



CHAPTER IV RESULTS AND DISCUSSION

4.1 Adsorption Isotherm of CTAB onto Silica Hi-Sil[®]255

The adsorption isotherm of CTAB adsorption at the solution pH of 8 and 30°C on Hi-Sil[®]255, an amorphous precipitated silica, was measured and found to have a plateau value of 600 μmol s of CTAB per g of silica (Figure 4.1). The experimentally determined critical micelle concentration (CMC) of 900 μM was very close to the 920 μM reported by Rosen (1989). The initial CTAB concentration giving the equilibrium bulk concentration below CMC for a ratio of 1 kg of silica per 12.5 l is 54,000 μmolar , which is consistent with that reported by Chaisirimahamorakot (2001).

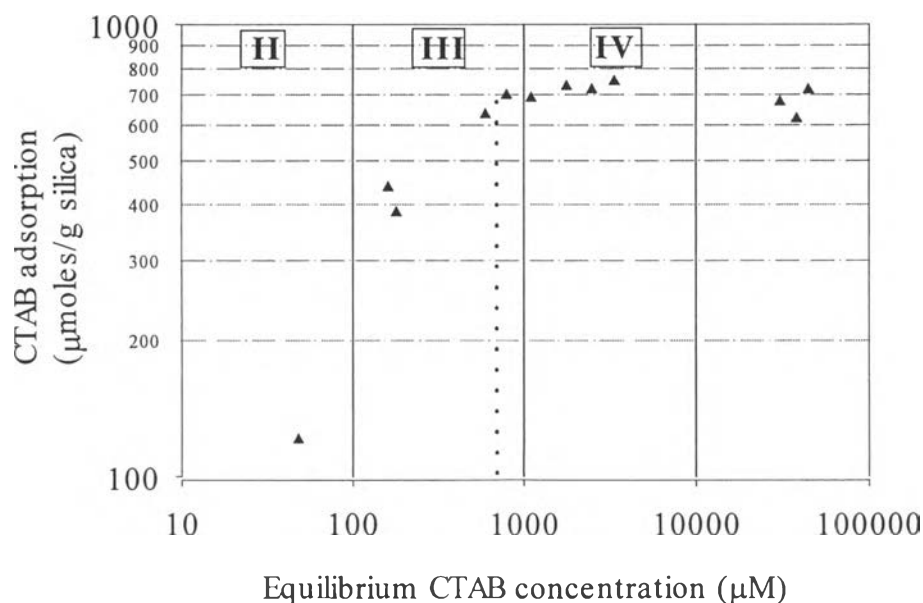


Figure 4.1 Adsorption isotherm of CTAB onto silica Hi-Sil[®]255 at pH 8 and 30°C.

4.2 Determination of Steady State Time of the Studied System

Based on the previous results reported by Chaisirimahamorakot (2001), the *in situ* polymerization experiment was carried out by using 20 g styrene-isoprene charged per kilogram silica at 70°C with 30 min retention time. It is necessary to know how long the studied system takes to equilibrate. The effluent samples were then taken at different interval times. The effluent samples were analyzed for TOC. The carbon content value represents the amount of CTAB and styrene-isoprene monomers dissolving in the aqueous samples. As seen in Figure 4.2, the TOC is stable almost at the beginning of the startup time. The results indicate that the polymerization reaction occurs immediately once the monomers enter into the reactor since the reaction is very sensitive to temperature. Therefore, for each experimental run, the effluent from the reactor was collected in the product tank until the system was shut down.

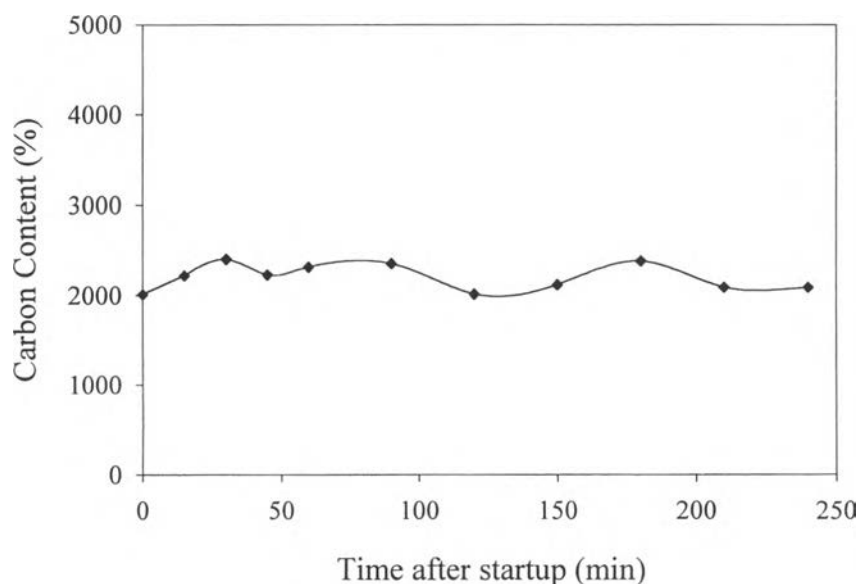


Figure 4.2 Carbon content in effluent samples at different time after startup.

4.3 Surface Characterization of Modified Silicas

The admicellar polymerization process has been known to affect a variety of physical characteristics of silicas, including BET surface area and mean agglomerate particle size (Thammathadanukul *et al.*, 1996). All samples were given a designation consisting of a number indicating the amount of monomer (styrene-isoprene) loading (5, 20 and 30 g of co-monomers per kg of silica), and a letter representing polymerization times of 30, 45 and 60 min is denoted by L, M and H, respectively.

4.3.1 BET Surface Area

All modified silica samples had BET surface areas less than that of the unmodified silica, some by as much as 20% (see Figure 4.3). For any given co-monomer loading, the modified silicas with 30 min retention time had the lowest surface area, while the highest surface area was obtained with 45 min retention time. Though the reason for this is unclear, the following scenario is a possible explanation. At low co-monomer loadings, the small aggregates of polymer were formed both on the surface and in the pore causing a decrease in the surface area.

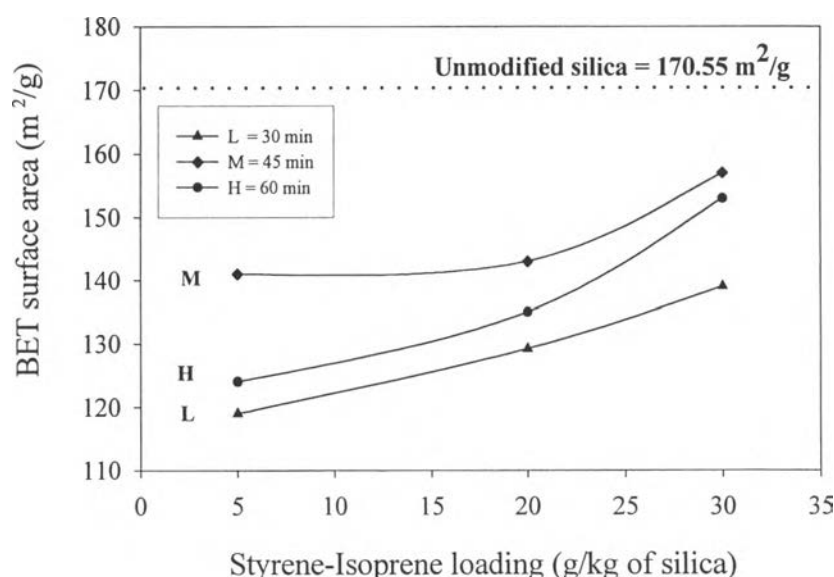


Figure 4.3 BET surface areas of modified silicas as a function of retention time and styrene-isoprene loading.

At high monomer loadings, most of polymers were formed in the large droplet that may be formed only on the surface; therefore, during the washing process or sieving process, significant amount of these surface aggregates might be removed, exposing the silica surface.

4.3.2 Mean Agglomerate Particle Size

Figure 4.4 shows the effect of retention time and co-monomer loading on the mean agglomerate particle size. As seen from the figure, the mean agglomerate particle size of all modified silicas increased, some by as much as 65%. The effect of the monomers loading on the mean agglomerate particle size was more pronounced than the retention time. At 5 g co-monomer loading, all samples at three different retention times had the highest degree of agglomeration as compared to the other two higher monomer loadings.

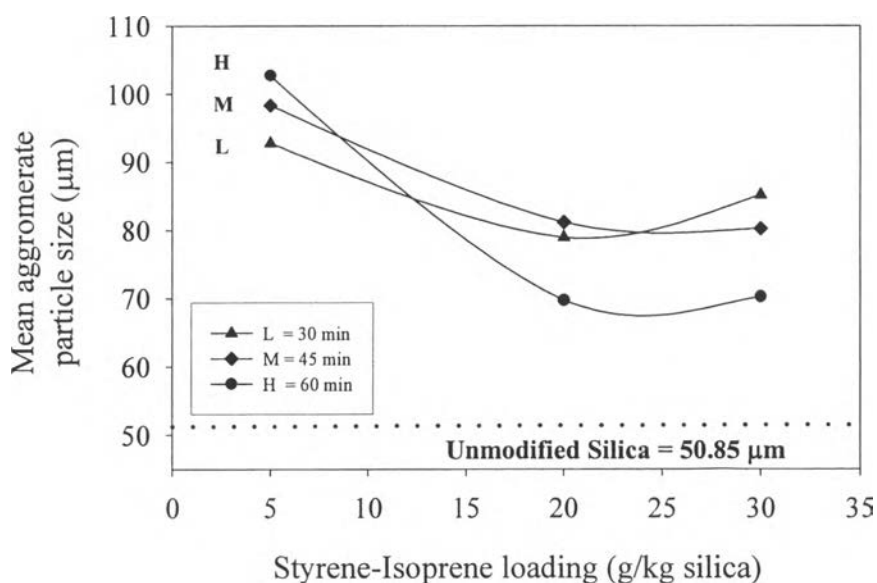


Figure 4.4 Mean agglomerate particle size of modified silicas as a function of retention time and styrene-isoprene loading.

Chaisirimahamorakot (2001) concluded that the increase in the mean agglomerate particle size was resulted from the formation of polymer bridges between silica particles. The observed trends may be due to the change in the distribution of monomers within the admicelle at different co-monomer loadings. At

low monomer loadings, the monomer(5) are evenly distributed, making the joining of contacting particles likely. At intermediate and high monomer loadings, the monomers may begin to separate within the admicelle, forming “pools” of monomer, enriching some areas, depleting others, which would again decrease the likelihood of particles joining. It had previously been stated that the reason for a decrease in the aggregate size might be due to the processing of the silica, specifically, grinding it back to powder by forcing it through a sieve (Chinpan, 1996).

4.3.3 Morphology of Modified Silicas

The scanning electron micrographs of the unmodified silica and the modified silicas are shown in Figures 4.5 to 4.8. Comparisons between the unmodified and modified silica images also showed that the particle size of silica increased after the polymerization of styrene-isoprene on the silica surface. Interestingly, the surfaces of most modified silica samples appeared rough as compared to the surface of the unmodified silica. The polymerization of the co-monomer styrene-isoprene on the silica surface resulted in the rough appearance.

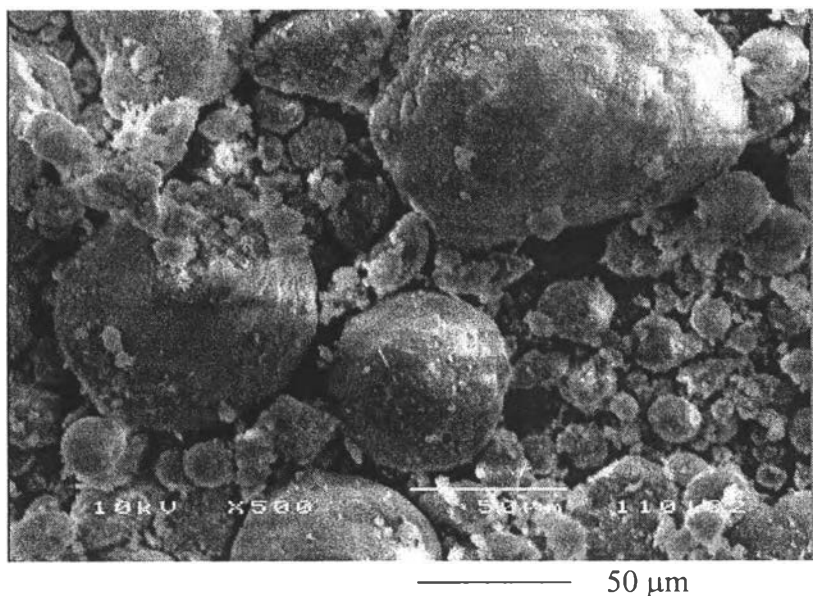
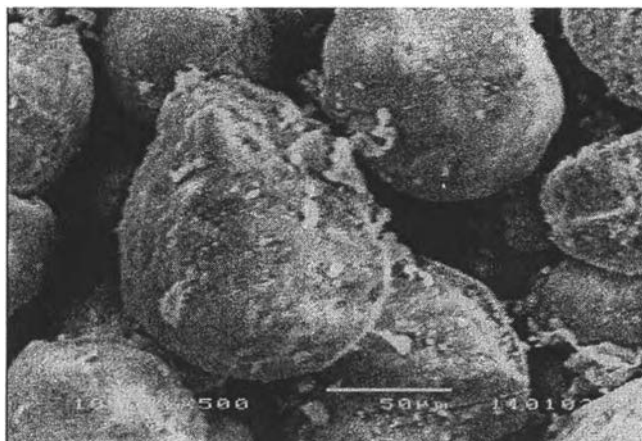
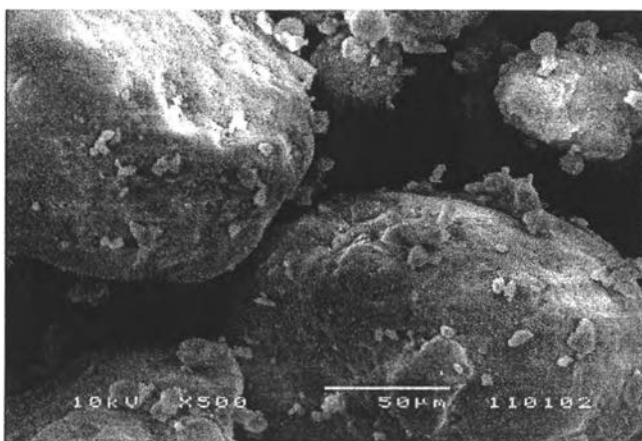


Figure 4.5 Scanning electron micrographs of unmodified silica, Hi-Sil[®]255.

A. 5L



B. 5M



C. 5H

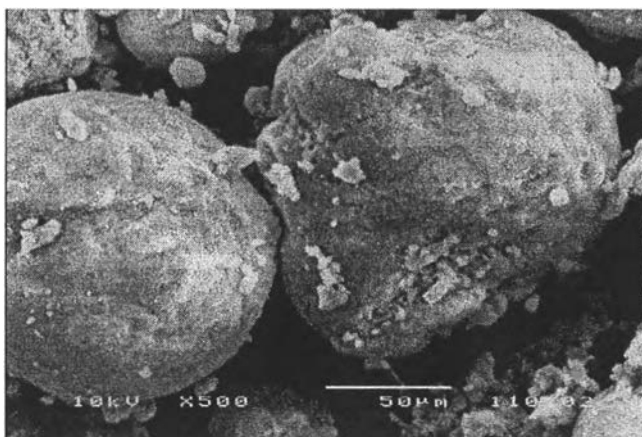
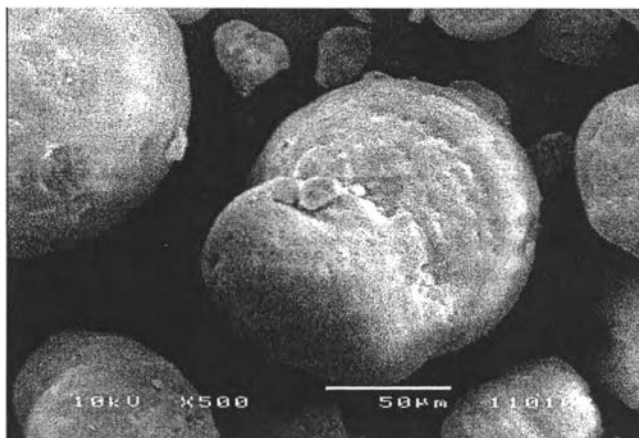
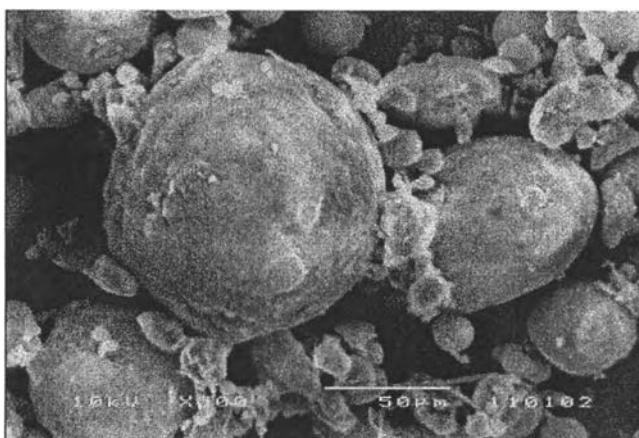


Figure 4.6 Scanning electron micrographs of modified silica, 5 g of co-monomer loading, at 500X magnification.

