

จุฬาลงกรณ์มหาวิทยาลัย
รายงานฉบับสมบูรณ์ของโครงการวิจัย
ทุนอุดหนุนการวิจัยจากงบประมาณแผ่นดิน ประจำปี 2547

ชื่อผู้วิจัย หัวหน้าโครงการ ผู้ช่วยศาสตราจารย์ ดร. วราวุฒิ ตั้งพสุธาตล
ภาควิชาเคมี คณะวิทยาศาสตร์
ผู้ร่วมงานวิจัย อาจารย์ ดร. อมราวรรณ อินทศิริ
ภาควิชาเคมี คณะวิทยาศาสตร์
ผู้ช่วยวิจัย นางสาวดารณี นันตวานิช นิสิตระดับมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

โครงการวิจัยเรื่อง การเพิ่มความแข็งแรงของยางพาราแบบใช้ซิลิกาโดยกระบวนการโซลเจลในลา
เทกซ์
Silica reinforcement of natural rubber by sol-gel process in latex

ประเภทของการวิจัย การวิจัยและพัฒนา

สาขาวิชา วิทยาศาสตร์เคมีและเภสัช กลุ่มวิชาการ เคมีพอลิเมอร์

ได้รับเงินอุดหนุนโครงการวิจัย

ปีการเงิน 2547 โครงการ 1 ปี

จำนวนเงินทั้งสิ้น 282,000 บาท

รายงานฉบับสมบูรณ์ ซึ่งเป็นผลงานระหว่างเดือน ตุลาคม 2546 ถึงเดือน กันยายน 2547

วันที่ส่งรายงานฉบับแก้ไข 1 สิงหาคม พ.ศ. 2548

ลงชื่อผู้วิจัยหลัก
(ผู้ช่วยศาสตราจารย์ ดร. วราวุฒิ ตั้งพสุธาตล)

เฉพาะเจ้าหน้าที่
วันที่ได้รับรายงาน
วันที่ส่งไปยังคณะกรรมการ
วันที่ตอบรับจากคณะกรรมการ
วันที่ส่งกองคลัง

ABSTRACT

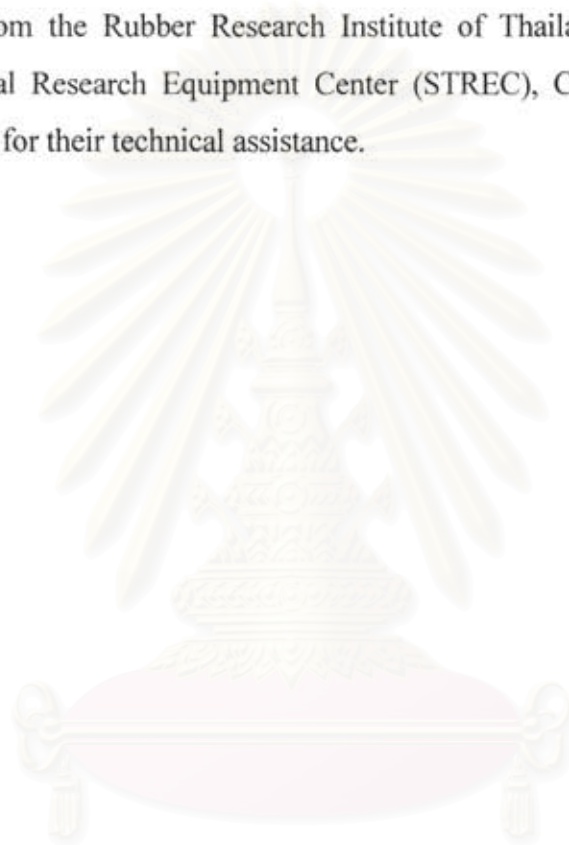
Beside carbon black, silica powder is the other important filler used to reinforce various colored rubber products. In order to improve the compatibility between silica particles and rubber phase, this work has focused on preparing an NR composite, reinforced by silica generated inside the NR matrix or '*in situ*'. The silica particle was formed by a sol-gel process of tetraethoxysilane (TEOS) dispersed in NR latex. The latex used was concentrated latex having 60% rubber content, and already contained water and ammonia, two ingredients needed for the sol-gel reaction. The conversion of TEOS to silica was close to 100%, and the particles size was about 44 nm in diameter, determined by TEM. The silica particles scattered evenly in the rubber. A statistical analysis method, named 'two-level factorial design', was used to study the influence of the amount of TEOS, ammonia, and gelation time on the mechanical properties of the composite. Silica content as high as 19% was prepared successfully. The composite had a tensile modulus of 3.7 MPa and a tear strength value of 41 N/mm. It was also found that the composite containing *in situ* silica had a higher tensile modulus and tear strength than a composite that was prepared by conventionally mixing with silica powder.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

ACKNOWLEDGEMENTS

The funding of this work was supported by Chulalongkorn University. Silica powder was provided by PPG-Siam Silica Co., Ltd. NR latex was also donated by Thai Rubber Latex Corporation (Thailand) public Co., Ltd. I appreciate the technical assistance by The staff from the Rubber Research Institute of Thailand and from Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University are also thanked for their technical assistance.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Contents

ABSTRACT	i
ACKNOWLEDGEMENT	ii
CHAPTER 1	1
1.1 Statement of Problems	1
1.2 Objective	1
1.3 Scope of the Investigation	2
CHAPTER 2	3
2.1 Filler Reinforcement System [5]	3
2.2 Description of Curing Parameters [5]	4
2.3 Sol-gel Process	5
2.4 Experimental Design-2 ^k Factorial Design [11,12]	6
CHAPTER 3	9
3.1 Materials	9
3.2 Chemicals	9
3.3 Instruments and Apparatus	9
3.4 Methods	11
CHAPTER 4	19
4.1 Mixing of NR latex and TEOS	19
4.2 Effect of gelation temperature on the composites	19
4.3 Conversion of TEOS to Silica	20
4.4 Physical Appearance of the NR-Silica Composites	20
4.5 Experimental Design for Study Factors that Influence Mechanical Properties of NR-Silica Composite	23
4.6 Comparison Between <i>in situ</i> Silica and Mechanically Mixed Silica	29
CHAPTER 5	34
5.1 Conclusion	34
5.2 Future Direction	34

CHAPTER 1

INTRODUCTION

1.1 Statement of Problems

Natural rubber (NR) is an important agriculture product essential for manufacturing. Usually, inorganic fillers are mixed with rubbers to reinforce the rubber products. Beside carbon black, silica (SiO_2) is the other important filler used in the rubber industry. The products obtained from mixing with silica are colorless or white. Therefore, other colors can be added to these products.

A problem of silica-reinforced rubber is incompatibility between silica and rubber, resulting in poor mechanical properties. A well-known method for improving the reinforcement effect is to treat silica surface by 'silane coupling agent' to promote interaction with rubber. Another method is to add silane coupling agent during NR-silica mixing process. Until recently, *in situ* synthesis of silica particles inside NR matrix has been widely studied as a new compounding method for NR composite (see section 2.3). The '*in situ* generation' of silica was accomplished by means of sol-gel process of tetraethoxysilane or TEOS, a precursor for silica particles, which was carried out in NR sheets.

Since Thailand can produce NR latex in a great quantity, this work was therefore decided to mix TEOS directly into the latex. The mixture was then baked in order to induce the sol-gel process of the silane, thus silica particles was formed while the latex was dried to become NR-silica composite. Water and ammonia, two major components needed to induce the sol-gel process, are already present in the latex. This might be a novel and alternate method to prepare the corresponding composites that could save energy consumption required to prepare the rubber sheets.

Therefore, this focus of research was to prepare silica-reinforced NR composite by using the sol-gel process of TEOS in NR latex. Mechanical properties of the composite filled with '*in situ* generated' silica and 'mechanically mixed' silica were also compared.

1.2 Objective

The objective of this project was to utilize natural rubber latex to prepare silica-reinforced natural rubber composite by sol-gel reaction of tetraethoxysilane (TEOS) in the latex.

1.3 Scope of the Investigation

The stepwise investigation was carried out as follows:

1. Literature survey for related research work.
2. Prepare silica reinforcement of NR by sol-gel process in latex.
3. Carry out the sol-gel process of TEOS in NR latex and prepare the silica-NR composites. Experimental factors being investigated were the amount of TEOS, ammonia, gelation temperature and time.
4. Study the effect of experimental factors on mechanical properties by using two-level factorial design.
5. Characterize the morphology of silica generated in the composites by SEM and TEM
6. Determine the amount of silica generated in the composites by thermogravimetric method.
7. Determine curing behavior and mechanical properties of NR-silica composites according to ASTM methods.
8. Make a comparison between the NR composites filled with *in situ* silica and mechanically mixed silica
9. Summarize the results.

CHAPTER 2

THEORETICAL AND LITERATURE REVIEW

2.1 Filler Reinforcement System [5]

2.1.1 Reinforcement Concepts

Reinforcement basically relates to composites built from two or more structural elements or components of different mechanical characteristics. The strength of one of these elements is imparted to the composite. One typical example of reinforcement is that of concrete with embedded steel rods or cable where the high tensile strength of the steel is imparted to the concrete to give it increased flexural and impact strength. A strong bond must develop between the reinforcing materials and the embedding matrix.

2.1.2 Effect of Particle Size on Elastomer Reinforcement

Modulus and tensile strength of the composite are very much dependent on the particle size of the filler. Small particles have a much greater effect than coarse ones. Particle size is directly related to the reciprocal of surface area per gram of filler; thus the effect of smaller particles actually reflects their greater extent of interface between polymer and solid material.

The reduction in properties at higher loading is a dilution effect, general to all fillers, merely due to a diminishing volume fraction of polymer in the composite. If the volume percentage of filler becomes so high that there is not enough rubber matrix to hold the filler particles together, strength approaches zero. Before this stage of loading is reached, the compound attains a level of stiffness where it becomes brittle and, at the normal rate of testing (e.g. 50 cm per minute) such a brittle compound would show poor strength. The place of the maximum is also dependent on the particle size of the filler.

A summary of the main influence of each of the four filler characteristics is given below:

- 1) Smaller particle size (larger external surface area)
Results: higher tensile strength, higher hysteresis, higher abrasion resistance, higher electrical conductivity for carbon blacks, higher Mooney viscosity. Minor effects on: extrusion shrinkage and modulus.
- 2) Increase in surface activity (physical adsorption)

Results: higher modulus at higher extension (300% up), higher abrasion resistance, higher adsorptive properties, higher “bound rubber”, lower hysteresis

3) Increase in persistent structure and anisometry

Results: lower extrusion shrinkage, higher modulus and medium extension (up to 300%), higher Mooney viscosity, higher hysteresis, longer incorporation time. Better dispersion, low electrical resistivity for carbon blacks. This property particularly is interrelated with surface activity; structure changes on fillers without surface activity (graphitized black) show the effects indicated above only rather faintly. When a filler’s surface activity is high (and constant), variations in its structure have the greatest effect on its rubber properties.

