สมบัติเชิงกลและเชิงความร้อนของยางธรรมชาติเสริมแรงโดยซิลิกาดัดแปรโดยออร์แกโนแอลคอกซีไซเลน

นางสาวอภิญญา ตันเลิศ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

MECHANICAL AND THERMAL PROPERTIES OF NATURAL RUBBER REINFORCED BY ORGANOALKOXYSILANE-MODIFIED SILICA

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2014

Thesis Title	MECHANICAL AND THERMAL PROPERTIES OF NATURAL RUBBER REINFORCED BY ORGANOALKOXYSILANE-MODIFIED SILICA
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อภิญญา ตันเลิศ : สมบัติเชิงกลและเชิงความร้อนของยางธรรมชาติเสริมแรงโดยซิลิกาดัดแปรโดยออร์แกโนแอลคอกซีไซเลน (MECHANICAL AND THERMAL PROPERTIES OF NATURAL RUBBER REINFORCED BY ORGANOALKOXYSILANE-MODIFIED SILICA) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ศิริลักษณ์ พุ่มประดับ, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ. ดร.ภัทรพรรณ ประศาสน์สารกิจ, 116 หน้า.

งานวิจัยนี้ศึกษาการดัดแปรพื้นผิวของอนุภาคซิลิกาที่เตรียมผ่านกระบวนการโซล-เจลด้วยสารประกอบออร์แกโนแอลคอกซีไซเลน ซึ่งทำหน้าที่เป็นตัวดัดแปรพื้นผิว ได้แก่ เมอร์แคปโทรโพรพิลไตรเมทอกซีไซเลน ฟีนิลไตรเมทอกซีไซเลน ฟีนิลไตรเอทอกซีไซเลน และไตรเมทอกซีไซริลโพรพิลอะนิลีน ภาวะที่เหมาะสมของการดัดแปรพื้นผิวของอนุภาคซิลิกา คือการใช้อัตราส่วนโดยโมลของตัวดัดแปรพื้นผิวต่อเตตระเอทอกซีไซเลนเป็น 0.4 ทำปฏิกิริยาที่อุณหภูมิห้องเป็นเวลา 24 ชั่วโมง พิสูจน์เอกลักษณ์ของอนุภาคซิลิกาดัดแปรพื้นผิวโดยเทคนิคอินฟราเรดสเปกโทรสโกปี ทดสอบสมบัติความไม่ชอบน้ำโดยการวัดมุมสัมผัสของน้ำ และทดสอบความสามารถในการเป็นสารป้องกันการเสื่อมสภาพโดยใช้สารละลายดีพีพีเอช ศึกษาผลของอนุภาคซิลิกาดัดแปรที่มีต่อสมบัติเชิงกลเชิงความร้อนและความทนทานต่อการเสื่อมสภาพด้วยโอโซนของยางธรรมชาติวัลคาไนตเซตทั้งในน้ำยางข้นและยางแห้ง พบว่าความเข้ากันได้ระหว่างอนุภาคซิลิกาดัดแปรกับยางธรรมชาติดีขึ้น ส่งผลต่อการปรับปรุงสมบัติเชิงกลของยางธรรมชาติวัลคาไนตเซตได้ นอกจากนี้อุณหภูมิการสลายตัวเริ่มต้นของยางธรรมชาติวัลคาไนเซตที่เติมด้วยอนุภาคซิลิกาดัดแปรสูงขึ้น และอนุภาคซิลิกาดัดแปรสามารถหน่วงการเสื่อมสภาพด้วยโอโซนของยางธรรมชาติวัลคาไนตเซตได้เมื่อเปรียบเทียบกับยางธรรมชาติวัลคาไนเซตที่เติมด้วยอนุภาคซิลิกาที่ไม่ผ่านดัดแปร ดังนั้นอนุภาคซิลิกาดัดแปรมีบทบาททั้งทางด้านสารเสริมแรงและสารป้องกันการเสื่อมสภาพสำหรับผลิตภัณฑ์ยางธรรมชาติ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5472150023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: NATURAL RUBBER (NR) / SOL-GEL PROCESS / SURFACE MODIFICATION

APINYA TUNLERT: MECHANICAL AND THERMAL PROPERTIES OF NATURAL RUBBER REINFORCED BY ORGANOALKOXYSILANE-MODIFIED SILICA. ADVISOR: ASSOC. PROF. SIRILUX POOMPRADUB, Ph.D., CO-ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, Ph.D., 116 pp.

This research studied the surface modification of silica particles that prepared via a sol-gel process by organoalkoxysilane as modify agents such as MpTMS, PhTMS, PhTES and ATMS. The optimum condition to modify the surface of silica particles was the use of mole ratio of modify agents to TEOS of 0.4 at ambient temperature for 24 h. The characterizations of modified silica particles by fourier transform infrared spectroscopy (FTIR), hydrophobic properties by water contact angle measurement and determination of antioxidant activity by using 2, 2-diphenyl-1-picrylhydrazyl (DPPH) solution were carried out. The effects of modified silica particles on the mechanical, thermal properties and ozone resistance of natural rubber (NR) vulcanizates both the concentrated latex and solid rubber were also investigated. The good compatibility between modified silica particles and NR matrix was observed, resulting in the improvement of mechanical properties. In addition, the initial temperature of decomposition of NR vulcanizates filled with modified silica particles was highly and the modified silica particles could retard the ozone-induced degradation compared with NR vulcanizares filled with unmodified silica particles. Therefore, the modified silica particles played the role as either reinforcing filler or antidegradant for NR product.

Field of Study: Petrochemistry and Polymer Science
Academic Year: 2014

Student's Signature ....
Advisor's Signature ....
Co-Advisor's Signature ....

ACKNOWLEDGEMENTS

The author would like to express their sincere gratitude to advisor, Assoc. Prof. Dr. Sirilux Poompradub for her encouraging guidance, supervision, invaluable help and helpful suggestion throughout this research. Thanks are also extended to co-advisor, Prof. Dr. Pattarapan Prasassarakich, Prof. Dr. Tharapong Vitidsant, Assoc. Prof. Dr. Voravee Hoven, and Assoc. Prof. Dr. Chakrit Sirisinha from Mahidol University for serving as the chairman, committee and external committee, respectively and for their worthy comments and suggestions.

The authors gratefully acknowledge the funding support from Toyo Tire & Rubber Co., Ltd., Japan. Many thanks are going to the Program in Petrochemistry and Polymer Science and all technicians of the Department of Chemical Technology, Faculty of Science, Chulalongkorn University.

Finally, the author would like to express their gratitude to family members for their love, willpower, understanding and great support throughout their study. Also, special thanks are expanded to my relation and my friends for friendships, their help, cheerful moral support and encouragement.

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LIST OF ABBREVIATIONS

AM-Si : Modified silica particles by ATMS

ASTM : American Society for Testing and Materials

ATMS : N-3-(trimethoxysilyl) propyl aniline

BRC : Bound rubber content

°C : Degree celsius

C-Si : Commercial silica particles

DMA : Dynamic mechanical analysis

DPPH : 2, 2-diphenyl-1-picrylhydrazyl

DRC : Dry rubber content

DSC : Differential Scanning Calorimetry

FTIR : Fourier Transform Infrared Spectroscopy

JIS : Japanese Industrial Standards

MBTS : Mercaptobenzothiazole disulfide

mm : Millimeter

MM-Si : Modified silica particles by MpTMS

MpTMS : 3-Mercaptopropyltrimethoxysilane

nm : Nanometer

NR : Natural rubber

PEG : Polyethylene glycol

PhE-Si : Modified silica particles by PhTES

PhM-Si : Modified silica particles by PhTMS

phr : Part per hundred part of rubber

PhTES : Phenyltriethoxysilane

PhTMS : Phenyltrimethoxysilane

SEM : Scanning Electron Microscopy

TEM : Transmission Electron Microscopy

TEOS : Tetraethoxysilane

TGA : Thermal Gravimetric Analysis

U-Si : Unmodified silica particles

ZnO : Acitve zinc oxide

CHAPTER 1

INTRODUCTION

1.1 Introduction

Natural rubber (NR) is widely used in many fields such as automotive, medical, sport and aircraft industries because it has excellent the mechanical and dynamic properties for example high flexibility, tensile strength and tear resistance [Nakason C. et al. (2005)]. However, the use of NR products is necessary to reinforce with fillers since the additional reinforcement can be improved the other mechanical properties, in particularly, hardness, modulus, tensile strength and abrasion resistance [Rattanasom N. et al., (2009)]. In efforts to adjust those properties, a wide varieties of particulate fillers such as carbon black and silica particles are necessarily added into NR for various purpose in order to gain the appropriate properties, and the most important are reinforcement that reduction in material costs and enhancement of strength and abrasion resistance are obtained [Rattanasom N. et al., (2012)]. Therefore, NR is usually mixed with a reinforcing filler to increase the mechanical properties and stability of its.

However, NR is highly susceptible to resistance for ageing with heat, ozone and radiation because the chemical structure has the carbon-carbon double bond in main chains [Vinod V. S. et al., (2002)], which it is considered as a disadvantage of the usage. Therefore, there has been an attempt to improve this disadvantage with the developed formulation for rubber compounding by adding some additives, e.g. an antidegradants or antioxidants in order to increase lifetime of rubber [Ambelang J. C. et al., (1963)]. The antioxidant can be classified as two category by chemical structure of functional groups. The first category is phenol derivatives e.g. butylated hydroxytoluene. The substances in this group are no effect on discoloration of rubber products. Subsequently, the latter category is amine derivatives e.g. N-Isopropyl-N’-phenyl-p-phenylenediamine. This group is more effective to prevent the highly oxygen and thermal than phenol derivatives, but it is severe discoloration of products [Poompradub S. et al., (2011)].

The reinforcing filler to get the attention is generally silica particles. Silica has excellent tear strength, high abrasion resistance and low rolling resistance compared to other fillers and is non-black reinforcing filler widely used for producing colored rubber products. This is simply due to its white color and the most importantly due to its small primary particle size giving rise to noticeably high reinforcing efficiency compared to other white fillers. However, silica is less compatible with non-polar elastomers such as NR, BR and SBR due to the different polarity. High polarity of silica particles is due to the silanol groups on silica surface, which can lead to the strong silica-silica interaction by hydrogen bonding [Chonkaew W. et al., (2011)]. Therefore, several attempts have been made to develop methods to enhance the dispersion of silica in rubber matrix. These include the addition of dispersing agents as silane coupling such as bis(3-triethoxysilylpropyl) tetrasulfane (Si-69) [Sae-oui P. et al., (2004)], and the generated silica nanoparticles prepared by a sol–gel method with silane precursor of tetraethoxysilane (TEOS) [Chaichua B. et al., (2009)]. Additionally, one of the improvement of silica particle is the modification of silica surface that has been functionalized with silane compounds containing organic chains. Surface modified silica particles are widely used in a range of different applications. Normally, the functional groups on silica surface can act to control the surface properties of silica particles such as hydrophobic properties, chemical reactivity and thermal properties that depend on the substitution of organic groups. The modified silica surface is generally used to achieve by several method, which is popularly used the co-reaction of organoalkoxysilane with silica precursor.

The aims of work is the improvement of mechanical and thermal properties of NR reinforced silica particles including the enhanced compatibility between rubber matrix and silica particles. The silica particles were prepared by sol-gel process of tetraethoxysilane (TEOS) as silica precursor, and co-condensation of TEOS with organoalkoxysilanes which was various types of organic group. The modify agents that was used for the modification of silica surface are 3-mercapto propyltrimethoxysilane (MpTMS), phenyltriethoxysilane (PhTES), phenyltrimethoxy silane (PhTMS) and N-3-(trimethoxysilyl) propyl aniline (ATMS). The functional groups of modified agent can act as an antioxidant to prolong the lifetime of rubber and increase the hydrophobic properties of silica particles in order to improve the compatibility between silica particles and rubbery matrix. The modified silica particles were used as a reinforcement with NR matrix by using 2 method, “latex” and “solid”. The modified silica particles were mixed with NR and curing agents by a two-roll-mill. Finally, the effect of modified silica particles on the morphology, cure characteristics, mechanical, thermal and dynamic mechanical properties of NR vulcanizates filled with modified silica particles were investigated and all results were compared to those of unmodified silica particles filled one. Moreover, the different dispersion of silica particles in rubbery matrix (both latex and solid) was studied by scanning electron microscope (SEM).

1.2 Objectives

1.2.1 To prepare the modified silica particles by sol-gel process with 3-mercaptopropyltrimethoxysilane (MpTMS), phenyltrimethoxysilane (PhTMS), phenyltriethoxysilane (PhTES), and N-3-(trimethoxysilyl) propyl aniline (ATMS)

1.2.2 To characterize the modified silica particles

1.2.3 To investigate the mechanical and thermal properties of composite materials

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1.3.5.2 Solid rubber: the modified silica particles (20 phr) were mixed with solid rubber including curing agents on a two-roll-mill

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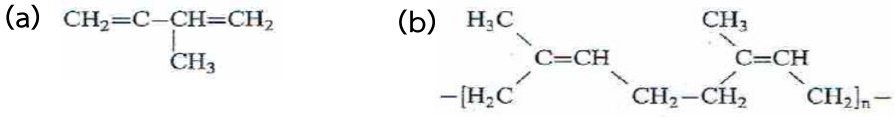
CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Natural rubber

NR is the most of important natural resource which obtained from *Hevea brasiliensis* that originally grown on plantations by small holder in the jungles of Brazil and is also found in the milky latex of the humble milkweed and dandelion. This tree grown most readily in a band within 5° of the equator, in places where the annual rainfall exceeds 80 in/year, the temperature is 25-35 °C, and low altitudes prevail [Barlow F. W., (1993)]. In 1876, Hevea tree was introduced to tropical in Asia by Sir Henry Wickman H.N. Ridley, and it was first grown in the south of Thailand in 1899. Today, more than 80% of NR comes from southeast asia (Malaysia, Indonesia and Thailand). NR still has a considerable technical and commercial importance. The worldwide production amounted to 5.5 million tons in 1992, representing 34% of the total rubber production (15 million tons) and the global consumption of natural rubber increased to 6 million tons in 1995 [Feldman D. et al., (1996)]. The chemical structure of NR is the repeating unit of isoprene (C_5H_8), which is a homopolymer with molecular weight ranging from 1 to 2.5×10^6. It has a cis-1, 4 configuration content of almost 100%, which means that carbon atoms 1 and 4 are both on the same side of the double bond [Day G., (2009)]. The linear structure of isoprene was proposed by Pickles providing the structure isomerism with *cis-* repeating unit as shown in Figure 2.1 [Day G., (2009)].



$$CH_2{=}C{-}\underset{CH_3}{\underset{|}{CH}}{=}CH_2$$

Figure 2.1 Structure of natural rubber: (a) isoprene monomer and (b) cis-repeating unit.

2.1.1 NR latex

NR comes from the milky sap or latex that a cut of rubber-bearing fluid which the latex exudes from the rubber tree followed a vertical channel at the lower end into a small cup, as shown in Figure 2.2 [Ciesielski A., (2000)]. In the cutting process, the latex flows for about 4 h and the coagulation is protected by adding a little amount of liquid ammonia in the cup. At the end of flow, the latex is collected in tanks [Barlow F. W., (1993)]. NR latex that is a dispersion of rubber particles (0.1-1.6um) in water, consists of rubber hydrocarbon 30-45 %weight, non-rubber constituents 3-5 %weight, and the rest is water. The non-rubber constituents comprise of proteins, amino acids, carbohydrates, lipids, as well as other organic and mineral components [Sarkawi S. S. et al., (2013)]. However, the non-rubber constituents can affect the reactivity of the rubber molecule, this will be considered at the appropriate point. The ratio of the rubber to non-rubber components varies from source to source [Ciesielski A., (2000)]. The typical compositions of NR latex were listed in Table 2.1.

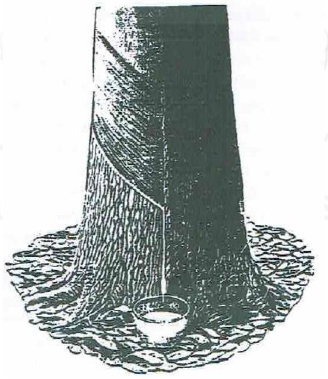


Figure 2.2 Tapping latex from the rubber tree.

Table 2.1 Typical composition of NR latex.

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

2.1.2 Dry rubber

The dry rubber production brings the field latex, stabilized against coagulation by ammonia or other materials that screened to remove foreign matter, diluted and the rubber coagulated with acid. Then, the coagulum is squeezed between contrarotating rollers to remove the water and serum after that dried to a moisture content of less that 1% by heat. Somewhat, the squeezing operation uses a copious supply of iron-free water to wash the coagulum on the roll mills to reduce all traces of serum that remains the coagulated rubber. Iron-free water is used to prevent oxidative deterioration of the rubber in storage [Barlow F. W., (1993)] . The main components of a typical mixture of fresh latex and dry rubber are illustrated in Table 2.2 [Feldman D. et al., (1996)]. There are two generic classifications of dry rubber as are follows: the crepes and sheets. The conventional crepes and sheets are classified by the International Standards of Quality and Packing for Natural Rubber Grades [Day G., (2009)].

Table 2.2 Composition of fresh latex and dry rubber.

Composition	Latex (% by weight)	Dry rubber (% by weight)
Rubber hydrocarbon	36	93.7
Proteins	1.4	2.2
Carbohydrates	1.6	0.4

2.1.3 Properties of NR

The general properties of NR were summarized in Table 2.3. NR has a glass transition temperature (Tg) of approximately -75 °C. In general, NR is an important materials in the rubber industry, in particularly the manufacture of rubber tires, as it possesses the excellent mechanical properties. Vulcanizated products of NR have the high elasticity, high tensile strength and modulus, especially at higher strain levels and temperatures. Due to its high structural regularity, NR tends to crystalline spontaneously of polymer chain at low temperature that causes stiffening and easily reversed by warming or when is stretched. Furthermore, NR has very good abrasion resistance which makes a significant choice for slurry pump liners and impellers as well as for tank linings. It has a very good dynamic mechanical properties and is used in tires, rubber springs and vibration mounts. The advantages include low compression set and stress relaxation, good electrical insulation and resistance to tear and fatigue. In the solvent followed the polarity rule, NR that has double bonds in the main chain shows the poor resistance to petroleum oils having carbon and hydrogen atoms, while the better resistance to alcohols and ketones is obtained [Ciesielski A., (2000)].

However, NR vulcanizates are susceptible to inherent weather resistance and to attack by atmospheric heat, oxygen, ozone and UV light. Ozone attack is of most concern for thin products that are subjected to stretching in service [Nagdi K., (1993)]. Thus, the drawback of the ozone and weather resistance can be improved by blending with a saturated rubber or by incorporating of antidegradants to protect in the NR products.

Table 2.3 Physical properties of NR.

Properties	Value
Specific gravity	0.92 g/cm^3
Refractive index (20 °C)	1.52
Coefficient of cubical expansion	0.00062 /°C
Cohesive energy density	63.7 cal/cc.
Heat of combustion	10,700 cal/g
Thermal conductivity	0.00032 cal/sec/ cm^3/°C
Dielectric constant	2.37
Power factor (1,000 cycles)	0.15-0.2 *
Volume resistivity	10^{15}-10^{19} ohms/cc.
Dielectric strength	1000 V/mm

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

2.2 Improvement of NR

There are several methods in order to improve the some properties of NR materials to be specific applications such as the chemical modification of NR structure and the addition of additives or reinforcing filler.

2.2.1 Modification of NR

NR has been modified in many ways since the establishment of a continuous supply of plantation rubber. Some of these modifications such as chlorinated rubber, have passed their peak of acceptance as other materials supplanted them. The modification highly affects its physical properties [Barlow F. W., (1993)]. The most of classical organic chemistry reactions of modification may therefore be applied to NR, in particular the addition reaction with various chemical reagents (hydrogenation, halogenation and hydrochlorination). The chemical modification of NR has generally followed two directions: improving undesirable properties such as low heat and hydrocarbon oil resistance, and transforming NR into new polymeric materials for specific application such as photocrosslinkable rubbers and thermoplastic elastomer. The chemical modification of NR may be carried out under various conditions including in organic solution, aqueous medium and surface modifications. The reaction may be by one-, two- or even three-step modification to obtain the required properties. Modified NR products have attained some commercial applications as follows: epoxide natural rubber (ENR), deproteinized natural rubber (DPNR) and oil-extended natural rubber (OENR) [Barlow F. W., (1993)].

2.2.2 Addition of additives

NR has some undesirable properties such as low heat resistance, poor ageing properties as well as low oil and flame resistance. These drawbacks may be due to the high unsaturation of the molecular chain and non-polar character of NR. To overcome these drawbacks, rubber manufactures adjust by the additional additive in rubber compounding formulation. The popularly additives were used for the improved these drawbacks are as follows: antidedegradant and flame retardant.

2.2.3 Incorporation of reinforcements

The inclusion of reinforcement is necessary to apply the usage of NR materials, which the reinforcing fillers can be improved the performance related mechanical properties of rubber such as resistance to tear and abrasion. The common reinforcing fillers for mixing with NR matrix are carbon black, calcium carbonate and silica particles.

2.3 Antidegradants

Antidegradants is a relatively recent descriptive term covering materials whose addition the useful life of a rubber and those protect rubber products against degradation by a variety of forces. The major need for antidegradants is in the unsaturated elastomers such as NR, SBR, BR, nitrile rubber, and neoprene that lead to reactive and more prone to degradation. Most prominent degradants are oxygen, ozone, dynamic fatigue, heat, and light (UV). The most antidegradants are generally classified into two classes as antioxidants and antiozonants. Antioxidants provide protection from oxygen degradation by slowing the reaction of oxygen with rubber. Antiozonants prevent deterioration of the rubber from attack by ozone. These products may be lost by volatilization during vulcanization or high-temperature service, or by extraction by water or other fluids [Ignatz-Hoover F., (2009)].

2.3.1 Types of antidegradant

Antidegradants are generally classified into two classes with two characteristic performance features are as follows: antioxidants and antiozonants [Ignatz-Hoover F., (2009)]. However, antioxidants are considered either discoloring or non-discoloring.

2.3.1.1 Non-discoloration antioxidants

These antioxidants are most of phenolic antioxidants that consist of six categories: (1) hindered phenols, (2) hindered bisphenols, (3) hydroquinones, (4) phosphites, (5) organic sulfur compounds, and (6) hindered amine and nitroxyl compounds [Ignatz-Hoover F., (2009)]. The structure of commonly phenolic antioxidants is shown in Figure 2.3 [Ciullo P. A. et al., (1996)]. There are many products that popularly used one to three categories, but only a few in the other another three classes. All are used to protect against oxygen, heat and light.

(1) Hindered phenols

Products in this class that are more volatile than other higher molecular weight antioxidants and are not as persistent. They provide moderate protection at a low-to-moderate cost. It is also of interest that phenol itself is not an antioxidant, i.e., substitution in one or both ortho positions (to the OH) is necessary. These products are used in latex, general mechanical goods, and shoe products.

(2) Hindered bisphenols

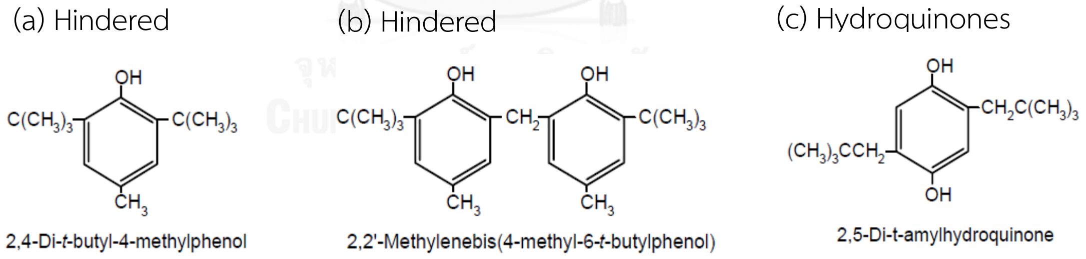
These are two examples of the bisphenols where two hindered phenol groups are linked together with an alkylene or alkylidine bridge in the ortho or para position. Other the bisphenols are bridged by sulfur. The bisphenols are generally the most potent and persistent of the non-staining antioxidants, but are also the most expensive. The alkylene- or alkylidine-bridged antioxidants tend to give the best non-discoloring characteristics, 4, 4’-Butylidene-bis-(6-t-butyl-m-cresol) are particularly effective in NR latex for many uses. Phenolic antidegradants are prone to losses through volatilization; the bis compounds, because of their higher molecular weight, are less prone to these losses.

(3) Hydroquinones

This is somewhat of a specialty class, used primarily for tack retention in uncured rubber films and adhesives, and as stabilizers for some synthetic rubbers such as NBR and BR. They are only active in uncured rubber, not in sulfur-cured rubber products, where they not only do not work as antioxidants, but impart severe scorch problems.

2.3.1.2 Discoloration antioxidants

This most class of materials is amine antioxidants that consist of various types of mono-and di-amines, which are very effective antioxidants, but impart mid to severe discoloration. The most widely used products can be divided into four classes are as follows: (1) phenylnaphthylamines, (2) dihydroquinolines, (3) diphenylamine derivatives and (4) paraphenylenediamines [Ignatz-Hoover F., (2009)]. The structure of commonly amine antioxidants is shown in Figure 2.4 [Ciullo P. A. et al., (1996)].



