CHAPTER IV

RESULTS AND DISCUSSION

4.1 Adsorption of surfactants

In this part of the study, the adsorption of Arquad®T-50 and Teric®X-10 on silica has been performed for single and mixed surfactant systems.

4.1.1 Adsorption Isotherm

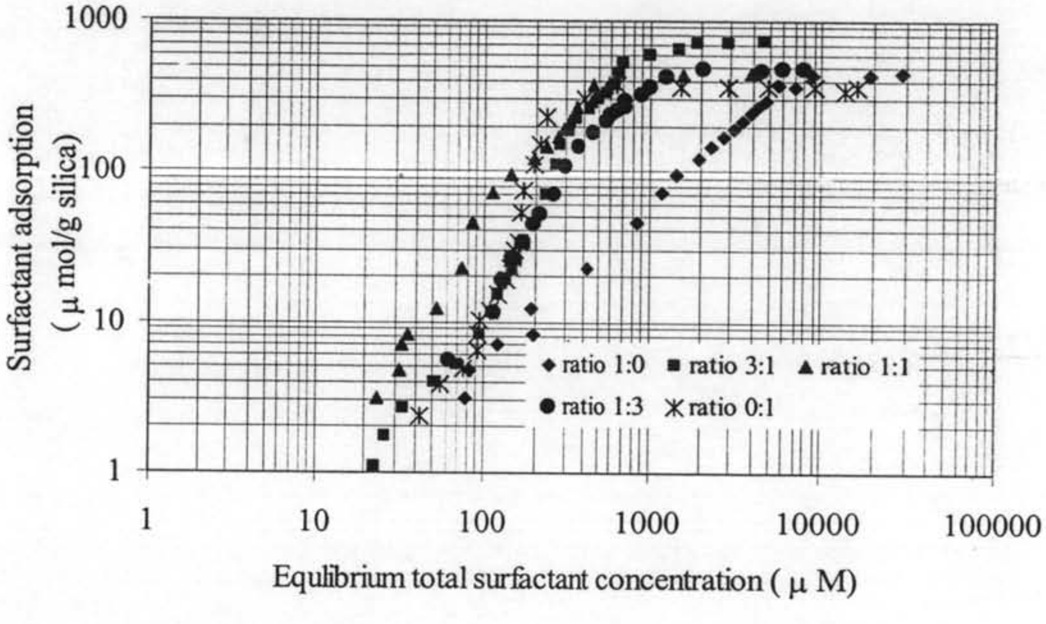


Figure 4.1 Adsorption isotherm of surfactants onto silica Hi-Sil®255 at pH 8 and 30°C at various Arquad®T-50:Teric®X-10 molar ratios.

Figure 4.1 shows the adsorption isotherms for the various mixtures of surfactants. In those systems that were predominantly cationic surfactant, regions II, III, and IV of the standard adsorption isotherm for ionic surfactants on polar surfaces can be seen. Plateau region adsorption for Arquad®T-50 on the silica is approximately 450 μmol/g silica. The CMC of Arquad®T-50 adsorbed on silica is approximately 5,000 μM.

The adsorption of Teric®X-10 is shown in Figure 4.1, plotted on a log-log scale, where the isotherms show the characteristic sigmoidal shape. From the figure, the CMC of Teric®X-10 is ≈300 μM and the maximum adsorption of Teric®X-10 on the silica is ≈350 μmol/g silica.

Comparing the adsorption of Arquad®T-50 and Teric®X-10, it can be noticed that Arquad®T-50 preferentially adsorbs onto the silica as indicated by a much higher plateau amount. This is attributed to the strong electrostatic interaction between cationic head groups of Arquad®T-50 and negatively charged surface of silica. This is also due to the much smaller head group area of the cationic surfactant, which would lead to a tighter packing of the molecules on the surface.

For mixed surfactant systems, the adsorption of Arquad®T-50 and Teric®X-10 was studied at several initial molar ratios. The adsorption of surfactants can be presented in terms of total surfactant concentration (Arquad®T-50 and Teric®X-10). It was found that the Arquad®T-50 to Teric®X-10 molar ratio 3:1 provides the highest surfactant adsorption, ≈700 μmol/g silica. The molar ratios 1:1 and 1:3 resulted in the surfactant adsorption of 600 and 500 μmol/g silica, respectively. It can be noticed that a higher amount of adsorbed surfactant is obtained in the mixed surfactant systems than the individual systems, and that it increases with increasing the Arquad®T-50:Teric®X-10 molar ratio. The increase in the adsorption of the mixed systems is likely due to the decrease in the electrostatic repulsion between head groups due to the presence of the nonionic surfactant between cationic surfactant molecules (Rosen, 1989). Consequently, the adsorptions of the mixed surfactants on the silica surface are relatively closely packed compared to that of the single surfactant systems. From the above results, the 3:1 surfactant molar ratio was chosen for further experiments due to its high maximum surfactants adsorption. In addition, the highest improvement of rubber properties testing results were obtained from this surfactant molar ratio (Supanam, 2005).

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

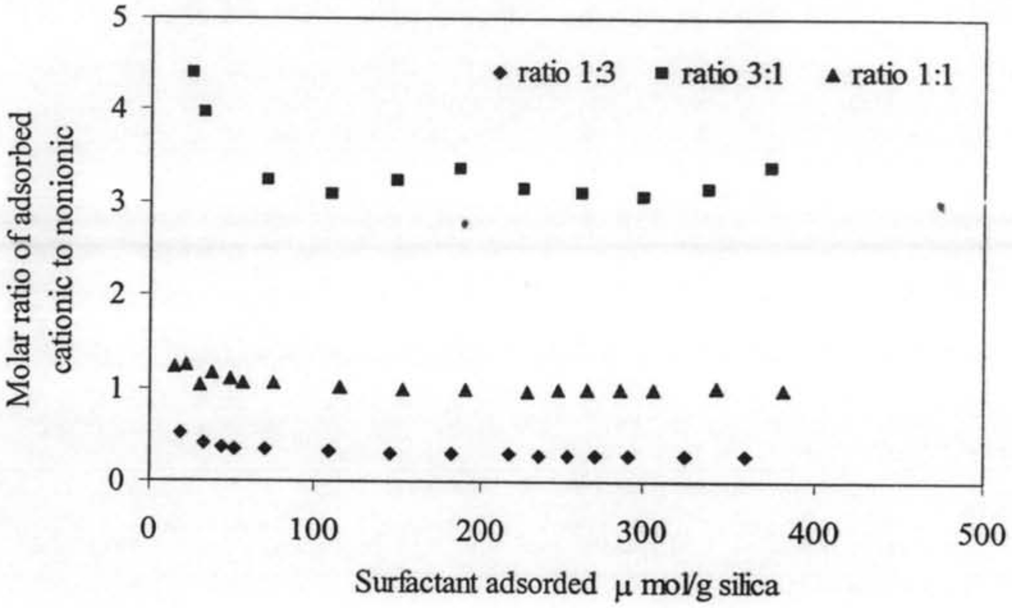


Figure 4.2 Molar ratios of surfactant adsorbed onto silica (Hi-Sil®255) at various Arquad®T-50:Teric®X-10 molar ratios and different total adsorbed surfactants.

For the mixed surfactant systems, amounts of each surfactant adsorbed can be predicted roughly by measuring the molar ratios (Arquad®T-50 to Teric®X-10) of 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 measured by a UV-Visible Spectrophotometer (UV-2550, Shimadzu). The result indicates that, at low surfactant adsorption, the obtained molar ratios of adsorbed surfactants are higher than the initial ratios of the mixed surfactants in the solution. It means that, initially, the cationic surfactant is more preferentially adsorbed onto the silica surface than the nonionic surfactant. After cationic surfactant adsorbed, nonionic surfactant adsorbed onto the hydrophobic tail of adsorbed cationic so the molar ratios of adsorbed surfactants is close to the initial ratios of the mixed surfactants in the solution. It can also be observed from the experiments that the ratio of the amount of each surfactant adsorbed onto the precipitated silica is quite close to that of the feed solution as shown in Figure 4.2. For example, for the 1:1 molar ratio mixed surfactant system, the adsorbed Arquad®T-50 accounts for approximately 50% of the total adsorbed amount of surfactants and adsorbed Teric®X-10 accounts for the other 50% in the system. For all molar ratios of the mixed surfactants, the same trends of the adsorbed Arquad®T-50 to adsorbed Teric®X-10 are similar to that of the feed mixture.

4.1.3 Zeta Potential of Silica Adsorbed with Surfactants

The charge of the silica after surfactant adsorption was examined by a zeta meter to determine the monolayer adsorption of surfactant (Figure 4.3). Since the silica surface is negatively charged, it can be neutralized by the positively charged head groups of the cationic surfactant.

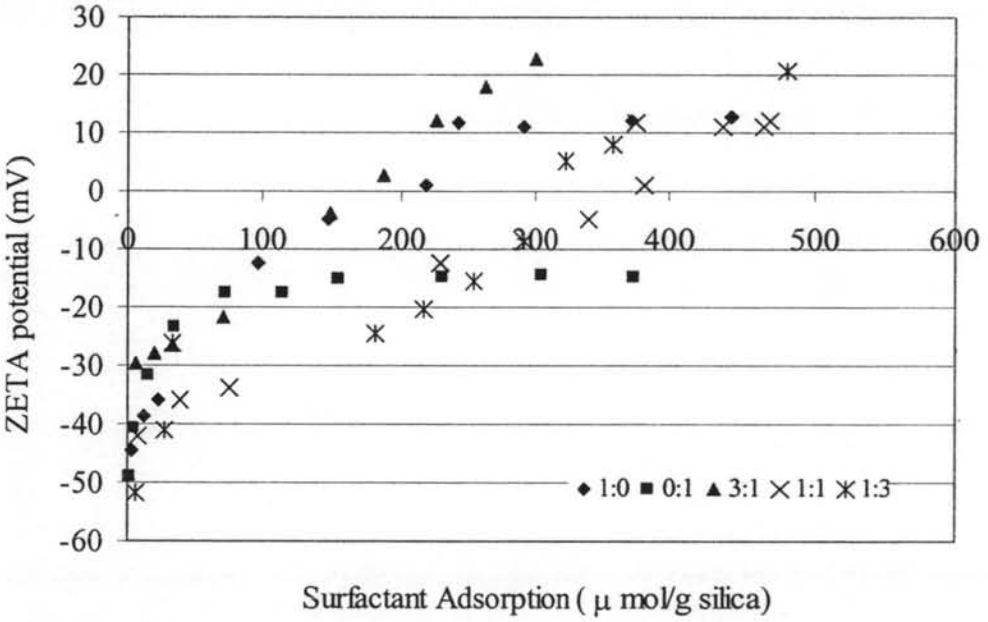


Figure 4.3 Charge on silica surface at difference total surfactants adsorbed with various Arquad®T-50:Teric® X-10 molar ratios.

At the zero charge, the silica surface was completely covered with monolayer of the surfactant. The monolayer adsorption at the mixed surfactants ratios 1:0, 3:1, 1:1 and 1:3 are 240, 210, 380 and 300 μmol/g silica, respectively. However, at the Arquad®T-50 to Teric®X-10 molar ratio 0:1, the silica surface cannot be neutralized by the nonionic surfactant because it dose not has the charge on the head group. The monolayer adsorption at the 3:1 ratio of the mixed surfactants was used for further experiments at a low level of surfactant adsorption.

4.2 Adsolubilization Isotherm

The adsolubilization of styrene and isoprene in the mixed surfactants system at the molar ratio 3:1 of Arquad®T-50 and Teric®X-10 adsorption onto the silica at pH 8 was investigated. Adsorption isotherm data were used to determine surfactant feed concentrations at three levels that would equilibrate at three different levels of adsorption, 500 μmol/g silica (high), 350 μmol/g silica (medium) and 200 μmol/g silica (low), and that would equilibrate below the CMC of surfactant system being studied to prevent the micelle formation. The amount of organic solute was varied. The solubility limits of solutes in water are 3.07 mM and 8.0 mM for styrene and isoprene, respectively (Daubert and Danner,1989).

4.2.1 Single Solute Adsolubilization

The relation between the amount of adsolubilized styrene and the equilibrium styrene concentration is shown in Figure 4.4. The solubilization of styrene increases with increasing the amount of the adsorbed surfactant. The maximum adsolubilization of styrene is 60 μmol/g silica at the high surfactant adsorption level. The results suggest that the adsolubilization of styrene can be related to the amount of the surfactant adsorbed on the silica. As expected, when the equilibrium concentration of styrene increases, the amount of the adsolubilized styrene increases. Figure 4.5 demonstrates the relationship between the partition coefficient (K) and the styrene mole fraction in the admicelle, assuming a constant surfactant adsorption. The partition coefficients (K) of styrene remain relatively constant as mole fraction of styrene in the admicelle increases. The location or combination of locations within the admicelle at which a particular monomer molecules and the structure of the compound. When the monomer is non-polar and has low solubility in water, such as the alkenes or other hydrophobic organic compounds are preferentially adsorbed in the core region of surfactant aggregates, whereas the polar organic compounds stay in the palisade layer or at the interface between surfactant aggregate and aqueous solution. Since styrene is a slightly polar organic solute, this implies that that styrene is adsolubilized into both the palisade layer and the core of the admicelle, as would be expected from the known behavior of aromatics in micelles (Rouse *et al.*, 1995).

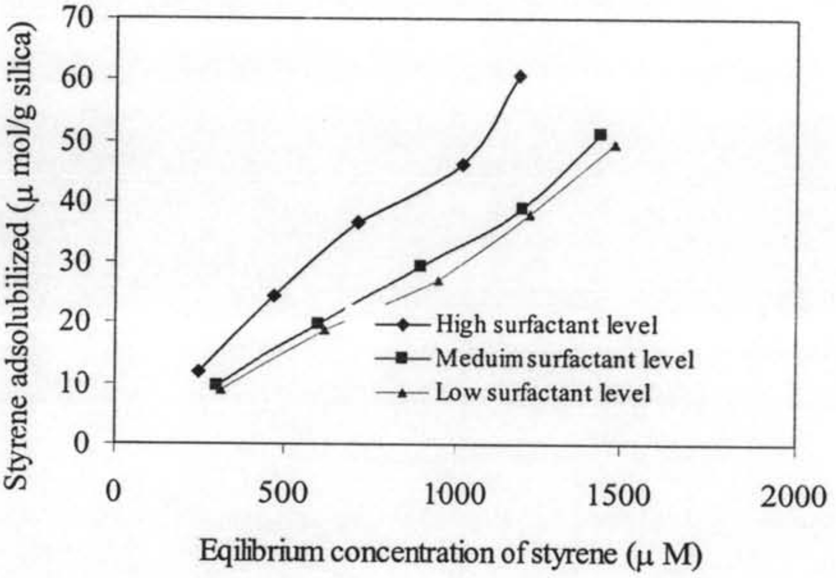


Figure 4.4 Adsolubilization isotherm of styrene in various surfactant adsorption levels.

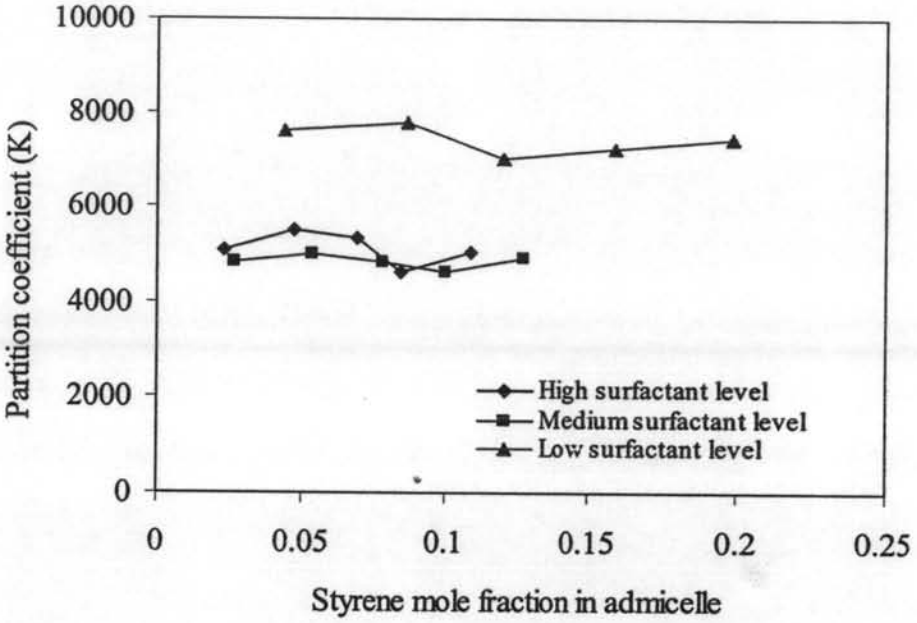


Figure 4.5 Partition coefficient (K) of styrene adsolubilization in various surfactant adsorption levels.

