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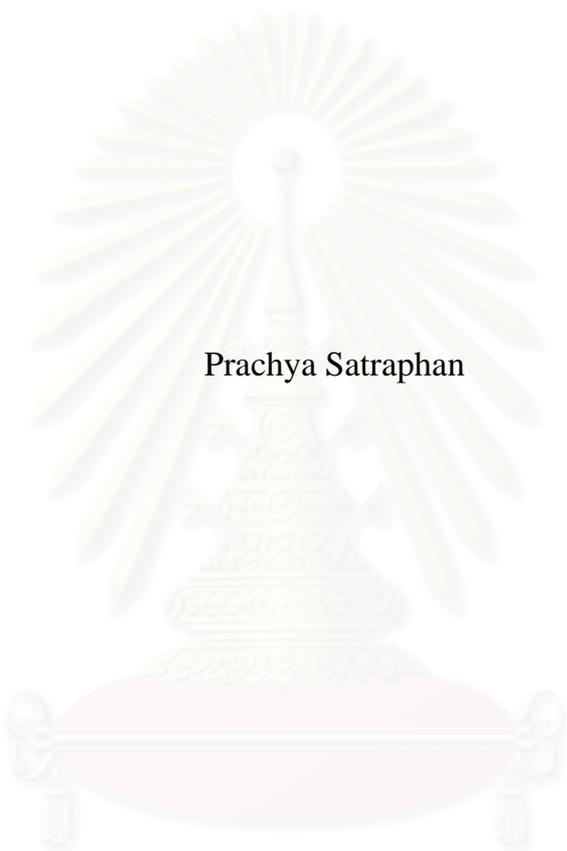
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REINFORCEMENT OF NATURAL RUBBER AND METHYL METHACRYLATE
GRAFTED NATURAL RUBBER FILMS BY *IN SITU* SILICA



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สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย
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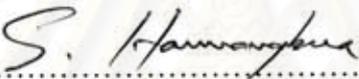
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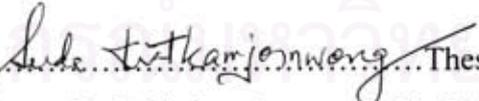
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วัตถุประสงค์ของงานวิจัยนี้คือ การเตรียมฟิล์มบางจากยางธรรมชาติที่กราฟต์ด้วยเมทิลเมทาคริเลตและเสริมแรงด้วยซิลิกาที่ถูกร่างขึ้นภายใน การกราฟต์เมทิลเมทาคริเลตกระทำโดยใช้ตัวริเริ่มคู่ ปฏิกริยาแบบรีดอกซ์ที่เป็นควิมิน ไฮโดรเปอร์ออกไซด์/เทตระเอทิลินเพนตามีน เมื่อวิเคราะห์ลาเท็กซ์ ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) พบว่า อนุภาคยางประกอบด้วยโครงสร้างแบบ เปลือกหุ้มแกนกลางที่มีแกนกลางเป็นยางธรรมชาติและชั้นเปลือกประกอบด้วยพอลิเมทิลเมทาคริเลต หลังจากกราฟต์แล้วนำน้ำยางที่ได้มาผสมกับเทตระเอทอกซีไฮเลนซึ่งเป็นสารตั้งต้นของซิลิกา ในขั้นนี้ พบว่ามีไฮเลนแทรกอยู่ในชั้นเปลือกรอบๆ อนุภาคยางธรรมชาติ ไฮเลนเปลี่ยนรูปไปเป็นซิลิกาโดย กระบวนการ โซล-เจลในขั้นตอนการคงรูปร่างที่อุณหภูมิ 80 องศาเซลเซียส เมื่อวิเคราะห์สัณฐานวิทยา ของยางธรรมชาติที่มีปริมาณเมทิลเมทาคริเลตในสัดส่วนต่างๆ โดยกล้องจุลทรรศน์อิเล็กตรอนแบบ ส่องกราด (SEM) และเครื่องอะตอมมิกฟอร์ซไมโครสโกปี (AFM) พบว่า อนุภาคซิลิกาที่เกิดในยาง ธรรมชาติที่กราฟต์ด้วยเมทิลเมทาคริเลต มีแนวโน้มจับตัวเป็นกลุ่มก้อนเล็กน้อย แต่ยังคงกระจาย ตัวอย่างสม่ำเสมอ และยังพบว่า การเพิ่มสัดส่วนของเมทิลเมทาคริเลตต่อยางธรรมชาติทำให้ค่ารากที่ สองของกำลังสองเฉลี่ยของความขรุขระบนพื้นผิวเพิ่มขึ้นและส่งผลให้ความเหนียวของฟิล์มยาง ธรรมชาติลดลง ยางธรรมชาติที่กราฟต์ด้วยเมทิลเมทาคริเลตและมีซิลิกาเกิดขึ้นภายใน ให้ค่ามอดูลัสที่ 500 เปอร์เซ็นต์ของการยืดและความต้านแรงดึงเพิ่มขึ้นอย่างเล็กน้อย แต่เปอร์เซ็นต์การยืดตัวของ ฟิล์มลดลง

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PRACHYA SATRAPHAN: REINFORCEMENT OF NATURAL RUBBER
AND METHYL METHACRYLATE GRAFTED NATURAL RUBBER
FILMS BY *IN SITU* SILICA. THESIS ADVISOR: ASST. PROF. VARAWUT
TANGPASUTHADOL, Ph.D. THESIS CO-ADVISOR: PROF. SUDA
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The objective of this research was to prepare thin rubber films from natural rubber (NR) grafted with methyl methacrylate (MMA) and reinforced by *in situ* generated silica. The MMA grafting was carried out using cumene hydroperoxide/tetraethylene pentamine (CHPO/TEPA) redox system as an initiator pair. The latex contained particles having a core-shell structure, where the core was comprised of NR and the shell layer was formed by PMMA, as revealed by transmission electron microscopy (TEM) analysis. The grafted NR latex was then mixed with tetraethoxysilane (TEOS), a precursor of silica. In the latex state, TEOS was discovered embedded in the MMA shell surrounding the NR particles. The silane was converted to silica particles by sol-gel process that was induced during film vulcanizing at 80°C. The influences of NR:MMA weight ratio on the surface morphology of the composites were investigated by scanning electron microscopic (SEM) and atomic force microscopic (AFM) methods. With the presence of grafted MMA, the silica tends to slightly aggregate, but remained dispersed throughout the entire NR matrix. It was also found that increasing weight ratio of MMA in the rubber resulted in an increase of root-mean-square roughness of the surface and led to a reduction of the film tackiness. The presence of both grafted MMA and silica particles led to slight increases in modulus at 500% elongation and tensile strength, but decreases elongation at break of the composite film.

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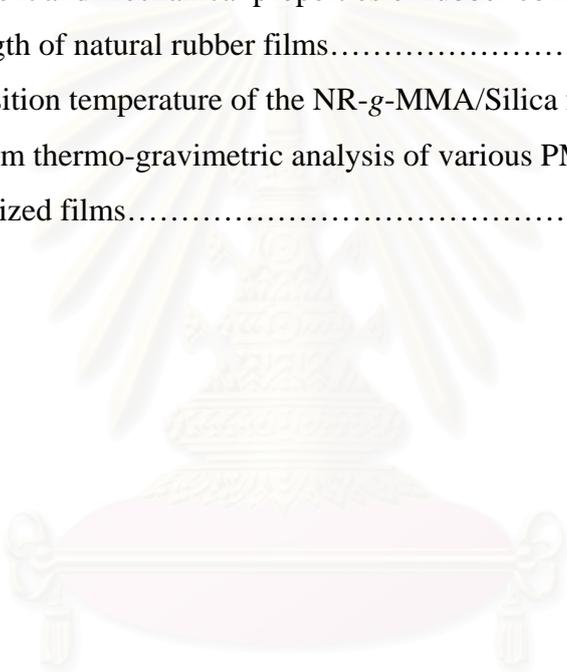
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LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
ASTM	American Society for Testing and Materials
°C	Degrees Celsius
CHPO	Cumene hydroperoxide
DRC	Dry rubber content
DSC	Differential scanning calorimetry
EDX	Energy dispersive X-ray spectrometer
ENR	Epoxidized natural rubber
FT-IR	Fourier transform infrared spectroscopy
GE	Grafting efficiency
HA	High ammonia
MD	Machine direction
MMA	Methyl methacrylate
MPa	Megapascal
N	Newton
NBR	Acrylonitrile-butadiene rubber
NR	Natural rubber
phr	Parts per hundred parts of rubber

PMMA	Poly(methyl methacrylate)
PVA	Polyvinyl alcohol
RMS	Root mean square
SBR	Styrene-butadiene rubber
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
T _g	Glass transition temperature
TBHP	<i>tert</i> -Butylhydroperoxide
TEM	Transmission electron microscopy
TEOS	Tetraethoxysilane
TEPA	Tetraethylenepentamine
TGA	Thermal gravimetric analysis
ZDEC	Zinc diethyldithiocarbamate
ZMBT	Zinc mercaptobenzothiazole

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CHAPTER I

INTRODUCTION

1.1 The purpose of the investigation

Natural rubber (NR) is versatile in a wide range of application, due to its distinct properties such as high elongation, and excellent resilience. Nevertheless, there are some weak points, such as low tensile strength, tensile modulus, and poor creep characteristics. In efforts to extend its use, various approaches have been implemented to improve the properties of NR based products. One of the modification techniques of NR is the reinforcement of NR by silica particles. In case of NR thin film production, silica reinforcement is achieved by mixing aqueous silica slurry with the NR latex [1]. However, in the mixing process, silica particles tend to aggregate together due to intermolecular hydrogen bonds between hydroxyl groups on the silica surface [2]. In order to overcome this problem, generation of silica particles in the NR matrix was introduced. The *in situ* silica formation is achieved by a sol-gel process of silica precursor such as tetraethoxysilane (TEOS) in the latex. This process has been developed and applied to a variety of polymers, including acrylonitrile-butadiene rubber (NBR) [3], styrene-butadiene rubber (SBR) [3,4], epoxidized natural rubber (ENR) [5], natural rubber (NR) [6], polybutadiene [7], poly(methyl methacrylate) (PMMA) [8], and polyurethane [9].

Moreover reducing the tackiness of NR has been another important and necessary property in the rubber industry. One method is to graft a secondary polymer onto the NR. Poly(methyl methacrylate) (PMMA) modified NR has been marketed since the mid 1950s under the trade name “Heveaplus”, with *tert*-butylhydroperoxide (TBHPO) as the initiator [10]. Graft copolymerization of MMA onto NR in emulsion polymerization process by using three different initiator systems; cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA), TBHPO/TEPA and potassium persulfate ($K_2S_2O_8$)/sodium thiosulfate ($Na_2S_2O_3$) were extensively studied [11]. CHPO/TEPA was found to give the highest grafting efficiency. It was reported

that, the graft copolymer of MMA onto NR simultaneously improved the physical properties and reduce the tackiness of rubber film [12, 13]. In the current work, an attempt was made to prepare graft copolymers of NR and MMA using CHPO/TEPA as a redox initiator system. The grafted NR was then subjected to silica reinforcement by *in situ* generation of silica inside the NR-g-MMA latex. The vulcanized rubber films having different weight ratios of NR:MMA, dry rubber content (DRC) and various amounts of added TEOS in the latex were examined in order to achieve the improvement of rubber film properties.

1.2 Objective

The aim of this research was to reinforce MMA grafted NR films by *in situ*-formed silica particles. The effects of MMA on silica particle distribution and reinforcement ability of the *in situ* silica were investigated.

1.3 Scope of the investigation

In this research, the necessary procedures to carry out the successful research are as follows:

1. Literature survey of the research work.
2. Graft copolymerization of methyl methacrylate onto NR particles in latex using a redox initiator system via emulsion polymerization.
3. Preparation of the grafted NR/silica composites by sol-gel process of TEOS.
4. Characterization of the morphology of the grafted NR/silica composites.
5. Mechanical property analysis of the grafted NR/silica composites.
6. Result summarization.

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 Amazonia. To harvest rubber, a small cut is made in the bark and a milky-substance called latex flows out. Today, 85% of the world's natural rubber comes from the Far East (Malaysia, Indonesia, Thailand, Sri Lanka, and India) [14].

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

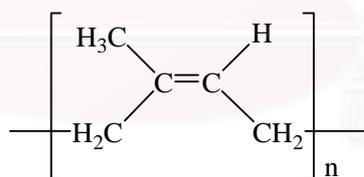


Figure 2.1 cis-1,4-polyisoprene.

2.1.3 Natural rubber latex

Natural rubber latex is a raw material derived from a rubber tree called the *Hevea brasiliensis*. It is a white milky fluid containing approximately 60% water, 35% rubber, and 5% proteins, amino acids and some carbohydrates. The natural rubber latex is harvested manually by cutting a spiral groove in the tree and allowing the fluid to drain. The raw natural rubber 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 natural rubber latex varied between wide limits are given in Table 2.1. The following composition is typical:

Table 2.1 Typical proportions of composition in natural rubber latex [15]

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 typically from 30 to 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 total solids and dry rubber content of fresh latex is of the order of 3%.

Natural rubber latex as it emerges from the tree (field latex) has a dry rubber content (DRC) of about 30 to 40%, the average being about 33%. Although field latex can be preserved with ammonia or 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 natural rubber latex to 60% or more to reduce the transportation costs and enhance suitability for various latex processes. Concentrated latexes are 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 latices. This is due in part to the partial removal of non-rubber constituents in several concentration processes [15].

2.1.3 Modification of natural rubber

Natural rubber has been modified in many ways since the establishment of a continuous supply of plantation rubber. Modification highly affects its physical properties. Even thermoplastic or resinous materials can be obtained by a modification of rubber. The most well known types of modification are oxidation, hydrogenation, halogenation, hydrochlorination, chlorosulphonation, and free radical addition or grafting [16].

2.2 Polymer grafting on natural rubber

2.2.3 Grafting copolymer

In graft copolymerization, polymer side chains are formed and attached to preformed macromolecules of different chemical composition. The simplest case of graft copolymer can be represented by the following structure [17],



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

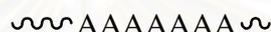
Graft copolymer is a high polymer, the molecules of which consist of two or more polymeric parts, of different compositions, chemically united together. A graft copolymer may be produced, for example, by polymerizing a given kind of monomer with subsequent polymerization of another kind of monomer onto 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 crosslinks between the different materials would also produce a graft copolymer.

During a free radical graft copolymerization, monomer B is intended to be grafted onto backbone polymer A, but usually the final product of a graft copolymerization will contain the following three species.

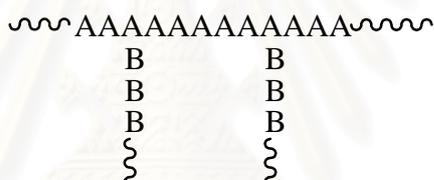
1. Homopolymer B which results from homopolymerization of monomer B.



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 the backbone poly-A.



The graft efficiency was found depend on 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 compete with polymer radicals for the monomer in order to form graft copolymers.
3. Competition between the various termination processes for the free polymer radicals.

The efficiency of the graft process will be affected by the mode of termination.

2.2.2. Natural rubber-graft-methyl methacrylate [18]

The graft copolymer of natural rubber with methyl methacrylate has been commercialized since the mid 1950s under the trade name “Heveaplus MG”, by a graft copolymerization by *tert*-butylhydroperoxide (TBHPO) initiator [10]. The Heveaplus MG materials have been used in two general ways. The first, and probably most importance in term of current consumption, is as solution of latex-based adhesives or bonding agent to bond rubber to poly(vinyl chloride), leather, textiles, and metals. The second is in the manufacture of hard rubber products and blends well with natural rubber in all proportions.

In 1993, Oommen and Thomas [19] studied the NR/PMMA blends compatibilized with NR-*g*-PMMA. PMMA was prepared by polymerizing MMA using benzoyl peroxide, while graft copolymers of NR and PMMA in the latex stage were prepared by using a redox initiator consisting of CHPO and TEPA. The reaction was performed at room temperature for about 24 hr. NR and PMMA in the ratio (60/40) were blended together in toluene with and without the addition of graft copolymer. The solvent was then evaporated to obtain a film. Addition of the copolymer led to reduce the size of dispersed PMMA. Moreover, the mechanical properties of the blends are also improved by the addition of the graft copolymer.

