CHAPTER IV
RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared Spectroscopy

In order to confirm the formation of polystyrene on the surface of natural rubber, spectra of the products were compared to the spectra of standard polystyrene. Figure 4.1 showed the spectra of modified surface of natural rubber with styrene monomer concentration of 300 mM and using CTAB surfactant (pH8). FTIR spectra represented the benzene ring which are aromatic C-H stretching at 3100-3000 cm^{-1}, aromatic C=C stretching at 1600 cm^{-1}, 1500 cm^{-1}, 1450 cm^{-1} and C-H deformation (out-of-plane) at 700 cm^{-1}. This result was as same as the extract polystyrene from cotton fiber in literature (Pongprayoon et al., 2002).
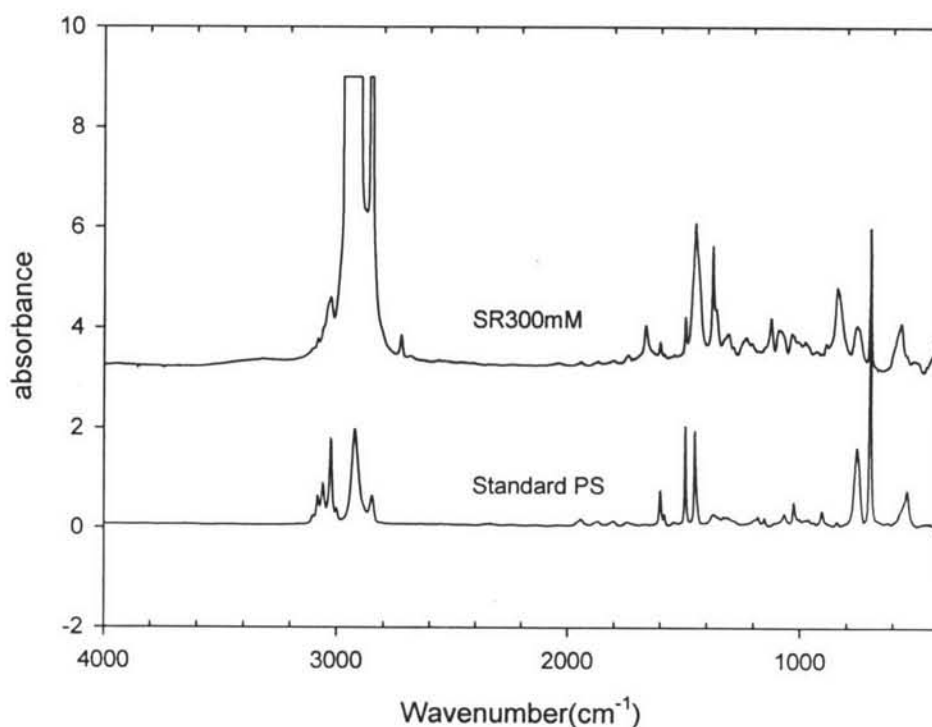

Figure 4.1 FTIR spectra of the CTAB admicellar polymerization on natural rubber at pH 8 for styrene concentration 300 mM.

The spectra of standard polystyrene, natural rubber and admicellar modified natural rubber with the concentration of styrene from 100 to 300 mM at pH8 and the mole ratio of styrene: initiator fixed at 1:0.1 were showed in Figure 4.2. The polystyrene modified natural rubber showed the same peaks as presented in the standard polystyrene. It can be concluded that the admiellar modified natural rubbers with all concentrations of styrene monomer show the characteristic peaks of polystyrene.
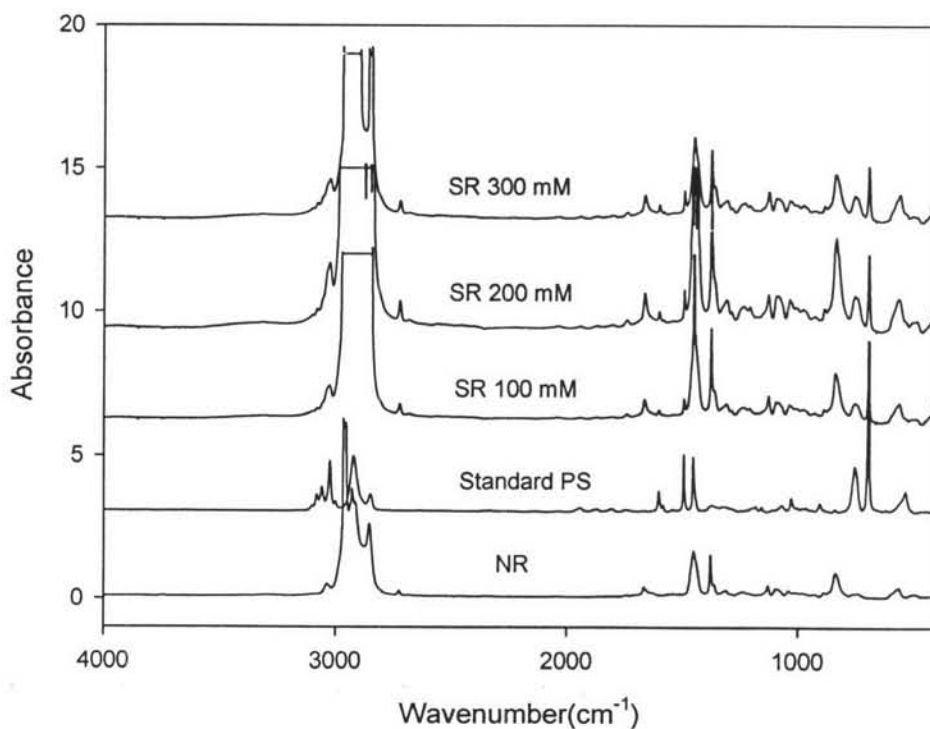

Figure 4.2 FTIR spectra of natural rubber, standard polystyrene and modified with styrene concentrations 100-300 mM by using CTAB surfactant.

The FTIR results by using SDS surfactant show in Figure 4.3. The admicellar modified natural rubbers show the characteristic peaks of polystyrene especially at high concentration of styrene monomer.
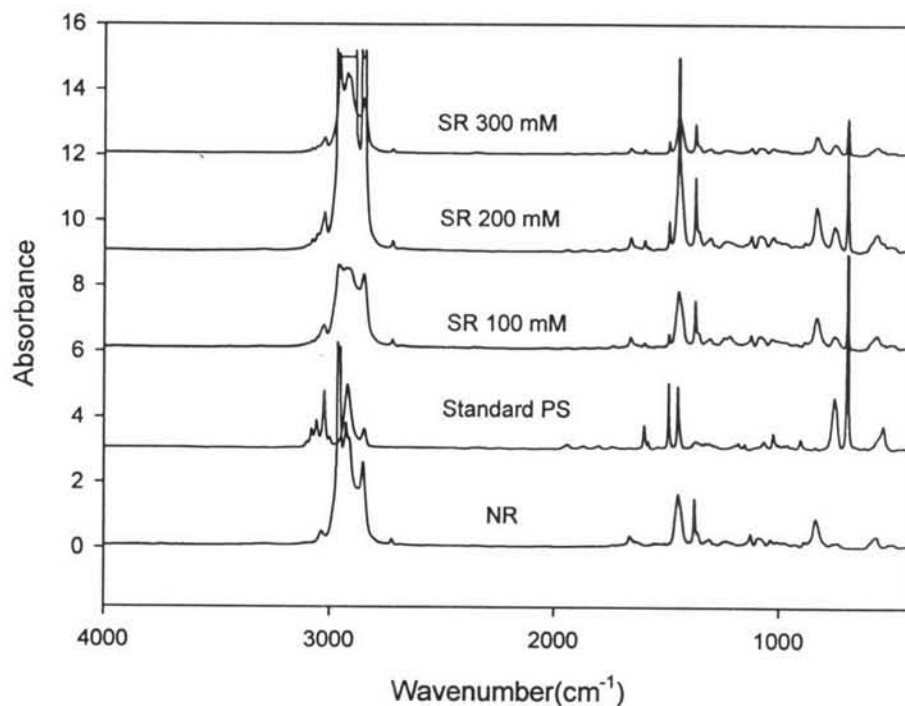
Figure 4.3 FTIR spectra of natural rubber, standard polystyrene and modified natural rubber with styrene concentrations 100-300 mM by using SDS surfactant

4.2 Appearance of Admicellar Modified Natural Rubber

The color of the dry admicellar modified natural rubbers at different concentrations of styrene showed in Figure 4.4. The color of the product varied from very light yellow to opaque white with styrene concentration as well as the apparent stiffness. In other words, the product turns to opaque white at high styrene concentration. The natural rubber color change occurred from chain degradation with light after that bacteria can destroy natural rubber easily. Polystyrene film can protect natural rubber from light and bacteria so it can improve color property. Furthermore the admicellar modified natural rubber can process to the thin polymer film by using compression molding at 200°C after that the color of admicellar modified natural rubber change a little.
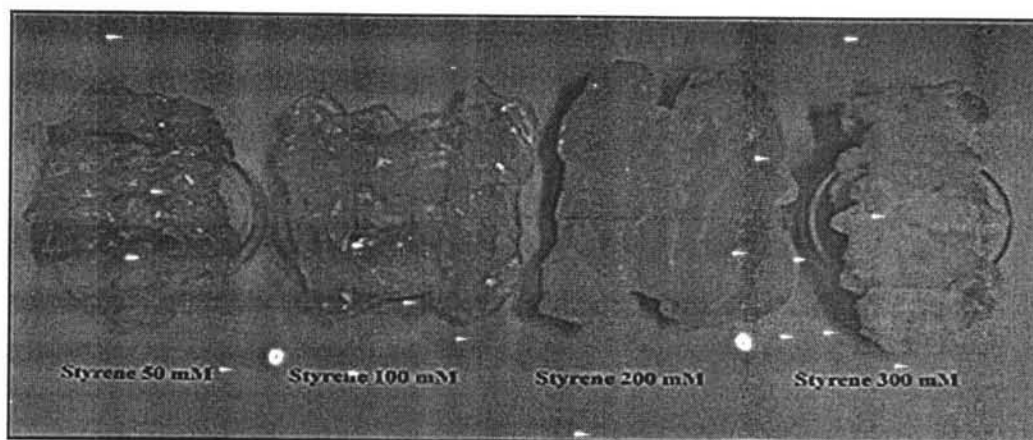
Figure 4.4 The color of modified natural rubber at different concentration of styrene monomer.