(a) Hindered

2,4-Di-*t*-butyl-4-methylphenol

(b) Hindered

2,2'-Methylenebis(4-methyl-6-*t*-butylphenol)

(c) Hydroquinones

2,5-Di-t-amylhydroquinone

Figure 2.3 Phenolic antioxidant types: (a) hindered phenols, (b) hindered bisphenols and (c) hydroquinones.

(1) Phenylnaphthylamines

The phenylnaphthylamines are among the oldest of the antioxidants and were used extensively until the early 1990s. Their decline are the result of suspected toxicity problems rather than displacement by a technically superior product. This class of chemicals offers good heat, oxidation, and flex fatigue protection.

(2) Dihydroquinolines

This group includes very potent and widely used general purpose antioxidants including polymerized 1, 2-dihydro-2, 2, 4-tri methylquinoline. They are good general antioxidants and also effective against heavy metal prooxidants such as nickel and copper ions. The polymeric nature of dihydroquinolines results in low volatility and migratory properties in a vulcanizates. Thus, there is minimum loss of protectant through extraction or diffusion, durability and high-temperature are improved.

(3) Diphenylamine Derivatives

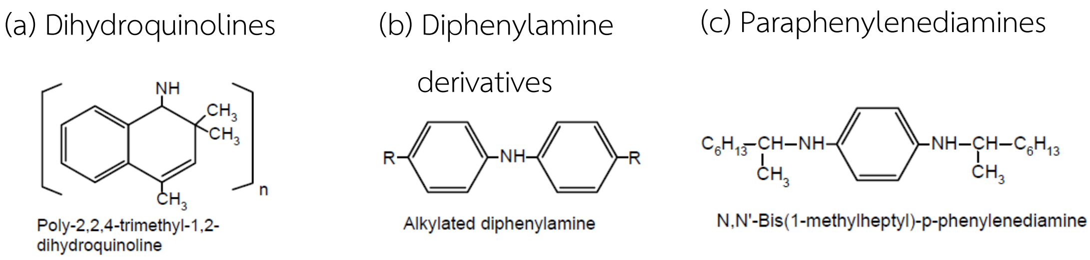
One group of this class often provides antioxidant protection that uses to be slightly less than the polymerized dihydroquinolines, depending upon ageing temperatures. They are very mildly the discoloration and very effective in neoprene and nitrile rubbers. A second group of this class is derived from the reaction of ketones with diphenylamine, e.g., high temperature reaction product of acetone and diphenylamine. These are quite effective antioxidants and better for flex cracking and fatigue resistance than the alkylated diphenyalmines, but they are also more discoloring.

(4) Paraphenylenediamines

These are very effective antioxidants. Generally, there are three categories of paraphenylenediamines (PPD) are as follows: (1) dialkyl PPD is the substituent R groups that are alkyls and this class tend to include higher levels of scorch in a compound, (2) alkyl-aryl PPD that one group is an aromatic ring and other groups is alkyl group shows to be better protection, safety including slower migratory properties, and (3) diaryl PPD that contains two aromatic pendant groups is less active than alkyl-aryl PPD and also tend to bloom, rendering them unsuitable for many applications.

2.3.1.3 Antiozonants

The selection of antiozonants depends very much on the application, and there are very different requirements for static ozone protection compared to dynamic ozone protection. Most applications involve both static and dynamic conditions of strain [Rodgers B. et al., (2013)]. There are only four classes of materials classified as an antiozonant, and some of these limited in performance are as follows: (1) petroleum waxes, (2) nickeldibutyldithiocarbamate (NBC), (3) 6-ethoxy-2, 2, 4-trimethyl-1, 2-dihydroquinoline (ETMQ) and (4) paraphenylenediamines. The antiozonant is popularly used as a class of paraphenylenediamines in the rubber industry. In general, there are three classes of paraphenylenediamines are as follows: (1) dialkyl PPD often provides superior ozone protection in a static environment, in particularly the absence of wax. They also tend to be more sensitive to oxidation and may not persist in rubber products as other materials, (2) alkyl-aryl PPD offers superior dynamic protection when combined with wax, and (3) Diaryl PPD is generally low cost but have lower activity than the alkyl-aryls PPD. Diaryl PPD may cause bloom problems at effective use levels, i.e., 2 phr or more.



(a) Dihydroquinolines (b) Diphenylamine derivatives (c) Paraphenylenediamines

Figure 2.4 Amine antioxidant types: (a) dihydroquinolines, (b) diphenylamine derivatives and (c) paraphenylenediamines.

2.3.2 Properties of antidegradants

The performance and properties of antidegradants are the primary criterion used to select the proper applications including the other criteria such as staining, volatility, solubility and concentration or usage level [Rodgers B. et al., (2013)].

2.3.2.1 Staining or discoloration

The first performance property considered is staining or discoloration. Staining is caused by antioxidant migration and physical transference to adjacent material. The extent and intensity of staining is determined by the chemaicl nature of the antidegradant and its mobility. In general, phenolic antidegradants are non-discoloring resulting in the choice for light-colored stocks, while amine antidegradants should not be used for colored products due to the discoloring.

2.3.2.2 Volatility

The molecular weight and chemical structure of molecule determine its volatility. Generally, the greater molecular weight is the lower the volatility. The volatility of antidegradants affects rubber testing and results may vary widely depending upon the volatility of the antidegradant. Throughout the service life of a rubber article, the volatility is important from the standpoint of loss of antidegradant.

2.3.2.3 Solubility and Migration

A third important property of antidegradants is their relative solubility in rubbers, detergents, or solvents which the rubbers come in contact. Solubility in the rubber and the contacting media results in a partitioning or transfer of a portion the antidegradant into the contact media, causing a net depletion of antidegradant in the rubber article. The solubility of an antidegradant in rubber depends upon its chemical structure, the type of rubber, and temperature. Poor solubility results in blooming that occurs when a chemical is readily crystallizable quantities larger than the solubility limit are used. The solubility of antidegradants in solvent or water is also important. Their extraction in service, such as in hydraulic hose or in articles subject to detergent cleaning, laundering or dry cleaning, can be a serious problem.

2.3.2.4 Chemical Stability

The stability of antidegradant toward heat, oxygen is important if it is to have maximum effectiveness for long periods. Many antioxidants are subjected to oxidative reactions with the development of colored species; the amine antioxidants are particularly sensitive. Antioxidants fall into two general categories, primary and secondary. Primary antioxidants are hydrogen atom donors and act as a chain stoppers, stopping the free radical chain reaction of oxidation. Secondary antidegradants are considered to be peroxide decomposers. These chemicals convert peroxides to more stable products without the detrimental free radical chain reactions.

2.3.2.5 Concentration level

Determining the proper level of antidegradant to use is a complex question whose answer depends upon cost, polymer type, end-use application, staining requirements, solubility limits. The p-phenylenediamines offer best oxidation resistance at about 0.5 phr and best antiozonant protection at 2 to 4 phr, whlie the phenolic antioxidants are effective at 0.5 to 1.0 phr.

2.3.3 Antidegradants protective mechanisms

Three variables in the compound formulation can be optimized to resist degradation; polymer types, cure systems and antidegradant systems. The deterioration process starts with the formation of free radical species. The backbone of rubber chain represented by RH which can be break, leading to the cleaved rubber chain and then, the rubber radical can react with oxygen or ozone to form a rubber peroxide. Therefore, the antidegradants (HA) are added in the system, which can play to act as the decomposition of peroxides are converted into non-radical products, resulting in the stopping of the radical chain reactions [Barlow F. W., (1993)]. In general, the phenols and amines used by the compounder stop the chain reaction by interposing themselves in it. The resultant free radical can link up with a like radical to form a stable product or react with another peroxide radical.

$$RH \longrightarrow R^{\bullet} + H^{\bullet}$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + HA \longrightarrow ROOH + A^{\bullet}$$

$$ROO^{\bullet} + A^{\bullet} \longrightarrow ROOA$$

where HA represents the antidegradant.

2.4 Reinforcement by particulate fillers

The use of particulate fillers in rubber is almost as old as the use of rubber itself that has been extensively studied, particularly in the 1960s and 1970s. The concept of reinforcement relates basically to composites built from two or more components of the different physical and mechanical properties whereby the strength of one of these elements is imparted to the composite and combined with the set of favorable properties of the other component. The particulate fillers are added to rubber compounds to improve the cure, physical and mechanical properties, reduce the cost and impart color to the rubber product. However, the efficiency of reinforcement by particulate fillers is depending on types of particulate fillers. In addition, the degree of reinforcement by particulate fillers is directly related to the average particle size, particle shape, and particle-size distribution, including a variable amount of particulate fillers, which also have significant effects on the reinforcement [Donnet J.-B. et al., (2013)].

2.4.1 Classification of particulate fillers

In the classifying the particulate fillers in rubber use to increase its usefulness or to make a cost-competitive product. Typically, the chemical composition of particulate fillers and its effect on the properties of rubber product can be classified into three categories [Waddell W. H. et al., (2009)].

2.4.1.1 Non-reinforcing or mineral fillers

Non-reinforcing or mineral fillers such as calcium carbonate and talcum are naturally occurring materials that are mined and ground to a specific particle size. This fillers can be used in rubber but just confer them a very slight improve for the properties of rubber product because of their large size.

2.4.1.2 Semi-reinforcing fillers or extending fillers

Semi-reinforcing fillers or semi active fillers such as kaolin clay, alumina trihydrate have the medium particle size and low cost. These fillers impart the high modulus, tensile strength, stiffness, and good abrasion resistance to rubber compounds, but their properties are lower than reinforcement by reinforcing fillers.

2.4.1.3 Reinforcing fillers or synthetic fillers

Reinforcing fillers, or synthetic fillers such as metal oxide, precipitate calcium carbonate, precipitate silica and silicates are generally manufactured by precipitation of soluble materials under controlled conditions to provide tailored properties. They may be found as colloidal particles that are spherical shape which may be covalently bonded groupings of individual particles. Reinforcement properties are the function of colloidal particle size and shape, the aggregate dimensions and morphology, and the ability of agglomerates to break down during mixing including the composition and surface chemistry.

2.4.2 Factors influencing reinforcement with particulate fillers

The characteristics which determine the properties of particulate fillers will impart to a rubber composite are particle size, structure, surface area, specific surface activity and number of particulate fillers.

2.4.2.1 Particle size

The particle size of particulate fillers is mainly associated with the efficiency of reinforcement that the particle size decreases, its specific surface area increases gives the good reinforcement. These can contribute to improve the mechanical properties in terms of modulus, tensile strength, hardness, tear resistance, and reduce the rupture of rubber chain flexing and stretching [Rothon R. N. et al., (1995)].

Fillers with particle size greater than 10,000 nm (10 μm) are therefore generally avoided because they can reduce performance rather than reinforce or extend. Fillers with particle sizes between 1,000 and 10,000 nm (1 to 10 μm) are used primarily as diluents and usually have no significant affect, positive or negative on rubber properties. Semi-reinforce fillers, which range from 100 to 1,000 nm (0.1 to 1 μm) can improve the properties in terms of strength and modulus. The really reinforcing fillers with particle size in range of 10 to 100 nm (0.01 to 0.1 μm) significantly improve the properties of rubber product. The particulate fillers such as carbon black 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 [Ciullo P. A. et al., (1996)].

2.4.2.2 Structure

The term of structure refers to the aggregation of primary particles resulting in deviation from the spherical shape leading to lower packing density and higher void volume. In general, the structure is determined by the genesis of the filler, by its chemistry, its crystal structure which is very important in determining the stiffness or rigidity of a composite and the surface smoothness of a component, i.e. virtually all the important properties of a composite [Rothon R. N. et al., (1995)].

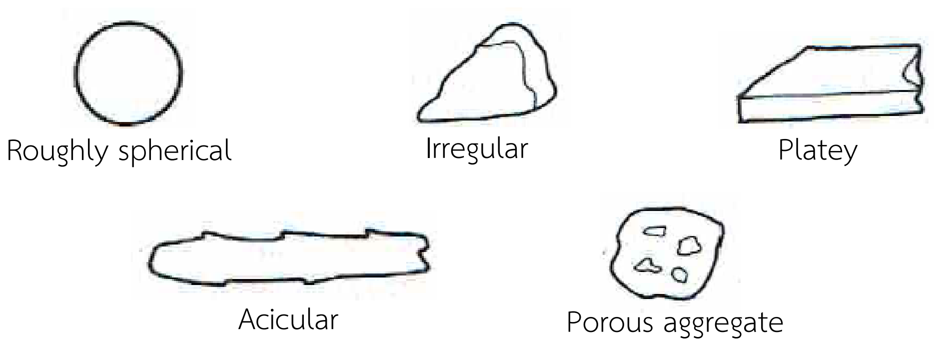


Figure 2.5 Some particle types in common fillers.

All particulate fillers commonly are used as microscopic in size imposing major difficulties both in how to measure and then to describe including the quantify shape. The shape of particulate filler is an important factor in the use of filler in elastomer affecting the dispersion in rubber and the properties of rubber composite. The typical particles likely to be found in fillers such as roughly spherical, blocky, irregular, platey, acicular, etc, as shown in Figure 2.5 [Rothon R. N. et al., (1995)]. The blacks and precipitated inorganics used for reinforcement have generally round primary particles but function as anisometric acicular aggregates. The round particles clump together into chains or bundles that can be very dense or open and lattice-like. These aggregate properties – shape, density, size – define their structure. Filler aggregates in elastomer matrix have a tendency to form agglomerates, especially at high loading, leading to chain like filler structure or cluster, generally termed as secondary structure or filler network. Such a network has a significant affects to the processability and properties of filled rubber [Ciullo P. A. et al., (1996)].

2.4.2.3 Surface area

Surface area is the most important single factor, which determines the degree of reinforcement is the development of a large polymer-filler interface. The surface area is the area of surface present in unit weight of fillers and frequency used as a measurement of filler particle size by different techniques such as gas adsorption or dye adsorption. The surface area of particulate fillers is related to its particle size and it is the basis of considerations of dispersibility and processability. A filler must make intimate contact with the rubber chains if it is going to contribute to the reinforcement of the rubber-filler composite. Fillers that have a high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains. Particles with a planar shape have more surface 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 [Ciullo P. A. et al., (1996)].

2.4.2.4 Specific surface activity

The specific surface activity denotes the chemical composition of the filler surface. The nature of the filler surface may be varying in a chemical sense, having different chemical groups, e.g., hydroxyl or metal oxide in white fillers and carbonyl, quinone, lactone in carbon black. The specific surface activity is a very important role in determining the nature of the interaction between filler and polymer, effecting the rate of cure with many vulcanizing systems [Boonstra B. B., (1982)]. A filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. 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 on the filler surfaces. The non-black fillers generally offer less affinity and surface activity toward the common elastomers. This can be compensated to a greater or lesser extent by certain surface treatments [Ciullo P. A. et al., (1996)].

2.4.2.5 Number of particulate fillers

The formulation of rubber compound have to use the appropriate number of particulate fillers in order to obtain the required properties because the excess amount of filler can result to loss the original properties of rubber. The number of particulate fillers depends on several factors such as the method and condition of mixing the rubber compound including the composition of rubber compound.

2.5 Silica materials

Nowadays, it is well known that the particulate fillers as a reinforcing fillers are popularly used in the rubber industry, which are carbon black or silica. The reinforcement by carbon black is limited for some applications, as the colorful product due to its black fillers. For this reason, silica is available used to replace the carbon black owing to its similar properties such as high tensile strength, tear and abrasion resistance. Silica gives the utmost in reinforcement with rubbers of nonblack fillers because it offers a number of advantages such as the improvement of the mechanical properties in terms of tear and abrasion resistance, reduction in heat buildup and the increase in compound adhesion in multicomponent products. In general, silica consists of silicon and oxygen arranged in a tetrahedral structure of three-dimensional lattice, which the formula is $SiO_2 \cdot xH_2O$ [Rodgers B. et al., (2013)].

2.5.1 Classification of silica

There are commonly two major categories, which the primary differentiation among silica products are the natural or synthetic, based on origin, that translates to a division between crystalline and amorphous form [Ciullo P. A., (1996)]. Natural silica is crystalline that classified for most of their uses under the term “sand and gravel” is non-reinforcing or semi-reinforcing fillers. The natural silica with high mineralogical and chemical purity is nevertheless produced in substantial quantities. It is generally characterized as off-white to white and abrasive, with low surface area, binder demand and cost. Synthetic silica is generally used as reinforcing fillers and characterized as amorphous with a high purity, surface area, liquid absorption, and ultimate particles size. These include the precipitated silica also known as hydrated silica and the fumed silica also known as pyrogenic or anhydrous silica, which results in a relatively high density of surface silanol groups.

2.5.1.1 Ground crystalline silica

Crystalline silica is produced by grinding high-purity quartz, quartzite, sandstone, or silica sand. It can be used a non-reinforcing or semi-reinforcing fillers for low cost rubber articles due to low chemical inertness and relatively low surface area. To minimize the health hazards of exposure to airborne crystalline silica, particles size are large in the range of 2 to 20 µm [Waddell W. H. et al., (2009)].

2.5.1.2 Biogenic silica

Biogenic silica is often referred to as diatomaceous earth because the primary deposits are the exoskeletons formed by diatoms that have extracted silicic acid from sea water and formed amorphous silica shells. Diatomaceous earth from sedimentary rocks often contains up to 30% organic matter and inorganic impurities requiring separation or treatment to remove crystalline content. In general, biogenic silica is used as a semi-reinforcing filler or as a carrier for liquid compounding ingredients. It often has a substructure of extremely small particles less than 50 Å in diameter which have a surface of silanol groups [Waddell W. H. et al., (2009)].

2.5.1.3 Fumed silica

Fumed silica is produced by thermal method, which the original process was developed by the Degussa Company in Germany in the 1940s and the product marketed, as it still is, under the brand name Aerosil [F.W. Barlow, (1993)]. Coming of the furnace, fumed silica was obtained in a fluffy form due to its high temperature of formation which presents a very stable morphology, and a pure silica with fewer silanol groups and water content on the surface compared with precipitated silica. This confers a high dispersibility and reactivity to fumed silica. The fumed silica is primary particles size of 7 to 40 nanometers that the primary particles collide and fuse into branched or chain-like clusters [Ciullo P. A., (1996)]]. However, fumed silica has the relatively high cost, affecting the lower usage of its in the industry. Most of this silica is used in the compounded with silicone rubber.

2.5.1.4 Precipitate silica

Precipitated silica is obtained by precipitation that is made by the action of acids on water glass. The acid is usually sulfuric acid, the water glass an alkaline solution of sodium silicate. The hydrated precipitated silica is filtered out and washed to remove the sodium sulfate. It is then dried and grinded that the formed size of the aggregates reduced. This results to obtain the small rigid and to maintain the high dispersibility [Barlow F. W., (1993)]. However, the particle size conventionally reported is that of primary particles (10 to 30 nanometers), although it is the aggregates (30 to 150 nanometers) that are the actual functional particles [Ciullo P. A., (1996)]. The physical and chemical properties of precipitated silica can vary according to the manufacturing process. The effectiveness of reinforcement can control from suspension pH, temperature and salt content that can change the ultimate particle and aggregate size of precipitated silica from solution. In elastomer compounding, the reinforcing fillers approximately 75% of precipitated silica were produced, which precipitated silica is highly reinforced tough white or light-colored compounds. It can improve the tear strength, resistance to flex fatigue, and heat ageing of a wide variety of manufactured rubber products such as conveyor, hoses and bumper pads. Nevertheless, the application of precipitated silica is commonly treated with silane coupling agents to promote better matrix compatibility and improved compound properties [Waddell W. H. et al., (2009)].

2.5.2 Surface chemistry of silica

The surface chemistry plays an important role in the reinforcement of particulate fillers, especially in the interaction of fillers and polymer with contributions ranging from electrostatic interactions to covalent bonding to the polymer backbone. However, surface chemistry also strongly affects the interaction of fillers with other chemicals in the rubber compound, particularly active metal oxides, curatives and antidegradants [Waddell W. H. et al., (2009)].

The silica surface consists of two types of functional gropus, siloxane bond (Si-O-Si) and silanol group (Si-OH). The surface content in silanol group can be divided into three categories: isolated, germinal and vicinal as illustrated in Figure 2.6 [Waddell W. H. et al., (2009)]. The isolated silanol includes the hydroxyl group that located at a distance sufficiently far from neighboring hydroxyl groups to prevent hydrogen bonding. Isolated hydroxyl exist predominantly on dehydrated silica, pyrogenic silica and to a lesser extent on precipitated silica. The germinal silanols are two hydroxyl group on the same silicon atom, while the vicinal silanols are associated of silanol groups on adjacent silicon atom. Vicinal hydroxyls are stronger adsorption sites and hence, have stronger reinforcement effect than isolated hydroxyl. However, the silica surface hydration that caused by water vapor absorption is affected to highly polar and hydrophilic as a result of its polysiloxane structure and surface silanol concentration. The hydroxyl groups on the silica surface show the surface acidity which they have a retarding effect on vulcanization rates of accelerator sulfur compound and vucanizate properties. To illustrate the influence of the surface hydroxyl groups and hydration levels, the physical moisture contents are almost impossible to control due to the strong desiccant of silica and the release of moisture during with rubber [Rodgers B. et al., (2013)].

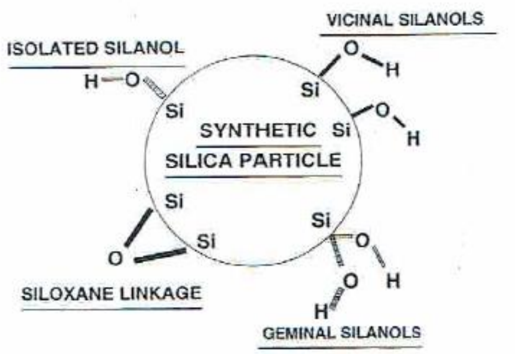


Figure 2.6 Silica surface groups: siloxane (Si-O-Si), and isolated, germinal and vicinal silanols (-Si-OH).

2.5.3 Problems usage of silica

In general, silica produces relatively greater reinforcement in more polar elastomers such as NBR and CR than in nonpolar polymers such as SBR and NR. The defectiveness of silica to reinforce in nonpolar polymers may present the silanol groups on the surface, which limited for some applications due to the rapid absorption of moisture. The high levels of hydration or moisture content are generally affect to the dispersion and distribution of silica in rubber product which are generally recognized to be determined by the state of aggregation and agglomeration. Aggregates are covalently bonded to one another via siloxane bonds which can physically agglomerate though intermolecular hydrogen bonding of surface silanol groups of one aggregate to a silanol group of other aggregate [Rodgers B. et al., (2013)]. Therefore, the compounding recipes of silica reinforced in rubber have been developed which include the polar compounds such as glycerin and glycols to decrease their influence on the vulcanization system by hydrogen bonding and blocking off the surface hydroxyl groups. In addition to these compounding methods, other techniques have been tried to improve the reinforcing performance of silica, including the heat treatment and chemical promotion of the rubber-filler, addition of silane coupling agents, in-situ generated silica by sol-gel methods and chemical modification of surface. Some of these methods promises for raising the rubber reinforcement performance of silica to a level commensurate with its large surface area.

2.6 Improvement of silica particles

There are many methods to improve the surface of silica particles in order to increase the reinforced ability of its with rubbery matrix such as the generated silica particles inside rubbery matrix via a sol-gel process, the addition of silane coupling agents, the treatment silica surface by heat and the chemical modification of surface by using organoalkoxysilane.

2.6.1 In situ generated silica by sol-gel method

In the early 1980s, Mark and Pan proposed the silica generated in situ by using sol-gel process of tetraethoxysilane (TEOS). They assumed that excellent reinforcement can be achieved when very fine silica particles are incorporated and dispersed well in rubbery matrix because the sol-gel reaction is considered to be a novel technique [Ikeda Y. et al., (1997)].

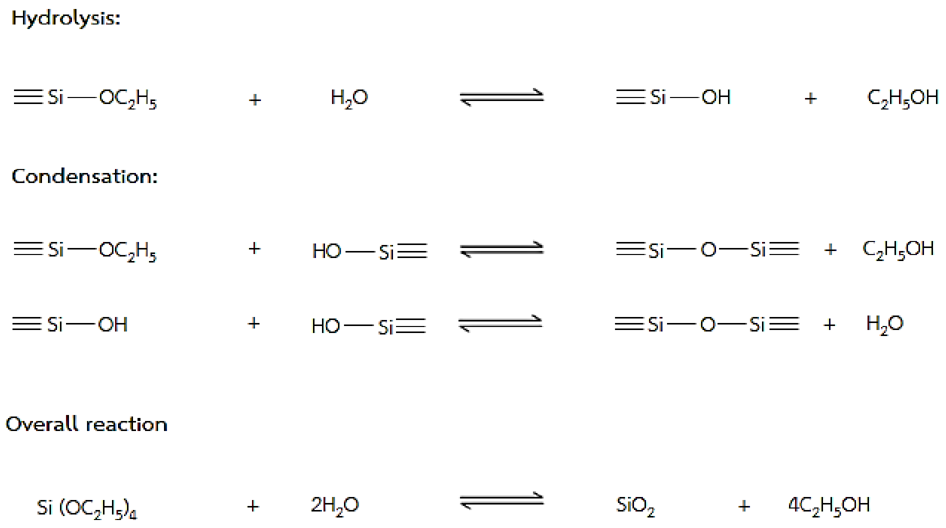


Figure 2.7 The hydrolysis and condensation reaction of TEOS to form silica.

