

Silica-Reinforced Natural Rubber Prepared by the Sol–Gel Process of Ethoxysilanes in Rubber Latex

V. Tangpasuthadol,¹ A. Intasiri,¹ D. Nuntivanich,² N. Niyompanich,² S. Kiatkamjornwong³

¹Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

²Program of Petrochemistry and Polymer Sciences, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

³Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Received 29 March 2007; accepted 19 January 2008

DOI 10.1002/app.28120

Published online 28 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Silica-reinforced natural rubber (NR) composite was prepared by using tetraethoxysilane (TEOS) as a precursor to generate silica particles inside the rubber. The silica was generated *in situ* by the sol–gel process of TEOS that was mixed directly into commercial-graded NR latex having 60% dry rubber content and 0.7% ammonia. The conversions of TEOS to silica inside the rubber were ranging from 90 to 97%. The silica particles dispersed evenly without extensive aggregation with sizes between 100 and 500 nm, as determined by scanning electron microscopy (SEM). An experimental design methodology, namely “two-level factorial design,” was used to evaluate the influence of the amounts of TEOS, ammonia, and gelation time on the tensile modu-

lus, tensile strength, and tear strength of the vulcanizates. The mechanical properties were significantly affected by the amount of TEOS added into the latex. Ammonia in the amount of 0.7% (w/w) present in the commercial latex was found to be sufficient for the conversion reaction of TEOS to silica. Bis-(3-triethoxysilylpropyl)tetrasulfide or TESPT, a coupling agent regularly used in rubber industry, was also added with TEOS to prepare the silica-filled composite. The presence of TESPT resulted in an increase of the mechanical properties and the rate of sulfur cure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 424–433, 2008

Key words: rubber; silicas; composites

INTRODUCTION

Nowadays silica powder has been increasingly used to reinforce rubber products. A problem of silica-reinforced rubber is the incompatibility between the hydrophilic silica and hydrophobic natural rubber (NR), resulting in poor mechanical properties. A well-known method for improving the reinforcement effect is to treat the silica surface with “silane coupling agent” to promote interaction with rubber. It generally improves the dispersion of silica in the rubber matrix.

In 1982, J. E. Mark has reported a new approach for preparing silica-filled composite by generating silica particles inside polydimethylsiloxane matrix,¹ hence the word “*in situ*” is used. Since then the *in situ* formation of silica has been widely explored as a new compounding method for silica-filled rubber

composite, such as polydimethylsiloxane,² synthetic rubber,^{3–5} and natural rubber.^{6–9} This was achieved by immersing solid rubber sheet in tetraethoxysilane (TEOS) (Fig. 1), a liquid precursor of silica, together with an acid/base catalyst. This was then followed by heat treatment ($\sim 50^\circ\text{C}$) of the swollen rubber sheet, to initiate the sol–gel process of TEOS inside the rubber matrix. During the sol–gel process, inorganic silica was generated through a series of chemical reactions as shown in Scheme 1. The ethoxysilane ($-\text{Si}-\text{OC}_2\text{H}_5$) can undergo hydrolysis by water to form silanol group ($-\text{Si}-\text{OH}$). This hydrolysis step can be accelerated by base such as hydroxide ion in the system, since the OH^- can react faster than a water molecule. The resulting silanol group can then react further with ethoxysilane or another silanol to form a siloxane linkage ($-\text{Si}-\text{O}-\text{Si}-$) with the release of water or ethanol. Networks of siloxane linkages will thus form silica (SiO_2) that can be observed as white particles embedded inside the rubber matrix.

Although the incorporation of TEOS into solid rubber by the swelling method can be limited by the shape of the rubber sheet, an alternative method is to directly add a measured amount of TEOS into rubber latex. The TEOS-mixed latex can then be introduced into a mold of a desired shape. This is

Correspondence to: V. Tangpasuthadol (varawut.t@chula.ac.th).

Contract grant sponsor: The Thailand Research Fund (Research Team Promotion Grant); contract grant number: RTA4780004.

Contract grant sponsor: The Thai Government Research Fund.

Journal of Applied Polymer Science, Vol. 109, 424–433 (2008)
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TABLE II
Experimental Variables and Their Levels Used in the
2³ Factorial Design

Variables	Codes	Level	
		Low (-)	High (+)
TEOS content (phr)	T	10	50
NH ₃ content (%)	N	0.7 ^a	3.2
Gelation time (days)	G	5	10

^a as received from the supplier

kg/cm². Vulcanized composite sheets of about 2-mm thick were obtained.