A. 20L



B. 20M



C. 20H

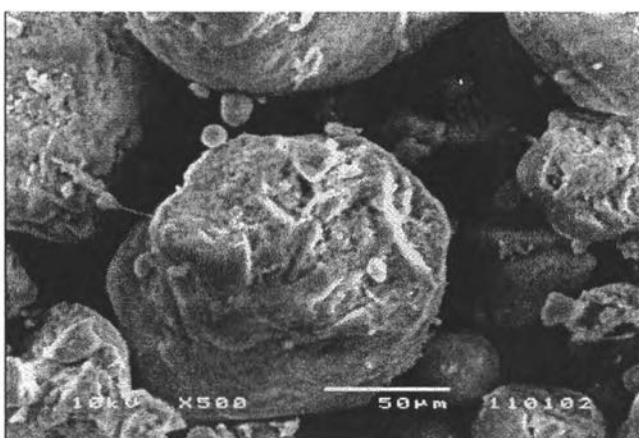
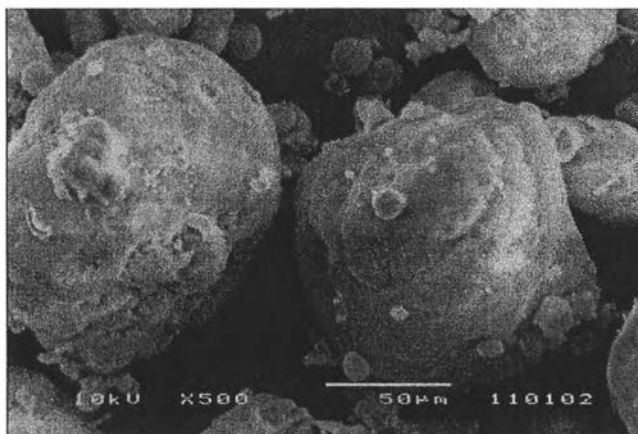
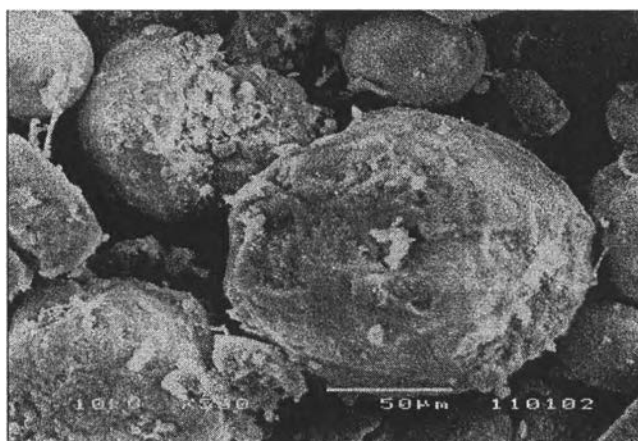


Figure 4.7 Scanning electron micrographs of modified silica, 20 g co-monomer loading, at 500X magnification.

A. 30L



B. 30M



C. 30H

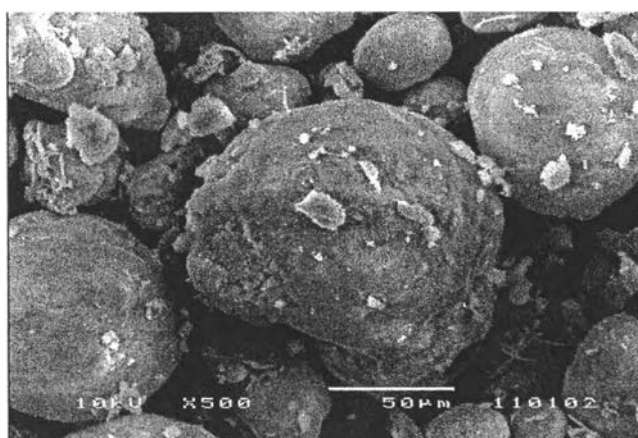


Figure 4.8 Scanning electron micrographs of modified silica, 30 g co-monomer loading, at 500X magnification.

4.3.4 The Formation of Poly(styrene-isoprene)

In order to determine, in a qualitative sense, how firmly the styrene-isoprene co-polymer was attached to the surface of the silica. The polymer from the modified silicas was extracted by refluxing with tetrahydrofuran (THF). Figure 4.9 illustrates the FT-IR spectra of Hi-Sil[®]255 (unmodified silica) showing two peaks of silanol group (Si-OH) peak at a number 3430 cm^{-1} and silicon dioxide (Si-O₂) peak at a number $1100\text{-}1200\text{ cm}^{-1}$. Figure 4.10 shows the FT-IR spectra of CTAB having two dominant peaks of CH₂, CH₃ stretching peak at a number $2700\text{-}2900\text{ cm}^{-1}$ and amino group peak at a number 1500 cm^{-1} . The extracted material was analyzed by FT-IR in order to prove the existence of poly(styrene-isoprene) on the silica surface and the spectra compared to the standard reference spectra of poly(styrene-*co*-isoprene) (Aldrich 18,292-3) (Figure 4.11). The characteristic benzene ring functional group peak at the wave number of 700 cm^{-1} proves the existence of styrene and aliphatic carbon double bond (C=C) peak at a number of 1600 cm^{-1} proves the presence of isoprene, amino group of CTAB peak at a number of 1500 and silicon dioxide (Si-O₂) peak at a number of $1100\text{-}1200\text{ cm}^{-1}$ were also found. The spectra of all extracted materials are shown in Figures 4.12-4.20. The spectra provide an evidence of the existence of poly(styrene-isoprene) on the silica surface. A mass balance on the system again showed that it was not possible to extract all of the polymer on the surface, with approximately 60% of the polymer being extractable. The inability to fully extract the polymer using refluxing tetrahydrofuran again demonstrates that the polymer is quite firmly embedded in the silica pores.

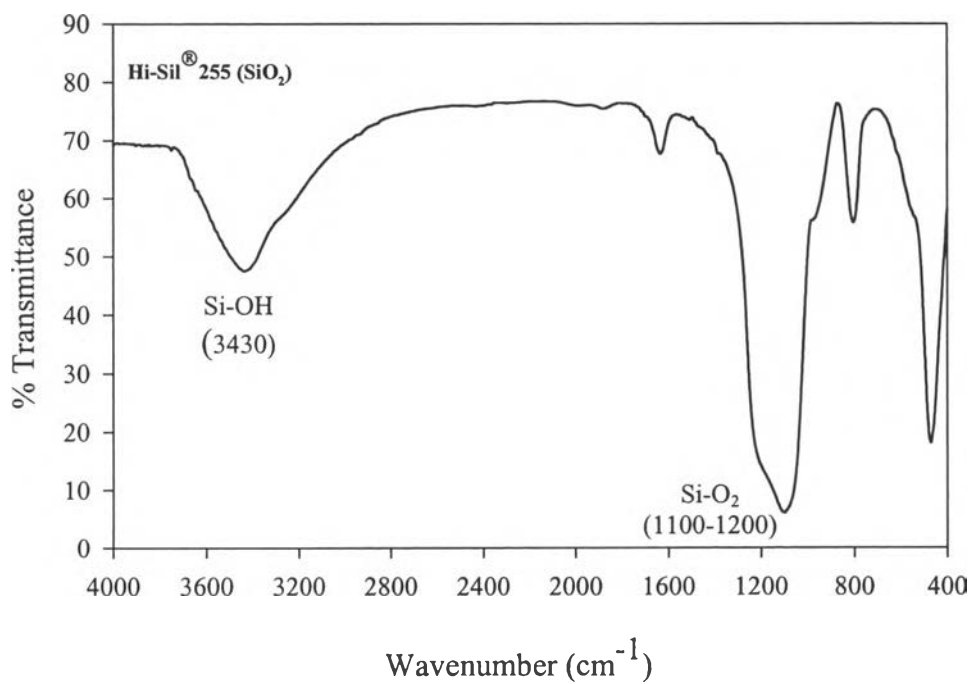


Figure 4.9 FT-IR spectrum of unmodified silica (SiO₂).

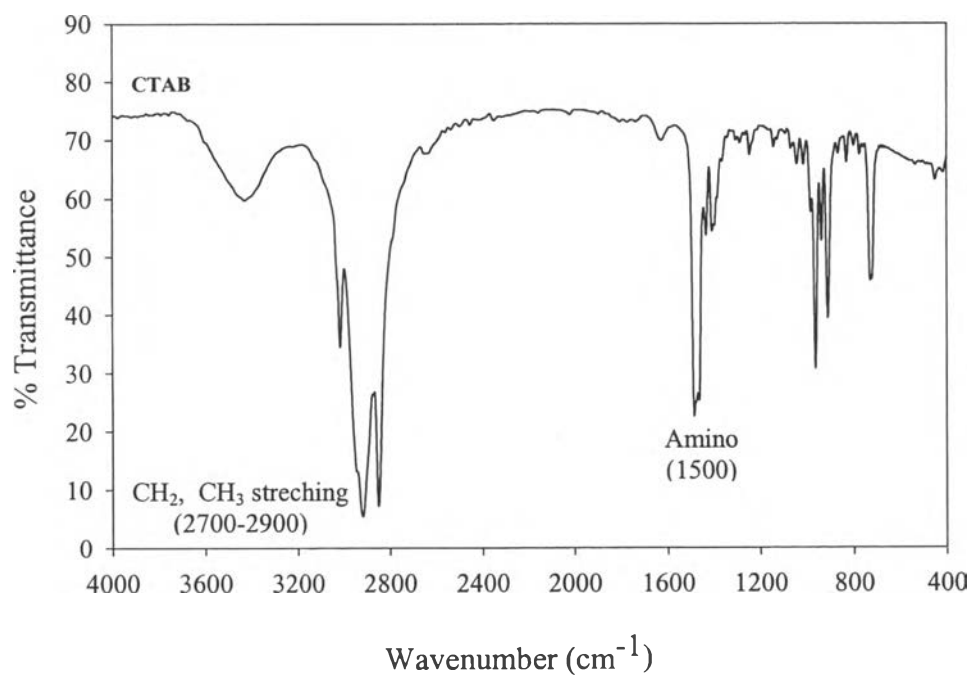


Figure 4.10 FT-IR spectrum of Hexadecyltrimethylammonium bromide (CTAB).

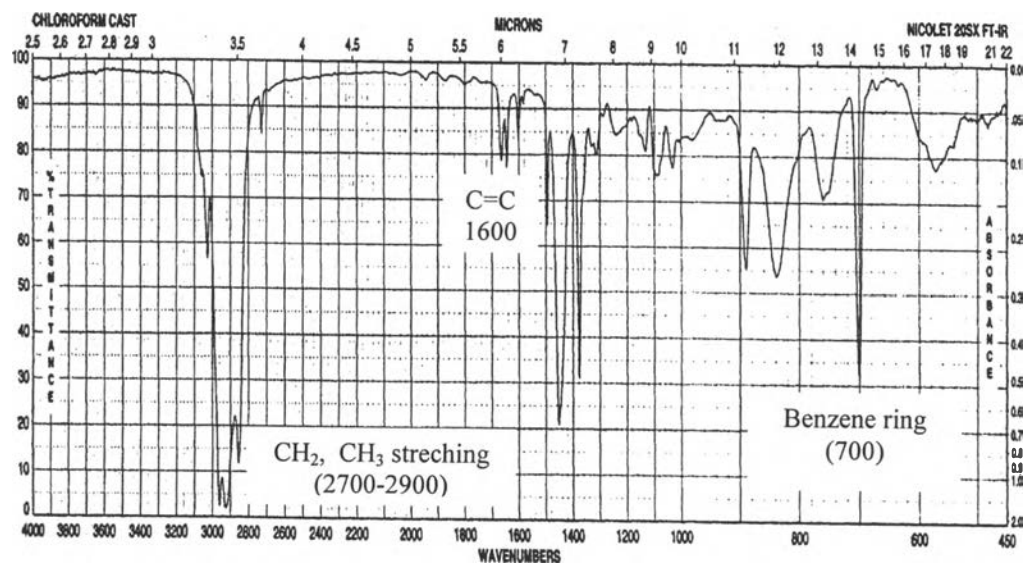


Figure 4.11 FT-IR spectrum of Poly(styrene-*co*-isoprene), ABA block copolymer from Aldrich 18,292-3.

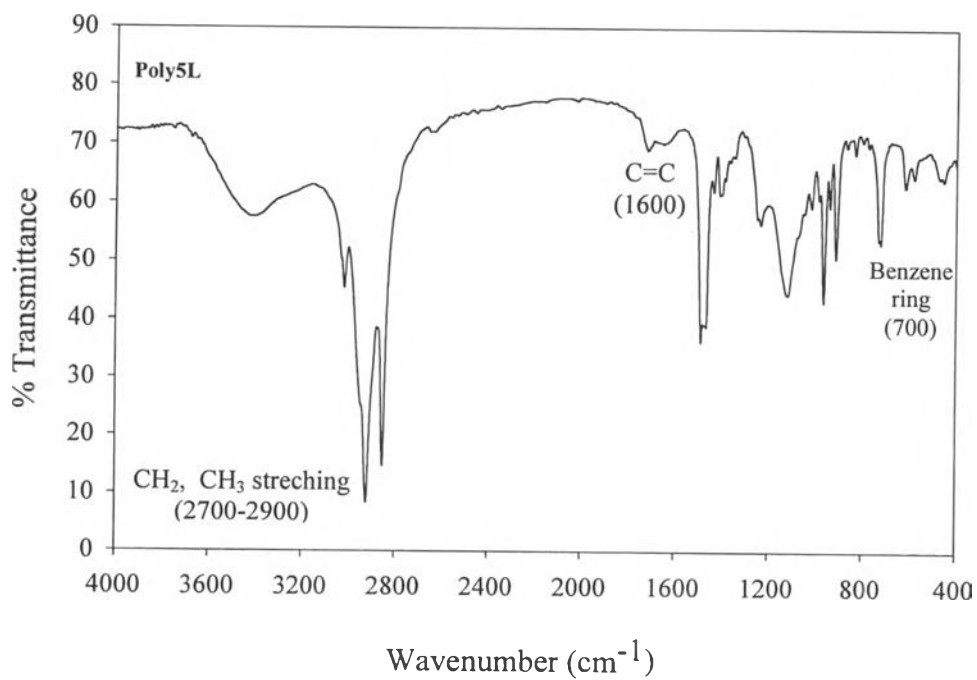


Figure 4.12 FT-IR spectrum of the extracted material (poly5L).

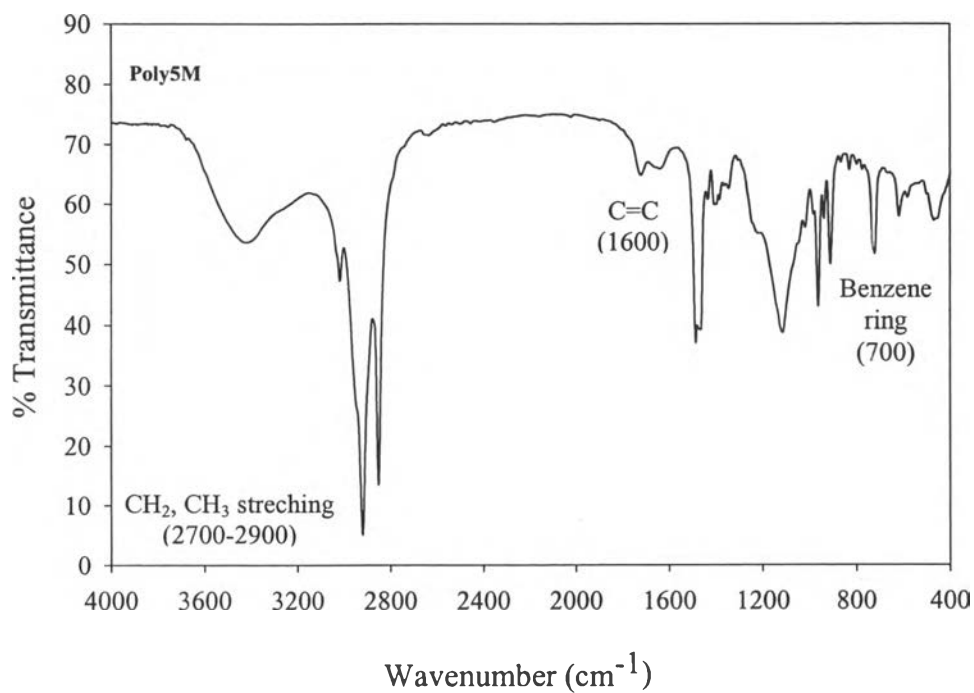


Figure 4.13 FT-IR spectrum of the extracted material (poly5M).

