CHAPTER IV

RESULTS AND DISCUSSION

4.1 Optimization of Gelation Time for the Sol-Gel Process of Silanes in Latex

Gelation time is the length of time during which the sol-gel process of silane proceeded in the NR latex. There are reports that different types of silane compounds have different rates of sol-gel reaction [34, 35]. In this section, the concentrated NR latex mixed with 50 phr TEOS with and without TESPT were studied for %conversion of TEOS to silica, morphology and distribution of *in situ* silica, as well as cure characteristics, swelling in toluene, and mechanical properties of the composite

### 4.1.1 % Conversion of TEOS to Silica

Here the silica contents in the NR-silica composites were determined prior to further sulfur vulcanization. The data are shown in Table 4.1.

From Table 4.1, the conversion of TEOS to generate *in situ* silica (*entry 2-7*) is mostly above 93%, indicating that nearly all TEOS that was added into the latex had turned into silica during the sol-gel process. When comparing among silica contents obtained after various gelation times, the amount of *in situ* generated silica and %conversion are not significantly different from one another.

Table 4.1 Comparison between silica content and %conversion of TEOS to silica of NR vulcanizates with and without silica reinforcement

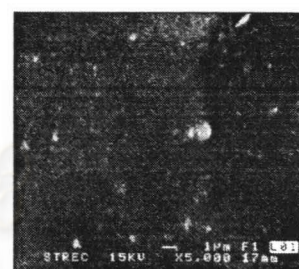| Entry	Sample	Gelation time (days)	Residual ash (phr)	Silica content (phr)	%Conversion
1	NR	-	0.17 ± 0.02	0	0
2		5	13.69 ± 0.15	13.52 ± 0.15	94
3	NR/50 phr TEOS	7	13.65 ± 0.56	13.48 ± 0.56	94
4		10	13.80 ± 0.03	13.63 ± 0.03	95
5		5	14.61 ± 0.22	14.44 ± 0.22	93
6	NR/50 phr TEOS/ 5 phr TESPT	7	13.54 ± 0.49	13.37 ± 0.49	86
7		10	14.87 ± 0.47	14.70 ± 0.47	95

4.1.2 Distribution and Size of *In Situ* Generated Silica in the NR Matrix
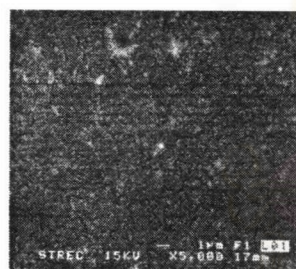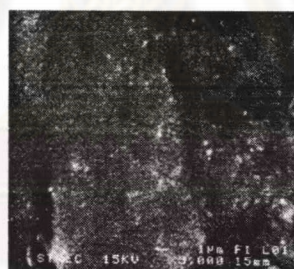
a) gelation time 5 days   b) gelation time 7 days   c) gelation time 10 days

d) gelation time 5 days   e) gelation time 7 days   f) gelation time 10 days

Figure 4.1 SEM micrographs of NR-silica composites, without TESPT (a-c) and with 5 phr TESPT (d-f)

The fracture surfaces of the composites were analyzed by SEM (Fig. 4.1). White spots represent the silica particles that were formed inside the rubber matrix (black-toned color). The silica particles are well dispersed in the NR matrix. When comparing among the three gelation times, no significant difference of silica distribution and size could be noticed.

4.1.3 Cure Characteristics of NR-Silica Compounds

Cure time and scorch time were the two cure characteristics being investigated. Both values were obtained from the cure curves of each composite. The influence of gelation time on cure characteristics of NR-silica compounds performed at 150 °C are shown in Table 4.2.

Table 4.2 Comparison between cure characteristics of NR vulcanizates with and without silica reinforcement

Entry	Sample	Gelation time (days)	Scorch time (min)	Cure time (min)
1	NR	-	2.76	4.22
2	NR/50 phr TEOS	5	3.12	4.76
3		7	3.19	4.82
4		10	3.11	4.85
5	NR/50 phr TEOS/ 5 phr TESPT	5	2.38	4.27
6		7	1.45	3.18
7		10	2.17	3.93