4.3 The Moiecular Weight of Polystyrene after Admicellar Polymerization

4.3.1 The Effect of Salt on the Molecular Weight of Polystyrene

The CTAB concentration was fixed at 2,800 µM while the styrene monomer was varied from 50, 100, 200, 300 mM. The styrene: initiator mole ratio was varied from 1:0.04 and 1:0.1. The effect of salt on the molecular weight of polystyrene showed in Tables 4.1 and 4.2. The molecular weight of polystyrene was increased slightly under salt addition with the ratio between styrene: initiator was 1:0.04 and 1:0.1. At low concentration, the peak pattern of polystyrene cannot be found in low concentration of styrene monomer because it was hindered by peak pattern of natural rubber of which the concentration was much higher than that of styrene monomer.

Table 4.1 The molecular weight of polystyrene by using CTAB surfactant. Styrene concentrations varied from 50, 100, 200, 300 and the styrene: initiator ratio at 1: 0.04 with and without salt

%wt of PS in admicellar modified NR	Styrene Monomer (mM)	CTAB, V50, 1:0.04	MWD	CTAB, V50, 1:0.04, NaBr 0.3mM	MWD
4.97	50	-	-	-	-
9.46	100	-	-	-	-
17.29	200	311,851	3.51	332,986	3.25
23.87	300	310,273	3.67	329,281	3.56

Table 4.2 The molecular weight of polystyrene by using CTAB surfactant. Styrene concentrations varied from 50-300mM and the styrene: initiator ratio at 1: 0.1 with and without salt

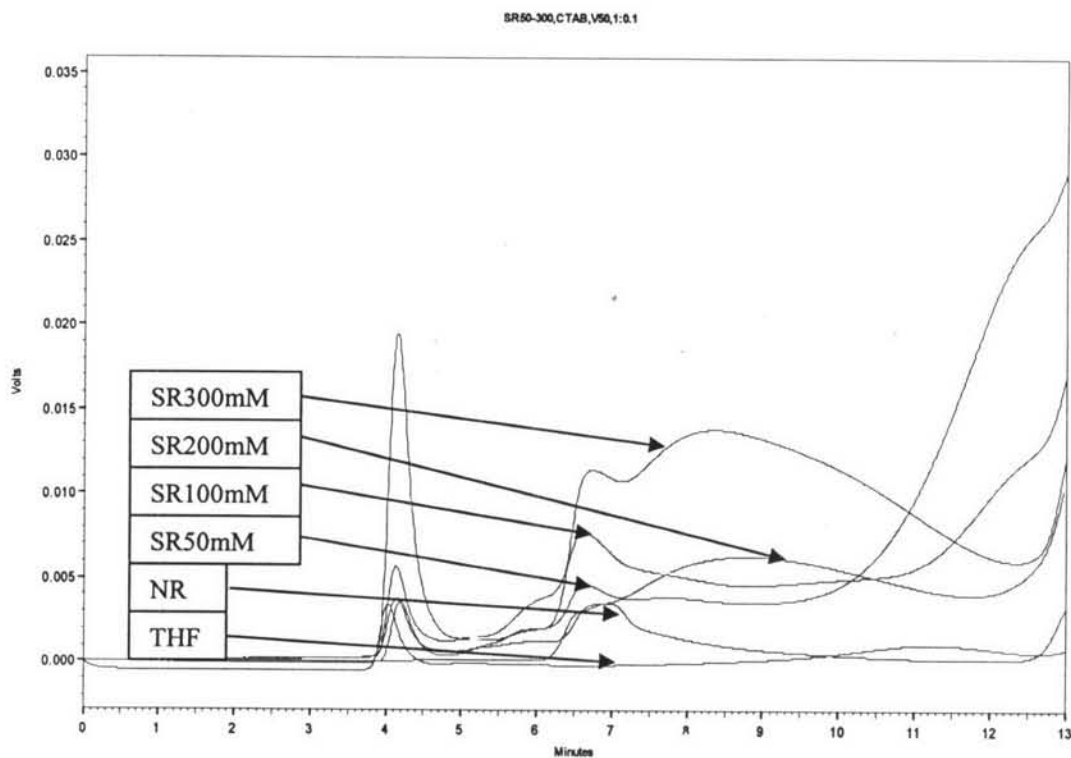| %wt of PS in admicellar modified NR	Styrene Monomer (mM)	CTAB, V50, 1:0.1	MWD	CTAB, V50, 1:0.1, NaBr 0.3 mM	MWD
4.97	50	-	-	-	-
9.46	100	296,346	3.24	258,182	3.12
17.29	200	295,526	3.17	332,674	3.64
23.87	300	299,980	3.68	330,644	3.87

Figure 4.5 The molecular weight chromatograms from GPC showing varied styrene monomers from 50-300 mM at fixed CTAB concentration of 2,800 µM without salt (Note: Peak at elution time about 4 min was belonging to mobile phase, THF).
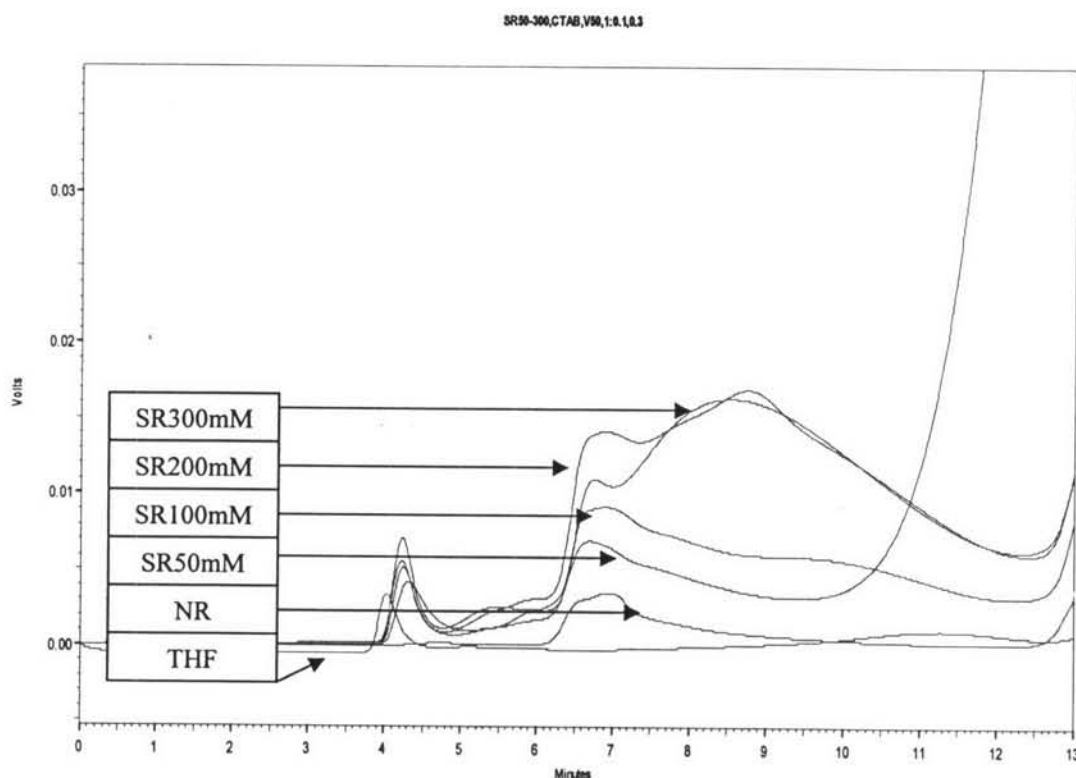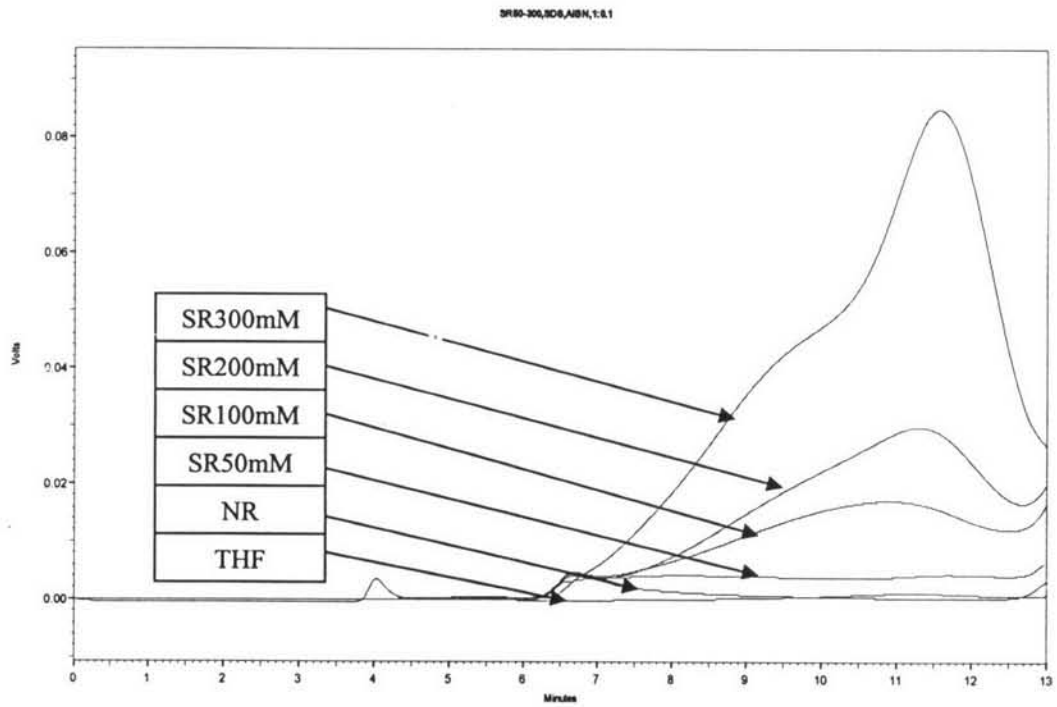
Figure 4.6 The molecular weight chromatograms from GPC with varied styrene monomer from 50-300 mM at fixed CTAB concentration of 2,800 μM with NaBr 0.3 mM (Note: Peak at elution time about 4 min was belong to mobile phase, THF).

