

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Surface Characterization and Polymer Analysis

Table 4.1 show the effect that surface modification has on silica physical properties, including mean agglomerate particle size, surface area and pore volume. The data show that the modification of precipitated silica by *in-situ* polymerization of styrene-isoprene onto the silica surface significantly reduces nitrogen BET surface area and increases the mean agglomerate particle size. The decrease in surface area may result from the polymer product and remaining surfactant covering part of the silica and filling part of the pore volume. The increase in mean agglomerate particle size may be due to the polymer forming on the surface or to aggregates being joined by polymer "bridges". However, the change in pore volumes for the modified silicas was not uniform. The samples modified using 5, 30 and 40 grams of comonomer per kilogram of silica decrease in pore volume but the samples modified using 10 and 20 grams of comonomer per kilogram of silica show increases in pore volume. There is no appearant simple explanation for this trend.

Table 4.1 Silica Physical Properties

SILICA	CO-MONOMER REACTOR CHARGE (g monomer/kg Silica)	BET SURFACE AREA (m ² /g)	PORE VOLUME (cm ³ /g)	PARTICLE SIZE (μm)
Hi-Sil 255	0	151	1.033	18.72
SI-1	5	121	0.837	22.04
SI-2	10	117	1.314	22.91
SI-3	20	100	1.047	23.16
SI-4	30	114	0.454	22.44
SI-5	40	118	0.692	23.03

Figures 4.1-4.6 are the Transmission electron micrographs of unmodified silica, Hi-Sil 255, and all five modified silicas. The micrographs showed that modified silicas develop a higher degree of agglomeration of the silica particles than the unmodified silica. The higher observed degree of agglomeration of modified silica than unmodified may be due because the polymerization process leads to strong aggregate-aggregate interaction, or it may be due to the processing of the modified silica, consisting of drying followed by regrinding the filter cake to a powder in a sieve.

The affect of the modification process on the silica surface is also showed from the Scanning electron micrographs in figures 4.7- 4.12 for unmodified silica and all five modified silicas. The SEM micrographs showed a similar increase in particle agglomeration. There are however, no other obvious changes in the silica surfaces.

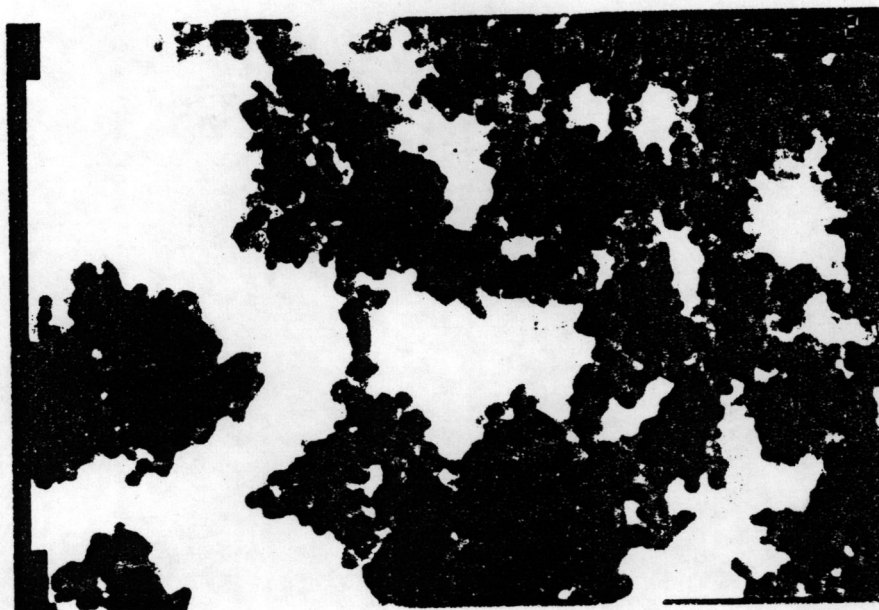


Figure 4.1 Transmission electron micrographs of unmodified silica, Hi-Sil®255, at 73,000X Magnification.

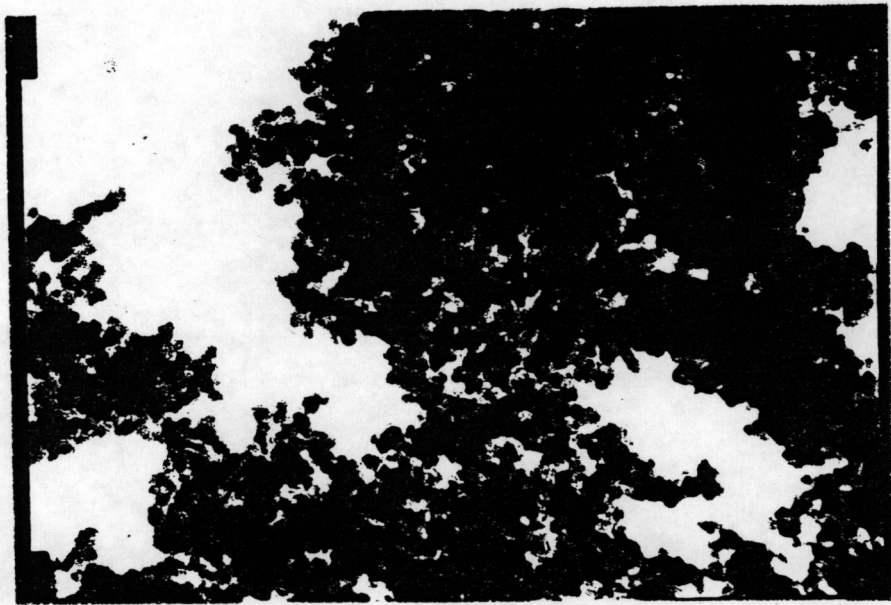


Figure 4.2 Transmission electron micrographs of modified silica, SI-1,
at 73,000X Magnification.

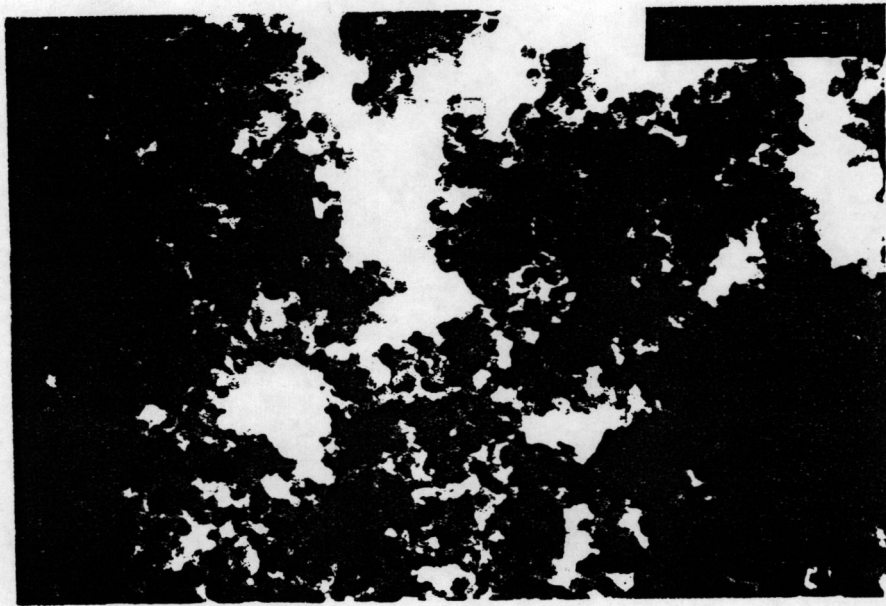


Figure 4.3 Transmission electron micrographs of modified silica, SI-2, at 73,000X Magnification.

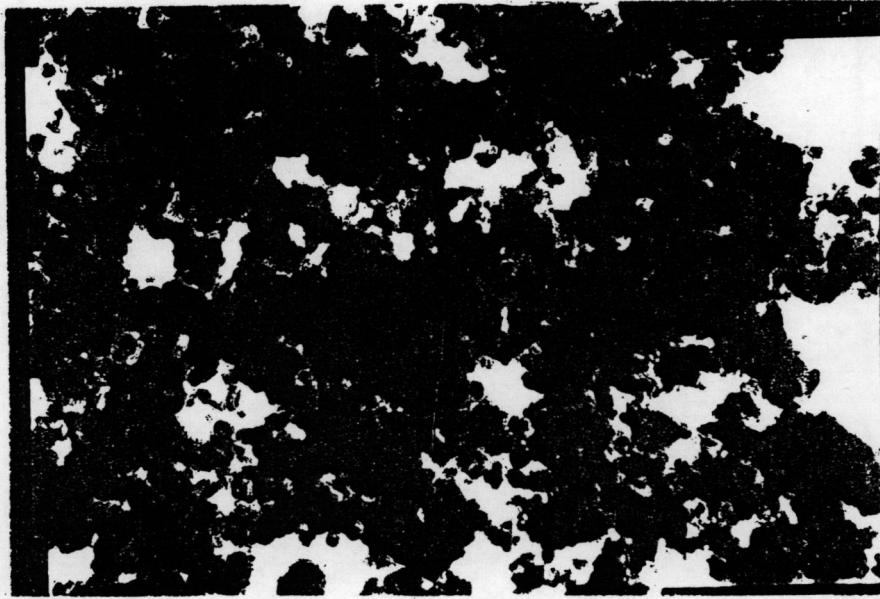


Figure 4.4 Transmission electron micrographs of modified silica, SI-3,
at 73,000X Magnification.

