CHAPTER IV

RESULTS AND DISCUSSION

The aim of this work was to use tetraethoxysilane and alkyltrialkoxysilane as a precursor to generate *in situ* silica in the NR dipped film. The effect of types of alkoxysilane on *in situ* silica formation was studied in 5 parts as follows:

4.1. *In situ* silica formation in natural rubber latex

4.2. Morphology of *in situ* silica–NR composite films

4.3. Swelling study

4.4. Mechanical properties

4.5. Thermal properties

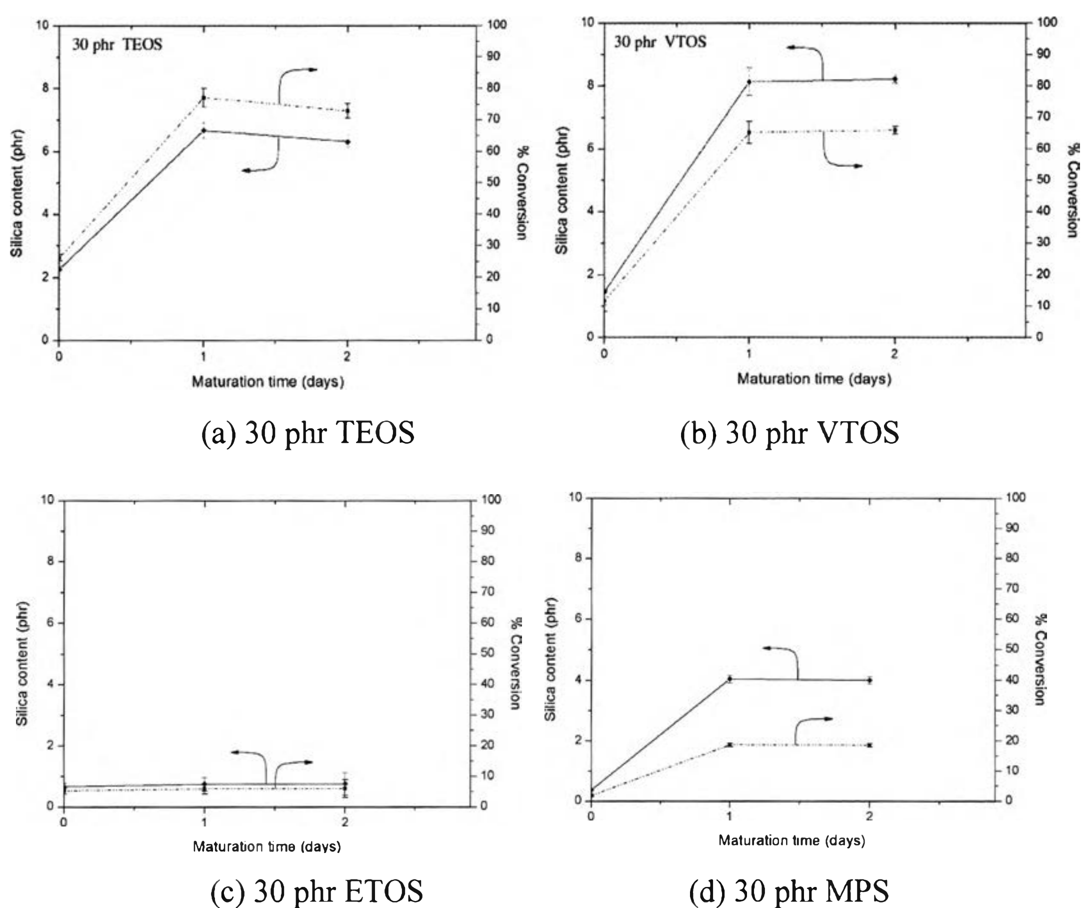
4.1 *In situ* silica formation in natural rubber latex

4.1.1 Effect of maturation time on natural rubber latex

The NR latex (30% DRC) was mixed with vulcanizing agent and alkoxysilanes with the amount listed in Table 3.2. The mixed latex must maintain its colloidal stability during maturation and dipping steps. The latex maturation is one of the most significant steps in manufacturing latex products. The maturation of latex compounds is the period after which the latex compound is stored prior to use in the dipping process. The crosslink in latex can slowly take place at room temperature [28]. Moreover, it is believed that the added alkoxysilane can slowly undergo hydrolysis and condensation to form low molecular weight silicon oxide. This is because the latex used contains ammonia that is a catalyst to accelerate the sol-gel process of those alkoxysilane in the latex. It is therefore worth exploring the effect of latex maturation time on silica formation in the composite. The latex was mixed with vulcanizing agent and 30 phr of one type of alkoxysilane (TEOS, VTOS, ETOS, or MPS).

After the latex was maturated at a certain length of time, the latex compound was used in the former dipping step, followed by film drying at 80°C. The *in situ*

generated silica in the dipped films was determined. The silica contents in the NR/silica dipped films obtained by the sol-gel process of each alkoxysilane after maturated for up to 2 days are shown in Figure 4.1. It can be seen that the silica content in rubber matrix and the conversion ability of TEOS, VTOS, and MPS to silica were dramatically increased after just one day of maturation at room temperature and remained unchanged thereafter. But the silica content in the ETOS-added film was rather low and did not increase at all during the 2-day time (Fig. 4.1c).



(a) 30 phr TEOS (b) 30 phr VTOS

(c) 30 phr ETOS (d) 30 phr MPS

Figure 4.1 Changes of silica content and % conversion of silane to silica as a function of latex maturation times for NR latex mixed with vulcanizing agent and (a) 30 phr TEOS, (b) 30 phr VTOS, (c) 30 phr ETOS, and (d) 30 phr MPS.

The result of TEOS precursor was in agreement with the reported by Satraphan [6]. It was most likely that the sol-gel process occurred during room-temperature maturation, leading to the formation of oligomer of polysiloxane. This

can also reduce silane loss, due to evaporation, during the dipping step. The difference in the extent of conversion of each individual silane is further discussed in the next topic. From these results the latex maturation time of 1 day before dipping process was used to prepare the NR/silica dipped films in this study.

4.1.2 Sol-gel process of different alkylalkoxysilanes in latex

In this section different types of alkoxysilanes were investigated for their potential use as precursors to generate silica in the NR latex. The effect of silane types was studied in terms of the silica content and % conversion. The silica content and degree of conversion are shown in Table 4.1.

For single silane type, the highest to lowest conversion of silane to silica are TEOS, VTOS, MPS, and ETOS (Entry 2–8). This finding is in agreement with the results in similar system reported earlier [7, 22]. It can be explained in terms of the structure and polarity of the silane. Each TEOS molecule contains 4 ethoxy groups, therefore undergoing hydrolysis and condensation to form silica fast and almost completely [6, 7]. The other three alkoxysilanes; VTOS, ETOS, and MPS, on the other hands, contain one alkyl substituent connected to the silicon atom. For the ETOS and VTOS, their sizes of ethyl and vinyl are similar, but the vinyl group is more polarized than the ethyl. VTOS should be more compatible with the polar medium and, thus, more reactive during the sol-gel process in the rubber matrix than the ETOS. The methacryloxypropyl group in MPS contains long carbon chain, this bulky group can somewhat inhibit the attack of water or base at the silicon atom during the sol-gel process.

Table 4.1 Analysis of the silica content and degree of conversion from alkylalkoxysilane to silica in the NR/silica dipped films prepared from various types of silane precursors.

