



CHAPTER IV RESULTS AND DISCUSSION

4.1 Adsorption of Surfactants

4.1.1 Adsorption Isotherm of Surfactants onto Silica Hi-Sil[®]255

Adsorption isotherms with various CTAB to Triton X-100 molar ratios, 0:1, 1:3, 1:1, 3:1 and 1:0, were obtained to determine the maximum adsorption concentration. The maximum surfactant adsorbed is determined when the surfactant is completely adsorbed on the silica surface in the bilayer structure. A further increase in surfactant concentration beyond its CMC, the excess surfactants will form multilayer or even micellar structure. From the adsorption isotherm results, in our previous works relating to the bilayer adsorption structure the surfactant concentration, slightly lower than the maximum surfactant concentration, was used to investigate the improvement of the properties of modified silicas for rubber compounds. Figure 4.1 shows surfactant adsorption at the feed pH of 8 and 30°C on Hi-Sil[®] 255, an amorphous precipitated silica. Pure CTAB (1:0 molar ratio of CTAB:Triton X-100)

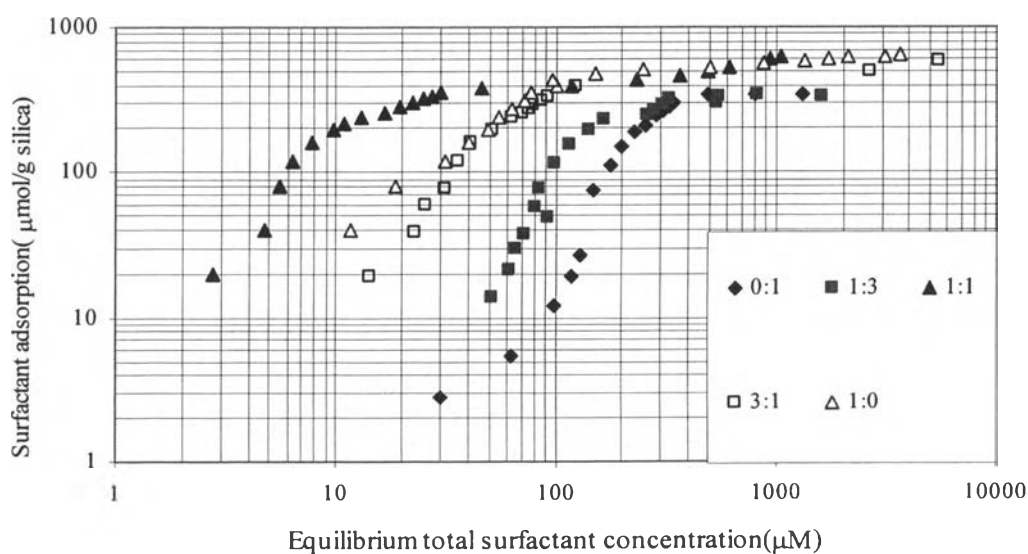


Figure 4.1 Adsorption isotherm of surfactants onto silica Hi-Sil[®] 255 at pH 8 and 30 °C at various CTAB : Triton X-100 molar ratios.

shows the highest of the maximum adsorption 600 μmol of CTAB per g of silica. The maximum total surfactant adsorption was found to decrease with decreasing molar ratio of CTAB to Triton X-100. The minimum adsorption concentration at 300 μmol of Triton X-100 per g of silica, was obtained with pure Triton X-100. Interestingly, at a molar ratio of CTAB to Triton X-100 of 1:1, the maximum adsorption of total surfactant onto the silica surface is almost as high as that of the pure CTAB system and it also gives the lowest equilibrium concentration of total surfactant shown in Figure 4.1. The results imply that the 1:1 molar ratio of CTAB : Triton X-100 provides both the best packed admicelles and micelles. The selected surfactant concentrations used to prepare the modified silica was 290, 320, 390, 510 and 600 μmol s per gram of silica for ratios of CTAB to Triton X-100, 0:1, 1:3, 1:1, 3:1 and 1:0, respectively.

4.1.2 Molar Ratios of Surfactant Adsorbed onto Silica Hi-Sil[®]255

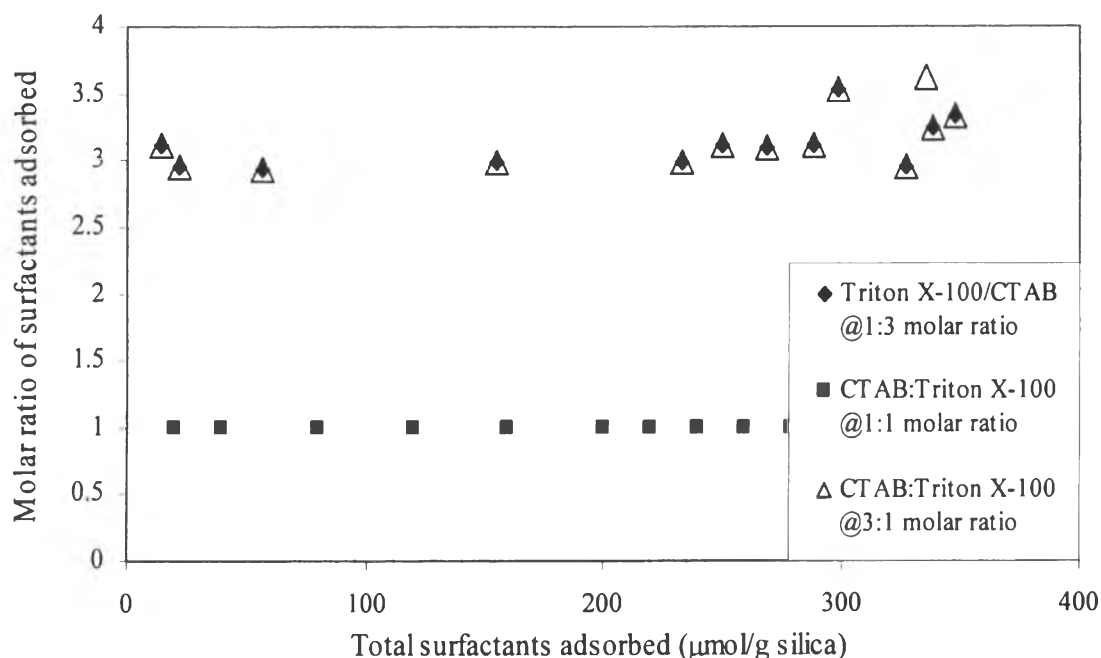


Figure 4.2 Molar ratios of surfactant adsorbed onto silica Hi-Sil[®]255 at various CTAB : Triton X-100 molar ratios and different total surfactants adsorbed.

The total surfactant concentrations before and after adsorption were measuring using a Total Organic Carbon analyzer (TOC). The total concentration of Triton X-100 was determined by a UV VIS spectrometer. Then, the molar ratio of CTAB to Triton X-100 could be calculated. It was found that the molar ratio of CTAB to Triton X-100 adsorbed on silica surface was very much the same as that of the initial ratio of mixed surfactants in the solution (Figure 4.2.).

4.1.3 Adsorption Concentration in Monolayer Region

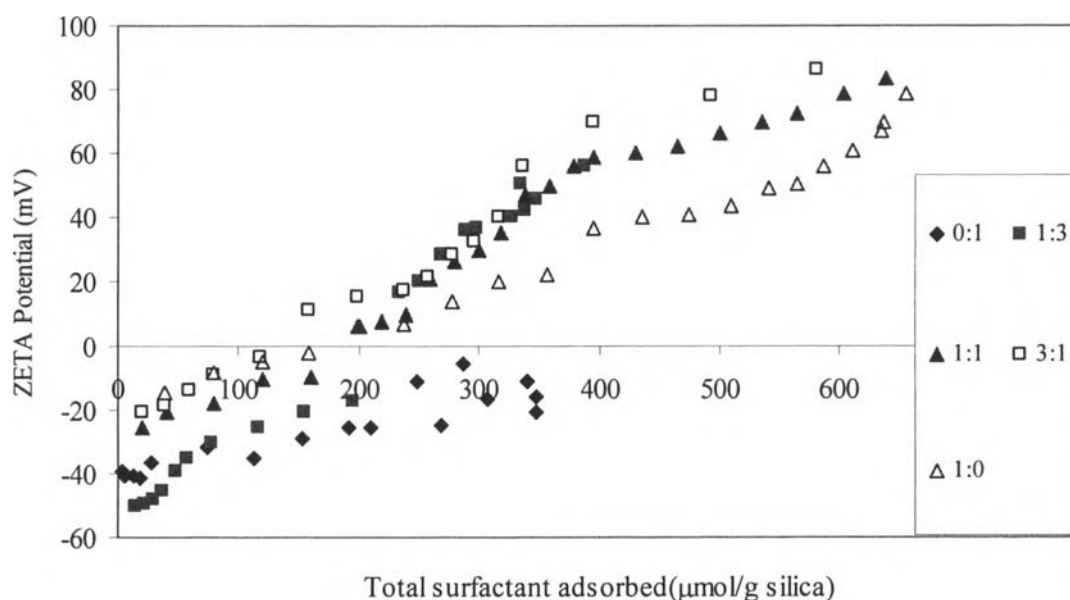


Figure 4.3 Charge on silica surface on different total surfactants adsorbed at various CTAB : Triton X-100 molar ratios.

Since it is very difficult to identify any monolayer coverage accurately from the adsorption isotherm (See Figure 4.2), the amount of total surfactants adsorbed in the monolayer structure on the silica surface (μmol per g of silica) was verified by a Zeta meter. Due to the negatively charged silica surface, the adsorption of the positive head group of CTAB on the silica surface results in the depression of the negative charges. Therefore, the neutral surface is obtained theoretically when CTAB completely covers the surface of silica in the monolayer structure. Figure 4.3 shows Zeta potential of the silica surface as a function of amount of total surfactants

adsorbed at different molar ratios of CTAB to Triton X-100. For pure CTAB, the adsorption of surfactant of 200 $\mu\text{mol/g}$ silica was obtained for the monolayer coverage. A decrease in the molar ratio of CTAB to Triton X-100 resulted in decreasing the total surfactants adsorbed for the monolayer coverage structures. For the monolayer structures at 1:3, 1:1, 3:1 and 1:0 molar ratios of CTAB to Triton X-100, the total surfactants adsorbed on the surface of silica were 240, 200, 160 and 200 μmol per g of silica, respectively. However, in the case of pure Triton X-100 as shown in Figure 4.3, the monolayer structure cannot be verified by the ZETA potential measurement because the negative surface of silica cannot be neutralized by Triton X-100 which is known as nonionic surfactant.

4.2 Surface Characterization of Modified Silicas

For the polymerization experiments, both monolayers and bilayers of surfactants adsorbed were selected to investigate their effects on the properties of the polystyrene-isoprene films formed on the silica surface at different molar ratios of CTAB to Triton X-100. For the case of the monolayer structure with any given molar ratio of CTAB to Triton X-100, the amount of total surfactants adsorbed at Zeta potential of zero obtained from Figure 4.3 was used to determine the equilibrium surfactants concentration from the adsorption isotherm plot shown in Figure 4.3.

Finally, a total amount of surfactants required is the summation of these two values to be used to prepare the feed solution. For the bilayer structure, the CMC as the equilibrium surfactants concentration and the maximum adsorption were used to calculate the total amount of surfactants, instead.

4.2.1 Morphology of Modified Silicas

The scanning electron micrographs (SEM) of the modified and unmodified silicas with both monolayer and bilayer structures at various molar ratios of CTAB to Triton X-100 are shown in Figures 4.4. All modified silica micrographs show obviously increases in the particle size compared with that of the unmodified one because of the formation of the poly-styrene-isoprene film on the silica particles as well as the agglomeration during the polymerization. Interestingly, the particle

surface became much smoother after the modification process and the modified silicas with the bilayer structures appeared much more spherical and smoother as compared to those with monolayer structures.