When compare the scorch and cure times of the NR-silica composites within the same group (*entry 2-4* and *entry 5-7*) in Table 4.2, it was found that changing the gelation time from 5 to 10 days did not cause any significant changes in those two values. Moreover it should be noted here that the scorch and cure times of *in situ* filled silica-NR vulcanizates (without TESPT, *entry 2-4*) are longer than those of NR without silica (*entry 1*). The addition of 5 phr TESPT (*entry 5-7*) helps reduce both scorch and cure times to values that even lower than the NR vulcanizate (*entry 1*). These observations in fact fit well with the theory. As mentioned earlier in Chapter 2

that the silanol group on the surface of silica particles can reduce the sulfur curing process, by interacting with the activator (ZnO) and the amine accelerators instead. After the incorporation of TESPT, the amount of silanol groups should decrease, and also TESPT contains sulfur units that can participate in sulfur vulcanization. This leads to strong chemical linkages between the silane coupling agent and rubber molecule. Thus vulcanization of *in situ* filled silica-NR composite is achieved faster in the presence of TESPT than without it.

4.1.4 Swelling of the NR-Silica Composites

Table 4.3 shows the swelling ratio of the *in situ* silica-NR vulcanizates. The swelling ratio is calculated from the weight of rubber matrix that was swollen in toluene, and it is inversely proportional to the degree of crosslinking. The swelling ratios of NR-silica vulcanizates without TESPT (*entry 2-4*) are higher than those of the composites with TESPT (*entry 5-7*). These results suggest that TESPT increases the crosslinking in the NR. Since TESPT can react with both silanol groups on the silica surface and the double bonds of NR polymer chain, therefore increasing chemical bonds between NR and silica particles. Finally when increase the gelation time, the swelling ratio of NR-silica vulcanizates does not change significantly.

Table 4.3 Comparison between swelling ratio in toluene of NR vulcanizates with and without silica reinforcement

Entry	Sample	Gelation time (days)	Swelling ratio (%)
1	NR	-	292.98 ± 0.67
2		5	260.49 ± 1.79
3	NR/50 phr TEOS	7	273.57 ± 0.77
4		10	250.19 ± 3.50
5		5	237.76 ± 0.95
6	NR/50 phr TEOS/ 5 phr TESPT	7	232.07 ± 3.73
7		10	234.79 ± 4.08

4.1.5 Mechanical Properties of the NR-Silica Composites

The mechanical properties of NR-silica vulcanizates– tensile modulus at 300% elongation (M300), tear strength and hardness, are listed in Table 4.4. All reported mechanical properties of the *in situ* silica-NR vulcanizates (*entry 2-7*) are higher than those of the gum vulcanizate (*entry 1*). The addition of TESPT (*entry 5-7*) obviously raises all mechanical properties to higher values. This confirms the reinforcement capability of silica particles and the role of TESPT as a co-curing agent in the NR vulcanizate. Again, when comparing among the same sample groups (*entry 2-4* and *entry 5-7*), increase in the gelation time does not significantly affect the mechanical properties.

Table 4.4 Comparison between mechanical properties of NR vulcanizates with and without silica reinforcement

Entry	Sample	Gelation time (days)	M300 (MPa)	Tear strength (N/mm)	Hardness
1	NR	-	2.19 ± 0.01	30.76 ± 3.71	39.5 ± 1.10
2	NR/50 phr TEOS	5	3.22 ± 0.40	40.81 ± 0.65	43.1 ± 2.76
3		7	3.33 ± 0.90	38.55 ± 3.78	42.7 ± 0.92
4		10	3.04 ± 0.25	41.55 ± 1.02	43.5 ± 2.44
5	NR/50 phr TEOS/ 5 phr TESPT	5	4.43 ± 0.14	46.35 ± 0.31	47.1 ± 1.27
6		7	4.17 ± 0.20	47.22 ± 2.52	46.2 ± 0.99
7		10	4.07 ± 0.52	45.28 ± 6.10	45.6 ± 0.64

In this section, the interaction of *in situ* generated silica and the coupling agent, TESPT were evaluated. The roles of silica as a reinforcing filler and TESPT a co-curing agent were confirmed in this vulcanizate system. Lastly, the gelation time of 5 days seems to be appropriate for the sol-gel process of TEOS in the concentrated NR latex to get a complete reaction.

4.2 Experimental Design for Study on the Influential Factors on the Mechanical Properties of NR-Silica Composites

The 2^3-factorial design was carried out to study the factors thought to influence the mechanical properties such as tensile modulus, tear strength and hardness. The 3 factors focused here were the amount of TEOS (T), TESPT (C) and ammonia (N) added to concentrated NR latex. Each factor was presented at the two levels; high and low.