Entry	Code	Silane amount (phr)				*In situ* silica content (phr)	Conversion (%)
		TEOS	VTOS	ETOS	MPS		
1	VNR[1]	-	-	-	-	0	0
2	30T	30	-	-	-	6.7 ± 0.3	77 ± 3.0
3	25T	25	-	-	-	5.1 ± 0.1	70 ± 1.0
4	20T	20	-	-	-	4.0 ± 0.1	70 ± 1.9
5	15T	15	-	-	-	2.3 ± 0.1	53 ± 1.6
6	30V	-	30	-	-	8.2 ± 0.4	65 ± 3.5
7	30E	-	-	30	-	0.8 ± 0.2	6 ± 1.7
8	30M	-	-	-	30	4.0 ± 0.1	19 ± 0.6
9	25T5V	25	5	-	-	5.6 ± 0.3	60 ± 3.5
10	20T10V	20	10	-	-	5.2 ± 0.1	52 ± 0.6
11	15T15V	15	15	-	-	3.9 ± 0.1	37 ± 0.4
12	25T5E	25	-	5	-	5.0 ± 0.2	54 ± 2.2
13	20T10E	20	-	10	-	4.8 ± 0.2	48 ± 2.2
14	15T15E	15	-	15	-	2.2 ± 0.2	21 ± 1.4
15	25T5M	25	-	-	5	5.2 ± 0.4	48 ± 3.2
16	20T10M	20	-	-	10	4.9 ± 0.1	38 ± 0.8
17	15T15M	15	-	-	15	3.7 ± 0.1	25 ± 0.4

[1]VNR = vulcanized NR films

The conversion of TEOS to silica in the NR/silica dipped film was the highest at 77.1 %. It is slightly lower when compared with earlier reports [5, 7], that the amount of silica formed *in situ* was >90 %. The dry rubber content (DRC) in the NR latex also played an important role in the conversion of silane to silica. The 60 %DRC NR latex was used in those works [5, 7] but in this work the latex was diluted to 30% DRC to suit the dipping process. This result is expected because 30% DRC NR latex contains a large amount of water that the addition of increasing polarity and

hydrogen-bonding capability reduces the final gel density [29] and it was in agreement with the result of the density of sintered gels prepared from TEOS that the bulk density of sintered gels prepared from TEOS increases with water-to-silicon ratio (W/Si) up to 10 but decreases for much higher W/Si (W/Si > 25) [30].

Since it was proven that the conversion of ETOS and MPS (Entry 7-8) to silica could not be achieved quantitatively, attempts were made to generate a higher amount of silica inside the dipped films by using a mixture of TEOS and the alkylated silanes (Entry 9-17) as silica precursors. When comparing the silica content and the % conversions obtained from various ratios of TEOS and alkyltrialkoxysilanes, the degree of silane conversions in the rubber vulcanizate decreased when increasing the amount of alkyltrialkoxysilane. This result was not surprising since some alkylated silanes had low reactivity during the sol-gel process.

From the study, it was clear that the mixture of TEOS and alkylalkoxysilanes was required to generate silica inside the NR latex. In this work, however the total amount of alkoxysilane added into the latex was limited to 30 phr. If a higher amount was added, the latex tended to become unstable, resulting in rubber aggregation.

4.2 Morphology of *in situ* silica and NR

4.2.1 Morphology of *in situ* silica and NR in the latex compounds

Rubber particles and *in situ* silica particles in the latex were analyzed by TEM. The shape of ruthenium-stained NR particles in the latex appeared to be spherical as shown in Figure 4.2. In this work the size of NR particles was found to be in the range of 0.1 to 1 μm.

In the latex compound mixed with TEOS (Fig. 4.2a), the *in situ* generated silica particles were observed as dark particles surrounding the rubber particle. When compared with the TEM micrograph of NR particle in Figure 4.2, the surface of silica-rubber particle was rather rough. Similar silica-rubber particles were also observed in the sample prepared from the latex compound mixed with VTOS (Fig. 4.2b) and MPS (Fig. 4.2d). For the latex compound mixed with ETOS (Fig. 4.2c), there was no silica present in the analyzed sample. This finding is in agreement with

the results of silica content that the amount of *in situ* silica particle from ETOS was very low. Moreover, in the case of the latex compound mixed with VTOS, free-standing aggregates of *in situ* silica were also observed (Fig. 4.2e).

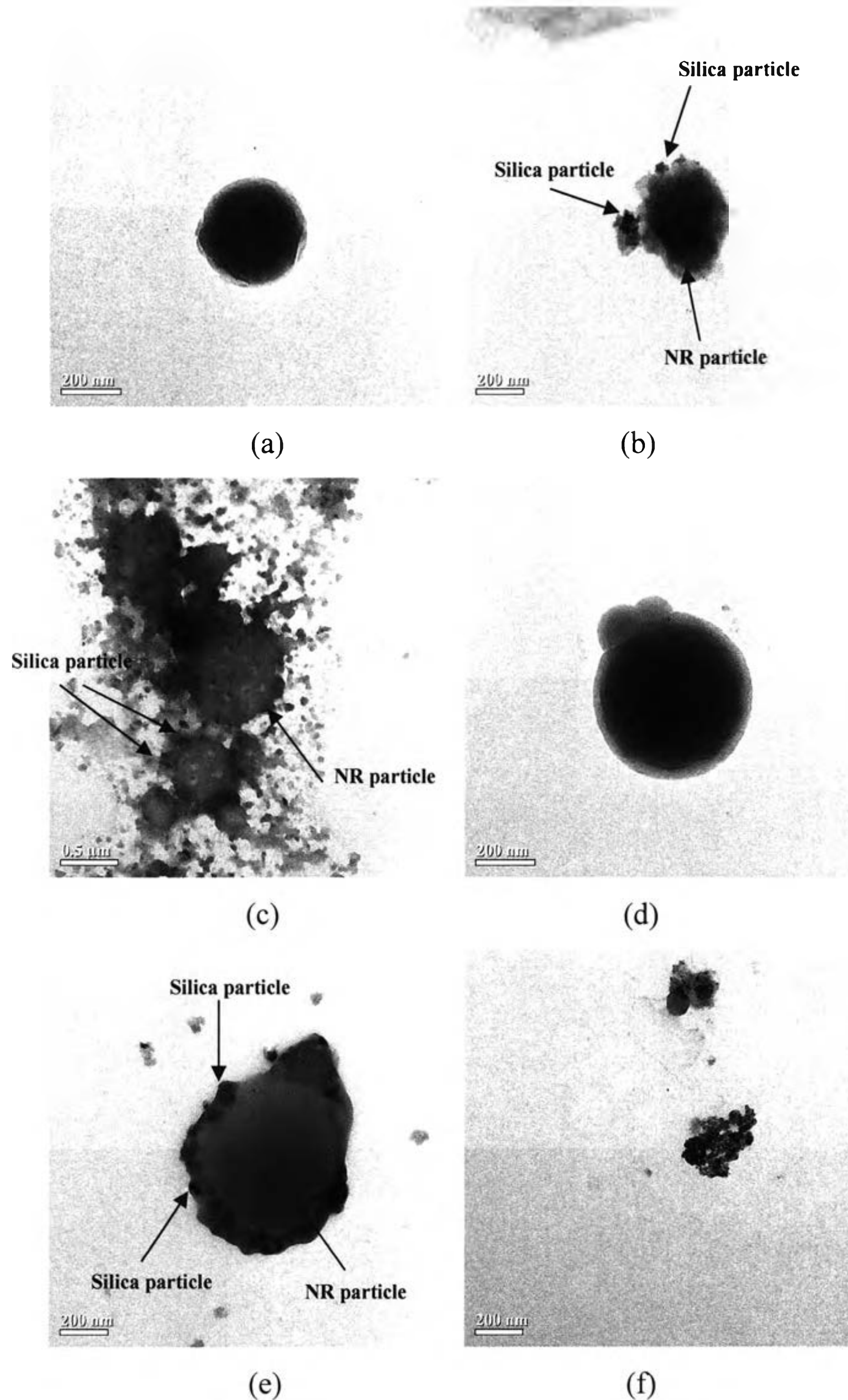


Figure 4.2 TEM micrographs of NR particle in (a) non-modified latex, in the latex that was mixed with (b) TEOS, (c) VTOS, (d) ETOS, and (e) MPS; (f) aggregates of *in situ* silica found in the latex mixed with VTOS.

Figure 4.3 shows the TEM micrographs of the natural rubber latex mixed with the mixture of TEOS and alkyltrialkoxysilanes. For TEOS-VTOS (Figure 4.3a) and TEOS-MPS (Figure 4.3c), *in situ* silica particles were observed around the NR particle. For the mixture of TEOS and ETOS (Figure 4.3b), it was not clear whether *in situ* silica particles were around NR particle. However this particle has a rough surface than NR particle in natural rubber latex (Figure 4.2). Figure 4.3d shows the free-standing aggregated silica particles found in the TEOS-VTOS mixed latex.