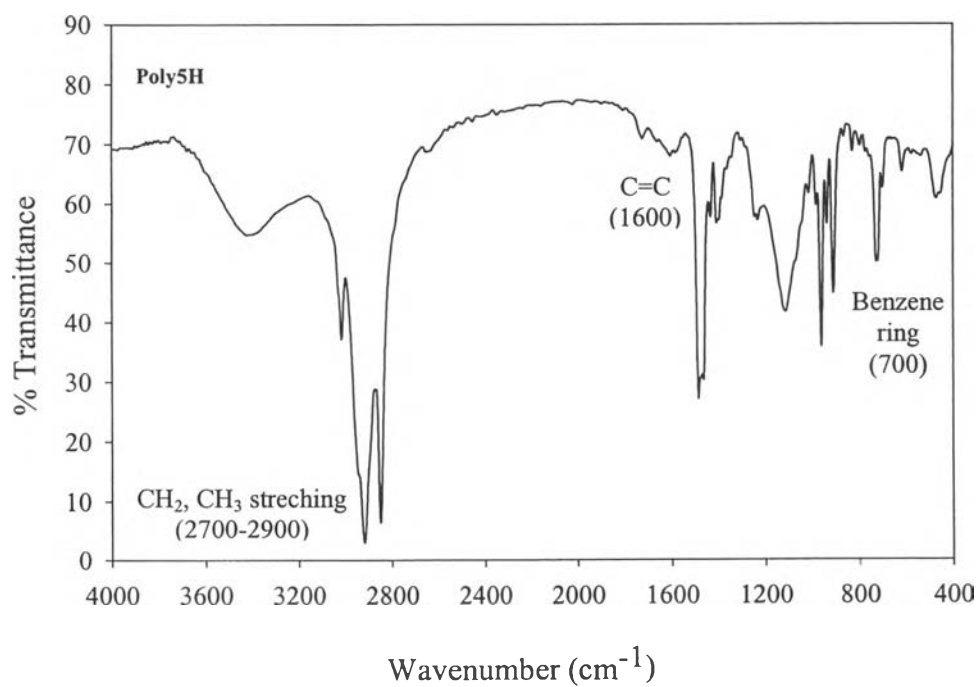


Figure 4.14 FT-IR spectrum of the extracted material (poly5H).

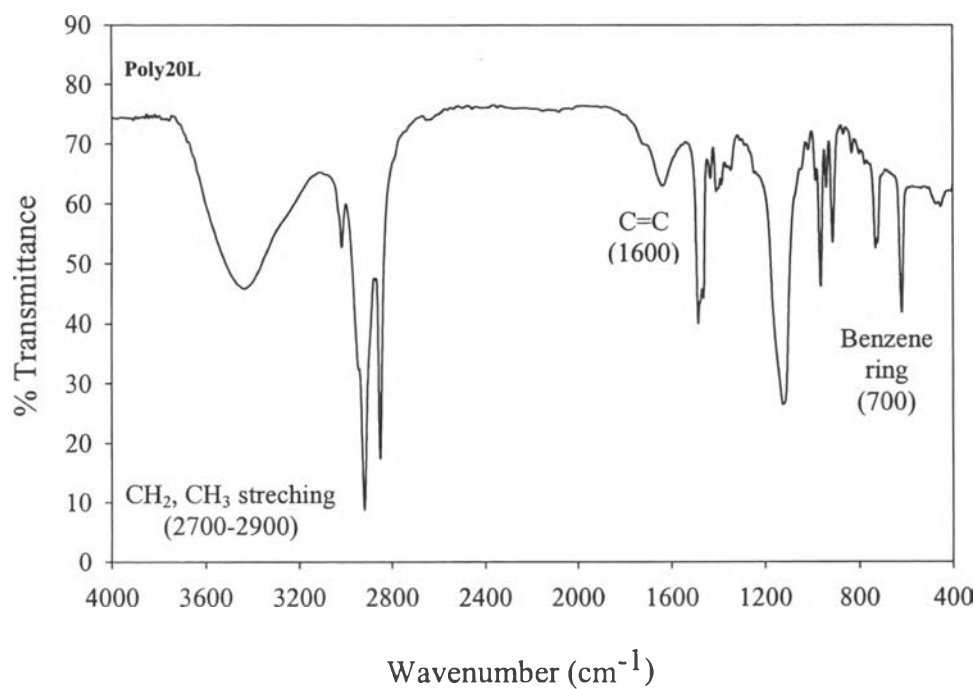


Figure 4.15 FT-IR spectrum of the extracted material (poly20L).

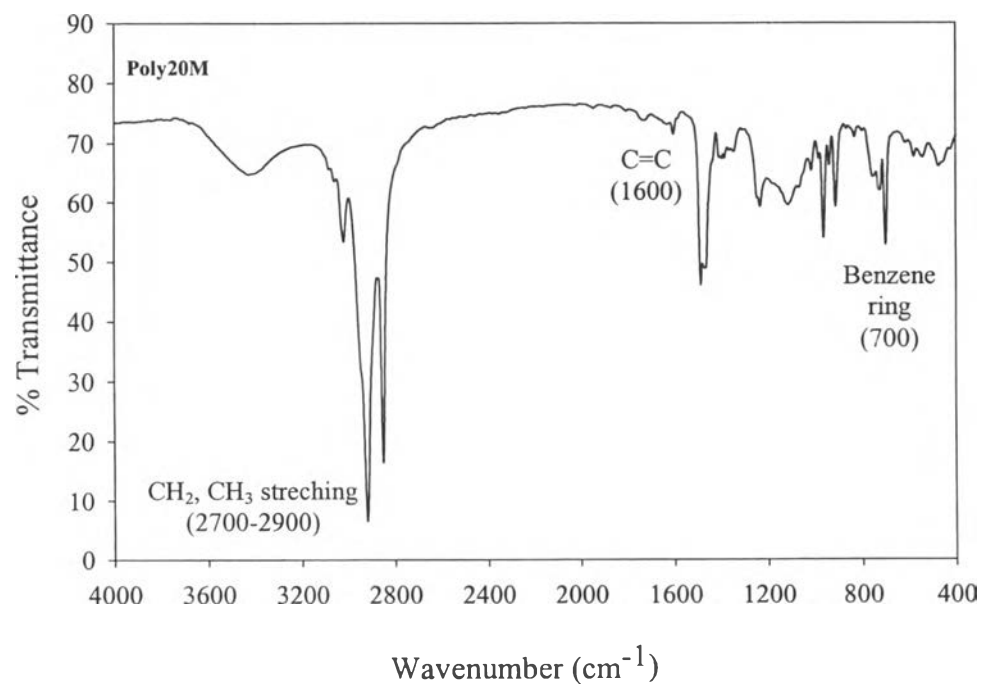


Figure 4.16 FT-IR spectrum of the extracted material (poly20M).

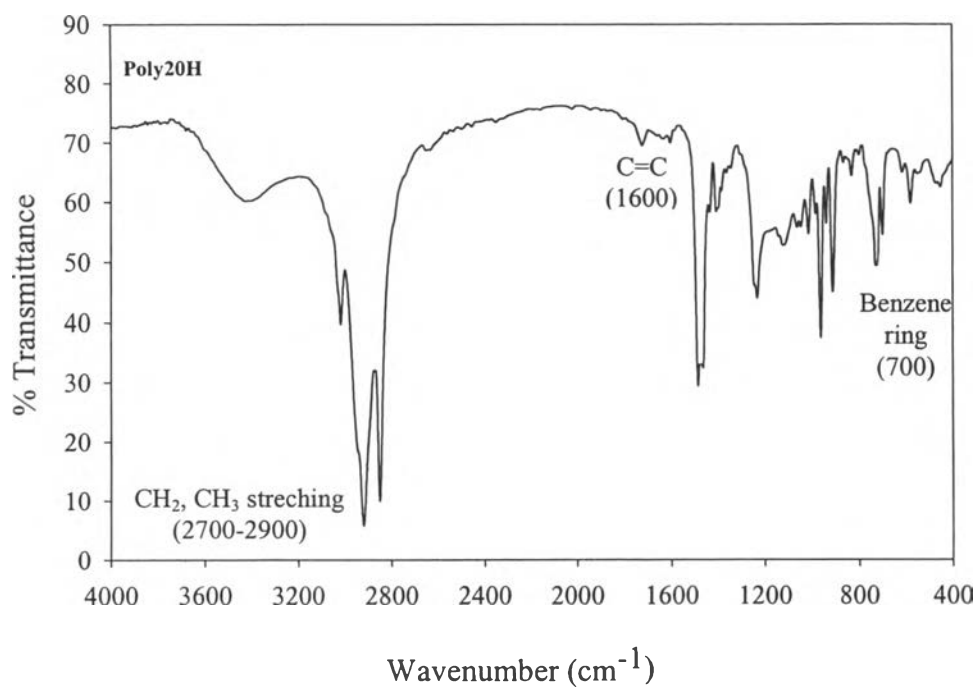


Figure 4.17 FT-IR spectrum of the extracted material (poly20H).

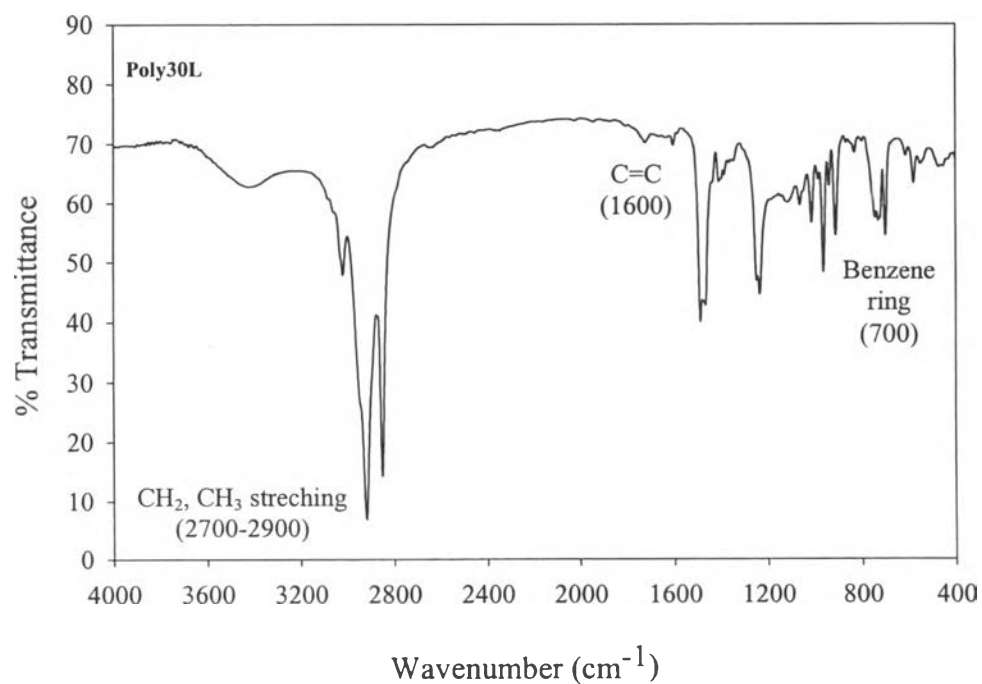


Figure 4.18 FT-IR spectrum of the extracted material (poly30L).

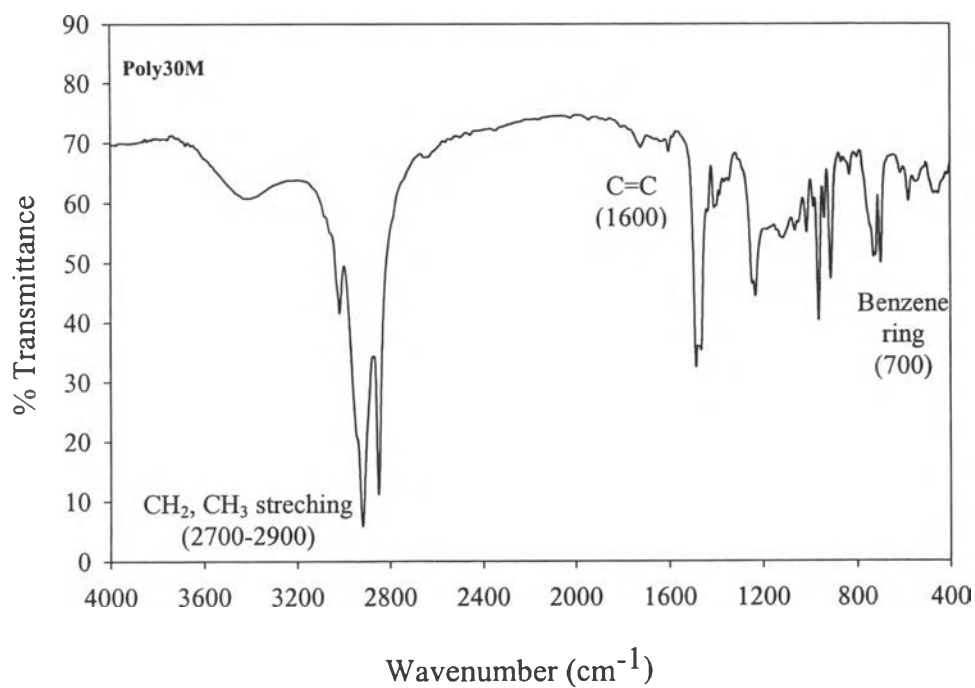


Figure 4.19 FT-IR spectrum of the extracted material (poly30M).

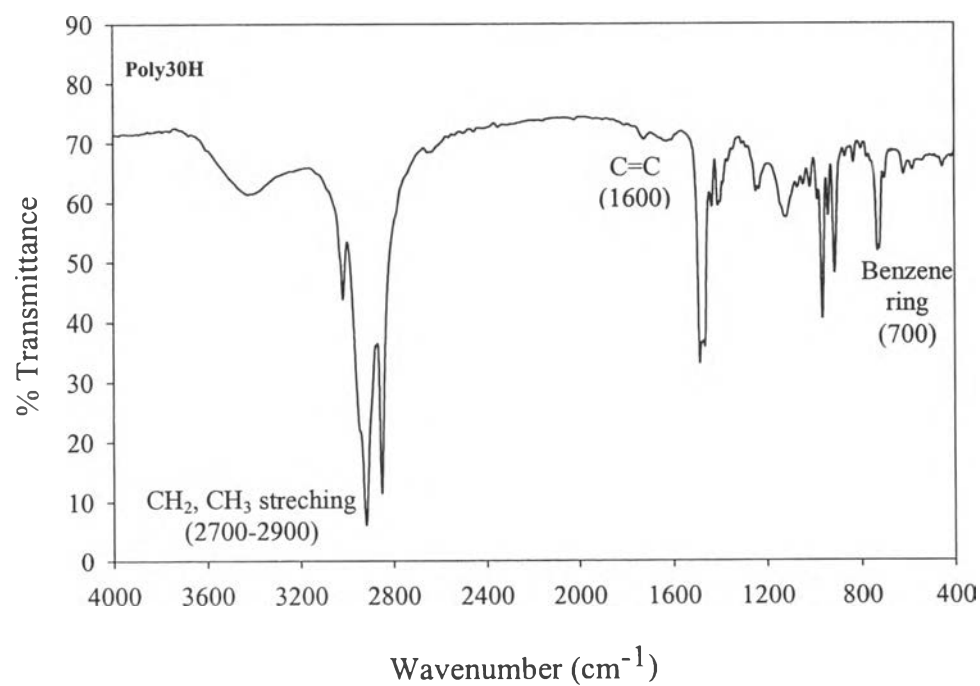


Figure 4.20 FT-IR spectrum of the extracted material (poly30H).

4.3.5 Determination of Amounts of Poly(styrene-isoprene) formed on the silica surfaces

All samples were examined by thermogravimetric analysis in order to verify the existence of poly(styrene-isoprene) forming on the silica surfaces. Figure 4.21 shows the water loss from the unmodified silica below 150°C. Thus, any weight change of the modified silicas above 150°C should be the result of the surface modification. Figure 4.22 shows the decomposition of CTAB between 200 to 300°C. Figure 4.23 shows the decomposition of CTAB adsorbed onto the silica, which appears to occur in two steps, the first from 170 to 300°C and the second from 300 to 450°C. The second peak of the weight loss may result from the stronger bonding, chemisorption, between CTAB and silica.

To predict the decomposition temperature of poly(styrene-isoprene) of the modified silicas, a sample was prepared by depositing polystyrene dissolved with THF onto the silica surface. Figure 4.24 shows that the decomposition of polystyrene takes place between 350 and 480°C. The decomposition of poly(styrene-isoprene) from the admicellar polymerization modified silica is shown in Figure 4.25. The graphs clearly show the decomposition of CTAB from 200 to 280°C and 300 to 450°C while that of the polymer is from 280 to 400°C.