2.6.1.1 Sol-gel method

The sol-gel method is used to produce the nanomaterial with complicated structure and shape, i.e. porous structure, thin films and dense powder that are popularly used in a range of wide such as selective adsorption, coating materials and medical industries. It is well known that this method can control of the distribution of components in molecule via a pre-orientation of the network affecting the high potential for application.

Generally, the sol-gel reaction divided into two steps of hydrolysis and followed by the condensation reaction. The hydrolysis reaction replaces the alkoxide group (OC_2H_5) with a hydroxyl group (OH). Subsequently, the condensation reaction involves the silanol groups that produce siloxane bonds (Si-O-Si) including the obtained water and alcohol as a by-products as shown in Figure 2.7 [Ikeda Y. et al., (1997)]. This method may be explained as the formation of the oxide network through the occurred hydrolysis and condensation reactions of precursor in a liquid. A sol is a stable dispersion of colloidal particles or polymer in a solvent that may be amorphous or crystalline. The sol particles may interact by van der waals forces or hydrogen bonds. A gel is irreversible and consists of a three dimensional continuous network which is built from agglomeration of particles. The gel may also be formed from linking polymer chains that are interactions of covalent bonds [Brinker C. J. et al., (1990)]. These reactions are concurrent and demonstrate some reversibility depending on the several parameter such as the nature of precursors, the molar ratio of reactants, type of catalysts or solvents including pH and temperature.

2.6.2 Coupling agents

Coupling agents are able to form a strong physical or chemical bond between a filler and the polymer. By so doing, the properties of the composite can be significantly improved [Skelhorn D., (1995)]. One point of fundamental importance when selecting a coupling agent is to ensure that is able to react with both the filler and polymer. There are several types of coupling agents commercially significant such as silanes, titanates, that silanes are the most widely used in this manner for improving the bonding of filler to rubber. In addition, the coupling agents are intended to function in the same way as the chemical promoters by reacting with both the filler surface groups and elastomer chains. Most commercial silane coupling agents are alkoxy based and only contain one organic group attached to silicon which the general formula is $R\text{-}Si\text{-}(OR)_3$ [Kuhn C. et al., (1996)].

Silane coupling agent is a bifunctional compound developed commercially to improve the reinforcing efficiency of silica by enhancing the rubber to filler interaction via the chemical linkage [B. Rodgers, et al., (2013)]. It is composed of two functionally active groups, i.e., the readily hydrolysable alkoxy group and the organo-functional group. The former can react chemically with the silanol groups on the silica surface to form stable siloxane linkages, which is relatively non-polar, is more compatible with rubbers and also can participate in the sulfur vulcanization to form chemical linkages with rubbers. Nowadays, many attempts have been made to study the role and various types of silane coupling agent in improving processability and increasing the effectiveness reinforcement of silica [Sae-oui P. et al., (2006)].

Recently, it has been reported that there are three well-known silane coupling agents and these have similar properties such as bis-(3-triethoxysilylpropyl) tetrasulfane (TESPT) [Ansarifar A. et al., (2004)] and 3-thiocyanatopropyl triethoxysilane (Si-264) [Sae-oui P. et al., (2005)]. One of the most effective silane coupling agents for vulcanizable hydrocarbon rubber is ɤ-mercaptopropyltrimethoxysilane [Dannenberg E. M., (1975)]. The mechanism of silane coupling agent with a silica involves the hydrophobation reaction of the alkoxy group in which silane coupling agent reacts with a surface silanol group of the silica, followed by the formation of the sulfur-containing function of silane coupling agent with rubber to afford a covalently bonded structure. The possible mechanism for reaction of silane coupling agent in silica-filled rubber systems is shown in Figure 2.8 [Dannenberg E. M., (1975)].

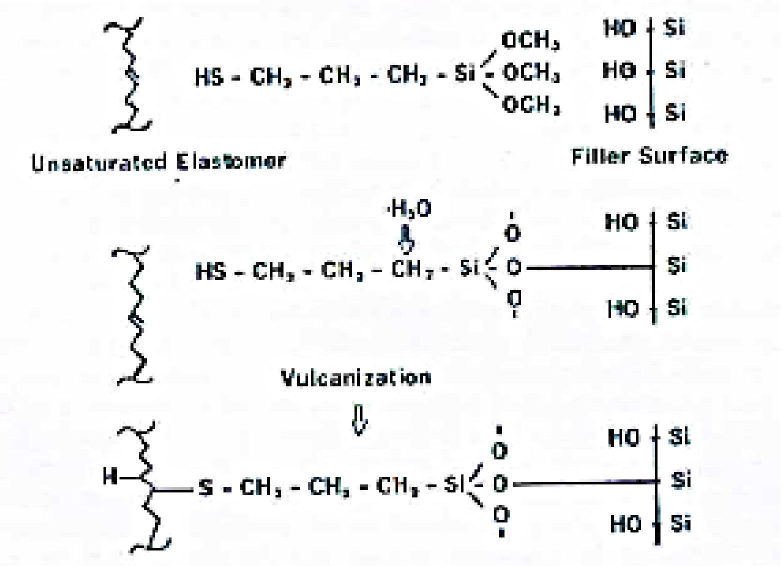


Figure 2.8 The possible mechanism for reaction of silane coupling agent in silica-filled rubber systems.

2.6.3 Heat treatment and chemical promotion

The heat treatment and chemical promoter methods have shown beneficial effects on rubber compounds filled silica show a significant change in properties after heat treatment of the additional effect is obtained if a promoter is added before heat treatment. The properties i.e. tensile strength, modulus increased due to the enhanced wetting and interaction between silica and rubber, resulting in the improvement of dispersion by the layer of attached rubber. However, this method may speculate that the increase in rupture energy is compensated by the reduced degree of hysteretic strain-energy dissipation resulting in no not change in reinforcement [Dannenberg E. M., (1975)].

2.6.4 Surface modification

The surface modification that is commercial chosen to bond an organic molecule chemically to the filler surface has covered the importance of the filler surface and of the polymer-filler interface in determining processing, reinforcement and other properties of composites. The modification of surface of fillers may be brought about in a variety of ways. The filler may be precoated or added the coating agent during compounding and make its way to the in-situ coating of filler surface. The relative importance of the various factors will vary depending on the nature of the coating and filler, and the composite processing conditions. Where the filler is precoated, various methods may be used to depend on the nature of the filler, the coating and the filler preparation procedure. When the filler is produced from aqueous solution, it is often advantageous to add a water-dispersable form of the coating prior to filtration and drying.

The important when modifying filler surfaces are the modifier reacts with the surface, the thickness and structure of the coating layer and interactions with the matrix. The most common functionalities of surface modifier used to produce bonding with the fillers with metal hydroxyl present, especially silica particles are alkoxysilane or called organosilane. The organosilane compounds are in widespread use for modifying the surface of fillers which this compounds has the general formula of $(R)_{4-n}$-Si-X where n = 1-3. The group X is a hydrolysable group chosen to react with surface hydroxyls of the filler to produce a stable bond. The group R is attached through a hydrolytically stable carbon-silicon bond and may be contained a reactive organic functionality. In general, organosilanes are complex species that often have the potential of reacting with themselves in the presence of moisture as well as with filler surface [Rothon R. N., (1995)]. Normally, the surface of silica contains the siloxane and silanol. Thus, silica modification can occur via the reaction of a particular molecule with either the siloxane (nucleophilic substitution at the Si) or silanol (direct reaction with the hydroxyl groups), although it is generally accepted that it is the reaction with the silanol function that main modification pathway [Dash S. et al., (2008)]. The reaction between organosilane or organoalkoxysilane and silica surface function at silanol groups is popularly method in which functional groups are attached to the silica surface. The kinds of organoalkoxysilane are necessary to use for improving the interfacial adhesion or chemical bonding of silica surface with the polymer.

Recently, the surface modification of silica have been reported to improve the dispersion of silica within rubber matrix, demonstrating the effective reinforcement of surface chemistry of silica particles [Waddell W. H. et al., (2009)]. The complete wetting and dispersion of high surface area silica are essential for good reinforcement in polymer matrix, and the silica surface provided for attaching with organic groups to increase the degree of hydrophobicity and chemical reactivity with the polymer matrix. The hydrophobic surface treatments of silica can be improved the surface adhesion, dispersion including the mechanical properties such as tensile strength, modulus and hardness with reinforced polymer [Dannenberg E. M., (1975)].

2.7 Literature reviews

Z. Wu et al. [Wu Z. et al., (2006)] prepared the silica spheres with aminopropyl (APTES) and phenyl (PhTES) groups through a one-step process by using a precursor as TEOS and ammonia solution as a basic catalyst. The spherical shape of modified silica particles were observed, and their exhibited characteristic changes in the surface properties, especially isoelectric point (IEP), water vapor and organic dye adsorption. The particles modified with APTES showed the highest IEP and dye adsorption due to the higher reactivity of APTES and the hydrophobic attraction, respectively. The particles modified by PhTES showed the lowest water vapor adsorption because their surface is more hydrophobic than those of TEOS and APTES.

V. Purcur et al. [Purcar V. et al. (2012)] fabricated the hydrophobic and antireflective coatings of hybrid films by sol-gel process, using TEOS as a silica precursor and methyltriethoxysilane (MTES), vinyltriethoxysilane (VTES), octyltri ethoxysilane (OTES) and PhTES as modifying agents. The hydrophilic properties represented the silica film from synthesized with TEOS only due to the hydroxyl groups on the surface, which can interact with water leading to the deterioration of the silica network. In case of surface modification with organic groups, the change in hydrophilic to hydrophobic was obtained, and the film prepared with TEOS+OTES showed the strong hydrophobic character of surface due to less polar of organic group.

S. Štandeker et al. [Štandeker S. et al., (2011)] modified the silica aerogel with mercapto (-HS) functional group via a sol-gel process using mercapto propyltrimethoxysilane (MpTMS) as a modifier. The modified silica aerogel was obtained to use the new adsorbent to remove Cu(II) and Hg(II) from water. The modified silica aerogels were used as an adsorbent, which showed the high adsorption potential for removal of Cu(II) and Hg(II) ions from aqueous solutions and more than 99.0%. Optimal conditions of adsorption on these modified silica aerogels, Cu(II) and Hg(II) removal were the efficiently performed at the pH 4 and 6, respectively, and the equilibrium time for Cu(II) and Hg(II) ions was reached within 2h.

C. H. Lee et al. [Lee C. H. et al., (2011)] prepared the surface modification through a continuous two-step sol-gel process with different silane compounds (MTES, vinyltrimethoxysilane (VTMS), 3-amino(propyl) trimethoxysilane (ApTMS) and MpTMS). All of alkoxy groups of the silane modifying agents were hydrolyzed and non-hydrolzable organo-chains were introduced on the surface of TEOS-derived silica nanoparticles. The modified silica particles were also the spherical shape which had the size in the range of 100-150 nm. The high contact angles and low wettability were obtained from the surface functionalized with methyl and vinyl groups, while ApTMS and MpTMS functionalized silica particles were hydrophilic due to the presence of amine and mercapto groups.

X. Liang et al. [Liang X. et al., (2011)] improved the sorption performance of sepiolite for heavy metals. Sepiolite was functionalized by nanotexturization in aqueous sepiolite gel and surface grafting in toluene with MpTMS. After surface modification, the surface areas decreased owing to the bulk size of the mercapto ligand, but the crystal structure did not change obviously. The surface modification can increase the sorption capacities for Pb(II) and Cd(II). In terms of operating simplicity and large scale production, the nanotexturization was better than the surface grafting in toluene. These results suggested that mercapto functionalized sepiolite could provide a potential remedy for heavy metal contamination in soils and water.

A. V. Rao et al. [Rao A. V. et al., (2010)] prepared the silica films by a single step base catalyzed sol-gel process, using MTES and phenyltrimethoxysilane (PhTMS) as co-precursor. The IR spectra showed an increase in the intensity of Si-Phenyl, Si-C and C-H peaks, and decrease in the intensity of O-H peaks with an increase in PhTMS/MTES molar ratio, clearly indicating the enhanced chemical modification of the silica surface by organic groups. The silica films with maximum static water contact angle of 164° and minimum sliding angle of 4° have been obtained from the PhTMS/MTES molar ratio of 0.22. These silica films could show the high potential for the development of self-cleaning coatings applications.

R. K. Goyal et al. [Goyal R. K. et al., (2013)] studied the poly (etherether ketone) nanocomposites reinforced with PhTMS treated silica nanoparticles. The good dispersion of treated silica nanoparticles in the matrix were observed as resulted in SEM micrographs. However, some silica aggregates were obtained at the higher silica loading. The thermal stability of the nanocomposites was more than 560 °C and the char yield of the nanocomposites significantly increased. The dielectric constant and dissipation factor were reduced slightly for the nanocomposites compared to those of pure poly (etheretherketone). These nanocomposites were inherently fire retardant materials with free from any halogen compounds, whereas commercials epoxy based laminates contain about 25% bromine compounds.

Q. Pen et al. [Pan Q. et al., (2013)] synthesized the antioxidant functionalized silica through reaction of precipitated silica and antioxidant coupling agent which is synthesized by (3-glycidyloxypropyl) trimethoxysilane and N-phenyl-1, 4-phenylene diamine in order to improve the dispersion of silica in rubber matrix and to study the reinforcement and antioxidant effect that incorporated into SBR matrix. The antioxidant functionalized silica/SBR composites had shorter optimum cure time, but much higher tensile strength than the neat silica/SBR composites. The antioxidant functionalized silica/SBR composites were more stable than the SBR filled with neat silica or TESPT modified silica in thermal oxidative and damp heat ageing.

K. C. Chang et al. [Chang K. C. et al., (2014)] studied the effects of N-3-(trimethoxysilyl) propyl aniline (ATMS)–modified silica particles on the physical properties of as-prepared polyaniline-silica composite. After surface treatments, the presence of organic groups occurred, indicating the incorporation of aniline functional groups. The well dispersibility of aniline-modified silica particles in matrix was obtained, and the polyaniline/aniline-modified silica mesoporous exhibited the better thermal stability, thermal insulation properties and mechanical strength, as well as increased the wettability of water droplets.

CHAPTER 3
EXPERIMENTAL

3.1 Chemicals

The chemical agents used in this research are shown in Table 3.1.

Table 3.1 The chemical agents used in this research.

Chemical agents	Company
High ammonia natural rubber (NR) latex (DRC of 60%)	Thai Rubber latex Co., Ltd. (Thailand)
NR (STR 5L)	PAN Innovation Co., Ltd. (Thailand)
Tetraethoxysilane (TEOS)	Sigma-Aldrich Co., Ltd. (USA)
Phenyltriethoxysilane (PhTES)	Sigma-Aldrich Co., Ltd. (USA)
Phenyltrimethoxysilane (PhTMS)	Sigma-Aldrich Co., Ltd. (USA)
3-Mercaptopropyltrimethoxysilane (MpTMS)	Sigma-Aldrich Co., Ltd. (USA)
N-3-(trimethoxysilyl) propyl aniline (ATMS)	Sigma-Aldrich Co., Ltd. (USA)
Absolute ethanol (99.9%)	Qrec chemicals Co., Ltd. (Thailand)
Ammonia solution (28%)	Qrec chemicals Co., Ltd. (Thailand)
Acetone commercials	Ajex chemicals Co., Ltd. (Thailand)
Commercial silica particles (Hisill-255)	PPG-Siam Silica CO., Ltd, (Thailand)
Active zinc oxide (ZnO)	PAN Innovation Co., Ltd. (Thailand)
Steric acid	PAN Innovation Co., Ltd. (Thailand)
Mercaptobenzothiazole disulfide (MBTS)	PAN Innovation Co., Ltd. (Thailand)
Polyethylene glycol (PEG)	PAN Innovation Co., Ltd. (Thailand)
Sulfur	PAN Innovation Co., Ltd. (Thailand)

3.2 Equipments

The equipments used in this research are as follows:

(1) Erlenmeyer flask 100, 250 and 500 ml

(2) Beaker 100, 250, 600 and 1000 ml

(3) Duran bottle 500 and 1000 ml

(4) Hotplate and magnetic stirrer

(5) Pipette 1, 5, 10 and 25 ml

(6) Cylinder 10, 25 and 100 ml

(7) Paper filter no. 5 and 42

(8) Buchner funnel

(9) Suction flask

(10) Glass funnel

(11) Glass plate

(12) Magnetic bar

(13) Parafilm

(14) Aluminium foil

3.3 Procedure

In this research, the modification of silica particles was prepared by a sol-gel process and then the modified silica particles were used as a reinforcement with NR matrix by using 2 method, “latex” and “solid”. The modified silica particles were mixed with NR and curing agent by a two-roll-mill, and vulcanized. Finally, the morphology, mechanical, thermal and dynamic mechanical properties of NR vulcanizates filled with silica particles were investigated. The flow diagram of this research was shown in Figure 3.1.

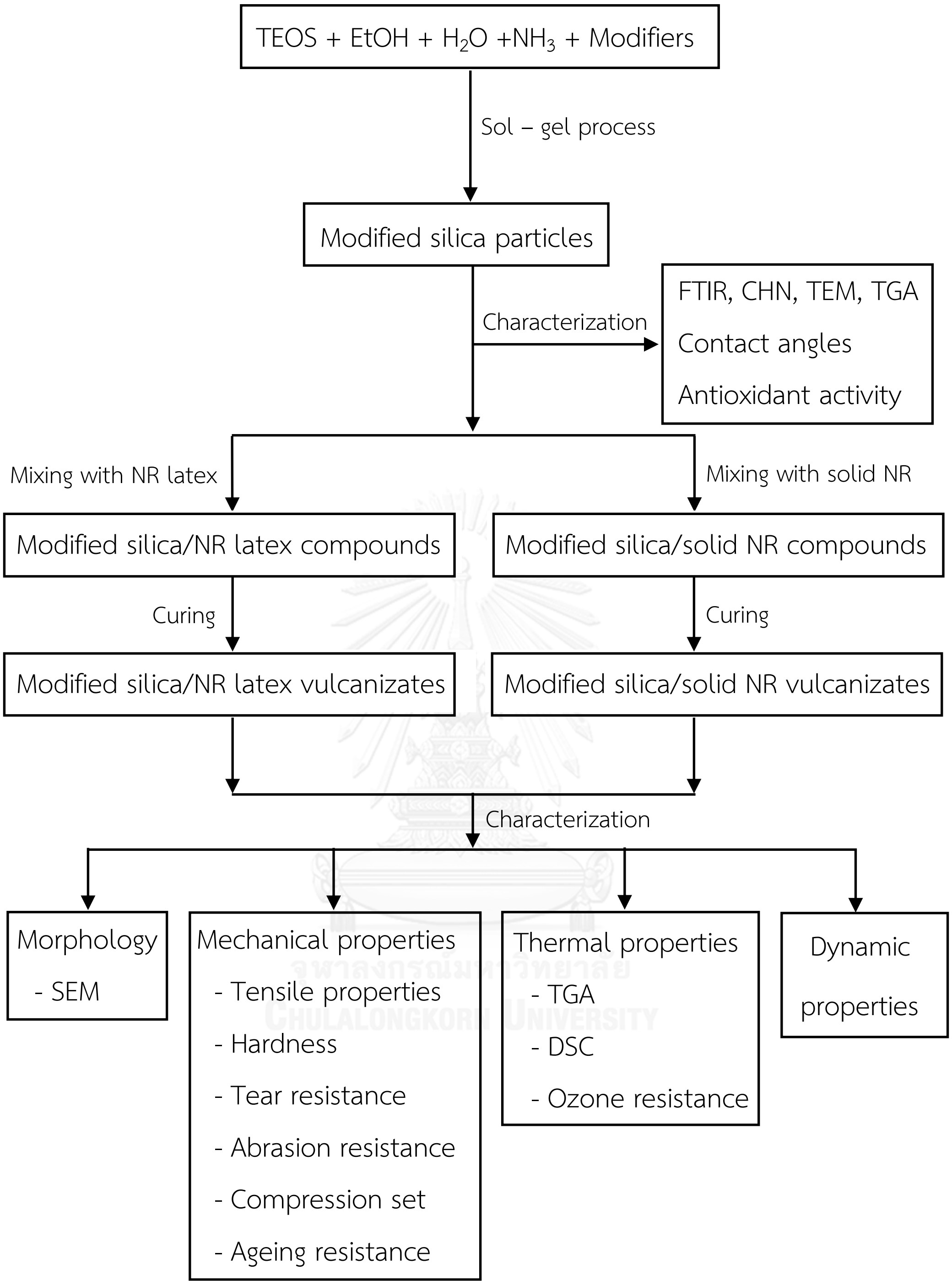


Figure 3.1 Overview procedures.

3.4 Preparation of modified silica particles

The modified silica particles were prepared by mixing two solutions at ambient temperature [Theppradit T. et al., (2014)], which the first solution was added into the second solution under stirring. The first solution was the mixture of 3.0 ml TEOS and 23.0 ml EtOH, and the second solution was the mixture of 1.0 ml 28% ammonia solution, 7.0 ml deionized water and 18.0 ml EtOH, so the total volume of the solution was about 52 ml. After 4 h of reaction, the modifier at various molar ratios (0.04, 0.4, 1.0 and 2.0) was added into the mixture solution, and the reaction was continued for additional 20 h with stirring. Especially, in the case of ATMS, 23.0 ml EtOH were necessary added into the reaction in order to not only decrease the suspension viscosity but also ease for processing sol-gel reaction. For the preparation of unmodified silica particles, the total reaction time was 24 h without the addition of modifier. The silica particles with/without modifier were separated by centrifugation at 5000 rpm for 25 min, then the silica particles were washed by deionized water and dried at 110 °C in an oven until the weight was constant.

The sample labels of the silica particles are as follows; “U-Si” means the unmodified silica particles, “MM-Si” means the modified silica particles by MpTMS, “PhM-Si” means the modified silica particles by PhTMS, “PhE-Si” means the modified silica particles by PhTES, “AM-Si” means the modified silica particles by ATMS, and “C-Si” means the commercial silica as a reference, respectively.

3.5 Characterization of modified silica particles

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups on the silica surface were confirmed by FTIR (Spectrum One, PerkinElmer, USA) (Figure 3.2 (a)). The samples were prepared in a KBr disk under high pressure. The FTIR spectra were recorded in ranges of 4000 to 400 cm^{-1} with resolution of 4 cm^{-1}.

3.5.2 CHN analysis

The contents of carbon, hydrogen and nitrogen on the silica surface were confirmed by CHNS/O analyzer (PE-2400, PerkinElmer, USA) (Figure 3.2 (b)). The samples of 2-3 mg were added into tin capsules, and then burnt in pyrolysis reactor at temperature of 1000 °C under a constant flow helium steam. The mixing combustion was separated by chromatographic column and detected with thermo conductivity detector.

3.5.3 Contact angles measurement

The hydrophobicity of modified silica particles was observed by a Ramé-hart instrument (USA) (Figure 3.3 (a)) at ambient temperature. The samples were prepared by sticking the dispersed modified silica particles on the glass plate with adhesive type. Then, the deionized water was place on the surface of samples, and the average contact angle values were obtained by measuring the same sample at five different positions.

3.5.4 Transmission Electron Microscopy (TEM)

The morphology of modified silica particles was studied by TEM (JEOL, JEM-2100, Japan) (Figure 3.3 (b)) operating at 80 kV. The modified silica particles were suspended in ethanol and then dropped onto a copper grid to dry at room temperature.

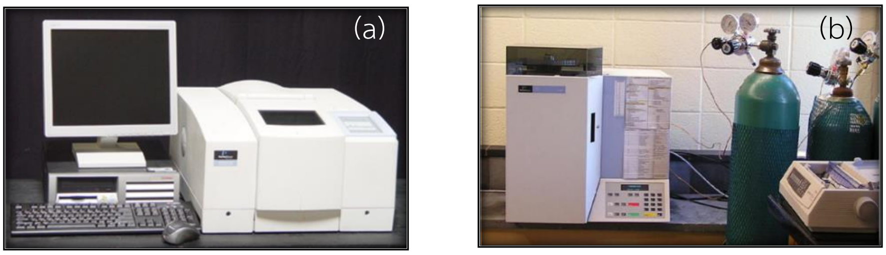


Figure 3.2 (a) Fourier transform infrared spectrometer and (b) CHNS/O analyzer, respectively.

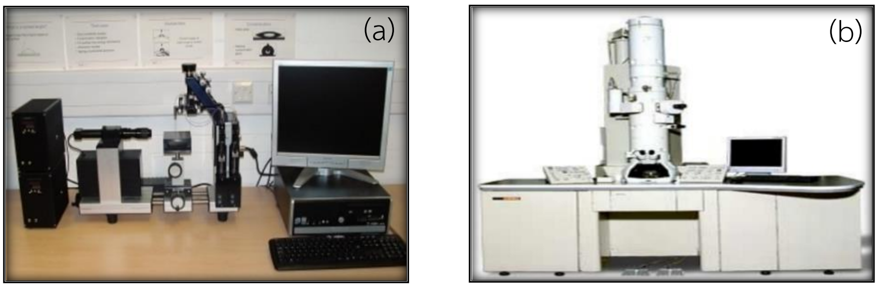


Figure 3.3 (a) Ramé-hart instrument and (b) Transmission electron microscope, respectively.

3.5.5 The antioxidant activity by DPPH method

The antioxidant activity of modified silica particles was measured by 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method. The suspension of samples was spotted by capillary tube onto TLC plate and dried at room temperature, after that DPPH solution was sprayed onto TLC plate. The antioxidant activity was observed by color change of DPPH solution from violet to yellow within five minutes.