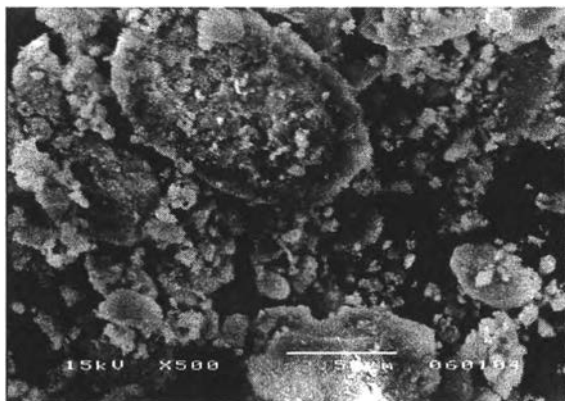


Figure 4.4 Scanning electron micrograph of unmodified silica, Hi-Sil[®]255.

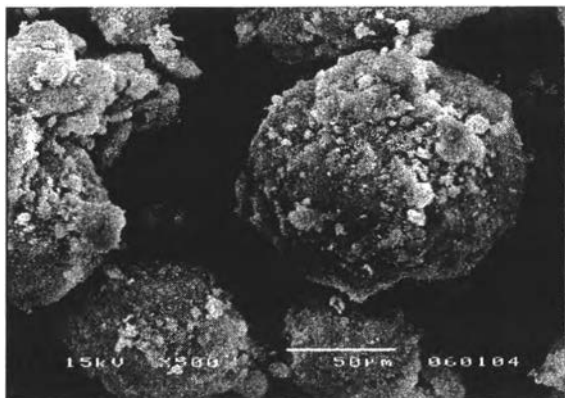


Figure 4.5 Scanning electron micrograph of the modified silica surface in monolayer with 1:3 CTAB: Triton X-100 molar ratio.

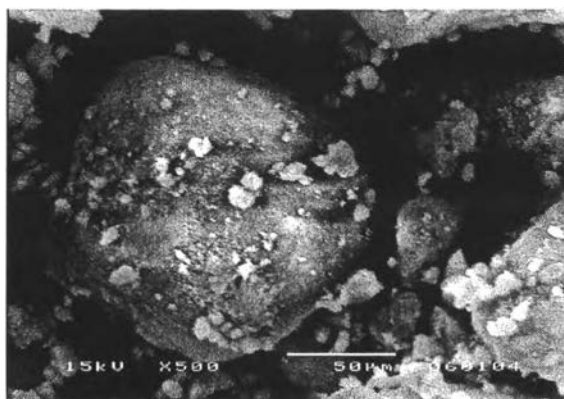


Figure 4.6 Scanning electron micrograph of the modified silica surface in monolayer with varies of 1:1 CTAB: Triton X-100 molar ratio.

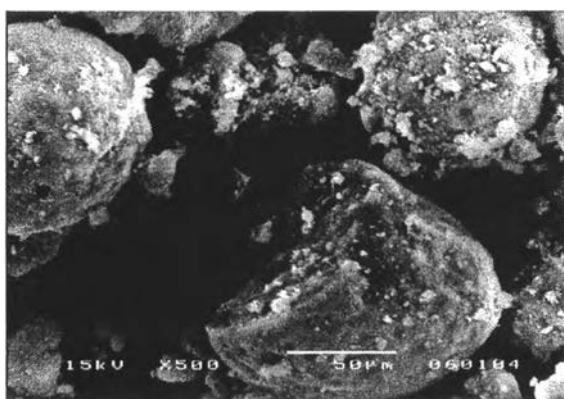


Figure 4.7 Scanning electron micrograph of the modified silica surface in monolayer with varies of 3:1 CTAB: Triton X-100 molar ratio.

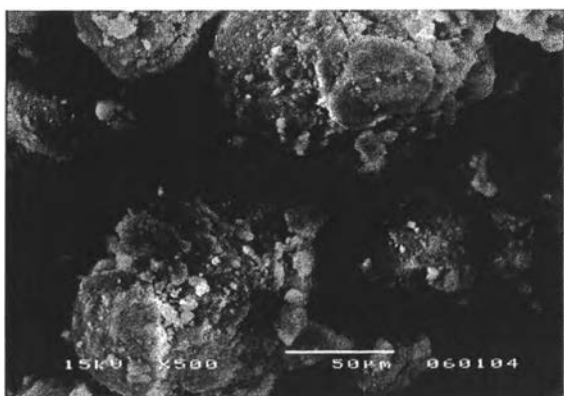


Figure 4.8 Scanning electron micrograph of the modified silica surface in monolayer with varies of 1:0 CTAB: Triton X-100 molar ratio.

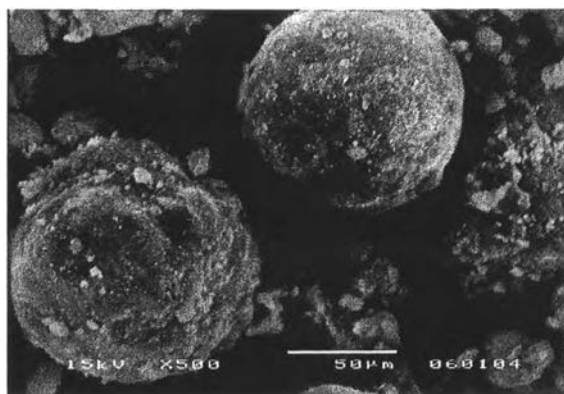


Figure 4.9 Scanning electron micrograph of the modified silica surface in bi- layer with varies of 0:1 CTAB: Triton X-100 molar ratio.

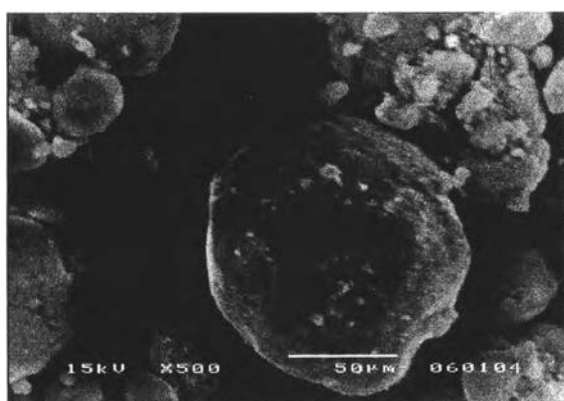


Figure 4.10 Scanning electron micrograph of the modified silica surface in bi- layer with varies of 1:3 CTAB: Triton X-100 molar ratio.

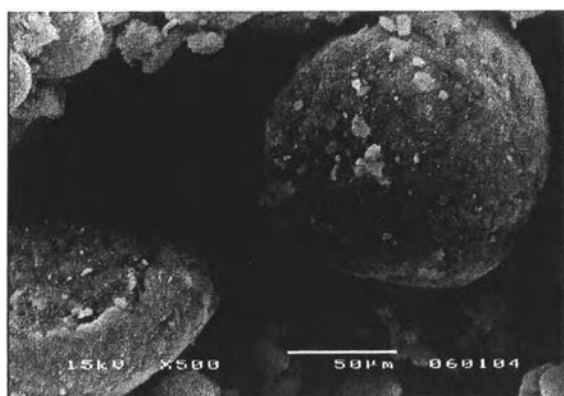


Figure 4.11 Scanning electron micrograph of the modified silica surface in bi- layer with varies of 1:1 CTAB: Triton X-100 molar ratio.

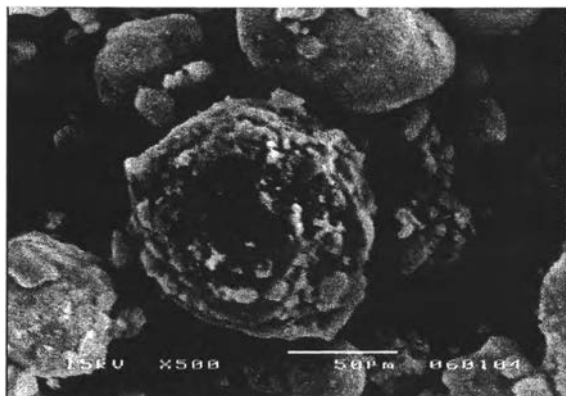


Figure 4.12 Scanning electron micrograph of the modified silica surface in bi-layer with varies of 3:1 CTAB: Triton X-100 molar ratio.

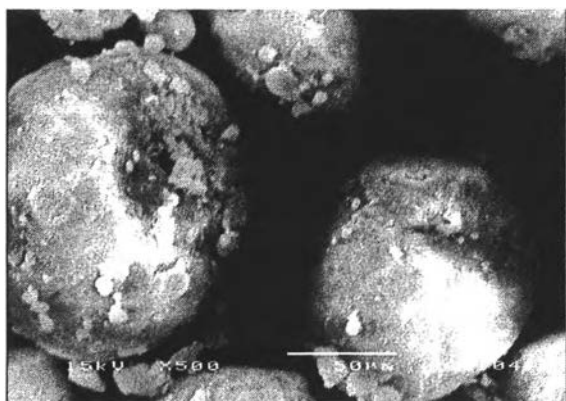


Figure 4.13 Scanning electron micrograph of the modified silica surface in bi-layer with varies of 1:0 CTAB: Triton X-100 molar ratio.

4.2.2 BET Surface Area

The surface areas of modified and unmodified silicas were determined by a BET surface area analyzer. The silica surface area is reduced significantly after the modification as shown in Figure 4.5. The modified silica surface with the bilayer structure had slightly lower surface area than that with the monolayer structure. For either monolayer or bilayer structure for the modification, the surface area of the modified silica does not depend on the molar ratio of CTAB to Triton X-100 dedicating the amount of poly(styrene-isoprene) may be the same.

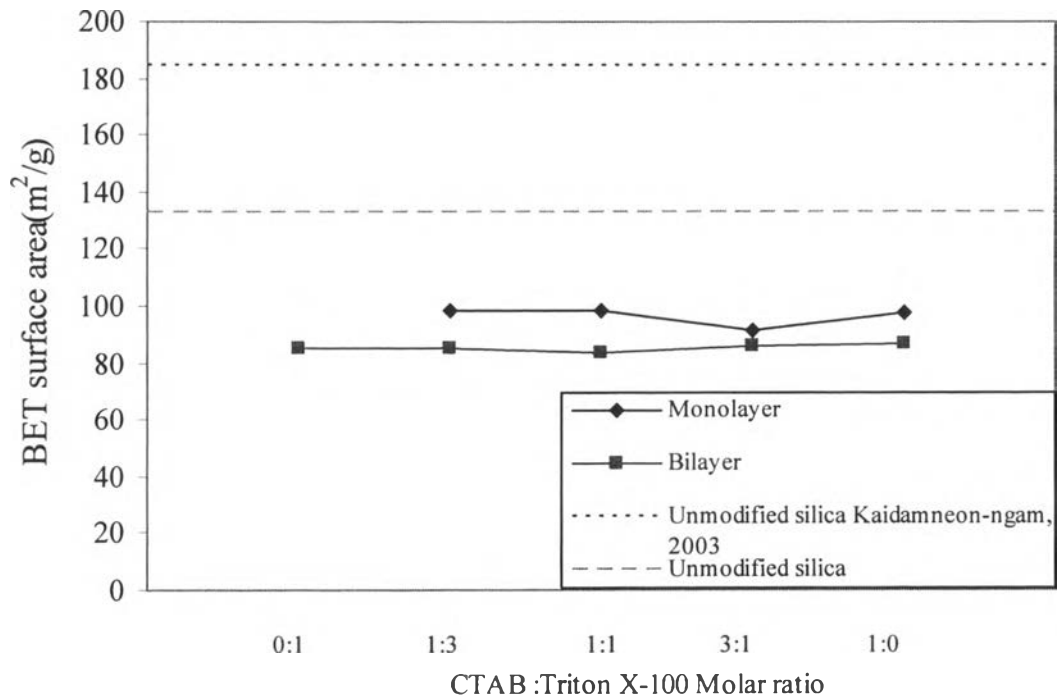


Figure 4.14 BET surface areas of modified and unmodified silicas.