Factorial design for variable screening

A 2³ factorial experimental design was used to evaluate the effect of three variables on the tensile modulus, tensile strength, and tear strength of the composite. The three target variables were TEOS content (T), %NH₃ (N), and gelation time (G). Therefore a total of 2³ or 8 runs were carried out with two replicates. Each variable was studied at low (-) and high (+) levels as shown in Table II. Values for main and interaction effect were then calculated by

$$\text{Effect} = \bar{y}_+ - \bar{y}_- \quad (1)$$

where \bar{y}_+ and \bar{y}_- are average values for the responses at high and low levels of each variable. For principal effects, the averages simply refer to the results at the high (+) and the low (-) levels, independent of the level of the other variables. For a binary interaction, \bar{y}_+ is the average of the results for two variables at high-high and low-low levels, whereas \bar{y}_- is the average of the results when one of the variables involved is at a high level and the other is at a low level.

In this study, two replicated experiments were performed, whose standard errors (E) in the effect values were calculated by

$$E = \{\Sigma(\text{SD})/2N\}^{1/2} \quad (2)$$

where SD is the standard deviation of two replicates and N is the number of experiments performed. The E value was used to determine which variable was likely to be important. If the effect value is larger than E, that effect has a significant influence on the tested property.

Characterization

Dispersion of silica

The rubber composite was cryogenically fractured under liquid nitrogen. The samples were then sput-

ter-coated with gold and the photographs were taken with a scanning electron microscope (JEOL JSM-6400).

Silica content

A weighed sample (~ 50 mg) of silica-NR composites placed in an aluminum oxide cup was heated in air to 850°C in an oven (Carbolite GM 11/7). The temperature was then held for 15 min at 850°C. The silica content was calculated by

$$\text{Silica content (phr)} = 100(W_1/W_2) \quad (3)$$

where W_1 was the weight of remaining ash, W_2 was the composite weight. The conversion of TEOS to silica was calculated using

$$\text{Conversion (\%)} = 100(W_3/W_4) \quad (4)$$

where W_3 was the amount of *in situ* generated silica in the sample, which was obtained from eq. (3) and W_4 was the theoretical amount of silica being generated assuming quantitative conversion of TEOS to silica by



Mechanical tests

The tensile properties of the vulcanizates were measured according to ASTM D412 using a tensile testing machine (Instron Corp. Series IX Automated Materials Testing System 6.05el 1011) at a crosshead speed of 500 mm/min. Values reported for each sample were based on an average of six measurements. Tear properties were measured using LLOYD Instruments (LS 500) according to ASTM D624 (Die C) at a crosshead speed of 500 mm/min. Values reported for each sample were averaged from six measurements. The tensile properties were measured along the grain direction whereas the tear properties were measured perpendicular to the grain direction.

Determination of curing behavior

A moving-die rheometer (Monsanto MDR2000) was used for determining vulcanization characterization of the rubber compounds. The Mooney viscosity of the specimen measured by using a Mooney viscometer based on ASTM D1646.

RESULTS AND DISCUSSION

In situ formation of silica

TEOS is in a liquid state at room temperature, with a boiling point of 163–167°C. It is also immiscible

TABLE III
The Silica Content and % Conversion of TEOS to Silica Generated in Rubber Composites

Added TEOS (phr)	<i>In situ</i> generated silica content (phr)	% Conversion
0	0	0
10	2.73 ± 0.26	95 ± 9
20	5.27 ± 0.16	91 ± 3
30	7.75 ± 0.19	90 ± 2
40	10.49 ± 0.08	91 ± 1
50	13.98 ± 0.83	97 ± 6
60	16.20 ± 0.29	94 ± 2
70	19.23 ± 0.15	95 ± 1

with water. It was however found in this study that certain amounts of TEOS could be mixed by gentle stirring with the concentrated latex without phase separation. It was possible that natural emulsifiers-phospholipids and proteins, that covered and helped

sustaining the rubber particles in the latex also aided the mixing of the hydrophobic TEOS. The silane compound was most likely adsorbed on the rubber particles. It was however found that if the added TEOS content was higher than 70 phr (parts per one hundred parts dry rubber), excess TEOS phase-separated out of the latex as floating droplets. Therefore the TEOS content in the latex was limited at 70 phr in this study.

The conversion of TEOS to silica inside the rubber matrix was determined before sulfur curing to avoid ash content resulting from ZnO, one of the curing chemicals. The amount of silica generated in the composites increased when the TEOS amount added into the latex increased (Table III). The percent conversions from TEOS to silica were between 90 and 97% by mole. It was, however, found that no correlation between the percentage of TEOS conversion and the initial amount of TEOS added into the latex

