.92 g/cm^3
Refractive index (20 ˚C)	1.52
Coefficient of cubical expansion	0.00062 /°C
Cohesive energy density	63.7 cal/cc.
Heat of combustion	10,700 cal/g
Thermal conductivity	0.00032 cal/sec/cm^3/°C
Dielectric constant	2.37
Power factor (1,000 cycles)	0.15-0.2*
Volume resistivity	10^{15} ohms/cc.
Dielectric strength	1,000 V/mm

* The power factor is reduced to 0.0015 and the resistivity substantially increased in deproteinized rubber.

2.1.2 NR latex

NR latex is a white milky fluid containing approximately 60% water, 35% rubber and 5% proteins, amino acids and some carbohydrates. NR latex is harvested manually by cutting a spiral groove in the tree and following the fluid to drain. The raw NR latex is then combined with other chemicals to create the durability, flexibility and strength required for a myriad of medical and consumer products. The proportions of composition in NR latex varied between wide limits are given in Table 2.2. The following composition is typical:

Table 2.2 Typical proportions of composition in NR latex

Composition	Content (% by weight)
Water	55
Rubber hydrocarbon	35
Proteins	4.5
Acetone extract	3.9
Lipins, amino acid, etc.	0.2
Quebrachitol	1.0
Inorganic salts	0.4

The total solid of fresh field latex varies typical from 30 – 40 %. The latex has a rubber content varies between the limits of 25 and 35%, depending on factors such as type of tree, tapping method, soil condition and season. The difference between the solids and dry rubber content of fresh latex is of the order of 3%

NR latex as it emerges from the tree (field latex) has dry rubber content (DRC) of about 30 – 40 %, the average being about 33%. Although field latex can be preserved with ammonia of fixed alkali, its low rubber content and high non-rubber solid content severely limit its usefulness. Hence it is necessary to increase the DRC in the NR latex to 60% or more to reduce the transportation costs and enhance suitability for various latex processes. Concentrated latex is economically useful as they contain less water to be shipped from the plantations; they are also more efficient in the manufacture of finished products directly from latex. Additionally, latex concentrates tend to be more uniform in quality than do field lattices. This is due in part to the partial removal of non-rubber constituents in several concentration processes [21].

2.1.3 Modification of natural rubber

NR 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 a modification rubber. The most well known types of modification are oxidation, hydrogenation, halogenations, hydrochioronation, chlorosulphonation and free radical addition or grafting [22].

2.2 Polymer grafting on natural rubber

2.2.1 Grafting copolymer

In graft copolymerization, polymer side chains are formed and attached to preformed macromolecules of different chemical compositions. The simplest case of graft copolymer can be represented by the following structure in Figure 2.2, where a sequence of A units is referred to as the main chain or backbone, the sequence of B units is the side chain of graft.

Figure 2.2 Graft copolymer [23].

Graft copolymer is a high polymer, the molecules of which consist of two or more polymeric parts of different compositions, chemically united together. A graft copolymer may be produced, for example, by polymerizing a given kind of monomer onto the product of the first polymerization. The union of two different polymers by chemical reaction between their molecular end groups or by a reaction producing crosslink between the different materials would also produce a graft copolymer. During a free radical graft copolymerization, monomer B is intended to be graft onto backbone polymer A, but usually the final product of a graft copolymerization will contain the following three species.

1. Homopolymer B which results from homopolymerization of monomer B.
2. Homopolymer A which is the original backbone polymer A not attacked by free radicals and therefore not involved in graft copolymerization.
3. Graft copolymer which has graft of poly-B branching out from poly-A.

The graft efficiency was found to depend on the following competing reaction:

1. Competition between monomer and backbone for the initiator radicals. When the peroxide initiator radical attacks the rubber, it results in the formation of a rubber radical capable of initiating graft copolymerization.
2. Competition between monomer and backbone for the growing polymer radicals. The resulting rubber radical then needs to complete with polymer radicals for the monomer in order to form graft copolymer.
3. Competition between the various termination processes for the free polymer radicals.

The mechanism of grafting copolymerization onto NR chains consists of 3 steps: initiation, propagation and termination. Cumene hydroperoxide (CHPO) used as an initiator will decompose to alkoxy radicals ($RO^\bullet$). For initiation step, alkoxy radicals might attack either the monomer (M) (Eq. 2.1) or the rubber molecule (Eq. 2.2) to produce monomer radicals ($M_n^\bullet$) and polyisoprene radicals ($NR^\bullet$), respectively as grafting sites. During formation of the graft copolymers, the surfaces of latex particles become the loci of polymerization. α-Methylenic hydrogen atoms (H) of NR (NR–H) can also become the site of graft copolymerization due to its more active. The alkoxy radical can attack α - methylenic hydrogen atoms to form polyisoprene radicals ($NR^\bullet$) to initiate monomers for producing graft copolymer radicals ($NR–M_n^\bullet$) (Eq. 2.3). For propagation step, $NR–M_n^\bullet$ attacks M to form graft copolymers ($NR–M_{n+1}$) (Eq. 2.4) or $M_n^\bullet$ attacks M to form free copolymer radicals ($M_{n+1}^\bullet$) (Eq. 2.5). Then, the M and $NR–M_n^\bullet$ will either combine with $NR^\bullet$ to terminate the process or transfer to NR via chain transfer agent (A) to form $NR–M_n^\bullet$ (Eq. 2.6-2.10). Finally, the $NR–M_n^\bullet$ can also terminate the process by reacting with free copolymers (Eq. 2.10-2.13) on the surfaces of latex particles [5].

Initiation:

Attacking monomer:

$$RO^\bullet + M \longrightarrow M_n^\bullet \tag{2.1}$$

Attacking rubber:

$$RO^\bullet + NR\text{–}H \longrightarrow NR^\bullet + ROH \tag{2.2}$$

Reinitiation:

$$NR^\bullet + M \longrightarrow NR\text{–}M_n^\bullet \tag{2.3}$$

Propagation:

Propagation of graft polymerization:

$$\mathrm{NR}-\mathrm{M}_n^{\bullet} + \mathrm{M} \longrightarrow \mathrm{NR}-\mathrm{M}_{n+1}^{\bullet} \tag{2.4}$$

Propagation of free polymerization:

$$\mathrm{M}_n^{\bullet} + \mathrm{M} \longrightarrow \mathrm{M}_{n+1}^{\bullet} \tag{2.5}$$

Chain transfer to macromolecules:

Transfer to monomer:

$$\mathrm{NR}-\mathrm{M}_n^{\bullet} + \mathrm{M} \longrightarrow \mathrm{M}_1^{\bullet} + \mathrm{NR}^{\bullet} - \mathrm{M}_n \tag{2.6}$$

Transfer to rubber:

$$\mathrm{NR}-\mathrm{M}_n^{\bullet} + \mathrm{NR{-}H} \longrightarrow \mathrm{NR}^{\bullet} + \mathrm{NR} - \mathrm{M}_n\mathrm{H} \tag{2.7}$$

$$\mathrm{M}_n^{\bullet} + \mathrm{NR{-}H} \longrightarrow \mathrm{NR}^{\bullet} + \mathrm{M}_n\mathrm{H} \tag{2.8}$$

Transfer to chain-transfer agent:

$$\mathrm{M}_n^{\bullet} + \mathrm{A} \longrightarrow \mathrm{A}^{\bullet} + \mathrm{M}_n \tag{2.9}$$

$$\mathrm{NR}-\mathrm{M}_n^{\bullet} + \mathrm{A} \longrightarrow \mathrm{A}^{\bullet} + \mathrm{NR} - \mathrm{M}_n\mathrm{H} \tag{2.10}$$

Termination by combination:

$$\mathrm{M}_n^{\bullet} + \mathrm{M}_m^{\bullet} \longrightarrow \mathrm{M}_{n+m}^{\bullet} \tag{2.11}$$

$$\mathrm{NR}-\mathrm{M}_n^{\bullet} + \mathrm{NR}-\mathrm{M}_m^{\bullet} \longrightarrow \mathrm{NR}-\mathrm{M}_{n+m} - \mathrm{NR} \tag{2.12}$$

$$\mathrm{NR}-\mathrm{M}_n^{\bullet} + \mathrm{M}_m^{\bullet} \longrightarrow \mathrm{NR}-\mathrm{M}_{n+m} \tag{2.13}$$

Normally, there are two methods to synthesize graft copolymers.

1. The side chain polymer can be directly linked by a suitable chemical reaction to the backbone polymer.
2. The backbone polymer can be initiated to occur active sites such as free radicals or ions to be used for polymerization of suitable monomers resulting the side chain polymer.

2.3 Vulcanization

2.3.1 Definition of Vulcanization [24]

Vulcanization is a process generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network as illustrated in Figure 2.3. According to the retractile force to resist a deformation is proportional to the number of network supporting polymer chains per unit volume of elastomer. A supporting polymer chain is a linear polymer molecular segment between network junctures. An increase in the number of junctures or crosslinks gives an increase in the number of supporting chains. In an unvulcanized linear high polymer (above its melting point), only molecular chain entanglements constitute junctures. Vulcanization, thus, is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. A crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon to carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber, mixed with vulcanizing agents, in a mold under pressure.

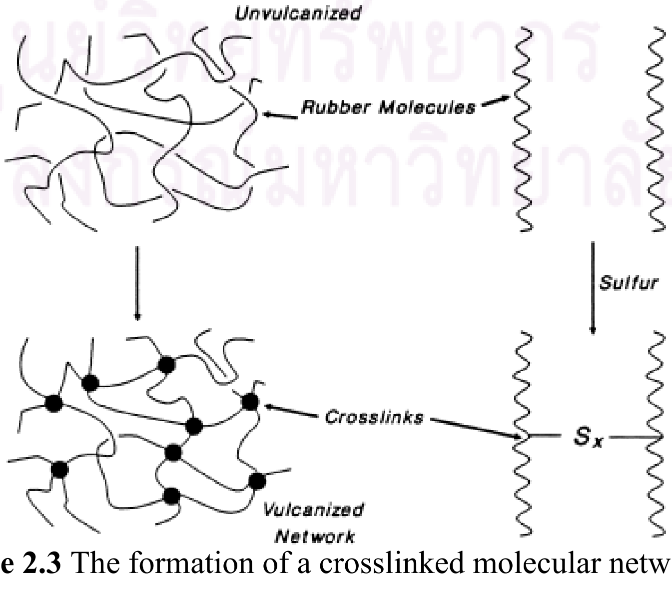


Figure 2.3 The formation of a crosslinked molecular network.

2.3.2 Description of Curing Parameters [25]

A cure curve in Figure 2.4 provides information on scorch safety or cures induction time, cure rate, state of cure, optimum cure time when modulus no longer increases significantly, and the tendency of the compound to degrade upon overcure as follows:

Scorch is a premature vulcanization in which the stock becomes partly vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound so that it can no longer be processed. Scorching is a result of both the temperature reached during processing and an amount of time the compound is exposed to elevated temperatures. This period of time before vulcanization is generally referred to as a “scorch time”. It is important that vulcanization dose not start until the processing is complete.

Rate of cure is the rate at which crosslinking and the development of the stiffness (modulus) of the compound occur after the scorch point. As the compound is heated past the scorch point, the properties of the compound change from a soft to a tough elastic material. During the curing step, crosslinks are introduced, which connect the long polymer chains of the rubber together. As more crosslinks are introduced, the polymer chains become more firmly connected and the stiffness or modulus of the compound increases. The rate of cure is an important vulcanization parameter since it in part determines the time the compound must be cured.

State of cure is a general term used to indicate the development of property of the rubber as cure progresses. As the crosslinking or vulcanization proceeds, the modulus of the compound increases to various “states of cure”. Technically, the most important state is the so-called “optimum”. Since all properties imparted by vulcanization do not occur at the same level of cure, the state of optimizing may not be the best for other properties.

Cure time is the time required during the vulcanization step for the compounded rubber to reach the desired state of cure.

Overcure is the cure time which is longer than optimum. Overcure may be of two types. In one type, the stock continues to harden, the modulus rises, and tensile and elongation fall. In other cases, including most NR compounds, reversion occurs with overcure and the modulus and tensile strength decreases.

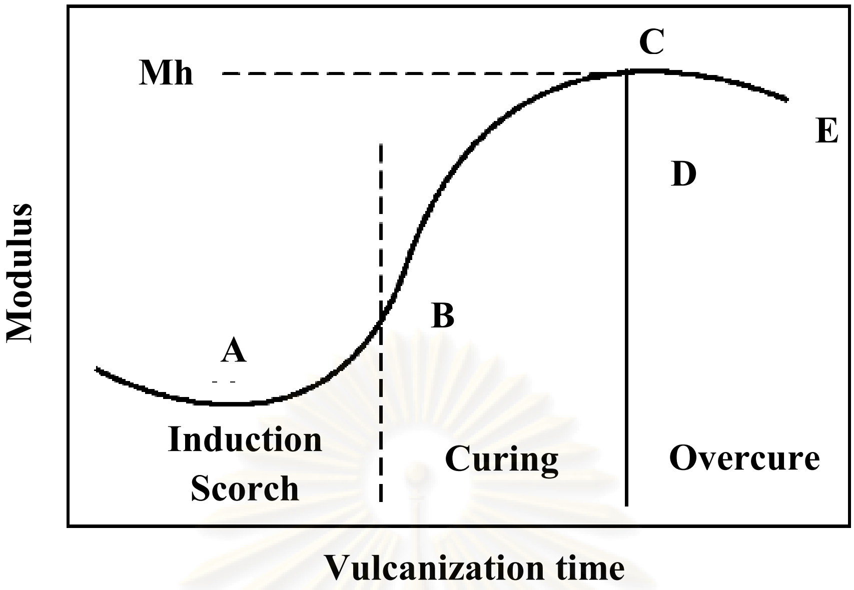
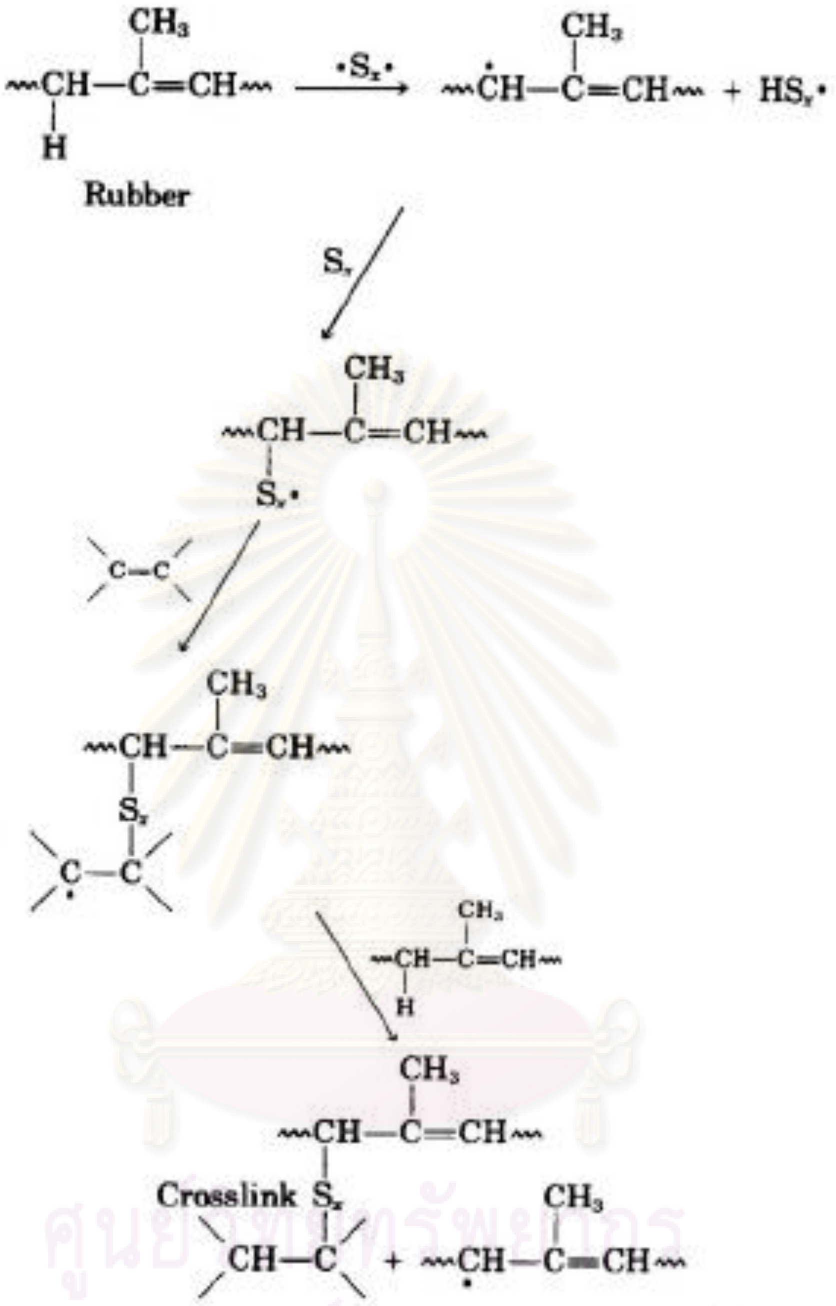


Figure 2.4 Cure curve from oscillating disk rheometer where A represents scorch safety, B cure rate, C state of cure, D optimum cure, and E reversion.

2.3.3 Sulfur Vulcanization [23]

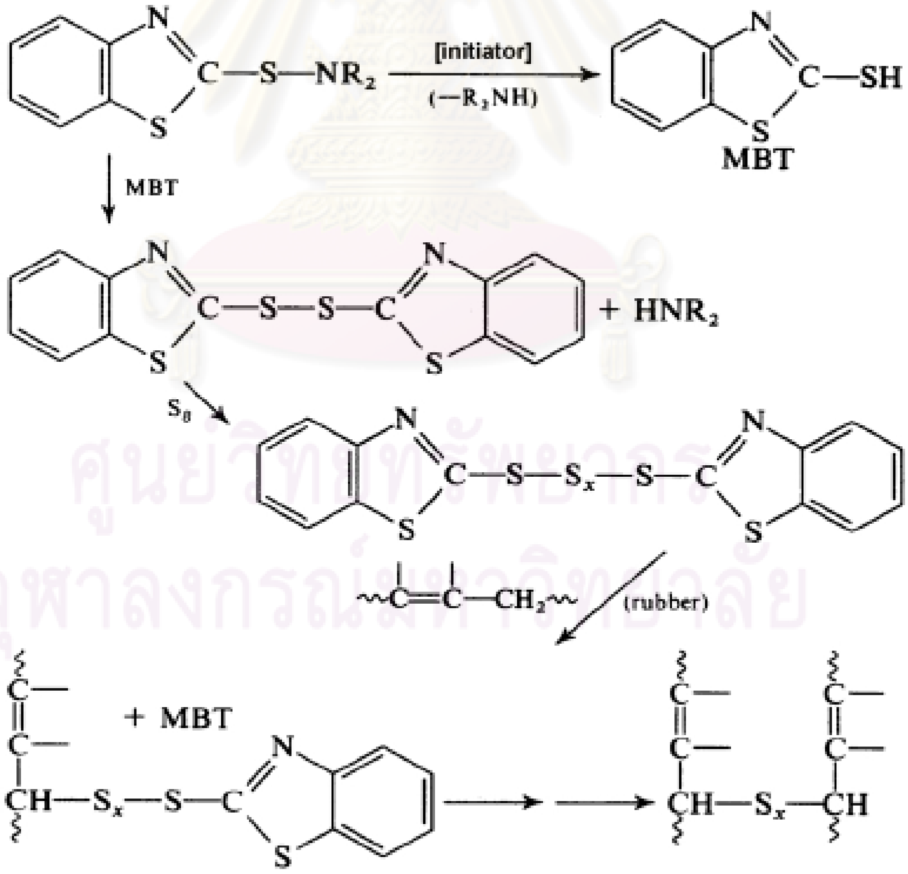
Initially, vulcanization was accomplished by using elemental sulfur at a concentration of 8 parts per 100 parts of rubber (phr). It required 5 hours at 140°C.The addition of zinc oxide reduced the time to 3 hours. The use of accelerators in concentrations as low as 0.5 phr has since reduced the time to as short as 1 to 3 minutes. As a result, elastomer vulcanization by sulfur without accelerator is no longer of much commercial significance. Even though unaccelerated sulfur vulcanization is not of commercial significance, its chemistry has been the object of much research and study. The chemistry of unaccelerated vulcanization is controversial. Many slow reactions occur over the long period of vulcanization. Some investigators have felt that the mechanisms involved free radicals as shown in scheme 2.1.