The modification of NR by graft copolymerization with MMA monomer was extensively studied by Charmondusit et al. [20]. In 1998, Charmondusit et al. studied the grafting of methyl methacrylate and styrene onto NR in emulsion process. The rubber macroradicals reacted with methyl methacrylate and styrene monomers to form graft copolymers. The particle structure of grafted NR was core-shell type by TEM observation. The grafted NR properties were strongly influenced by the reaction temperature. The grafted NR prepared using 100 parts by weight of monomer per 100 parts by weight of NR, 1.5 parts by weight of emulsifier, and 1.5 parts by weight of initiator performed at 70°C showed a high grafting efficiency and graft ratio. The grafted NR product could be used as an impact modifier for poly(vinyl chloride) (PVC) resin to form PVC/grafted NR product blends by mechanical blending and

compression molding. The good mechanical properties of blends were obtained at 10 and 15 phr of the grafted NR.

In 2001, Thiraphattaraphun et al. [21] studied the blends of NR-*g*-MMA and PMMA. The graft copolymerization of the MMA monomer onto NR using potassium persulfate as the initiator was carried out. The grafting efficiency increased with increasing initiator concentration up to 0.75 phr, but decreased with an increase in temperature above 55°C. The tensile strength and hardness increased but impact energy decreased with increasing PMMA content.

The grafted natural rubber latex used in the dipping process was studied by Lu et al. [22]. In 2002, Lu et al. studied the blending NR latex with MMA-*g*-NR latex (MGL). The blends were prevulcanized by sulfur system. The films of prevulcanized blends were formed by a dipping process with calcium nitrate ethanol solution as a coagulant. By blending NRL with MGL, they increased the modulus, antiaging properties, and tear strength of the blended films, but there was no adverse effect on the tensile strength.

In 2004, Kovuttikulrangsie et al. [23] prepared dipped film from PMMA blended deproteinized natural rubber (DPNR) or natural rubber low-ammonia (NR-LA) latex and DPNR-*g*-PMMA coated DPNR and NR-LA latex. The DPNR-*g*-PMMA coated films had lower friction coefficient than those of PMMA blended films. The physical properties in term of modulus at 500% elongation, tensile strength, and elongation at break of those rubbers were achieved for the rubber examination and surgical glove specification.

The grafting of polymer in seed emulsion polymerization occurs on the entry of radicals from the aqueous phase into the polymer particle, where they add to a double bond or abstract hydrogen from the hydrocarbon chain.

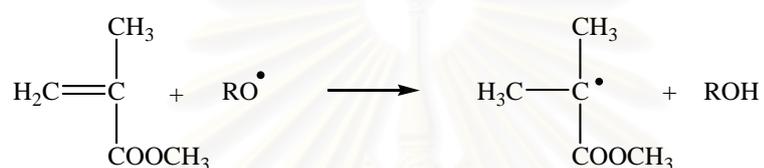
If, in a system containing polymer and growing chains of monomer, chain transfer to polymer (*i.e.*, abstraction of an atom such as hydrogen, or halogen, from polymer) occurs by the growing chains of monomer units, polymerization of the

monomer can take place at these newly formed reactive sites. The product is a graft copolymer. The grafting mechanism is characterized by reaction [11]:

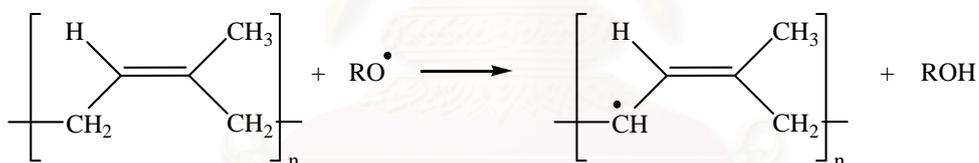
Initiation:



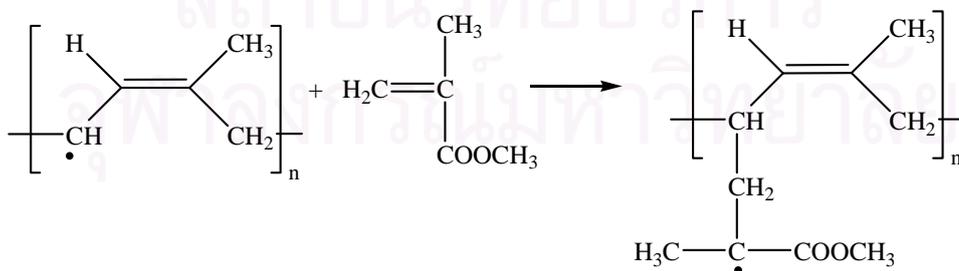
Attacking monomer:

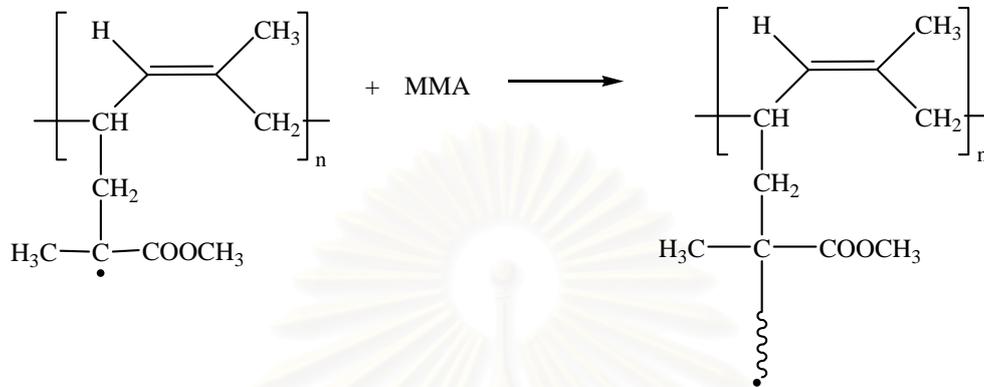
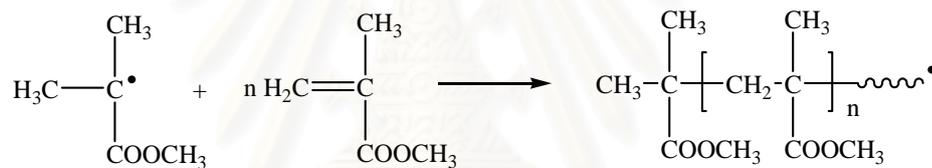
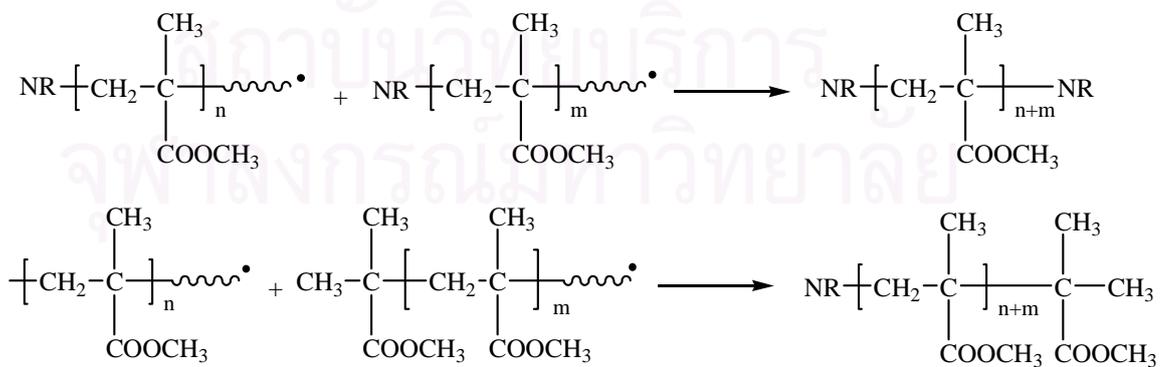


Attacking rubber:

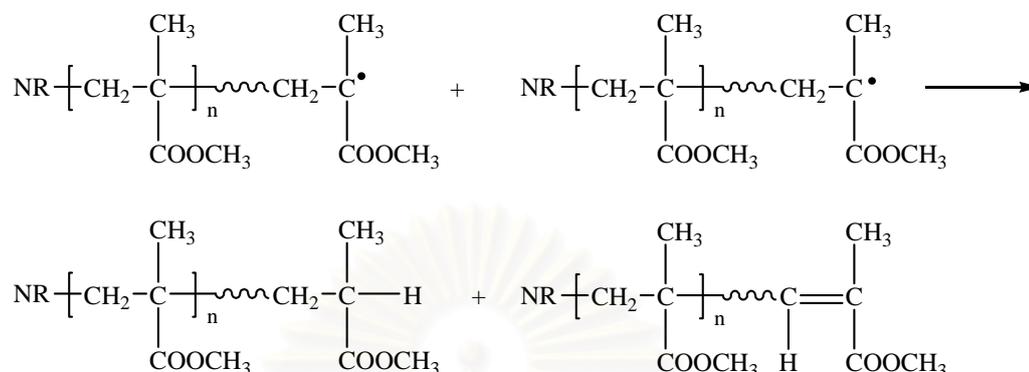


Re-initiation:



Propagation:*Propagation of graft polymerization:**Propagation of free polymerization:***Termination:***Termination by combination:*

Termination by disproportionation:



Scheme 2.1 Mechanism of the graft copolymerization of MMA onto NR.

The initiators decompose to yield the radicals. The free initiator radicals may promote grafting in two different ways. First, the free initiator radicals reacted with MMA monomer and polyisoprene simultaneously. The generated free radical intermediates were highly reactive with both the double bond and the alpha methylenic groups in NR, to form the graft copolymer. The end product of the polymerization process was a latex *i.e.*, PMMA grafted NR polymer particles disperse in a continuous aqueous phase.

2.2.3 Core-shell mechanism

Latex particles with different morphological structures can be prepared from seeded emulsion polymerization technique. These particles typically comprise an inner soft polymer sphere, *i.e.*, the “core” and an outer hard polymer “shell”.

Both redox and thermal initiator could be used to prepare NR-based core-shell latex particles. Kochthongrasamee et al. [11] studied the graft copolymerization of MMA onto NR prepared by emulsion polymerization by three different initiator systems; CHPO/TEPA, TBHPO/TEPA and $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_3$. The CHPO/TEPA initiator concentration of only 1.0 phr at 60°C gave the highest percentage grafting efficiency and percentage of grafted NR. To promote a greater grafting efficiency and yield a lower homopolymer content of PMMA, grafting promoter (vinyl *neo*-decanoate: VneoD) was added. Since the peroxide is soluble in both the monomer

and the NR particle, whereas the activator TEPA is water soluble, the free radicals are produced at the particle/water or monomer droplet/water interface. The MMA monomer absorbed at or near surface of NR particles where the redox partners met and the emulsion polymerization took place. The PMMA phase was, therefore, locked into core-shell configuration [24]. The location of the components of the redox couple CHPO/TEPA is shown in Figure 2.2.

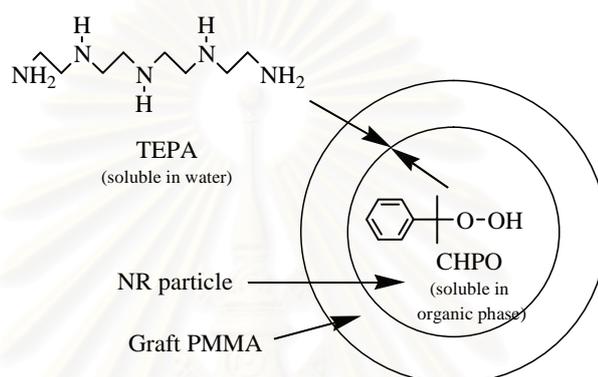


Figure 2.2 The polymerization of MMA in NR latex.

2.3 Fillers for rubber

Fillers may be of two types, reinforcing and non-reinforcing. Non-reinforcing fillers are characterized by extremely weak interactions with the rubber. They include chalk, silica flour, diatomaceous earth, mica, and kaolin etc. They are used to raise the viscosity of the compounds in the unvulcanized state and to increase the Shore hardness and the modulus of elasticity of the vulcanized rubbers. Improvements in tear strength can also be achieved in the case of surface-treated fillers. Reinforcing fillers are primarily and fine-particle silica. The reinforcing effect can be attributed to the bond between the filler and the rubber. These filler-rubber interactions result in increased viscosity and changes to the glass transition temperature (T_g) and the crystallization behavior. On the other hand, filler-rubber bonds improve the mechanical properties but can also lead to premature stiffening (creep hardening) of the rubbers. Almost all natural rubber compounds utilize either carbon black or inorganic fillers such as precipitated and fumed silica, clay, ground or precipitated calcium carbonate, titanium dioxide, zinc oxide and several others as reinforcing agents and/or extenders for rubber compounds.

2.3.3 Filler properties [25]

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

Particle Size – If the size of the 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 generally 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-reinforcing 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.

Surface Area – Filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Fillers that have a high surface area have more contact area available and therefore have 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 to 250 m^2/g . Most reinforcing precipitated silica range from 125 to 200 m^2/g ; typical hard clay ranges from 20 to 25 m^2/g .

Structure – The shape of an individual particle of reinforcing filler (e.g. carbon black or precipitated silica) is of less importance 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 acicular (needle-like) aggregates.

For reinforcing fillers which exist as aggregates rather than discrete particles, carbon black and silica in particular, a certain amount of structure that existed at manufacture is lost after compounding. The high shear forces encountered in rubber milling will break down the weaker aggregates and agglomerates of aggregates. The structure that exists in the rubber compound, the persistent structure, is what affects processability and properties.

Surface Activity – A 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.

2.3.3 Reinforcing fillers [26]

Particulate fillers can increase the strength of an amorphous rubber more than 10-fold. For a filler to cause significant reinforcement, it must possess high specific surface area, *i.e.*, the particles must be small, less than $1\ \mu\text{m}$ in size. Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Two types of fillers that are most effective for reinforcing rubber are carbon black and silica. They can be produced with a primary particle size as small as $100\ \text{\AA}$, corresponding to a surface area of a few hundred square meters per gram (m^2/g) of filler.

Two other important characteristics of fillers are structure and surface chemistry. Structure relates to irregularity in shape of filler aggregates (Figure 2.3), determined by the extent and manner of clustering of primary particles. A filler aggregate with high structure has a large void volume within the space it pervades, in which rubber molecules may become "occluded". The combination of occluded

rubber and filler then becomes the reinforcing entity, so that the effective volume fraction of filler is increased (Aggregates are not broken down into primary particles upon mixing with rubber). Generally, reinforcement is enhanced by high structure and strong bonding between filler and rubber. Silica fillers are often treated with silane coupling agents to bond them chemically to rubber, or the coupling agents may be added directly to the rubber compound [26].

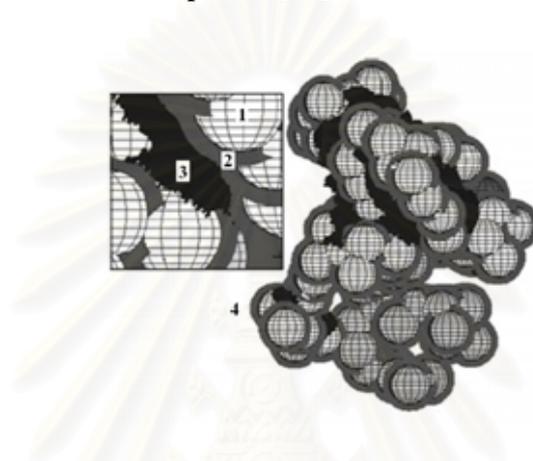


Figure 2.3 Structure of the material: (1) filler, (2) polymer layer around particles, (3) occluded polymer and (4) matrix [27].

2.3.3 Silica

Fine particle silica gives the utmost in reinforcement in rubbers of the nonblack fillers; the silicates would probably be in second place. Amorphous silica consists of ultimate particles of the inorganic silicon dioxide $(\text{SiO}_2)_n$, where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Because of its numerous and longstanding uses in other applications, silica surface chemistry is clearly better known than that of carbon black [28]. Silica surface chemistry is mainly defined by the surface content in silanols Si-OH ; silanols can be “isolated”, $\text{O}=\text{Si-OH}$, or “geminated”, $\text{O}=\text{Si}(\text{OH})_2$. They are generally highly associated by hydrogen bonds (Figure 2.4).