3.5.6 Thermogravimetric analysis (TGA)

The thermal stability of modified silica particles was carried out by a TG/DTA Perkin-Elmer Pyris Diamond (USA) (Figure 3.4). The samples of 10 mg were placed in a platinum pan and heated from ambient temperature up to 1000 °C under nitrogen with a heating rate of 10 °C/min.

Figure 3.4 Thermogravimetric analyzer.

3.6 Preparation of NR vulcanizates

In the case of using NR latex, 100 phr of NR latex (based on the DRC of 60%) were mixed with silica particles (10 and 20 phr) under stirring until the ingredient was homogenously dispersed. NR suspension was then precipitated by acetone and dried at 40 °C in a vacuum oven until the weight was constant. The obtained rubber filled silica particles was mixed with curing agents by a two-roll mill at ambient temperature. In the case of using solid rubber, 100 phr of NR (STR 5L) were mixed with silica particles (20 phr) and curing agents on a two-roll mill at ambient temperature. The formulations for rubber compounding are as follows: 5 phr zinc oxide, 2 phr stearic acid, 3 phr sulfur, 1.8 phr MBTS and 0.33 phr PEG based on silica content, respectively.

The cure characteristics of NR compounds were determined by using a Moving Die Rheometer (TECHPRO rheotech MD+) at 150 °C according to ASTM D5289. Subsequently, NR vulcanizates were performed by compression molding at the pressure of 150 kg/m^2 under the temperature of 150 °C with the optimum cure time (tc_{90}).

The sample code used in this study are as follows: “L” and “S” mean the NR vulcanizates prepared by latex and solid rubbers, respectively. The unfilled NR vulcanizates were represented by “LNR and SNR”. “U” and “C” mean the NR vulcanizates filled with U-Si particles and C-Si particles, respectively, “MM” means the NR vulcanizates filled with MM-Si particles, “PhM” means the NR vulcanizates filled with PhM-Si particles, “PhE” means the NR vulcanizates filled with PhE-Si particles, “AM” means the NR vulcanizates filled with AM-Si particles. The silica contents in a part by weight per hundred part of rubber (phr) were designed by the number after the sample code.

3.7 Measurements of NR vulcanizates

3.7.1 Morphology

The morphology of NR vulcanizates filled with/without modified silica particles was studied by SEM (JEOL, JSM-6480LV, Japan) operating at 15 kV. The fracture surfaces after the tensile testing were cut and stitched on a SEM stub and then sputter-coated with gold before SEM analysis.

3.7.2 Swelling ratio

The swelling ratio of NR vulcanizates filled with/without modified silica particles was determined according to ASTM D471. The specimens were cut into the sized of 20 × 20 × 2 mm and immersed in toluene until they reached equilibrium within 7 days at ambient temperature. Then, the specimens were taken out and surface liquid was rapidly removed by blotting with filter paper [Chaichua B. et al., (2009)]. The swelling ratio of the polymer (Q) was calculated according to Eq. (3.1):

$$Q = \frac{W_2 - W_1}{W_1} \tag{3.1}$$

where W_1 and W_2 are the weights of the specimen before swelling after immersion (g), respectively.

3.7.3 Crosslinking density

The crosslink density of NR vulcanizates filled with/without modified silica particles can be calculated by Flory-Rehner equation [Satraphana P. et al., (2009)], as seen in Eq. (3.2):

$$\eta_c = \frac{-\ln(1-V_r) - V_r - \chi V_r^2}{\left(V_s V_r^{\frac{1}{3}}\right) - \left(\frac{2V_s V_r}{f}\right)} \tag{3.2}$$

where η_c is the crosslink density of the rubber (mol/cm^3), V_s is the molar volume of the toluene (106.2 cm^3/mol), χ is the NR-toluene interaction parameter (χ = 0.3795), V_r is the volume fraction of rubber in the swollen gel, which was calculated based on Eq. (3.3) and f is the functionality of the crosslinks for the sulfur curing system (f = 4) [Satraphana P. et al., (2009)].

$$V_r = \frac{\left(\frac{W_1}{\rho_r} - \frac{W_\mathrm{f}}{\rho_\mathrm{f}}\right)}{\left(\frac{W_1}{\rho_r} - \frac{W_\mathrm{f}}{\rho_\mathrm{f}}\right) + \left(\frac{W_2 - W_1}{\rho_s}\right)} \tag{3.3}$$

where W_1 and W_2 are the weights of the specimen before swelling after immersion (g), respectively. W_f is the weight of filler in the rubber vulcanizates (g), ρ_r is the density of the composite materials (g/cm^3), ρ_f is the density of silica particles from sol–gel reaction (1.92 g/cm^3), and ρ_s is the density of toluene (0.862 g/cm^3) [Satraphana P. et al., (2009)].

3.7.4 Bound rubber content

The filler to rubber interaction of NR vulcanizates filled with/without modified silica particles was determined by the bound rubber content based on the gravimetric method. 1 g of specimen of rubber filled with/without silica particles was immersed in toluene 80 ml for a total of 7 days at ambient temperature. After that, the rubber gel was filtered out by glass funnel, and then rubber gel was dried in an oven for 1 day at 80 °C [Chokanandsombat Y. et al., (2012)]. The percentage of bound rubber contents can be calculated from Eq. (3.4):

$$R_B = \frac{W_{fg} - W\left[\frac{m_f}{m_f + m_p}\right]}{W\left[\frac{m_p}{m_f + m_p}\right]} \times 100 \tag{3.4}$$

where W_{fg} is the weight of filler-rubber gel (g), W is the weight of test specimen before immersion (g), m_f is the weight of filler in the rubber filled with silica particles (g) and m_p is the weight of rubber in the rubber filled with silica particles (g) [Chokanandsombat Y. et al., (2012)].

3.7.5 Tensile properties

A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded, which tensile properties indicate that the material will react to forces being applied in tension load to vulcanized rubber. Tensile properties start with preparation and measurement of the specimens for testing, which covered are test the tensile stress, tensile strength and elongation at break. Specimens may be in the shape of dumbbells (Figure 3.5).

The tensile properties of NR vulcanizates filled with/without modified silica particles were measured using an Universal Testing Machine (INSTRON 3366, USA) according to ASTM D412 at ambient temperature (28±2 °C) and a crosshead speed of 500 mm/min with load cell of 1 kN. The specimens were cut by a die C into the dumbbell shape, and thickness of specimen was 2.0 mm. At least five specimens were tested and the average value ±SD was reported.

The tensile strength and elongation (at any degree of extension) can be calculated [Ciesielski A., (2000)], as follows to Eqs. (3.5) and (3.6), respectively:

$$TS = \frac{F_{(BE)}}{A} \tag{3.5}$$

where TS is the tensile strength (MPa), $F_{(BE)}$ is the force magnitude at rupture (N) and A is the cross-sectional area of unstrained specimen (m^2)

$$E = \frac{L - L_0}{L_0} \times 100 \tag{3.6}$$

where E is the elongation in percent (of original bench mark distance), L is the observed distance between bench marks on the extended specimen (mm) and L_0 is the original distance between bench marks (mm).

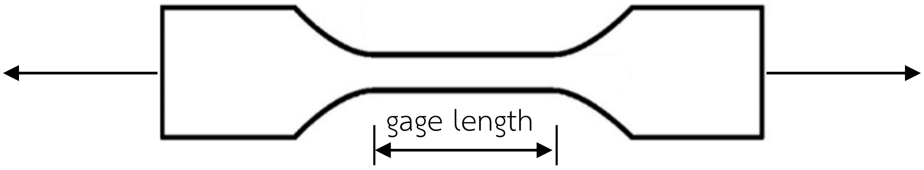


Figure 3.5 Dumbbell shape for tensile test.

3.7.6 Hardness

Hardness value is defined as the resistance that a rubber surface offers against penetration by an indenter, and relates to the deformation of the rubber surface [Tangudom P. et al., (2013)]. Hardness measurement based on either initial indentation or indentation after a specified period of time, or both which the durometer is commonly instrument for testing hardness of rubber vulcanizates [Ciesielski A., (2000)].

The hardness of NR vulcanizates filled with/without modified silica particles was carried out by following ASTM D2240 at ambient temperature (28±2 °C) using a Shore A (Figure 3.6 (a)) hardness tester (WALLACE, UK). The surface of the specimens was flat and parallel over an area to permit the presser foot to contact the specimen over an area having a radius of at least 6.0 mm from the indentor point. The five hardness values were average from contacting of specimen after five seconds of test.

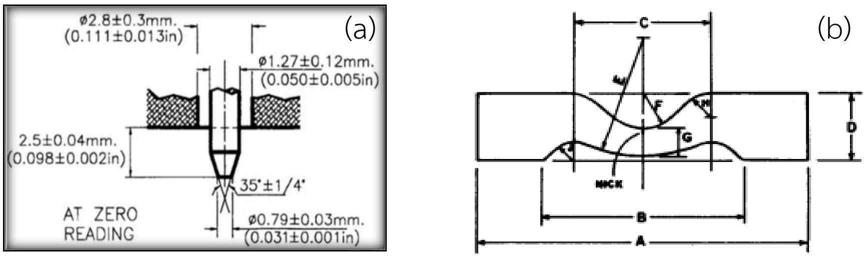


Figure 3.6 (a) Shore A for hardness test and (b) Die B for tear strength test, respectively.

3.7.7 Tear resistance

The tear of rubber is a mechanical rupture process initiated and propagated at a site of high stress concentration caused a cut, defect, or localized, which define the different technique for measuring the resistance to tear according to ASTM D624 [Dick J. S., (2009)]. In this study, the standard test pieces are designed as die B, as shown in Figure 3.6 (b) The force acts on the test piece in a direction substantially parallel to the tab ends of the specimen (45° to the 90° center angle) in the direction of grip separation.

The tear resistance of NR vulcanizates filled with/without modified silica particles was measured using an Universal Testing Machine (INSTRON 5566, USA). The specimens for tear test were cut from the rubber vulcanized sheets using die B at ambient temperature (28±2 °C). Its thickness was measured at three place across the width, near the center by using a micrometer before testing, and a crosshead speed of 500 mm/min with load cell of 1 kN. The average values of five measurements were reported. The tear strength can be calculated as Eq. (3.7):

$$T_s = \frac{F}{d} \tag{3.7}$$

where T_S is the tear strength (kN/m), F is the maximum force (N) and d is the median thickness of each specimen (mm).

3.7.8 Abrasion resistance

Abrasion resistance is one of the most important properties of a rubber compound, which must reliant the many properties including the materials resilience, modulus, tear strength and hardness [Dick J. S., (2009)]. Abrasion resistance is the ability of material to bear the force action such as rubbing or scraping [Tabsan N. et al., (2010)], which is usually thought of in terms of volume loss that can be defined as the loss of material that results from mechanical action on a rubber surface. The abrasion resistance of NR vulcanizates filled with/without modified silica particles was carried out according to DIN 53516 using the DIN abrasion tester (ZWICK, UK) (Figure 3.7 (a)). The specimens were in cylinder shape having diameter of 16 mm and height of 6 mm. The force of 12.5 N was used to compress the specimen and abrasion speed was 0.32 m/s. The specimens were weighted before and after testing. Volume loss (mm^3) of the specimen was calculated following the Eq. (3.8):

$$Volume\ loss = \frac{(W_S \times 200)}{(W_r \times D_S)} \times 100 \qquad (3.8)$$

where W_s is the weight loss of the specimen (g), W_r is the weight loss of the standard rubber (g) and D_s is the density of the specimen (g/cm^3).

3.7.9 Compression set

Compression set tests are intended to measure the ability of rubber compounds to retain elastic properties after prolonged action of compressive stress at a constant strain. A test specimen is compressed to either a deflection or by a specified force and maintained under this condition at specified time and temperature [Pal K. et al., (2009)].

In this study, the compression set of NR vulcanizates filled with/without modified silica particles was measured according to ASTM D395 Method B (CEAST 6425/006) (Figure 3.7 (b)). The specimens were prepared as a cylinder shape having 6 mm of thickness. Then, the specimens were pressed at 25% strain and placed in oven at 70 °C for 22 h. When the time was ripe, the specimens were cooled to room temperature and the deformation of a test specimens was measured 30 min after removal from a suitable compression device. After the measurement of residual deformation, the compression set can be calculated according to Eq. (3.9):

$$C_B = \frac{t_0 - t_i}{t_0 - t_n} \times 100 \tag{3.9}$$

where C_B is the compression set (Test Method B) in percentage of the original deflection, t_0 is the original thickness of specimen (mm) and t_i is the final thickness of specimen (mm) and t_n is the thickness of spacer bar (mm).

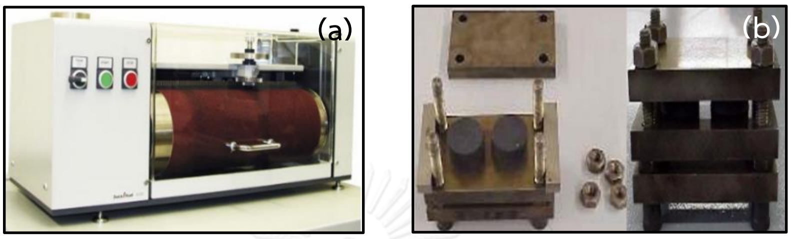


Figure 3.7 (a) DIN abrasion tester and (b) Compression set device method B, respectively.

3.7.10 Thermal ageing resistance

Thermal ageing testing is a procedure to determine the effect of elevated temperatures on the physical properties of vulcanized rubber, which testing is performed for a specified period and temperature [Dick J. S., (2009)]. This test method indicated that rubber product must resist the deterioration of physical properties with time caused by oxidative and thermal ageing. The specimen are exposed to the deteriorating air at specified elevated temperatures, which physical properties are changed. Therefore, these properties were compared with the properties determined on the original specimens according to test method D 412.

The thermal ageing resistance of NR vulcanizates filled with/without modified silica particles was measured according to ASTM D573. The specimens were prepared as a dumbbell shape in test method of tensile properties, and aged in an air circulating oven at 100 °C for 22 h, then cooled at room temperature for at least 18 h before testing [Prasertsri S. et al., (2012)]. The tensile properties (modulus, tensile strength and elongation at break) of aged specimens were considered in the same as the unaged specimens, and a least three specimens must be used to determine the original physical properties of each sample. The calculation of tensile retention from thermal ageing test was calculated based on Eq. (3.10):

$$Tensile\ retention\ (\%) = \frac{TS_{aged}}{TS_{unaged}} \times 100 \tag{3.10}$$

where TS_{unaged} and TS_{aged} are tensile strength of unaged and aged specimens (MPa), respectively.

3.7.11 Thermal stability

3.7.11.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out by a TG/DTA Perkin Elmer Pyris Diamond to analyze the thermal stability of NR vulcanizates filled with/without modified silica particles. The samples of 10 mg were placed in a platinum pan and heated from room temperature up to 1000 °C at a constant heating rate of10 °C/min with a flow rate of nitrogen gas of 50 ml/min. The thermal stability could be explained by the initial temperature of decomposition (T_{id}), the temperature of maximum weight loss (T_{max}), and activation energy of decomposition (E_t). The activation energy was calculated by the integral method of Horowiiz and Metzger [Chaichua B. et al., (2009)], using Eqs. (3.11) and (3.12):

$$ln\left[ln\left(\frac{1}{1-\alpha}\right)\right] = \frac{E_t\ \theta}{RT_{max}^2} \tag{3.11}$$

$$\alpha = \frac{(W_i - W)}{(W_i - W_f)} \tag{3.12}$$

where α is the decomposed fraction, W is the weight at chosen temperature (mg), W_i is the weight at initial temperature (mg), W_f is the weight at final temperature (mg), R is the gas constant, and θ is given by $T\text{-}T_{max}$: T is chosen temperature and T_{max} is temperature of maximum weight loss.

3.7.11.2 Differential scanning calorimetry (DSC)

Glass transition temperature (T_g) of NR vulcanizates filled with/without modified silica particles was performed using a differential scanning calorimeter (Mettler Toledo, 822^e, Switzerland) (Figure 3.8 (a)). The samples of 10 mg were planced in aluminum pan and cooled to -100 °C under a nitrogen atmosphere, and heated up to 150 °C with the scan rate of 20 °C /min.

3.7.12 Ozone resistance

This test method is used to estimate the effect of exposure, under surface tensile strain conditions, either dynamic or static, in atmosphere containing specified levels of ozone concentration. The test is carried out to measure the ozone cracking which takes place when specified strain is imposed on vulcanized rubber. The significance of these test methods lies in the ability to differentiate between the degree of ozone resistance, which judged by the appearance and magnitude of the formation of cracks in the surface of materials [Dick J. S., (2009)]. Generally, test pieces are usually placed under a less degree of tension e.g. by bending around a mandrel or stretching under conditions to a controlled atmosphere containing ozone, and the cracks are recorded by standard photographs.

The ozone resistance of NR vulcanizates filled with/without modified silica particles was followed the physical testing standard methods of rubber according to Japanese Industrial Standard (JIS) K 6259. The specimens were stretched by 20% using a sample holder for 48 h period in a light ozone-free atmosphere [Poompradub S. et al., (2011)] The specimens were exposed in an ozone atmosphere of 50 pphm (part per hundred million) at 40 °C in an ozone cabinet (TOYOSEIKI, JAPAN).

3.7.13 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis, which are the storage modulus (E'), loss modulus (E") and loss tangent (tan δ), as a function of temperature were investigated by using a dynamic mechanical analyzer (Mettler Toledo, 816e, Switzerland) (Figure 3.8 (b)). The specimens were cut in a shape having its thickness of 2.00 mm, width of 8.00 mm and length of 6.00 mm, respectively. The tests were performed in tension mode at a constant frequency of 10 Hz, a strain of 0.1% and a temperature range of -80 ^{o}C to 100 ^{o}C with the scan rate of 2 ^{o}C/m under a nitrogen atmosphere.

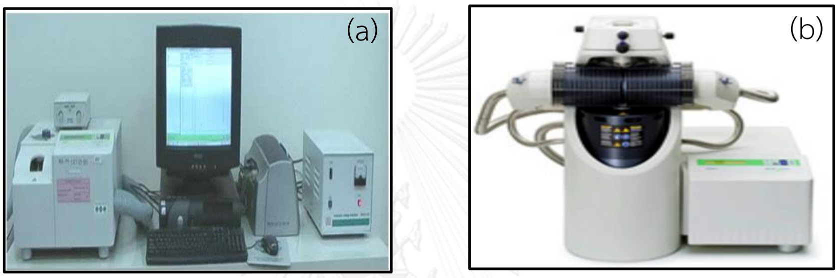


Figure 3.8 (a) Differential scanning calorimeter and (b) Dynamic mechanical analyzer, respectively.

CHAPTER 4

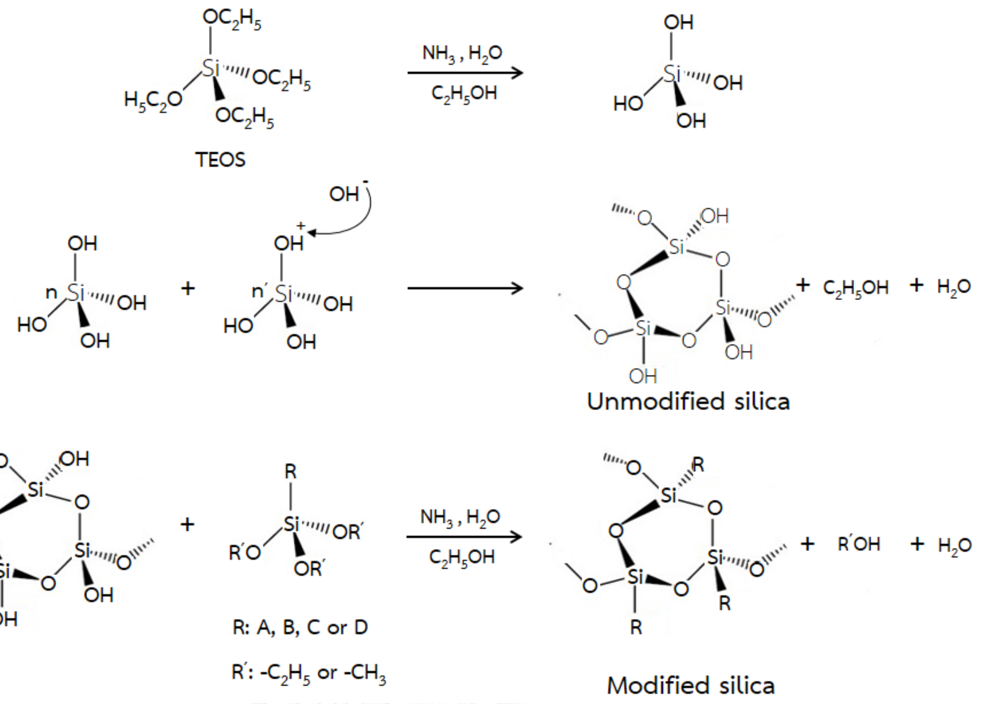
RESULTS AND DISCUSSION

4.1 Modification of the silica particles

4.1.1 Reactions of the modified silica particles

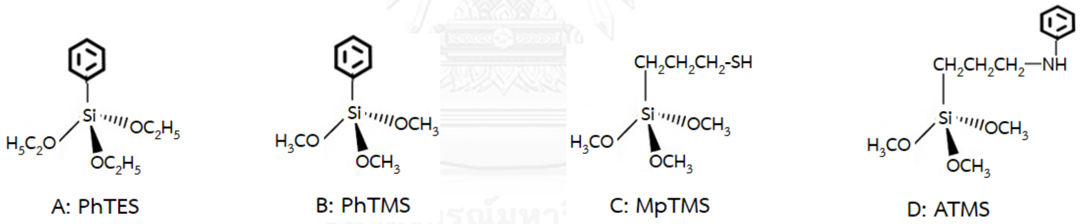
The proposed mechanism for modification of silica particles by sol-gel process was shown in Figure 4.1. Initially, TEOS is hydrolyzed in ethanol and ammonia solution as a catalyst to generate the silanol groups (Si-OH) on the silica surface. The hydroxide anions (OH^-) played a role of catalyst for condensation step. This step is leading to the formation of Si-O-Si groups, which their form the silica networks to produce silica particles [Al-Oweini R. et al., (2009)]. The modification of silica surface was achieved by co-condensation of TEOS with various types of organic groups of organoalkoxysilanes which was phenyl, mercapto and amine groups. After 4 h of sol – gel reaction, the modifier (MpTMS, PhTMS, PhTES or ATMS) was added into the reaction. The alkoxy groups of each modifier were readily hydrolyzed and reacted with silanol groups on the silica surface, while the organic groups of modifier were expected to exist on the silica surface [Theppradit T. et al., (2014)].

(a)



(b)

Structure of modifier



Structure of modified silica particles

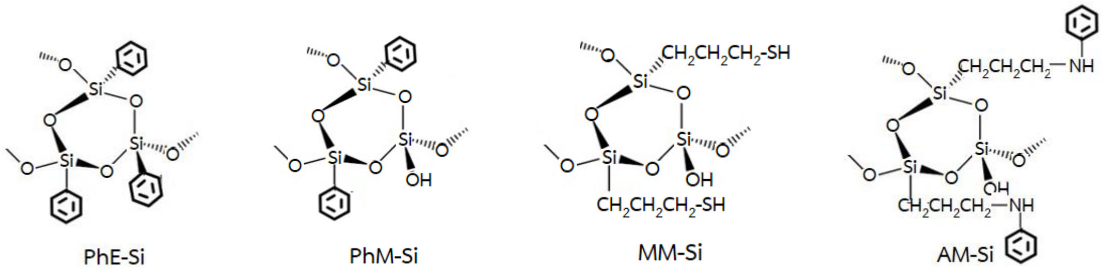


Figure 4.1 (a) Modification of the silica particles, and (b) structure of each modifier and modified silica particles.

4.1.2 Effect of the reaction time

In this study, the reaction temperature for synthesis silica particles via a sol – gel process was carried at ambient temperature. Figure 4.2 shows the effect of time on synthesized unmodified silica particles (U-Si). The increasing reaction time resulted the increasing yield for produced silica particles and the percentage of silica yield became constant (96%) at the reaction time of 24 h. Accordingly, the optimum condition for the synthesized silica particles was the reaction time of 24 h at ambient temperature by using basic catalyst as ammonia solution in order to save time and energy.

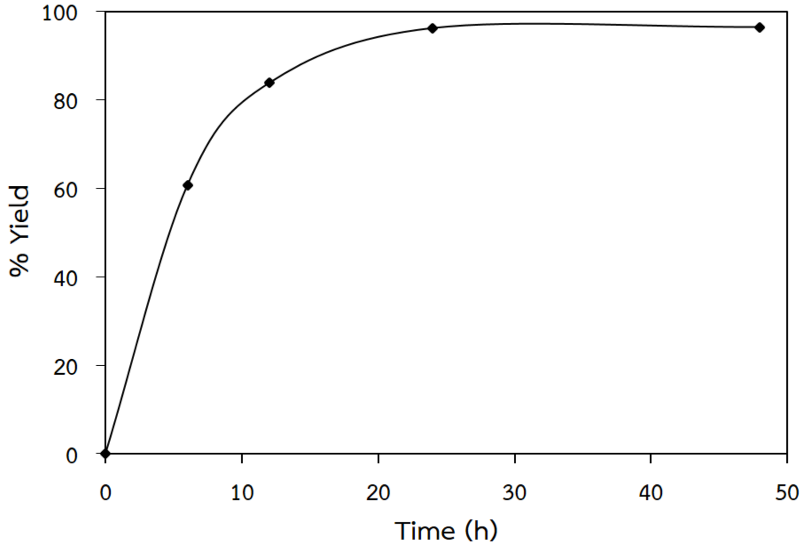


Figure 4.2 Effect of reaction time on % yield of unmodified silica particles.

