# CHAPTER IV

RESULTS AND DISCUSSION

4.1   Sol-Gel Process of Alkyltriethoxysilanes in Latex

4.1.1   Conversion of Silanes to Silica

As clearly mentioned in Chapter I, the aim of this work was to use alkyltriethoxysilane as a precursor to create silica *in situ*. Therefore, the first step was to evaluate whether the selected alkyltriethoxysilane can be converted to silica in the NR matrix in comparison with TEOS.

The silica content found in the NR-silica composites and %conversion are shown in Table 4.1. The conversion of TEOS to silica in the NR matrix was as high as 92%. The TEOS molecule contains four ethoxy group, therefore undergoing hydrolysis and condensation to form silica almost completely as found in earlier report [11, 12]. The other three alkyltriethoxysilanes-V30, E30, and B30-, on the other hands, contain one alkyl group connected to the silicon (Fig. 4.1). From Entries 2, 3, and 4, it was found that the presence of the alkyl group in the silane resulted in a remarkable reduction in the %conversion, and also the amount of silica in the NR.

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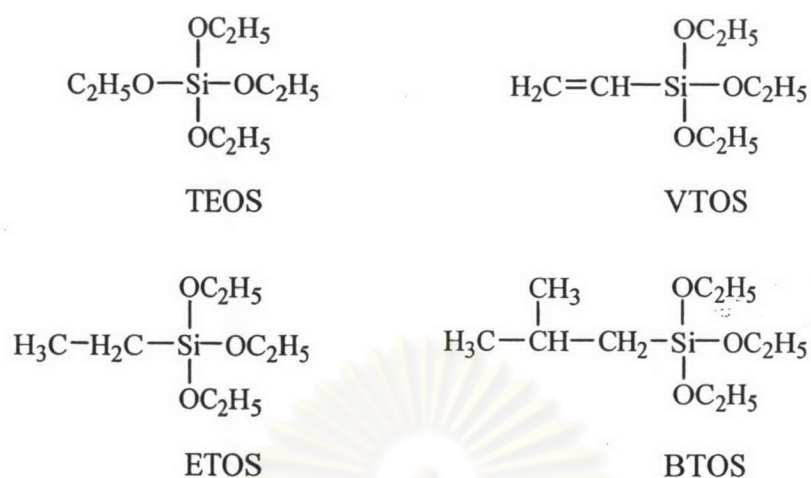
Figure 4.1 Chemical structures of TEOS, VTOS, ETOS and BTOS used in this study

Table 4.1 Analysis of the content and %conversion of *in* situ generated silica in the NR composites prepared from various types of ethoxysilanes.
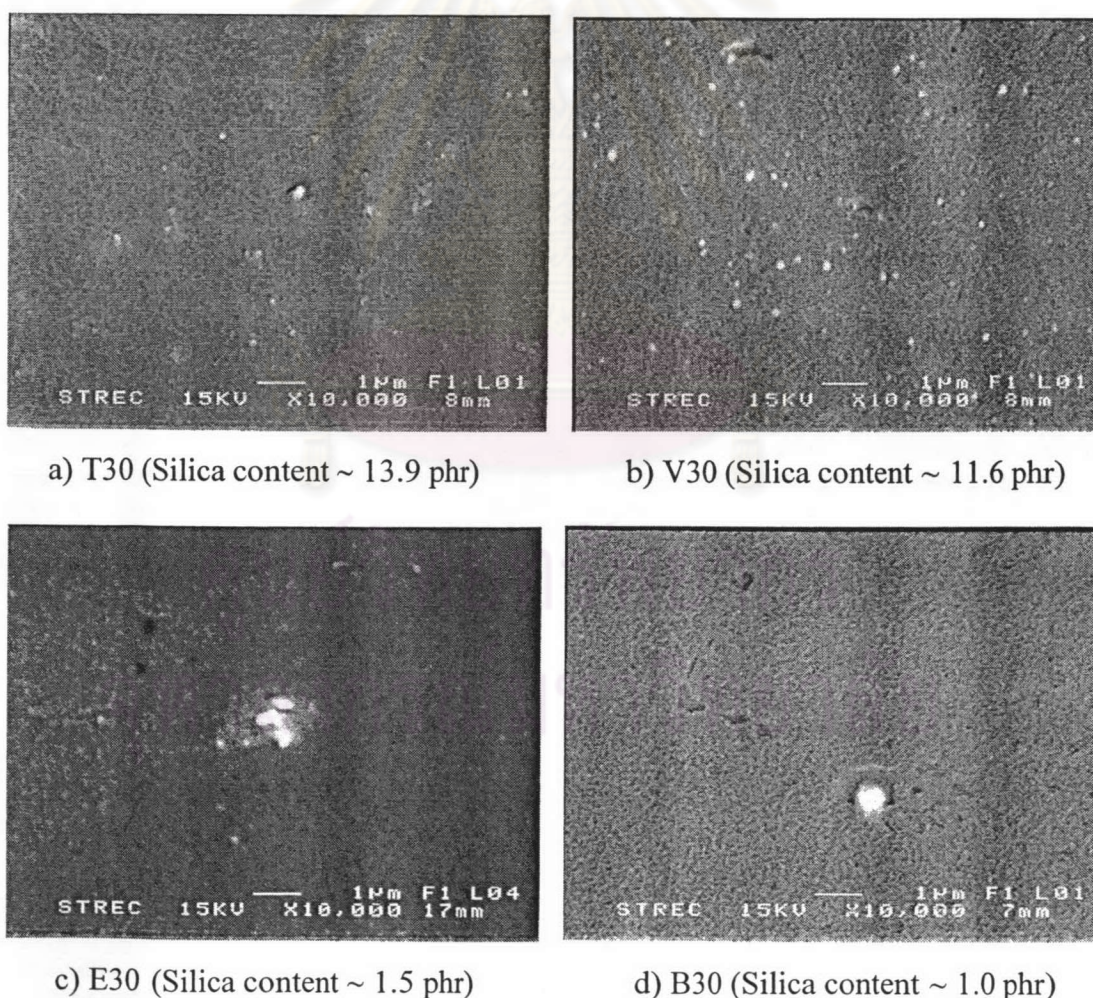
Entry	Sample	TEOS (mmol)	VTOS (mmol)	ETOS (mmol)	BTOS (mmol)	Silica content (phr)	%Conversion to silica
1	T30	30.0	-	-	-	13.9 ± 0.5	92.6
2	V30	-	30.0	-	-	11.6 ± 0.2	58.2
3	E30	-	-	30.0	-	1.5 ± 0.4	7.2
4	B30	-	-	-	30.0	1.0 ± 0.3	3.7

