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PHYSICAL PROPERTIES OF MMA GRAFTED NATURAL RUBBER FILM
REINFORCED WITH IN SITU SILICA

Miss Wasinee Sakathok

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

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การปรับปรุงความเข้ากันได้และการยึดติดของยางธรรมชาติ (NR) ที่กราฟต์ด้วยเมทิลเมทาครีเลต (MMA) กับซิลิกาโดยใช้สารไฮโดรเจนที่มีพันธะคู่สองชนิดคือ แกมมาเมทาคริลอกซีโพรพิล ไทรมเมทอกซีไฮโดรเจน (γ -MPS) และ ไวนิล ไทรมเมทอกซีไฮโดรเจน (VTES) เป็นสารคู่ควบ ชั้นแรก เป็นการกราฟต์น้ำยางธรรมชาติ (30%DRC) ด้วย MMA มอนอเมอร์ ผ่านกระบวนการอิมัลชันพอลิเมอร์เรชัน โดยใช้ควีนไฮโดรเปอร์ออกไซด์/เททระเอทิลีนเพนเตน เป็นตัวริเริ่มปฏิกิริยาแบบรีดอกซ์ อนุภาคยางที่กราฟต์แล้วมีลักษณะที่ส่วนของยางเป็นแกนกลาง และมีชั้นรอบนอกเป็นพอลิเมทิลเมทาครีเลต ผลวิเคราะห์จากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) เพื่อสร้างซิลิกาให้เกิดขึ้นภายในยางที่กราฟต์ดังกล่าว ชั้นต่อมาจึงได้กราฟต์ NR-g-MMA ด้วย γ -MPS หรือ VTES เพื่อสร้างซิลิกาให้เกิดขึ้นภายในยางที่กราฟต์ดังกล่าว จึงได้นำเททระเอทอกซีไฮโดรเจนมาผสมอนุภาคเคลือบของคอมพอสิตที่ได้ มีลักษณะเป็นซิลิกาไหลหุ้มอนุภาคยางที่อยู่เป็นแกนกลาง เมื่อวิเคราะห์ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) พบว่า ซิลิกากระจายตัวได้ค่อนข้างดีในเนื้อยาง ร้อยละของการเปลี่ยนรูปจาก γ -MPS-TEOS และ VTES-TEOS ไปเป็นซิลิกามีค่าอยู่ระหว่างร้อยละ 60-90 ผลการทดสอบสมบัติเชิงกลชี้ให้เห็นว่า หมู่ไว้นิลของอนุภาคซิลิกาที่เกิดขึ้นภายในมีบทบาทสำคัญต่อการเสริมแรงของฟิล์มยาง

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WASINEE SAKATHOK: PHYSICAL PROPERTIES OF MMA GRAFTED NATURAL RUBBER FILM REINFORCED WITH *IN SITU* SILICA. ADVISOR: ASST. PROF. VARAWUT TANGPASUTHADOL, Ph.D., CO-ADVISOR: PROFESSOR SUDA KIATKAMJORNWONG., Ph.D., 67 pp.

The improvement in the compatibility and adhesion between natural rubber (NR) grafted with methylmethacrylate (MMA) and silica by two types of vinylated silane, γ -methacryloxypropyltrimethoxysilane (γ -MPS) and vinyltriethoxysilane (VTES) as a coupling agent was reported. In the first step, the NR latex (30%DRC) was grafted with MMA monomer via emulsion polymerization using cumene hydroperoxide/tetraethylene pentamine (CHPO/TEPA) redox system as an initiator. The latex core and PMMA shell feature was found by transmission electron microscopic (TEM) analysis. Graft copolymerization of NR-g-MMA with γ -MPS or VTES was then proceeded. To generate silica in the grafted NR latex, tetraethoxysilane (TEOS) was mixed with the latex mixture. The composite latex particles appeared to be a core-shell structure with the silica sol forming encompassing the NR core. The silica particles were well dispersed in the rubber matrix as observed by SEM. The conversions of γ -MPS-TEOS and VTES-TEOS to silica particles in the composite were between 60 to 90%. The results of mechanical test suggested that the vinyl group on the *in situ* generated silica played an important role in the reinforcement of rubber films.

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LIST OF ABBREVIATIONS

NR	: Natural rubber
NRL	: Natural rubber latex
MMA	: Methylmethacrylate
PMMA	: Poly(methylmethacrylate)
γ -MPS	: Methacryloxypropyltrimethoxysilane
VTES	: Vinyltriethoxysilane
TEOS	: Tetraethoxysilane
δ	: Chemical shift
ATR-FTIR	: Attenuated total reflectance fourier transform spectroscopy
NMR	: Nuclear magnetic resonance spectroscopy
TEM	: Transmission electron microscopy
T_g	: Glass transition temperature
$CDCl_3$: Deuterated chloroform
ppm	: Parts per million (unit of chemical shift)
Phr	: Parts per hundred of rubber
DRC	: Dry rubber content
CHPO	: Cumene hydroperoxide
TEPA	: Tetraethylenepentamine
GE	: Grafting efficiency
SEM	: Scanning electron microscopy
RMS roughness	: root mean square roughness

CHAPTER I

INTRODUCTION

1.1 Statement of the Problem

Natural rubber (NR) latex obtained from natural resources of *Hevea brasiliensis* tree, known as *cis*-1,4-polyisoprene has been widely used in various applications such as balloon, condom and medical glove due to its excellent physical properties, comfort and feel. Unfortunately, the tack and high surface friction of NR glove are still problems and required some improvement. One of the methods for overcoming these problems is to graft a secondary polymer onto NR. Grafting a plastic with higher glass transition temperature such as poly(methyl methacrylate) (PMMA) onto NR has been recently developed in order to increase the surface hardness, roughness and to decrease the friction coefficient of rubber [1-3]. Moreover, reinforcement of NR by mixing with silica particles has become routinely performed in many rubber products, especially automobile tires. However, the presence of the polar hydroxyl groups on the silica surface can result in strong filler-filler interactions, caused by the strong hydrogen bond between particles. This can lead to aggregation of silica particles inside the rubber matrix; therefore poor reinforce efficiency occurs. Recently there were many reports on the formation of silica particles in the rubber matrix. The *in situ* formation of silica was achieved by a sol-gel process of tetraethoxysilane or TEOS, which was directly mixed with the latex. The advantage of the *in situ* generated silica over conventional mixing is the rubber and silica are able to interact more intimately, lowering the agglomeration of silica particles, resulting higher mechanical properties of the composite than conventional mixing [4]. An alternative method to improve rubber-filler interactions is to use a silane coupling agent. The use of silane coupling agent was chosen to enhance the compatibility between organic and inorganic components. Its chemical structure contains two different functional groups-one can react with the polymeric matrix and another can chemically bond to the surface of the silica [5]. The main role of coupling agents is to promote adhesion during the developments of mechanical and electrical properties such as tensile and flexural strength, fracture

toughness, tensile modulus, bulk electrical properties, dielectric coefficient, etc [6]. Among the silane coupling, the most commonly used one is γ -methacryloxypropyl trimethoxysilane (γ -MPS). The vinyl group in γ -MPS can be incorporated into the polymer chains by conventional free radical copolymerization reaction, while methoxysilyl group in the other end of the chain, undergoes hydrolysis/condensation to form siloxane bond (Si-O-Si) with other alkoxy silane molecules, i.e. TEOS and/or other γ -MPS molecules [7] resulting in crosslinking sites in the hybrid film. Beside γ -MPS, Vinyltriethoxysilane (VTES), a silane coupling agent, was reportedly used functional silane in polymer silica composites [4]. The VTES is capable of bonding to an organic material as γ -MPS does. The structures of their hydrocarbon moieties displayed similar polarity to that of rubber, but had different sizes.

In the present work, the graft copolymerization of NR with MMA (NR-*g*-MMA) was prepared using CHPO/TEPA as a redox initiator system. To reinforce the MMA grafted rubber, *in situ* generation of silica from TEOS was performed. The silane coupling agent, γ -MPS and VTES were also used to improve the adhesion and compatibility of silica/NR-*g*-MMA composites.

1.2 Research Objectives

In this work, our aim was to prepare a hybrid structure of silica and rubber by utilizing γ -methacryloxypropyl trimethoxysilane (γ -MPS) and vinyltriethoxysilane (VTES) as the coupling agent to improve the compatibility between the NR grafted with MMA (NR-*g*-MMA) and the *in situ* generated silica particles (from TEOS). Evidences of *in situ* silica formation as well as the grafting of MMA, and γ -MPS, and VTES were also investigated. Beside the *in situ* silica formation behavior, morphology, and mechanical properties of the grafted NR/silica composite films were analyzed.

1.3 Scope of the investigation

The stepwise investigation was carried out as follows:

1. Literature survey for method for preparation of *in situ* silica containing NR film
2. Preparation of grafted copolymers of methylmethacrylate onto NR latexes particles *via* seeded emulsion polymerization.
3. Grafting of γ -MPS in the latex containing NR-*g*-MMA.
4. Grafting of VTES in the latex containing NR-*g*-MMA.
5. Preparation of *in situ* silica/NR-*g*-MMA- γ -MPS composites by a sol-gel process of TEOS
6. Investigation the chemical structure of grafted NR/silica composites
7. Characterization of the morphology of grafted NR/silica composites
8. Characterization of the mechanical property of grafted NR films
9. Result interpretation and summary

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural rubber

Natural rubber 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*). This raw material is usually tapped from the rubber tree, which is native to ammonia. To harvest rubber, a small cut is made in the bark and a milky substance called latex flow out. Today, 85% of the world natural rubber comes from the South East Asia (Malaysia, Indonesia, and Thailand).

2.2 Natural rubber latex (NRL)

Natural rubber latex (NRL), a white milky fluid, collected by tapping from *Hevea brasiliensis* tree or Para rubber tree, is a native of the tropical rain forest in Brazil. Most of the world's natural rubber comes today from South-East Asia, mainly Thailand, Malaysia, and Indonesia [8]. In recent years, Thailand has been the world's leader in natural rubber production and exportation. The chemical structure of natural rubber is known as *cis*-1,4-polyisoprene as shown in Figure 2.1. NR has retained a leading place among commodity and engineering elastomers.

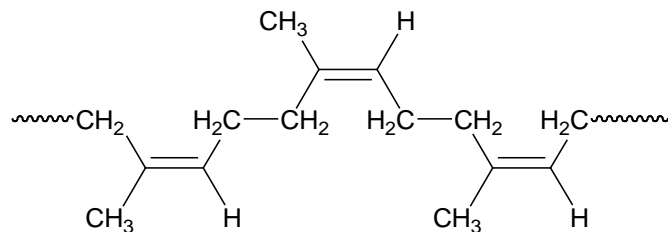


Figure 2.1 Chemical structure of natural rubber (*cis*-1,4-polyisoprene).

The colloidal suspension of natural rubber particles in aqueous phase are known as field latex. Field latex consists of rubber hydrocarbon particles and non-rubber

components suspended in an aqueous phase. Field latex consists of only about 36% dry rubber and 4% non-rubber substances. The non-rubber components include proteins, carbohydrates, liquids which are antioxidants and activators of cure, and trace elements including potassium, manganese, phosphorus, copper and iron which can act as catalysts for oxidation [9]. Its composition varied according to the clones of rubber, age of rubber tree, and tapping method. A typical composition of a field latex and dry rubber is shown in Table 2.1.

Table 2.1 Compositions of field latexes

Composition	Content (% by weight)
Dry rubber	36.0
Proteinous substance	1.0-1.5
Carbohydrates	1.6
Sugar, Lipids, Resinous substance	1.0-2.5
Inorganic matter	0.5
Water	58.5

Rubber particles in natural rubber latex are spherical droplets of hydrocarbon, which are stabilized by the negative charge of surface absorbed proteins and phospholipids as revealed in Figure 2.2 [10].

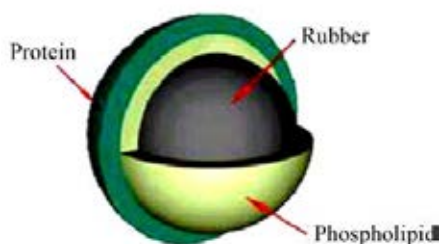


Figure 2.2 The structure of rubber particle [10]

About 10% of natural rubber is not processed into dry rubber but sold as latex. Latex concentrate is usually made by centrifugation-spinning at high speeds to separate off a cream of about 60% rubber from a liquid of about 5% rubber, from which dry skim rubber is made. Another concentrate, made by evaporation, evaporated latex concentrate, has higher rubber content and so slightly different properties. Finally, the latex concentrate is mixed with a chemical, such as ammonium alginate, which makes the rubber particles rise to the top of the liquid, like cream, when left to stand for several weeks. All latex concentrates are chemically treated to prevent coagulation.

2.3 Modification of natural rubber

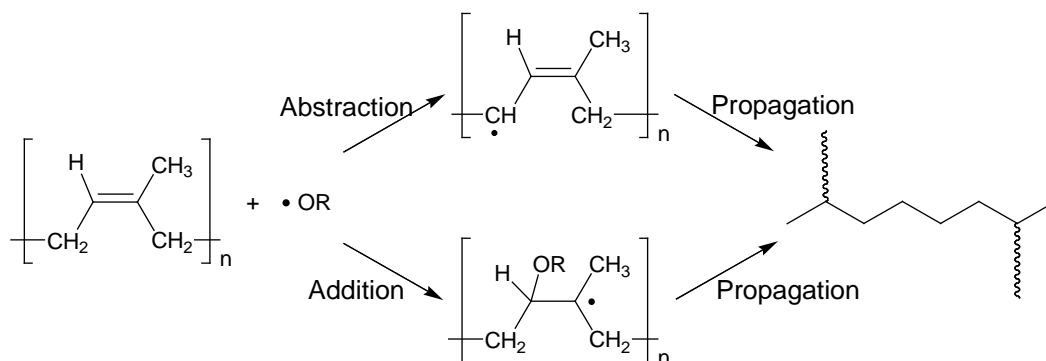
Natural rubber has been modified in many ways since the establishment of a continuous supply of rubber plantation. Modification highly affects its physical properties. Even thermoplastic or resinous materials can be obtained by a modification of rubber, the most well known types of modification are oxidation,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

2.3.1 Graft copolymers from natural rubber

Graft copolymerization has been used as a common method for modifying NR in a latex form. Reactions involving free radicals have been the most widely applied in a grafting process, and such reactions have been used with a wide range of polymers and monomers. Free radical initiators may promote grafting in two different ways when added to a monomer/polymer system. The grafting of secondary polymer onto polyisoprene may be induced in two pathways (Scheme 2.1).

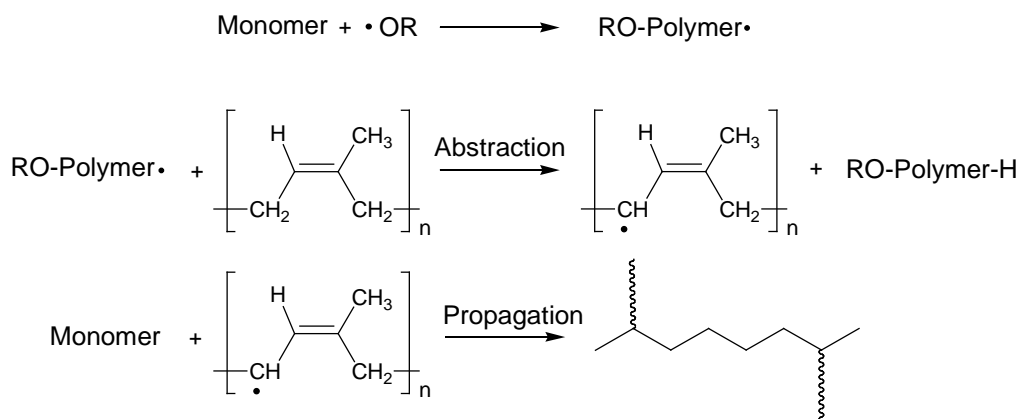
Direct attack of rubber by initiator radical:

The first method is through a grafting site which the initiator-derived radicals either add across the double bond or abstract hydrogen atoms from polyisoprene backbone [11].



Chain transfer with polymer via abstraction:

In the second method, the growing long chain radical (RO-polymer \bullet) undergoes chain transfer with the polymer, probably by hydrogen abstraction, leading to the initiator of a graft [12].



Scheme 2.1 Graft copolymerization pathways

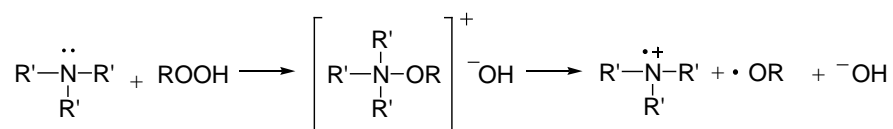
2.3.2 Mechanism of grafting

The following reaction in Scheme 2.2 is proposed for the graft copolymerization of vinyl monomers onto natural rubber by free-radical method [13].

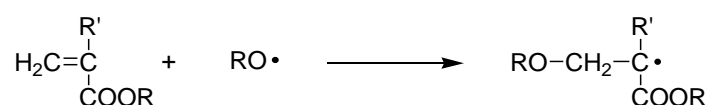
Redox initiation:

This type of initiation can produce the radicals by many oxidation-reduction reactions. These can be used to initiate polymerization. In a redox initiation, the hydroperoxide was induced by amine activator decomposition to yield alkoxy radicals (RO \bullet). The alkoxy radical might interact with either the monomer or the rubber

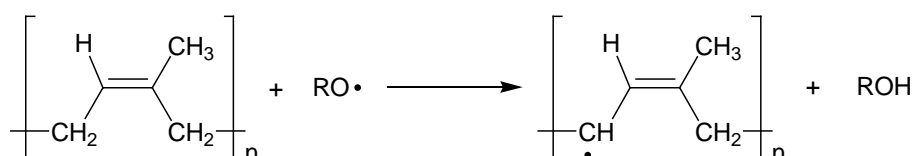
molecule to produce macroradical, which initiated grafting sites. It is possible for the α -methylene hydrogen atoms in the natural rubber, which are more active, to become the sites of graft copolymerization.



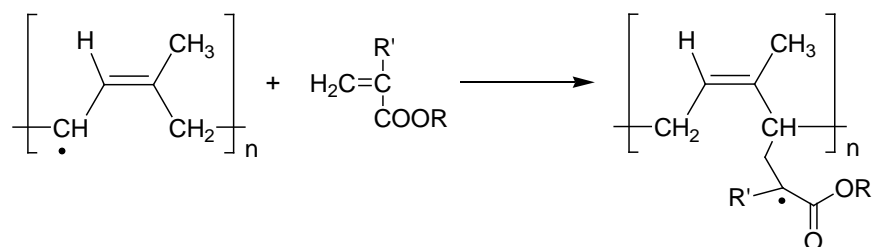
Monomer attack:



NR attack:



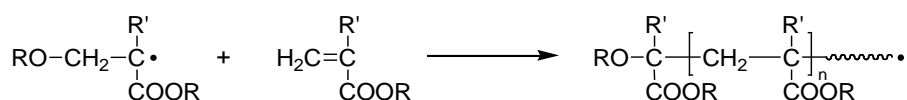
Re-initiation:



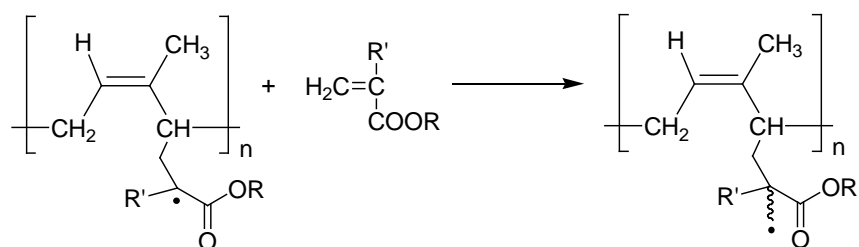
Propagation:

The alkoxy radicals ($\text{RO}\cdot$) not only can attack the α -methylene hydrogen atoms to produce polyisoprene radicals, which initiate monomers to form the graft copolymers, but can also initiate monomers to form free homopolymer radicals.