4.2.1 Silica Content and %Conversion of TEOS to Silica

Table 4.5 Factor level for factorial designed experiments and silica content of the composites

Entry	Factor			Silica content (phr)	%Conversion
	TEOS (T)	TESPT (C)	Added ammonia (N)		
1	-	-	-	2.68 ± 0.11	87
2	+	-	-	13.22 ± 0.38	90
3	-	+	-	3.64 ± 0.19	91
4	+	+	-	13.44 ± 0.61	87
5	-	-	+	2.97 ± 0.26	96
6	+	-	+	13.28 ± 0.31	91
7	-	+	+	3.66 ± 0.20	92
8	+	+	+	14.19 ± 0.25	91

TEOS : +(50 phr), -(10 phr)

TESPT : +(5 phr), -(1 phr)

added ammonia : +(2.5 %w/w), -(0 %w/w)

Table 4.5 shows the amount of silica, and %conversion of the *in situ* silica-NR composites. The amount of *in situ* silica is 3-4 phr for the sample having 10 phr TEOS. The silica content increased to ~14 phr when 50 phr TEOS was added to the latex. The conversion of TEOS to generate *in situ* silica is 86-96 % indicating that

nearly all TEOS have turned into silica during the sol-gel process inside the NR matrix.

4.2.2 Factors that Influence the Mechanical Properties

The results obtained from the three modes of mechanical property measurement of the *in situ* silica-NR vulcanizates are shown in Table 4.6.

Table 4.6 The mechanical properties of the *in situ* silica-NR vulcanizates

Entry.	Factor			M300 (MPa)	Tear strength (N/mm)	Hardness
	TEOS (T)	TESPT (C)	Added ammonia (N)			
1	-	-	-	2.47 ± 0.22	34.04 ± 3.07	40.6 ± 2.00
2	+	-	-	3.46 ± 0.61	44.80 ± 1.45	43.8 ± 1.50
3	-	+	-	2.93 ± 0.29	33.67 ± 7.50	41.5 ± 0.72
4	+	+	-	4.17 ± 0.20	47.22 ± 2.52	46.2 ± 0.99
5	-	-	+	2.38 ± 0.25	35.50 ± 2.95	41.2 ± 1.54
6	+	-	+	3.78 ± 0.40	42.23 ± 1.63	44.1 ± 1.66
7	-	+	+	2.78 ± 0.14	35.89 ± 4.38	43.0 ± 1.65
8	+	+	+	4.43 ± 0.53	38.66 ± 2.49	44.4 ± 1.98

From these results, 'estimated effects' for each mode of the three mechanical properties (responses) are calculated by Eq. 3.4. The standard error (E) for all 7 estimated effects for each response can be calculated by Eq. 3.5. By using Eq. 3.4, the main and the interaction effects between the high and low levels were determined, while Eq. 3.5 was used to calculate the errors between three repeated experiments. The data are shown in Table 4.7.

Table 4.7 Values of estimated effect for the 2^3-factorial design of *in situ* silica-NR vulcanizates

Calculated effect	M300 (MPa)	Tear strength (N/mm)	Hardness
Main			
TEOS content (T)	$1.322^a \pm 0.149^b$	8.453 ± 1.520	3.083 ± 0.638
TESPT content (C)	0.553 ± 0.149	-0.283 ± 1.520	1.333 ± 0.638
Added ammonia content (N)	0.083 ± 0.149	-1.858 ± 1.520	0.117 ± 0.638
Two-factor interaction			
TC	0.125 ± 0.149	-0.295 ± 1.520	0.000 ± 0.638
TN	0.208 ± 0.149	-3.705 ± 1.520	-0.917 ± 0.638
CN	-0.030 ± 0.149	-1.305 ± 1.520	-0.300 ± 0.638
Three-factor interaction			
TCN	-0.002 ± 0.149	-1.686 ± 1.520	-0.767 ± 0.638

[a] The estimated effect is obtained from Eq. 3.4.

[b] The standard error (E) is obtained from Eq. 3.5.

In order to identify the effect that significantly influenced the properties of the NR-silica composites, the E values of each response must be taken into account by comparing with the absolute value of all 7 estimated effects in the same response. If the absolute estimated effect value is larger than E, that effect is considered significant. (Detailed calculation of the estimated effects and standard errors are shown in Appendix A.)

