CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 Appearance of Admicelled PS-NR

Figure 4.1 showed the appearance of admicelled PS-NR with various styrene concentrations. The color of products was varied from light yellow to opaque white as increase in concentration of styrene monomer. In addition, the rigidity of admicelled PS-NR was also increased due to the increment of styrene monomer concentration. However, their color would be changed a little after processing with thermal (Preechasup *et al.*, 2006).
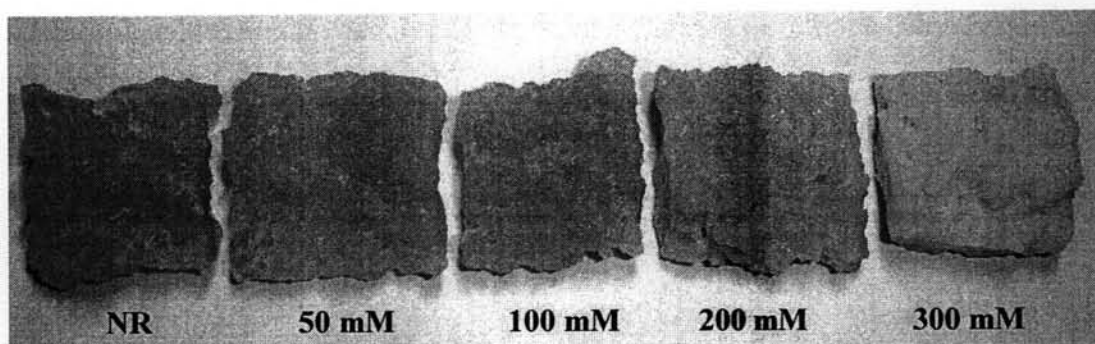

Figure 4.1 Appearance of admicelled PS-NR with various styrene concentrations.

4.2 Characterizations of Admicelled PS-NR

4.2.1 Fourier-Transform Infrared Spectroscopy

FTIR was used to analyze the benzene rings of styrene for ensuring the achievement of coating styrene on natural rubber particles by admicellar polymerization method. Figure 4.2 shows infrared spectra of admicelled PS-NR with different styrene monomer concentrations compared with pure PS and NR. The absorption band of aromatic C-H stretching at 3100-3000 cm^{-1}, aromatic C=C stretching at 1600-1400 cm^{-1} and C-H deformation (out of plane) at 700 cm^{-1} indicating the benzene ring of PS were observed. The absorption band of NR was also found in admicelled PS-NR at any styrene concentration especially at 837 cm^{-1}

indicating the presence of C=CH wagging. It could be seen that the spectra intensities at 1600-1400 and 700 cm^{-1} were clearly observed as increase of styrene monomer concentration in natural rubber. The admicelled PS-NR with any different concentrations of styrene showed the same peaks as presented in standard polystyrene corresponding to previous work (Preechasup *et al.*, 2006). Therefore, the formation of admicellar polymerization of styrene on natural rubber particles could be confirmed.
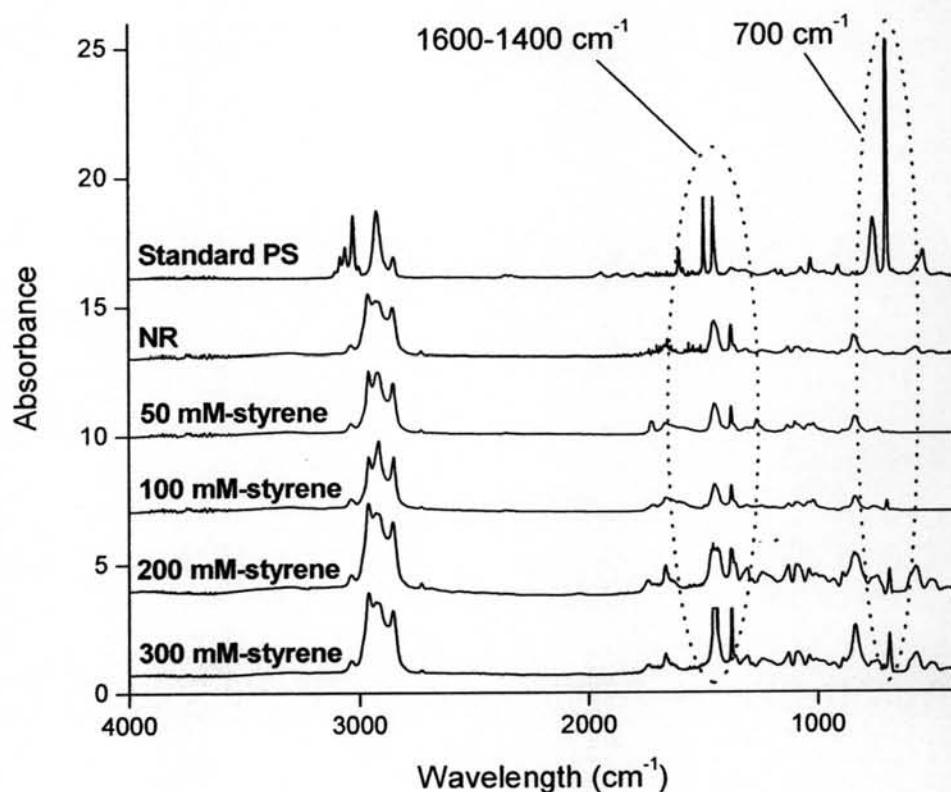

Figure 4.2 Infrared spectra of admicelled PS-NR compared with pure PS and NR.