4.1.3 Effect of the molar ratio of modifier to TEOS

Figure 4.3, Figure 4.4, Figure 4.5 and Figure 4.6 show the FTIR spectra of modified silica particles by MpTMS (MM-Si), PhTMS (PhM-Si), PhTES (PhE-Si) and ATMS (AM-Si) at various molar ratios of modifier to TEOS. The molar ratio was varied as follows: 0.04, 0.4, 1.0 and 2.0. As seen the FTIR spectra of MM-Si particles, the absorption bands of C-H stretching and Si-C stretching appeared at 2950 and 690 cm^{-1}. In the case of PhTMS and PhTES as modifier, the peak of C-H stretching, C-H bending, Si-C stretching and aromatic ring at 2997, 1431, 739 and 697 cm^{-1} were observed, while by using ATMS, the peaks at 1605, 1507 and 697 cm^{-1} were attributed to the C=N stretching, C=C stretching and aromatic ring, respectively. However, the absorption band of Si-OH stretching at 948 cm^{-1} tended to be decreased due to the substitution by organic groups of modifier, and the presence of each peak intensity increased with increasing molar ratios of modifier to TEOS. It can be seen that the each peak at molar ratio of modifier to TEOS of 0.04 showed the low transmittance, while at molar ratio of modifier to TEOS of 0.4, all absorption peaks was obviously observed. Accordingly, the condition at molar ratio of modifier to TEOS of 0.4 was chosen for the modification of silica surface.

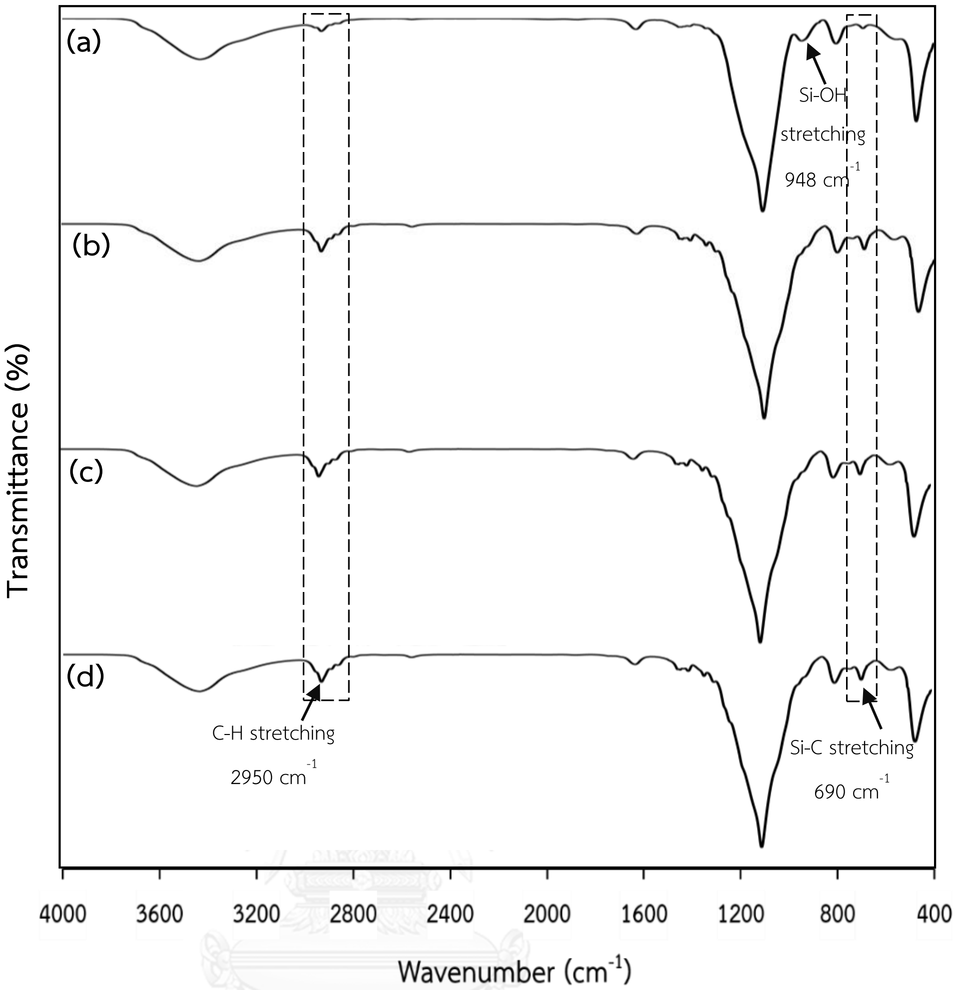


Figure 4.3 FTIR spectra of MM-Si at various molar ratios of MpTMS to TEOS: (a) 0.04, (b) 0.4, (c) 1.0 and (d) 2.0, respectively

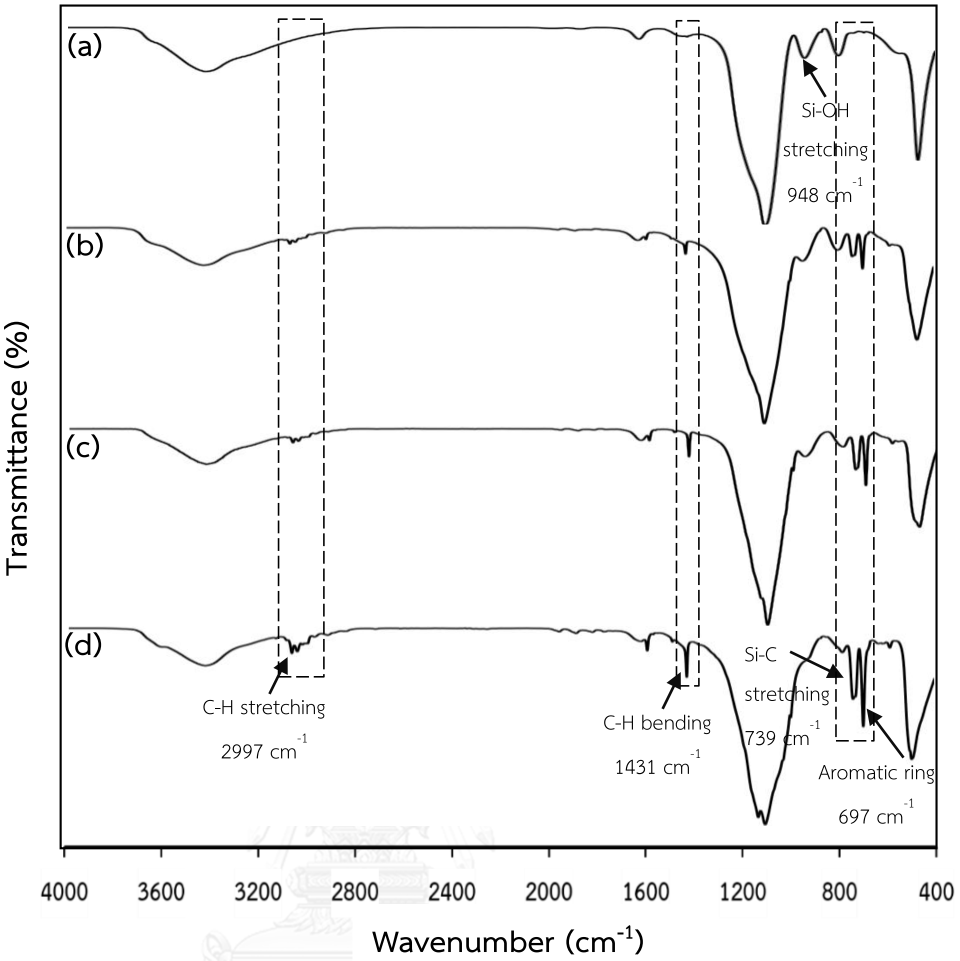


Figure 4.4 FTIR spectra of PhM-Si at various molar ratios of PhTMS to TEOS: (a) 0.04, (b) 0.4, (c) 1.0 and (d) 2.0, respectively.

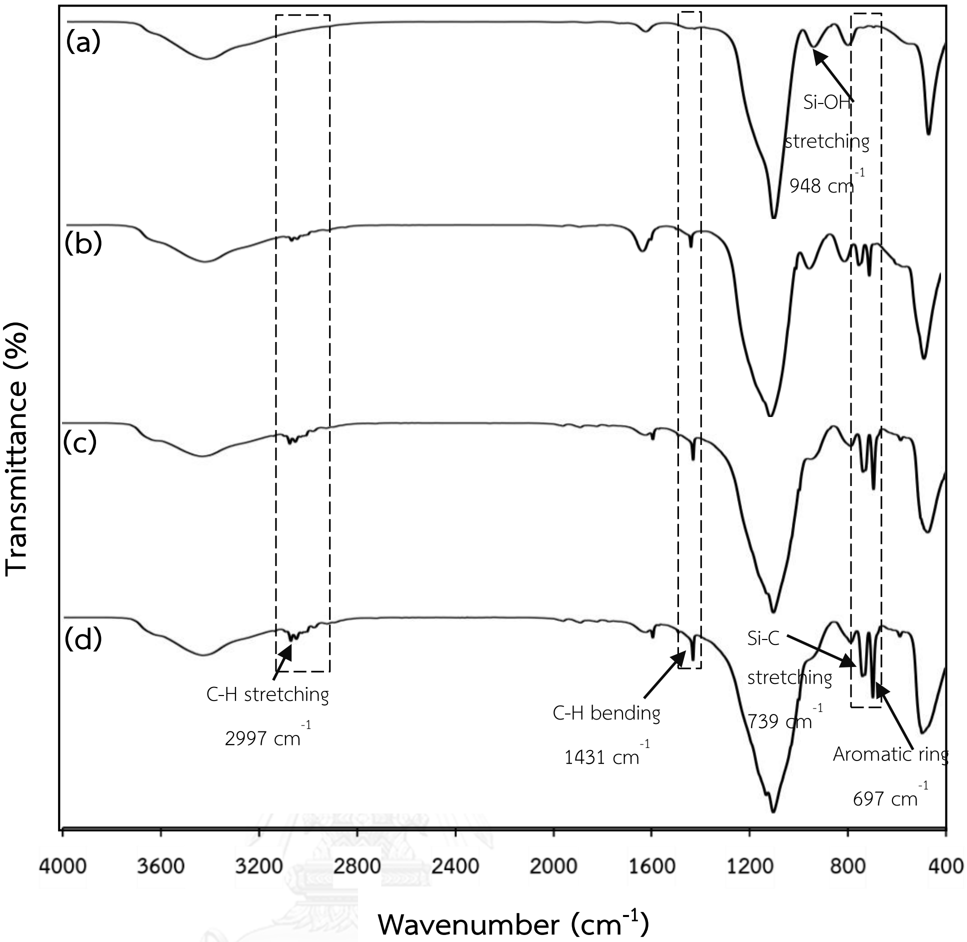


Figure 4.5 FTIR spectra of PhE-Si at various molar ratios of PhTES to TEOS: (a) 0.04, (b) 0.4, (c) 1.0 and (d) 2.0, respectively.

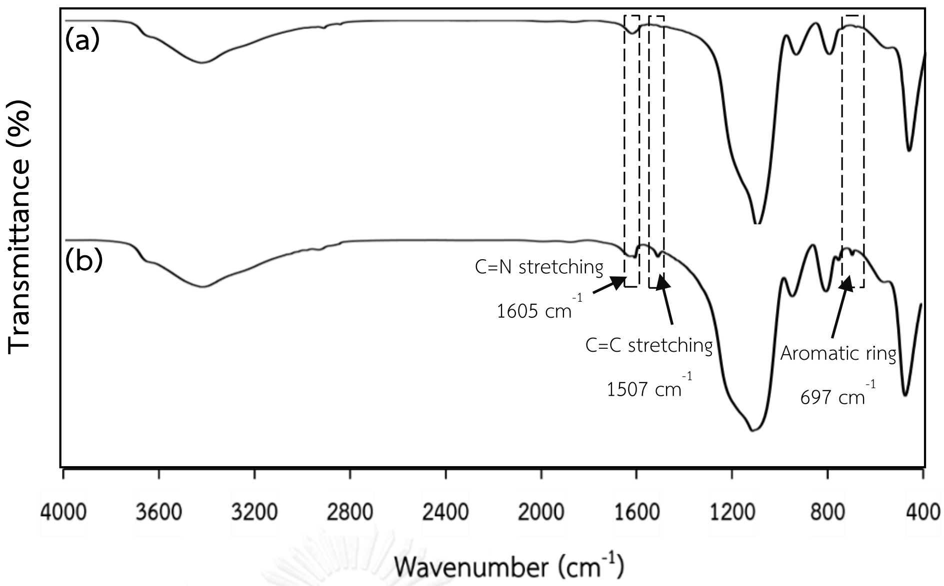


Figure 4.6 FTIR spectra of AM-Si at various molar ratios of ATMS to TEOS: (a) 0.04 and (b) 0.4, respectively.

4.2 Characterization of the modified silica particles

4.2.1 FTIR spectra of modified silica particles

The FTIR spectra of the unmodified or modified silica particles compared to commercial silica (C-Si) were shown in Figure 4.7. The FTIR spectra of C-Si and U-Si (Figure 4.7 (a) and Figure 4.7 (b)) revealed that the absorption band at 3434 cm^{-1} was corresponding to the overlapping of the O-H stretching of hydrogen-bonded in water molecules and the SiO-H stretching of surface silanol groups hydrogen-bonded to molecular water [Al-Oweini R. et al., (2009)]. The O-H bending of O-H groups appeared at 1631 cm^{-1} and the peak at 948 cm^{-1} was represented the Si-O in-plane stretching of silanol groups [Al-Oweini R. et al., (2009)]. The adsorption of water molecules on the surface was due to the existence of silanol groups and therefore to the hydrophilic nature of silica surface. The absorption bands appeared at 1107 and 802 cm^{-1} were attributed to the Si-O asymmetric and symmetric stretching of Si-O-Si bond, respectively [Rublo F. et al., (1997)]. The Si-O-Si bending of Si-O-Si bond appeared at 471 cm^{-1}, which was directly related to the existence of densed silica networks, and the oxygen atoms played the role of bridges between each silicon site [Al-Oweini R. et al., (2009)]. Additionally, it is clearly observed that the peak area of Si-O in-plane stretching at 948 cm^{-1} in case of C-Si (4.23 Area•cm^{-3}) was higher than that of U-S (3.75 Area•cm^{-3}) due to the high contents of silanol groups on the silica surface [Kohjiya S. et al., (2005)].

After modification by MpTMS (MM-Si) (Figure 4.7 (c)), the absorption bands due to the C-H stretching and bending of chain methylene ($-CH_2-$) groups were appeared at 2950 and 1431 cm^{-1}, respectively, and the S-H stretching of thiol group (-SH) was appeared at 2560 cm^{-1} [Štandeker S. et al., (2011)]. Moreover, the adsorption band at 690 cm^{-1} was corresponding to the Si-C stretching of the functional group containing the thiol group [Hernandez G. et al., (1999)].

In the case of PhM-Si and PhE-Si as seen in Figure 4.7 (d) and Figure 4.7 (e), the C-H stretching and C=C in-plane stretching of phenyl group were appeared at 2997 and 1595 cm^{-1}, respectively [Moriones P. et al., (2011)]. The band at 1431 cm^{-1} was attributed to the combination of two vibrations: the phenyl C=C stretching and C-H bending of phenyl group [Al-Oweini R. et al., (2009)]. The absorption bands at 697 and 739 cm^{-1} were corresponded to the aromatic ring vibration [Al-Oweini R. et al., (2009)] and Si-C stretching of phenyl group [Purcar V. et al., (2012)], respectively. Finally, by using ATMS (AM-Si) (Figure 4.7 (f)), the N-H stretching of N-H bond [Subramani S. et al., (2004)] and the C-H stretching vibration of -CH_2 groups [Štandeker S. et al., (2011)] were appeared at 3675 and 2981 cm^{-1}. The characteristic peaks of aniline groups appearing at 1605 and 1507 cm^{-1} were assigned to the stretching of C=N and C=C, corresponding to the quinone - and aromatic ring vibrations [Chang K. C. et al., (2014)]. Additionally, the peak at 697 cm^{-1} was corresponding to the aromatic ring vibration. It is clearly seen that for all modified silica particles, the peak at 948 cm^{-1} seemed to be weakened due to the substitution of silanol groups by organic groups of each modifier. Accordingly, the modified silica particles were successfully prepared by sol-gel process.

4.2.2 Elemental analysis of the silica surface

Table 4.1 shows the result of elemental analysis of unmodified and modified silica particles by CHN analyzer. The U-Si found only hydrogen content due to the silanol groups on surface which could be absorbed the moisture. After the modified silica surface, the contents of organic groups coated on the silica surface containing the carbon, hydrogen or nitrogen were appeared and depending on the chemical structure for each modifier.

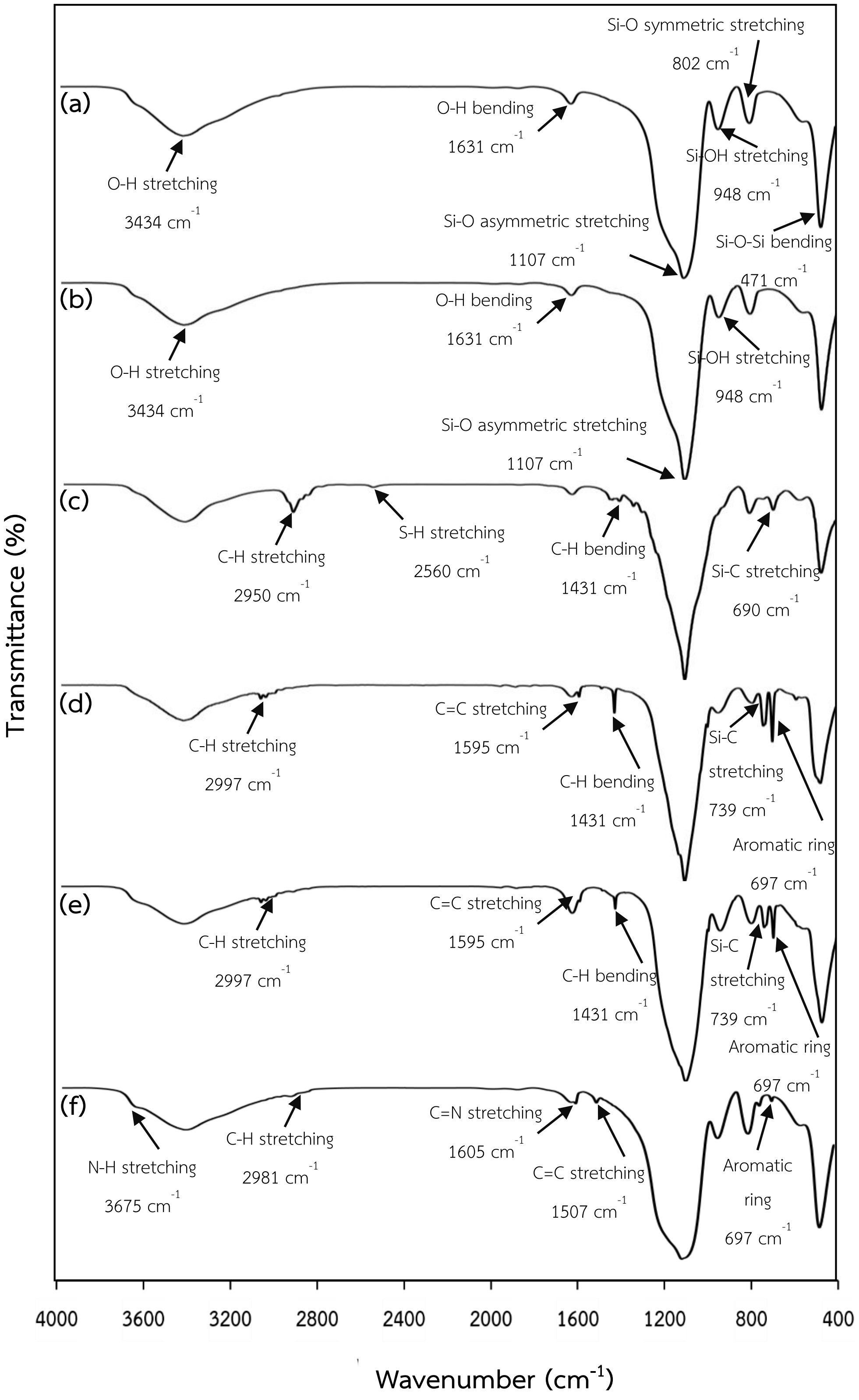


Figure 4.7 FTIR spectra of (a) C-Si, (b) U-Si, (c) MM-Si, (d) PhM-Si, (e) PhE-Si and (f) AM-Si.

Table 4.1 CHN analysis of silica particles.

Sample code	% Carbon	% Hydrogen	% Nitrogen
U-Si[1]	0.00	1.06	0.00
MM-Si[2]	7.32	1.42	0.00
PhM-Si[3]	17.81	1.24	0.00
PhE-Si[4]	17.26	1.20	0.00
AM-Si[5]	11.58	1.29	1.41

[1]unmodified silica particles, [2]modified silica particles with MpTMS, [3]modified silica particles with PhTMS, [4]modified silica particles with PhTES, [5]modified silica particles with ATMS.

4.2.3 Hydrophobicity of the silica surface

The hydrophobicity of unmodified and modified silica particles was anticipated by the contact angle of water droplet on the surface as shown in Table 4.2. The contact angle of U-Si could not be measured because the large number of silanol groups presented on the silica surface which were the major sources of hydrophilicity as they promote the water adsorption [Hegde N. D. et al., (2006)]. After surface modification, the contact angle of modified silica particles could be determined due to the decrease of polarity on the silica surface. The hydrophobicity of MM-Si, PhM-Si and PhE-Si was almost comparable, while the hydrophilicity was significantly increased in the case of AM-Si due to the presence of amine group. Accordingly, the modified silica particles may improve the compatibility NR matrix and silica particles.

Table 4.2 Contact angle and average particles size of silica particles.

Sample code	Contact angle (°)	Average particles size (nm)
U-Si	N/A	200±0.05
MM-Si	131 ± 0.84	227±0.12
PhM-Si	132 ± 1.0	265±0.08
PhE-Si	134 ± 0.4	282±0.07
AM-Si	93 ± 0.4	298±0.12

4.2.4 Morphology of the modified silica particles

TEM micrographs of the unmodified and modified silica particles were shown in Figure 4.8. The silica particles were in a spherical shape with uniform size and shape. It is clearly seen that the modified silica particles were covered by thin film on the silica surface. The average particle size of U-Si, MM-Si, PhM-Si, PhE-Si and AM-Si was summarized in Table 4.2. The particle size of modified silica tend to be increased with increasing the molecular weight of substituted groups for each modifier; the substituted groups for MpTMS ($-CH_2CH_2CH_2SH$ = 75 g/mole), PhTMS and PhTES ($-C_6H_5$ = 77 g/mole), ATMS ($-CH_2CH_2CH_2-NH-C_6H_5$ = 134 g/mole). The U-Si particles (Figure 4.8 (a)) were intensively fused into aggregates due to the presence of silanol groups on the silica surface, while the high dispersion of modified silica particles (Figure 4.8 (b), Figure 4.8 (c) and Figure 4.8 (d)) could be observed owing to the presence of non-polar groups on the silica surface leading to the increase of hydrophobicity. In the case of AM-Si (Figure 4.8 (e)), the aggregation was clearly observed since the presence of amine group on silica surface being more hydrophilicity which make silica surface easily fuse into the aggregates.

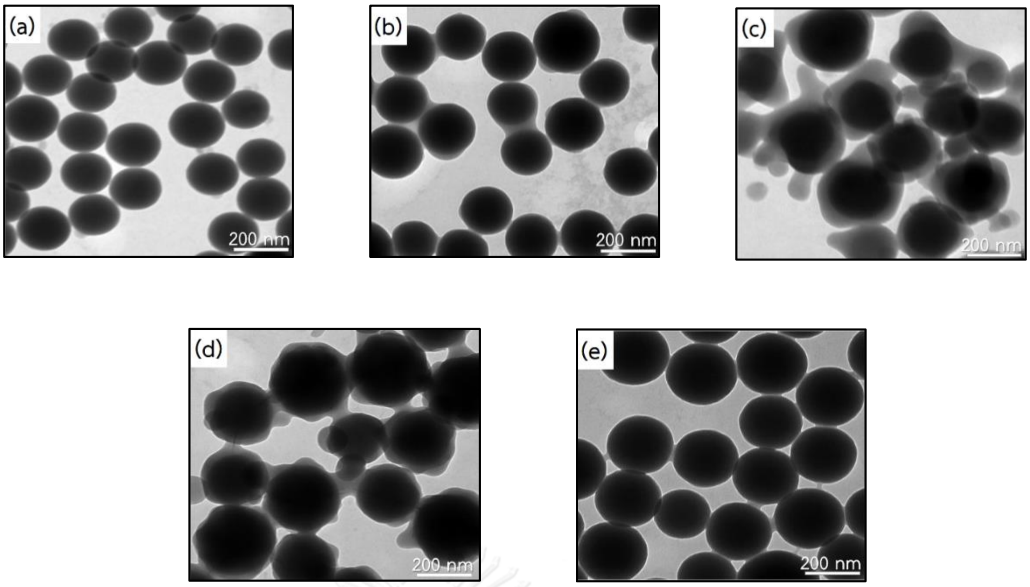


Figure 4.8 TEM micrographs of silica particle: (a) U-Si, (b) MM-Si, (c) PhM-Si, (d) PhE-Si and (e) AM-Si.