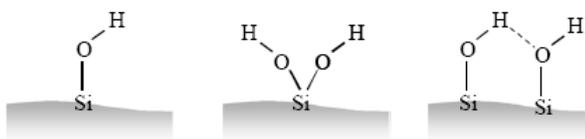


Figure 2.4 “Isolated”, “geminated” and associated silanols [28].

The hydrolysis reaction replaces alkoxide groups (OR) with hydroxyl groups (OH). Subsequent condensation reactions involving the silanol groups produce siloxane bonds (Si-O-Si) plus the by-products alcohol (ROH) or water. Under most conditions, condensation commences before hydrolysis is complete. Because water and alkoxy silanes are immiscible, a mutual solvent such as alcohol is normally used as a homogenizing agent. However, gels can be prepared from silicon alkoxide-water mixtures without added solvent, since alcohol produced as the by-product of the hydrolysis reaction is sufficient to homogenize the initially phase separated system. It should be noted that alcohol is not simply a solvent.

2.4.3 *In situ* formation of silica in a polymeric matrix

Recently, a sol-gel process of TEOS was applied to prepare silica for reinforcing many types of rubbers: e.g. polymer, synthetic rubber and natural rubber.

In 1995, Huang and Qiu [8] prepared the hybrid material incorporating poly(methyl methacrylate) with tetraethoxysilane (TEOS) by using the *in situ* sol-gel process. The bonding between the organic phase and inorganic phase was formed by a coupling agent, (3-trimethoxysilyl)propylmethacrylate (MSMA). This material showed high optical transparency and great hardness. Increasing the silica content would increase the thermal decomposition temperature of the hybrid material, but higher content of silica would make the product become stiffer and easily crack.

In the same year, Hashim et al. [5] prepared silica reinforced vulcanizates using TEOS and epoxidized natural rubber (ENR). The rubber was first procured with 3-aminopropyltriethoxysilane (APS) by heat pressing at 180°C for a range of cure time. The resultant rubber sheets or vulcanizates were swelled in TEOS, and subsequently subjected to a sol-gel reaction in butylamine aqueous solution. Hydrolysis and condensation of the TEOS resulted in the formation of silica particles in the rubber network yielding silica-containing vulcanizates. Silica content as high as 28% and TEOS-to-silica conversion of over 60% were observed. When prepared under certain reaction conditions, the sol-gel vulcanizates obtained were more rigid and stronger than a typical sulfur-cured ENR vulcanizate that contained comparable amount of silica. The sol-gel technique could be employed to prepare high-modulus

vulcanizates with tensile strength comparable to or better than the one prepared by the conventional method.

In 1997, Ikeda and Kohjiya [6] studied the *in situ* formed silica particles in rubber vulcanizate by the sol-gel method. *In situ* silica filling butadiene rubber (BR) was carried out by the sol-gel process using TEOS. BR was sulfur cured, and the resulting crosslinked BR was subjected to soaking in TEOS at 30 °C for 24 hr, followed by standing at 50°C for 72 hr to conduct the *in situ* sol-gel reaction of TEOS. The resulting vulcanizates contained silica particles, which were prepared by the *in situ* filling technique. They were subjected to tensile and dynamic mechanical measurement, differential scanning calorimetry and transmission electron microscopic observation. The *in situ* formed silica was dispersed homogeneously in the rubber matrix. The size of *in situ* silica was influenced by the crosslinking density, probably because it was formed in the crosslinked rubber networks. Compared to the conventional silica-filled BR vulcanizate, which was prepared by mechanical mixing of the silica particles, the new vulcanizates with the *in situ* formed silica showed better mechanical properties.

In 2002, Yoshikai et al. [3] 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 SBR and NBR (nitrile rubber). The sol-gel process of TEOS then proceeded in a mixture of latex, water and a catalyst. 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 were over 25 MPa.

In 2003, Kohjiya and Ikeda [32] 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.

In 2004, Zhou and Mark [7] studied the *in situ* generated silica particles in *trans*-1,4-polybutadiene (*t*PBD). *t*PBD networks crosslinked with dicumyl peroxide (DCP) were reinforced by *in situ* silica formed by sol-gel process. Changing the degree of crosslinking by changing the amount of DCP, or changing the amounts of the sol-gel components [TEOS and the catalyst dibutyltin diacetate (DBTDA)], changed the silica generated with regard to the amount precipitated, particle size, and degree of dispersion. Stress-strain measurements in continuous extension indicated good reinforcement, even at relatively small amounts (around 2 %wt) of silica.

Until 2007, Ma et al. [33] prepared the acrylic resin/nano-silica composite by physical blending of acrylic resin and nano-silica, which was synthesized via the sol-gel process of TEOS and catalyzed with alkali. DSC indicated the glass transition temperature (T_g) of acrylic resin/nano-silica ($T_g = -26.7^\circ\text{C}$) was slightly higher than that of the acrylic resin ($T_g = -29.6^\circ\text{C}$). The nano-silica particles were useful for the composite to improve the strength and toughness evidently. Swelling characterization confirmed that the water resistance of acrylic resin/nano-silica was improved by 55.94% and the solvent resistance in acetone by 54.79% when compared with acrylic resin.

2.5 Tackiness on rough surfaces

Roughness of the counter-face has two opposing effects on rubber friction and tackiness. As the roughness is increased the true area of contact and hence the friction will be reduced. However, roughness will also increase the deformation in the rubber and hence the viscoelastic loss of energy in the bulk rubber, which will contribute to the total frictional energy dissipation. Lubricants such as non-swelling fluids or dust, greatly reduce friction on smooth surfaces but the effect is smaller on rough surfaces [34]. Bhushan [35] also indicated an increase in surface roughness resulting in the decrease of interfacial adhesion. Adhesion is affected by the real area of contact. If two surfaces are placed together, because of surface roughness, the real area of

contact is usually very much smaller than the geometrical area. Materials with higher roughness exhibit lower real area of contact, which leads to lower adhesion.

Tack is normally determined from the force required to separate two components joined by a soft viscoelastic bonding material. It is a concept normally applied to the initial stages of bonding but is relevant for longer periods in certain applications. The tack of an adhesive has been defined as the property that enables it to form a bond with the surface of another material upon brief contact under light pressure. Tack depends on the surface energies of the adhesive and surface where bonding takes place and on the cohesive strength of the adhesive [36]. Classic theories of tack assumed that it occurs in two phase systems due to the disperse phase acting as a viscous liquid that wets the substrate with an elastic continuous phase providing the strength. This does not account for tack of modern single phase systems. Current theories suggest that tack is due to viscoelasticity. For a material to be tacky, the glass transition temperature of the adhesive should be substantially below the application temperature. Zosel [37] reported that the highest tack levels are achieved when the application temperature is around 50-70°C above T_g . Zosel also reported that high tack strength was also associated with the formation of filament structures in the adhesive as the adherents are pulled apart. Therefore, the tack will depend on the pressure applied, the time history of the applied pressure and on the rheological properties of the adhesive.

2.6 Characterization of mechanical properties

Mechanical tests provide the only method to obtain engineering-type evaluations of new polymers. Such 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, multiple tests on similar samples are needed before valid results can be obtained [38].

2.6.3 Tensile Properties

If rubber is stretched, squashed or otherwise mechanically deformed, the scientist says that a deformation (change in shape) called strain has been applied to the material, as

a result of an applied pressure called stress. There are certain clearly defined modes of strain, such as tensile (stretch), compression (squash), shear (a combination of tensile and compression), and torsion (twist).

The most used strain mode in the quality control rubber laboratory is tensile. In this test, a piece of rubber is stretched until it snaps (tensile at break). The test piece often goes through a considerable amount of elongation before break occurs (up to around 900%, depending on the compound).

Tensile testing is accomplished by first molding a flat sheet of rubber about 2 mm thick, from which dumbbell shaped pieces are die cut (Figure 2.6).



Figure 2.6 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 unstretched 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:

$$\frac{L - L_0}{L_0} \times 100$$

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. Modulus numbers at 500% elongation is commonly measured on thin film rubber products. 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 [39].

2.6.3 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 [40].

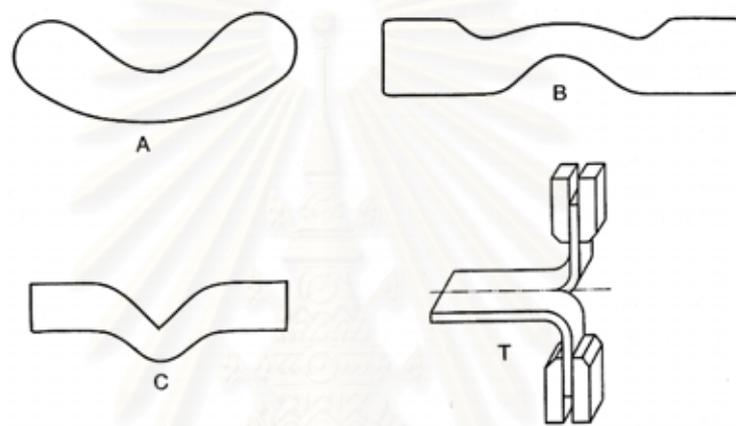


Figure 2.7 Shaping of standard tear specimens, A, B, C, and T [40].

Figure 2.7 shows the shapes of some commonly used tear test pieces which are described in ASTM D624. Die B is a crescent-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 accordance with fracture mechanics, tearing energy theoretically is a basic material property that is truly independent of the cut geometry and geometry of the rubber specimen. Most standard tear tests do not measure tearing energy. The most common shape in ASTM is that cut by die C. If the apex in the die is not kept sharp and well defined, it can result in higher apparent values of tear.

2.7 Swelling

Linear polymers are capable of dissolving in appropriate solvents to form homogeneous polymer solutions. However, if crosslinks are introduced to tie the chains into an infinite network, the polymer can no longer dissolve. Instead the solvent is absorbed into the polymer network, giving rise to the phenomenon of swelling. The degrees of swelling thus reached for common elastomers remain moderate, depending on the solvent quality and the crosslink density. Evidently, for a given solvent, the higher crosslink density of the rubber the lower is the swelling, and conversely for a given degree of crosslink density a more powerful solvent will give a higher degree of swelling. This relationship is quantitatively expressed by Flory-Rehner equation:

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = V_s \eta_{swell} \left(V_r^{1/3} - \frac{2V_r}{f} \right)$$

This is used quite often to calculate the crosslink density (η) from swelling measurements. V_s is the molar volume of the solvent and V_r is the volume fraction of the rubber in the swollen gel.

χ is the interaction constant (for natural rubber usually about 0.4 in good solvents) dependent on the cohesive energy density of solvent, polymer, and swollen gel [41].

The ASTM standard for measuring resistance of rubber to liquids is ASTM D 471-98. The preferred method for volume change measurements is the gravimetric method, in which the test piece is weighed in air and in a liquid before and after

immersion. The volume change is then calculated on the basis that volume is proportional to the weight in air minus the weight in liquid.

The effect of liquids on tensile and hardness properties can be measured by two procedures specified in ASTM D 471-98. In one procedure, properties are measured immediately after removal from immersion; in the other, measurement takes place after removal from immersion and subsequent drying [26].



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CHAPTER III

EXPERIMENTALS

3.1 Materials

High ammonia natural rubber latex (HA, 0.7%) with 60% dry rubber content (DRC) and 50% dispersion of vulcanizing agents were purchased from the Rubber Research Institute of Thailand. Tetraethoxysilane (TEOS; Fluka, >98%), methyl methacrylate (MMA; Fluka, Purum), the stabilizer oleic acid, the buffer potassium hydroxide (KOH; Fluka), sodium dodecyl sulfate (SDS; Fluka, >99.5%), cumene hydroperoxide (CHPO; Fluka, purity ~80%) and tetraethylenepentamine (TEPA; Fluka, purity ~85%) were used as received. Ammonia solution was purchased from BDH, England.

3.2 Procedures

3.2.1 Preparation of grafted NR latex

Graft copolymerization of MMA onto NR particles in the latex was synthesized by emulsion polymerization technique. The high ammonia natural rubber latex (30% DRC) was placed in a round bottom reactor. Potassium hydroxide solution (10% w/v, 0.2 phr), and sodium dodecylsulfate solution (10% w/v, 1.0 phr) were then added while stirring. The latex mixture was deoxygenated by bubbling nitrogen gas for approximately 15 min at room temperature. The stabilizer, oleic acid (10 phr) was added to the latex mixture and mixed thoroughly for 15 min. The MMA monomer was then added continually while stirring for 30 min to allow the latex particles to absorb monomer. The mixture was warmed up to 60°C, the initiator (CHPO) was then added. After 15 min of mixing, the amine activator (TEPA) was added. The bipolar redox initiating system was employed at 1:1 ratio (CHPO:TEPA) for a total amount of 1.0 phr. The reaction was allowed to proceed for 2 hr under continuous stirring and nitrogen atmosphere.

3.2.2 Preparation of sulfur vulcanized NR latex containing TEOS

The amount of latex mixture and vulcanizing agents are shown in Table 3.1. The mixture was stirred at 300 rpm by a mechanical stirrer for 2 hr at room temperature. After that, a predetermined amount of TEOS was added into the latex compound with stirring for 10-15 min to obtain a homogeneous milky mixture. Finally the mixture was filtered through a wire mesh to separate coagulated solid phase. The latex compound was matured for 2 days at room temperature before used for dipping process.

Table 3.1 Compound formulation

Ingredients	NR (phr ^a)
NRL	100.0
Sulfur	2.5
Wingstay L	1.0
Zinc mercaptobenzothiazole (ZMBT)	0.5
Zinc diethyldithiocarbamate (ZDEC)	1.5
ZnO	2.0

^a phr = part per one hundred parts rubbers by weight

3.2.3 Dipping process

A glass former used for the dipping process was cleaned and dried before being coated with 20% w/v calcium nitrate solution. A film was prepared by slowly dip the former into the latex compound for 12 sec. The coated former was then dried at 80°C for 15 min. A film was then leached with water at 80°C and put into an oven at 80°C for 24 hr to complete the vulcanization.

3.3 Characterization of the grafted NR

3.3.1 Grafting efficiency

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

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

The amounts of homo-PMMA grafted and ungrafted NR in the product were determined by solvent extraction using a Soxhlet apparatus. The ungrafted NR was extracted by light petroleum (60-80°C) for 72 hr. The residue was dried to constant weight in an oven at 70°C. To remove homo-PMMA, the residue was further extracted in acetone (60°C) for 72 hr. Grafted NR content was determined by the residual weight after the extraction of the two homopolymers. %Grafting efficiency and %Grafted NR are defined as the mass of NR-g-PMMA divided by total PMMA produced.

$$\% \text{ Grafting efficiency} = \left(\frac{\text{The residual weight after 2 extractions}}{\text{The total weight of polymer formed}} \right) \times 100 \quad (3.2)$$

The amount of grafted NR was therefore calculated by

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

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

3.3.2 Morphology of grafted NR

JEOL transmission electron microscope (JEM-2100) was used to examine the morphology of rubber particles after MMA grafting at 120 kV. The MMA-g-NR latex was diluted with distilled water to obtain a DRC of 0.75% (10 ml). A drop of 0.5% ruthenium tetroxide (RuO₄) was added into the diluted latex and stirred for 24 hr. A

drop of the diluted latex sample was deposited onto a carbon-coated Formvar film grid and allowed to dry overnight in a desiccator. The substrate grid was finally stained by exposed to RuO₄ vapor in a glass-covered dish at room temperature for 24 hr.

3.3.3 Fourier transformation infrared spectroscopy (FT-IR)

The grafted NR film was dissolved in chloroform and casted on a KBr cell of 1 mm thickness. Composition of the NR film sample was determined by Fourier transform infrared spectrophotometer (Perkin Elmer model 1760x) in the range of 4000-400 cm⁻¹ with 32 scans at a resolution of 4 cm⁻¹.