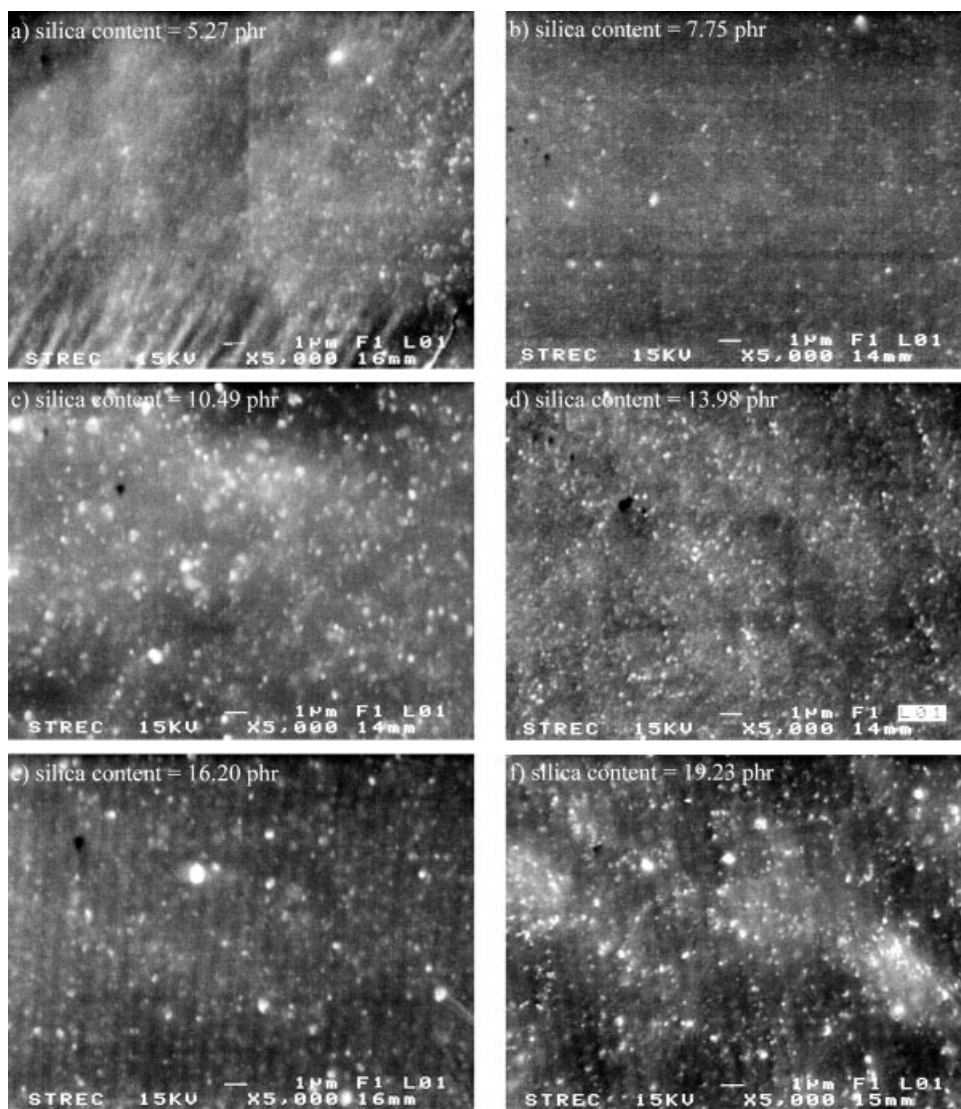


Figure 2 Scanning electron micrographs of the fractured surfaces of uncured NR filled with *in situ* generated silica.

TABLE IV
Design Matrix and the Results (M300, Tensile Strength, and Tear Strength) Obtained for the Mechanical Properties of *In Situ* Silica-NR Vulcanizates

Runs	Variables			M300 (MPa)	Tensile strength (MPa)	Tear strength (N/mm)
	T	N	G			
1	-	-	-	1.87 ± 0.137	15.87 ± 1.28	33.57 ± 1.54
2	-	-	+	2.02 ± 0.192	16.22 ± 2.40	32.29 ± 1.49
3	-	+	-	2.09 ± 0.188	17.76 ± 2.76	32.59 ± 1.37
4	+	-	-	2.61 ± 0.344	23.48 ± 3.08	36.44 ± 1.63
5	+	+	+	2.96 ± 0.391	24.90 ± 1.42	37.81 ± 1.70
6	+	+	-	2.70 ± 0.227	22.07 ± 1.71	37.98 ± 1.95
7	+	-	+	2.80 ± 0.278	24.63 ± 1.35	40.95 ± 1.79
8	-	+	+	2.38 ± 0.270	18.80 ± 2.31	34.20 ± 1.96

could be established. The results suggested that nearly all TEOS mixed in the latex had turned into silica during the sol-gel process in basic condition at 50°C for a period of 5 days. It was believed that non-converted TEOS possibly evaporated during the heating step since the organosilane were quite volatile even at room temperature.

The resulting *in situ* silica-NR composite turned more opaque with increasing silica contents. No loosely bound silica particles were found on the rubber sheet. SEM analysis for the fractured surface of the composites having different silica contents (listed in Table III) are shown in Figure 2. In the micrographs, the silica particles are present as white spots dispersed in the rubber matrix (dark area). The micrograph of the sample with 10 phr TEOS (2.7 phr silica) was not shown since the presence of silica was hardly seen. When increasing the added TEOS content, the number of white spots increases without major particle aggregation. Estimation of the particle sizes from the scanning electron micrographs suggested that the particles were mostly smaller than 500 nm in diameter.