2.2 Description of Curing Parameters [5]

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

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

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

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

Overcure- A cure which is longer than optimum is an “overcure.” Overcures may be of two types. In one type, the stock continues to harden, the modulus rises, and

tensile and elongation fall. In other cases, including most natural rubber compounds, reversion occurs with overcure and the modulus and tensile strength decrease.

2.3 Sol-gel Process

The sol-gel technique is used to prepare inorganic glasses at low temperatures. A classic example is the reaction of tetraethoxysilane (TEOS) to give silica glass (SiO_2). The reaction of TEOS takes place in two steps, hydrolysis and condensation, to produce SiO_2 (Fig. 2.1).

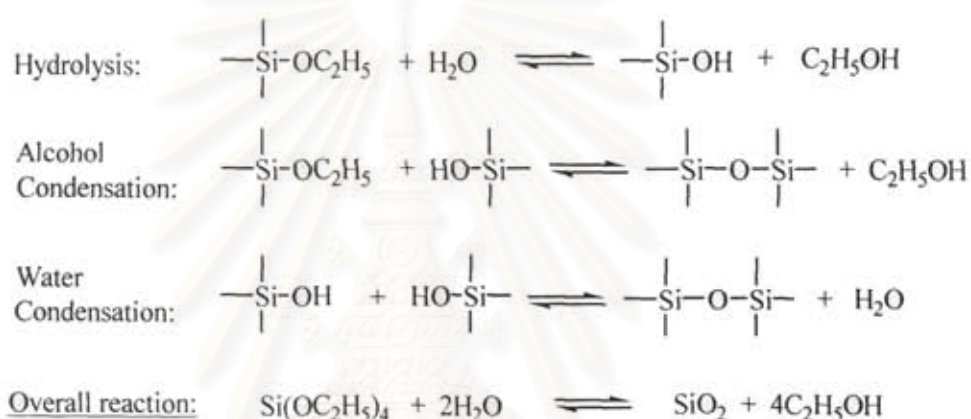


Figure 2.1 Hydrolysis and condensation reaction of TEOS to form silica.

Sol-gel process in polymers

Recently, a sol-gel process of TEOS was applied to prepare silica for reinforcing various types of rubbers, e.g. natural rubber [13], synthetic rubber [14-18]. In general, thin rubber sheet was swollen in TEOS (with or without solvent), followed by soaking in acid or base catalyst. The soaked sheet was then heated to induce the sol-gel reaction of TEOS. *In situ* silica-filled rubber was obtained.

Ikeda Y. et al. [18] studied the effect of catalyst on *in situ* silica reinforcement of SBR (styrene butadiene rubber). They found that basic catalyst (n-butylamine) was needed for the sol-gel process of TEOS in the SBR vulcanizate. There was also a report that the scorch time of *in situ* silica-NR composite was shorter than that of the composite obtained by mechanically mixing [13]. This indicated that curing in the former reached an optimum value faster than the latter.

The disadvantages of the silane swelling method for the NR sheet are time-consuming and uncontrollable TEOS content in the solid rubber. A solution to this problem is to directly add TEOS in the polymer latex. This method was successfully implemented in a number of reports for silica-reinforced SBR [19], poly(butyl methacrylate) [20], polyacrylamide [21], and polyimide [22]. In one of the report

[19], the ratio of water and TEOS in the latex mixture governed the size of silica particles. The size reached a nanometer-order level, leading to a drastic increase of tensile strength of the composite.

2.4 Experimental Design- 2^k Factorial Design [11,12]

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on response. There are several special cases of the general factorial design that are important because they are widely used in research work and also because they form the basis of other designs of considerable practical value.

The most important of these special cases is that of k factors, each at only one two levels. These levels may be quantitative or may be qualitative such as the presence and absence of a factor, the high and low levels of a factor. A complete replicate of such a design requires $2_1 \times 2_2 \times \dots \times 2_k = 2^k$ observations and is called a 2^k factorial design. It is particularly useful in the early stages of experimental work, when there are likely to be many factors to be investigated. It provides the smallest number of runs which k factors can be studied in a complete factorial design. Consequently, these designs are widely used in factor screening experiments. Because there are only two levels for each factor, it is assumed that the response is approximately linear over the range of the factor levels chosen.

Suppose that 3 factors, A, B and C, each at two levels, are of interest. The design is called a 2^3 factorial design. Using the "+" and "-" notation to represent the high and low levels of the factors, the eight runs in the 2^3 design are listed in Table 2.1. This is called a design matrix. There are actually 3 different notations that are widely used for the runs in the 2^k design. The first is the + and - notation, often called the geometric notation. The second notation uses 1 and 0 to denote high and low factor levels, respectively, instead of the plus and minus sign. The final notation is the use of lowercase letter labels to identify the treatment combinations. These different notations are illustrated in Table 2.1 for the 2^3 design.

Table 2.1 The design matrix and different notation for the 2^3 design

Run	A	B	C	A	B	C	labels
1	-	-	-	0	0	0	(1)
2	+	-	-	1	0	0	<i>a</i>
3	-	+	-	0	1	0	<i>b</i>
4	+	+	-	1	1	0	<i>ab</i>
5	-	-	+	0	0	1	<i>c</i>
6	+	-	+	1	0	1	<i>ac</i>
7	-	+	+	0	1	1	<i>bc</i>
8	+	+	+	1	1	1	<i>abc</i>

There are seven degrees of freedom between the eight treatment combinations in the 2^3 design. Three degrees of freedom are associated with the main effects of A, B and C. Four degrees of freedom are associated with interactions; one each with AB, AC and BC and one with ABC.

Next a value called 'effect' must be determined from the design matrix. The effect is the difference between average value of the *high* and the *low* levels of each factor.

$$Effect = \hat{y}_+ - \hat{y}_-$$

The effects are calculated by using the columns of contrast coefficients, illustrated in Table 2.2. The contrasts for the main effects are the sign used in the design matrix. These are applied to the responses and then divided by 4, since this is the number of comparison mode. Thus, to calculate the A effect:

$$A \text{ Effect} = \frac{-y_1 + y_2 - y_3 + y_4 - y_5 + y_6 - y_7 + y_8}{4}$$

The other main effects could be calculated in a similar manner. Note that each effect has four – and four + signs associated with it.

An interaction effect, e.g. AB effect, can be calculated by

$$AB \text{ Effect} = \frac{+y_1 - y_2 - y_3 + y_4 + y_5 - y_6 - y_7 + y_8}{4}$$

Table 2.2 The columns of contrast coefficients for the 2^3 design

A	B	C	AB	AC	BC	ABC	y
-	-	-	+	+	+	-	y ₁
+	-	-	-	-	+	+	y ₂
-	+	-	-	+	-	+	y ₃
+	+	-	+	-	-	-	y ₄
-	-	+	+	-	-	+	y ₅
+	-	+	-	+	-	-	y ₆
-	+	+	-	-	+	+	y ₇
+	+	+	+	+	+		y ₈

If replicate experiments are also performed, whose *standard errors* (E) in the effect values are calculated,

$$E = \left(\frac{\sum V}{2N} \right)^{1/2}$$

where V is the variance of replications and N is the number of experiments performed. The standard error (E) is used to determine which factor is likely to be important or significant. If the effect value is larger than the standard error, that effect has a significant influence on the tested property.

Detailed method for experimental design carried out in this research is shown in Experimental chapter.

จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER 3

EXPERIMENTAL

3.1 Materials

- Concentrated and high-ammonia NR latex with %DRC of 60% (Thai Rubber Latex Corporation (Thailand) Public Co., Ltd. and Rubber Research Institute of Thailand)
- NR block STR5L (Teck Bee Hang Co., Ltd)
- Silica: Hi-Sil 255-S (F-10-02) (PPG-Siam Co., Ltd (Thailand))

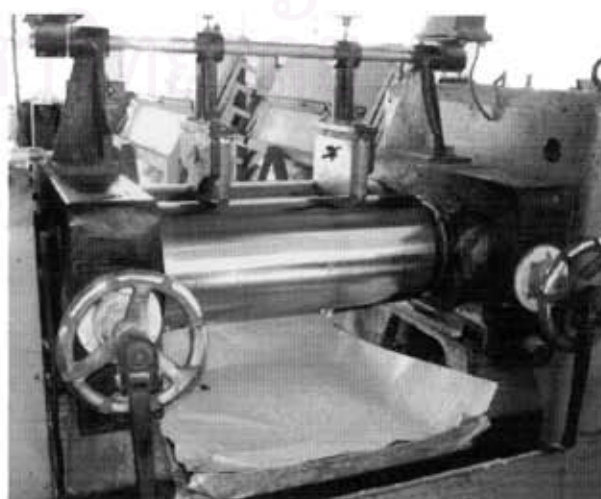
3.2 Chemicals

- | | |
|--|---------------------------------|
| • Tetraethoxysilane (TEOS) | : Fluka |
| • Ammonia solution (NH ₃) | : Fluka |
| • Styrene monomer | : Fluka |
| • Zinc oxide (ZnO) | : Univentures Public Co., Ltd. |
| • Stearic acid | : Imperial (Thailand) Co., Ltd. |
| • Tetramethyl thiuram disulfide (TMTD) | : Flexsys Co., Ltd. |
| • Mercaptobenzothiazole disulfide (MBTS) | : Flexsys Co., Ltd. |
| • Sulfur | : Loxley public Co., Ltd. |
| • Wingstay L (Antioxidant) | : Goodyear Co., Ltd. |

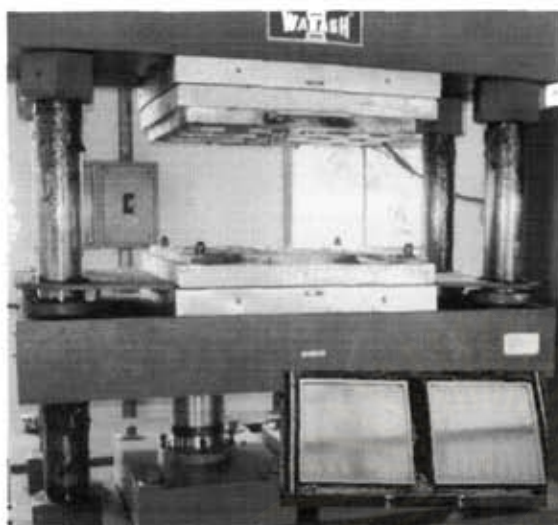
3.3 Instruments and Apparatus



Mechanical stirrer- IKA RW 20 DZM.n
(Germany)



Two-roll mill- Model R11-3-FF (Japan)



Compression molding hydraulic- Model V75h-18-BPX, Serial 9593 (USA)



Compressed air sample cutter- Model SDAP-100-N Intro Enterprise Co., Ltd. (USA)



Hardness testing- Durometer Hardness system (Shore A) Model 716 (USA)



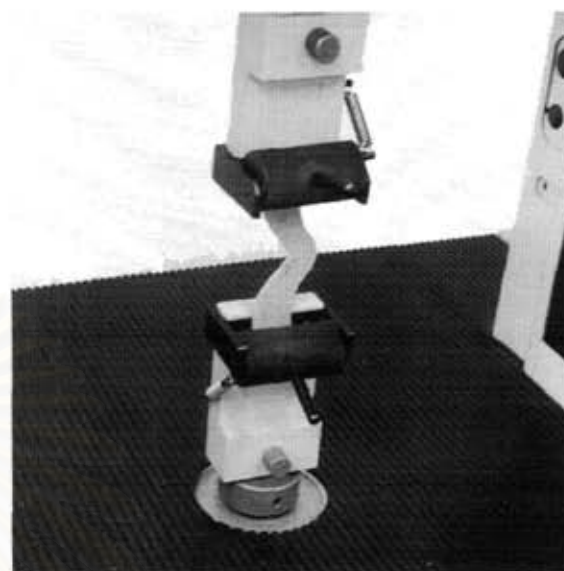
Rheometer- Monsanto MDR2000 (USA)



Mooney viscometer- Visc. Tech. (USA)



Tensile testing machine- Instron Corporation Series IX Automated Materials Testing System 6.05 Model 1011 (USA)



Tear testing machine- LLOYD Instruments LS 500 (USA)

- Scanning electron microscope JEOL, Model JSM-6400 (Japan)
- Transmission electron microscope JEOL, JEM -1220 (Japan)
- High temperature oven Carbolite GM 11/7 (England)

3.4 Methods

3.4.1 *In situ* Generation of the Silica in NR Matrix

The silica was generated in the natural rubber matrix by a method shown in Fig. 3.1, with a detailed explanation as follows.