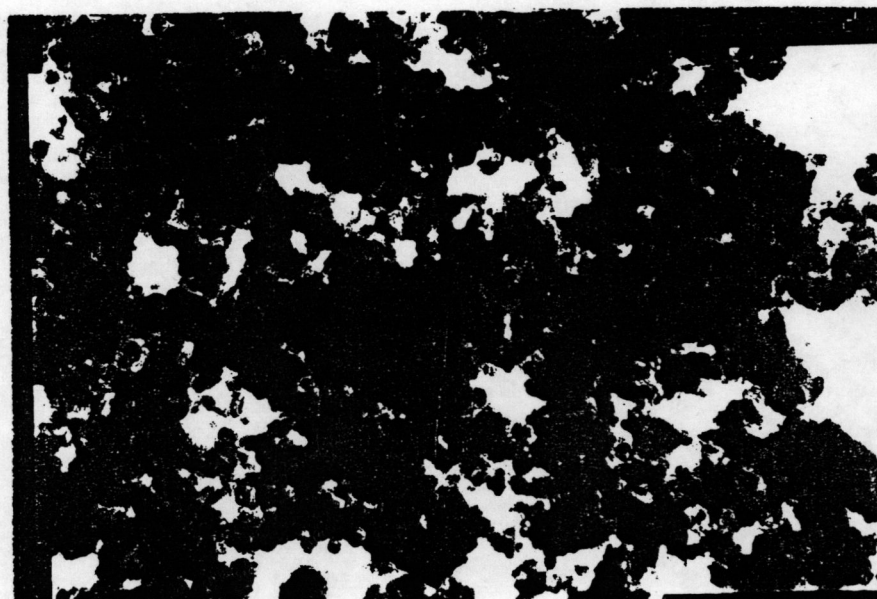


Figure 4.4 Transmission electron micrographs of modified silica, SI-3,
at 73,000X Magnification.

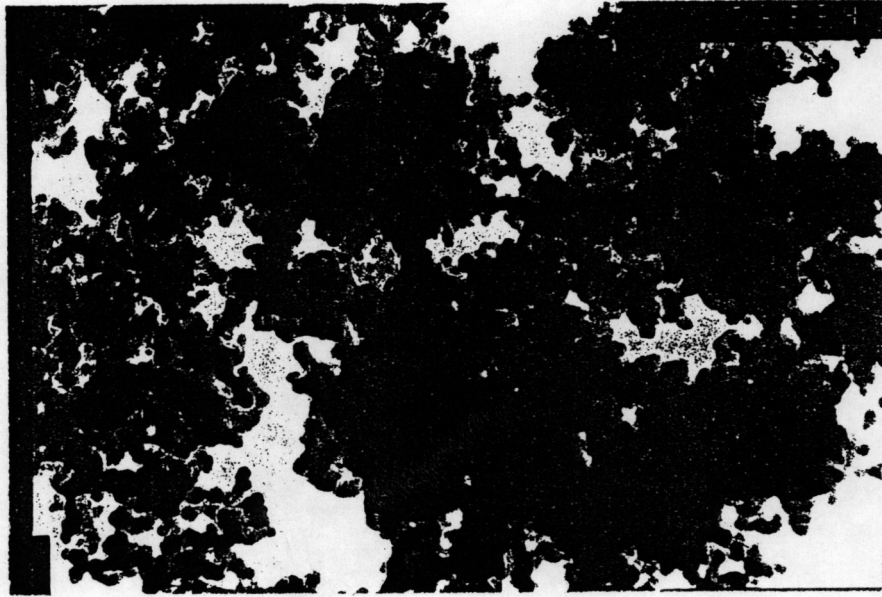


Figure 4.5 Transmission electron micrographs of modified silica, SI-4, at 73,000X Magnification.



Figure 4.6 Transmission electron micrographs of modified silica, SI-5, at 73,000X Magnification.

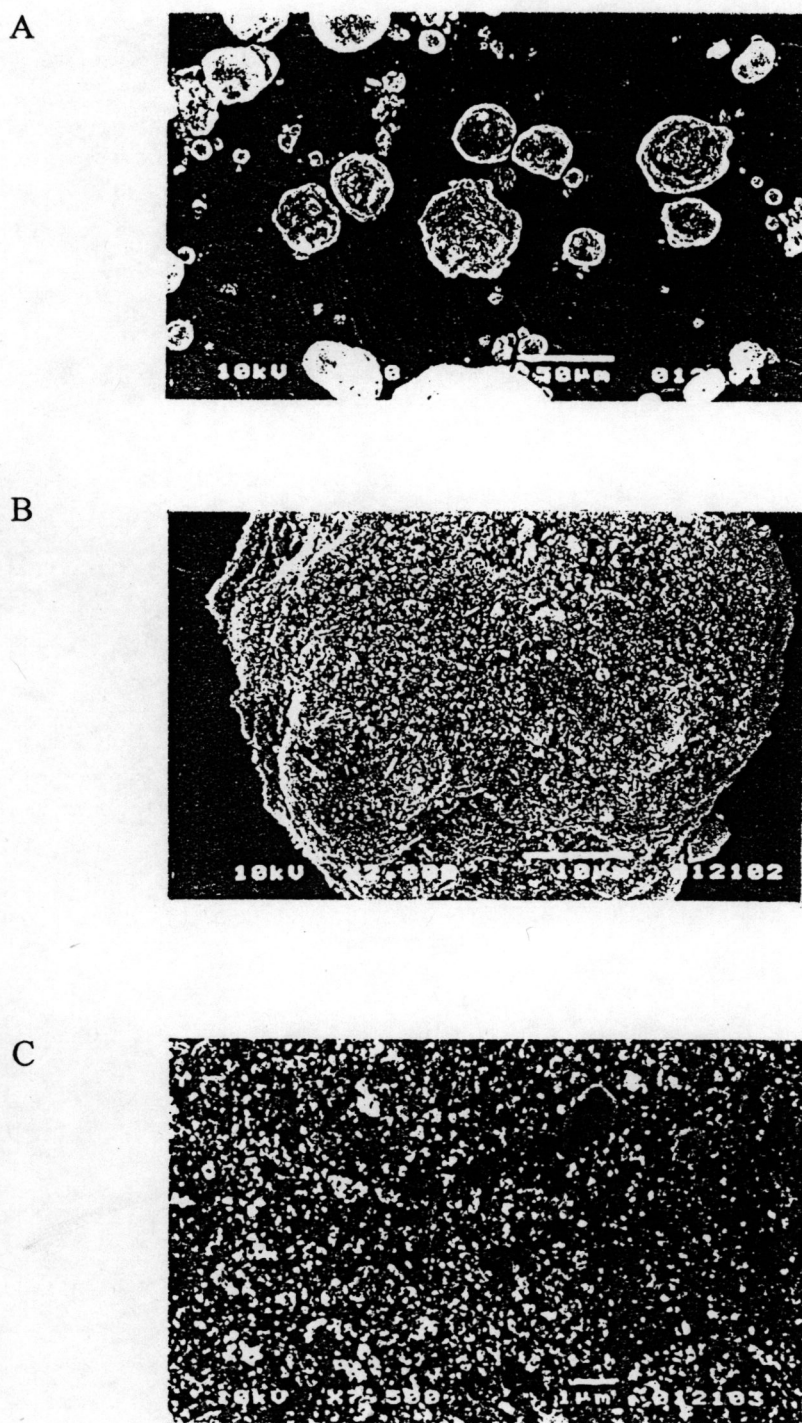


Figure 4.7 Scanning electron micrographs of unmodified silica, Hi-Sil[®]255, A. at 350X Magnification, B. at 2,000X Magnification, C. at 7,500X Magnification.

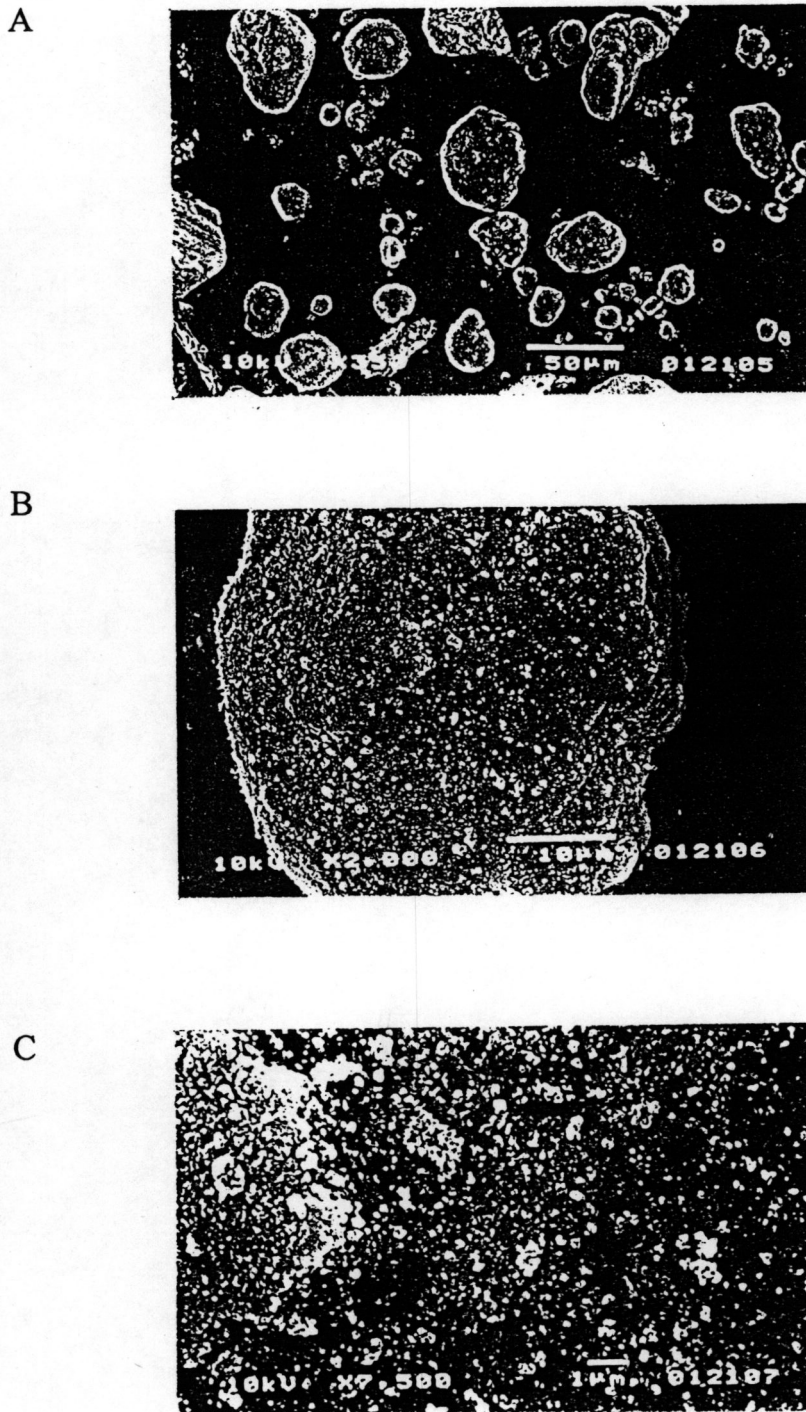
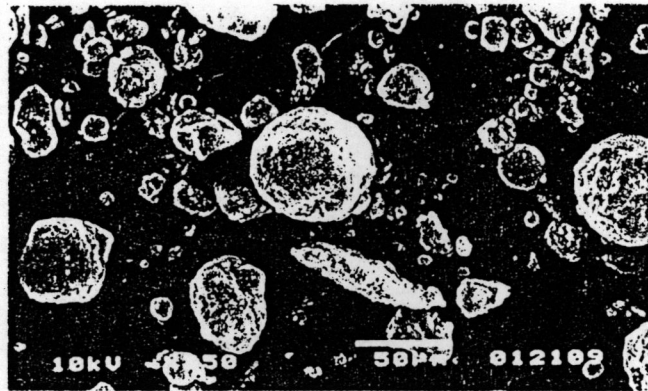
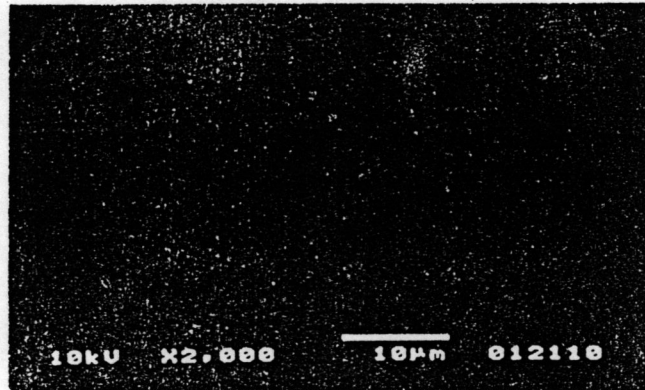