Propagation of free polymerization (homopolymer):



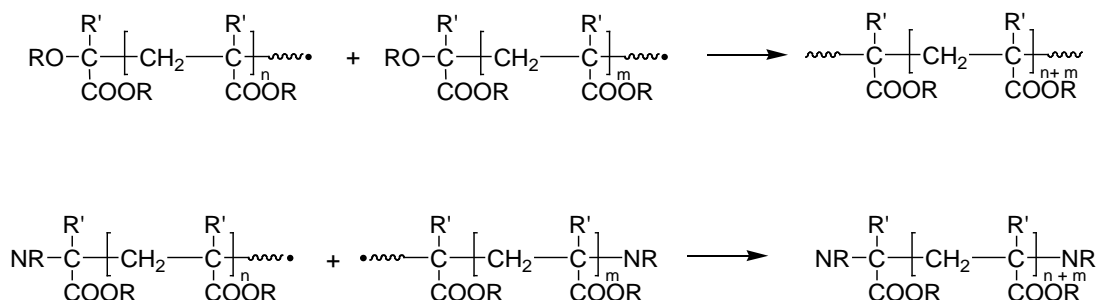
Propagation of graft polymerization:



Termination:

Moreover, the free homopolymer radicals can terminate by combination or disproportionation to form free homopolymers. The end product of the graft copolymerization process is composed of graft copolymers and free homopolymer phase in a reaction.

Combination and disproportionation:



Scheme 2.2 Mechanism of graft copolymerization of secondary polymer

The Natural Rubber Research Organizations had investigated processes for grafting polymers to natural rubber using free radical chemistry. Graft copolymer of poly(methyl methacrylate) onto natural rubber under trade name of “Heveaplus-MG”, by a graft copolymerization by *tert*-butylhydroperoxide (*t*-BHPO) has been commercialized since mid 1950s. The chemical modification of NR by grafting with vinyl monomers combines the properties of both NR and the polymer of the monomer grafted. It has gained considerable importance as it leads to polymers with altered and improved properties for the production of new materials. The most promising graft copolymer based on NR, thus far obtained, is that derived from methyl methacrylate (MMA) and styrene (ST) [13]. The graft copolymer may be prepared by graft copolymerization of NR in the latex form, since the NR, an unsaturated elastomer having the existence of double bonds in its chains, can be readily grafted with a variety

of monomers, using the well-established technique of seeded emulsion polymerization. The couple redox initiators have been extensively used to initiate the graft polymerization of secondary polymers at moderate temperature. In 2002, Arayapranee, *et al.* [13] chose the couple redox initiator of cumene hydroperoxide (CHPO)/sodium formaldehyde sufoxylatedihydrate/EDTA-chelated Fe^{2+} to prepare the graft copolymerization of MMA and ST onto NR. The hydroperoxide oxidizes the iron (II) ions, thus introducing alkoxy radicals that can be used to initiate polymerization. Moreover, the produced iron (III) ions, in turn, oxidize the reducing agent, being they reduced to iron (II) ions once again. Recently, the effect of various types of redox initiator systems including CHPO/TEPA, *t*-BHPO/TEPA, $\text{K}_2\text{S}_2\text{O}_8/\text{K}_2\text{S}_2\text{O}_5$, and $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_3$ were studied on the graft copolymers of dimethylaminoethyl methacrylate (DMAEMA), dimethylaminoethyl acrylate (DMAEA), and MMA [11] onto NR by emulsion polymerization. The CHPO/TEPA was found to be the most effective redox initiating system and has been widely applied to prepare graft copolymers of NR and MMA later [11-12,14]. It was also found that CHPO/TEPA gave the highest percentage grafting efficiency and lowest yield of homopolymer content of PMMA because the partition ability of CHPO into NR phase is higher than that of *t*-BHPO and $\text{K}_2\text{S}_2\text{O}_8$.

2.3.3 Core shell mechanism

The couple redox initiator of CHPO/TEPA could be used to prepare NR-based core-shell latex particles. CHPO is soluble in organic phase (NR particles phase and monomer), whereas the amine activator, TEPA, is soluble in aqueous phase. The initiators present in the graft copolymerization of secondary polymers onto NR particles, therefore, seem to be appropriate to create sites of grafting by the abstraction reaction over addition to allylic double bonds acting predominantly at the interface of NR particles as illustrated in Figure 2.3. Therefore, the free radicals are mostly generated only at the surface of NR particles. This leads to low conversion of copolymers.

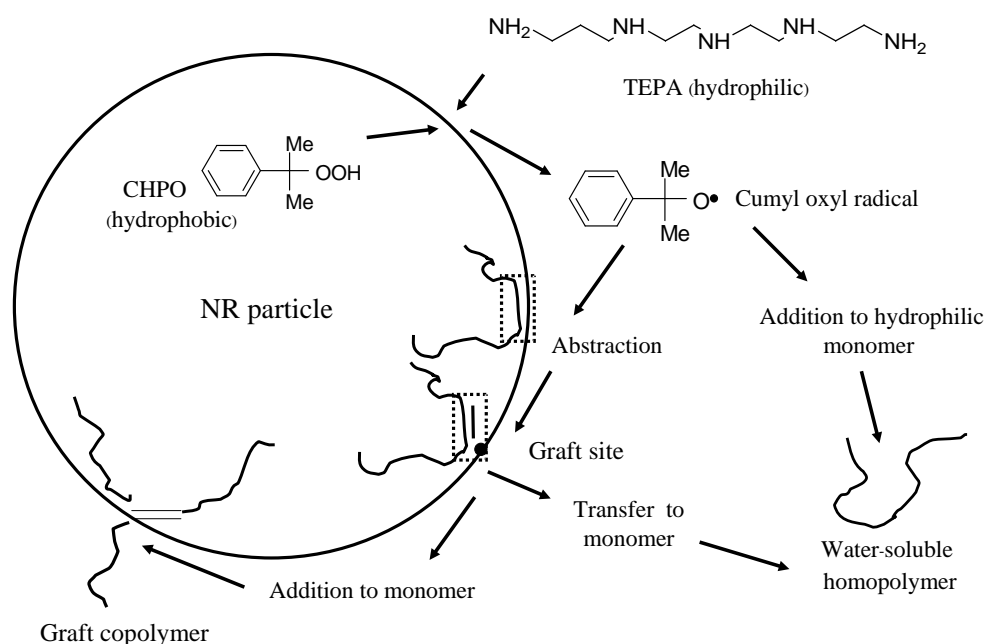
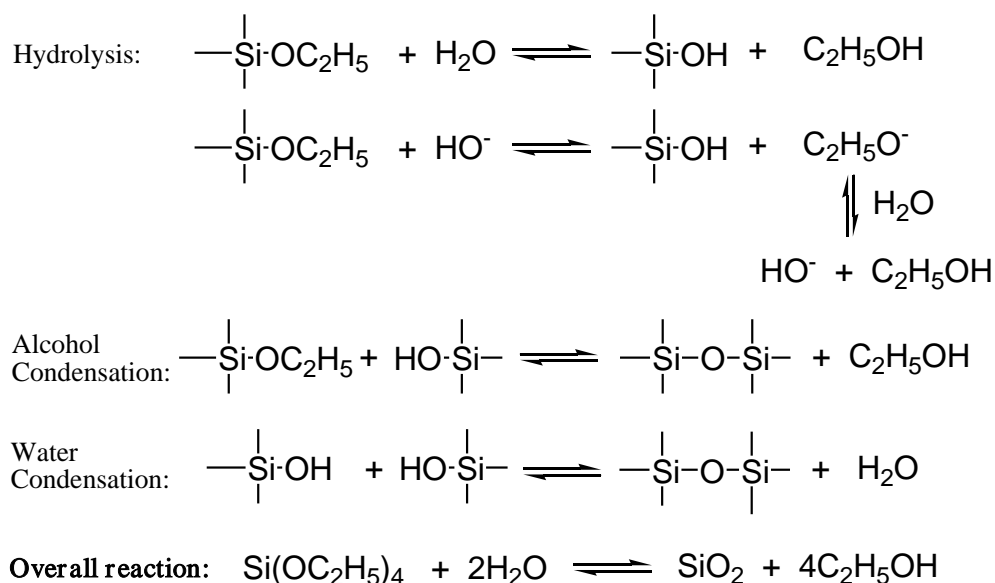


Figure 2.3 Schematic routes of the possible grafting reaction by using the bipolar redox initiator (CHPO/TEPA) systems *via* seeded emulsion polymerization [12]

2.4 Silica formation by sol-gel process of TEOS

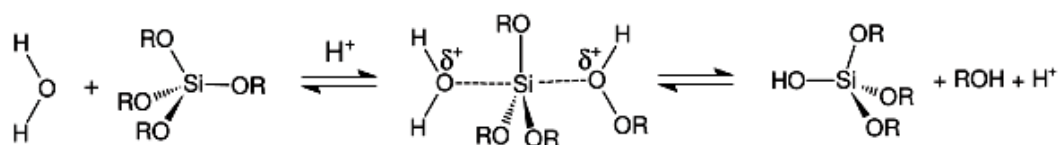
The sol-gel process occurs in liquid solution of metal alkoxide precursors such as tetraethoxysilane or tetraethylorthosilicate, TEOS, which, by means of hydrolysis and condensation reactions, leading to the formation of a new phase, called ‘sol’. The sol is made of solid particles of a diameter of few hundreds of nanometer suspended in a liquid phase. Then the particles condense into a new phase, called ‘gel’ in which a solid macromolecule is immersed in a liquid phase (solvent). Hydrolysis and condensation reaction of TEOS or other metal alkoxides to form silica is shown in Scheme 2.4. Initially, metal alkoxides react readily with water. The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the metal atom (so that all of the OR groups are replaced by OH groups). Two partially hydrolyzed molecules can link together in a condensation reaction. By definition, condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon containing molecules by the process of polymerization.



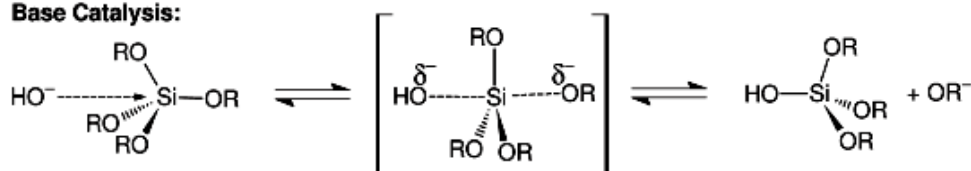
Scheme 2.3 Hydrolysis and condensation reaction of TEOS to form silica

The mechanisms of acid and base-catalyzed hydrolysis are shown in Scheme 2.4.

Acid Catalysis:



Base Catalysis:



Scheme 2.4 Differences in mechanism depending on the type of catalyst used in the silicon-based sol-gel process [15].

A sol-gel process of TEOS was applied to prepare silica for reinforcement of rubbers. In 2000, Kohjiya and Ikeda [16] studied *in situ* silica in natural rubber (NR) matrix. Preparation of the silica filled rubber compound was performed by the sol-gel method. The NR sheet was immersed in TEOS for 48 h at room temperature before being crosslinked by sulfur. The silica-silica interaction of *in situ* silica seemed to be weaker than that of silica-rubber to result in better dispersion compared with the conventional silica. The *in situ* silica particles showed good reinforcement effect on the

NR vulcanizate without the silane coupling agent. The *in situ* silica was homogeneously dispersed in the natural rubber matrix.

In 2002, Yoshikai *et al.* [17] reported a study on silica reinforcement of synthetic diene rubbers by a sol-gel process of TEOS in the latex. The TEOS was mixed directly into the latex of styrene butadiene rubber (SBR) and nitrile rubber (NBR). The sol-gel process of TEOS then proceeded in a mixture of latex. The silica content in the compounds, particle size and reinforcing behavior of silica were found to depend on the amount of TEOS added and the molar ratio of water to TEOS. The average particle size of silica was reported to be smaller than 100 nm. The tensile strength of SBR and NBR was over 25 MPa.

In 2003, Kojiya and Ikeda [18] prepared the *in situ* silica reinforcement of NR by the sol-gel reaction of TEOS using n-butylamine as a catalyst. γ -mercaptopropyl trimethoxysilane was used for modifying the silica surface. The reaction of TEOS in raw NR was conducted before the processing for NR vulcanizates. The *in situ* silica with coupling agent afforded the lowest viscosity compared not only with conventional silica but also with a carbon black. Lower hydrophilicity of the *in situ* silica surface may result in less filler-to-filler interaction in the reason of better performances.

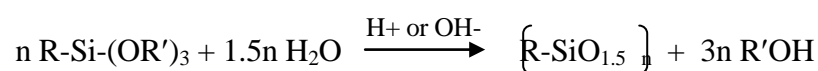
A “green” (eco-friendly) composite was prepared by Ikeda and Kameda. In 2004, Ikeda and Kameda [19] prepared *in situ* silica nano-particles by a sol-gel reaction of tetraethoxysilane (TEOS) in natural rubber (NR), which was prepared by the NR sheets immersing in TEOS. The swelling degree of NR in TEOS was important for controlling the *in situ* silica content in NR. The *in situ* silica was nano-particle sized, and its particle size became larger with the increase of silica content from ca. 10 nm to ca. 40 nm for 10–40 phr loadings in the NR matrix, respectively. The excellent reinforcement effect of *in situ* silica for the NR vulcanizates was observed when increasing the *in situ* silica content. The *in situ* silica filling in NR is a good method to prepare the rubbery nano-composites with unique characteristics.

In 2009, Chaichua *et al.* [20] investigated the parameters of *in situ* silica formation in natural rubber by a sol-gel reaction. The NR sheets were immersed in TEOS at room temperature for 3 h. THF was the suitable solvent for the sol-gel reaction. N-hexylamine was the most efficient base catalyst to produce the high amount

of *in situ* silica in the rubbery matrix compared with n-butylamine. It was because the longer chain of n-hexylamine easily penetrated into NR matrix. The higher the mole ratio of TEOS to H₂O, the higher the silica content was obtained. The Mooney viscosity of the *in situ* silica filled NR vulcanizates showed a lower value compared with that of the commercial filled ones. The mechanical properties of the *in situ* silica composite materials, i.e., the moduli and compression set, were improved compared with the commercial silica filled NR vulcanizates.

2.5 Silica formation by sol-gel process of Organotrialkoxysilanes

Organotrialkoxysilanes are typically co-polymerized with another sol-gel monomer-generally tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). The sol-gel polymerization of organotrialkoxysilanes involving hydrolysis and condensation that usually results in the formation of *low* molecular weight silica are shown in Scheme 2.5.



Scheme 2.5 Hydrolysis and condensation of trialkoxysilane to give polysilsesqui-oxane

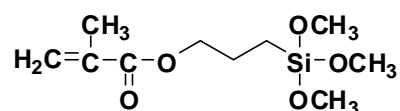


Figure 2.4 The chemical structure of γ -MPS

The first commercially available coupling agent was the highly reactive 3-mercaptopropyl trimethoxysilane for sulfur-cured compound and vinyltrimethoxysilane and 3-methacryloxypropyl trimethoxysilane (the structure of γ -MPS is shown in Figure 2.4) for peroxide-cross-linked rubber compounds. With the addition of these silanes a remarkable increase in the reinforcement of white-filled compounds was achieved [21].

In 2000, Loy, *et al.*[22] examined the sol-gel chemistry of organotrialkoxysilanes having different organic groups with methoxide or ethoxide substituents on silicon, at varying monomer concentrations, and under acidic, neutral, and the basic conditions. Polysilsesquioxane gels were prepared by the sol-gel polymerization of organotrialkoxysilane. They found that the large substituent group of organotrialkoxysilane led to the formation of oligomers and polymers in the form of oils and resins. Formation of gels from organotrialkoxysilane is significantly hindered by phase separation of oligomeric or polymeric silsesquioxanes and, to a lesser extent, by sterically bulky organic substituents.

In 2009, Siramanont, *et al.* [4] studied the sol-gel process of alkyltriethoxysilanes that was dispersed in natural rubber latex to generate alkylated silica particles inside the rubber matrix. Three types of alkyltriethoxysilanes were chosen, i.e., vinyltriethoxysilane (VTOS), ethyltriethoxysilane (ETOS), and i-butyltriethoxysilane (BTOS). The alkylated silica particles were formed in the rubber matrix by a certain combination of TEOS and alkyltriethoxysilanes. 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 study on hardness, tensile, and tear properties revealed that the uses of *in situ*-generated silica and alkylated silicas resulted in a better reinforcement capability to the rubber vulcanizates than did the conventionally added silica powder.

In 2011, Dirè *et al* [23] prepared hybrid silica nanoparticles by hydrolysis–condensation of organotriethoxysilanes with a wide range of organic functions and without tetraalkoxysilane addition. The degree of condensation of the silsesquioxane networks is high even when precursors bearing long alkyl chains have been used. Regular shaped spheres functionalized by vinyl, methyl, ethyl, phenyl, amyl, octyl, 3-aminopropyl groups were obtained, with sizes in the range 100–400 nm.

2.6 Silane coupling agent

A high silica–rubber interaction is achieved by chemical coupling using bifunctional silanes. For the application of the silica–silane filler system, prereacted

silica–silane products can be used, but *in situ* modification of the silica with the silane during the mixing process is more common. The silica–silane filler system is needed for industrial rubber goods that require high reinforcement combined with the possibility to manufacture white or colored products such as seals, hoses, and profiles. In some dynamic applications the silica–silane filler system is needed to reduce the heat buildup. Silane coupling agents that provide a chemical link between the filler and the rubber are needed. The use of silanes allows a modification of the polar silica surface that makes the silica more compatible with the rubber matrix.

The γ -MPS, trialkoxysilane acting as coupling agents are mainly prepared for coating application. Up to now, there are no literatures reporting the preparation of γ -MPS and couple with TEOS for generating *in situ* silica in the rubber matrix. In this study, γ -MPS is first used to improve compatibility between NR matrix and silica from TEOS.