4.2.2 Thermogravimetric Analysis

The samples of admicelled PS-NR with various styrene concentrations, pure PS and NR were heated up from ambient temperature to 600 °C at heating rate of 10°C/min to investigate their thermal stability. In Figure 4.3, it could be seen that the degradation temperatures of admicelled PS-NR were increased as increase in styrene monomer concentration. The NR and pure uncrosslinked PS exhibited almost comparable thermal stability and both degraded around above 360°C (Thomas *et al.*, 2001). Due to this technique of admicellar polymerization, the decomposition for all cases of admicelled PS-NR products did not clearly show two transitions of natural rubber and polystyrene like the blending method. A little changing in slope that reveals two compositions was observed only as shown in Figure 4.4. At higher styrene concentration, especially the admicelled PS-NR with 300 mM-styrene, it clearly showed that two decomposition temperatures of natural rubber and polystyrene were about 380°C and 420°C, respectively (Preechasup, 2006). It could be seen that, after natural rubber was completely decomposed at 400°C and then started the polystyrene decomposition, the content of polystyrene can be measured at this point of temperature and corresponded to the real content used in synthesis system as shown in Appendix A (Table A1). Thus, the content of polystyrene could be measured and confirmed by this technique.

Furthermore, it should be noted that water soluble protein in NR latex is almost 15 μg/g (see Table B1 in Appendix B) while those of admicelled PS-NR are slightly lower (12-15 μg/g). The rather high water soluble protein in admicelled PS-NR has to account for nitrogen content added from CTAB surfactant. So, the remaining protein in admicelled PS-NR should be much lower than the obtained value. This means that admicelled PS-NR is safer to use for medical application or less allergic.

Table 4.1 Decomposition temperatures of admicelled PS-NR

Samples	Degradation Temperature ($^{\circ}$C)			Residue (%)
	Onset	Peak	End point	
PS	390	412	430	0.77
NR	354	378	414	0.57
50 mM-styrene	351	365	407	0.63
100 mM-styrene	352	368	412	0.95
200 mM-styrene	362	377	417	0.85
300 mM-styrene	369	380	426	0.28
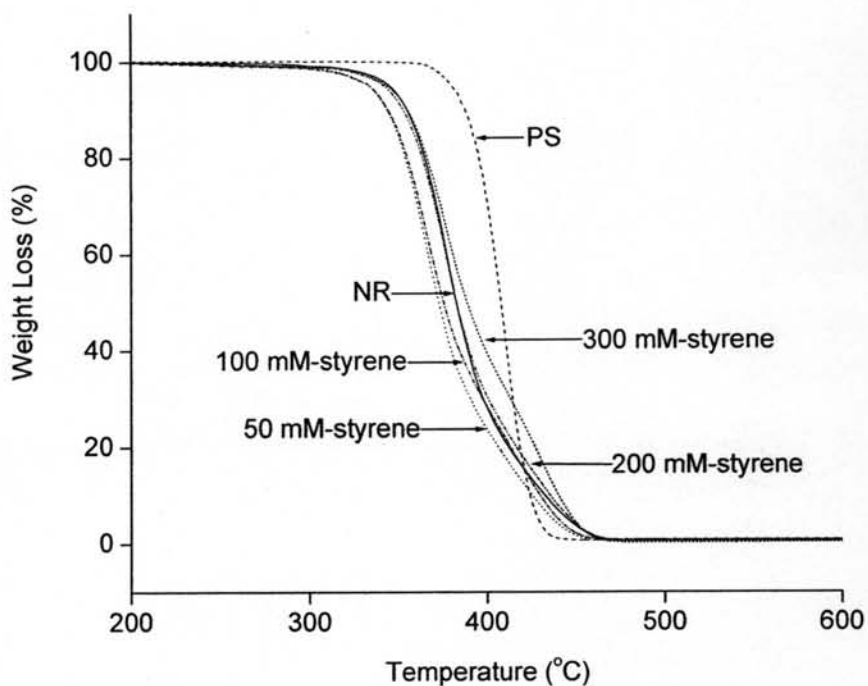
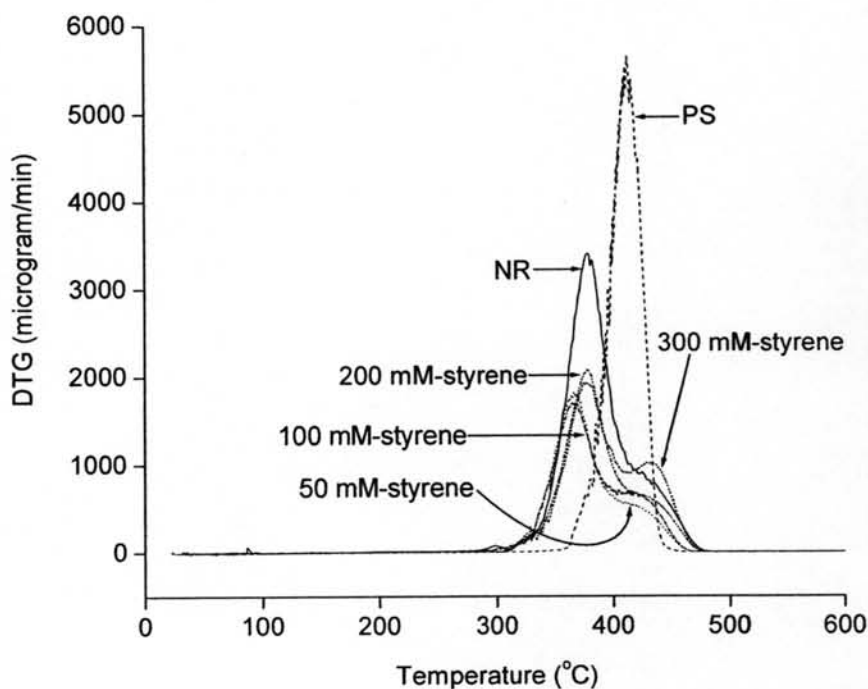**Figure 4.3** TGA results of admicelled PS-NR, pure PS and NR.