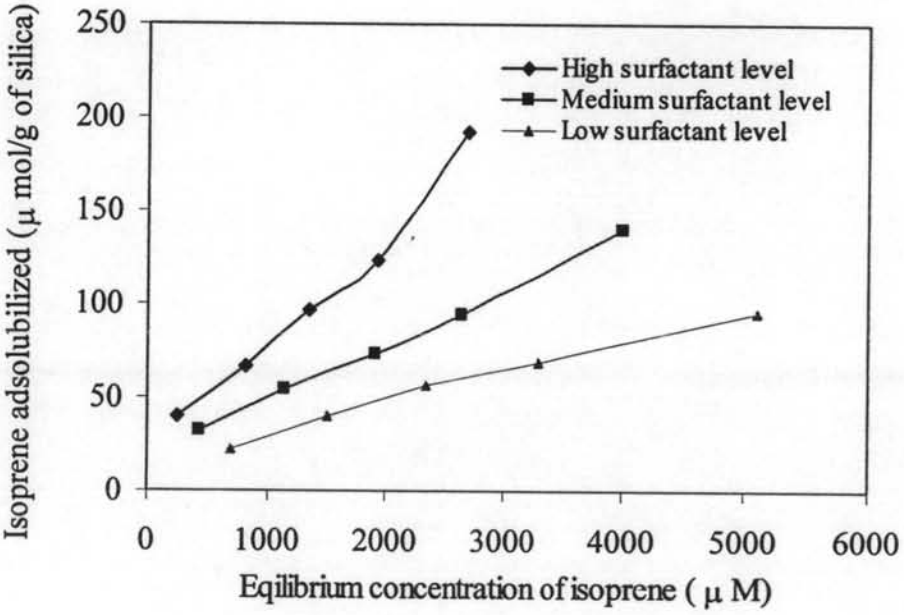


Figure 4.6 Adsolubilization isotherm of isoprene in various surfactant adsorption levels.

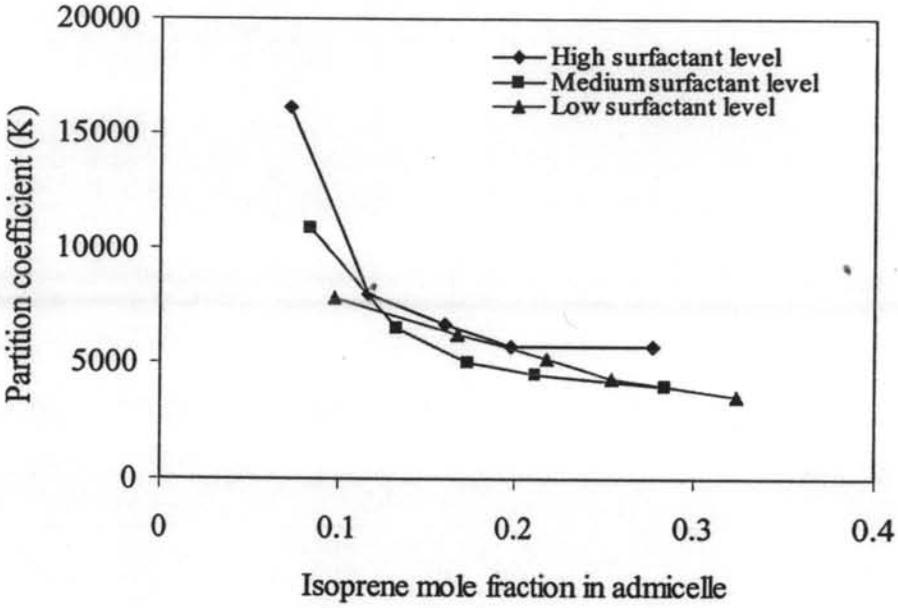


Figure 4.7 Partition coefficient (K) of isoprene adsolubilization in various surfactant adsorption levels.

Figure 4.6 shows the plot of isoprene adsolubilization versus the bulk equilibrium concentration of isoprene for the mixed surfactant system at various surfactant adsorption levels. Generally, the results suggest that the adsolubization of isoprene in the mixed Arquad®T-50 to Teric®X-10 systems can be related to the amount of the surfactant adsorbed on the silica. The maximum adsolubilization of isoprene is 190 μmol/g silica at the high surfactant adsorption level. As expected, the amount of isoprene solubilized increases with the increasing of the equilibrium concentration of isoprene. Comparing the adsolubilization of styrene and isoprene, the amount of isoprene adsolubilized in the mixed surfactant systems of Arquad®T-50 to Teric®X-10 is higher than styrene for all studies surfactant adsorption levels because of the structure of organic solute. The structure of isoprene is linear, which has two branches so it is easy to penetrate into admicelles while the styrene has a benzene ring and branch as a structure thus making it more difficult for the branched-structure benzene to penetrate into the admicelle than isoprene.

The partition coefficient of isoprene gradually reduces with increasing mole fraction in the admicelle Figure 4.7, which agrees with previous work

(Kitiyanan *et al.*, 1996). Thus, the behavior of the partition coefficient suggests that isoprene partitions primarily into the palisade regions of the admicelle since isoprene is a polar organic solute and has no attached branch and the head and palisade regions of the admicelle.

4.2.2 Adsolubilization of Co-monomer

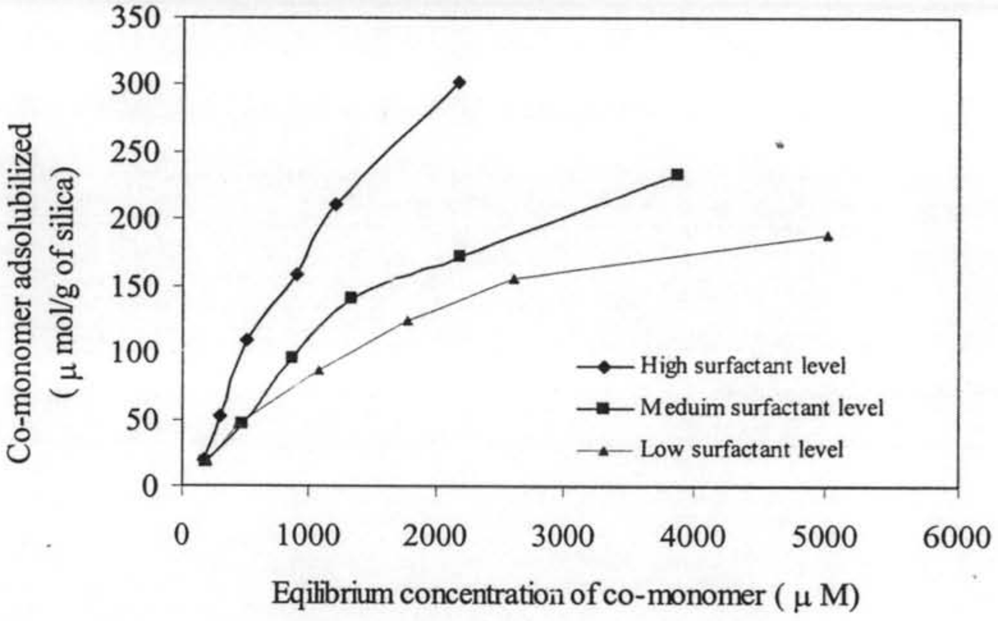


Figure 4.8 Adsolubilization isotherm of co-monomer in various surfactant adsorption levels.

In the co-monomer system, the amount of styrene adsolubilized is slightly increased in the presence of isoprene while the isoprene adsolubilized is significantly enhanced in the presence of styrene showing a synergistic effect, possibly due to swelling of the admicelle due to the addition of adsolubilizate. Figure 4.8 shows the amount of styrene-isoprene mixtures adsolubilization at different surfactant adsorption levels. The high surfactant adsorption level shows the highest adsolubilization, which is 300 μmol/g silica. For the medium and low surfactant adsorption levels, the maximum of co-monomer adsolubilization are 230 and 190 μmol/g silica, respectively. The calculated mole ratio of the adsorbed mixed surfactants and the adsolubilized co-monomer are used in the modification silica surface procedure, 32:1, 16:1, 8:1 and 4:1.

4.3 Characterization

4.3.1 Electrostatic Charge and Hydrophobicity

Table 4.1 Electrostatic charge on unmodified and modified silica surface

Modified silica at various mole ratios of adsorbed surfactant : adsolubiized co-monomer	Zeta Potential (mV)		
	H	M	L
32:1	14.51	-8.15	-37.35
16:1	24.85	-6.66	-36.35
8:1	34.52	-2.89	-16.10
4:1	35.85	-2.51	-6.65
Unmodified silica	-38.11		

where H, M, and L represent the high, medium and low surfactant adsorption level, respectively.

Surface charge properties of silica powder in aqueous suspensions were determined using the Zeta Potential Meter (Table 4.1). Normally, the silica surface is negatively charged at pHs above 3. Silica modified by the admicellar polymerization process should have polymer formed on the surface. If the upper layer of surfactant was removed, the electrostatic charge should be zero because the polymer is exposed to the water. Moreover, the electrostatic charge from the experiment not only has the negative charge but also the positive charge. The negative charge may be from the charge of silica surface because the surfactant and copolymer does not continuously coat on the silica particle. At the low and medium surfactant adsorption the silica is negatively charged. At high surfactant adsorption, the modified silica is positively charged. It implies that not all upper layer surfactant is removed thus the cationic head group exposed to the aqueous solution, or that sufficient surfactant is entrapped in and under the polymer to provide this charge. In addition, the results suggest that the silica surface charge tends to be positively charged when the mole ratio of adsorbed surfactant : adsolubilized co-monomer decreases because there are higher amount of the copolymer coated on the surface.

Table 4.2 Hydrophobicity of modified and unmodified silica by the contact angle measurement

Modified silica at various mole ratios of adsorbed surfactant : adsolubiized co-monomer	Contact angle		
	H	M	L
32:1	43.06	43.69	41.58
16:1	44.93	43.64	42.51
8:1	47.08	46.60	43.67
4:1	52.48	51.66	49.86
Unmodified silica	26.07		

where H, M, and L represent the high, medium and low surfactant adsorption level, respectively.

The contact angle test is used to observe the hydrophobicity of the modified silica by placing a drop of water on the silica then the angle is taken from a tensiometer. The contact angle test results are shown in Table 4.2. For unmodified silica, the water droplet spreads to cover a wide area, showing that the contact angle is low and the surface is hydrophilic (low hydrophobicity). For all modified silica, the water droplet forms a sphere on the surface and the contact angle is higher than that of the unmodified silica. In addition, the results show that the hydrophobicity of the modified silica increases with an increase in the amount of adsorbed surfactant and styrene-isoprene mixtures. Polymer formation on silica has good water resistance as shown by the higher hydrophobicity.

4.3.2 Amount of Polymer Formation

Thermal gravimetric analysis is used to examine the modified silicas. The TGA for unmodified silica is shown in Figure 4.9. Unmodified silica shows weight loss of water below 150°C. Normally, the weight change above 150°C might be the result of the surface modification of modified silica. Figure 4.10 show the decomposition of polystyrene from 350 to 480°C (Chaisirimahamorakot, 2001). Poly(styrene-isoprene) decomposed from 200-280°C as shown in Figure 4.11. Figure 4.12 evidently shows the peak decomposition of Arquad®T-50 which occurs at 180 to 280°C while the decomposition of Teric®X-10 is between 240-420°C (Figure 4.13). Figure 4.14 shows that Arquad®T-50 adsorbed onto the silica also decomposes in two steps as CTAB, the first step from 180 to 300°C and the second step from 300 to 400°C. The second step may be from the stronger bonding between silica and Arquad®T-50 (Supanam, 2005).

The decomposition of mixed surfactants, Arquad®T-50 and Teric®X-10, adsorbed onto the silica at difference mole ratios of adsorbed surfactant : adsolubilized co-monomer at difference levels of surfactants concentration is shown in Figures 4.15 - 4.17. For all surfactant adsorption levels, the weight loss appear in two steps, the first peak is 200 to 300°C for the decomposition of Arquad®T-50 while the second peak for weight loss of Teric®X-10 as well as Arquad®T-50 chemisorbed onto the silica is at 300 to 480°C.

Figures 4.18 to 4.30 show TGA results of different modified silicas. All modified silica samples consisting of Arquad®T-50 again show two step decomposition at the same temperature ranges as mentioned before. The first step is Arquad®T-50 decompostion and the second is the decomposition of Arquad®T-50 chemisorbed, Teric®X-10 and poly(styrene-isoprene) onto the silica.

The quantity of formed copolymer can be studied from the percent weight loss of TGA results. All mass losses were evaluated on the second degradation step at temperatures >300°C. 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 mixed 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 4.3 shows percent of polymer present on the modified silicas approximately. It was found that the greater amount of polymer depositing on the silica occurs with high surfactant adsorption level and low mole ratio of adsorbed surfactant : adsolubilized co-monomer. There is also a good correlation between the TGA and the contact angle test, which shows that the hydrophobicity of the modified silica increases with an increase in the amount of adsorbed surfactant and styrene-isoprene mixtures. That may be due to the higher amount of polymer coated on the silica leads to high water resistance.

Table 4.3 Amount of polymer present on the modified silicas.

Modified silica at various mole ratios of adsorbed surfactant : adsolubilized co-monomer	Amount of Polymer (%)		
	H	M	L
32:1	0.214	0.173	-
16:1	0.311	0.240	-
8:1	0.475	0.459	0.154
4:1	0.547	0.623	0.263

where H, M, and L represent the high, medium and low surfactant adsorption level, respectively.

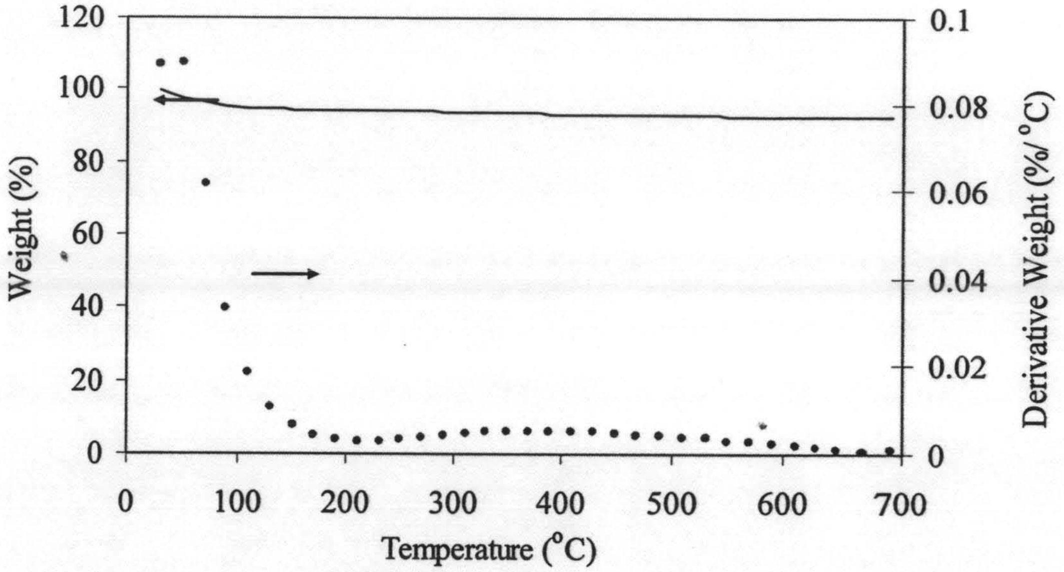


Figure 4.9 TGA results of unmodified silica Hi-Sil®255.