4.2.5 Antioxidant activity of the modified silica particles

The antioxidant activity of the unmodified or modified silica particles was determined by DPPH method for the estimation of the antioxidative (hydrogen-donating) of materials. In general, the molecule of DPPH is characterized as a stable free radical due to the delocalization of the spare electron over the molecule as a whole, so that the molecule cannot dimerise, as would be the case with most other free radicals. The delocalization also gives rise to the deep violet color [Molyneux P., (2004)]. The photographs of antioxidant activity of unmodified or modified silica particles were shown in Figure 4.9. The U-Si particles did not show the antioxidant activity due to no color change of DPPH solution, while MM-Si, PhM-Si, PhE-Si and AM-Si particles showed the antioxidant activity due to the change of DPPH solution from violet to yellow within five minutes.

It can be explained that a solution of DPPH being mixed with that of a substance (modified silica particles) can donate a hydrogen atom, then this gives rise to the reduced form diphenylpicrylhydrazine (DPPH-H) with the loss of this violet color. There would be expected to be a residual pale yellow color from the picryl group still present [Rajesh M. P. et al., (2011)]. However, in the case of MM-Si, the yellow color was clearly observed because the chemical structure of MpTMS contained sulfur atom which was normally yellow. Therefore, in this case there is no effect on the antioxidant activity from MM-Si particles. Accordingly, the antioxidant activity was expected from its phenyl and amine groups containing in the modified silica surface.

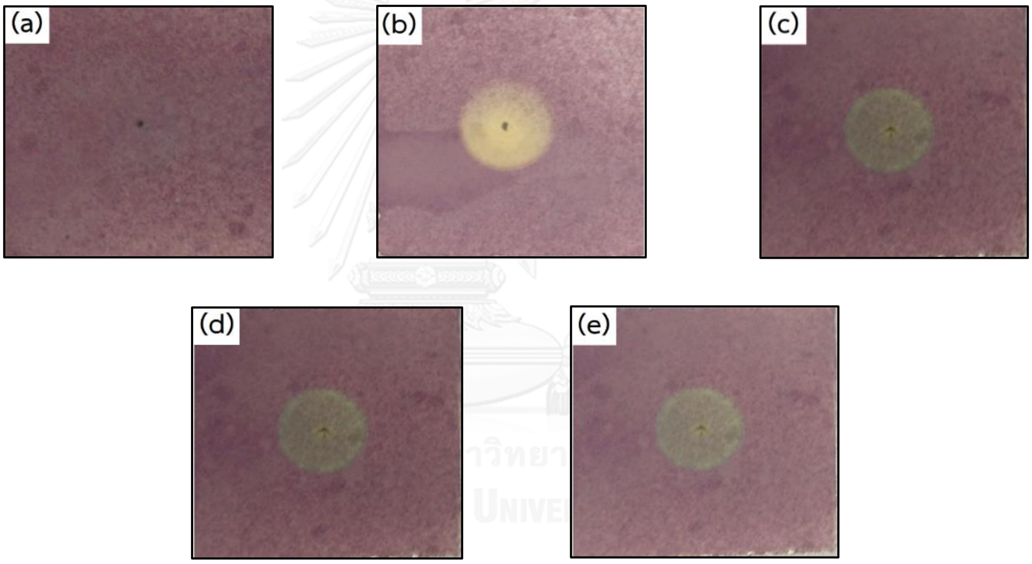


Figure 4.9 Photographs of antioxidant activity of silica particles: (a) U-Si, (b) MM-Si, (c) PhM-Si, (d) PhE-Si and (e) AM-Si by DPPH method.

4.2.6 Thermal stability of the modified silica particles

Figure 4.10 shows thermogravimetric analysis (TGA) of the unmodified or modified silica particles. The U-Si showed only a one step of decomposition, while the modified silica particles showed two steps of decomposition. In the range of 80 - 120 °C, the weight loss for all samples was due to the evaporation of residual such as water and ethanol in the amount of 6.15% (U-Si), 3.07% (PhE-Si), 4.05% (PhM-Si), 3.38% (MM-Si) and 3.53% (AM-Si), respectively. It was found that the highest weight loss (in the range of 80 - 120 °C) was obtained by U-Si. This result referred that U-Si contained the high amount of silanol groups on the silica surface resulting in the reactively adsorbed moisture, while the weight loss of modified silica was less than that of U-Si due to the decrease in polarity of silica surface.

After the modification, the weight loss appeared in the range of 250 - 650 °C due to the decomposition of hydrocarbon for each modifier in the amount of 4.08% (U-Si), 12.94% (PhE-Si), 11.85% (PhM-Si), 20.12% (MM-Si) and 14.42% (AM-Si), respectively. However, it can be seen that the decomposition temperature in this range for PhM-Si and PhE-Si was shifted to the higher temperature than that of MM-Si and AM-Si because they contained aromatic group, which required the higher energy to decompose compared to long chains hydrocarbon of MM-Si and AM-Si. According to TGA results, the thermal stability of modified silica particles tended to be increased as follows: phenyl groups > amine groups > mercapto groups, respectively.

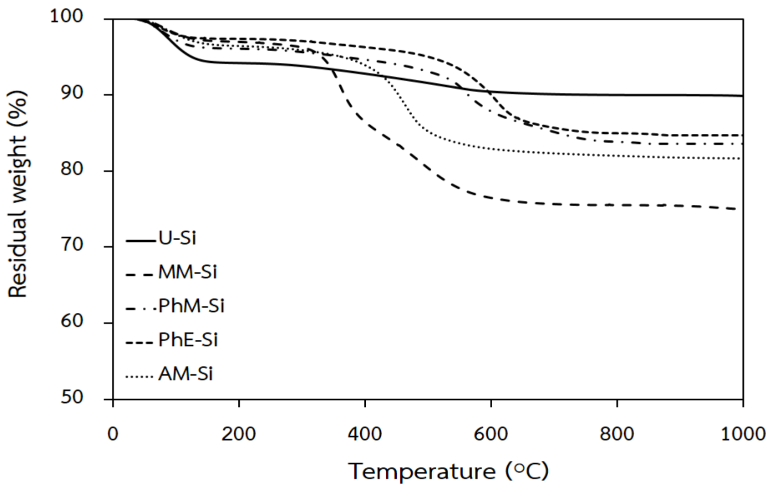


Figure 4.10 TGA curves of the silica particles.

4.3 Properties of NR vulcanizates

4.3.1 Cure characteristics of NR vulcanizates

Table 4.3 summarizes the cure characteristics of NR vulcanizates filled with unmodified or modified silica particles compared to commercial silica particles. The scorch time (t_{s2}) and curing time (t_{c90}) of composite materials increased after filling with unmodified silica or modified silica particles compared to those of NR vulcanizates without the reinforcing filler (LNR and SNR), and also increased with increasing silica contents. This is because the silanol groups on the silica surface may react with activator as well as accelerator and the number of active sulfurating agents, which are necessary for vulcanization, was subsequently reduced [Rattanasom N. et al., (2012)] and [Chonkaew W. et al., (2011)].

By including the same silica content, the t_{s2} and t_{c90} values of NR vulcanizates filled with C-Si particles (LC-10, LC-20 and SC-20) were longer than those of NR vulcanizates filled with U-Si particles (LU-10, LU-20 and SC-20). It may be because the silica particles were synthesized by the sol-gel reaction of TEOS, which was expected that the content of silanol groups on the surface was lower than those of C-Si particles [Poompradub S. et al., (2014)]. This result was confirmed by decreasing the peak area of Si-O in-plane stretching of silanol groups, as discussed in section 4.2.1.

After filling the modified silica particles, the t_{s2} and t_{c90} values of NR vulcanizates filled with MM-Si particles (LMM-10, LMM-20 and SMM-20) were shorter than those of NR vulcanizates filled with U-Si particles. It is because the MM-Si particles contained sulfur in the molecular structure, thus sulfur may play a role to promote the crosslink of rubber chains [Ansarifar A. et al., (2005)]. However, the t_{s2} and t_{c90} values of PhM-Si, PhE-Si and AM-Si particles filled in NR vulcanizates were longer values than those of NR vulcanizates filled with U-Si particles due to the steric effect of phenyl group to retard the vulcanization. In the case of AM-Si particles filled in NR vulcanizates (LAM-10 and LAM-20), the t_{s2} and t_{c90} values showed the shorter than those of NR vulcanizates filled with PhM-Si particles (LPhM-10 and LPhM-20) or PhE-Si particles (LPhE-10 and LPhE-20). This is because the amine groups containing the structure of

AMTS could act the co-accelerator [Surya I. et al., (2013)]. In addition, It can been seen that the t_{s2} and t_{c90} values of NR vulcanizates prepared by NR latex were shorter than those of NR vulcanizates prepared by NR solid because NR latex containing ammonia solution that was added for the preservation of latex may be promote agent and sulfur, resulting in activation of vulcanization system.

Additionally, it can be seen that the minimum torque (M_L), maximum torque (M_H) and the difference between M_H and M_L (ΔM) of NR (both latex and rubber) vulcanizates filled unmodified or modified silica particles were increased compared to LNR and SNR, and increased with increasing silica contents. This results indicated that rigid fillers did not prevent the vulcanization [Pan Q. et al., (2013)]. It was also found that the increase in ΔM values of composite materials indicated the higher degree of crosslinking (Table 4.4), which was related to the stiffness of material [Carli L. N. et al., (2011)]. These explanations could be confirmed by the swelling ratio and crosslink density as discussed in next section.

The swelling ratio and crosslink density of NR vulcanizates filled unmodified or modified silica particles were summarized in Table 4.4. Generally, the rubber swelling is influenced by various factors such as crosslink type, elastomer type and density, amount and type of filler [Hassan H. H. et al., (2012)]. The swelling ratio is inversely related to the results of crosslink density from calculation based on Flory-Rehner equation (Eqs. (3.2) and (3.3)). The swelling ratio of NR vulcanizates filled with silica particles was lower than those of LNR and SNR and it was decreased with increasing silica loading. This is a result for the formation of more crosslink in the vicinity of the silica particles owing to the chain segment and facilitates the crosslink formation [Poompradub S. et al., (2014)], therefore; an increase in the filler-rubber interaction is constructed.

Considering at the same silica content, it is interesting to note that NR vulcanizates filled with MM-Si particles (LMM-10, LMM-20 and SMM-20) showed the lowest swelling ratio compared to NR vulcanizates filled with other modified silica due to chemical structure of MM-Si particles containing sulfur atom that affect to the increased vulcanization.

Table 4.3 Cure characteristics of NR vulcanizates filled with silica particles.

Sample code	Scorch time; t_{s2} (min)	Minimum torque; M_L (dNm)	Maximum torque; M_H (dNm)	$M_H - M_L$ (ΔM) (dNm)	Curing time; t_{c90} (min)
LNR	2.15	0.08	3.14	3.06	3.87
LC-10	4.42	0.17	4.91	4.75	6.75
LU-10	3.25	0.11	4.82	4.71	5.85
LMM-10	2.86	0.06	6.43	6.57	5.49
LPhM-10	4.15	0.07	5.01	4.94	6.80
LPhE-10	4.69	0.10	4.94	4.84	7.56
LAM-10	3.27	0.10	5.44	5.32	5.83
LC-20	4.54	0.55	6.35	5.80	6.86
LU-20	3.42	0.33	5.99	5.66	5.93
LMM-20	3.28	0.13	6.82	6.69	5.74
LPhM-20	5.56	0.34	5.36	5.02	8.81
LPhE-20	5.58	0.25	5.32	5.07	8.85
LAM-20	3.83	0.21	5.78	5.57	6.64
SNR	6.32	0.08	3.77	3.69	12.13
SC-20	7.90	0.51	6.43	5.54	16.97
SU-20	7.69	0.26	5.28	5.02	15.13
SMM-20	7.49	0.21	7.43	7.22	13.44
SPhM-20	9.35	0.12	5.54	5.42	17.45
SPhE-20	9.78	0.14	5.45	5.31	17.73

L: NR latex, S: NR solid

Table 4.4 Swelling ratio, crosslink density and bound rubber content of NR vulcanizates filled with silica particles.

Sample code	Swelling ratio; Q	Density of material; ρ_r (g·cm^{-3})	Crosslink density; $\eta_c \times 10^{-4}$ (mol·cm^{-3})	Bound rubber content (%)
LNR	4.14 ± 0.15	0.969	1.18 ± 0.08	35.53 ± 0.74
LC-10	3.52 ± 0.14	1.013	1.38 ± 0.10	47.49 ± 2.03
LU-10	3.35 ± 0.20	1.011	1.52 ± 0.16	52.77 ± 3.54
LMM-10	2.15 ± 0.29	1.023	3.41 ± 0.29	61.60 ± 1.74
LPhM-10	3.15 ± 0.24	1.004	1.71 ± 0.23	64.11 ± 0.67
LPhE-10	3.25 ± 0.16	1.000	1.57 ± 0.20	67.41 ± 2.89
LAM-10	3.27 ± 0.10	1.008	1.54 ± 0.08	58.28 ± 3.39
LC-20	3.13 ± 0.04	1.056	1.41 ± 0.04	68.39 ± 1.15
LU-20	2.93 ± 0.08	1.042	1.64 ± 0.08	77.48 ± 1.72
LMM-20	1.97 ± 0.02	1.031	3.46 ± 0.04	78.22 ± 0.45
LPhM-20	2.43 ± 0.06	1.019	2.39 ± 0.11	82.33 ± 2.47
LPhE-20	2.48 ± 0.10	1.029	2.26 ± 0.16	86.76 ± 0.74
LAM-20	2.66 ± 0.10	1.035	1.79 ± 0.13	77.09 ± 0.99
SNR	4.00 ± 0.08	0.968	1.26 ± 0.05	36.59 ± 1.52
SC-20	3.03 ± 0.01	1.066	1.49 ± 0.01	61.60 ± 2.06
SU-20	2.80 ± 0.01	1.064	1.73 ± 0.01	70.14 ± 2.52
SMM-20	1.87 ± 0.05	1.054	3.64 ± 0.06	75.07 ± 2.01
SPhM-20	2.35 ± 0.01	1.051	2.43 ± 0.02	76.93 ± 0.73
SPhE-20	2.43 ± 0.02	1.051	2.28 ± 0.03	78.52 ± 0.35

4.3.2 Filler to rubber interaction of NR vulcanizates

The filler to rubber interaction was determined by using bound rubber measurement. The bound rubber is defined as the percentage of the polymer that remains bound to the filler when the compounds is extracted with a good solvent such as toluene at room temperature. The amount of bound rubber is a function of the interaction between polymer and filler, the surface area of filler, the solvent used in the extraction and the concentration of filler in the composites [Aranguren M. I. et al., (1997)].

The percentage of bound rubber contents (BRC) after extraction with toluene can be calculated from Eq. (3.4) and showed in Table 4.4. Most of the BRC formed in the NR vulcanizates filled with silica particles may be chemical or physical bonds. The BRC of NR vulcanizates filled silica particles increased with increasing silica content, resulting in more filler to rubber interaction. At the same silica content, the BRC of NR vulcanizates filled with C-Si particles (LC-10, LC-20 and SC-20) were lower than those of NR vulcanizates filled with U-Si particles (LU-10, LU-20 and SU-20) due to high silanol groups which led to a stronger filler to filler network as seen in SEM micrographs for further discussion, reflecting in the weak interaction with rubber.

In the case of NR vulcanizates filled with modified silica, the higher BRC was obtained. It was indicated that the hydrogen bond in the silica to silica interactions were destroyed, as results in the increase in filler to rubber interaction. This results related to the hydrophobicity of modified silica surface, resulting in the increased compatibility of the modified silica with rubber matrix. Moreover, the BRC of composite materials prepared by NR both latex and solid was almost comparable.

4.3.3 Morphology of NR vulcanizates

The morphology of NR vulcanizates filled with unmodified or modified silica particles from the cross-sectioned surface was observed by SEM as shown in Figure 4.11. The black areas indicated the rubbery matrix, and white spots represented the dispersed phase of silica particles. At 10 phr of silica particles, the C-Si particles tended to be aggregated, resulting in the poor distribution of C-Si particles in rubbery matrix. In contrast, the U-Si particles were well dispersed in rubbery matrix. It may be due to the different amount of silanol groups on silica surface as discussed previous. When the modified silica particles filled in NR vulcanizates, the good dispersion was obtained because the silica surface was coated by non-polar groups indicating the different interfacial adhesion. By increasing the amount of silica particles, the C-Si and U-Si particles showed the agglomerates or aggregates, while the modified silica particles were well dispersed in rubbery matrix. In the case of NR vulcanizates prepared by NR solid, the dispersed features of silica particles in NR vulcanizates were similarly with the prepared by NR latex compared to the same silica content. Accordingly, the good compatibility between rubbery matrix and modified silica particles was overcome and would be resulted to improve in mechanical properties.

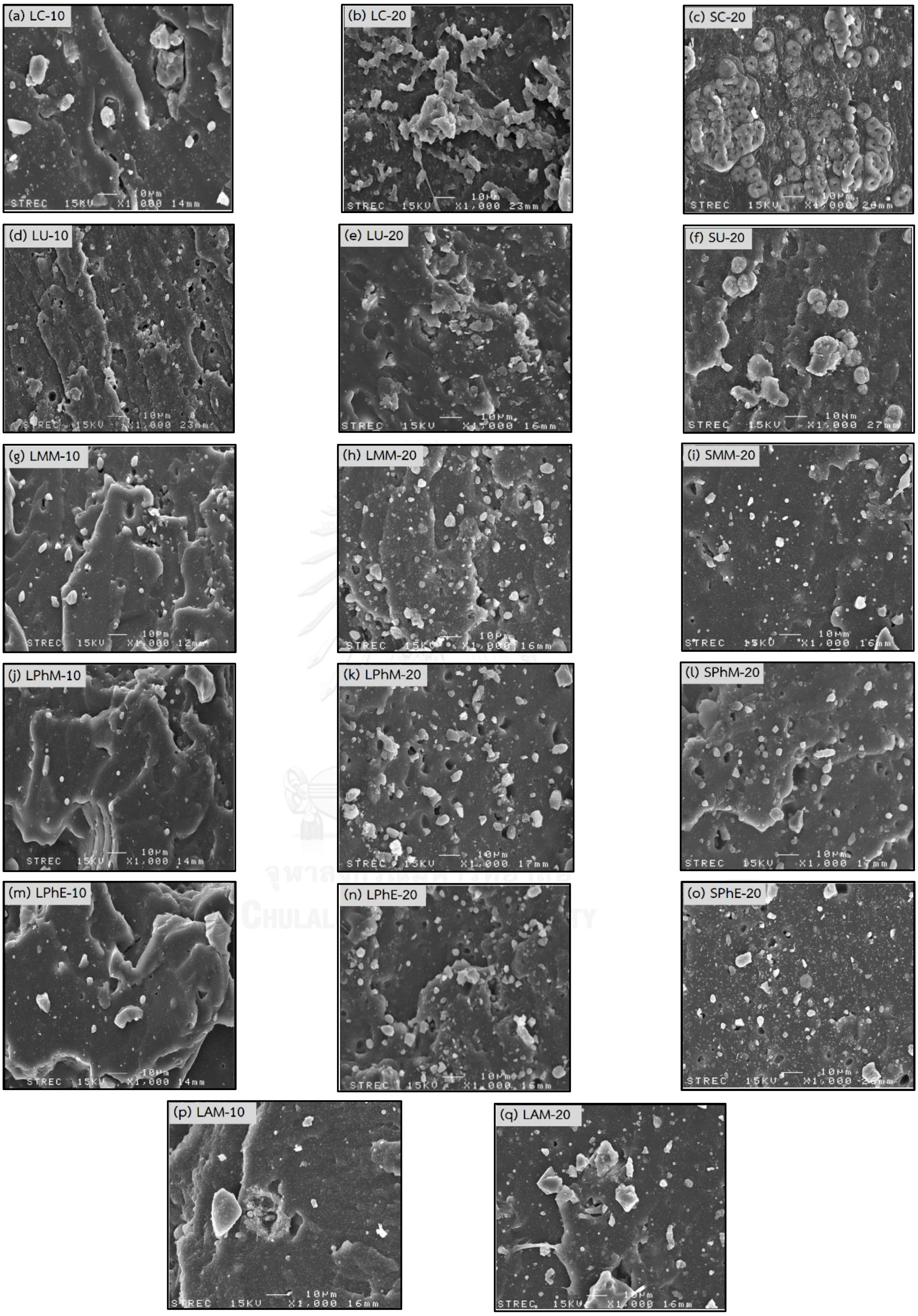


Figure 4.11 SEM micrographs of NR (latex and solid) vulcanizates filled with unmodified and modified silica particles.

4.3.4 Mechanical properties of NR vulcanizates before and after ageing

Figure 4.12 shows tensile properties of NR vulcanizates filled with unmodified or modified silica particles. These properties of NR vulcanizates prepared by NR latex was similar to those of NR solid. The moduli at 300% elongation (M_{300}) of NR vulcanizates were progressively increased with adding the silica particles, and increased with increasing silica loading compared to those of LNR and SNR due to the reinforcing effect of silica particles [Chaichua B. et al., (2009)]. Generally, the factors affecting the influence to the reinforcement of silica particles are the surface chemistry of filler as well as the filler structure, the specific surface area and the average particles size [Sae-oui P. et al., (2004)]. At the same silica content, the M_{300} values of NR vulcanizates filled with C-Si particles were lower than those of NR vulcanizates filled with U-Si particles. Although the C-Si particles had the smaller average particle sizes (40-60 nm), they contained many numbers of silanol groups (confirmed by FTIR). This result indicated that the large number of silanol groups on the silica surface of C-Si particles may result the aggregates or agglomerates affecting to the poor compatibility between rubbery matrix and silica particles. The M_{300} values of NR vulcanizates filled with modified silica particle were lower than those of NR vulcanizates filled with U-Si particles because the average particle sizes of modified silica particles (in the range of 227-298 nm) were larger than those U-Si particles (in the range of 200 nm). Usually, the smaller particle size, the higher reinforcement effect was obtained [Fu S. Y. et al., (2008)]. However, the tensile strength (T_B) and elongation at break (E_B) of NR vulcanizates filled with unmodified or modified silica particles did not show the difference compared with LNR and SNR.

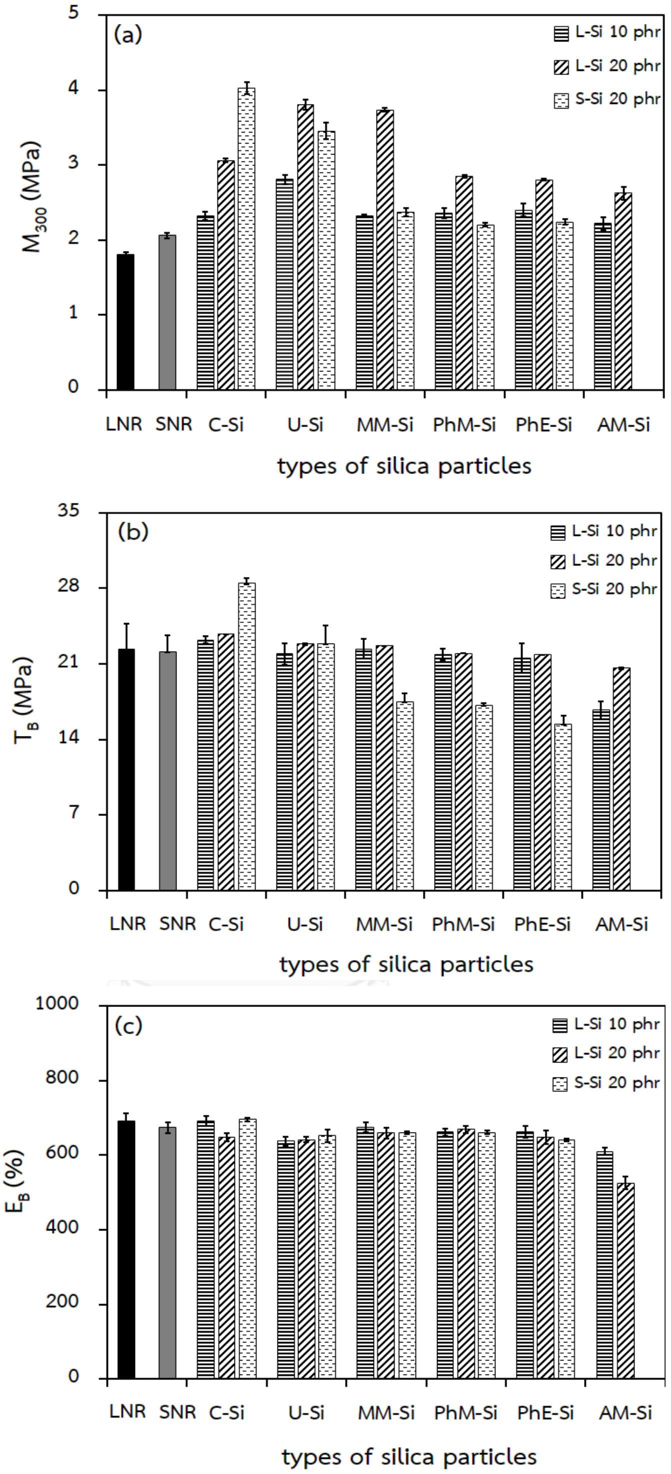


Figure 4.12 Tensile properties of NR (both latex and solid) vulcanizates filled with silica particles: (a) modulus at 300% elongation (M_{300}), (b) tensile strength (T_B) and (c) elongation at break (E_B).