Figure 4.4 DTG results of admicelled PS-NR, pure PS and NR.

4.3 Rheological Properties

4.3.1 Rheological Behavior of Admicelled PS-NR Using Circular Die

4.3.1.1 *Pure Admicelled PS-NR*

- Effect of L/D Ratio on Apparent Shear Stress

The effects of L/D ratio and apparent shear rate on the apparent shear stress of admicelled PS-NR with 50 mM-styrene and 100 mM-styrene at 130, 140, 150, 160 and 170 °C were shown in Figure 4.5 (a)-(e). In all the cases the apparent shear stress increased with increasing apparent shear rate. This is due to the applied force disturbed the long chain polymer from its equilibrium position and the molecules got disentangled (higher orientation) in the direction of applied force causing to increase in pressure and apparent shear stress (Thomas *et al.*, 1997). An increase in L/D ratio results in higher the pressure drop across the die channel. However, even the pressure drop was higher, but the measured apparent shear stress was decreased causing by increase in die length. Moreover, admicelled PS-NR with

100 mM-styrene was higher in apparent shear stress than that of 50 mM-styrene at any particular shear rate, L/D ratio and temperature according to higher MW (see Appendix C, Table C1) at higher styrene content.
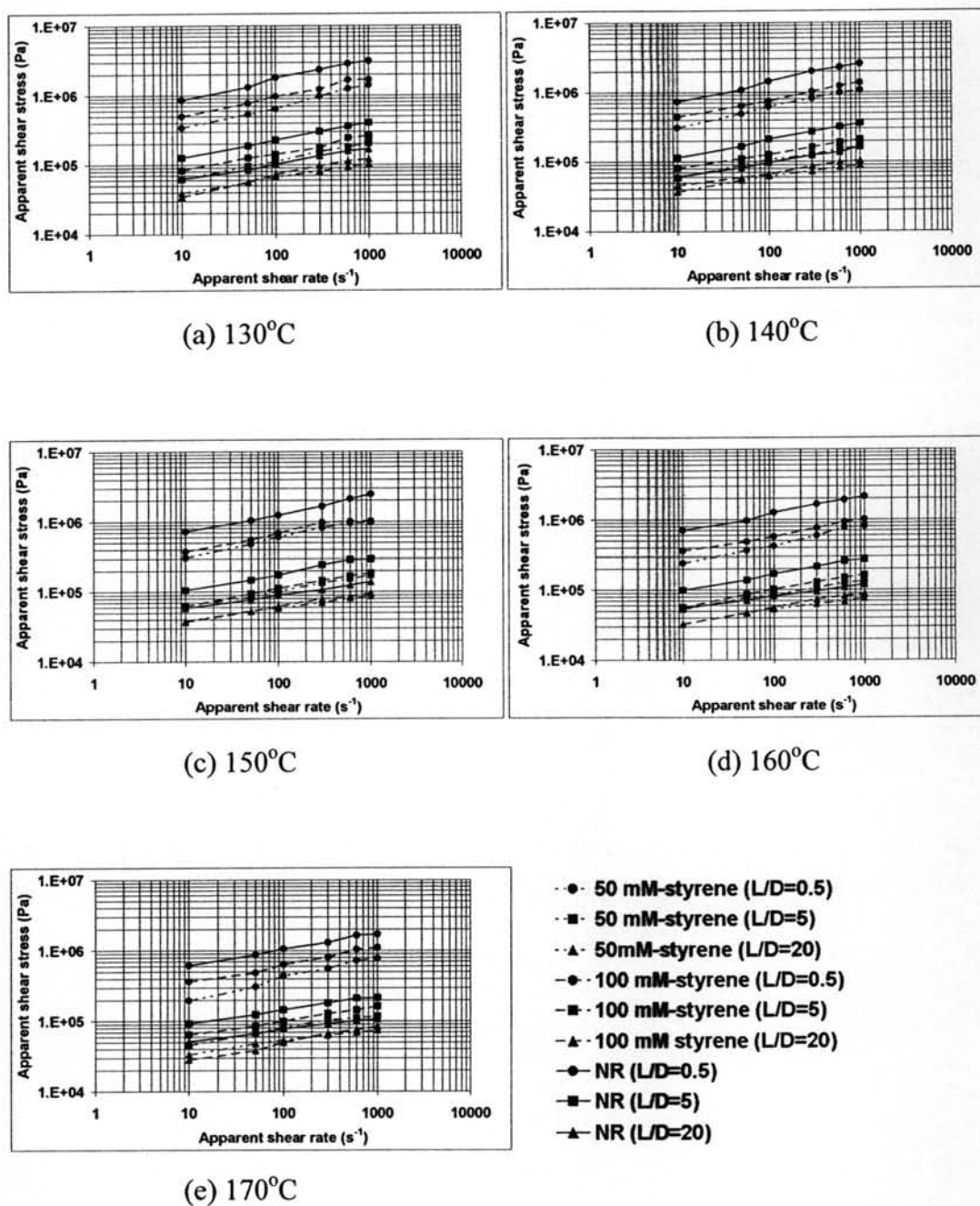