As mentioned earlier, it was expected that TEOS underwent hydrolysis and condensation reaction to form silica in the rubber latex environment consisting of 60% dry rubber, 40% water, and about 0.7% ammonia (by weight). In this study the amounts of

added TEOS were 10 to 70 phr, the molar ratios of water : TEOS : NH₃ in the latex were therefore varied from 14 : 0.14 : 0.25 to 14 : 1 : 0.25. It can be seen that the amount of water was in excess for the sol-gel process in all samples. The quantity of ammonia needed to accelerate the sol-gel process was only in a catalytic amount since the hydroxide ion was regenerated at the end of the reaction. More discussion on the effect of ammonia content on the generation of silica and mechanical properties is in the next section. A study on the effect of molar ratios of water : TEOS : NH₃ on silica formation was reported earlier by Yoshikai et al.¹⁰ for the preparation of SBR and NBR reinforced by *in situ* silica. It was concluded in the report that as the ratio of H₂O/TEOS increased from 8.1 to 15.3, the size of *in situ* silica particles decreased. In this study, however, no clear correlation between the amount of added TEOS and the size of silica was found. It was possibly because the H₂O/TEOS ratios in this study were ranged from 14 and higher, much more than the range studied by Yoshikai et al.

Screening design for variables influencing the mechanical properties of NR-silica composite

The influences of different variables and their interactions on the mechanical properties of NR-silica

TABLE V
Estimated Effects and Standard Errors of the Variables and Interactions Obtained by Factorial Design for Mechanical Properties of *In Situ* Silica-NR Vulcanizates

Variables/Interactions	M300	Tensile strength	Tear strength
Main effect			
TEOS (T)	0.681 ± 0.044	6.61 ± 0.96	5.13 ± 0.68
NH ₃ (N)	0.212 ± 0.044	0.83 ± 0.96	-0.17 ± 0.68
Gelation time (G)	0.221 ± 0.044	1.34 ± 0.96	1.17 ± 0.68
Two-factor interaction			
TN	-0.083 ± 0.044	-1.41 ± 0.96	-0.63 ± 0.68
TG	0.003 ± 0.044	0.65 ± 0.96	1.00 ± 0.68
NG	0.054 ± 0.044	0.59 ± 0.96	-0.45 ± 0.68
Three-factor interaction			
TNG	-0.017 ± 0.044	0.25 ± 0.96	-1.89 ± 0.68

TABLE VI
ANOVA Results Showing the Significance of Main Effects and Interactions

Source of variance	M300		Tensile strength		Tear strength	
	<i>F</i> -ratio	<i>P</i> -value	<i>F</i> -ratio	<i>P</i> -value	<i>F</i> -ratio	<i>P</i> -value
<i>T</i>	237.684	<0.0001	47.433	0.0001	56.988	<0.0001
<i>N</i>	22.960	0.0014	0.748	0.4122	0.060	0.8129
<i>G</i>	25.182	0.0010	1.958	0.1993	2.944	0.1245
<i>TN</i>	3.536	0.0968	2.145	0.1812	0.869	0.3784
<i>TG</i>	0.005	0.9475	0.455	0.5188	2.159	0.1799
<i>NG</i>	1.497	0.2560	0.378	0.5557	0.436	0.5277
<i>TNG</i>	0.140	0.7183	0.068	0.8010	7.742	0.0238

Critical value of $F_{1,8} = 7.571$ ($P = 0.05$)¹⁶
Italic numbers indicated the significant effect.

composite including tensile modulus at 300% elongation (M300), tensile strength, and tear strength were determined using an experimental design namely 2^3 factorial design. The factorial design was used as an important first step to obtain the significant effects and interactions of the variables as well as to indicate the direction of further experiments to improve the composite properties.

Table IV shows the design matrix and the results (tensile modulus, tensile strength and tear strength) obtained in each run. From the values of M300, tensile strength and tear strength, the influence of each variable and their interactions could be determined by the calculation of estimated effects and their standard errors (Table V). The influence of factors or interactions was considered as significant if the estimated effect was higher than the standard errors. Thus, for the tensile modulus at 300% elongation, the significant factors were *T*, *G*, *N*, *TN*, and *NG* but with different magnitudes. However, among these significant factors, the effect of TEOS content seemed to be much more important than the others due to its highest estimated effects. Considering the effects on tensile strength, *T*, *TN*, and *G* were three leading variables with the TEOS content being more important than the other two factors. Also, the negative

sign of the estimated effect of *TN* indicated that having NH_3 at low level (0.7%) was preferable in preparing a composite with high tensile strength. In case of the tear strength, the significant variables were *T*, *TNG*, *G* and *TG*, with *T* was the most significant factor. Increasing the amount of the main variables (*T* and *G*) resulted in an increase in tear strength. The minus sign of the estimated effect of *TNG* indicated that increasing the amount of one variable caused a reduction of tear strength. Considering Table IV, the highest tear strength was obtained from the experimental run no. 7 (*T*+, *N*-, *G*+). This can be interpreted that high NH_3 content can lower the tear strength. Therefore the ammonia content should be limited to a low value.