The %conversion of the three alkyltriethoxysilanes in fact decreased when the number of carbon and hydrogen atoms in the alkyl group increased from vinyl (VTOS), to ethyl (ETOS), and *i*-butyl (BTOS). This finding is in agreement with the results reported earlier by Douglas [19] for aqueous system. These results can be explained in terms of the structure and polarity of the silanes. The *i*-butyl group in BTOS is larger and less polar than the ethyl and vinyl groups in ETOS and VTOS. Increasing the steric bulkiness of the organic substituent has an inhibitory effect on the hydrolysis and condensation reaction during the sol-gel process. The silanes with smaller ethyl and vinyl groups are more readily hydrolyzed and condensed to afford large silica than those with bulkier *i*-butyl group. BTOS therefore forms only low molecular weight resin and tends to phase-separate out of the polar medium due to the

low polarity of the butyl group. For the ETOS and VTOS, their sizes are similar, but the vinyl group is more polar than the ethyl. It is more compatible with the polar medium and, thus, more reactive during the sol-gel process in the rubber matrix than the ethyl group. In addition, a small amount of yellow liquid was also found separating out of the semi-dry sample containing BTOS. This liquid could be the silane that was not completely transformed during the sol-gel process.

4.1.2 Morphology and Distribution of Silica in the Composites

The fractured surfaces of the NR composites filled with *in situ* silica generated from different silanes before sulfur vulcanization were analyzed by SEM (Fig. 4.2).

a) T30 (Silica content ~ 13.9 phr)   b) V30 (Silica content ~ 11.6 phr)

c) E30 (Silica content ~ 1.5 phr)   d) B30 (Silica content ~ 1.0 phr)

Figure 4.2 SEM micrographs of the *in situ* silica-filled NR composites

The white spots are the silica particles that were formed inside the rubber matrix (black-toned color). Only one or few white spots were seen in the samples E30 and B30 (Fig. 4.2 c and d), corresponding to the low amount of silica reported in Table 4.1.

4.2 Sol-Gel Process of TEOS/Alkyltriethoxysilanes in Latex

Since it was proven that the conversion of alkyltriethoxysilanes to silica could not be achieved quantitatively, attempts were made to generate silica inside the rubber matrix by using a mixture of TEOS and alkyltriethoxysilanes (Table 4.2). The experiment was designed such that mole ratios of all mixed silanes and the total amount were equal. When comparing among the silica contents obtained between various molar ratios of alkyltriethoxysilane and TEOS, the silica content in the composite decreased when increasing the amount of alkyltriethoxysilane. This result was not surprising since it was shown in section 4.1 that some alkyltriethoxysilanes had low reactivity during the sol-gel process.

Table 4.2 Analysis of the content and %conversion of *in* situ generated silica in the NR composites prepared from various amounts and types of ethoxysilanes. The amount of latex used was 20 grams.

Entry	Sample	TEOS (mmol)	VTOS (mmol)	ETOS (mmol)	BTOS (mmol)	Silica content (phr)	%Conversion to silica
1[1]	T30	30.0	-	-	-	13.9 ± 0.5	92.6
5	V10T20	20.0	10.0	-	-	12.7 ± 0.5	75.9
6	V20T10	10.0	20.0	-	-	12.6 ± 0.3	69.2
7	E10T20	20.0	-	10.0	-	10.4 ± 0.4	61.9
8	E20T10	10.0	-	20.0	-	7.3 ± 0.3	39.6
9	B10T20	20.0	-	-	10.0	9.2 ± 0.1	47.2
10	B20T10	10.0	-	-	20.0	5.5 ± 0.2	23.7

[1] The sample T30 was listed here for comparison purpose.

From the study in section 4.1 and 4.2, it was clear that the mixture of alkyltriethoxysilanes and TEOS was required to quantitatively generate silica inside the NR latex in order to produce NR-silica composites with high silica content. In the next section, the contents of alkyltriethoxysilanes were kept at less than 20% of the total silanes (alkyltriethoxysilane and TEOS), in order to maintain high silica content in the composite.