(a) 130°C

(b) 140°C

(c) 150°C

(d) 160°C

(e) 170°C

- ·●· 50 mM-styrene (L/D=0.5)
- ·■· 50 mM-styrene (L/D=5)
- ··▲· 50mM-styrene (L/D=20)
- ─●·100 mM-styrene (L/D=0.5)
- ─■··100 mM-styrene (L/D=5)
- ─▲··100 mM styrene (L/D=20)
- ─●─ NR (L/D=0.5)
- ─■─ NR (L/D=5)
- ─▲─ NR (L/D=20)

Figure 4.5 Logarithmic plots of apparent shear stress versus apparent shear rate for admicelled PS-NR with 50 mM and 100 mM-styrene at different temperature.

- Effect of L/D ratio on Apparent Shear Viscosity

The effects of L/D ratio and apparent shear rate on the apparent shear viscosity of admicelled PS-NR with 50 mM and 100 mM-styrene at 130, 140, 150, 160 and 170 °C were shown in Figure 4.6 (a)-(e). The result showed that the apparent shear viscosity of all cases at any L/D ratio decreased as increase in apparent shear rate which indicates the pseudoplastic behavior of admicelled PS-NR. The pseudoplasticity is according to random chain orientation and highly entangled state of the NR molecules which under high shear, get disentangled and become oriented resulting in a reduction of viscosity (Thomas et al., 1997). The measured apparent shear viscosity of NR was similar to the results of Nakason et al. (2002) at particular L/D ratio which could be certainly used to compare with admicelled PS-NR. The admicelled PS-NR with 100 mM-styrene exhibited higher shear viscosity than that of admicelled PS-NR with 50 mM-styrene. This shows the comparatively higher plastic-like behavior of admicelled PS-NR at higher content of styrene. However, it found to be lower the apparent shear viscosity of both admicelled PS-NRs when compared with NR, it could be presumed that, this might be come from the less amount of styrene used in the synthesis, thus it acts as the molecular plasticizing action on the viscosity in modified NR. In addition, there is slight difference between apparent shear viscosity of both admicelled PS-NRs using L/D ratio of 20 at any particular temperature. It can be seen that the increase in L/D ratio is not significantly prominent in the melt state of both admicelled PS-NRs.
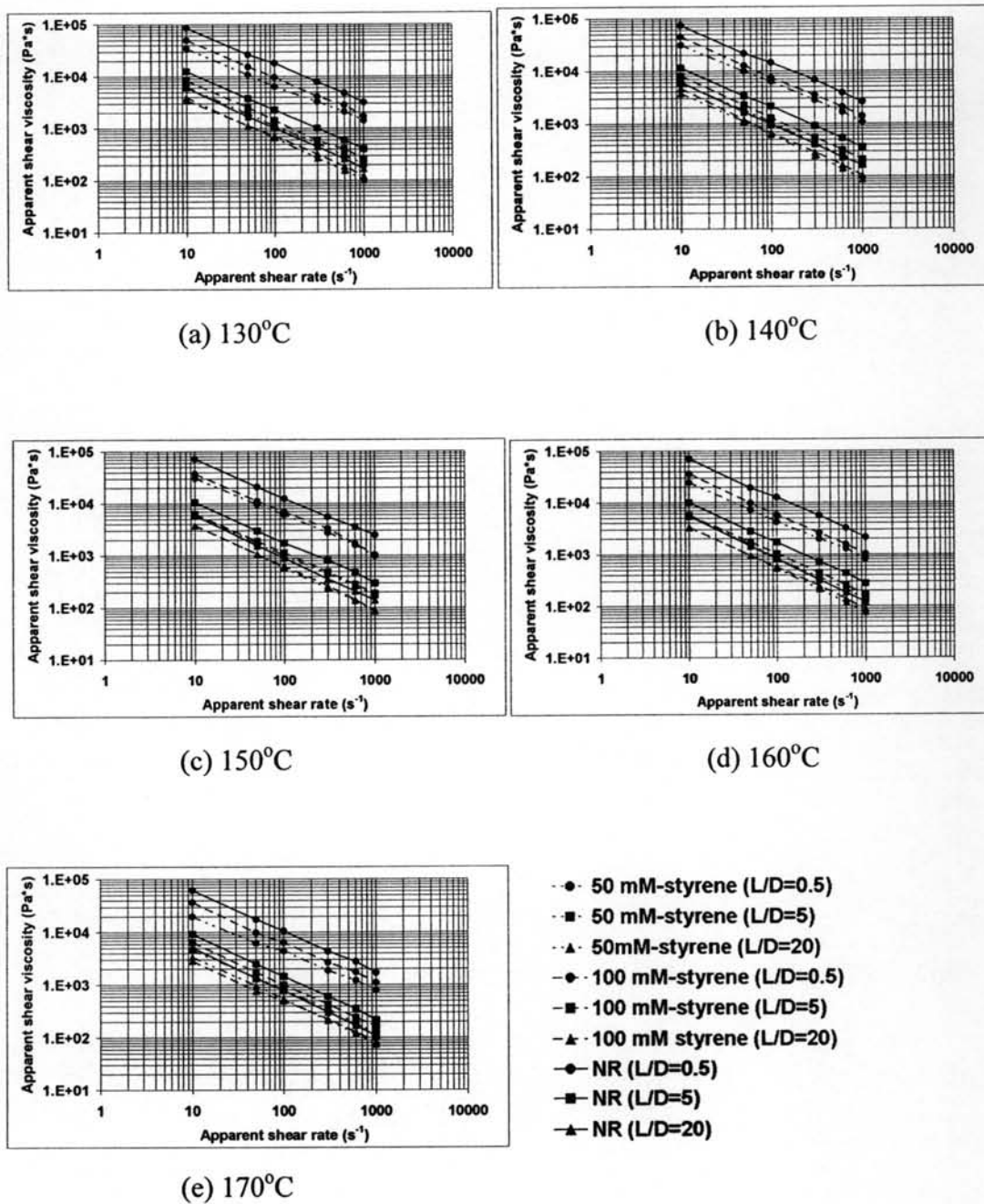
(a) 130°C