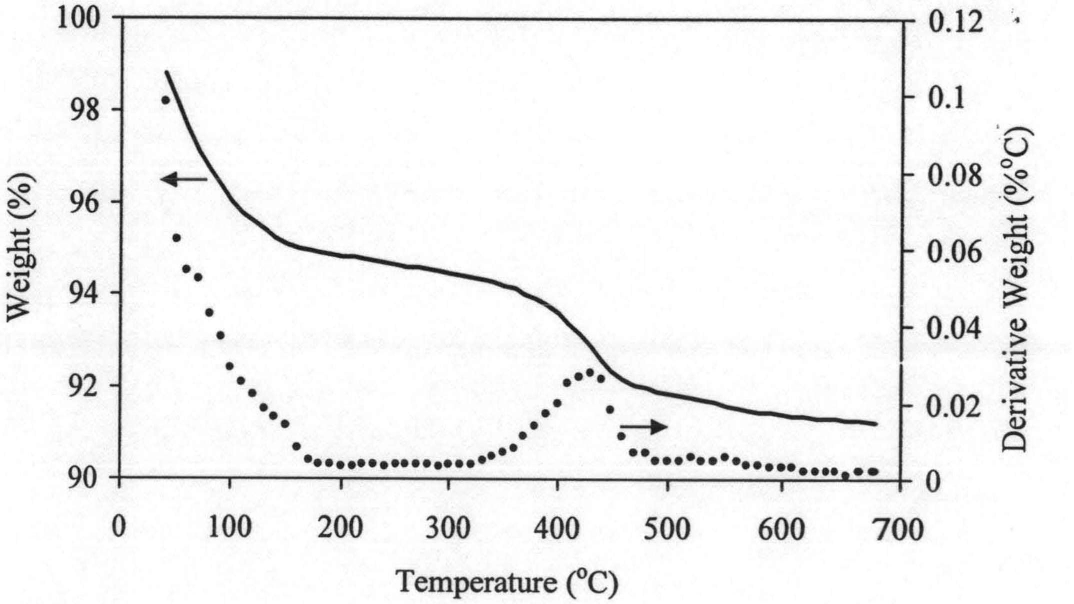


Figure 4.10 TGA results of silica Hi-Sil®255 adsorbed with polystyrene (Chaisirimahamorakot, 2001).

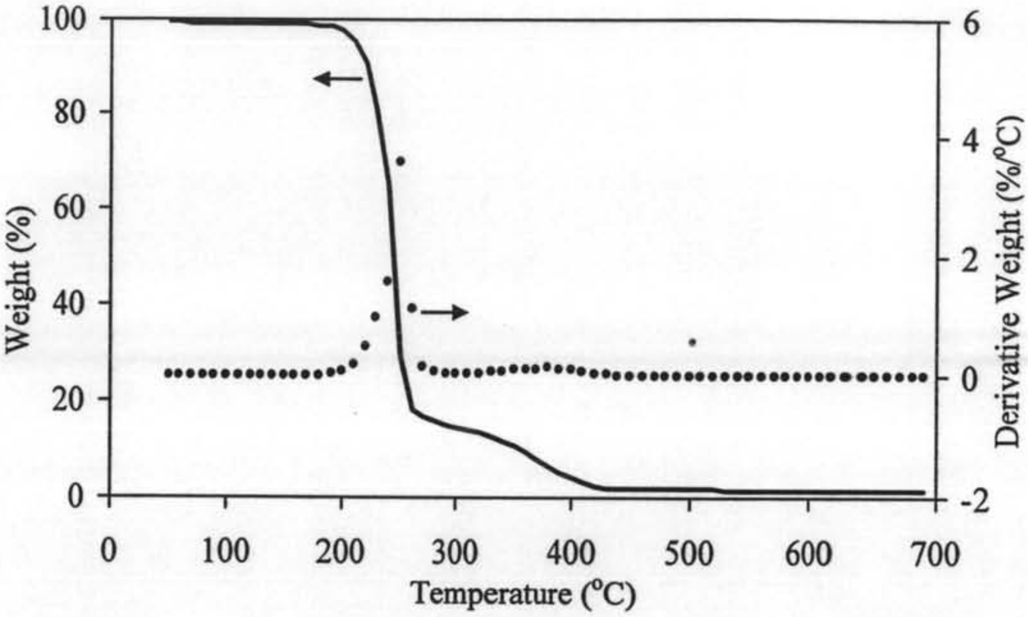


Figure 4.11 TGA results of poly(styrene-isoprene).

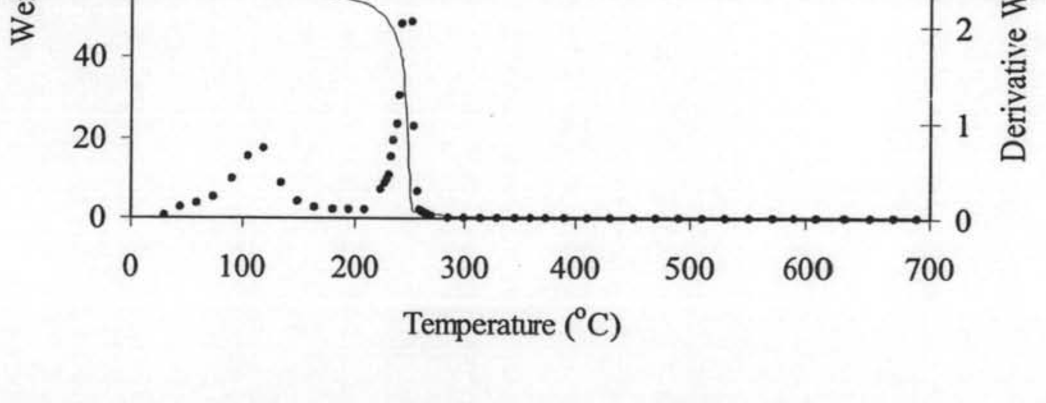


Figure 4.12 TGA results of Arquad®T-50.

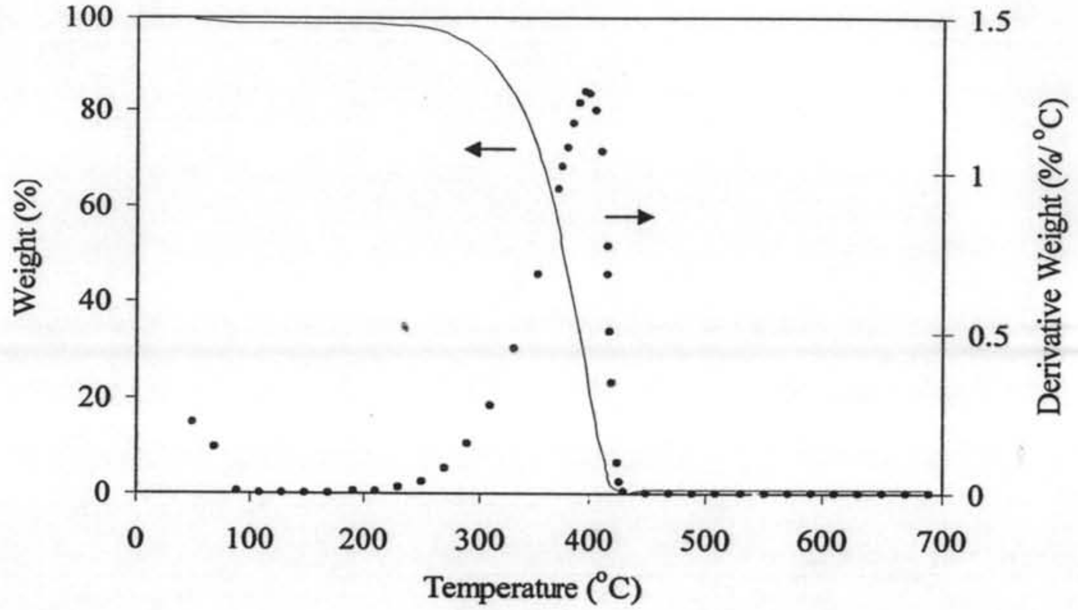


Figure 4.13 TGA results of Teric®X-10.

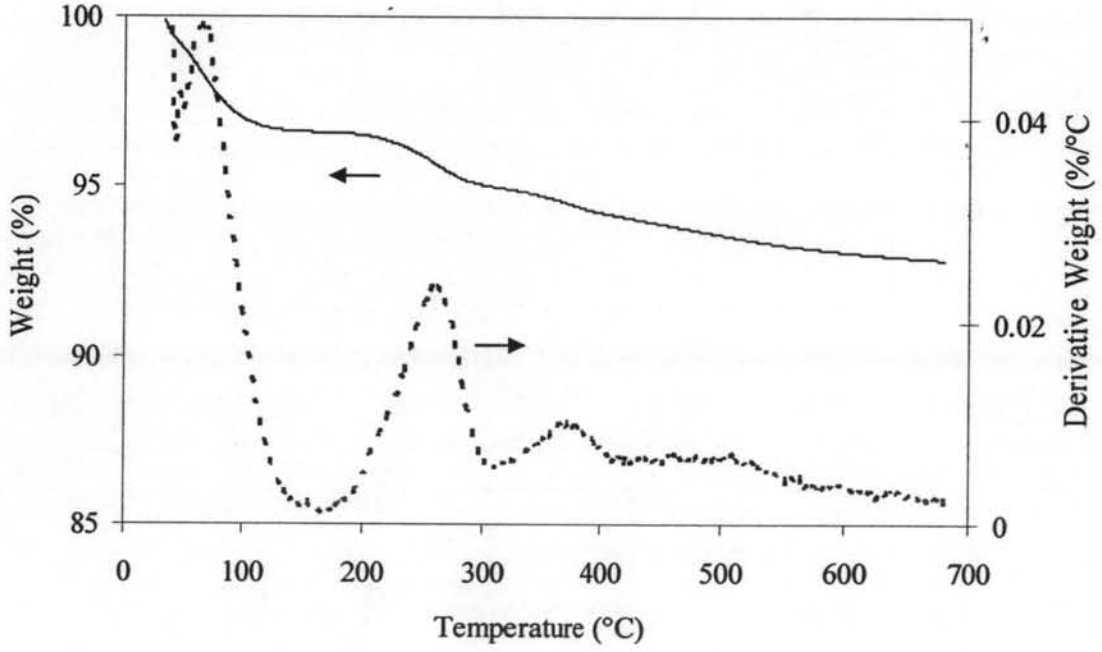


Figure 4.14 TGA results of silica Hi-Sil®255 adsorbed with Arquad®T-50.

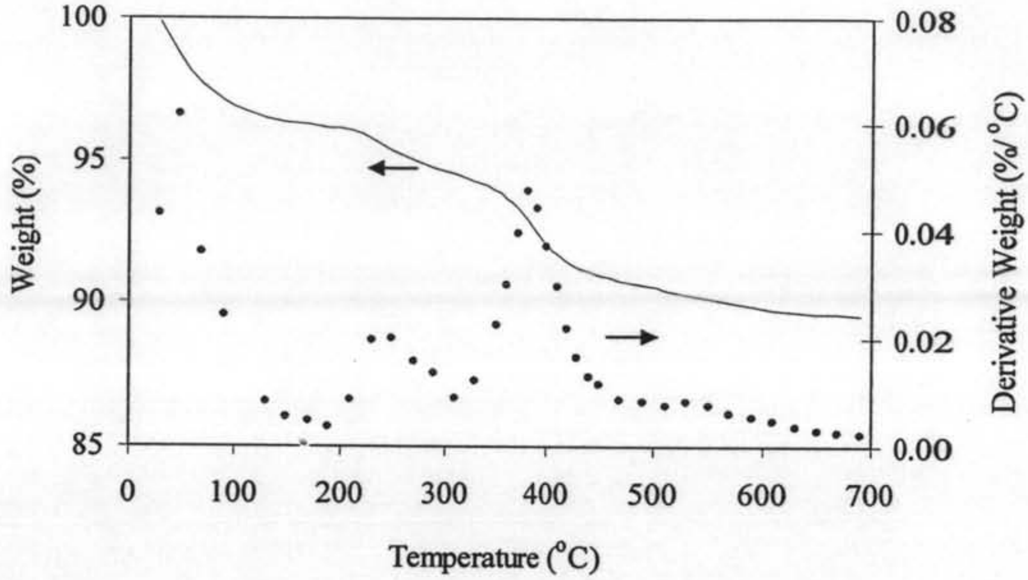


Figure 4.15 TGA results of silica Hi-Sil®255 adsorbed with low surfactant adsorption level.

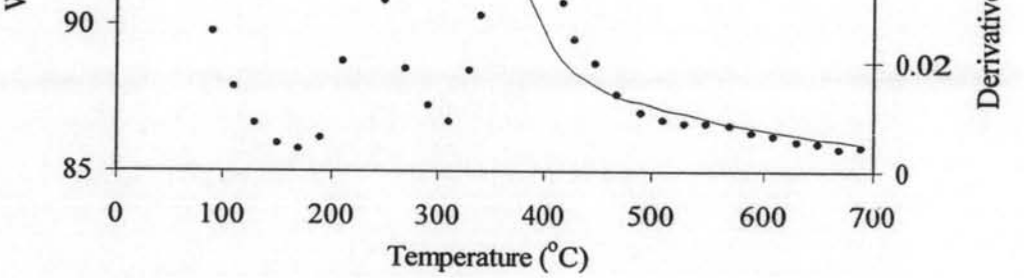


Figure 4.16 TGA results of silica Hi-Sil®255 adsorbed with medium surfactant adsorption level.

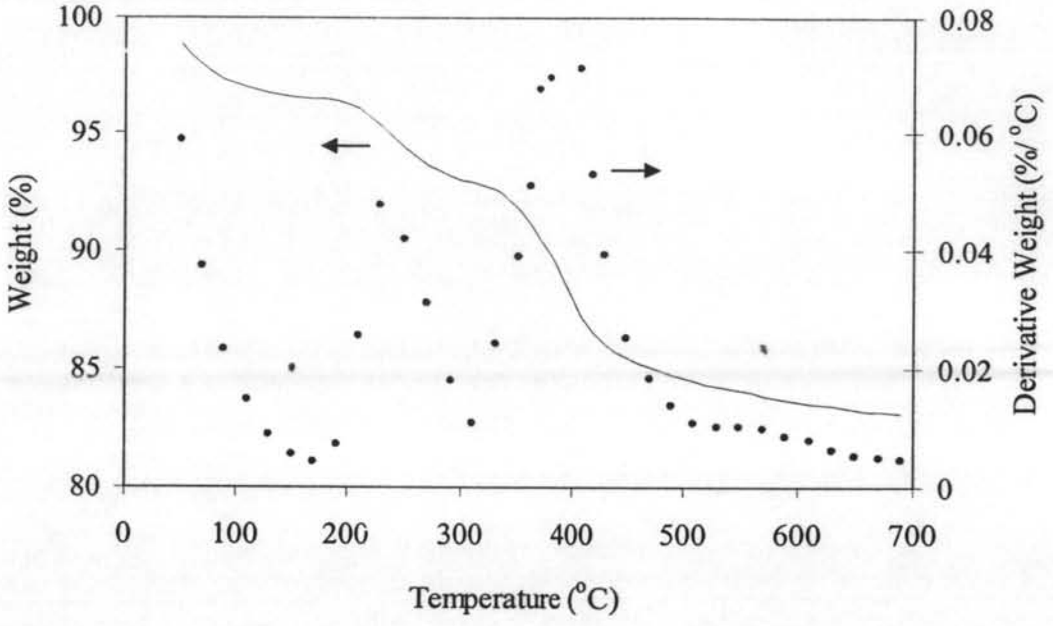


Figure 4.17 TGA results of silica Hi-Sil®255 adsorbed with high surfactant adsorption level.