In 2001, Tissot *et al.* [7] prepared polystyrene latex particles coated with a silica shell. In a first step, γ -MPS molecules were incorporated into polystyrene latex particles. The pH of the suspension was adjusted to 7 (to slow down γ -MPS hydrolysis and condensation reactions). In the second step, the trimethoxysilyl groups trapped into the organo-mineral seed latexes were reacted with TEOS in water under basic conditions to yield silica-coated latex particles. The structure of the copolymer was characterized by ^{13}C and ^{29}Si solid-state CP-MAS NMR and IR spectroscopy was found to incorporation of γ -MPS units in the copolymer chain by free radical polymerization. The results from TEM showed clearly that the formation of a smooth and regular silica layer on the seed particles was highly dependent on the nature of the latex core. It is presumed that the success of the seeded growth process in this system is due to the unique hybrid structure of the copolymer.

In 2005, Ni *et al* [24] synthesized core-shell nanoparticles with a polystyrene core and a hybrid copolymer shell via emulsion polymerization of styrene and subsequent addition of γ -MPS to produce the shell by copolymerization reaction of γ -MPS with the residual amount of styrene. Along with the copolymerization process, hydrolysis and polycondensation reactions were taking place in the presence of the aqueous phase, resulting in cross-linking of the alkoxysilane monomer which chemical

process has a strong influence on the latex particles size and on the shell microstructure.

In 2006, Zhang *et al* [25] synthesized polystyrene latex nanoparticles bearing silanol groups on their surfaces via miniemulsion polymerization using γ MPS as the functional comonomer and oil-soluble AIBN as the initiator at neutral conditions. FTIR and ^{29}Si NMR spectra showed that the condensation of silanol groups was suppressed effectively. ζ -potential and XPS analyses demonstrated that the silanol groups were enriched at the surfaces of the latex particles and could be tailored by MPS concentration. These silanol-functionalized latex particles could be easily coated with silica or other inorganic or organic compounds to prepare novel hybrid particles and hollow microspheres.

In the same year (2006), Zu *et al.* [26] prepared polymethylmethacrylate/SiO₂ nanocomposite particles through microemulsion polymerization by using the silica particles coated with 3-(trimethoxysilyl)propyl methacrylate (MSMA) in both acidic and alkaline conditions. Nanocomposite microemulsion, based on the charge attraction between silanol particles and cation initiators, at low pH values such as pH 2 the surface of silanol precursor had few charges, and as a result, every hybrid particle had only one silica core, while at high pH values such as pH 9, the large negative surface charge caused autocondensation between silanols and thus led to the formation of cellular structures in the hybrids. The structure of the hybrid was also affected by the amount of silanol and the coupling agent in the system. Increasing either silanol or the coupling agent caused the change of hybrid structures from a regular core-shell structure to a cellular structure.

In the same year Yeh *et al* [27] successfully synthesized a hybrid coating consisting of organic PMMA and inorganic silica by using 3-(trimethoxysilyl)propyl methacrylate (MSMA) as a coupling agent. In this work, MSMA was first copolymerized with MMA monomer at a specific feeding ratio by using benzoyl peroxide as initiator. Subsequently, the as prepared copolymer was then co-hydrolyzed with various contents of tetraethyl orthosilicate (TEOS) to afford chemical bondings to the forming silica networks. The hybrid sol-gel coatings in the form of coating were found to show advanced corrosion protection effect on cold rolled steel (CRS) coupons

relative to the pure PMMA based on the electrochemical measurement of the corrosion potential, polarization resistance and corrosion current.

CHAPTER III

METHODS AND MATERIALS

3.1 Chemicals

High ammonia natural rubber latex (NRL, 0.7% (w/w) NH_4OH) with 60% dry rubber content was purchased from the Rubber Research Institute of Thailand (Bangkok). The stabilizer oleic acid (Fluka, Lab grade) and potassium hydroxide (KOH; Fluka), the emulsifier sodium dodecyl sulfate (SDS; Fluka, 99.5%), methyl methacrylate (MMA; Aldrich, 99%), the couple redox initiator cumene hydroperoxide (CHPO; Fluka, 80%), the amine activator tetraethylenepentamine (TEPA; Fluka, 85%), γ -methacryloxypropyl trimethoxysilane (γ -MPS; Aldrich, 98%), vinyltriethoxysilane (VTOS; Aldrich, 98%) tetraethoxysilane (TEOS; Aldrich, 98%), toluene (Merck, AR grade), and petroleum ether (Merck, 98%) were used without additional purification. Ammonia solution (25% (w/v)) was purchased from BDH (England).

3.2 Methods

3.2.1 Preparation of peroxide-prevulcanized natural rubber latex

In this work, a bipolar redox initiating system of CHPO/TEPA acts as the peroxide vulcanizing agent. The high ammonia natural rubber latex (60% dry rubber content, DRC) was diluted by adding 0.7% (v/v) ammonia solution to obtain latex with 30% DRC. The latex was charged into a round-bottomed flask and deoxygenated by nitrogen gas purging through the latex for 30 min at room temperature. Next, the latex was heated up to 50°C under N_2 atmosphere, followed by CHPO and TEPA initiator addition. The bipolar redox initiating system was employed at 1:1 ratio (CHPO:TEPA) for a total amount of 1.5 phr. The reaction was allowed to proceed for 1 h under continuous stirring and N_2 atmosphere. After prevulcanization step, the latex was rapidly cooled down to room temperature to prevent further vulcanization, and was then

filtered through a wire mesh to separate coagulated solid phase. Pre vulcanized natural rubber latex was obtained.

3.2.2 Preparation of pre vulcanized NR grafted with MMA and γ -MPS or VTOS

The grafting was divided into 2 steps. The pre vulcanized latex was first grafted with MMA, followed by γ -MPS or VTOS. In the first step, the stabilizer, KOH (0.25 phr), SDS (1 phr) solutions, and oleic acid (10 phr) were mixed into the latex (30%DRC) with N₂ bubbling at room temperature. The MMA monomer was then added dropwise continually while stirring to allow the latex particles to absorb the monomer. Then the latex mixture was heated up to 50°C, followed by CHPO and TEPA (1:1) initiator addition for a total amount of 1.0 phr. The reaction was allowed to proceed for 1 h under continuous stirring and N₂ atmosphere. In the second step, the latex mixture was rapidly cooled down to room temperature, followed by the addition of more CHPO/TEPA for a total amount of 0.5 phr. γ -MPS or VTOS was then added with continually stirring to allow the latex particles to absorb the monomer. The grafting was achieved by heating the latex mixture at 80°C for 2 days in ambient atmosphere.

3.2.3 Preparation of *in situ* silica formation from TEOS

A predetermined amount of TEOS was added into the latex mixture to obtain a homogeneous milky mixture. The latex was then filtered through a wire mesh screen to separate a small amount of coagulated solid. The latex mixture was poured into a petri dish. The dish was then closed and sealed to reduce ammonia evaporation and was dried in an oven (80°C) for 2 days. Rubber-silica hybrid films were obtained. Formulations of the latex compound for the preparation of grafted NR are shown in Table 3.1.

Table 3.1 Formulations of the latex compounds for the preparation of grafted NR

Code	NR (phr) ^a	MMA (phr)	γ -MPS (phr)	VTES (phr)	TEOS (phr)
NR-g-MMA	30	17.65	-	-	-
NR-g- γ -MPS	30	-	17.65	-	-
NR-g-VTES	30	-	-	17.65	-
NR-g-MMA-TEOS	30	17.65	-	-	20
NR-g-MMA- γ -MPS	30	14.12	3.53	-	-
NR-g-MMA-VTES	30	14.12	-	3.53	-
NR-g-MMA- γ -MPS/TEOS	30	14.12	3.53	-	5,10,15,20
NR-g-MMA-VTES/TEOS	30	14.12	-	3.53	5,10,15,20

a = parts per hundred of rubber

3.3 Characterization of grafted NR

3.3.1 Determination of grafting results

The conversion of MMA to PMMA was defined as the ratio of total weight of PMMA formed (free PMMA and grafted PMMA) and total weight of MMA monomer charged into the reaction (eq. 3.1):

$$\% \text{ conversion} = \frac{\text{Total weight of PMMA formed}}{\text{Weight of MMA charged}} \times 100 \quad (3.1)$$

The weight of homo or free PMMA, ungrafted NR (free NR), and grafted NR were determined after a solvent soxhlet extraction method. The ungrafted NR was extracted by light petroleum ether (60-80°C) for 48 h. The residue was dried to a constant weight in an oven at 70°C. The residue was further extracted by acetone for 48 h to remove the free PMMA. Calculation for grafting efficiency is based on the weight

ratio of grafted PMMA and total PMMA (homo PMMA and grafted PMMA) formed as shown in eq. 3.2:

$$\% \text{ grafting efficiency} = \frac{\text{Total weight of grafted PMMA}}{\text{Weight of PMMA formed}} \times 100 \quad (3.2)$$

The percentage of grafted NR in the total polymer added and formed in the system was calculated by eq. (3.3).

$$\% \text{ grafted NR} = \left(\frac{b}{a + b + c} \right) \times 100 \quad (3.3)$$

where a, b, and c are the weights of ungrafted NR, grafted NR, and homo PMMA, respectively.

3.3.2 Attenuated total reflectance-Fourier transform infrared (ATR FT-IR) spectroscopy

The composition of NR film sample was determined by Fourier transform infrared spectrometer in the range of 4000-400 cm^{-1} . IR spectra were collected using a Nicolet 6700 FT-IR spectra. The IR spectra were acquired by using the Omnic ESP in a range of 4000-500 cm^{-1} .

3.3.3 Transmission Electron Microscopy (TEM) for morphology

Morphology of NR particles before and after grafting was observed by JEOL transmission electron microscopy (TEM, Model JEM-2100, Japan) at 120 kV. The grafted NR latexes were diluted 400 times by deionized water. A drop of the diluted latex was deposited on a carbon-coated Formvar® grid. Then, the substrate grid was stained by a drop of chemical staining vapor, RuO_4 , in a glass-covered dish at room temperature for 24 h and dried overnight in a desiccator. The substrate grid was additionally stained by exposure to RuO_4 vapor in a glass-covered dish at room temperature for 24 h. Only the double bonds in the chemical structure of NR were reacted with the chemical staining vapor.

3.3.4 Scanning Electron Microscopy (SEM) for surface analysis

An SEM was used to analyze the fractured surface of the composite films. The samples were fractured under liquid nitrogen. The fractured samples were then sputter-coated with gold. The photographs were taken on a JOEL JSM-6480LV SEM. The SEM photographs were used to estimate the degree of silica particle dispersion. Measurements were done at 15 kV at 1,000 and 10,000 magnifications. Energy dispersive X-ray spectrometer (EDX) detector was carried at an elevation angle of 35° in order to determine atomic type on the analyzed surface.

3.3.5 Atomic force microscopy (AFM) for surface roughness and morphology

AFM images were recorded with Scanning Probe Microscope model NanoScopeIV®, Veeco, U.S.A.. Measurement were performed in air using a tapping mode. Silicon nitride tip with a resonance frequency of 267-298 kHz and a spring constant of 20-80 N/M was used. The root mean square roughness (R_q) of the rubber surfaces was computed from NanoScope software by using the following:

$$R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n (Z_i - m)^2}$$

where, Z_i is the height of the profile at n^{th} point, n is the number of points selected, and m is the height of the mean line that fits in the middle of the profile.

3.3.6 Silica content in the composites

The silica content was determined by cutting the grafted NR composites films into small pieces to have a weight of ~50 mg. After an exact weight was determined, the sample was heated at 850°C for 15 min in an oven. The weight of the remaining ash was calculated for the silica content by equations 3.4 and 3.5

$$\text{Weight of silica in the sample } (W_I) = W_a - W_0 \quad (3.4)$$

where W_a is the weight of sample's ash, and W_0 is the weight of ash from silica-free sample. The silica content in phr unit was calculated as follows;

$$\text{Silica Content} = 100 (W_1/W_2) \quad (3.5)$$

where W_1 is the weight of silica in the sample, W_2 the weight of the rubber.

The conversion of the silane to silica was calculated using equation 3.6,

$$\text{Conversion (\%)} = 100 (W_3/W_4) \quad (3.6)$$

where W_3 is the obtained amount of the *in situ* generated silica in the sample, and W_4 is the theoretical amount of generated silica based on the added amount of silane in the latex. The results reported were averaged from three specimens.

3.3.7 Mechanical properties

3.3.7.2 Tensile properties

The tensile properties of the grafted NR composites were measured following the JIS K6251-8 test method. The testing was performed on a Hounsfield H10KS universal testing machine (Hounsfield, Redhill, UK) using dumbbell-shaped specimens. The specimens were cut into dumbbell shape specimens using a die cutter with the dimension as shown in Figure 3.1. For each sample, at least 5 specimens were tested with the crosshead speed of 500 mm/min.

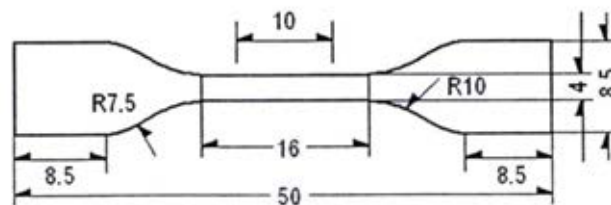


Figure 3.1 Schematic diagram of tensile test specimen (JIS K6251-8)

3.3.7.2 Tension Set

The grafted NR composite films were cut into the size of 5×60 mm as shown in Figure 3.2. Two lines which were about 10 mm apart were marked on the sample. The distance between the two lines was measured by a digital caliper. The sample was extended until distance the between t he two lines was twice that of the original length, and was held for 10 min. After 10 min, the sample was allowed to retract for 10 min. The final distance between the two lines was measured.

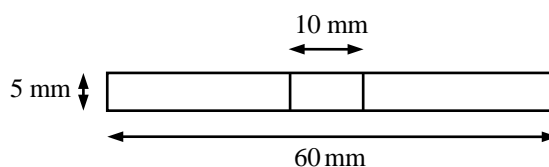


Figure 3.2 Schematic diagram of tension test specimen

The tension set was calculated using the following equation

$$\text{Tension set (\%)} = 100 ((L_f - L_i)/L_i) \quad (3.4)$$

where L_i is the initial distance between two lines, and L_f is the final distance between two lines.

3.3.8 Swelling measurements of NR/Silica composites

Circular specimens with a diameter of 0.5 mm were cut out from the grafted NR composite films. Specimens of known weights were immersed in toluene at room temperature for 24 h to allow the swelling to reach diffusion equilibrium. Then, the specimens were immediately blotted out with filter paper to get rid of toluene on the on the surface. Their weights were then determined. From the differences of sample masses, the degree of swelling was calculated by:

$$\text{Degree of swelling (\%)} = 100 ((W_f - W_i)/ W_i) \quad (3.5)$$

where W_i is the initial weight of the specimen, and W_f is the final (swollen) weight of the specimen.

CHAPTER IV

RESULTS AND DISCUSSION

The aim of this work was to prepare a hybrid structure of silica and rubber by utilizing γ -methacryloxypropyl trimethoxysilane (γ -MPS) and vinyltriethoxysilane (VTES) as the coupling agent between the *in situ* generated silica particles and MMA-grafted rubber chains to improve the compatibility between the two moieties. The silica particles were produced inside the rubber matrix from the sol-gel process of tetraethoxysilane or tetraethyl orthosilicated (TEOS). In this chapter, the results have been divided into 3 parts. The first part clarifies the grafting of MMA, γ -MPS, and VTES on the rubber (in the latex form), followed by peroxide vulcanization of the grafted rubber latex. The second part reveals details on the formation and characterization of silica in the grafted NR via the sol-gel process of TEOS together with the siloxane side groups of each of the two vinylated silanes. In the final part, mechanical properties tests of the silica–rubber hybrid materials are presented.

4.1 Preparation of grafted NR and peroxide vulcanization

4.1.1 Grafting of MMA on NR (in latex)

As mentioned in chapter 3, graft copolymerization of MMA was carried out in a latex medium *via* seeded emulsion polymerization. At the first step, the high ammonia NR latex with 60% DRC was diluted by 0.7% ammonia solution in order to obtain NR latex having 30% DRC. A potassium hydroxide solution (10% w/v) was added to maintain the latex stability as well as the basic condition of the latex during grafting. Sodium dodecyl sulfate (SDS) was added as an emulsifier to prevent foaming and to preserve the colloidal stability of the latex. After the addition of MMA, it was believed that MMA was absorbed on the surface of rubber particles. CHPO/TEPA was chosen as the couple redox initiator to generate radicals onto the surface of NR particles to form the grafted PMMA shell around the seed NR particles. This method has been found to

give high grafting efficiency and low free homopolymer yield [28]. The weight ratio of NR:MMA was fixed at 85:15, as it was an optimum amount to produce less tack film reported earlier by Satraphan *et al* [14]. After the completion of grafting process, the resulting products still consisted of ungrafted (free) NR, free homo PMMA, and the desired grafted copolymer (NR-*g*-MMA). Consequently, the undesired free NR and free homopolymer were extracted out by solvent soxhlet extraction method. The free NR was extracted by petroleum ether while the free PMMA was removed by extracting in acetone.

Grafting characteristic was studied by determine the amount of graft copolymer and homo-polymer formed during the grafting step. The percentages of monomer conversion, graft copolymer, free homopolymer, and grafting efficiency (GE) of NR-*g*-MMA prepared in this work were compared to those of sulfur-cured grafted NR reported by Satraphan *et al* [14] (Table 4.1). The grafting efficiencies of the two methods were about the same.

Table 4.1 The conversion of MMA, amount of graft copolymer, homopolymers, and grafting efficiency of MMA on NR in latex state

Sample	MMA conversion (%)	Grafted NR (%)	Free homopolymer (%)		%GE
			NR	PMMA	
NR- <i>g</i> -MMA ¹	96.3	78.6	17.9	3.5	77.5
NR- <i>g</i> -MMA	62.2	80.7	17.6	1.7	89.5

¹prepared by Satraphan *et al* [14]

After the soxhlet extraction of the NR-*g*-MMA, the grafted NR was analyzed for its functional groups by ATR-FTIR technique. The FTIR spectra of NR showed the absorption bands at 3032, 2958, and 838 cm^{-1} corresponding to of the stretching vibration of olefinic =C-H, aliphatic -C-H, and out of plane bending vibration of aliphatic -C-H, respectively (Figure 4.1). Two distinct new peaks of the grafted NR were found at 1725 and 1147 cm^{-1} , corresponding to the C=O stretching and C-O-C stretching of MMA. This evidence confirmed the grafting of MMA on the NR.