(b) 140°C

(c) 150°C

(d) 160°C

Legend:
- ⋯●⋯ 50 mM-styrene (L/D=0.5)
- ⋯■⋯ 50 mM-styrene (L/D=5)
- ⋯▲⋯ 50mM-styrene (L/D=20)
- —●— 100 mM-styrene (L/D=0.5)
- —■— 100 mM-styrene (L/D=5)
- —▲— 100 mM styrene (L/D=20)
- —●— NR (L/D=0.5)
- —■— NR (L/D=5)
- —▲— NR (L/D=20)

(e) 170°C

Figure 4.6 Logarithmic plots of apparent shear viscosity versus apparent shear rate for admicelled PS-NR with 50 mM and 100 mM-styrene at different temperature.

- Effect of Temperature on Apparent Shear Stress and
Apparent Shear Viscosity

Figures 4.7-4.9 shows the effects of temperature on the apparent shear stress and apparent shear viscosity of admicelled PS-NR by using L/D ratio of 0.5, 5 and 20. In all cases, the apparent shear stress trended to decrease with increasing the temperature at any particular shear rate. This is because the long chain polymer with lower molecules vibration at lower temperature was rather difficult to flow by disturbing of applied force than that of higher temperature to change their equilibrium position of molecular chain. In comparison with the results of NR/PS blends at any blend compositions from Asaletha *et al.