4.2.3 Mean Agglomerate Particle Size

An increase in the mean agglomerate particle size of the modified silicas may simply be attributed to the subsequent polymerization step to form the organic polymer-layer on the silica surface. Figure 4.15 shows the effect of the molar ratio of CTAB to Triton X-100 on the mean agglomerate particle size silica after the modification. An increase in the mean agglomerate particle size of all modified silicas may be due to the development of polymer bridges between silica particles (Chaisirimahamorakot, 2001). For any given molar ratio of CTAB to Triton X-100, the mean agglomerate particle size of the modified silica with the bilayer structure was larger than that with the monolayer structure.

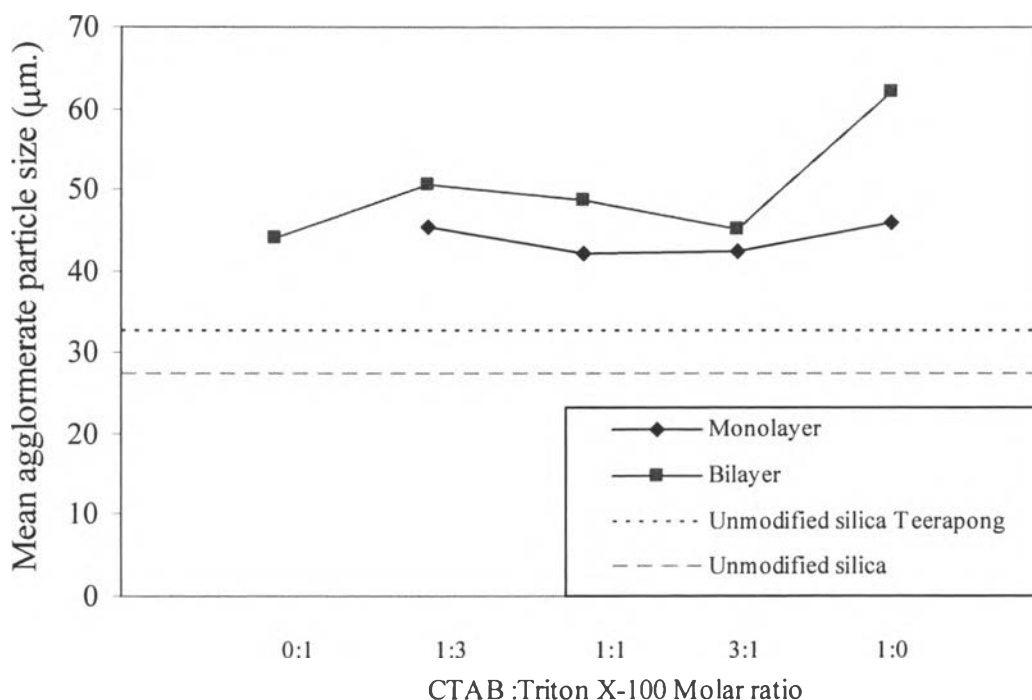


Figure 4.15 Mean agglomerate particle size of modified and unmodified silicas at different molar ratios of CTAB : Triton X-100.

4.2.4 The Verification of the Existence of Poly(styrene-isoprene)

All samples were examined by TGA in order to verify the existence of poly(styrene-isoprene) forming on the silica surfaces. The water loss from the unmodified silica below 150°C is shown in Figure 4.16. Figure 4.17 shows the decomposition of pure CTAB between 200 to 300°C. Figure 4.18 shows the decomposition of Triton X-100 between 400 to 450°C. Interestingly, the decomposition of CTAB adsorbed onto the silica occurs in two steps; the first step from 170 to 300°C and the second step was 300 to 450°C (Figure 4.19.). The second peak of the weight loss may result from the stronger bonding between silica and CTAB molecules.

Samples of modified silicas were dissolved with THF to extract the poly(styrene-isoprene) onto silica for TGA analysis. The decomposition of the poly(styrene-isoprene) sample appears in the temperature range from 350 to 480°C as shown in Figure 4.20. Poly(styrene-isoprene) was decomposed from the admicellar polymerization modified silica as shown in Figure 4.21. Figure 4.19 evidently shows

the decomposition of CTAB taking place between 200 to 280°C and 300 to 450°C while the polymer started from 280 to 400°C. The TGA results of all modified silicas with both monolayer and bilayer structured at different molar ratios of CTAB to Triton X-100 are shown in Figures 4.22. – 4.30.

All modified silicas had two dominant peaks at two temperature range of 200°-280°C and 350°-450°C. The first peak corresponds to the decomposition of CTAB while the second peak exhibits the decomposition of CTAB, poly(styrene-isoprene) and Triton X-100.

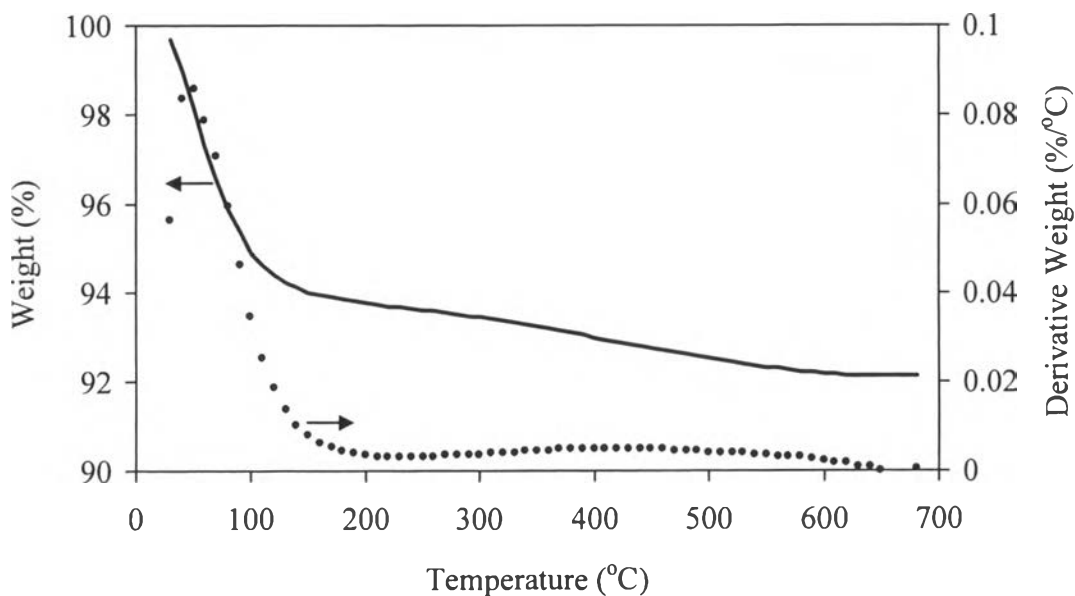


Figure 4.16 TGA results of unmodified silica Hi-Sil[®]255.

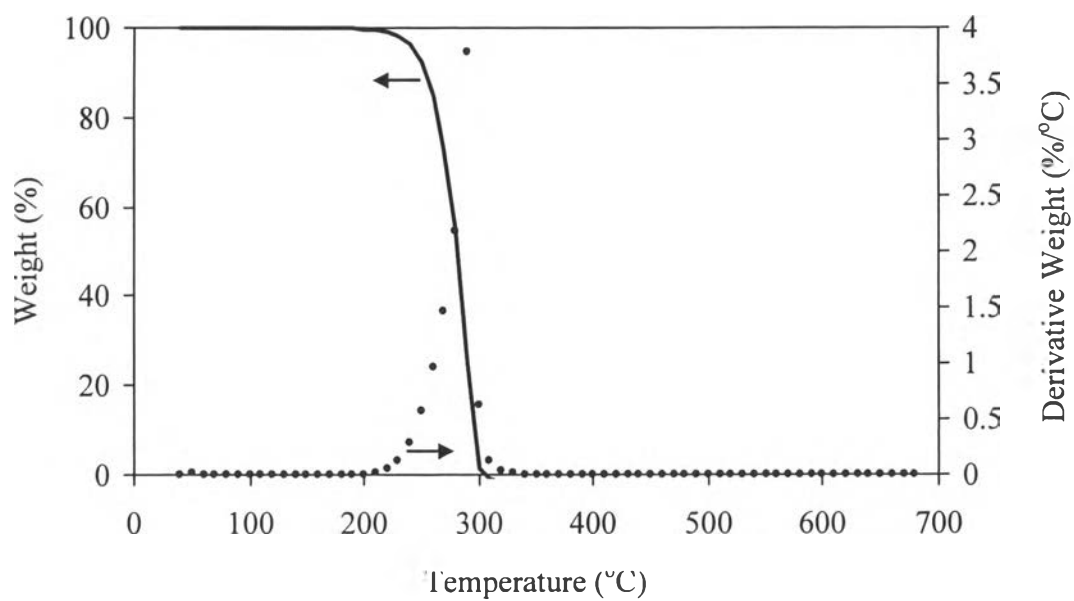


Figure 4.17 TGA results of CTAB.

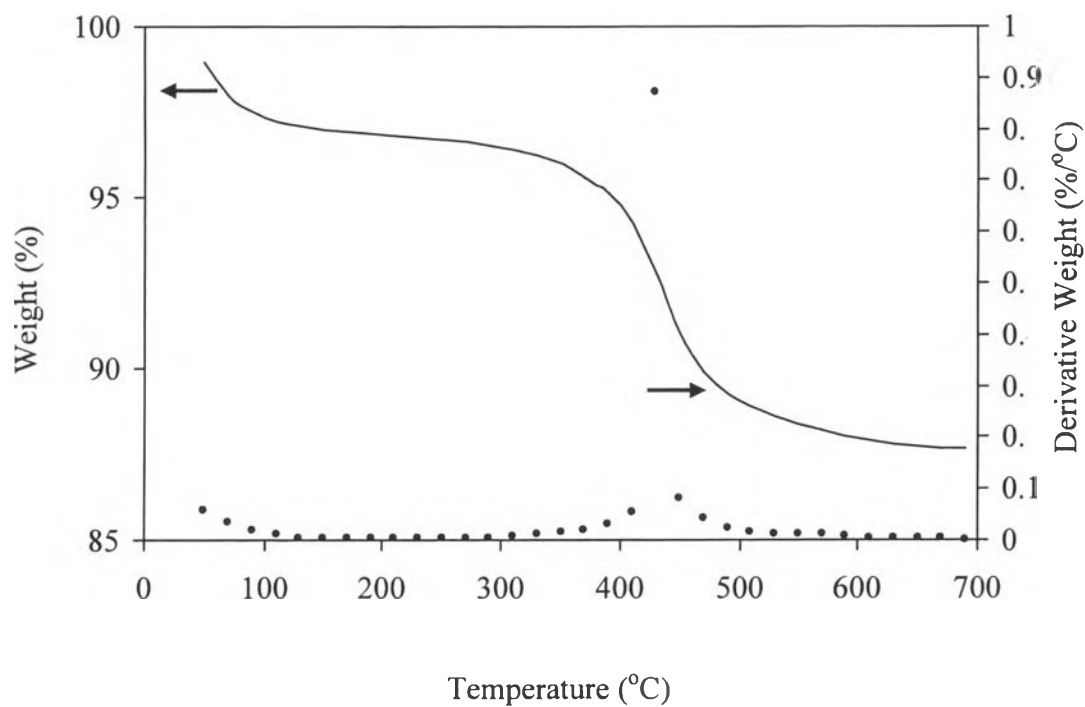


Figure 4.18 TGA results of Triton X-100.