The concentrated natural rubber latex (DRC 60%, NH_3 0.7%) was placed in a wide-mouth glass container or beaker. TEOS of the required amount (10 to 70 phr) was added into the latex with stirring at 750-800 rpm by a mechanical stirrer. The stirring was allowed to proceed for 10-15 minutes to obtain a homogeneous milky mixture. The mixture was immediately poured into a glass bowl and tightly closed with wrapping film. The mixture was heated in a 50 °C oven to let the sol-gel reaction to proceed. After 5-10 days, the wrapping film was removed and the composite was left in the oven for another 48-hour period. Partially dry composites was then fed through a two-roll mill operated at 50°C for 10-15 minutes to get rid of water and ammonia retained in the samples.

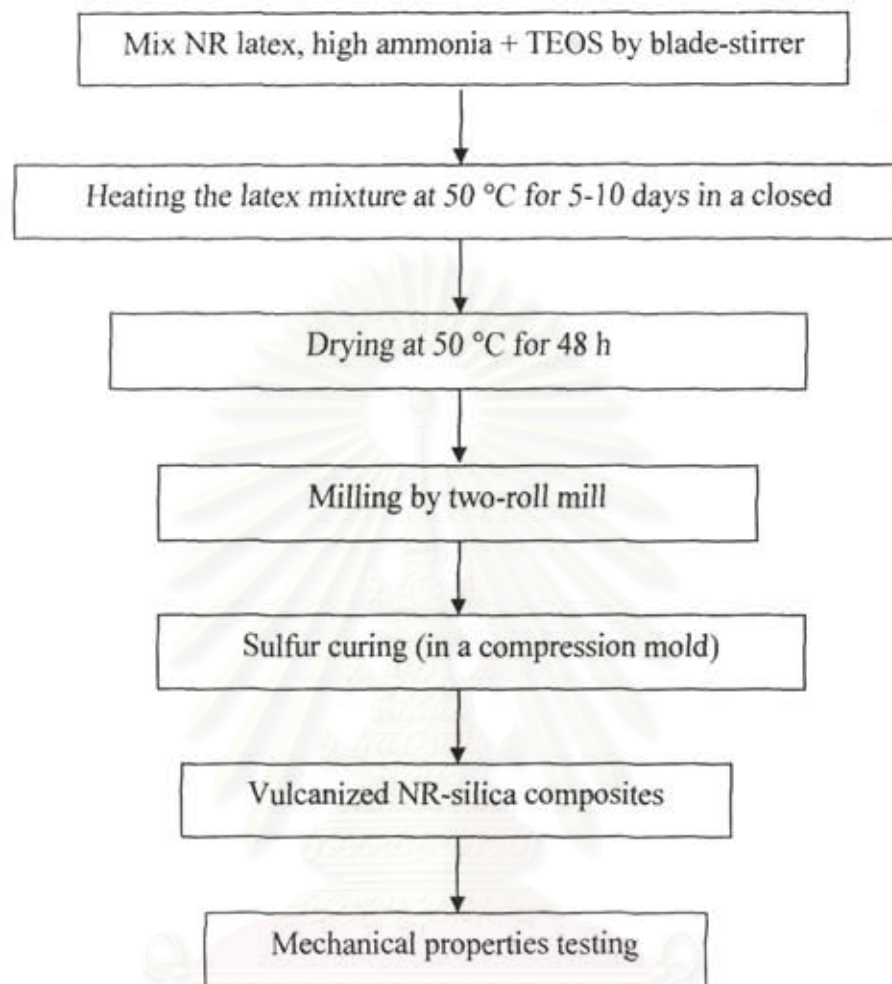


Figure 3.1 Experimental scheme for the preparation of NR-silica composite

3.4.2 Determination of the Silica Content

A piece of NR-silica composite (ca. 50 mg), prepared from the method in 3.4.1, was placed in an aluminum oxide cup and heated under air atmosphere, from 0 °C to 850 °C in an oven. The temperature was then held for 15 min at 850 °C. The silica content was calculated from the weight of remaining ash by Eq. 3.1.

$$\text{Silica content (\%)} = 100 (W_1/W_2) \quad \text{Equation 3.1}$$

And the conversion of TEOS to silica was also calculated using Eq. 3.2,

$$\text{Conversion (\%)} = 100 (W_3/W_4) \quad \text{Equation 3.2}$$

where W_1 was the weight of residue ash, and W_2 was the initial weight of the sample. W_3 was the weight of *in situ* generated silica in the sample, which was obtained from

Eq. 3.1. W_4 was the theoretical weight of silica being generated assuming quantitative conversion of TEOS into silica by



3.4.3 Vulcanization of NR-silica composite

The recipe of the compound rubber is presented in Table 3.1. Detailed procedure is as follows.

The *in situ* silica-NR composite was fed to the two-roll mill having a preset temperature of 70 °C. Then, all materials were added slowly to the rubber. The mixing proceeded until homogeneous compound was obtained. The sheet was cut off the roll and placed on a flat, dry, clean place. Small pieces were removed to test for Mooney viscosity and cure meter before vulcanization. The sheet was then placed into a preheated square-shape mold for compression at 150 °C and a pressure of 150 kg/cm² for a prescribed time. The vulcanized composite sheets of ca. 2 mm thickness were obtained. The composite prepared by mixing STR5L with silica powder was also prepared by the same vulcanization method stated earlier.

Table 3.1 Formulation for sulfur-vulcanization of the NR-silica composite

Materials	Quantity (phr*)
ZnO	3.0
Stearic acid	2.0
TMTD	0.3
MBTS	1.0
Sulfur	2.0
Wingstay L	1.0

* phr = parts per 100g rubber

3.4.4 Determination of Curing Behavior and Mechanical Properties

Determination of curing behavior and mechanical properties of vulcanized NR-silica composites were investigated by following the ASTM test methods as follows:

Rotorless Cure Meter (ASTM D5289)

The moving-die rheometer (Monsanto MDR2000) was used for determining vulcanization characterization of the rubber compounds.

A test specimen of vulcanized rubber compound is cut into a circular form. A sample shall be 30 mm in diameter and 11.5 mm in thickness. It is then placed in a

die cavity which is closed under positive pressure and maintained at the vulcanization temperature. The cavity is formed by two dies, one of which is oscillated through a rotary amplitude. This action produces a torsion strain in the test piece and torque which depends on the stiffness (shear modulus) of the rubber compound. The envelope curve, which is defined as the amplitude of the oscillating force or torque, is continuously recorded as a function of time. The stiffness of the rubber test piece increases as vulcanization proceeds. The time required to obtain a vulcanization curve (Fig. 3.1) is a function of the test temperature (150 °C) and the characteristics of the rubber compound. The test results reported are normally chosen from the following parameters: minimum (M_L) and maximum (M_{HF}) torque in dN.m unit, scorch time (t_{s2}) and cure time ($t_c(90)$) in min.

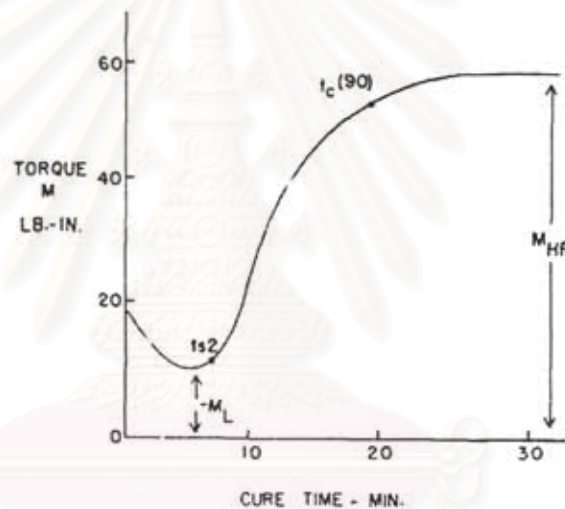


Figure 3.2 A typical vulcanization curves which attains an equilibrium torque

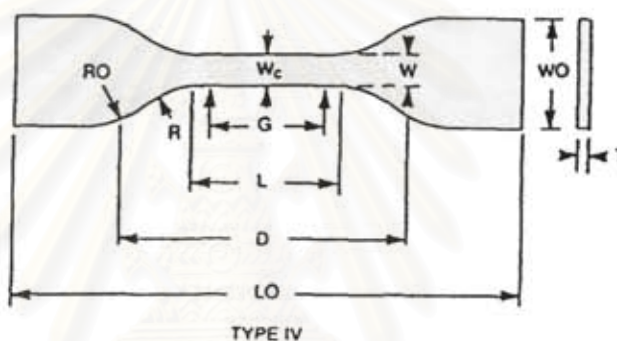
Mooney Viscometer (ASTM D1646)

A Mooney viscometer measures the effect of temperature and time on the viscosity of rubber. The test specimen consists of two pieces which completely fill the test chamber. One piece is placed above the rotor and the other beneath it. The rubber is squeezed into the cavity under considerable pressure and temperature. The rotor is continuously rotated at 2 rpm in one direction for a specified time. The resistance to this rotation offered by the rubber is measured in arbitrary torque units as the Mooney viscosity (MV) of the specimen. The viscometer is adjusted so that it will read zero torque when run empty, and 100 ± 0.5 when a torque of 8.30 ± 0.02 N-m is applied to the rotor shaft. The temperature for viscosity determination is 100 °C. The sample is allowed to warm up for one minute after the platens are closed. The motor is then started and reading taken at 4 min.