In addition, to assess and confirm the significant factors affecting each mechanical property of *in situ* silica-NR vulcanizates, the analysis of variance (ANOVA) was performed. For simplicity, only *F*-ratios and *P*-values are given in Table VI. The *F*-ratios measure the contribution of each variable or interaction on the variance of the results. The *P*-values indicate the statistical significance of each of the variables or interactions. The significant factor was verified by considering the *F*-ratio and the *P*-value. The influence of factor or interaction was considered as significant if the *F*-ratio was higher than *F*-critical value [critical value of $F_{1,8} = 7.571$ ($P = 0.05$)].¹⁶ Moreover, when its *P*-value was less than 0.05, a factor had a statistically significant effect at the 95% confidence level. As seen, in case of tensile modulus, all main effects especially the TEOS content were significant whereas for the tensile strength the significant factor was only the TEOS content. For the tear strength, TEOS and the three-factor interaction (*TNG*) were the significant factors.

According to the results described above, the amount of TEOS added into the latex played a crucial role in the mechanical properties of the composite. Increase in the gelation time from 5 to 10 days also increased the M300, tensile strength, and in some case, tear strength, but at a much lower magni-

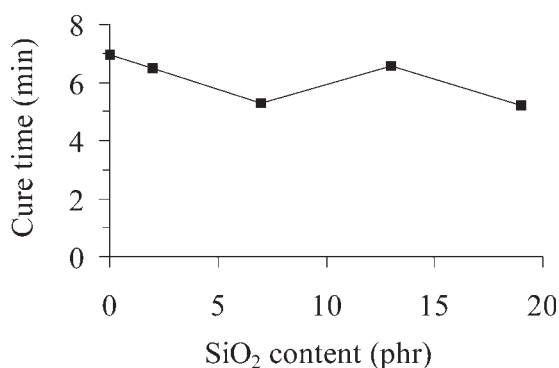


Figure 3 Changes in cure time (t_{90}) as a function of silica contents for the *in situ* silica-NR vulcanizates.

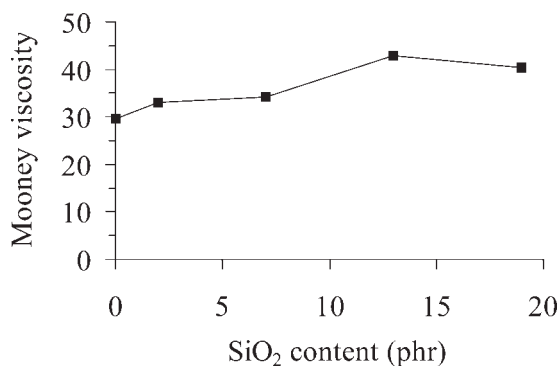


Figure 4 Changes in Mooney viscosity as a function of silica contents for the *in situ* silica-NR vulcanizates.

tude than the effect from TEOS. The effects of ammonia content on the mechanical properties were rather low. It was thus stated that the standard ammonia content of 0.7% in the commercial-grade concentrated latex was sufficient to initiate the formation of silica from TEOS dispersed in the latex.

Effect of TEOS content on the curing and mechanical properties of the composite

As from the previous results, the content of TEOS was the major variable affecting the mechanical properties of the *in situ* silica-NR vulcanizate. Therefore, a set of NR-silica composite samples was prepared and analyzed for curing behavior and mechanical properties as a function of TEOS content. The gelation time was fixed at 5 days and the ammonia content was kept at its original value of 0.7%.

During the sulfur curing step, it was found that increasing the silica content somewhat lowered the cure time or t_{90} , but not very significantly (Fig. 3). This result in fact contradicted a usual retardation effect by silica during sulfur vulcanization that was caused by the adsorption of accelerators by the silica-

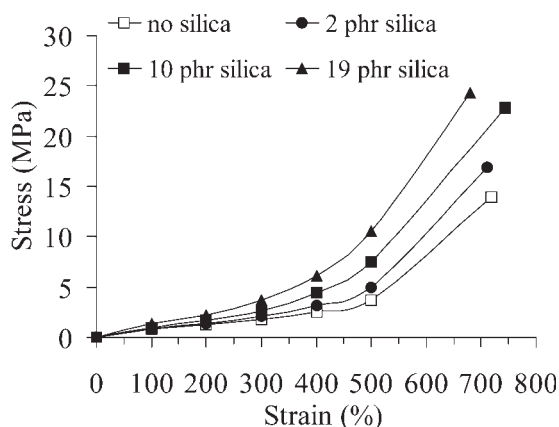


Figure 5 Stress–strain curves of the *in situ* silica-NR vulcanizates having various silica contents.

groups on the silica surface. It could be possible that the silica content (up to 19 phr) in this study was not high enough to exhibit the cure retardation. The Mooney viscosity of the composites increased as expected when increasing silica contents (Fig. 4). This is the result of having many inorganic domains block the free movement of the rubber chain. However it should be noted here that the magnitude of viscosity change is not high.