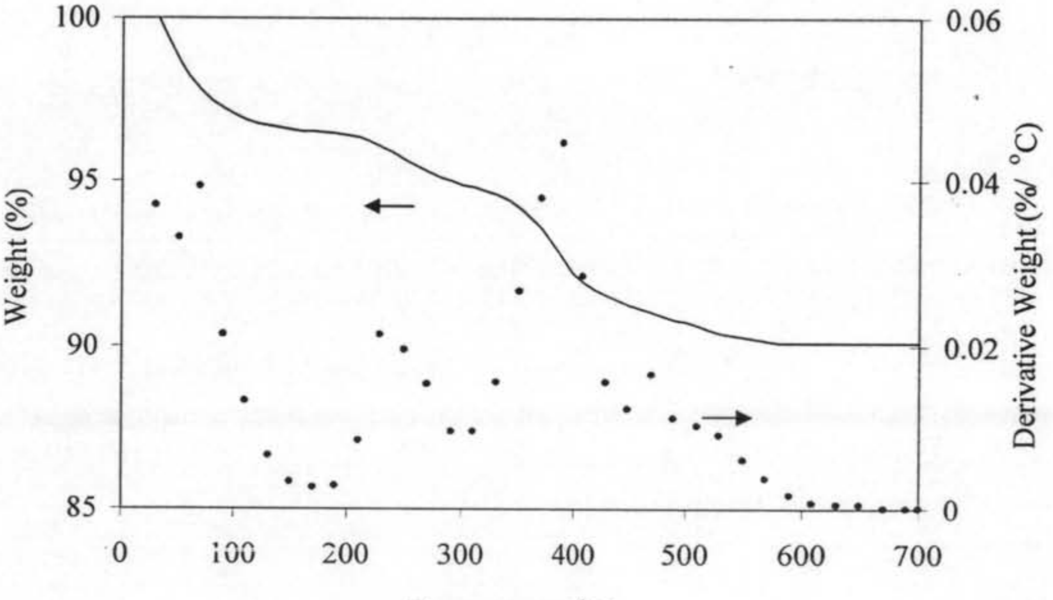


Figure 4.18 TGA results of silica Hi-Sil®255 adsorbed with 4:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at low surfactant adsorption level.

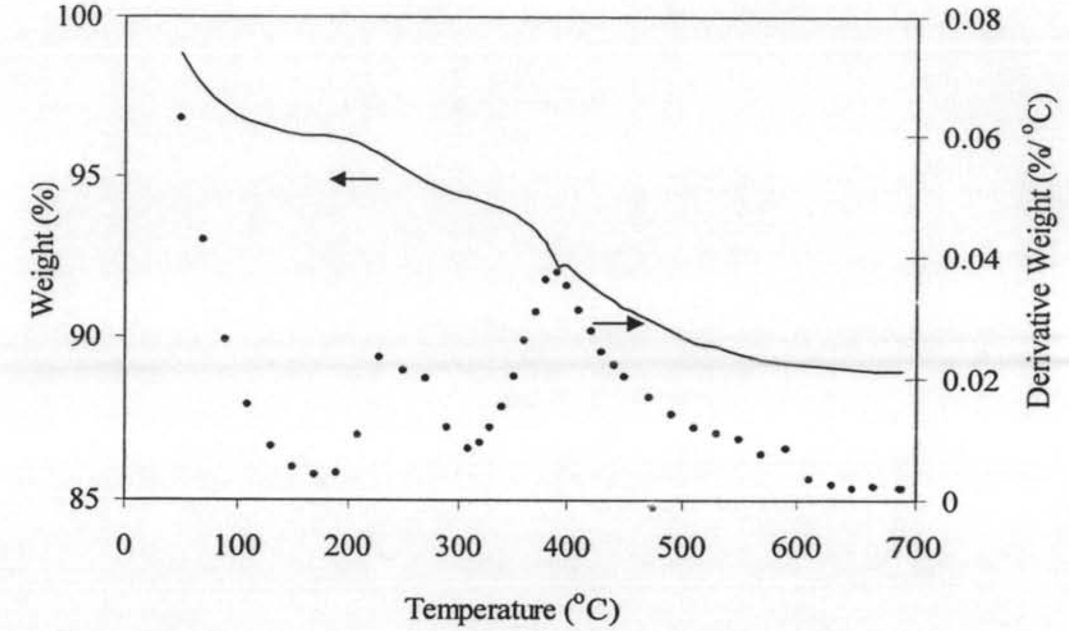


Figure 4.19 TGA results of silica Hi-Sil®255 adsorbed with 8:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at low surfactant adsorption level.

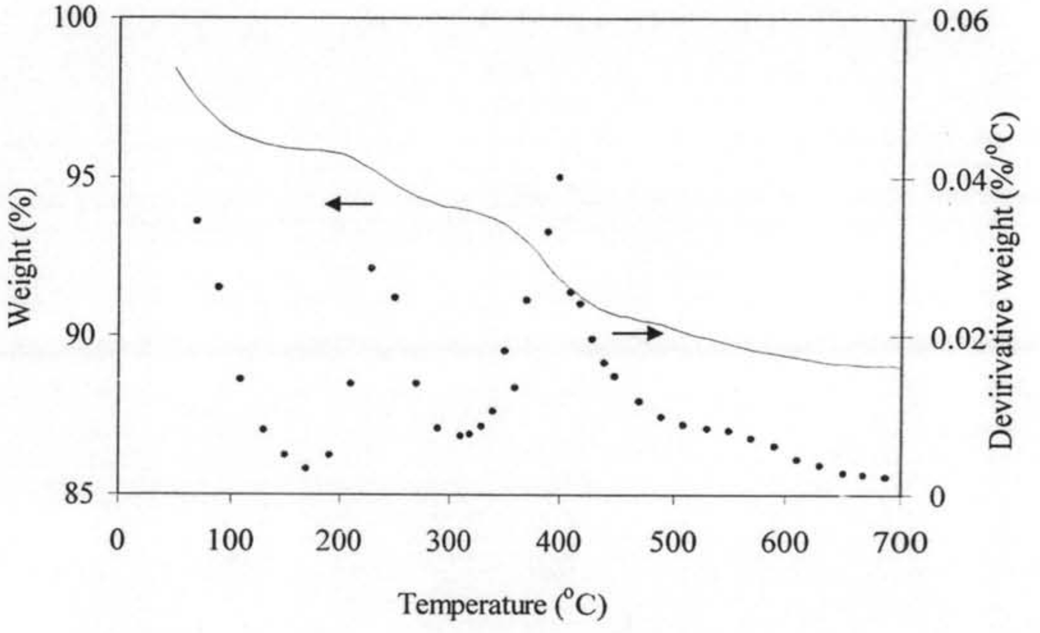


Figure 4.20 TGA results of silica Hi-Sil®255 adsorbed with 16:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at low surfactant adsorption level.

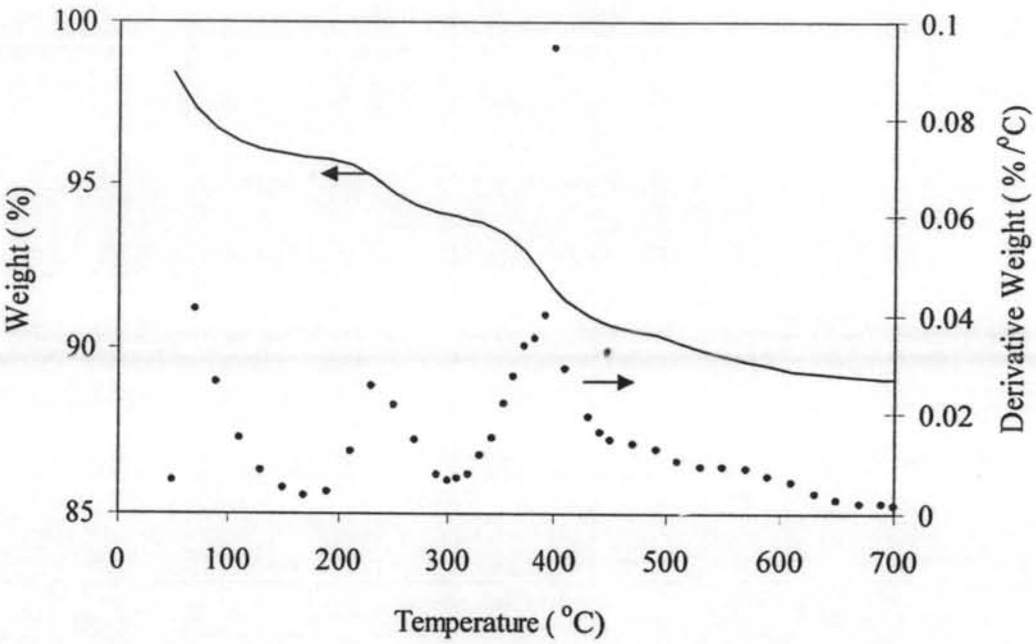


Figure 4.21 TGA results of silica Hi-Sil®255 adsorbed with 32:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at low surfactant adsorption level.

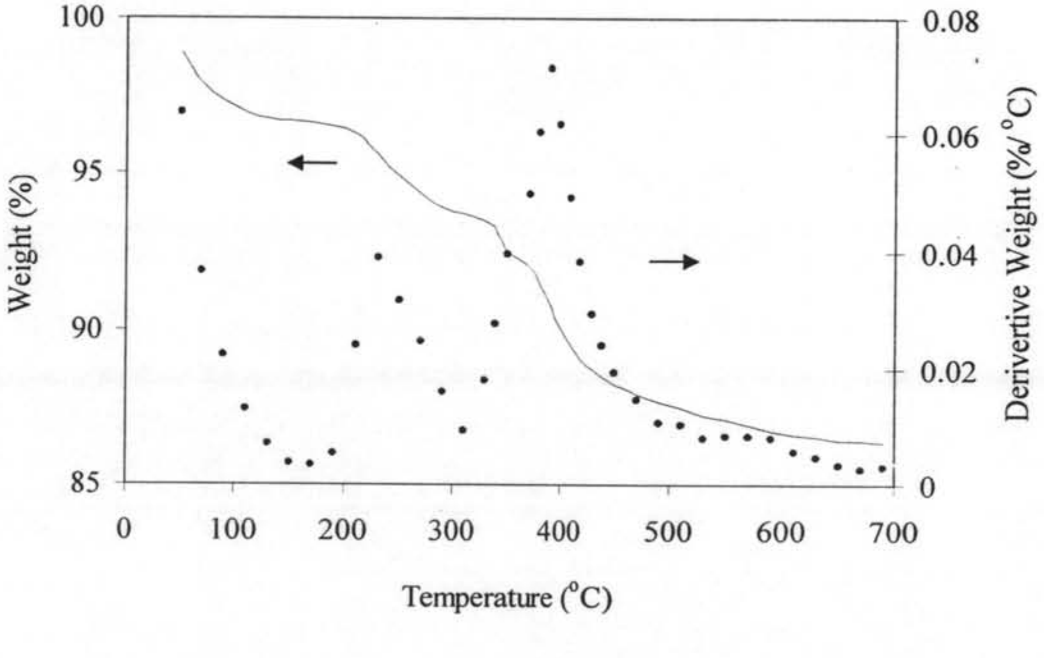


Figure 4.22 TGA results of silica Hi-Sil®255 adsorbed with 4:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at medium surfactant adsorption level.

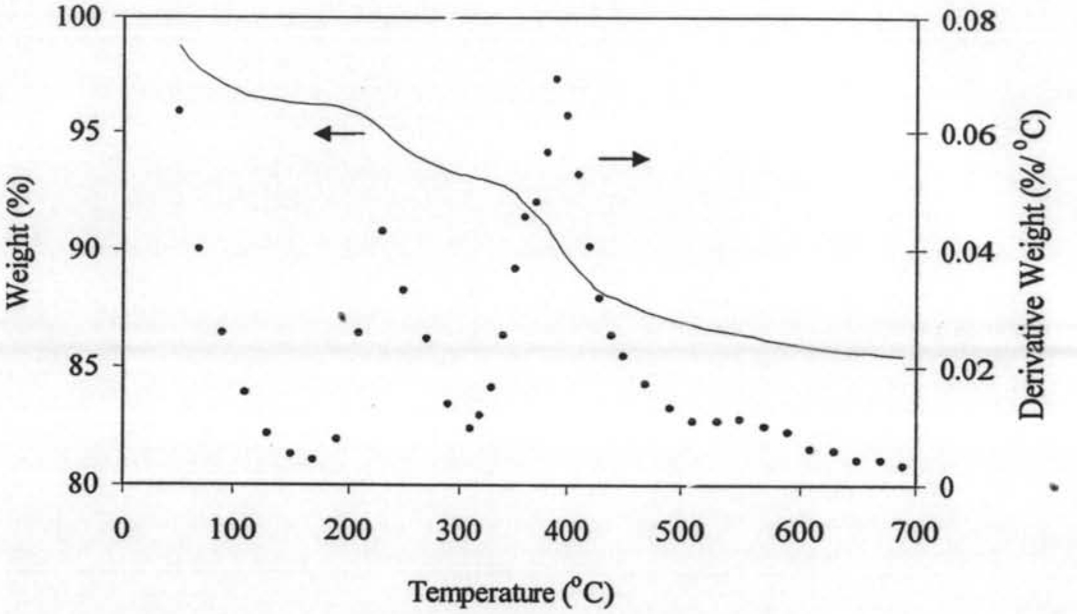


Figure 4.23 TGA results of silica Hi-Sil®255 adsorbed with 4:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at medium surfactant adsorption level.

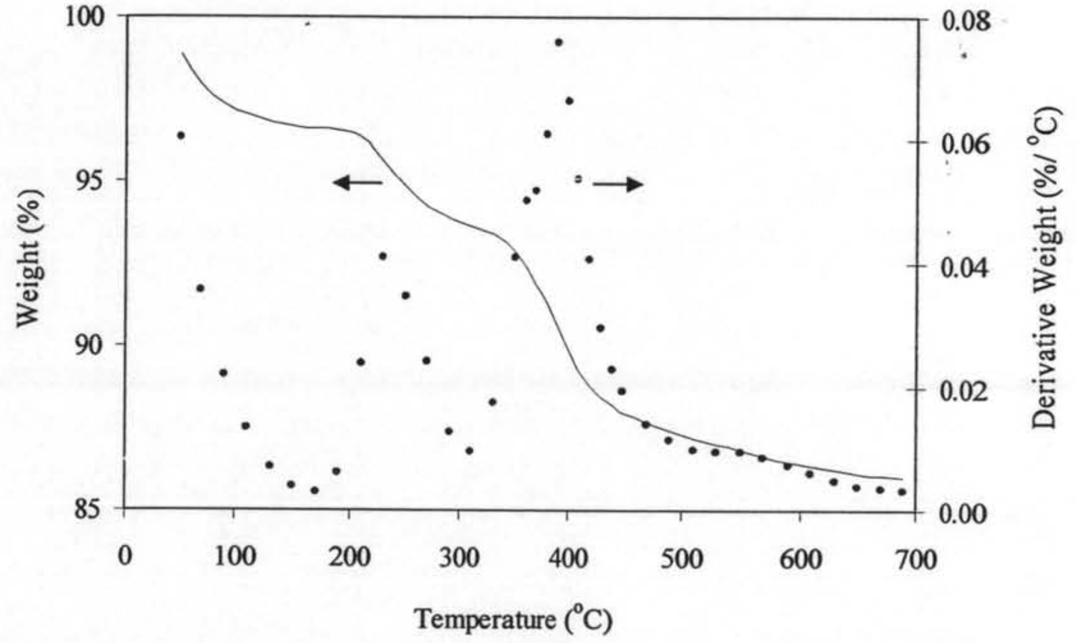


Figure 4.24 TGA results of silica Hi-Sil®255 adsorbed with 8:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at medium surfactant adsorption level.