<u>M300</u>

From Table 4.7, it was found that factors that influence M300 of the silica-NR vulcanizates are T and C, which confirmed by the factorial design study in Tables 4.6 and 4.7. The M300 increases significantly when increasing the amounts of TEOS and TESPT added into the latex. High ammonia value does not affect the M300. Therefore, for a practical method, a silica-NR vulcanizate having a high M300

requires high TEOS and high TESPT contents without the need to add more ammonia into the concentrated NR latex which already contains 0.7% NH_3.

Tear strength

The T, N, TN and TCN are the main and combined factors that influence the tear strength significantly. Noted that the effective values of N, TN and TCN are *negative*, suggesting that increase in the NH_3 in the system would reduce the tear strength of the composite. The adversed effect of ammonia agreed well with the study made by Nuntivanich [10] using the same sol-gel process but without the coupling agent. Therefore, a composite with large tear strength can be obtained by adding a large amount of TEOS but limit the ammonia content to a low amount. For TESPT, no obvious trend could be made from this data set.

Why the high ammonia caused a reduction in tear strength? No conclusive reason could be made but one possible explanation might relate to the formation kinetics of silica particles. Since hydrolysis and condensation of TEOS in latex was known to depend on pH. The change in the ammonia content from 0.7% to 3.2% could somewhat affect the silica particle in terms of molecular weight and, thus, size. Due to time limitation, analysis on this issue by TEM has not yet been performed.

Hardness

The factors that influence hardness are T, C, TN and TCN. As expected, the hardness increased when increasing TEOS and TESPT contents. Additional ammonia does not significantly affect the hardness. Also, increase the ammonia content but decrease the amount of TEOS and TESPT resulted in a reduction of hardness.

The highest hardness was obtained from experiment 4 (T+, C+, N-) (Table 4.6). This implies that ammonia is the factor that should be limited to a low value. For practical usage, the composite with high hardness requires high TEOS, TESPT and no need to add more ammonia into the latex.

4.3 Effects of TESPT Content on the Properties of NR-Silica Composites

In this section, the properties of *in situ* silica-NR composite were studied by varying the amount of TESPT to 1, 5, and 10 phr.
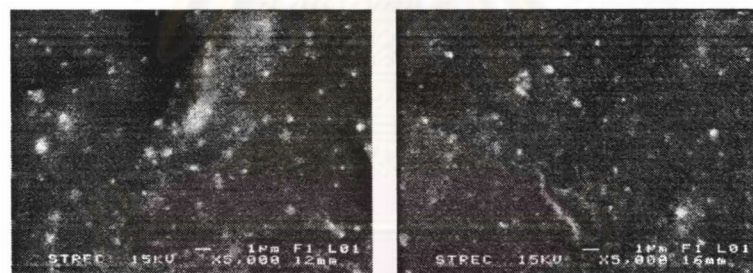
4.3.1 Morphology and Distribution of Silica in the Composites
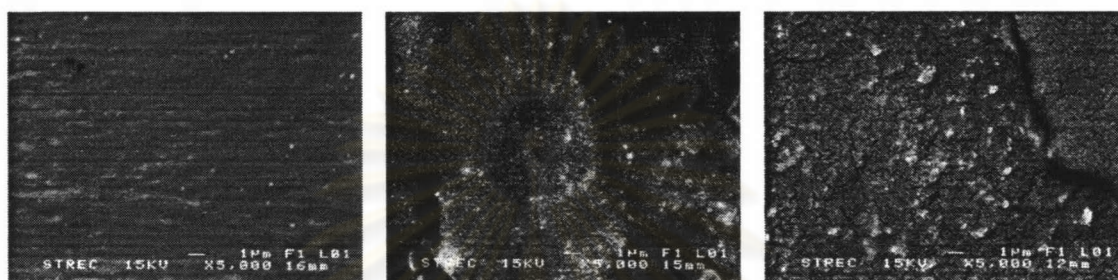
a) NR vulcanizate   b) NR/50 phr TEOS   c) NR/50 phr TEOS/ 1 phr TESPT

d) NR/50 phr TEOS/5 phr TESPT   e) NR/50 phr TEOS/10 phr TESPT

Fig 4.2 SEM micrographs of NR-silica composites

The fracture surfaces of the composites were analyzed by SEM (Fig 4.2). White spots represent the silica particles and black area is the rubber matrix. The silica particles are evenly dispersed in the NR matrix. In order to accurately determine silica particle size in the range of sub-micron, silica-NR composite was subjected to analysis by TEM.