Figure 4.8 Scanning electron micrographs of modified silica, SI-1,
A. at 350X Magnification, B. at 2,000X Magnification,
C. at 7,500X Magnification.

A



B



C

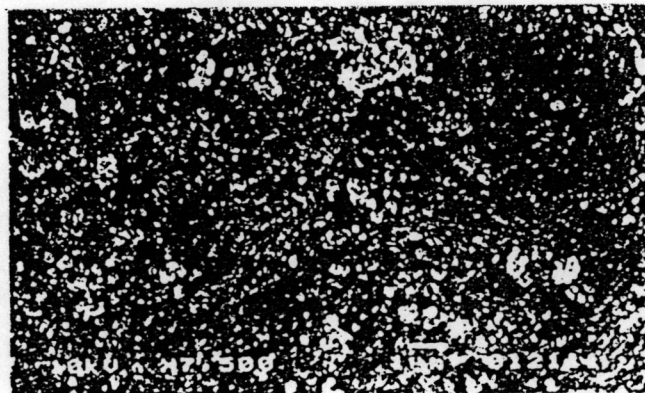
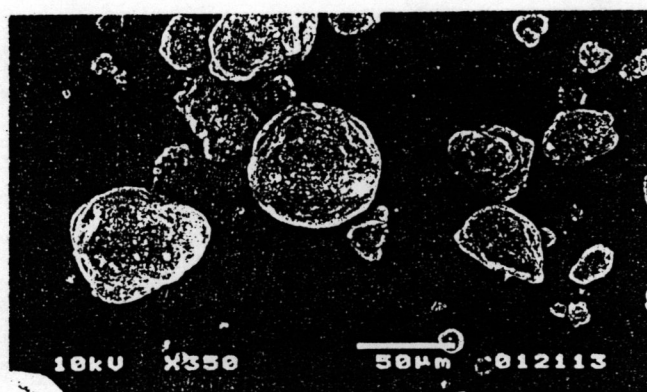
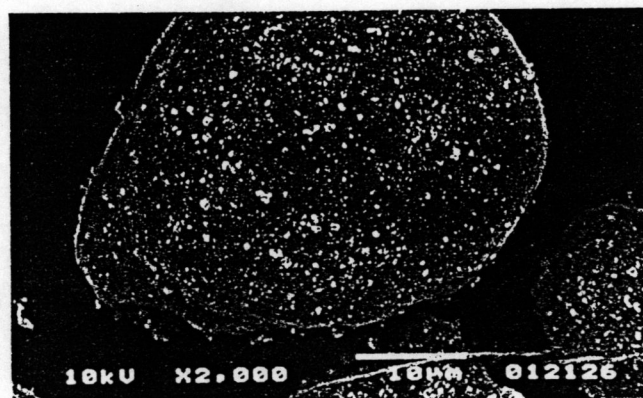


Figure 4.9 Scanning electron micrographs of modified silica, SI-2, A. at 350X Magnification, B. at 2,000X Magnification, C. at 7,500X Magnification.

A



B



C

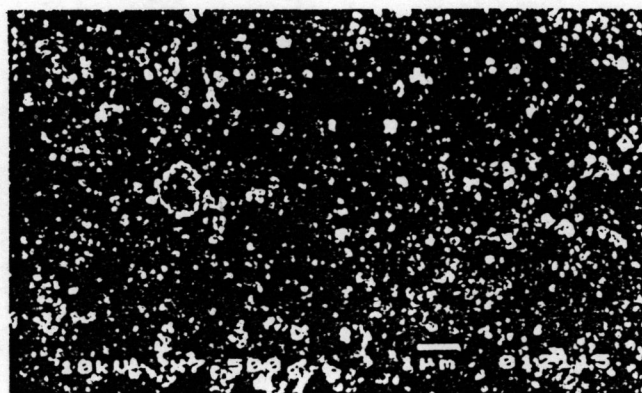
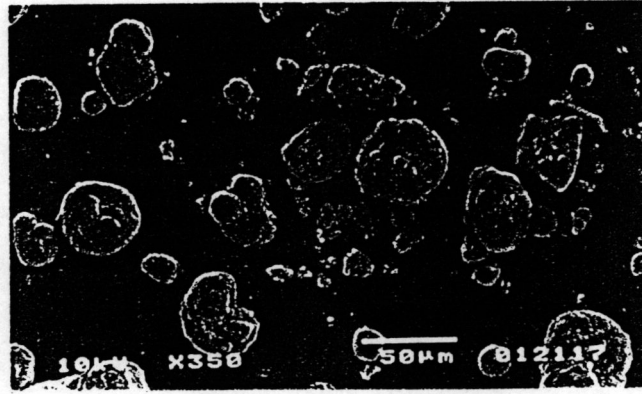
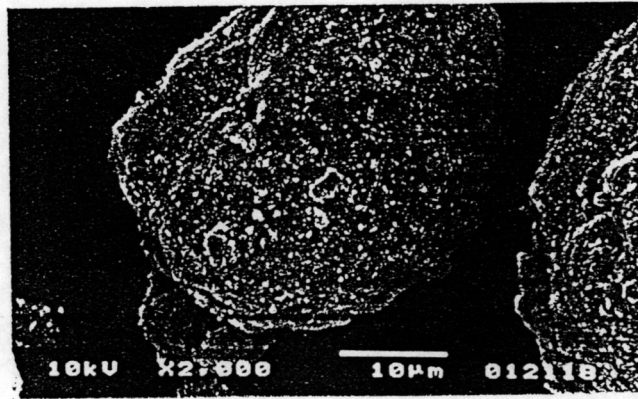


Figure 4.10 Scanning electron micrographs of modified silica, Si-3,
A. at 350X Magnification, B. at 2,000X Magnification,
C. at 7,500X Magnification.

A



B



C

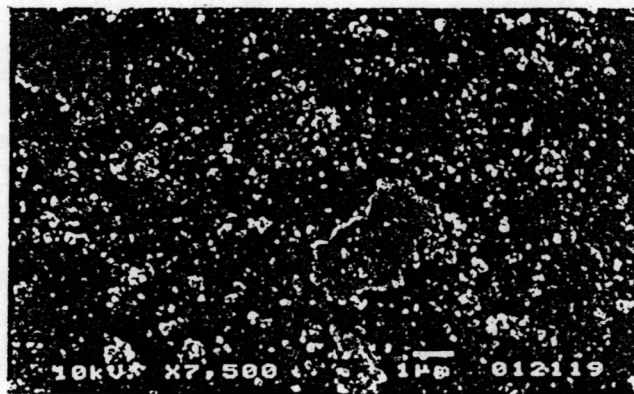
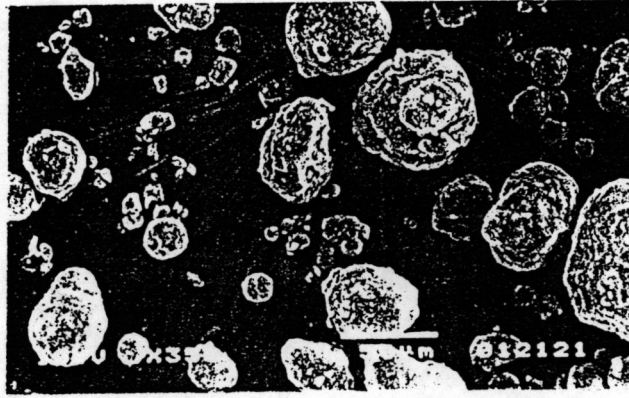
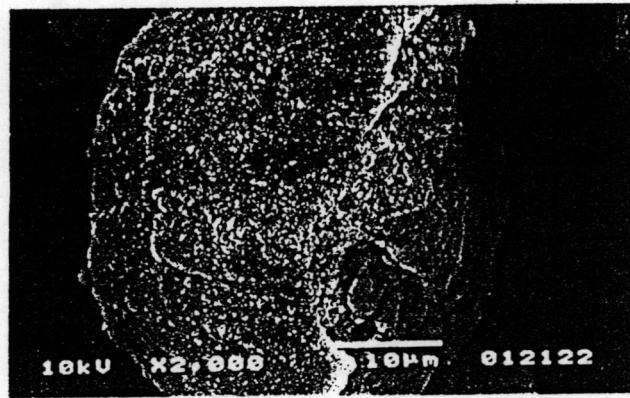


Figure 4.11 Scanning electron micrographs of modified silica, SI-4,
 A. at 350X Magnification, B. at 2,000X Magnification,
 C. at 7,500X Magnification.