Tensile Properties (ASTM D412)

Tensile strength, elongation and modulus are determined. The vulcanized rubber is stamped with a compressed air sample cutter into a dumbbell shape (Type IV) as illustrated in Fig. 3.2. The specimens are cut from a 2.0 mm thick rubber sheet. The testing is performed on a tensile testing machine. Results reported for each sample are averages of 6 specimens. Measurement condition is as follows:

Temperature	25 °C
Humidity	60 %
Sample rate	10.00 pts/sec.
Crosshead speed	500 mm/min.



W : 6 mm	WO : 19 mm	G : 25 mm	R : 14 mm	T : 4 mm or under
L : 33 mm	LO : 115 mm	D : 65 mm	RO : 25 mm	

Figure 3.3 A schematic of the specimen for tensile test (Type IV)

Tear Strength (ASTM D624)

The vulcanized rubber is stamped with a compressed air sample cutter (Model SDAP-100-N) using a "Die C" (Figure 3.3). The cutting edges of which shall be kept sharp and free of all nicks to avoid leaving ragged edges on the specimens. It is important that the apex of 90° angle shall be sharpened to provide a sharp corner. The sample thickness is 1.9-2.0 mm. Results reported for each sample are averages of 6 specimens. The tear testing condition is shown as follows:

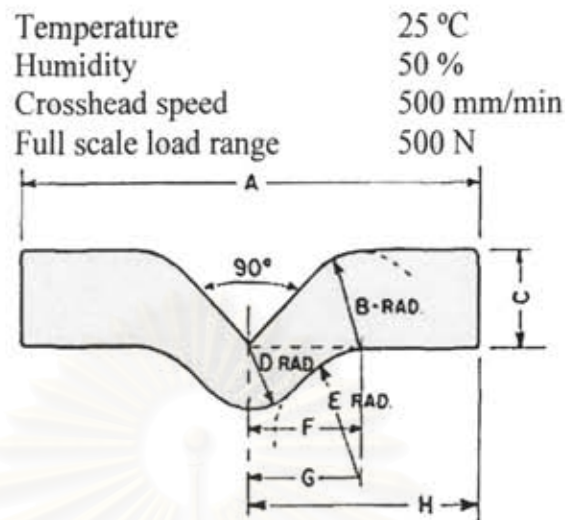


Figure 3.4 A schematic diagram of tear test specimen (Die C).

Hardness (ASTM D2240)

For the assignment of the specimen for hardness testing, the test specimen is at least 6 mm in thickness. In this experiment, the test specimens are composed of plied pieces to obtain the necessary thickness. Type A Durometer is used to measure the hardness.

The specimen is placed on a hard and horizontal surface. The presser is held on a vertical position with the point of the indenter at least 12 mm from any edge of the specimen. The presser is applied to the specimen. After the presser foot is in firm contact with the specimen, the scale reading is taken within 30 s. Measurements are made at five different points distributed over the specimen. The median of these measurements is used as the hardness value. The conditions of testing are as follows:

Temperature	25 °C
Relative humidity	50%
Number of pieces plied	3 pieces

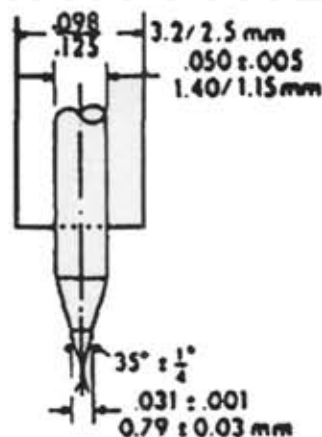


Figure 3.5 A schematic of indenter for type A Durometers.

3.4.5 Scanning Electron Microscopy

The NR-silica composite sheet was frozen in liquid nitrogen and then fractured. The sample was placed on the double sided sticky tape on a specimen stub and sputtered with gold before viewing. Morphology of the composite of the fractured surface was obtained by using SEM.

3.4.6 Transmission Electron Microscopy

The NR-silica composite was embedded in polystyrene to make the specimens harder. The specimen was cut to be a small piece and placed in osmium tetroxide (OsO_4) vapor for 24 h in order to stain the NR phase. The staining not only enhanced the contrast for the microscopic viewing of the composites but also hardened the rubber phase. The specimens were prepared to be ultra-thin films using a microtome. The specimen was placed on a copper grid, which was coated with Formvar[®]. The thin film sections of NR-silica composite was also observed by TEM. The accelerating voltage was 80 kV.

3.4.7 The Design of Two-Level Factorial Experiments

Factorial design is widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. For an experiment having k independent factors, each was studied at “low” and “high” levels. The low level is coded as -1 and the high level is coded as +1.

In this study, a 2^3 design requires a total of 8 runs. It is performed to evaluate three main effects and five interaction effects of each factor on the mechanical properties of NR-silica composite. The three factors are TEOS content, added ammonia solution, and gelation time. Details are shown in Table 3.2.

Table 3.2 Factors and levels used in the experimental design.

Factor	Unit	Level	
		(Low = -1)	(High = +1)
TEOS content (T)	phr	10	50
Added ammonia solution (N)	%	0	2.5
Gelation time (G)	days	5	10

Values for main and interaction effects were calculated from the factorial design results. Both types of effects were calculated using the Eq. 3.1.

$$Effect = \hat{y}_+ - \hat{y}_- \quad \text{Eq. 3.3}$$

where \hat{y}_+ and \hat{y}_- are the averaged values for the responses at the high and low levels of each factor.

In this study, three replicate experiments were performed, whose standard errors (E) in the effect values were calculated by Eq. 3.2.

$$E = \left(\frac{\sum V}{2N} \right)^{1/2} \quad \text{Eq. 3.4}$$

where V is the variance of three replicates and N is the number of experiments performed. The standard error was used to determine which factor was significant. If the effect value was larger than the standard error, that effect had a significant influence on the tested property.

The standard error is used to determine which factor is likely to be important. In this research, the estimated effects are calculated from 2 repeated experiments. Therefore standard error from the 2 experiment sets are used to determine which effect is significant. If the effect value is larger than the standard error, that effect has a significant influence on the tested property.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Mixing of NR latex and TEOS

TEOS is immiscible with water, but natural emulsifier present in the latex aids the mixing. When adding a small amount of TEOS, the mixture remains homogeneous and becomes more viscous when increasing TEOS content. But when the TEOS amount is larger than 70 phr, the mixture is so viscous that a homogeneous mixture can not be obtained. Rubber also tended to aggregate at the stirring blade. The latex-TEOS mixtures were left standing for no more than 15 min before the gelation (heating) step.

4.2 Effect of gelation temperature on the composites

A suitable gelation temperature for preparing the *in situ* silica-NR composites was studied by using 25 g conc. NR latex mixed with 17 and 50 phr TEOS. Three gelation temperatures; 50, 60 and 70°C, were evaluated. Results on their physical appearances are shown in Table 4.1. It was found that the composites turned brown when the gelation temperature reached 70°C. This suggested that the rubber could be thermally degraded if the heating was set at high temperature. Therefore in order to prevent rubber degradation, the gelation time of 50°C was chosen to be used as the gelation temperature for all samples in this project. The previously planned heating temperature of 40°C was omitted because it would possibly require a long heating time to obtain a dry rubber sheet starting from the NR latex.

Table 4.1 Visual appearance of *in situ* silica-NR composites (before vulcanization) after various gelation temperature (gelation time= 5 days)

Temperature (°C)	TEOS amount (phr)		
	0	17	50
50	yellowish transparent sheet	yellowish slightly opaque sheet	Yellowish opaque sheet
60	yellowish transparent sheet	yellowish slightly opaque sheet	Yellowish opaque sheet
70	brownish transparent sheet	brownish slightly opaque sheet	Brownish opaque sheet

4.3 Conversion of TEOS to Silica

Silica content in the NR composite was determined prior to sulfur curing. Data are shown in Table 4.2.

Table 4.2 The silica content and %conversion of TEOS to silica of the sol-gel process in NR

Sample code*	Added TEOS (phr)	Residue ash at 850 °C (%)	Silica content (%)	Conversion from TEOS to silica (%)
I0	0	0.17 ± 0.01	0	0
I2	10	2.82 ± 0.26	2.73 ± 0.26	94.63
I5	20	5.04 ± 0.09	5.27 ± 0.16	91.48
I7	30	7.22 ± 0.19	7.75 ± 0.19	89.67
I10	40	9.53 ± 0.08	10.49 ± 0.08	91.05
I13	50	12.44 ± 0.83	13.98 ± 0.83	97.10
I16	60	14.12 ± 0.29	16.20 ± 0.29	93.77
I19	70	16.30 ± 0.15	19.23 ± 0.15	95.40

* The sample is coded as “In”, where n indicated the silica percentage found in the sample.

The NR without TEOS was found to contain about 0.71% (w/w) residue ash when being heated at 850°C. This amount was subtracted from %residue ash of the other TEOS-filled samples. The amount of silica in the composites increases with increasing the amount of TEOS added to the latex. In all cases, the conversion from TEOS to silica (SiO₂) is 89-97% by mole, indicating that nearly all TEOS has turned into silica during the sol-gel process.

4.4 Physical Appearance of the NR-Silica Composites

4.4.1 General Observation

During the gelation (heating) step of the rubber-TEOS mixtures, their texture gradually became tofu-like. Upon drying, the rubber sheet turned yellow with a certain degree of opaqueness depending on the amount of TEOS added.

Appearances of some composites listed in Table 4.2 are shown in Fig. 4.1. The composites become more opaque with increasing silica contents. No differences could be made between the composites containing *in situ* and mechanically-mixed silica. One key observation made is that when the composite containing mechanically mixed silica is scratched, some silica powder in fact falls off. This does not occur with the composite containing *in situ* silica.