4.3.2 The Size of Silica Particle in the Composites

Since SEM is not an effective method to determine the size of particle in the sub-micron range, TEM is used to analyze a sample of *in situ* silica-NR composite.

Figure 4.3 shows the TEM photographs of the NR-silica composites with and without TESPT. The presence of TESPT further made *in situ* silica particles very fine and homogeneous comparing to the NR-silica vulcanizate without TESPT. The single particle was measured on the picture by using a ruler. An average diameter, out of five different silica particles, is 123 ± 7.63 nm for the vulcanizate without TESPT and 37 ± 1.65 nm for the vulcanizate with TESPT. The additional presence of TESPT provided a higher number of initiating sites for *in situ* silica formation, resulting in a greater number of silica particles with smaller sizes [31].
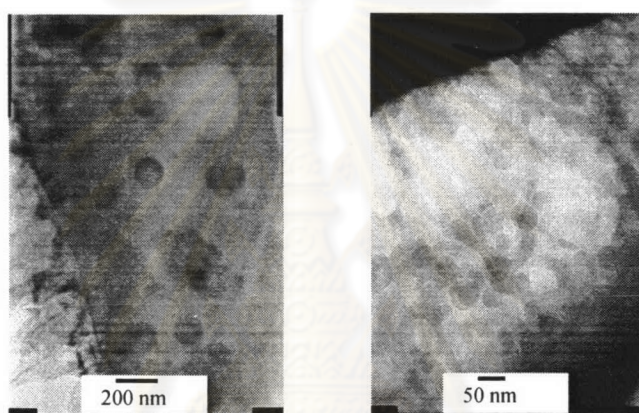

Fig 4.3 TEM photographs of the NR-silica composites

4.3.3 Cure Characteristics of NR-Silica Composites

The influence of TESPT content on the cure characteristics of silica-NR vulcanizate is shown in Table 4.8. The addition of TESPT caused Δtorque (difference between the maximum and minimum torques) to increase but reduces both scorch time (ts_2) and optimum cure time (t_{90}). It is known that the increase in torque during vulcanization is proportional to the number of crosslinks formed per unit volume of rubber [24]. Therefore, it is evident that TESPT acts as a co-curing agent in the sulfur vulcanization process. Thus, the rate of vulcanization reaction is faster. At 10 phr TESPT, however, the ts_2 and t_{90} tend to increase, indicating a slower curing rate. The behavior was possible due to the fact that at 10 phr, TESPT was in excess and might plasticize the system.

Table 4.8 Cure characteristics of *in situ* silica-NR vulcanizates

TEOS (phr)	TESPT (phr)	ts_2 (min)	t_{90} (min)	Torque $_{max}$ (dNm)	Torque $_{min}$ (dNm)	ΔTorque (dNm)
0	0	2.76	4.22	6.42	0.74	5.68
10	0	3.25	4.82	6.68	0.71	5.97
	1	2.65	4.46	6.34	0.70	5.64
	5	2.21	3.97	7.06	0.71	6.35
	10	2.33	3.86	8.70	0.77	7.93
50	0	3.19	4.82	6.56	0.71	5.85
	1	2.48	4.27	7.03	0.77	6.26
	5	1.45	3.18	7.83	0.59	7.25
	10	2.88	5.23	9.72	1.04	8.68