* (1998), they found the decrease of shear viscosity as increase of temperature and its viscosity become to increase again at temperature above 165°C causing by chain crosslinking without curing agent at higher temperature. This can be shown that the admicelled PS-NR was better thermal stability than NR/PS blends especially at higher temperature e.g. 170°C. However, the apparent shear stress and shear viscosity were found to be lower than that of NR at any temperature according to the reason explained earlier. However, the tendency of changing in apparent shear viscosity using L/D ratio of 20 at different temperature was not prominent.
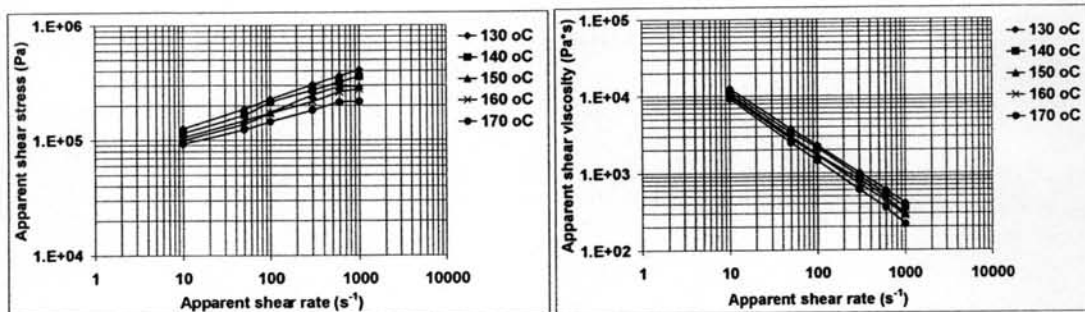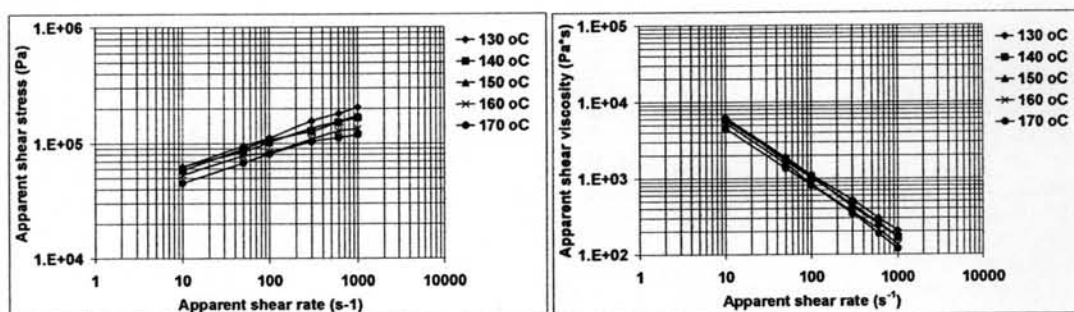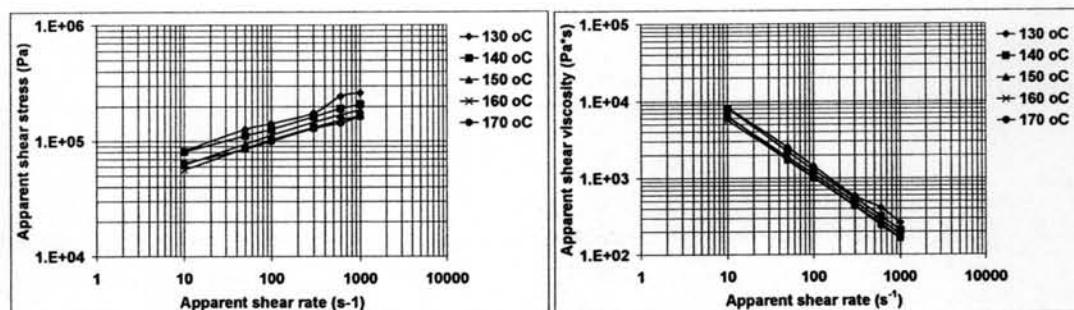
(a) NR
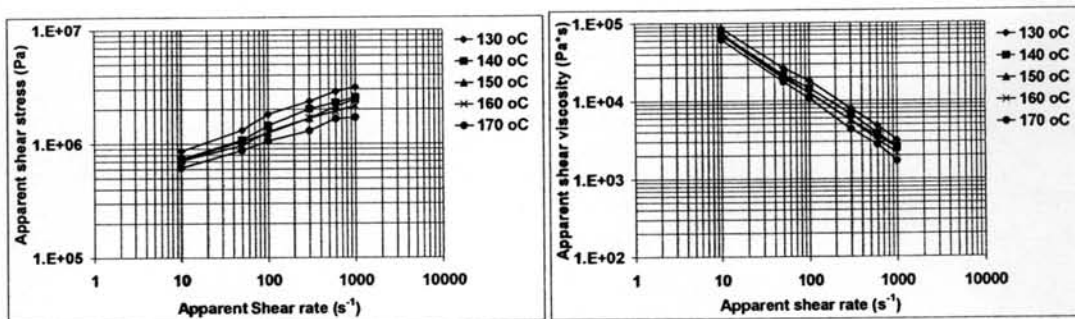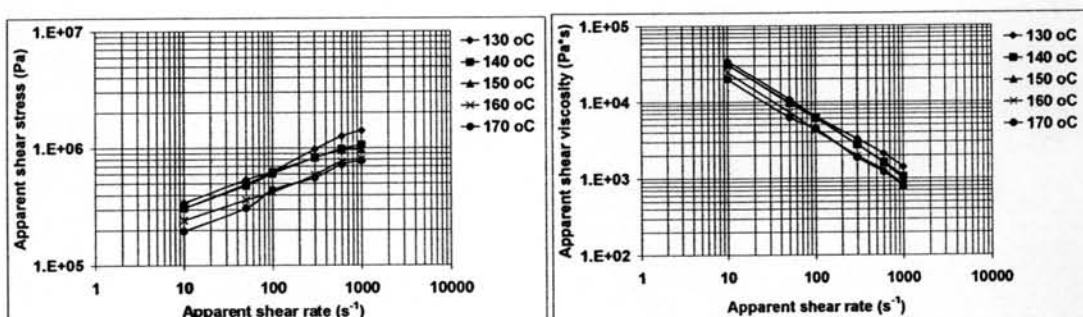
(b) 50 mM-styrene
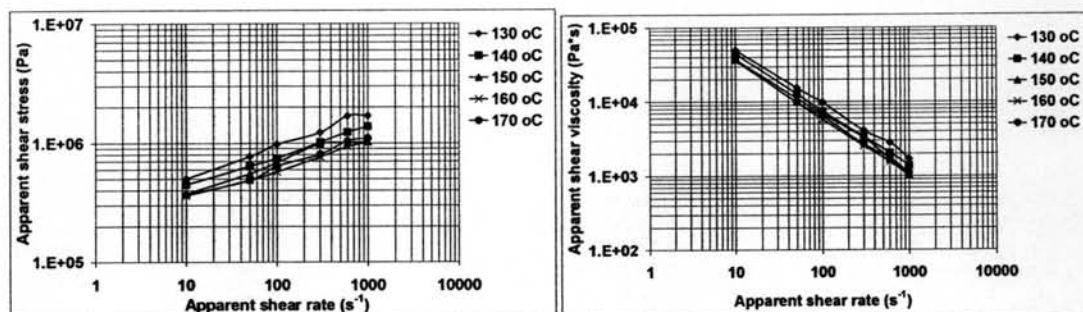
(c) 100 mM-styrene