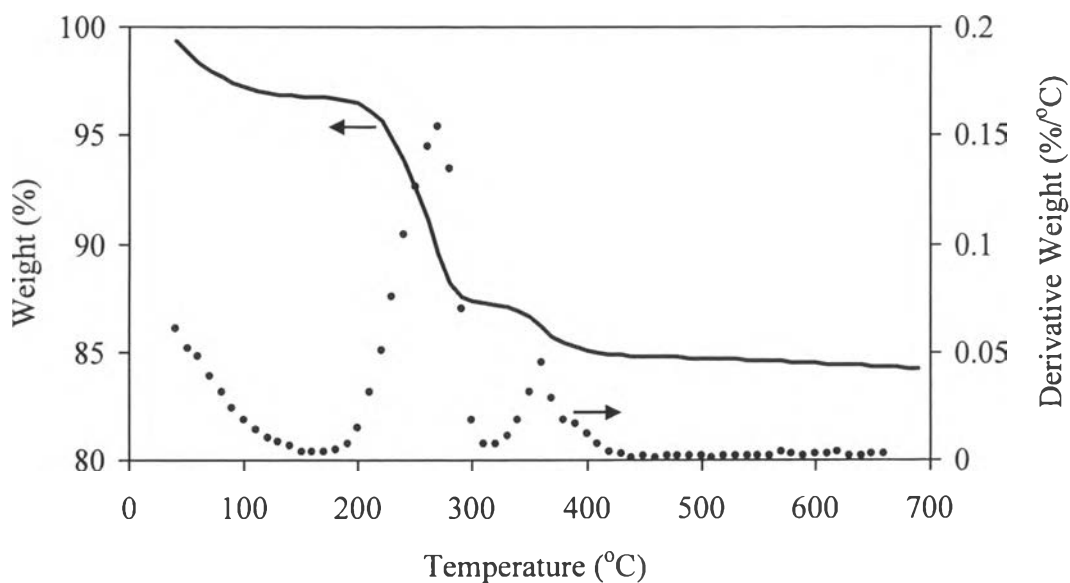


Figure 4.19 TGA results of silica Hi-Sil[®]255 adsorbed with CTAB (Chaisirimahamorakot, 2001).

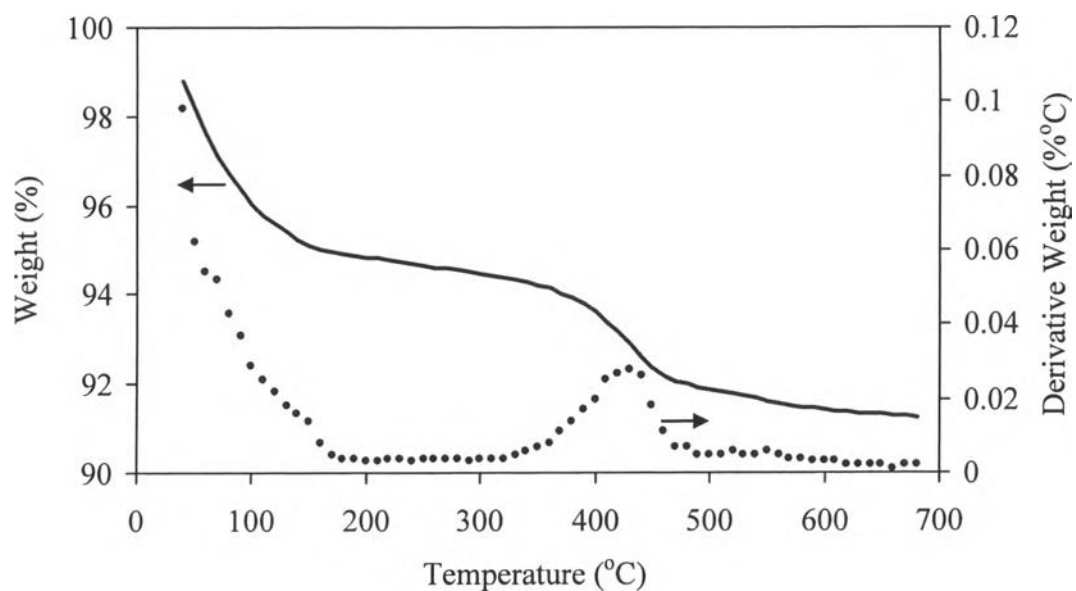


Figure 4.20 TGA results of silica Hi-Sil[®]255 adsorbed with poly(styrene-isoprene) extracted from the modified silica (Chaisirimahamorakot, 2001).

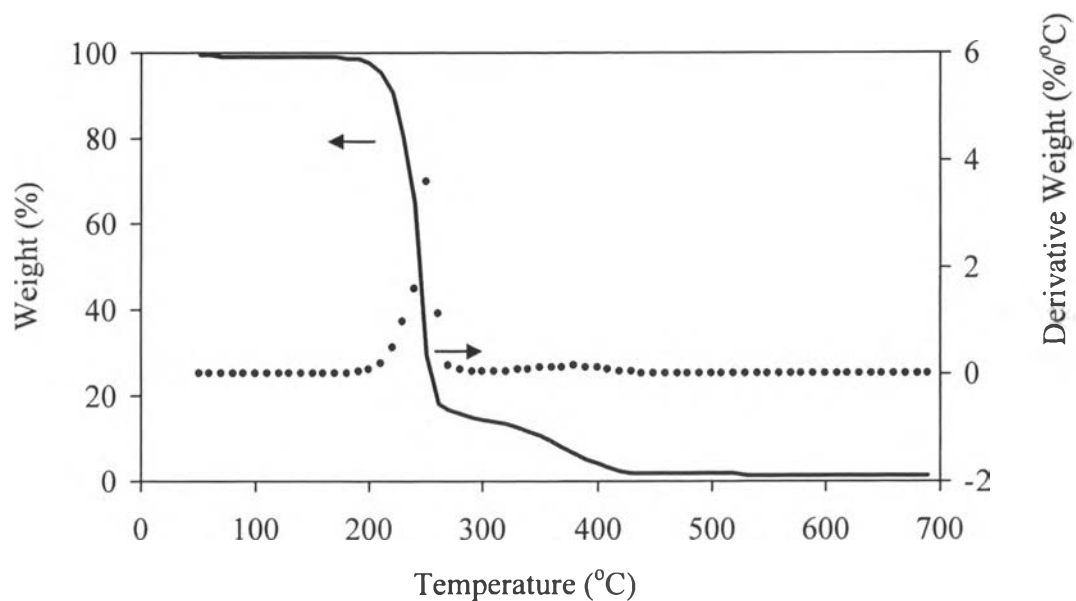


Figure 4.21 TGA results of poly(styrene-isoprene) polymerized in CTAB (Chaisirimahamorakot, 2001).

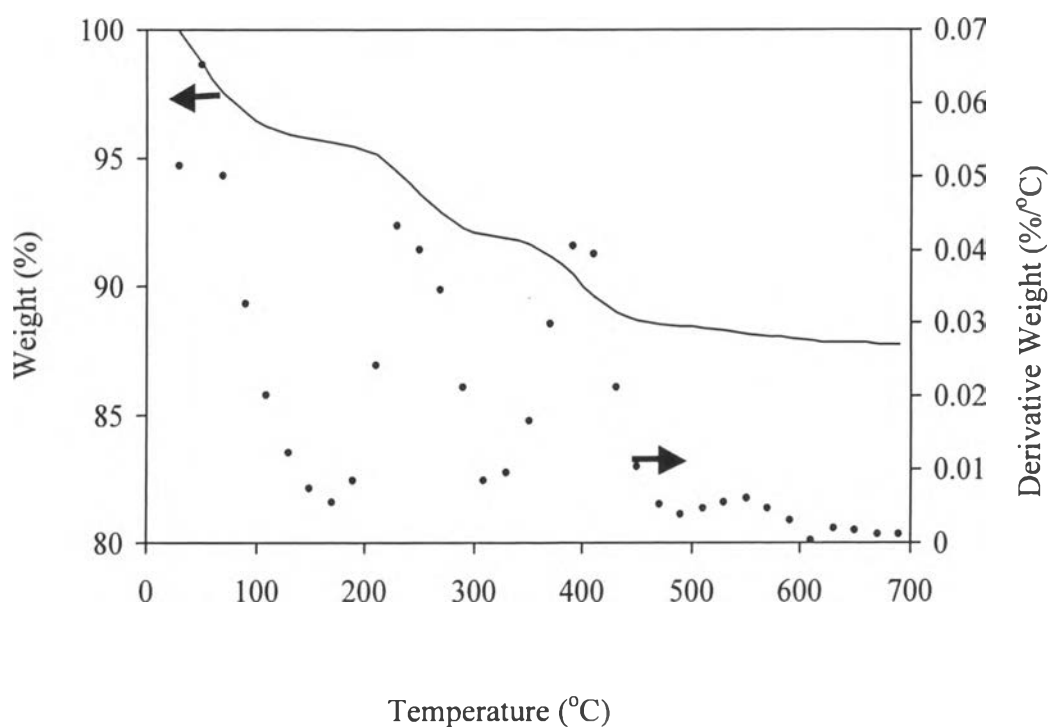


Figure 4.22 TGA results of the modified silica surface in monolayer with varies of 1:0 CTAB: Triton X-100 molar ratio.

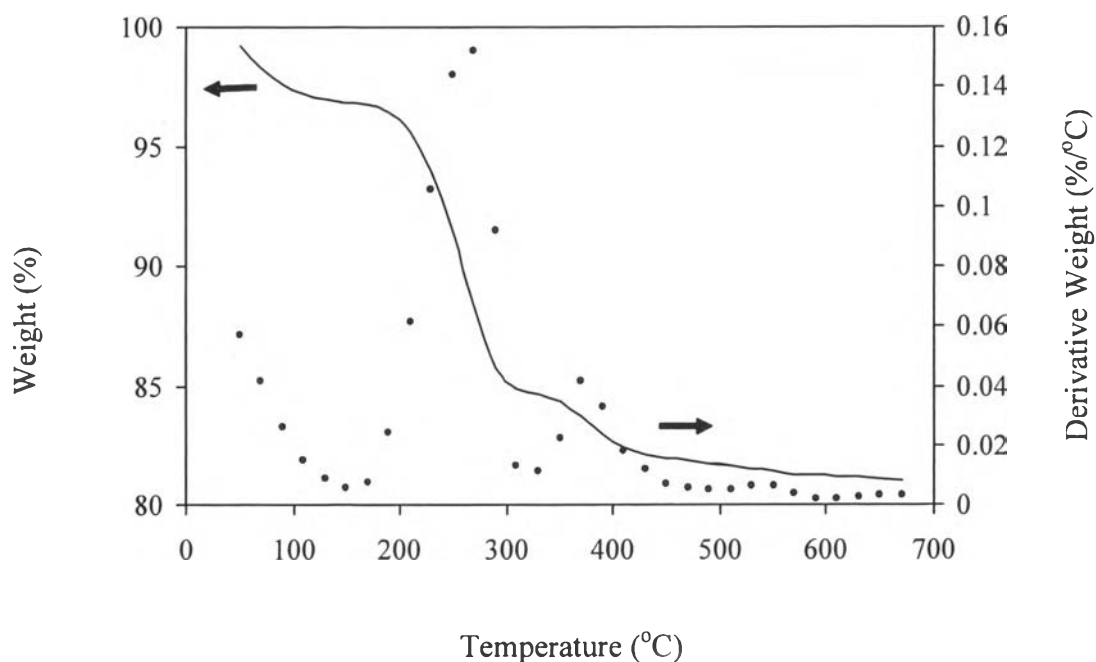


Figure 4.23 TGA results of the modified silica surface in bilayer with varies of 1:0 CTAB: Triton X-100 molar ratio.