A



B



C

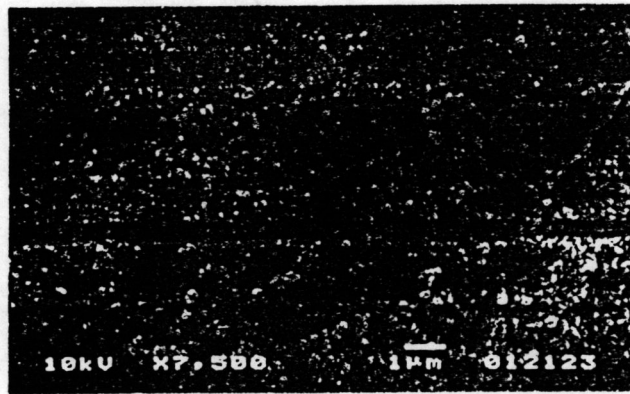


Figure 4.12 Scanning electron micrographs of modified silica, SI-5,
A. at 350X Magnification, B. at 2,000X Magnification,
C. at 7,500X Magnification.

The presence of polystyrene-isoprene copolymer on the silica powder was tested qualitatively by observing the hydrophobicity of the coated silica powder. All copolymer modified silica powders floated on the surface of water, while unmodified silica sank. This phenomena occurs because, after the surfactant was partially removed by washing, the hydrophobic tails part of the surfactant and co-polymer remained on the silica surface, making the pore more hydrophobic and prevents water into the powder.

In order to verify co-polymer formation on the silica, styrene-isoprene copolymer from the coated silicas was extracted by using refluxing THF. The extracted material and the silica after extraction were analyzed using FTIR and TGA. Both FTIR spectra and TGA proved the existence of poly(styrene-isoprene) on the silica surface. The TGA data indicated that silica modified by using 20 grams of styrene/isoprene co-monomer per kilogram of silica charged to the reactor (SI-3), has the greatest amount of co-polymer formed on the silica surface. Further, increasing the co-monomer charge to the reactor may result in a decrease in co-polymer formed on the silica surface. The explanation for this may be due to a diffusion effect. At a higher reactor charge of styrene/isoprene co-monomer, rapid polymerization at the pore mouth may block the pore and inhibit further development of the thin film. The authors are not prepared at this point to speculate further on the possible details of this mechanism.

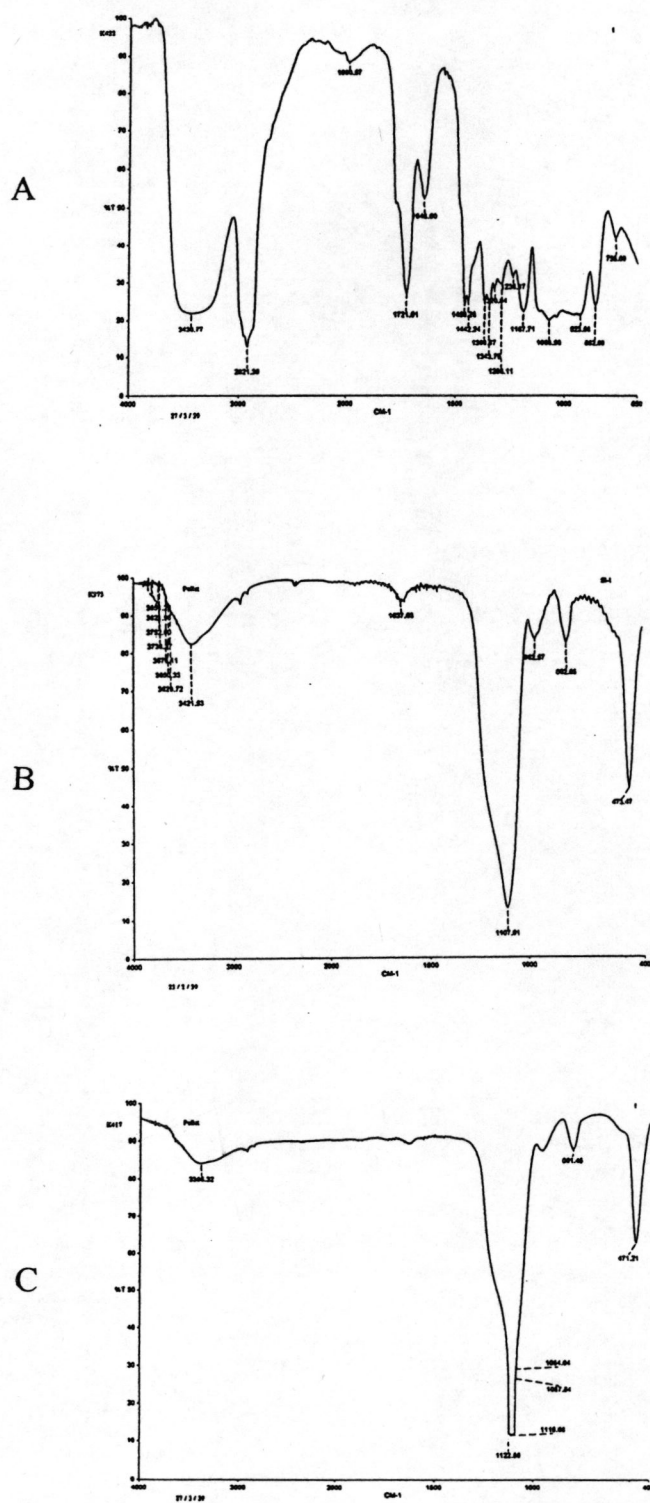


Figure 4.13 FTIR spectra of SI-1, A. Extracted material, B. Silica before extraction, C. Silica after extraction.

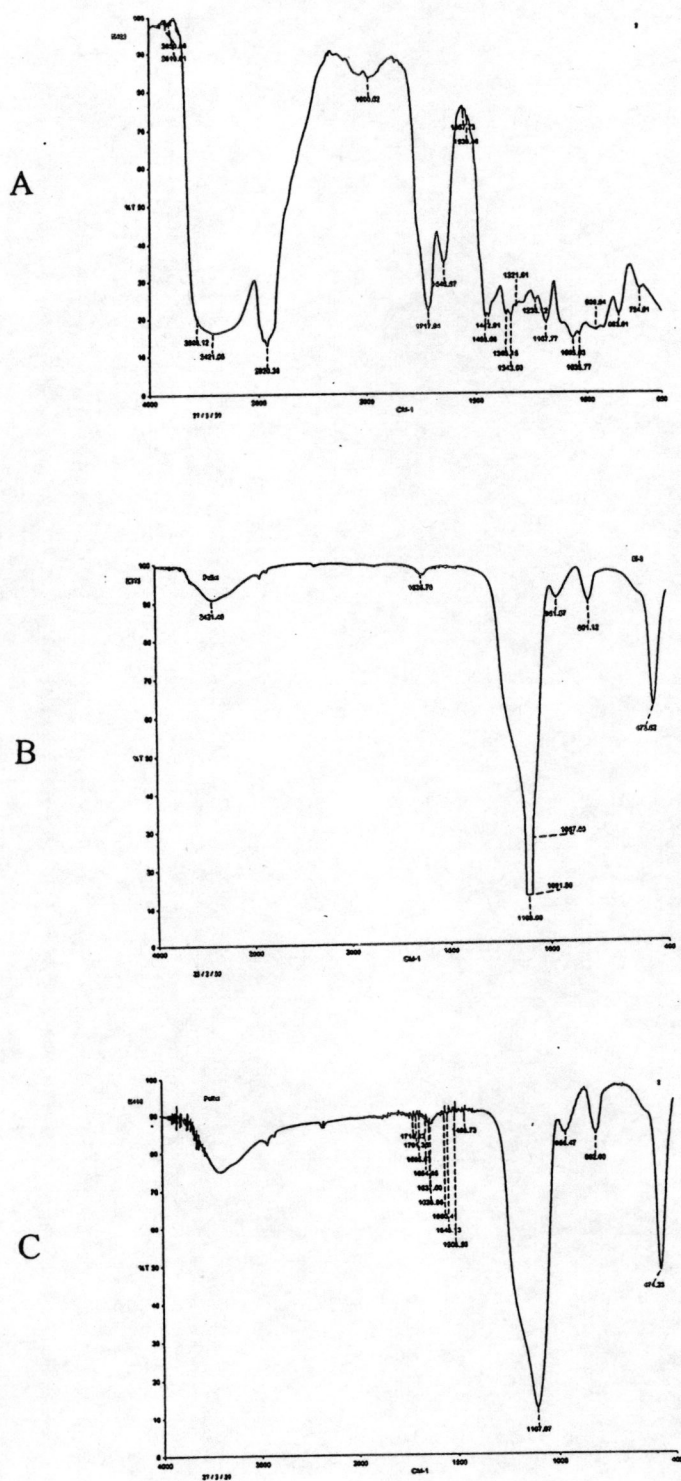


Figure 4.14 FTIR spectra of SI-2, A. Extracted material, B. Silica before extraction, C. Silica after extraction.