4.3   Preparation of *In Situ* Silica-NR Composites

In this section, *in situ* silica-NR composites were prepared by the sol-gel process of mixed TEOS/alkyltriethoxysilanes in the concentrated NR latex. Again, the experiment was designed such that mole ratios of all mixed silanes and the total amount were equal. Characterization and mechanical testing were performed in terms of %conversion of silanes to silica, morphology and distribution of *in situ* silica, cure characteristics, swelling in toluene, tensile modulus at 300% elongation (M300), tensile strength, and tear strength of the composite.

4.3.1   Silica Content and %Conversion of Silanes to Silica

The silica contents of the NR-silica composites were determined prior to sulfur vulcanization. The silica content in the NR-silica composites and %conversion are shown in Table 4.3.

Table 4.3 Analysis of the content and %conversion of *in* situ generated silica in the NR composites prepared from various amounts and types of ethoxysilanes. The amount of latex used was 670 grams.

Entry	Sample	TEOS (mmol)	VTOS (mmol)	ETOS (mmol)	BTOS (mmol)	Silica content (phr)	%Conversion to silica
11	NR	-	-	-	-	0	0
12	T100	100.5	-	-	-	14.1 ± 0.4	93.8
13	V5T95	95.5	5.0	-	-	14.2 ± 0.4	92.9
14	V10T90	90.5	10.0	-	-	13.9 ± 0.3	90.1
15	V20T80	80.4	20.1	-	-	14.1 ± 0.3	88.4
16	E20T80	80.4	-	20.1	-	13.4 ± 0.4	83.4
17	B20T80	80.4	-	-	20.1	11.9 ± 0.3	68.2

From Table 4.3, the %conversion of TEOS to silica in the composites is the highest at the average of 93.8%. The presence of alkyltriethoxysilane causes the conversion to decrease depending on the silane types. Mixture of 20% BTOS and 80%TEOS yields a composite with the lowest conversion and the lowest silica content.

4.3.2 Morphology and Distribution of Silica in the Composites

The fractured surfaces of the silica-filled NR vulcanizates after sulfur cure were analyzed by SEM (Fig. 4.3). The detail composition is listed in Table 4.3. White spots represent the silica particles and black area is the rubber matrix.
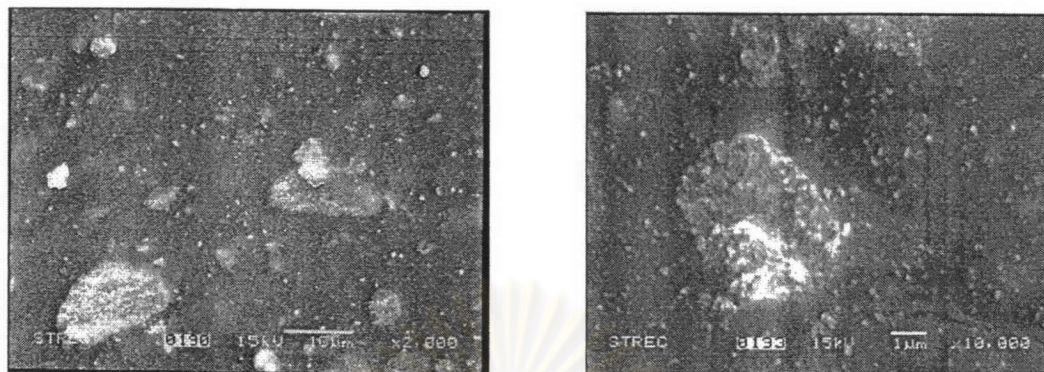
A) NR vulcanizate filled with mechanically mixed silica (14.0 phr silica)
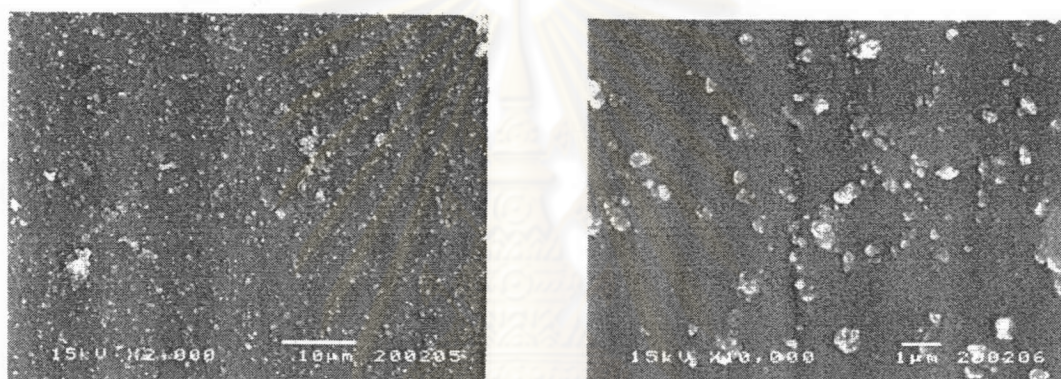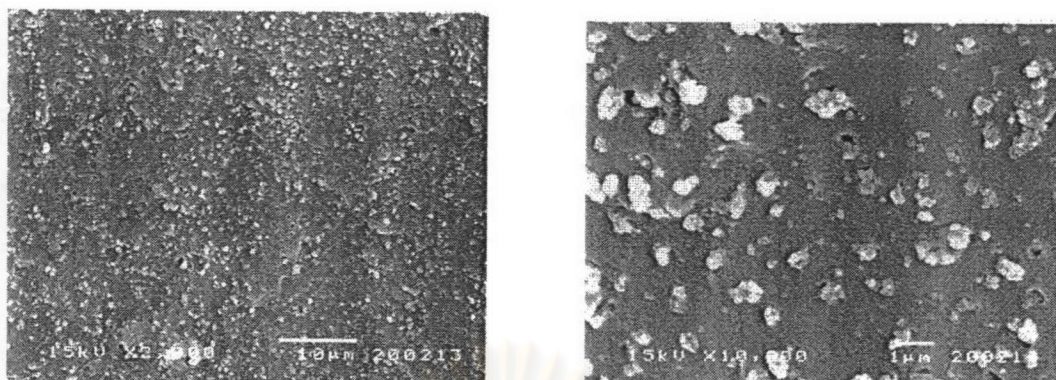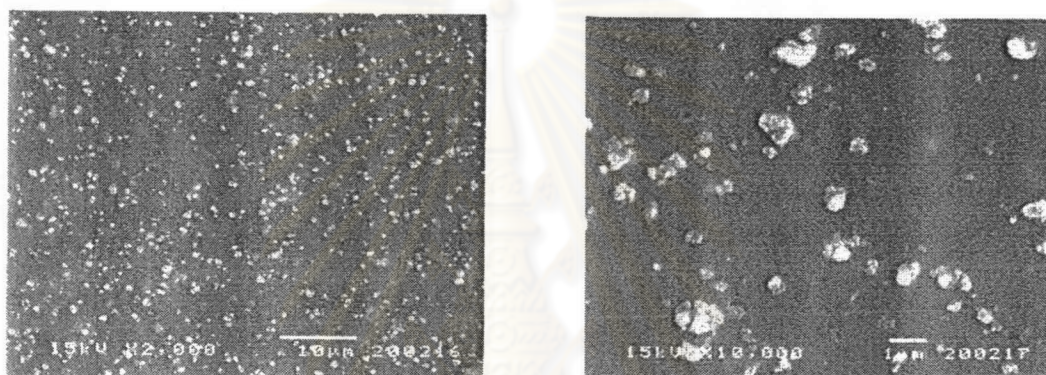