Figure 4.7 Logarithmic plots of apparent shear stress and apparent shear viscosity versus apparent shear rate for admicelled PS-NR using L/D ratio of 0.5.
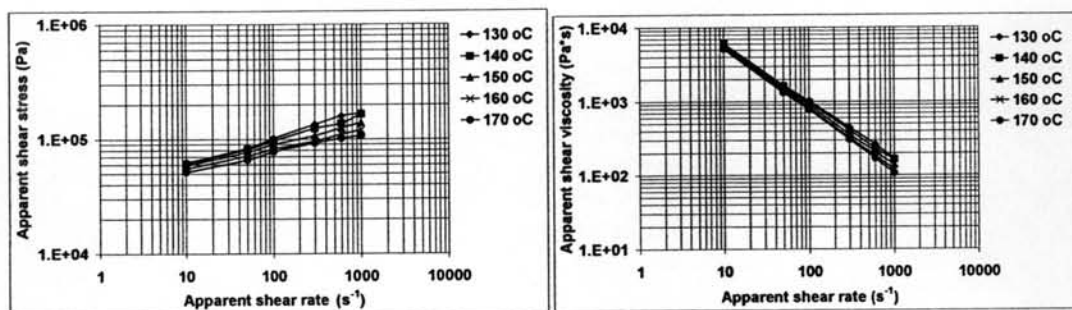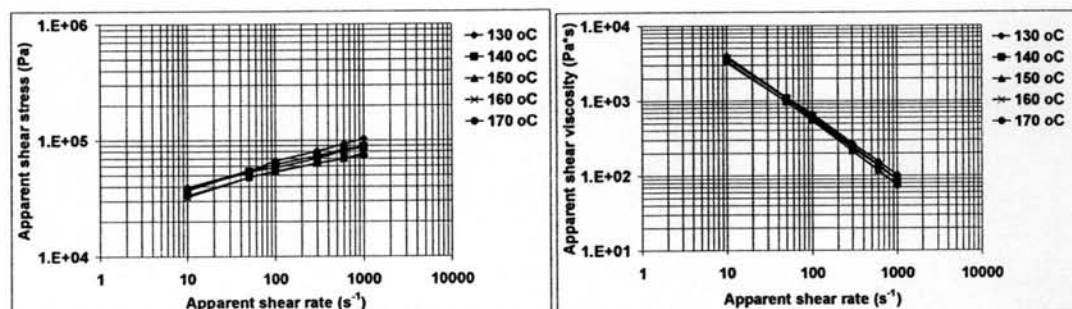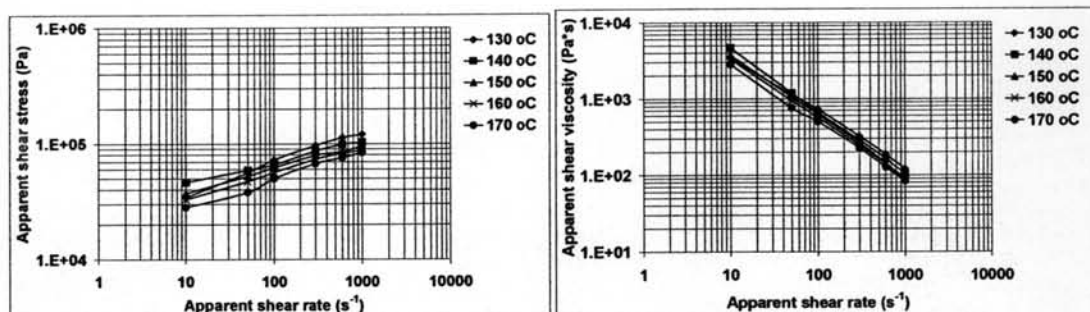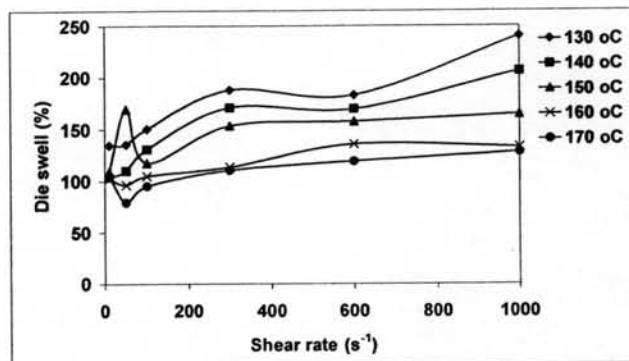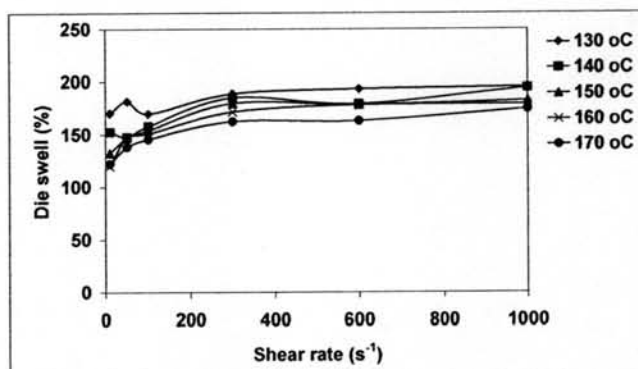
(a) NR

(b) 50 mM-styrene

(c) 100 mM-styrene

Figure 4.8 Logarithmic plots of apparent shear stress and apparent shear viscosity versus apparent shear rate for admicelled PS-NR using L/D ratio of 5.