The stress–strain curve of the composite (Fig. 5) was typical of rubber. We found that having *in situ* silica in the range of 2–19 phr did not affect the ultimate elongation of the composite. However the tensile modulus (M300), ultimate strength, and tear strength of the vulcanizates were affected by changing the amount of silica generated in the rubber. The

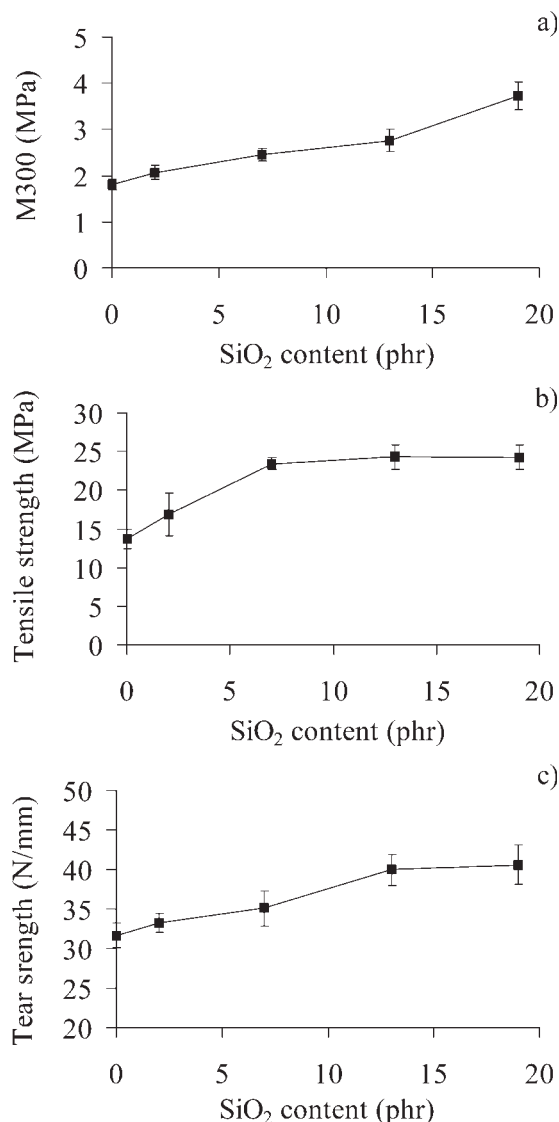


Figure 6 Influence of silica contents on (a) tensile modulus at 300% elongation, (b) tensile strength, and (c) tear strength of the *in situ* silica-NR vulcanizates.