B) T100 (14.1 phr silica)
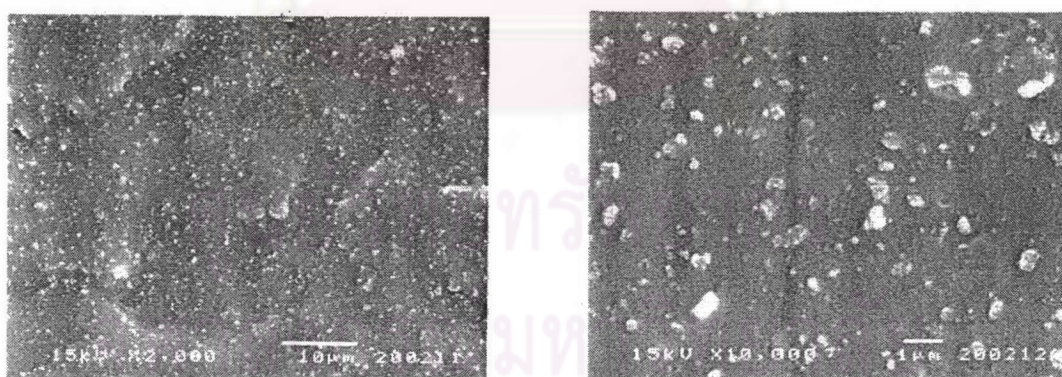
C) V20T80 (14.1 phr silica)

Figure 4.3 *continued on the next page*

D) E20T80 (13.4 phr silica)

E) B20T80 (11.9 phr silica)