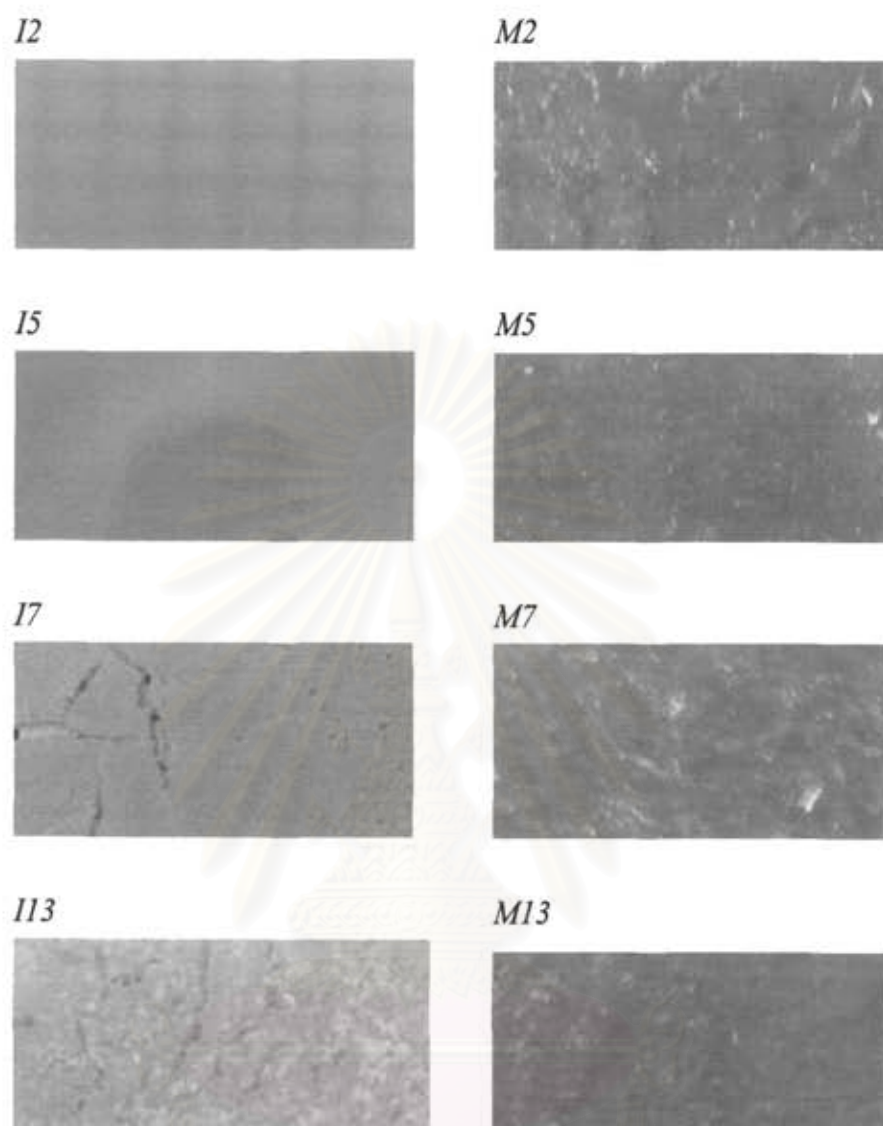


Figure 4.1 Photographs of NR composites filled with *in situ* silica (*I*) and mechanically mixed silica (*M*) (Sample codes are listed in Table 4.2.)

4.4.2 Morphology and Distribution of Silica in the Composites

The fracture surfaces of the composites listed in Table 4.2 were analyzed by using SEM (Fig. 4.2). White spots represent silica particles and black area is the rubber matrix. It seems that the silica particles are evenly dispersed in the NR matrix.

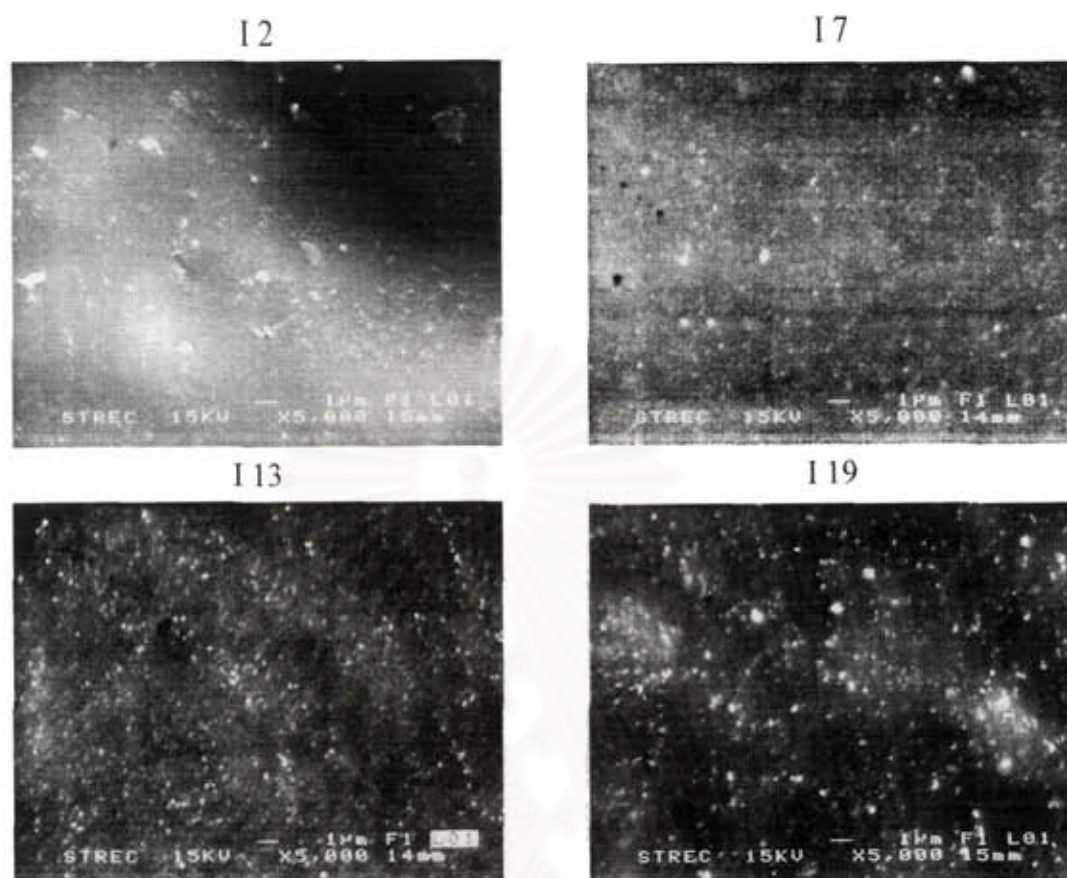


Figure 4.2 SEM micrographs of NR-silica composites filled with *in situ* silica (Sample codes are listed in Table 4.2.)

4.4.3 The Size of Silica Particle in the Composites

From these SEM micrographs, it was not clear whether the particle size was affected by the amount of TEOS. TEM was therefore used to analyze the size of silica aggregates from a sample of *in situ* silica-NR composite. Practically a cryogenic slicing machine is needed to cut out a thin rubber specimen. Unfortunately the machine was unoperational at the time of this study, the rubber sample was therefore hardened by embedding the composite in polystyrene, then sliced to obtain a thin specimen for the TEM. It should be noted here that, since the composite was swollen in styrene, silica might disperse differently from the original state. Therefore only the size but not the distribution of silica in the NR matrix was determined.

Two TEM photographs of the composite having 10% silica (*I10*) are shown in Fig. 4.3. The silica particles aggregate to form clusters having various shapes and sizes. Single silica particle was measured on the picture using a ruler. An average diameter, out of five different silica particles, is 44.4 ± 0.1 nm.

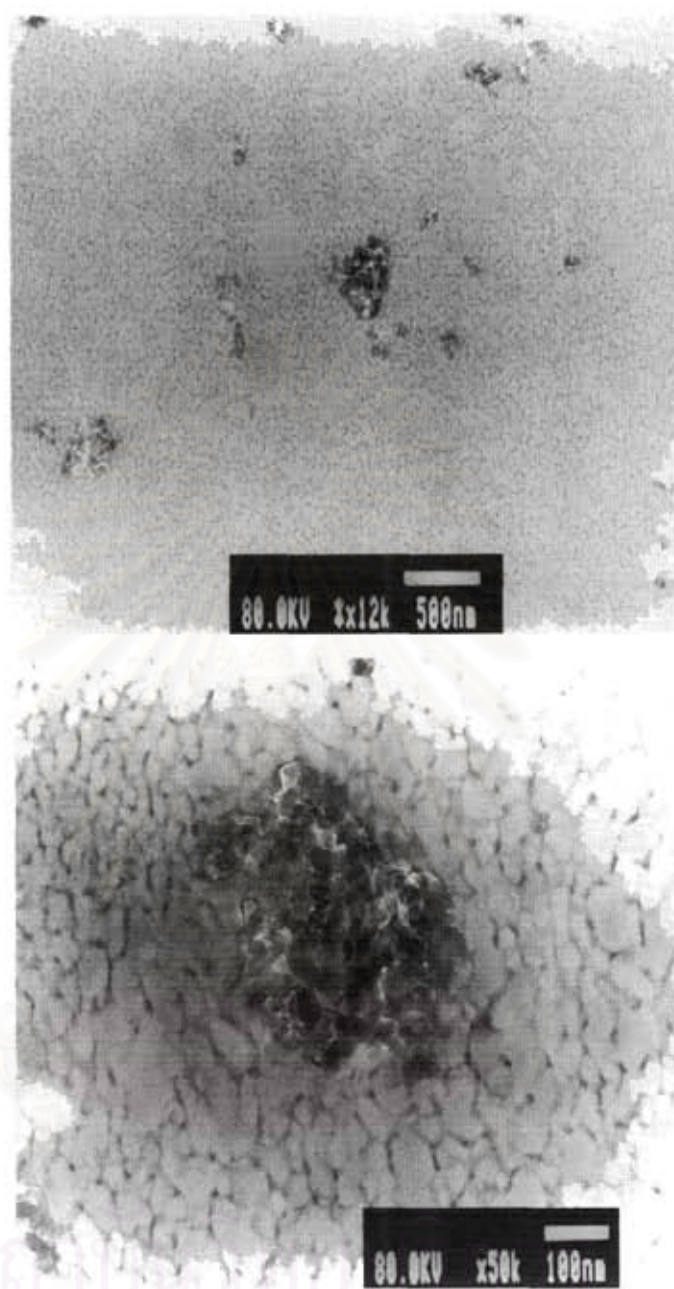


Figure 4.3 TEM images of NR-silica composite with 10 % *in situ* silica (I 10)

4.5 Experimental Design for Study Factors that Influence Mechanical Properties of NR-Silica Composite

The factorial design at two-level was carried out in order to study the factor thought to influence the mechanical properties such as tensile modulus, tensile strength, and tear strength. The three factors ($k=3$) that were focused here are TEOS content (T), added ammonia (N), and gelation time (G). Each factor is present at two levels- high and low. The 2^3 factorial design with two replicates was used. A table of

+ and - signs for the 2^3 factorial design and the average response data are shown in Table 4.3.