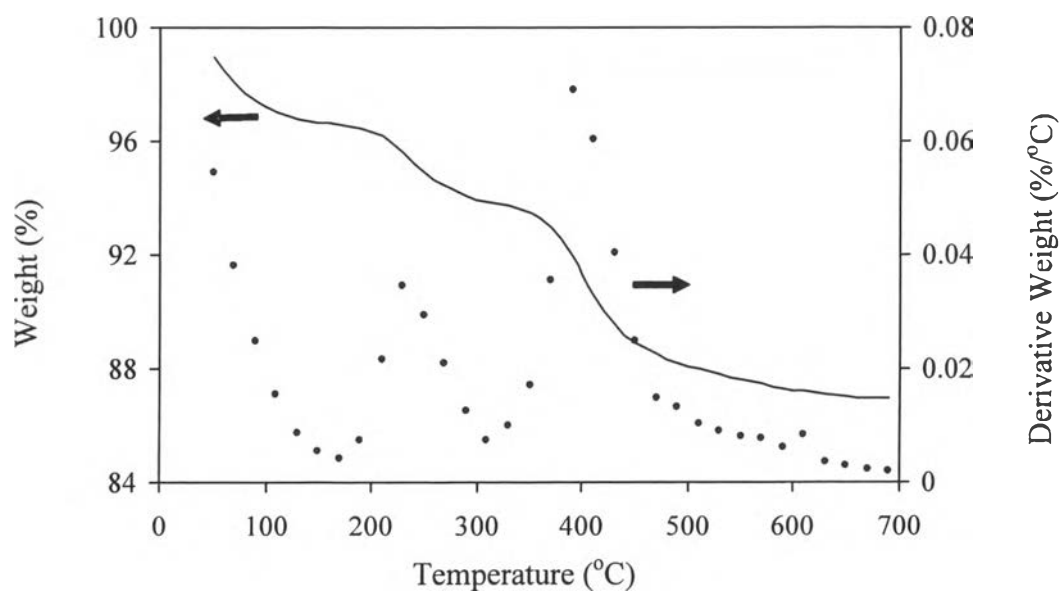


Figure 4.24 TGA results of the modified silica surface in monolayer with varies of 1:3 CTAB: Triton X-100 molar ratio.

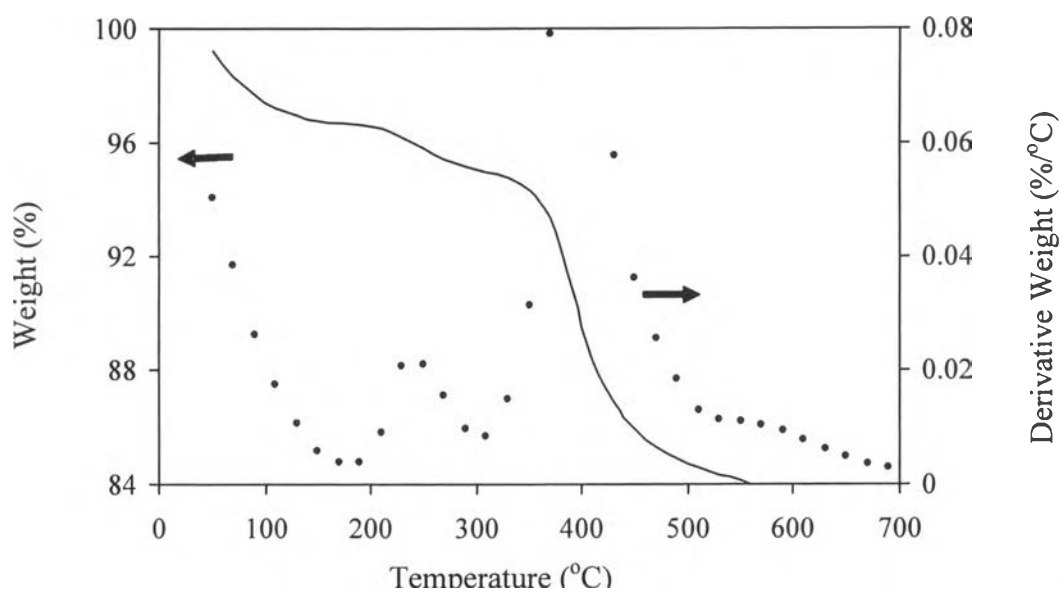


Figure 4.25 TGA results of the modified silica surface in bilayer with varies of 1:3 CTAB: Triton X-100 molar ratio.

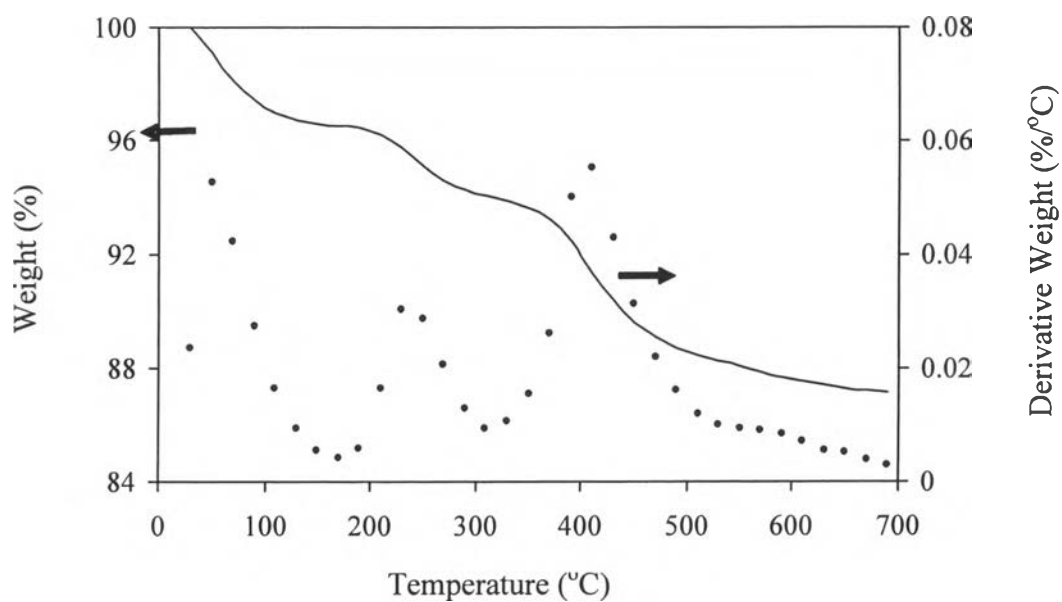


Figure 4.26 TGA results of the modified silica surface in monolayer with varies of 1:1 CTAB: Triton X-100 molar ratio.

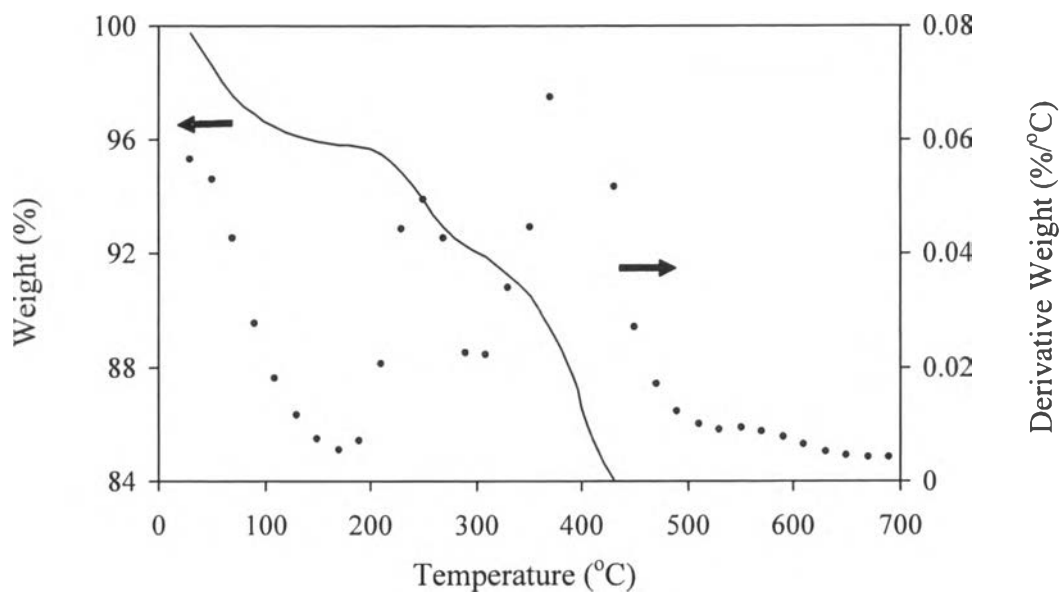


Figure 4.27 TGA results of the modified silica surface in bilayer with varies of 1:1 CTAB: Triton X-100 molar ratio.

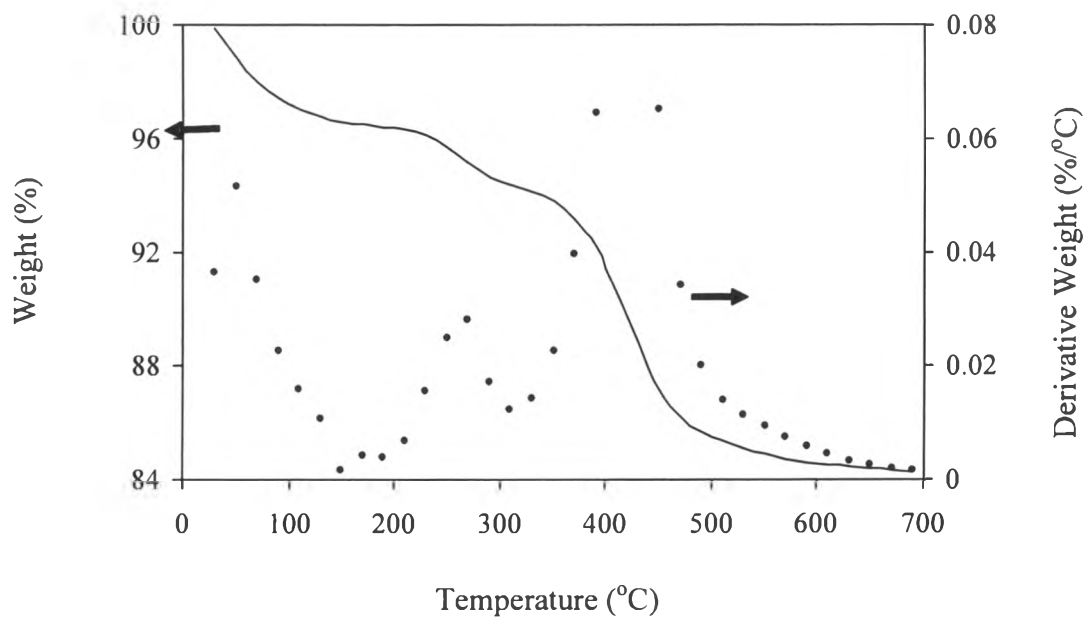


Figure 4.28 TGA results of the modified silica surface in monolayer with varies of 3:1 CTAB: Triton X-100 molar ratio.

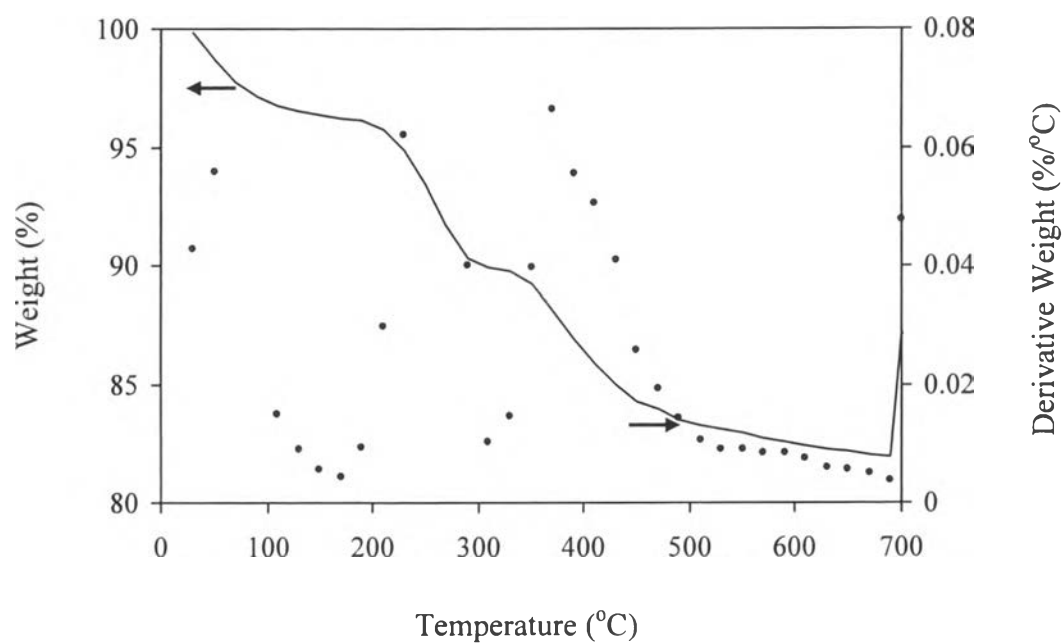


Figure 4.29 TGA results of the modified silica surface in bilayer with varies of 3:1 CTAB: Triton X-100 molar ratio.