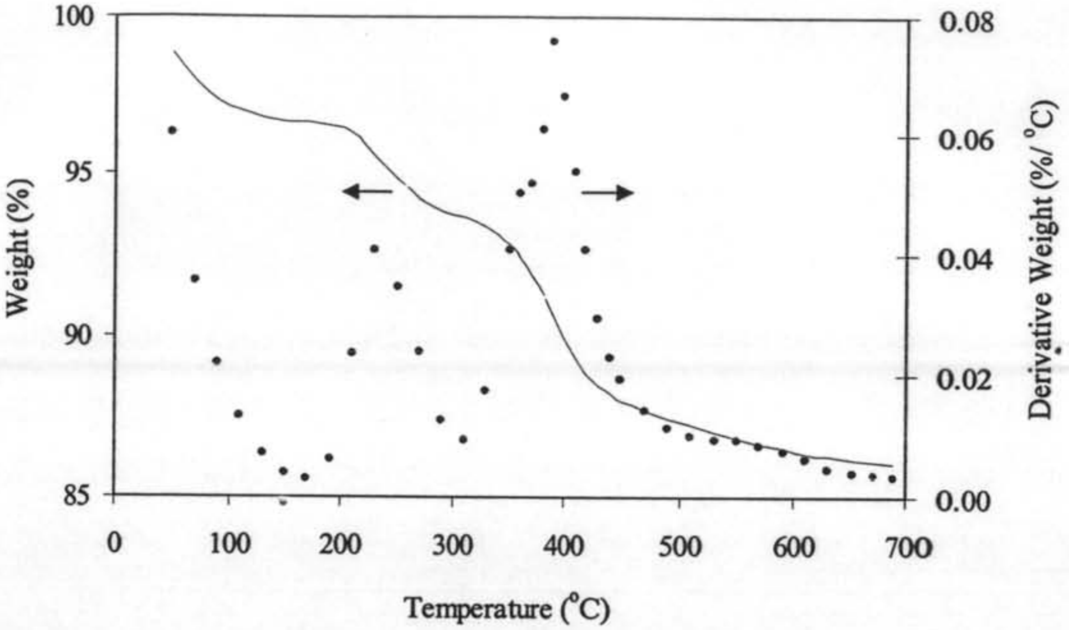


Figure 4.25 TGA results of silica Hi-Sil®255 adsorbed with 16:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at medium surfactant adsorption level.

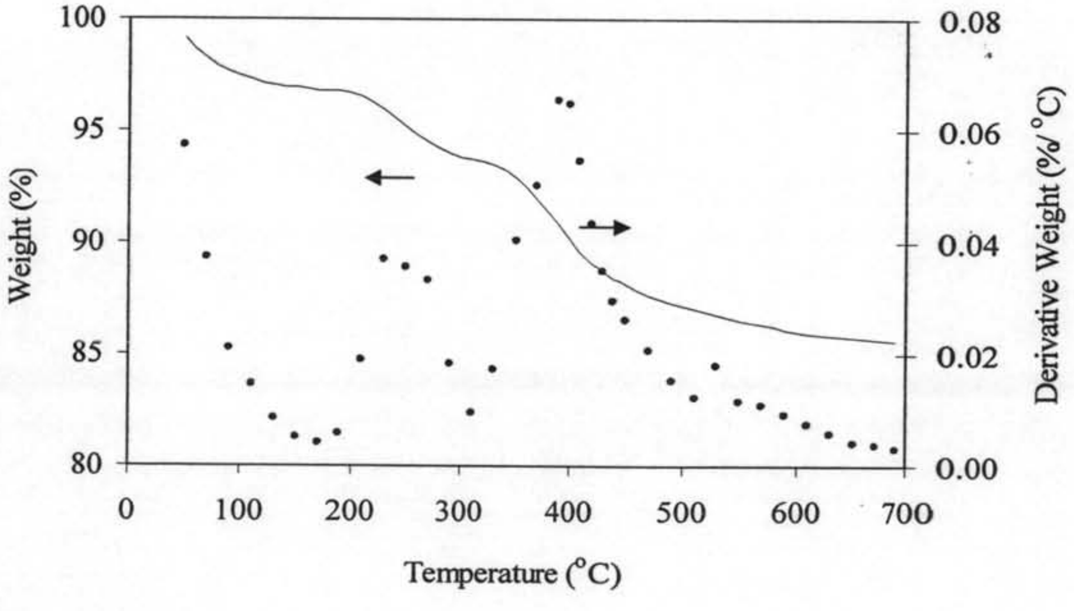


Figure 4.26 TGA results of silica Hi-Sil®255 adsorbed with 32:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at medium surfactant adsorption level.

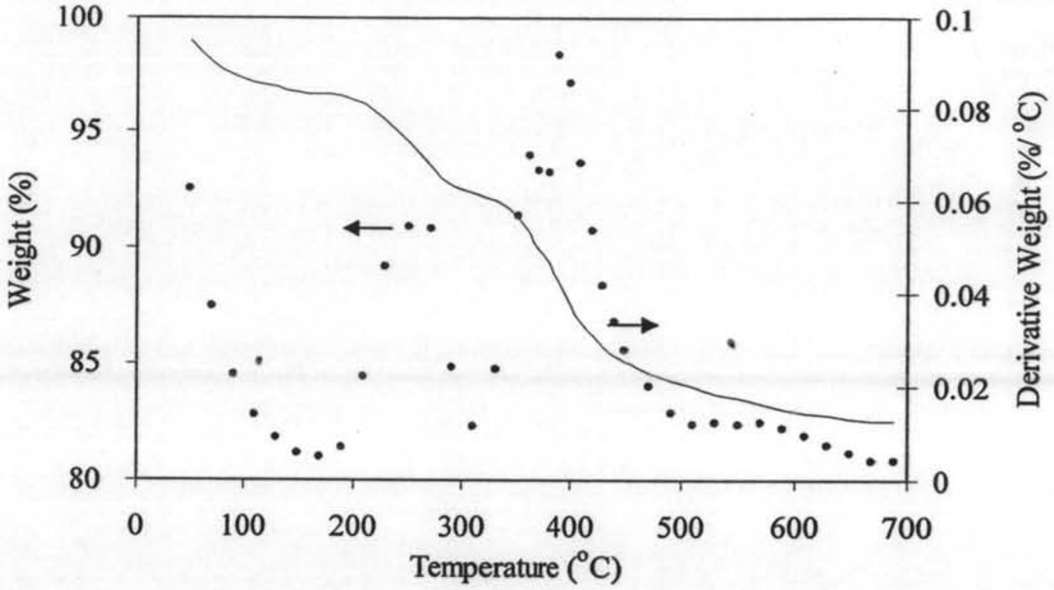


Figure 4.27 TGA results of silica Hi-Sil®255 adsorbed with 4:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at high surfactant adsorption level.

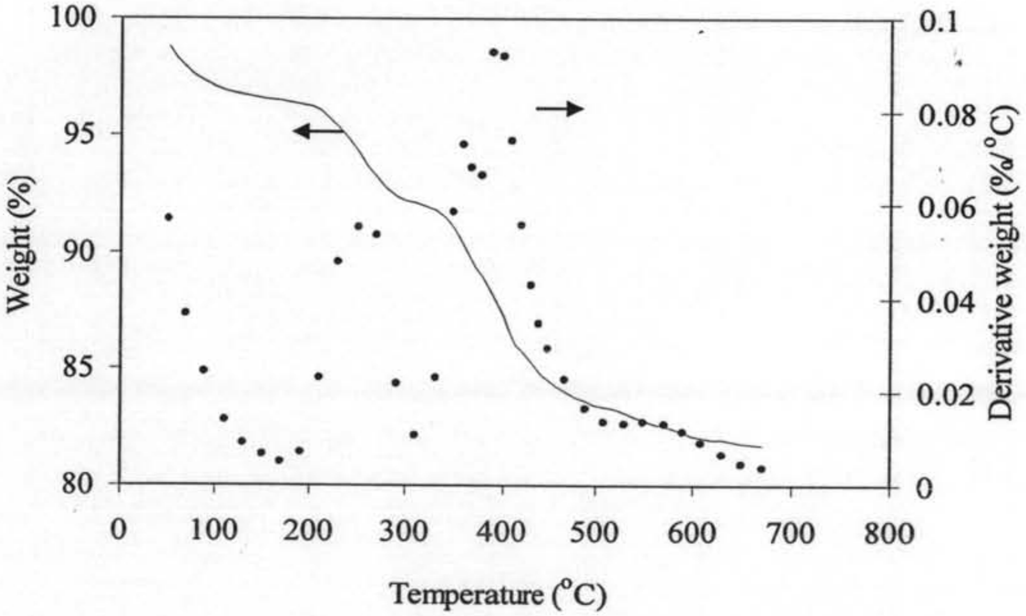


Figure 4.28 TGA results of silica Hi-Sil®255 adsorbed with 8:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at high surfactant adsorption level.

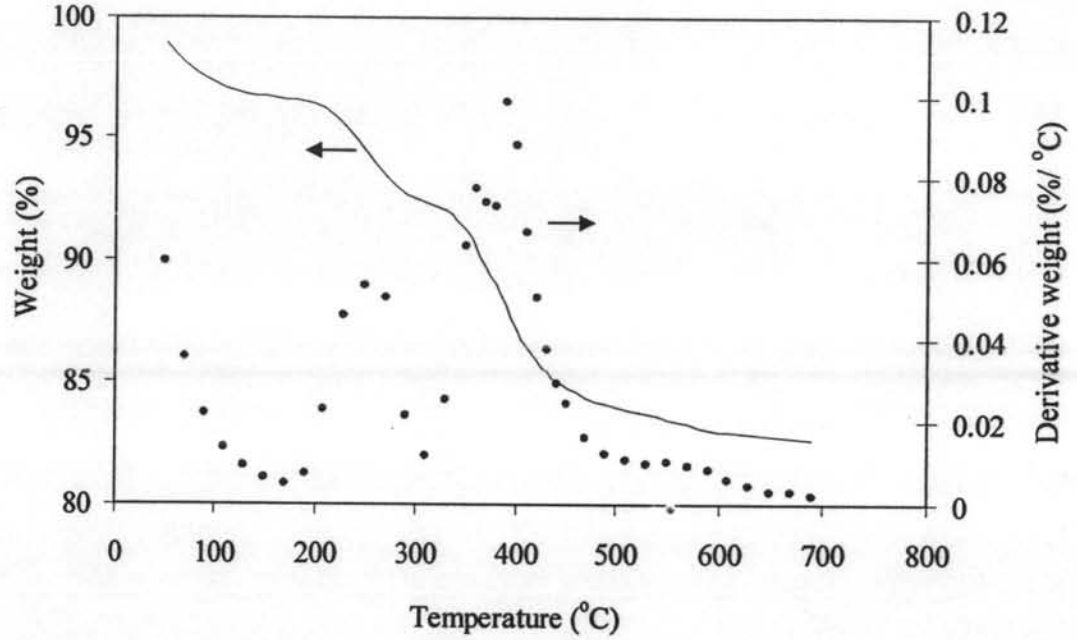


Figure 4.29 TGA results of silica Hi-Sil®255 adsorbed with 16:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at high surfactant adsorption level.

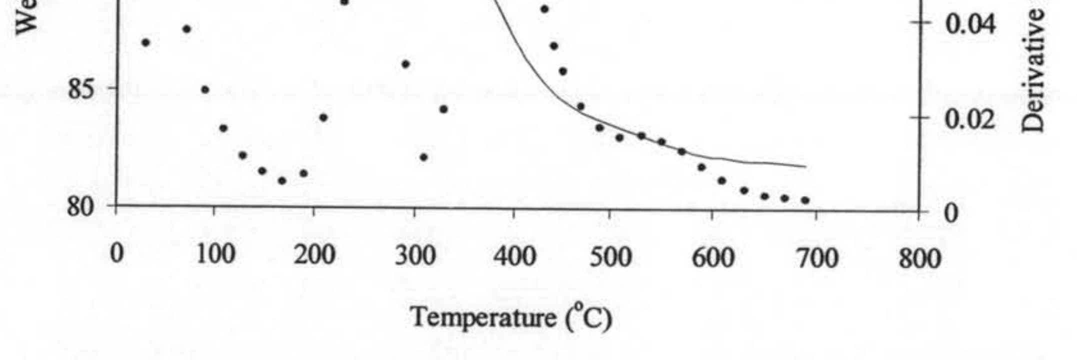


Figure 4.30 TGA results of silica Hi-Sil®255 adsorbed with 32:1 mole ratio of surfactant adsorption to mixtures of styrene-isoprene adsolubilized at high surfactant adsorption level

4.3.3 Molecular Weight Measurement

The molecular weight of the extracted polymer was determined using gel permeation chromatography (GPC). Table 4.4 illustrates the number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and molecular weight distribution (MWD) of the extracted polymer from modified Hi-Sil®255. As a result, the weight average molecular weights of the extracted polymer form Hi-Sil®255 ranges between 1,233 and 2,664. The GPC curves of the extracted polymer showed only one peak. The copolymer in this MW range is probably due to polymerization within monomer-rich regions within the admicelle (See and O'Haver, 2004). Comparing the polymer at the difference levels of surfactant adsorption shows that at high surfactant adsorbed level, the weight average molecular weights of the extracted polymer is higher than medium and low surfactant adsorbed levels. The admicelle is probable "patchy" on the surfaces at the lower coverage, and perhaps so at the high coverage. Therefore, some polymerizations occur in small aggregates that do not contain sufficient monomer to form high molecular weight polymer. The patchy admicelle would also have more exposure to surrounding water which would increase the rate of termination. Thus, to obtain high molecular weight polymer, high surfactant adsorbed level is preferable. In the same way, the low mole ratios of adsorbed surfactant : adsolubilized co-monomer causes an expected increase in the molecular weight. The decrease in the mole ratios of adsorbed surfactant : adsolubilized co-monomer increases the copolymer molecular weight. That may be due to the swell of the surfactant layer at low mole ratios and the increase in the density of co-monomer per surfactant molecule.

Table 4.4 $\overline{M}_n$, $\overline{M}_w$ and MWD of extracted polymer for modified silica

Modified silica at various mole ratios of adsorbed surfactant : adsolubiized monomer	H			M			L		
	$\overline{M}_n$	$\overline{M}_w$	MWD	$\overline{M}_n$	$\overline{M}_w$	MWD	$\overline{M}_n$	$\overline{M}_w$	MWD
32:1	2172	1233	1.0523	1620	1956	1.2075	1615	1831	1.1339
16:1	2363	2413	1.0209	1913	2054	1.0738	1621	2000	1.2339
8:1	2545	2578	1.0129	1999	2176	1.0886	1669	2015	1.2077
4:1	2640	2664	1.0094	2205	2269	1.0288	1962	2163	1.1024

where H, M, and L represent the high, medium and low surfactant adsorption level, respectively.

4.3.4 Surface Area and Particles size

Table 4.5 shows the BET specific surface area of the modified surface compared with unmodified silica. As expected, the BET specific surface area of the modified silica decreases about 27% and the mean agglomerate particle increases up to 15% after surface modification via admicellar polymerization process. These results suggested that the polymer covers or obstructs the pores of silica leading to decrease in the BET specific surface area of the modified silica. In addition, these results show a good correlation between the increasing of particle size and a reduction in the BET specific surface area of the modified silica.

The increase in the mean agglomerate particle size may simply be attributed to the subsequent reprocessing of the modified silicas or it could be a result of the organic polymer-forming process. The result does not indicate significant effects of the surfactant adsorption level and mole ratios of adsorbed surfactant : adsolubiized co-monomer on the mean agglomerate particle size. However, the mean agglomerate particle sizes of all modified silicas increase and that may result from the development of polymer bridges between silica particles (Chaisirimahamorakot, 2001).

Table 4.5 Effect of the modification on the BET N_2 surface area and mean agglomerate particle size of the modified silicas

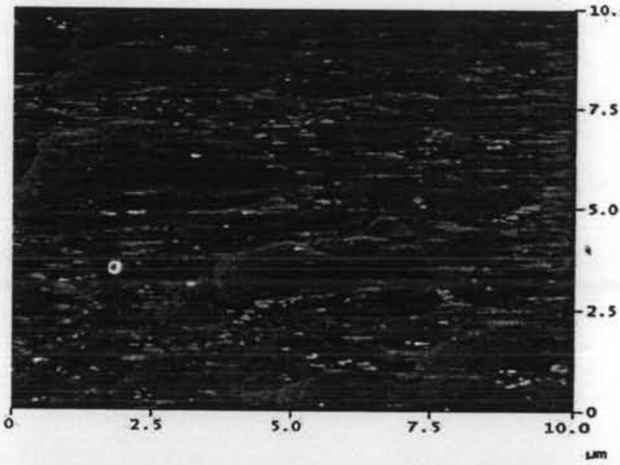
Modified silica at various mole ratios of adsorbed surfactant : adsolubiized monomer	BET N_2 Surface area (m^2/g)			Mean Agglomerate Paticle Size (μm)		
	H	M	L	H	M	L
32:1	130.2	141.4	141.7	33.05	30.27	30.98
16:1	127.1	138.8	139.6	33.36	32.21	33.68
8:1	123.4	122.7	134.7	33.76	33.02	33.81
4:1	122.8	119.6	127.9	37.06	33.92	33.72
Unmodified silica	180.2			28.52		

where H, M, and L represent the high, medium and low surfactant adsorption level, respectively.