Scheme 2.1 Vulcanization of NR crosslinking via free radicals.

2.3.4 Accelerated Sulfur Vulcanization

Vulcanization by heating with sulfur alone is a very inefficient process with approximately 40-50 sulfur atoms incorporated into the polymer per crosslink. Sulfur is wasted by the formation of long polysulfide crosslinks, vicinal crosslinks, and intramolecular cyclic sulfide structures. Commercial sulfur vulcanizations are carried out in the presence of various additives, referred to as accelerators, which greatly increase the rate and efficiency of the process. The most used accelerators are sulfenamide derivatives of 2- mercaptobenzothiazole (MBT). Actually, the use of accelerators alone as illustrated in scheme 2.2 usually gives only small increases in crosslinking efficiency. Maximum efficiency is achieved by using accelerators together with a metal oxide and fatty acid. The latter substances are referred to as the activator. Zinc oxide and stearic acid are the most commonly used. The fatty acid solubilizes the zinc oxide by forming the zinc carboxylate salt. Vulcanization is achieved in minutes using the accelerator–activator combination compared to hours for sulfur alone. Analysis of the crosslinked product showed a large decrease in the extent of the wastage reactions. The crosslinking efficiency in some systems is increased to slightly less than two sulfur atoms per crosslink. Most of the crosslinks are monosulfide or disulfide with very little vicinal or cyclic sulfide units.



Scheme 2.2 Acceleration of NR vulcanization**.**

2.4 Composite

The word “composite” in composite material signifies that two or more materials are combined to form a useful material. The advantage of composite is that it usually exhibits the best qualities of its constituents and often some qualities that neither constituent possesses [26]. The properties that can be improved by forming a composite material include:

- strength
- stiffness
- corrosion resistance
- wear resistance
- attractiveness
- weight
- fatigue life
- temperature-dependent behavior
- thermal insulation
- thermal conductivity
- acoustical insulation
- adsorption

2.4.1 Composition of Composite Materials

2.4.1.1 Matrix

Matrix, that is continuous phase, is a major constituent into which the reinforcement is embedded. It holds reinforcing material together and also determines the physical properties of the end products. In structural applications, the matrix is usually a light metal such as aluminium or titanium, which is added by fiber glass reinforcing material. The composite obtained is used for automobile part to reduce weight of vehicle. Moreover, the other matrix can be ceramics, polymers, and wood.

2.4.1.2 Reinforcing Materials

The reinforcing materials are embedded into the matrix. They can normally enhance stiffness, strength and sometimes improve toughness. Properties of composite are directly related to their atomic arrangement and their content. The particle reinforcing materials are arranged in matrix as fiber, they can improve strength higher than wide dispersed in composite. Different shapes of reinforcing materials are as follows:

- fiber/filament
- needle
- globular
- woven
- aggregate
- platelet
- flake
- particulate

Reinforcing materials are classified according to their shapes. For example, fiber reinforcing materials and particulate reinforcing materials.

2.4.2 Classification and Characteristics of Composite Materials

There are three commonly accepted types of composite materials:

(A) Fibrous composites (Figure 2.5)
(B) Laminate composites (Figure 2.6)
(C) Particulate composites (Figure 2.7)

2.4.2.1 Fibrous Composites

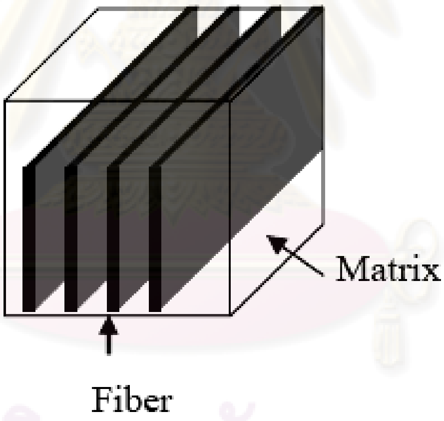


Figure 2.5 Fibrous composite structure.

Fibrous composites consist of fibers of high strength and modulus embedded in or bonded to a matrix with distinct interfaces between them. Long fibers are inherently much stiffer and stronger than the same material in bulk. For example, plain plate glass fractures at stresses of only a few thousand psi; however, glass fibers have strengths of 400,000 to 700,000 psi in commercial fiber and about 1,000,000 psi in laboratory fiber. The geometry of a fiber is crucial and must be considered in applications. Moreover, the fiber has lower paradox than the bulk; since, the crystals are aligned in the fibers.

2.4.2.2 Laminate Composites

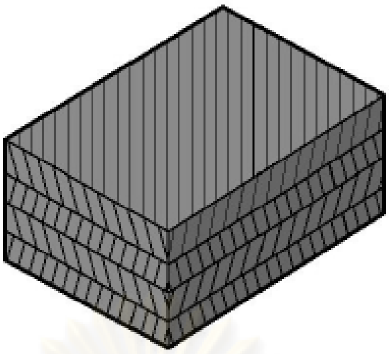


Figure 2.6 Laminate composite structure.

Laminate composites consist of layers of at least two different materials that are bonded together. Lamination is used to combine the best features of the constituent layers in order to achieve a more useful material. The properties that can be enhanced by lamination are strength, stiffness, low weight, corrosion resistance, wear resistance, beauty or attractiveness, thermal insulation, acoustical insulation, etc.

2.4.2.3 Particulate Composites

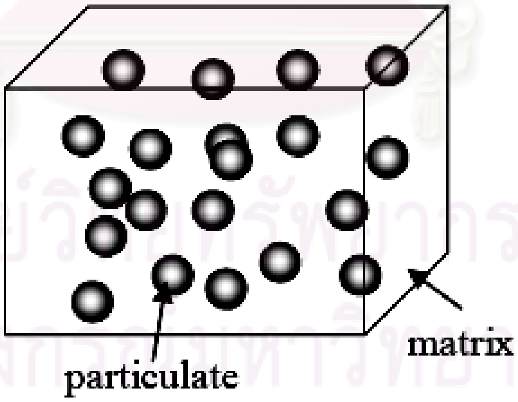


Figure 2.7 particulate composite structures.

Particulates are the cheapest reinforcing materials. Particulate composites consist of particulates of one or more materials regularly suspended in the matrix. Hence, these composites are isotropic; that is, they have the same mechanical properties in all directions [27].

2.4.3 Filler properties [28]

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

2.4.3.1 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 reinforce. 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-reinforce 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.

2.4.3.2 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.

2.4.3.3 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 blacks and precipitated inorganic used for reinforcement have generally round primary particles but function as anisometric (needle-like) aggregates.

2.4.3.4 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.

2.5 Silica Materials

Silica is an inorganic polymer with the general structural formula of $(SiO2)_n$. Typically, silica can be classified according to the International Union of Pure and Applied Chemistry (IUPAC) in three types depending on its pore size [29].

1. Microporous silica with pore diameter smaller than 2 nm.
2. Mesoporous silica with pore diameter between 2 and 50 nm.
3. Macroporous silica with pore diameter larger than 50 nm.

Silica was used as the reinforcing filler. Silicon dioxide or silica is particularly the main component of the crust of the earth. Combined with the oxides of magnesium, aluminum, calcium, and iron, it forms the silicate minerals in our rocks and soil. The general formula of silica is $SiO_2 \cdot xH_2O$. Due to its properties such as chemical resistance, high thermal and mechanical stability, silica is thus widely used as reinforcing filler in rubber. There are essentially two types of silica commonly used as reinforcing filler [30].

2.5.1 Type of Silica

2.5.1.1 Precipitated Silica

Silica used as reinforcing fillers is mainly obtained by precipitation. The process basically consists in the preparation of a silica glass by alkaline fusion of pure sand and an alkaline salt. Then this glass is solubilized in water at high temperature and acid precipitated. The silica suspension obtained is then filtered, washed, and dried. In order to obtain reinforcing silica, much care must be taken in precipitation recipes to obtain small rigid objects and drying conditions to maintain high dispersibility.

2.5.1.2 Fumed Silica

Fumed silica is obtained by high temperature oxydecomposition of SiH_4, or other methyl hydride precursors ($SiHMe_3$, SiH_2Me_2) Coming out of the furnace, fumed silica was obtained in a fluffy form, and because of their high temperature of formation, they present a very stable morphology and few surface silanols compared to precipitation silica. This confers a high dispersibility and reactivity to fumed silicas but, because of their higher price, they are rarely used in the rubber industry.

$$nSiH_4 + 2nO_2 \rightarrow nSiO_2 + 2nH_2O$$

The structure of silica particle (as seen in Figure 2.8) is containing siloxane bond (Si-O-Si) and silanol group (Si-OH). The latter can be divided into three types: vicinal, geminal and isolated silanol. Vicinal or H-bonded or associated silanols are Si-OH groups. Geminal silanols are silanediols groups. An isolated silanol includes an OH group located at a distance sufficiently far from neighboring hydroxyl groups to prevent hydrogen bonding as shown in Figure 2.9.

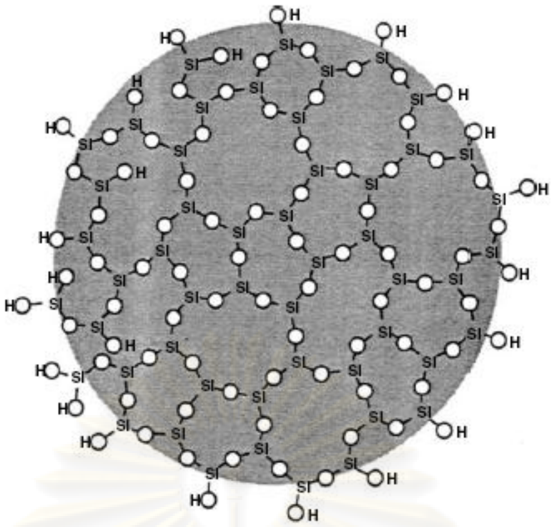


Figure 2.8 Structure of silica particle [24].

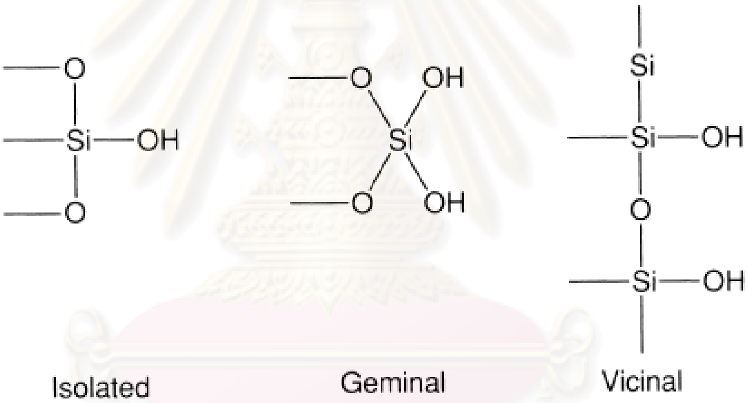


Figure 2.9 Typical silanol groups on silica [24].

The dispersion and the distribution of silica are generally recognized to be determined by the state of aggregation and agglomeration, which are schematically shown in Figure 2.10. Aggregates are three-dimensional clusters of ultimate particles, covalently bonded to one another via siloxane bonds. Aggregates can physically agglomerate through intermolecular hydrogen bonding of surface silanol groups of one aggregate to a silanol group of other aggregate [31].

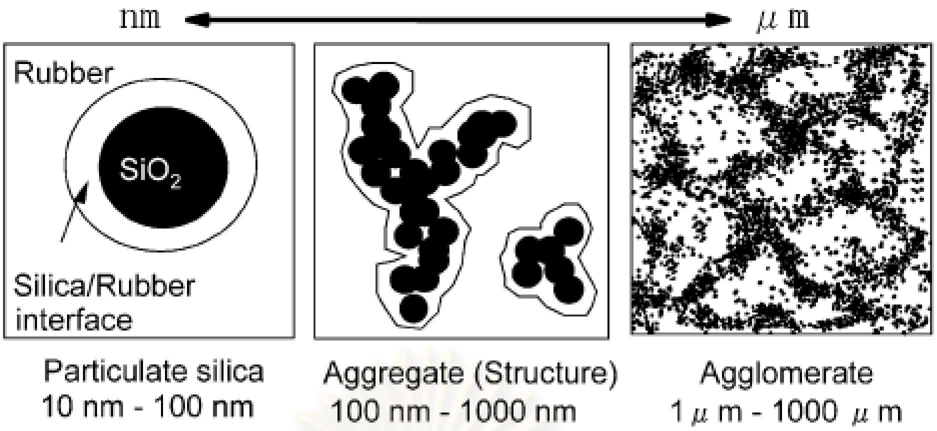


Figure 2.10 Sketches of a primary particle, aggregates and agglomerate occurring in silica [31].

2.5.2 Sol-Gel Process [32]

The sol-gel process may be described as "formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid". A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid. A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel, the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved. Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films as shown in Figure 2.11.

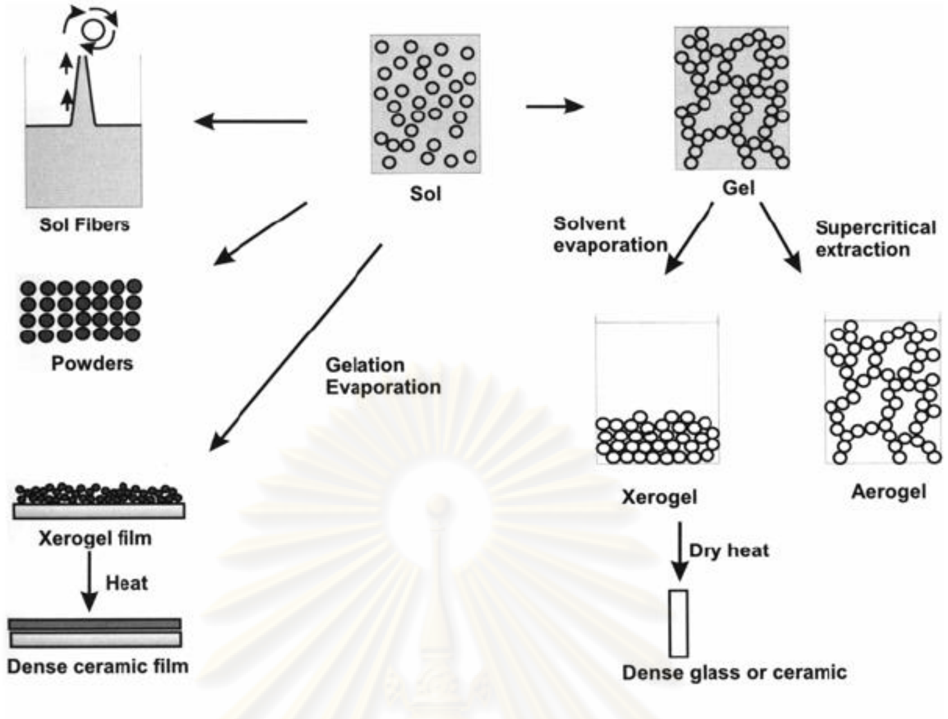
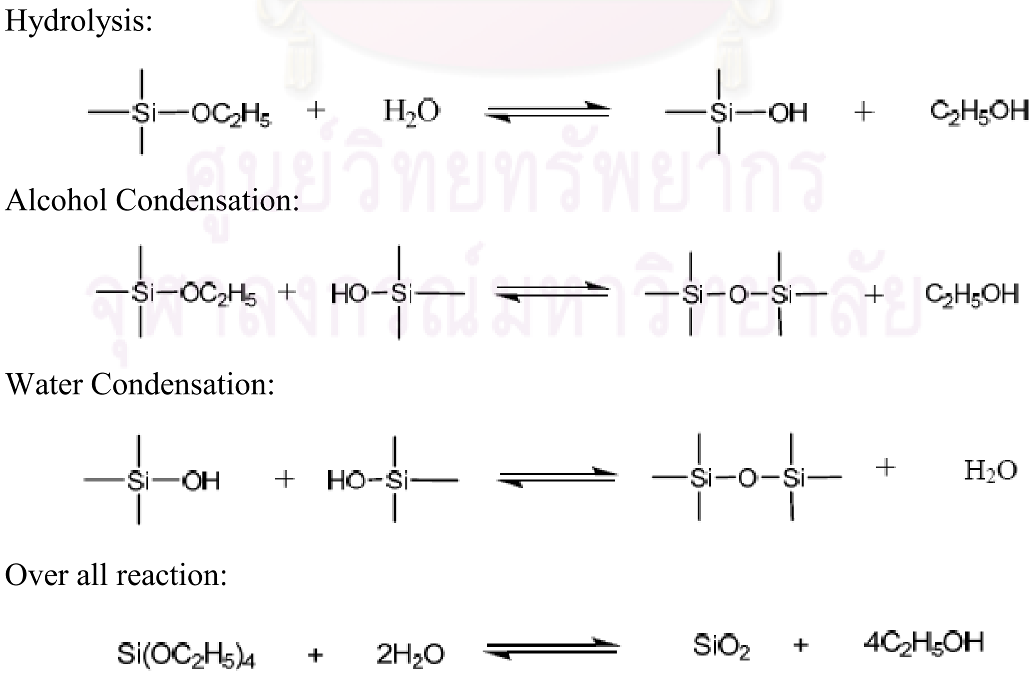


Figure 2.11 Sol-gel process options [25].

The sol-gel reaction takes place into two steps of hydrolysis and followed by the condensation reactions. Water and alcohol are the by-products of the sol-gel reaction as shown in Scheme 2.3.



Hydrolysis:

Alcohol Condensation:

Water Condensation:

Over all reaction:

$Si(OC_2H_5)_4 + 2H_2O \rightleftharpoons SiO_2 + 4C_2H_5OH$

Scheme 2.3 Hydrolysis and condensation reactions of TEOS to form silica [32].

2.5.3 Parameters which Influence the Sol-Gel Process

2.5.3.1 Types of Precursor

The stability and reactivity of the silicon alkoxides are influenced by a steric factor. The hydrolysis reaction was slow down by bulky ligands. Reactivity of different type of precursors are as follows:

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

2.5.3.2 The Ratio between Alkoxide and Water (RW)

The reaction states that a water ratio of RW = 2 (OR/H_2O) 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.

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH$$

2.5.3.3 Types of Catalyst Used

The dependence of the reaction rate with pH is different for acid and base catalyzed systems as shown in Figure 2.12. The polymerization process is divided into three approximate pH domains: <pH 2, pH 2-7, and pH>7. 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. 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 ionized above pH 7 so that particle growth occurs without aggregation or gelation.