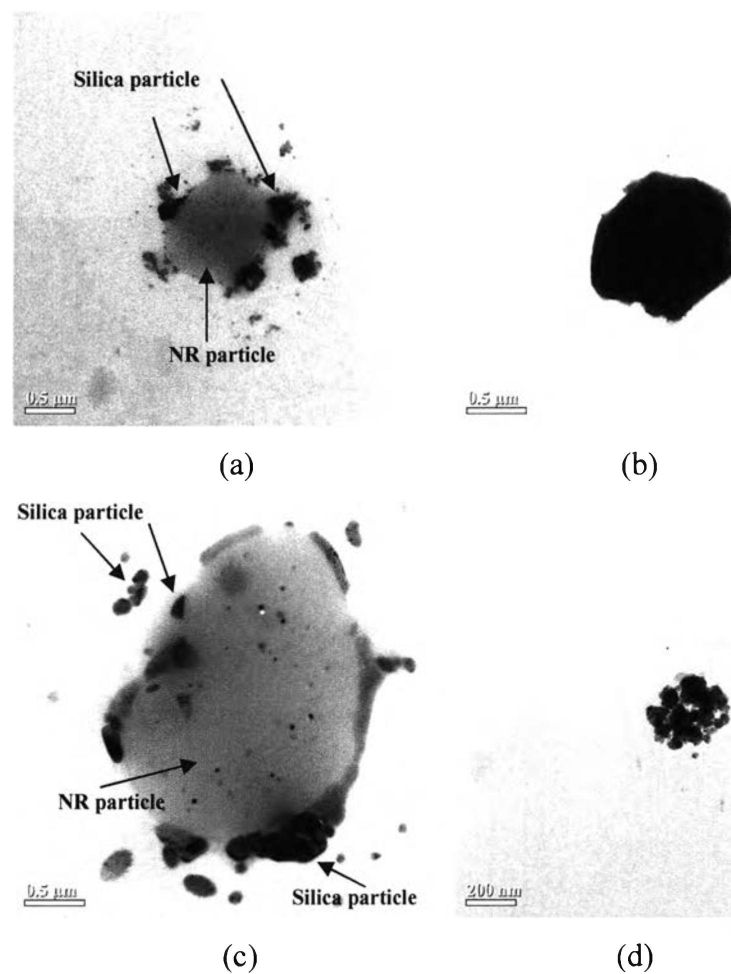


Figure 4.3 TEM micrograph of NR particle in natural rubber latex mixed with (a) TEOS and VTOS, (b) TEOS and ETOS, (c) TEOS and MPS; and (d) aggregates of *in situ* silica particle found in the latex mixed with TEOS and VTOS.

4.2.2 Morphology of *in situ* silica in the NR composite films

Two SEM micrographs and selected EDX plots of the cross-sectioned surface of silica-free vulcanized NR films (VNR) from dipping process are shown in Fig. 4.4. The EDX technique was used to identify atomic type of a selective area of the rubber matrix. In Figure 4.4a the EDX spectrum shows no Si peak at 1.7 KeV on the fractured surface. A significant amount of particles seen in the micrograph (Fig. 4.4b) were ZnO particles from the vulcanizing agents (ZDEC, ZMBT, and ZnO), as identified by the EDX spectrum indicating Zn peak at 1.0 KeV. The black area represents the NR matrix.

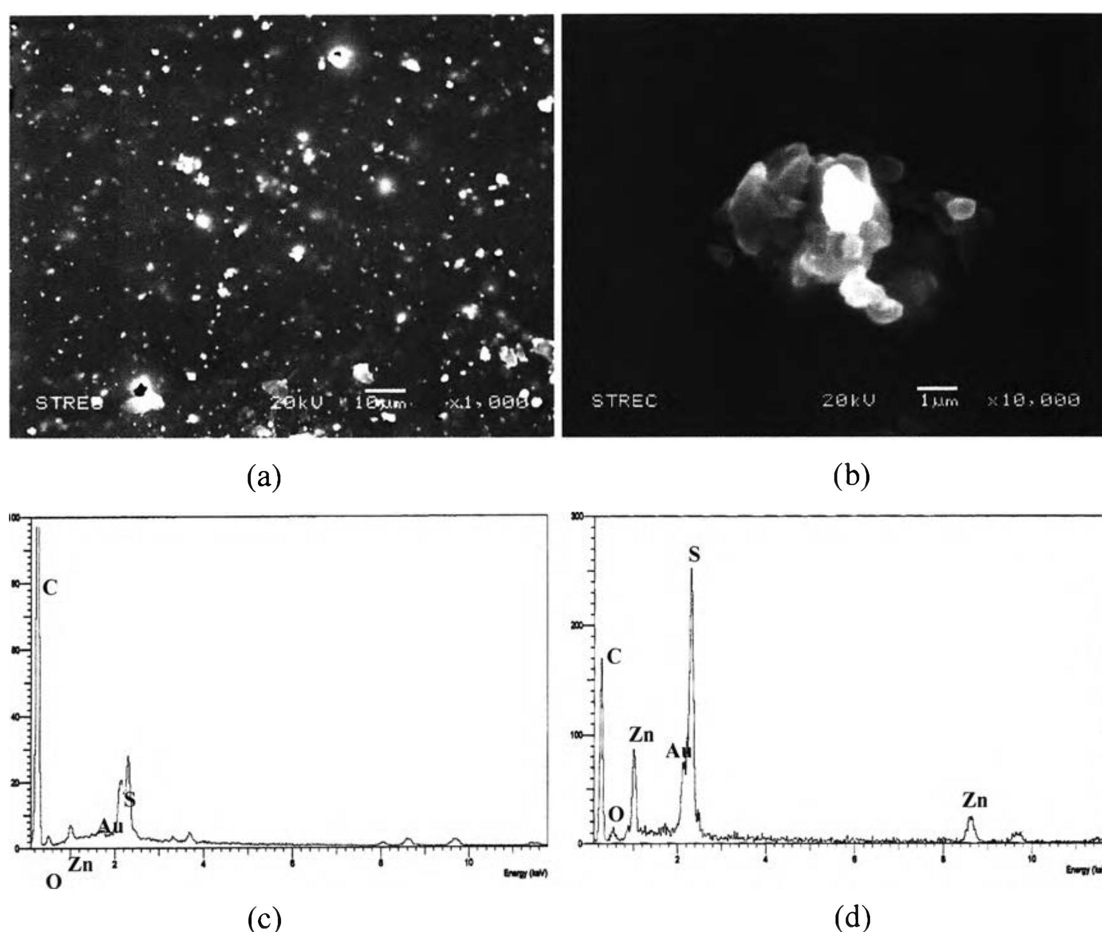


Figure 4.4 The SEM-EDX micrographs of VNR films (without silica): (a) SEM at 1,000 magnifications, (b) SEM at 10,000 magnification (c) EDX spectrum at 1,000 magnifications, and (d) EDX spectrum at 10,000 magnification.

SEM-EDX micrographs of cross-sectioned surface of the *in situ* silica aggregates generated from TEOS in the NR/silica dipped films (30T) are shown in Figure 4.5a. In Figure 4.5b the *in situ* silica particle can be clearly observed, and it was identified by EDX spectrum showing Si peak at 1.7 KeV in Figure 4.5c.