Figures 4.5-4.6 also showed natural rubber molecule weight chromatogram and suggested that natural rubber was come out at elution time about 6.5 min. This natural rubber elution peak was not changed when styrene and initiator were added. Besides, the modified natural rubber can be totally dissolved in solvent THF thus it can be concluded that natural rubber was not involved in polymerization of styrene and initiator cannot attack natural rubber.

In acid condition, the SDS concentration was fixed at 24,000 μM and the concentration of styrene monomer was varied from 50 to 300 mM. The styrene: initiator mole ratio was 1:0.04. The results were showed in Table 4.3. The MW of polystyrene under salt addition was observed to be about 199,510-157,150 which increasing significantly when comparing to the MW of polystyrene in no salt addition (99,490-86,955). It is probably suggested that salt can decrease the repulsion

between surfactant head group (Pongprayoon, 2002) therefore the surfactant was able to increase its adsorption at the surface of natural rubber which can prevent the agglomerate of natural rubber and also resulted in increasing the adsolubilization of styrene monomer.

The GPC chromatograms in Figure 4.7 and Figure 4.8 showed the peak of polystyrene at elution time between 7-13 min. The elution time of polystyrene that synthesize form the same styrene concentration compare between with and without salt. It showed short elution time occurred in adding salt condition. It can be concluded salt can improved the high molecular weight of polystyrene. Furthermore, at low concentration, peak of polystyrene was not clearly found.

Table 4.3 The molecular weight of polystyrene by using SDS surfactant. Styrene concentration varied from 50-300 mM and the styrene: initiator ratio at 1:0.04 under condition with and without salt

Styrene Monomer (mM)	SDS, AIBN, 1:0.04	MWD	SDS, AIBN, 1:0.04, NaBr 0.3mM	MWD
50	-	-	-	-
100	99,075	4.12	199,510	3.65
200	86,955	3.89	176,446	3.84
300	99,490	3.64	157,150	3.69

Figure 4.7 The molecular weight chromatogram from GPC that varied styrene monomer from 50-300 mM and fixed SDS concentration at 24,000 μM without salt (THF elution time about 4 min).
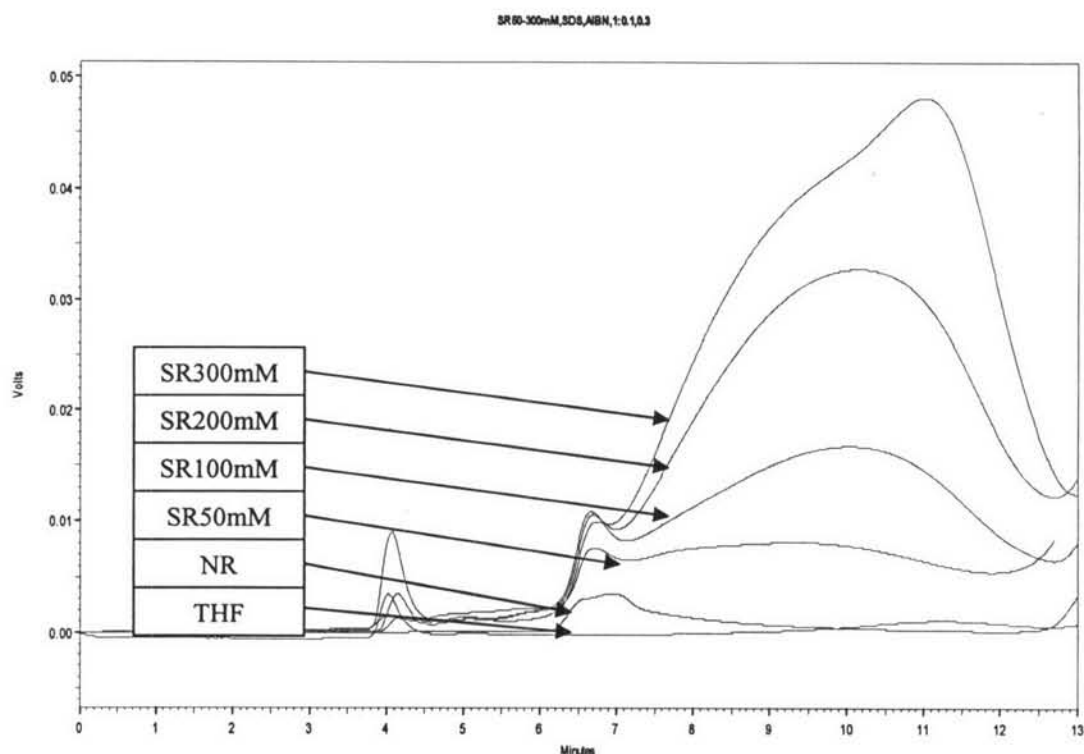
Figure 4.8 The molecular weight chromatograms from GPC that varied styrene monomer from 50-300 mM and fixed SDS concentration at 24,000 μM with salt 0.3 mM (THF elution time about 4 min).

4.3.2 The Effect of Varying Amount of Initiator

In this experiment, the concentration of CTAB surfactant and styrene monomer was fixed at 2,800μM and 100, 200 mM respectively. The mole ratio between styrene: initiator was varied to be 1:0.04, 1:0.1, 1:0.2. The chromatogram of GPC in Figure 4.9 and the results in Table 4.4 shows that molecular weight of polystyrene was 311,981, 296,823 and 160,965 with increasing initiator ratio at fixed concentrations of styrene monomer at 200 mM and 277,585 and 193,149 for V50 0.1 and 0.2 mole/mole styrene with styrene concentration of 100 mM. The observation would conclude that by increasing the amount of initiator, the molecular weight of polystyrene was decreased and its MWD or PDI became wider (Pongprayoon, 2002).

Table 4.4 The effect of varying amount of initiator from 0.04, 0.1 and 0.2 mole/mole styrene on the molecular weight of polystyrene (Using CTAB).

Styrene : Initiator	Styrene 100mM	MWD	Styrene 200Mm	MWD
1: 0.04	-	-	311,981	3.11
1:0.1	277,585	3.12	296,823	2.98
1:0.2	193,149	3.29	160,965	3.51
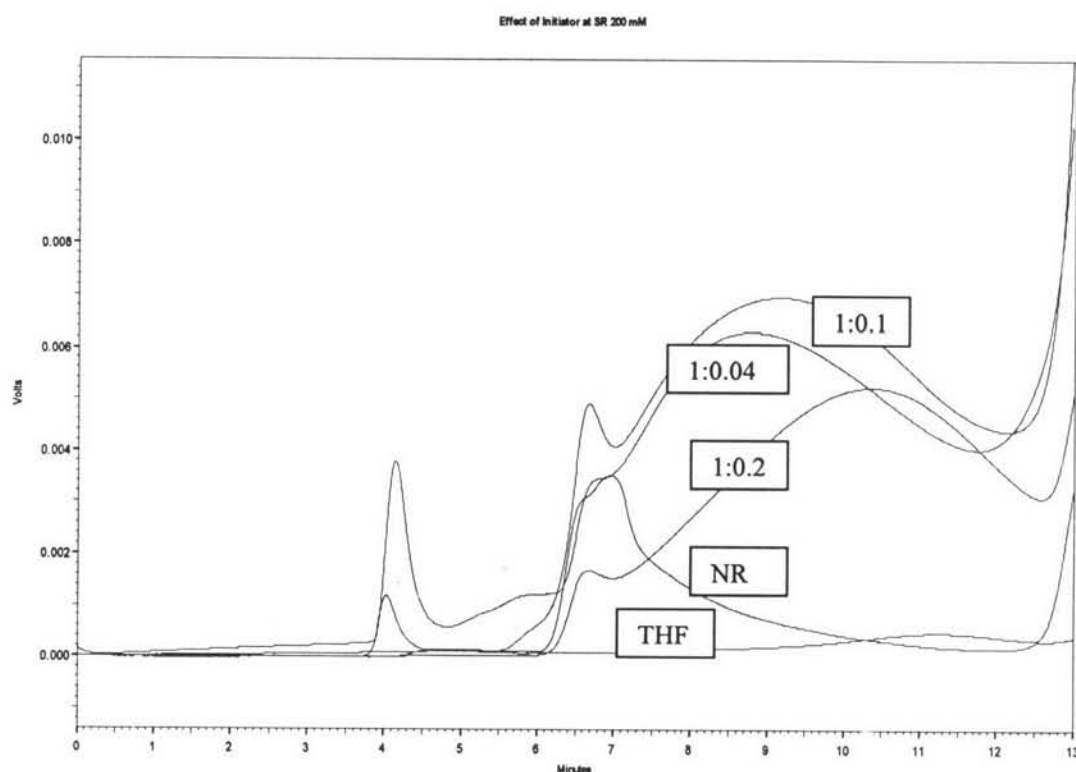
Figure 4.9 The molecular weight chromatograms of (a) THF, (b) NR and admicellar modified NR prepared by fixed Styrene:V50 mole ratio at (c) 1:0.04, (d) 1:0.1 and (e) 1:0.2 (styrene concentration at 200 mM and using CTAB surfactant).