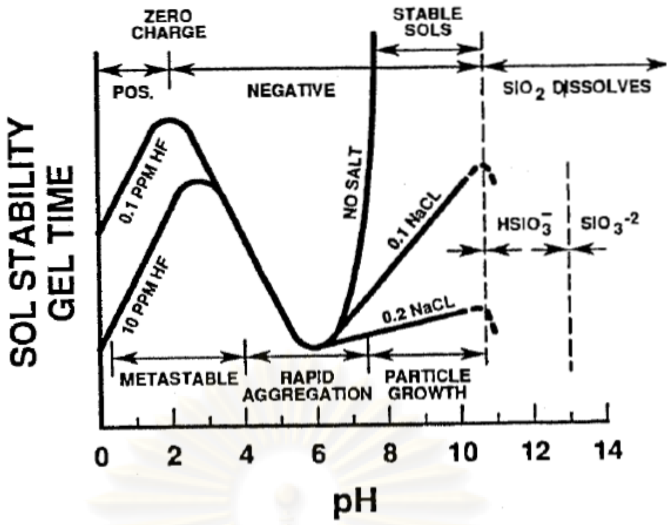


Figure 2.12 Effect of pH in the colloidal silica-water system [32].

2.5.3.4 Types of Solvent

The polarity, dipolar moment, viscosity, 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.

2.6 Literature Reviews

Yamamoto and Ohata [33] studied on the new macromolecular silane coupling agents synthesized by living anionic polymerization. Well-defined end-triethoxysilylated poly (styrene)s and poly (tert-butylmethacrylate)s were successfully prepared by living anionic polymerization. End-triethoxysilyl groups of these polymers were hydrolyzed by acidic and basic catalysts and then converted to silanol groups. These polymers were grafted onto inorganic particles such as silica, alumina and titania by a favorable choice of catalyst. The graft inorganic powders were finely dispersed in a medium having a strong affinity for the graft chain. The surface properties such as surface tension of the graft inorganic materials were the same as the properties of the graft polymers. The properties were easily changed through treatment of the graft polymer chain.

Arayapranee et al. [5] studied on the synthesis of graft copolymers from NR using CHPO redox initiator. The graft copolymerization of ST and MMA mixtures onto NR seed latex using the redox initiation system is dependent on the main process factors such as the amount of initiator, emulsifier, and chain-transfer agent; monomer-to-rubber ratio; and temperature. An increase in the concentration of initiator up to 2 phr increased both the grafting efficiency and grafting level. The grafting yield increased with increasing temperature up to 70°C and then decreased, suggesting that a large amount of free radicals, produced at higher temperature, may combine by themselves. The emulsifier amount has a small effect on grafting ST and MMA onto NR. The grafting efficiency decreased as monomer to rubber ratio increased, indicating that the graft copolymerization occurs on the surface of the latex particles. The grafting decreased as the amount of chain-transfer agent increased because of the decrease of macroradical formation.

Xavier et al. [34] studied on the thermoplastic ionomers based on ST-g-NR. Zinc neutralized sulfonated ST-g-NR (SGNR) could be prepared by reacting ST-g-NR with acetyl sulfate followed by neutralization of the sulfonic acid with zinc acetate. The analytical techniques: X-Ray Fluorescence Spectroscopy (XRFS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), respectively showed that the acetyl sulfate conversion is about 32% and the neutralization of the sulfonic acid is 96%. Thermogravimetric analysis studies showed the improved thermal stability of the ionomer. It also revealed that thermal stability increased with increasing ionic content of the polymer. The modified SGNR has tensile strength about ten times the strength of unvulcanised graft copolymer.

Chuayjuljit et al. [35] studied on the use of natural rubber-*g*-polystyrene (NR-g-PS) as a compatibilizer in casting NR/PS blend films. NR/PS blend films with weight ratios of 70/30, 60/40, and 50/50 were prepared using NR-*g*-PS as the compatibilizer. Copolymers with molar ratios of 90/10, 80/20, and 70/30 were synthesized via emulsion copolymerization using *tert*-butyl hydroperoxide (t-BuHPO)

/tetraethylene pentamine (TEPA) as an initiator. The copolymers were subsequently added into the blends at 0, 5, 10, 15, 20, 25, and 30 phr. The film prepared from 80/20 NR-*g*-PS showed higher tensile and tear strength, as well as finer domain size of the dispersed phase, than those prepared from 90/10 and 70/30 NR-*g*-PS. However, the mechanical properties of the films were decreased at high loading of the copolymers.

Arayapranee and Rempel [36] studied on the preparation of a NR core/polymer shell in a nanomatrix by graft copolymerization. The graft copolymerization of a vinyl monomer onto NR seed latex with a redox initiation system was dependent on the main process factors, including the reaction time, amount of initiator, and amount and type monomer. Graft efficiency (GE) dramatically increased with increasing reaction time up to 5 h and then hardly varied. GE increased with increasing amount of initiator up to 5.0×10^{-2} mmol/g of rubber and then decreased marginally, which suggested that an excess of free radicals may have combined by themselves and lessened the chain length of the grafts. GE decreased as monomer content increased, which indicated that the graft copolymerization occurred on the surface of the latex particles. The results showed that the GE of the ST graft NR was higher than that of the MMA graft NR under the same conditions. The difference between the GE of the ST graft NR and that of the MMA graft NR was due to the nature of the monomer.

Ikeda et al. [37] studied on the preparation of high performance nanocomposite elastomer and effect of reaction conditions on *in situ* silica generation of high content in NR. The effects of amine catalyst and its reaction condition on the sol-gel reaction of TEOS in the uncrosslinked NR matrix were investigated in detail aiming to obtain a high *in situ* silica generation in NR. The primary alkylamines with pertinent hydrocarbon segments, i.e., n-hexylamine, n-heptylamine and n-octylamine, gave the high contents up to ca. 80 phr of homogeneous *in situ* silica particles in NR matrix with fairly homogeneous dispersion within the reaction time of ca.10 h. The amount of *in situ* silica increased with the increase of concentration of n-hexylamine. Due to the higher solubility in water, n-hexylamine was found to be the most preferable catalyst for the effective *in situ* silica generation.

Tangpasuthadol et al. [38] studied on the silica-reinforced NR prepared by the sol-gel process of ethoxysilanes in rubber latex. Silica can be generated successfully by the sol–gel process of TEOS mixed with commercial concentrated NR latex at

508C. Statistical analysis of the data showed that the TEOS content had the most significant effect on the mechanical properties. It was also found that 0.7% ammonia content present in the commercial-grade concentrated latex was sufficient to initiate the sol–gel process of the silane. Therefore no additional ammonia was required to add to the latex with the resultant benefits in costs and time saving in the preparation of NR composite reinforced by *in situ* generated silica.

Siramanont et al. [39] studied on the sol-gel process of alkyltriethoxysilane in latex for alkylated silica formation in NR. The preparation of composite containing *in situ* generated silicas and alkylated silica can be achieved by the use of commercially available concentrated NR latex with 0.7% ammonia. The alkylated silica particles were formed in the rubber matrix by a certain combination of TEOS and alkyltriethoxysilanes containing vinyl, ethyl, or butyl functional group. The silane conversion to silica in the NR matrix was almost complete for TEOS, but decreased when the alkyl group of the alkyltriethoxysilanes increased in size. The alkylated silicas were well dispersed in the NR matrix with the size of less than 100 nm, and not depending on the silane types. The uses of *in situ*-generated silica and alkylated silicas resulted in a better reinforcement capability to the rubber vulcanizates than did the conventionallyadded silica powder. Among the three alkyltriethoxysilanes, VTOS seemed to be the most promising silane that was able to enhance the tensile modulus and resistance to tear of the rubber vulcanizates.

Chaichua et al. [40] studied on the *in situ* silica reinforcement of NR by sol–gel process via rubber solution. The effects on the curing, mechanical, dynamic mechanical and thermal properties were found to significantly change. The Mooney viscosity and curing time both increased with increasing *in situ* silica contents and were lower than that of the commercial silica filled vulcanizate for the same level of silica. The moduli (M_{50}, M_{100}, and M_{300}) and compression set of *in situ* silica filled NR vulcanizates was also improved compared with the commercial silica filled ones. The storage modulus at 25 °C suggested that the silica– silica interaction of the *in situ* silica was weaker, resulting in a better dispersion in the rubbery matrix, compared with the commercial silica. Thus, in conclusion due to the overall characteristics of the *in situ* silica generated using TEOS, this sol–gel reaction via NR solution was more useful and practical for industrial-scale synthesis than via NR latex.

CHAPTER III
EXPERIMENTALS

3.1 Chemicals

Chemicals	Company
1. High ammonia NR latex (solids content of 60%)	Thai Rubber Latex Corp. Co. LTD., Thailand
2. Styrene monomer (A.R grade)	Siam Chemical Industry, Thailand
3. Sodiumdodecyl sulfate (A.R grade)	Ajax Finechem, Australia
4. Potassium hydroxide (A.R grade)	Ajax Finechem, Australia
5. Iso – propanol (A.R grade)	Ajax Finechem, Australia
6. Cumene hydroperoxide (A.R grade)	Merck, Germany
7. Tetraethylene pentamine (A.R grade)	Merck, Germany
8. Sodium hydroxide (A.R grade)	Ajax Finechem, Australia
9. Tetraethoxysilane (A.R grade)	Fluka, USA
10. Active zinc oxide (Commercial grade)	Pan Innovation Ltd., Thailand
11. Stearic acid (Commercial grade)	Imperial Industrial Chemicals Co. Ltd., Thailand
12. Polyethylene glycols (Commercial grade)	Pan Innovation Ltd., Thailand
13. Mercaptobenzothiazole disulfide (Commercial grade)	Pan Innovation Ltd., Thailand
14. Silica (Hisil-255)	PPG-Siam Silica Co., Ltd., Thailand
15. n-hexylamine (A.R grade)	Sigma - Aldrich

3.2 Equipments

1. Beaker, 50, 100, 250, 600, 1,000 mL
2. Round bottom flask, 250 mL
3. Soxhlet extractor
4. Heating mantle
5. Hotplate and magnetic stirrer
6. Overhead stirrer
7. Condenser
8. Magnetic bar
9. Dropper
10. Stirring rod
11. Water pump
12. Water bath
13. Thermometer
14. Apparatus for graft copolymerization reaction as seen in Figure 3.1

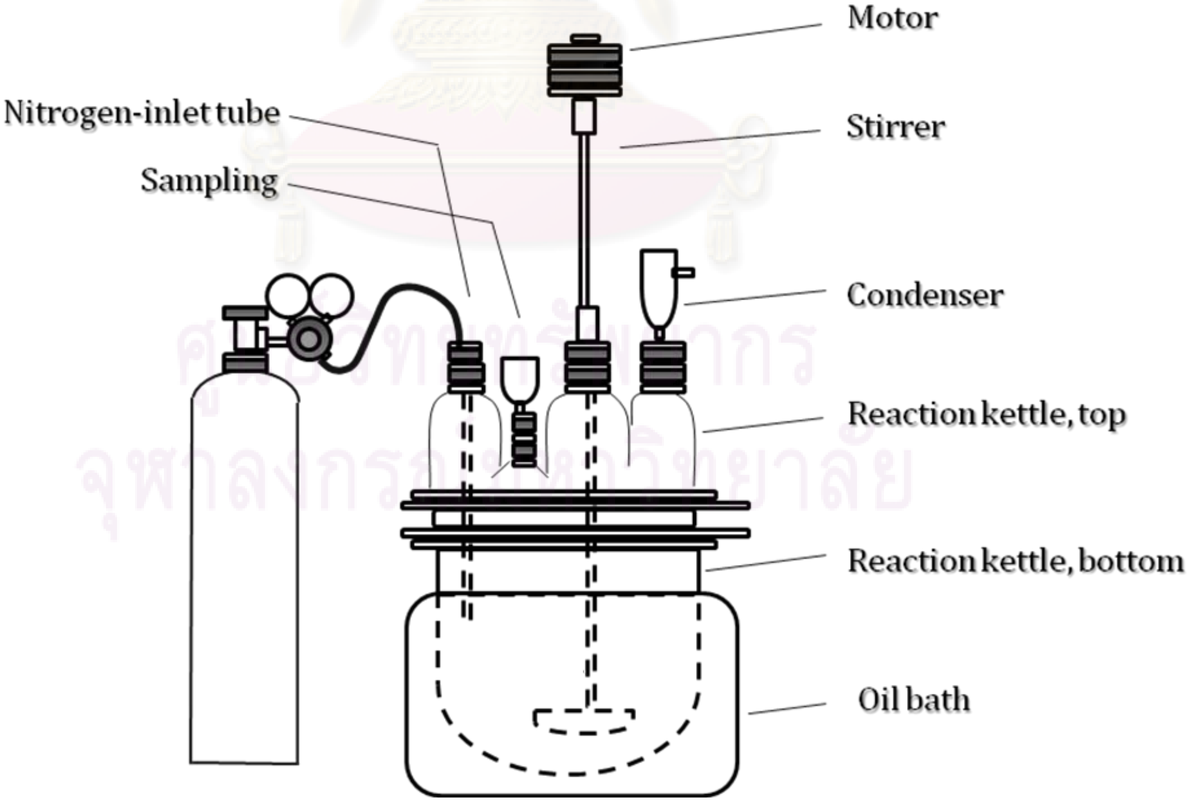


Figure 3.1 Apparatus set up to synthesize the graft copolymer.

3.3 Procedure

In this study, ST-g-NR was synthesized and modified with TEOS. ST-g-NR was modified by using 2 methods, “solid rubber” and “latex solution”. Modified ST-g-NR was then vulcanized, and finally, the mechanical properties of vulcanized graft copolymer were investigated. The overall procedures used in this study are showed in Figure 3.2.

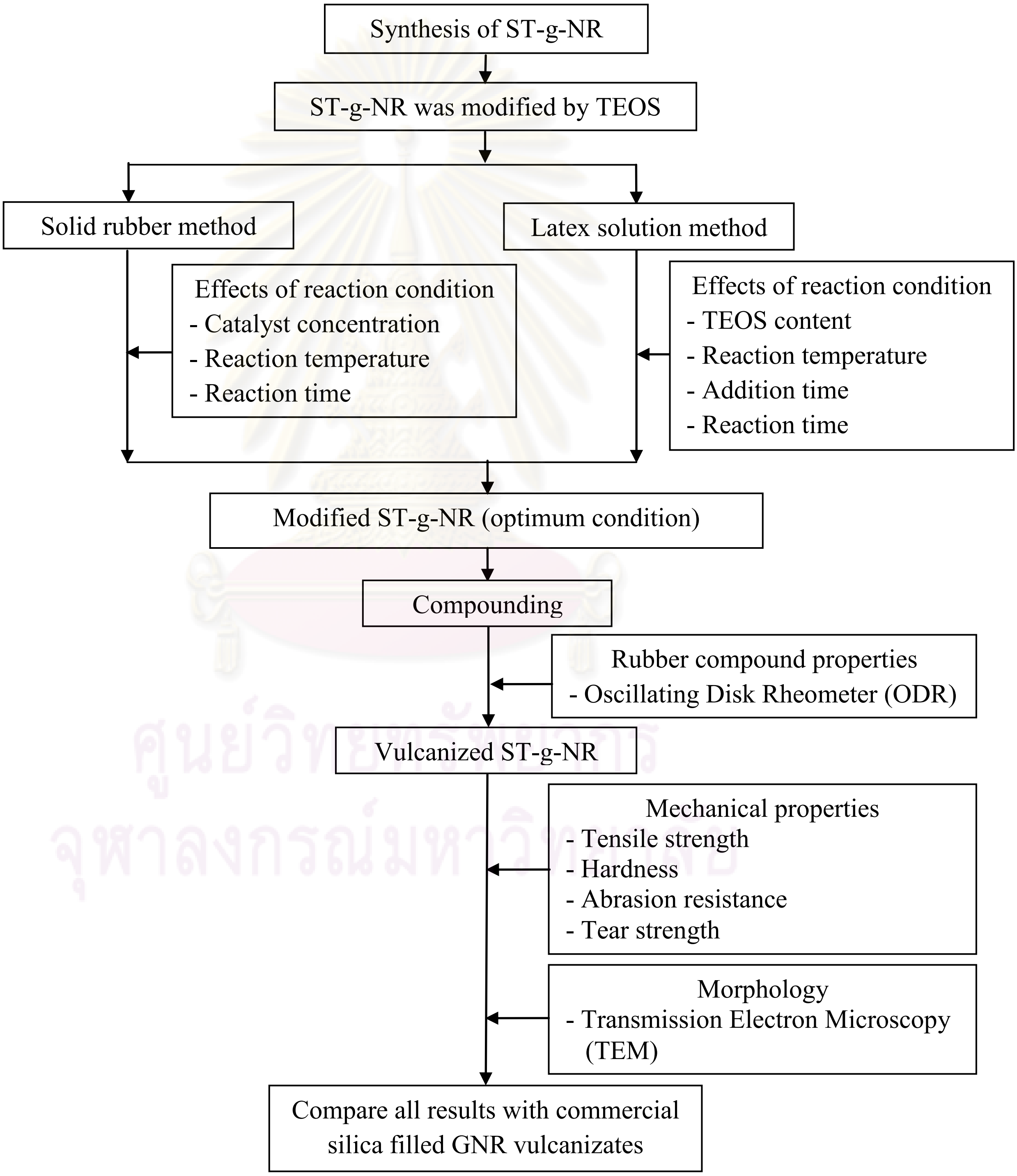


Figure 3.2 Overview procedures.

3.3.1 Purification of Styrene Monomer

Styrene monomer was washed to eliminate inhibitor with 10% sodium hydroxide and followed by deionized water until the pH of solution was equal 7. Then, sodium sulfate anhydrous was added and solution was evaporated in order to remove water. Finally, styrene monomer was contained in amber glass bottle and keep at 0 -10 °C.

3.3.2 Synthesis of ST-g-NR

The NR latex and deionized water were charged to the reactor (Figure 3.10). After that, potassium hydroxide (as a buffer), sodiumdodecyl sulfate (as an emulsifier) and iso-propanol (as a stabilizer) were fed into a reactor, respectively. The recipe for the preparation of ST-g-NR is represented in Table 3.1. Dissolved oxygen in reactor was removed by purging nitrogen gas for 30 min through the mixture. The ST and tetraethylene pentamine (TEPA) as an activator agent were fed into the reactor. The redox initiation system, consisting of cumene hydroperoxide (CHPO) and TEPA at a ratio of 1: 1, was used. The NR latex was swollen with the monomer for 30 min at 50°C before the initiator CHPO was added. The polymerization reaction was performed at a stirring speed of 200 rpm for 8 h. The preparation procedure was shown in Figure 3.3.