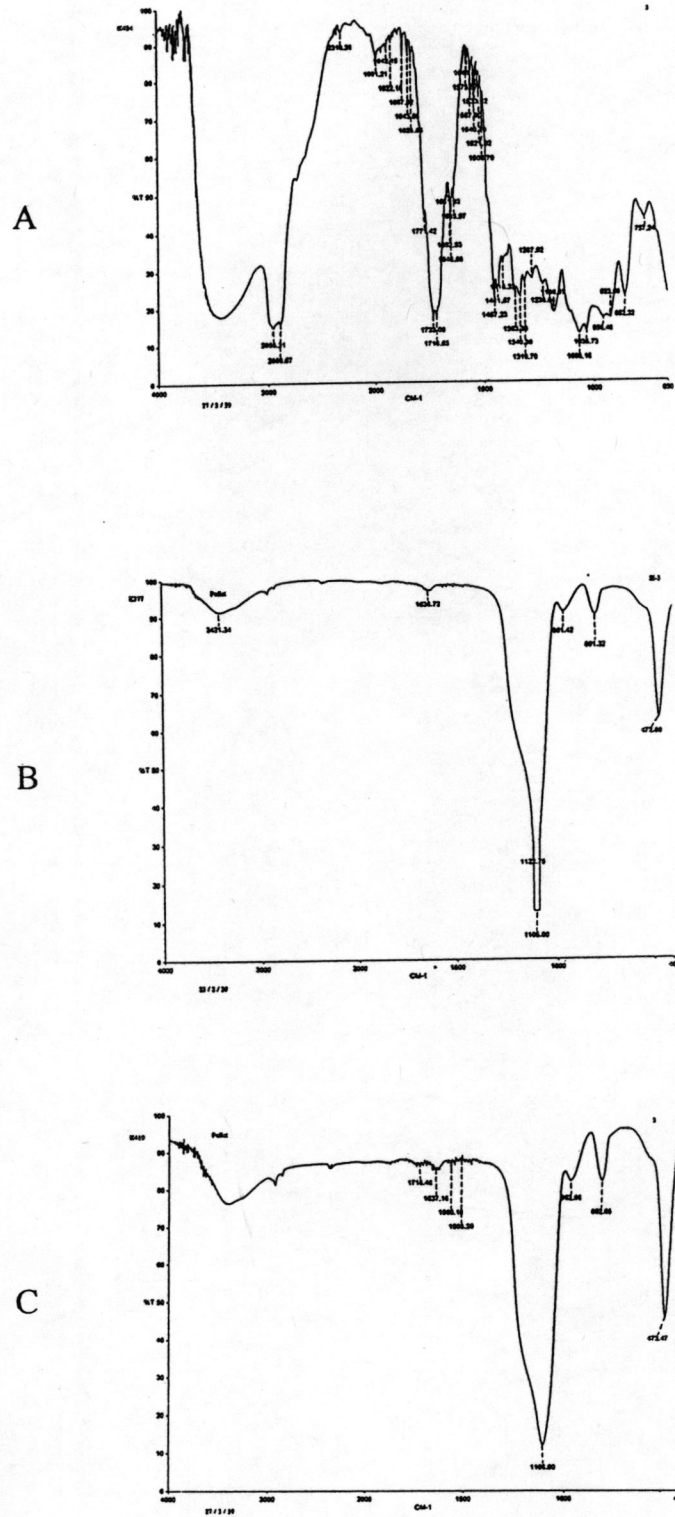


Figure 4.15 FTIR spectra of SI-3, A. Extracted material, B. Silica before extraction, C. Silica after extraction.

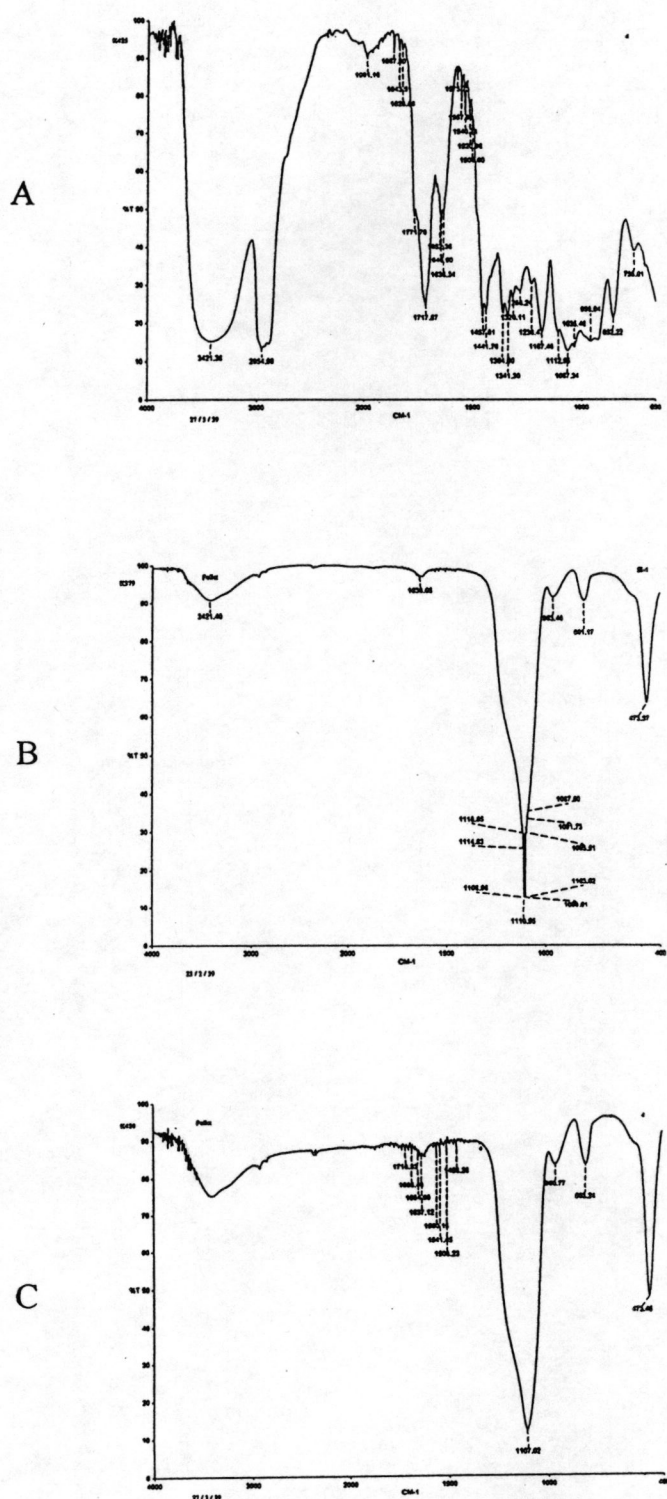


Figure 4.16 FTIR spectra of SI-4, A. Extracted material, B. Silica before extraction, C. Silica after extraction.

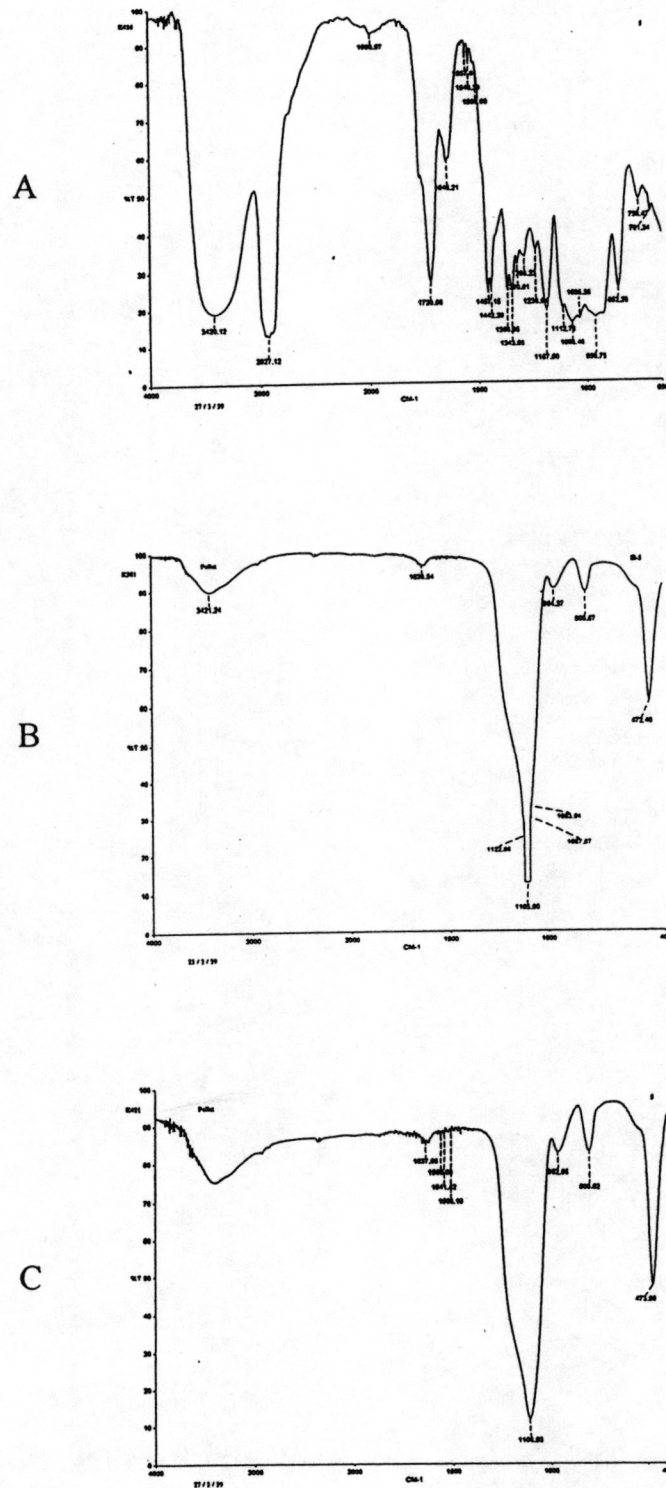


Figure 4.17 FTIR spectra of SI-5, A. Extracted material, B. Silica before extraction, C. Silica after extraction.

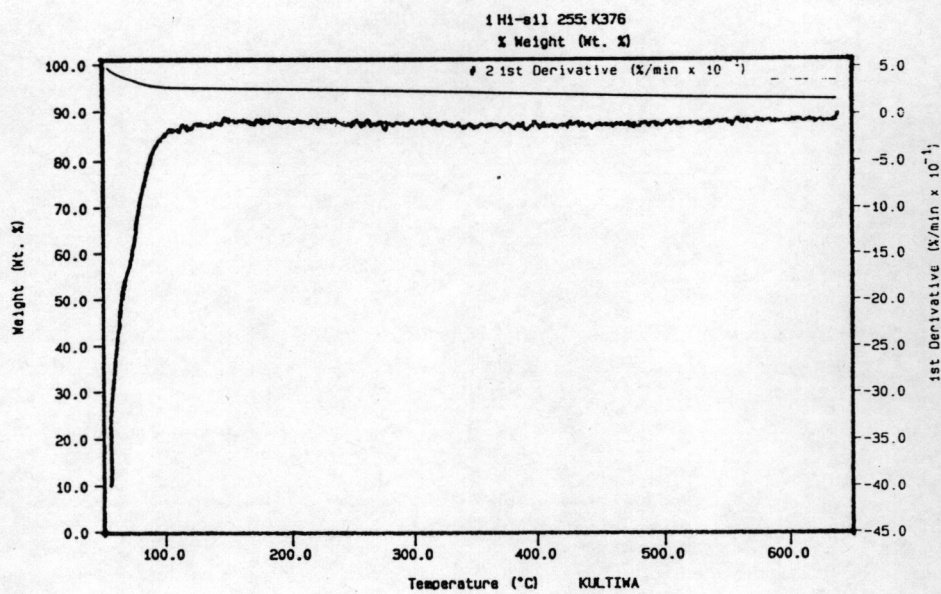
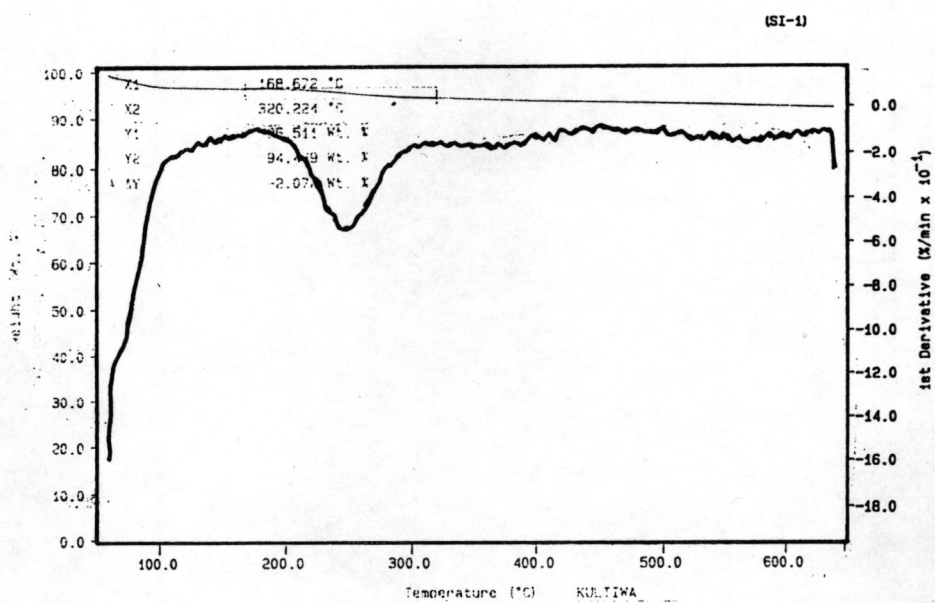