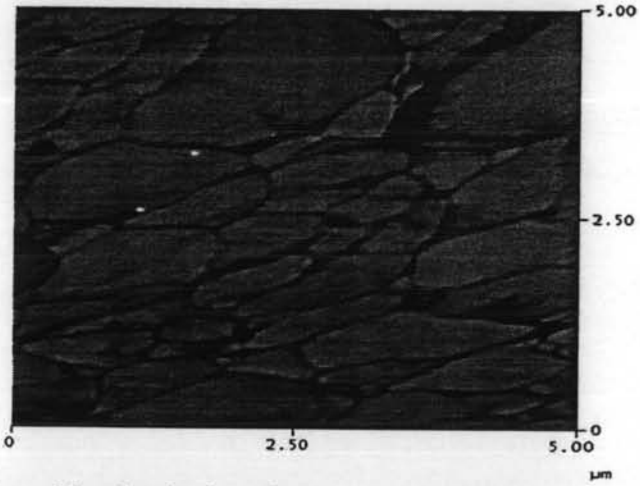
4.3.5 Atomic Force Micrograph of Modified and Unmodified Silica

AFM images (Figure 4.31) show the morphology of the unmodified and modified silica. The phase image can be used to interpret the hardness of sample surface. "Soft" samples will be seen as regions of darker contrast while hard areas will appear brighter in contrast. Thus, silica will appear light and polymer dark. From the figures, a) shows the atomic micrograph of the unmodified silica, the valleys and edges of the primary particles not clearly appear. However, it can be observed that the grain boundary of modified silica is bigger than the unmodified silica; which may be due to the higher amount of formed polymer as shown in Figure b) and c). Furthermore, the particle size of the unmodified silica is smaller than the modified silica as well as the investigating from particle size analyzer.

a) Hi-Sil®255



b) Modified silica with adsorbed surfactant : adsolubiized co-monomer,4:1H



c) Modified silica with adsorbed surfactant : adsolubiized co- monomer, 16:1H

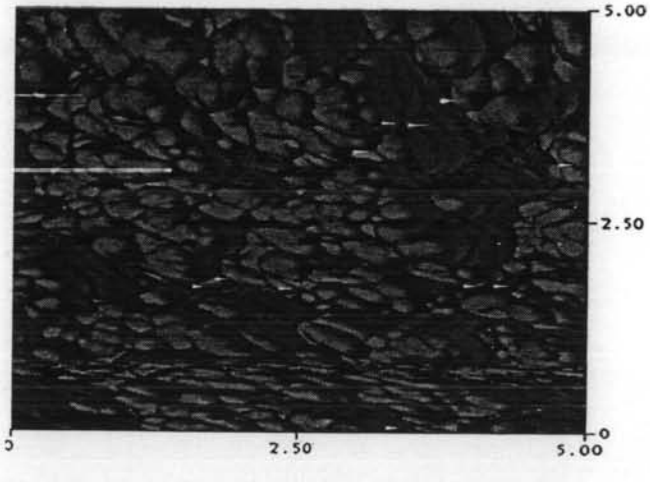


Figure 4.31 Atomic force micrograph of unmodified silica.

4.4 Rubber Compound Physical Properties

The effect of both the surfactant adsorption level and the molar ratio of adsorbed surfactant : adsolubilized co-monomer on rubber compound physical properties was studied. The surfactant adsorption level of mixed surfactant has no significant effect on the cure time. All different modified silicas at various mole ratios of adsorbed surfactant : adsolubilized co-monomer, 4:1 to 32:1 resulted in the cure time of about 6.2 min as seen in Figure 4.32. Comparing with the result from previous works, the cure time in the present work is slightly higher than the other systems. Compared to the unmodified silica, it can be seen that the modified silica can reduce the cure time. That is due to the copolymer on the modified silica reducing the adsorption of additives into pore of the silica. Thammathadanukul *et al.* (1996) concluded that the decrease in the cure time is consistent with the copolymer formation within the silica pores, covering some of the surface silanol groups, thereby reduced their interaction toward the polar chemical additives used for rubber vulcanization.

Figures 4.33 and 4.34 shows comparison of the 100% and 300% modulus@ before aging of the modified silicas with the unmodified silica and previous works. The 100% modulus of the modified silicas is lower than the modified silica from other systems except the result from 4:1 and 16:1 molar ratios of adsorbed surfactant : adsolubilized co-monomer at the high surfactant adsorption level. For the 300% modulus, the results suggest that 16:1 molar ratio of the adsorbed surfactant : adsolubilized co-monomer at the high surfactant adsorption level shows the highest increase in the modulus compared with other different modified conditions.

Most modified silicas in this work show slight improvement of the tensile strength@ before aging of the rubber compounds as compared to the unmodified silica except the result from 16:1 molar ratio of the adsorbed surfactant: adsolubilized co-monomer at the high surfactant adsorption level (Figure 4.35).

The tear strength @before aging of rubber compounds is shown in Figure 4.36. The improvement is almost three times of the unmodified silica. The low level of surfactant adsorption shows the highest improvement compared with the results from previous study and other modified condition.

Again, the abrasion loss values of all twelve modified silicas are decreased compared with the unmodified silica and did not show a significant impact due to the mole ratio of the adsorbed surfactant : adsolubiized monomer and surfactant adsorption level as shown in Figures 4.37. The results indicate that all modified silicas improve the resilience values (Figures 4.38). From Figure 4.39, the compression set of all modified silicas are significantly reduced compared to that of the unmodified silica and the previous work systems. The modified silicas at 8:1 mole ratio of the adsorbed surfactant : adsolubiized co-monomer at the low surfactant adsorption level provides greater performance than the other modified silicas at present study.

Figure 4.40 shows a comparison of the hardness of different rubber compounds. The result does not show significant improvement on the hardness value. For the flex cracking resistance testing, the results are in Figure 4.41. The flex cracking properties dramatically decrease compared with the unmodified silica.

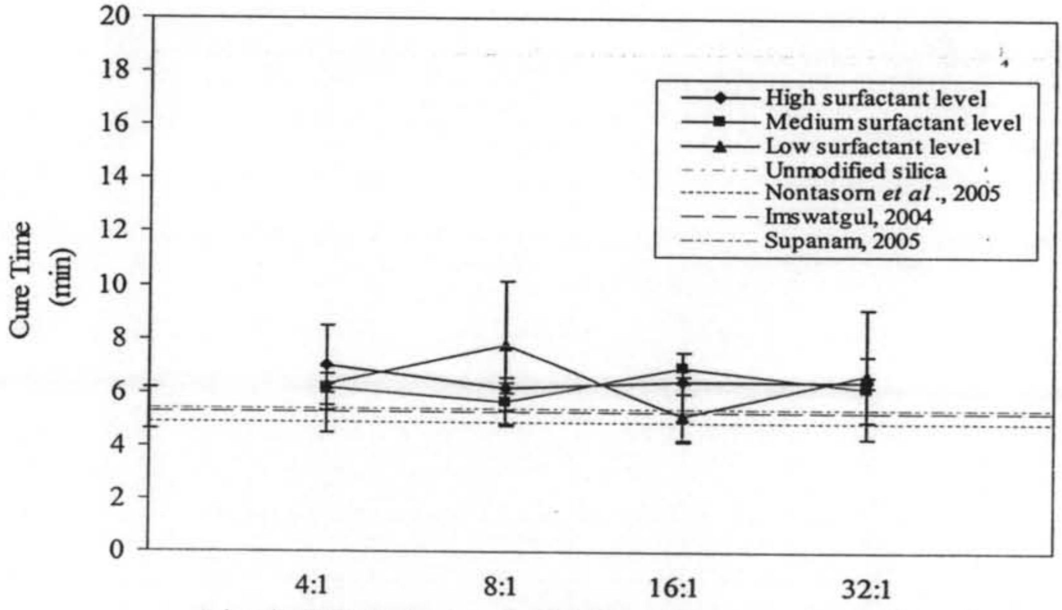


Figure 4.32 Cure time of modified silicas prepared with different adsorbed surfactant : adsolubilized monomer mole ratios and different surfactant adsorption levels.

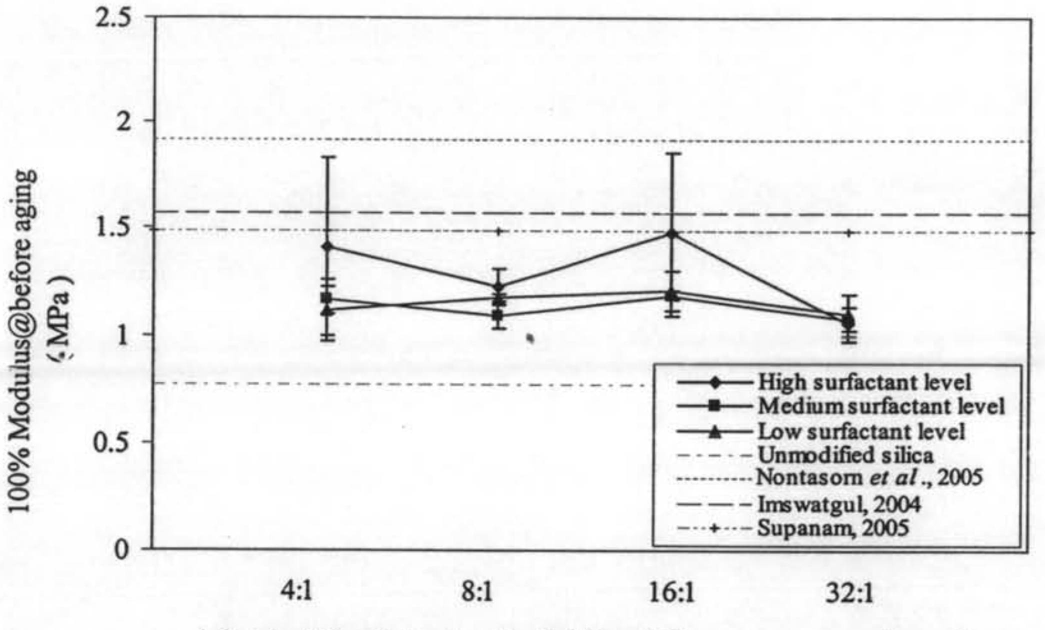


Figure 4.33 100% modulus @before aging of rubber compounds with different modified silicas.

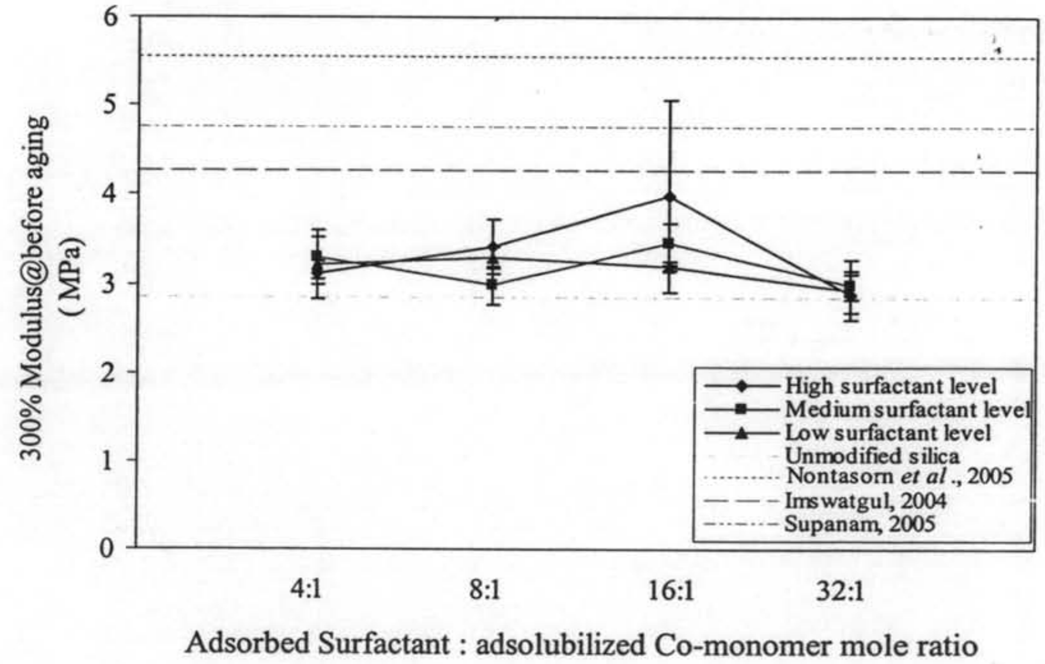


Figure 4.34 300% modulus @before aging of rubber compounds with different modified silicas.

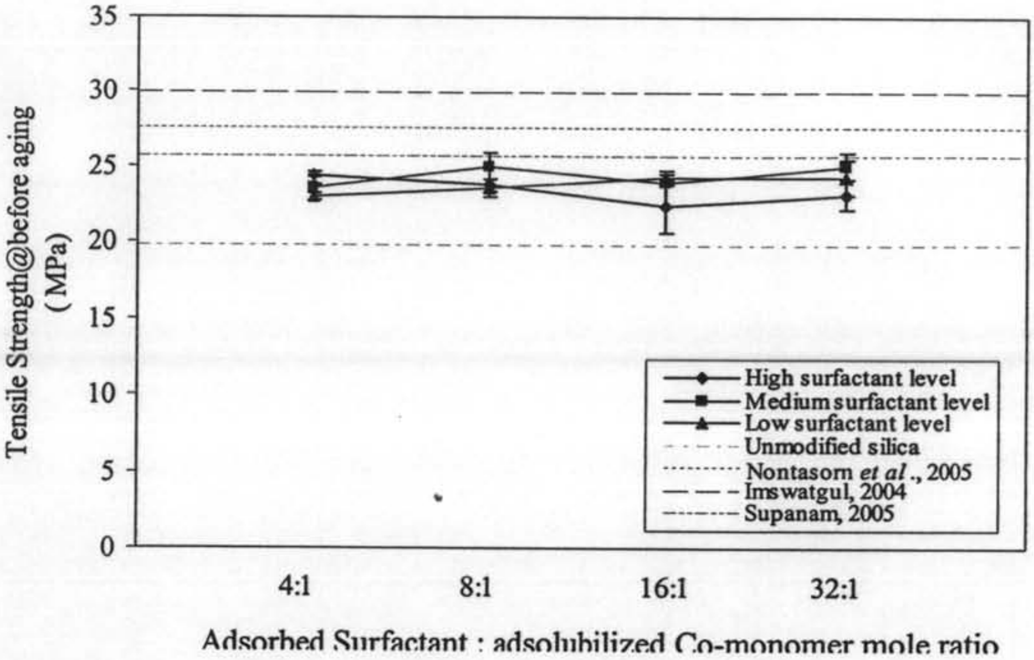


Figure 4.35 Tensile strength @before aging of rubber compounds with different modified silicas.

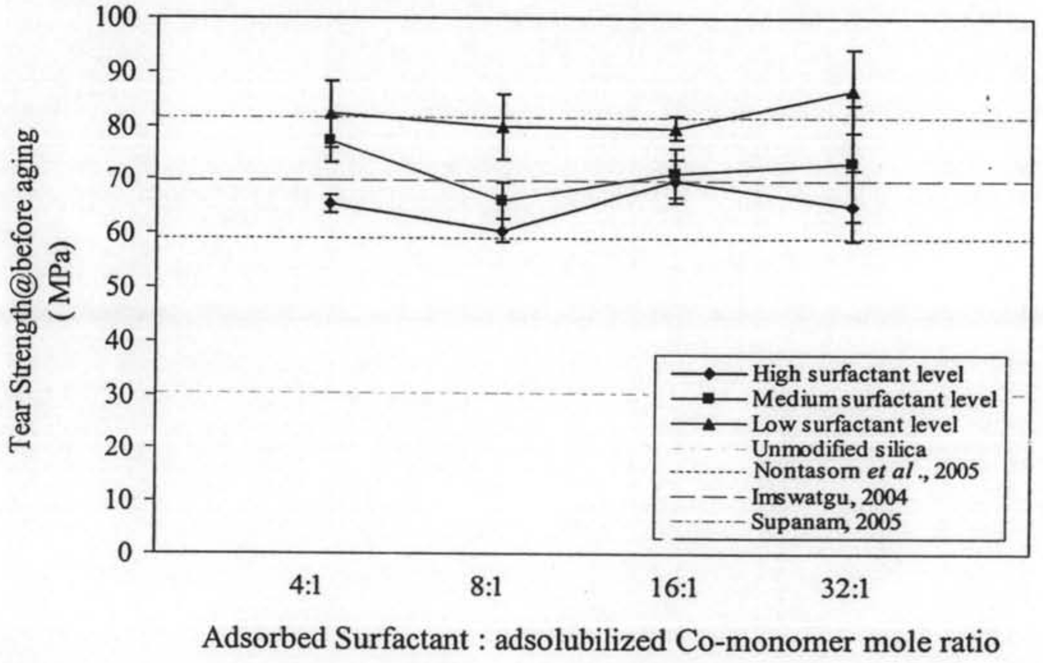


Figure 4.36 Tear strength @before aging of rubber compounds with different modified silicas.