Table 3.1 Recipe for the preparation of ST-g-NR [4]

Materials	Content (g)
NR latex	100
Water	200
Iso-propanol	3
Potassium hydroxide	0.3
Sodiumdodecyl sulphate	0.9
Styrene monomer	60
TEPA	1.2
CHPO	1.2

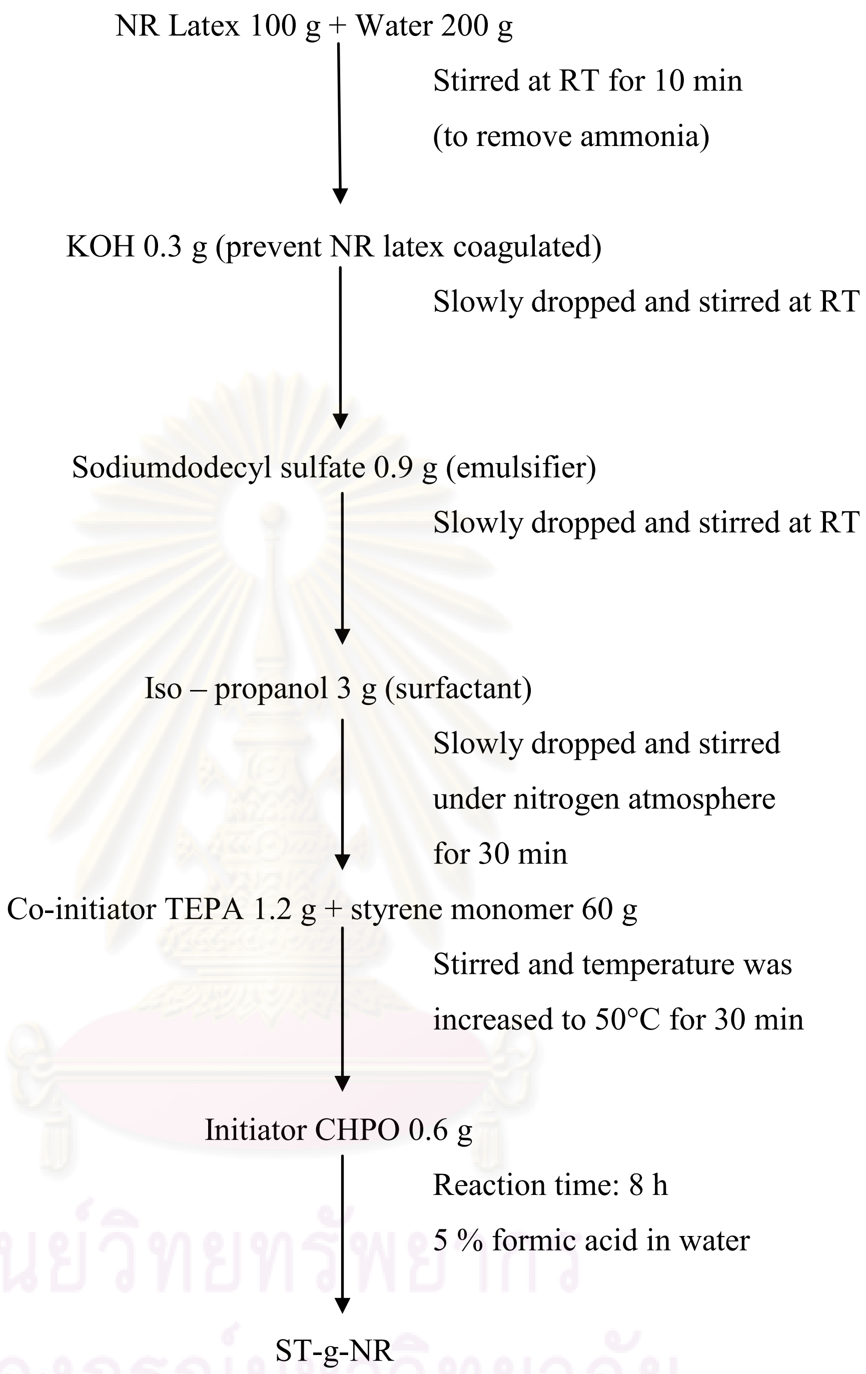


Figure 3.3 Preparation of ST-g-NR by using CHPO/TEPA initiation.

3.3.3 Modified ST-g-NR by TEOS via Sol – Gel Process in Solid Rubber

3.3.3.1 Swelling Degree of ST-g-NR

The swelling times used for immersing ST-g-NR in TEOS at 40°C and room temperature were varied to determine the suitable swelling degree. The ST-g-NR sheets of 1.5 mm x 1.5 mm x 1 mm were prepared by a two – roll mill. The rubber sheets were immersed in TEOS at various times in range of 1 – 24 h at 40°C and room temperature. Table 3.2 present the conditions to find the maximum degree of swelling of graft copolymer in TEOS at 40°C and room temperature. All calculations were presented in Appendix A.1.

Table 3.2 Conditions for swelling of ST-g-NR in TEOS

Experiments	Temperature (°C)	Time (step one) (h)	Swelling degree (%)	Time (step two) (h)	Swelling degree (%)
ST 1	40 and 30	1 and 24	195	1 and 1	89
ST 2	40 and 30	2 and 24	192	1 and 2	142
ST 3	40 and 30	4 and 24	206	1 and 4	177
ST 4	40 and 30	8 and 24	210	1 and 8	185
ST 5	40 and 30	12 and 24	212	1 and 12	191
ST 6	40 and 30	16 and 24	220	1 and 16	196
ST 7	40 and 30	20 and 24	223	1 and 20	197
ST 8	40 and 30	24 and 24	229	1 and 24	201
ST 9	40 and 30	30 and 24	228	1 and 30	198

3.3.3.2 *In Situ* Generation of Silica in ST-g-NR Matrix

The flowchart of preparation of ST-g-NR by using solid rubber method is shown in Figure 3.4. ST-g-NR sheets of ca. 1 mm were prepared by two-roll mill. The rubber sheets of 70 mm x 70 mm x 1 mm were immersed in TEOS at 40 °C for 1 h and at room temperature for 16 h in a container. The swollen sheets were then immersed in aqueous solution of n-hexylamine. Catalyst concentration and temperature of sol-gel reaction were varied according to Table 3.3. Rubber sheets were sampling at 1, 2, 3, 4 and 5 days after immersion in catalyst solution. Finally, the rubber sheets were dried under vacuum at 40°C until the weight of sample was constant. All calculations were presented in Appendix A.2 – A.4.

Table 3.3 Experimental variables for sol-gel reaction in solid rubber

Experiment	Swelling in TEOS		Sol-gel in n-hexylamine	
	Temperature (^{0}C)	Time (h)	Concentration of catalyst (mol/l)	Temperature (^{0}C)
1	40 and 30	1 and 16	0.064	40
2	40 and 30	1 and 16	0.008	40
3	40 and 30	1 and 16	0.064	50
4	40 and 30	1 and 16	0.008	50

3.3.4 Modified ST-g-NR by TEOS via Sol – Gel Process in Latex Solution

The flowchart of preparation of ST-g-NR by using latex solution method is shown in Figure 3.4. The reaction temperature, TEOS content and addition time of TEOS were varied to investigate the effect of reaction conditions on *in situ* silica content. The conditions of the sol–gel reaction of TEOS in ST-g-NR are summarized in Table 3.4. For investigating the effect of addition time of TEOS on the *in situ* silica content, TEOS was added into reactor before starting graft copolymerization reaction (before N_2 was purged) and after finishing graft copolymerization reaction as seen in Figure 3.5. The effect of TEOS on graft copolymerization reaction was also investigated. The modified ST-g-NR was sampling at 1, 2, 3, 4 and 5 days after TEOS was added.

Table 3.4 Experimental variables for sol-gel reaction in latex solution

Experimental	Variables		
	TEOS content (phr)	Temperature (°C)	Addition time of TEOS
1	10	50	B[a]
2	20	50	B
3	10	60	B
4	20	60	B
5	20	50	A[b]
6	40	50	A
7	60	50	A
8	80	50	A

[a] Before starting graft copolymerization reaction

[b] After finishing graft copolymerization reaction

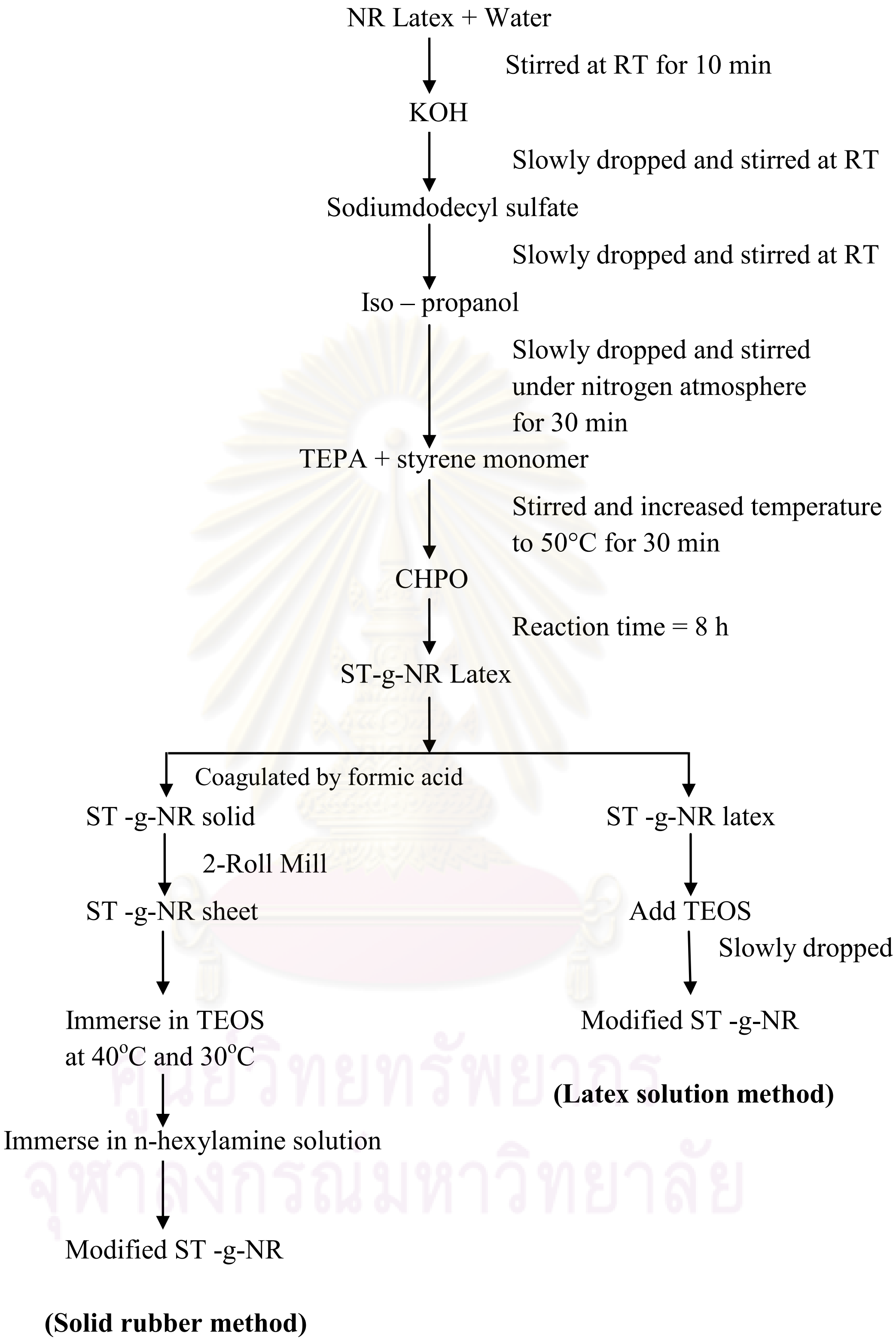


Figure 3.4 Preparation of modified ST-g-NR by using solid rubber and latex solution methods.

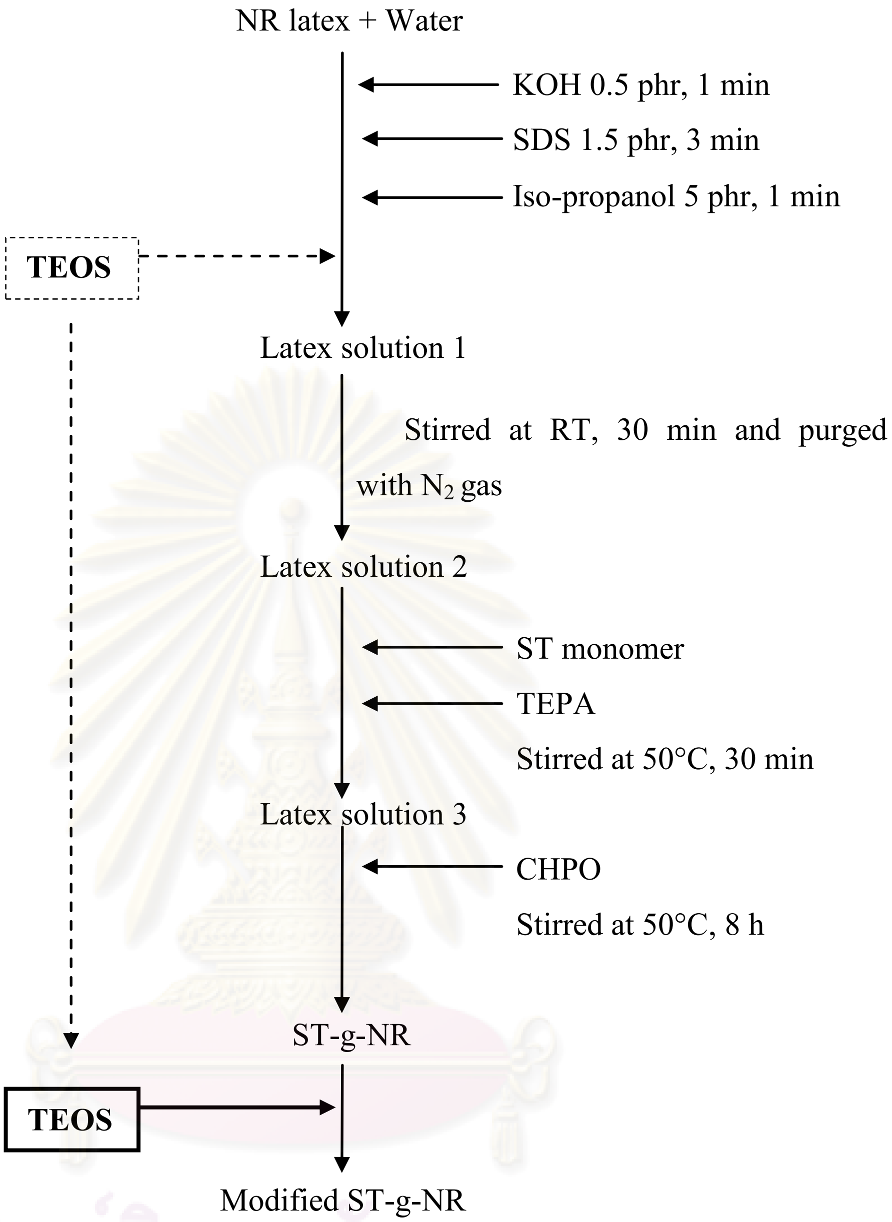


Figure 3.5 Comparative procedures of two addition methods of TEOS in sol-gel reaction.

3.3.5 Sulfur Vulcanization

The recipe of compounds is shown in Table 3.5. Modified or non-modified ST-g-NR was blended with NR until the surface of blend was smooth. Then, rubber blend was mixed with active zinc oxide, stearic acid, mercaptobenzothiazole disulfide (MBTS), polyethylene glycols (PEG) and sulfur, respectively. The obtained rubber sheet was then compressed into a square-shape at 150°C and a pressure of 150 kg/cm^2. Vulcanized rubber sheets of about 2 mm thick were obtained. The cure time (t_{90}) was determined by Oscillation Die Rheometer. In this study, modified or non-modified ST-g-NR vulcanizates with *in situ* silica and commercial silica were represented by "In" and "Si", respectively. The silica content in a part by weight per hundred part of rubber (phr) was indicated by the number after the sample code. Modified ST-g-NR with solid rubber and latex solution method were represented by "S" and "L", respectively after the number of silica content.

Table 3.5 Formulations for rubber compounding in parts by weight per hundred parts

Ingredients	NR-V	GNR-V	Si-12	In-12-S	In-12-L	In-25-S
NR	100	50	50	50	50	50
ST-g-NR	-	50	50	-	-	-
In situ filled ST-g-NR	-	-	-	62	62	75
Conventional silica	-	-	12	-	-	-
Active zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
MBTS[a]	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	3	3	3	3	3	3
PEG[b]	-	-	0.40	0.40	0.40	0.83

[a] Mercaptobenzothiazole disulfide

[b] Polyethylen glycol

3.4 Characterization

3.4.1 Soxhlet Extraction

Amount of homopolymer (PS), graft NR and free NR in product was determined by solvent extraction. The free NR was extracted by light petroleum at 60-80°C for 24 h. The residue was dried in an oven at 40°C until weight constant. To remove homopolymer, the residue was further extracted in methyl ethyl ketone at 80°C for 24 h. The percentage of free natural rubber, free homopolymer, grafted natural rubber, grafting efficiency (GE) and conversion of graft copolymerization were calculated by the following equations:

$$\text{Free natural rubber (\%)} = \frac{\text{Total weight of free natural rubber}}{\text{Total weight of the gross polymer}} \times 100 \quad (3.1)$$

$$\text{Free homopolymer (\%)} = \frac{\text{Total weight of free homopolymer}}{\text{Total weight of the gross polymer}} \times 100 \quad (3.2)$$

$$\text{Grafted natural rubber (\%)} = \frac{\text{Total weight of graft copolymer}}{\text{Total weight of the gross polymer}} \times 100 \quad (3.3)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Total weight of monomers grafted}}{\text{Total weight of the monomers polymerized}} \times 100 \quad (3.4)$$

$$\text{Conversion (\%)} = \frac{\text{Total weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \quad (3.5)$$

3.4.2 Characterization of Graft Copolymer

To determine the presence of ST-g-NR, the graft copolymer product was extracted by petroleum ether and methyl ethyl ketone, respectively. The obtained ST-g-NR was characterized by FTIR and ^{1}H-NMR. FTIR spectra were recorded on a Perkin Elmer FTIR spectrum RX-I Fourier Transform Infrared Spectrometer, Japan. ST-g-NR sample 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}. NMR spectra of ST-g-NR were taken in a Varain FTNMR spectrometer, UK operating at a proton resonance frequency of 400 MHz.

3.4.3 *In Situ* Silica Content

Modified ST-g-NR was carried out by using TG/DTA to determine *in situ* silica generated in ST-g-NR. TGA was carried out by using a Perkin Elmer Pyris Diamond Thermogravimetric/Differential thermal Analyzer, USA. A modified ST-g-NR sample (ca.10 mg) was placed in a platinum pan and heated under air at room temperature up to 1000^{o}C using the heating rate of 10^{o}C/min.

Silica content and the conversion of TEOS to silica were calculated by using equation (3.6) and (3.7), respectively [10].

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

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

$$\text{Conversion (\%)} = 100 \times (W_3/W_4) \qquad (3.7)$$

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

$$Si(OC_2H_5)_4 + 2H_2O \rightleftarrows SiO_2 + 4C_2H_5OH \qquad (3.8)$$

3.4.4 Morphology by Transmission Electron Microscopy (TEM)

The dispersion and particle size of the filler in NR vulcanizates are studied by using TEM. TEM observation was then carried out with a transmission electron JEOL JEM-2010, Germany. The accelerating voltage was 200 kV. Ultra thin films of the 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.

3.4.5 Mechanical Testing

Mechanical tests are performed routinely in materials laboratories and in industrial research laboratories. Because most tests result in destruction of the sample and because such tests do not have a high degree of reproducibility, multiples tests on similar samples are needed before valid results can be obtained [41].

3.4.5.1 Tensile Testing

Tensile testing is accomplished by first molding a flat sheet of rubber about 2 mm thick, from which dumbbell shaped pieces are die cut (as shown in Figure 3.6)

Figure 3.6 Dumbbell shaped test piece for tensile testing

The test pieces are then stretched in a tensile testing machine and the force required to stretch the samples is measured. Values of stress (force divided by the unstrecthed cross sectional area of the straight portion of the dumbbell) are recorded at various levels of extension, up to the break point. The extension is measured as percent elongation and is defined as:

$$\frac{L - L_0}{L_0} \; x \; 100$$

where: L is the stretched length and L_0 is the original length.

Tensile stress before the sample breaks, give the modulus of the sample. For the rubber chemist, modulus means the tensile value (stress) at a given elongation. Note that the modulus, as defined here for rubber is not equivalent to the modulus as understood by an engineer, which is equal to stress over strain [42]. In this study, the tensile properties of the vulcanized samples were measured according to ASTM D412 using Lloyd Universal Testing Machine LR 10 K PLUS, England at 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.