Figure 4.18 TGA of unmodified Hi-Sil[®]255.

A



B

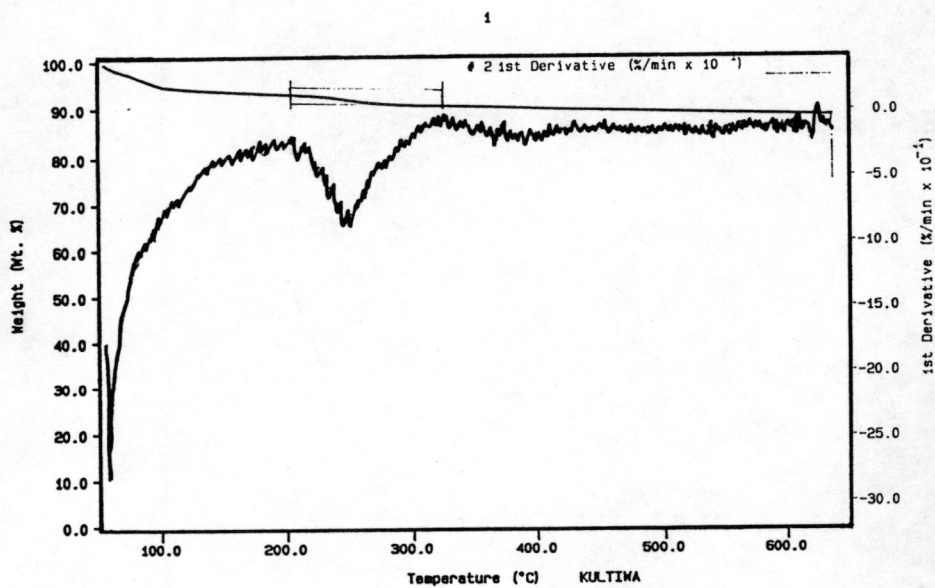
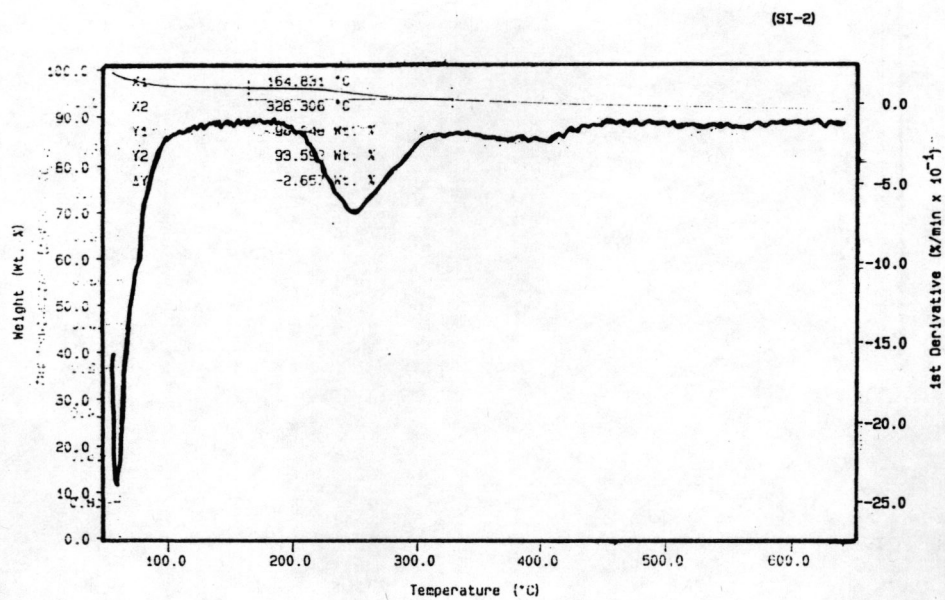


Figure 4.19 TGA of modified Silica, SI-1, A. Silica before extraction, B. Silica after extraction.

A



B

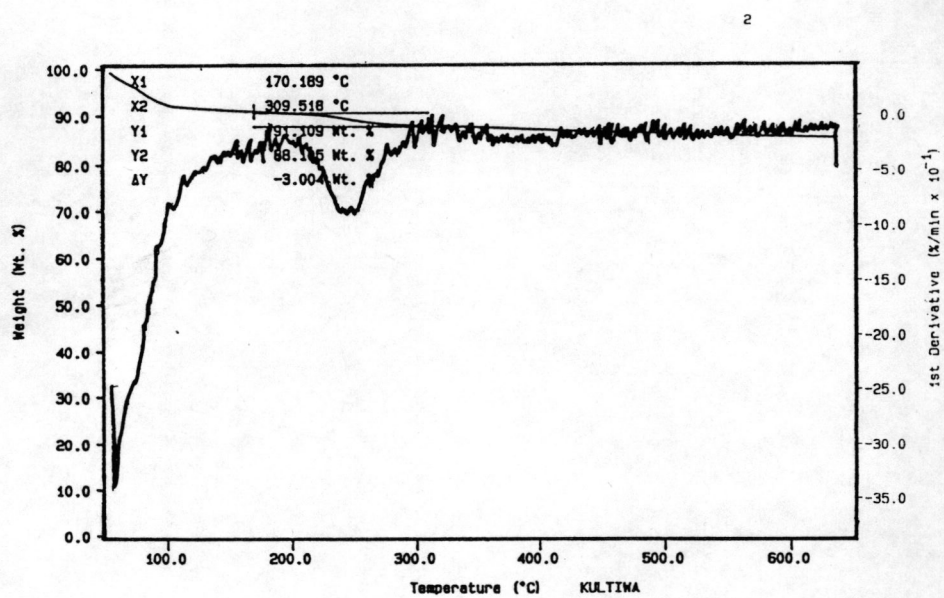
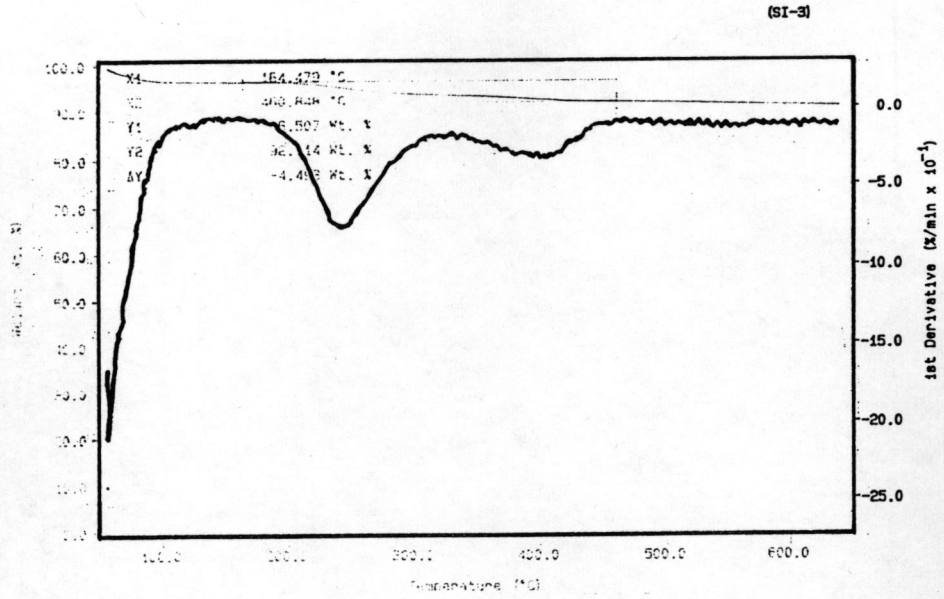


Figure 4.20 TGA of modified Silica, SI-2, A. Silica before extraction, B. Silica after extraction.