Figure 4.3 Scanning electron micrographs of NR vulcanizate filled with mechanically mixed silica (A) and NR vulcanizates filled with *in situ* silica (B-E).
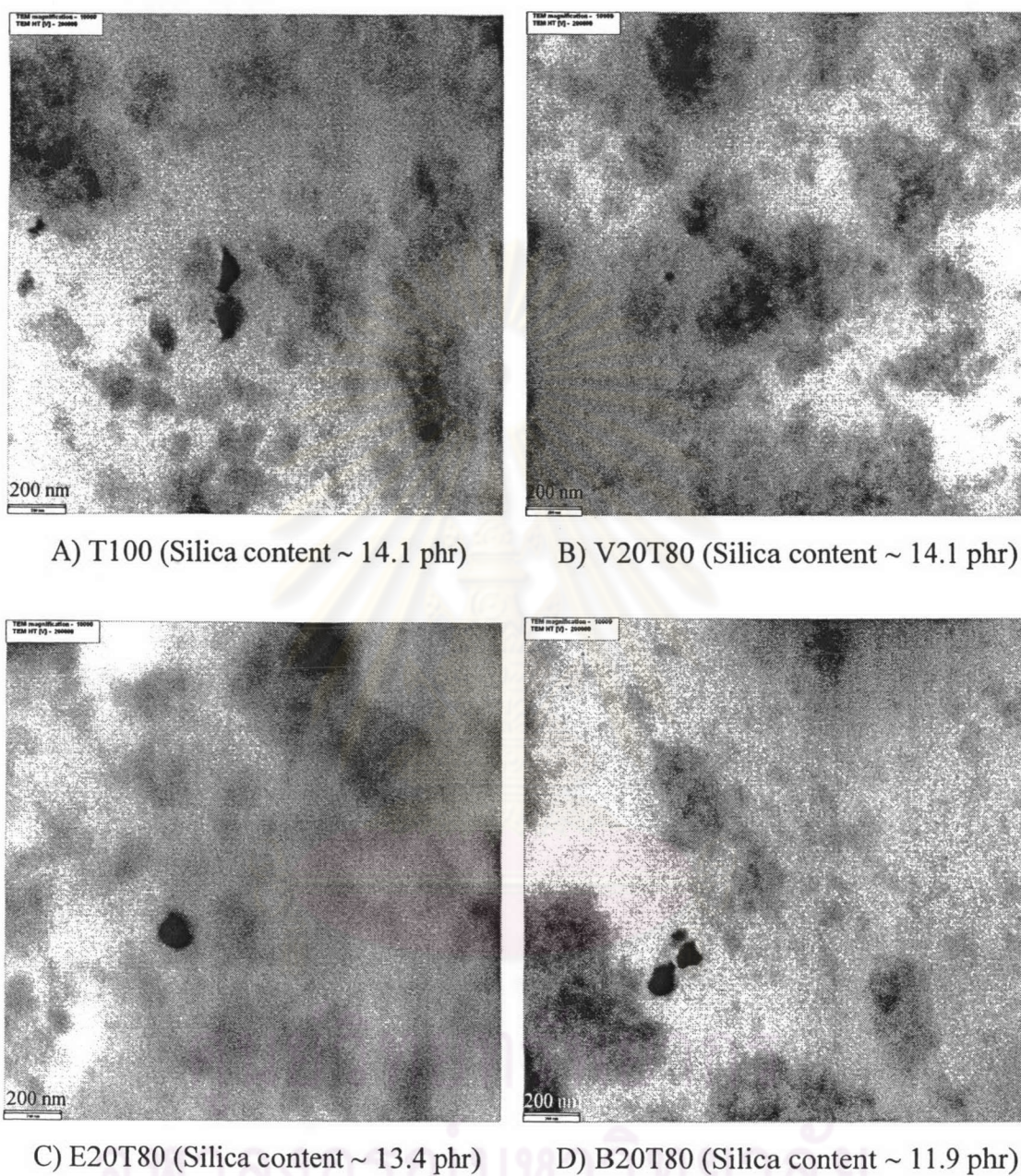
[Images on the left- 2,000× magnification; on the right- 10,000× magnification]

Agglomeration is clearly observed in the micrograph of the vulcanizates mechanically mixed with silica (Hisil-255) (Fig. 4.3 A). The silica particles aggregated to form clusters having various sizes. While the silica generated *in situ* are well dispersed in the NR matrix without noticeable agglomeration (Fig 4.3 B-E).

When comparing among different types of the silane precursors in Fig. 4.3 B-E, no significant difference of silica distribution and size could be observed visibly.

4.3.3 The Size of Silica in the Composites

A) T100 (Silica content ~ 14.1 phr)   B) V20T80 (Silica content ~ 14.1 phr)

C) E20T80 (Silica content ~ 13.4 phr)   D) B20T80 (Silica content ~ 11.9 phr)

Figure 4.4 TEM images of the *in situ* silica-filled NR vulcanizates

TEM was used to analyze the *in situ* silica-filled NR vulcanizates after sulfur vulcanization. Figure 4.4 shows the TEM images of the NR-silica composites prepared using various silanes. The dark spots seen throughout the micrographs are the silica particles.

Area estimation of the black spots from the TEM images (Fig. 4.4) was in agreement with the amount of silica reported in Table 4.2. In addition, no significant difference of size distribution of the *in situ* generated silica in all samples can be observed visibly. It seems that the types of alkyl group in the alkyltriethoxysilane used in this system have no effect on the size distribution of the silica particles in the rubber matrix. The smallest silica size measured by the scale bar in the TEM images is found to be around 40 nm.

It is possible to state that the mixing step by a two-roll mill during curing can cause aggregation of silica particles. If this should be the case, the comparison of silica size and distribution cannot be done. The author suggests that in order to establish the correlation between the type of alkyltriethoxysilane and size of silica particles, the TEM analysis should be performed on the un-milled sample. Unfortunately in this study, a very thin and un-milled (uncured) cannot be obtained since only the fully cured rubber can be sliced into a very thin sheet even by using a microtome operated at cryogenic state.

4.3.4 Solid-State ^{29}Si NMR Analysis

A solid-state ^{29}Si CPMAS NMR technique, which enhances the sensibility of silicon atoms near the OH or CH_x groups, was used to evaluate the structure of silica particles dispersed in the rubber composites. All NR-silica composites were cured by the sulfur vulcanization as shown in Table 3.1.