3.4.5.2 Hardness

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions which do not puncture the rubber. Hardness must be expressed in terms of instrument parameters rather than in basic units. The springloaded pocket durometer is the most common instrument for measuring hardness of elastomers. The shore durometer (ASTM D2240) in particular is generally used. In this instrument, the scale runs from zero hardness for a liquid to 100 for a hard plane surface such as glass. The type A durometer is used for soft stocks, up to a reading of 90. Above 90, the type D durometer having a different indentor shape and different stiffness spring is used. In this study, the hardness was measured according to ASTM D2240 using a Shore- type-A Lever Loader REX GAUGE 2000 & OS-2 Stand, UK. The reported values were an average of six measurements.

3.4.5.3 Abrasion Resistance [43]

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. Abrasion test results are known to be variable; therefore, it is important to control and standardize the abradant used in the test. It is also required to relate the test results to a standard reference vulcanizate. The rubber test piece with a holder traverses a rotating cylinder 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 build up on the abradant paper. In this study, abrasion resistance was measured by Happen Abrasion testing machine, England according to DIN 53516 (ZWICK) at room temperature. The cylindrical in shape of samples used was 16 mm in diameter and had a minimum thickness of 6 mm.

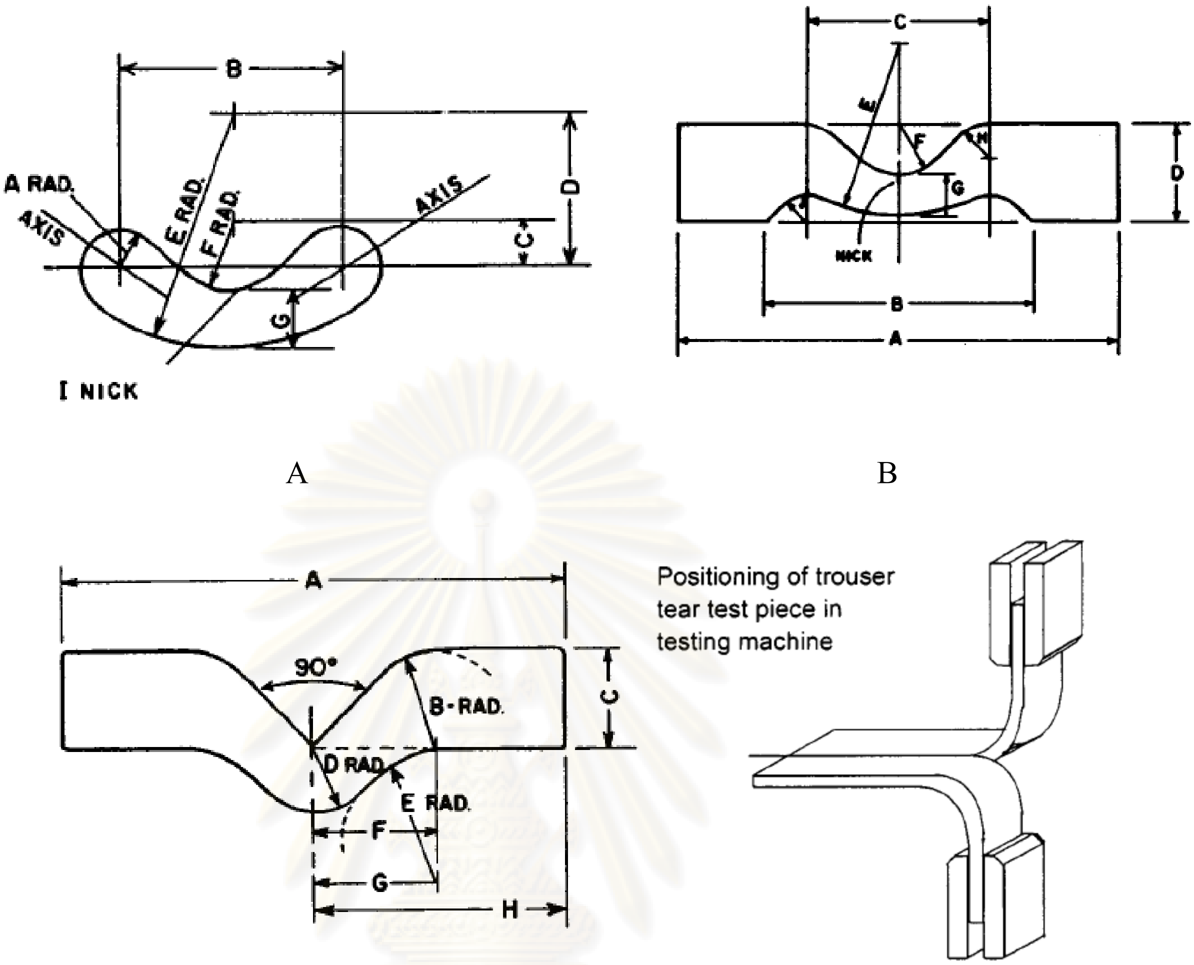
3.4.5.4 Tear Resistance

High stress concentration on a rubber product applied at a cut or defect area during service can lead to the propagation of a tear or rupture. Tear characteristics for a compound can be related to the compound's crosslink density and state of cure, as well as filler type and loadings. Various tear tests place a deliberate flaw in a rubber specimen to try to relate to the tear propagating force. Figure 3.7 shows the shapes of some commonly used tear test pieces which are described in ASTM D264. Die B is acrescent-shaped test piece with large ends for better gripping in a tensile tester. This specimen is nicked with a razor blade to a specified depth to help initiate a tear. The Die C test piece has an angle to help initiate a tear and does not necessarily require a cut nick. The die T Trouser tear specimen is separated by a shear force from the tension applied in opposite directions to each leg at right angles to the plane of the test piece. The tear strength (T_S) is reported as kilonewton-meter^{-1} of thickness from the formula:

$$T_s = F / d$$

where F = maximum force (in N), for dies B and C, and the median or mean for die T (trouser), and d = test piece thickness in mm.

In this study, the tear properties were measured by using a Hounsfield H10KS testing machine, England according to ASTM D624-02. The specimens were cut using die C. The gauge length was 70 mm and the crosshead speed was 500 mm/min. The reported values were an average of three measurements.



A B

C T

Figure 3.7 Shaping of standard tear specimens A, B, C and T

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Graft Copolymer

4.1.1 Grafting Efficiency

The graft copolymerization reaction of ST with NR was prepared by using redox initiation system with emulsion polymerization reaction. The obtained graft copolymer product was extracted by petroleum ether (PE) and methyl ethyl ketone (MEK), respectively. The amount of free NR, free polymer (ST) and graft NR in graft copolymer product were then calculated by following equations (3.1) - (3.3) and the results were summarized in Table 4.1. The graft copolymer products were composed of 63.28 wt% graft copolymer and the unreacted NR and ST, which were about 18.78 wt % and 17.94 wt %, respectively. The graft efficiency of ST-g-NR was obtained up to 51%.

4.1.2 Characterization

After solvent extraction, the graft copolymer was characterized by FTIR and ^{1}H-NMR in order to determine the presence of ST-g-NR. FTIR spectra of NR and ST-g-NR samples are shown in Figure 4.1. Peaks at 835 and 1216 cm^{-1} correspond to C=C and C–C stretching of NR, respectively. The peak at 1373 cm^{-1} corresponds to C–H stretching of NR. The evidence of aromatic structure of PS is pronounced with the peaks at 3033 cm^{-1}, 1661 cm^{-1} and 698 cm^{-1} corresponding to the aromatic C–H stretching, aromatic C=C stretching and the monosubstituted benzene ring, respectively. ^{1}H-NMR spectrum of ST-g-NR is shown in Figure 4.2. The peak at 5.12 ppm corresponds to the NR. The signals at 6.5–7.5 ppm correspond to the phenyl group of PS. These results from FTIR and ^{1}H-NMR indicate that ST monomers were successfully grafted onto NR.

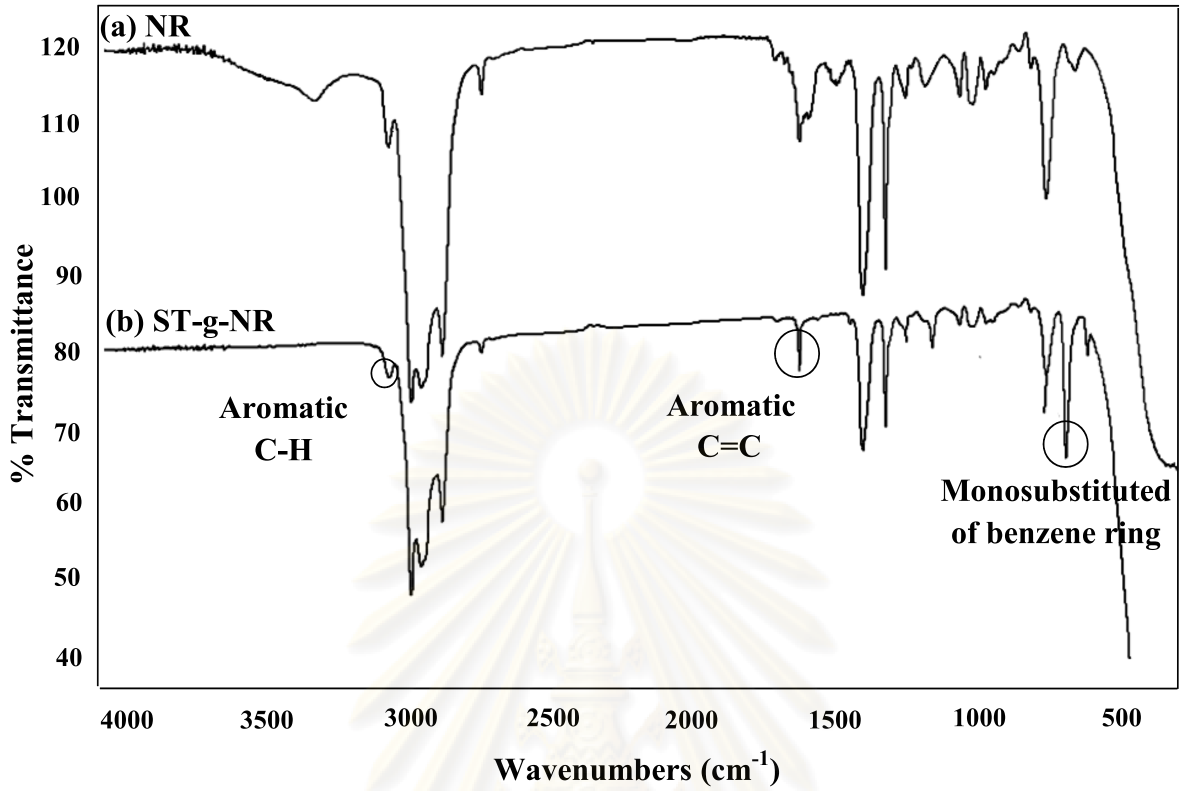


Figure 4.1 FTIR spectra of NR and ST-g-NR.

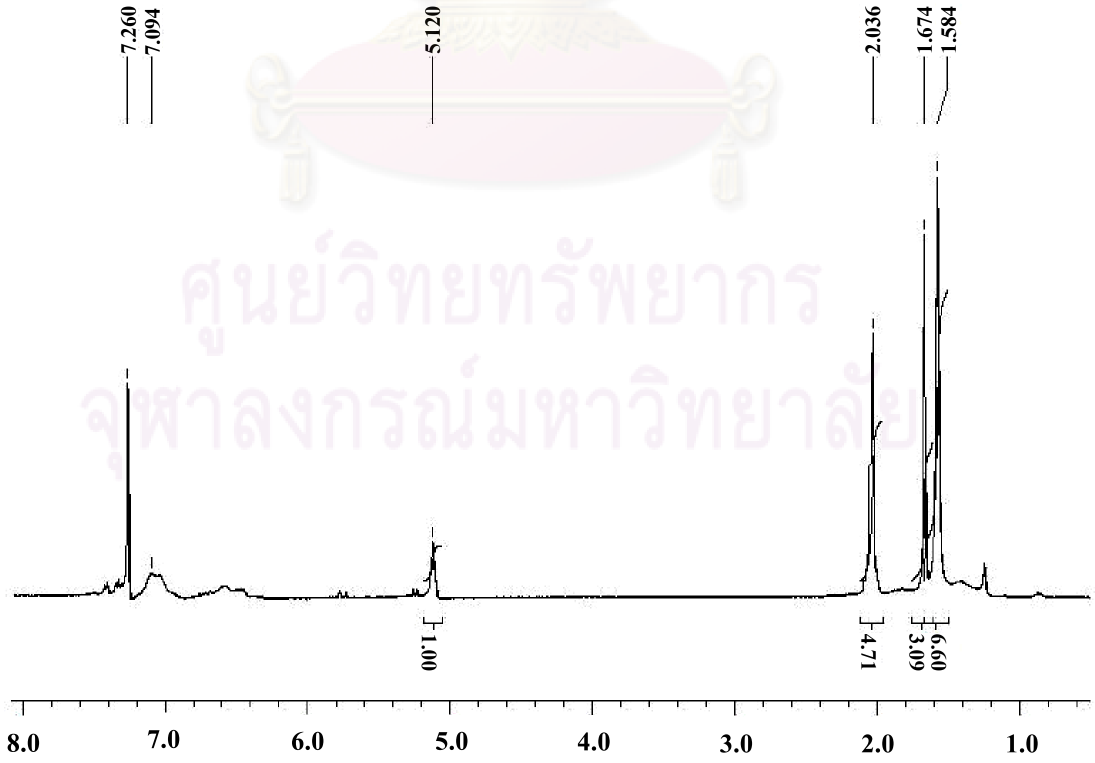


Figure 4.2 ^{1}H NMR spectrum of ST-g-NR.

Table 4.1 Grafting efficiency, free NR, free polymer and graft NR for ST-g-NR

Grafting Properties	Value [a] (%)
Free NR	18.78
Free polymer	17.94
Graft NR	63.28
Grafting Efficiency	51.07

[a] See the calculations in Appendix A.5

4.2 Sol-gel Reaction of Graft Copolymer Using Solid Rubber Method

In this study, the sol-gel reaction of graft copolymer was prepared by using two methods which are the solid rubber and latex solution method. The solid rubber of ST-g-NR was modified by TEOS. ST-g-NR sheets were immersed in TEOS at 40°C and then at room temperature. The obtained swollen sheets were immersed in n-hexylamine solution. In order to find the suitable condition for sol-gel reaction, the effects of catalyst concentration and reaction temperature on *in situ* silica content were investigated. The obtained *in situ* silica from solid rubber method should be nearly equal the *in situ* silica content which was prepared via latex solution method.

4.2.1 Swelling Degree of Graft Copolymer

In order to find the highest swelling degree of immersing ST-g-NR in TEOS, the ST-g-NR sheets of 1.5 mm x 1.5 mm x 1 mm were immersed in TEOS at 40°C and then at room temperature at various times in range of 1 – 30 h (as seen in Table 3.2). Figure 4.3 shows the relationship between swelling degree and immersing time of ST-g-NR in TEOS at 40°C and 30°C, respectively. At 40°C, the significant change of immersing ST-g-NR in TEOS was not observed due to the limitation of diffusion and the final swelling degree of ST-g-NR was about 230% at 30 h. Under the temperature of 30°C, the swelling degree of ST-g-NR was rapidly increased in the first six hours and then it was approached to the equilibrium after 16 h. The optimum swelling degree of ST -g-NR was about 200%. Thus, in order to keep the short time to carry out the sol-gel process and obtained optimum swelling degree, the suitable condition to immerse ST-g-NR in TEOS was at 40°C for 1 h, after that TEOS was decreased to 30°C for 16 h. Moreover, the rise in the immersing temperature was effective to increase the swelling degree of ST-g-NR in TEOS. However, the high swollen ST-g-NR was too soft to be satisfactorily handled as a thin sheet. The lowering temperature to 30°C, after immersing the NR sheet at 40°C for 1 h, allowed increasing the degree of swelling of ST-g-NR in TEOS and to make the swollen ST-g-NR sheet hard enough for handling [13].

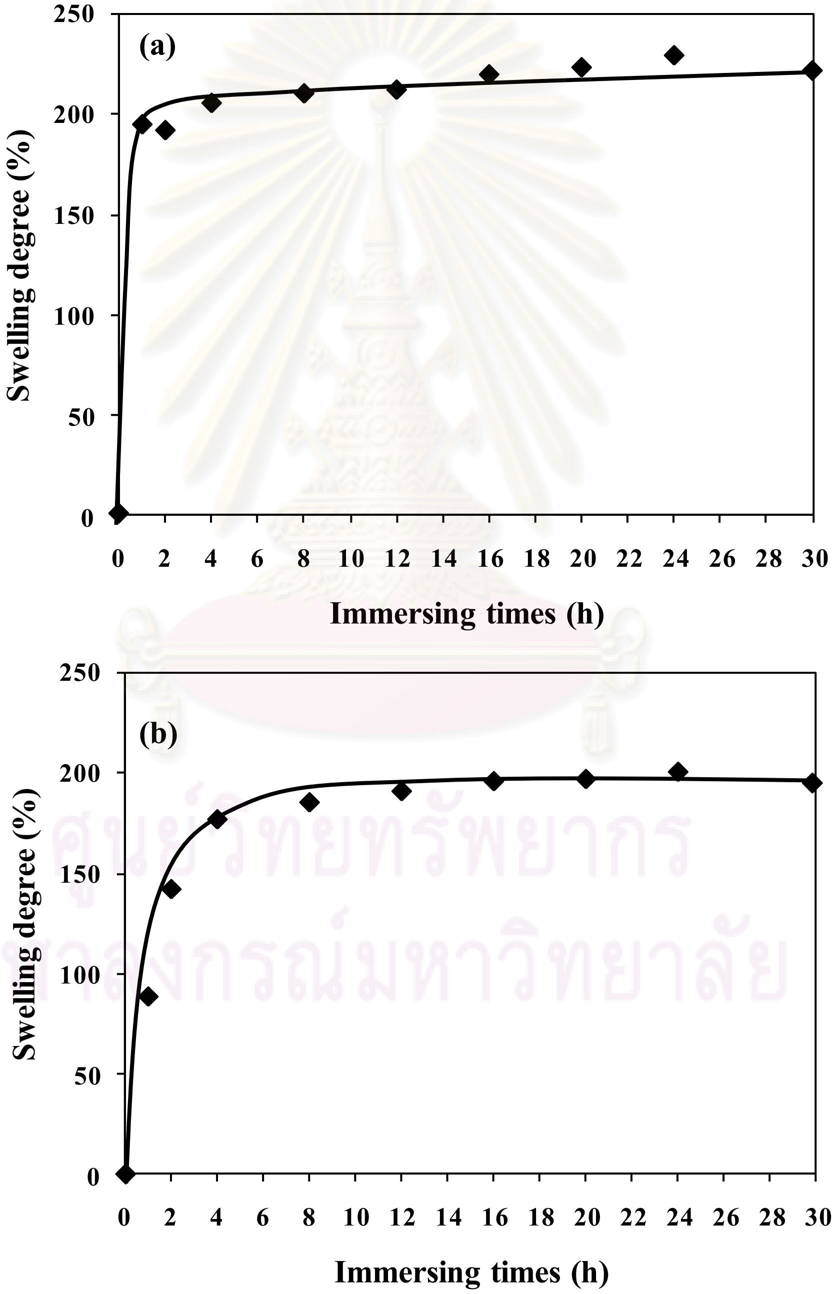


Figure 4.3 The relationship between swelling degree and immersing time of modified ST-g-NR in TEOS at (a) 40^0C and (b) 30^0C, respectively.