A



B

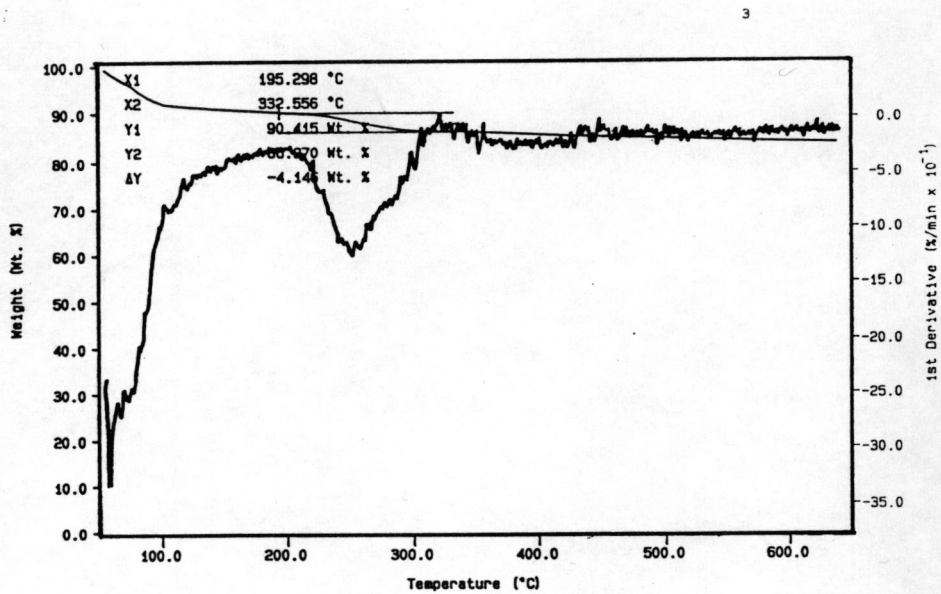
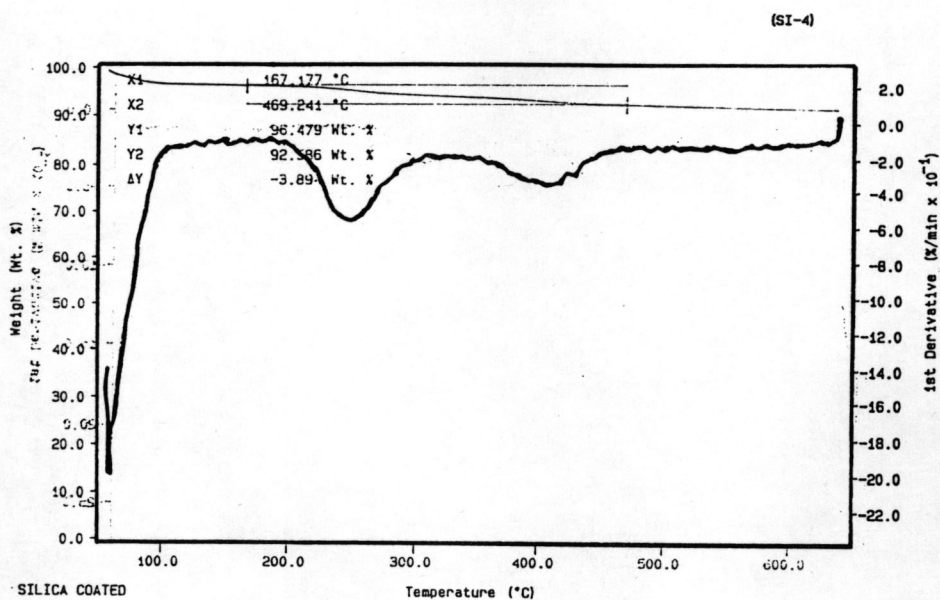


Figure 4.21 TGA of modified Silica, SI-3, A. Silica before extraction, B. Silica after extraction.

A



B

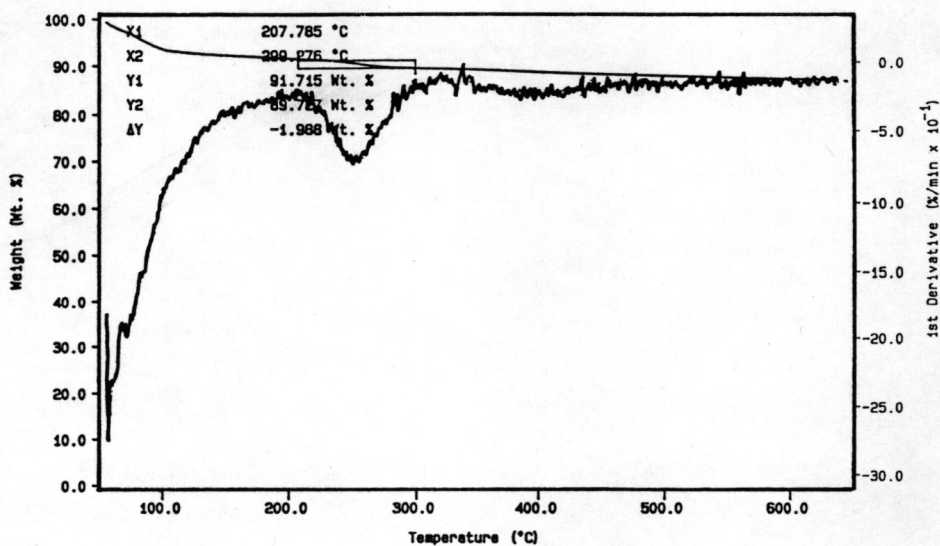
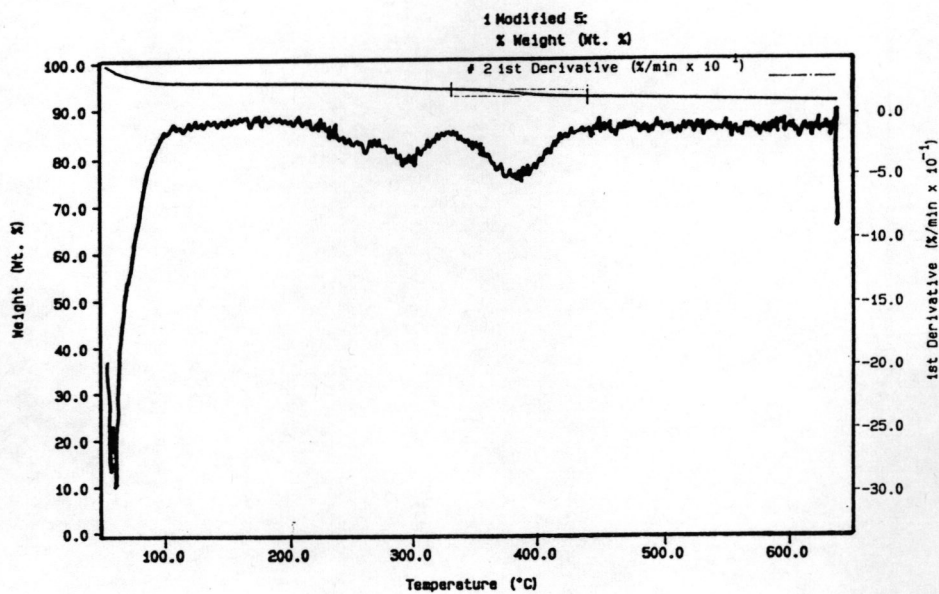


Figure 4.22 TGA of modified Silica, SI-4, A. Silica before extraction, B. Silica after extraction.

A



B

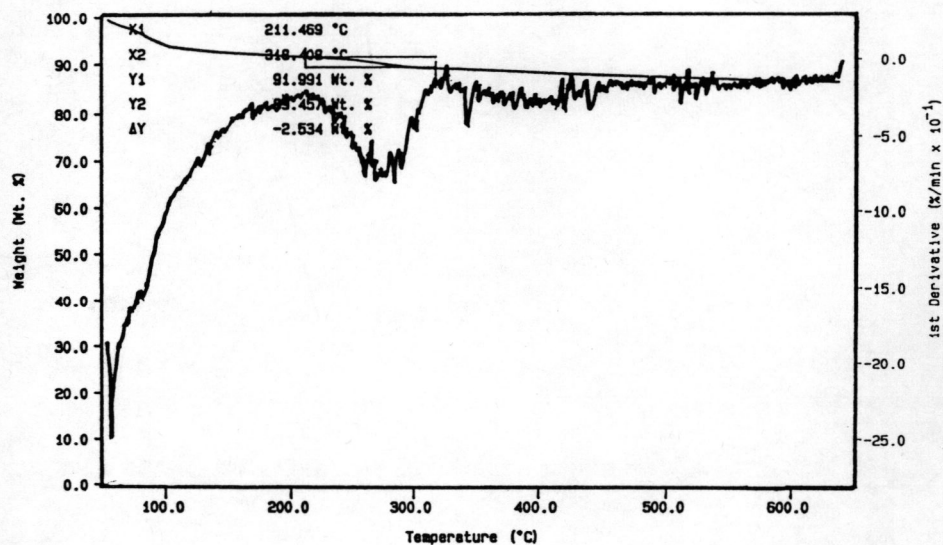


Figure 4.23 TGA of modified Silica, SI-5, A. Silica before extraction, B. Silica after extraction.

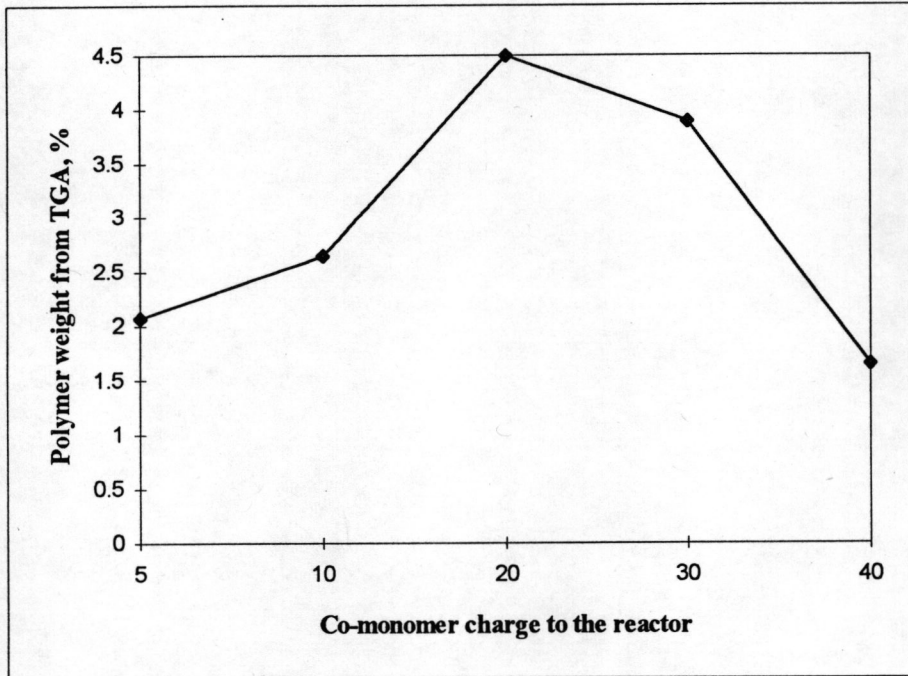


Figure 4.24 The amount of polymer versus co-monomer charge.