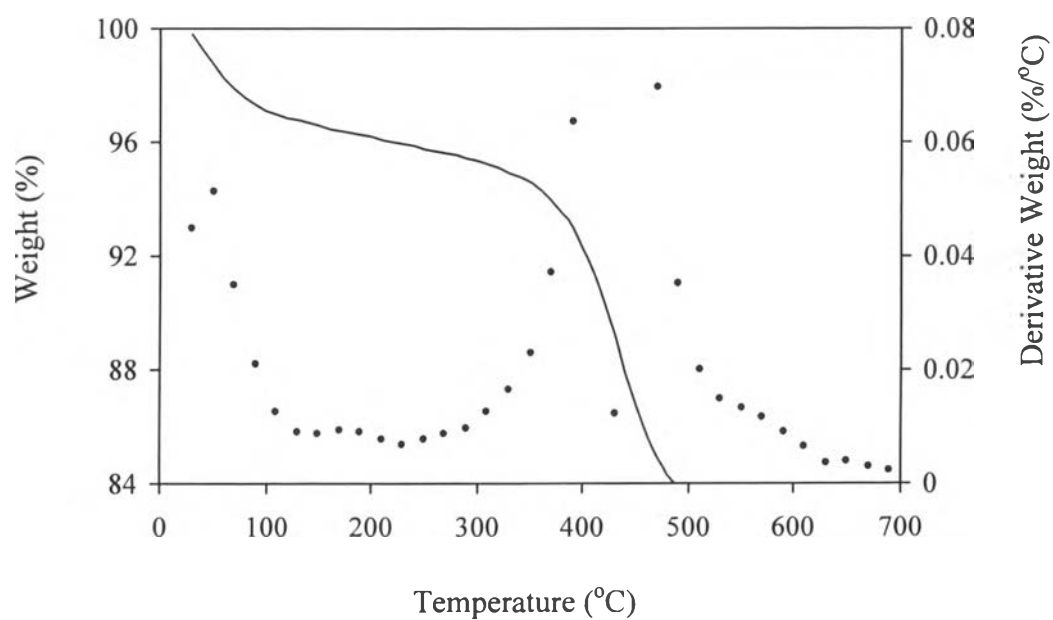


Figure 4.30 TGA results of the modified silica surface in bilayer with varies of 0:1 CTAB: Triton X-100 molar ratio.

4.3 Rubber Compound Physical Properties

The effects of the molar ratio of CTAB to Triton X-100 as well as the surfactant adsorption structures on rubber compound physical properties were investigated systematically. As can be seen from Figure 4.31, the adsorption structures of mixed surfactants exhibit in significant effect on the cure time. Both monolayer and bilayer structures of various molar ratios of CTAB to Triton X-100 from 1:3 to 3:1 gave the cure time of about 5.3 min which is in the same range as the previous results with the bilayer structure (Kaidamneon-ngam, 2003 ; Thammathadanukul, 1996)

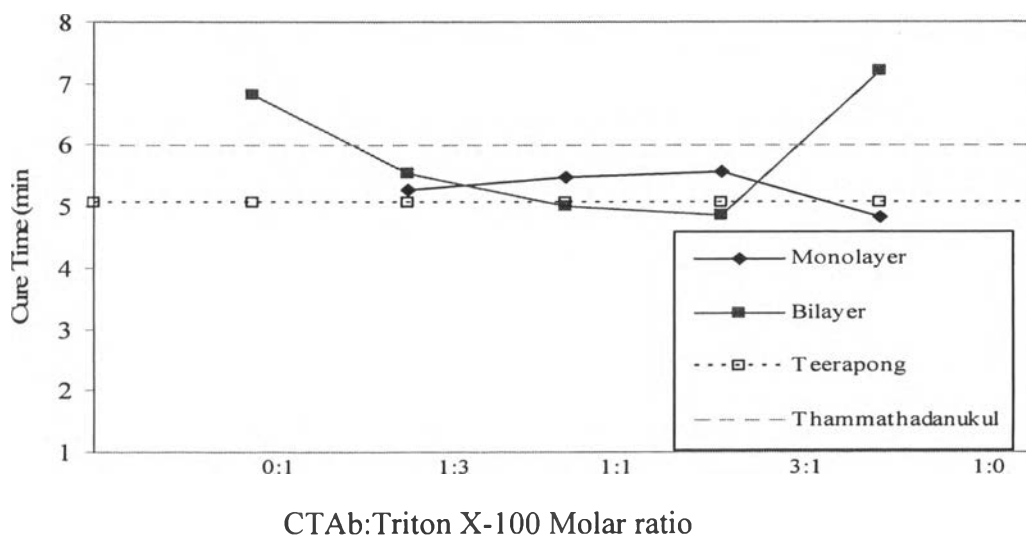


Figure 4.31 Cure time of modified silicas prepared with different CTAB to Triton X-100 molar ratios and different adsorption structures.

Several physical properties of rubber compounding with the modified silicas such as compression set, resilience, tear, hardness and abrasion, are shown in Figures 4.32 - 4.40. The results showed that various molar ratios of CTAB to Triton X-100 had significant effect on most physical properties except the resilience property which was the best with pure CTAB (Figure 4.35). Type of surfactant adsorption structures on the silica surface affected the physical properties of the rubber compound, for example, the bilayer structure yielded better compression set and abrasion than those derived from the monolayer structure. On the other hand, the

hardness of composite rubber modified by the monolayer structure is better than that of the bilayer structure silica, as shown in Figures 4.32 - 4.34.

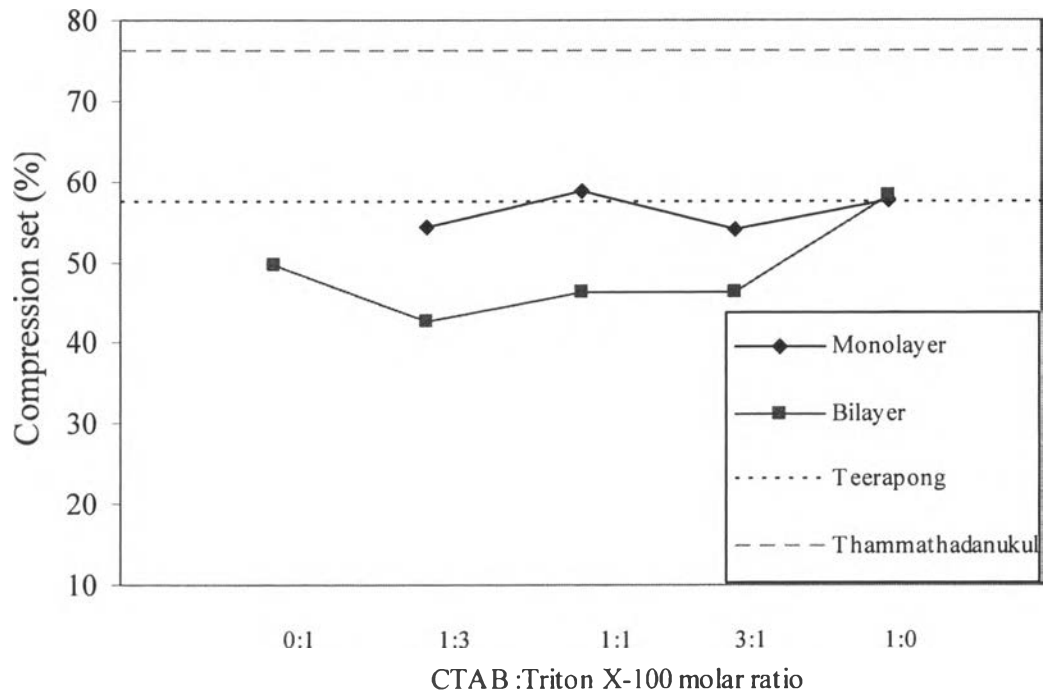


Figure 4.32 Compression set of rubber compounds with different modified silicas.

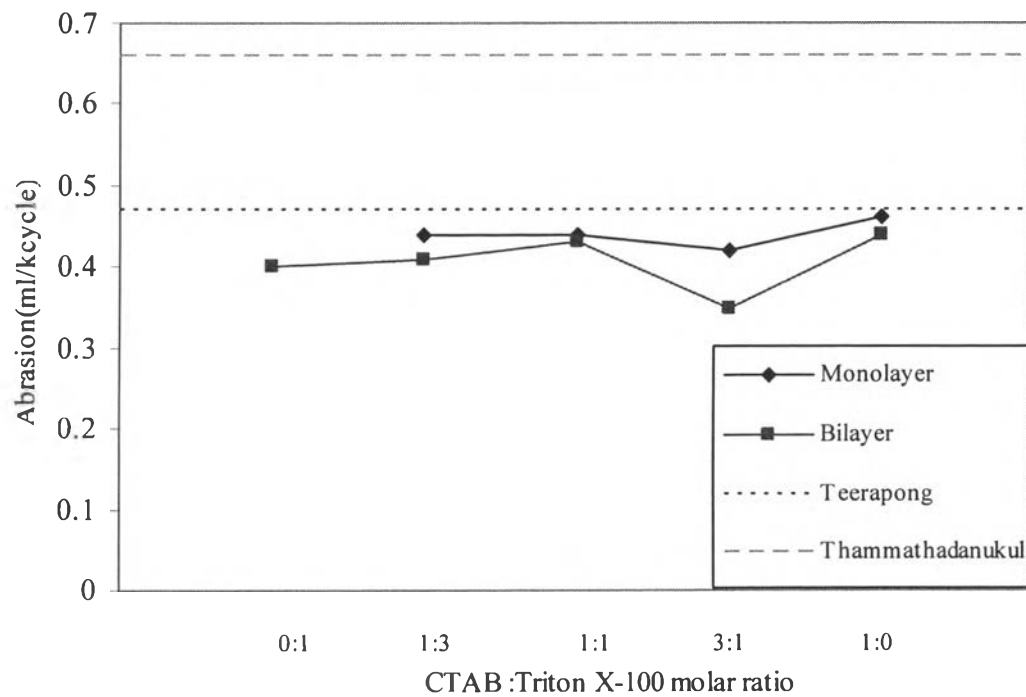


Figure 4.33 Abrasion set of rubber compounds with different modified silicas.

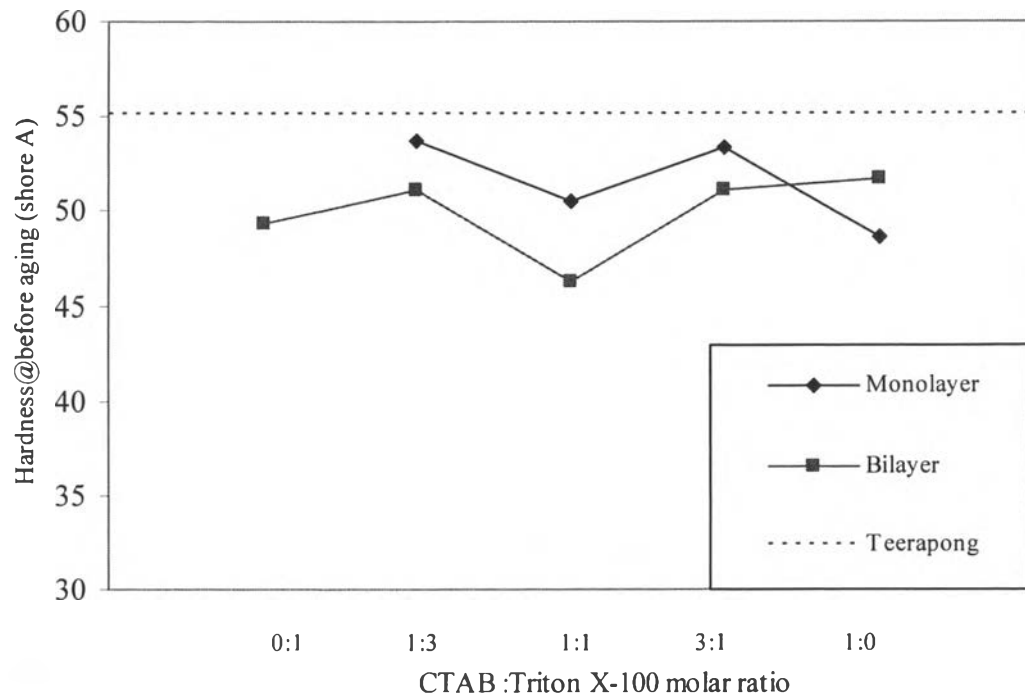


Figure 4.34 Hardness@before aging of rubber compounds with different modified silicas.