3.4 Characterization of the grafted NR/silica composites

3.4.1 Silica content in the composites

The silica content was determined by cutting the NR/silica composite into small pieces (ca. 50 mg). They were placed in aluminum oxide cups and heated under air atmosphere, from room temperature to 850°C in an oven (Carbolite GM 11/7). The temperature was kept at 850°C for 30 min. The weight of the remaining ash was calculated for the silica content by [42]:

$$\text{Silica content (phr)} = 100 (W_1/W_2) \quad (3.4)$$

The conversion of silanes to silica was calculated using:

$$\text{Conversion (\%)} = 100 (W_3/W_4) \quad (3.5)$$

where, W_1 was the weight of silica in the sample, and W_2 was the weight of the rubber. W_3 was the amount of *in situ* generated silica in the sample, which was obtained from equation. 3.4. W_4 was the theoretical amount of silica generated.

3.4.2 Microscopic analysis

3.4.2.1 Atomic force microscopy (AFM)

AFM images were recorded with Scanning Probe Microscope model NanoScopeIV[®], Veeco, USA. Measurements were performed in air using 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 were computed from NanoScope software by using the following:

$$R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n (Z_i - m)^2} \quad (3.6)$$

where, Z_i is the height of the profile at the 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 profile.

3.4.2.2 Scanning electron microscope (SEM)

Both of the ungrafted and grafted composite films were fractured under liquid nitrogen. The samples were then sputter-coated with gold and the photographs were taken on a JEOL JSM-6480LV SEM. The SEM photographs were used to determine the degree of silica dispersion. Measurements were done at 15 kV, and a magnification of 2,000 and 10,000. The energy dispersive X-ray spectrometer (EDX) detector has an elevation angle of 35°.

3.4.3 Thermal Properties

3.4.3.1 Differential scanning calorimetry (DSC)

The calorimetric studies were conducted on a DSC 204 F1 Phoenix[®] differential scanning calorimetry. A rubber sample (~10 mg) was scanned from -100 to 220°C at a heating rate of 20°C/min. The analyses were done under nitrogen atmosphere. The glass transition temperature was taken as the onset of the heat capacity change.

3.4.3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed in a thermal analyzer NETZSCH STA 409C. A piece of rubber sample (~20 mg) was placed into an aluminium oxide crucible and scanned from 25 to 700°C at a heating rate of 20°C/min. The measurements were done under air atmosphere at the flow rate of 50 mL/min.

3.4.4 Mechanical properties

Tensile properties were measured with Hounsfield H10KS universal testing machine (Hounsfield, Redhill, UK), according to JIS K6251-8 at grip length of 10 mm, and crosshead speed of 500 mm/min. Rubber samples of 0.2 to 0.4 mm thick were cut into dumbbell shape specimens using Wallance die cutter as shown in Figure 3.1. Tensile properties of the specimens were measured in the machine direction (MD). Each data point was an average value obtained from measurement of four specimens.

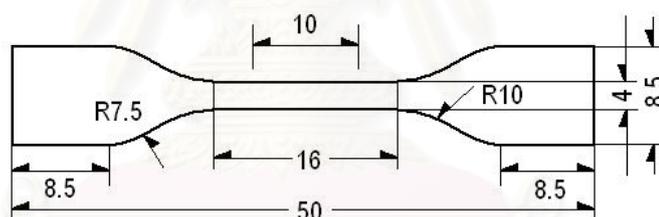


Figure 3.1 Schematic diagram of tensile test specimen (JIS K6251-8).

The tear properties were measured using a Hounsfield H10KS universal testing machine, according to ASTM D624-91. The specimens were cut using die C (Figure 3.2) and the thickness of each specimen at the notch was measured using a micrometer. The gauge length was 70 mm and the crosshead speed was 500 mm/min. The values reported for each sample were averaged from three specimens.

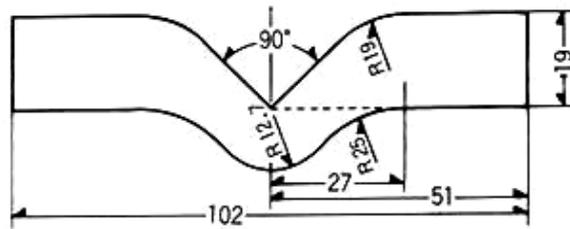


Figure 3.2 Schematic diagram of tear test specimen (ASTM D624 Die C).

Tackiness of the ungrafted and grafted films was measured using PICMA Tack Tester (Toyo Seiki Kogyo Co., Ltd., Japan) under the load of 500 g, pressing time of 30 sec and a peeling speed of 25 mm/min. Six samples were used for tackiness test. An average of results was taken as the resultant value. All tests were controlled at 25°C and 60% relative humidity.

3.4.5 Swelling measurements of grafted NR/Silica composites

Circular specimens with a diameter of 30 mm, were cut out from the vulcanized films. Thickness and diameter of the specimens were measured by digital calipers. Specimens of known weights were immersed in toluene at room temperature for 24 hr to allow the swelling to reach diffusion equilibrium. Then, the specimens were immediately blotted with filter paper. Their weights were then determined. From the differences of sample masses, the degree of swelling was calculated by:

$$\text{Degree of swelling (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (3.7)$$

where, W_1 and W_2 were the initial and final (swollen) weights of the sample (g).

Crosslink density (η) was calculated by using Flory-Rehner equation [43]:

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = V_s \eta_{swell} \left(V_r^{1/3} - \frac{2V_r}{f} \right) \quad (3.8)$$

where, V_r is volume fraction of rubber in swollen gel, V_s is molar volume of the toluene (in this work being 106.2 cm³/mole), χ is the rubber-solvent interaction

parameter ($\chi = 0.3795$ for NR-toluene system), η_{swell} is the crosslink density of the rubber (mole/cm³), and f is the functionality of the crosslinks ($f = 4$ for sulfur curing system).

The value of V_r was calculated:

$$V_r = \frac{\left(\frac{W_1}{\rho_{cr}} - \frac{W_{filler}}{\rho_{filler}} \right)}{\left(\frac{W_1}{\rho_{cr}} - \frac{W_{filler}}{\rho_{filler}} \right) + \left(\frac{W_2 - W_1}{\rho_{toluene}} \right)} \quad (3.9)$$

where, W_1 and W_2 were weights of the crosslinked rubber before and after toluene uptake (g), W_{filler} is the weight of the silica in the crosslinked rubber matrix (g), ρ_{cr} is the density of the crosslinked rubber (g/cm³), ρ_{filler} is the density of sol-gel silica from TEOS (1.92 g/cm³) [29], and $\rho_{toluene}$ is the density of toluene (0.862 g/cm³).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Grafting MMA onto NR latexes

In the grafting process, the high ammonia preserved NR latex with 60% DRC was diluted to 30% DRC by 0.7% ammonia solution. Potassium hydroxide solution (10%w/v) was added to maintain the stability as well as the basic condition of the latex during the grafting and maturation period. SDS, an emulsifying agent, was also added with gentle stirring in order to produce emulsions and provide colloidal stability.

Grafting of MMA on NR was carried out in latex stage. First the rubber particles in the latex had to be swollen with the MMA monomer. Then the redox initiation system, formed by CHPO/TEPA, produced radicals that was able to initiate polymerization. The redox couple should generate radicals predominantly near the surface of the rubber particle which is the desired locus of polymerization, leading to the formation of a PMMA layer around the seed particle. The grafting was studied by varying the weight fraction of NR:MMA from 95:5 to 85:15.

Grafting efficiency was studied by analyzing the amount of graft copolymer and homopolymers formed during the grafting step. The percentages of monomer conversion, graft copolymer, and free homopolymer, and grafting efficiency (GE) are listed in Table 4.1. The percentages of monomer conversions of the graft reaction were higher than 90%, and not significantly affected by the range of NR:MMA ratios in this study. Also no marked difference was observed for the free NR contents in the graft copolymers. Free PMMA increased slightly with increasing the weight ratio of MMA monomer. The graft co-polymerization largely occurs around the surface of the latex particles. As the MMA shell layer become thick, the access of MMA monomer to the radical propagation chain tends to be more difficult. This should result in the increase of homo-PMMA formation in the system. Still the GE increased with increasing the MMA fraction from 5 to 15 %wt. The increase of GE with MMA

fraction was most likely because higher monomer concentrations led to more monomer radicals, which were produced by an electron-transfer reaction from primary free radicals [44].

Table 4.1 Grafting efficiency of MMA on NR latex

Weight ratio of NR:MMA	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		GE (%)
			NR	PMMA	
95:5	94.96	79.14	19.19	1.67	66.3
90:10	97.76	77.64	19.40	2.96	71.1
85:15	96.28	75.84	20.96	3.21	78.7

An individual rubber particle in the latex was analyzed by TEM. The surface of ruthenium-stained NR particles in the latex appears to be spherical with somewhat sharp edge (Figure 4.1a). For the MMA-grafted NR particles, semi-transparent layer covering the seed particle is present (Figures 4.1b to 4.1d). Because the Ru-staining occurs exclusively at unsaturated chemical bonds, i.e. C=C, PMMA is therefore not stained very well and appears as semi-transparent object in the micrograph. When the weight percentage of MMA monomer increased, the thickness of the grafted MMA layer around the core particles also increased. In the sample with the highest MMA content, the shell layer of PMMA in Figure 4.1d was joined by semi-transparent PMMA phase with some small area of rubber domain. In addition, one also sees faintly stained small particles dispersed in the emulsion phase. They are probably agglomeration of homo-PMMA particles occurring at the expense of grafting process.

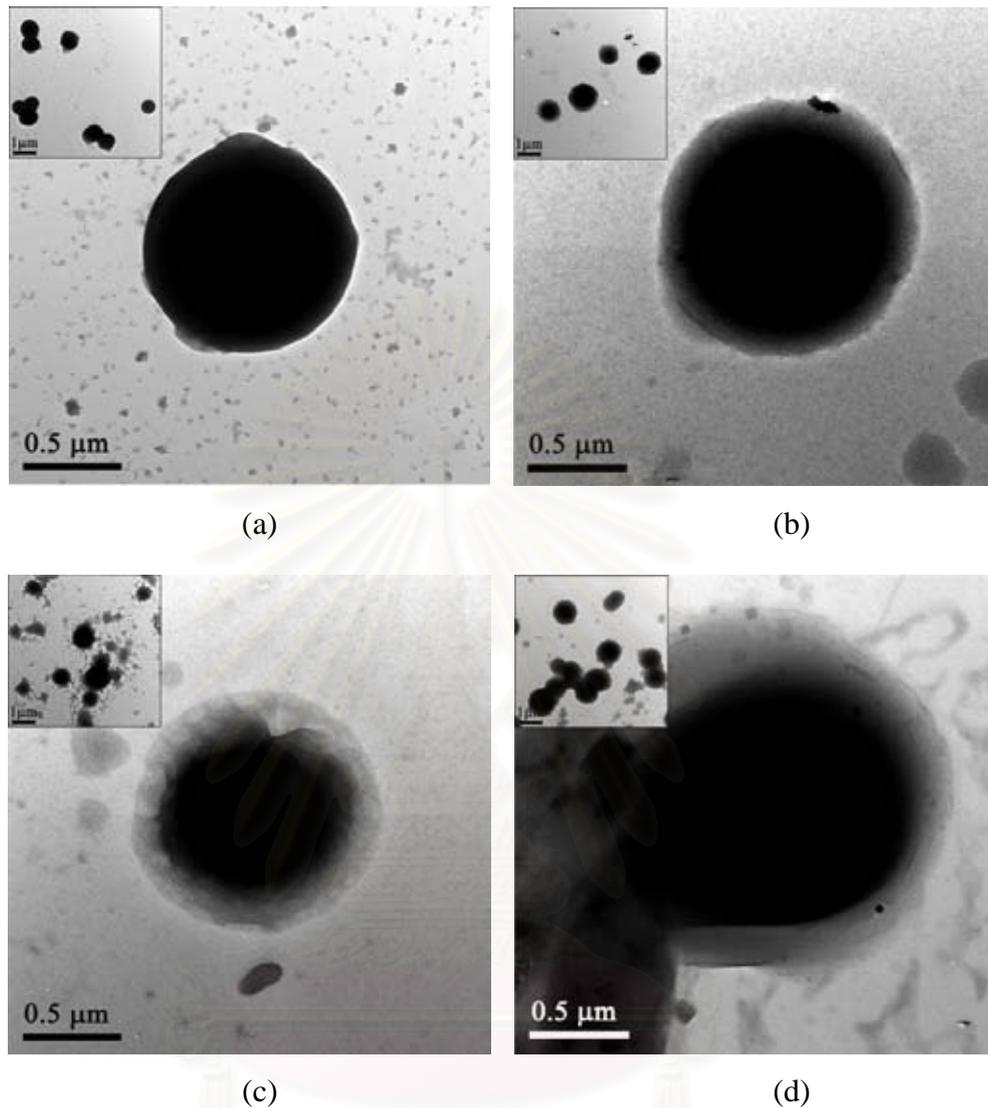


Figure 4.1 TEM micrographs of rubber particles in (a)NR latex (100:0), (b)NR-g-MMA 95:5, (c)90:10, and (d)85:15.

4.2 *In situ* silica formation in the MMA grafted NR

Rubbers are conventionally reinforced with particulate reinforcing fillers such as synthetic silica, usually precipitated silica. Generally, silica is normally highly hydrophilic in nature and has a strong tendency to form agglomerates. Certain degrees of agglomeration can result in loss of mechanical properties. Accordingly, various methods have been offered to provide efficient dispersions of silica in the rubber latex. Treating silica with coupling agent in aqueous suspension to form silica slurry

is usually used [1, 45]. Alternatively, the silica particles can also be produced from a sol-gel process of TEOS. The goal of this work was to prepare *in situ* silica/NR composite film by latex dipping process. In this section, the preparation parameters affecting the silica formation in MMA grafted NR were investigated and discussed.

4.2.1 Effect of maturation time on latex compound

In this work, the latex was mixed with vulcanizing agents and TEOS. The mixed latex therefore has to maintain its colloidal stability during maturation and dipping steps. The latex compound maturation is one of the most significant steps in manufacturing latex products. The maturation of latex compounds is the period after which the latex compound is stored prior to use in the dipping process. The crosslinking in latex can slowly take place at room temperature [46]. Moreover, it was believed that the sol-gel process of TEOS was also occurring during maturation. This was because there were 2 major ingredients required for the sol-gel process in the latex, i.e. water and ammonia as the base catalyst. It was therefore worth exploring the effect of latex maturation time on silica content in the composites. The latex being investigated was prepared from ungrafted NR latex with DRC of 50%. The latex was mixed with vulcanizing agents and 10 phr of TEOS.

The silica contents of the NR/silica composites obtained by the sol-gel process of TEOS after various maturation times are shown in Figure 4.2. It can be seen that the silica content in rubber matrix and the conversion ability of TEOS to silica were dramatically increased after just one day of maturation and remained unchanged thereafter.

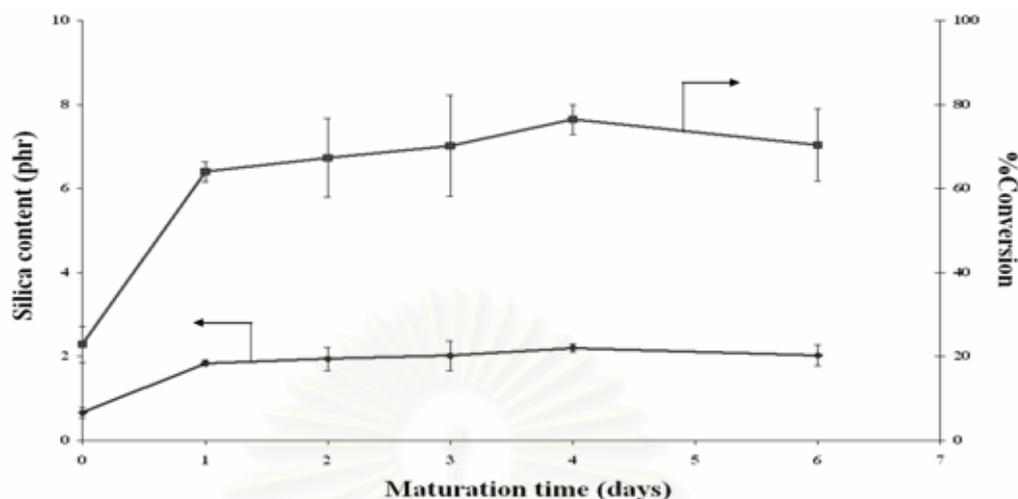


Figure 4.2 Changes of silica content and %conversion of TEOS to silica as a function of latex maturation times for the NR latex mixed with vulcanizing agent and TEOS.