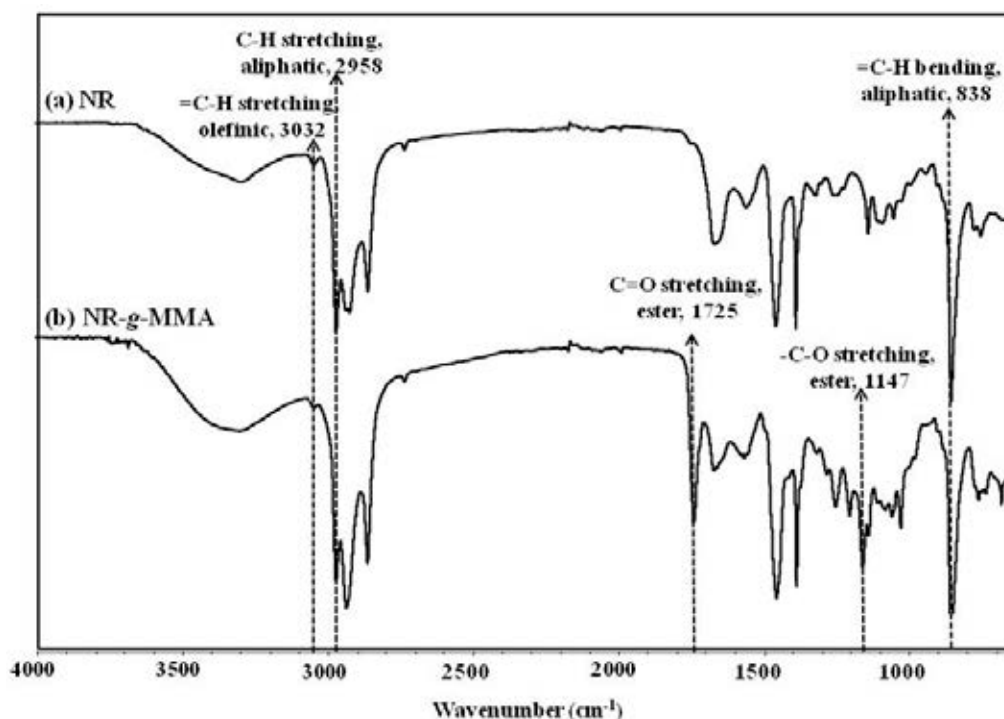


Figure 4.1 FTIR spectra of (a) NR, and (b) NR-*g*-MMA

The grafting of NR latexes was performed in the presence of CHPO/TEPA. Oil-soluble nature of CHPO and water-soluble characteristic of TEPA allowed the generation of radicals at the NR–water interface. This facilitates the polymerization of the secondary polymers at the interface of NR particles, which provided the formation of a shell layer around the core NR particles as core-shell morphology [12]. Transmission electron microscopy (TEM) was employed to investigate the morphology of grafted NR particles obtained. The morphology of the grafted and ungrafted NR

particles was studied by using RuO_4 staining at $\text{C}=\text{C}$ bonds of NR to improve the contrast and gradation between the NR and non-NR phase in the composite of latex particles [28]. The shape of ruthenium-stained NR particles in the latex appeared to be a dark sphere with clear boundaries (Figure 4.2 (a)). After the MMA grafting, a semi-translucent layer of grafted PMMA covering the dark-toned seed rubber particle was observed to have core-shell morphology (Figure 4.2 (b) and (c)). Because the ruthenium-staining occurred solely at the unsaturated chemical bonds ($\text{C}=\text{C}$) on the NR chain, PMMA was not stained at all and appeared as semi-transparent shade in the micrograph. This evidence suggested that the grafting took place at the surface of the NR seed particle in the latex to give PMMA outer shell layer.

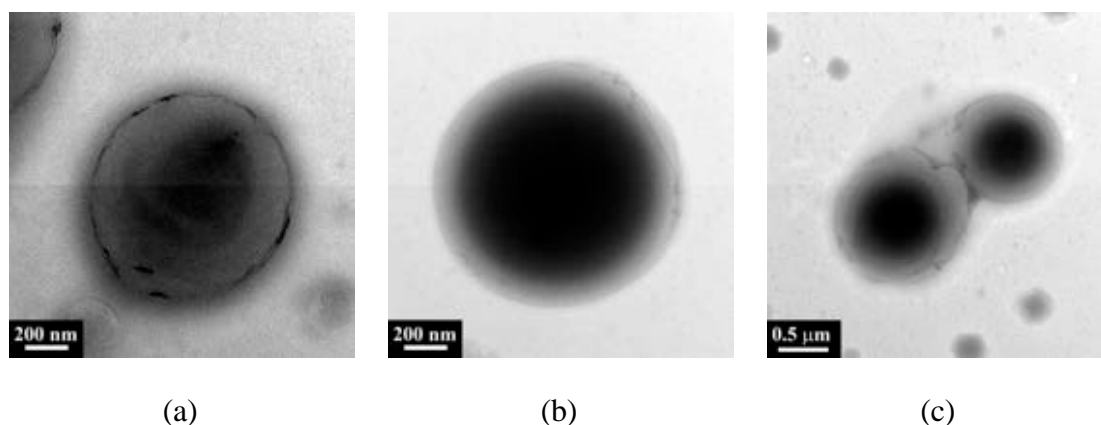


Figure 4.2 Transmission electron micrographs of NR latex particles (a) and NR-g-MMA particles (b and c; different magnifications) [All samples were stained with 1% RuO_4 vapor before analysis.]

A scanning electron microscope (SEM) was employed to investigate the cryogenically fracture surfaces of the specimens. Figure 4.3 displays the SEM micrographs that revealed the fracture surfaces of NR and NR-g-MMA. The NR-g-MMA surface was rougher than that found for the NR. The grafting between the hard plastic (PMMA) and elastomer (natural rubber) components leads to aggregates and globular shape of the particles.

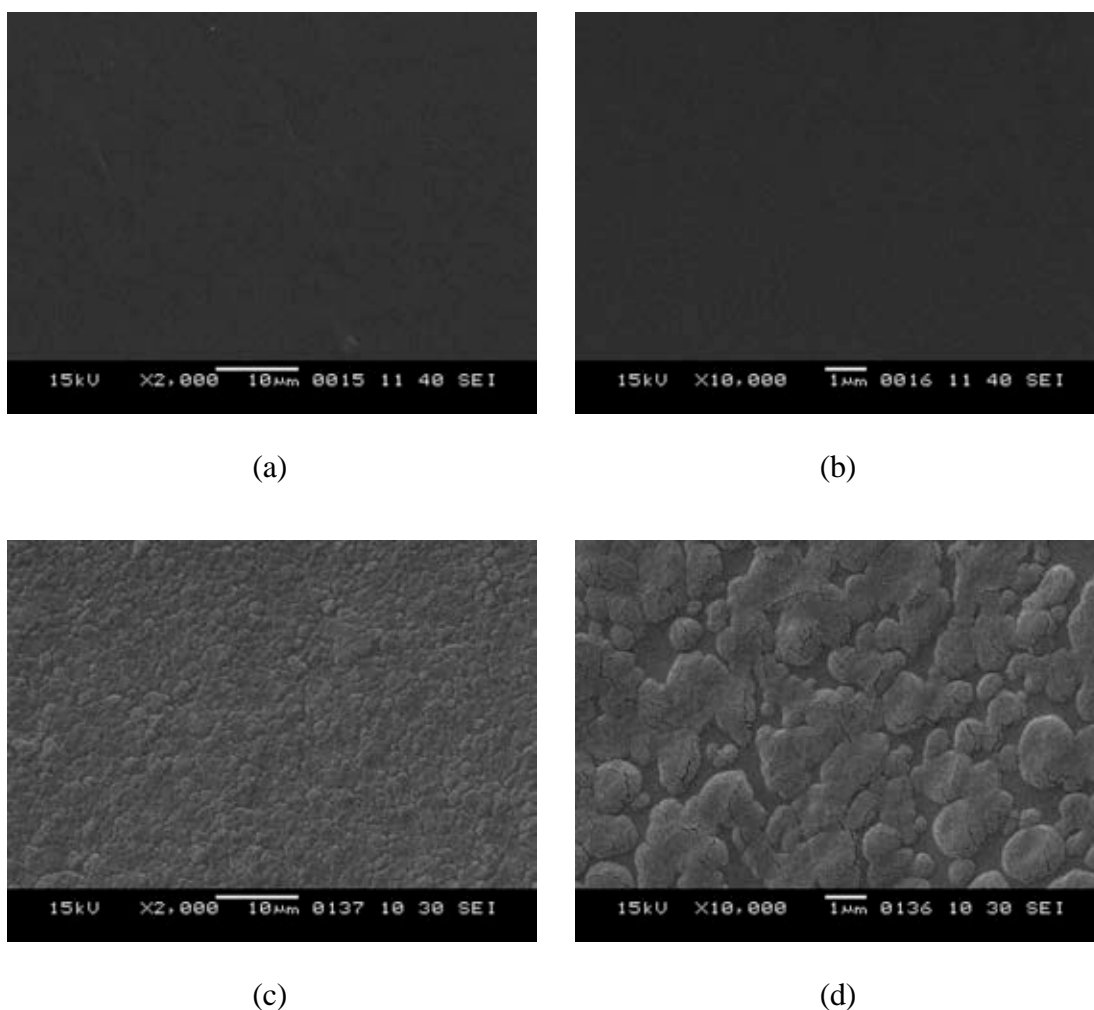
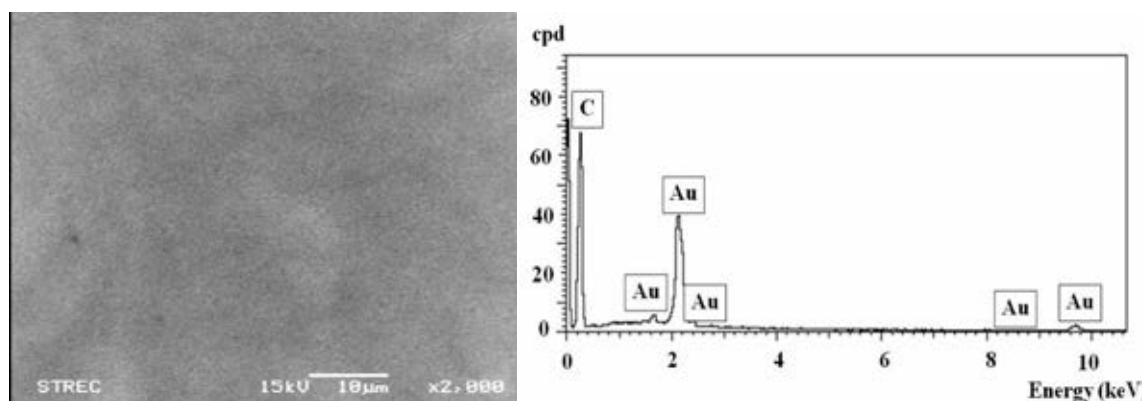
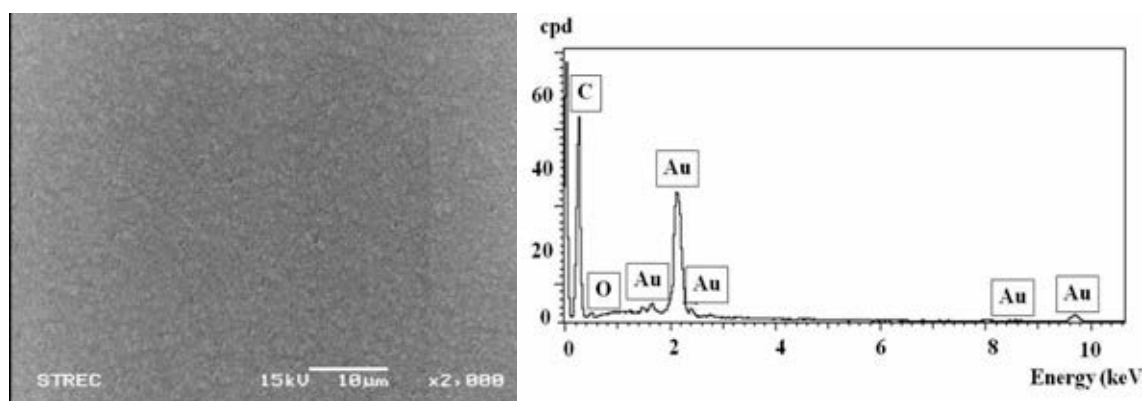


Figure 4.3 The fractured surfaces of NR (a) at 2000 magnification, (b) at 10000 magnification, NR-g-MMA (c) at 2000 magnification, and (d) at 10000 magnification by SEM

Furthermore, the fractured surface of NR and NR-g-MMA films were analyzed for elements in the grafted copolymer at a selected area of the rubber matrix by EDX technique. In Figure 4.4 (a), the SEM-EDX spectrum of NR shows very low-intensified O (oxygen atom) peak at 0.5 KeV on the fractured surface. After the MMA grafting, a peak of O atom at 0.5 KeV is clearly observed, supporting that the MMA was successfully grafted onto NR chains.



(a) NR



(b) NR-g-MMA

Figure 4.4 The SEM-EDX micrographs of (a) NR and (b) NR-g-MMA films

4.1.2 Grafting of γ -MPS with NR-g-MMA latexes

In this work, graft copolymerization between NR and MMA was firstly prepared. Then the addition of γ -MPS was performed with the goal to graft γ -MPS on the NR-g-MMA particles in the latex. Theoretically, γ -MPS after being activated by radical initiator can be grafted on the double bond of NR chains and/or coupling with the grafted PMMA radical chain end. The grafting of γ -MPS on NR was performed using a similar procedure for graft copolymerization of MMA. The chemical structure of NR-g- γ -MPS was verified by ^{13}C NMR and ATR-FTIR analysis. The grafting

efficiency of γ -MPS on NR in the latex state cannot be determined by gravimetric method using soxhlet extraction as done in the case of NR-*g*-MMA. This was because γ -MPS tended to form alkylated silica particles when it was heated up, preventing an accurate measurement of the weight of the polymer being extracted. ^{13}C NMR spectroscopy was therefore used to determine changes of the key functional groups from the olefinic carbon-carbon double bond in γ -MPS molecule to become the saturated C-C single bond when the grafting was accomplished. The NMR spectrum of γ -MPS molecule was determined in CDCl_3 , while that of the NR-*g*- γ -MPS was analyzed in solid state due to dissolution problem of the grafted vulcanizate. The solid state ^{13}C NMR spectrum of NR was run as a reference as illustrated in Figure 4.5. The signals of two ethylenic carbons were observed at 135.40 (*a*) and 125.80 (*b*) ppm. The signals at 32.02 (*c*) and 27.25 (*d*) ppm were assigned to two methylene carbon atoms. The signal of methyl carbon (*e*) appeared at 24.19 ppm. All signals indicated the carbon atoms of *cis*-1,4-polyisoprene of NR [29].

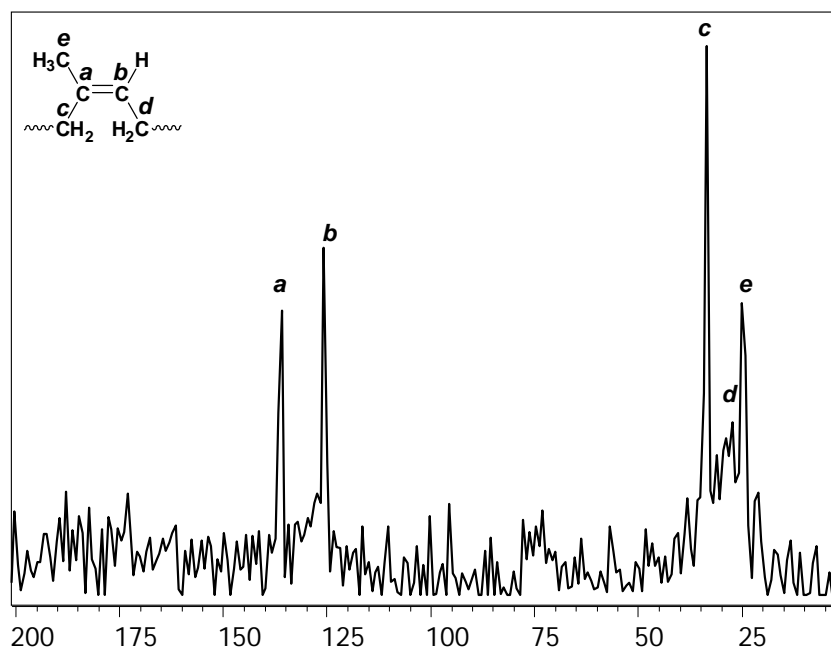


Figure 4.5 Solid stated C^{13} NMR spectrum of NR film

^{13}C NMR analysis of γ -MPS monomer in CDCl_3 (Figure 4.6) revealed the carbon signals of two ethylenic carbons at 136.48 (a) and 125.11 (b) ppm. The signal at 168.37 (c) ppm was assigned to carbonyl carbon of γ -MPS. The carbon signals of three methylene groups were appeared at 66.67 (d), 21.20 (e), and 6.69 (f) ppm. The carbon signal of methoxy groups was observed at 50.65 (g) ppm. The carbon signal of methyl was found at 18.54 (h) ppm [30].

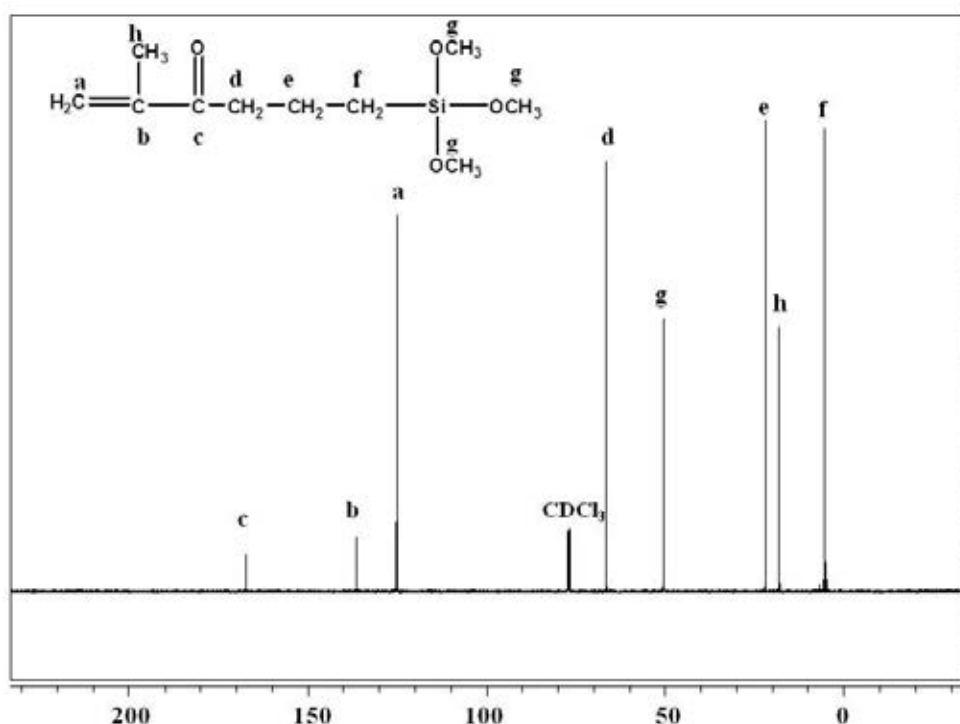


Figure 4.6 Liquid state ^{13}C NMR spectra of γ -MPS

From the solid-state ^{13}C NMR spectrum of NR-*g*- γ -MPS (Figure 4.7), two new peaks appeared at 45.55 ppm due to the quaternary carbon atom and at 175.09 ppm due to the C=O groups bonded to aliphatic carbon atom [31]. These two functional groups would only be obtained after a success of the γ -MPS grafting on the rubber. Moreover, the disappearance of carbon signal of methoxy silyl groups of γ -MPS at 50.65 ppm indicated that those groups were completely hydrolyzed in the latex medium and possibly went to condense with another γ -MPS molecule to form ‘siloxane’ bond (-Si-O-Si-).