Figures 4.26 to 4.34 show the TGA results of different modified silicas before and after the THF extraction. The TGA results of all modified silica samples again showed a two-step decomposition process. The first-step is the CTAB deformation at 150 to 300°C. The second one is CTAB chemisorbed on the silica as well as poly(styrene-isoprene) decomposition at 300 to 400°C. To calculate the amount of polymer present, the amount of CTAB decomposing is calculated from the first weight drop, and this is subtracted from the weight loss at the second peak. The amount of extracted polymer was then calculated. It was found that not all polymers could be extracted from the modified silica as confirmed by O'Haver *et al.* (1994). The Figure 4.35 shows the amount of polymer deposit as a function of the monomers loading and the retention time. The results show a good correlation between a reduction in the BET surface area and an increase in the amount of

polymer deposit. As shown in Table 4.1, the 5 g co-monomer loading with 30-min retention time results in the highest polymer formed on the silica surface.

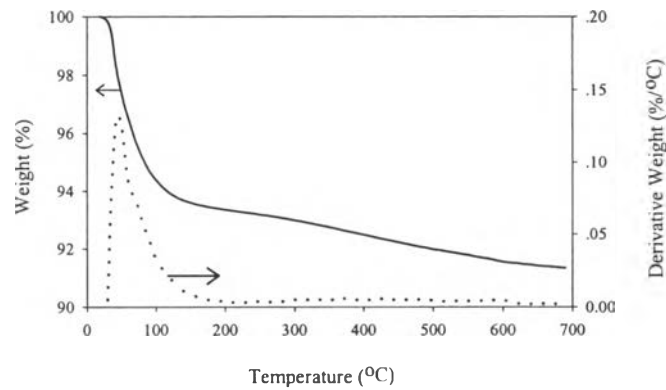


Figure 4.21 TGA result of unmodified silica Hi-Sil[®]255.

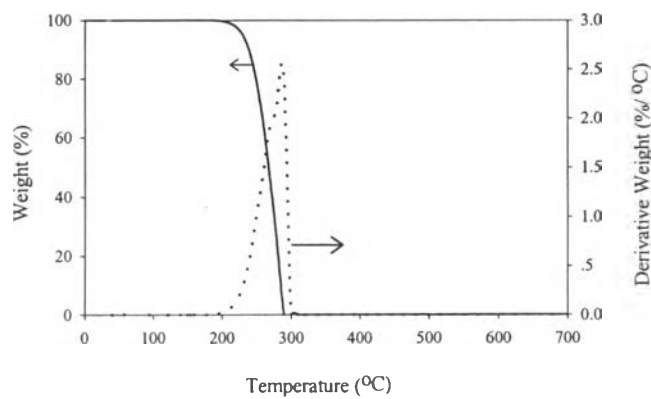


Figure 4.22 TGA result of Hexadecyltrimethylammonium bromide (CTAB).

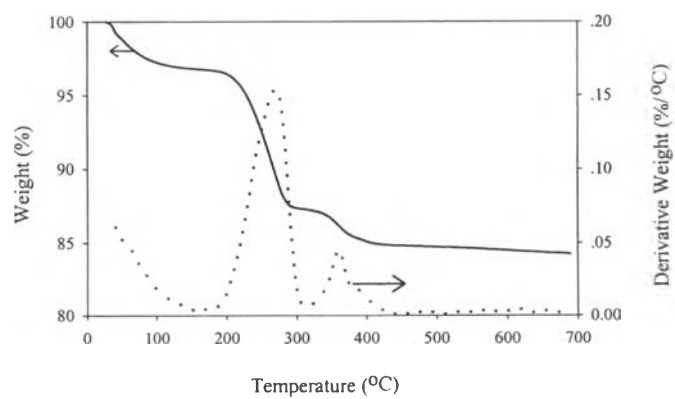


Figure 4.23 TGA results of silica Hi-Sil[®]255 adsorbed with CTAB (Chaisirimahamorakot, 2001).

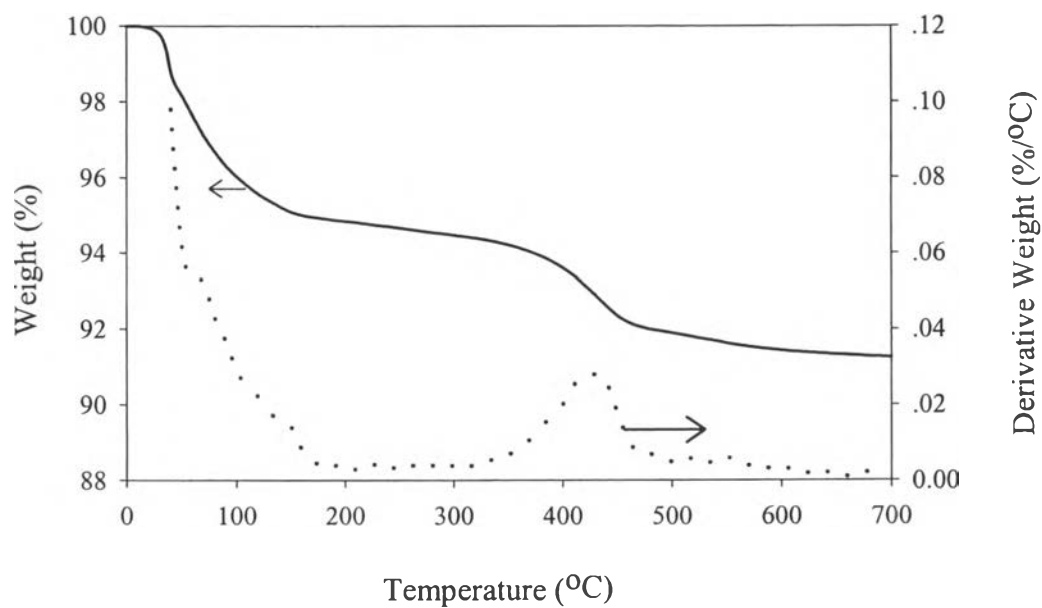


Figure 4.24 TGA results of silica Hi-Sil[®]255 adsorbed with polystyrene (Chaisirimahamorakot, 2001).

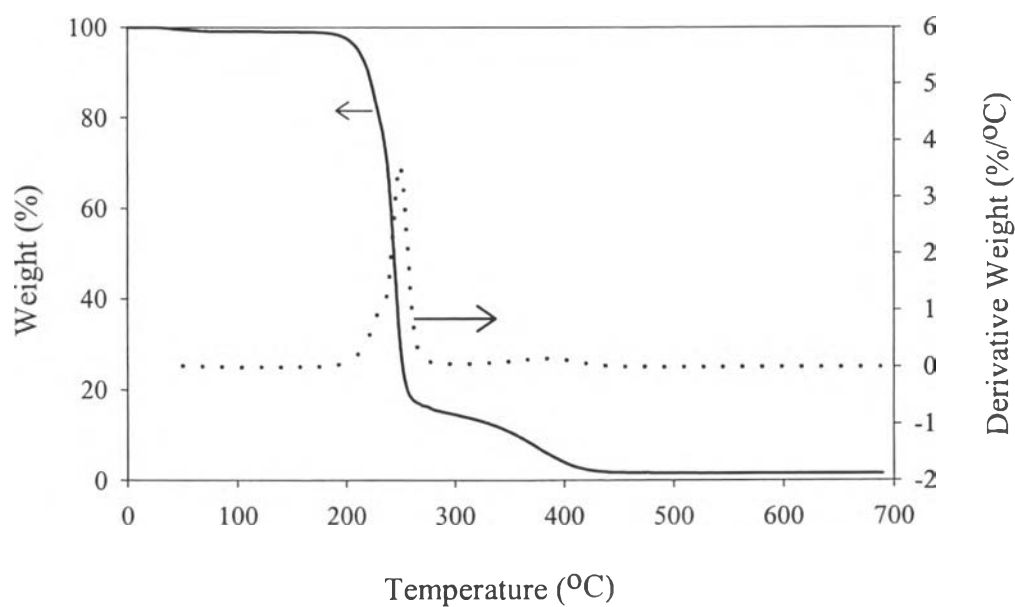
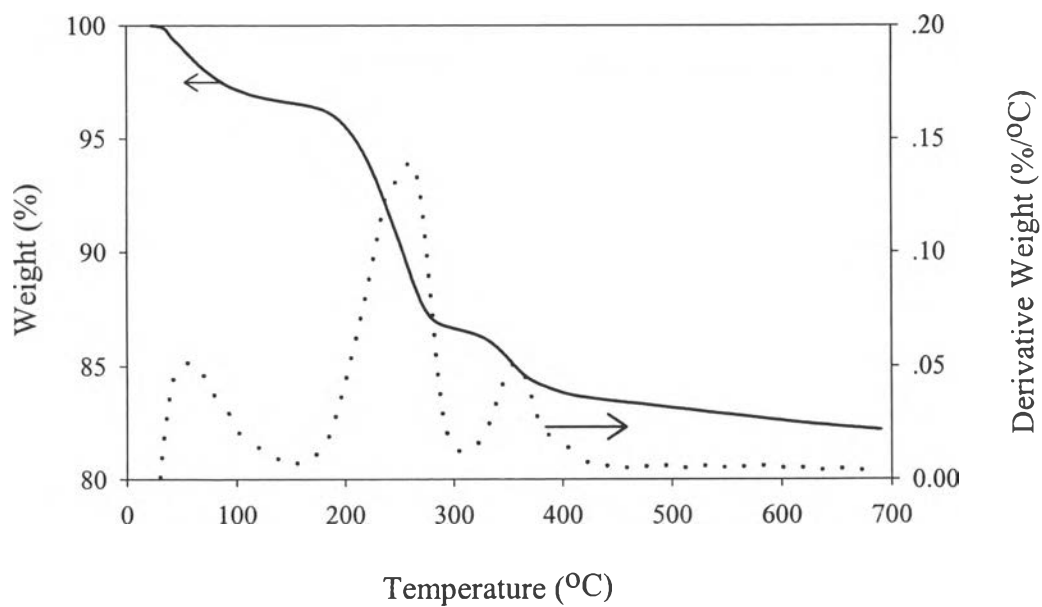


Figure 4.25 TGA results of poly(styrene-isoprene) polymerized in CTAB (Chaisirimahamorakot, 2001).

A. Modified silica before extraction



B. Modified silica after extraction

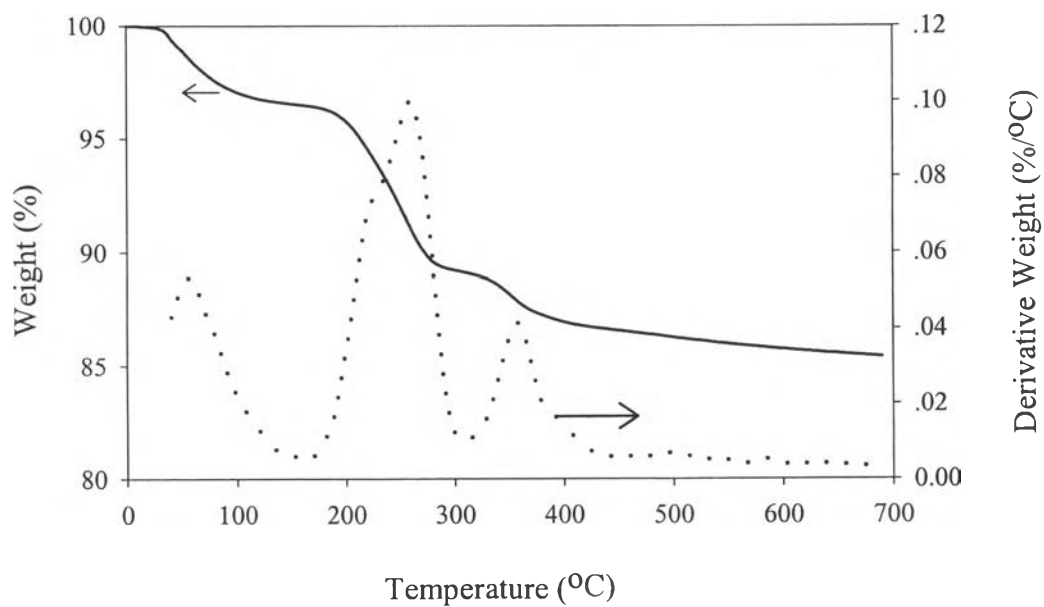
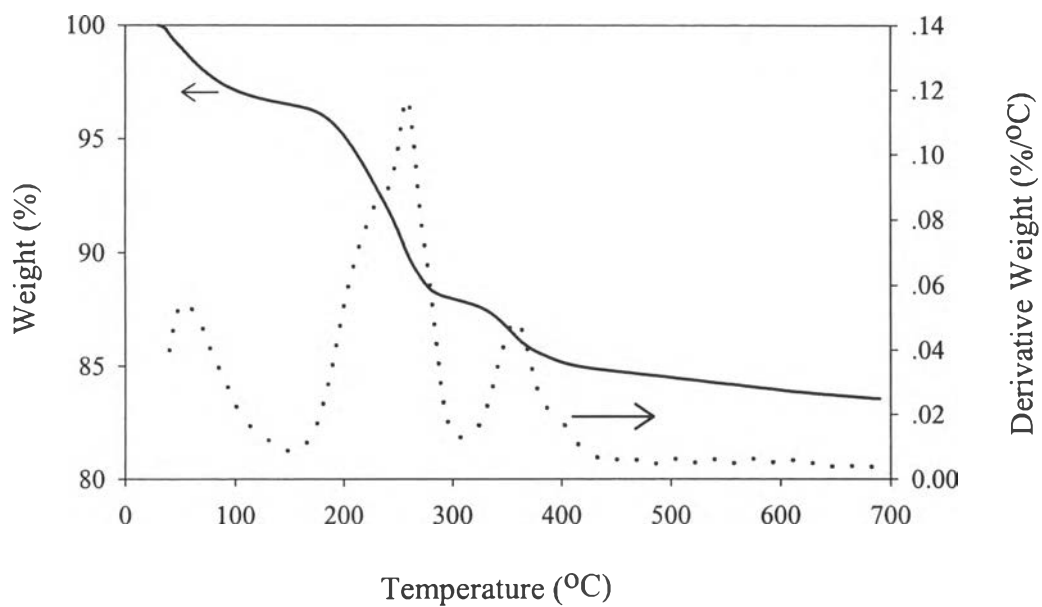


Figure 4.26 TGA results of modified silica 5L.

A. Modified silica before extraction



B. Modified silica after extraction

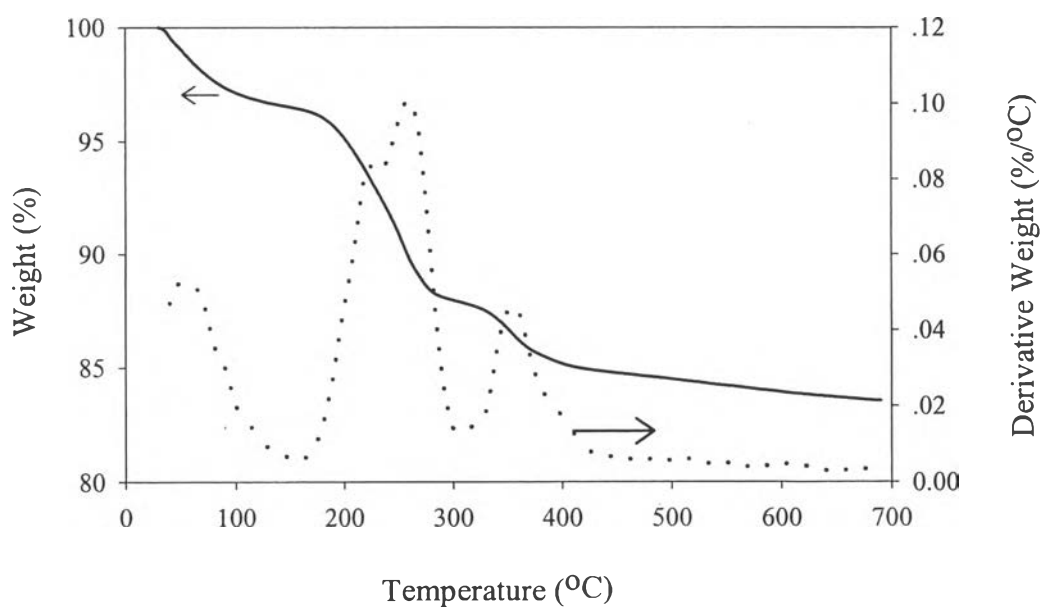
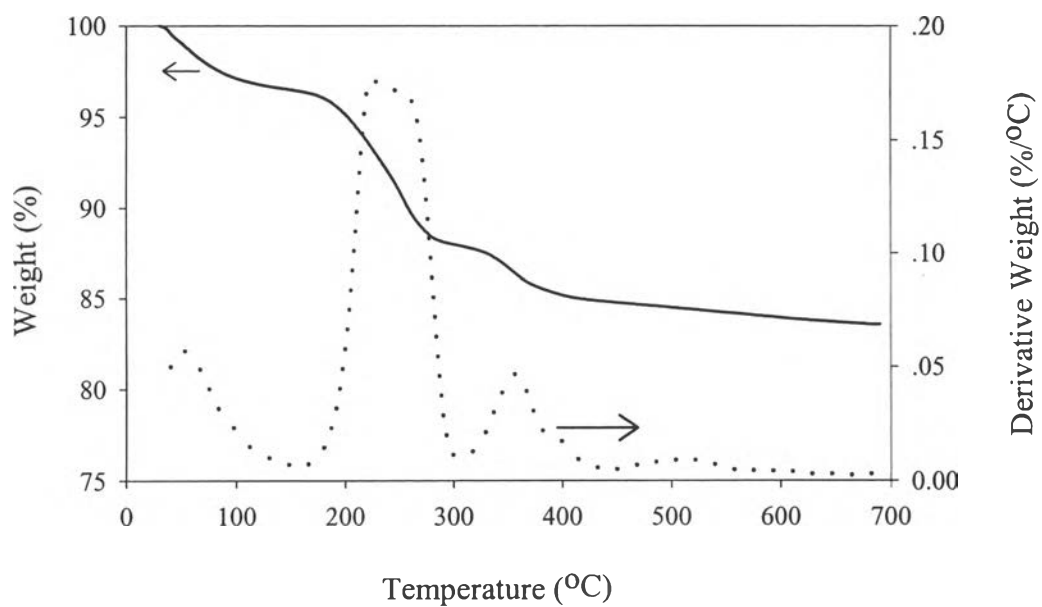


Figure 4.27 TGA results of modified silica 5M.