4.4 Phase Morphology of Modified Natural Rubber

Surface morphology of the modified natural rubber emulsion obtained after reaction was observed by optical microscope at magnification 800X (see Figure 4.10). The results exhibited core-shell structure which the core of natural rubber particles was coated with polystyrene film as shell, especially at high concentration of styrene monomer (Figure. 4.10d), the large thickness of polystyrene film was obtained (Srinarang, 2004).
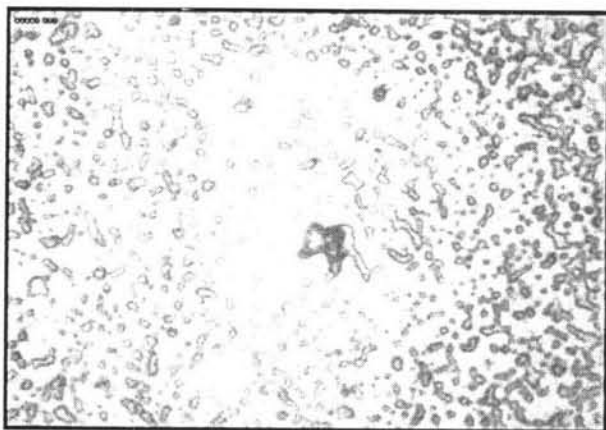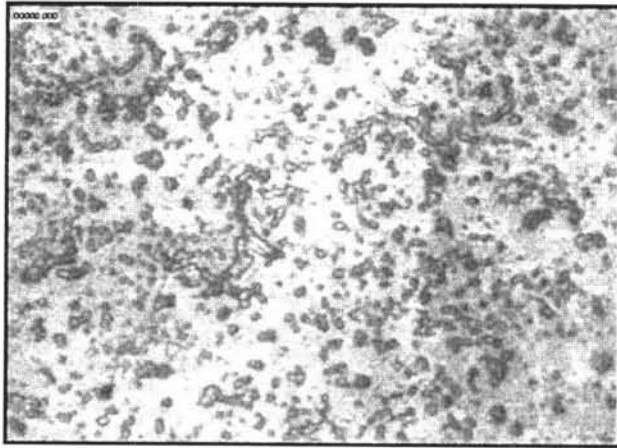

(4.10a) SR 50 mM
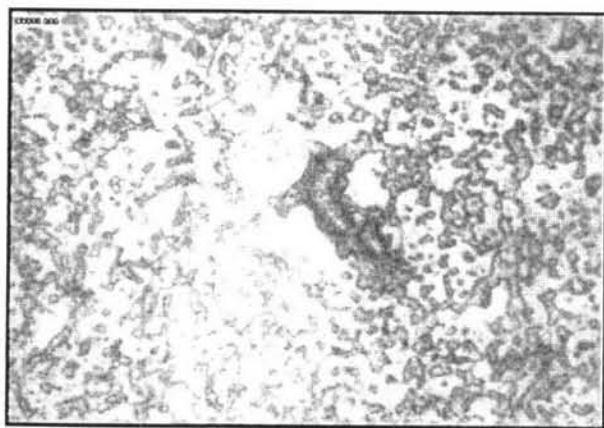
(4.10b) SR 100 mM
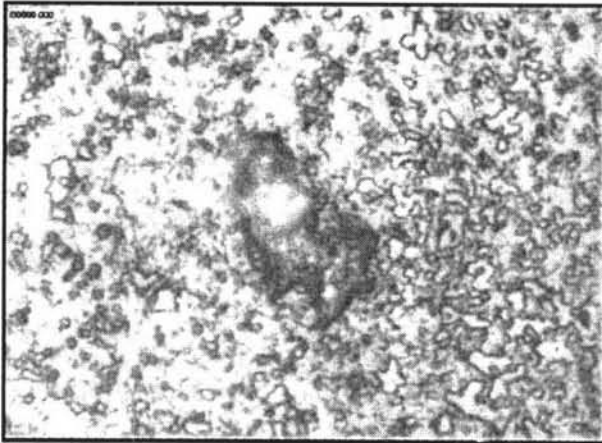
(4.10c) SR 200 mM

(4.10d) SR 300 mM

Figure 4.10 The phase morphology of admicellar modified natural rubber with (4.10a) SR 50 mM, (4.10b) SR 100 mM, (4.10c) SR 200 mM, (4.10d) SR 300 mM by using optical microscope at different of styrene monomer concentrations.

The phase morphologies of dried modified natural rubber by SEM after OsO_4 were showed in Figures 4.11 and Figure 4.12. The mole ratio between styrene: initiator was fixed at 1:0.1 and CTAB concentration was 2,800 µM. Styrene concentration was varied from 50-300 mM. These figures showed natural rubber round particles of about 0.5-1 µm were coated with polystyrene film (Kawahara, 2003). The polystyrene film connected and held each natural rubber particles. In Figure (4.12f) showed the ring of polystyrene film around the natural rubber particles with about 0.3-0.5 µm thick.

The phase morphology of modified natural rubber was compared between salt and no salt condition showed in Figure 4.13. The phase morphology in salt condition showed polystyrene film wrapping around natural rubber particles more clearly than the phase morphology in no salt addition.

SEM images with SDS surfactant in Figure 4.14 showed the morphology of modified natural rubber particles was not clearly investigated since the natural rubber may agglomerate in acid condition, therefore the reaction was occurred more difficult. The synthesized polystyrene may not make full coverage around natural rubber particles and thus allowing natural rubber to coalescence when drying. This makes natural rubber phase size has wider distribution while polystyrene can form into better continuous film.
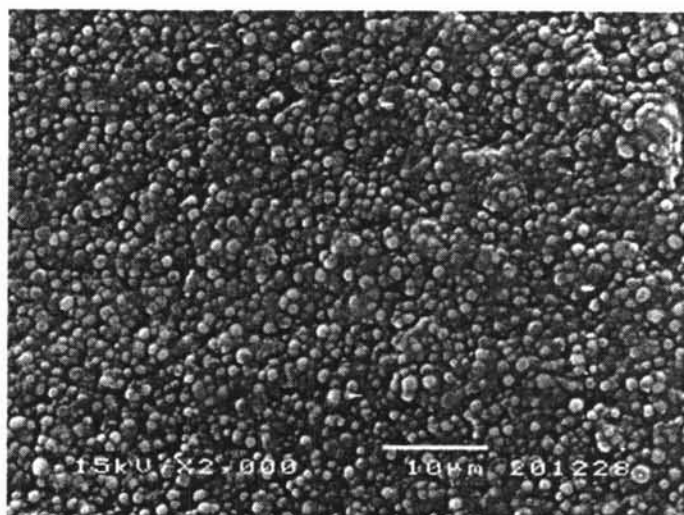
Figure 4.11 The phase morphology of admicellar modified natural rubber with styrene monomer concentration 300 mM (Using CTAB, S:I = 1:0.4).
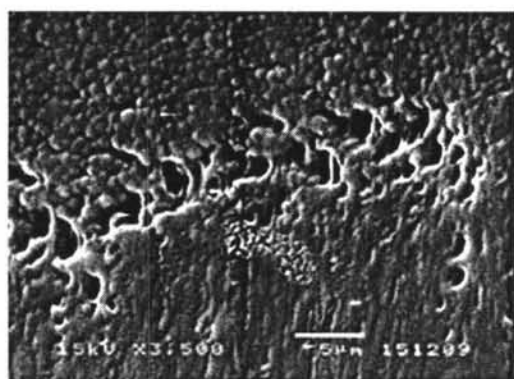
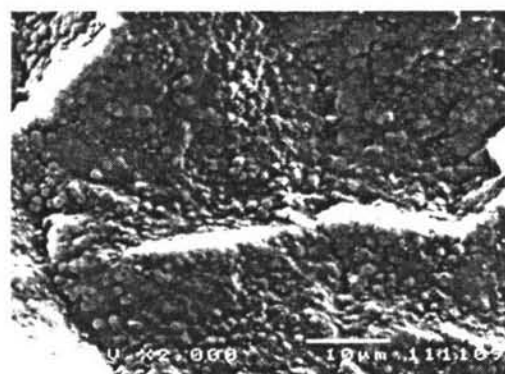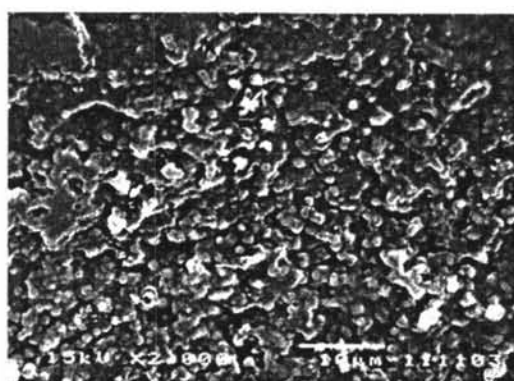(4.12a) NR
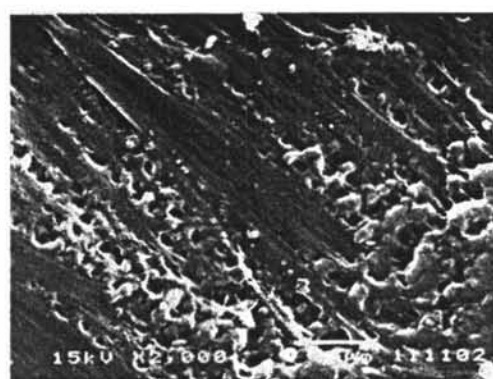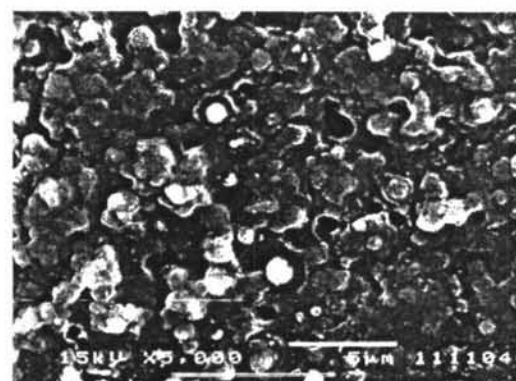