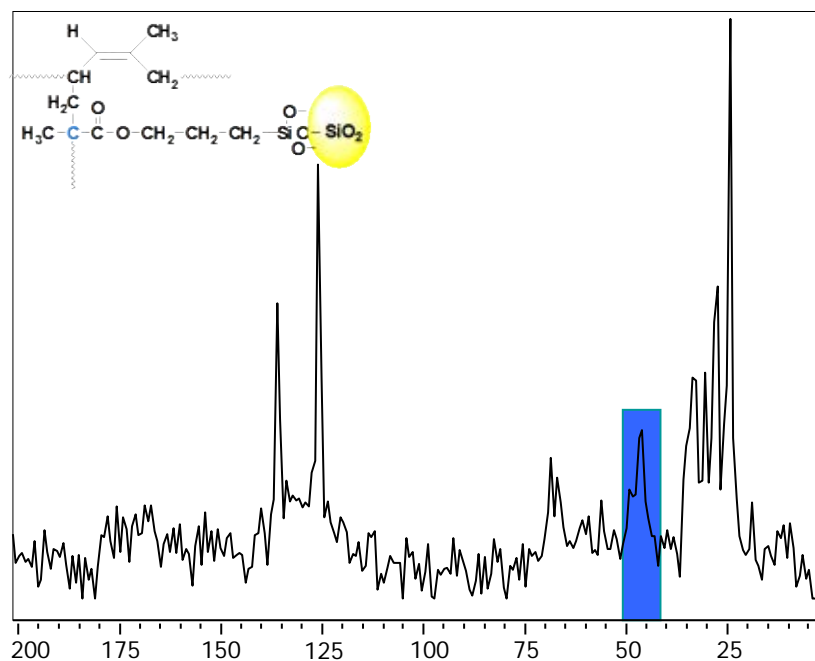


Figure 4.7 Solid state ^{13}C NMR spectra of NR-g- γ -MP

Furthermore, a physical mixture of NR and γ -MPS (NR/ γ -MPS) was prepared and analyzed by the NMR (Figure 4.8) with the aim to compare the spectrum pattern of unreacted methacrylate group of γ -MPS with the reacted one. This sample was prepared by direct mixing γ -MPS with NR latex without heating but with the same drying step. The NMR result clearly shows that no quaternary carbon signal at 44.55 ppm was observed as found in the grafted system in which the vinyl group of γ -MPS was transformed to the saturated C-C single bond.

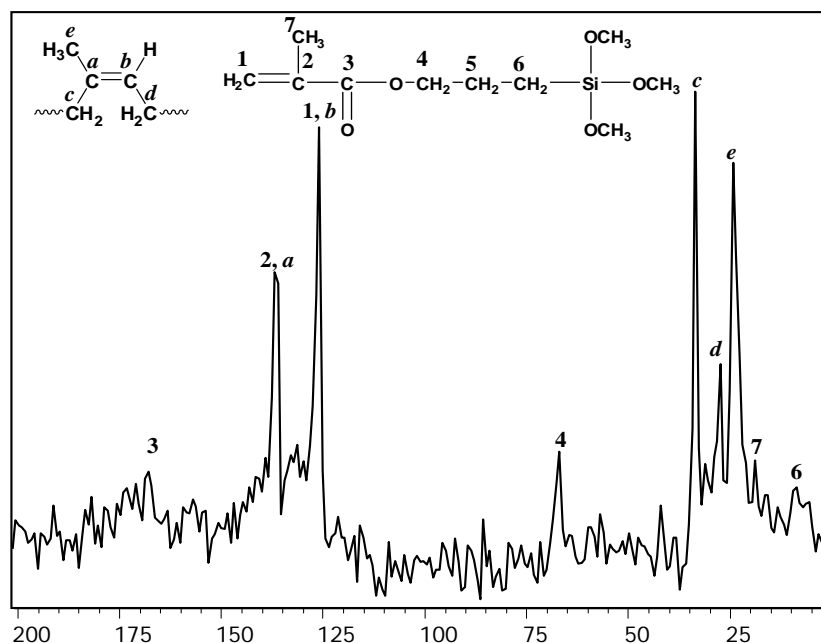


Figure 4.8 Solid state ^{13}C NMR spectra of a physical mixture of NR and γ -MPS

The latex of NR- g - γ -MPS, NR- g -MMA- γ -MPS, and their ungrafted analogs (physical mixtures); NR/ γ -MPS and NR- g -MMA/ γ -MPS, were characterized by TEM with the aim to observe single rubber particles and the location of grafted MMA and γ -MPS. All samples for TEM analysis were stained by RuO_4 which only reacted with the carbon-carbon double bond ($\text{C}=\text{C}$) of the NR to increase contrast and gradation of the NR particles. NR- g - γ -MPS gives NR core surrounded by alkylated silica particles as darkish round tiny particles (Figure 4.9 (a)). For NR/ γ -MPS, the NR core is also surrounded by the silica particles but as loosely clusters (Figure 4.9 (b)), different from the *in situ* silica particles obtained after grafting. This can indicate that the loosened agglomerates of the ungrafted γ -MPS to form silica would become more compact by the linkage between the nanoparticles offered by the grafting reaction.

For NR- g -MMA- γ -MPS, core-shell morphology containing dark-shaded silica nanoparticles generated from γ -MPS and grey-shaded PMMA shell growing outward from seed rubber particle was also obtained (Figure 4.9 (d)). When comparing between NR- g -MMA- γ -MPS and its mixed analog (NR- g -MMA/ γ -MPS), the shape and location of *in situ* formed silica was, however, not really different (Figure 4.9 (e)). In addition, *in situ* formed silicas unbound to the rubber particles are seen widely dispersed in the

emulsion phase (Figure 4.9 (c), (f), (g)). These dispersed particles probably are the ungrafted γ -MPS homopolymer in which dark-shaded silica are also observed. These results indicate that γ -MPS can undergo a sol-gel process to create *in situ* alkylated silica at either the rubber shell by grafting or copolymerization with NR-*g*-MMA latex particles or remaining in the continuous phase in the form of low molecular weight cyclic oligomers.

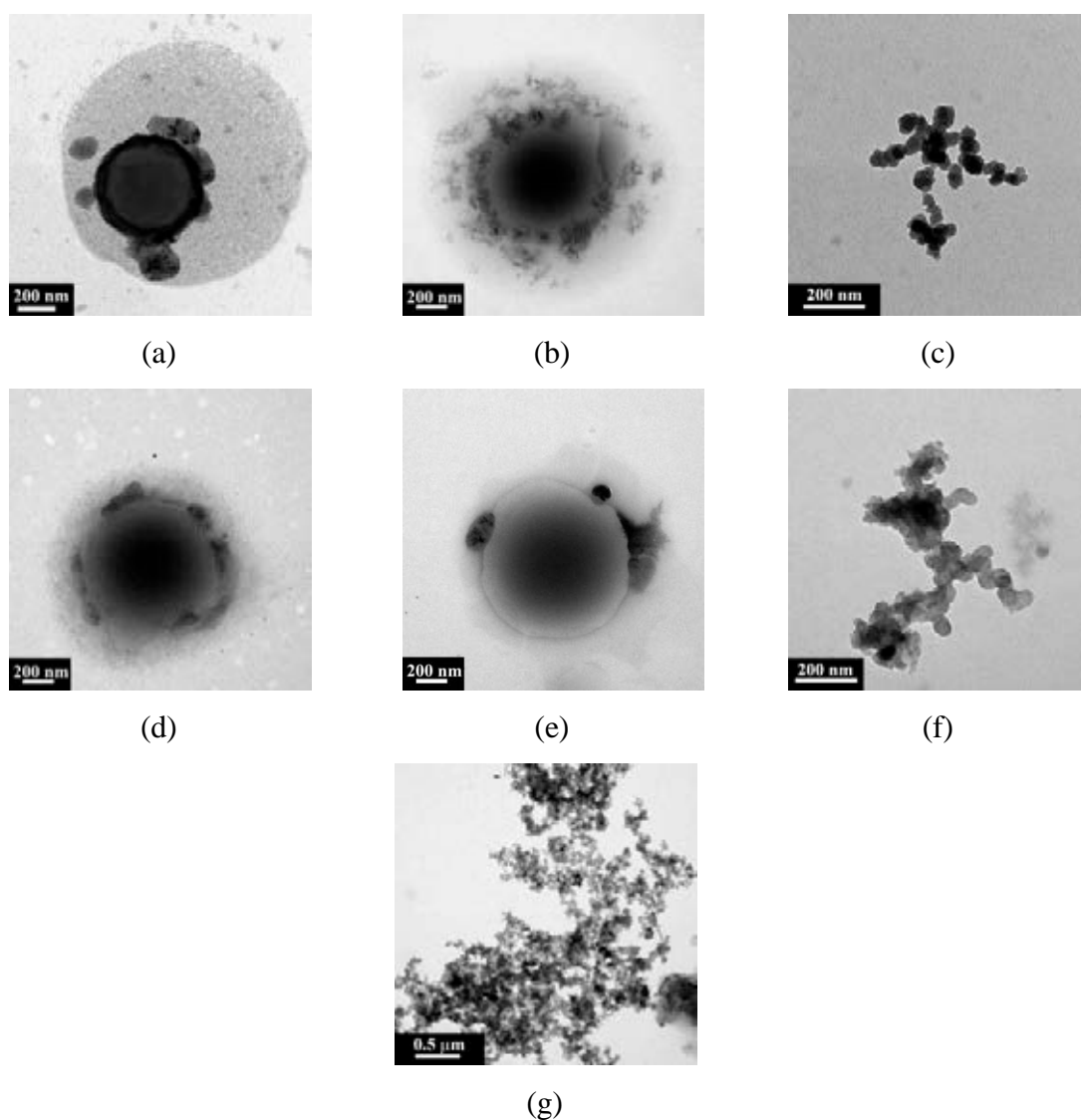
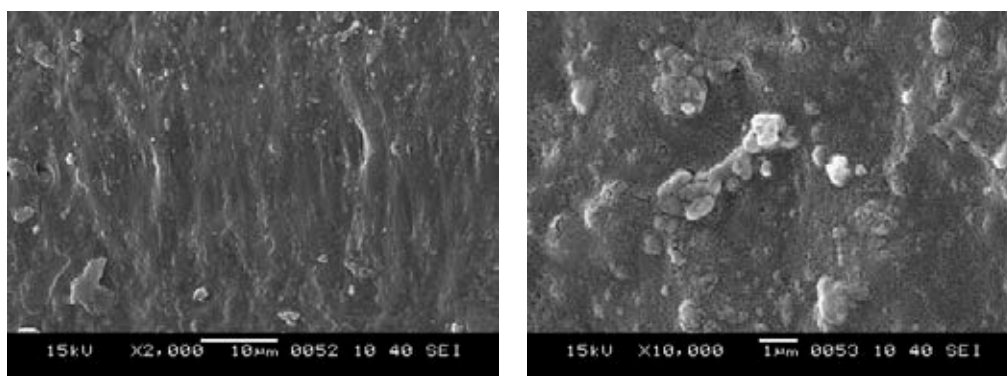
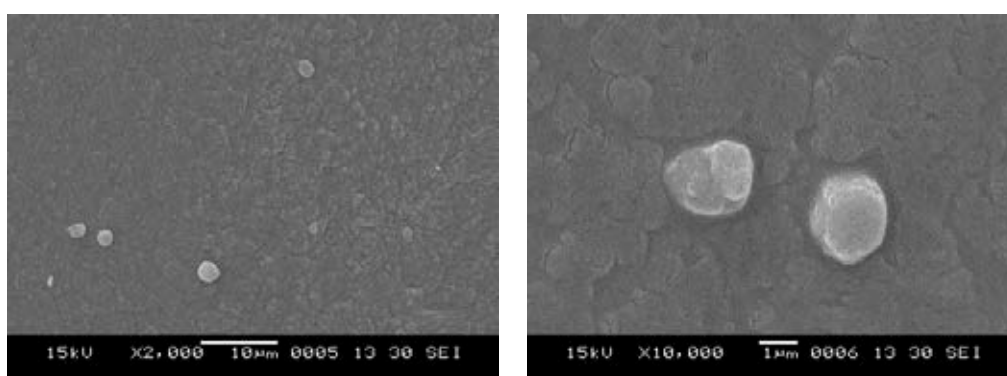


Figure 4.9 Transmission electron micrographs of (a) NR-*g*- γ -MPS, (b) NR/ γ -MPS, (c) unbound silica particles found in NR-*g*-MMA- γ -MPS, (d) NR-*g*-MMA- γ -MPS, and (e) NR-*g*-MMA/MPS, (f) unbound silica particles found in NR-*g*- γ -MPS, and (g) unbound silica particles found in NR/ γ -MPS



(a) NR-g-MPS (3.53 phr alkylated silica)



(b) NR-g-MMA-MPS (1.23 phr alkylated silica)

Figure 4.10 Scanning electron micrographs of (a) NR-g-MMA- γ -MPS (3.53 phr of γ -MPS) and (b) NR-g- γ -MPS (17.65 phr of γ -MPS)

The fractured surfaces of the *in situ* silica filled NR-g-MMA composites were analyzed by SEM (Figure 4.10). Silica particles in the NR-g-MMA- γ -MPS and NR-g- γ -MPS composite which contains 3.53 phr and 17.65 phr of γ -MPS are shown in Figure 4.10 (a) and (b), respectively. The white spots represent silica particles and the dark area represents NR and NR grafted with MMA. It can be clearly seen that the alkylated silica was successfully generated by γ -MPS as a silica precursor with particle size in the range of microscale. Furthermore, the rubber phase of NR-g-MMA is rougher than the pristine NR (Figure 4.3 (a)-(b)). Moreover, the fractured surface of NR-g-MMA- γ -MPS film was analyzed for element types at a selected sample area by EDX technique. In Figure 4.11, the SEM-EDX spectrum shows Si peaks at 1.75 KeV, supporting that the silica particle was successfully generated in the grafted NR film.

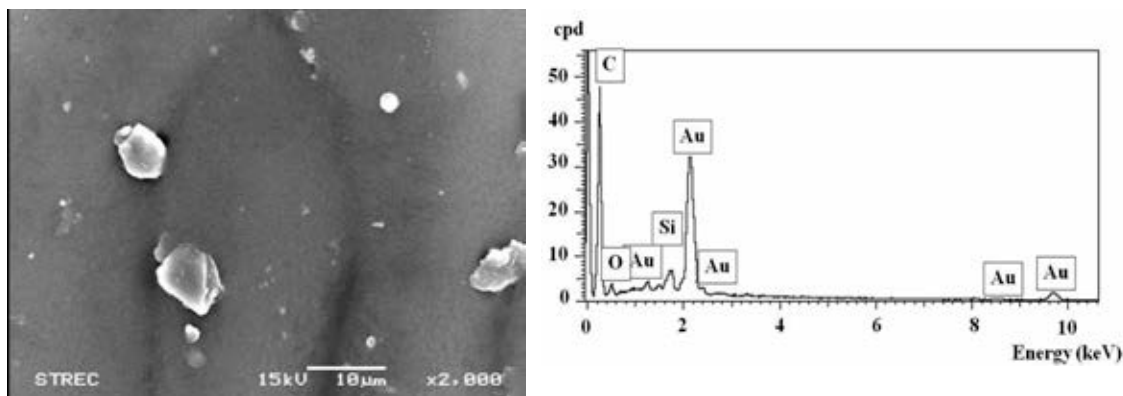


Figure 4.11 EDX spectra of NR-g-MMA- γ -MPS

4.1.3 Grafting of VTES with NR-g-MMA latexes

Vinyltriethoxysilane (VTES), a silane coupling agent is capable of bonding to an organic material as γ -MPS does. The distance between the vinyl group and silicon atom of VTES is shorter than γ -MPS. Graft copolymerization of VTES was carried out in latex medium *via* seeded emulsion polymerization. The reaction was performed using a similar procedure for the graft copolymerization of MMA and γ -MPS. The chemical structure of NR-g- γ -VTES and NR-g-MMA-VTES were also investigated by ATR-FTIR analysis.

The ATR-FTIR analyzed results of the grafted NR are shown in Figure 4.12. The ATR-FTIR spectrum of NR (Figure 4.12 (a)) displays the characteristic transmission peaks at 3032, 2958, and 844 cm^{-1} corresponding to =C-H stretching of olefinic, C-H stretching of aliphatic, and =C-H bending of aliphatic, respectively. When NR was grafted with VTES, a new strong band at 1128-1051 cm^{-1} appeared, assigning to Si-O-Si band of condensed silica network as shown in Figure 4.12 (b). If the condensation reaction was not completed, Si-OH groups would also be existed. When VTES was grafted with NR-g-MMA, the new strong band at 1128-1051 cm^{-1} also appeared similarly to that of the NR-g-VTES, assigning to Si-O-Si band of the silica network, indicating that ethoxysilyl groups of VTES can condense with other ethoxysilyl groups to form a siloxane network. These result confirmed the existence of *in situ* silica generated with VTES in the grafted NR film. Furthermore, the addition of

MMA in the grafting system resulted in the existence of the new sharp peak at 1722 cm^{-1} corresponding to ester C=O stretching of MMA which was grafted onto NR backbone.

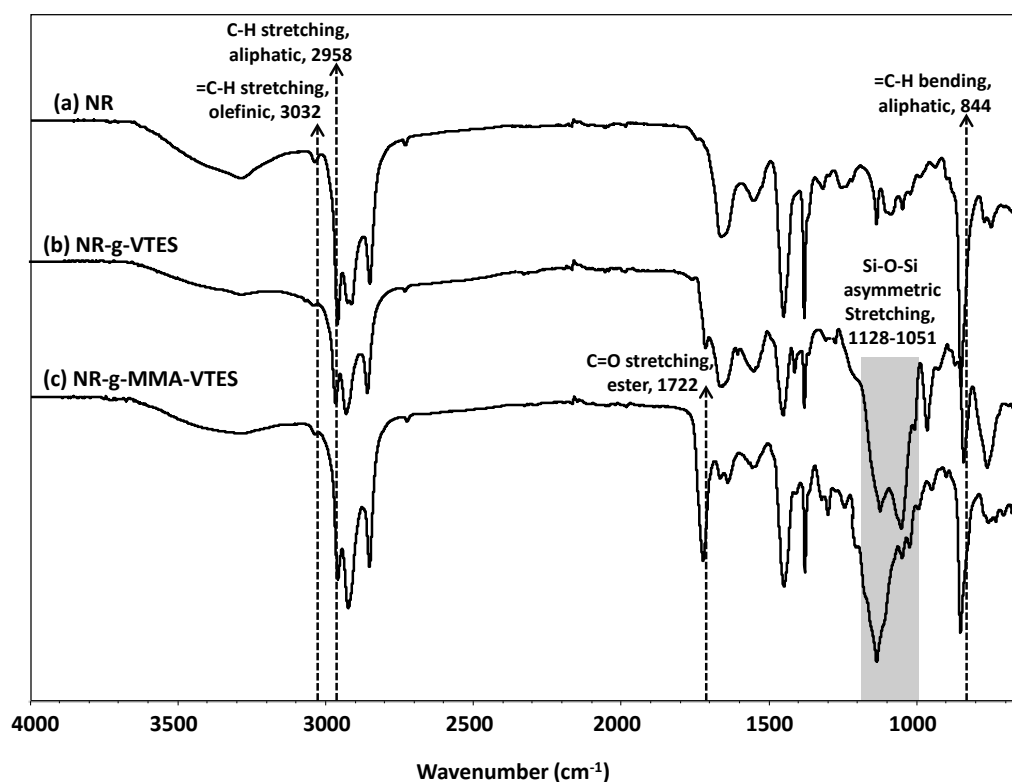


Figure 4.12 ATR-FTIR spectra of (a) NR, (b) NR-g-VTES, and (c) NR-g-MMA-VTES

In order to observe the morphology of NR-g-MMA-VTES, the TEM technique was used to determine the location of *in situ* silica generated by VTES and the presence of the grafted PMMA. This sample was also stained with RuO_4 in order to increase the contrast and gradation of organic parts which have weak interaction with the electrons. For NR-g-MMA-VTES, a representative core-shell morphology containing dark-shaded silica nanoparticles generated from VTES and grey-shade PMMA shell surrounded seed rubber particle was observed (Figure 4.13 (a)). In addition, small and dark particles are seen widely dispersed in the emulsion phase (Figure 4.13 (b)). These dispersed particles probably are the ungrafted VTES homopolymer particles. These results also

indicate that VTES can undergo a sol-gel process to create *in situ* alkylated silica as was found in the case of γ -MPS.