4.2.2 Effect of Catalyst Concentration

According to the previous result, ST-g-NR was immersed in TEOS at 40°C for 1 h and at 30^{o}C for 16 h, respectively. The maximum swelling degree of ST-g-NR was about 200%. The obtained swollen sheets were then immersed in n-hexylamine solution at 50^{o}C with various catalyst concentrations. Figure 4.4 shows the effect of catalyst concentration on the *in situ* silica content and the percentage of TEOS conversion in modified ST-g-NR. By using n-hexylamine as base catalyst, the *in situ* silica content was increased with increasing catalyst concentration. The rate of reaction, which was considered from the slope of curve, was also increased with the increase of catalyst concentration. By using n-hexylamine concentration of 0.008 M, the *in situ* silica content was reached to the equilibrium for 2-3 days about 40 phr, while at concentration of 0.064 M, the highest silica content was obtained up to 50 phr within 24 h. This result indicates that the sol-gel reaction was reached to the equilibrium faster when the catalyst concentration increased. Since more concentration of base catalyst could accelerate the dissociation of water in order to produce more nucleophilic hydroxyl anion in a rapid first step of hydrolysis reaction (as seen in Scheme 2.3). Hydroxyl anions attacked the silicon atom on TEOS, resulting in the acceleration for the production of hydroxyl group on the TEOS surface [37]. This result was corresponding to the previous work of Ikeda *et al.* [37]. They studied the effect of amine (*n*-hexylamine) on the *in situ* silica generation in NR and found that the amount of generated *in situ* silica increased with increasing *n*-hexylamine concentration. However, the sol-gel reaction in this study at the concentration of 0.1816 M *n*-hexylamine could not be performed due to the limitation of the catalyst solubility in water, resulting in phase separation. The percentage of TEOS conversion in Figure 4.4 (b) was also shown the similar results as seen in Figure 4.4 (a). According to this result, the catalyst concentration used was at 0.064 M.

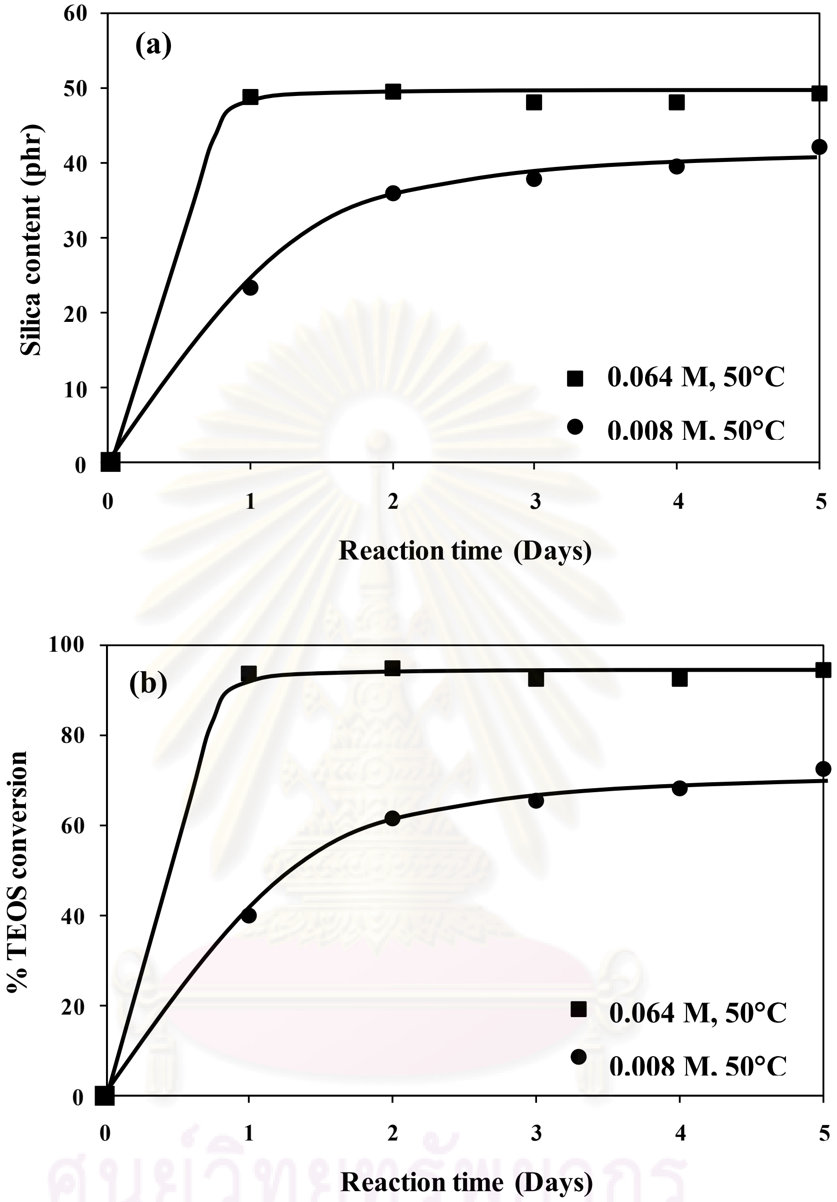


Figure 4.4 Effect of n-hexylamine catalyst concentration on (a) *in situ* silica content and (b) % TEOS conversion by using solid rubber method.

4.2.3 Effect of Reaction Temperature

Figure 4.5 shows the effect of temperature of sol-gel reaction on the *in situ* silica content and the percentage of TEOS conversion in modified ST-g-NR. The increase of reaction temperature from 40°C to 50°C gave the increase of *in situ* silica content. At 40°C, the *in situ* silica content was increased with the increase of immersing time, and the *in situ* silica content seemed to be constant when the reaction time was progressed about 2-3 days. At 50°C, the *in situ* silica content was reached to the equilibrium after 1 day for the sol-gel reaction. The *in situ* silica content was 46 and 50 phr at 40°C and 50°C, respectively. As a rule, the higher the reaction temperature, the higher the yield of *in situ* silica content was obtained. However, at 40°C, the TEOS convert to silica which was about 95% and the *in situ* silica content was nearly equal to the condition of 50°C (different about 8%). Thus, the reaction temperature for sol-gel reaction of ST-g-NR in this study was used at 40°C for a mild condition. According to the obtained results, we can conclude that the optimum condition of sol-gel reaction in ST-g-NR was the use of 0.064 M of n-hexylamine as base catalyst at 40°C for 3 days. Under this condition, the *in situ* silica was produced up to 46 phr.

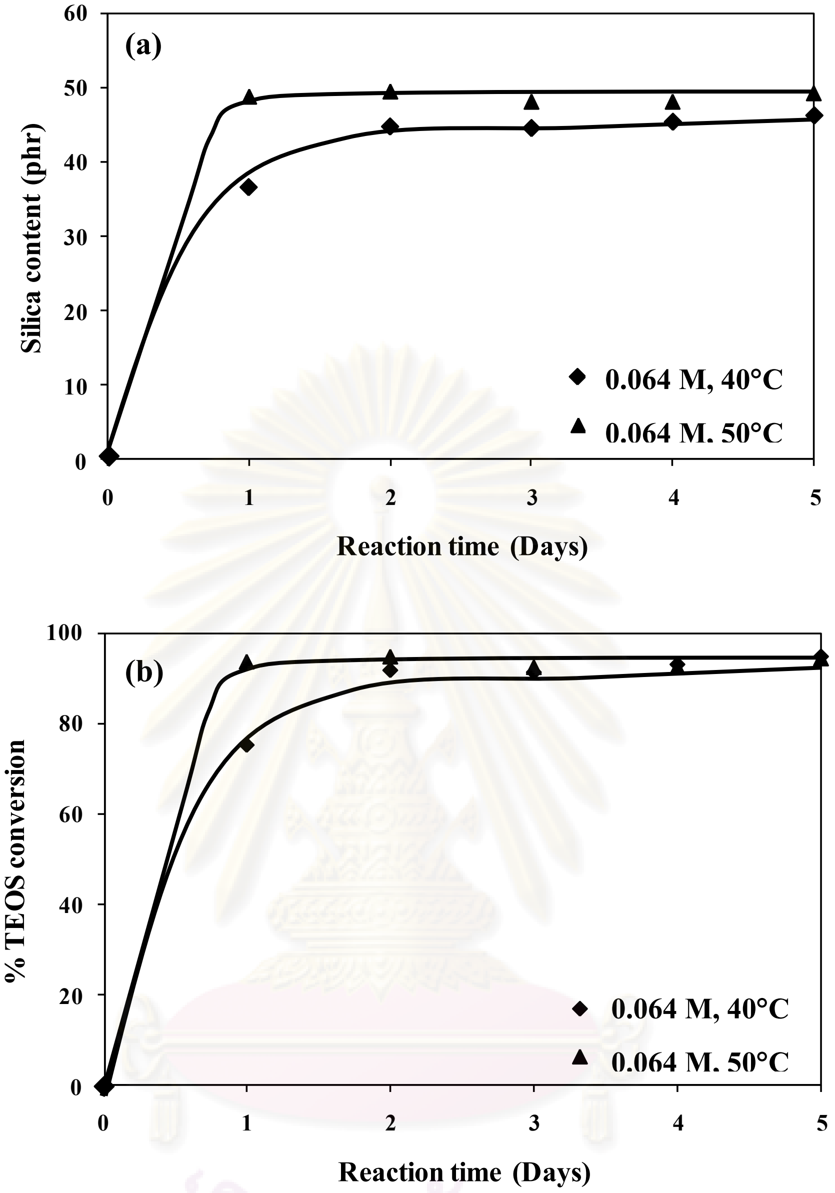


Figure 4.5 Effect of reaction temperature on (a) *in situ* silica content and (b) % TEOS conversion by using solid rubber method.

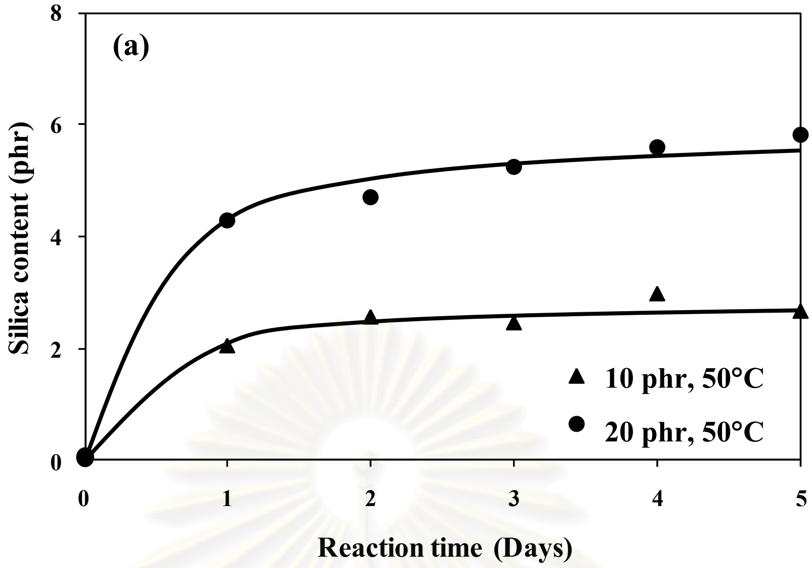
4.3 Sol-Gel Reaction Graft Copolymer Using Latex Solution Method

The other way to modify ST-g-NR used in this study was the latex solution method. TEOS was also added into ST-g-NR in latex form either before starting graft copolymerization or after finishing graft copolymerization. In order to find the suitable condition for the sol-gel reaction, the effects of TEOS content, reaction temperature and addition time of TEOS on the *in situ* silica content were investigated. We hope that the *in situ* silica content generated in ST-g-NR matrix both solid rubber and latex solution method should be nearly equal.

4.3.1 Adding TEOS before Starting Graft Copolymerization Reaction

4.3.1.1 Effect of TEOS Content

ST-g-NR was prepared by using graft copolymerization reaction under reaction temperature of 50^0C. While the graft copolymerization reaction was progressed, at the same time the sol-gel reaction was also occurred. The various amounts of TEOS were added into latex before starting graft copolymerization. Figure 4.6 shows the effect of TEOS content on the amount of *in situ* silica in modified ST-g-NR and the percentage of TEOS conversion. The *in situ* silica content increased with the increase of TEOS content. By using TEOS content of 10 phr, the *in situ* silica content was increased with increasing reaction time, however it seemed to be constant after 3 days for the sol-gel reaction. By using TEOS content of 20 phr, the *in situ* silica content was increased with the increase of reaction time. Moreover, the conversion of TEOS was reached almost 100% after 4 day for the sol-gel reaction. According to these results, TEOS was used as the precursor to generate *in situ* silica particles in rubbery matrix, so the higher amount of *in situ* silica was obtained by the increase of TEOS content.



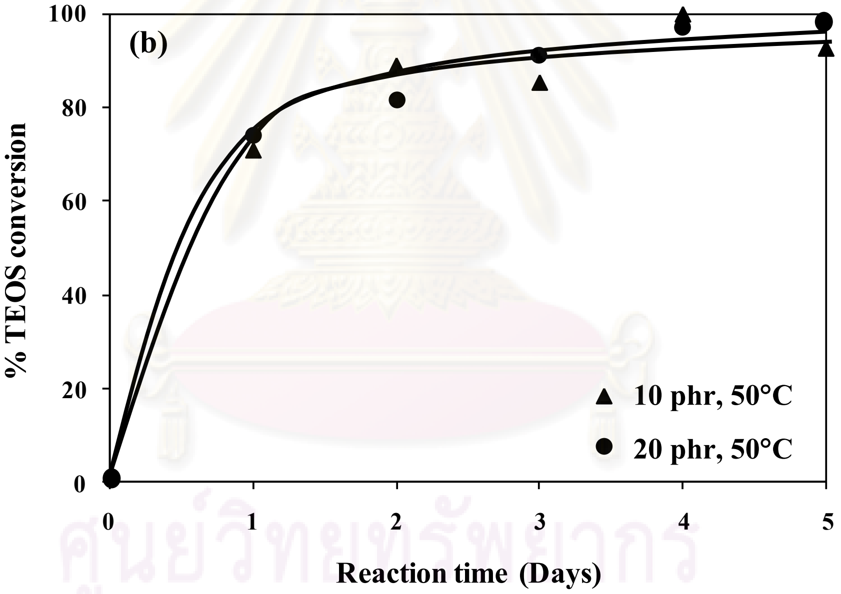


Figure 4.6 Effect of TEOS content on (a) *in situ* silica content and (b) % TEOS conversion by using latex solution method (TEOS was added before starting graft copolymerization).

4.3.1.2 Effect of Reaction Temperature

The other factor investigated by modifying ST-g-NR was the reaction temperature. In this study, the reaction temperature for the sol-gel reaction was examined at 50^{o}C and 60^{o}C by fixing the TEOS content at 20 phr and the sol-gel reaction occurred before starting graft copolymerization reaction. Figure 4.7 shows the effect of reaction temperature on the amount of *in situ* silica in modified ST-g-NR and the percentage of TEOS conversion. It is clearly seen that the increase of reaction temperature from 50^{o}C to 60^{o}C resulted the insignificant change of *in situ* silica content in rubbery matrix. The TEOS conversions of both conditions were also comparible and it was reached to 100% after 5 days. However, the initial reaction rate of reaction at 50^{o}C was lower than that of 60^{o}C. From the Arrhenius Equation (4.1), the term of –E_a/RT was decreased when the increase of reaction temperature, resulting in the increase of reaction rate (k). Although the increase of temperature results the rate of reaction increased, the *in situ* silica content in ST-g-NR matrix at the equilibrium was insignificant change. Thus, in order to keep the low temperature to carry out the sol-gel process as the soft condition, the reaction temperature was used at 50°C.

$$\ln\ k = \frac{-E_a}{RT} + \ln\ A \qquad (4.1)$$

Where k is the rate constant of chemical reaction, E_a is activation energy, T is reaction temperature, A is the pre-exponential factor and R is the gas constant.

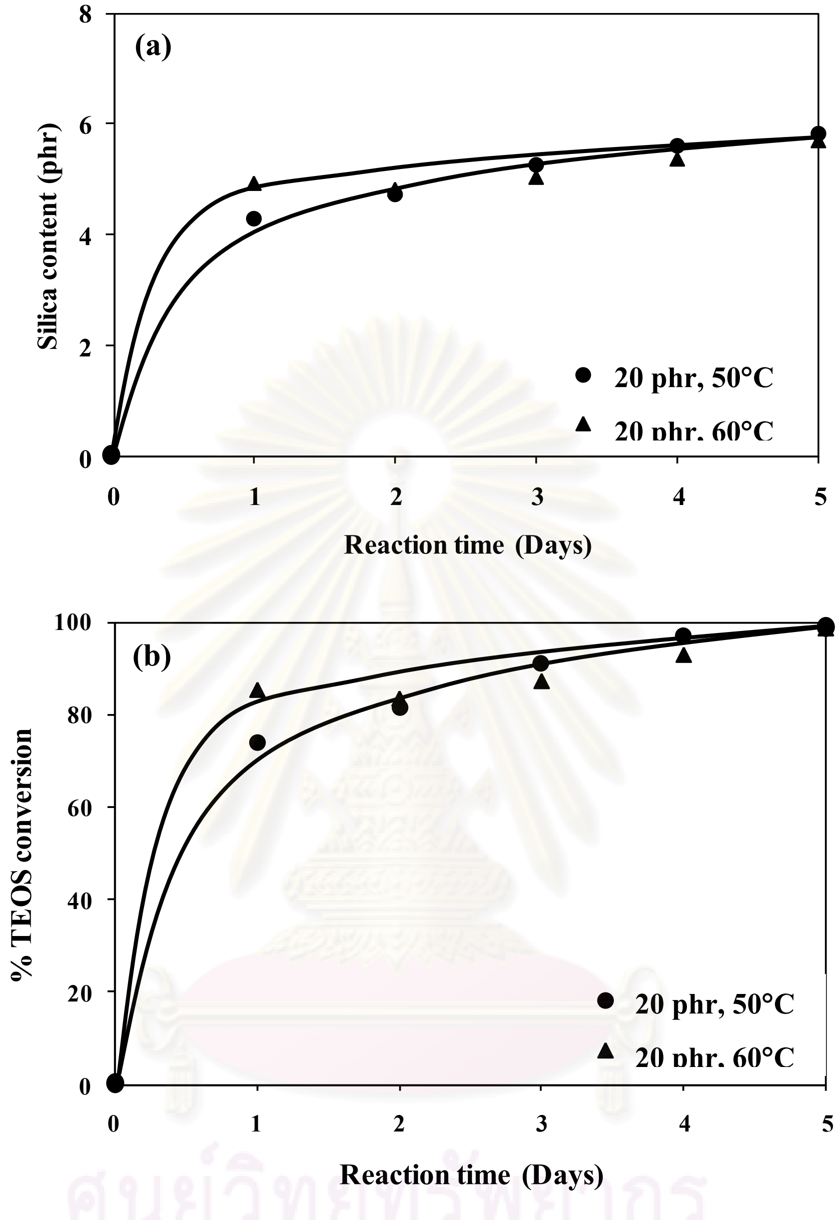


Figure 4.7 Effect of reaction temperature on (a) *in situ* silica content and (b) % TEOS conversion by using latex solution method (TEOS was added before starting graft copolymerization reaction).