(4.12b) SR 50 mM
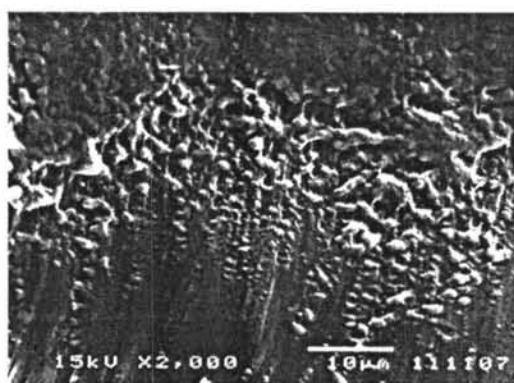
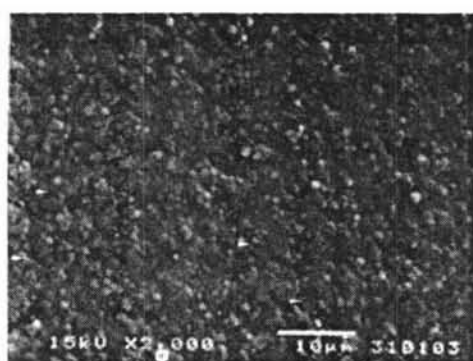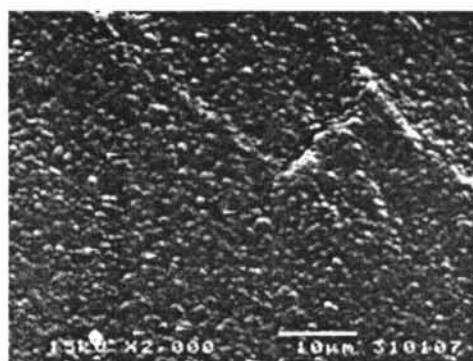(4.12c) SR 100 Mm

(4.12d) SR 200 mM

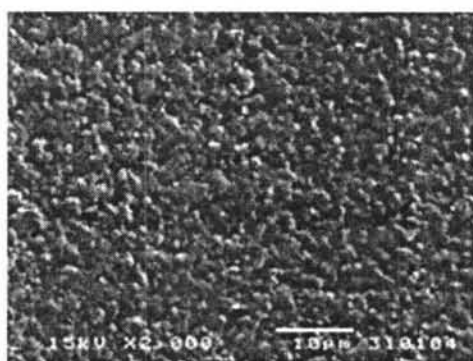(4.12e) SR 300 mM

(4.12f) SR 300 mM at 5000x

Figure 4.12 The SEM cross section micrographs of natural rubber (a) and admicellar modified natural rubber with SR 50 mM, SR 100 mM, SR 200 mM, SR 300 mM at 2000x and SR 300 mM at 5000x (CTAB; S:I=1;0.1).
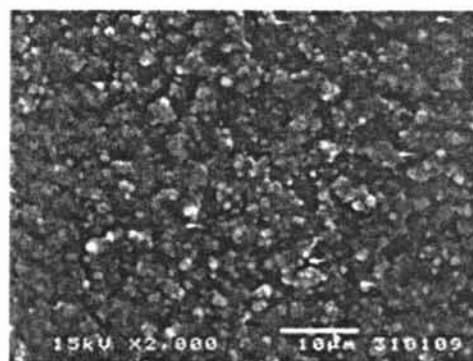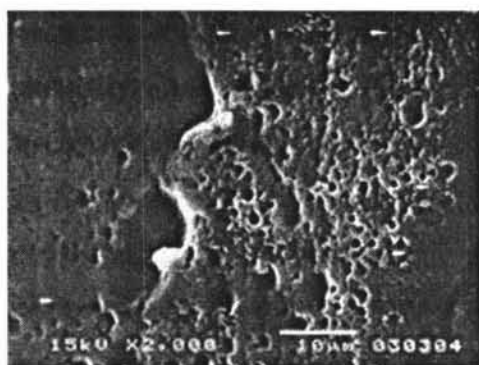
(4.13a) SR 200 mM
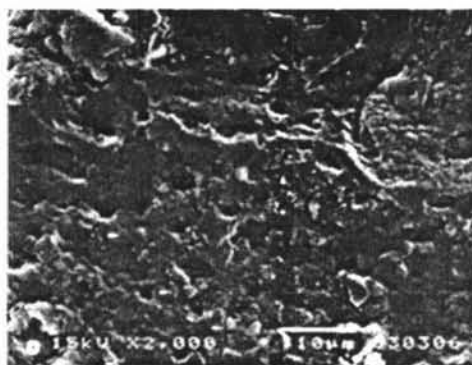
(4.13b) SR 200 mM, NaBr0.3 mM

(4.13c) SR 300 mM

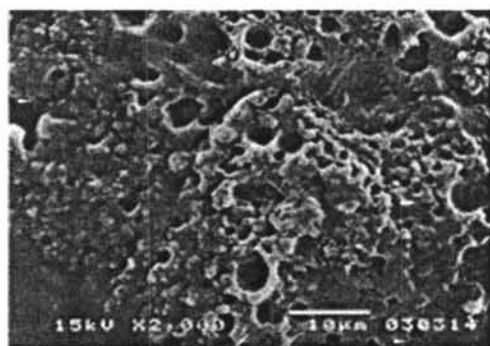(4.13d) SR 300 mM, NaBr0.3 mM

Figure 4.13 The SEM cross section micrographs of admicellar modified natural rubber with and without salt (CTAB; S:I=1:0.1).

(4.14a) SR 100 mM   (4.14b) SR 200 mM

(4.14c) SR 300 mM

Figure 4.14 The SEM cross section micrographs of admicellar modified natural rubber with styrene concentration at 100-300 mM by using SDS surfactant and S:I=1:0.1 under adding salt condition (Etching by petroleum ether to extract rubber phase before staining with OsO_4).

4.5 Thermogravimetric Properties

For CTAB surfactant and ratio between styrene: initiator fixed at 1:0.1, Figure 4.15 showed that the degradation temperatures of natural rubber were about 380°C while the admicellar modified natural rubbers showed two decomposition temperatures which were about 380°C and 420°C, the latter temperature came from the decomposition temperature of pure polystyrene. Moreover, there is no evidence of thermal degradation occurring within temperature range of 30-130°C. It reveals that the residual monomer is not found in the product.

The DTG results in Figure 4.16 also exhibited two peaks of DTG in pure natural rubber at high concentration of styrene monomer. It showed that the admicellar modified natural rubber was composed of two components.

For modified natural rubber with SDS surfactant and mole ratio between styrene: initiator fixed at 1:0.1, the thermogram in Figure 4.17 showed the decomposition temperatures of admicellar modified natural rubbers with styrene monomer. It was clearly observed that with styrene concentration at 300 mM, the decomposition temperature when compared to those of the modified natural rubber with low styrene monomer concentrations. However, from the DTG results in Figure 4.18, two peaks in all of concentration of styrene monomer were shown. It revealed that the modified natural rubber was composed of two components.
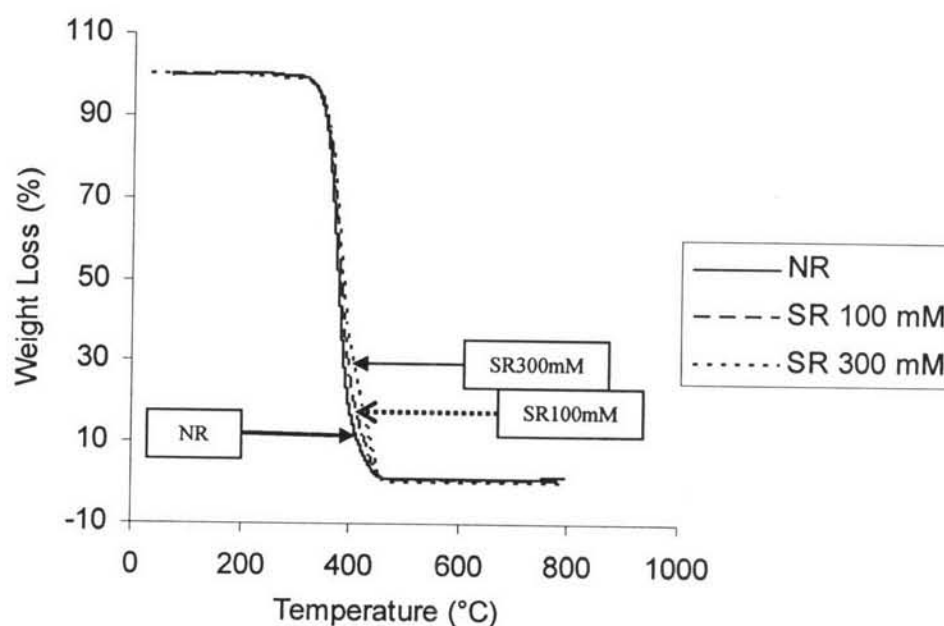