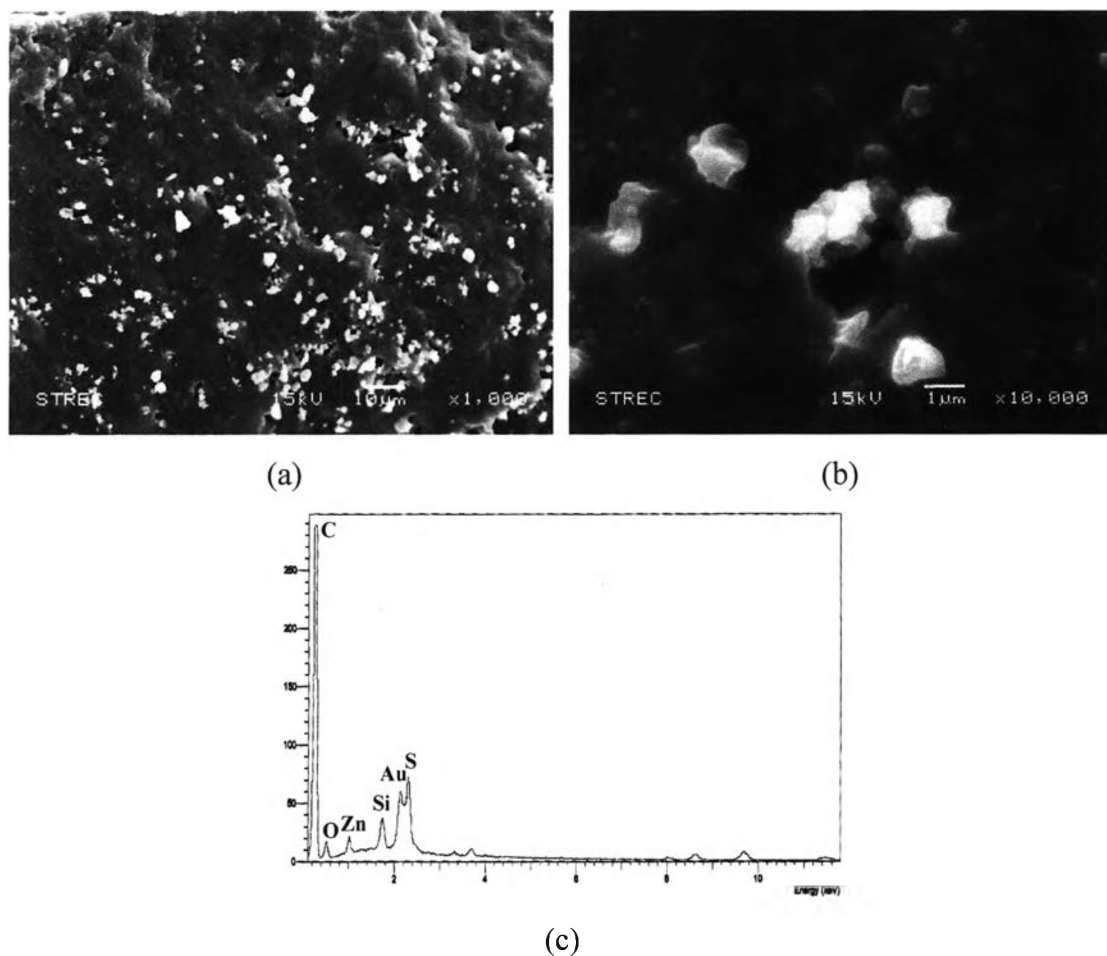
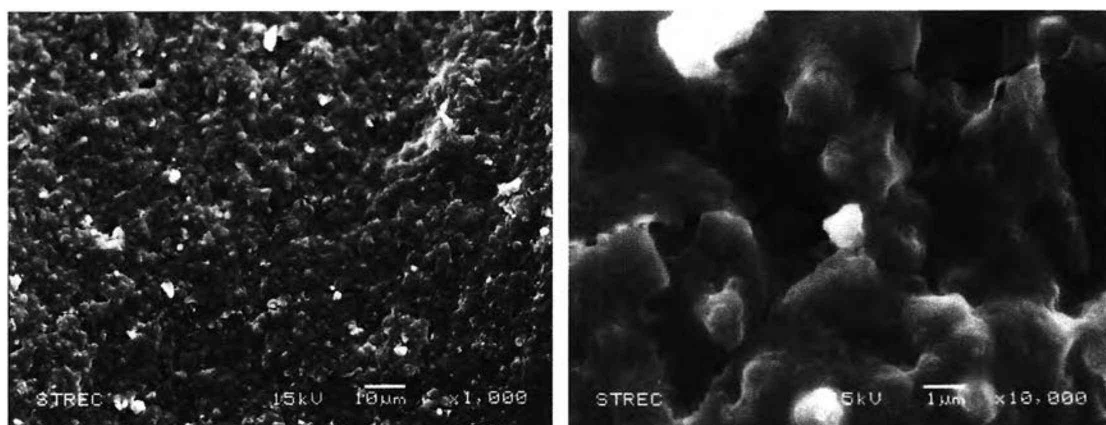
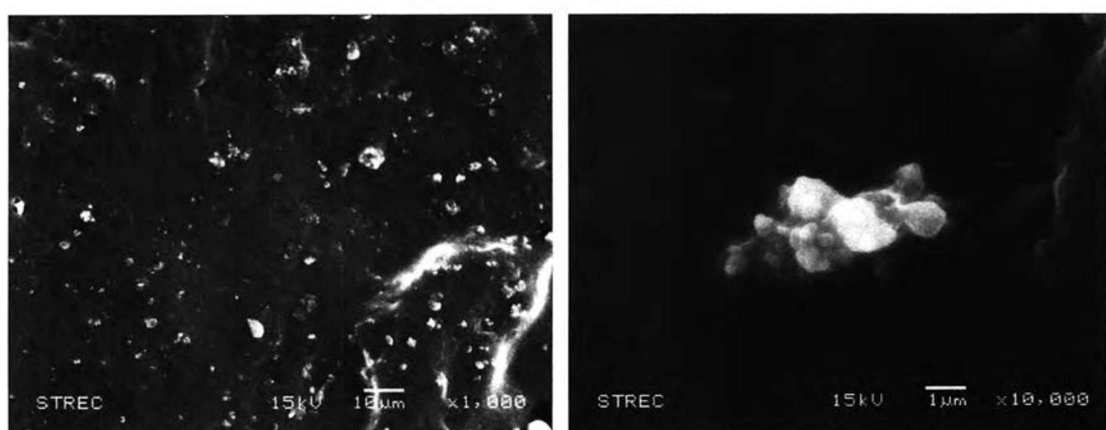


Figure 4.5 The SEM-EDX micrographs of 30T (6.7 phr silica): (a) at 1,000 magnification; (b) at 10,000 magnification; (c) EDX spectrum.

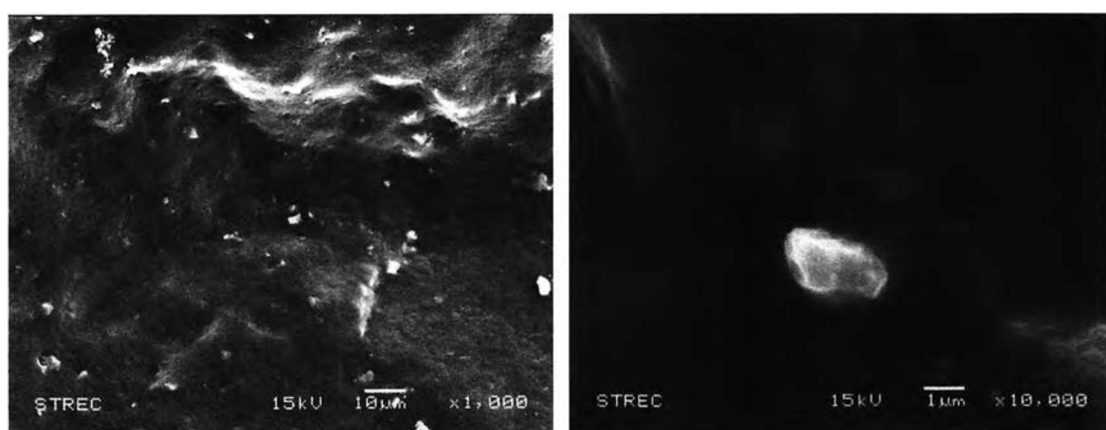
The SEM micrographs showing the fractured surface of the NR/Silica dipped films containing *in situ* formed silica generated from single alkoxysilane are shown in Fig. 4.6. At 1,000 magnifications, some white spots are zinc particles (about 3.9 phr) and some are silica particles but the white spots at 10,000 magnifications represent the silica particles, as identified by the EDX method. From the micrographs, the silica and ZnO particles are regularly dispersed in the vulcanizate matrix.



(a) VTOS (8.2 phr silica)



(b) ETOS (0.8 phr silica)



(c) MPS (4.0 phr silica)

Figure 4.6 The SEM micrographs of the NR/silica dipped films: (a) VTOS, (b) ETOS, and (c) MPS; [left figures: 1,000 magnifications, right figures: 10,000 magnifications].

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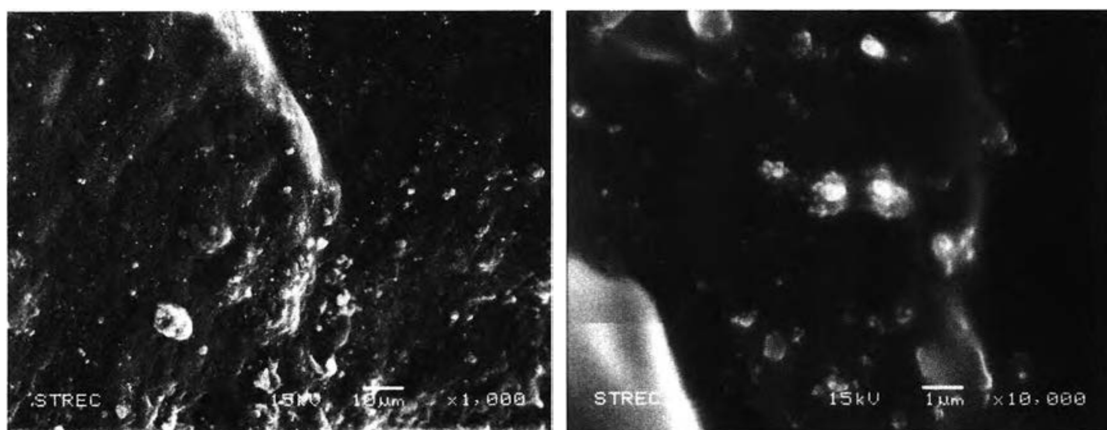
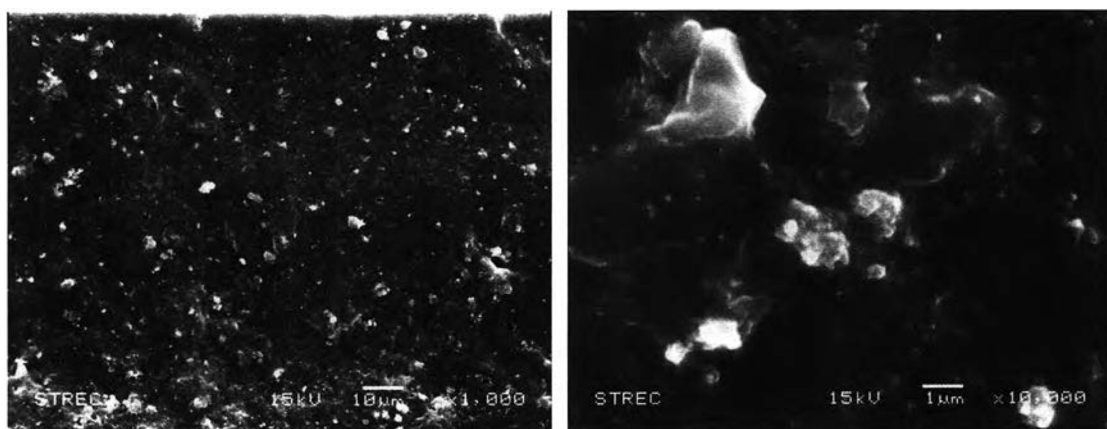
Figure 4.7 shows the fractured surface of the NR/silica dipped films containing *in situ* silica generated from the mixture of TEOS and alkyltrialkoxysilane. The features in all pictures were similar to those belonging to the films containing *in situ* silica generated from the single alkoxysilane (Fig. 4.6).

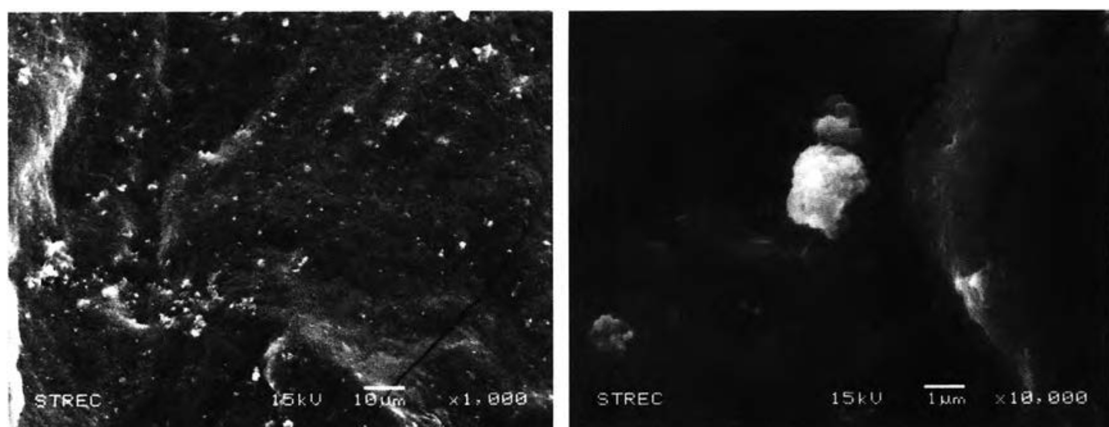


(a) 25T5V (5.6 phr silica)

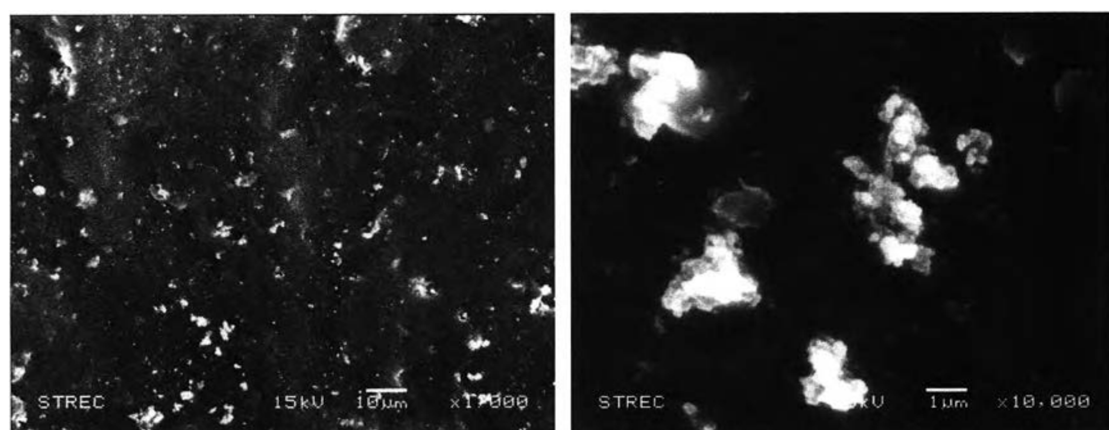


(b) 20T10V (5.2 phr silica)

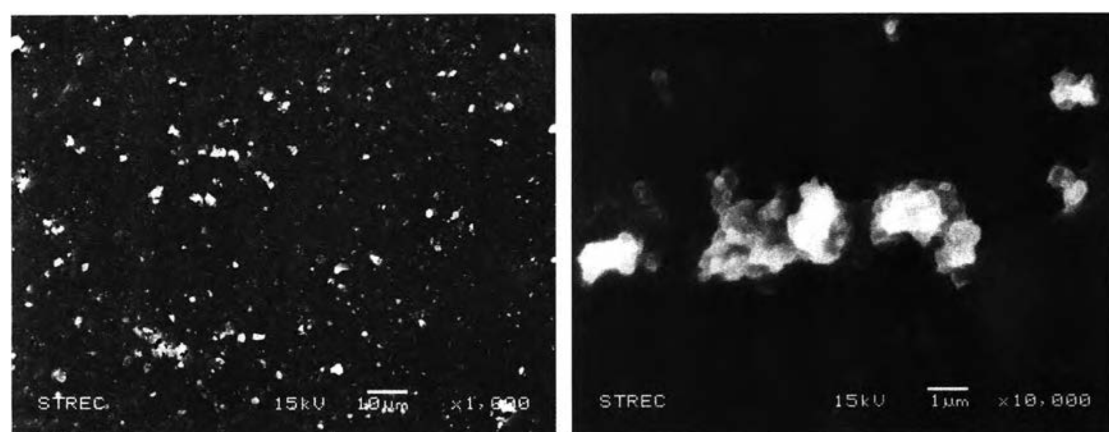
Figure 4.7 *continued*



(c) 25T5E (5.0 phr silica)

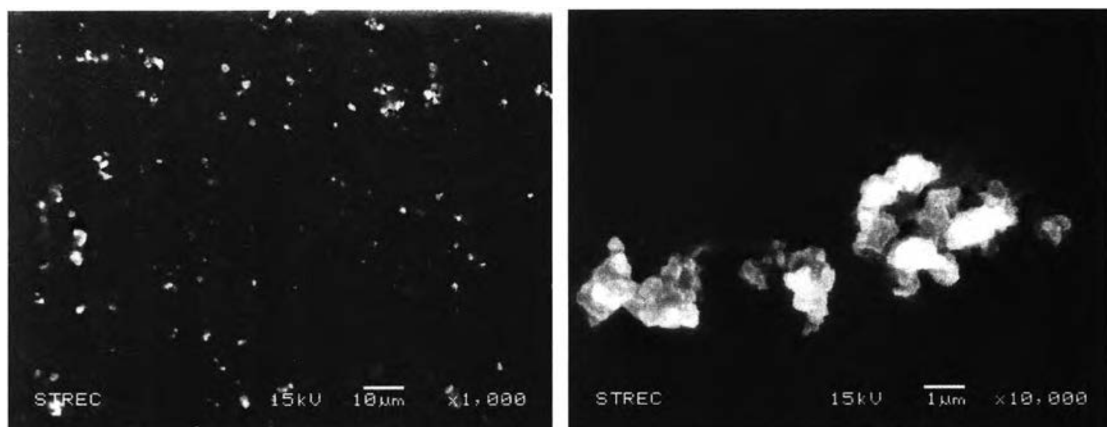


(d) 20T10E (4.8 phr silica)



(e) 25T5M (5.2 phr silica)

Figure 4.7 *continued*



(f) 20T10M (4.9 phr silica)

Figure 4.7 The SEM micrographs of the NR/silica dipped films: (a) 25T5V; (b) 20T10V; (c) 25T5E; (d) 20T10E; (e) 25T5M; (f) 20T10M; [left figures: 1,000 magnifications, right figures: 10,000 magnifications].

From the SEM micrographs, the silica particles of all precursors form aggregate with various sizes in the range from nanoscale to microscale without any clear correlation to the silane type.

4.3 Swelling of the NR/silica dipped films

The crosslink density of an elastomer can be determined from swelling measurements. In a crosslink 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 dipped NR films filled with various types of silane precursor are shown in Fig. 4.8.

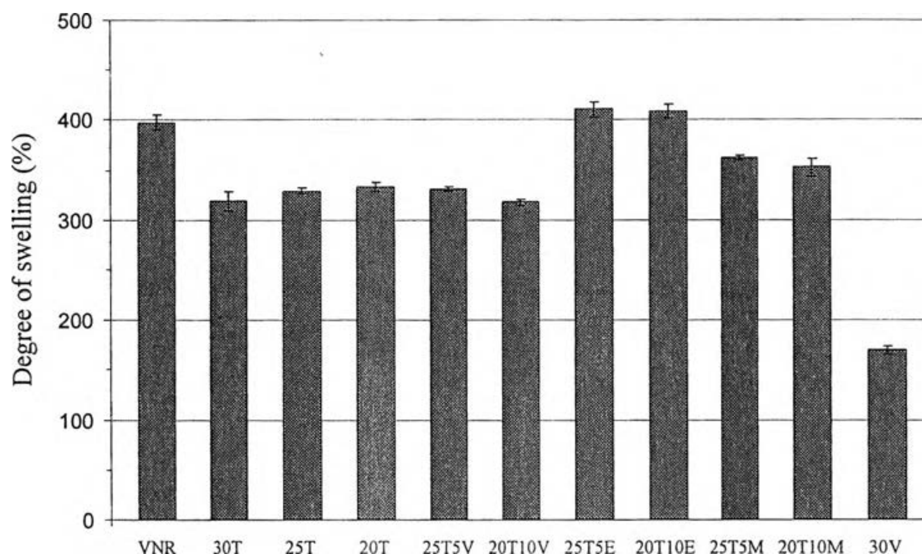


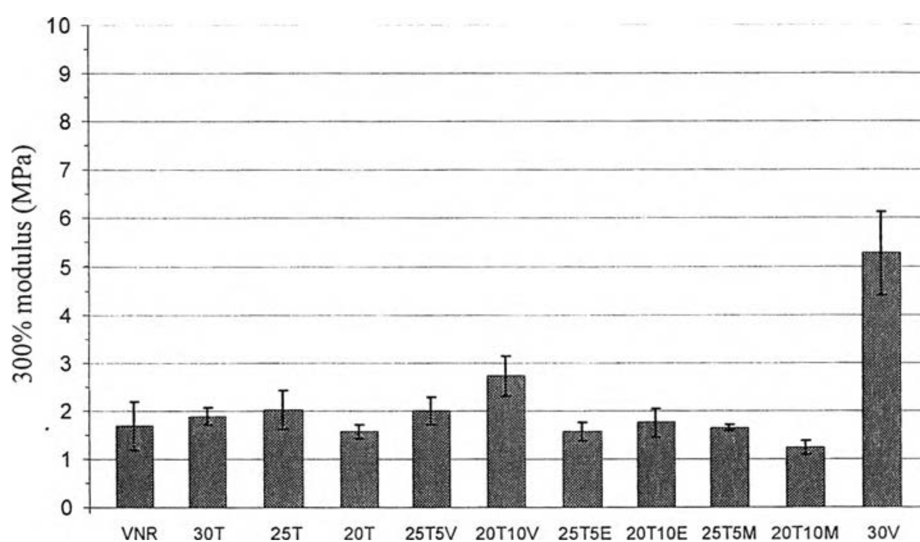
Figure 4.8 Degree of swelling of the dipped NR films filled with *in situ* silica generated by various types of alkoxysilane precursor, compared with silica-free dipped rubber film (VNR).

From Figure 4.8, the swelling behaviors of all *in situ* silica contained vulcanizes except 25T5E and 20T10E significantly decreased compared to VNR (without silica). This was because chain motions of rubber in the matrix become restricted by the silica. For 25T5E and 20T10E the degree of swelling slightly increased compared to VNR. This was because ETOS in the matrix possibly led to the formation of ethyl group on silica surface, replacing the silanol group (-Si-OH). The overall polarity of the composites could decrease and thus resulted in the increased diffusion of low polar toluene used in the experiment into the dipped film. When comparing among various silanes, it was found that the degree of swelling of 30V was the lowest.

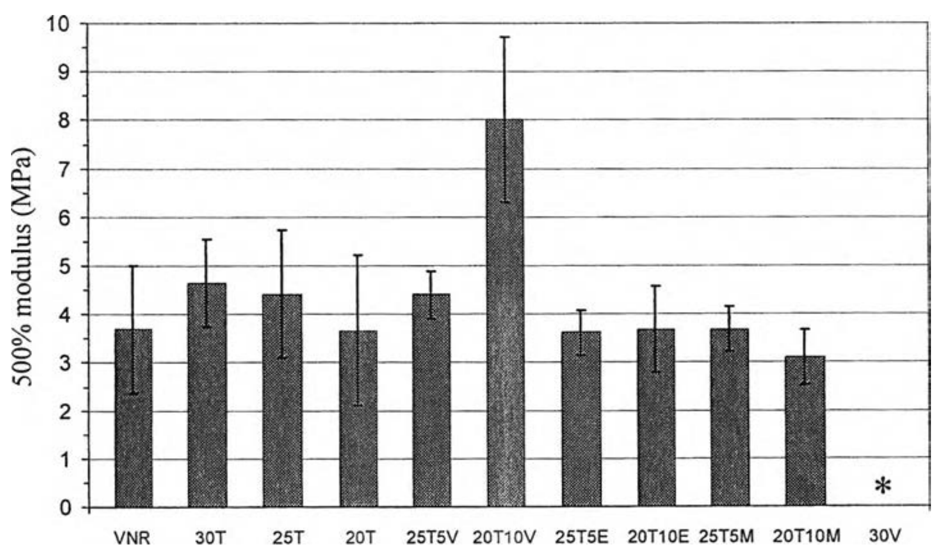
4.4 Mechanical properties

4.4.1 Tensile properties

Tensile properties of the dipped films were investigated in terms of tensile modulus at 300% and 500% elongation, tensile strength, and elongation at break. Results are shown in Figure 4.9.