A. Modified silica before extraction



B. Modified silica after extraction

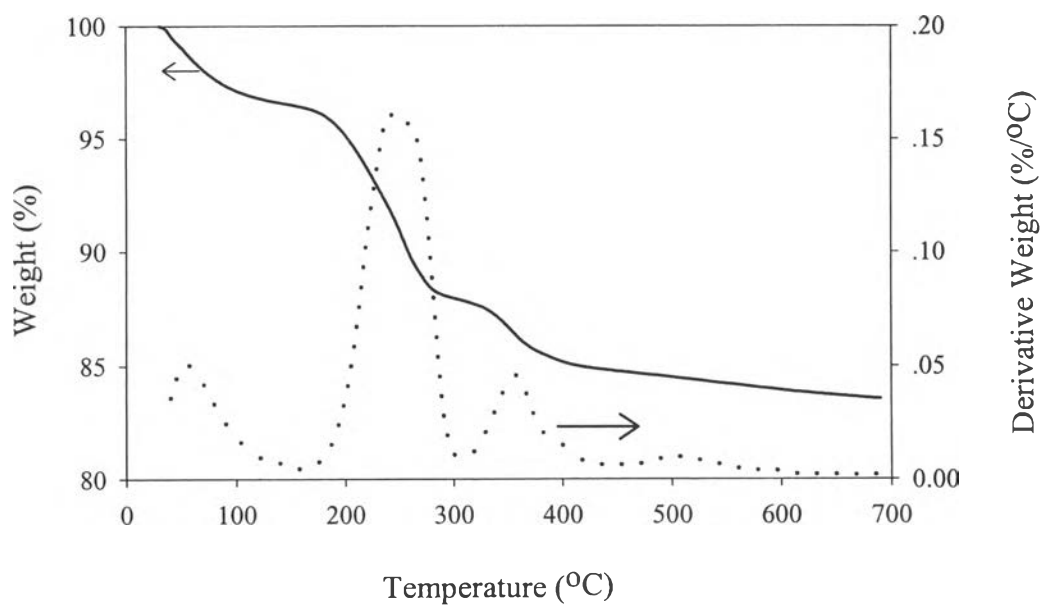
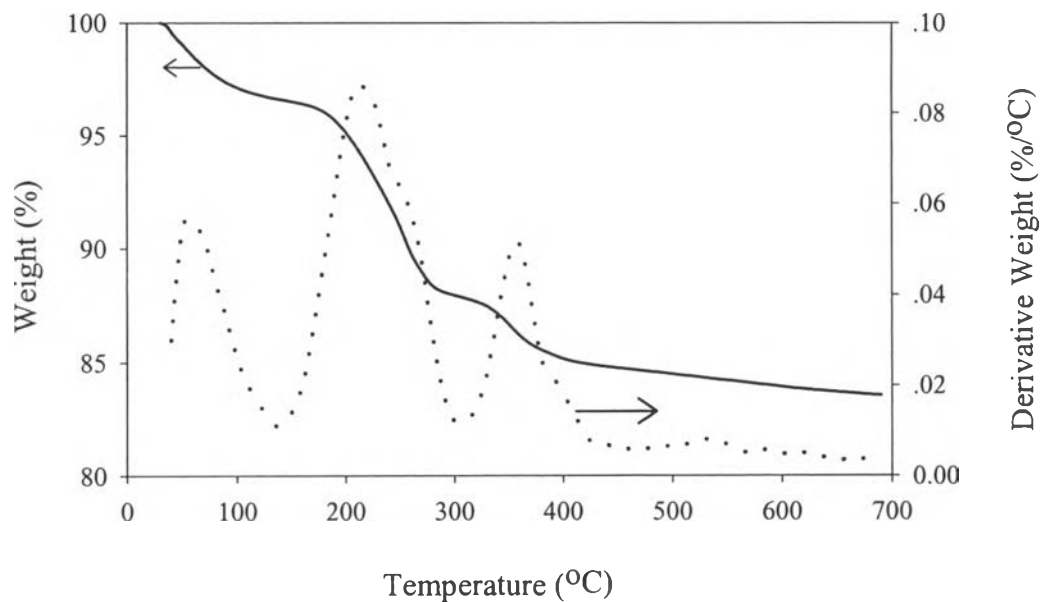


Figure 4.28 TGA results of modified silica 5H.

A. Modified silica before extraction



B. Modified silica after extraction

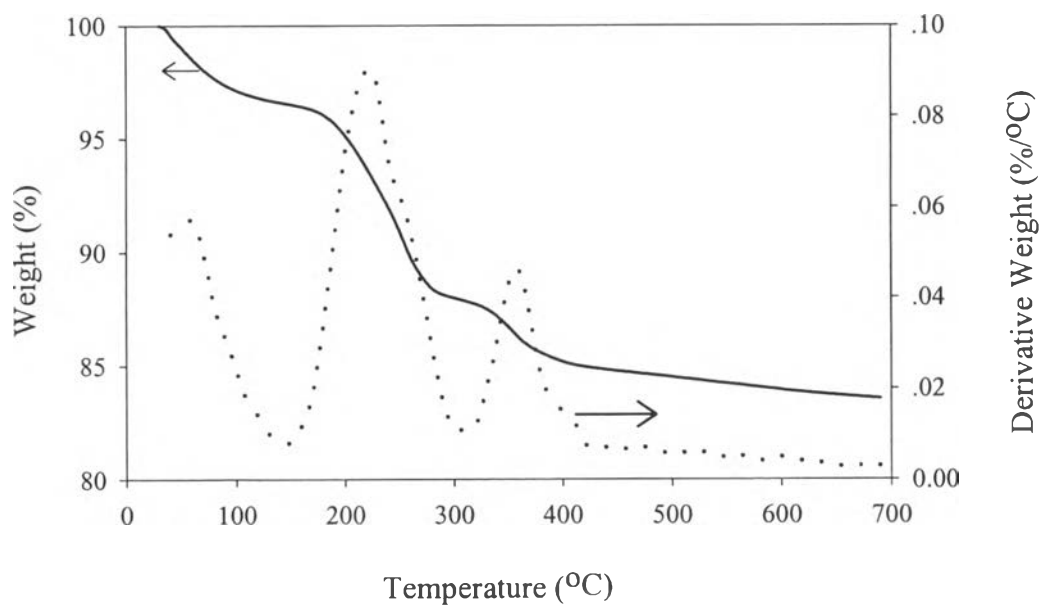
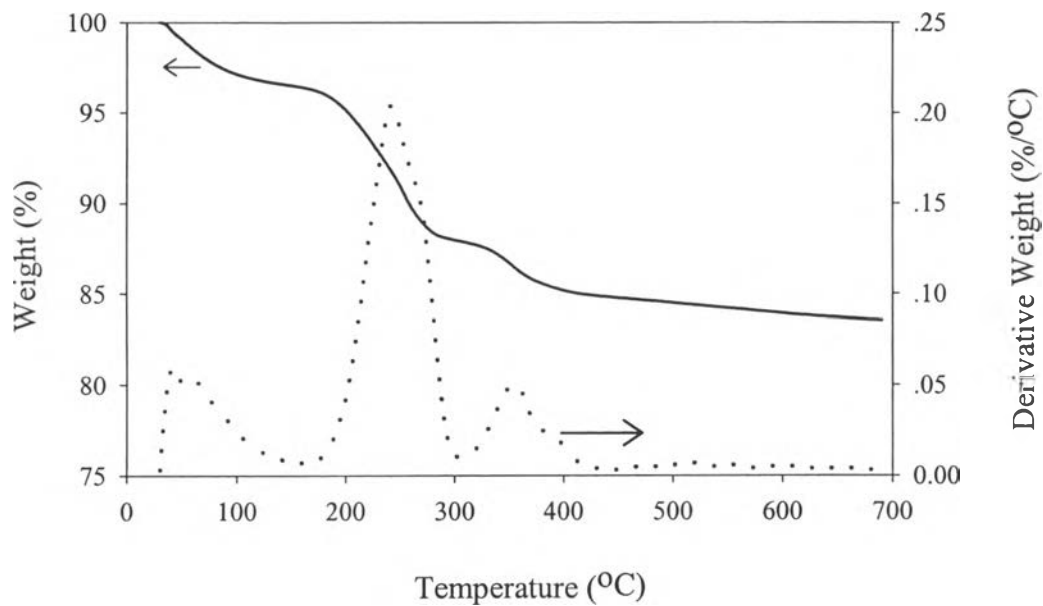


Figure 4.29 TGA results of modified silica 20L.

A. Modified silica before extraction



B. Modified silica after extraction

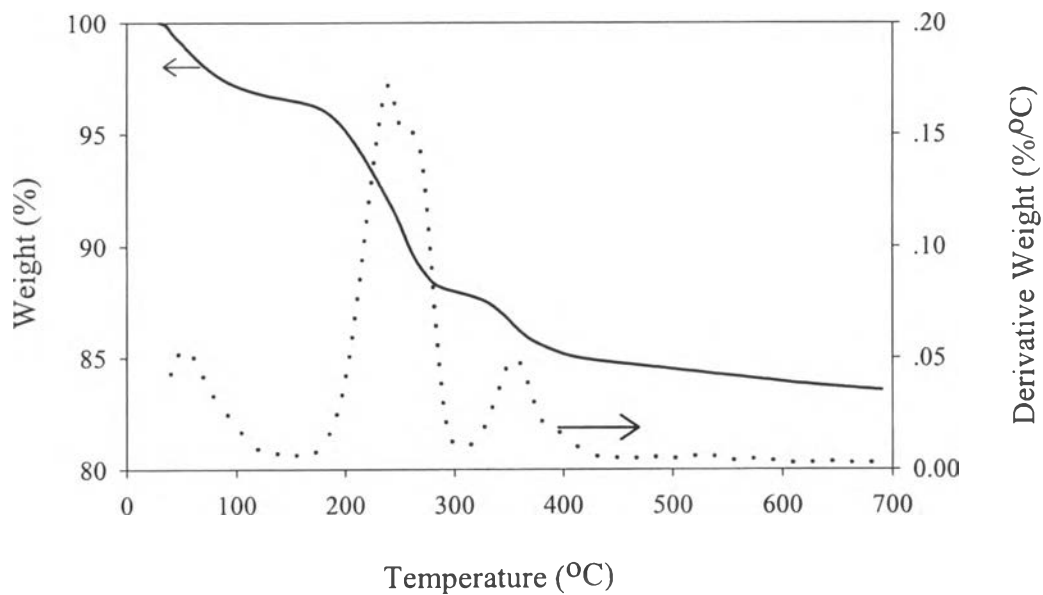
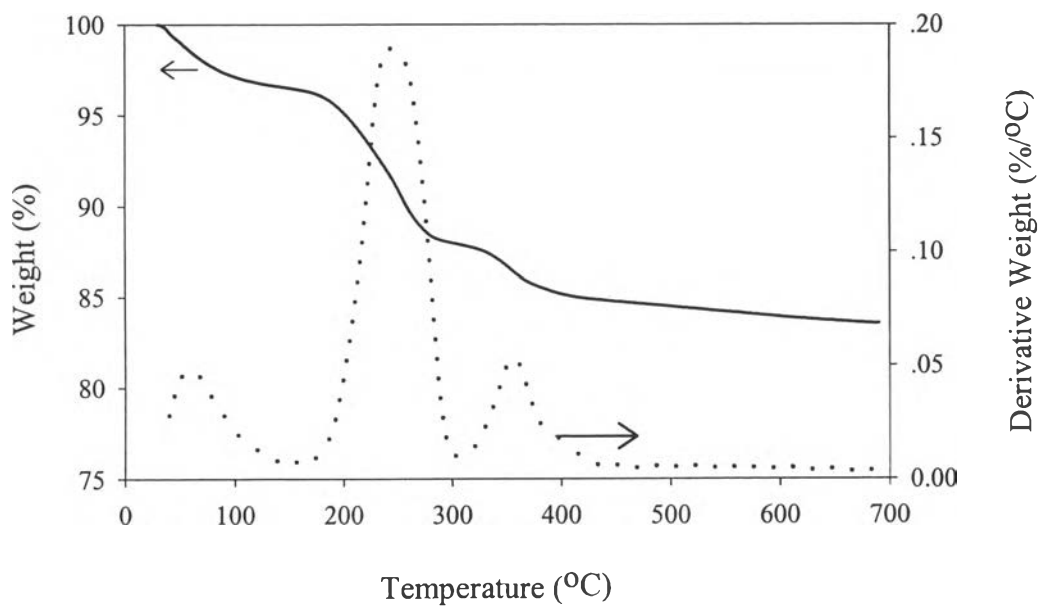


Figure 4.30 TGA results of modified silica 20M.

A. Modified silica before extraction



B. Modified silica after extraction

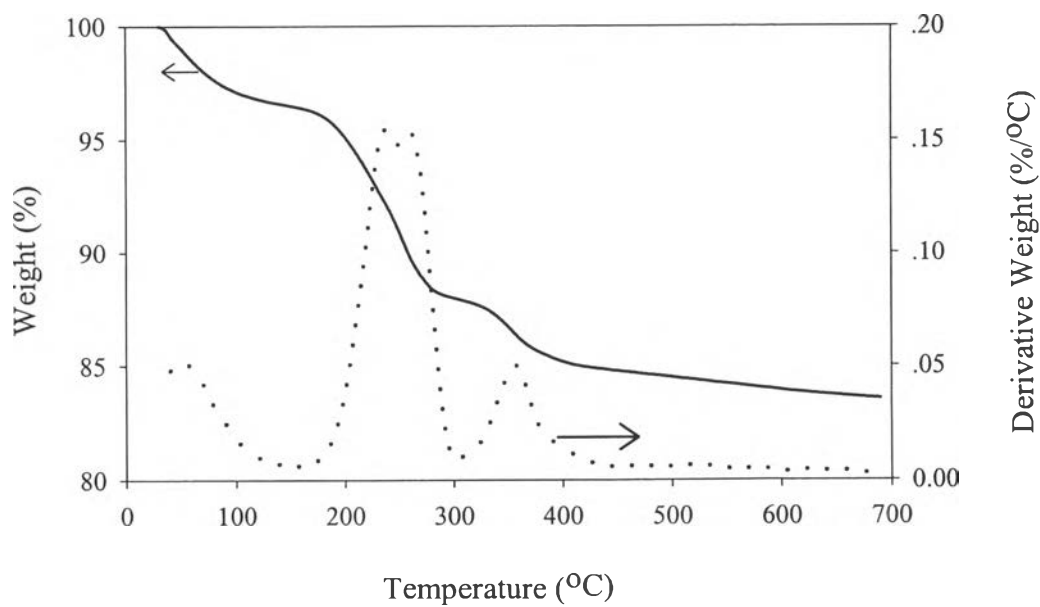
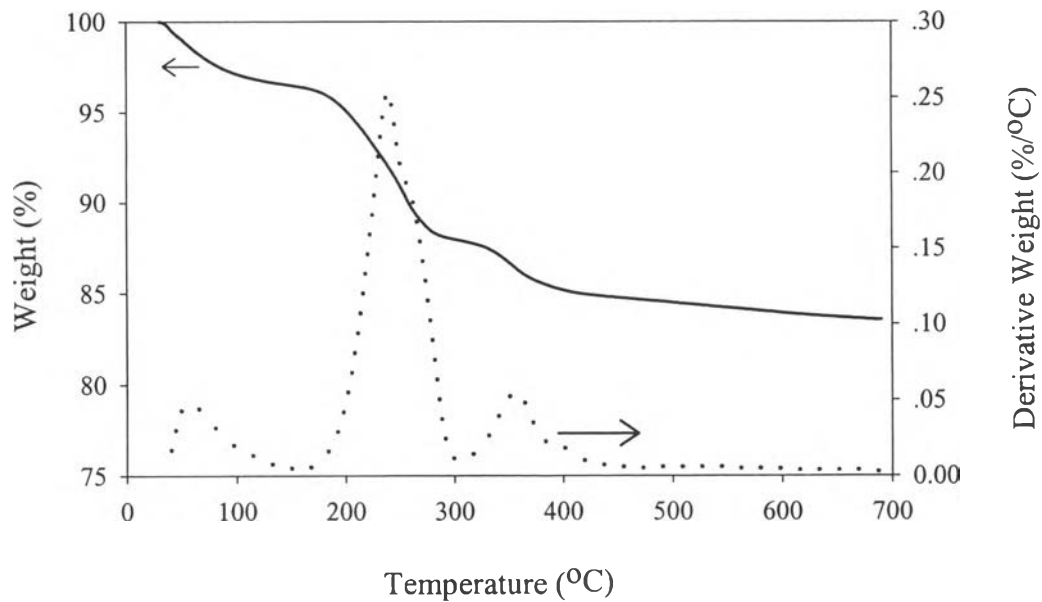


Figure 4.31 TGA results of modified silica 20H.