The mechanical properties in terms of hardness, tear strength, abrasion resistance and compression set of NR vulcanizates filled with unmodified or modified silica particles were shown in Figure 4.13. The mechanical properties in terms of hardness, tear strength, abrasion resistance and compression set of NR vulcanizates prepared by NR latex and solid showed the similar result. The hardness value is defined as the resistance that a rubber surface offers against penetration by an indenter, and relates to the deformation of the rubber surface [Tangudom P. et al., (2013)]. All composite materials showed the higher hardness compared to those of LNR and SNR and the hardness of composite materials increased with increasing silica loading. This result suggested that the resistance to indentation was more when the inclusion of rigid phase as silica particles in NR vulcanizates was obtained.

Figure 4.13 (b) shows the tear strength of NR vulcanizates filled with unmodified or modified silica particles. The tear strength is the force per unit thickness used to initiate a rupture or tear of the materials [Nakason C. et al., (2005)]. All composite materials showed the comparable tear strength and each value for composite was higher than those of LNR and SNR due to the increase in crosslink density of composites. It is referred that the modification of silica particles surface in this study did not inhibit the role of silica on the tear resistance. This observation was associated with the ability of silica particles to transfer the tearing force, and also probably due to the compatibility between the reinforcing filler and rubber phase [Poompradub S. et al., (2014)].

Abrasion resistance of NR vulcanizates filled with unmodified or modified silica particles was determined in terms of volume loss as seen in Figure 4.13 (c). The lower the volume loss, the greater the abrasion resistance is overcome. The abrasion resistance is the ability of material to bear the force action such as rubbing or scraping [Tabsan N. et al., (2010)]. Moreover, the crosslink density, hardness, modulus of the rubber vulcanizates are important factor controlling the abrasion resistance [Malas A. et al., (2014)]. It also was found that the abrasion resistance of NR vulcanizates filled with silica particles tended to be increased with increasing silica loading. The result revealed that the addition of silica particles may hinder the loss of rubbery matrix during abrasion process [Wang L. L. et al., (2012)]. Considering at the same silica content, the NR vulcanizates filled with U-Si particles showed the lowest volume loss because U-Si particles having smaller particles size exhibited better abrasion, resulting in the improvement of wear behavior of material. However, the volume loss of NR vulcanizates with modified silica particles was increased. Accordingly, the improvement of abrasion resistance of composite materials was affected by not only the structure but also the particles size of reinforcing filler.

Compression set of NR vulcanizates filled with unmodified or modified silica particles was represented in Figure 4.13 (d). Compression set is a measure of the ability of rubber to retain their elastic properties after prolonged compression at a constant strain under a specified set of conditions, and it is permanent set of rubber compound [Pal K. et al., (2009)]. The compression set of NR vulcanizates tended to be increased when the silica loading was increased. At the same silica loading, the compression set for NR vulcanizates filled with C-Si particles showed the highest value due to the aggregation and agglomeration of C-Si particles, as resulted in the SEM micrographs, which may retard the recovery of rubber chains. However, the compression set of NR vulcanizates tended to reduce by filling with unmodified or modified silica particles. It may be due to the good interfacial adhesion between silica particles and rubbery matrix. Additionally, the compression set of NR vulcanizates filled with modified silica particles was lower than those of NR vulcanizates filled with U-Si particles. This result referred that the improvement of hydrophobicity on silica surface made filler particles and rubbery matrix more compatible. Accordingly, the improvement of compression set might arise due to not only the good interfacial adhesion between filler and rubbery matrix but also the surface properties of filler.

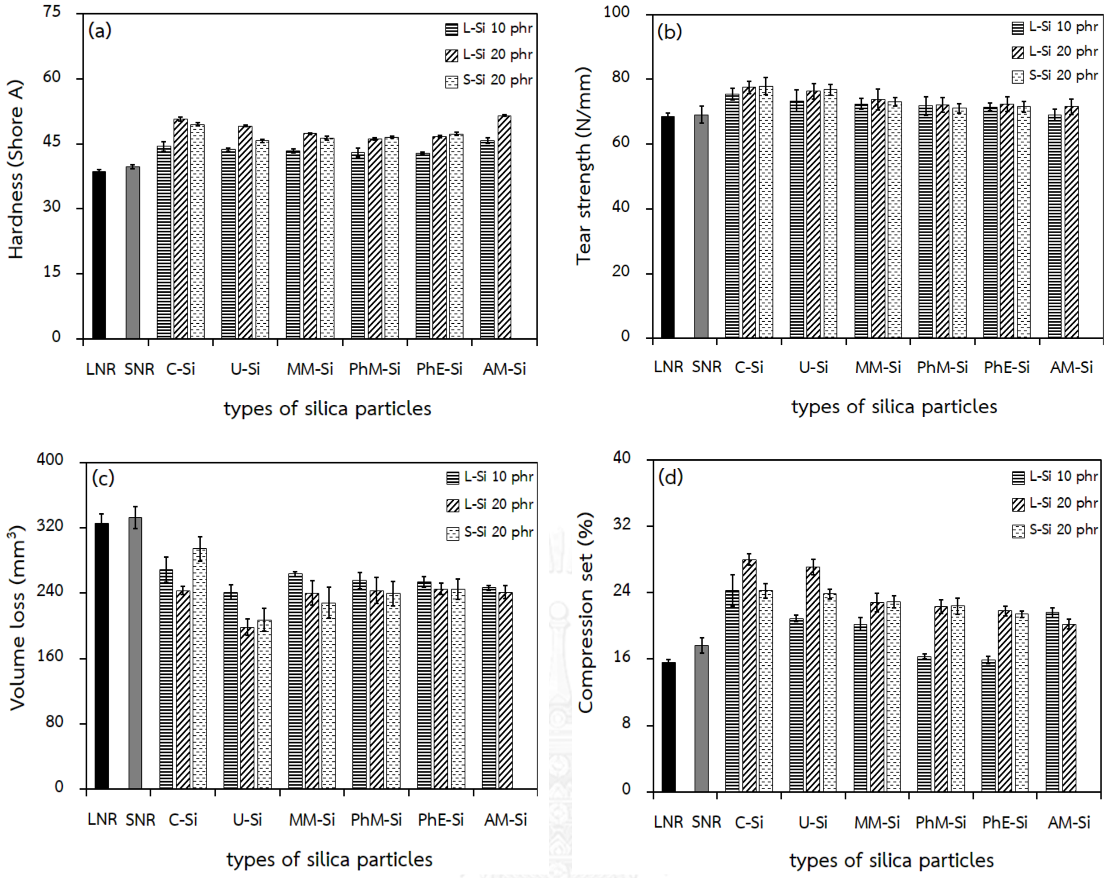


Figure 4.13 Mechanical properties of NR (both latex and solid) vulcanizates filled with silica particles: (a) hardness and (b) tear strength, (c) volume loss and (d) compression set.

Figure 4.14 and Figure 4.15 show the mechanical properties after ageing of NR vulcanizates filled with unmodified or modified silica particles prepared by NR latex and solid. The same behavior for thermal ageing properties was observed in the both cases. The moduli at 100% elongation (M_{100}) (Figure 4.14 (a) and Figure 4.15 (a)) of all composite materials after thermal ageing was higher than those of before thermal ageing, while T_B and E_B values tended to decrease after ageing at high temperature. This is simply attributed to the formation of crosslinks, which was well known as post curing effect. The increase in crosslink density via post curing effect caused the reduction in mobility of rubber chain [Rattanasom N. et al., (2012)]. Furthermore, the thermal ageing properties was reported in terms of tensile retention as calculated from Eq. (3.10), shown in Figure 4.14 (d) and Figure 4.15 (d). As can be seen, the tensile retention of all composite materials is less than 100%. The tensile retention of NR vulcanizates filled with modified silica particles gave greater than those of NR vulcanizates filled with unmodified silica particles. It may be because the modified silica particles restricted the polysulfidic linkages after ageing, leading to the higher thermal ageing properties.

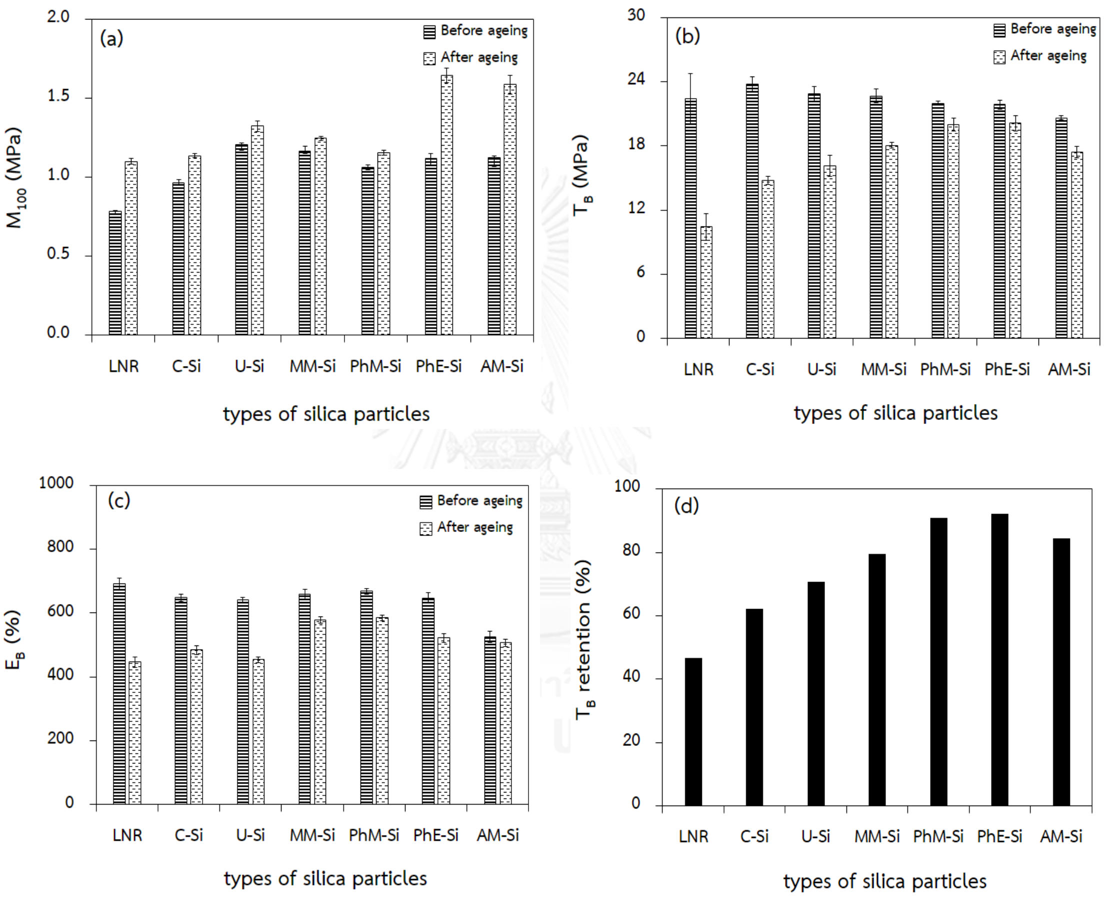


Figure 4.14 Mechanical properties after ageing of NR latex vulcanizates filled with silica particles (20 phr): (a) modulus at 100% elongation (M_{100}) before and after ageing, (b) T_B before and after ageing, (c) E_B before and after ageing and (d) tensile retention.

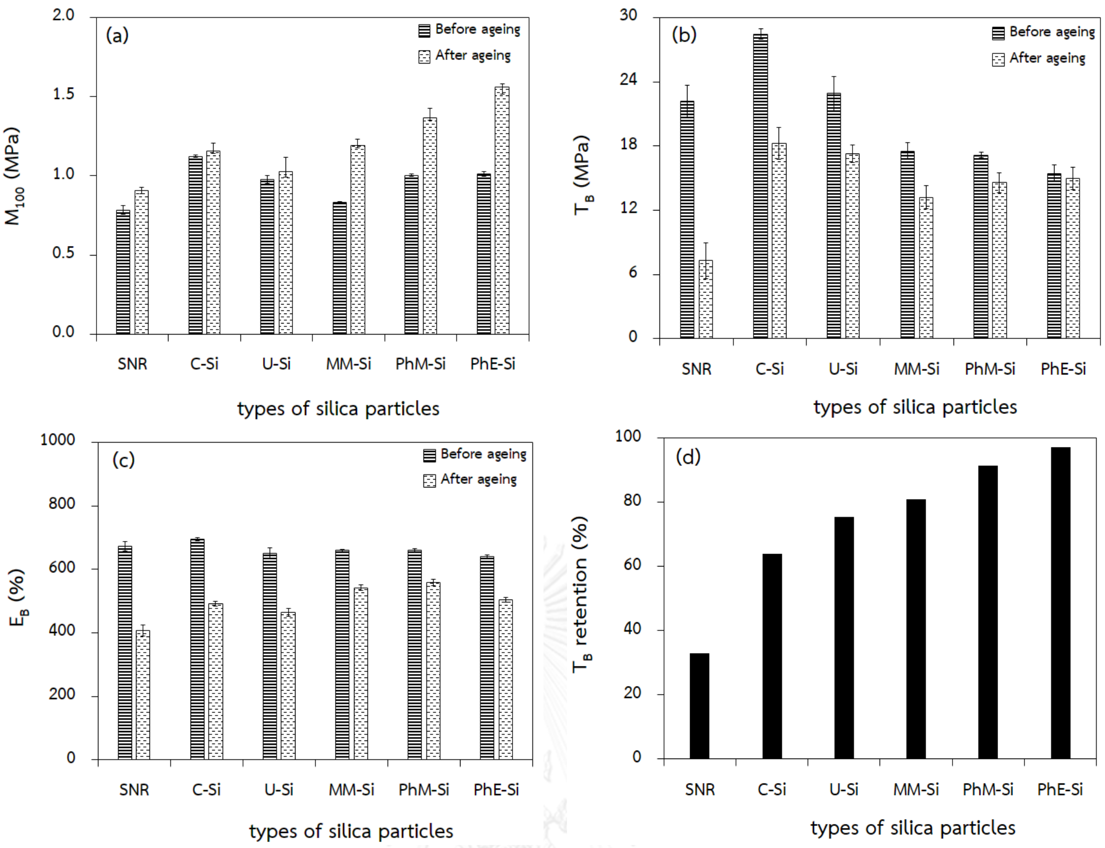


Figure 4.15 Mechanical properties after ageing of NR solid vulcanizates filled with silica particles (20 phr): (a) M_{100} before and after ageing, (b) T_B before and after ageing, (c) E_B before and after ageing and (d) tensile retention.

4.3.5 Thermal properties of NR vulcanizates

In this study, the thermal stability of NR vulcanizates was considered as the ability to maintain the required properties at a desired temperature, which TGA and DSC techniques was used to investigate. The TGA curves of NR vulcanizates filled with unmodified or modified silica particles in nitrogen atmosphere at a heating rate of 10 °C/min were shown in Figure 4.16. The thermal behavior of NR vulcanizates prepared by NR latex was found to be similar to that of NR vulcanizates prepared by NR solid. TGA behaviors for all composite materials evidenced a one – stage weight loss during thermal decomposition.

The thermal decomposition of NR vulcanizates began around 285 to 291 °C and completed around 374 to 400 °C which was correspond to the NR degradation. The initial temperature decomposition (T_{id}) and the temperature of maximum rate of weight loss (T_{max}) of the sample were listed in Table 4.5. The T_{id} and T_{max} values of NR vulcanizates increased when the addition of silica content increased. This is because silica particles were effective to act as physical barrier to prevent the transport of volatile decomposed product out of composite materials [Theppradit T. et al., (2014)]. At the same silica particles loading, the T_{id} and T_{max} values of NR vulcanizates filled with silica particles (C-Si or U-Si particles) were improved (13.4 to 16.6 °C) compared to those of LNR. It is interesting to note that the T_{id} and T_{max} values of modified silica particles filled in NR vulcanizates were shifted to the higher temperature (more than 3 to 50 °C) compared with those of NR vulcanizates filled with U-Si particles. Based on these descriptions, it can be concluded that the presence of phenyl or amine groups on the surface of modified silica particles could enhanced the thermal stability of composite materials due to the resonance effect of phenyl or amine groups [Rhein R. A., (1983)]. Additionally, the E_t values of NR vulcanizates were calculated from Eqs (3.11) and (3.12). The E_t values was progressively increased when the modified silica was used as reinforcing filler.

The glass transition temperature (T_g) of NR vulcanizates filled with unmodified or modified silica particles was also summarized in Table 4.5. It should be noted that the T_g values of NR vulcanizates slightly increased when the unmodified and modified silica particles were added. Considering at the same silica content, the T_g values of NR vulcanizates filled with C-Si or U-Si particles was higher than those of unfilled NR. The T_g values of NR vulcanizates filled with modified silica particles, especially, PhE-Si and PhM-Si particles were higher than those of NR vulcanizates filled with U-Si particles. The increase of T_g values of NR vulcanizates was probably ascribed to the interactions between the modified silica particles and NR molecules and might be due to the relaxation of tightly bound modified silica by the NR matrix [Satraphana P. et al., (2009)]. Normally, the T_g of polymer is affected by the chemical structures of the main chain and molecular size of the substituted groups which control the chain mobility. In the case of NR rubber, the T_g values of NR vulcanizates located at the same temperature around – 60 °C, indicating that the addition of unmodified and modified silica particles did not affect on the glass transition behavior of NR.

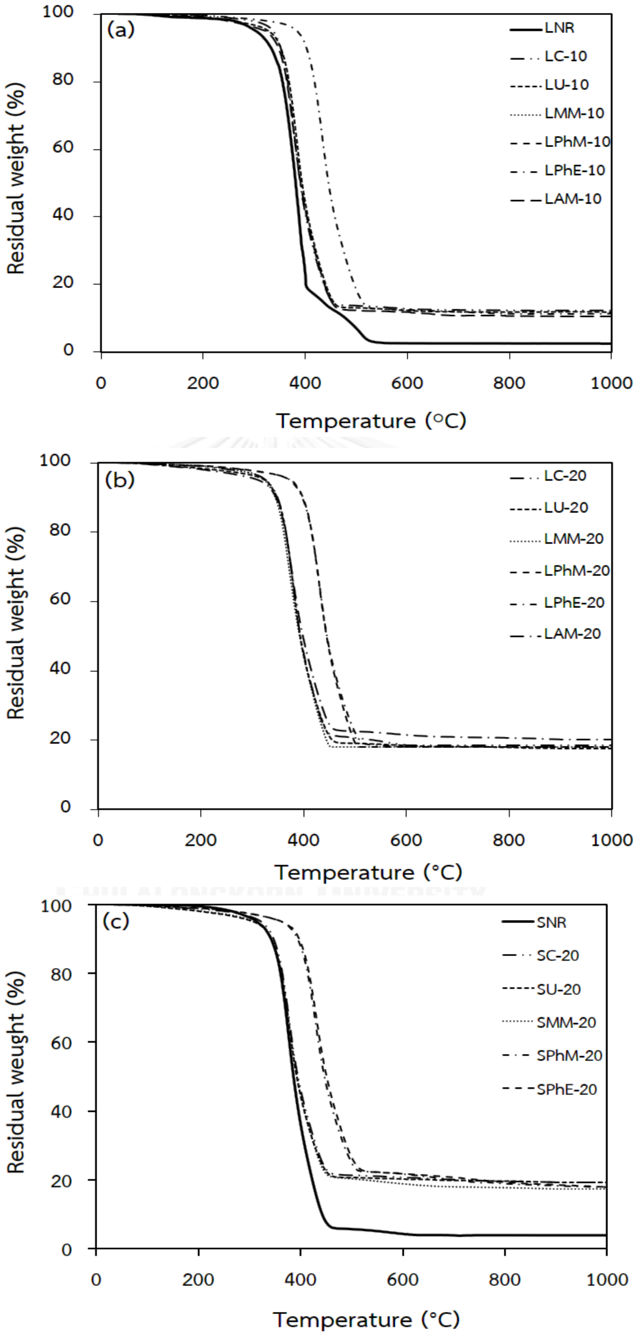


Figure 4.16 TGA curves of NR vulcanizated filled with silica particles: (a) 10 phr of silica in NR latex, (b) 20 phr of silica in NR latex and (c) 20 phr of silica in NR solid.

Table 4.5 Thermal properties of NR vulcanizates filled with silica particles.

Sample code	T_{id}[a] (°C)	T_{max}[b] (°C)	E_t[c] (kJ/mol)	T_g[d] (°C)
LNR	291.23	382.15	18.56	- 62.1
LC-10	309.38	376.41	20.69	- 61.2
LU-10	311.38	378.96	21.20	- 58.9
LMM-10	314.73	380.55	22.02	- 58.4
LPhM-10	339.26	431.04	24.31	- 58.1
LPhE-10	344.17	433.62	25.32	- 58.2
LAM-10	312.33	380.06	23.84	- 58.7
LC-20	315.91	378.19	21.51	- 59.7
LU-20	318.74	379.65	23.37	- 58.2
LMM-20	322.45	381.25	25.61	- 57.6
LPhM-20	358.56	434.35	29.54	- 55.5
LPhE-20	360.20	436.86	30.58	- 55.2
LAM-20	320.16	380.71	27.62	- 56.5
SNR	285.58	374.41	16.73	-60.2
SC-20	305.56	377.85	20.42	-59.7
SU-20	308.67	378.41	22.54	-59.1
SMM-20	310.61	380.13	24.79	-57.8
SPhM-20	345.16	430.00	28.67	-57.5
SPhE-20	351.84	431.96	29.26	-57.1

[a] initial decomposition temperature, [b] temperature of maximum rate of weight loss, [c] activation energy of decomposition, [d] glass transition temperature.

4.5.3 Ozone resistance of NR vulcanizates

In general, many unsaturated rubbers are susceptible to degradation by ozone. The greater level of double bonds in the unsaturated rubber, the higher the susceptibility to ozonation is obtained [Simma K. et al., (2009)]. Chemicals are added to rubber products to impart effective resistance to ozone ageing under both static and dynamic service conditions of the rubber articles [Poompradub S. et al., (2011)]. The effect of unmodified or modified silica particles (at 20 phr) on the ozone resistance of NR vulcanizates were shown in Figure 4.17. The type numberless of cracking was separated as four types, which the each type was defined as follows: C-2 type is the cracking that recognizable by naked eye, C-3 type is the cracking which is deep and comparatively large less than 1 mm, C-4 type is cracking which is deep and large (1-3 mm) and C-5 type is cracking which is not less than 3 mm, or which is probably followed by cutting.

The cracking traces on the surface of NR vulcanizates prepared by NR latex and solid were similarly obtained. The cracking traces of LNR and SNR (C-4 type) were clearly observed on the surface after exposure to 50 pphm of ozone for 48 h due to the presence of C=C bond in the structure of NR, which caused the degradation by ozone attack [Poompradub S. et al., (2011)]. The C-Si and U-Si particles filled in NR vulcanizates showed the C-4 type of cracking traces, while NR vulcanizates filled with modified silica exhibited the cracking traces of C-3 type. This result indicated that the modified silica particles played to act the chemical antiozonants in order to prevent the ozonolysis of rubber product. For the antiozonants in this study, it may be related to the scavenging theory [Layer R. W. et al., (1990)]. The scavenging theory states that antiozonant functions by migration to the rubber surface due to its exceptional reactivity towards ozone and the scavenging theory is based on the fact that antiozonants react much more rapidly with ozone than do the double bonds of the rubber they protect [Layer R. W. et al., (1990)]. According to this theory, the modified silica particles could diffuse the surface of rubber in order to scavenge the ozone, and the initial reaction with ozone was rapidly reacted, resulting in more slowly ozonolysis of NR vulcanizates.