The NMR spectra of the *in situ* silica-NR vulcanizates (sample T100) are shown in Figure 4.5. For T100 (Fig. 4.5 A) the signal at -109.2 ppm can be assigned to the siloxane groups which are attributed to silicon atoms without the hydroxyl group, $Si(O-Si)_4$ (conventionally called Q^4). The signal at -101.4 ppm represents free silanols which are attributed to silicon atoms that have one hydroxyl group, $(Si-O)_3Si-OH$ (called Q^3). A Q^2 signal, relating to geminal silanols, $(Si-O)_2Si-(OH)_2$, is not shown because of its low abundance.
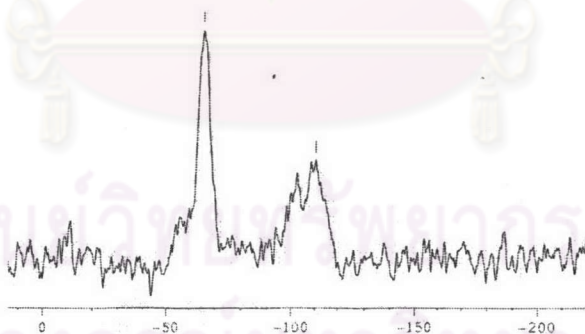
A) T100
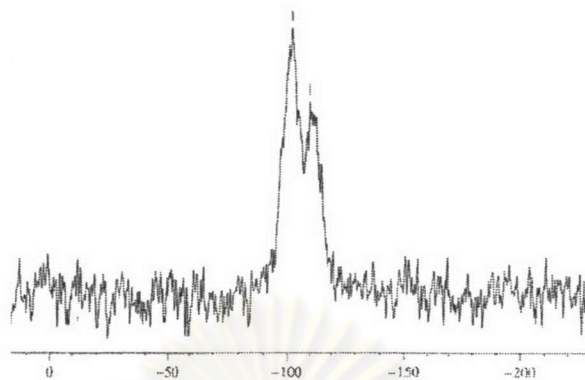
B) V20T80
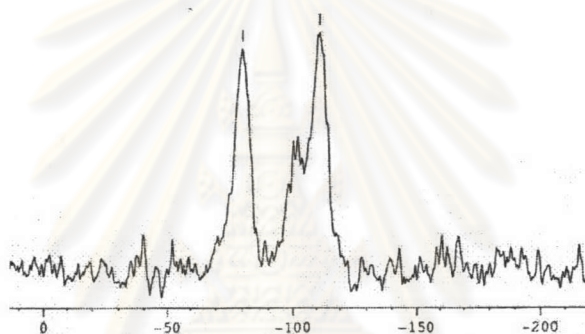
C) E20T80

Figure 4.5 ^{29}Si CP/MAS NMR spectra of A) T100, B) V20T80 and C) E20T80

The *in situ* silica-filled NR vulcanizates with TEOS/VTOS and TEOS/ETOS illustrated in the NMR spectra of V20T80 and E20T80 are shown in Figure 4.5 B) and C), respectively. The Q^3 and Q^4 signals are seen in both spectra at about -110 and -100 ppm, respectively. In addition, a signal assigned to silicon atoms in which one bond is connected to the alkyl group, $(Si-O)_3Si-R$ (T peak) is observed at -79.9 ppm for

V20T80 (Fig. 4.5 B) and at -65.8 ppm for E20T80 (Fig. 4.5 C). The signal intensity of the siloxane groups (Q^4) in E20T80 are lower in proportion than those in V20T80. This indicates that the hydrolysis and condensation reactions of ETOS are less complete than those of VTOS in the rubber latex.

Another distinct difference can be made for the silanol peak at -100.0 ppm (Q^3). For T100, the signal intensity of the Q^3 is higher than the Q^4. On the other hand, the Q^3 in V20T80 and E20T80 are both lower than that of the Q^4. It clearly indicates that the use of VTOS and ETOS to generate silica in the composites can replace the silanol with the alkyl end group on the silica particles.

4.3.5   Cure Characteristics of NR-Silica Compounds

The cure characteristics of NR-silica compounds in terms of scorch and cure times were obtained from the cure curves of each composite. The scorch and cure times of all samples are plotted in Fig. 4.6 (data presented in Appendix A). It can be seen that both scorch and cure times of all silica filled composites are higher than those of the NR vulcanizates. It is due to the fact that the silanol groups on the surface of silica particles can reduce the sulfur curing process, by interacting with the activator (ZnO) and the amine accelerators instead.

When comparing the vulcanizates between the mechanically mixed silica (NR-mix) and the *in situ* silica (T100, V5T95, V10T90, V20T80, E20T80, and B20T80), both scorch and cure times of NR-mix are longer than those of the *in situ* silica-filled NR vulcanizates. This suggests that the amount of silanol groups on the *in situ* generated silica was lower than that on the conventional silica surface [30].
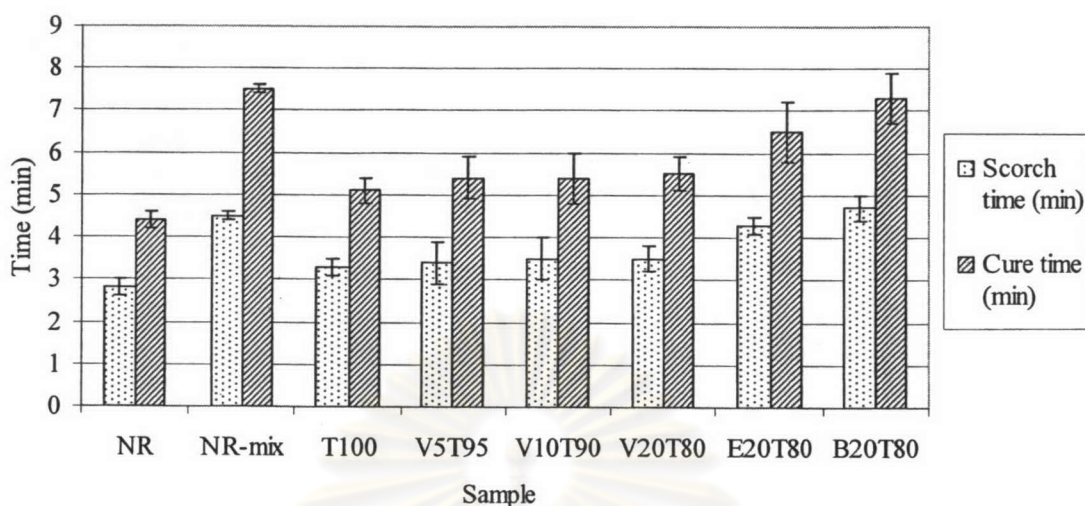
Figure 4.6 Scorch and cure times of the silica-filled NR vulcanizates