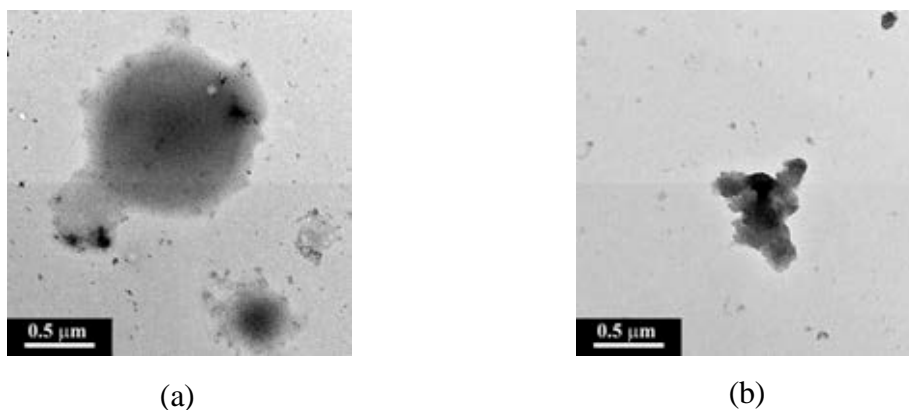


Figure 4.13 Transmission electron micrographs of (a) NR-g-MMA-VTES and (b) unbound silica particles found in NR-g-MMA- γ -MPS

In order to observe the morphology of composite film, the SEM was used to analyze the fracture surface of NR-g-MMA-VTES as shown in Figure 4.14. It can be clearly seen that silica particles were successfully generated by VTES as a silica precursor with a particle size in the range of microscale.

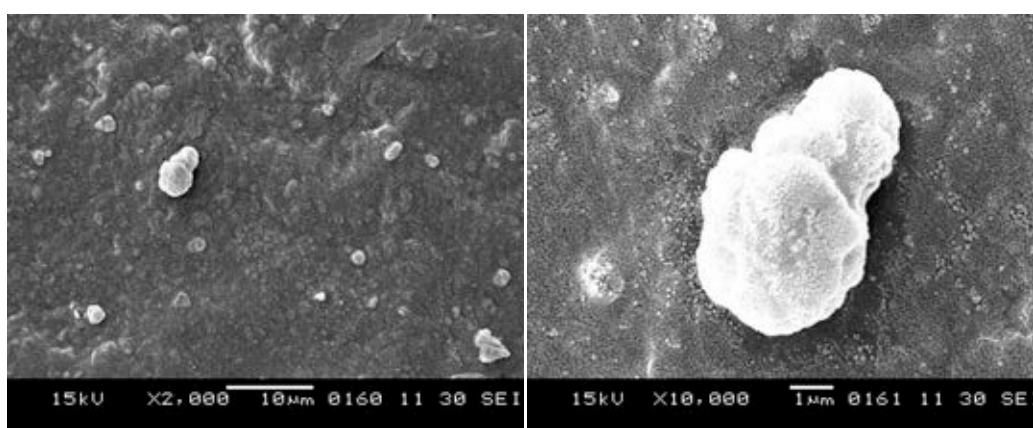


Figure 4.14 Scanning electron micrographs of NR-g-MMA- γ -MPS (3.53 phr of γ -MPS)

In addition the fractured surface of NR-g-MMA- γ -MPS film was analyzed for element types at a selected sample area by EDX technique. In Figure 4.15, the SEM-

EDS spectrum shows Si peaks at 1.75 KeV, supporting that the silica particle was successfully generated in the grafted NR film.

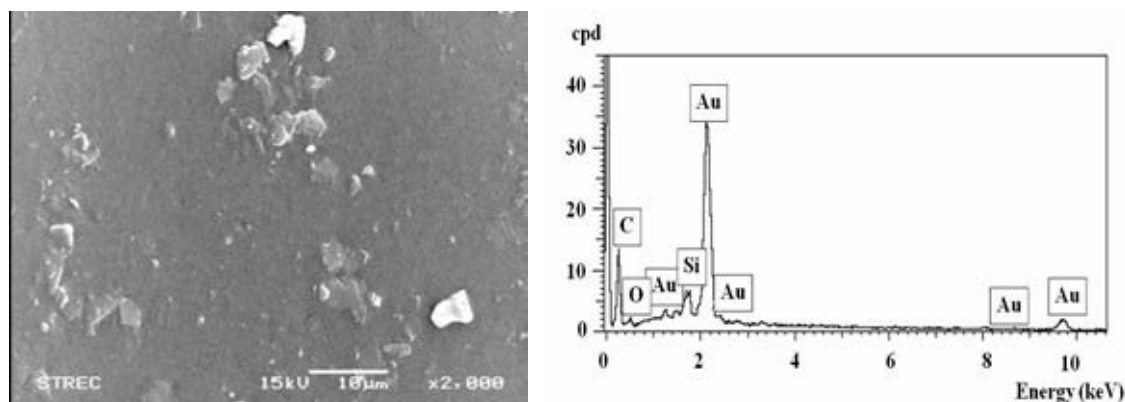


Figure 4.15 EDX spectra of NR-g-MMA-g-VTES

4.2 *In situ* formation of silica from TEOS in the grafted NR composites

4.2.1 General observations

The appearances of the composite films prepared in this study are shown in Figure 4.16. When MMA was grafted with NR latex, the obtained film became transparent with yellowish color (Figure 4.16 (a)). When alkoxy silane was added in the latex compound, it was clearly seen that the films became more opaque when silica particles were present in the rubber sheet. Moreover, the silica is embedded into the rubber matrix without observing any fall-off during storage. Nevertheless, the grafted films were stiffer and less tacky than ungrafted NR film.

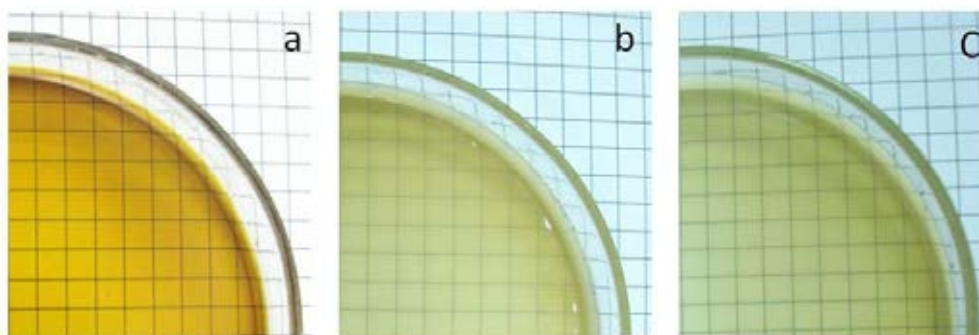


Figure 4.16 Photographs of (a) NR-g-MMA, (b) NR-g-MMA- γ -MPS/TEOS and (c) NR-g-MMA- γ -VTES/TEOS

4.2.2 FT-IR Spectroscopy analysis of the *in situ* silica

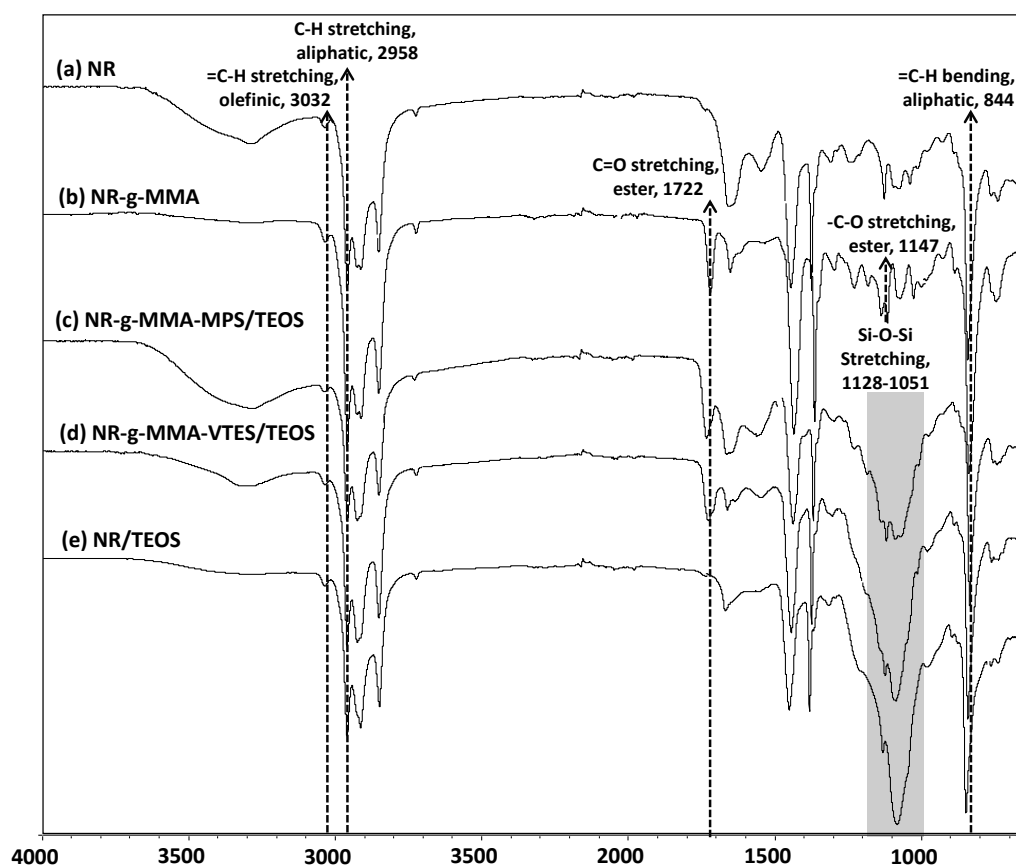
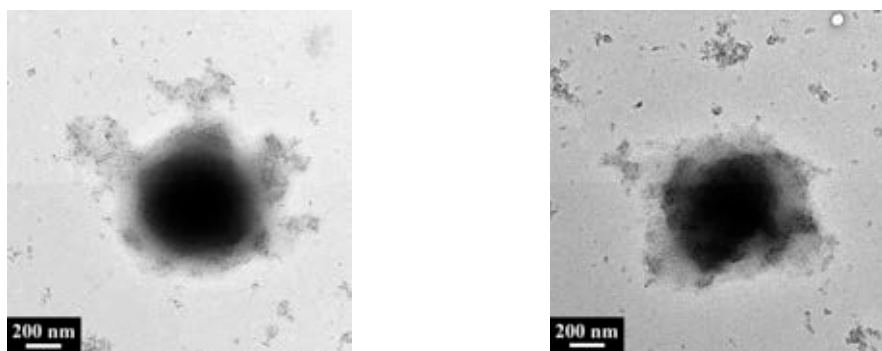


Figure 4.17 FTIR spectra of (a) NR, (b) NR-g-MMA, (c) NR-g-MMA- γ -MPS/TEOS, (d), NR-g-MMA- γ -VTES/TEOS, and (e) NR/TEOS

ATR-FTIR analysis results of silica/NR composites are revealed in Figure 4.17. The ATR-FTIR spectrum of NR (Figure 4.17 (a)) displays the characteristic transmission peaks at 3032, 2958, and 844 cm^{-1} , corresponding to =C-H stretching of olefinic, C-H stretching of aliphatic, and =C-H bending of aliphatic, respectively. When MMA was grafted onto NR backbone, the signal at 1722 and 1147 cm^{-1} appeared indicating that the C=O and C-O-C groups in the methacrylate of MMA. The silica generated in the composites exhibits the IR band at 1128–1051 cm^{-1} , assigning to the Si–O–Si bridging bonds in Figure 4.17 (c-e). Those FT-IR results also confirm the existence of silica in the composite films.

4.2.3 Morphology observation by transmission electron microscopy (TEM) of the in situ silica composites



(a) NR-g-MMA- γ -MPS/TEOS

(b) NR-g-MMA- γ -VTES/TEOS

Figure 4.18 The transmission electron micrographs of (a) NR-g-MMA- γ -MPS/TEOS and (b) NR-g-MMA- γ -VTES/TEOS

In order to observe the morphology of NR-g-MMA- γ -MPS/TEOS and NR-g-MMA- γ -VTES/TEOS were investigated by TEM (Figure 4.18). This sample was stained with RuO_4 in order to increase the contrast and gradation of organic parts which have weak interaction with the electrons. It can be clearly seen that the grafted NR/silica particles pronounced core-shell morphology, with the silica sol forming surrounding the NR core. Silica particles have a uniform dark appearance with the particle size in the range of nanoscale. For NR-g-MMA- γ -MPS/TEOS, the representative core-shell

morphology containing dark-shaded silica nanoparticles was generated from γ -MPS, TEOS and grey-shade PMMA shell surrounded seed rubber particle gave the silica coated NR-g-MMA (Figure 4.18 (a)). Similar silica-grafted NR particles were also observed in the sample prepared from NR-g-MMA-VTES mixed with TEOS (Figure 4.18 (b)). Furthermore, free-standing aggregates of *in situ* silica were also observed in latex mixture of the both cases. The observation indicated that the loosened agglomerated of the unbound silicas also exists due to polycondensation of the silane was promoted by a locally high TEOS concentration, and silanes coupling was introduced on the latex surface and/or possibly into the hybrid latex core [7]. Indeed, due to its hydrophobic character, TEOS can easily enter the polymer particles and chemically react with methoxy group of γ -MP and ethoxy group of VTES or other TEOS, but only at the rubber latex surface that TEOS can react with water and hydroxide ion.

4.2.4 Content of *in situ* silica and percentage of conversion of γ -MPS, VTES, and TEOS to silica

The content and the percentage of conversion of silica in the grafted NR composite films are listed in Table 4.2. The amount of *in situ* formed silica in all samples was determined from the weight of remaining ash after sample pyrolysis. In the case of single silane system that γ -MPS, VTES, and TEOS act as an *in situ* silica precursor (NR-g- γ -MPS, NR-g-VTES, and NR/TEOS), it was observed the percentage of conversion of TEOS to form silica was the highest and VTES was higher than γ -MPS. TEOS underwent hydrolysis and condensation to form silica at an average 85%. Because the TEOS molecule contains four ethoxy groups, therefore it underwent an almost completion of a sol-gel process to form silica as found in earlier reports [5]. For VTES and γ -MPS, the vinyl group of VTES is polarized than methacryloxypropyl group of γ -MPS therefore VTES should be more compatible with the polar medium and, thus, more reactive during the sol-gel process in the rubber matrix than the γ -MPS. Moreover, it was observed that the conversion of γ -MPS was only 28% (from sample NR-g- γ -MPS), which was much lower than the conversion of TEOS to silica reported

elsewhere (up to 80-90 %) [4-5,14]. The results can be explained in terms of the structure and polarity, hydrolysis and condensation reaction during the sol-gel process of γ -MPS. The methacryloxypropyl group in γ -MPS is less polar and very bulky, therefore the sol-gel process of γ -MPS proceeded very slowly and limitedly. When comparing the silica content and the conversions obtained from the mixed precursor of TEOS and alkyltrialkoxysilanes, the degree of silane conversions in the composite films decreased when addition the amount of alkyltrialkoxysilane. On the other hand the *in situ* silica content increased with increasing TEOS amount from 5 to 20 phr. This result was not surprising since alkylated silanes had low reactivity during the sol-gel process. However, the amount of TEOS added into the latex was limited to 20 phr. When a higher TEOS amount was added, the latex tended to become unstable, resulting in rubber aggregation.