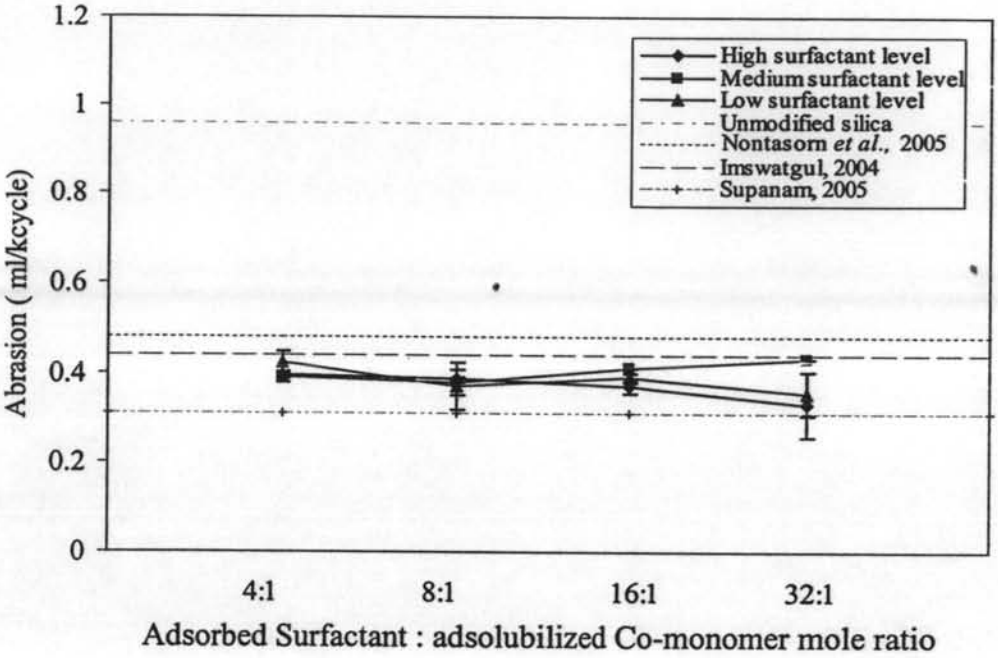


Figure 4.37 Abrasion set of rubber compounds with different modified silicas

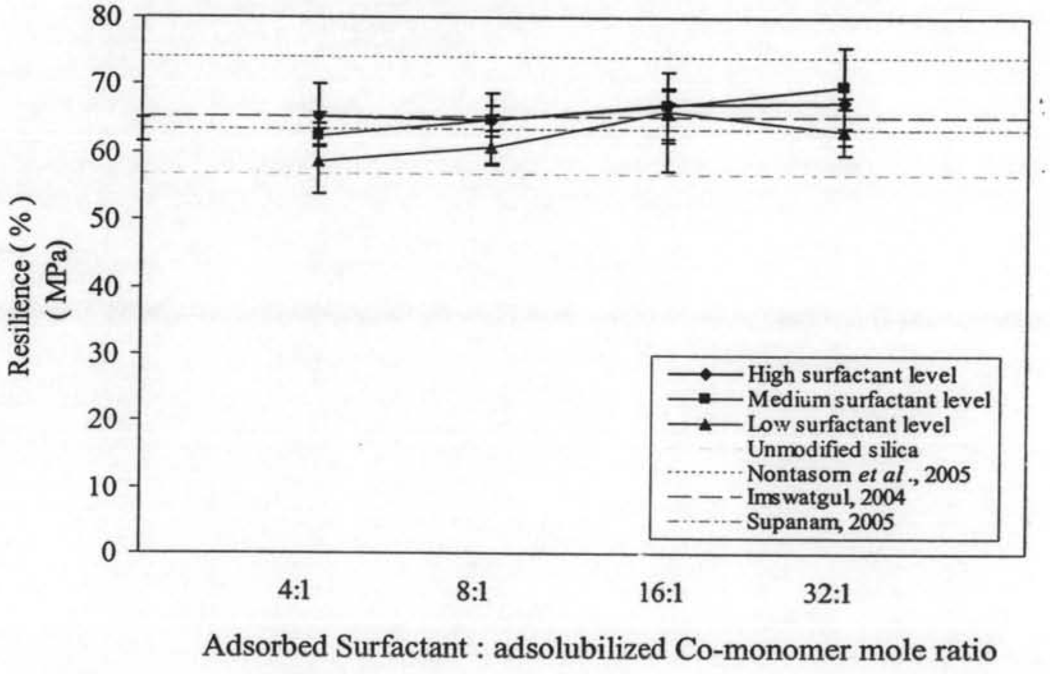


Figure 4.38 Resilience of rubber compounds with different modified silica

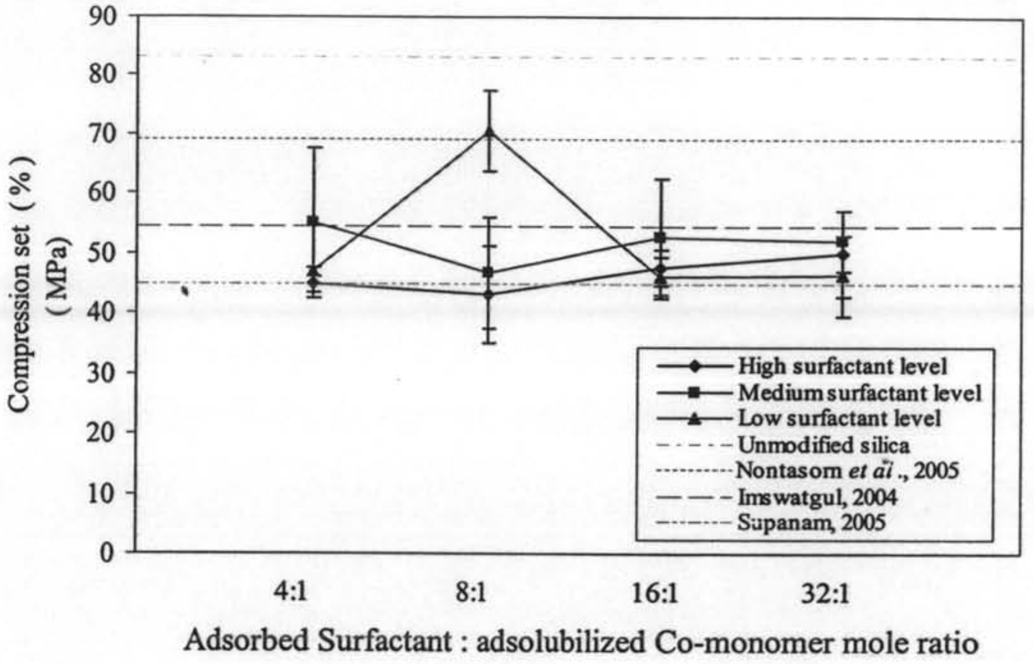


Figure 4.39 Compression set of rubber compounds with different modified silicas.

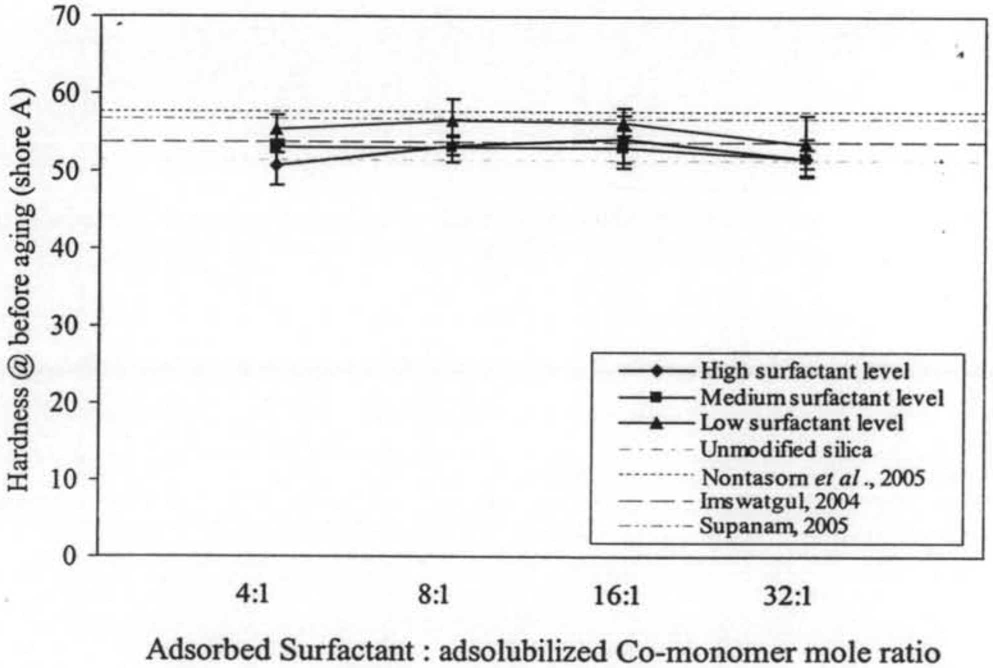


Figure 4.40 Hardness @before aging of rubber compounds with different modified silicas.

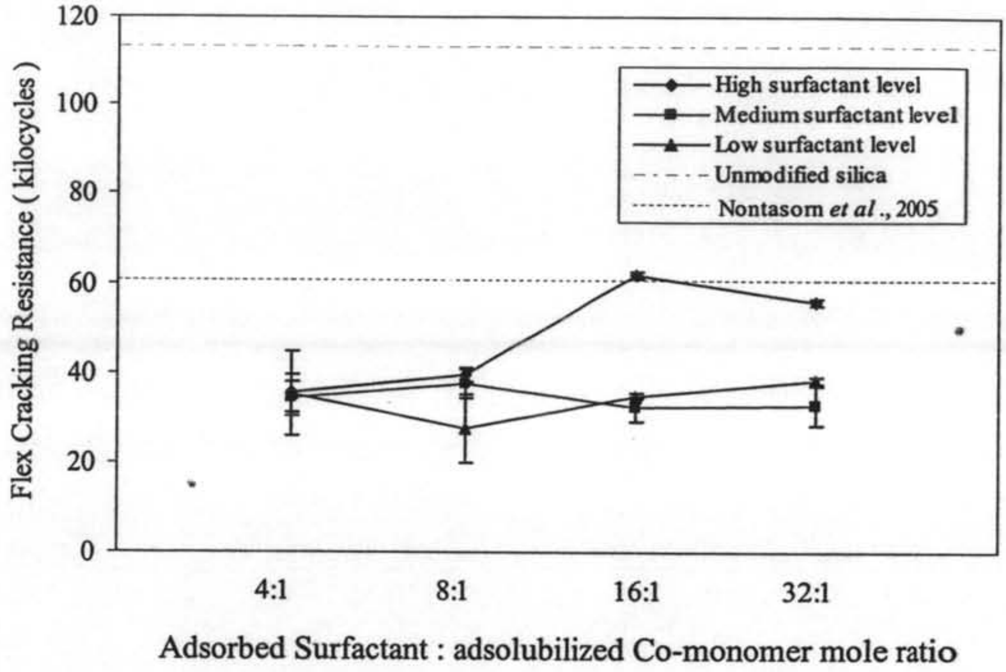


Figure 4.41 Flex cracking resistance of rubber compounds with different modified silicas.

Table 4.6 shows the rubber compound physical properties using different modified silicas. 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 "12" in order to determine the optimum condition of the silica modification system. Qualitative summary of rubber physical properties using different modified silicas is shown in Table 4.7. The results suggest that the best rubber physical properties are obtained from the 16:1 mole ratio of adsorbed surfactant : adsolubilized co-monomer at high surfactant adsorption level.

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 4.8. The percent improvement of surface-modified silica rubber physical properties is shown in Tables 4.9. The "+" designation indicates a greater than 10% improvement in the property over the 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 4.10 shows the positive impact of improvement in resilience of the modified silica compared to the unmodified silica in almost all different mole ratios of adsorbed surfactant : adsolubilized co-monomer and surfactant adsorption level.

Tables 4.11 and 4.12 show the qualitative summary of surface-modified silica rubber physical properties compared to the modified silica using CTAB surfactant and 1:3 mixed surfactant, CTAB and TritonX-100, of the previous studies, Nontasorn *et al.* (2005) and Imsawatgul (2004), 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 with the commercial grade surfactants that have more impurities. However, all modified silicas give the positive improvements in tear strength, abrasion loss, resilience and compression set relative to the previous studies.

Qualitative summary of rubber physical properties obtained from the present study compared to the modified silicas of the previous study (Supanam, 2005) at 3:1 surfactant molar ratios, Arquad®T-50 and Teric®X-10, at 30 min polymerization time is shown in Table 4.13. Table 4.14 presents the percent improvement of surface-modified silica rubber physical properties as compared to the modified silica of the previous study (Supanam, 2005). The positive effect of improvement in resilience was observed in almost all surfactants molar ratios. The other properties are close to those form Supanam (2005).

Therefore, the mole ratio of adsorbed surfactant : adsolubilized co-monomer and surfactant adsorption level 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 the rubber compound physical properties were obtained; thus, commercial grade surfactant can be used to modify silica surface in order to reduce the production cost as demonstrate in Table 4.15.