Table 4.3 The sign of each factor and averaged response data from 2 replicate experiments

Experiment	Factors			Silica content (%)	Modulus 300% elongation (MPa)	Tensile strength (MPa)	Tear strength (N/mm)
	TEOS (T)	Added NH ₃ (N)	Gelation time (G)				
ED 1	-	-	-	2.69 ± 0.23	1.87 ± 0.137	15.87 ± 1.28	33.57 ± 1.54
ED 2	-	-	+	2.82 ± 0.12	2.02 ± 0.192	16.22 ± 2.40	32.29 ± 1.49
ED 3	-	+	-	2.68 ± 0.08	2.09 ± 0.188	17.76 ± 2.76	32.59 ± 1.37
ED 4	+	-	-	13.00 ± 0.05	2.61 ± 0.344	23.48 ± 3.08	36.44 ± 1.63
ED 5	+	+	+	13.17 ± 0.25	2.96 ± 0.391	24.90 ± 1.42	37.81 ± 1.70
ED 6	+	+	-	13.29 ± 0.38	2.70 ± 0.227	22.07 ± 1.71	37.98 ± 1.95
ED 7	+	-	+	13.51 ± 0.67	2.80 ± 0.278	24.63 ± 1.35	40.95 ± 1.79
ED 8	-	+	+	2.54 ± 0.08	2.38 ± 0.270	18.80 ± 2.31	34.20 ± 1.96

TEOS: + (50 phr), - (10 phr); added NH₃: + (2.5 %), - (0 %); gelation time: + (10 days), - (5 days)

In order to conclude which effects influence the mechanical properties of the composites, comparison of the estimated effects with their standard error was considered. If the estimated effect is larger than the standard error, that effect is considered significant. The estimate of effects and their standard error were obtained from Eq.3.3 and 3.4. The results from this study are as follows:

4.5.1 Stress-Strain Curves of 8 Experiments in Experimental Design

Figure 4.4 shows stress-strain curves of the eight (2^3) experiments in factorial design. All curves are those exhibited by elastomeric materials.

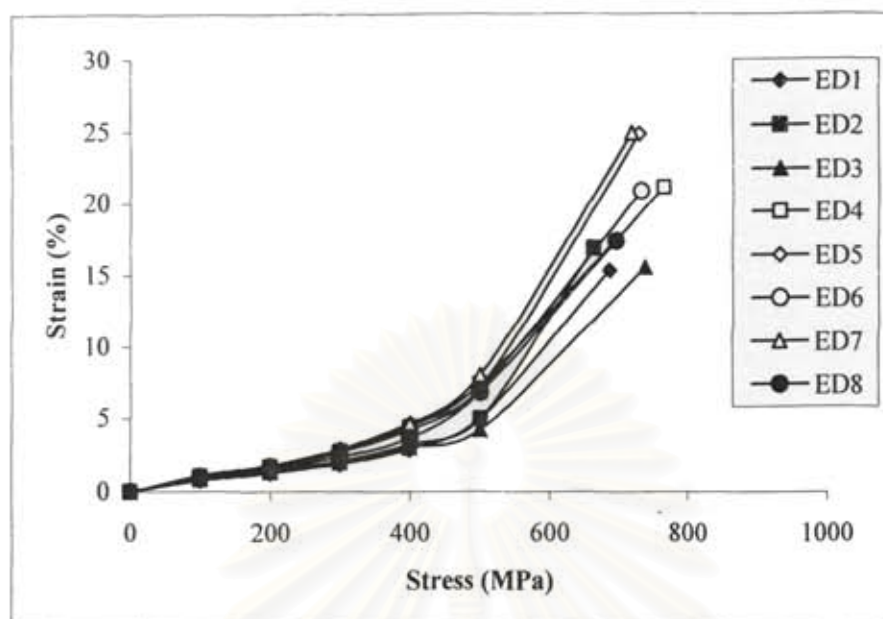


Figure 4.4 Stress-strain curves of 8 (2^3) experiments (Keys for sample labels are listed in Table 4.2)

4.5.2 Effects on Tensile Modulus at 300% Elongation (M300)

The estimated effects of the factorial analysis on tensile modulus along with the standard error of the effects are given in Table 4.4.

Table 4.4 The estimated effects on tensile moduls at 300% elongation (M300)

Effect	Estimated effect	Standard error
<u>Main effect</u>		
TEOS (T)	0.681	± 0.044
NH ₃ (N)	0.212	± 0.044
Gelation time (G)	0.221	± 0.044
<u>Two factor interaction</u>		
TN	-0.083	± 0.044
TG	0.003	± 0.044
NG	0.054	± 0.044
<u>Three factor interaction</u>		
TNG	-0.017	± 0.044

It was found that factors that influence M300 are T, N, G, TN and NG. Nevertheless, the estimated effects value of NG is close to the standard error, indicating that NG is not highly significant for the M300 of these composites.

The three main effects are plotted against M300 (Fig. 4.5). It can be seen that increasing T, N, and G result in an increase of M300. However, the N effect is less important than the others [Fig.4.5(c)]. Note from the TN interaction effect [Fig. 4.5(d)] that additional ammonia does not significantly affect the tensile modulus when TEOS content is high. Therefore, a composite with large M300 value can be obtained by adding a large amount of TEOS but limiting the ammonia content to a low amount. For practical usage, a high M300 value requires high TEOS content, long gelation time, and no need to add more NH_3 into the latex which already contains about 0.7% NH_3 .

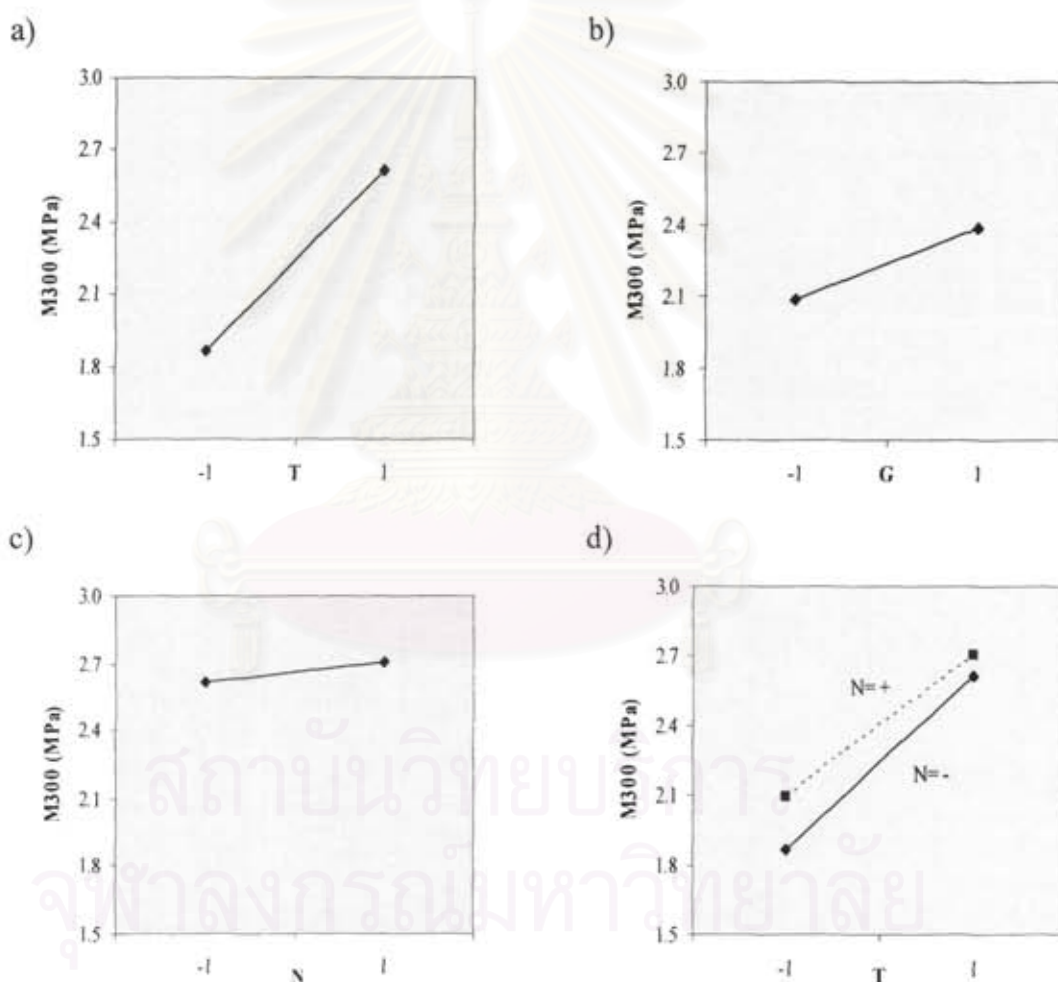


Figure 4.5 The effect of (a)T, (b)G, (c)N and (d)TN interaction on M300

4.5.3 Effects on Tensile Strength

The estimated effects of the factorial analysis on tensile strength are given in Table 4.5 along with the standard error of the effects. It is found that factors that influence tensile strength of the composites are T, G and TN.

Table 4.5 The estimated effects on tensile strength of the NR composites

Effect	Estimated effect	Standard error
<u>Main effect</u>		
TEOS (T)	6.61	± 0.96
NH ₃ (N)	0.83	± 0.96
Gelation time (G)	1.34	± 0.96
<u>Two factor interaction</u>		
TN	-1.41	± 0.96
TG	0.65	± 0.96
NG	0.59	± 0.96
<u>Three factor interaction</u>		
TNG	0.25	± 0.96

The results of main effect T and G shown in Fig 4.6(a) and (b), indicating that increasing T and G (high TEOS content and long gelation time) would result in an increase of tensile strength. The TN interaction effect is plotted in Fig. 4.6(c). From the plot, when using high TEOS content, increasing ammonia becomes less effective in increasing the tensile strength. Therefore, a composite with highest tensile strength can be obtained by adding a large amount of TEOS but limit the ammonia content to a low amount. In another word, there is no need to add more ammonia to the concentrated NR latex that already contains 0.7% NH₃.