Figure 4.15 The TGA results of natural rubber and modified natural rubber with SR 100 mM and SR 300 mM by using CTAB surfactant.
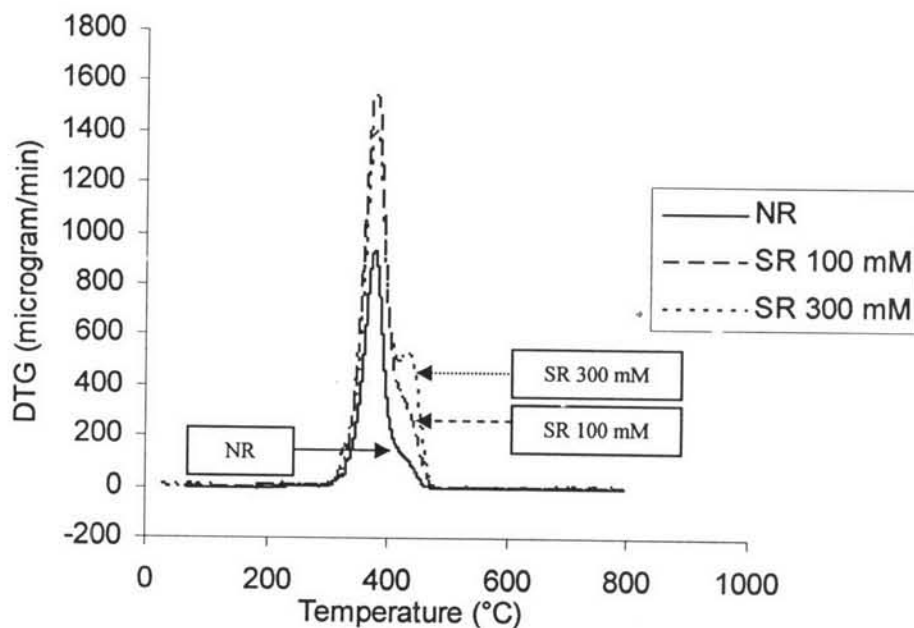
Figure 4.16 The DTG results of natural rubber and modified natural rubber with SR 100 mM and SR 300 mM by using CTAB surfactant, S:I=1:0.1.
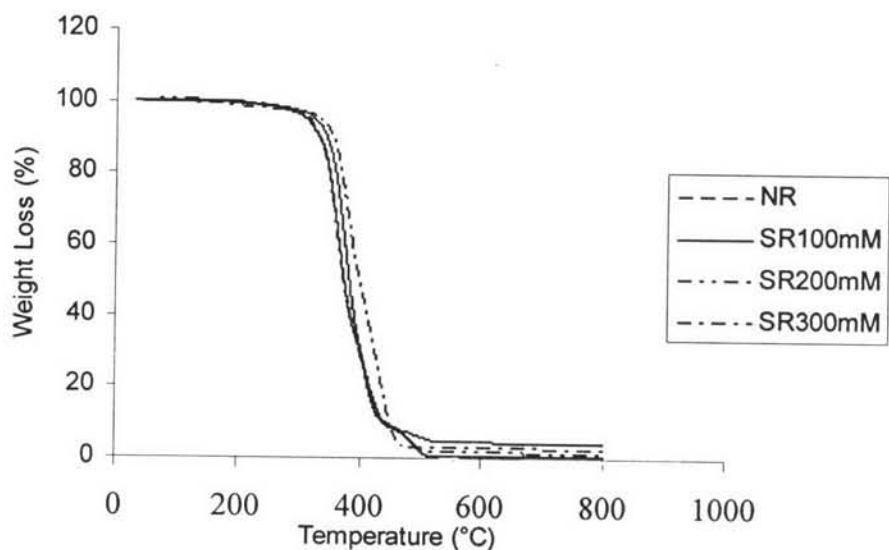

Figure 4.17 The TGA results of natural rubber and admicellar modified natural rubber with SR 100, 200 and 300 mM by using SDS surfactant, S:I=1:0.04.
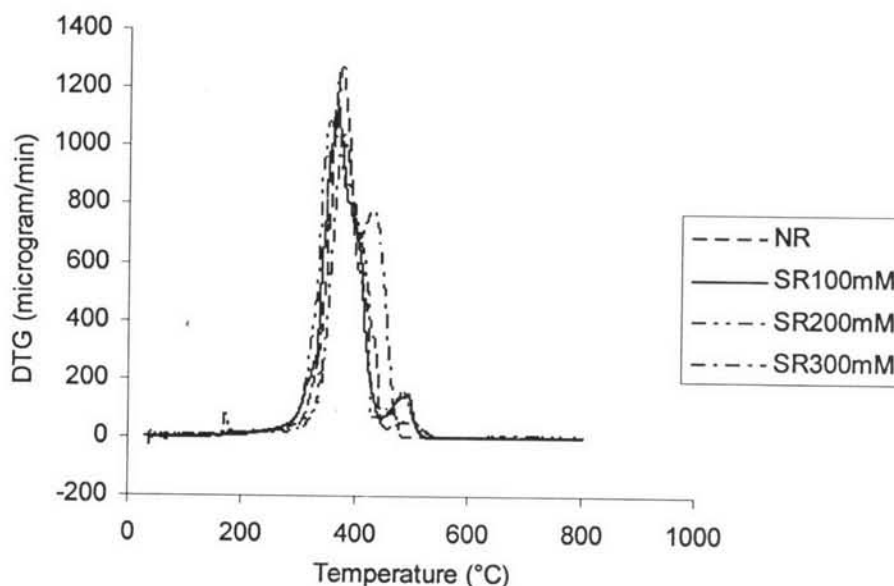
Figure 4.18 The DTG results of natural rubber and admicellar modified natural rubber with SR 100, 200 and 300mM by using SDS surfactant, S:I=1:0.04.

4.6 Dynamic Mechanical Thermal Analysis Property (DMTA)

Mechanical properties of admicellar modified natural rubbers were determined by using DMTA. This method reveals the storage modulus E', loss modulus E" and tan δ over a range of temperature from -90 to 100°C. Therefore glass transition temperatures of the admicellar modified natural rubber can be determined. It showed the tan δ peak in Figure 4.19. The peak of tan δ in pure natural rubber was sharpened but it tend to broaden for admicellar modified natural rubber with high styrene concentration. The size of the tan δ peak and the fall in E' in the transition region is proportional to the volume fraction of the rubber component (Katime, 1994). However all peaks was occurred at the same position therefore the tan δ showed the composition of polystyrene in modified natural rubber (Hourston, 1991). In other words, there is only one T_g found for the admicellar modified natural rubber at about -43 to -51°C. This suggest that the admicellar polymerization is a unique method to prepare a well miscible core-shell structure of PS-NR and also the area of tan δ peak could reflect relaxation or mobility of polystyrene as well as natural rubber. Figure 4.19 reveals that as styrene content increase. The tan δ peak

becomes lower or stiffer with increasing polystyrene. As temperature increases beyond T_g the tan δ of the admicellar modified natural rubber samples become higher than that of natural rubber or their chains become better relaxation than natural rubber chains. This indicates better flow than natural rubber or higher viscous than elasticity and hence it could be better possible than natural rubber. This better flow property is contributed to smaller molecular weight of polystyrene.
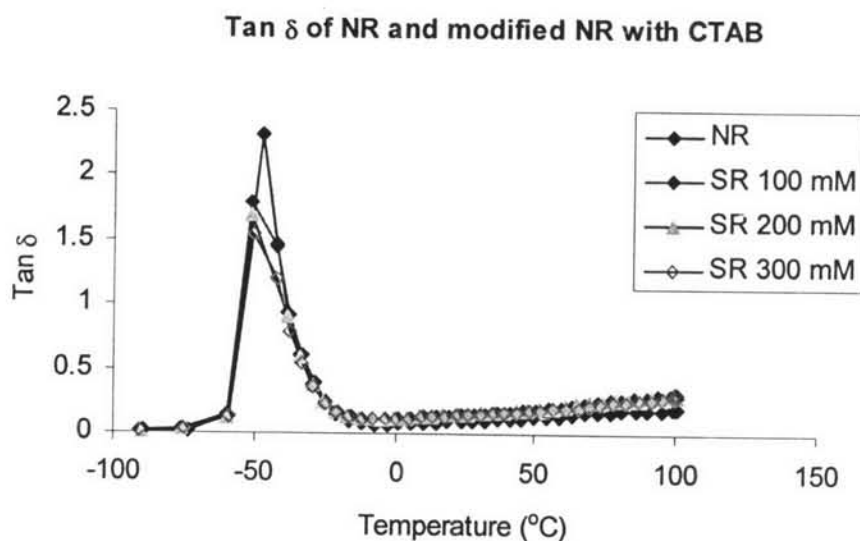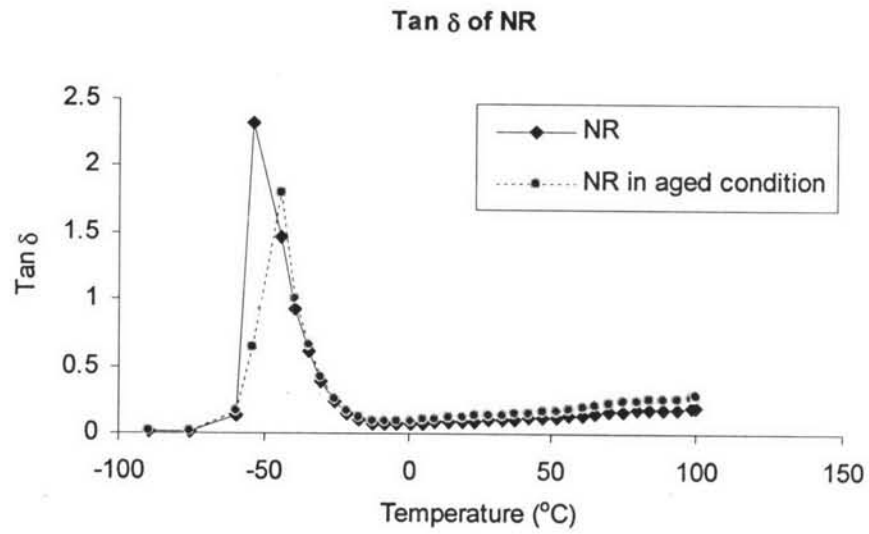
Tan δ of NR and modified NR with CTAB

Figure 4.19 Tan δ of natural rubber and modified natural rubber with CTAB surfactant.

From plots of tan δ versus temperature in Figure 4.20, the tan δ in all admicellar modified natural rubber using CTAB and SDS were shown. Only tan δ of the aged samples CTAB and SDS with high styrene concentration tend to increasing slightly starting at around 67°C which is the β-transition (Hourston, 1991), but the pure natural rubber and modified natural rubber with low styrene monomer concentration in SDS surfactant was not showed. This could be attributed to the β relaxation of long chain polystyrene that is clearly observed after aging.