A. Modified silica before extraction



B. Modified silica after extraction

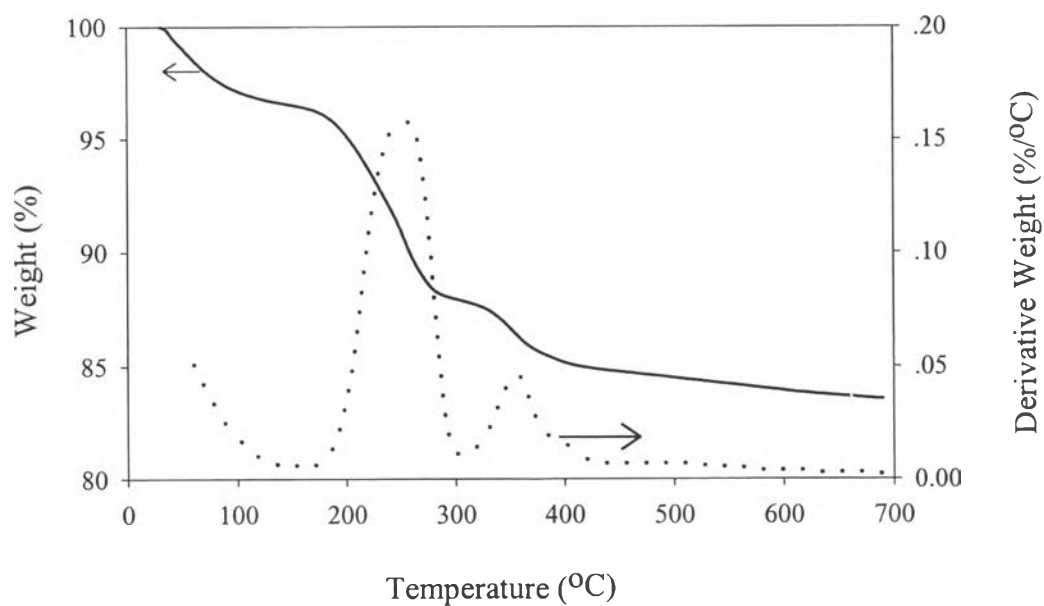
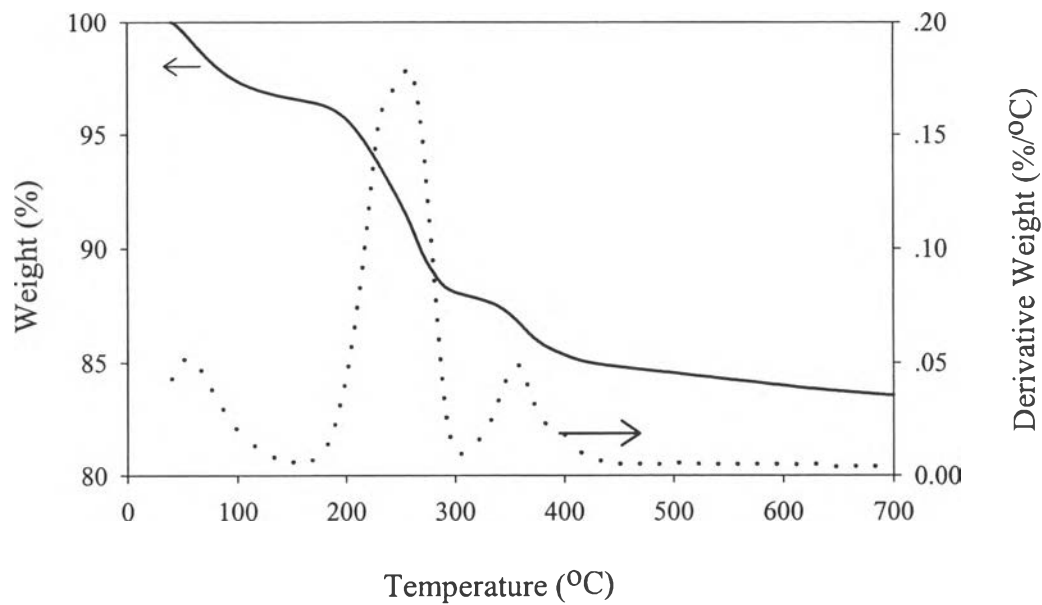


Figure 4.32 TGA results of modified silica 30L.

A. Modified silica before extraction



B. Modified silica after extraction

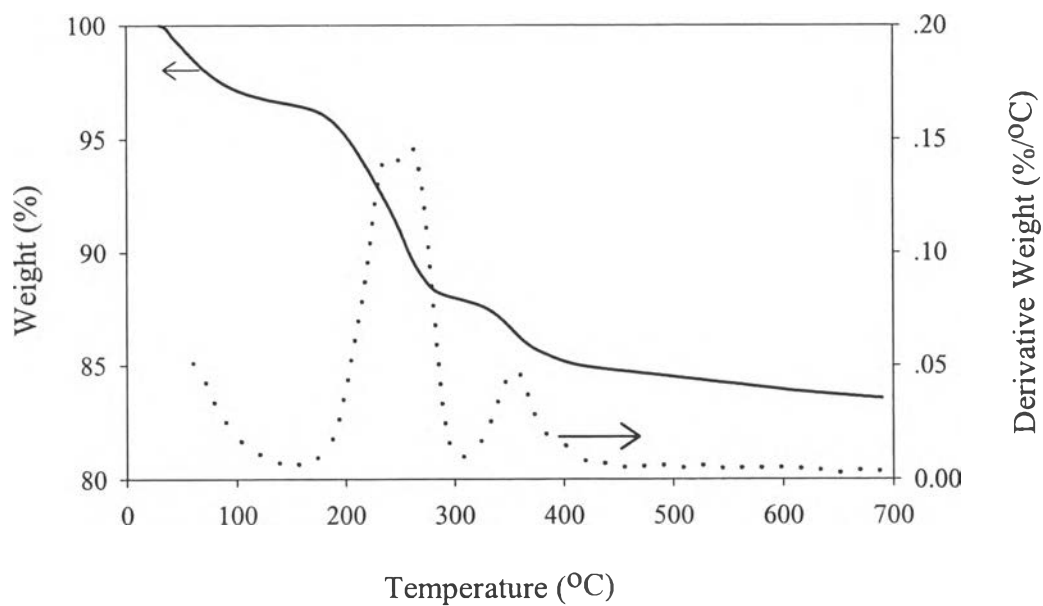
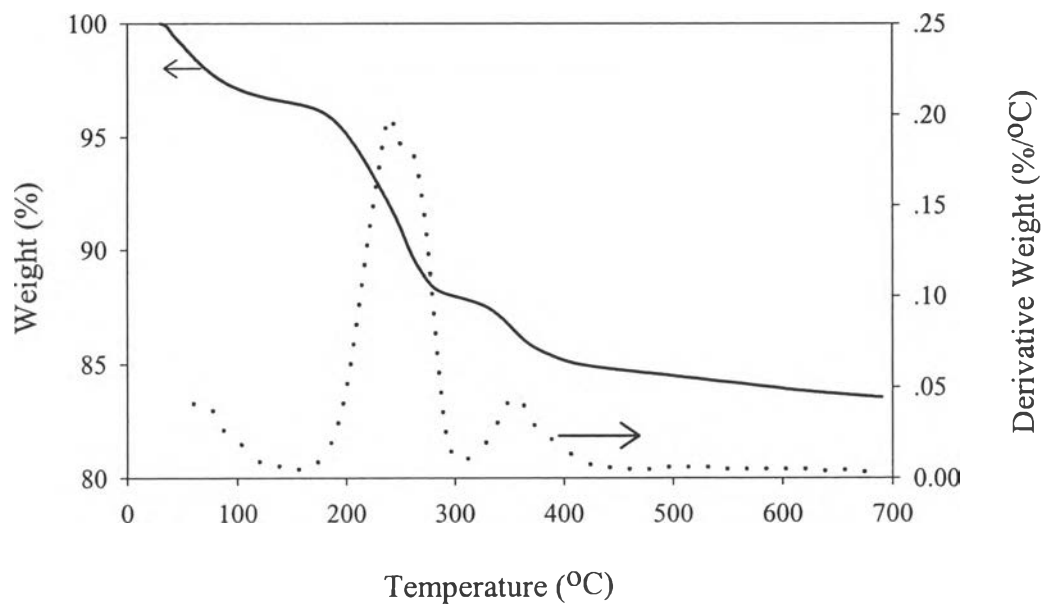


Figure 4.33 TGA results of modified silica 30M.

A. Modified silica before extraction



B. Modified silica after extraction

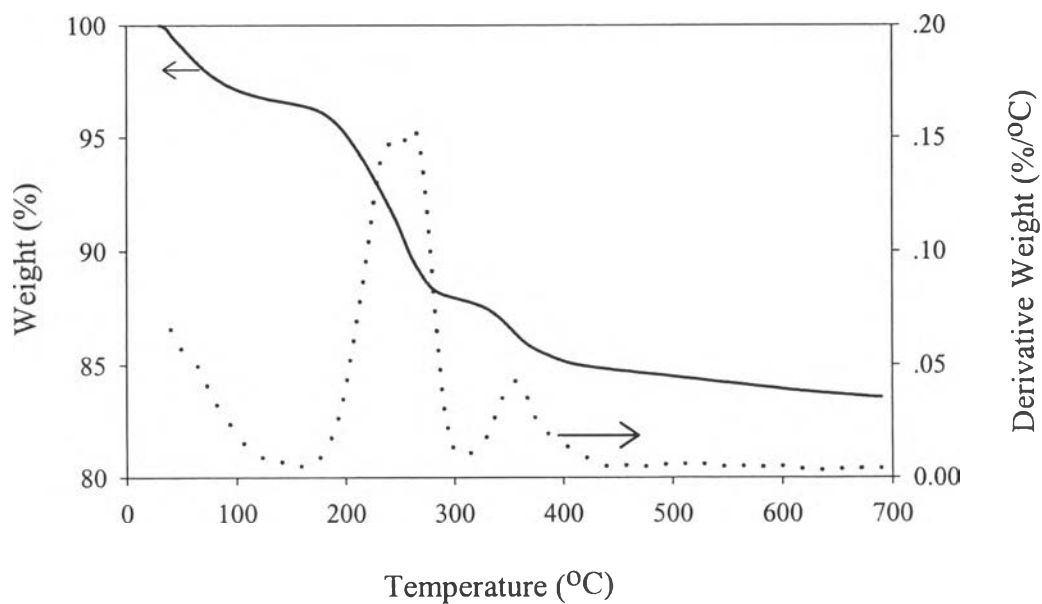


Figure 4.34 TGA results of modified silica 30H.

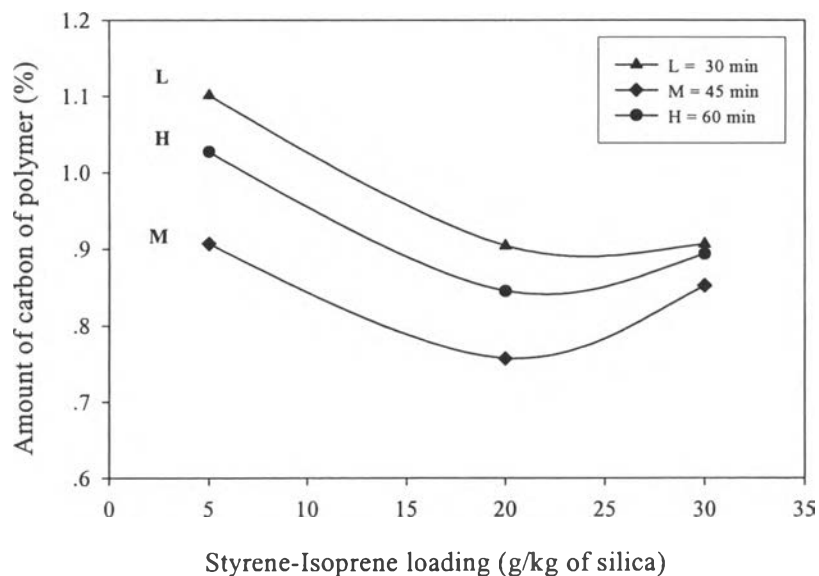


Figure 4.35 The amount of %carbon of polymer of modified silicas as a function of retention time and styrene-isoprene loading.

Table 4.1 Amount of polymer on the silicas before and after the THF extraction

Sample		TGA		
Monomer Loading (g/kg silica)	Retention Time*	Amount carbon of polymer (%)**		% Extracted Polymer
		Before THF Extraction	After THF Extraction	
5	L	1.101	0.223	87.810
	M	0.907	0.316	59.078
	H	1.027	0.315	71.217
20	L	0.904	0.307	59.724
	M	0.757	0.170	58.731
	H	0.845	0.184	66.087
30	L	0.906	0.262	64.491
	M	0.852	0.221	63.087
	H	0.893	0.212	68.146

* L = 30 min, M = 45 min, H = 60 min

** with respect to the weight loss of SI_CTAB

4.4 Rubber Compound Physical Properties

All nine modified silicas having different amounts of styrene-isoprene copolymer were further investigated their effects on rubber compound physical properties. The results are summarized exclusively in Tables 4.2 and 4.3. Table 4.2 also includes the results of the unmodified and modified silica from Thammathadanukul *et al.* (1996) while the results of the modified silicas with 5, 20, 30 g co-monomer loadings from Chinpan (1996) are provided in Table 4.3. Both results of the previous works were obtained from batch reactors.

The data show that the modified silicas produced with different co-monomer loadings and retention times had slight differences in compound physical properties. As can be seen from Figure 4.36, the cure time of all modified silicas from the present study does not depend on both the co-monomer loading and the retention time. Interestingly, the cure times of all modified silicas from the present study were much lower than those of the previous works. This may be due to the better uniform polymer layer coating on the silica surface by the continuous process as compared to batch process.