4.3.4 Solid-state ^{29}Si NMR

Silicon-29 CP/MAS NMR spectra of the *in situ* silica-NR vulcanizates are shown in Fig 4.3. Without the coupling agent (TESPT), two peaks are easily recognized: one peak, at -101.4 ppm, is attributed to silicon atoms that have one hydroxyl group, $(Si-O)_3Si-OH$ (conventionally called Q^3), and the other at -109.2 ppm is due to the silicon atoms without hydroxyl group, $Si(Si-O)_4$ (called Q^4). A Q^2 signal, relating to geminal silanols, $(Si-O)_2Si-(OH)_2$, is not shown because of its low abundance [36]. When TESPT is added, an additional peak is observed at -67.9 ppm which are attributed to silicon atoms that one bond is connected to an alkyl, $(Si-O)_3Si-R$ (or T^3) [36, 37]. Moreover when adding TESPT, the intensity of Q^3 signal decreases but the Q^4 increases. The results imply that the reaction between TESPT and TEOS leads to a reduction in the density of silanol groups on the silica surface.
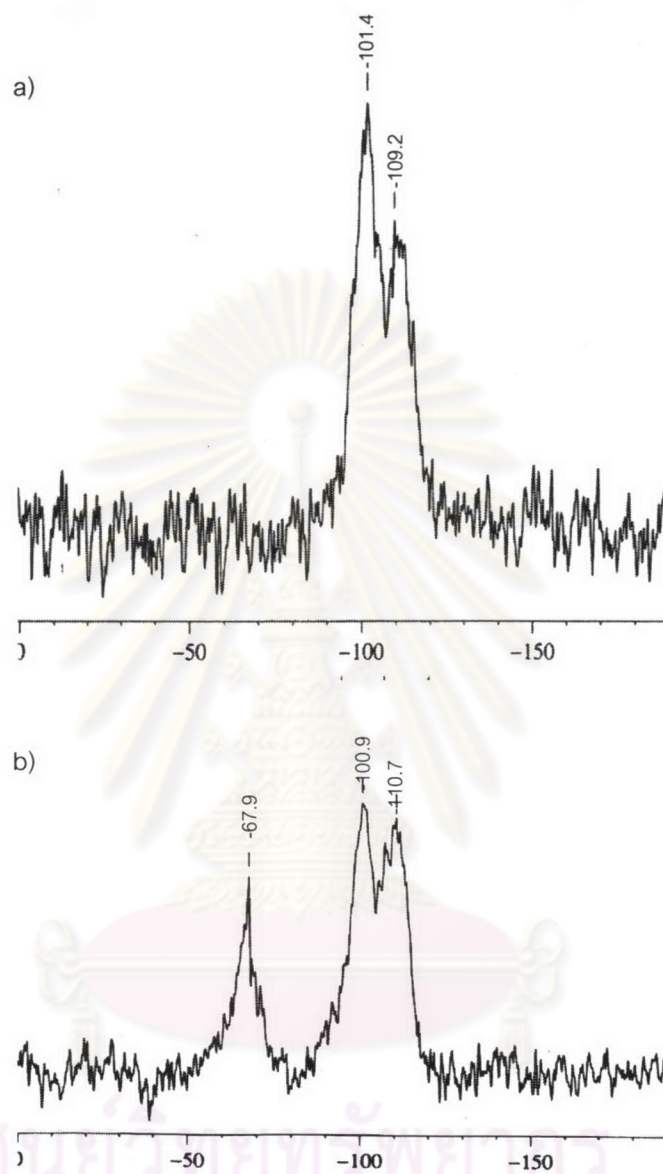
Fig 4.4 ^{29}Si CP/MAS NMR spectra of a) without TESPT and b) with TESPT