Tan δ of NR

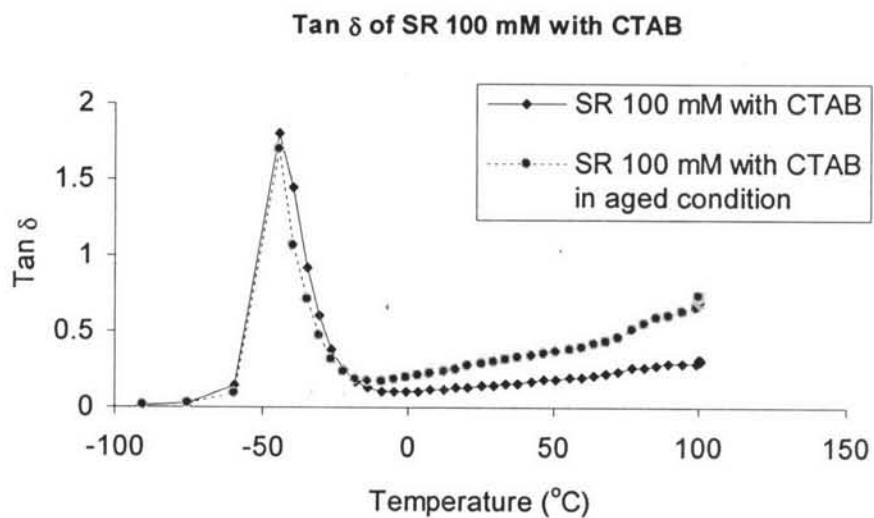(a) Tan δ of aged and unaged natural rubber.
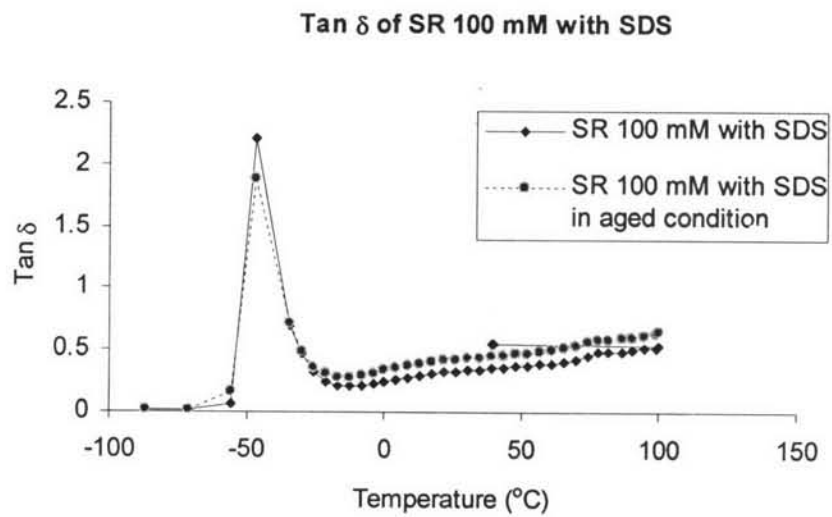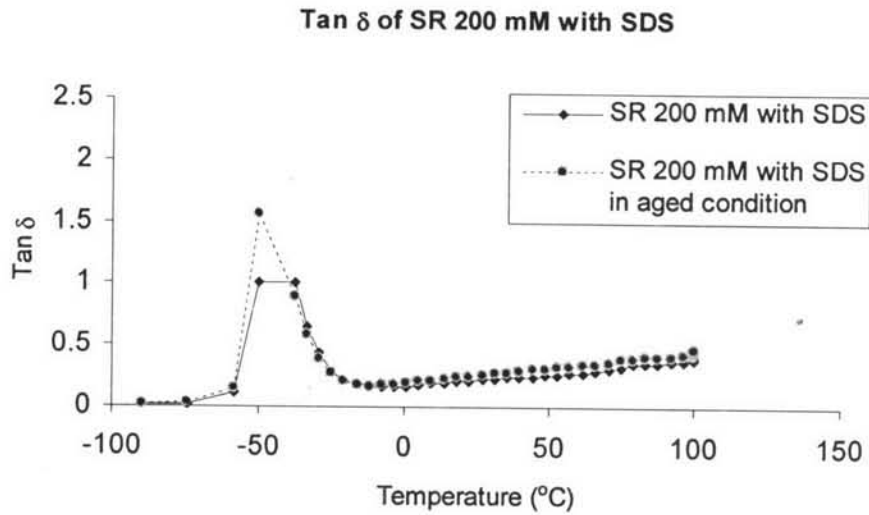
Tan δ of SR 100 mM with SDS

(b) Tan δ of aged and unaged modified natural rubber with SR 100 mM in SDS.

Tan δ of SR 200 mM with SDS

(c) Tan δ of aged and unaged modified natural rubber with SR 200 mM in SDS.

Tan δ of SR 300 mM with SDS

(d) Tan δ of aged and unaged modified natural rubber with SR 300 mM in SDS.

Tan δ of SR 100 mM with CTAB

(e) Tan δ of aged and unaged modified natural rubber with SR 100 mM in CTAB.

Tan δ of SR 200 mM with CTAB

(f) Tan δ of aged and unaged modified natural rubber with SR 200 mM in CTAB.

Tan δ with SR 300 mM with CTAB
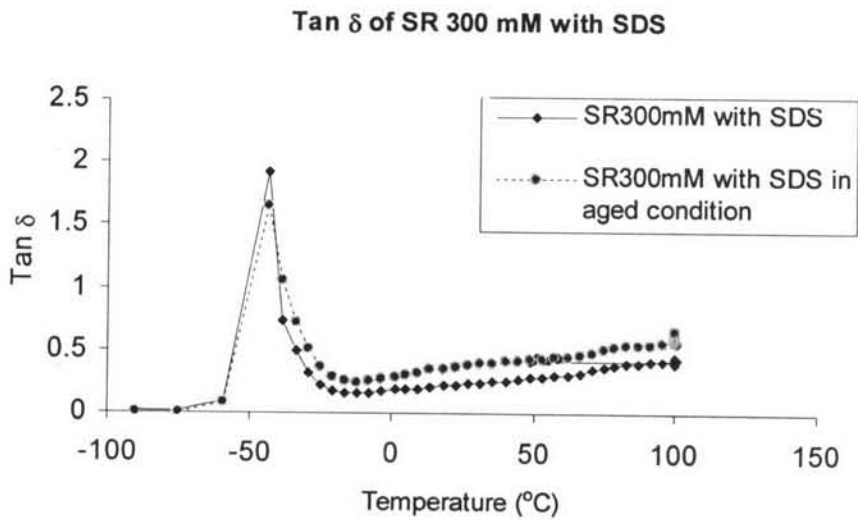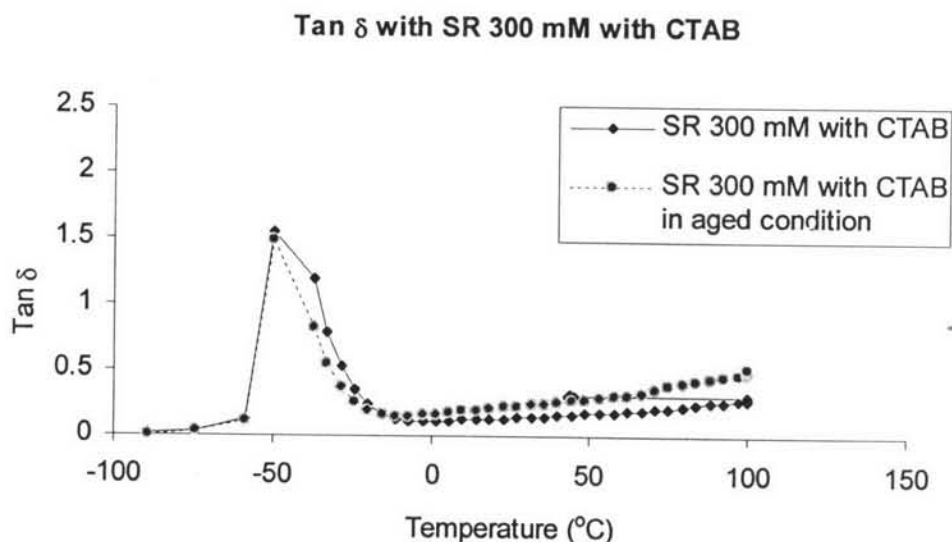
(g) Tan δ of aged and unaged admicellar modified natural rubber with SR 300 mM in CTAB.

Figure 4.20 Tan δ of pure natural rubber and modified natural rubber with CTAB and SDS surfactant in aged and unaged condition.

The storage and loss modulus of admicellar modified natural rubber compared to those of pure natural rubber were shown at 30°C in table 4.5. The storage modulus of the admicellar modified natural rubber are lower than that of pure natural rubber but after aging, the storage modulus are much improved while natural rubber is deteriorated, especially for those modified with CTAB. The same behavior was also found for loss modulus. This suggested that admicellar polymerization of polystyrene on natural rubber is not only induced better flow or viscous property but also improved thermal property by strengthening, so call thermal strengthening, like annealing instead of causing thermal degradation.

Table 4.5 Storage modulus, loss modulus and tan δ of aged and unaged modified natural rubber at 30°C

Sample	Results		
	E' (MPa)	E" (MPa)	Tan δ
NR	0.5499	0.05715	0.1039
NR,A	0.1829	0.02578	0.1409
SR100mM, CTAB	0.1812	0.02795	0.1543
SR100mM, CTAB,A	0.3548	0.1109	0.3126
SR200mM, CTAB	0.3473	0.05450	0.1569
SR200mM, CTAB,A	0.3885	0.09315	0.2398
SR300mM, CTAB	0.2305	0.03511	0.1523
SR300mM, CTAB,A	0.4453	0.1062	0.2385
SR100mM, SDS	0.6518	0.2209	0.3388
SR100mM, SDS,A	0.5193	0.2239	0.4312
SR200mM, SDS	0.2792	0.06500	0.2328
SR200mM, SDS.A	0.3597	0.09721	0.2702
SR300mM, SDS	0.4150	0.1020	0.2459
SR300mM, SDS,A	0.2600	0.1027	0.3949