When comparing the cure characteristics of all six *in situ* silica-filled NR vulcanizates, it was found that the scorch and cure times of T100, is at the shortest. These values increased slightly for the V5T95, V10T90, and V20T80 samples, and significantly increased for the E20T80 and B20T80 samples. It could be most likely that the increases of cure and scorch times of E20T80 and B20T80 were caused by the low silica content in the composites. The silica content of B20T80 (Table 4.3) was the lowest, therefore less silica was present to inhibit the flow of rubber. For T100, V5T95, V10T90, and V20T80 samples, all of these four samples contained similar amount of silica but the samples with VTOS seemed to have a slightly longer cure and scorch times. A possible explanation is that in TEOS filled sample, silica had a tendency to aggregate, retarding the flow of the rubber composite. The vinyl group in VTOS-filled samples, however, can possibly reduce the aggregation, thus, allowing more rubber flow.

4.3.6 Swelling of the NR-Silica Composites

The crosslink density of an elastomer can be determined from swelling measurements. In a crosslinked network, swelling takes place slowly and continues until the retractable forces in the extended molecular strands in the network balance

the forces tending to swell the network. The degrees of swelling of the silica-filled NR vulcanizates are shown in Figure 4.7 and whose data was shown in Appendix A.
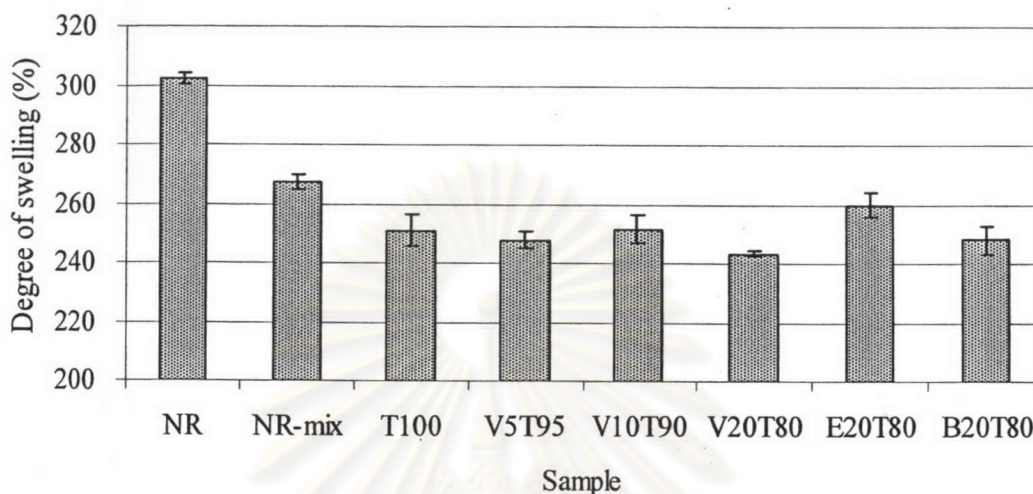
Figure 4.7 Degree of swelling of the silica-filled NR vulcanizates

From Figure 4.7, the swelling behavior of the silica-filled NR vulcanizates is significantly decreased compared to that of the neat vulcanizate (without silica). This is because chain motions of rubber in the silica-filled vulcanizates become restricted by the silica.

For NR-mix, the degree of swelling is higher than those of *in situ* silica-filled NR vulcanizates resulting from the size of silica particle. The *in situ* silica must possess high specific surface area to interact with the rubber. Therefore, the extents of swelling in the solvent for the vulcanizates filled with *in situ* silica were reduced.

When comparing among various silanes, it was found that the swelling of *virginal* silica-filled NR vulcanizates (T100) are similar to those of other modified silica-NR vulcanizates. The use of alkyltriethoxysilanes does not significantly affect the swelling.

4.3.7 Mechanical Properties of the NR-Silica Composites

In this section, all NR vulcanizates were tested for tensile modulus (at a 300% elongation or M300), tensile strength, and tear strength. The results are plotted as shown in Figure 4.8.

The mechanical properties of the NR vulcanizates shown in Figure 4.8 clearly indicate that all the reported mechanical properties of the silica-filled NR vulcanizates are higher than those of the neat NR vulcanizate (without silica). These in fact are due to reinforcing properties of the silica.