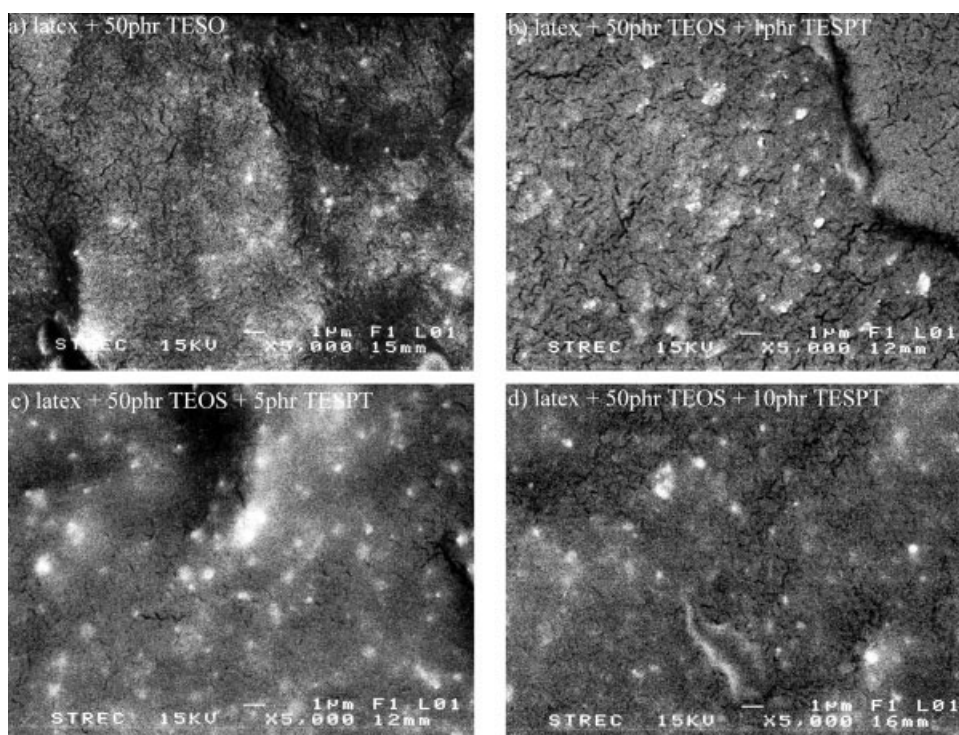


Figure 7 Scanning electron micrographs of the fractured surfaces of the vulcanizates prepared from mixtures of concentrated rubber latex, a fixed contents of TEOS (50 phr) and varying amounts of TESPT.

M300 [Fig. 6(a)] increased almost twofold from 1.8 to 3.7 MPa when the *in situ* silica content was increased from 0 to 19 phr. The tensile strength or strength at break increased with *in situ* silica contents but remained rather constant at about 24 MPa when %SiO₂ was above 8 phr and up to 19 phr [Fig. 6(b)]. Some studies reported that upon increasing the silica content the tensile strength also increased to a maximum. With further addition of silica, the tensile strength decreased possibly due to silica aggregation.^{17,18} However in this study, the SEM revealed no major aggregation of *in situ* generated silica in the vulcanizate containing as high as 19 phr (Fig. 2), therefore no decreasing of tensile strength was observed. Finally, the tear strength was also found to increase with *in situ* silica content in the vulcanizates [Fig. 6(c)]. These results in fact confirm the role of silica as reinforcing filler for the NR vulcanizate.

Role of TESPT in the *in situ* silica-NR composites

In this section, TESPT, an organotriethoxysilane with tetrasulfide group in the molecule, was investigated for its role as a coupling agent between the *in situ* generated silica and the rubber chain. TESPT was added together with TEOS into the commercial-grade concentrated latex. The resulting silica-filled vulcanizates were analyzed for silica dispersion microscopically by SEM. The fractured surfaces of

the vulcanizates prepared from latex mixtures containing a fixed contents of TEOS (50 phr) and varying amounts of TESPT (0–10 phr) are shown in Figure 7. Usually TESPT was used to enhance compatibility between silica and rubber and prevent aggregation of silica particles in rubber. It was however found from this study that the dispersion of *in situ* silica in the rubber matrix was not affected by the addition of TESPT in the amounts of up to 10 phr. This might be due to the fact that no extensive aggregation of the *in situ* generated silica occurred even without the addition of TESPT.

The investigation on the role of TESPT was then focused on cure characteristics and mechanical properties of the vulcanizates. The contents of *in situ* generated silica, cure characteristic and mechanical properties of the vulcanizates prepared from conc. latex mixed with 50 phr TEOS and 5 phr TESPT are listed in Table VII. From the Table, it is clear that the addition of 5 phr TESPT resulted in about 1% increase of *in situ* silica in the composite.

For cure properties, it was found that scorch and cure times of the *in situ*-filled silica-NR vulcanizates without TESPT (entry 2, Table VII) were longer than those of vulcanizate without silica (entry 1). The addition of 5-phr TESPT with TEOS during the latex mixing step (entry 3) helped reduce both scorch and cure times to the values that were lower than those of the vulcanizate without silica. These observations

TABLE VII
Comparison Between Cure Characteristics and Mechanical Properties of *In Situ* Silica-NR Vulcanizates With and Without Silica Reinforcement (50°C, 5 days)

Entry	Sample	Silica content (%)	Scorch time (min)	Cure time (min)	M300 (MPa)	Tear strength (N/mm)	Hardness
1	NR	0	2.76	4.22	2.19 ± 0.01	30.76 ± 3.71	39.5 ± 1.10
2	NR + 50 phr TEOS	13.52 ± 0.15	3.12	4.76	3.22 ± 0.40	40.81 ± 0.65	43.1 ± 2.76
3	NR + 50 phr TEOS + 5 phr TESPT	14.44 ± 0.22	2.38	4.27	4.43 ± 0.14	46.35 ± 0.31	47.1 ± 1.27

in fact fitted well with the theory that, without the coupling agent, the silanol group of silica particles reduced the sulfur curing by adsorbing the curing chemicals onto their surfaces. After the incorporation of TESPT, the amount of silanol groups should decrease. TESPT also contained sulfide units that could participate in the sulfur vulcanization. This led to strong chemical linkages between the silane coupling agent and the rubber chain. Thus vulcanization of *in situ*-filled silica-NR composite was achieved faster in the presence of TESPT than without it.