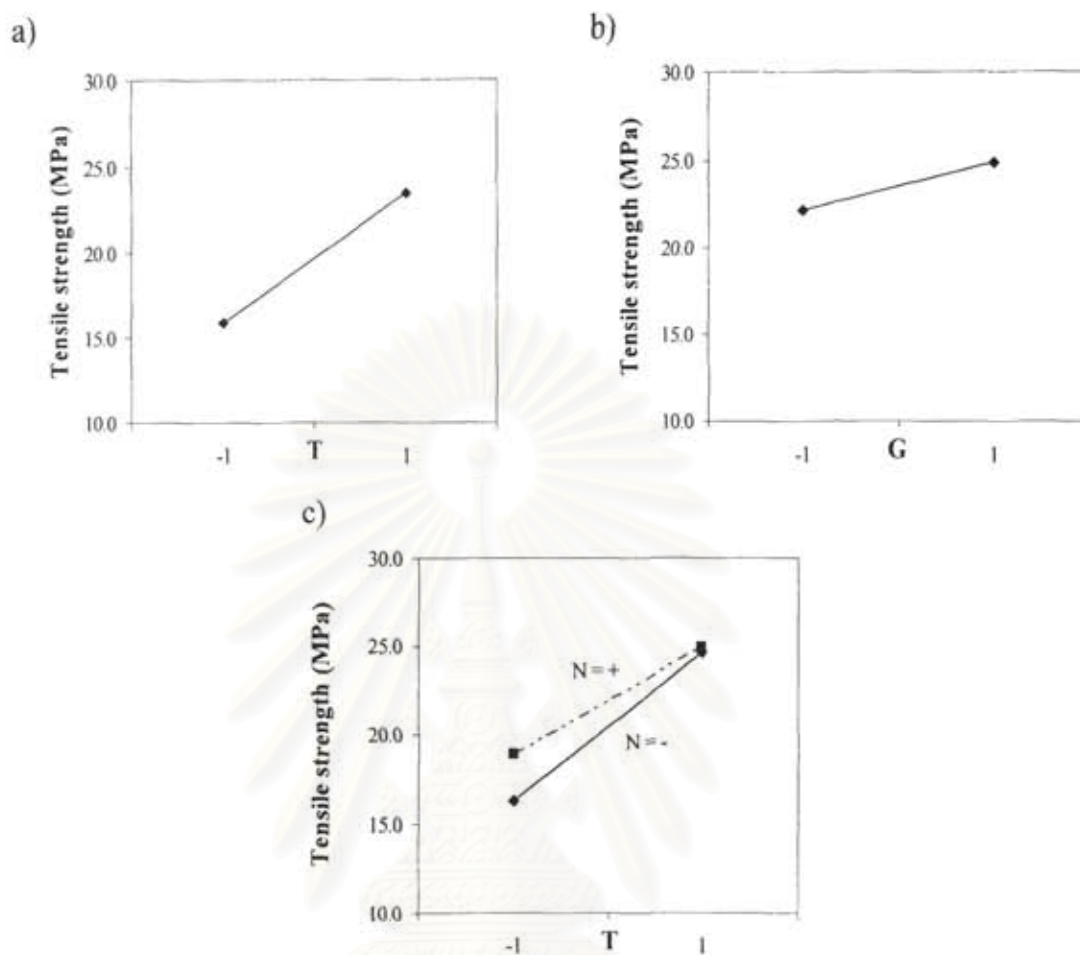


Figure 4.6 The effect of (a)T, (b)G and (c)TN interaction on tensile strength

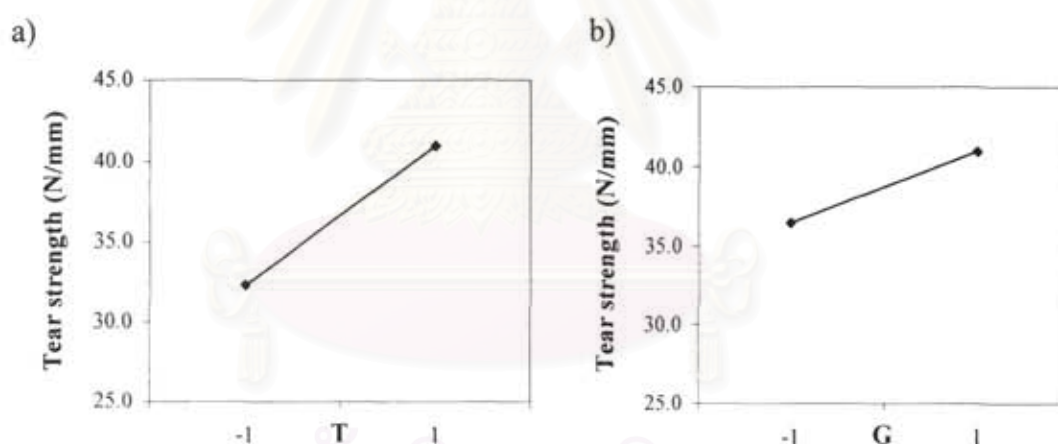
4.5.4 Effects on Tear Strength

The estimated effects of the factorial analysis on tear strength are given in Table 4.6 along with the standard error of the effects. Factors that influence tear strength of the composites are T, G, TG and TNG. Nevertheless, the estimated effects value of TG is close to the standard error, suggesting that TG interaction effect does not significantly affect the tear strength of these composites.

For the main effects- T and G (Fig. 4.7), increasing either factor will result in an increase of tear strength. It is also found that the three-interaction effect (TNG), however, gives a minus sign. This indicates that increasing the amount of one factor can cause a reduction of tear strength. From Table 4.3, the highest tear strength was obtained from sample ED7 (T+, N-, G+). This implies that NH_3 is the one that should be limited to a low value. Moreover the results from Table 4.6 suggest that NH_3 does not have a significant effect on the tear strength when compare to other main effects. Therefore, for practical usage, composites with high tear strength would require high TEOS content (50 phr), long gelation time (10 days), and no need to add more NH_3 into the latex.

Table 4.6 The estimated effects on tear strength

Effect	Estimated effect	Standard error
<u>Main effect</u>		
TEOS (T)	5.13	± 0.68
NH ₃ (N)	-0.17	± 0.68
Gelation time (G)	1.17	± 0.68
<u>Two factor interaction</u>		
TN	-0.63	± 0.68
TG	1.00	± 0.68
NG	-0.45	± 0.68
<u>Three factor interaction</u>		
TNG	-1.89	± 0.68

**Figure 4.7 The effect of (a) T and (b) G on tear strength**

4.6 Comparison Between *in situ* Silica and Mechanically Mixed Silica

In this section, curing time, Mooney viscosity, tensile modulus, tensile strength, and tear strength of the composite containing *in situ* silica were analyzed, and then compared to the composites that were mechanically mixed with an equal amount of silica. The silica powder used here was an industrial grade that was used regularly in composite industries. Comparison between the *in situ* silica and mechanically mixed silica was made as follows.

4.6.1 Stress-Strain Curve

The stress-strain curves of NR-silica composites listed in Table 4.3 are shown in Fig. 4.8. All curves are those exhibited by elastomeric materials. Discussions on tensile modulus and strength of the composite filled with *in situ* silica and mechanically-mixed silica are in the following section.

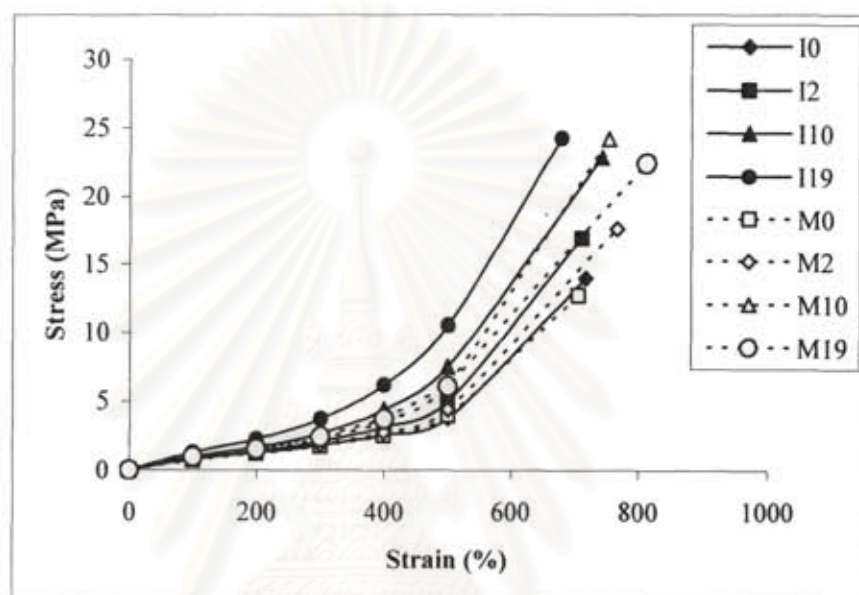


Figure 4.8 Stress-strain of NR-silica composite having various silica contents ('Ix' and 'Mx' denote composites filled with n% *in situ* silica and n% mechanically-mixed silica respectively.)

4.6.2 Cure Time

A plot of cure time or t_{90} versus the amount of silica in the composites was shown in Fig. 4.9. The t_{90} of the composite containing mechanically mixed silica is *higher* than that of the composite having *in situ* silica. This means that the composite filled with mechanically mixed silica needs a longer time to complete curing process than the one with *in situ* silica.

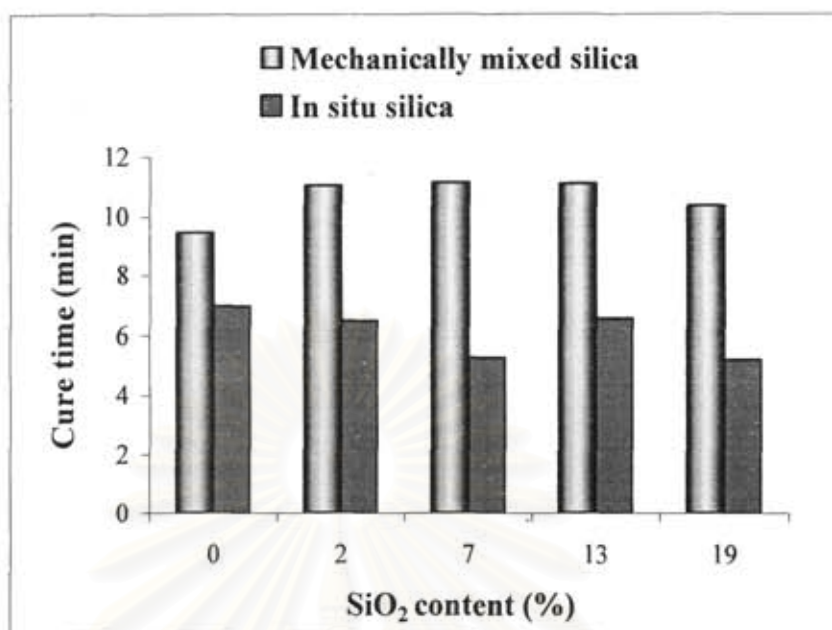


Figure 4.9 Cure time (t_{90}) of NR-silica composite having various silica contents

4.6.3 Mooney Viscosity

In general the Mooney viscosity (ML1+4 @100°C) of the composites increased, as expected, when increasing the silica contents (Fig. 4.10). The viscosity of the composite with conventionally mixed silica powder is higher than the one with *in situ* silica. According to Ikeda [13], the silica powder in the rubber matrix can aggregate and forms pseudo-network structure. This leads to a significant increase of viscosity. Here, the viscosity results suggest that the degree of aggregation of the composite having *in situ* silica is *less* than that in the conventionally mixed silica. It is possible that the interaction among the *in situ* silica particles is smaller than that among the conventionally mixed silica powder.

4.6.4 Tensile Modulus at 300% Elongation (M300)

The bar-graph in Fig. 4.11 exhibits the effect of silica loading on tensile modulus. The modulus of the composite containing *in situ* silica is slightly higher than the one with mechanically mixed silica. The difference becomes more distinct at high silica content.