4.2 Rubber Compound Testing

4.2.1 Effect of the amount of comonomer loading on the silica surface

Five surface modified silicas, differing in the amount of styrene-isoprene copolymer, were used to investigate the effect of these various modifications on rubber compound physical properties. The results of rubber compound physical testing of all modified silicas are summarized in Table 4.2. The table also includes earlier results using unmodified Hi-Sil 255 (Thammathadanukul et al, accepted). The data show that the different copolymer-modified silicas produced significant differences in compound physical properties. Silica modified by polymerizing styrene-isoprene comonomers at a ratio of 20 g of comonomer per kg of silica onto the silica surface (SI-3) affords the minimum in compound cure time. This may be due to the greater amount of styrene-isoprene copolymer formed on the silica surface as indicated by the TGA (Figure 4.24). There are also significant differences in mooney viscosity, which are directly related to the differences in the mean particle size of all modified silicas (Evan and Waddell, 1994).

A comparative study of cured rubber compound physical properties shows that the silica modified by using a reactor charge of 20 grams of styrene-isoprene co-monomer charge per kilogram of silica afforded the maximum in rubber reinforcing properties for some properties, such as tensile strength, modulus@ 100%, modulus @ 500%, tear strength, and resilience. This modified silica also gives the minimum in abrasion loss, compression set, and hardness. However, this sample also had the minimum on flex cracking resistance. The results demonstrate that differences in performance arise due to differences in the amount of co-polymer coating on the silica surface.

Depending on the application, there may be an optimum amount of co-polymer coating on the silica which is beneficial in rubber compound reinforcement. The silica modified by polymerizing styrene-isoprene copolymer with the ratio of 20 grams of comonomer per kg of silica appears to be the more desirable surface modification for use in the natural rubber compound if flex cracking resistance, hardness and fatigue are within acceptable limits.

Table 4.2 Rubber Compound Physical Properties

PROPERTY	Hi-Sil 255 [†]	SIR-1	SIR-2	SIR-3	SIR-4	SIR-5
Mooney Viscosity ML1+4 (100 °C)	-	84.4	87.4	76.2 *	81.4	94.4
T ₉₀ , min:sec @ 150 °C	18:38	13:17	11:07	8:47*	12:47	14:41
Tensile strength, MPa	19.84	21.83	22.97	25.20*	21.05	17.99
Modulus @ 100 %, MPa	0.77	2.014	2.267	2.385	2.323	2.394*
Modulus @ 300 %, MPa	2.84	3.612	4.062	4.299*	3.985	3.999
Modulus @ 500 %, MPa	-	9.359	10.451	11.51*	9.812	9.515
Elongation @ Break, %	749.5	759.5*	751.1	742.3	736.6	698.0
Tear strength, N/mm	30.27	57.97	58.83	67.91*	45.94	31.94
Hardness, shore A	51.40	53.67	54.35	52.61	55.47*	55.03
Resilience, %	56.7	49.33	46.87	54.26*	44.45	43.90
Abrasion loss, mg/1000 cycles	0.960	0.768	0.715	0.567*	0.691	0.733
Compression set, %	-	72.16	73.38	67.69*	77.20	75.86
Flex cracking resistance, kilocycles	113.10	55.41	54.48	50.54	58.28	65.26
Fatigue	-	95.08*	92.32	88.55	94.62	53.93

† Results from Thammathanukul, et al, accepted.

* Indicates a desirable maximum or minimum in physical property variation with comonomer reactor charge.

Table 4.3 show physical properties of the rubber compound after aging at 100° C for 22 hours. The data shows that the silica modified by using a reactor charge of 20 grams of styrene/isoprene co-monomer loading on silica give the maximum in tensile strength and resilience. However, the maximum for modulus @ 100%, and hardness are now given by the silica modified by a reactor charge of using 30 grams of styrene/isoprene co-monomer per kilogram of silica (SI-4), the maximum for elongation @ break is given by the silica modified by reactor charge of using 5 grams of styrene/isoprene co-monomer per kilogram of silica (SI-1), and the maximum performance for modulus @ 300%, modulus @ 500%, and for tear strength are now given by the silica modified by using a reactor charge of 10 grams of styrene/isoprene co-monomer per kilogram of silica (SI-2).

Table 4.3 Rubber Compound Physical Properties after Aging

PROPERTY	SIR-1	SIR-2	SIR-3	SIR-4	SIR-5
Tensile strength, MPa	22.94	22.95	23.43 *	22.54	18.19
Modulus @ 100 %, MPa	3.815	4.268	3.964	4.368 *	4.202
Modulus @ 300 %, MPa	6.514	7.250 *	6.719	7.221	6.771
Modulus @ 500 %, MPa	15.395	16.641*	16.203	15.686	14.250
Elongation @ Break, %	816.7 *	724.9	755.7	629.8	582.7
Tear strength, N/mm	73.59	80.02 *	68.18	72.36	55.67
Hardness, shore A	58.56	59.94	56.87	61.44 *	58.76
Resilience, %	50.68	52.40	53.76 *	47.45	45.26

4.2.2 Effect of percent silica loading on model rubber compound

Filler aggregates in an elastomer matrix are known to have a tendency to form agglomerates, especially at high loading, leading to chain-like filler structures or clusters. These are generally termed secondary structures or filler networks, even though they are not comparable to the continuous polymer network. Such structures have significant effects on the properties of filled rubber. To explore the impact of silica-loading in a rubber compound, five different compounds were prepared with percent silica loadings of 10, 20, 30, 40, and 50 parts per hundred (PHR). The modified silicas used in this study were prepared using a reactor charge of 20 grams of styrene-isoprene comonomer per kg of silica, the charge that produced the most effective reinforcing silica in the first part of this study.

The results are summarized in Table 4.4. The data show that the addition of silica to a compound rapidly increases the viscosity. The mooney viscosity increased dramatically from 48.83 to 69.80 as the percent silica loading increased. This is due to the incompatibility of silica with rubber, so that as the percent silica level in rubber compound increases, the silica to silica attraction becomes more dominant, with the result that larger aggregates are formed, which impede polymer flow, and increase the filled rubber compound stiffness.

Cure time, tensile strength, and elongation @ break increase with silica loading up to the 40 PHR level. Time to 90 % cure increases from 4:34 to 5:48 minutes, tensile strength increases from 22.39 to 26.53 MPa and elongation @ break increases from 618.8 to 654.4 %. Modulus @100%, modulus @ 300%, modulus @ 500%, tear strength, hardness, and compression set all increase significantly as the percent silica loading increased. Modulus

@100% increases from 2.207 to 3.536 MPa, modulus @ 300% increases from 3.007 to 5.794 MPa, modulus @ 500% increases from 12.480 to 15.794 MPa. The tear strength increases from 38.79 to 59.13 N/mm, hardness varied from 44.59 to 59.57 shore A, and the compression set after 24 hours at 100°C can be varied from 47.09 to 58.96 %. Abrasion loss also decreased from 0.821 to 0.471 ml/1000 cycles. However, an increase in silica loading in the rubber compound results in a decrease in resilience, flex cracking resistance, and fatigue. From the data, the resilience dropped from 72.89 to 60.35 %, flex cracking resistance dropped from 67.22 to 35.56 kilocycles and fatigue of the cure rubber compound dropped from 212.82 to 108.45.

Table 4.4 Rubber Compound Physical Properties

PROPERTY	10 PHR	20 PHR	30 PHR	40 PHR	50 PHR
Mooney Viscosity ML1+4 (100 °C)	48.83	57.03	63.2	67.8	69.80*
T ₉₀ , min:sec @ 150 °C	4:34 *	4:40	5:11	5:48	5:18
Tensile strength, MPa	22.39	25.44	26.42	26.53*	24.81
Modulus @ 100 %, MPa	2.217	2.672	2.909	3.222	3.536*
Modulus @ 300 %, MPa	3.667	4.437	4.849	5.105	5.794*
Modulus @ 500 %, MPa	12.480	14.379	15.108	15.026	15.794*
Elongation @ Break, %	618.8	632.1	643.8	654.4*	618.8
Tear strength, N/mm	38.79	44.75	53.34	58.55	59.13*
Hardness, shore A	44.59	46.72	48.76	53.0	59.57*
Resilience, %	72.89*	71.17	68.53	65.67	60.35
Abrasion loss, mg/1000 cycles	0.821	0.568	0.471*	0.505	0.489
Compression set, %	47.09*	48.15	48.52	50.32	58.96
Flex cracking resistance, kilocycles	67.22	70.86*	47.80	43.47	35.56
Fatigue	212.82*	200.03	164.16	112.58	108.45

Table 4.5 shows the compound physical properties for each sample after aging 22 hours at 100°C. Tensile strength and elongation @ break values decrease during aging, but still increase with silica loading up to a silica level of 40 PHR. Tensile strength varied from 6.82 to 23.42 MPa and elongation @ break varied from 329.4 to 568.9 %. Modulus @100%, modulus @ 300%, tear strength, and hardness increase with increasing silica level. Modulus @100% increases from 3.066 to 5.015 MPa, and modulus @ 300% increases from 5.066 to 8.796 MPa. Both of these measurements are higher than before aging for all silica loading levels. Tear strength increases from 33.89 to 51.76 N/mm as loading increases, but the values at each silica loading level are less than the value before aging. Hardness of the compound increases with aging and varies from 48.97 to 65.78 shore A.

The data suggest that a silica loading of 40 PHR may be the maximum for achieving optimum rubber performance. Beyond this level, there appears to be a dilution effect, where there is not enough rubber matrix to hold the silica particles together. Figures 4.35- 4.56 graphically display compound data for each property listed in Table 4.4 and 4.5

Table 4.5 Rubber Compound Physical Properties after Aging

PROPERTY	10 PHR	20 PHR	30 PHR	40 PHR	50 PHR
Tensile strength, MPa	6.82	11.60	20.75	23.42*	19.71
Modulus @ 100 %, MPa	3.066	3.726	3.908	4.316	5.015*
Modulus @ 300 %, MPa	5.066	6.419	6.512	7.121	8.796*
Modulus @ 500 %, MPa	11.920	-	18.807	18.050	19.522*
Elongation @ Break, %	329.4	373.9	527.3	568.9*	483.9
Tear strength, N/mm	33.89	39.13	46.41	51.33	51.76*
Hardness, shore A	48.97	52.49	54.15	58.08	65.78*
Resilience, %	75.55*	74.31	73.15	68.04	62.13