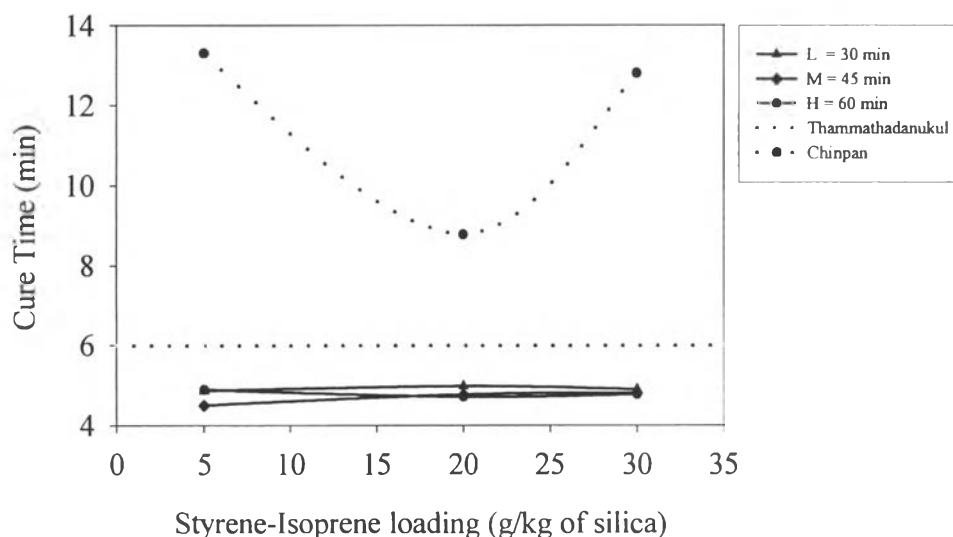


Figure 4.36 Cure time of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

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 (Thammathadanukul *et al.*, 1996)

Property	Hi-Sil®255*	Batch**	5L	5M	5H	20L	20M	20H	30L	30M	30H
Cure Time (min)	18.63	5.98	4.86	4.50	4.89	4.97	4.77	4.71	4.89	4.80	4.77
100%Modulus @before aging (MPa)	0.77	1.33	1.92	2.34	2.22	2.51	1.91	1.88	1.65	1.96	2.08
200%Modulus @before aging (MPa)	1.57	2.54	3.29	3.68	3.57	3.93	3.21	3.13	2.88	3.20	3.37
300%Modulus @before aging (MPa)	2.84	4.19	5.55	5.82	5.53	6.32	5.13	4.78	4.56	5.01	5.22
Tensile Strength @before aging (MPa)	19.84	26.43	27.54	27.44	27.51	26.98	26.86	28.00	27.10	26.99	25.62
Tear Strength @before aging (N/mm)	30.27	75.37	58.94	56.12	56.55	56.95	59.96	58.35	59.09	55.45	53.31
Hardness @before aging (shore A)	51.40	55.30	57.67	57.30	56.77	58.73	57.23	56.63	55.94	58.13	59.10
Hardness @after aging (shore A)	52.80	55.70	59.77	62.53	62.30	62.93	60.40	59.47	58.37	61.81	63.10
Flex cracking (kcycle)	113.00	35.84	60.44	70.25	72.16	30.77	37.76	32.37	35.50	21.16	19.60
Abrasion (ml/kcycle)	0.96	0.66	0.48	0.48	0.53	0.51	0.49	0.52	0.56	0.53	0.57
Resilience (%)	56.70	73.60	74.20	74.70	65.40	76.70	72.20	75.00	77.50	79.90	75.90
Compression set (%)	83.11	76.02	69.06	66.90	69.92	71.71	66.28	63.52	63.69	67.04	68.17

5, 20, 30: styrene-isoprene loading, g per kg silica

L, M, H: the retention time of polymerization, 30, 45, 60 min, respectively

* Unmodified silica, ** Styrene-isoprene co-monomer (Results from Thammathadanukul *et al.*, 1996)

Table 4.3 Rubber compound physical properties using different modified silicas obtained from the present study compared to the modified silicas of the previous batch system with different monomer loadings (Chinpan,1996)

Property	Batch* (5)**	5L	5M	5H	Batch* (20)**	20L	20M	20H	Batch* (30)**	30L	30M	30H
Cure time (min)	13.30	4.86	4.50	4.89	8.78	4.97	4.77	4.71	12.80	4.89	4.80	4.77
100%Modulus @before aging (MPa)	2.01	1.92	2.34	2.22	2.39	2.51	1.91	1.88	2.32	1.65	1.96	2.08
300%Modulus @before aging (MPa)	3.61	5.55	5.82	5.53	4.30	6.32	5.13	4.78	3.99	4.56	5.01	5.22
Tensile Strength @before aging (MPa)	21.80	27.54	27.44	27.51	25.20	26.98	26.86	28.00	21.10	27.10	26.99	25.62
Tear Strength @before aging (N/mm)	58.00	58.94	56.12	56.55	67.90	56.95	59.96	58.35	45.90	59.09	55.45	53.31
Hardness @before aging (shore A)	53.70	57.67	57.30	56.77	52.60	58.73	57.23	56.63	55.50	55.94	58.13	59.10
Flex cracking (kcycle)	55.41	60.44	70.25	72.16	50.54	30.77	37.76	32.37	58.28	35.50	21.16	19.60
Abrasion (ml/kcycle)	0.77	0.48	0.48	0.53	0.57	0.51	0.49	0.52	0.69	0.56	0.53	0.57
Resilience (%)	49.30	74.20	74.70	65.40	54.30	76.70	72.20	75.00	44.50	77.50	79.90	75.90
Compression set (%)	72.20	69.06	66.90	69.92	67.70	71.71	66.28	63.52	77.20	63.69	67.04	68.17

5, 20, 30: styrene-isoprene loading, g per kg silica

L, M, H: the retention time of polymerization, 30, 45, 60 min, respectively

* Results from Chinpan, 1996

** Amount of styrene-isoprene co-monomers, g/kg silica

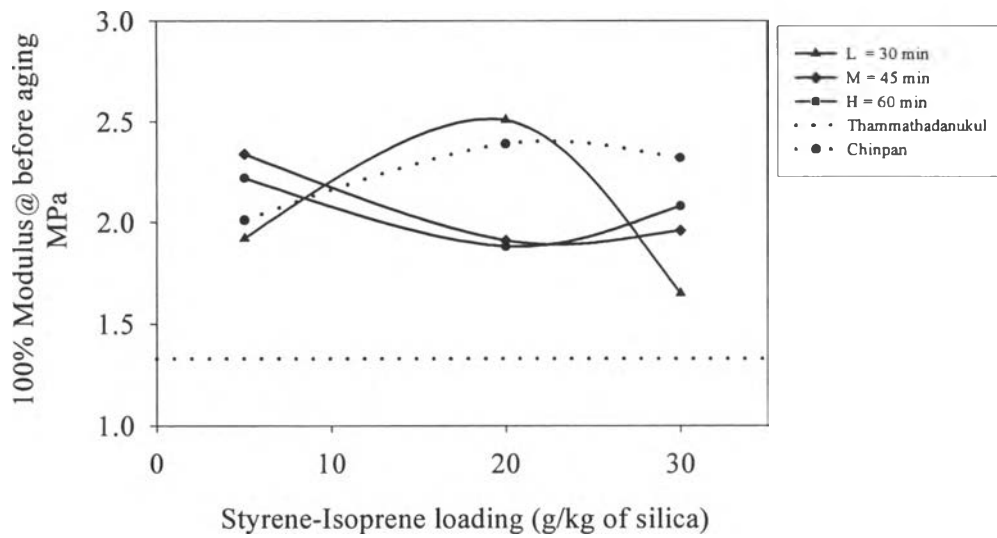


Figure 4.37 100% Modulus @ before aging of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

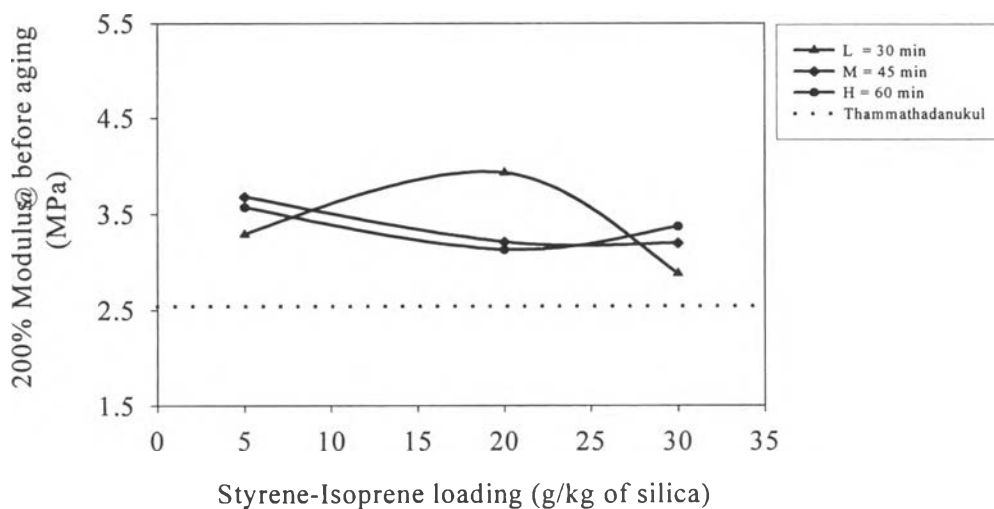


Figure 4.38 200% Modulus @ before aging of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

Figure 4.37 shows the results of 100% modulus @ before aging from the continuous system of the present study are about 54% higher than those of the batch system from Thammathadanukul, while they are not significantly different from those of the batch system from Chinpan.

Figure 4.38 to 4.40 show that for any given co-monomer loading and retention time modified silicas of the present study have 200% modulus @ before aging, 300% modulus @ before aging and tensile strength @ before aging greater than those of the batch systems. Again, the good consistency of polymer deposit on the silica surface by the continuous process attributed to the better tensile strength as compared to the batch system.

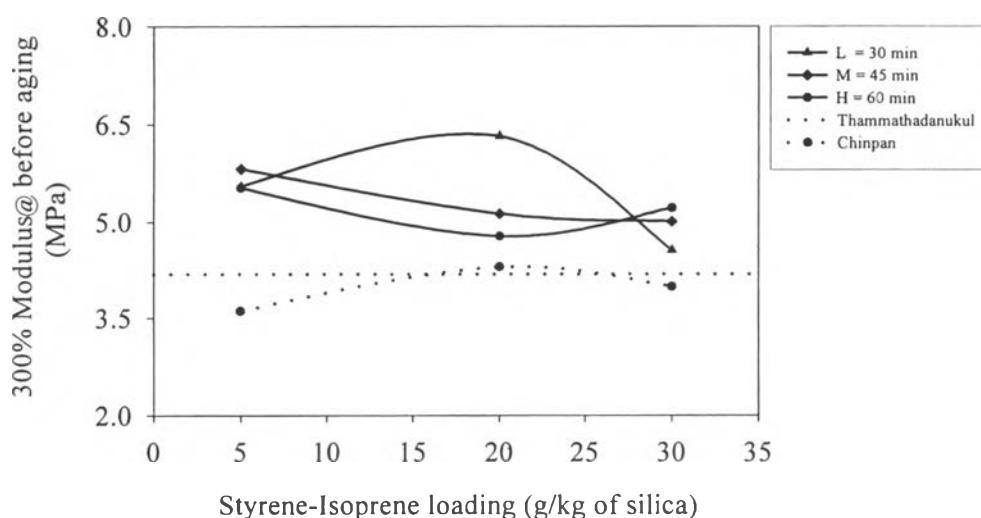


Figure 4.39 300% Modulus @ before aging of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

As seen from Figure 4.41, all of the samples using the modified silica of the present study show lower improvement of tear strength @ before aging than those of the batch system from Thammathadukul about 25%. The modified silicas produced at 5 and 20 g co-monomer loadings and at any retention time had lower improvement than those of the batch system from Chinpan about 2% and 14% respectively, while the ones produced at 30 g co-monomer loading at any retention time had greater improvement than those of the batch system from Chinpan about 20%.

For the results of hardness @ before aging, all of the modified silica obtained from the present study give greater improvement than those of the batch systems from Thammathadanukul and Chinpan about 4% and 7%, respectively (see Figure 4.42).

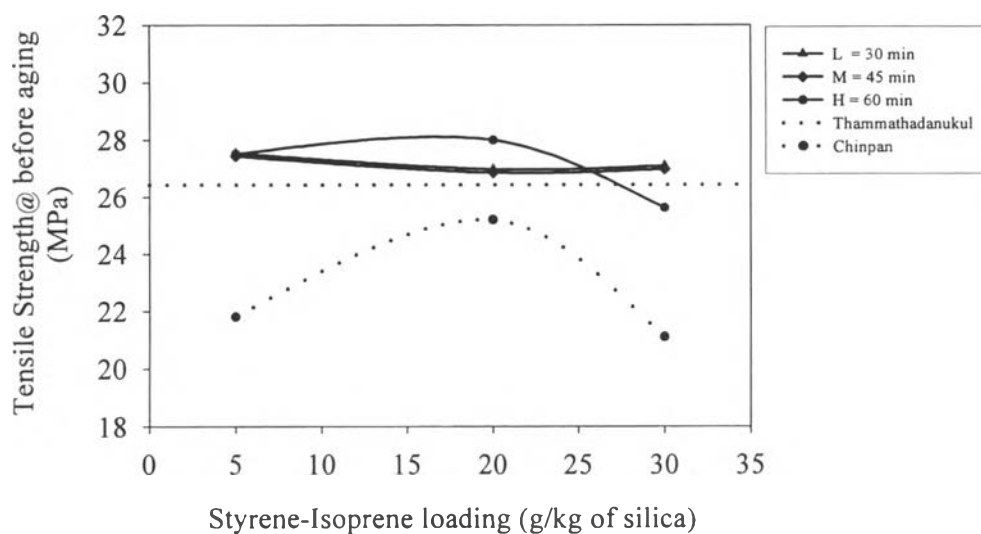


Figure 4.40 Tensile strength @ before aging of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

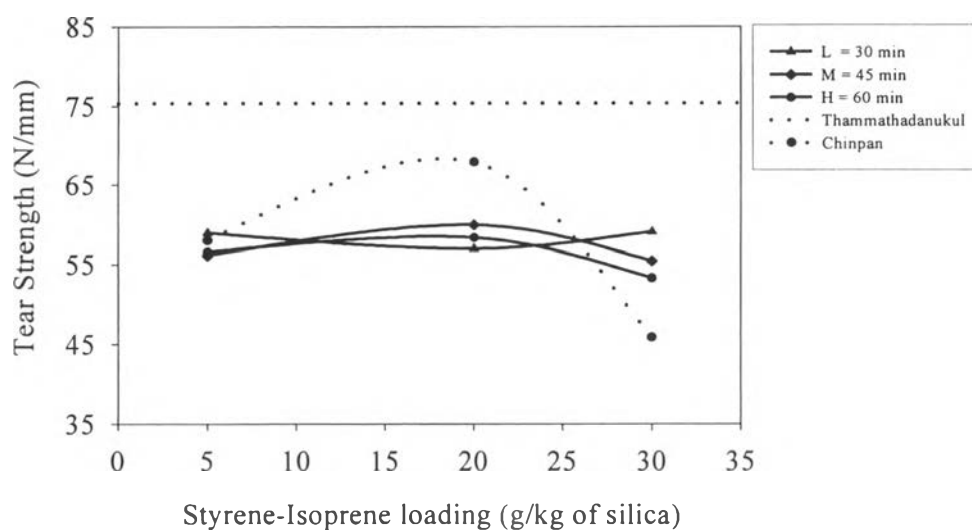


Figure 4.41 Tear strength @ before aging of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

Figure 4.43 shows the results of flex cracking, the modified silicas produced at 5 g co-monomer loading and at any retention time provide higher overall improvement than those of the batch systems while the modified silicas produced at 20 and 30 g co-monomer loadings at any retention time show lower improvement than those of the batch systems. Moreover, all of the modified silicas obtained from

both the present study and the previous works were found to have lower improvement in flex cracking as compared to the unmodified silica.

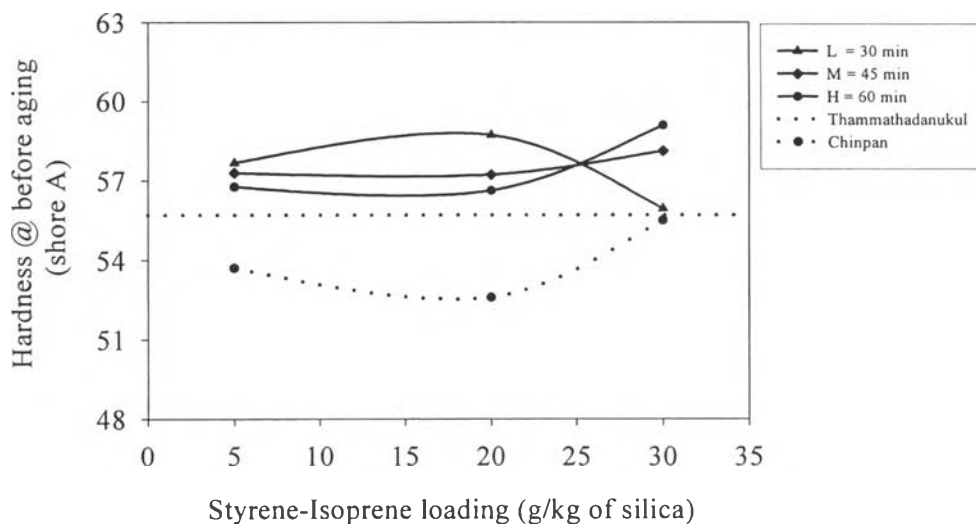


Figure 4.42 Hardness @ before aging of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

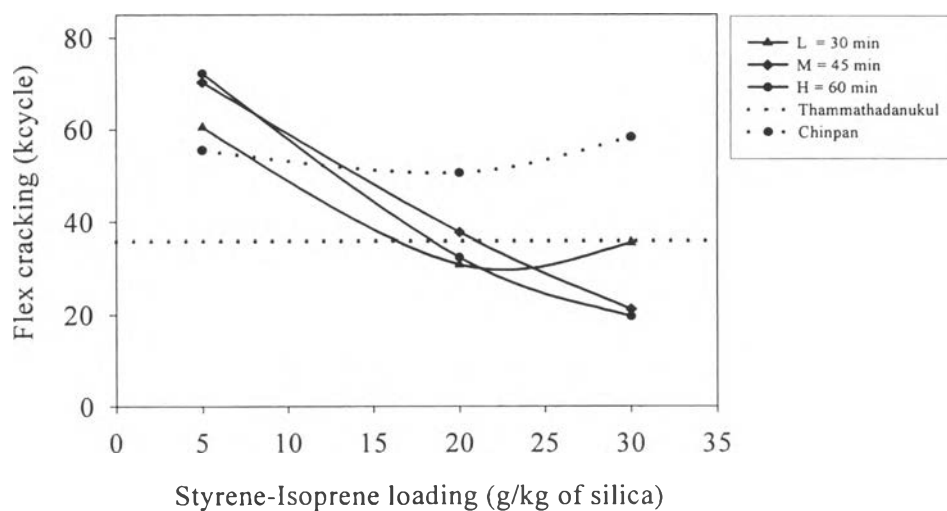


Figure 4.43 Flex cracking of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

As seen from Figure 4.44, all of the samples using the modified silicas produced from the continuous system of the present study show greater overall improvement in abrasion resistance than those of the batch systems. For the

modified silicas of this study, a lower co-monomer loading resulted in improving abrasion resistance. It can be explained that the continuous system can produce more uniform polymer layer and better surface coverage resulting in better bonding between the modified silica particles and rubber as compared to those produced from the batch system.