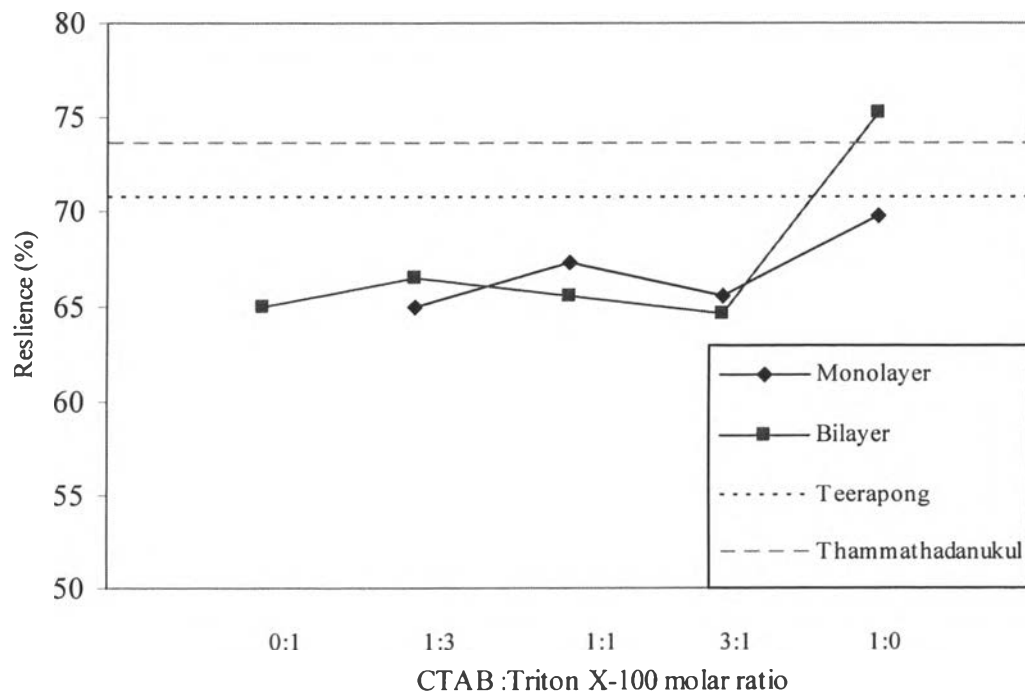


Figure 4.35 Resilience of rubber compounds with different modified silicas.

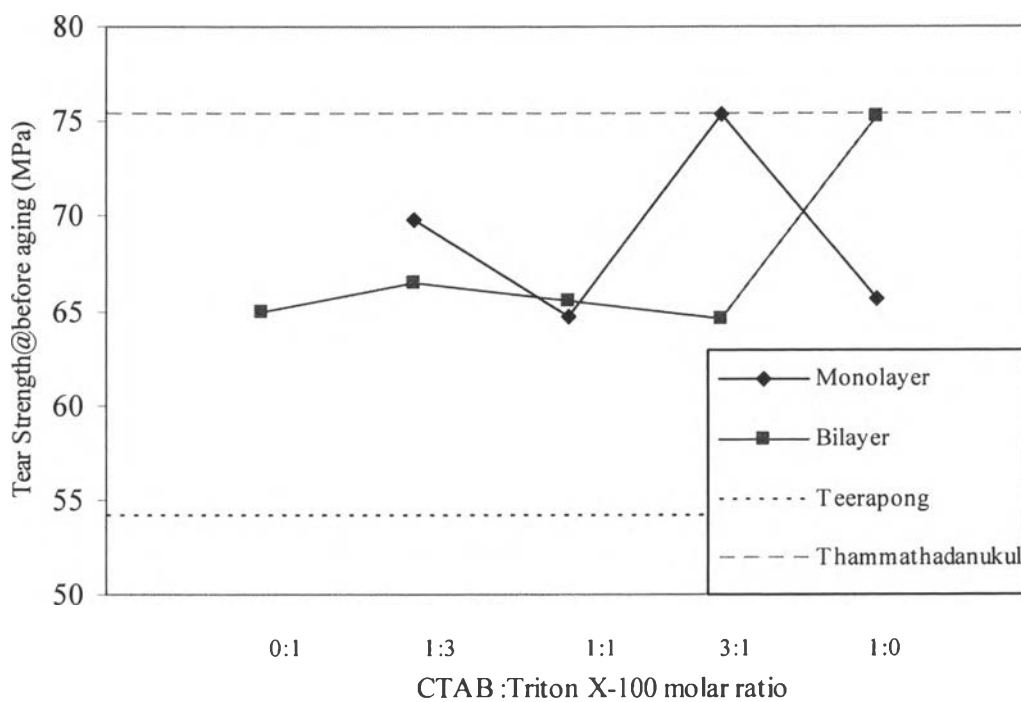


Figure 4.36 Tear strength@before aging of rubber compounds with different modified silicas.

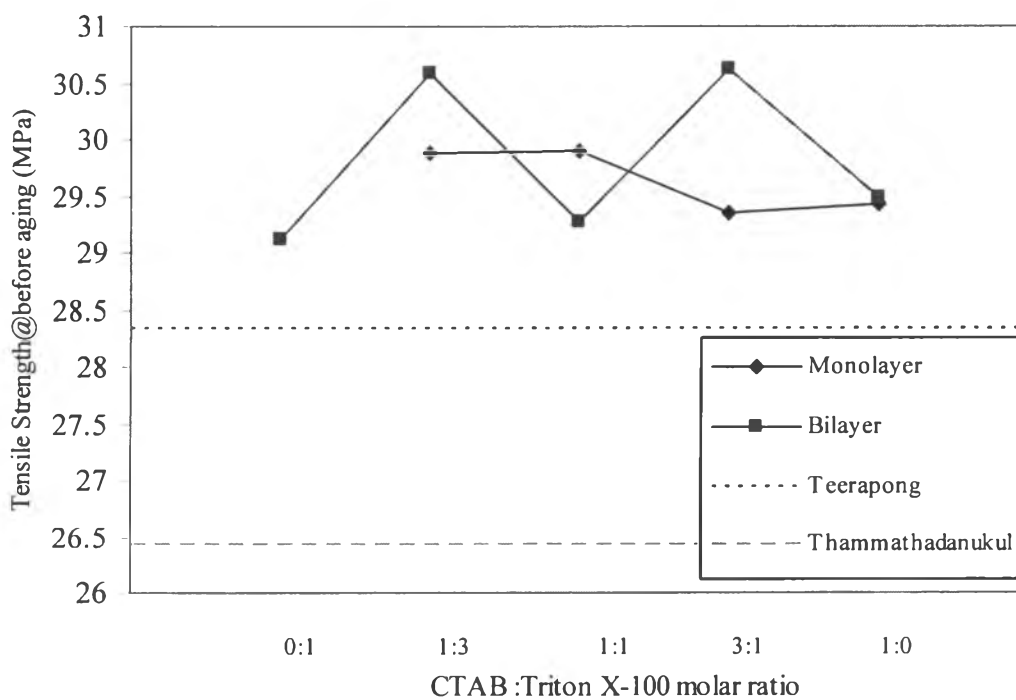


Figure 4.37 Tensile strength@before aging of rubber compounds with different modified silicas.

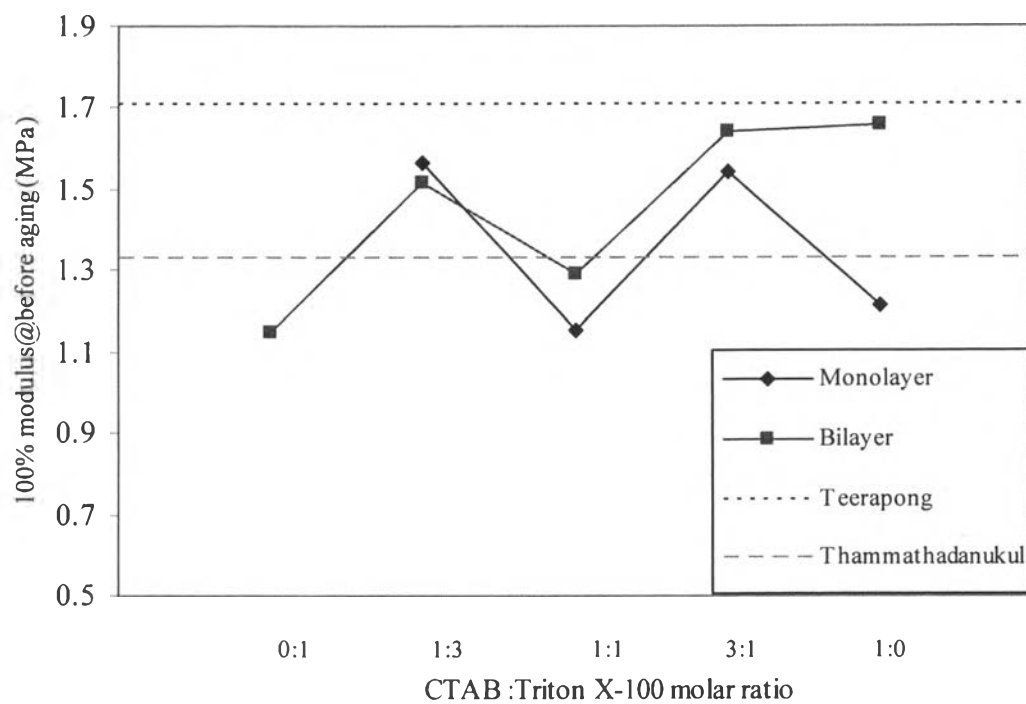


Figure 4.38 100% modulus@before aging of rubber compounds with different modified silicas.

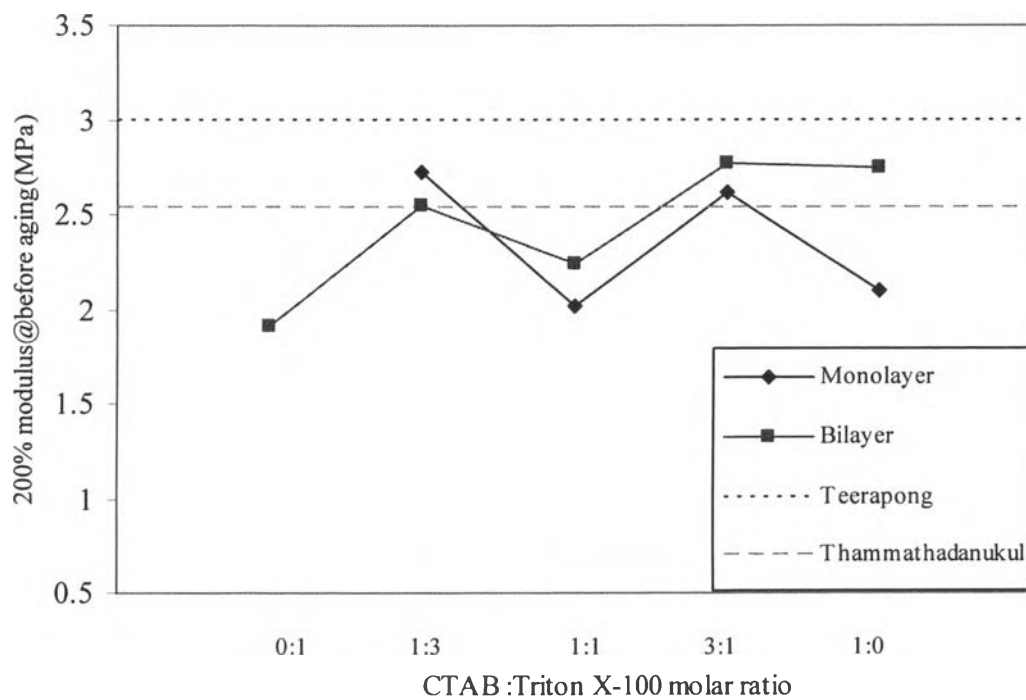


Figure 4.39 200% modulus@before aging of rubber compounds with different modified silicas.