4.3.1.3 Effect of TEOS on Graft Copolymerization

The modified ST-g-NR after finishing the sol-gel reaction was then subjected to extract by using PE and MEK in the order to analyst the percentage of graft NR, free NR and free ST, respectively. Figure 4.8 show the results of % graft NR, % free ST and % free NR of modified and non-modified (without sol-gel reaction) ST-g-NR, respectively. The percentages of graft NR in modified ST-g-NR were lower than that in the non-modified ST-g-NR about 28.49%. It is referred that the sol-gel reaction may retard the graft copolymerization of ST monomer and NR chain. Generally, graft copolymers are produced when vinyl monomers of styrene are attached to the unsaturated backbone of NR through the carbon-to-carbon bonds. However, the sol-gel process was occurred during the graft copolymerization, it was possible to explain that the natural emulsifiers-phospholipids and proteins, that covered and helped sustaining the rubber particles in the NR latex also aided the mixing of the hydrophobic TEOS. The silane compound was most likely adsorbed on the NR particles [38]. These results indicated that the graft copolymerization of ST onto NR was obstructed resulting in the higher free ST content (as seen in Figure 4.8 (b)). Moreover, two factors of TEOS content and reaction temperature had also affected % graft NR, % free ST and % free NR in modified ST-g-NR. The % graft NR was decreased, while % free NR was increased with the increasing of TEOS content and reaction temperature. It may be explained that TEOS can be obstructing graft copolymerization similar the above reason. With the increase of reaction temperature, the yield of free radical concentration increase and the free radicals then might be acting as radical scavengers, which results in decreasing the initiator amount [5]. These problems were then improved by changing the addition time of TEOS. Therefore, in the next step, ST-g-NR was modified by using TEOS which was added after finishing graft copolymer.

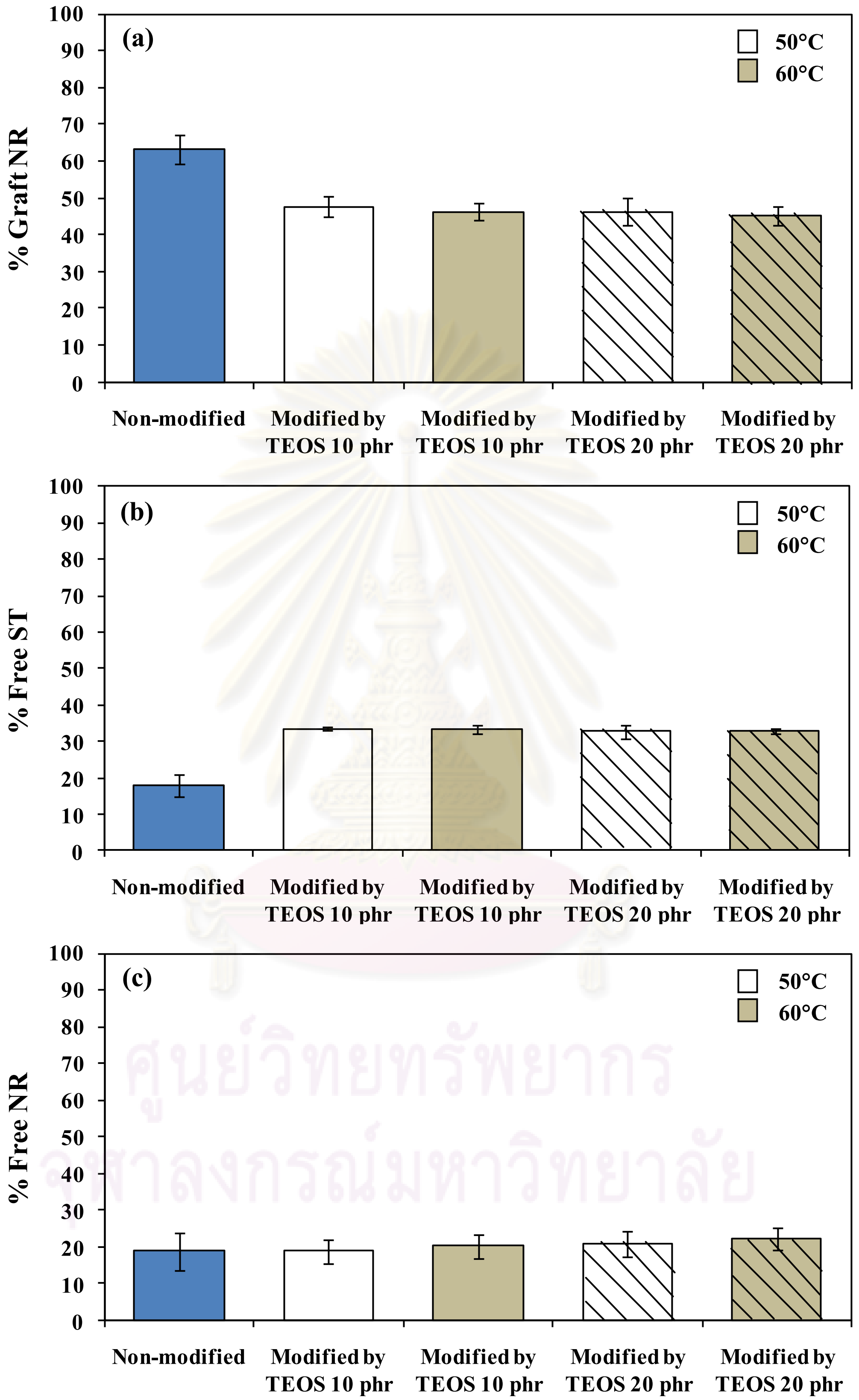


Figure 4.8 The percentage of (a) graft NR, (b) free ST and (c) free NR of modified and non-modified ST-g-NR.

4.3.2 Adding TEOS after Finishing Graft Copolymerization Reaction

4.3.2.1 Effect of Addition Time of TEOS

Figure 4.9 shows the effect of addition time on the amount of *in situ* silica in modified ST-g-NR and the percentage of TEOS conversion, respectively. In this section, TEOS was added after finishing graft copolymerization and the results was compared with the result obtained before starting graft copolymerization. TEOS content was fixed at 20 phr and the reaction temperature was 50^{o}C. In the case of adding TEOS before starting graft copolymerization, the *in situ* silica content was increased with the increase of reaction time and it was nearly constant after 4 days. The similar result was also obtained adding TEOS after finishing graft copolymerization. However, the initial rate of reaction in the case of modified ST-g-NR after finishing graft copolymerization was lower than that of before starting graft copolymerization. In this study, the graft copolymerization was carried out for 8 h. The pH of the ST-g-NR latex from the beginning of reaction to the end of reaction was decreased from 11 to 10. This result referred that the activity of NH_3 in ST-g-NR latex acting as the base catalyst for sol-gel process became decreased during the graft copolymerization resulting in the decrease of reaction rate compared with adding TEOS before starting graft copolymerization. Further reaction time, the *in situ* silica generated in ST-g-NR matrix in both reactions at the equilibrium was insignificant change (the difference was about 0.6%).

4.3.2.2 Effect of TEOS Content

Figure 4.10 shows the effect of TEOS content on the amount of *in situ* generated silica in modified ST-g-NR under the reaction temperature of 50^{0}C. The *in situ* silica content increased with increasing TEOS content. The rate of sol-gel reaction was also increased with the increase of TEOS content. For all conditions of the sol-gel reaction, the generated *in situ* silica was reached to the equilibrium for 7 days. However, by adding TEOS more than 80 phr, the ST-g-NR latex was rapidly coagulated. This result was corresponding to the previous work of Tangpasuthadol *et al.* [38]. They studied the generation of *in situ* silica in NR latex and found that if the added TEOS content was higher than 70 phr, excess TEOS phase-separated out of the latex as floating droplets. Therefore the TEOS content in the latex was limited at 70 phr. In this study, the added TEOS content was reached up to 80 phr. It was because the emulsifier in graft copolymerization reaction helped sustaining the latex phase. According to this result, the maximum amount of TEOS which could be added in ST-g-NR was 80 phr, and the *in situ* silica was obtained up to 24 phr under reaction temperature of 50°C.

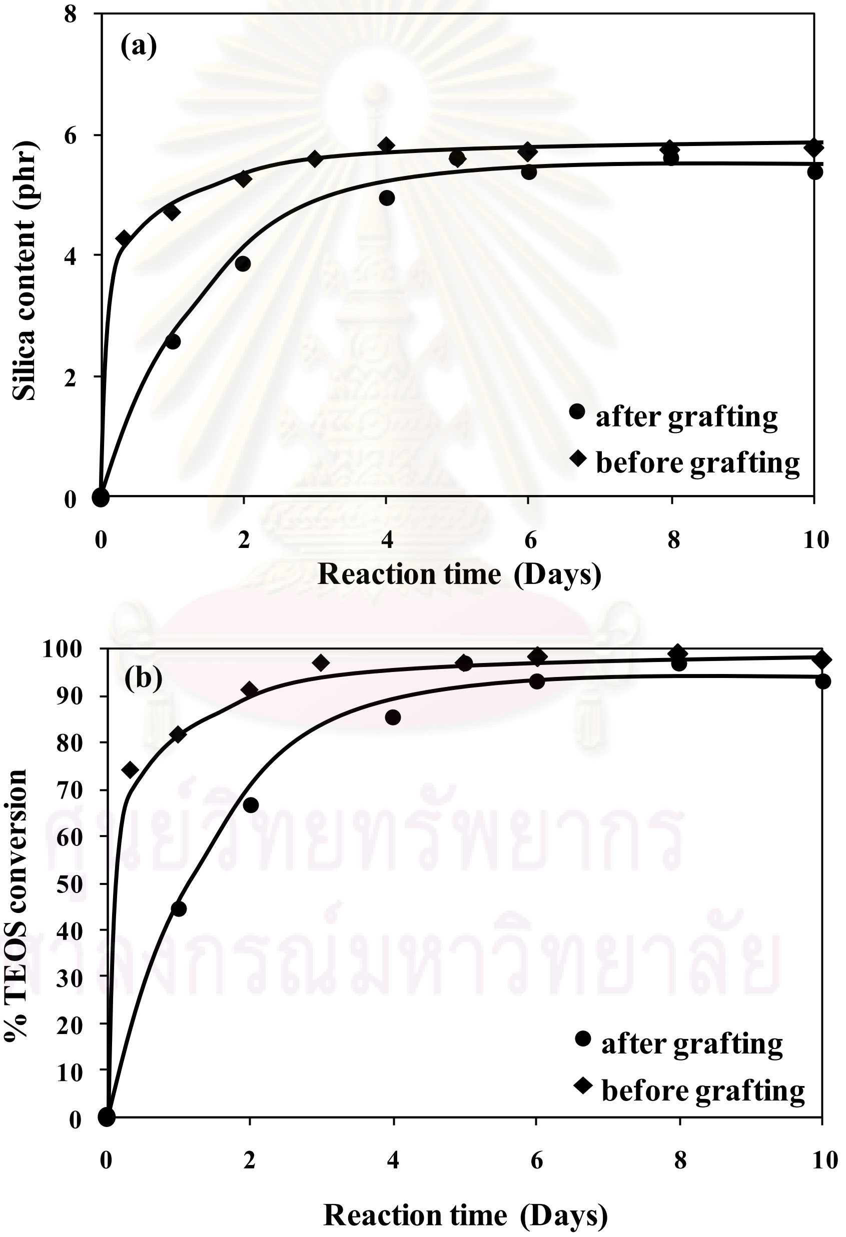


Figure 4.9 Effect addition time on (a) *in situ* silica content and (b) % conversion by using latex solution method.

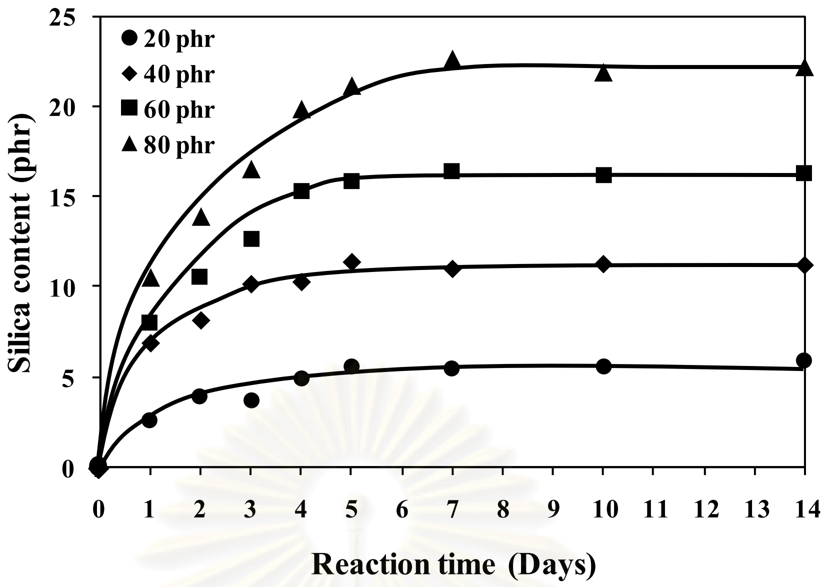


Figure 4.10 The amount of *in situ* silica content in modified ST-g-NR by adding TEOS after finishing graft copolymerization reaction.

4.4 The Comparison of Advantages and Disadvantages between Solid Rubber and Latex Solution Method

In this study, the *in situ* silica was synthesized via the sol-gel process by using TEOS as the precursor in ST-g-NR matrix. Two methods used in this study were prepared in ST-g-NR solid rubber and ST-g-NR latex solution. The advantages of sol-gel reaction via the solid rubber were simple to carry out, easy to control many factors, high generated silica content, well silica dispersion and short reaction time. Additionally, when adding the high content of TEOS, the sol-gel reaction of ST-g-NR was not coagulated. The disadvantages of sol-gel reaction in the solid rubber were the use of high volume of TEOS and need to use base catalyst.

The advantages of sol-gel reaction via the latex solution were needlessly used organic solvent and the base catalyst (due to NH_3 in NR latex can be using as base catalyst). Additionally, the well dispersion of *in situ* silica in polymer matrix was obtained. The disadvantages of sol-gel reaction via the latex solution were long reaction time and difficult to control many factors, because in the liquid state, ST-g-NR latex trended to be coagulated when the high amount of TEOS was added.

In the order to investigate the effect of *in situ* silica content on mechanical properties both in solid rubber and latex solution method, the *in situ* silica filled ST-g-NR was prepared according to the following conditions: Two concentrations (24 and 50 phr) of *in situ* silica generated in ST-g-NR via solid rubber method were prepared by using 0.008 M n-hexylamine at 40°C for 1 day and using 0.064 M n-hexylamine at 50°C for 1 day, which were achieved the *in situ* silica content about 24 and 50 phr, respectively. In the case of latex solution method, the same amount of *in situ* silica (24 phr) was prepared in order to compare with solid rubber method. ST-g-NR was subjected to the sol-gel reaction under 50°C by using TEOS 80 phr for 7 days. The *in situ* silica content was obtained about 24 phr. Finally, the compounding of *in situ* silica filled ST-g-NR was prepared according to the formulations that shown in Table 3.5.

4.5 Cure characteristic

The cure characteristics of the NR vulcanizates, GNR vulcanizates with and without silica are presented in Table 4.2. The curing time of GNR vulcanizates was lower than NR vulcanizates. During the graft copolymerization reaction, ST monomer was grafted onto NR chains and growing up to PS at the same time. The reactive NR chain was decreased with the increase of the percentage of graft NR. It has affected to the efficiency of curing agent due to the lower reactive NR chains of ST-g-NR. Moreover, the steric effect of PS chain has also affected to the curing time. PS on NR chains may prevent the vulcanization of NR.

The curing time of *in situ* silica filled GNR vulcanizate increased with *in situ* silica contents increased due to the surface properties of *in situ* silica. The surface of silica particles contains silanol groups, which are acidic and highly reactive. The silanol groups can react quickly with the curing agents. The efficiency of the curing agent is reduced leading to an increase in the curing time of the *in situ* silica filled NR vulcanizate [31]. Moreover, the curing time of the In-12-S and In-12-L vulcanizate was lower than that of the Si-12 vulcanizate. By using Atomic Force Microscopy (AFM), it was reported that the surface silanol group contents of the *in situ* formed silica was lower than that of the commercial silica, and thus the curing time of *in situ* silica filled samples decreased due to lower amount of surface silanol groups [16].

Table 4.2 Cure time of NR and GNR vulcanizates with and without silica at 150^{o}C

Sample code	Curing time (min)
NR	7.20
GNR	5.14
Si-12	7.05
In-12-L	6.65
In-12-S	6.81
In-25-S	12.9

4.6 Mechanical Properties

The rubber compounds with and without *in situ* silica was prepared by the two-roll mill and the effects of silica content (both *in situ* silica and commercial silica) on mechanical properties was investigated. Figure 4.11 shows the tensile properties of NR vulcanizate and GNR vulcanizate with and without silica, respectively. The modulus at 300% elongation (M_{300}) and tensile strength (T_B) of NR vulcanizate increased when mixed with ST-g-NR, while the elongation at break (E_B) of GNR vulcanizate was lower than that of NR vulcanizate. This was due to the increase of the hard segment of PS which makes the rubber chain more stiffness. By adding silica 12 phr, the M_{300} and T_B of GNR vulcanizate trend to be increased due to the reinforcement effect of silica. The stress applied from an external force to the composite was transferred to the filler through the filler-matrix interface [44]. M_{300}, T_B and E_B of commercial silica filled GNR vulcanizates were lower than those of *in situ* silica filled GNR vulcanizates either solid rubber or latex solution methods at the same silica content. Additionally, the tensile properties of both samples prepared via solid rubber and latex solution methods were comparable. When the *in situ* silica content in GNR matrix prepared by solid rubber method increased, the M_{300} of GNR vulcanizate increased, while T_B and E_B decreased respectively. This result referred that the brittleness of composite materials was increased when the increase of silica content leading to the decrease of elasticity of composite materials [26].

Figure 4.12 shows the tear strength, abrasion loss and hardness of NR vulcanizate and GNR vulcanizates with and without silica, respectively. The tear strength in GNR vulcanizate was improved when compared with NR vulcanizate. The increase of hard segment of PS in NR chain may be the main reason for the increasing of tear strength [45]. By adding silica 12 phr, the tear strength in GNR vulcanizates trended to be increased due to the reinforcement effect of silica. The tear strength in GNR vulcanizates among 3 samples (Si-12, In-12-L and In-12-S) were comparable. However, when the *in situ* silica content in GNR matrix prepared by solid rubber method increased, the tear strength trended to decrease due to the increase of brittleness in silica filled GNR vulcanizates.

The abrasion resistance of NR vulcanizate was increased when mixed with ST-g-NR due to the increase of hard segment of PS molecule in NR chain. By adding silica 12 phr, the abrasion resistance of GNR vulcanizates trended to be increased due to the reinforcement effect of silica. The abrasion resistance in GNR vulcanizates among 3 samples (Si-12, In-12-L and In-12-S) were comparable. However, when the *in situ* silica content in GNR matrix prepared by solid rubber method increased, the abrasion resistance rapidly decreased. This result could be explained that the rubbery matrix was not enough to hold the silica particles together leading to simply lose the rubber composite volume [46].

The hardness of NR vulcanizates increased when mixed with ST-g-NR due to increasing hard segment of PS. The hardness of GNR vulcanizates increased with increasing silica content. The hardness in GNR vulcanizates among 3 samples (Si-12, In-12-L and In-12-S) were comparable.