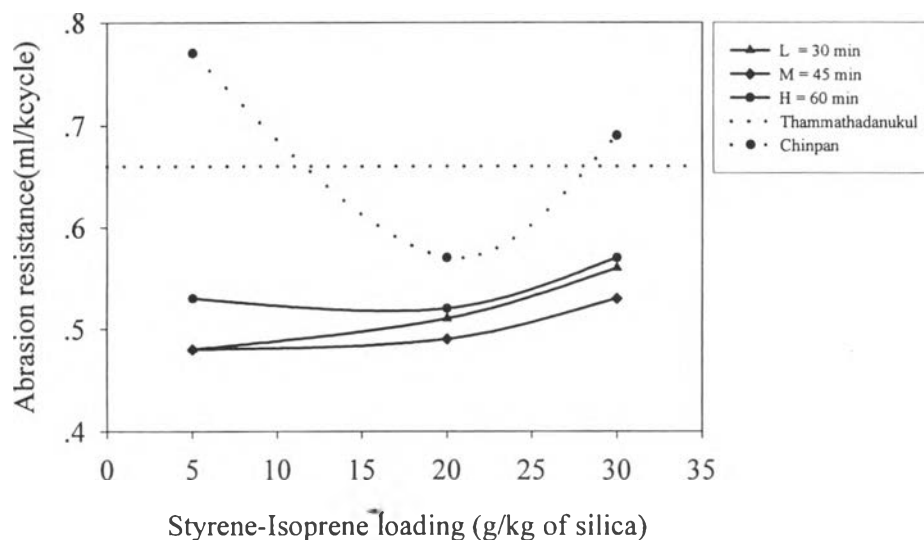


Figure 4.44 Abrasion resistance of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

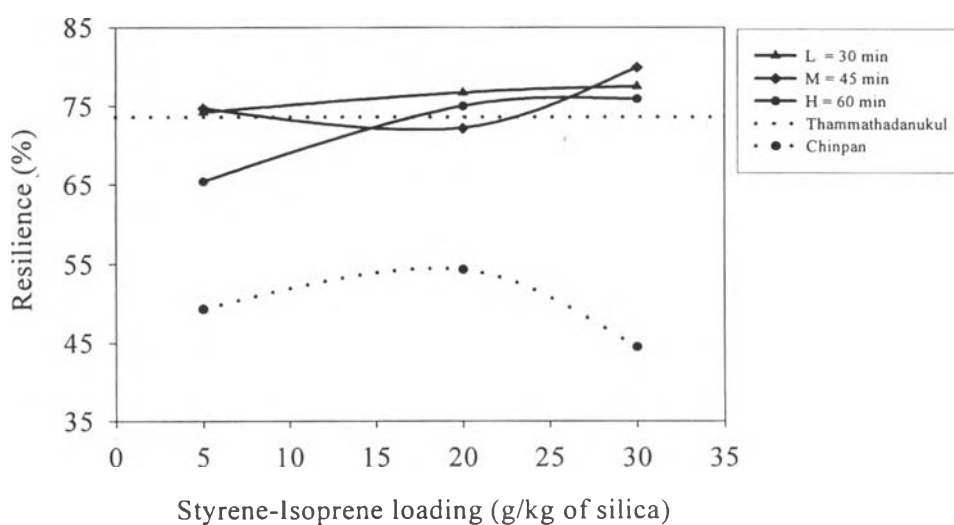


Figure 4.45 Resilience of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

As seen in Figure 4.45, the results of resilience of the modified silicas produced from the continuous system show 50% improvement as compared to those of the batch system studied by Chinpan. It can be concluded that the continuous system lead to increase performance of rubber compound. For compression set property, all of the samples from continuous system provided lower compression set than batch system from Thammathadanukul.

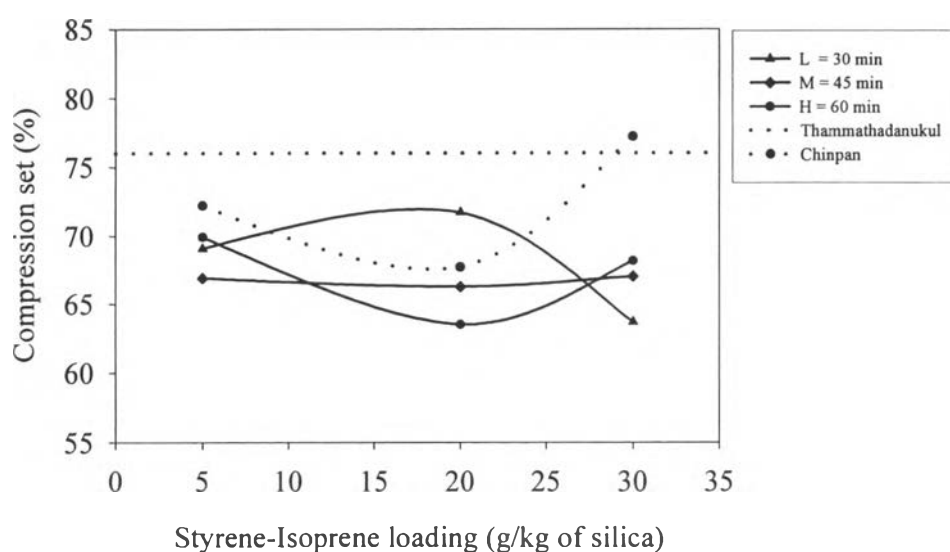


Figure 4.46 Compression set of modified silicas as a function of retention time and styrene-isoprene loading as compared to the previous works.

The impacts of the different surface-modified silicas on various rubber physical properties in comparison between the present study and the previous works are summarized qualitatively in Tables 4.4 and 4.5, with the + designation meaning improvement of greater than 10%, the – designation meaning a negative or undesirable effect greater than 10%, and the = meaning no significant effect of lower than 10% as compared to those of two previous batch works. The total score of each modified silica is calculated by assigning +1 value to the positive effect, –1 to the negative effect and 0 to no significant effect. Tables 4.6 and 4.7 show the actual percentage in improvement/degradation of all modified silicas of the present study on the rubber compound physical properties as compared to the previous works using batch system.

As can be seen the results from Table 4.4 and 4.5, significant improvement in the rubber compound properties can be achieved by the admicellar polymerization with the continuous reactor and the results show overall greater improvement than the batch reactors. It is possibly due to the consistency of the polymerization in the continuous reactor. Moreover, the continuous reactor can be easily controlled to specifically modify silicas to improve certain rubber compound properties.

As seen from Table 4.4, the comparative scores of the rubber compound physical properties show that all modified silicas significantly improve the cure time, modulus, and abrasion resistance but having only a negative effect on the tear strength. Comparing with batch system from Thammathadanukul, the sample at any co-monomer loading and retention time are improved 100% modulus @ before aging, 200% modulus @ before aging, 300% modulus @ before aging, and abrasion resistance, while they are not improved tear resistance.

Table 4.5 also show comparative scores of all modified silicas produced at 5, 20, 30 g co-monomer loadings from the continuous reactor as compared those obtained from the batch reactor conducted by Chinpan. Again, the results indicated the improvement in the cure time, 300% modulus @ before aging, tensile strength @ before aging, abrasion resistance, and resilience values with the modified silicas. The tear strength values of the rubber compound were maximized at 30 g co-monomer loading, while the compound using 20 g co-monomer loading had the poorest tear strength as compared to that of the batch system. There were also significant compound performance differences in the flex cracking resistance among different co-monomer loadings. At 20 and 30 g co-monomer loadings, the modified silicas adversely reduced the number of flexing cycles required to reach the same grade of cracking.

Table 4.8 shows the rubber compound physical properties of nine samples with the modified silicas from the continuous reactor. Table 4.9 shows the qualitative summary by ranking the results from low to high quality of each physical property using a number “1” to “9” in order to determine the optimum conditions of the silica modification system. In this study, the styrene-isoprene modified silica at 5 g co-monomer loading with low retention time (5L) had the lowest surface area, and also had the highest particle size and the amount of polymer formed on the surface.

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	5L	5M	5H	20L	20M	20H	30L	30M	30H
Cure time	+1	+1	+1	+1	+1	+1	+1	+1	+1
100%Modulus @before aging	+1	+1	+1	+1	+1	+1	+1	+1	+1
200%Modulus @before aging	+1	+1	+1	+1	+1	+1	+1	+1	+1
300%Modulus @before aging	+1	+1	+1	+1	+1	+1	0	+1	+1
Tensile Strength @before aging	0	0	0	0	0	0	0	0	0
Tear Strength @before aging	-1	-1	-1	-1	-1	-1	-1	-1	-1
Hardness @before aging	0	0	0	0	0	0	0	0	0
Hardness @after aging	0	+1	+1	+1	0	0	0	+1	+1
Flex cracking	+1	+1	+1	-1	0	0	0	-1	-1
Abrasion	+1	+1	+1	+1	+1	+1	+1	+1	+1
Resilience	0	0	-1	0	0	0	0	0	0
Compression set	0	+1	0	0	+1	+1	+1	+1	+1
Comparative Score	+5	+7	+5	+4	+5	+5	+4	+5	+5

5, 20, 30: styrene-isoprene loading, g per kg silica

L, M, H: the retention time of polymerization, 30, 45, 60 min, respectively

Table 4.5 Qualitative summary of surface-modified silica rubber physical properties as compared to the modified silicas of the previous batch system with different monomer loadings (Chinpan, 1996)

Property	5L	5M	5H	20L	20M	20H	30L	30M	30H
Cure time	+1	+1	+1	+1	+1	+1	+1	+1	+1
100%Modulus @before aging	0	+1	+1	0	-1	-1	-1	-1	-1
300%Modulus @before aging	+1	+1	+1	+1	+1	+1	+1	+1	+1
Tensile Strength @before aging	+1	+1	+1	0	0	+1	+1	+1	+1
Tear Strength @before aging	0	0	0	-1	-1	-1	+1	+1	+1
Hardness @before aging	0	0	0	+1	0	0	0	0	0
Flex cracking	0	+1	+1	-1	-1	-1	-1	-1	-1
Abrasion	+1	+1	+1	+1	0	0	+1	+1	+1
Resilience	+1	+1	+1	+1	+1	+1	+1	+1	+1
Compression set	0	0	0	0	0	0	+1	+1	+1
Comparative Score	+5	+7	+7	+3	0	+1	+5	+5	+5

5, 20, 30: styrene-isoprene loading, g per kg silica

L, M, H: the retention time of polymerization, 30, 45, 60 min, respectively

Table 4.6 Percent improvement of surface-modified silica rubber physical properties as compared to the modified silicas of the previous batch system (Thammathadanukul *et al.*, 1996)

Property	5L %	5M %	5H %	20L %	20M %	20H %	30L %	30M %	30H %
Cure time	19	25	18	17	20	21	18	20	20
100%Modulus @before aging	44	76	67	89	44	41	24	47	56
200%Modulus @before aging	30	45	41	55	26	23	13	26	33
300%Modulus @before aging	32	39	32	51	22	14	9	20	25
Tensile Strength @before aging	4	4	4	2	2	6	3	2	-3
Tear Strength @before aging	-22	-26	-25	-24	-20	-23	-22	-26	29
Hardness @before aging	4	4	3	6	3	2	1	5	7
Hardness @after aging	7	12	12	13	8	7	5	11	13
Flex cracking	69	96	101	-14	5	-10	-1	-41	-45
Abrasion	27	27	20	23	26	21	15	20	14
Resilience	1	1	-11	4	-2	2	5	9	3
Compression set	9	12	8	6	13	17	16	12	11

5, 20, 30: styrene-isoprene loading, g per kg silica

L, M, H: the retention time of polymerization, 30, 45, 60 min, respectively

Table 4.7 Percent improvement of surface-modified silica rubber physical properties as compared to the modified silicas of the previous batch system with different monomer loadings (Chinpan, 1996)

Property	5L %	5M %	5H %	20L %	20M %	20H %	30L %	30M %	30H %
Cure time	63	66	63	43	46	46	62	62	63
100%Modulus @before aging	-5	16	10	5	-20	-21	-29	-16	-11
300%Modulus @before aging	54	61	53	47	19	11	14	26	31
Tensile Strength @before aging	26	26	26	7	7	11	29	28	22
Tear Strength @before aging	2	-3	-2	-16	-12	-14	29	21	16
Hardness @before aging	7	7	6	12	9	8	1	5	7
Flex cracking	9	27	30	-39	-25	-36	-39	-64	-66
Abrasion	38	38	31	10	14	8	19	23	18
Resilience	50	51	33	41	33	38	74	80	71
Compression set	4	7	3	-6	2	6	18	13	12

5, 20, 30: styrene-isoprene loading, g per kg silica

L, M, H: the retention time of polymerization, 30, 45, 60 min, respectively

Table 4.8 Rubber compound physical properties using different modified silicas

Property	5L	5M	5H	20L	20M	20H	30L	30M	30H
100%Modulus @before aging (MPa)	1.92	2.34	2.22	2.51	1.91	1.88	1.65	1.96	2.08
100%Modulus @after aging (MPa)	2.36	2.47	2.35	2.53	2.2	2.23	2.03	2.38	2.56
200%Modulus @before aging (MPa)	3.29	3.68	3.57	3.93	3.21	3.13	2.88	3.20	3.37
200%Modulus @after aging (MPa)	4.26	4.12	3.98	4.14	3.75	3.91	3.67	4.13	4.33
300%Modulus @before aging (MPa)	5.55	5.82	5.53	6.32	5.13	4.78	4.56	5.01	5.22
300%Modulus @after aging (MPa)	7.02	6.52	6.11	6.41	5.7	6.18	5.85	6.48	6.66
Tensile Strength @before aging (MPa)	27.54	27.44	27.51	26.98	26.86	28.00	27.10	26.99	25.62
Tensile Strength @after aging (MPa)	25.68	22.67	24.56	23.81	22.92	23.58	25.8	25.34	23.25
Tear Strength @before aging (N/mm)	58.94	56.12	56.55	56.95	59.96	58.35	59.09	55.45	53.31
Tear Strength @after aging (N/mm)	54.49	53.96	55.55	53.51	53.24	55.84	58.09	54.31	54.22
Hardness @before aging (shore A)	57.67	57.30	56.77	58.73	57.23	56.63	55.94	58.13	59.10
Hardness @after aging (shore A)	59.77	62.53	62.30	62.93	60.40	59.47	58.37	61.81	63.10
Flex cracking (kcycle)	60.44	70.25	72.16	30.77	37.76	32.37	35.50	21.16	19.60
Abrasion (ml/kilocycle)	0.48	0.48	0.53	0.51	0.49	0.52	0.56	0.53	0.57
Resilience (%)	74.20	74.70	65.40	76.70	72.20	75.00	77.50	79.90	75.90
Compression set (%)	69.06	66.90	69.92	71.71	66.28	63.52	63.69	67.04	68.17
Heat build up (°C)	15.33	15.95	18.35	18.16	19.67	14.8	18.86	18.21	19.50

Table 4.9 Qualitative summary of rubber physical properties using different modified silicas

Property	5L	5M	5H	20L	20M	20H	30L	30M	30H
100%Modulus @before aging	4	8	7	9	3	2	1	5	6
100%Modulus @after aging	5	7	4	8	2	3	1	6	9
200%Modulus @before aging	5	8	7	9	4	2	1	3	6
200%Modulus @after aging	8	5	4	7	2	3	1	6	9
300%Modulus @before aging	7	8	6	9	4	2	1	3	5
300%Modulus @after aging	9	7	3	5	1	4	2	6	8
Tensile Strength @before aging	8	6	7	3	2	9	5	4	1
Tensile Strength @after aging	8	1	6	5	2	4	9	7	3
Tear Strength @before aging	7	3	4	5	9	6	8	2	1
Tear Strength @after aging	6	3	7	2	1	8	9	5	4
Hardness @before aging	6	5	3	8	4	2	1	7	9
Hardness @after aging	3	7	6	8	4	2	1	5	9
Flex cracking	7	8	9	3	6	4	5	2	1
Abrasion	8	8	3	6	7	5	2	3	1
Resilience	3	4	1	7	2	5	8	9	6
Compression set	3	6	2	1	7	9	8	5	4
Heat build up	8	7	4	6	1	9	3	5	2
Total	105	101	83	101	61	79	66	83	84

Based on the total scores shown in Table 4.9, the superior characteristics of the rubber compound physical properties can be obtained with silica modified with 5 g co-monomer loading at 30 min retention time. These results suggest that the modified silicas at 5 g co-monomer loading with low retention time are the optimum modification condition to improve the rubber properties. Moreover, the modified silica obtained under the optimum conditions as mention above needs only small amounts of co-monomers.