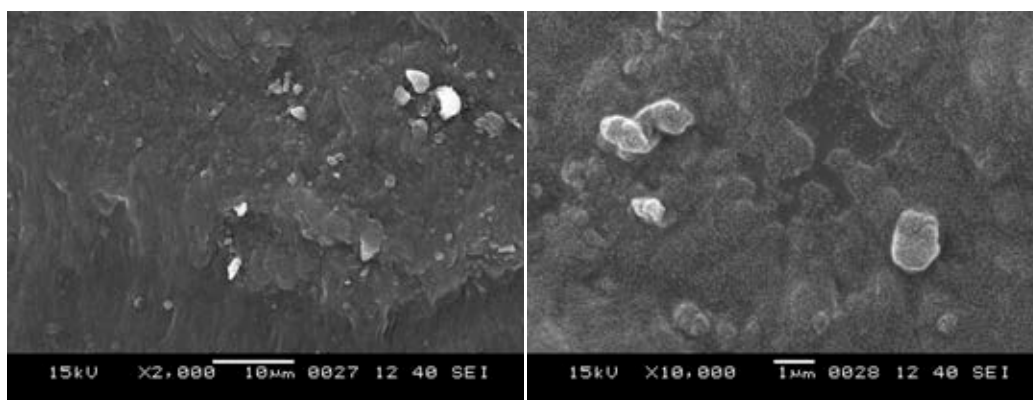
Table 4.2 The silica content and percentage of conversion of γ -MPS, VTES, and TEOS to silica in various types of rubber vulcanizates

Samples	Amount of silane (phr)			silica content (phr)	Conversion (%)
	γ -MPS	VTES	TEOS		
NR	-	-	-	-	-
NR- <i>g</i> -MMA	-	-	-	-	-
NR- <i>g</i> - γ -MPS	17.65	-	-	3.53 \pm 0.11	28
NR- <i>g</i> -VTES	-	17.65	-	4.16 \pm 0.44	57
NR/TEOS	-	-	17.65	4.52 \pm 0.47	88
NR- <i>g</i> -MMA- γ -MPS	3.53	-	-	1.23 \pm 0.11	48
NR- <i>g</i> -MMA-VTES	-	3.53	-	1.25 \pm 0.23	86
NR- <i>g</i> -MMA- γ -MPS/TEOS5	3.53	-	5	2.48 \pm 0.40	62
NR- <i>g</i> -MMA- γ -MPS/TEOS10	3.53	-	10	3.21 \pm 0.34	72
NR- <i>g</i> -MMA- γ -MPS/TEOS15	3.53	-	15	4.36 \pm 0.40	63
NR- <i>g</i> -MMA- γ -MPS/TEOS20	3.53	-	20	6.00 \pm 0.48	59
NR- <i>g</i> -MMA-VTES/TEOS5	-	3.53	5	2.69 \pm 0.24	89
NR- <i>g</i> -MMA-VTES/TEOS10	-	3.53	10	2.98 \pm 0.34	68
NR- <i>g</i> -MMA-VTES/TEOS15	-	3.53	15	3.38 \pm 0.60	58
NR- <i>g</i> -MMA-VTES/TEOS20	-	3.53	20	5.30 \pm 0.26	73
NR- <i>g</i> -MMA/TEOS20	-	-	20	4.56 \pm 0.19	79

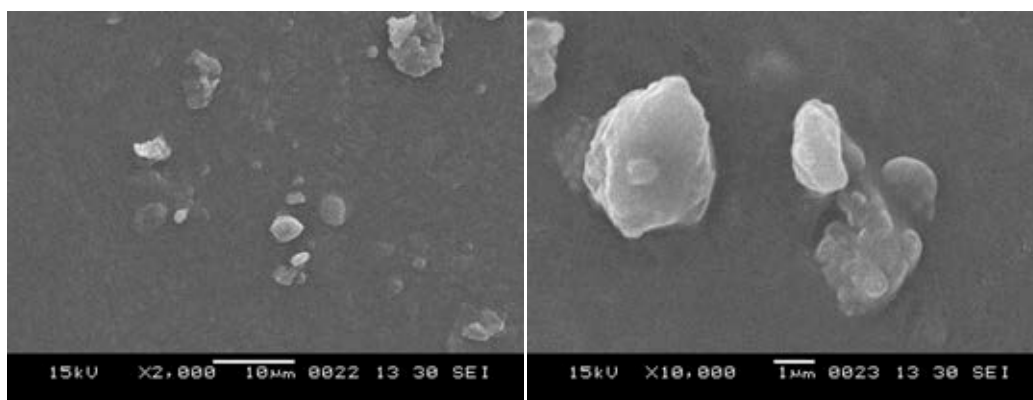
4.2.5 Morphology observation by scanning electron microscopy (SEM) of the *in situ* silica composites

Figure 4.19 shows the fractured surface of the grafted NR/silica films containing *in situ* silica generated from the mixture of TEOS and alkyltrialkoxysilane. The white

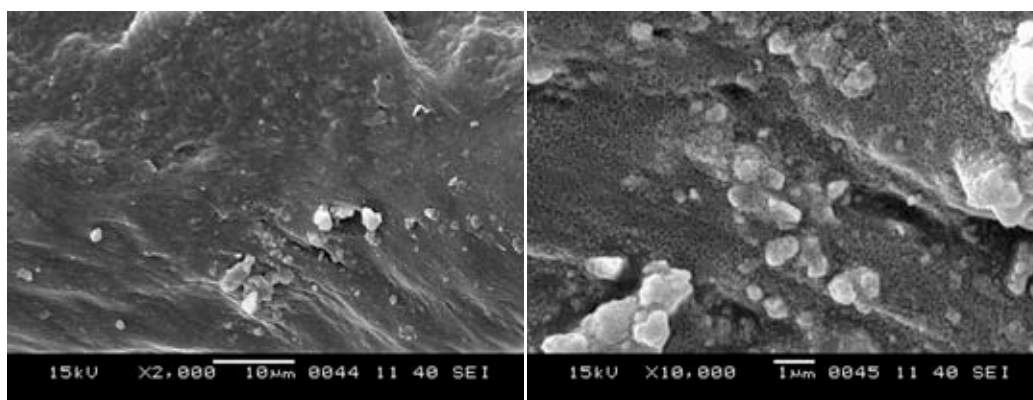
and grey tone color represented the *in situ* silica particles and the black tone color indicated the NR matrix as identified by EDX technique. The formation of silica aggregation (silica particles fused into aggregated) was clearly seen. Although, the primary particle size of the “*in situ*” formed silica cannot be observed by SEM, the silica aggregates were regularly dispersed in rubber matrix. In the case of NR-*g*-MMA-TEOS20 (Figure 4.19 (i)), the silica generated from TEOS tended to be agglomerated and formed clusters having various sizes because of a low interaction between silica from TEOS and NR-*g*-MMA along with a strong silica-silica interaction by hydrogen bonding to cause silica aggregations. In the case of the NR-*g*-MMA- γ -MPS/TEOS composites (Figure 4.19 (a)-(d)), the silica generated from the mixed precursors, it was observed that the silica particle size was increased when increasing TEOS amount. In the case of NR-*g*-MMA-VTES/TEOS composites (Figure (e)-(h)), the features in all micrographs were similar to those of the NR-*g*-MMA- γ -MPS/TEOS and the single precursor (TEOS alone). Moreover, the rubber phase was rougher when addition MMA in the graft copolymerization which was resulted from the non-homogenous phase distributions of hard phase PMMA. From the SEM micrographs, the silica particles of all precursors form aggregate with various sizes in the range from nano to microscale without any clear correlation to the silane type.



(a) NR-g-MMA-MPS-TEOS5

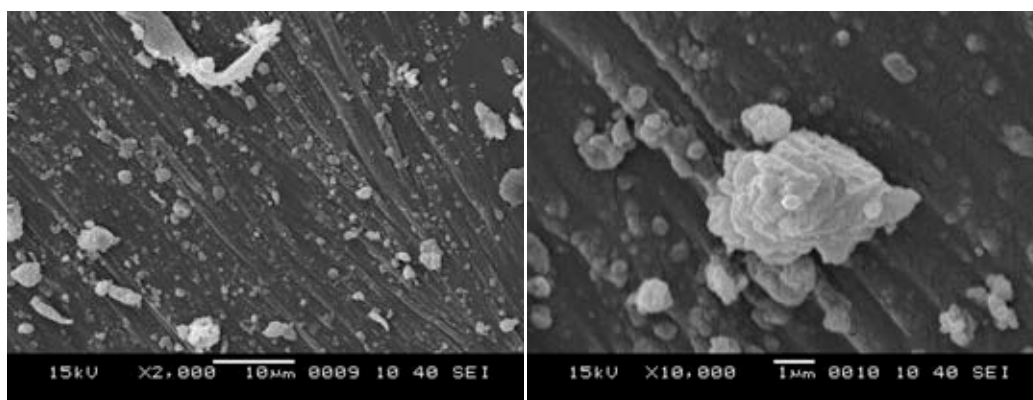


(b) NR-g-MMA-MPS-TEOS10

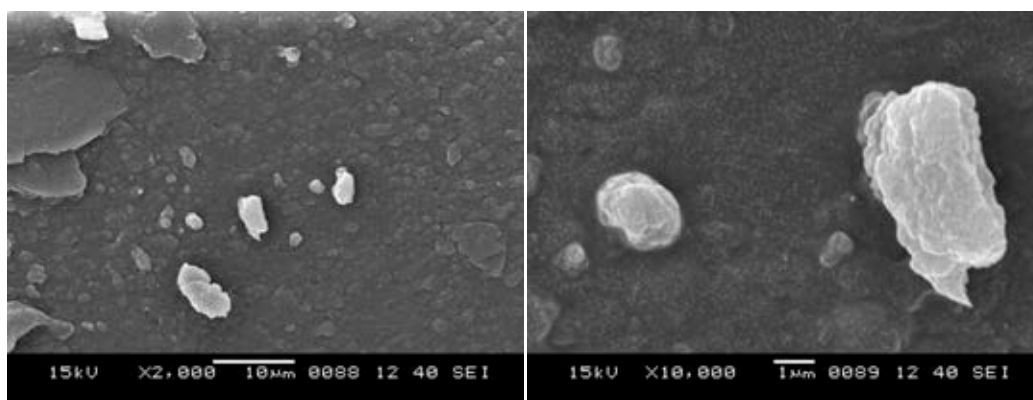


(c) NR-g-MMA-MPS-TEOS15

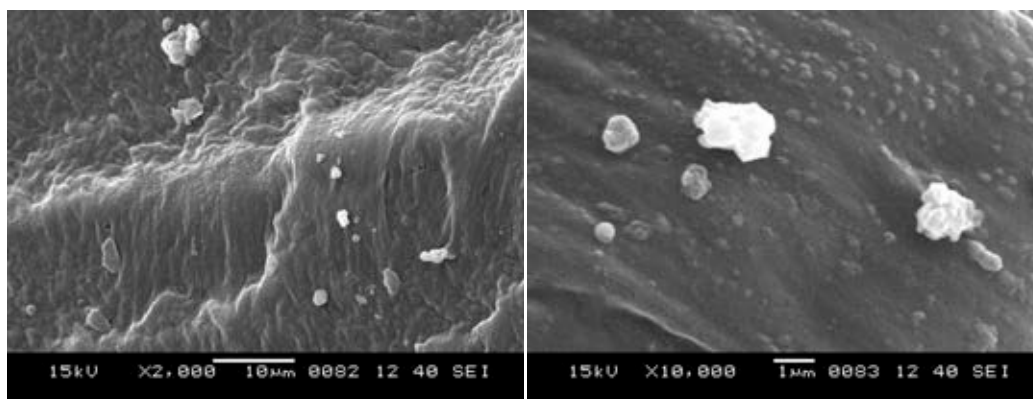
Figure 4.19 The scanning electron micrographs of *in situ* silica containing grafted NR (continued on the next page)



(d) NR-g-MMA-MPS-TEOS20

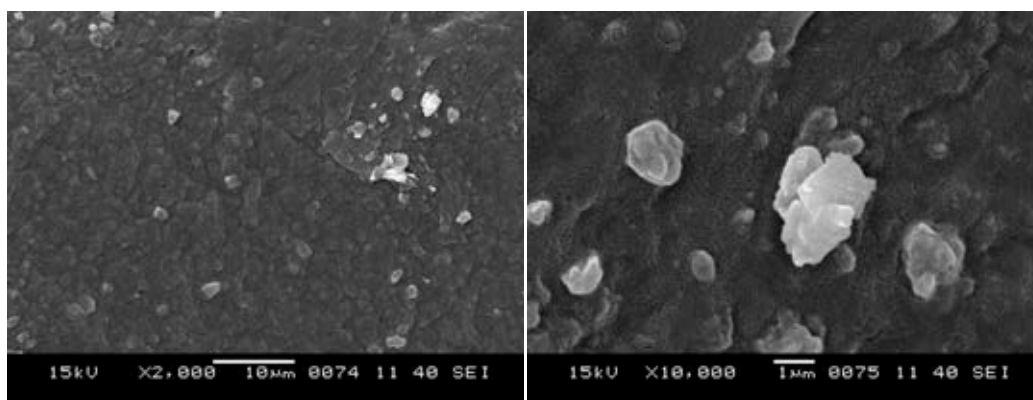


(e) NR-g-MMA-VTES-TEOS5

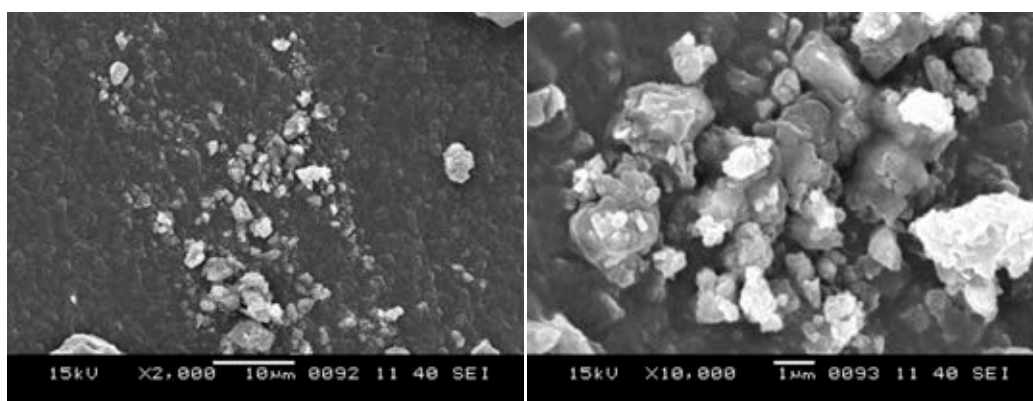


(f) NR-g-MMA-VTES-TEOS10

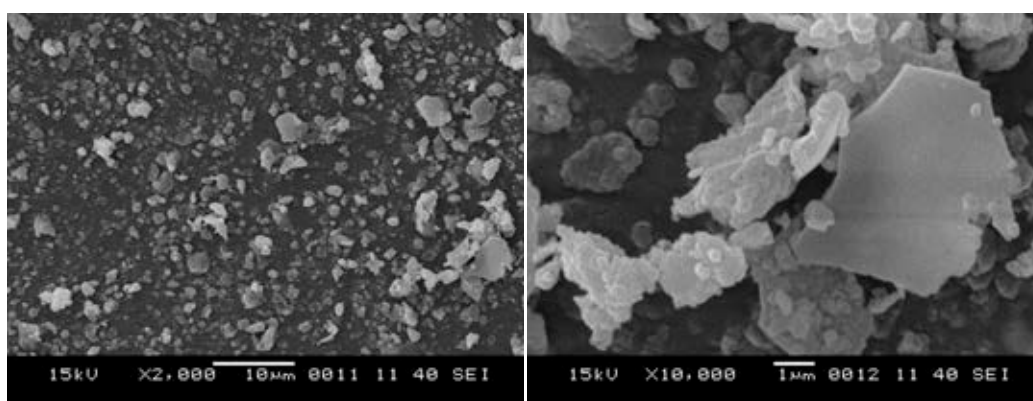
Figure 4.19 The scanning electron micrographs of *in situ* silica containing grafted NR (continued on the next page)



(g) NR-g-MMA-VTES-TEOS15



(h) NR-g-MMA-VTES-TEOS20



(i) NR-g-MMA-TEOS20

Figure 4.19 The scanning electron micrographs of *in situ* silica containing grafted NR

4.2.6 Surface morphology by atomic force microscopy of MMA grafted NR containing *in situ* silica

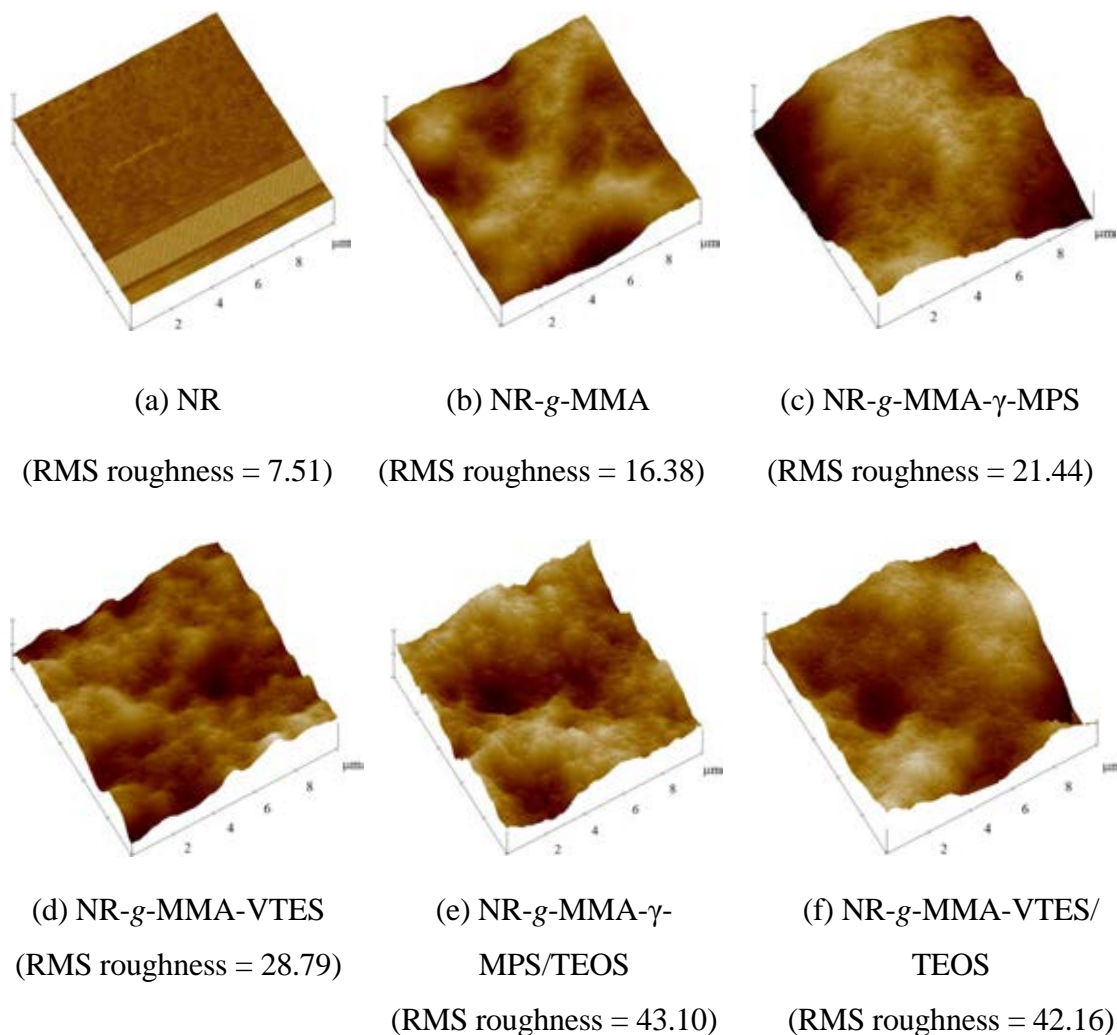


Figure 4.20 Surface analysis by AFM of the composite films

The surface roughness of the grafted NR films was analyzed by AFM (Figure 4.20). In Figure 4.20a shows the flat and smooth surface of the untreated NR. In addition, it can be clearly seen that addition MMA in the grafting reaction resulted in increases the surface roughness as shown in Figure 4.20(b). These results agree with Sruanganurak *et al.* [3], in which the deposition of PMMA nanoparticles onto polyacrylamide grafted NR via layer by layer method was obtained. The influence of *in*

situ silica on the surface morphology of the rubber composite was also investigated by AFM as displayed in Figure 4.20(c)-4.20 (f). These samples were prepared from the grafted NR latex with loading 12% MMA, 3% γ -MPS or VTES, and 10 phr TEOS content. It can be clearly seen that the silica-filled grafted NR increased the surface roughness. These results agree with Satraphan *et al.* [14], in which also studied the influence of MMA content and *in situ* silica on the surface morphology of the rubber composites. Calculation of root-mean-square (RMS) roughness of the sample surface allowed a detailed comparison of the surface roughness as shown in Figure 4.20.