4.3.5 Mechanical Properties of *In Situ* Silica-NR Vulcanizates

Figure 4.4 shows the mechanical properties of NR-silica vulcanizates – tensile modulus at 300% elongation (M300), tear strength and hardness (see data in Appendix B). In each plot, a comparison was made among samples prepared from 10 or 50 phr TEOS and 0, 1, 5, and 10 phr TESPT.
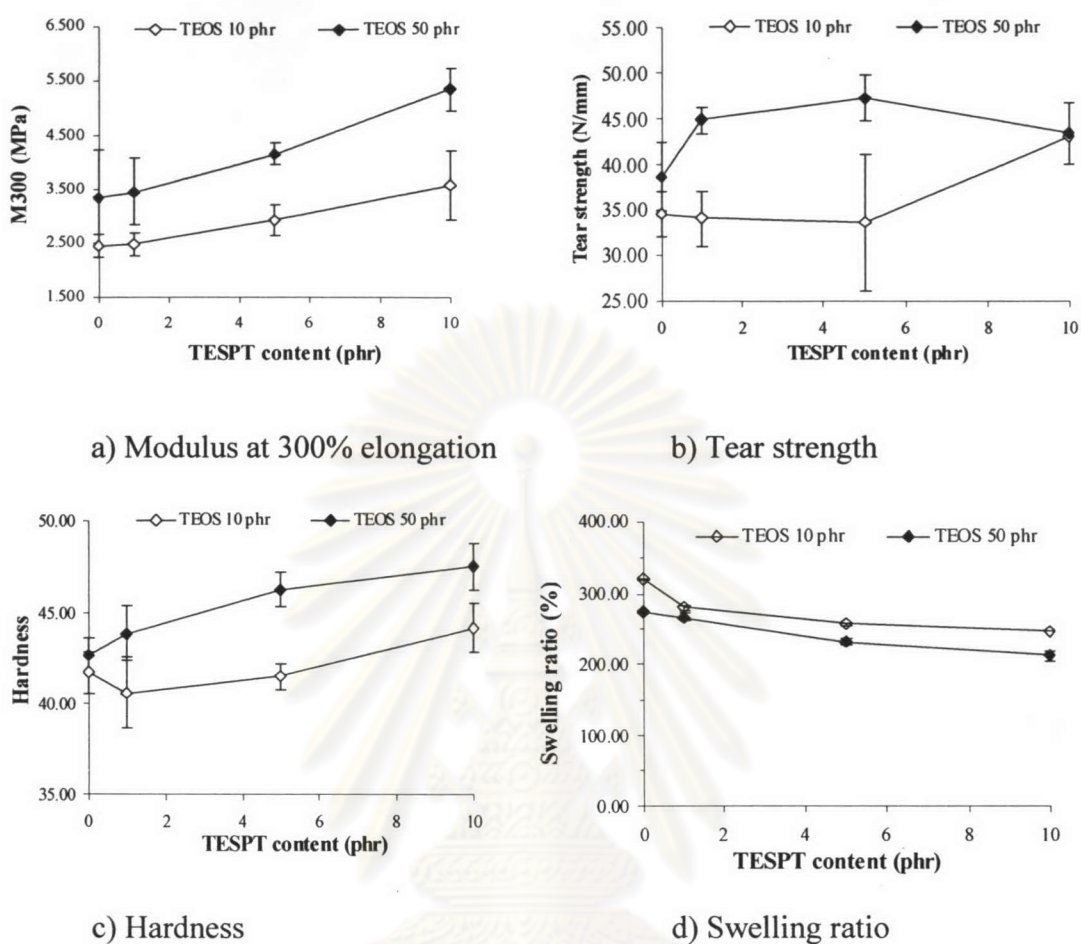
a) Modulus at 300% elongation

b) Tear strength

c) Hardness

d) Swelling ratio

Fig 4.5 Variation of the properties of silica-NR vulcanizates with TESPT content

As presented earlier M300, tear strength, and hardness increased with the presence of TESPT. The results are brought about by improved interaction between NR and silica. The tensile strength of the TESPT contained composites are 14-20 MPa. An adverse result was obtained from one formulation. When 10 phr TESPT was added to the latex mixture, the tear strength was reduced. This may be caused by the excess of TESPT. For practical usage, high mechanical properties and optimum cure characteristics require high TEOS content and TESPT 5 phr.

Crosslink density is directly related to the hardness of rubber vulcanizates. An explanation is the increased crosslink density with increasing TESPT content, as shown in swelling test results (Fig 4.4d). The swelling ratio (Q) was correlated closely to the crosslink density. The reciprocal swelling ratio is used to represent

crosslink density. The crosslink density of vulcanizates increases with increasing TESPT content. The crosslink density of vulcanizate with higher TEOS content (50 phr) is higher than that with lower TEOS content (10 phr). This is because the linkage between NR and TESPT-immobilized silica in the former case is more than that in the latter sample.

4.4 Methods of Adding the Coupling Agent (TESPT)

In this section, the author compared two methods of adding TESPT in the process of preparing *in situ* silica-NR vulcanizate. TESPT could be added together with TEOS, a major component for forming silica, or added after the sol-gel process of TEOS to silica in rubber was completed. These two possibilities may lead to two different schemes of modifying the silica particles.

In the first method, when TESPT is present with TEOS, it can participate in the sol-gel process. This would yield silica particles having their molecular weight and size limited by TESPT. But when TESPT is added to the already formed silica in the second method, here silica with desired size can form siloxane linkage with the added coupling agent. It is possible that the density of silanol groups obtained from these two methods would be different from each other, thus causing a different reinforcing efficiency.