When comparing the mechanical properties between NR-mix and all six *in situ* silica-filled NR vulcanizates (T100, V5T95, V10T90, V20T80, E20T80, and B20T80), it was found that all mechanical properties tested of the *in situ* systems are higher than those of the NR-mix. It could be due to the fact that the *in situ* silica seemed to be dispersed very homogeneously throughout the rubber matrix, which contributed effectively to the reinforcement [3]. Although the silica content in E20T80 and B20T80 are slightly lower than the silica content in NR-mix, the M300 and tensile strength of these two vulcanizates are still higher than those of the NR-mix. For tear strength, the values from NR-mix, E20T80, and B20T80 are almost the same.

Other observations relating to alkyltriethoxysilanes can be made as follows. The addition of VTOS in the formulation to prepare the vulcanizates (V5T95, V10T80 and, V20T80) somewhat increased the mechanical properties compared to the vulcanizate prepared from only TEOS (T100). The sample V20T80 has the highest M300 and tensile strength while the V10T90 has the highest tear strength. It suggests that VTOS should participate in a mechanism that promote phase compatibility between the NR phase and the silica phase through the alkyl group and enhances the mechanical property. It is possible that the vinyl groups on silica particles are crosslinked with sulfur.

For the other two silanes, the addition of ETOS and BTOS caused a reduction in all types of mechanical properties tested. For ETOS, the ethyl group has almost the same size as vinyl group but is short of the double bond needed for the crosslinking reaction. In the case of BTOS, the reason could be that the silica content in this sample was much lower than the others. Therefore, a specific remark for the effect of BTOS on the mechanical properties of the vulcanizate cannot be concluded.
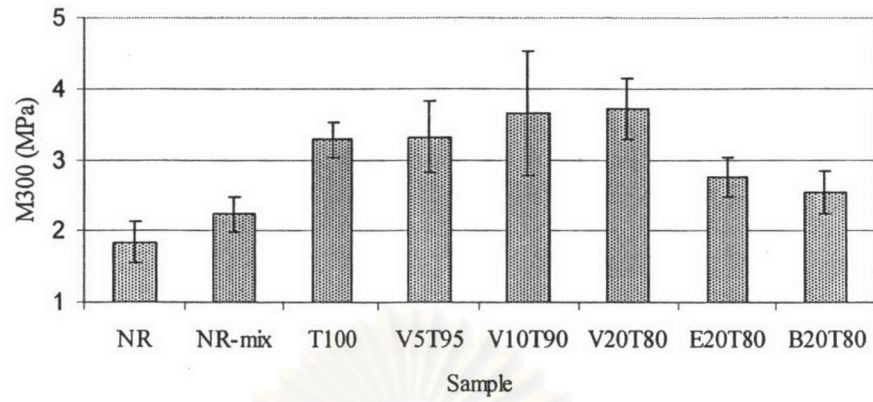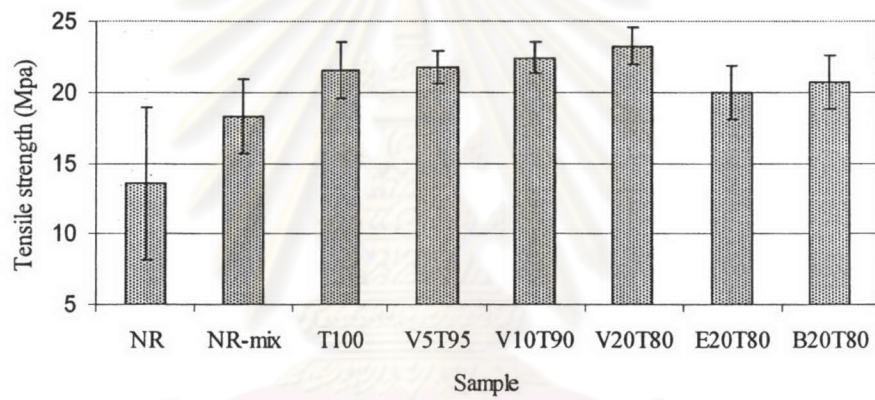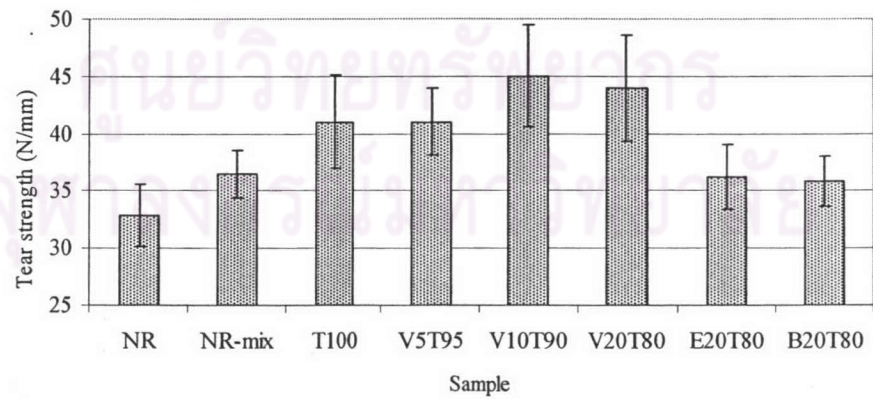
A) Modulus at 300% elongation

B) Tensile strength

C) Tear strength

Figure 4.8 Mechanical properties of the silica-filled NR vulcanizates