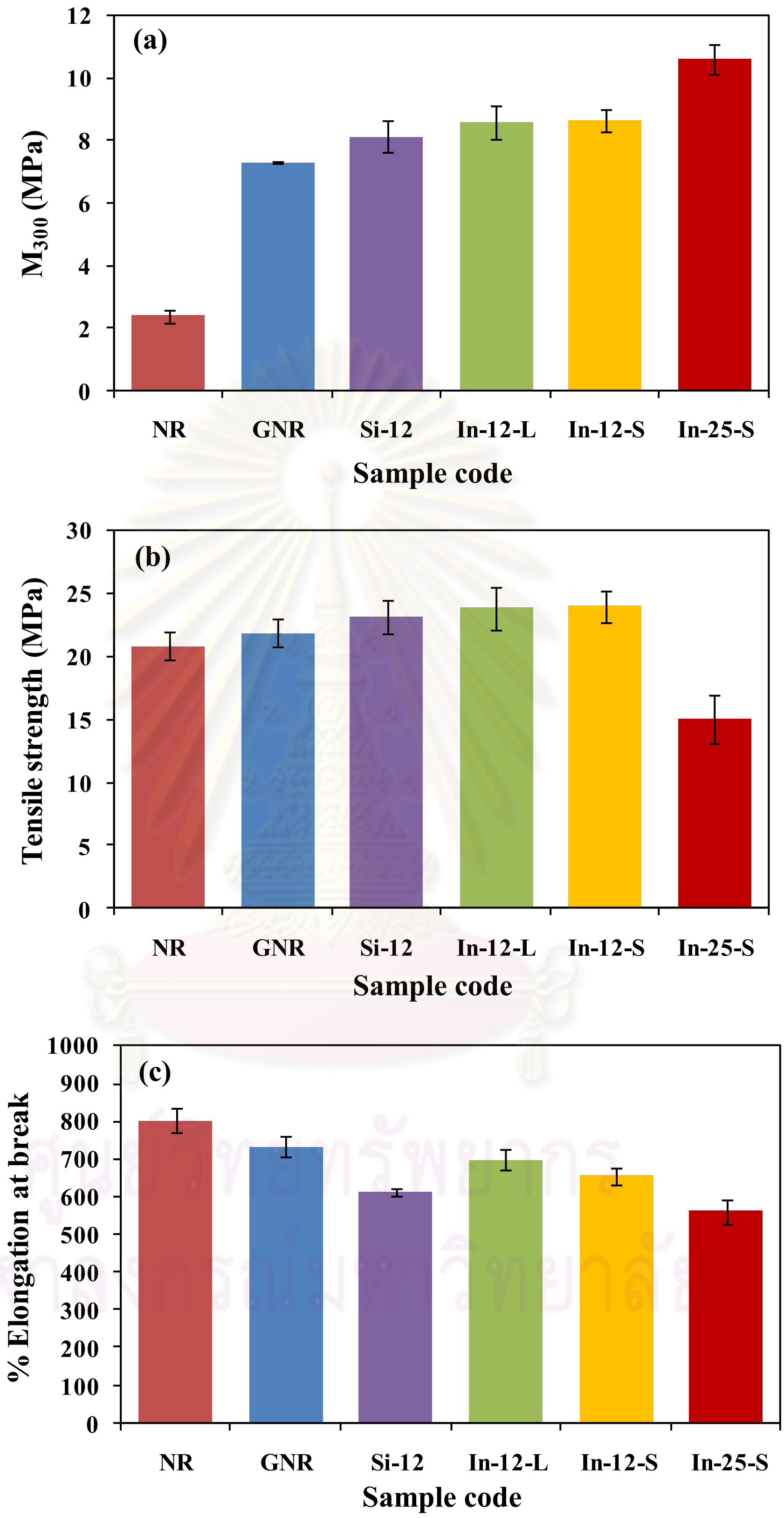


Figure 4.11 Mechanical properties of NR vulcanizate and GNR vulcanizate with and without silica (a) 300% modulus (M_{300}), (b) tensile strength and (c) elongation at break.

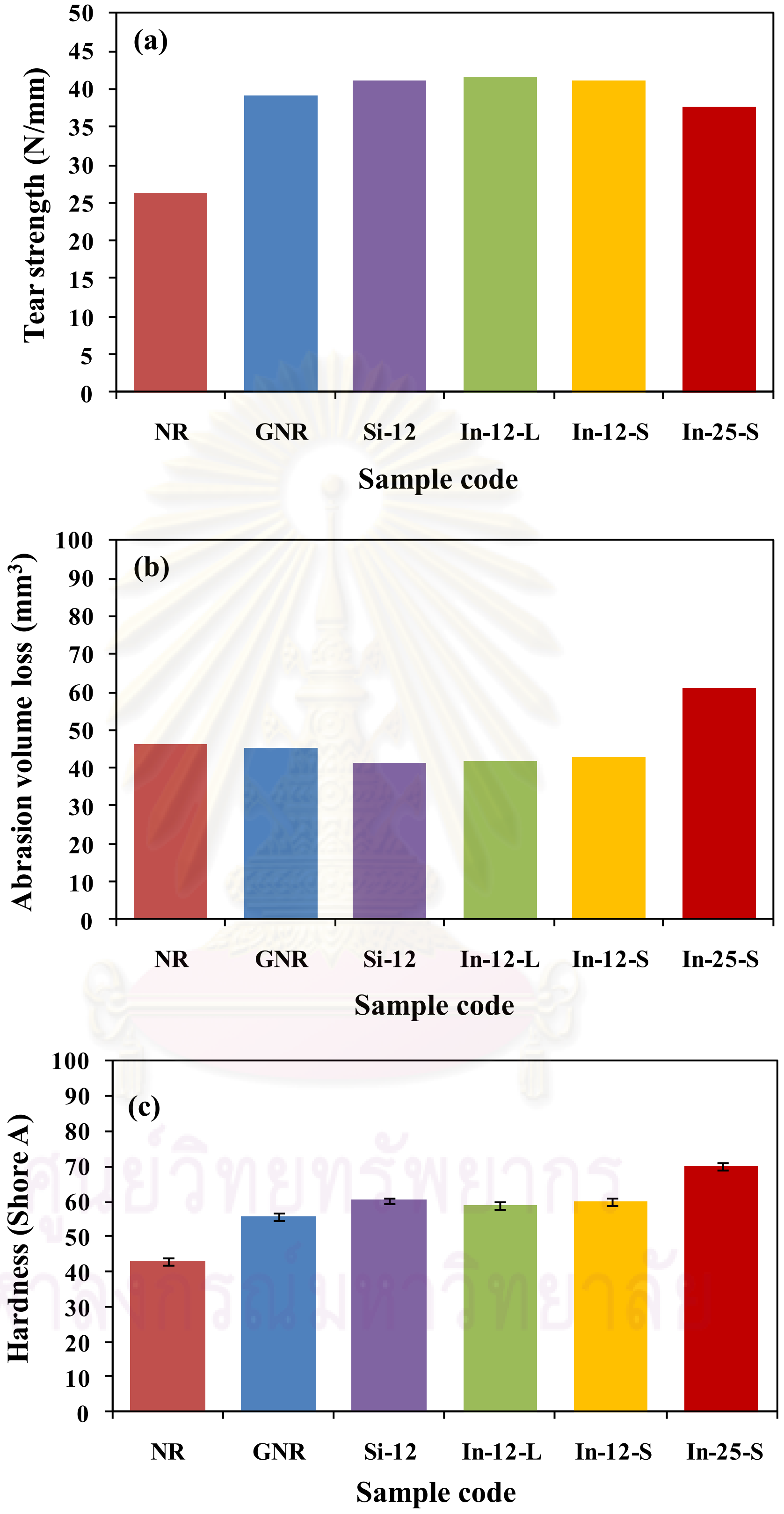


Figure 4.12 Mechanical properties of NR vulcanizate and GNR vulcanizate with and without silica (a) tear strength, (b) abrasion loss and (c) hardness.

4.7 Morphology of NR and GNR Vulcanizates

The surface morphology of silica filled GNR vulcanizates was characterized by TEM and the TEM images were shown in Figure 4.13. It was clearly seen that the 12 phr of commercial silica particles were aggregated to form agglomeration structure, while the *in situ* silica particles from latex solution and solid rubber methods were dispersed more homogeneously in GNR matrix at the same filler content (12 phr). The particle sizes of *in situ* silica of both methods were about 40 nm and those of commercial silica were about 60 nm. The smaller particle size, the larger surface area was acquired. According to this reason, we could obtain the good dispersion of *in situ* silica in GNR matrix. Additionally, the surface properties of nanofiller are the other factors which have influenced either the reinforcement effect or the dispersion in polymer matrix. The surface of precipitated silica is more polar and hydrophilic due to the presence of numerous silanol groups, so the commercial silica seems to be agglomerated easily than the *in situ* silica [47]. In the case of increasing the *in situ* silica content by solid rubber method, silica particles were well dispersed in GNR matrix, however, they seem to be agglomerated. The particle size of *in situ* silica which was prepared via either solid rubber or latex solution methods was comparable. These TEM results could support the results of tensile properties that the good dispersion of *in situ* silica in GNR matrix resulted in the improvement of tensile properties.

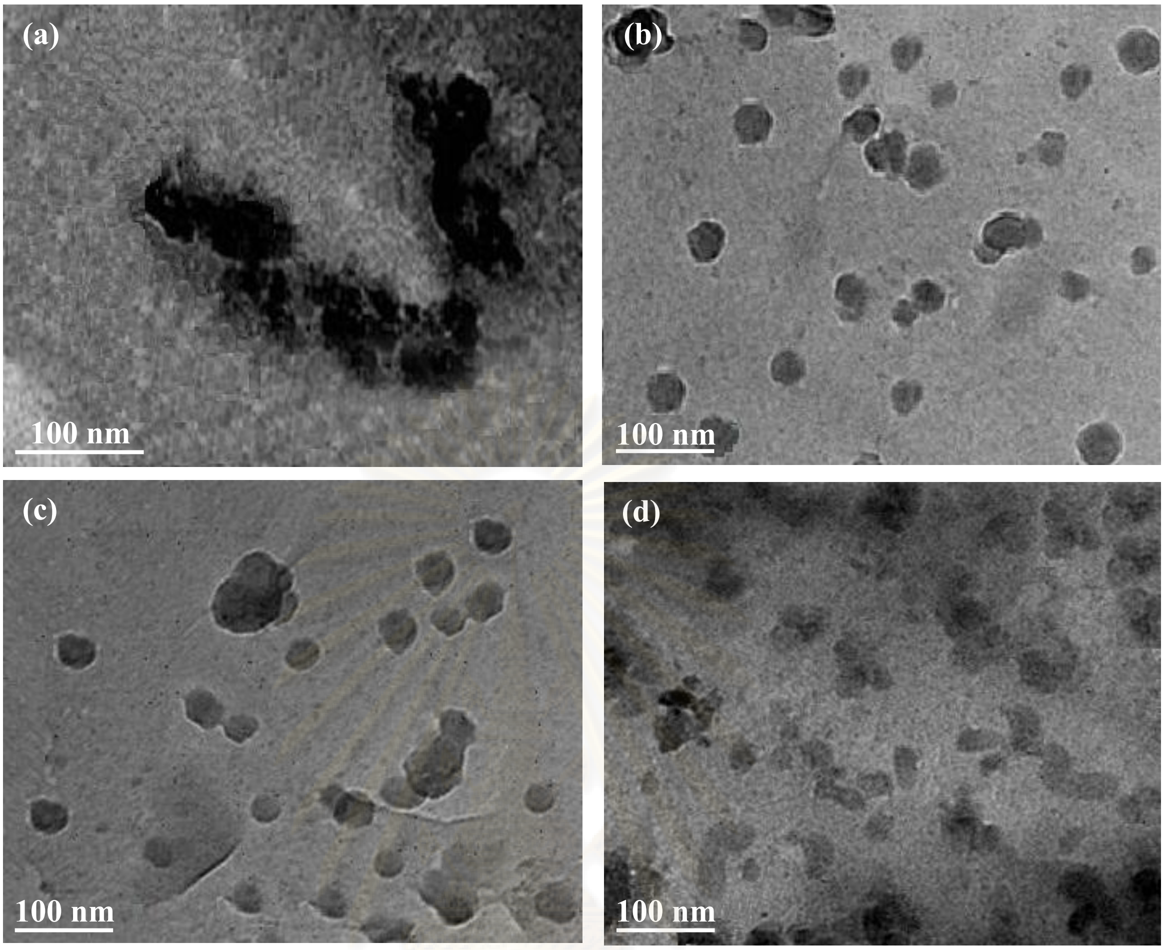


Figure 4.13 TEM photogragphs of NR and ST-g-NR vulcanizates with (a) commercial silica of 12 phr, (b) *in situ* silica 12 phr (latex solution method), (c) *in situ* silica 12 phr (solid rubber method) and (d) *in situ* silica 20 phr (solid rubber method).

CHAPTER V
CONCLUSION AND FUTURE DIRECTION

5.1 Conclusion

In this study, the graft copolymerization of ST-g-NR was synthesized by using CHPO/TEPA as an initiator. The structure of ST-g-NR was confirmed by FTIR and H^1-NMR analysis. The preparation of *in situ* silica filled was carried out by sol-gel reaction of TEOS via 2 methods, i.e., solid rubber method and latex solution method. In the case of solid rubber method, the effects of reaction time, reaction temperature and catalyst concentration were investigated. The *in situ* silica content increased with the increase of n-hexylamine concentration and reaction time, while the reaction temperature was independent of *in situ* silica content. The optimum condition was carried out by using 0.064 M n-hexylamine at the temperature of 40°C. *In situ* silica up to 50 phr was successfully filled in the ST-g-NR matrix. In the case of latex solution method, the effects of TEOS content, reaction temperature, addition time of TEOS and reaction time were investigated. The *in situ* silica content increased with the increase of TEOS content and reaction time, while the reaction temperature was independent of *in situ* silica content. The percentage of graft NR in modified ST-g-NR (before graft copolymerization) was less than that of modified ST-g-NR (after graft copolymerization). The optimum condition for latex method was the use of 80 phr TEOS at 50°C and the sol-gel reaction was carried out after graft copolymerization. The maximum *in situ* silica content about 24 phr was achieved. The mechanical properties were increased with increasing the *in situ* silica content in GNR vulcanizates (modified ST-g-NR). However, the mechanical properties tended to be decreased at the high *in situ* silica content. The mechanical properties of *in situ* silica filled GNR vulcanizate of both methods were higher than those of commercial silica filled rubber vulcanizate. It was because the *in situ* silica particles were well dispersed in the rubber matrix, while the commercial silica particles were agglomerated in rubber matrix.

5.2 Future Direction

1) Study in more parameters such as surfactant or catalyst type to increase TEOS content and decrease reaction time of sol-gel reaction by using latex solution method.

2) Study the effect of *in situ* silica filled ST-g-NR that use as compatibilizer in NR/PS blends on mechanical properties of NR/PS blends

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APPENDICES

APPENDIX A
CALCULATION

A.1 Calculation of swelling degree

$$Degree\ of\ swelling\ (\%) = \frac{Weight\ of\ NR\ sheet\ after\ swell - Weight\ of\ NR\ sheet\ before\ swell}{Weight\ of\ NR\ sheet\ before\ swell} x100$$

$$\text{Degree of swelling(\%)} = \frac{53.68 - 18.15}{18.15} \text{ x } 100 = 195.2\ \%$$

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 = 53.68 – 18.15 = 35.43 g

A.3 Calculation of amount of water (15 times of amount of TEOS)

Amount of water = 15 x 35.43 = 531.45 ml

A.4 Calculation of amount of n-hexylamine

MW of n-Hexylamine = 101.19 and n-hexylamine concentration used in this study was 0.064 mol/l

Water 1000 mL n-hexylamine 0.064 mol

Water 531.45 mL n-hexylamine = $\frac{0.064 \text{ x } 531.45}{1000}$ mol

= 0.034 mol

= 0.034 x 101.19 g = 3.44 g

A.5 Calculation of % Conversion, % Graft NR, % Free NR, % Free ST and % Graft efficiency

Weight of latex = 100 g
Weight of DRC = 60 g
Weight of monomer = 60 g
Product = 104.021 g
Sample **(S)** = 3.046 g
After PE **(A)** = 2.641 g
After MEK**(B)** = 2.013 g

- **% Conversion**

$$\text{Conversion} = \frac{104.021 - 60}{60} \times 100$$

$$= 73.37\ \%$$

- **% Graft NR**

$$\frac{B}{S} \times 100 = \frac{2.013}{3.046} \times 100$$

$$= 66.10\ \%$$

- **% Free NR**

$$\frac{S - A}{S} \times 100 = \frac{3.046 - 2.641}{3.046} \times 100$$

$$= 13.30\ \%$$

- **% Free ST**

$$\frac{A - B}{S} \times 100 = \frac{2.641 - 2.013}{3.046} \times 100$$

$$= 20.60\ \%$$

- **Total ST**

$$\text{Total ST} = 104.021 - 60$$

$$= 44.021 \text{ g}$$

- **Free ST**

$$\text{Free ST} = \frac{20.60 \times 104.021}{100}$$

$$= 21.43 \text{ g}$$

- **Graft ST**

$$\text{Graft ST} = 44.021 - 21.43$$

$$= 22.591 \text{ g}$$

- **% Graft efficiency**

$$\%\text{ Graft efficiency} = \frac{\text{Graft ST} \times 100}{\text{Total ST}} = \frac{22.591 \times 100}{44.021}$$

$$= 51.32\ \%$$

APPENDIX B

Table B.1 300% modulus of NR and GNR vulcanizate with and without silica

	NR	GNR	Si-12	In-12-L	In-12-S	In-25-S
300% Modulus (MPa)	2.09	7.58	8.46	8.95	8.18	10.50
	2.60	7.90	8.66	8.34	8.58	10.76
	2.44	6.88	7.86	8.56	8.85	10.64
	2.40	6.84	7.59	8.71	8.60	11.02
	2.36	7.31	8.12	8.37	8.99	10.26
Average	2.38	7.30	8.14	8.59	8.64	10.64
SD	0.19	0.46	0.44	0.26	0.31	0.29

Table B.2 Tensile strength of NR and GNR vulcanizate with and without silica

	NR	GNR	Si-12	In-12-L	In-12-S	In-25-S
Tensile strength (MPa)	20.88	21.78	25.59	23.19	24.45	14.97
	20.05	21.27	22.59	23.69	23.28	13.58
	20.04	21.63	22.05	24.05	25.00	16.33
	22.45	22.50	22.27	22.07	22.23	15.29
	20.85	22.64	23.08	25.87	25.12	15.04
Average	20.86	21.90	23.13	23.86	24.01	15.05
SD	1.14	1.44	1.31	1.66	1.28	0.98

Table B.3 Elongation at break of NR and GNR vulcanizate with and without silica

	NR	GNR	Si-12	In-12-L	In-12-S	In-25-S
Elongation at break (%)	805.37	776.58	622.64	707.49	660.99	547.34
	786.59	693.22	571.60	695.60	673.95	556.69
	839.67	729.16	614.45	659.59	611.93	572.78
	780.30	734.89	634.20	730.09	635.66	564.65
	800.01	734.01	610.74	701.95	697.85	560.40
Average	802.39	733.57	610.72	698.94	656.09	560.36
SD	23.15	29.58	23.65	25.56	33.37	9.43

Table B.4 Tear strength and Abrasion resistance of NR and GNR vulcanizate with and without silica

	NR	GNR	Si-12	In-12-L	In-12-S	In-25-S
Tear strength (N/mm)	26.4	39.1	41.2	41.5	41.2	37.7
Abrasion loss (mm^3)	46.4	45.2	41.4	41.7	42.8	61.0

Table B.5 Hardness of NR and GNR vulcanizate with and without silica

	NR	GNR	Si-12	In-12-L	In-12-S	In-25-S
Hardness	43.00	55.00	61.00	59.00	61.00	70.00
	43.00	57.00	60.00	59.00	60.00	71.00
	43.00	55.00	60.00	58.00	59.00	70.00
Average	43.00	55.67	60.33	58.67	60.00	70.33
SD	0.00	1.15	0.58	0.58	1.00	0.58

VITAE

Mr. Torpong Sittiphan was born on September 2, 1985 in Samutprakarn, Thailand. He received his Bachelor's degree in Petrochemicals and Polymeric Material, from the Faculty of Engineering and Industrial Technology, Silpakorn University in 2006. He has pursued Master's degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2007 and finished his study in 2010.

Presentation

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