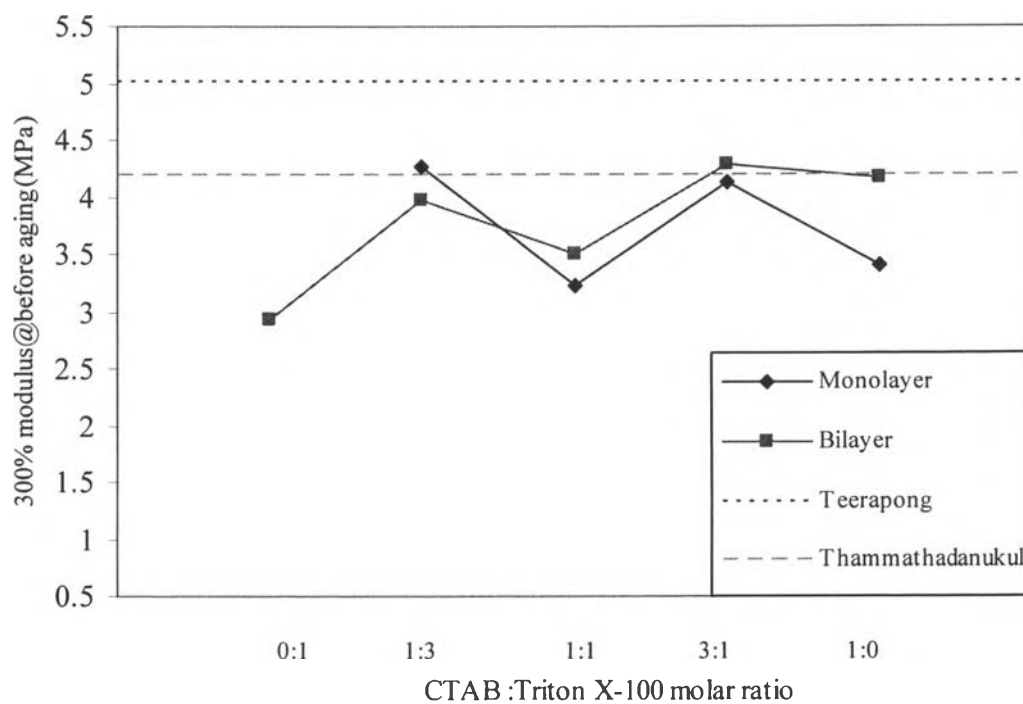


Figure 4.40 300% modulus@before aging of rubber compounds with different modified silicas.

All testing physical properties of rubber compounds using different modified silica are summarized in Table 4.1.

The present results of all testing physical properties of rubber compounds are also compared to the previous results as shown in Table 4.2.

Table 4.1 Rubber compound physical properties using different modified silicas

Property	B01	M13	B13	M11	B11	M31	B31	M10	B10
100%Modulus @before aging (MPa)	1.15	1.57	1.52	1.15	1.29	1.54	1.67	1.22	1.66
100%Modulus @after aging (MPa)	2.17	2.15	2.01	1.92	1.98	2.12	2.01	1.91	1.85
200%Modulus @before aging (MPa)	1.92	2.72	2.55	2.02	2.24	2.62	2.77	2.10	2.75
200%Modulus @after aging (MPa)	3.76	3.96	3.56	3.35	3.60	3.85	3.41	3.48	3.17
300%Modulus @before aging (MPa)	2.93	4.27	3.96	3.22	3.45	4.13	4.28	3.40	4.16
300%Modulus @after aging (MPa)	5.84	6.27	5.39	5.63	5.78	6.07	5.29	5.45	4.80
Tensile Strength @before aging	29.12	29.88	30.59	29.91	29.27	29.35	30.63	30.69	29.49
Tensile Strength @after aging (MPa)	27.90	28.00	25.70	26.90	27.30	26.20	25.60	25.60	27.70
Tear Strength @before aging (N/mm)	69.85	69.82	68.80	64.74	49.81	75.38	50.62	65.60	52.80
Tear Strength @after aging (N/mm)	48.56	57.60	49.20	54.61	51.81	54.98	46.09	55.26	51.26
Abrasion (ml/kcycle)	0.40	0.44	0.41	0.44	0.43	0.42	0.35	0.46	0.44
Resilience (%)	65.00	65.37	66.50	67.03	65.53	63.43	64.53	69.20	75.30
Compression set (%)	49.63	54.48	42.67	58.80	46.30	53.98	46.17	57.59	58.13
Hardness @before aging (shore A)	49.30	53.73	51.07	50.50	46.23	53.37	51.10	51.73	51.73
Hardness @after aging (shore A)	57.83	59.57	57.40	57.93	52.90	59.87	57.43	57.90	57.03

01,13,11,31,10 : ratio of surfactants, CTAB:Triton X-100 molar ratio

M,B : type of adsorption structure, monolayer, bi-layer, respectively

Table 4.2 Rubber compound physical properties using different modified silicas obtained from the present study compared to the modified silicas of the previous batch system with bilayer structure(Thammathadanukul *et al.*, 1996) and previous CSTR system with bilayer structure (Kaidamneon-ngam *et al.*, 2003)

Property	B10*	Batch**	B01	M13	B13	M11	B11	M31	B31	M10	B10
Cure time (min)	5.07	5.98	6.81	5.28	5.55	5.49	4.87	5.58	5.00	4.82	7.19
100%Modulus @before aging (MPa)	1.77	1.33	1.15	1.57	1.52	1.15	1.29	1.54	1.67	1.22	1.66
200%Modulus @before aging (MPa)	3.02	2.54	1.92	2.72	2.55	2.02	2.24	2.62	2.77	2.10	2.75
300%Modulus @before aging (MPa)	5.01	4.19	2.93	4.27	3.96	3.22	3.45	4.13	4.28	3.40	4.16
Tensile Strength @before aging	28.33	26.43	29.12	29.88	30.59	29.91	29.27	29.35	30.63	30.69	29.49
Tear Strength @before aging	54.12	75.37	69.85	69.82	68.8	64.74	49.81	75.38	50.62	65.6	52.8
Abrasion (ml/kcycle)	0.45	0.66	0.40	0.44	0.41	0.44	0.43	0.42	0.35	0.46	0.44
Resilience (%)	70.80	73.6	65.00	65.37	66.5	67.03	65.53	63.43	64.53	69.2	75.30
Compression set (%)	57.46	76.02	49.63	54.48	42.67	58.8	46.3	53.98	46.17	57.59	58.13

01, 13, 11, 31, 10 : ratio of surfactants, CTAB:Triton X-100 molar ratio

M, B: type of adsorption structures, monolayer, bilayer, respectively

* (Kaidamneon-ngam *et al.*, 2003)

** (Thammathadanukul *et al.*, 1996)

Table 4.3 Qualitative summary of rubber physical properties using different modified silicas as compared to the unmodified silica

Property	B01	M13	B13	M11	B11	M31	B31	M10	B10
100%Modulus @before aging (MPa)	2	7	5	1	4	6	9	3	8
100%Modulus @after aging (MPa)	9	8	5.5	3	4	7	5.5	2	1
200%Modulus @before aging (MPa)	1	7	5	2	4	6	9	3	8
200%Modulus @after aging (MPa)	7	9	5	2	6	8	3	4	1
300%Modulus @before aging (MPa)	1	8	5	2	4	6	9	3	7
300%Modulus @after aging (MPa)	7	9	3	5	6	8	2	4	1
Tensile Strength @before aging (MPa)	1	5	7	6	2	3	8	9	4
Tensile Strength @after aging (MPa)	8	9	3	5	6	4	1.5	1.5	7
Tear Strength @before aging (N/mm)	8	7	6	4	1	9	2	5	3
Tear Strength @after aging (N/mm)	2	9	3	6	5	7	1	8	4
Abrasion (ml/kcycle)	8	3	7	3	5	6	9	1	3
Resilience (%)	7	6	5	3	4	9	8	2	1
Compression set (%)	6	4	9	1	7	5	8	3	2
Hardness @before aging (shore A)	2	9	4	3	1	8	5	7	6.5
Hardness @after aging (shore A)	5	8	3	7	1	9	4	6	2
Total score	74	108	75.5	53	60	97	84	61.5	58.5

01,13,11,31,10 : ratio of surfactants, CTAB:Triton X-100 molar ratio

M,B : type of adsorption structures, monolayer, bi-layer, respectively

There are many properties, which has an important effect on the overall performance of modified rubber. For example, the tensile modulus, which represent how rigidity of rubber are, the higher the modulus, the better rigidity. The tear strength is the maximum force required to rip a rubber product. The tensile strength show how rubber resists undergoing determination. Thus, to determine the overall properties of modified rubber appropriately the scoring technique was applied. Each physical properties of modified rubber, such as tensile strength value were weighted to 9. The higher the value means the better properties. For example, the rubber which had highest modulus or tensile strength values were weighted to 9 while the worse properties were represented by value 1. after that, all scores from each properties were summarized, and the final value was used to represent overall performance of the modified rubber as show in Table 4.3.

For overall, the overall performance of rubber obtain from monolayer structure was better than those bilayer structure.

Table 4.4 Qualitative summary of surface-modified silica rubber physical properties as compared to the modified silicas of the previous batch system (Thammathadanukul *et al.* , 1996)

Property	B01	M13	B13	M11	B11	M31	B31	M10	B01
Cure time	+1	-1	0	0	-1	0	-1	-1	-1
100%Modulus @before aging	-1	+1	+1	-1	0	+1	+1	0	+1
200%Modulus @before aging	-1	+1	0	-1	-1	0	0	-1	0
300%Modulus @before aging	-1	0	0	0	-1	0	0	-1	0
Tensile Strength @before	+1	+1	+1	+1	+1	+1	+1	+1	0
Tear Strength @before aging	-1	0	0	-1	-1	0	-1	-1	-1
Abrasion	+1	+1	+1	+1	+1	+1	+1	+1	+1
Resilience	+1	+1	0	0	+1	+1	+1	0	0
Compression set	+1	+1	+1	+1	+1	+1	+1	+1	+1
Comparative Score	+1	+4	+4	-1	0	+5	+3	-2	+1

01,13,11,31,10 : ratio of surfactants, CTAB:Triton X-100 molar ratio

M,B : type of adsorption structure, monolayer, bi-layer, respectively

The effects of type of surfactants adsorption structures and the molar ratio of mixed surfactants of the modified silica on various physical properties of the rubber compound are shown qualitatively in Table 4.4, in which a “+” indicates greater than 10% improvement in the property over unmodified silica, 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.

The silica modification by the nonionic surfactant is successfully used to modify rubber compound. The properties of rubber compound modified by silica using the nonionic surfactant mixed with the cationic surfactant in monolayer adsorption structure are acceptable compared to those of rubber compound modified by silica using pure cationic surfactant (bilayer adsorption structure). However, the use of nonionic surfactant can reduce the cost of the modified silica about 3 time less than the modified silica using the pure cationic surfactant.