4.2.2 FT-IR Analysis of silica-filled rubber films

The infrared spectra of NR, PMMA, sol-gel silica, NR-*g*-MMA, and NR-*g*-MMA/silica samples are shown in Figure 4.3. Characteristic transmission peaks for NR were found at 3035, 2960, and 837 cm^{-1} correspond to the stretching vibration of olefinic =C–H, stretching vibration of –C–H and out-of-plane bending vibration of aliphatic =C–H, respectively. The evidence of MMA present in the graft copolymer was observed at 1733 for C=O and 1147 cm^{-1} for –C–O– of the ester functional groups in the MMA repeat unit. Moreover, analysis of the silica incorporated vulcanizates revealed additional characteristic signals of siloxane (Si–O–Si) stretching vibration from 1210 to 1095 cm^{-1} , bending vibration at 473 cm^{-1} and stretching vibration of the silanol groups (Si–OH) at 967 cm^{-1} . These results prove the existence of MMA and silica inside the rubber vulcanizates.

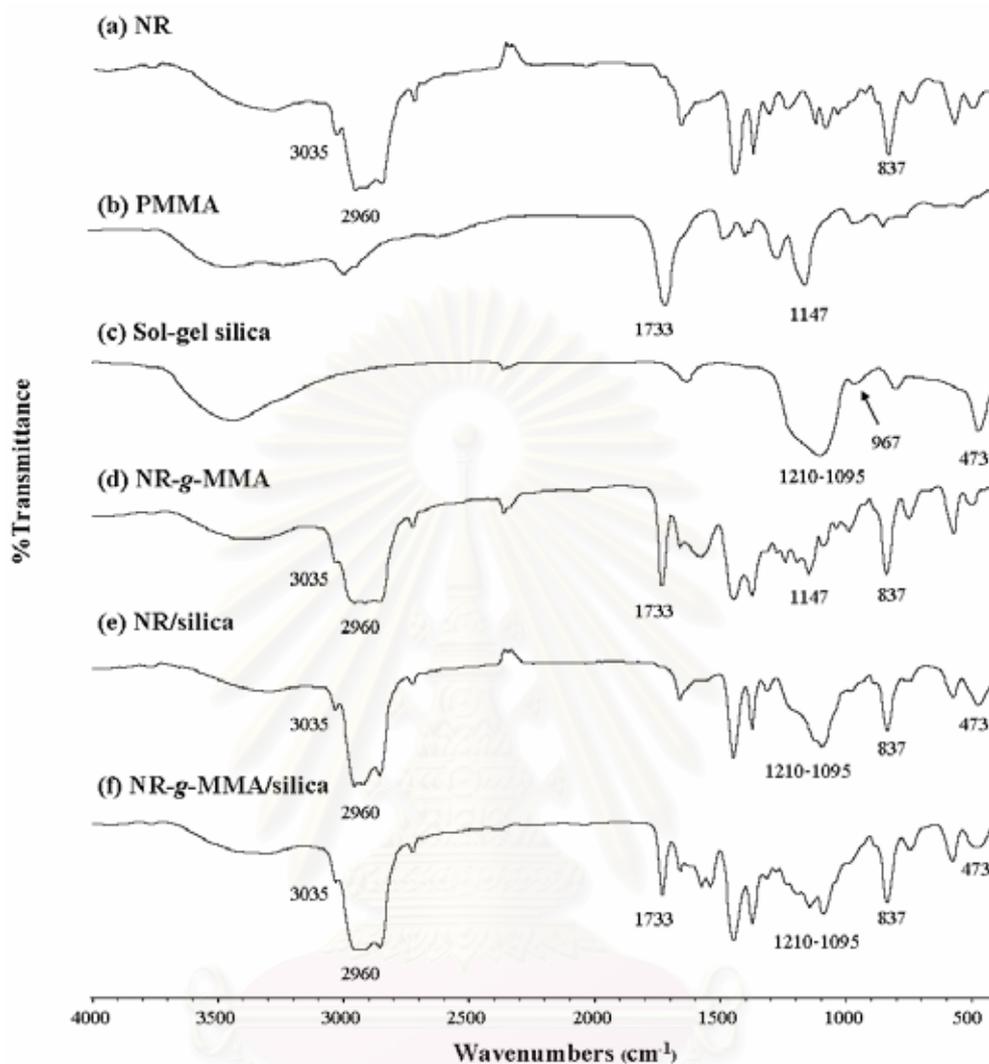


Figure 4.3 FT-IR spectra of (a)NR, (b)PMMA, (c)sol-gel silica, (d)NR/silica, (e)NR/silica, and (f)NR-g-MMA/silica.

4.2.3 The silica content and percentage conversion of TEOS to silica

Appearances of rubber composite films prepared by latex dipping are shown in Figure 4.4. The film thickness was 0.4 to 0.5 mm. Both the MMA grafted and ungrafted NR films were transparent, but the films obtained from the grafted latex appeared more yellowish than the film from ungrafted latex. Among the composite films prepared with and without the addition of TEOS, the film appearances were identical. No loosely bound *in situ* silica was observed. Nevertheless, the grafted films were stiffer and less tacky than all other ungrafted films.

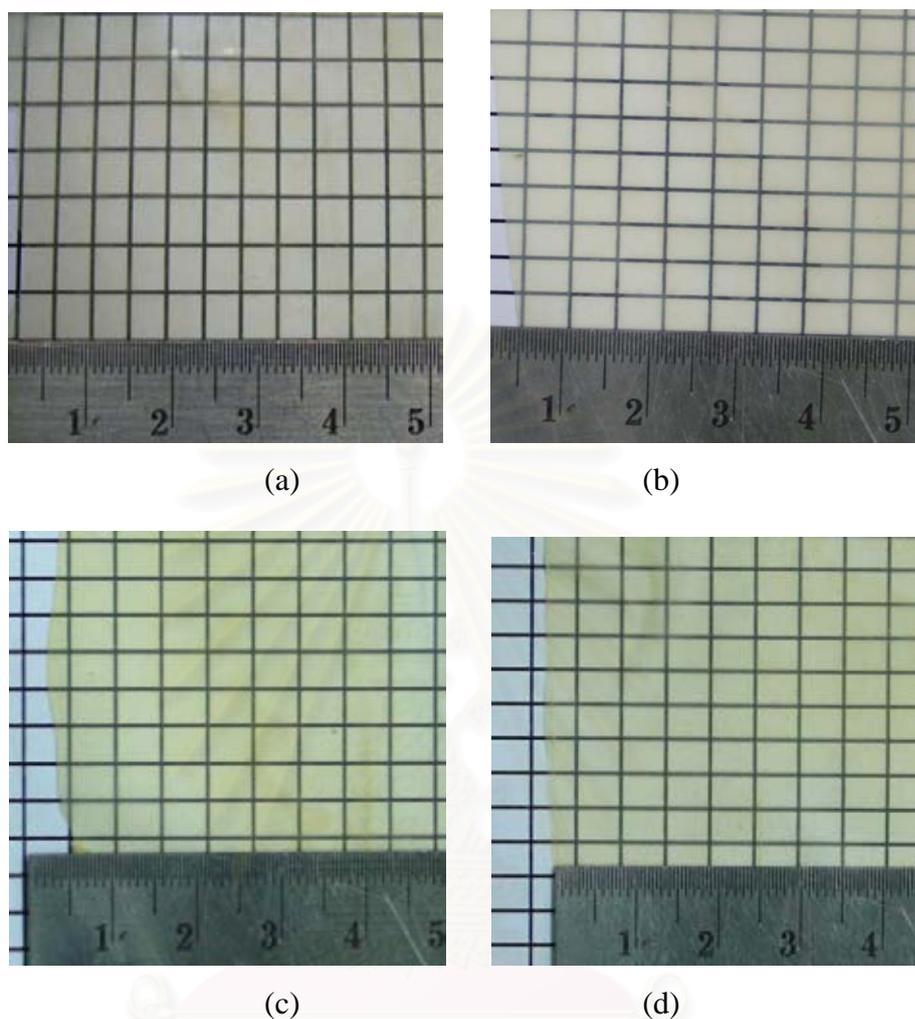


Figure 4.4 Visual appearances of the ungrafted NR films (a) without TEOS, (b) with 15 phr of TEOS added, and grafted NR films (c) without TEOS, and (d) with 15 phr of TEOS added.

The amount of *in situ* formed silica in all samples was determined from the weight of remaining ash after sample pyrolysis. It was found that the *in situ* silica content increased with not only increasing added TEOS amount from 5 to 15 phr, but also increasing weight fraction of MMA (Table 4.2). The conversions of TEOS to silica in the rubber were between 50 to 80%, probably because some portions of silane evaporated during the dipping and drying step. Upon closer data analysis, the conversion of TEOS to silica tended to increase when the weight fraction of MMA was increased from 0 to 15%. This implied that the PMMA shell layer enhanced the

compatibility between seed latex and hydrophobic TEOS. This brought about increases in silica content and %conversion of TEOS to silica. This inference was confirmed by TEM analysis performed on the MMA grafted latex (85:15) mixed with TEOS (Figure 4.5). These micrographs represented the morphology of NR particles grafted with MMA that was mixed homogeneously with 15 phr TEOS, a precursor of silica. It was clear that each NR particle assumed the core-shell structure but with rather rough surface (Figure 4.5a). Analysis of unstained sample in Figure 4.5b revealed a thin dark layer that formed around the core NR particles. The dark layer was most likely the evident of silicon in the form of silica surrounding the rubber core.

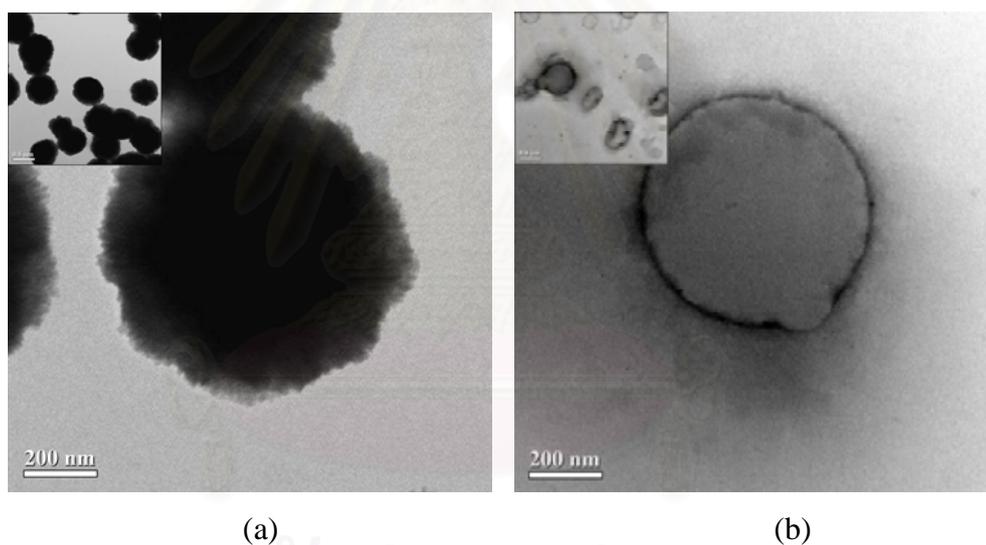


Figure 4.5 TEM micrographs of grafted NR particle(s) (a) 85:15 with TEOS 15 phr, and (b) 85:15 with TEOS 15 phr (un-stained).

The dry rubber content in the NR latex also played an important role in the content of *in situ* formed silica. Decreasing the amount of DRC led to a decrease of silica content significantly. This result is somewhat expected because TEOS is considered hydrophobic and can not be mixed very well with the diluted latex in which contains large amount of water (30 DRC). The separation and subsequently evaporation during mixing resulted in the lowering of the *in situ* silica content [3].

Furthermore, the more rubber latex particles can accommodate more added TEOS in the latex.

Table 4.2 The silica content and percentage of TEOS conversion to silica

Sample Name	Silica content (phr)	Conversion (%)
R30/5/100:0	0.81 ± 0.19	56
R30/10/100:0	1.54 ± 0.19	53
R30/15/100:0	1.86 ± 0.16	43
R30/5/95:5	1.12 ± 0.14	78
R30/10/95:5	2.19 ± 0.17	76
R30/15/95:5	1.97 ± 0.29	45
R30/5/90:10	1.14 ± 0.18	79
R30/10/90:10	2.42 ± 0.29	84
R30/15/90:10	2.49 ± 0.29	57
R30/5/85:15	1.17 ± 0.24	81
R30/10/85:15	2.37 ± 0.24	82
R30/15/85:15	2.65 ± 0.58	61
R30/5/blend*	1.19 ± 0.20	83
R30/10/blend*	2.48 ± 0.24	86
R30/15/ blend*	2.94 ± 0.32	68
R40/5/100:0	0.97 ± 0.19	68
R40/10/100:0	2.25 ± 0.20	78
R40/15/100:0	3.62 ± 0.25	84
R50/5/100:0	1.08 ± 0.26	75
R50/10/100:0	1.96 ± 0.27	68
R50/15/100:0	3.57 ± 0.30	82

Note- Rn/m/o = %DRC/amount of TEOS (phr)/weight fraction of NR:MMA

* = the blend containing 50 %wt of ungrafted latex (100:0) and 50 %wt of grafted latex (85:15)

4.2.4 Morphology of *in situ* silica-NR composite films

The two SEM-EDX micrographs of the cross-sectioned surface of non-silica and *in situ* silica incorporated NR vulcanized films are shown in Figure 4.6 and 4.7, respectively. An EDX technique was used to identify atomic type of a selective area in the rubber matrix. In Figure 4.6a the SEM-EDX spectrum shows no Si peak on the fractured surface. A significant amount of particles seen in the micrograph were thought to be the zinc and sulfur atoms from the vulcanizing chemicals. On the other hand, the silica formed inside the rubber matrix (containing ~3.5 phr) in Figure 4.6b was identified by the EDX as a strong peak of Si atom at 1.75 keV. These results indicate that silica particles were successfully generated in the composite films.

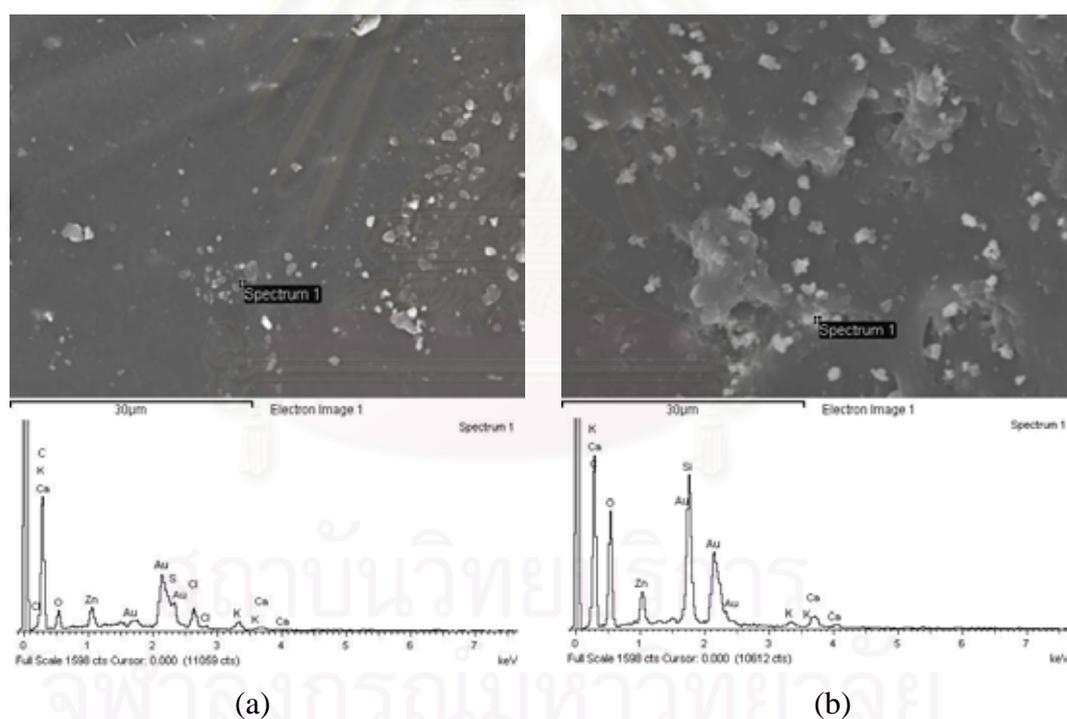
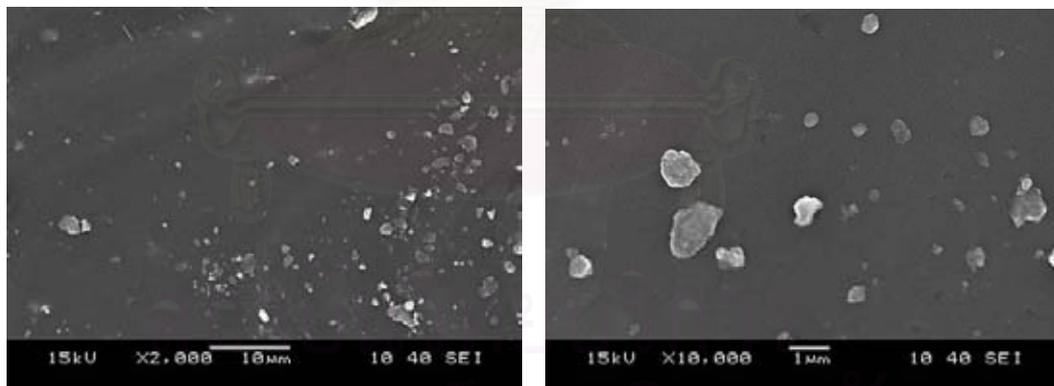


Figure 4.6 EDX spectra of (a)R30/0/100:0 and (b)R40/15/100:0 films.