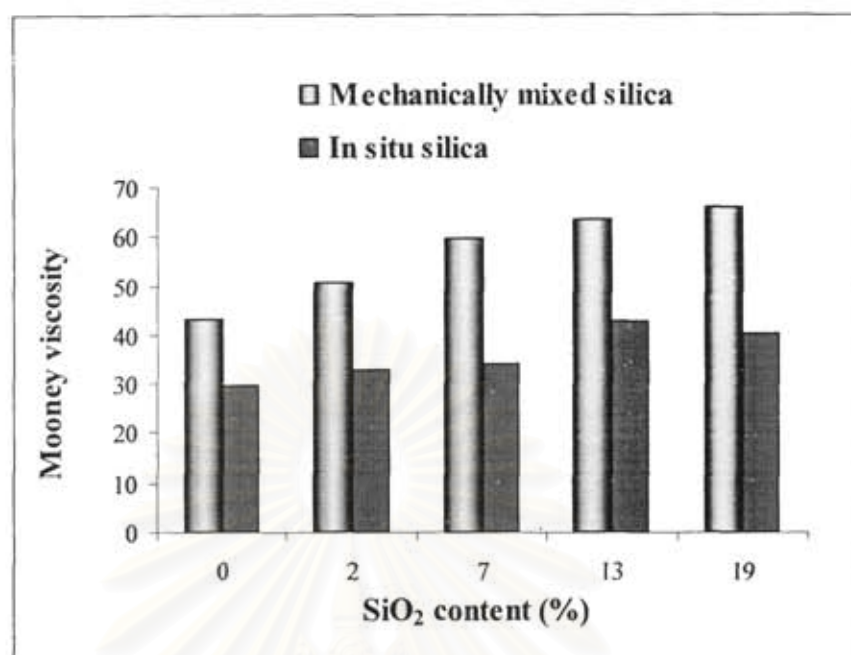


Figure 4.10 Mooney viscosity of NR-silica composite having various silica contents

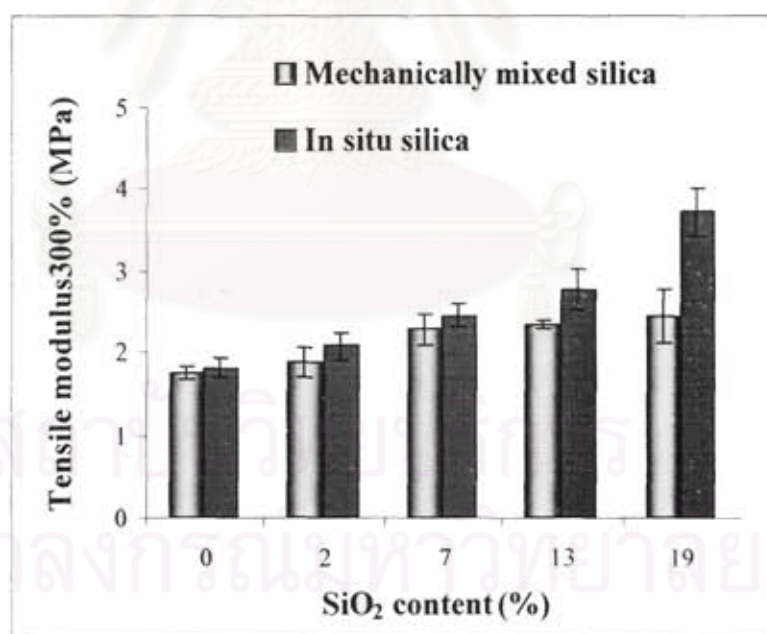


Figure 4.11 Tensile modulus at 300 % elongation of vulcanized NR-silica composite having various silica contents

4.6.5 Tensile Strength

From Fig. 4.12, it is clear that the tensile strength of the composites increases with increasing silica contents. However, the tensile strength values of the composite filled with two types of silica are not significantly different from one another in the samples being studied.

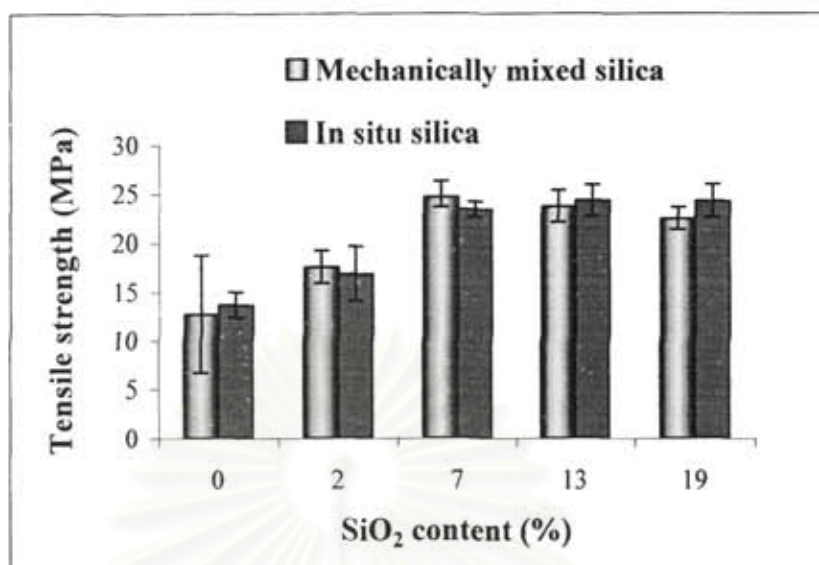


Figure 4.12 Tensile strength of vulcanized NR-silica composite having various silica contents

4.6.6 Tear Strength

Tear strength of the composite of *in situ* silica is higher than that of the mechanically mixed silica (Fig. 4.13). The difference in tear strength becomes more obviously at higher silica contents.

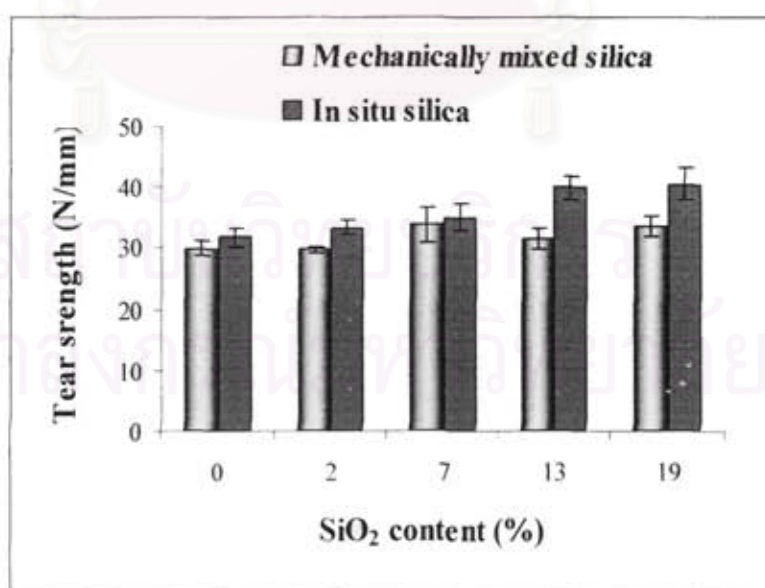


Figure 4.13 Tear strength of vulcanized NR-silica composite having various silica contents

These results suggest that generating the silica *in situ* results in a more efficient reinforcement than the mechanical mix method. This could be due to a better interface between silica and NR chain in the case of silica formed *in situ*.

CHAPTER 5

CONCLUSION AND FUTURE DIRECTION

5.1 Conclusion

The reinforcement of NR by silica generated *in situ* was achieved by sol-gel process of TEOS in the NR latex. Upto 70 phr TEOS can be mixed with the latex without causing aggregation of rubber. The resulting composite contained 19 phr silica. Analysis of the composites using SEM revealed that the *in situ*-formed silica particles were evenly dispersed in the NR matrix. The size of a single silica particle in the composite having 10% *in situ* silica observed by TEM was 44 nm.

The two-level factorial design experimental method was demonstrated to be a very useful tool to study the influence of the experiment factors on the mechanical properties of the composite. In this work, three analyses were carried out; tensile modulus at 300% elongation, tensile strength and tear strength. Statistic analysis of the data showed that TEOS content and gelation time had a significant effect on the mechanical properties. It was also found that the amount of ammonia present in the concentrated latex was enough to complete the sol-gel process of TEOS. A composite containing 19% of silica having tensile modulus at 300% elongation of 3.7 MPa, tensile strength of 24 MPa, and tear strength of 41 N/mm was obtained.

When comparing the mechanical properties of the composite with *in situ* silica to the one with mechanically-mixed silica, the former has a higher tensile modulus and tear strength than the latter.

5.2 Future Direction

- Develop a method that can increase the homogeneity of latex and TEOS in order to increase the added amount of TEOS and, thus, silica in the composite.

REFERENCES

1. Morton, M. *Rubber Technology*. 2nd ed., New York: Van Nostrand Reinhold Company, 1973, pp.466-467, 51-84, 87-128.
2. Kohjiya, S., Murakami, K., Iio, S. *et al.*, "In situ filling of silica onto "green" natural rubber by the sol-gel process." *Rubber Chem. Technol.*, **2001**, 74, 16-27.
3. Tanahashi, H., Osani, S., Shigekuni, K. *et al.*, "Reinforcement of acrylonitrile-butadiene rubber by silica generated *in situ*." *Rubber Chem. Technol.*, **1998**, 71, 38-52.
4. Ikeda, Y., and Kohjiya, S. "In situ formed silica particles in rubber vulcanizate by the sol-gel method." *Polymer*, **1997**, 38, 4417-4423.
5. Ikeda, Y., Tanaka, A. and Kohjiya, S. "Reinforcement of styrene-butadiene rubber vulcanizate by *in situ* silica prepared by the sol-gel reaction of tetraethoxysilane." *J. Mater. Chem.*, **1997**, 7, 1497-1503.
6. Kohjiya, S. and Ikeda, Y. "Reinforcement of general-purpose grade rubber by silica generated *in situ*." *Rubber Chem. Technol.*, **2000**, 73, 534-550.
7. Ikeda, Y., Tanaka, A. and Kohjiya, S. "Effect of catalyst on *in situ* silica reinforcement of styrene-butadiene rubber vulcanizate by the sol-gel reaction of tetraethoxysilane." *J. Mater. Chem.*, **1997**, 7, 455-458.
8. Yoshikai, K., Ohsaki, T. and Furukawa, M. "Silica reinforcement of synthetic diene rubbers by sol-gel process in the latex." *J. Appl. Polym. Sci.*, **2002**, 85, 2053-2063.
9. Tong, X., Tang, T., Zhang, Q-L. Feng, Z., Huang, B-T., "Polymer/silica nanoscale hybrids through sol-gel method involving emulsion polymers. I. Morphology of poly(butyl methacrylate)/SiO₂" *J. Appl. Polym. Sci.*, **2002**, 83, 446-454.
10. Jan, J.-S. and Park, H.-S., "Formation and structure of polyacrylamide-silica nanocomposites by sol-gel process" *J. Appl. Polym. Sci.*, **2002**, 83, 1817-1823.

11. Hsiue, G.-H., Chen, J.-K., and Liu, Y.-L., "Synthesis and characterization of nanocomposite of polyimide-silica hybrid from nonaqueous sol-gel process." *J. Appl. Polym. Sci.*, **2000**, 76, 1609-1618.
12. Morgan, E. *Chemometrics: Experimental Design*. John Wiley & Sons, **1991**, pp. 92-128.
13. Douglas, C. M. *Design and analysis of Experiments*. 5th ed. John Wiley & Sons, **2001**, pp. 218-244.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย