<div align="center">

**CHAPTER IV**

RESULTS AND DISCUSSIONS

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4.1 Adsorption of Surfactants

    4.1.1 <u>Adsorption of Surfactant onto the Liquid/Gas Interface</u>

        The dependence of the surface tension (γ) of surfactant solutions and their mixtures on the concentration (log C) in aqueous solution is shown in Figure 4.1. The surface tension of all surfactants and their mixtures is denoted by a number indicating the molar ratio of Arquad® T-50 : Teric® X-10 and were measured by the pendant drop method. The CMCs of each solution were determined from a break in the curve and are listed in Table 1.
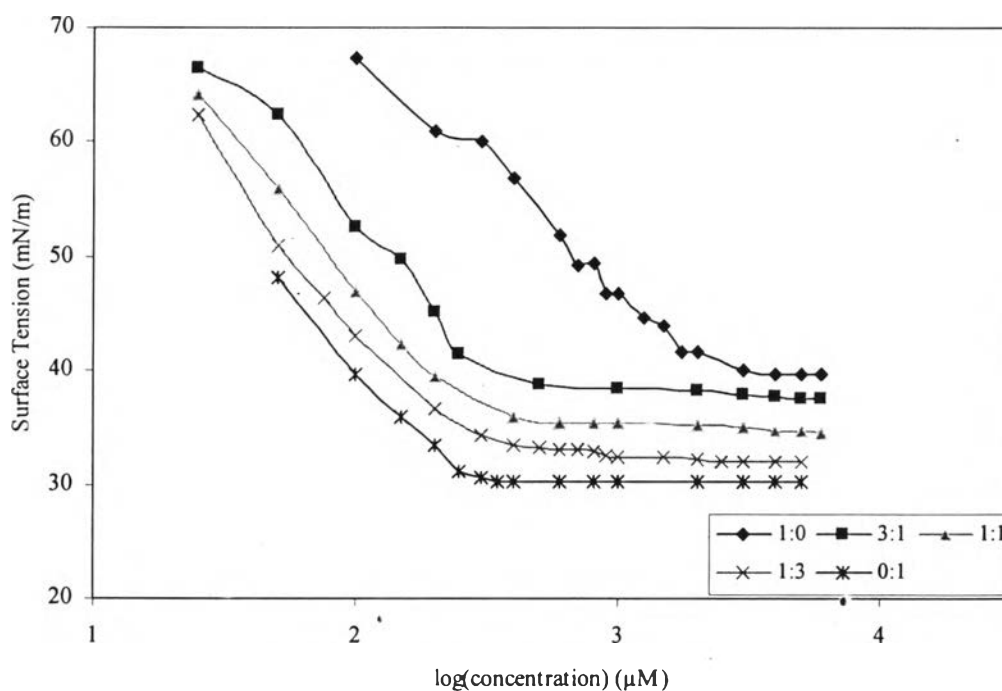
Figure 4.1 Surface tension of Arquad® T-50, Teric® X-10 and their mixtures versus the logarithm of the total concentration.

        According to the Gibbs law applied at equilibrium between the interfacial and bulk phase concentration, the adsorption of surfactant at the liquid/gas interface leads to the reduction in the surface tension of the solution. The surface

excess concentration (Γ) was calculated for dilute solutions (10^{-2} M or less) containing only one surfactant and no other material, using the Gibbs equation, Equation 4.1, (Rosen, 1989),

$$\Gamma = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right)_T , \qquad (4.1)$$

where R is the gas constant in $J \cdot mol^{-1}K^{-1}$, T the absolute temperature and n a constant which depends on the number of species constituting the surfactant and that are adsorbed at the interface; Γ can be obtained from the slope of the curve in Figure 4.1 as listed in Table 1 and has units of mol/1000 m^2 when γ is in $m \cdot Nm^{-1}$. The individual cationic surfactant is considered as a completely dissociated surfactant, n=2, and the nonionic surfactant as a neutral molecule, n=1. For mixtures of ionic and nonionic surfactant in aqueous solution in the absence of added electrolyte, the coefficient decreases from 4.606 to 2.303 with a decrease in concentration of the ionic surfactant at the interface (Rosen, 1989).

The area per molecule (a) at the interface, also listed in Table 1, can be calculated from the surface excess concentration, in square angstroms, from the following relation (Rosen, 1989)

$$a = \frac{10^{23}}{N\Gamma} , \qquad (4.2)$$

where N is Avogadro's number.

The results in Table 1 indicate that the CMCs of mixtures are less than the CMC of the cationic surfactant. These suggest that the interaction between the two surfactants is attractive and they form mixed micelles in the bulk solution (Ivanova et al., 1995). The least value of surface excess concentration (Γ) at liquid/gas interface was observed in the single cationic surfactant system. This is generally due to an electrical repulsion between the ionic heads of surfactant ions already at the interface whereas the highest value in the single nonionic surfactant

system owes to the hydrophobic interaction consequent in the more closely packed (Rosen, 1989).

Table 4.1 Physicochemical properties of surfactants at liquid/gas interface at 30 °C

| Surfactant	CMC (µM)	$\Gamma \times 10^6$ (mol/m^2)	Area/molecule (Å^2)
Cationic (Arquad® T-50)	3000	1.96	84.73
Mixed 3:1	335	2.83	58.55
Mixed 1:1	280	3.19	52.05
Mixed 1:3	278	3.95	42.54
Nonionic (Teric® X-10)	272	4.16	39.84

4.1.2 Adsorption of Surfactant onto the Silica Surface

The adsorption isotherms of cationic surfactant (Arquad® T-50), nonionic surfactant (Teric® X-10), and their mixtures onto precipitated silica (Hi-Sil® 255) at 30 °C and feed pHs of 5 and 8 are given in Figures 4.2 and 4.3, respectively. The amount of surfactant adsorption (µmol/g silica) was calculated from the difference in concentration of aqueous surfactant before and after reaching equilibrium of adsorption as determined by a Total Organic Carbon analyzer (TOC-V CSH, Shimadzu). The molar ratios of Arquad® T-50 to Teric® X-10 are denoted by 1:0 and 0:1 for single surfactant systems and 3:1, 1:1, and 1:3 for mixed surfactant systems.

In this experiment, pHs of 5 and 8 for the feed solution were used in order to study the effect of pH on the adsorption of surfactants on silica surface. The pH at which the net surface charge of silica is zero, the PZC, is about 2-3. At pHs above the PZC, the surface is negatively charged; thus, cationic surfactant will adsorb favorably on the surface of silica when the pH of contacting aqueous phase is greater than 3. More basic solutions (pH>8), though desirable in terms of the driving force for adsorption, were not used due to increasing solubility of silica in alkaline solution (Iler, 1979).
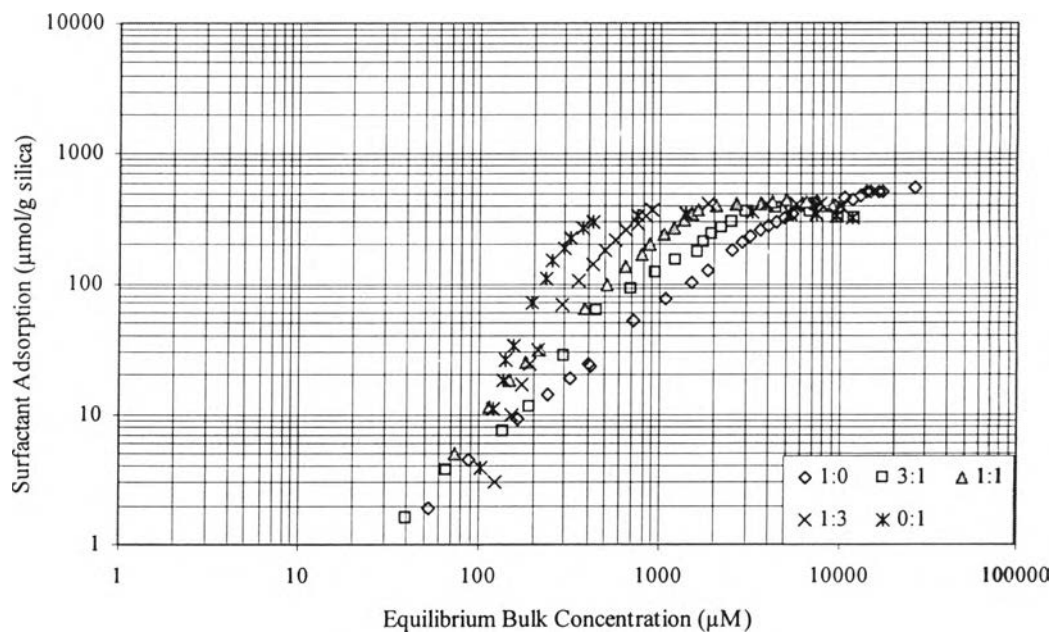
Figure 4.2 Adsorption isotherms of surfactants with various molar ratios of Arquad® T-50 (1:0) to Teric® X-10 (0:1) onto precipitated silica (Hi-Sil® 255) at pH 5 and 30°C.
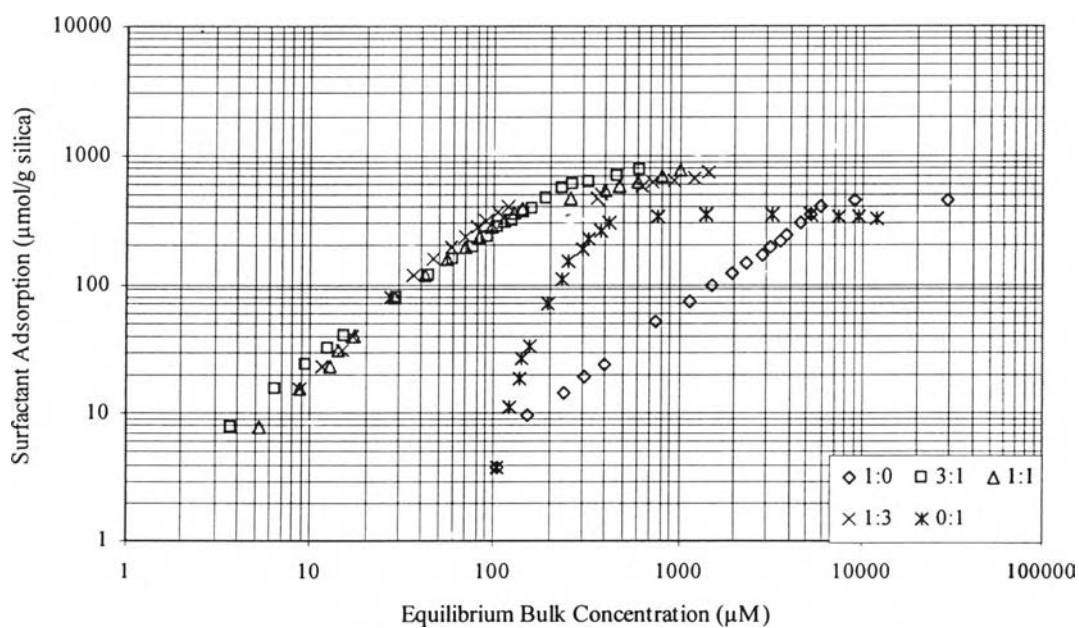
Figure 4.3 Adsorption isotherms of surfactants with various molar ratios of Arquad® T-50 (1:0) to Teric® X-10 (0:1) onto precipitated silica (Hi-Sil® 255) at pH 8 and 30°C.

Figures 4.2 and 4.3 suggest that the isotherms of pure cationic surfactant (1:0) do not fall into the four regions. At regions II and III, the surfactant adsorption increases sharply and it is where the surface aggregation occurs. The critical micelle concentration (CMC) of each surfactant marks the transition to the plateau region. As the surfactant concentration increases above the CMC the "excess" surfactant forms micelles in solution. For pure nonionic surfactant (0:1), adsorption isotherm is of the langmuir type. At low coverage, the surfactant molecule may lie prone on the surface; at higher coverage, the hydrophobic group may be displaced from the surface by the hydrophilic group and lateral interactions between adjacent hydrophobic groups (hemimicelle formation) may occur (Rosen, 1989).

At the feed solution of pH 5, a lower level of adsorption was observed in all mixtures composed of cationic surfactant because of the less negatively charged surface at pH 5. The pH of the feed solution does not significantly affect nonionic surfactant adsorption as seen by the similar maximum adsorption at both pHs.

Table 4.2 The maximum surfactant adsorption onto silica (Hi-Sil® 255) at pH 5 and 8 and 30°C

Surfactant	Maximum surfactant adsorption* (μmol/g of silica)	
	pH 5	pH 8
Cationic (Arquad® T-50)	420	440
Mixed 3:1	390	700
Mixed 1:1	415	620
Mixed 1:3	405	575
Nonionic (Teric® X-10)	305	305

* approximately predicted from adsorption isotherms

At pH 8, a higher amount of surfactant adsorption is obtained in mixed surfactant systems than individual systems and it increases with increasing the Arquad® T-50 : Teric® X-10 molar ratio. Therefore, the adsorption of surfactants onto silica surface is highly influenced by electrostatic attraction. The advantage of

mixed surfactant adsorption is thought to be due to the decrease in electrostatic repulsion between head groups of cationic surfactant when connected with the nonionic surfactant (Rosen, 1989). Consequently, the adsorptions of mixed surfactants onto the silica surface are relatively closely packed compared to that of single surfactant systems. Table 4.3 shows the data of the surface excess concentration (Γ) and area per molecule of surfactant adsorbed onto silica surface. These indicate that the surface excess concentration of the nonionic surfactant is lower than those of other systems caused from the slight interaction to the negatively charged surface.

Table 4.3 Physicochemical properties of surfactants adsorbed onto silica surface at pH 8 and 30°C

Surfactant	Properties at maximum adsorbed	
	$\Gamma \times 10^6$ (mol/m^2)	Area/molecule (Å^2)
Cationic (Arquad® T-50)	1.87	88.63
Mixed 3:1	2.98	55.66
Mixed 1:1	2.62	63.33
Mixed 1:3	2.45	67.89
Nonionic (Teric® X-10)	1.29	128.78

4.1.3 Molar Ratios of Adsorbed Surfactant on Silica (Hi-Sil® 255)

For mixed surfactant systems, it is difficult to determine the mechanism of adsorption. However, in this experiment, it can be predicted roughly by measuring the molar ratios (Arquad® T-50 to Teric® X-10) of the adsorbed surfactants onto silica (Hi-Sil® 255) at pH 8 and 30°C compared to the molar ratios of initial surfactant solutions. Total surfactant concentration after adsorption was determined by a Total Organic Carbon analyzer (TOC-V CSH, Shimadzu) and total Teric® X-10 concentration was analyzed by a UV-Visible Spectrophotometer (UV-2550, Shimadzu). Figure 4.4 shows the dependence of adsorbed Arquad® T-50 to Teric® X-10 molar ratio on the total amount of adsorption.
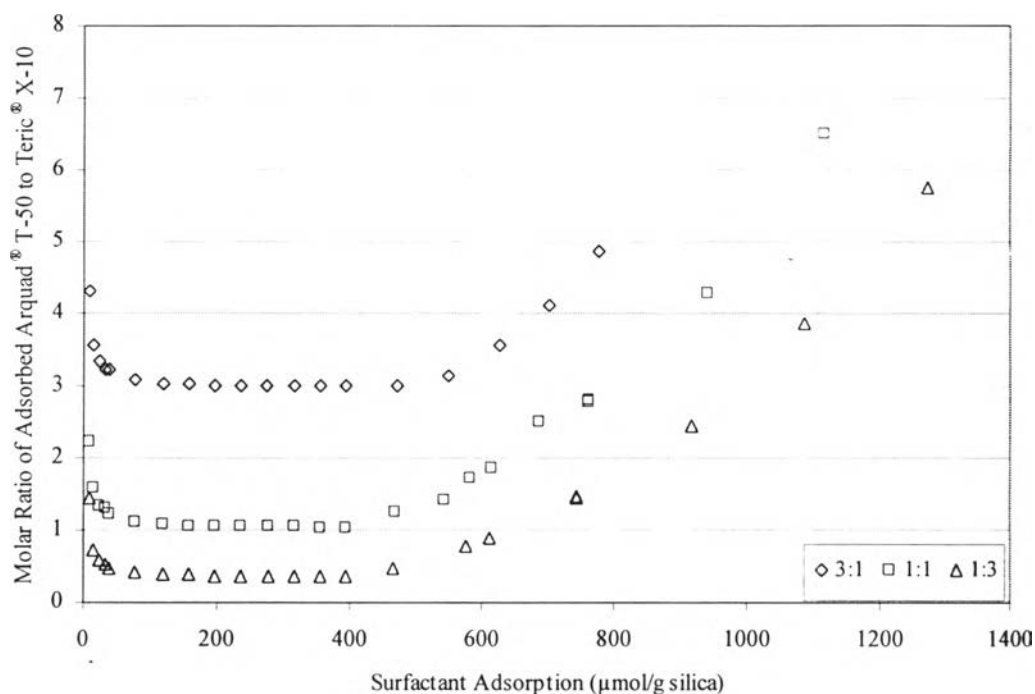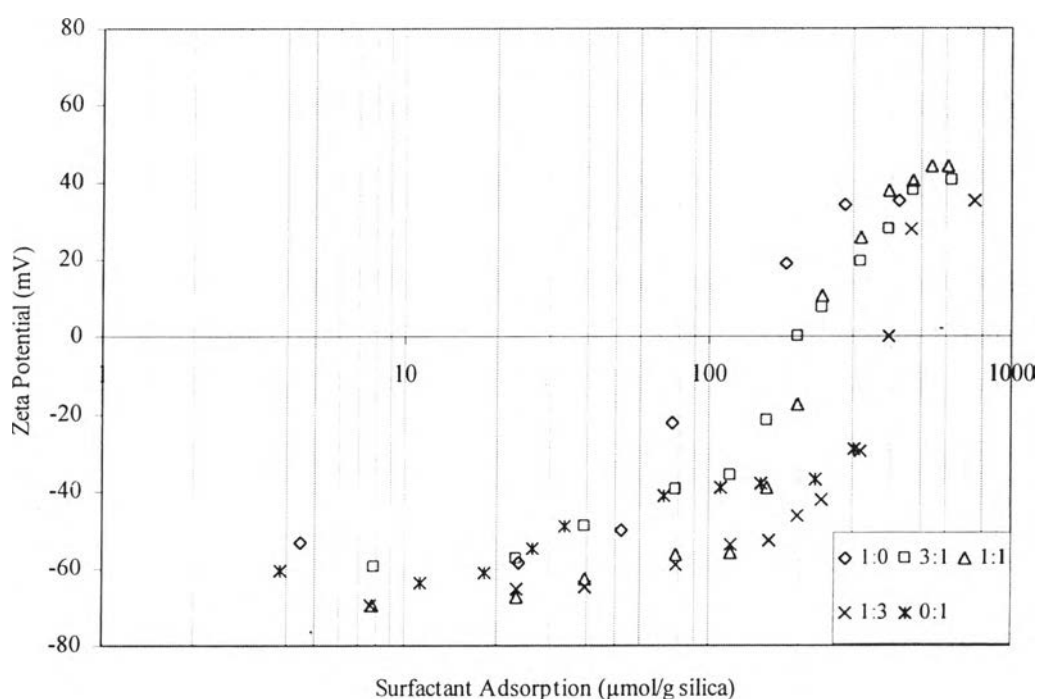
Figure 4.4 Molar ratios of surfactant adsorbed onto silica (Hi-Sil® 255) at various Arquad® T-50 : Teric® X-10 molar ratios and different total adsorbed surfactants.

For all examined molar ratios of of the Arquad® T-50 to Teric® X-10 the total surfactant adsorption isotherm trends are similar. The result indicates that at low surfactant adsorption the obtained molar ratios of adsorbed surfactants are higher than the initial ratios of mixed surfactant in the solution. That is, the cationic surfactant adsorbs more readily onto the silica surface than the nonionic surfactant. However, similar molar ratios between the adsorbed surfactants and initial solution were observed when the total amount of adsorbed surfactant increases. Once the adsorption is complete the cationic surfactant is preferably adsorbed resulting in an increasing in the adsorbed surfactant molar ratios (Figure 4.4). Moreover, the total amount of adsorption continues to rise, indicating tighter packing on the surface. The adsorption in this case may be due to the hydrophobic effect as that is responsible for micelle formation in aqueous solution of surfactant (Ivanova *et al.* 1995).

4.1.4 Zeta Potentials of Silica Adsorbed with Surfactants

In this study, the silica surface was modified by adsorption with low surfactant coverage. For all molar ratios of Arquad® T-50 : Teric® X-10, a suitable surfactant concentration in the polymerization process was based on the point that the value of zeta potential of silica surface equals zero measuring by ZETA-METER 3.0 Unit.

Figure 4.5 Zeta potential on silica surface at different total surfactant adsorbed with various molar ratios of Arquad® T-50 : Teric® X-10.

Figure 4.5 shows plots between zeta potential of silica surface and amounts of total adsorbed surfactant at different molar ratios of Arquad® T-50 : Teric® X-10. It was found that the decrease in the molar ratios resulted in increasing the total surfactant adsorbed at the zeta potential of zero. Due to the fact that only positively charged head groups of the cationic surfactant are able to balance the negative charge, as ratios of the cationic surfactant decrease, the total amount of adsorbed surfactant must increase. The total amounts of adsorbed surfactant at ratios of 1:0, 3:1, 1:1, and 1:3 which give a neutral surface are 395, 200, 195, and 100 μmol/g silica, respectively. However, in the case of Teric® X-10, as shown in

Figure 4.5, the complete surface coverage cannot be verified by the zeta potential measurement because the negatively charged surface cannot be neutralized by the nonionic surfactant.

4.2 Surface Characterization of Modified Silica

According to the adsorption isotherms and zeta potential measurement of all surfactant and their mixtures, the concentrations at which zeta potential is zero were selected for the modification process. The polymerization was carried out at retention times of 15 and 30 min. Their effects on the properties of the formed polystyrene-isoprene films on the silica surface were studied in terms of physical characteristics of the modified silica, including BET surface area and mean agglomerate particle size, and thermal analysis. All samples were given a designation consisting of a number indicating the molar ratio of mixed surfactants (Arquad® T-50 : Teric® X-10) and a letter representing the polymerization time as S and L referred to 15 and 30 min, respectively.

4.2.1 BET Surface Area

The surface areas of unmodified silica (Hi-Sil® 255) and modified silicas were determined by BET nitrogen surface area analyzer (Autosorb-1, Quantachrome), as shown in Figure 4.6 listed in Table 4.4. The data show that the modification of precipitated silica by admicellar polymerization reduces the BET nitrogen surface area by 10-40% for both polymerization times and all molar ratios of Arquad® T-50 to Teric® X-10. The changes in the surface area may be the result of the blocking of some of the micropore in the silica by the formed polymer (O'Haver et al., 1995; See, 2004). The surface areas were essentially the same for both retention times.
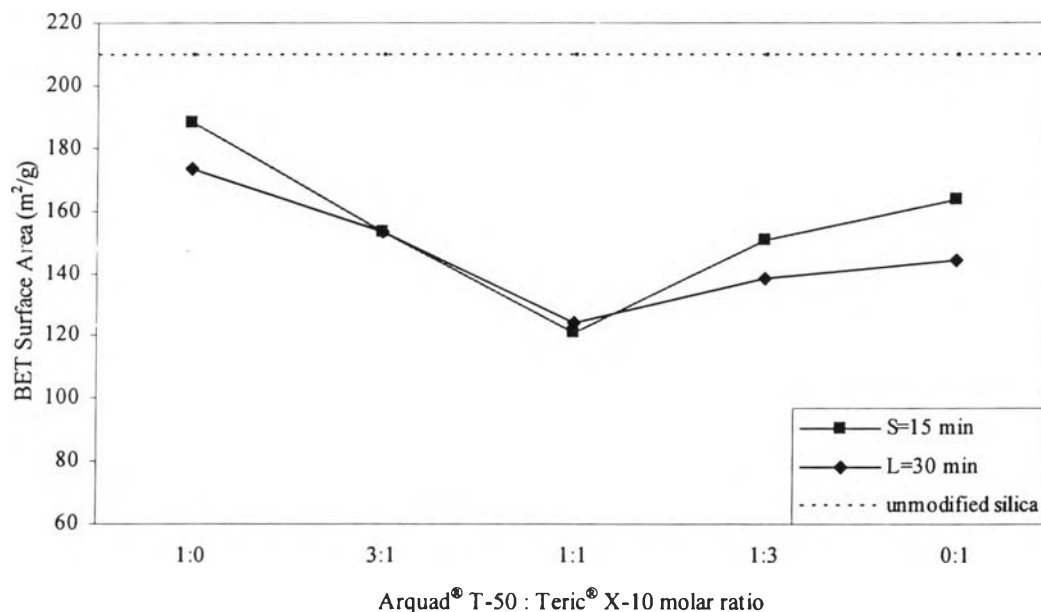
Figure 4.6 BET surface areas of modified and unmodified silica.

4.2.2 Mean Agglomerate Particle Size

The effect of the polymer film on mean agglomerate particle size of the modified silicas is shown in Figure 4.7 and Table 4.4. An increase in the mean agglomerate particle size by 20-30% was observed in all modified silicas. This may be due either to the organic polymer forming process or the subsequent processing of the silica. The polymerization process itself may cause linkages between the silica particles forming larger aggregates, or the processing of the treated silica, which consists of drying and regrinding it to a powder in a sieve, may result in a greater degree of agglomeration which would increase in particle size (O'Haver *et al.*, 1995). The differences in polymerization time show slightly different mean agglomerate particle sizes; therefore, the effect of polymerization times was not pronounced.
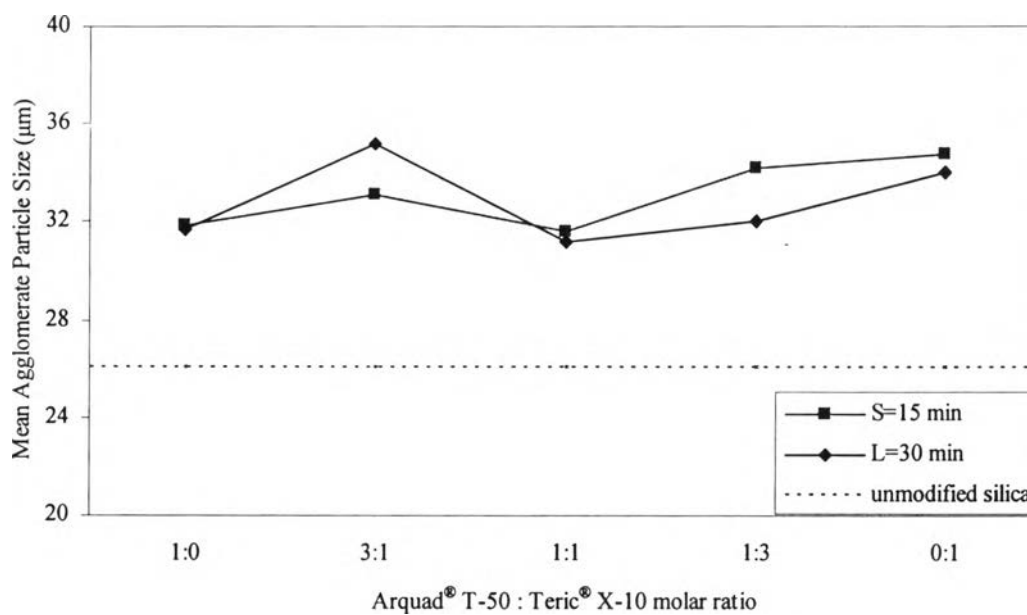
Figure 4.7 Mean agglomerate particle size of modified and unmodified silica.

Table 4.4 Effect of the the modification on the BET N_2 surface area and mean agglomerate particle size of the modified silicas

Silica	BET N_2 Surface Area (m^2/g)		Mean Agglomerate Particle Size (μm)	
	S = 15 min	L = 30 min	S = 15 min	L = 30 min
1:0	186.6	173.6	31.85	31.66
3:1	153.4	153.5	33.14	35.18
1:1	120.9	124.1	31.62	31.24
1:3	150.5	138.4	34.23	32.06
0:1	163.9	144.4	34.79	34.06
Hi-Sil® 255	209.5		26.68	

4.2.3 Thermogravimetric Analysis

All samples were examined by thermogravimetric analysis (TGA) in order to verify the existence of polymer forming on the silica surfaces. The water loss from the unmodified silica below 150 °C was shown in Figure 4.8. Consequently, the weight change above 150 °C might be the result of the surface modification of modified silicas. In order to predict the decomposition temperature of poly(styrene-isoprene) of the modified silicas, samples were prepared by depositing polystyrene dissolved with THF onto the silica surface. The decomposition of polystyrene occurred from 350 to 480 °C and is shown in Figure 4.9 (Chaisirimahamorakot, 2001). The decomposition of CTAB adsorbed onto the silica occurs in two steps; the first step was from 170 to 300 °C and the second step was from 300 to 450 °C (Figure 4.10). Poly(styrene-isoprene) decomposed from the admicellar polymerization modified silica as shown in Figure 4.11. The graphs evidently show the decomposition of CTAB taking place between 200 to 280 °C and 300 to 450 °C while the polymer started at above 300 °C.

Figure 4.12 shows the decomposition of Arquad® T-50 and propylene glycol (the impurity in Arquad® T-50) between 180 to 280 °C. Figure 4.13 shows the decomposition of Teric® X-10 to be between 250 to 420 °C. The decomposition of the surfactants Arquad® T-50, Teric® X-10 and their mixtures, adsorbed onto the silica at various molar is shown in Figures 4.14 to 4.18. Figure 4.14 shows that Aquard® T-50 also decomposed in two steps as CTAB, the first step from 180 to 300°C and the second step from 300 to 400°C. The second peak of the weight loss may result from the stronger bonding between silica and Aquard® T-50. For mixed surfactants, the decompositions appear in two steps, the first peak was 200 to 300 °C for the decomposition of Aquard® T-50 while the second peak for the decomposition of Teric® X-10 as well as Aquard® T-50 chemisorbed onto the silica at 300 to 480 °C (Figures 4.15-4.17). The decomposition of Teric® X-10 adsorbed onto the silica was observed in one step at 300 to 480 °C as shown in Figure 4.18.

Figures 4.19 to 4.23 show the TGA results of different modified silicas. All modified silica samples consisting of Aquard® T-50 (1:0, 3:1, 1:1 and 1:3 molar ratios) again showed two-step decomposition at the same temperature ranges as mentioned before. The first step was Aquard® T-50 decomposition and the second

was the deformation of Aquard® T-50 chemisorbed, Teric® X-10 and poly(styrene-isoprene) onto the silica. The modified silica with Teric® X-10 (0:1 molar ratio) was decomposed at 300 to 480 °C from Teric® X-10 and poly(styrene-isoprene) depositing on the silica. The amount of polymer depositing onto the silica was calculated from the comparison between first and second weight drops of modified silicas and the silicas adsorbed with surfactants. The higher weight loss of the second peak of the modified silica compared to silica adsorbed with surfactant at similar molar ratios indicates that there is polymer present on the silica and it was then calculated. Table 4.5 shows percent of polymer present on the modified silicas approximately. It was found that the greater amount of polymer depositing on the silica occur with longer polymerization time. However, for the modified silica with nonionic surfactant, it cannot find the amount of polymer. That may be due to the loss of some aggregates during the washing step. At various surfactant molar ratios, the highest percent of polymer present was observed in modified silica with 1:1 molar ratio of Aquard® T-50 to Teric® X-10. These results show a good correlation with the reduction in the BET surface area.
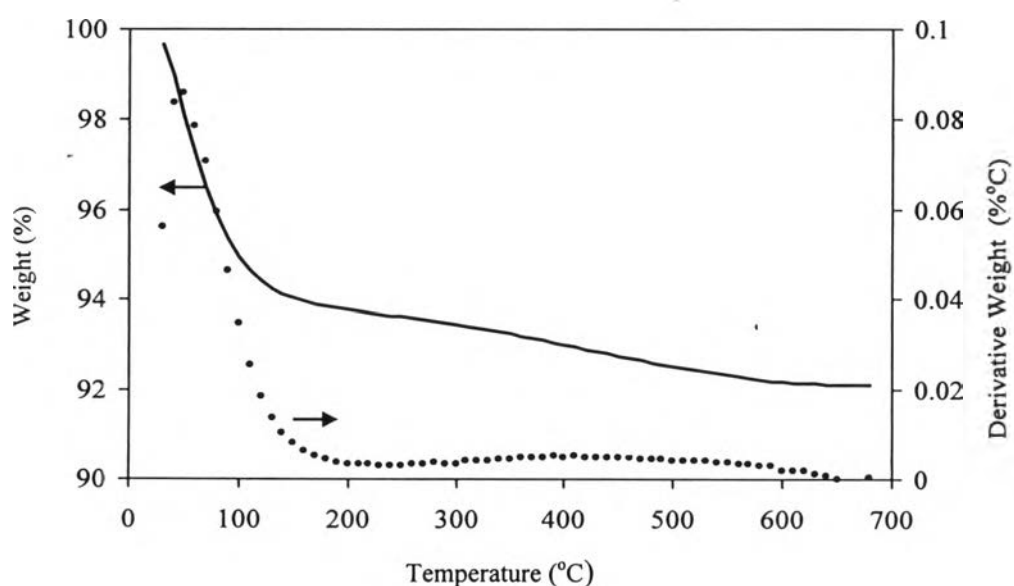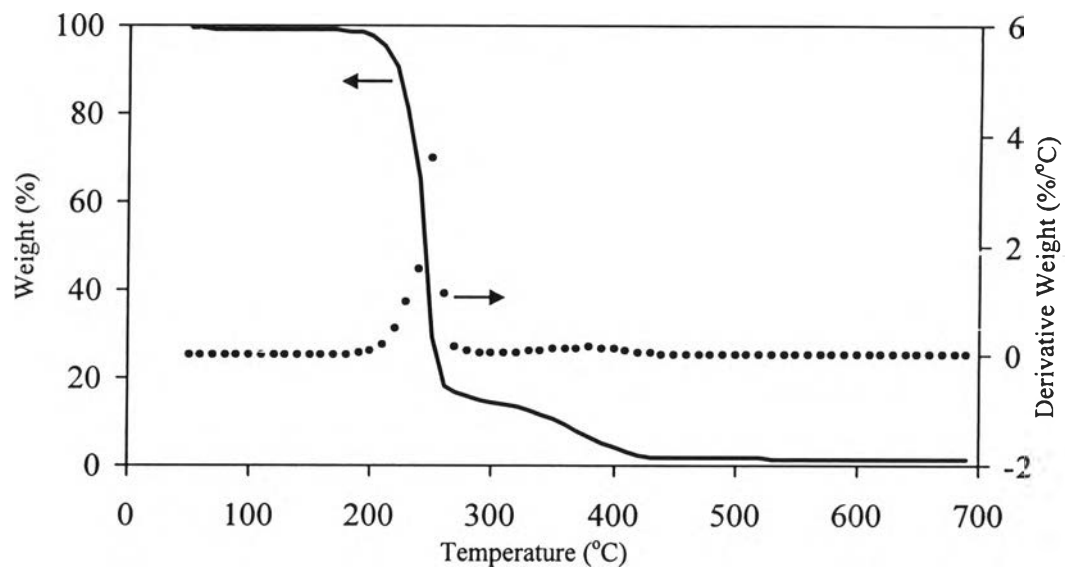

**Figure 4.8** TGA results of unmodified silica Hi-Sil®255 (Chaisirimahamorakot, 2001).
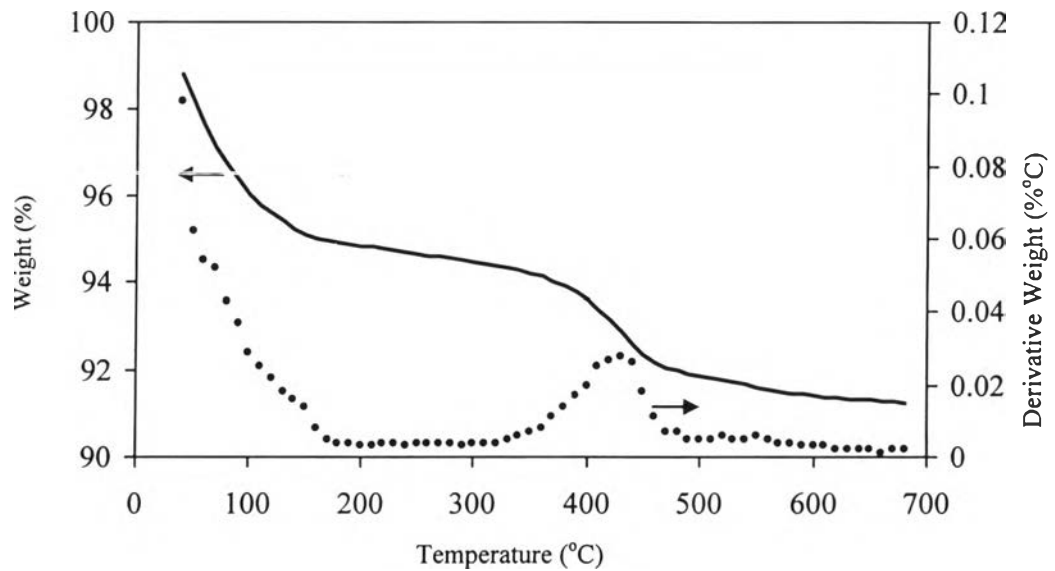
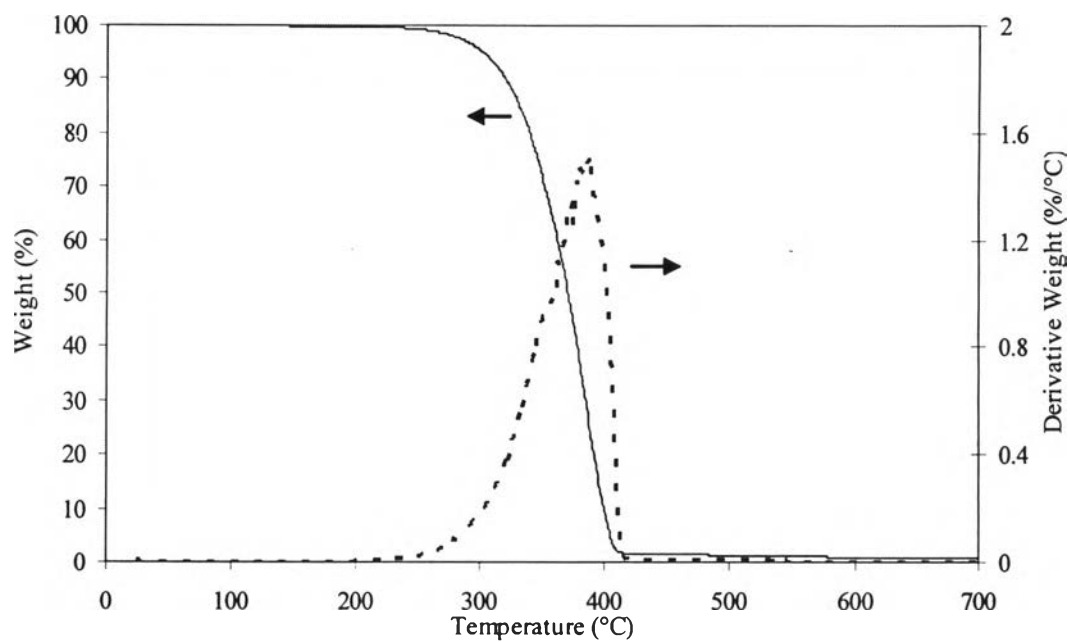**Figure 4.9** TGA results of silica Hi-Sil®255 adsorbed with polystyrene (Chaisirimahamorakot, 2001).
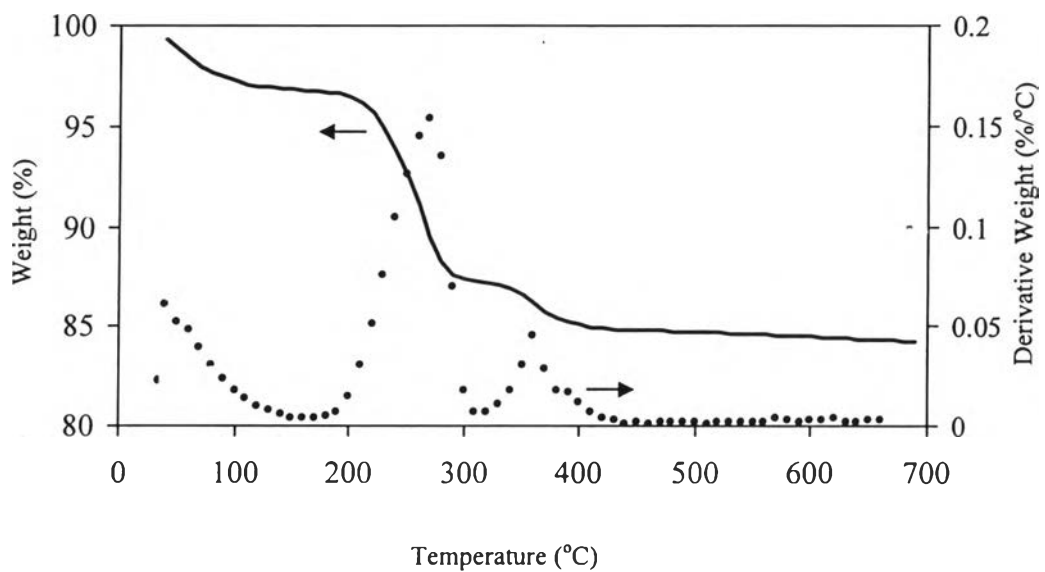
Figure 4.10 TGA results of silica Hi-Sil®255 adsorbed with CTAB (Chaisirimahamorakot, 2001).
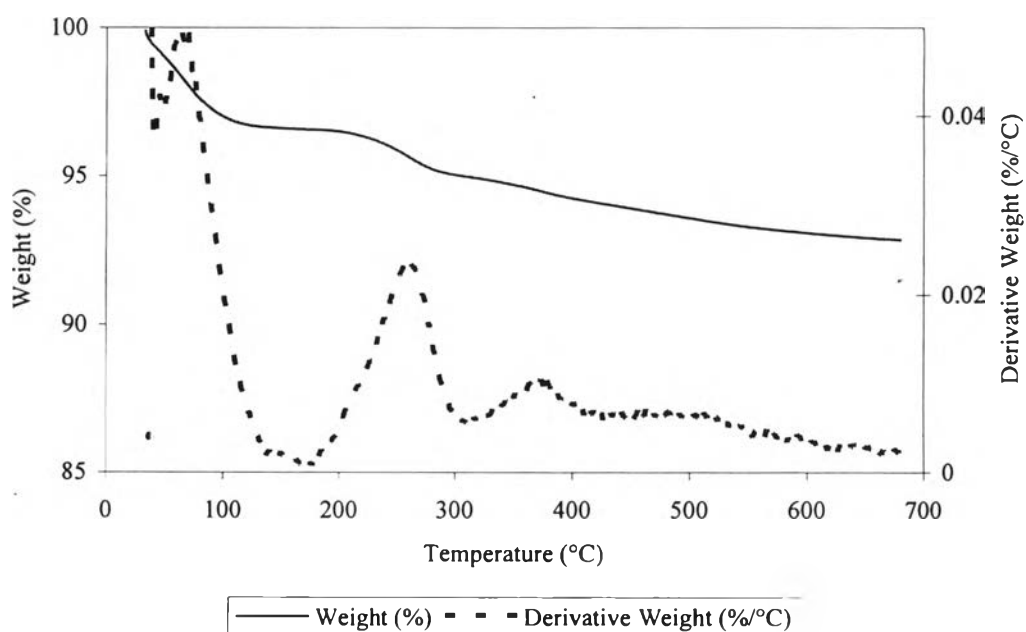
Figure 4.11 TGA results of poly(styrene-isoprene) polymerized in CTAB (Chaisirimahamorakot, 2001).
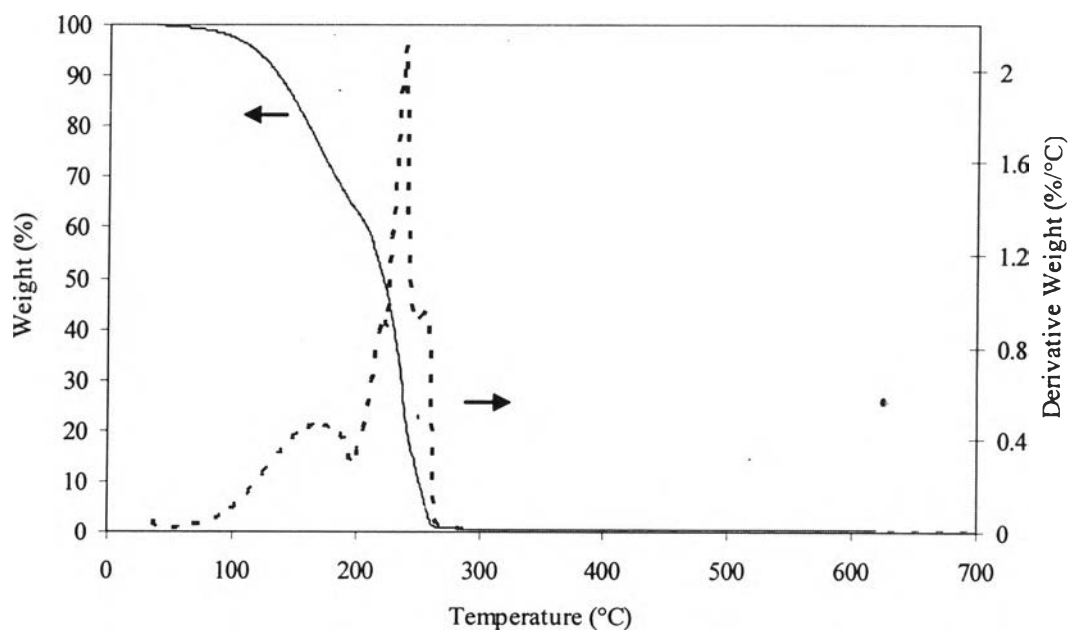
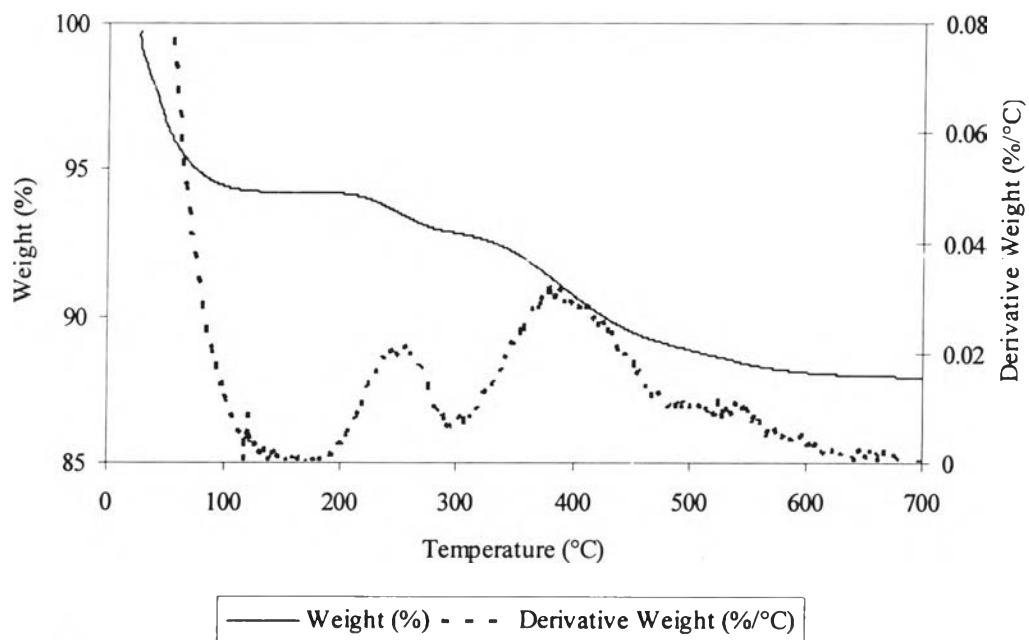**Figure 4.12** TGA results of Arquad® T-50.
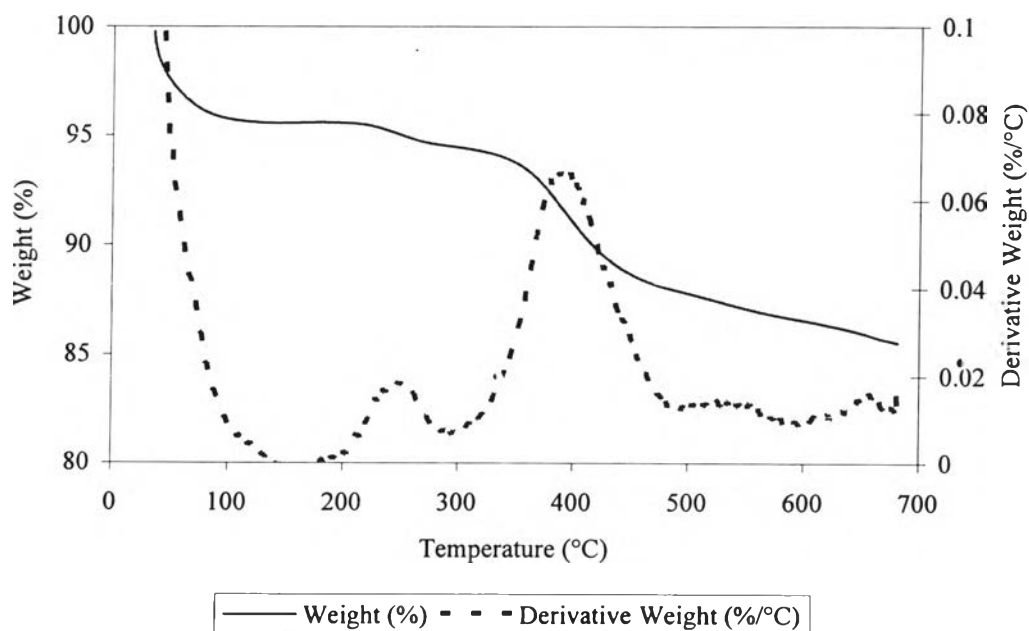
Figure 4.13 TGA results of Teric® X-10.

Figure 4.14 TGA results of silica Hi-Sil®255 adsorbed with 1:0 molar ratio of Arquad® T-50 to Teric® X-10.
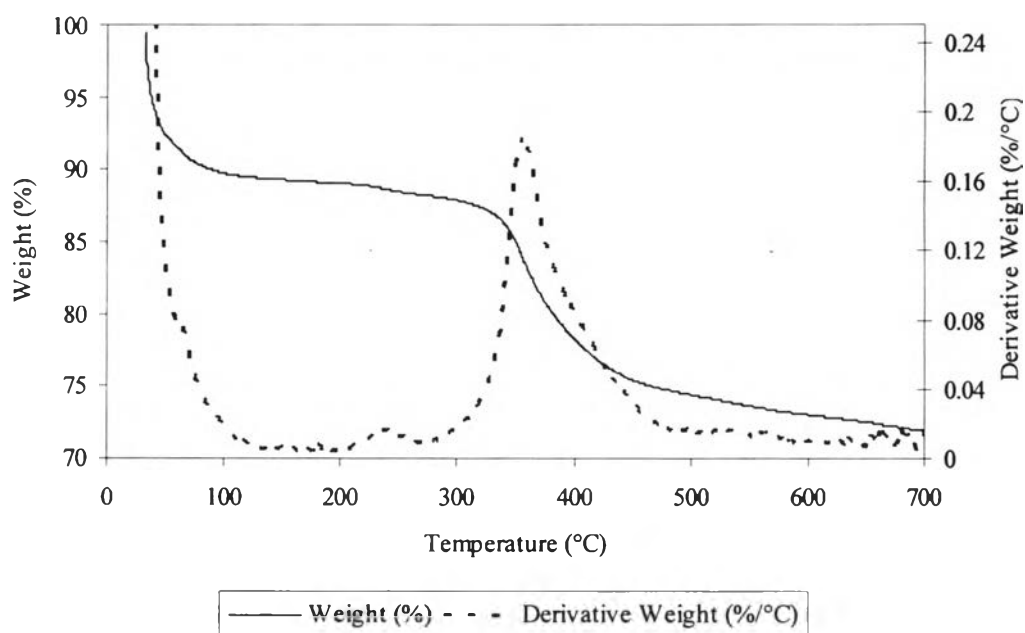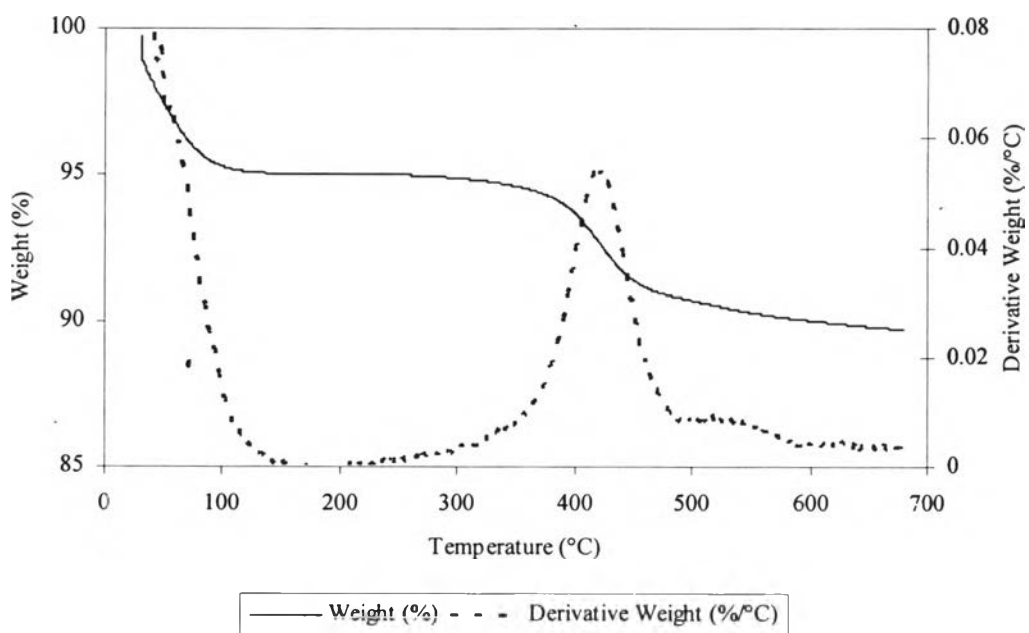
Figure 4.15 TGA results of silica Hi-Sil®255 adsorbed with 3:1 molar ratio of Arquad® T-50 to Teric® X-10.

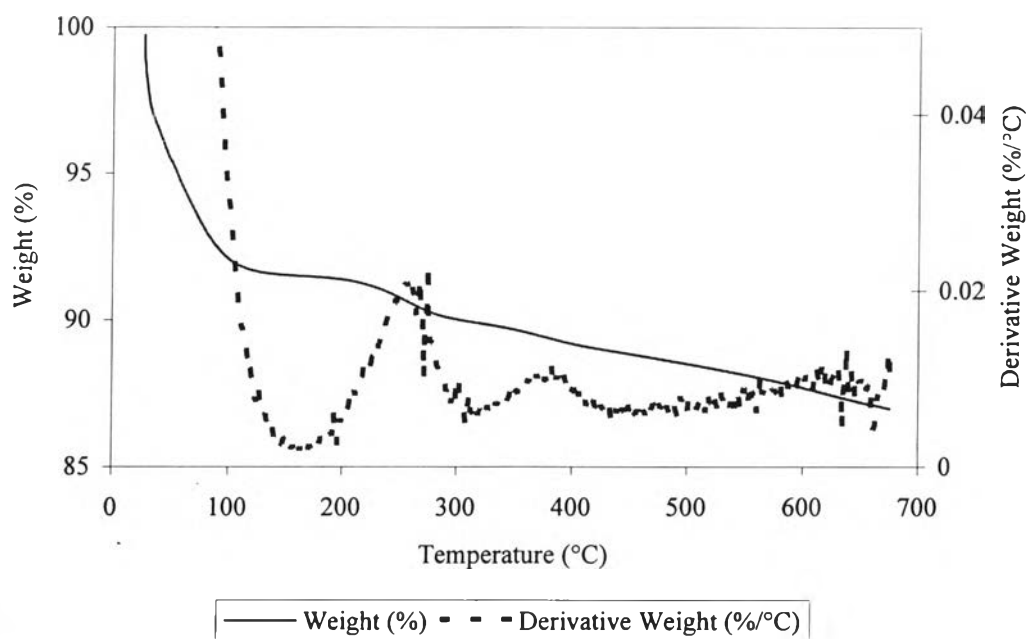**Figure 4.16** TGA results of silica Hi-Sil®255 adsorbed with 1:1 molar ratio of Arquad® T-50 to Teric® X-10.

Figure 4.17 TGA results of silica Hi-Sil®255 adsorbed with 1:3 molar ratio of Arquad® T-50 to Teric® X-10.
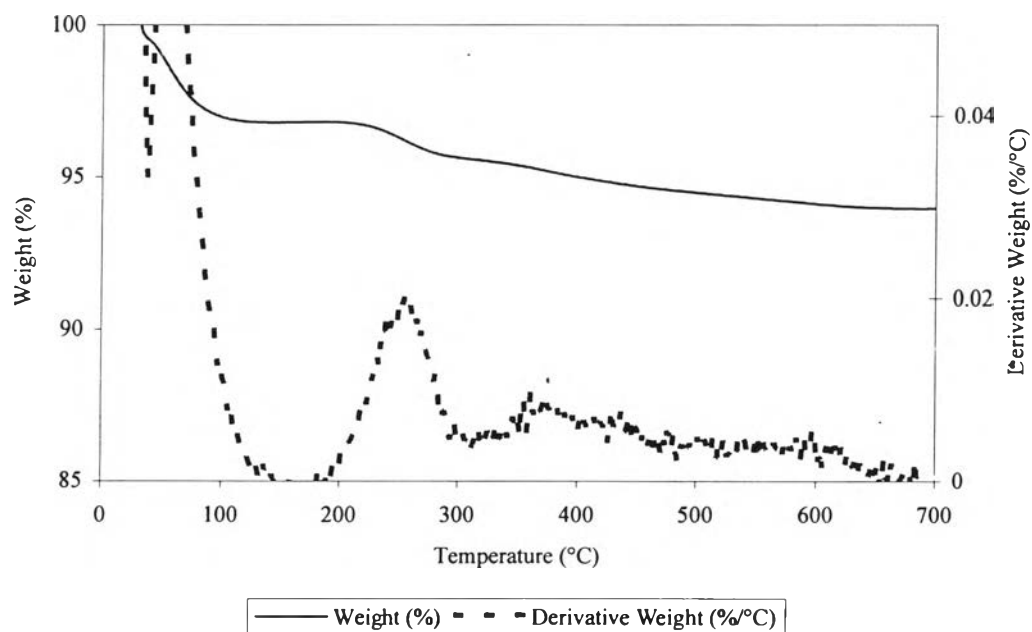

Figure 4.18 TGA results of silica Hi-Sil®255 adsorbed with 0:1 molar ratio of Arquad® T-50 to Teric® X-10.

A. S = 15 min

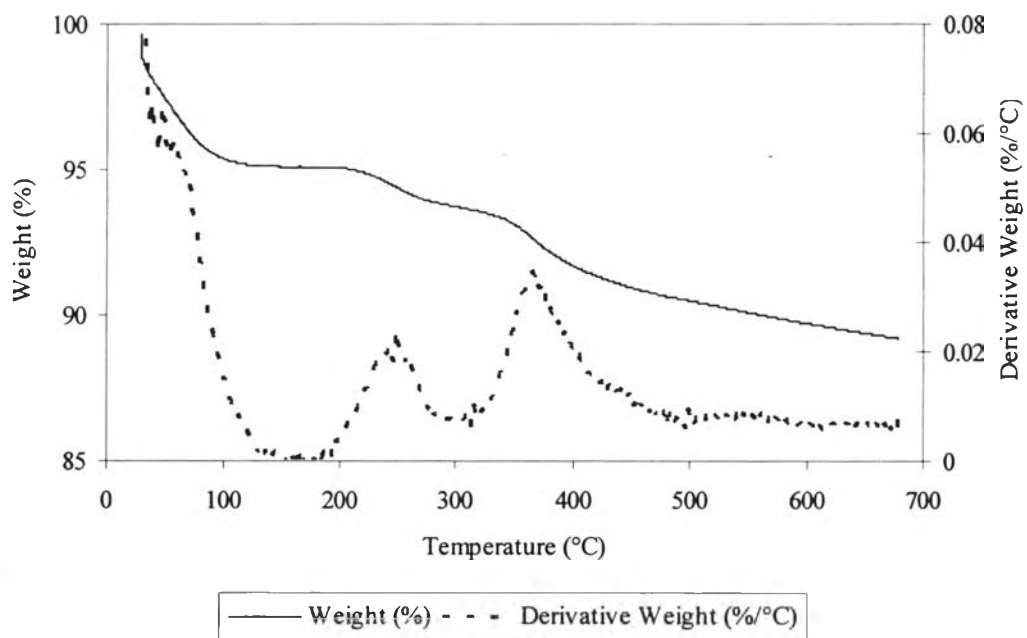B. L = 30 min

Figure 4.19 TGA results of the modified silica surface with 1:0 molar ratio of Arquad® T-50 to Teric® X-10.

A. S = 15 min

B. L = 30 min

Figure 4.20 TGA results of the modified silica surface with 3:1 molar ratio of Arquad® T-50 to Teric® X-10.

A. S = 15 min

A. S = 15 min graph: Weight (%) and Derivative Weight (%/°C) vs Temperature (°C)

Legend: Weight (%) - - - Derivative Weight (%/°C)

B. L = 30 min

B. L = 30 min graph: Weight (%) and Derivative Weight (%/°C) vs Temperature (°C)
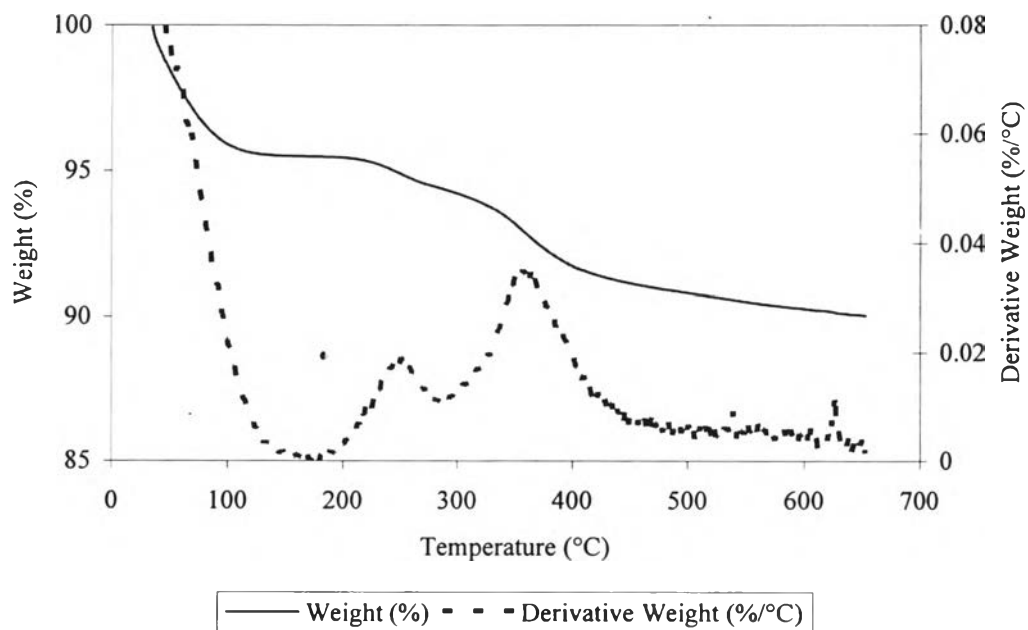
Legend: Weight (%) - - - Derivative Weight (%/°C)

Figure 4.21 TGA results of the modified silica surface with 1:1 molar ratio of Arquad® T-50 to Teric® X-10.
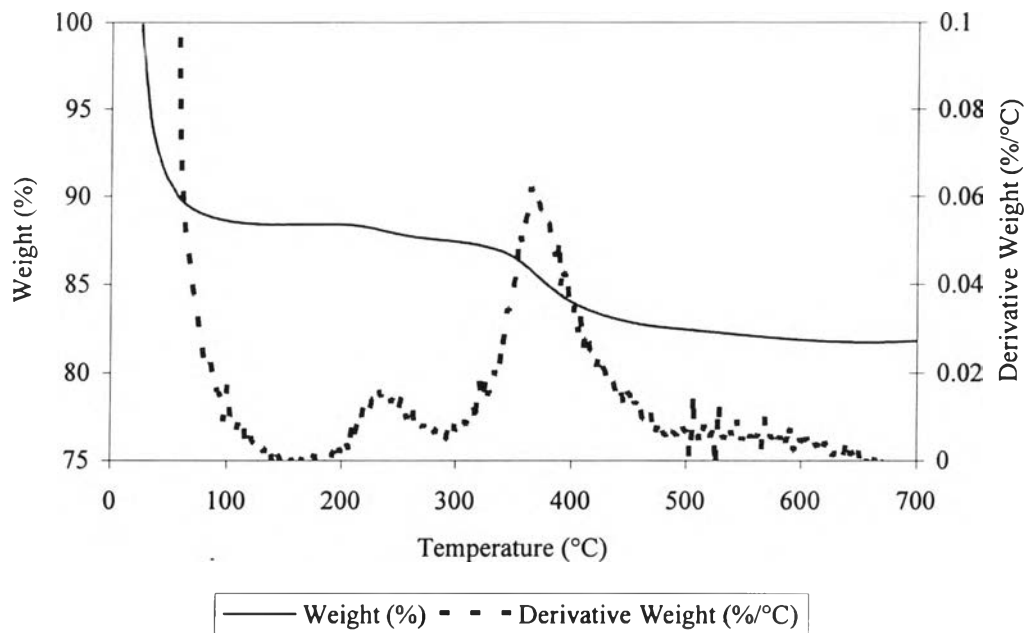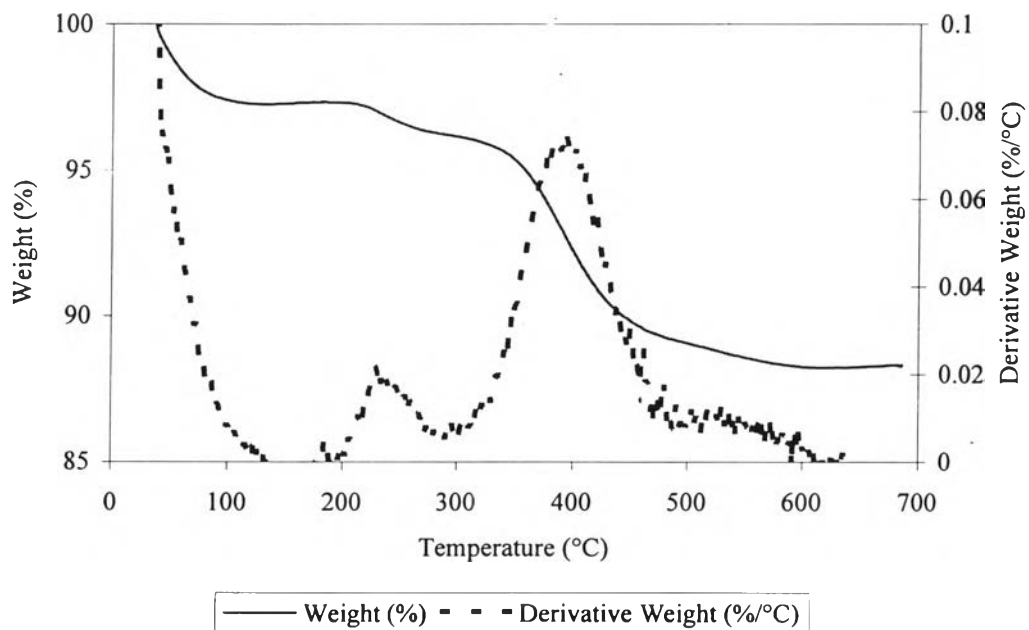
A. S = 15 min

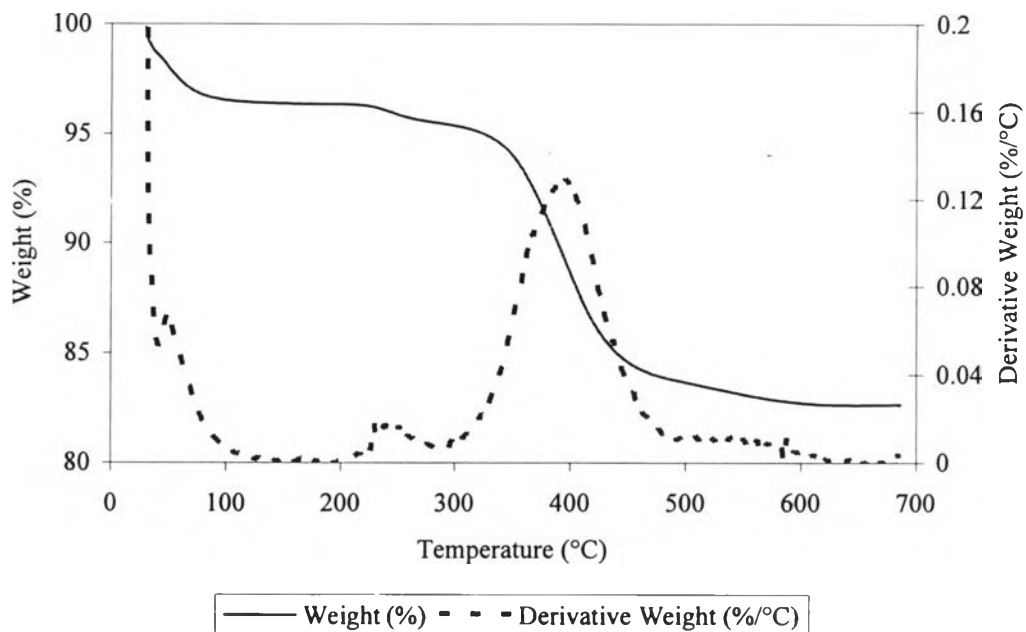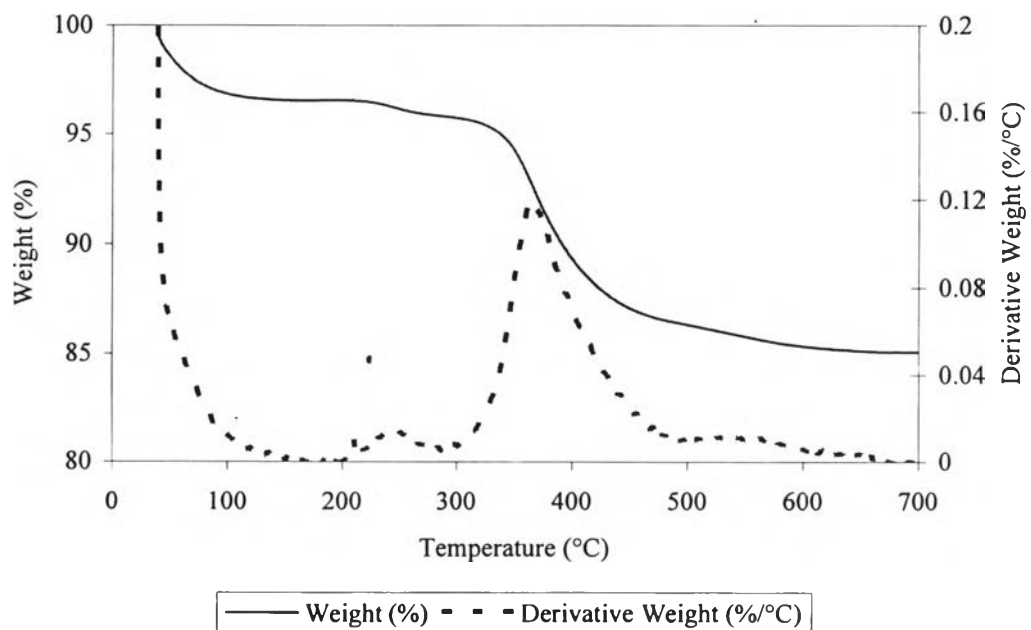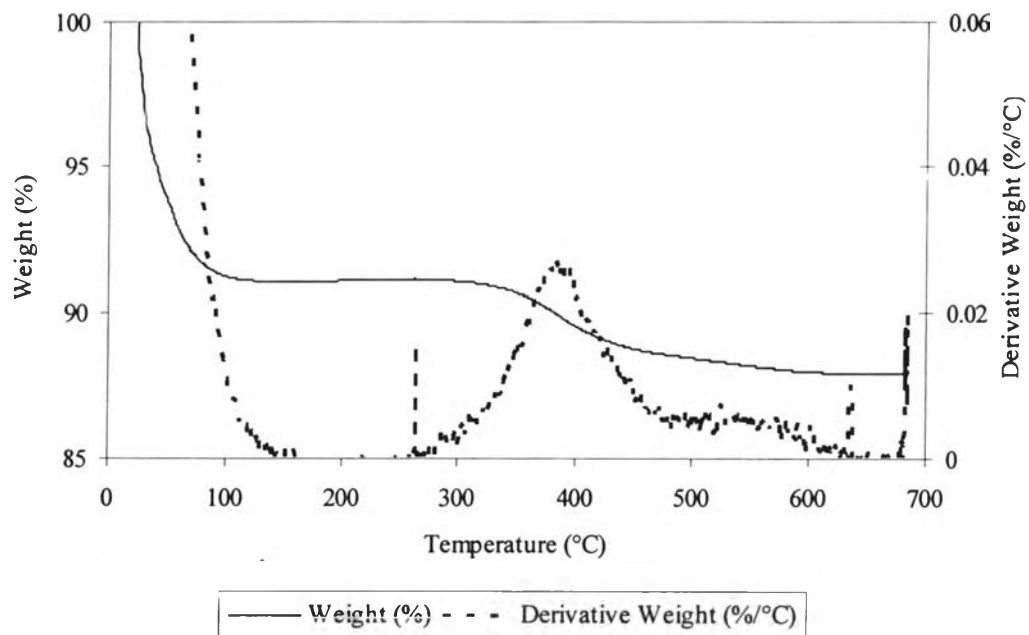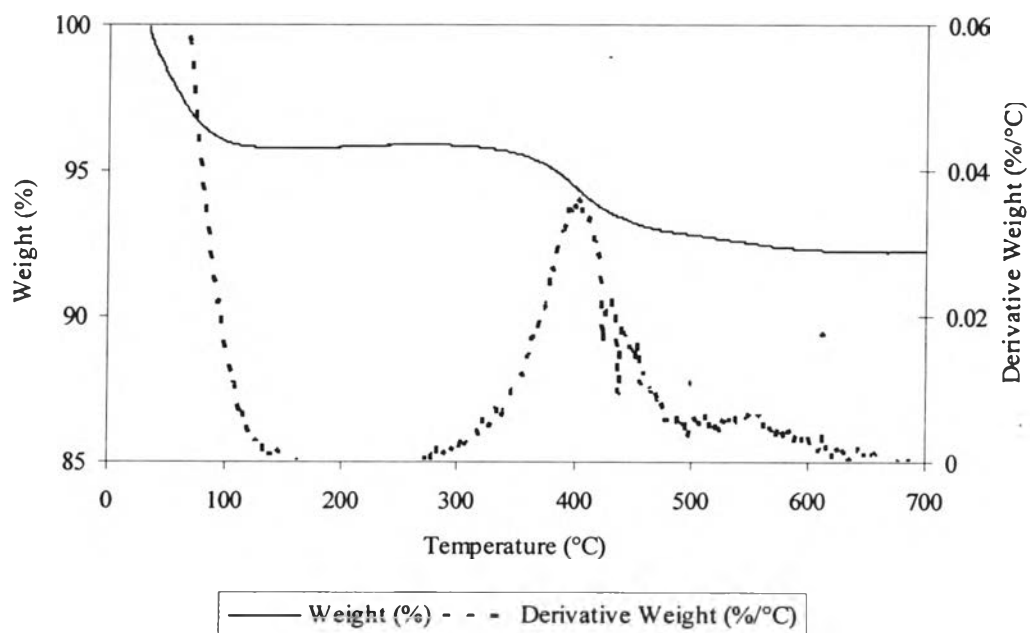

B. L = 30 min

Figure 4.22 TGA results of the modified silica surface with 1:3 molar ratio of Arquad® T-50 to Teric® X-10.

A. S = 15 min

B. L = 30 min

Figure 4.23 TGA results of the modified silica surface with 0:1 molar ratio of Arquad® T-50 to Teric® X-10.

Table 4.5 Amount of polymer present on the modified silicas.

| Modified Silica	Amount of Polymer (%)*	
	S = 15 min	L = 30 min
1:0	0.186	0.362
3:1	0.349	0.413
1:1	0.528	0.631
1:3	0.395	0.566

* with respect to weight loss of silica adsorbed with each surfactant molar ratio

4.3 Rubber Compound Physical Properties

All modified silicas having different surfactant molar ratios and polymerization times were further investigated for the impact of the modification on rubber compound physical properties. The results of performance data of all modified silicas studied in rubber compound (including the result of unmodified silica (Hi-Sil® 255)) are summarized in Table 4.6. Tables C1 and C2 (from Appendix C) show the present data compared to the results of previous work from Nontasorn (2002), Kiatdamneon-ngam (2003) and Imsawatgul (2004).

The data shows that the modified silicas with different surfactant molar ratios and polymerization times are slightly different in the compound physical properties. Figure 4.23 shows the effect of modified silicas on cure time of rubber compound. It can be seen that the modified silicas can reduce the cure time significantly as compared to the unmodified silica and these results are slightly different from the result of previous work. The data suggest that the cure time of modified silicas does not depend on both surfactants molar ratio and polymerization time except in pure Teric® X-10 at 15 min polymerization time. This system shows much higher cure time than other systems. That may be due to the low interaction between the surfactant and silica surface resulting in a less uniform layer coated on the surface.
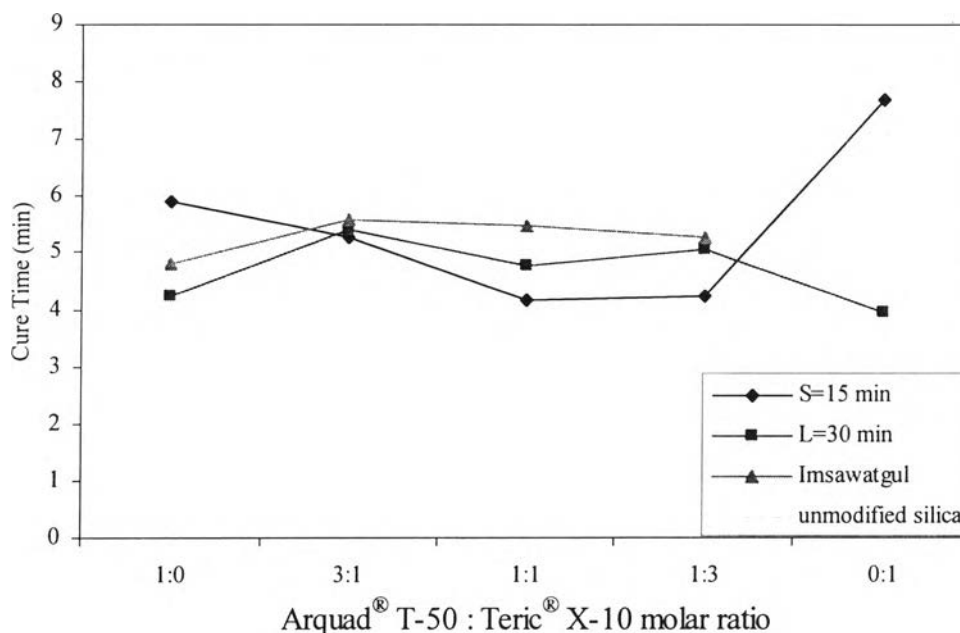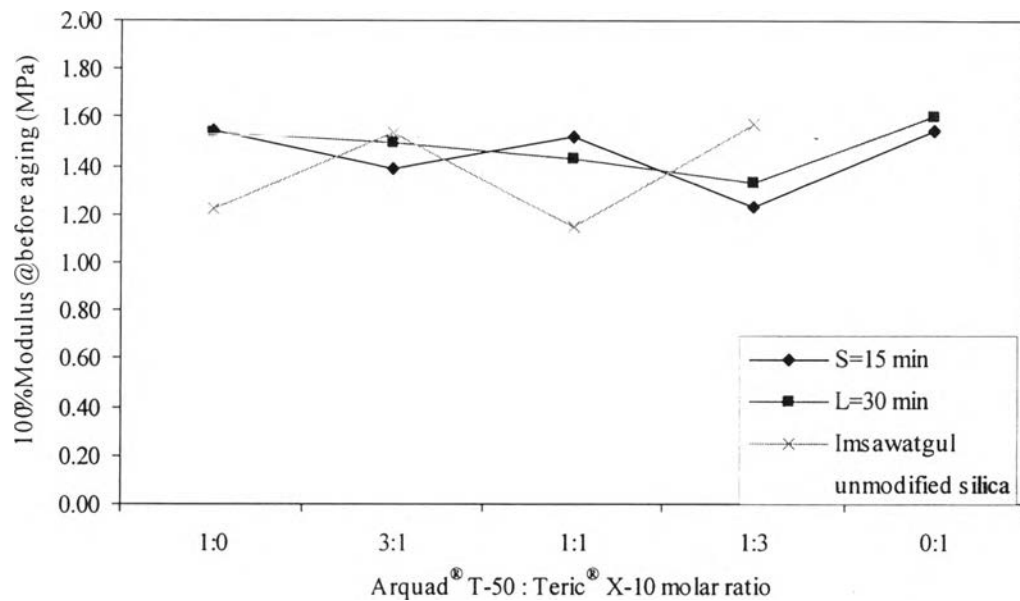
Figure 4.24 Cure time of modified silica compared to the previous work.

Figures 4.24 to 4.26 show the results of 100%, 200% and 300% modulus @ before aging of the modified silicas compared to the unmodified silica and previous work. The modified silicas show a slight increase in all modulus when compared to the unmodified silica, while they are not significantly different from those of the previous systems.

As seen from Figure 4.27, the tensile strength @ before aging of the modified silicas is not different from the unmodified silica but lower when compared to the previous results. In addition, the differences in the surfactant molar ratios and polymerization times do not significantly affect the tensile strength.

The tear strength @ before aging of the rubber compounds shows a slight decrease for the modified silica as compared to the unmodified silica but not much different when compared to the previous work, as seen from Figure 4.28. The resilience value of all modified silicas show slight improvement compared to the unmodified silica (Figure 4.30). From Figure 4.31, the modified silicas show significant reduction in compression set from the previous work and slightly lower compared to the unmodified silica. For the results of hardness @ before aging, the

modified silicas give better improvement than those of the previous work and slightly different from that of the unmodified silica, as can be seen from Figure 4.32.

Figure 4.25 100% modulus @ before aging of modified silica compared to the previous work.
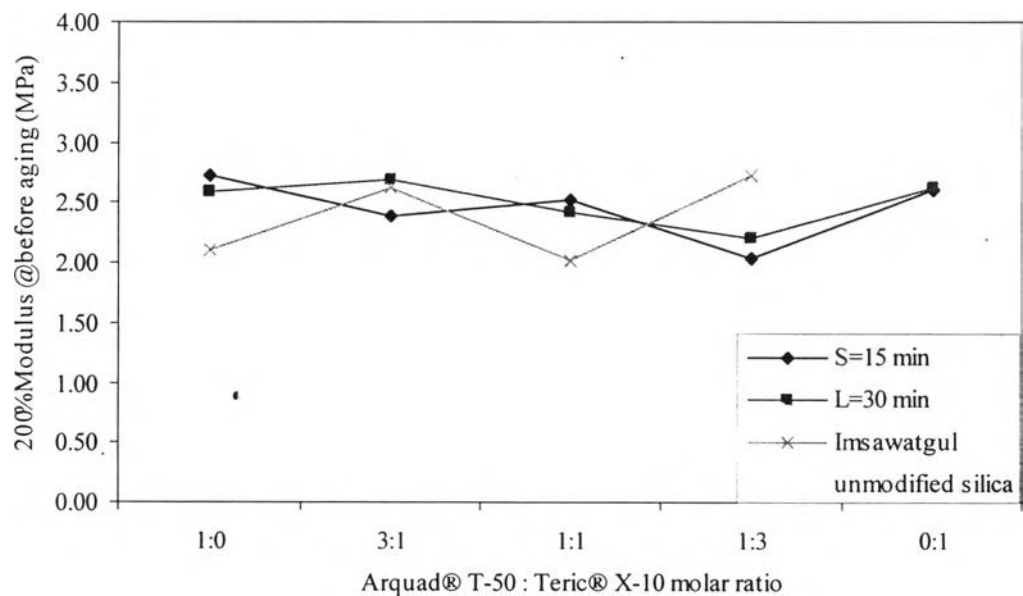
Figure 4.26 200% modulus @ before aging of modified silica compared to the previous work.
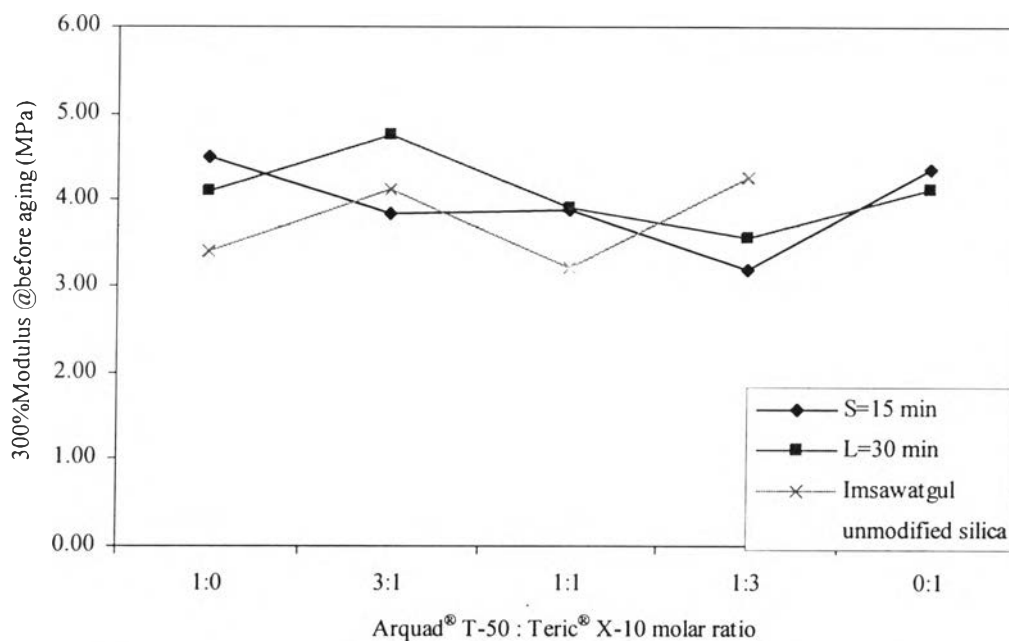
Figure 4.27 300% modulus @ before aging of modified silica compared to the previous work.
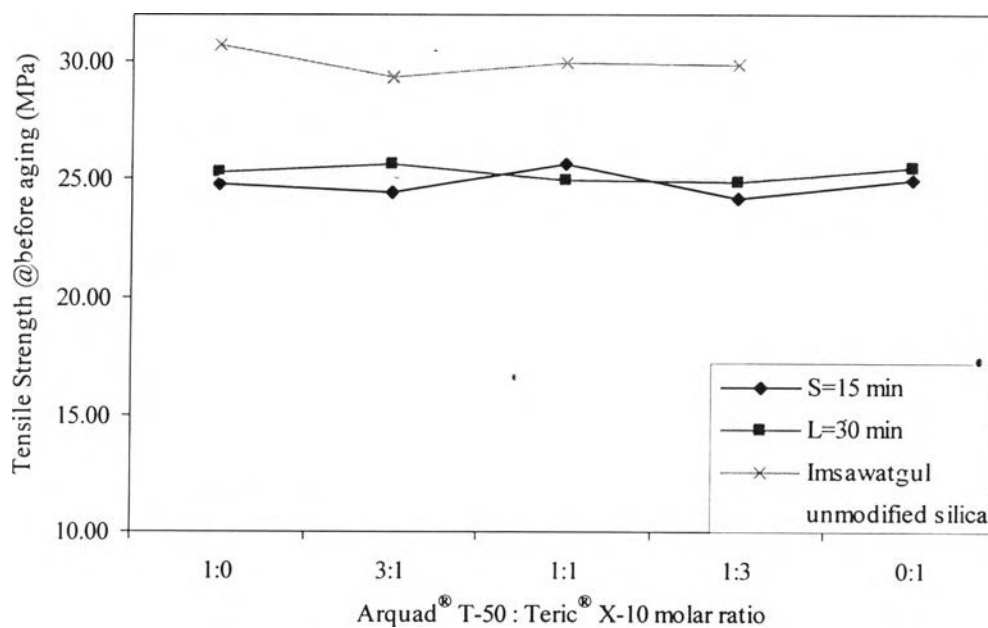
Figure 4.28 Tensile strength @ before silica.aging of modified compared to the previous work.
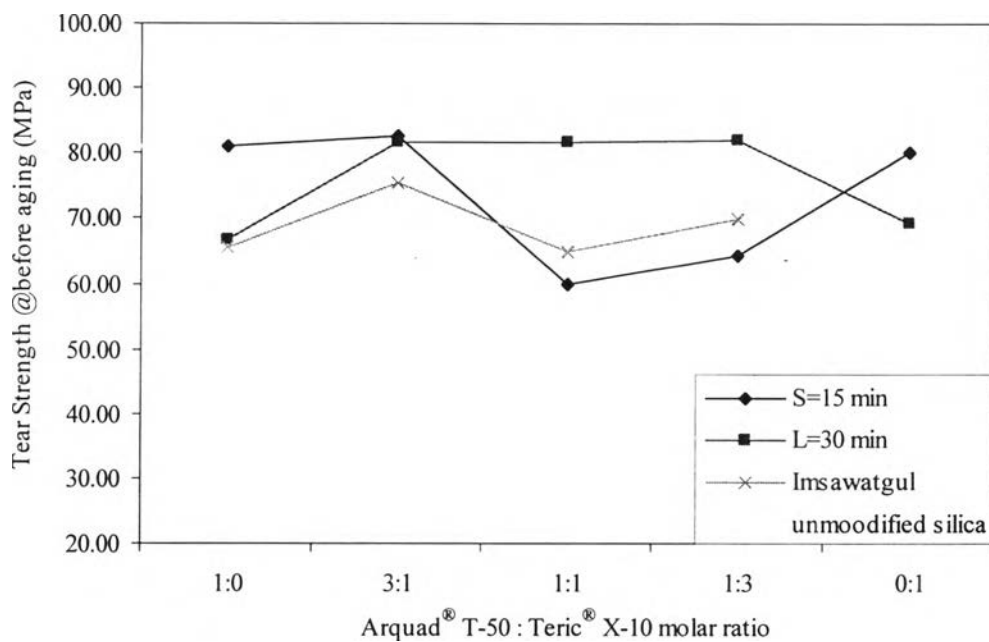
Figure 4.29 Tear strength @ before aging of modified silica compared to the previous work.

Figure 4.30 Abrasion loss of modified silica compared to the previous work

Figure 4.31 Resilience of modified silica compared to the previous work.

Figure 4.32 Compression set of modified silica compared to the previous work.

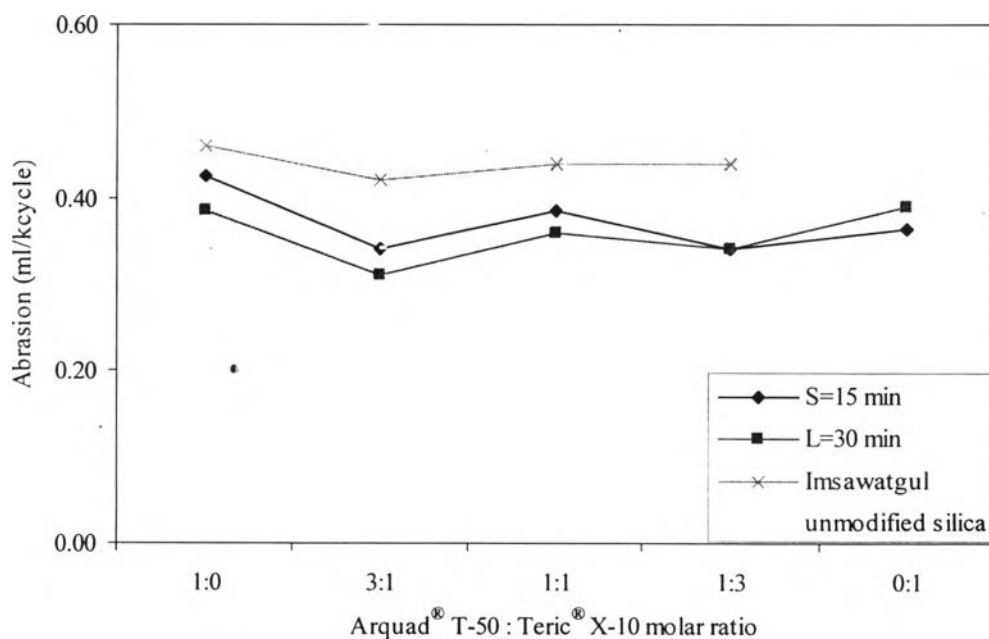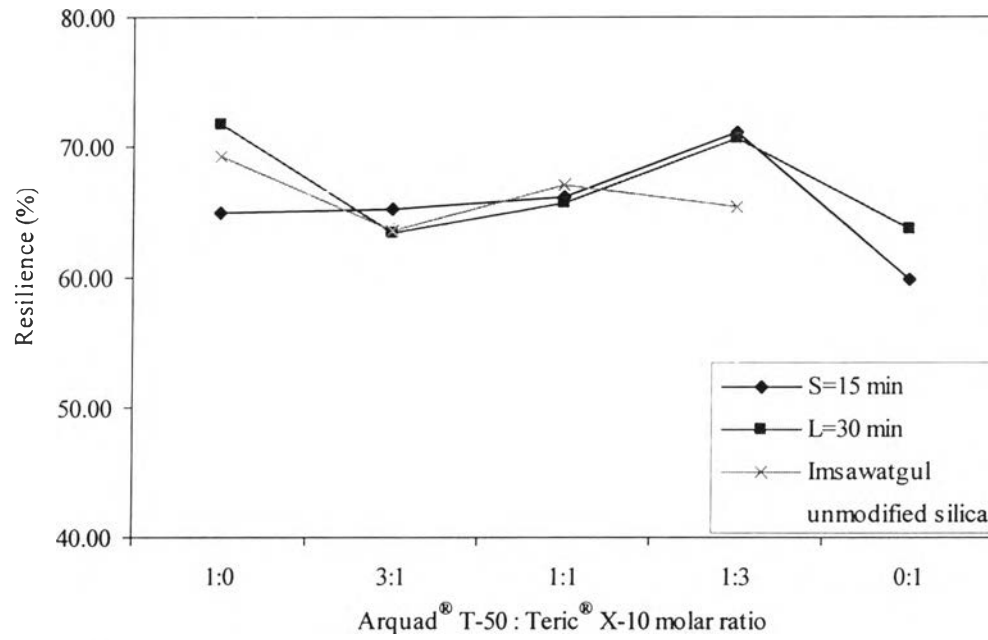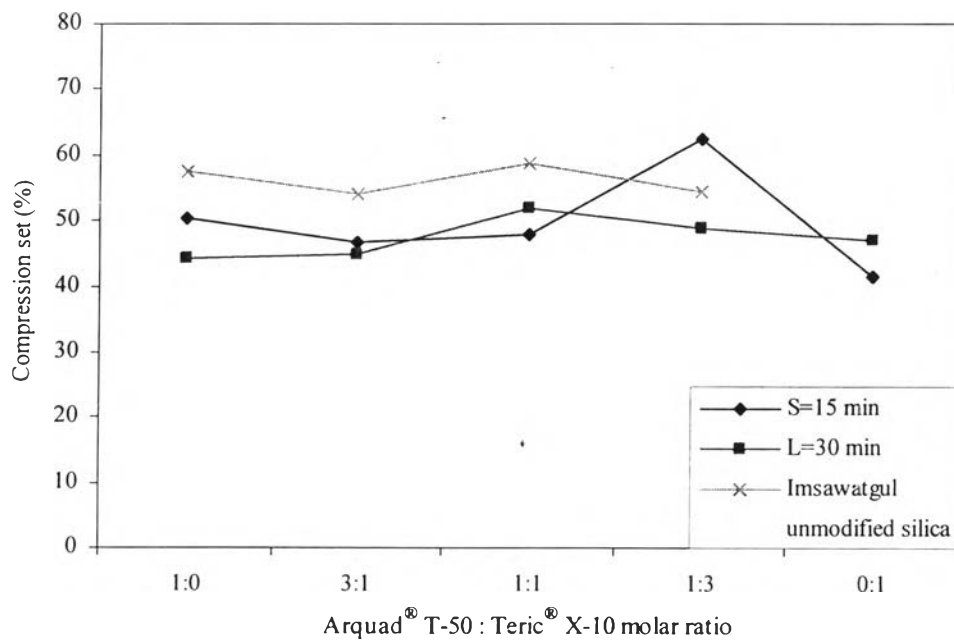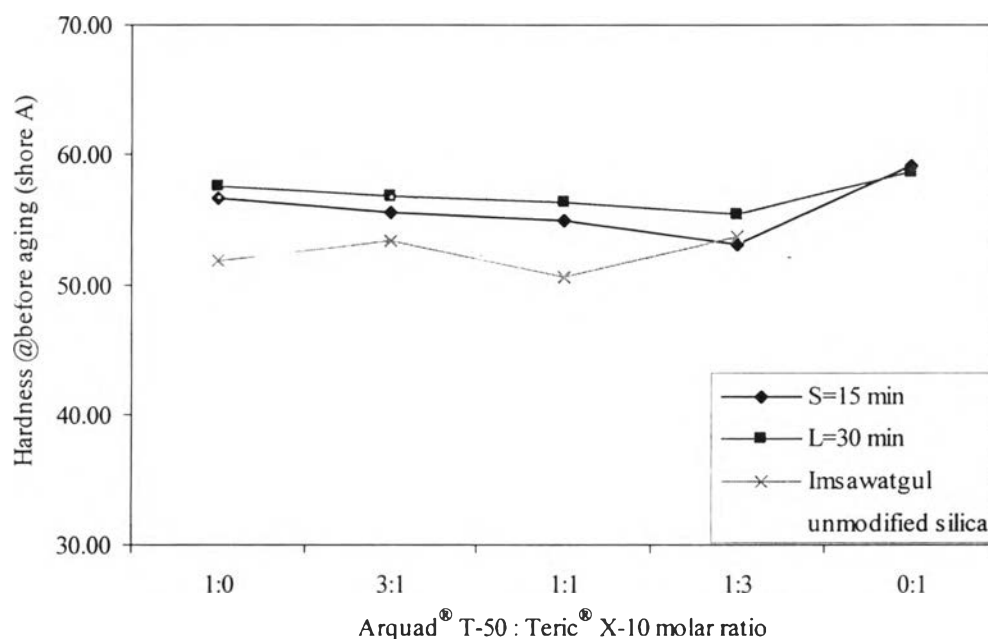**Figure 4.33** Hardness @ before aging of modified silica compared to the previous work.

The impacts of the different surface-modified silicas on various rubber physical properties of the present study in comparison with the unmodified silica and previous works are summarized qualitatively in Tables C3 to C6 (Appendix C). The percent improvements of surface-modified silica rubber physical properties are shown in Tables C7 to C9. The designation are meaning as a "+" indicates greater than 10% improvement in the property over unmodified silica or the previous studies, a "-" indicates a greater than 10% negative impact on the property, and an "=" indicates no significant difference. A "+" is given a value of 1; a "-" is given a value of -1; and an "=" is given a 0 values for qualitative calculation of overall improvement relative to the respective unmodified silicas or the modified silica of previous works.

Results from Table C3 show the positive impact of improvement in resilience of the modified silica when compared to the unmodified silica in almost all different surfactants molar ratios and polymerization times. The overall improvement in the physical properties was observed in 1:0, 3:1 and 0:1 molar ratio of surfactants. The highest overall improvement in the rubber physical properties over the

unmodified silica occur in the modification with 3:1 molar ratio of Arquad® T-50 to Teric® X-10 at 30 min polymerization time.

Tables C4 and C5 show a qualitative summary of surface-modified silica rubber physical properties compared to the modified silica using CTAB surfactant of the previous studies, Nontasorn (2002) and Kiatdamneon-ngam (2003), respectively. The negative impact on the various rubber physical properties with respect to the previous studies was observed. It may be due to the less uniform polymer coated on the silica surface when using the commercial grade surfactants that have more impurities. However, all modified silicas give the positive improvements in tear strength, abrasion loss and compression set relative to the previous studies

A qualitative summary of rubber physical properties obtained from the present study compared to the modified silicas of the previous study (Imsawatgul, 2004) at similar surfactant molar ratios and polymerization time is shown in Table C6. The positive effect of improvement in tear strength, abrasion loss and compression set was again observed in almost all surfactants molar ratios. The overall improvement was obtained with the 1:0, 3:1 and 1:1 molar ratios.

The qualitative summary of rubber physical properties using different modified silicas was shown in Table C10. To determine the overall properties of modified rubber, the results were compared qualitatively and summarized by ranking the result from low to high quality of each physical property using a number "1" to "10" in order to determine the optimum condition of the silica modification system. In this study, the modified silica with 3:1 molar ratio (Arquad® T-50 to Teric® X-10) and 30 min polymerization time shows the superior characteristics of the rubber compound physical properties. However, the rubber compound physical properties of modified silica with different polymerization times were slightly different. Therefore, the polymerization time can be minimized whereas the rubber properties are still maintained. Moreover, in comparison with the previous mixed surfactant system using CTAB and Triton X-100, the overall improvement in rubber compound physical properties were obtained, thus, commercial grade surfactant can be used to modify silica surface in order to reduce the production cost.

Table 4.6 Rubber compound physical properties filled with different modified silicas and unmodified silica (Hi-Sil® 255)

Property	Hi-Sil® 255	1:0		3:1		1:1		1:3		0:1	
		S	L	S	L	S	L	S	L	S	L
Cure Time (min)	7.07	5.89	4.25	5.27	5.41	4.15	4.77	4.25	5.06	7.68	3.95
100%Modulus @before aging (MPa)	1.34	1.55	1.54	1.39	1.49	1.52	1.43	1.23	1.33	1.54	1.60
100%Modulus @after aging (MPa)	1.89	2.30	1.81	2.18	2.41	1.83	2.16	1.85	2.06	2.12	1.84
200%Modulus @before aging (MPa)	2.25	2.72	2.59	2.38	2.69	2.52	2.41	2.04	2.21	2.61	2.62
200%Modulus @after aging (MPa)	3.37	4.00	3.11	3.75	4.18	3.18	3.67	3.14	3.40	3.64	3.20
300%Modulus @before aging (MPa)	3.71	4.49	4.10	3.84	4.75	3.88	3.91	3.18	3.57	4.37	4.13
300%Modulus @after aging (MPa)	5.36	6.34	4.83	5.68	6.67	4.85	5.76	4.80	5.16	5.58	4.96
Tensile Strength @before aging (MPa)	25.06	24.76	25.32	24.41	25.64	25.68	24.98	24.17	24.84	24.94	25.47
Tensile Strength @after aging (MPa)	24.79	22.38	24.07	21.03	22.53	23.00	21.65	21.90	21.68	22.94	23.99
Tear Strength @before aging (MPa)	83.70	81.05	66.85	82.43	81.59	59.83	81.74	64.31	81.83	79.96	69.31
Tear Strength @after aging (MPa)	62.44	59.07	54.67	54.60	56.15	57.57	54.34	50.73	49.25	64.16	60.67
Abrasion (ml/kcycle)	0.34	0.43	0.39	0.34	0.31	0.39	0.36	0.34	0.34	0.37	0.39
Resilience (%)	63.98	64.90	71.73	65.23	63.40	66.13	65.64	71.11	70.73	59.80	63.63
Compression set (%)	42.04	47.45	44.87	46.56	44.92	47.78	52.54	62.37	48.94	41.24	44.31
Hardness @before aging (shore A)	56.70	56.60	57.55	55.50	56.80	54.85	56.30	53.00	55.30	59.10	58.60
Hardness @after aging (shore A)	65.80	65.30	63.10	64.15	64.70	59.90	63.30	57.95	62.10	66.65	64.00

1:0, 3:1, 1:1, 1:3, 0:1 : ratio of surfactants, Arquad® T-50 to Teric® X-10 molar ratio

S, L : the retention times of polymerization, 15 and 30 min, respectively

4.4 Cost Reduction

In the admicellar polymerization process, the main cost of production has been from the cost of surfactants when using chemical grade surfactants that is unsatisfactory in the industrial application. However, the cost of modification can be reduced by using commercial grade surfactants, which is the objective of this work. Table 4.7 shows the prices of chemical grade and commercial grade surfactants used in previous works and present work, respectively. Cost of surfactants per one kilogram of silica calculated from previous and present systems is shown in Table 4.8. It was found that, with commercial grade surfactants, the surfactant cost decreased by 98% compared among the optimum conditions of each system while the rubber physical properties can be maintained.

Table 4.7 Prices of surfactants used in previous and present work

Surfactants		Price
Name	Type	(Baht/kg)
CTAB	Cationic	9,400
Titron X-100	Nonionic	4,200
Arquad®T-50	Cationic	230
Teric®X-10	Nonionic	210

Table 4.8 Cost of surfactant per one kilogram of silica comparing between previous and present work

Modification systems (at optimum)	Surfactants	Amount of surfactant used (g of surfactant/kg of silica)	Cost of surfactant (Baht/kg of silica)	% Cost reduction of present work (compared with previous works)
Previous 1*	CTAB	200	1880	98.99
Previous 2**	CTAB	146	1372	98.61
Previous 3***	CTAB TritonX-100	21 112	690	97.24
Present	Arquad®T-50 Teric®X-10	51 33	19	-

* Nontasorn (2002)

** Kaitdabneon-ngam (2003)

***Imsawatkul (2004)