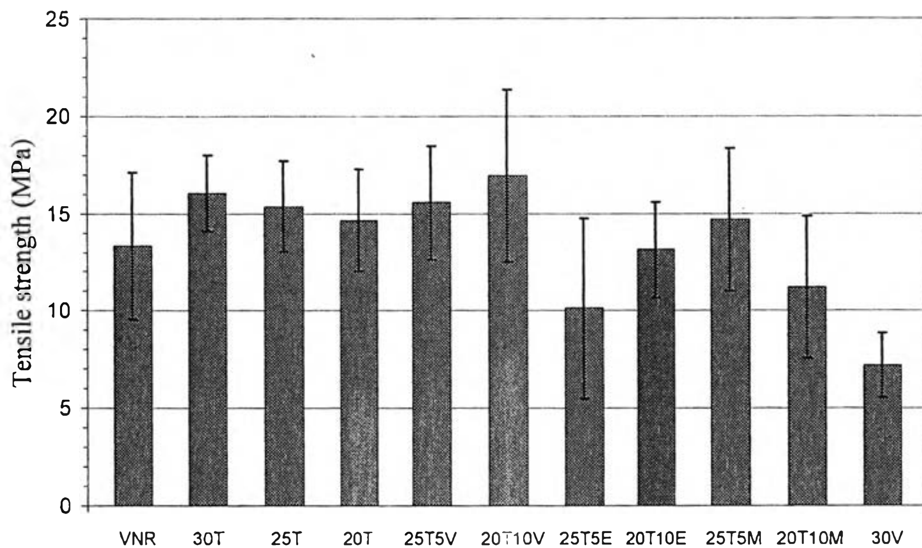


(a) 300% modulus

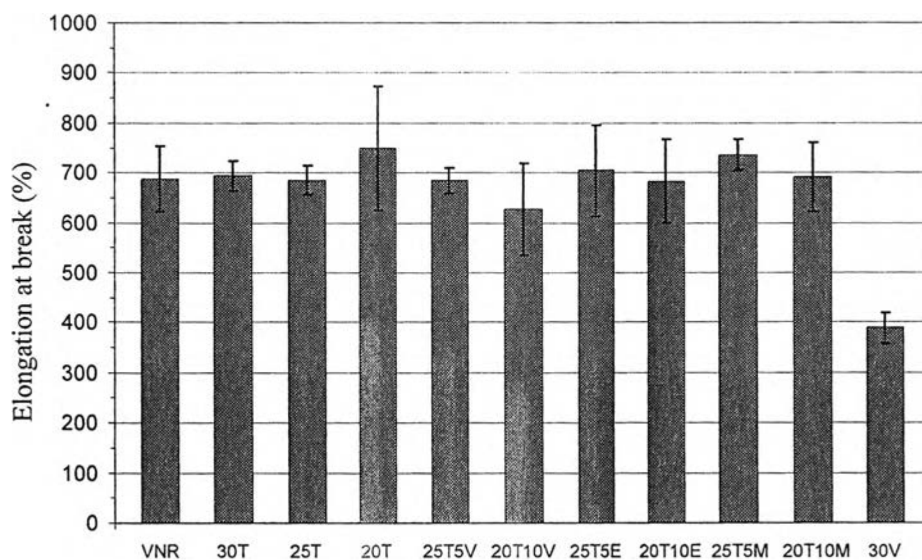


(b) 500% modulus

Figure 4.9 *continued*



(c) Tensile strength



(d) Elongation at break

Figure 4.9 Tensile properties of the dipped rubber films: (a) modulus at 300%, (b) modulus at 300% elongation, (c) tensile strength, (d) elongation at break. [*Sample 30V broke at < 500% elongation.]

For the dipped films that TEOS was the precursor for *in situ* silica (30T, 25T, and 20T), the modulus at 300% elongation (M300) of 25T was the highest, 30T had higher modulus than VNR and 20T had lower modulus than VNR. For modulus at 500% elongation (M500), 30T was highest modulus, 25T had higher modulus than VNR and 20T had slightly lower modulus than VNR. For tensile strength, the value of 30T was the highest, 25T and 20T had higher modulus than VNR. However, the M300, M500, and tensile strength of the dipped films containing *in situ* silica from TEOS (30T, 25T, and 20T) did not significantly different from that of VNR.

It seems that the vulcanized NR films can not be reinforced efficiently by the *in situ* silica that was generated by TEOS alone. Although the sample 30T tended to have higher modulus than VNR, the difference was not quite significant based on statistical analysis. For the used of only VTOS to generate *in situ* silica (30V), it was found that 30V had the highest M300. However, the tensile strength and elongation at break of 30V were the lowest at 7.19 ± 1.66 MPa and 388 ± 32 %, respectively. This reflects the tough and stiff characteristics of the rubber films filled with vinylated silica.

For the samples containing *in situ* silica generated from mixed TEOS-VTOS (25T5V and 20T10V), M300, M500, and tensile strength were all increased with increasing the weight ratio of VTOS in the TEOS-VTOS mixture. A quite interesting point should be made here that the total silica content in 25T5V was in fact *higher* that that of 20T10V. In other words, the modulus and tensile strength of 20T10V were higher despite its silica content was 5.2 ± 0.1 phr, lower than 5.6 ± 0.3 phr in sample 25T5V. These results were somewhat similar to the data from NR/silica films from TEOS-ETOS (25T5E and 20T10E), but not as significant as the TEOS-VTOS samples. In the case of NR/silica films obtained from TEOS-MPS (25T5M and 20T10M), the modulus and tensile strength were decreased when increasing the amount of MPS, because the amount of silica formed decreased when MPS content was increased.

In general the tensile strengths at break were not significantly different among all samples. However 20T10V still possessed the highest modulus. The elongations at break of all samples were found to be higher than 500%, except for the sample 30V.

No relation between the elongation at break and the type of silane precursor was observed.

It is noted here that among all samples only Sample 25T, 20T10V, 20T10E, and 20T10M contained approximately the same amount of *in situ* generated silica (5.0 ± 0.4 phr). These NR/silica film samples were therefore used to investigate the effect of silane types on the tensile properties of the films. It was found that vinyl group played an important role in the reinforcement of rubber films. The sample 20T10V was found to possess the highest modulus as observed from both M300 and M500 plots (Fig. 4.9a and 4.9b). Its tensile modulus was significantly higher than the silica-free film (VNR), and much higher than the others in the plot of M500.

Compared among the film samples with the same amount of *in situ* generated silica, the mixed TEOS-VTOS precursor provides very effective reinforcing ability for the dipped NR film. On the other hand, the mixed TEOS-ETOS and TEOS-MPS were not as efficient as a reinforced precursor as when TEOS was used alone.

These results indicate that the vinyl group in the *in situ* generated silica (from VTOS precursor) most likely takes part in the sulfur vulcanization process of the dipped film. Also only one-step heating at 80°C for 1 day can initiate both sol-gel and vulcanization processes, resulting in a reinforced hybrid thin rubber film.

4.4.2 Tension set

Figure 4.10 shows the results of tension set study. The tension set parameter, reflects the elasticity of rubber and is presented by the degree of film length change after the film was stretched for a certain length and time. Here the tension set percentages of all *in situ* NR/silica dipped films were between 2.3 to 4.3%. No difference between the *in situ* silica-reinforced and non-reinforced samples was observed. The use of TEOS and other alkyltrialkoxysilanes to generate silica in the dipped film did not significantly affect to the tension set. The resilience properties of rubber remained in all samples because it was lower than one of standard material (10%) [31].

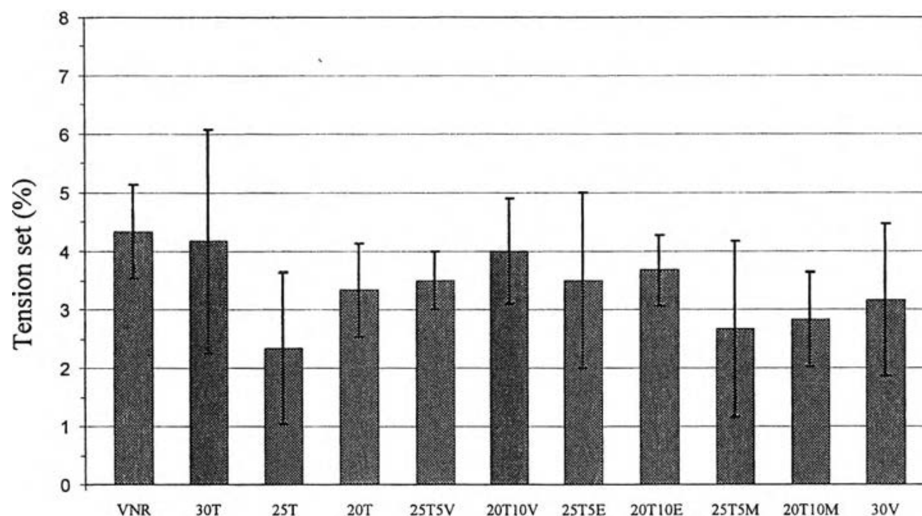


Figure 4.10 Result of tension set study of the dipped rubber films filled with *in situ* silica generated by various types of alkoxysilane precursor, compared with silica-free dipped rubber film (VNR).