Analyses of silica particles in the rubber matrix from the fractured surface of grafted and ungrafted films were carried out in terms of size and dispersion. The size distributions of the silica particles were in the range from nanoscale to microscale (Figure 4.7). The newly generated silica particles could have hydrophilic nature which

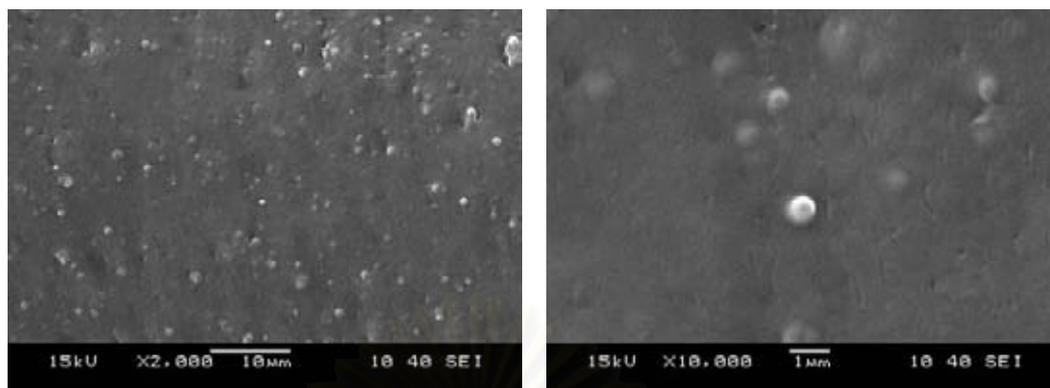
is in contrast with the NR particles having the hydrophobic nature therefore the silica particles tend to aggregate themselves to form a bigger size of agglomerate separated from the NR matrix polymer.

In addition, the primary silica particles were formed and coagulate into small aggregates when the natural rubber latex was grafted with MMA because MMA can accommodate the aggregated silica particles. Similarly, almost all the silica particles were aggregated when the weight of the dry rubber content (DRC) of latex was increased from 30 to 50 DRC. These results related to Yoshikai et al. [3], in which the influence of the amount of water on the silica formation by the sol-gel of TEOS in SBR and NBR latex were studied. These can be ascribed that the additional concentration of latex can induce compatibility and miscibility between rubber and TEOS that the precursor can lead to hydrolysis reaction, thereby the silica particles from condensation reaction can aggregate easily in the concentrated latex. Furthermore, the rubber phase is rougher with increase in MMA fraction used in the graft copolymerization, resulted from the non-homogenous phase distributions of hard phase PMMA.

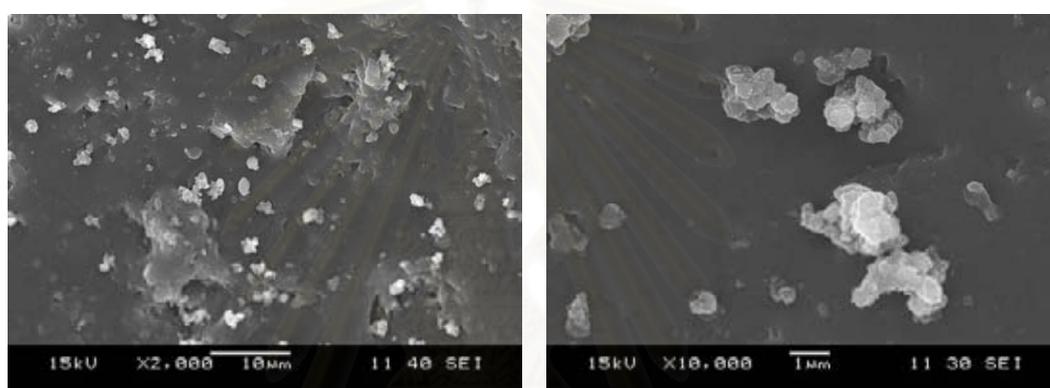


(a) R30/0/100:0 (without silica)

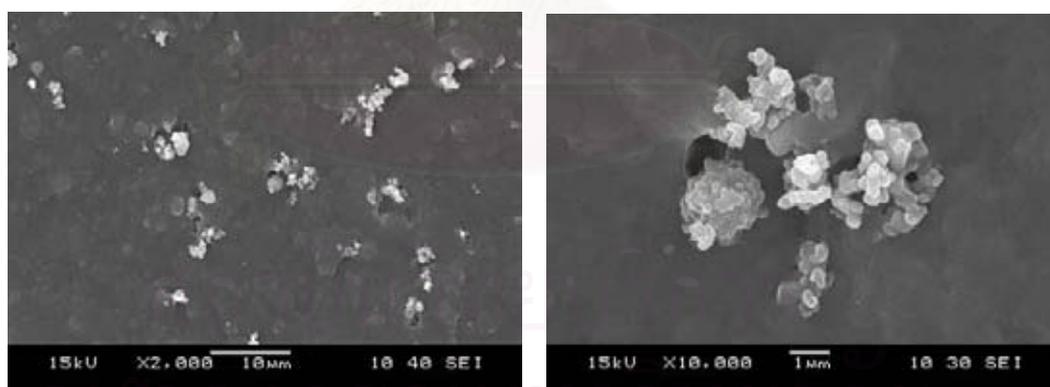
Figure 4.7 Scanning electron micrographs of the dipped NR films with cross sectioned surfaces: (a)R30/0/100:0; (b)R30/15/100:0; (c)R40/15/100:0; (d)R50/15/100:0; (e)R30/15/95:5; (f)R30/15/90:10; (g)R30/15/85:15, and (h)R30/15/blended film. *(continued on the next page)*



(b) R30/15/100:0 (1.86 phr silica)

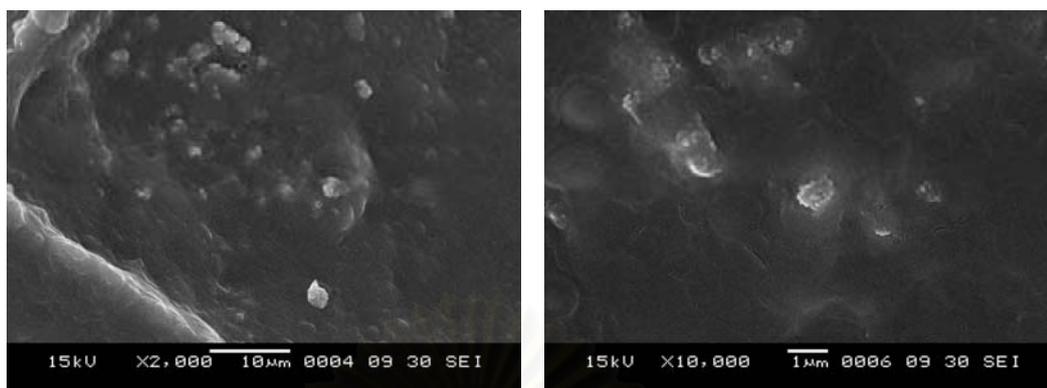


(c) R40/15/100:0 (3.62 phr silica)

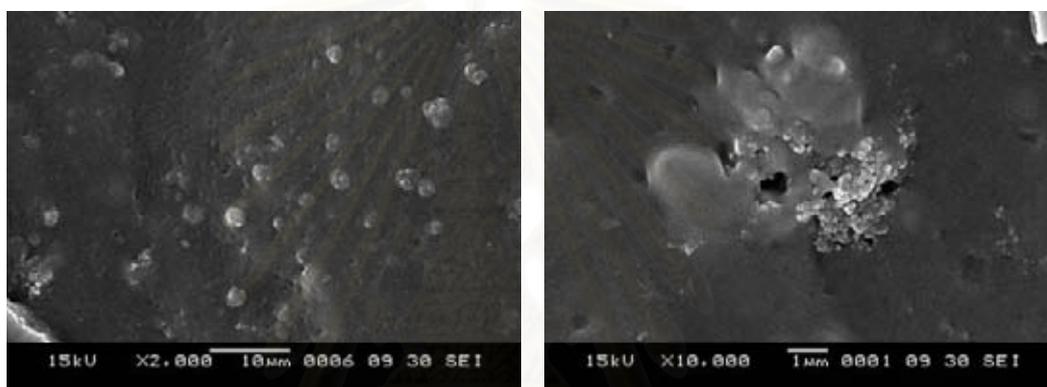


(d) R50/15/100:0 (3.57 phr silica)

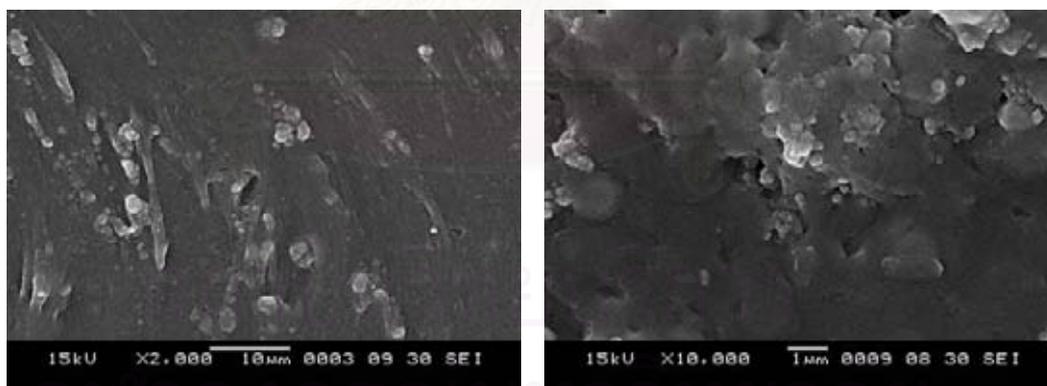
Figure 4.7 Scanning electron micrographs of the dipped NR films with cross sectioned surfaces: (a)R30/0/100:0; (b)R30/15/100:0; (c)R40/15/100:0; (d)R50/15/100:0; (e)R30/15/95:5; (f)R30/15/90:10; (g)R30/15/85:15, and (h)R30/15/blended film. *(continued on the next page)*



(e) R30/15/95:5 (1.97 phr silica)

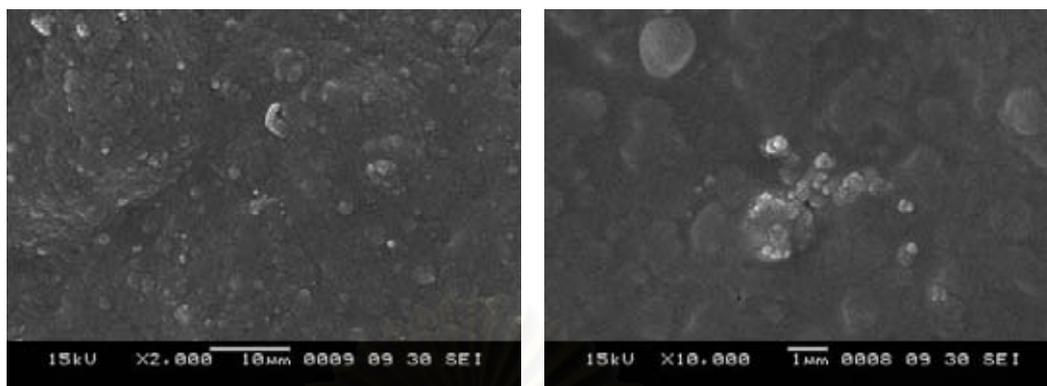


(f) R30/15/90:10 (2.49 phr silica)



(g) R30/15/85:15 (2.65 phr silica)

Figure 4.7 Scanning electron micrographs of the dipped NR films with cross sectioned surfaces: (a)R30/0/100:0; (b)R30/15/100:0; (c)R40/15/100:0; (d)R50/15/100:0; (e)R30/15/95:5; (f)R30/15/90:10; (g)R30/15/85:15, and (h)R30/15/blended film. *(continued on the next page)*



(h) R30/15/blended (2.94 phr silica)

Figure 4.7 Scanning electron micrographs of the dipped NR films with cross sectioned surfaces: (a)R30/0/100:0; (b)R30/15/100:0; (c)R40/15/100:0; (d)R50/15/100:0; (e)R30/15/95:5; (f)R30/15/90:10; (g)R30/15/85:15, and (h)R30/15/blended film.

4.3 Role of MMA on the tackiness of MMA grafted NR composite films

4.3.1 Surface characterization of MMA grafted NR by AFM

The surface roughness of the grafted NR films from different weight contents of grafted MMA was analyzed by AFM (Figure 4.8). It can be clearly seen that increasing MMA content in the grafting process resulted in an increase of roughness as shown in Figures 4.8a to 4.8d. These results agree well with Sruranganurak et al. [47], in which the deposition of PMMA nanoparticles onto polyacrylamide grafted NR was studied. The grafting of high- T_g and more rigid PMMA onto the low- T_g and more flexible NR can lead to void formation on the film surface. As the roughness increased, the true contact area therefore decreased, resulting in the reduction of the friction and tackiness of the rubber surface [34-35].

The influence of *in situ* silica on the surface morphology of the rubber composites was also investigated by AFM as shown in Figure 4.8e to 4.8h. These samples were prepared from the grafted NR latex having MMA contents varied from 0-15% and with a fixed 15 phr TEOS. The micrographs of the silica-filled and non-filled composites having the same MMA contents turned out to be very similar. With

the calculation of the root-mean-square (RMS) roughness of sample surface, detailed comparisons of these samples were possible.



Figure 4.8 Surface analysis by AFM of NR and MMA grafted NR films.

The RMS roughness values of all films analyzed by AFM were plotted against %wt of MMA (Figure 4.9). For the rubber samples without *in situ* silica, the surface roughness steadily increased with increasing the weight ratios of MMA in the grafting step. A similar trend was also reported by Sanguansap et al. [12]. The effect of *in situ* silica on the roughness can be discussed as follows. Without MMA grafting, the presence of silica in the composite did not cause significant changes in the surface roughness. It was however found that as the MMA content increased, the roughness tended to level off to about 56 nm when the MMA content reached the maximum at 15%. The roughness of the silica-filled NR-g-MMA sample was found to increase linearly with increase in MMA content. These results were possibly caused by the amounts of silica generated *in situ* in these four NR-g-MMA films were increasing from 1.86 to 2.65 phr for samples with MMA contents of 0-15.