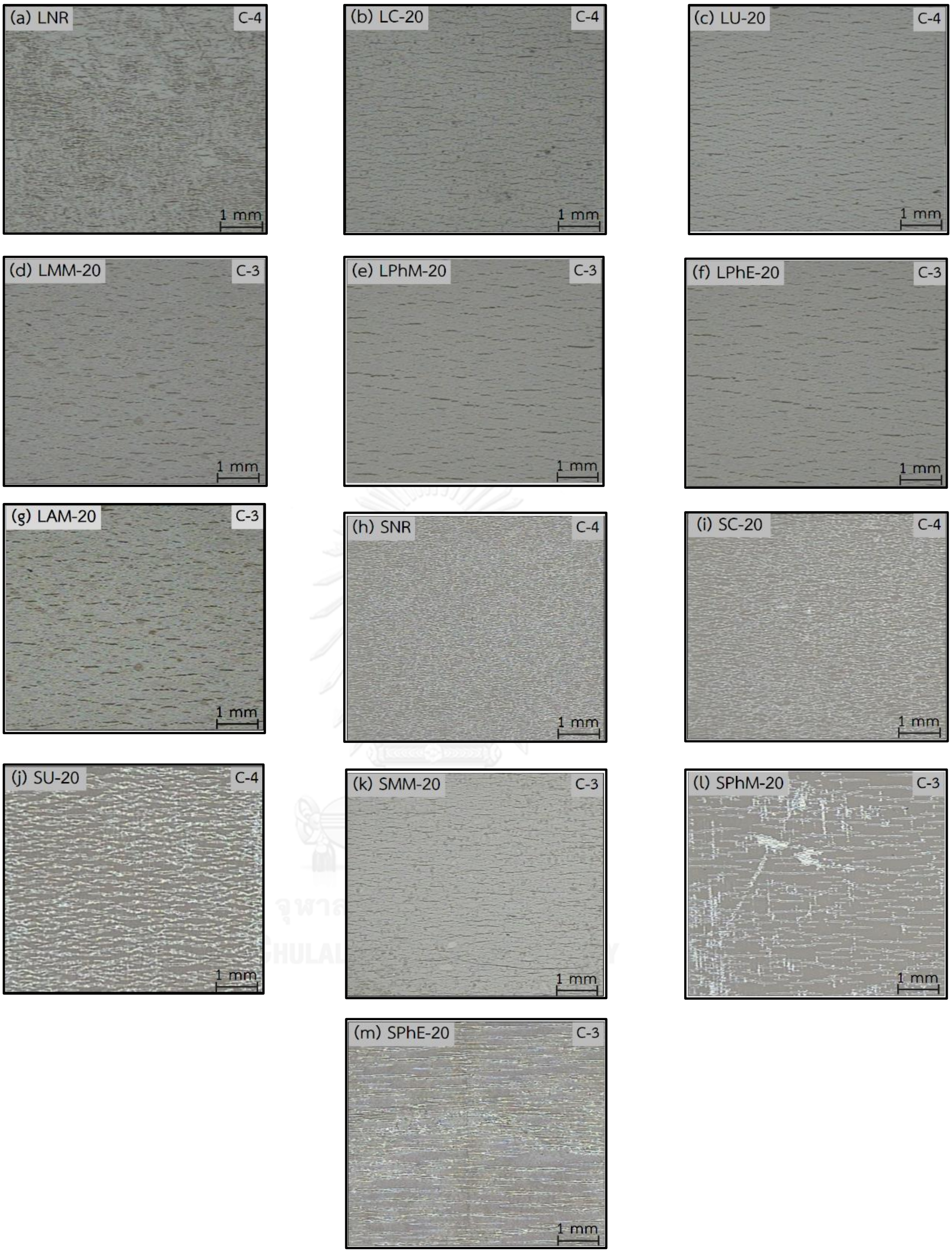


Figure 4.17 Ozone resistance of NR (both latex and solid) vulcanizates filled with silica particles.

4.5.4 Dynamic mechanical properties of NR vulcanizates

Dynamic mechanical analysis is useful for investigating of the viscoelastic behavior of rubber products. The variations in viscoelastic properties are usually expressed by storage modulus (E') and the mechanical damping behavior, in the form of loss tangent (tan δ), as summarized in Table 4.6. Figure 4.18 (a) represents the E' curves of unmodified and modified silica particles (20 phr) filled NR vulcanizates. E' is a measure of the maximum energy stored in the material during one cycle of oscillation. This provides valuable insight into the stiffness of the rubbers, representing the elastic nature of the materials [Thongsang S. et al., (2012)]. In the glassy region, the movement of chain segments was mostly frozen due to the dense packing, resulting in the higher E' values. At high temperature, the lose packing of chain segments led to decrease of E' values in the glass transition region. Considering E' values at 25 °C, it can be observed that NR vulcanizates filled with modified silica particles were higher E' values compared to LU-20 and LNR. This behavior was more pronounced in the rubbery region. This should be attributed to the stronger filler-to-rubber or filler-to-filler interactions resulting in the higher stiffness.

Figure 4.18 (b) demonstrates the tan δ that is defined from the ratio of E'' to E' curves of unmodified and modified silica particles filled NR vulcanizates. The damping peak usually occurs in the glass transition region, and is associated with the movement of side groups and molecular chains within the rubbers. Therefore, the higher the damping peak, the greater the E'' was obtained [Thongsang S. et al., (2012)]. It can be seen that the incorporation of silica particles filled NR vulcanizates decreased the damping peak of NR vulcanizates. This could be explained that loss energy during the mobility of rubber chains of NR vulcanizates filled with silica particles was lower than those of LNR. In addition, the maximum values in tan δ peak could be implied to the T_g value of sample. It was found that T_g values of NR vulcanizates filled with silica particles were shifted to higher temperature compared to LNR because silica particles acted to restrict the moving rubber chains. However, the T_g values of NR vulcanizates filled with C-Si particles was shifted to the lower temperature compared to U-Si particles filled NR vulcanizates because the C-Si particles were aggregated and agglomerated, resulting in the silica-silica network, as seen in SEM micrographs. These results indicated the poor compatibility between C-Si particles and NR matrix. In addition, T_g values of NR vulcanizates filled with modified silica particles were shifted to the lower temperature due to the strong rubber-to-filler interaction, leading to enhance the compatibility between modified silica particles and NR matrix. Accordingly, the modified silica particles can be reduced the degree of molecular mobility and improved the interaction of modified silica particles with NR matrix.

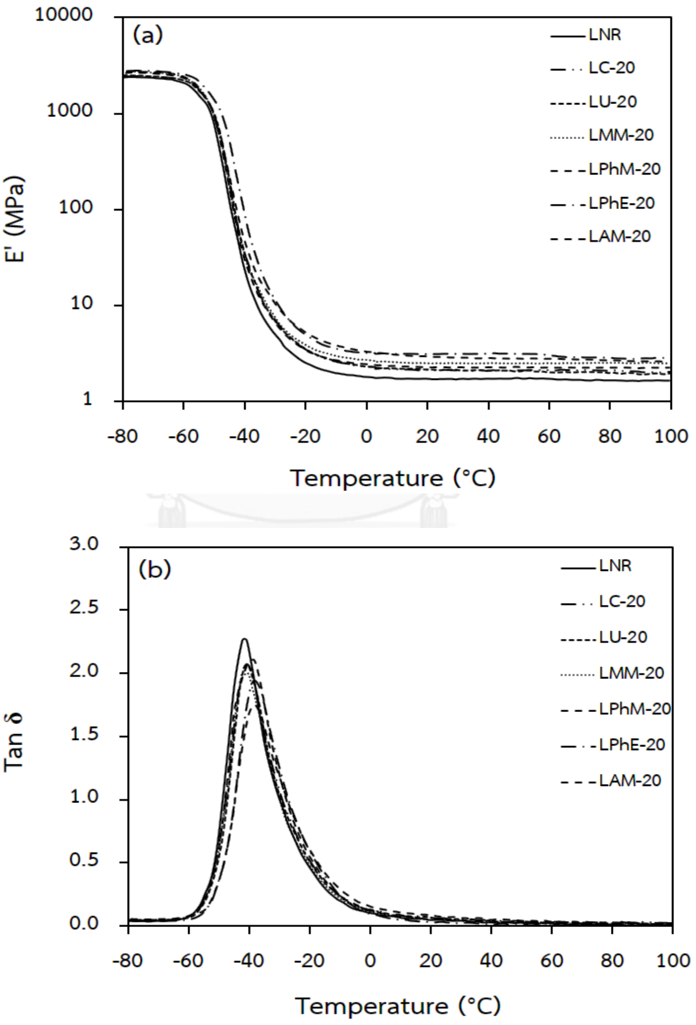


Figure 4.18 Dynamic properties as a function of temperature of NR vulcanizates filled with silica particles: (a) storage modulus (E') and (b) loss tangent (tan δ), respectively.

Table 4.6 Dynamic properties of NR vulcanizates filled with silica particles

Sample code	E' at 25 °C (MPa)	Peak height of tan δ	T_g (°C)
LNR	1.71	2.26	-40.9
LC-20	2.31	2.10	-40.7
LU-20	2.54	1.99	-40.0
LMM-20	2.62	1.95	-39.6
LPhM-20	2.71	1.92	-38.5
LPhE-20	2.84	1.90	-38.2
LAM-20	2.80	1.93	-38.5

CHAPTER 5
CONCLUSION

5.1 Conclusion

In this research, the surface modification of silica particles by organoalkoxysilane (PhTES, PhTMS, MpTMS and ATMS) as a modifier was successfully carried out via a sol – gel reaction of TEOS as a silica precursor. The optimum condition for the modification of silica surface was the use of the molar ratio of TEOS to modifier of 1:0.4 at ambient temperature for 24 h. After the surface modification, the hydrophobicity, particles size, and thermal stability of modified silica particles were increased, and the modified silica particles showed the antioxidant activity by DPPH method. Additionally, this research studied the influence of unmodified and modified silica particles on the mechanical, thermal, dynamic properties and ozone resistance of NR vulcanizates compared to commercial silica particles in order to improve the compatibility between NR matrix and silica particles and to prolong the lifetime of rubber product. The NR vulcanizates was prepared by using two methods are as follows: latex solution and solid rubber method. The well dispersion of modified silica particles filled NR vulcanizates both latex and solid rubber was observed leading to the good compatibility between modified silica particles and NR matrix. The properties of NR vulcanizates prepared by NR latex were similar to those of NR solid. The incorporation of modified silica particles can be improved the mechanical and thermal properties of NR vulcanizates. In addition, the NR vulcanizates filled with modified silica particles showed the better ozone resistance when compared to NR vulcanizates filled with unmodified silica particles. This is because the modified silica particles could diffuse to the rubber in order to scavenge the ozone, and the initial reaction with ozone was rapidly reacted. Accordingly, the modified silica particles obviously can improve the mechanical properties and prevent the degradation and ozonolysis of rubber product, which was comparable to irganox 1010.

5.2 Recommendations

5.2.1 Study the other functional groups of modify agents that can act as the antidegradants compounds to modify the surface of silica particles for improvement the thermal properties of NR.

5.2.2 Study the effect of modified silica particles that use as reinforcing filler on the other rubber vulcanizates in order to improve the compatibility between filler and rubber matrix including the mechanical and thermal properties.

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APPENDIX

APPENDIX A

Table A.1 Composition of concentrated natural rubber latex

Parameter	Unit	Spec	Content	Method
total solid content	%by mass	61.50 min	61.8843	ISO 124: 2008
dry rubber content	%by mass	60.00 min	60.1373	ISO 126: 2005
non-rubber content	%by mass	2.00 max	1.7470	W-CBI-QCC-20
Ammonia content	%by mass	0.65-0.75	0.7225	ISO 125: 1003
pH value (25.60)	-	11 max	10.51	ISO 976: 1996
KOH number	%by mass	0.85 max	0.5370	ISO 127: 1995
VFA number	-	0.05max	0.0258	ISO 506: 1992
M.S.T @55% TSC	sec	650 min	1050	ISO 35: 2004
magnesium content	ppm	60 max	18	W-CBI-QCU-46
viscosity	cps	-	61	ISO 1652: 2004
coagulum content	Pp	-	24	ISO 706: 1985

Table A.2 Composition of natural rubber (STR 5L)

Content name	Unit	Content
dirt, retaned on 46 aperture	% wt	0.009
ash	% wt	0.25
volatile matter	% wt	0.22
nitrogen	% wt	0.31
mooney viscosity ML (1+4) 100 °C	-	89.10

Table A.3 Properties of commercial silica as precipitated silica (Hisil 255)

Content name	Unit	Content
pH	5% suspension	6.9
moisture (as packed)	%	5.5
Na_2SO_4	%	1.17
bulk denity	g/cm^3	0.250
surface area	m^2/g	177

APPENDIX B

CALCULATION

B.1 The calculation of %yield of silica particles from TEOS via a sol-gel process

$$\%\text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

By theoretical yield can be calculated from the below equation

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

From equation; 1 mole of TEOS = 1 mole of SiO_2

In experimental; using 3.0 ml TEOS

= 0.01344 mole of TEOS

Therefore theoretical yield = 0.01344 mole of SiO_2

= 0.01344 mole × 60.08 g/mole

= 0.8075 g of SiO_2

The actual yield 24 h = 0.7768 g of SiO_2

$$\%\text{yield} = \frac{0.7768\ \text{g of}\ SiO_2}{0.8075\ \text{g of}\ SiO_2} \times 100 \quad = \quad 96.2\%$$

APPENDIX C

Table C.1 Peak area of silanol groups at Si-OH stretching 948 cm^{-1} of silica particles

Sample code	Peak area of Si-OH groups (A·cm^{-1})
C-Si particles	4.23
U-Si particles	3.75
MM-Si particles	0.67
PhM-Si particles	0.53
PhE-Si particles	0.56
AM-Si particles	0.84

Table C.2 CHN analysis of silica particles

Sample code	No.	Element contents		
		%Carbon	%Hydrogen	%Nitrogen
U-Si particles	1.	0.00	1.05	0.00
	2.	0.00	1.06	0.00
	3.	0.00	1.08	0.00
	Average	0.00 ± 0.00	1.06 ± 0.02	0.00 ± 0.00
MM-Si particles	1.	7.31	1.41	0.00
	2.	7.19	1.42	0.00
	3.	7.49	1.44	0.00
	Average	7.31 ± 0.14	1.42 ± 0.02	0.00 ± 0.00

Table C.2 (to) CHN analysis of silica particles

Sample code	No.	Element contents		
		%Carbon	%Hydrogen	%Nitrogen
PhM-Si particles	1.	17.83	1.24	0.00
	2.	17.92	1.26	0.00
	3.	17.67	1.23	0.00
	Average	17.81 ± 0.13	1.24 ± 0.02	0.00 ± 0.00
PhE-Si particles	1.	17.12	1.20	0.00
	2.	17.25	1.19	0.00
	3.	17.42	1.21	0.00
	Average	17.26 ± 0.15	1.20 ± 0.01	0.00 ± 0.00
AM-Si particles	1.	11.77	1.31	1.54
	2.	11.53	1.28	1.32
	3.	11.44	1.29	1.38
	Average	11.58 ± 0.17	1.29 ± 0.02	1.41 ± 0.11

Table C.3 Contact angle of silica particles

Sample code	No.	Contact angles of each molar ratio			
		0.04	**0.4**	**1.0**	**2.0**
MM-Si particles	1.	120	130	135	146
	2.	122	132	137	143
	3.	121	131	137	142
	4.	124	131	138	144
	5.	121	132	136	145
	Average	122 ± 1.52	131 ± 0.84	137 ± 1.14	144 ± 1.58
PhM-Si particles	1.	125	134	138	149
	2.	123	132	139	150
	3.	126	132	140	151
	4.	125	131	138	151
	5.	126	132	139	149
	Average	125 ± 1.22	132 ± 1.10	139 ± 0.84	151 ± 1.34
PhE-Si particles	1.	127	134	140	156
	2.	127	135	142	156
	3.	127	135	140	157
	4.	128	134	142	159
	5.	126	133	140	159
	Average	127 ± 0.71	134 ± 0.84	141 ± 1.10	157 ± 1.52

Table C.3 (to) Contact angle of silica particles

Sample code	No.	Contact angles of each molar ratio			
		0.04	**0.4**	**1.0**	**2.0**
AM-Si particles	1.	93	70	-	-
	2.	93	72	-	-
	3.	93	68	-	-
	4.	93	71	-	-
	5.	94	72	-	-
	Average	93 ± 0.45	70 ± 1.48	-	-

Table C.4 Tensile properties of NR vulcanizates before ageing

Sample code	M_{300} (MPa)	T_B (MPa)	E_B (%)
LNR	1.81 ± 0.03	22.39 ± 2.36	691.78 ± 19
LC-10	2.32 ± 0.05	23.24 ± 0.39	690.78 ± 14
LU-10	2.81 ± 0.07	21.95 ± 1.00	637.95 ± 12
LMM-10	2.33 ± 0.02	22.40 ± 0.94	673.78 ± 13
LPhM-10	2.36 ± 0.07	21.87 ± 0.54	661.34 ± 9
LPhE-10	2.40 ± 0.09	21.57 ± 1.35	662.37 ± 15
LAM-10	2.22 ± 0.08	16.73 ± 0.84	609.87 ± 10
LC-20	3.06 ± 0.02	23.75 ± 0.69	647.99 ± 11
LU-20	3.81 ± 0.06	22.84 ± 0.69	641.00 ± 7
LMM-20	3.74 ± 0.02	22.67 ± 0.63	659.38 ± 15
LPhM-20	2.85 ± 0.02	21.98 ± 0.18	668.52 ± 9
LPhE-20	2.81 ± 0.02	21.65 ± 0.39	647.62 ± 17
LAM-20	2.63 ± 0.09	20.63 ± 0.21	525.00 ± 17
SNR	2.06 ± 0.04	22.16 ± 1.49	673.25 ± 14
SC-20	4.03 ± 0.08	28.47 ± 0.49	695.04 ± 5
SU-20	3.45 ± 0.11	22.90 ± 1.62	651.63 ± 16
SMM-20	2.37 ± 0.06	17.53 ± 0.77	660.23 ± 4
SPhM-20	2.21 ± 0.02	17.15 ± 0.25	660.77 ± 5
SPhE-20	2.24 ± 0.04	15.43 ± 0.78	640.93 ± 4

Table C.5 Tensile properties of NR vulcanizates after ageing

Sample code	M_{100} (MPa)	T_B (MPa)	E_B (%)
LNR	1.10 ± 0.02	10.44 ± 1.23	446.65 ± 16
LC-20	1.41 ± 0.01	14.79 ± 0.37	484.27 ± 13
LU-20	1.32 ± 0.03	16.14 ± 0.97	454.44 ± 9
LMM-20	1.25 ± 0.01	18.04 ± 0.28	578.07 ± 10
LPhM-20	1.15 ± 0.01	19.97 ± 0.61	584.86 ± 8
LPhE-20	1.64 ± 0.05	20.11 ± 0.71	522.66 ± 14
LAM-20	1.58 ± 0.06	17.42 ± 0.56	506.95 ± 12
SNR	0.91 ± 0.02	7.28 ± 1.68	408.26 ± 17
SC-20	1.15 ± 0.05	18.24 ± 1.48	491.48 ± 8
SU-20	1.03 ± 0.09	17.30 ± 0.82	465.29 ± 12
SMM-20	1.19 ± 0.04	13.22 ± 1.08	542.62 ± 9
SPhM-20	1.36 ± 0.06	14.57 ± 0.93	558.93 ± 10
SPhE-20	1.56 ± 0.02	14.98 ± 1.05	503.74 ± 7

Table C.6 Mechanical properties of NR vulcanizates

Sample code	Hardness (shore A)	Tear strength (N/mm)	Volume loss (mm^3)	Compression set (%)
LNR	38.6 ± 0.5	68.6 ± 0.9	325 ± 11.5	15.6 ± 0.3
LC-10	44.4 ± 1.1	75.4 ± 1.8	269 ± 15.4	24.3 ± 1.9
LU-10	43.7 ± 0.4	73.4 ± 3.4	241 ± 9.2	20.9 ± 0.4
LMM-10	43.4 ± 0.5	72.4 ± 1.7	263 ± 3.0	20.2 ± 0.8
LPhM-10	43.0 ± 1.0	71.8 ± 2.9	255 ± 9.5	16.3 ± 0.3
LPhE-10	42.9 ± 0.2	71.4 ± 1.2	254 ± 6.0	15.9 ± 0.4
LAM-10	45.8 ± 0.6	68.9 ± 1.8	246 ± 2.8	21.6 ± 0.6
LC-20	50.7 ± 0.4	77.5 ± 1.9	243 ± 5	28.0 ± 0.7
LU-20	49.1 ± 0.2	76.3 ± 2.3	198 ± 10	27.1 ± 0.9
LMM-20	47.4 ± 0.2	73.8 ± 3.2	240 ± 15	22.8 ± 1.1
LPhM-20	46.2 ± 0.3	72.1 ± 2.2	243 ± 16	22.3 ± 0.8
LPhE-20	46.7 ± 0.3	72.3 ± 2.3	245 ± 7	21.8 ± 0.6
LAM-20	51.5 ± 0.2	71.5 ± 2.5	241 ± 8	20.2 ± 0.6
SNR	39.7 ± 0.4	69.1 ± 2.7	333 ± 13	17.7 ± 0.9
SC-20	49.5 ± 0.4	77.9 ± 2.6	294 ± 15	24.2 ± 0.9
SU-20	45.7 ± 0.3	76.8 ± 1.7	207 ± 14	23.8 ± 0.6
SMM-20	46.3 ± 0.5	73.0 ± 1.3	228 ± 17	22.9 ± 0.7
SPhM-20	46.6 ± 0.2	71.1 ± 1.4	239 ± 15	22.4 ± 0.9
SPhE-20	47.3 ± 0.4	71.5 ± 1.7	245 ± 13	21.4 ± 0.4

Table C.7 Properties of NR latex vulcanizates filled with antioxidant compounds (irganox 1010)

Properties	**LNR-I^c**	**LC-20-I^c**	**LU-20-I^c**
Cure characteristics			
t_{s2} (min)	3.58	3.53	3.48
t_{c90} (min)	5.96	7.32	6.05
ΔM (dN.m)	4.28	6.17	5.67
Mechanical properties			
$M_{300}{}^a$ (MPa)	3.35 ± 0.05	3.35 ± 0.05	4.00 ± 0.08
$T_B{}^a$ (MPa)	22.58 ± 0.55	22.58 ± 0.55	21.55 ± 0.49
$E_B{}^a$ (%)	659.38 ± 16	639.38 ± 16	632.24 ± 6
$M_{100}{}^b$ (MPa)	0.77 ± 0.01	1.59 ± 0.02	1.40 ± 0.02
$T_B{}^b$ (MPa)	13.73 ± 1.24	15.24 ± 1.95	16.68 ± 1.82
$E_B{}^b$ (%)	571.38 ± 17	505.42 ± 12	495.85 ± 8
Thermal properties			
T_{id} (°C)	295.68	318.74	321.49
T_{max} (°C)	385.81	388.52	390.37
T_g (°C)	-61.5	-61.0	-59.5

^{a} before ageing

^{b} after ageing

^{c} irganox 1010 1 phr

Table C.8 Properties of NR solid vulcanizates filled with antioxidant compounds (irganox 1010)

Properties	**SNR-I^c**	**SC-20-I^c**	**SU-20-I^c**
Cure characteristics			
t_{s2} (min)	4.09	8.48	7.65
t_{c90} (min)	9.62	13.73	12.75
ΔM (dN.m)	4.35	7.01	5.04
Mechanical properties			
$M_{300}{}^a$ (MPa)	2.03 ± 0.09	4.10 ± 0.10	3.63 ± 0.07
$T_B{}^a$ (MPa)	21.15 ± 1.91	28.00 ± 0.65	27.92 ± 0.74
$E_B{}^a$ (%)	675.86 ± 15	682.62 ± 12	680.76 ± 10
$M_{100}{}^b$ (MPa)	0.95 ± 0.01	1.67 ± 0.04	1.48 ± 0.02
$T_B{}^b$ (MPa)	9.29 ± 1.25	21.41 ± 2.56	16.97 ± 0.51
$E_B{}^b$ (%)	460.47 ± 15	498.71 ± 9	484.43 ± 9
Thermal properties			
T_{id} (°C)	292.36	310.59	315.82
T_{max} (°C)	380.19	382.24	385.58
T_g (°C)	-60.5	-60.0	-59.5

[a] before ageing

[b] after ageing

[c] irganox 1010 1 phr

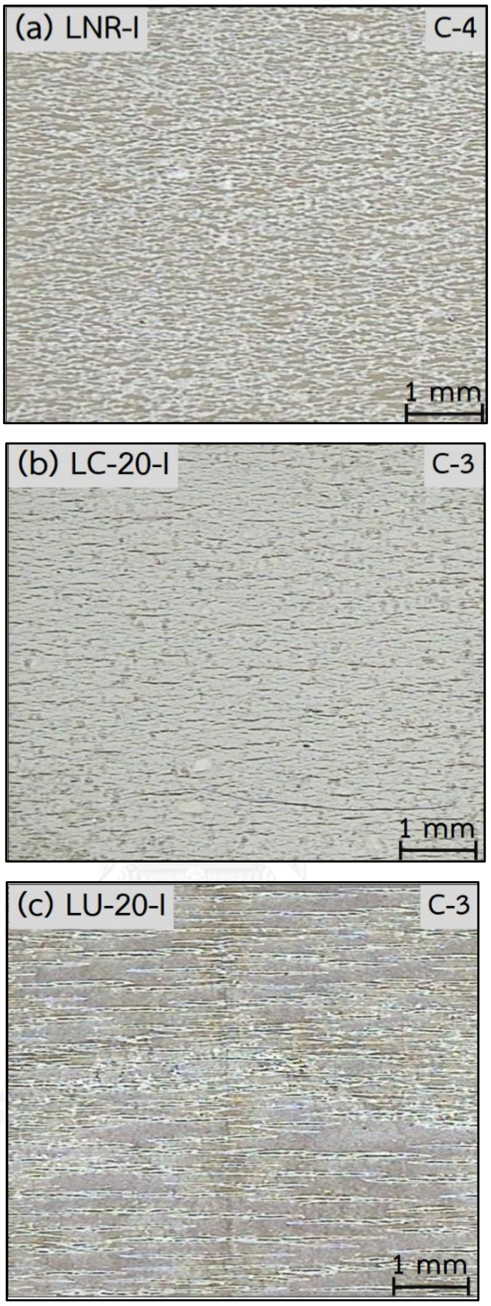

Figure C.1 Ozone resistance of NR latex vulcanizates filled with antioxidant compounds (irganox 1010)

VITA

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Presentation

2014 Effect of modified silica particles with phenyltriethoxysilane on mechanical and thermal properties of natural rubber composites, July 6-11, International Conference on 2014 IUPAC World Polymer Congress or MACRO 2014, Chiang Mai, Thailand