4.6 Tensile Testing

Blend samples between pure polystyrene and modified natural rubber with styrene monomer concentration 100-300mM at the ratio of 90:10 percent weight was the softer phase, investigated in tensile testing which showed in Figure 4.21 and 4.22. The presence of admicellar modified natural rubber was found to decrease Young's modulus of polystyrene when compared to the pure polystyrene. However, the unaged and aged blend samples gave the different results. The young's modulus of aged samples tended to increase significantly in the blend samples with admicellar modified natural rubber at high styrene concentration while Young's modulus of unaged sample were not changed. Thus, it can be concluded that the modulus can be

improved by aging condition. This suggests the aging helps to increase homogeneous mixing or better compatibilization between pure polystyrene and admicellar modified natural rubber.
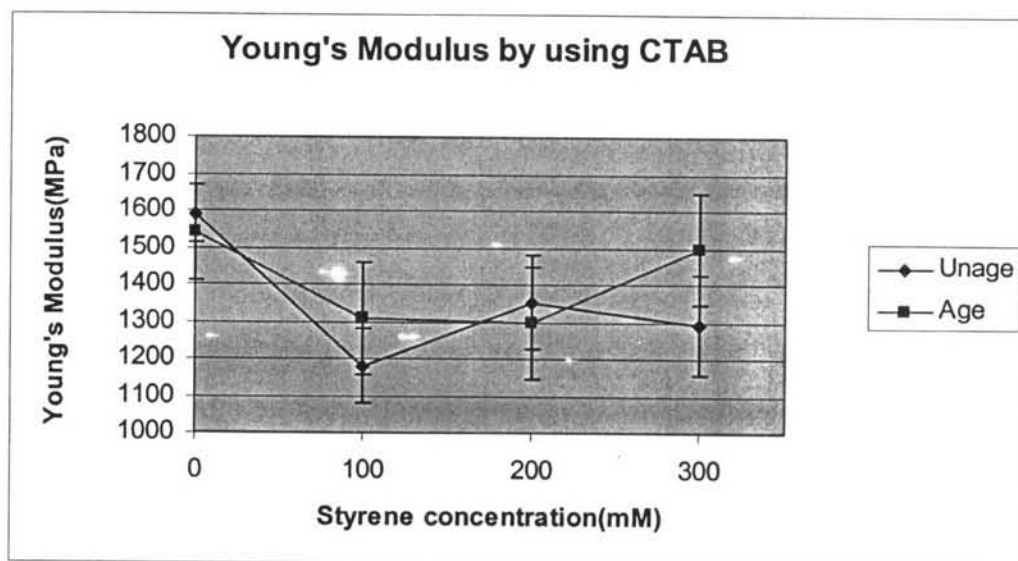

Figure 4.21 The Young's Modulus of pure polystyrene and the blend sample in condition without aging and aging using CTAB.
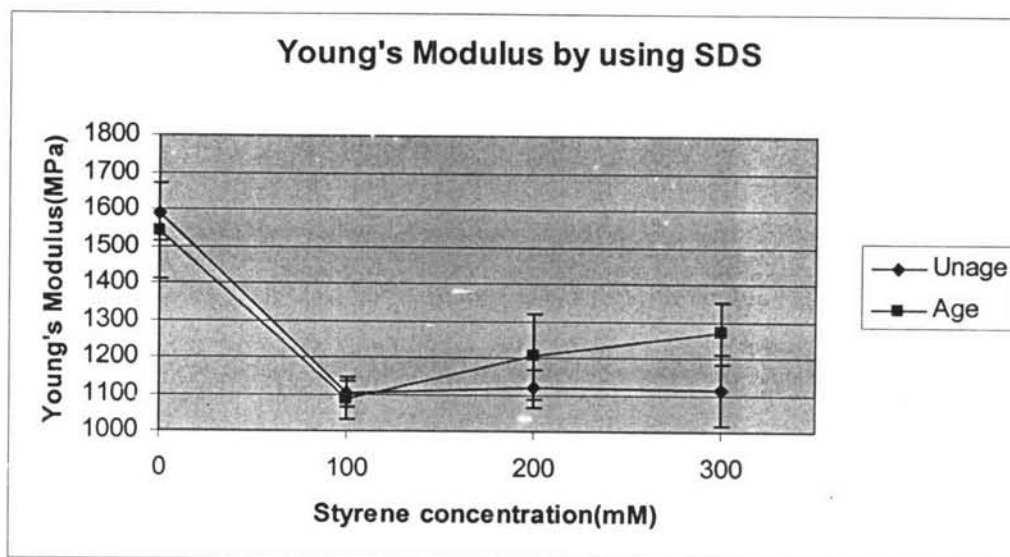

Figure 4.22 The Young's Modulus of pure polystyrene and the blend sample in condition without aging and aging using SDS surfactant.

The tensile strengths of blended samples using CTAB and SDS surfactants were shown in Figures 4.23-4.24. It was decreases dramatically when compare to the pure polystyrene in not aging condition. The lowest tensile strength occurred in styrene concentration at 200mM and it tended to increases slightly in styrene concentration at 300mM. From aging condition, the tensile strength of blended samples were exhibited the same trend as in not aging condition. However, tensile strength of blended samples with CTAB in aging condition has the lowest value in styrene concentration 300 mM. It can be concluded tensile strength of blended samples in aging and not aging smaller than pure polystyrene because it was not mixed homogeneously.
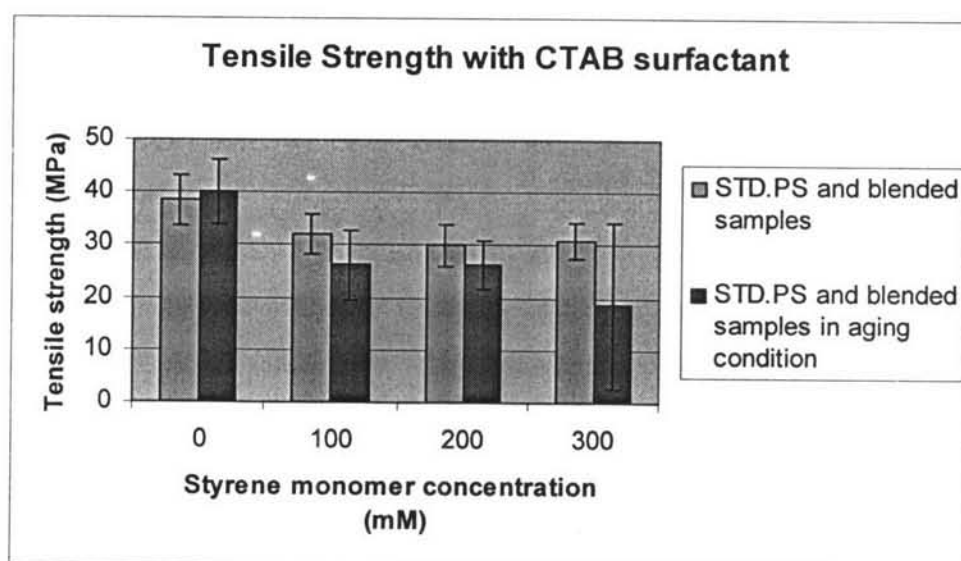

Figure 4.23 The tensile strength of pure polystyrene and blended samples with CTAB surfactant.
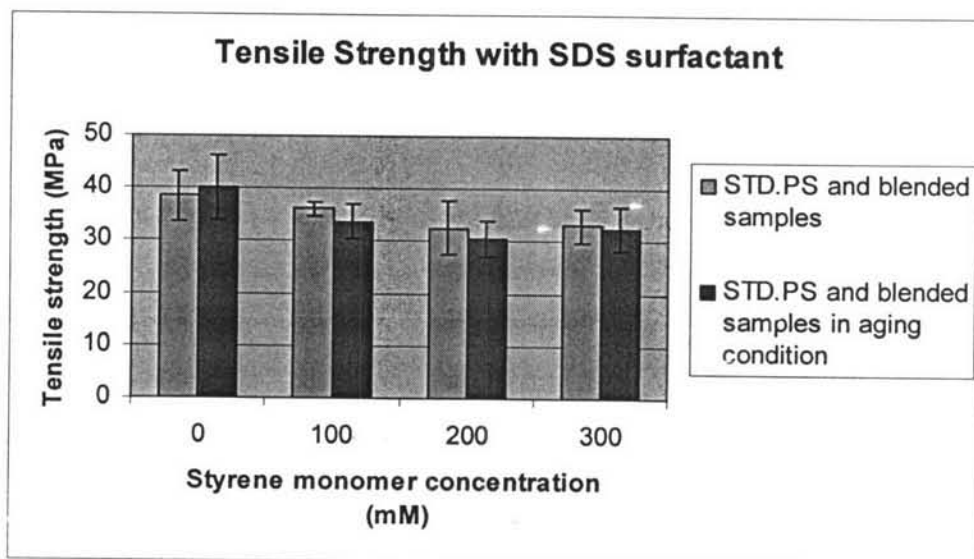
Tensile Strength with SDS surfactant

Figure 4.24 The tensile strength of pure polystyrene and blended samples with SDS surfactant.

Broken mechanism of blended sample showed in Figure 4.25, the blended sample showed craze mechanism while in pure polystyrene was not showed. It can be concluded, although the blended samples have low tensile strength and low modulus than pure polystyrene but it has a mechanism before break.
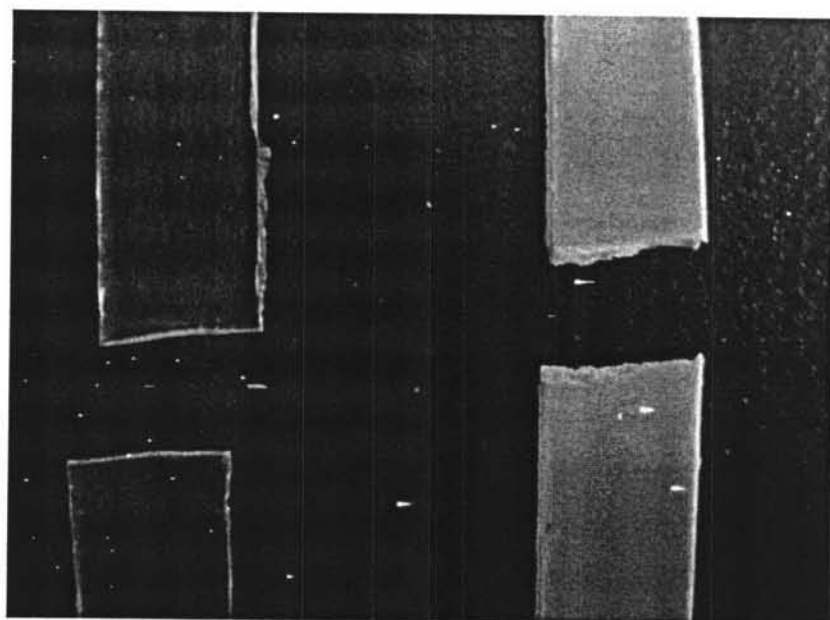

Figure 4.25 Pure polystyrene and blended sample after tensile testing.