Table 4.6 Rubber compound physical properties using different modified silica

Property	4:1L	8:1L	16:1L	32:1L	4:1M	8:1M	16:1M	32:1M	4:1H	8:1H	16:1H	32:1H
Cure Time (min)	6.33	7.76	5.11	6.70	6.16	5.64	6.95	6.19	7.01	6.17	6.43	6.41
100% Modulus @before aging (MPa)	1.12	1.17	1.21	1.10	1.16	1.09	1.19	1.08	1.41	1.23	1.48	1.05
100% Modulus @after aging (MPa)	1.50	1.44	1.35	1.40	1.46	1.23	1.45	1.34	1.39	1.47	1.65	1.35
200% Modulus @before aging (MPa)	1.98	2.06	2.00	1.87	2.02	1.90	2.10	1.87	1.94	2.11	2.55	1.82
200% Modulus @after aging (MPa)	2.69	2.63	2.39	2.62	2.63	2.40	2.68	2.43	2.49	2.61	2.93	2.41
300% Modulus @before aging (MPa)	3.22	3.29	3.19	2.94	3.29	2.98	3.46	3.00	3.12	3.42	3.99	2.90
300% Modulus @after aging (MPa)	4.12	4.14	3.80	4.19	4.15	3.82	4.31	3.90	4.00	4.02	4.63	3.76
Tensile Strength @before aging (MPa)	23.01	23.54	24.31	24.26	23.57	24.93	23.93	25.01	24.41	23.76	22.42	23.11
Tensile Strength @after aging (MPa)	20.55	20.46	22.32	20.88	20.45	20.53	21.37	22.34	21.80	21.64	20.73	21.79
Tear Strength @before aging (MPa)	82.05	79.95	79.70	86.71	77.25	66.01	71.20	73.17	65.54	60.53	69.70	65.26
Tear Strength @after aging (MPa)	53.33	61.75	54.29	56.76	54.37	51.27	54.95	55.75	49.37	52.47	50.51	53.48
Abrasion (ml/kcycle)	0.42	0.37	0.39	0.36	0.39	0.38	0.41	0.43	0.40	0.39	0.37	0.33
Resilience (%)	58.58	60.78	66.19	63.22	62.36	64.64	66.82	69.79	65.21	64.79	67.28	67.31
Compression set (%)	46.88	70.58	46.17	46.24	55.07	46.72	52.54	51.94	44.72	42.93	47.47	49.94
Hardness @before aging (shore A)	55.37	56.57	56.23	53.40	53.10	52.93	52.97	51.57	50.77	53.23	54.27	51.73
Hardness @after aging (shore A)	61.67	59.37	59.17	56.50	57.53	54.90	58.40	57.03	54.03	56.93	58.83	55.03
Flex Cracking Resistance (kilocycles)	35.05	27.42	34.51	38.28	34.42	37.43	32.25	32.81	35.30	39.57	61.82	55.84

Table 4.7 Qualitative summary of rubber physical properties using different modified silcas

Property	4:1L	8:1L	16:1L	32:1L	4:1M	8:1M	16:1M	32:1M	4:1H	8:1H	16:1H	32:1H
Cure Time (min)	7	1	12	4	10	11	3	8	2	9	5	6
100% Modulus @before aging (MPa)	5	7	10	4	6	3	8	2	9	11	12	1
100% Modulus @after aging (MPa)	11	7	3.5	6	9	1	8	2	5	10	12	3.5
200% Modulus @before aging (MPa)	6	9	7	2.5	8	4	10	2.5	5	11	12	1
200% Modulus @after aging (MPa)	11	8.5	1	7	8.5	2	10	4	5	6	12	3
300% Modulus @before aging (MPa)	7	8.5	6	3	8.5	4	11	5	1	10	12	2
300% Modulus @after aging (MPa)	7	8	2	10	9	3	11	4	5	6	12	1
Tensile Strength @before aging (MPa)	1	3	8	7	5	10	6	11	9	4	12	2
Tensile Strength @after aging (MPa)	4	2	11	6	1	3	7	12	10	8	5	9
Tear Strength @before aging (MPa)	11	10	9	12	8	4	5	6	2	1	7	3
Tear Strength @after aging (MPa)	5	12	7	11	8	3	9	10	1	4	2	6
Abrasion (ml/kcycle)	2	9.5	6	11	6	8	3	1	4	6	9.5	12
Resilience (%)	1	2	8	4	3	5	9	12	7	6	10	11
Compression set (%)	7	1	10	9	2	8	3	4	11	12	6	5
Hardness @before aging (shore A)	10	12	11	8	6	4	5	2	1	7	9	3
Hardness @after aging (shore A)	12	11	10	5	7	2	8	6	1	4	9	3
Flex Cracking Resistance (kilocycles)	9	1	8	4	7	11	5	6	10	12	3	2
Total	**116**	**112.5**	**129.5**	**113.5**	**112**	**86**	**121**	**97.5**	**88**	**127**	**149.5**	**73.5**

Table 4.8 Rubber compound physical properties using different modified silica samples obtained from the present study compared to the modified silica of the previous systems

Property	Hi-Sil®255[a]	Batch[b]	Silica1[c]	Silica2[d]	Silica3[e]	4:1L	8:1L	16:1L	32:1L	4:1M	8:1M	16:1M	32:1M	4:1H	8:1H	16:1H	32:1H
Cure Time (min)	18.63	5.98	4.86	5.28	5.41	6.33	7.76	5.11	6.70	6.16	5.64	6.95	6.19	7.01	6.17	6.43	6.41
100% Modulus @before aging (MPa)	0.77	1.33	1.92	1.57	1.49	1.12	1.17	1.21	1.10	1.16	1.09	1.19	1.08	1.41	1.23	1.48	1.05
300% Modulus @before aging (MPa)	2.84	4.19	5.55	4.27	4.75	3.22	3.29	3.19	2.94	3.29	2.98	3.46	3.00	3.12	3.42	3.99	2.90
Tensile Strength @before aging (MPa)	19.84	26.43	27.54	29.88	25.64	23.01	23.54	24.31	24.26	23.57	24.93	23.93	25.01	24.41	23.76	22.42	23.11
Tear Strength @before aging (MPa)	30.27	37.75	58.94	69.82	81.59	82.05	79.95	79.70	86.71	77.25	66.01	71.20	73.17	65.54	60.53	69.70	65.26
Abrasion (ml/kcycle)	0.96	0.66	0.48	0.44	0.31	0.42	0.37	0.39	0.36	0.39	0.38	0.41	0.43	0.40	0.39	0.37	0.33
Resilience (%)	56.7	73.6	74.2	65.37	63.4	58.58	60.78	66.19	63.22	62.36	64.64	66.82	69.79	65.21	64.79	67.28	67.31
Compression set (%)	83.1	76.02	69.06	54.48	44.92	46.88	70.58	46.17	46.24	55.07	46.72	52.54	51.94	44.72	42.93	47.47	49.94
Hardness @before aging (shore A)	51.4	55.3	57.67	53.73	56.8	55.37	56.57	56.23	53.40	53.10	52.93	52.97	51.57	50.77	53.23	54.27	51.73
Flex Cracking Resistance (kilocycles)	113.1	35.84	60.44	-	-	35.05	27.42	34.51	38.28	34.42	37.43	32.25	32.81	35.30	39.57	61.82	55.84

[a] Results from Thammathadanukul *et al.*, 1996

[b] Results from Thammathadanukul *et al.*, 1996; Styrene-isoprene co-monomer

[c] Results from Nontasorn *et al.*, 2005; modified silica with 200 g of CTAB, 5 g of styrene-isoprene loading

[d] Results from Imswatgul., 2004; modified silica with 1:3 ratio of surfactants, CTAB:Triton X-100 in monolayer structure at 30 min polymerizaiton time

[e] Results from Supanam,, 2005; modified with 3:1 ratio of surfactants, Arquad®T-50:Teric® X-10 in monolayer structure at 30 min polymerizaiton time

Table 4.9 Percent improvement of surface-unmodified silica rubber physical properties as compared to the unmodified silica of the previous study (Thammathadanukul *et al.*, 1996)

Property	**4:1L**	**8:1L**	**16:1L**	**32:1L**	**4:1M**	**8:1M**	**16:1M**	**32:1M**	**4:1H**	**8:1H**	**16:1H**	**32:1H**
Cure Time (min)	66.00	58.33	72.55	64.04	66.94	69.73	62.69	66.79	62.37	66.90	65.47	65.58
100% Modulus @before aging (MPa)	44.95	52.38	56.80	42.24	50.82	42.03	54.07	39.83	83.51	59.22	91.82	36.72
300% Modulus @before aging (MPa)	13.32	16.01	12.22	3.45	15.70	5.08	21.95	5.50	9.87	20.58	40.49	2.00
Tensile Strength @before aging (MPa)	15.98	18.67	22.55	22.30	18.78	25.65	20.63	26.08	23.02	19.77	13.00	16.48
Tear Strength @before aging (MPa)	171.1	164.1	163.3	186.5	155.2	118.1	135.2	141.7	116.5	100.0	130.3	115.6
Abrasion (ml/kcycle)	55.9	61.5	59.4	63.0	59.4	60.4	57.3	55.2	58.9	59.9	61.5	65.6
Resilience (%)	3.3	7.2	16.7	11.5	10.0	14.0	17.9	23.1	15.0	14.3	18.7	18.7
Compression set (%)	43.6	15.1	44.4	44.4	33.7	43.8	36.8	37.5	46.2	48.3	42.9	39.9
Hardness @before aging (shore A)	55.4	56.6	56.2	53.4	53.1	52.9	53.0	51.6	50.8	53.2	54.3	51.7
Flex Cracking Resistance (kilocycles)	-69.01	-75.7	-69.5	-66.2	-69.6	-66.9	-71.5	-71.0	-68.8	-65.0	-45.3	-50.6

Table 4.10 Qualitative summary of surface-modified silica rubber physical properties as compared to the unmodified silica of the previous study (Thammathadanukul *et al.*, 1996)

Property	**4:1L**	**8:1L**	**16:1L**	**32:1L**	**4:1M**	**8:1M**	**16:1M**	**32:1M**	**4:1H**	**8:1H**	**16:1H**	**32:1H**
Cure Time (min)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
100% Modulus @before aging (MPa)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
300% Modulus @before aging (MPa)	+1	+1	+1	+1	+1	0	+1	0	0	+1	+1	0
Tensile Strength @before aging (MPa)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
Tear Strength @before aging (MPa)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
Abrasion (ml/kcycle)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
Resilience (%)	0	0	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
Compression set (%)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
Hardness @before aging (shore A)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
Flex Cracking Resistance (kilocycles)	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Comparative Score	**+7**	**+7**	**+8**	**+8**	**+8**	**+7**	**+8**	**+7**	**+7**	**+8**	**+8**	**+7**

Table 4.11 Percent improvement of surface-modified silica rubber physical properties as compared to the modified silica of the previous study (Nontasorn *et al.*, 2005)

Property	4:1L	8:1L	16:1L	32:1L	4:1M	8:1M	16:1M	32:1M	4:1H	8:1H	16:1H	32:1H
Cure Time (min)	-30.3	-59.7	-5.2	-37.9	-26.7	-16.0	-43.0	-27.3	-44.2	-26.9	-32.4	-32.0
100% Modulus @before aging (MPa)	-41.9	-38.9	-37.1	-43.0	-39.5	-43.0	-38.2	-43.9	-26.4	-36.1	-23.1	-45.2
300% Modulus @before aging (MPa)	-42.0	-40.6	-42.6	-47.1	-40.8	-46.2	-37.6	-46.0	-43.8	-38.3	-28.1	-47.8
Tensile Strength @before aging (MPa)	-16.4	-14.5	-11.7	-11.9	-14.4	-9.5	-13.1	-9.2	-11.4	-13.7	-18.6	-16.1
Tear Strength @before aging (MPa)	39.2	35.7	35.2	47.1	31.1	12.0	20.8	24.1	11.2	2.7	18.3	10.7
Abrasion (ml/kcycle)	11.8	22.9	18.8	26.0	18.8	20.8	14.6	10.4	17.7	19.8	22.9	31.3
Resilience (%)	-21.1	-18.1	-10.8	-14.8	-16.0	-12.9	-9.9	-5.9	-12.1	-12.7	-9.3	-9.3
Compression set (%)	32.1	-2.2	33.1	33.0	20.3	32.4	23.9	24.8	35.2	37.8	31.3	27.7
Hardness @before aging (shore A)	-4.0	-1.9	-2.5	-7.4	-7.9	-8.2	-8.2	-10.6	-12.0	-7.7	-5.9	-10.3
Flex Cracking Resistance (kilocycles)	-42.0	-54.6	-42.9	-36.7	-43.0	-38.1	-46.6	-45.7	-41.6	-34.5	2.3	-7.6

Table 4.12 Percent improvement of surface-modified silica rubber physical properties as compared to the modified silica of the previous study (Imswatgul, 2004)

Property	4:1L	8:1L	16:1L	32:1L	4:1M	8:1M	16:1M	32:1M	4:1H	8:1H	16:1H	32:1H
Cure Time (min)	-19.9	-47.0	3.2	-26.9	-16.7	-6.8	-31.6	-17.2	-32.8	-16.8	-21.8	-21.5
100% Modulus @before aging (MPa)	-28.9	-25.3	-23.1	-30.2	-26.0	-30.3	-24.4	-31.4	-10.0	-21.9	-5.9	-32.9
300% Modulus @before aging (MPa)	-24.6	-22.8	-25.4	-31.2	-23.0	-30.1	-18.9	-29.8	-26.9	-19.8	-6.6	-32.2
Tensile Strength @before aging (MPa)	-23.0	-21.2	-18.6	-18.8	-21.1	-16.6	-19.9	-16.3	-18.3	-20.5	-25.0	-22.7
Tear Strength @before aging (MPa)	17.5	14.5	14.1	24.2	10.6	-5.5	2.0	4.8	-6.1	-13.3	-0.2	-6.5
Abrasion (ml/kcycle)	3.8	15.9	11.4	19.3	11.4	13.6	6.8	2.3	10.2	12.5	15.9	25.0
Resilience (%)	-10.4	-7.0	1.3	-3.3	-4.6	-1.1	2.2	6.8	-0.2	-0.9	2.9	3.0
Compression set (%)	14.0	-29.6	15.2	15.1	-1.1	14.2	3.6	4.7	17.9	21.2	12.9	8.3
Hardness @before aging (shore A)	3.0	5.3	4.7	-0.6	-1.2	-1.5	-1.4	-4.0	-5.5	-0.9	1.0	-3.7

Table 4.13 Percent improvement of surface-modified silica rubber physical properties as compared to the modified silica of the previous study (Supanam, 2005)

Property	4:1L	8:1L	16:1L	32:1L	4:1M	8:1M	16:1M	32:1M	4:1H	8:1H	16:1H	32:1H
Cure Time (min)	-17.1	-43.5	5.5	-23.8	-13.9	-4.3	-28.5	-14.4	-29.6	-14.0	-18.9	-18.5
100% Modulus @before aging (MPa)	-25.1	-21.3	-19.0	-26.5	-22.1	-26.6	-20.4	-27.7	-5.2	-17.7	-0.9	-29.3
300% Modulus @before aging (MPa)	-32.2	-30.6	-32.9	-38.1	-30.8	-37.2	-27.1	-36.9	-34.3	-27.9	-16.0	-39.0
Tensile Strength @before aging (MPa)	-10.3	-8.2	-5.2	-5.4	-8.1	-2.8	-6.7	-2.4	-4.8	-7.3	-12.6	-9.9
Tear Strength @before aging (MPa)	0.6	-2.0	-2.3	6.3	-5.3	-19.1	-12.7	-10.3	-19.7	-25.8	-14.6	-20.0
Abrasion (ml/kcycle)	-36.6	-19.4	-25.8	-14.5	-25.8	-22.6	-32.3	-38.7	-27.4	-24.2	-19.4	-6.5
Resilience (%)	-7.6	-4.1	4.4	-0.3	-1.6	2.0	5.4	10.1	2.9	2.2	6.1	6.2
Compression set (%)	-4.4	-57.1	-2.8	-2.9	-22.6	-4.0	-17.0	-15.6	0.4	4.4	-5.7	-11.2
Hardness @before aging (shore A)	-2.5	-0.4	-1.0	-6.0	-6.5	-6.8	-6.7	-9.2	-10.6	-6.3	-4.5	-8.9

Table 4.14 Qualitative summary of surface-modified silica rubber physical properties as compared to the unmodified silica of the previous study (Supanam, 2005)

Property	4:1L	8:1L	16:1L	32:1L	4:1M	8:1M	16:1M	32:1M	4:1H	8:1H	16:1H	32:1H
Cure Time (min)	-1	-1	0	-1	-1	0	-1	-1	-1	-1	-1	-1
100% Modulus @before aging (MPa)	-1	-1	-1	-1	-1	-1	-1	-1	+1	-1	0	-1
300% Modulus @before aging (MPa)	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Tensile Strength @before aging (MPa)	-1	0	0	0	0	0	0	0	0	0	+1	0
Tear Strength @before aging (MPa)	0	0	0	0	0	-1	-1	-1	-1	-1	0	-1
Abrasion (ml/kcycle)	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	0
Resilience (%)	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
Compression set (%)	0	-1	0	0	-1	0	-1	-1	+1	+1	0	-1
Hardness @before aging (shore A)	0	0	0	0	0	0	0	0	-1	0	0	0
Comparative Score	**-5**	**-4**	**-2**	**-3**	**-4**	**-3**	**-5**	**-5**	**-2**	**-3**	**0**	**-4**

Table 4.15 Production Cost of Modified Silica Surface

Surfactant	Cost of surfactants (Bath/kg modified silica)
CTAB[a]	2,430
CTAB:TritonX-100[b], (1:3)	870
Arquad®T-50:Teric®X-10[c], (16:1H)	64
Arquad®T-50:Teric®X-10[d], (16:1L)	27

[a] Nontasorn *et al.* (2005); modified silica with 200 g of CTAB

[b] Imswatgul (2004); modified silica with 1:3 ratio of surfactants

[c] Present work; modified silica with 16:1 mole ratio of surfactants adsorbed:co-monomer adsolubilized at high surfactant adsorption level

[d] Present work; modified silica with 16:1 mole ratio of surfactants adsorbed:co-monomer adsolubilized at low surfactant adsorption level

The price of CTAB, Triton X-100, Arquad®T-50 and Teric®X-10 are 9,400, 4,200, 230, and 150 Bath/kg, respectively.