In the following section, silica content, cure characteristics, particle morphology, and mechanical properties of the composites prepared by the two methods were compared. No difference in the silica content, %conversion of TEOS to silica, and its distribution in NR matrix could be observed (Table 4.9 and Fig. 4.5). But when comparing the scorch and cure times (Table 4.10), it was found that adding TESPT with TEOS resulted in shorter scorch and cure times than when adding the coupling agent later. It was likely that the density of silanol group on silica particles in the first case was lower than the second. The crosslink density and mechanical properties of the silica-NR composites prepared by both methods were not much different from the other as shown in the Table 4.11.
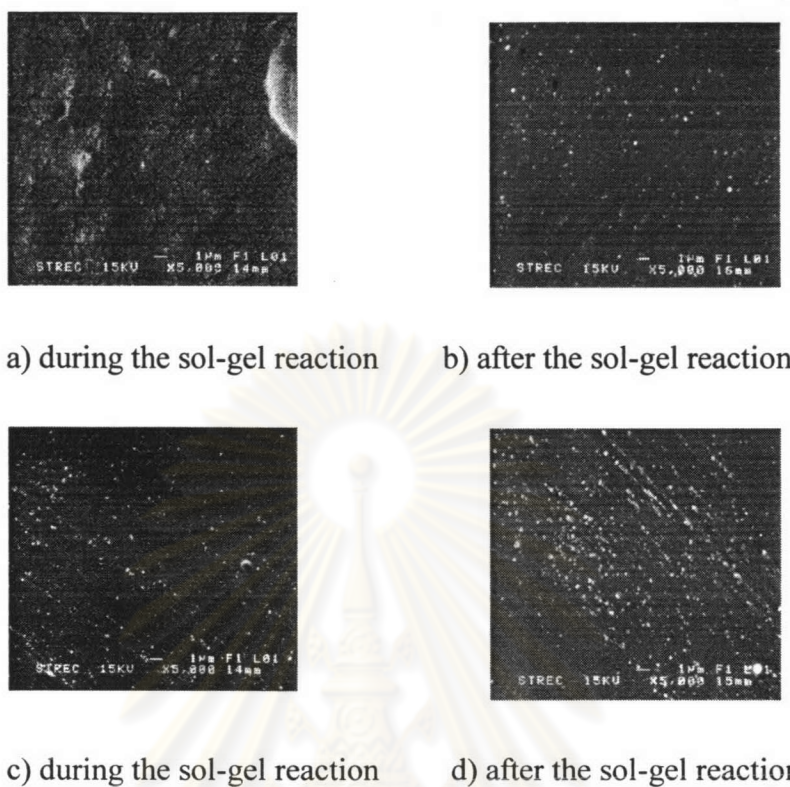
a) during the sol-gel reaction   b) after the sol-gel reaction

c) during the sol-gel reaction   d) after the sol-gel reaction

Fig 4.6 SEM micrographs of NR-silica composites, 10 phr of TEOS (a-b) and 50 phr of TEOS (c-d)

Table 4.9 The silica content and %conversion of TEOS to silica of the sol-gel process in NR

Sample	Order of adding TESPT*	Residual ash content (phr)	Silica content (phr)	%Conversion
NR	-	0.17 ± 0.02	0	0
NR/10 phr TEOS	before	3.81 ± 0.19	3.64 ± 0.19	91.09
	after	3.75 ± 0.26	3.58 ± 0.26	89.62
NR/50 phr TEOS	before	13.54 ± 0.49	13.37 ± 0.49	86.04
	after	14.59 ± 0.37	14.42 ± 0.37	92.79

* before = before sol-gel, after = after sol-gel process.

Table 4.10 Cure characteristics of NR-silica compounds

Sample	Order of adding TESPT	Scorch time (min)	Cure time (min)
NR	-	2.76	4.22
NR/10 phr TEOS	before	2.21	3.97
	after	2.63	4.96
NR/50 phr TEOS	before	1.45	3.18
	after	2.38	6.20

- before = before sol-gel, after = after sol-gel process.

Table 4.11 The swelling ratio and mechanical properties of the NR-silica composites

Sample	Adding TESPT	Swelling ratio (%)	M300 (MPa)	Tear strength (N/mm)	Hardness
NR	-	292.98 ± 0.67	2.19 ± 0.01	30.76 ± 3.71	39.5 ± 1.10
NR/10 phr TEOS	before	255.83 ± 1.94	2.93 ± 0.29	33.67 ± 7.50	41.5 ± 0.72
	after	266.77 ± 10.28	2.76 ± 0.08	28.09 ± 3.91	42.2 ± 1.70
NR/50 phr TEOS	before	232.07 ± 3.73	4.17 ± 0.20	47.22 ± 2.52	46.2 ± 0.99
	after	228.91 ± 2.50	5.35 ± 0.32	46.55 ± 2.91	47.3 ± 1.34

* before = before sol-gel, after = after sol-gel process.