The mechanical properties of NR-silica vulcanizates-M300, tear strength, and hardness, are also listed in Table VII. All reported mechanical properties of the *in situ* silica-NR vulcanizates (entry 2) were higher than those of the rubber vulcanizate without reinforcement (entry 1). The addition of TESPT (entry 3) led to significant increases of all reported mechanical properties. It should be noted that although the increase of silica content in the vulcanizate can contribute to the increase of mechanical properties, the magnitudes of reinforcement in the TESPT-filled samples were higher than the composite with higher silica content that were generated from TEOS alone (see Fig. 6). These results confirm the reinforcement capability of *in situ* silica and the possible role of TESPT as a cocuring agent in the NR vulcanizate.

Silicon-29 CP/MAS NMR spectra of the *in situ* silica-NR vulcanizates are shown in Figure 8. Without the coupling agent (TESPT), two peaks were identified as a Q³ peak for silicon atoms that have one hydroxyl group, (Si-O)₃-Si-OH, at -101.4 ppm and a Q⁴ peak for the silicon atoms without hydroxyl group, (Si-O)₄-Si, at -109.2 ppm. A Q² signal, relating to geminal silanols, (Si-O)₂-Si-(OH)₂, was not present because of its low abundance.¹⁹ When TESPT was added, an additional peak was observed at -67.9 ppm which was attributed to the silicon atoms connecting to the alkyl groups, (Si-O)₃-Si-R, also called T³ signal.^{19,20} Moreover the addition of TESPT led to a decrease in the intensity of the Q³ or an increase in the Q⁴ signals. The results implied that the reaction between

TESPT and TEOS caused a reduction in the density of silanol groups (-Si-OH) on the silica surface.

CONCLUSIONS

This study has shown that silica can be generated successfully by the sol-gel process of TEOS mixed

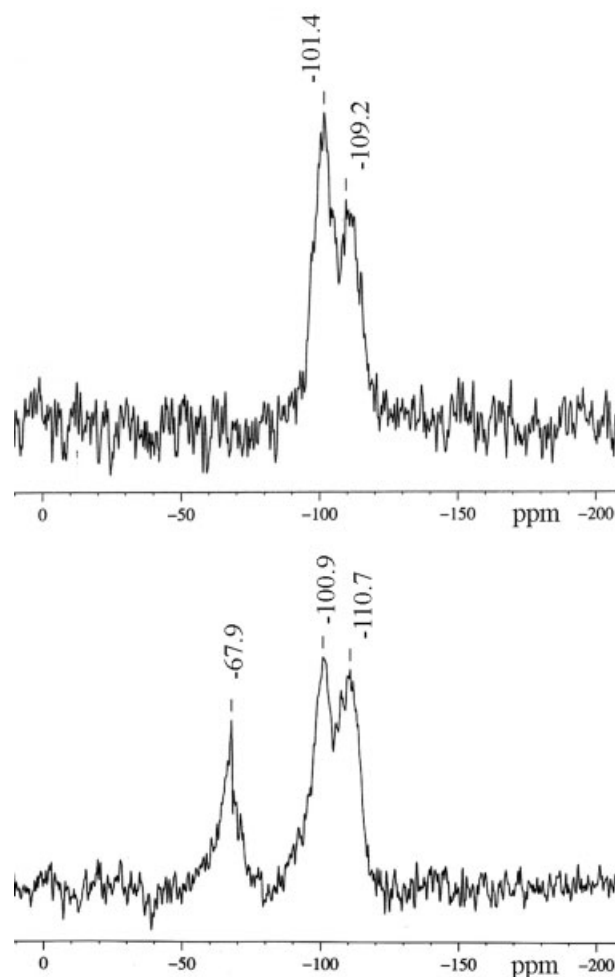


Figure 8 ²⁹Si CP/MAS NMR spectra of the *in situ* silica-NR vulcanizates without TESPT (upper) and with TESPT (lower).

with commercial concentrated NR latex at 50°C. The *in situ* generated silica particles were homogeneously dispersed inside the rubber matrix as revealed by SEM. The averaged diameter was estimated to be smaller than 500 nm. An experimental design was used to study variables that could affect the mechanical properties of the *in situ* silica-filled vulcanizates. Statistical analysis of the data showed that the TEOS content had the most significant effect on the mechanical properties. It was also found that 0.7% ammonia content present in the commercial-grade concentrated latex was sufficient to initiate the sol-gel process of the silane. Therefore no additional ammonia was required to add to the latex with the resultant benefits in costs and time saving in the preparation of NR composite reinforced by *in situ* generated silica. The addition of TESPT, a common silane coupling agent, together with TEOS into the latex reduced both scorch time (t_{s2}) and optimum cure time (t_{90}) of the vulcanizates. The M300, tear strength, and hardness of the *in situ* silica-NR vulcanizates were increased by the addition of 5 phr TESPT.

This research was supported by the Research Team Promotion Grant (for Prof. S. Kiatkamjornwong) from The Thailand Research Fund (RTA4780004). Appreciation is extended to J. Boonyawat, Y. Ikeda, and S. Kohjiya for their suggestions and comments.

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