The study of surface roughness was also extended to rubber films prepared by a one-to-one mixture of the grafted and ungrafted NR latexes, as denoted by R30/0/blend and R30/15/blend in Figure 4.8 and 4.9. The actual MMA contents in these blends were 7.5%. It was found that the RMS roughness values of the blends were lower than the expected values of the grafted latex with MMA contents of 7.5%. The rubber film with 2.94 phr of *in situ* silica (30/15/blend) was found to possess slightly higher roughness than the non-silica film.

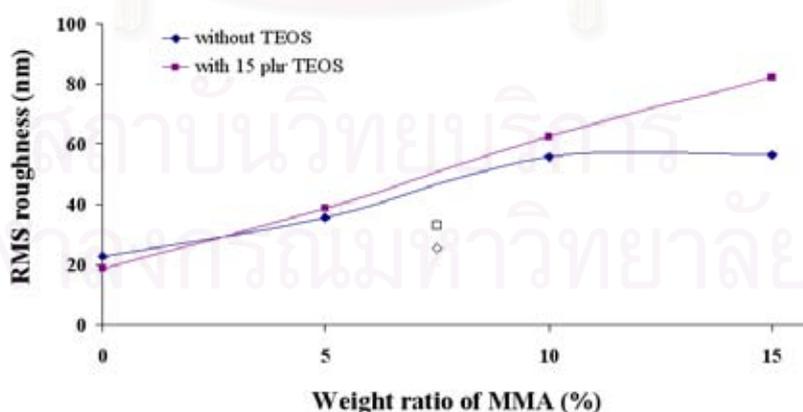


Figure 4.9 Changes of the root-mean-square (RMS) roughness of ungrafted and MMA grafted NR films as a function of MMA content used in the grafting step, that mixed with 15 phr TEOS (■), and without TEOS (◆). Two rubber samples prepared from R30/0/blend (◇) and R30/15/blend (□) are also plotted for comparison.

4.3.2 Tackiness strength

Determination of the tackiness strength of MMA-g-NR films showed that the tackiness dramatically decreased in the grafted sample with only 5% MMA by weight (Figure 4.10). In fact it was found that the tackiness did not change much when the MMA content was increased from 5 to 15% by weight. Therefore it is shown here that the increase in the surface roughness of the rubber film caused by high proportion of MMA grafting can reduce the tackiness of the film [48]. Further analysis on the effect of *in situ* silica in rubber on the film tackiness indicated that the presence of silica (1.86 to 2.65 phr) did not cause significant change to the film tackiness. It was possible because the amount of silica in the rubber was too low to affect the tack property.

For the films obtained from the blend latexes, the tackiness strength was found to be higher than the expected values if samples with 7.5% MMA grafting were analyzed. This result suggests that the non-grafted rubber exists partially on the film surface, causing the tackiness to increase slightly.

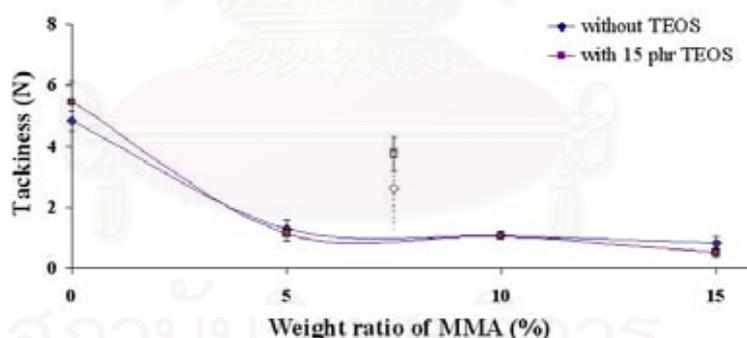


Figure 4.10 Changes of the tackiness strength of ungrafted and MMA grafted NR films as a function of MMA content used in the grafting step- mixed with 15 phr TEOS (■), and without TEOS (◆), R30/0/blend (◇) and R30/15/blend (□).

4.4 Swelling behavior

The vulcanization and swelling behavior of rubber composite can be studied in terms of degree of swelling in organic medium. The degree of swelling and the crosslink density of NR and NR-g-MMA in toluene are shown in Figures 4.11 and 4.12. In the same figures, the effect of *in situ* silica contents on the swelling behavior was also

investigated. When the organic parts were kept constant, it was found that the degree of film swelling in toluene decreased with increasing contents of *in situ* silica. The composites without silica inclusion swelled the most. Reportedly, silica particles can form a barrier to reduce toluene penetration into the crosslinked composites and restrict the rubber chain mobility. For the films having different ratios of NR:MMA, the degree of swelling tended to decrease while increasing the ratio of grafted MMA monomer in the matrix. The presence of MMA in the rubber films possibly led to an increase of polarity of the composite, and thus resulted in the decreased diffusion of less polar toluene into the film.

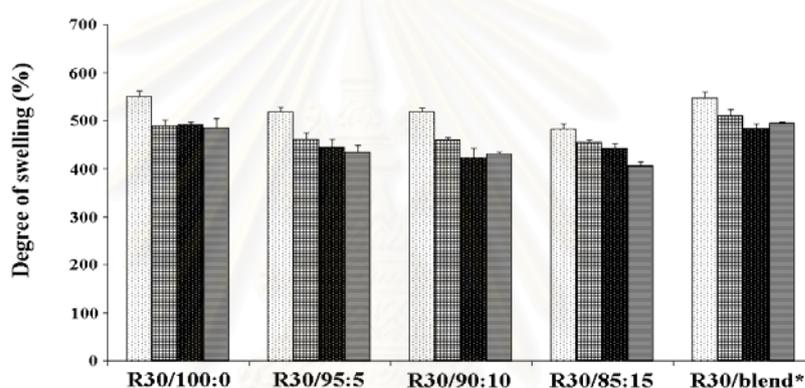


Figure 4.11 The degree of swelling of NR rubber, the modified NR and composite NR in toluene, when □ without TEOS; ▨ 5 phr of TEOS; ▩ 10 phr of TEOS; ■ 15 phr of TEOS; and *blended latex (containing 50 % wt of 100:0 and 85:15).

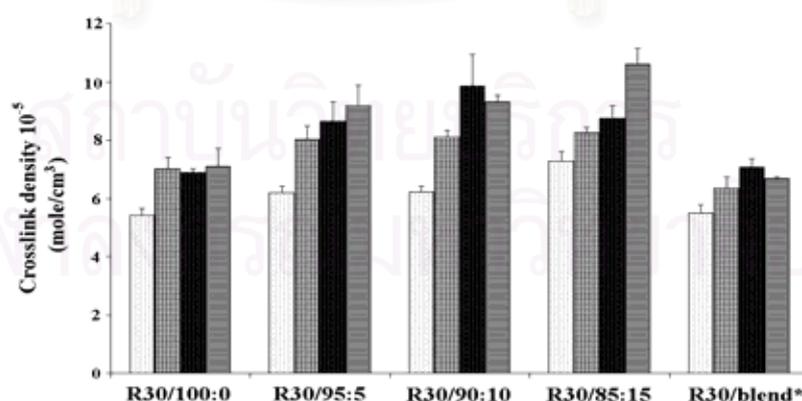


Figure 4.12 The crosslink density of the ungrafted and grafted natural rubber with various amounts of TEOS and different weight ratios of MMA, when □ without TEOS; ▨ 5 phr of TEOS; ▩ 10 phr of TEOS; ■ 15 phr of TEOS; and *blended latex (containing 50 % wt of 100:0 and 85:15).

4.5 Tensile and tear properties

4.5.1 Tensile properties

Mechanical properties of the rubber films were investigated in terms of tensile modulus at 500% elongation, tensile strength, and elongation at break as a function of NR:MMA ratios and *in situ* silica contents. Results are shown in Figure 4.13 and Table 4.3. Each formulation parameter is discussed as follows.

Dry rubber content (DRC)

One of the parameters investigated in this study was the dry rubber content or DRC of the latex used. It can be seen that the DRC in the NR latex from 30 to 50% with and without TEOS added led to an increase in modulus at 500% elongation of the films, but resulted in decreasing tensile strength. The correlation between elongation at break and %DRC could not be justified.

MMA content

As mentioned in the earlier section, increasing the MMA mole ratio in the grafting process resulted in the increase of grafted rubber. It was found that the modulus of the vulcanizates increased significantly when the MMA mole ratios were increased. The presence of MMA, however, caused the tensile strength and elongation at break to decrease. This can be explained by the fact that PMMA is a glassy thermoplastic with hard and brittle characteristics. An increase in the weight ratio of MMA for grafting would drastically reduce the elongation at break of the grafted rubber film [23, 49]. In general, the mechanical properties of most of the grafted NR latex do not meet the standards set in ASTM-D3577 and ASTM-D3578 specifications for rubber surgical gloves and examination gloves, but meet satisfactorily with the ASTM-D4679 specification for general purpose, household or beautician rubber gloves.

In order to cope with this problem, another set of vulcanized dipped films was prepared from a one-to-one blend of the grafted NR latex having 85:15 of NR:MMA and the ungrafted NR latex. In the sample, one half of the rubber was not grafted but the other half was grafted with PMMA. The mechanical test results of this latex

blends were also presented in comparison with other samples for the tensile modulus, tensile strength and elongation at break in Figures 4.13a to 4.13c respectively. It can be seen that the modulus at 500% elongation was approximately between the values of 5% to 10% MMA content, as expected for the sample with “7.5%” MMA. Interestingly, the tensile strength and the elongation at break were close to those of the ungrafted sample and distinctly higher than the values of the other grafted rubber films. The explanation of this observation can be related to the presence of ungrafted rubber in the blend that still possesses elastic properties. Therefore the films prepared from blend latexes can be elongated to higher degrees than all those grafted rubber films.

TEOS content

Upon increasing the TEOS contents added to the latex, the tensile modulus of the final films also increased. The *in situ* formed silica that was dispersed homogeneously in the rubber matrix contributed effectively to the composite reinforcement [50]. On the other hand, the presence of *in situ* silica caused the tensile strength to decrease for the films without MMA grafting. In the case of MMA grafted films, the tensile strength of the silica-incorporated samples were higher than those of the non-reinforced ones. However the values did not significantly change when increasing the silica content. The elongation at break was found to decrease with increasing the *in situ* silica content. It also seems that the combination of both MMA graft and *in situ* silica actually lowers the elongation property of the rubber films. This could be related the fact that aggregation of PMMA and possible *in situ* silica in the NR matrix resulted in lowering interaction between the rubber and non-rubber phases [51].

Table 4.3 Silica content and mechanical properties of rubber composite films

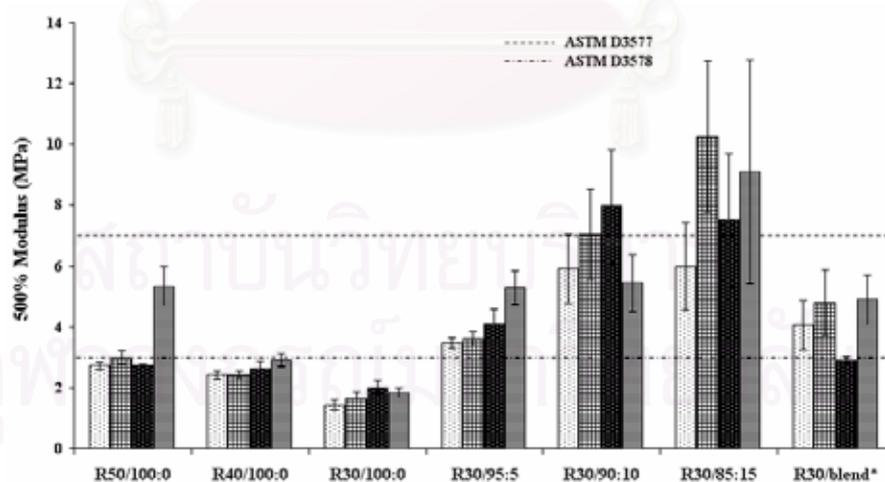
Entry	Silica content (phr)	Modulus at 500% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)
R50/0/100:0	0.00 ± 0.00	2.71 ± 0.11	18.94 ± 0.97	910 ± 29
R50/5/100:0	1.08 ± 0.30	2.99 ± 0.24	19.05 ± 1.21	876 ± 28
R50/10/100:0	1.96 ± 0.27	2.73 ± 0.04	18.83 ± 1.28	763 ± 23
R50/15/100:0	3.57 ± 0.30	5.33 ± 0.64	17.01 ± 1.74	696 ± 64
R40/0/100:0	0.00 ± 0.00	2.40 ± 0.14	18.63 ± 1.53	964 ± 19
R40/5/100:0	0.97 ± 0.19	2.43 ± 0.12	19.07 ± 0.90	944 ± 38
R40/10/100:0	2.25 ± 0.20	2.64 ± 0.22	18.88 ± 1.89	827 ± 42
R40/15/100:0	3.62 ± 0.25	2.89 ± 0.21	18.05 ± 1.41	813 ± 24
R30/0/100:0	0.00 ± 0.00	1.44 ± 0.17	22.23 ± 1.78	933 ± 27
R30/5/100:0	0.81 ± 0.19	1.63 ± 0.23	23.27 ± 1.09	885 ± 57
R30/10/100:0	1.54 ± 0.19	1.98 ± 0.26	21.90 ± 1.54	882 ± 45
R30/15/100:0	1.86 ± 0.16	1.83 ± 0.15	19.50 ± 0.91	865 ± 37
R30/0/95:5	0.00 ± 0.00	3.47 ± 0.18	11.13 ± 0.23	738 ± 30
R30/5/95:5	1.12 ± 0.14	3.61 ± 0.25	14.43 ± 1.13	731 ± 6
R30/10/95:5	2.19 ± 0.17	4.09 ± 0.50	12.47 ± 1.21	701 ± 22
R30/15/95:5	1.97 ± 0.29	5.29 ± 0.56	12.85 ± 0.77	659 ± 34
R30/0/90:10	0.00 ± 0.00	5.90 ± 1.15	11.05 ± 1.02	643 ± 36
R30/5/90:10	1.14 ± 0.18	7.05 ± 1.49	13.15 ± 0.75	602 ± 31
R30/10/90:10	2.42 ± 0.29	7.97 ± 1.88	12.89 ± 0.24	571 ± 33
R30/15/90:10	2.49 ± 0.29	5.44 ± 0.92	12.31 ± 0.43	535 ± 28

Table 4.3 (continued) Silica content and mechanical properties of rubber composite films

Entry	Silica content (phr)	Modulus at 500% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)
R30/0/85:15	0.00 ± 0.00	5.99 ± 1.44	11.36 ± 0.25	592 ± 29
R30/5/85:15	1.17 ± 0.24	10.26 ± 2.49	16.01 ± 0.64	569 ± 32
R30/10/85:15	2.37 ± 0.24	7.51 ± 2.18	16.83 ± 0.74	617 ± 39
R30/15/85:15	2.65 ± 0.58	9.12 ± 3.67	14.89 ± 1.22	571 ± 40
R30/0/blend*	0.00 ± 0.00	4.07 ± 0.81	18.70 ± 0.49	746 ± 30
R30/5/blend*	1.19 ± 0.20	4.78 ± 1.09	22.22 ± 0.96	723 ± 35
R30/10/blend*	2.48 ± 0.24	2.92 ± 0.11	21.39 ± 0.86	841 ± 8
R30/15/blend*	2.94 ± 0.32	4.88 ± 0.82	20.85 ± 0.52	765 ± 40

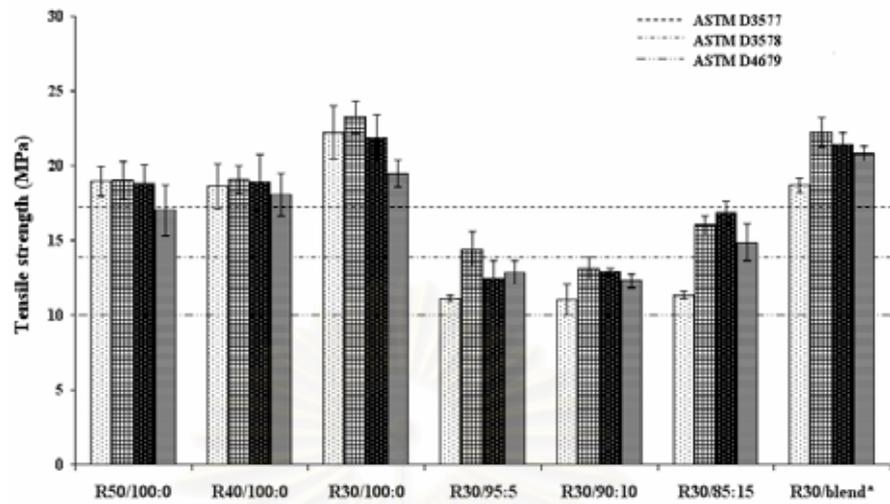
Note- Rn/m/o = %DRC/amount of TEOS (phr)/weight fraction of NR:MMA

* = the blend containing 50 %wt of ungrafted latex (100:0) and 50 %wt of grafted latex (85:15)

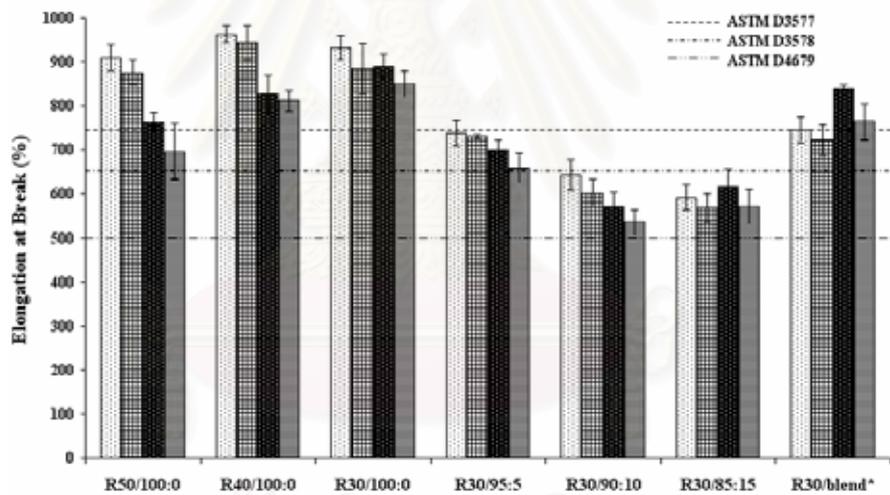


(a)500% modulus

Figure 4.13 Mechanical properties of rubber composite films: (a)500% modulus, (b)tensile strength, (c)elongation at break, when □ without TEOS; ▨ 5 phr of TEOS; ▩ 10 phr of TEOS; ■ 15 phr of TEOS; and *blended latex (containing 50 %wt of 100:0 and 85:15), (continued on the next page).