4.4.3 Tear properties

Tear testing of all NR/silica composites was performed on cast rubber sheets that were prepared from the same latex compound for dipping process. The sheet thickness was about 0.6 mm. Results are shown in Figure 4.11.

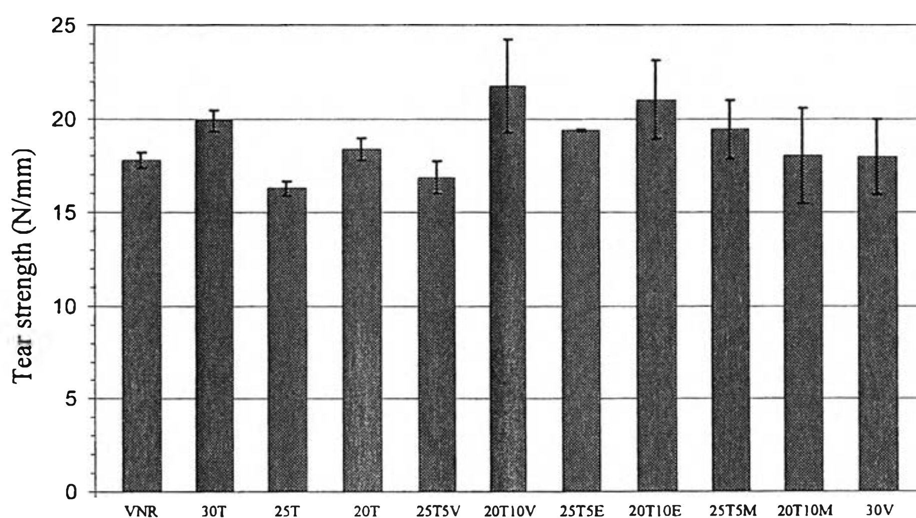


Figure 4.11 Tear strength of the cast sheets filled with *in situ* silica generated by various types of alkoxysilane precursor, compared with silica-free sample (VNR).

From the results only 3 samples had significantly higher tear strength than did the VNR. The highest tear strength belonged to 20T10V, followed by 20T10E and 30T, respectively. The other samples did not show any significant difference in the tear strength. Compared with the previous work in which the film samples were prepared by similar conditions (%DRC of NR latex, vulcanizing agent type, and procedure) [6], all samples from this work had slightly lower tear strength.

4.5 Thermal properties

The thermal stability of the dipped films studied by TGA is shown in Fig. 4.12 and Table 4.2. The air oxidative degradation of the vulcanized films took place in two steps. The first step of degradation was due to rubber decomposition in the temperature range of 300-450°C and accounting for about 80% of mass. The second step of degradation was between 450-600°C accounting for 8% of total mass, which is related to the degradation of sulfur vulcanizates. Some of polysulfide groups in sulfur crosslink were transformed to disulfide. This disulfide can be oxidized to sulfenic or thiosulfoxylic acids [32]. In addition there was an increase in the residual mass at 850°C from about 5.72% for the silica-free film (VNR) to 11.67% for the silica-incorporated sample (30V) due to the presence of *in situ* silica in the composites. However, the inclusion of silica in the dipped films does not enhance the thermal stability of the NR composite, probably because of the low silica content. However, Poompradub et al. [23] reported that the thermal stability of NR sheet vulcanizate containing 30 phr *in situ* silica (that were generated by immersing dry rubber sheet in TEOS) was improved, compared with silica-free NR sheet. The presence of the *in situ* silica as reinforcing filler, and resulted in the delayed decomposition process upon heating under O_2.

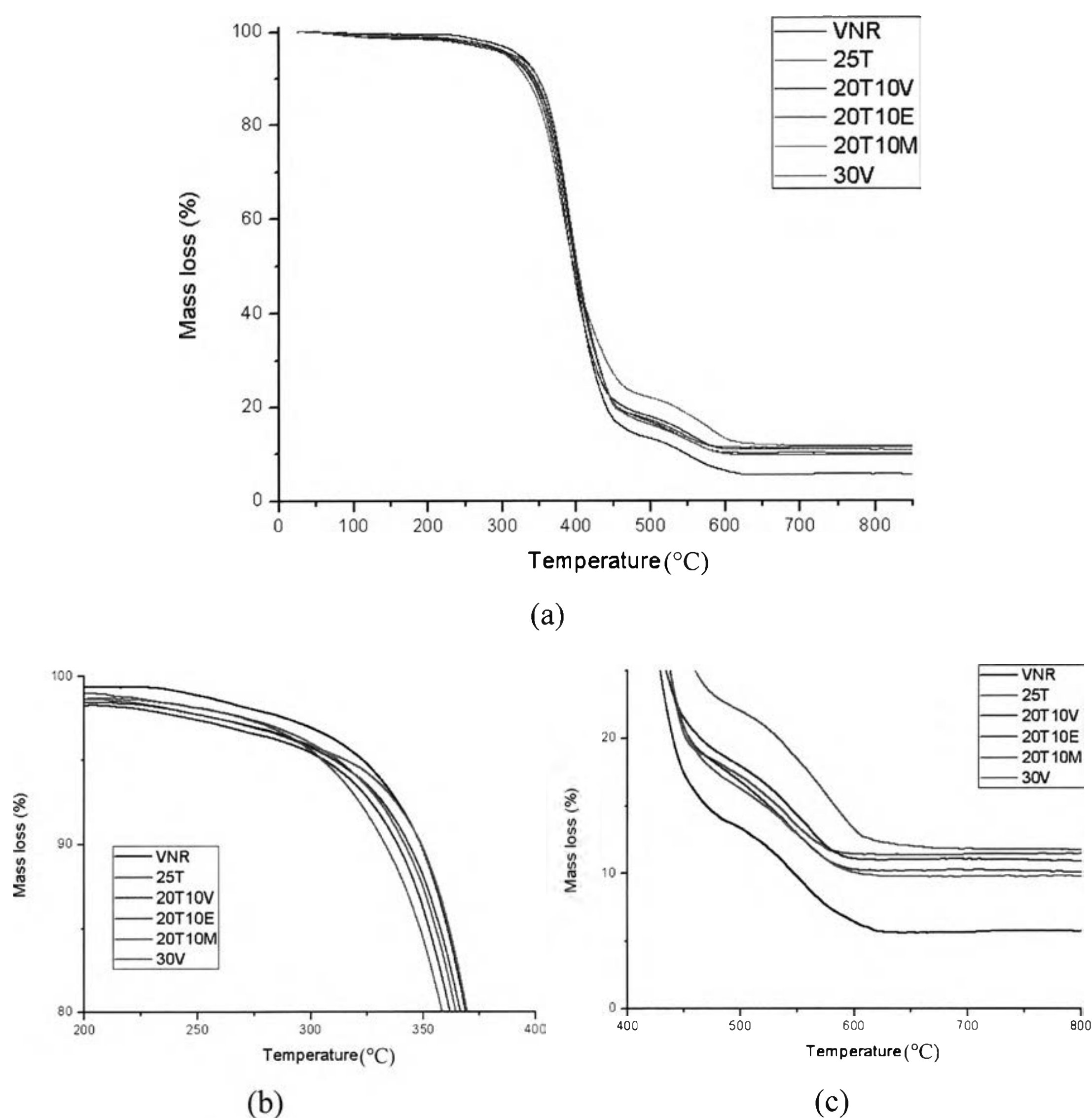


Figure 4.12 Thermo-gravimetric analysis in the range between (a) 0-850°C, (b) expanded 200-400°C, and (c) expanded 400-800°C, of dipped rubber films filled with *in situ* silica generated by various types of alkoxysilane precursor, compared with silica-free sample (VNR).

Table 4.2 Results from thermo-gravimetric analysis of various dipped films filled with *in situ* silica generated by various types of alkoxysilane precursor, compared with silica-free sample (VNR).

Sample	Onset (°C)	1st mass loss		2nd mass loss		Residual mass (%) at 850°C
		Peak (°C)	Mass loss (%)	Peak (°C)	Mass loss (%)	
VNR	350.6	391.0	86.14	540.0	8.08	5.72
25T	350.7	390.3	81.56	543.0	6.80	11.57
20T10V	343.3	383.9	81.59	562.4	7.59	10.85
20T10E	343.7	390.1	81.99	541.1	8.04	9.98
20T10M	344.0	390.1	83.20	539.4	6.88	9.88
30V	333.8	378.6	77.55	580.6	10.75	11.66