4.3 Testing

4.3.1 Swelling behavior

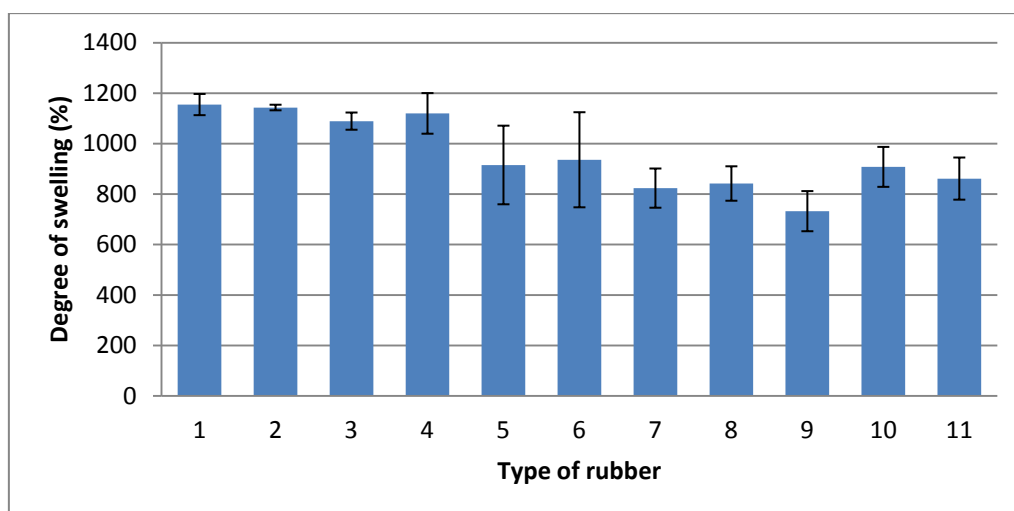


Figure 4.21 The degree of swelling of (1) NR, (2) NR-g-MMA, (3) NR-g-MMA- γ -MPS, (4) NR-g-MMA-VTES, (5) NR-g-MMA- γ -MPS-TEOS5, (6) NR-g-MMA-VTES-TEOS5, (7) NR-g-MMA- γ -MPS-TEOS10, (8) NR-g-MMA-VTES-TEOS10, (9) NR-g-MMA- γ -MPS-TEOS15, (10) NR-g-MMA-VTES-TEOS15, (11) NR-g-MMA-TEOS20

The vulcanization and swelling behavior of rubber composite were studied in terms of degree of swelling in an organic medium. The degrees of swelling of NR and

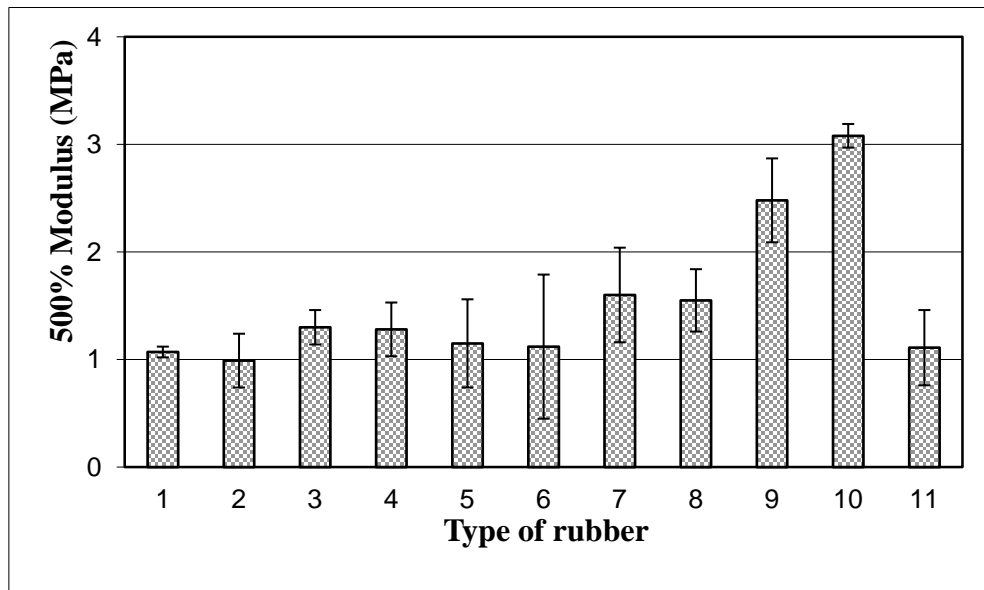
grafted NR vulcanized in toluene are shown in Figure 4.21. In the same figure, the effect of *in situ* silica contents on swelling behavior was investigated. From these histograms, it can be observed that the extent of swelling behavior of *in situ* silica containing grafted NR film decreased when compared to those of NR and NR-g-MMA films (without silica). This was because chain motions of rubber matrix become restricted by the silica particles. However, the effect of silica particles were not pronounced.

4.3.2 Mechanical properties

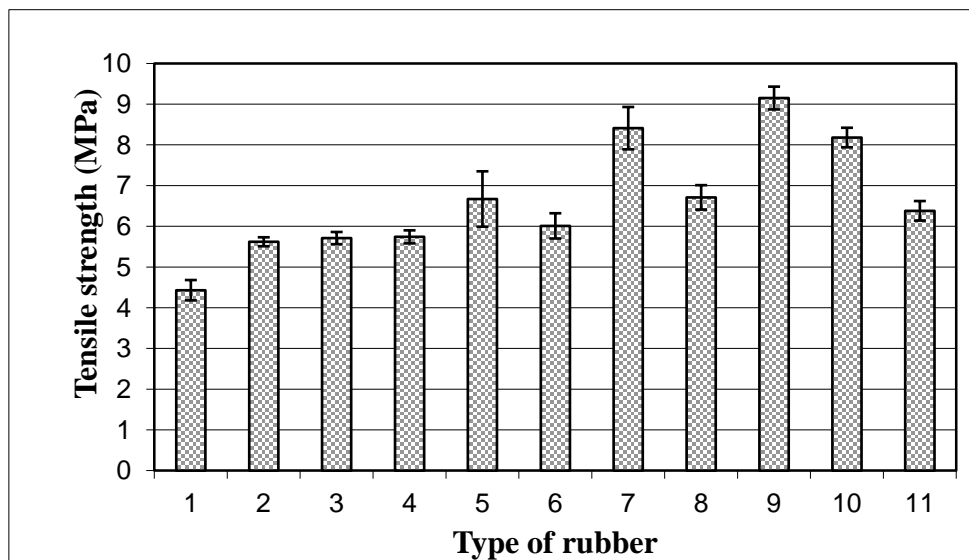
4.3.2.1. Tensile properties

Tensile properties of the composite films were investigated in terms of tensile modulus at 500% elongation, tensile strength at break, and elongation at break of the grafted NR containing *in situ* silica. The results are shown in Figure 4.22.

Considering the samples containing *in situ* silica generated from the mixed vinylated silica-TEOS, modulus at 500% elongation and tensile strength were all increased with increasing the amount of TEOS in the vinylated silica-TEOS mixture. When comparing to the unmodified NR, it was found that all modified NR have the higher modulus at 500% and tensile strength than does the unmodified NR. When comparing among the film samples with the same amount of *in situ* generated silica, the mixed precursor γ -MPS-TEOS provided effective reinforcing ability for the grafted NR film. Moreover, the mixed precursor VTES-TEOS is more effective for reinforcing ability when comparing with that containing only TEOS. It can be concluded that the vinyl group played an important role in the reinforcement of rubber films.

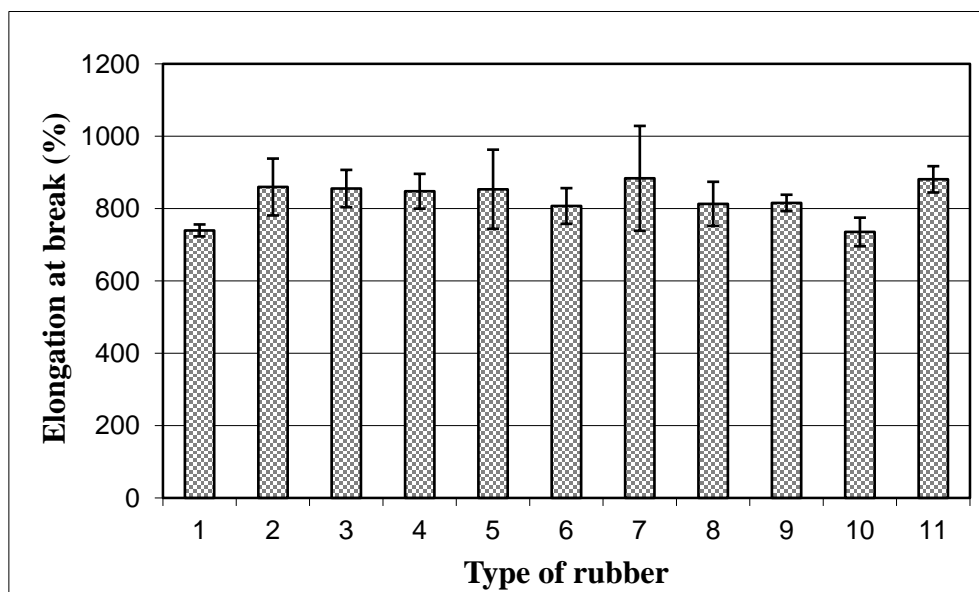


(a) 500% modulus



(b) Tensile strength

Figure 4.22 (continued on the next page)



(c) Elongation at break

Figure 4.22 Tensile properties of the rubber composite films: (a) modulus at 500%, (b) tensile strength, (c) elongation at break of (1) NR, (2) NR-*g*-MMA, (3) NR-*g*-MMA- γ -MPS, (4) NR-*g*-MMA-VTES, (5) NR-*g*-MMA- γ -MPS-TEOS5, (6) NR-*g*-MMA-VTES-TEOS5, (7) NR-*g*-MMA- γ -MPS-TEOS10, (8) NR-*g*-MMA-VTES-TEOS10, (9) NR-*g*-MMA- γ -MPS-TEOS15, (10) NR-*g*-MMA-VTES-TEOS15, and (11) NR-*g*-MMA-TEOS20

4.3.2.2 Tension set

Figure 4.23 shows the results of tension set study. The tension set property reflects the elasticity of rubber and is presented by the degree of film length change after the film was stretched for a certain length and time. Here the tension set percentages of all *in situ* silica containing the grafted NR films were between 2.7 to 4.8%. No difference between the *in situ* silica-reinforced and non-reinforced samples was observed. The use of TEOS and other alkyltrialkoxysilanes to generate silica in the grafted film did not significantly affect the tension set. The resilience properties of rubber remained in all samples because its tension set was lower than one of the standard material (10%).

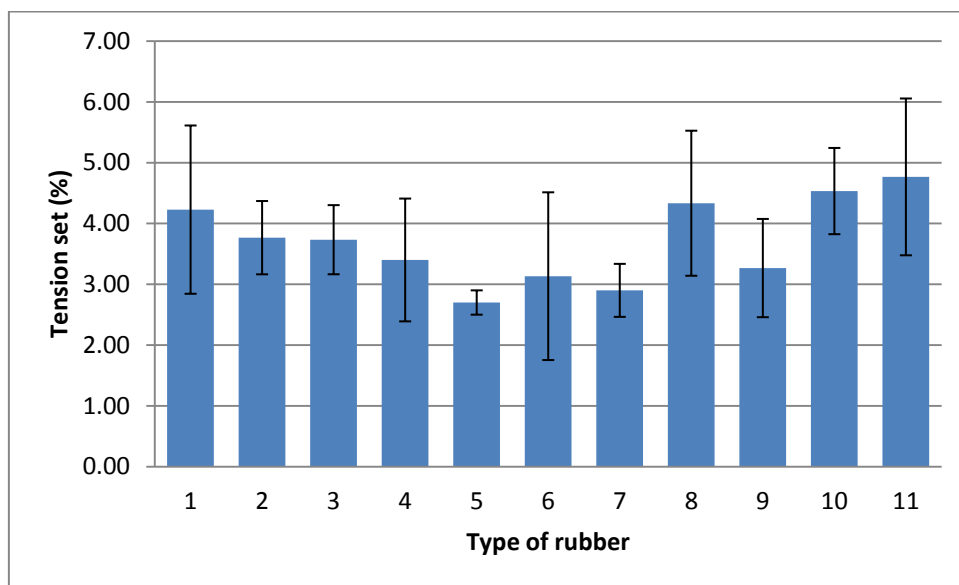


Figure 4.23 Result of tension set study of (1) NR, (2) NR-*g*-MMA, (3) NR-*g*-MMA- γ -MPS, (4) NR-*g*-MMA-VTES, (5) NR-*g*-MMA- γ -MPS-TEOS5, (6) NR-*g*-MMA-VTES-TEOS5, (7) NR-*g*-MMA- γ -MPS-TEOS10, (8) NR-*g*-MMA-VTES-TEOS10, (9) NR-*g*-MMA- γ -MPS-TEOS15, (10) NR-*g*-MMA-VTES-TEOS15, and (11) NR-*g*-MMA-TEOS20

CHAPTER V

CONCLUSION AND SUGGESTIONS

5.1 Conclusions

This investigation, the NR-*g*-MMA containing *in situ* generated silica was successfully prepared by the sol-gel process of TEOS by using γ -MPS and VTES as a silane coupling agent in the grafted rubber latex. The preparation was divided into 3 steps. Firstly, MMA monomer was grafted onto NR latex *via* seeded emulsion polymerization by using CHPO/TEPA as a redox initiator system. Secondly γ -MPS or VTES was sequentially grafted to the NR-*g*-MMA latex. Lastly TEOS was mixed into the NR-*g*-MMA- γ -MPS latex, followed by heating the latex mixture to initiate the sol-gel process of added silanes as well as to dry the rubber composite.

The formation of this rubber-silica hybrid was confirmed by ATR-FTIR, TEM and SEM. The strong IR absorption bands at 1730 cm^{-1} and 1147 cm^{-1} are attributed to the C=O stretching and C-O-C stretching of grafted MMA. Moreover, the IR band at $1122\text{-}1090\text{ cm}^{-1}$, assigning to the Si-O-Si bridging bond from the *in situ* generated silica. The core-shell structure with the PMMA shell surrounding the rubber core was observed by TEM. By addition of TEOS and vinylated silane, TEM clearly showed that PMMA and *in situ* silica nanoparticles resided in the shell layer of the NR core. The SEM images and EDX analysis confirmed that the *in situ* generated silica particles were fairly dispersed inside the rubber matrix. The conversions of silane to form silica from highest to lowest are TEOS (88%), VTOS (57%), and MPS (28%), depending on the size and polarity of the alkyl group in the silane. The silica increased with increasing TEOS loading.

The NR-*g*-MMA containing *in situ* generated silica affected the properties of the rubber films. The presence of grafted PMMA and *in situ* generated silica resulted in increased roughness of the film surface as confirmed by AFM. As a result, the film thickness was also reduced. Swelling behavior of the composite film in toluene revealed that the degree of swelling decreased with increasing silica content. This was because the *in situ* silica could restrict the rubber chain mobility.

The results of mechanical properties indicated that vulcanizate containing *in situ* silica obtained from mixed TEOS- γ -MPS possessed high tensile modulus. These results lead us to believe that vinyl groups in the *in situ* generated silica (from γ -MPS) probably take part in the rubber chain. For tension set, it was found that all composite films samples had low tension set values (<10%) and were not different from one another.

5.2 Suggestion for future works

A more overview of studies that need to be undertaken and directions that could be further explored are in the following aspects:

- Investigation of other possible techniques which also modify NR through chemical bonding such as photo-polymerization in a latex medium or solution medium.
- Investigation of the use low ammonia natural rubber latex to slow down hydrolysis and condensation of the sol-gel process to achieve good stability latex before applying.
- Investigation of the novel vulcanization system such as radiation vulcanization.

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APPENDIX

APPENDIX

Table A-1 The Degree of swelling (%) of the grafted NR composite films filled with *in situ* silica generated by various types of alkoxy silane precursor and silica-free NR film.

Sample	Average \pm SD
NR	1154 \pm 42
NR- <i>g</i> -MMA	1143 \pm 11
NR- <i>g</i> -MMA- γ -MPS	1189 \pm 34
NR- <i>g</i> -MMA-VTES	1119 \pm 80
NR- <i>g</i> -MMA- γ MPS/TEOS5	915 \pm 155
NR- <i>g</i> -MMA-VTES/TEOS5	936 \pm 188
NR- <i>g</i> -MMA- γ -MPS/TEOS10	823 \pm 77
NR- <i>g</i> -MMA-VTES/TEOS10	841 \pm 68
NR- <i>g</i> -MMA- γ MPS/TEOS15	732 \pm 79
NR- <i>g</i> -MMA-VTES/TEOS15	907 \pm 79
NR- <i>g</i> -MMA-TEOS	861 \pm 83

n=5

Table A-3 Silica content and tensile properties of the composit films.

Sample code	Modulus at 500% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)
NR	1.07±0.05	4.43±0.25	739±16.5
NR-g-MMA	0.99±0.25	5.62±0.11	859±78.63
NR-g-MMA- γ -MPS	1.30±0.16	5.71±0.15	855±51.58
NR-g-MMA-VTES	1.28±0.25	5.74±0.16	847±48.14
NR-g-MMA- γ -MPS/TEOS5	1.15±0.41	6.67±0.68	853±109.49
NR-g-MMA-VTES/TEOS5	1.12±0.67	6.01±0.31	807±49.4
NR-g-MMA- γ -MPS/TEOS10	1.60±0.44	8.41±0.52	883±144.92
NR-g-MMA-VTES/TEOS10	1.55±0.29	6.71±0.3	813±60.94
NR-g-MMA- γ MPS/TEOS15	2.48±0.39	9.15±0.28	815±22.65
NR-g-MMA-VTES/TEOS15	3.08±0.11	8.18±0.24	735±39.57
NR-g-MMA-TEOS	1.11±0.35	6.38±0.24	880±36.34

n=5

Table A-3 The tension set (%) of the grafted rubber films filled with *in situ* silica generated by various types of alkoxy silane precursor and silica-free rubber film.

Sample	Average \pm SD
NR	4.3 \pm 1.3
NR- <i>g</i> -MMA	3.77 \pm 0.6
NR- <i>g</i> -MMA- γ -MPS	3.73 \pm 0.5
NR- <i>g</i> -MMA-VTES	3.40 \pm 1.0
NR- <i>g</i> -MMA- γ MPS/TEOS5	2.70 \pm 0.2
NR- <i>g</i> -MMA-VTES/TEOS5	3.13 \pm 1.3
NR- <i>g</i> -MMA- γ -MPS/TEOS10	2.90 \pm 0.4
NR- <i>g</i> -MMA-VTES/TEOS10	4.33 \pm 1.1
NR- <i>g</i> -MMA- γ MPS/TEOS15	3.2 \pm 0.8
NR- <i>g</i> -MMA-VTES/TEOS15	4.53 \pm 0.7
NR- <i>g</i> -MMA-TEOS	4.77 \pm 1.2

n=5

VITAE

Miss Wasinee Sakathok was born on March 30th, 1985 in Surin, Thailand. She graduated with a Bachelor's degree of Science, majoring in Chemistry, Faculty of Science, Srinakharinwirot University in 2008. In the same year, she started as a Master Degree student with a major in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and finished her study in May 2012.

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