(b)Tensile strength



(c)Elongation at break

Figure 4.13 Mechanical properties of rubber composite films: (a)500% modulus, (b)tensile strength, (c)elongation at break, when □ without TEOS; ▨ 5 phr of TEOS; ▩ 10 phr of TEOS; ■ 15 phr of TEOS; and *blended latex (containing 50 %wt of 100:0 and 85:15).

4.5.2 Tear properties

The tear strengths of the ungrafted rubber composites containing *in situ* silica were relatively higher than that of the film without reinforcement (Table 4.4). The presence of PMMA grafts had, however, a pronounced effect on reducing the tear strength, i.e., all the MMA-g-NR films gave relatively lower tear strength than the ungrafted sample. Incorporation of *in situ* formed silica in the amount of 1.97 to 2.65 phr still could not improve the tear strengths. The grafted PMMA induced higher brittleness and weakness to the films which decreased resistance to tear and thus the lower tear strength [21].

Table 4.4 Tear strength of natural rubber films

Entry	Tear strength (N/mm)
R30/0/100:0	29.82 ± 2.76
R30/5/100:0	33.55 ± 5.82
R30/10/100:0	31.13 ± 4.43
R30/15/100:0	32.22 ± 5.50
R30/15/95:5	25.24 ± 1.16
R30/15/90:10	24.35 ± 1.22
R30/15/85:15	21.57 ± 1.44
R30/15/blend*	31.25 ± 1.38

Note- Rn/m/o = %DRC/amount of TEOS (phr)/weight fraction of NR:MMA

* = the blend containing 50 %wt of ungrafted latex (100:0) and 50 %wt of grafted latex (85:15)

The use of small-sized particles as reinforcement elements in polymer is a common method to improve the mechanical and/or electrical properties of composites. The improvement of the fracture mechanics properties by the addition of

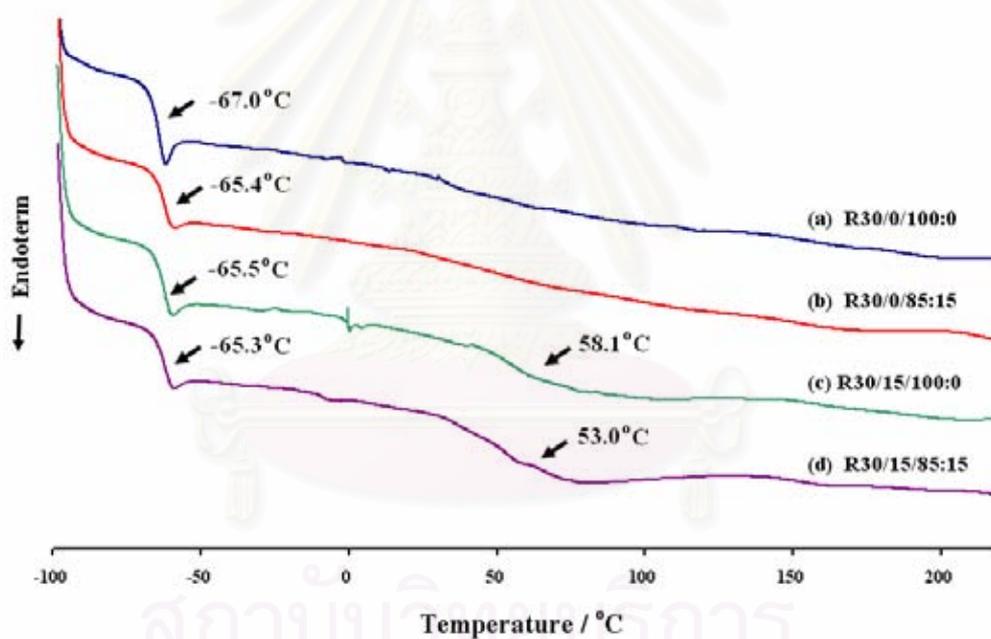
particles can be achieved when a sufficiently good interaction between the particles and the matrix polymer takes place and when the particles are well dispersed within the matrix. To reduce the size of agglomeration of silica particles, a good bonding between the silica particles and the matrix is to introduce a load transfer between them.

4.6 Thermal properties

Differential scanning calorimeter (DSC) is the most widely used instrument for studying the glass transition temperature (T_g) of bulk polymer systems. Table 4.5 and Figure 4.14 show the differential heat capacities as a function of temperature from which the changes were observed in the range of -67 to -65°C . The neat NR has a glass transition temperature of about -67°C whereas the PMMA grafted NR and silica incorporated NR composites have an almost constant glass transition temperature of about -65°C . The two PMMA grafted NRs have a single temperature peak which indicated that the grafted NR is miscible or homogeneous. This can be confirmed by the close solubility parameters of NR and PMMA at 16.6 and $19.4 \text{ MPa}^{1/2}$ respectively [52-53]. The increase in T_g in the grafted NR was probably caused by the rigid PMMA shell on the NR backbone. Although the amounts of PMMA grafted shell and the incorporated silica particles in NR were not high, their presence still had an appreciable shift in T_g to a higher end. In addition, the T_g of PMMA, usually appearing at 93 - 110°C , cannot be observed in Figure 4.14. The second transition temperatures at about 58.1 and 53.0°C in curves (c) and (d), respectively, was observed when the silica was formed inside the rubber matrix. This could be ascribed to the dipole-dipole interaction between the silica particles and the polar group in NR molecules. The observed transition might be due to the relaxation of tightly bound silica by the NR matrix [54-55]. Generally, the T_g of a polymer is affected by the chemical structures of the main chain, and molecular size of the substituent which control the chain mobility.

Table 4.5 Glass transition temperature of the NR-*g*-MMA/Silica films

Sample	NR:MMA (%wt)	TEOS (phr)	Silica content (phr)	T _{g1} (°C)	T _{g2} (°C)
T0/100:0	100:0	0	0.00	-67.0	-
T0/85:15	85:15	0	0.00	-65.4	-
T15/100:0	100:0	15	1.86	-65.5	58.1
T15/85:15	85:15	15	2.91	-65.3	53.0

**Figure 4.14** DSC curves of the MMA grafted NR and the silica incorporated NR grafted with MMA.

In order to observe air-oxidative degradation at high temperatures of the films, the three NR composites were subjected to thermo-gravimetric analysis (Figure 4.15 and Table 4.6). The air oxidative degradation of the vulcanized film took place in two steps. The first prominent and major peak obtained from rubber decomposition is in the temperature range of 300 to 450°C and accounting for about 90% of mass. This

first step of thermal oxidative degradation is attributed to the organic part of the vulcanized NR and its grafted portion. The second step of degradation was between 450 to 600°C and accounting for 5% mass. This part is related to the degradation of sulfur vulcanizates. Some of polysulfide groups in sulfur crosslink were transformed to disulfide. This disulfide can be oxidized to sulfenic or thiosulfoxylic acids [56]. In addition there was an increase in char residue at 700 °C from about 3.00 for non-silica rubber films to 4.98% for the silica-incorporated sample. The difference in mass residue is in fact due to the presence of *in situ* silica that was produced from 10 phr TEOS added during latex mixing step. However, the inclusion of silica in the NR graft does not enhance the thermal oxidative degradation of the NR composite, probably because of the low silica content.

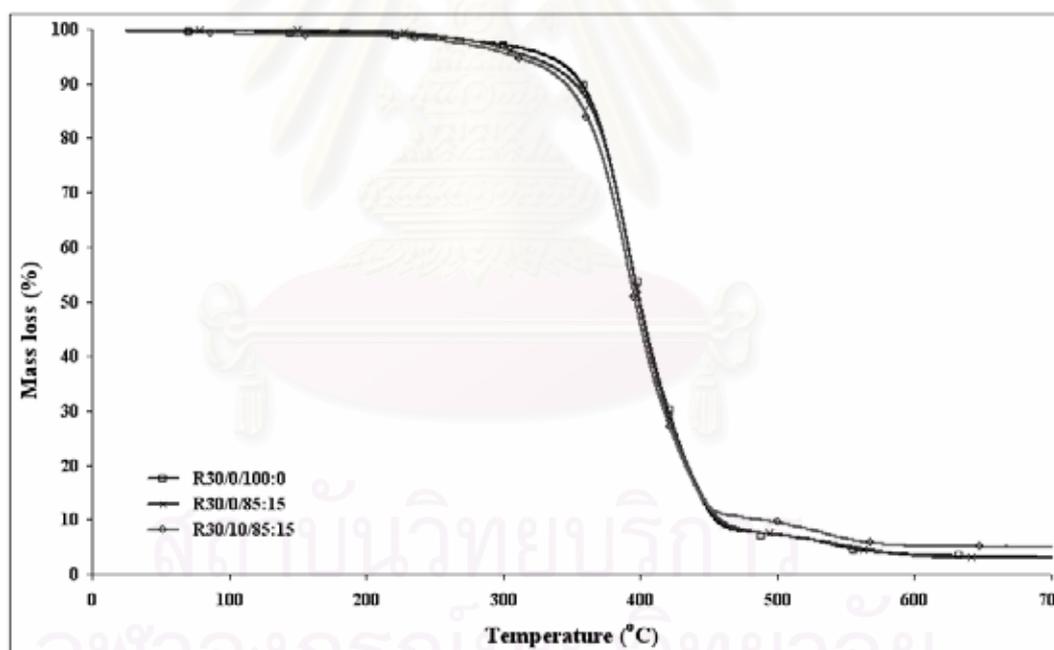


Figure 4.15 Thermo-gravimetric analysis of various MMA grafted NR vulcanized films.

Table 4.6 Results from thermo-gravimetric analysis of various PMMA grafted NR vulcanized films

Sample	First mass loss			Second mass loss			Residual Mass (%) at 700°C
	Temperature (°C)		Mass loss (%)	Temperature (°C)		Mass loss (%)	
	Onset	Peak		Onset	Peak		
R30/0/100:0	359.0	390.5	91.86	469.5	537.5	5.07	3.07
R30/0/85:15	358.6	391.0	92.46	489.5	537.2	4.52	3.02
R30/10/85:15	355.5	390.7	89.21	465.3	532.9	5.81	4.98

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CHAPTER V

CONCLUSIONS AND SUGGESTION

5.1 Conclusions

This work reports the method for preparing dipped rubber films from PMMA grafted NR latex that is reinforced by *in situ* generated silica. The preparation was divided into two steps. Firstly the NR latex was grafted with up to 15%wt MMA by using bipolar redox initiator. Secondly TEOS, a precursor of silica and vulcanizing chemicals were mixed with the grafted latex. The latex compound was formed into thin films by dipping process and followed by curing step.

The dipped film of grafted NR latex was yellowish transparent and stiffer than ungrafted NR film. No loosely bound silica particle was observed on the film surface. The structure of grafted NR was confirmed by FT-IR analysis. The IR spectrum showed new signals at 1733 and 1147 cm^{-1} corresponding to the ester group ($-\text{C}=\text{O}$, $-\text{C}-\text{O}-$) stretching vibration of MMA units. The core-shell structure with the PMMA shell surrounding the rubber core was observed by TEM. By mixing TEOS with grafted NR latex, TEOS was discovered embedded in the MMA shell surrounding the rubber particles. The SEM images confirmed that the *in situ* formed silica were dispersed inside the rubber matrix while the silica was identified by EDX technique as a strong peak of silicon atom at 1.75 keV. The conversions of TEOS to silica in the rubber were between 50 to 80%. The silica content increased with increasing both the weight fraction of MMA and the TEOS loading.

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

mobility. In addition the degree of swelling tended to decrease while increasing the ratio of grafted MMA monomer in the matrix.

The results of mechanical properties indicated that the *in situ* silica particles, which were generated by the sol-gel process of TEOS, exhibited the reinforcement effect on grafted NR films. But no significant changes in the tensile strength and modulus of the ungrafted films were observed for any amount of silica content. The drop of mechanical properties is probably due to the agglomerated particles in the composites. The grafted NR exhibited higher modulus at 500% elongation, but lower tensile strength, elongation and tear strength than the ungrafted vulcanizate. By the blending method, the modulus at 500% elongation was approximately between the values of 5 to 10% MMA content. The tensile strength and the elongation at break were suddenly higher than the other grafted sample results.

Thermal properties of the composite films were examined using DSC and TGA. Glass transition temperatures of all samples were found at -67°C for ungrafted rubber vulcanizates and increased to about -65°C for the MMA grafted and silica incorporated samples. The presence of grafted PMMA and *in situ* silica particles could observe a slight shift of T_g to a higher end. The evidence for interaction between the *in situ* silica particles and the rubber molecules was found as second T_g 's at $53\text{-}58^{\circ}\text{C}$. The air oxidative degradation of the NR samples was measured by TGA. The decomposition behavior of the pure NR, grafted NR and grafted NR/Silica composite are similar but the result shows an increase in the yield of char residue at 700°C about 2% when the *in situ* silica was generated from 10 phr TEOS added into the latex.

5.2 Suggestions for future work

The purpose of this section is to provide a more overview of studies that need to be undertaken, and directions that could be explored further in the following aspects:

- Investigate in more detail on the effect of graft copolymerization parameters like, *e.g.*, the monomer addition sequence, the polarity of monomers (such as

low-polarity polymer species, namely styrene and n-butyl methacrylate or high-polarity polymer species, namely ethyl methacrylate and acrylonitrile) and initiating systems (such as thermal, redox and photochemical initiating system) on the *in situ* silica formation, and any changes in the mechanical properties.

- Investigate the use of other alkyltriethoxysilanes (such as vinyltriethoxysilane and ethyltriethoxysilane) to prepare the grafted composite films with the aim to achieve optimal mechanical properties.
- Investigate of the blend ratios of NR and grafted NR latex by using *in situ* silica to prepare dipped composite films with the aim to either increase the reinforce ability and decrease the tack property.
- Explore the feasibility and potential advantages of grafted NR/silica composite films in the manufacturing industry.

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