(a) NR

(b) 50 mM-styrene

(c) 100 mM-styrene

Figure 4.9 Logarithmic plots of apparent shear stress and apparent shear viscosity versus apparent shear rate for admicelled PS-NR using L/D ratio of 20.
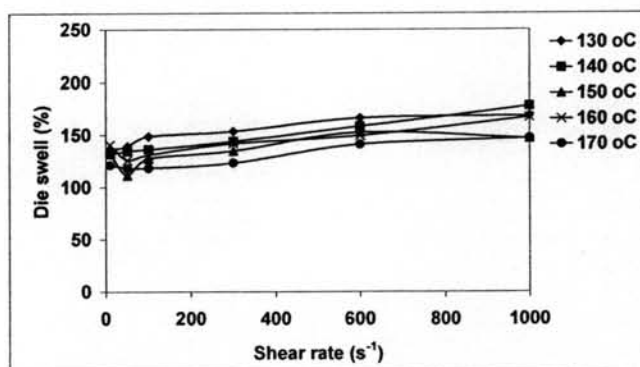
- Die Swell Ratio of Admicelled PS-NR

The extrudates of admicelled PS-NR were also measured for die swell to study their elastic property. Figures 4.10-4.12 showed the effect of temperature on die swell ratio of admicelled PS-NR at different L/D ratios and various apparent shear rates. It can be seen that the die swell of all cases decreased as increase in temperature at any particular L/D ratio, but it increased as increase in shear rate. This is because the less elastic recovery of the macro molecular chains under the influence of the applied shear stress at higher temperature. In comparison with the result of Asletha et al. (1998), without the compatiblizer, the blends of NR/PS found to be increase in die swell as increase of temperature, but the reverse trend is obtained when the compatibilizer of NR-g-PS was applied. Therefore, this is shown that the technique of admicellar polymerization can give us the higher compatability between NR and PS without adding any compatabilizer. In addition, the die swell of admicelled PS-NR with 50 mM-styrene was higher than that of admicelled PS-NR with 100 mM-styrene at particular shear rate, L/D ratio and temperatue, because the higher styrene content increased the plasticity or better chain relaxation of modified NR.
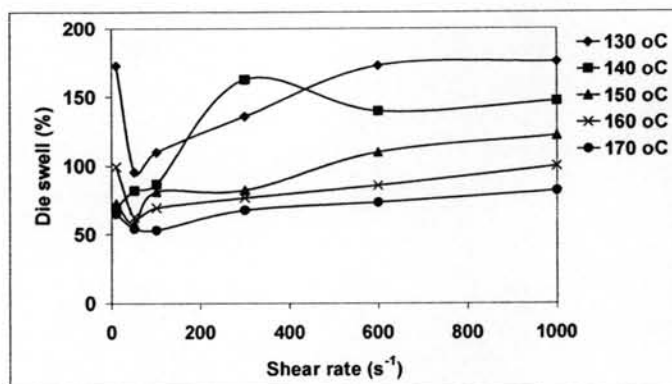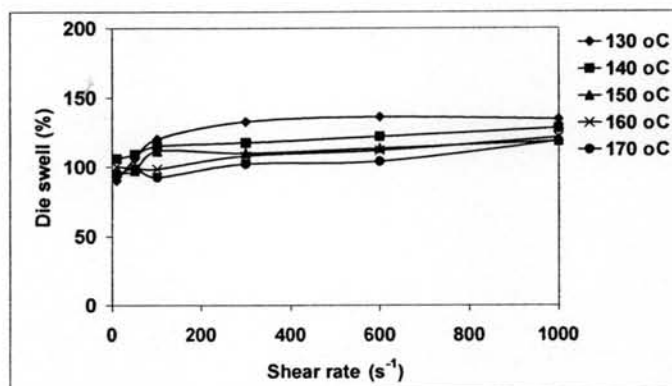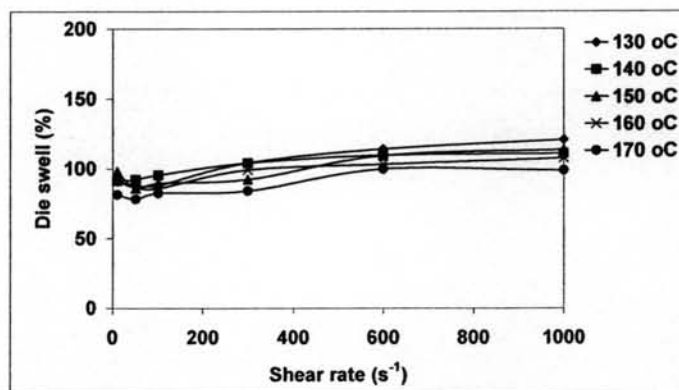
(a) NR

(b) 50 mM-styrene

(c) 100 mM-styrene

Figure 4.10 Plots of die swell versus shear rate for admicelled PS-NR using L/D ratio of 0.5.
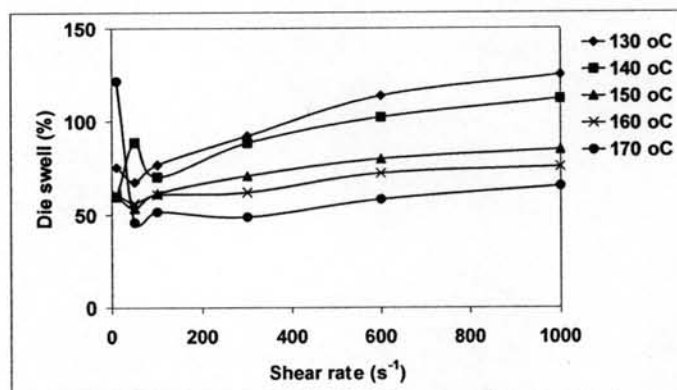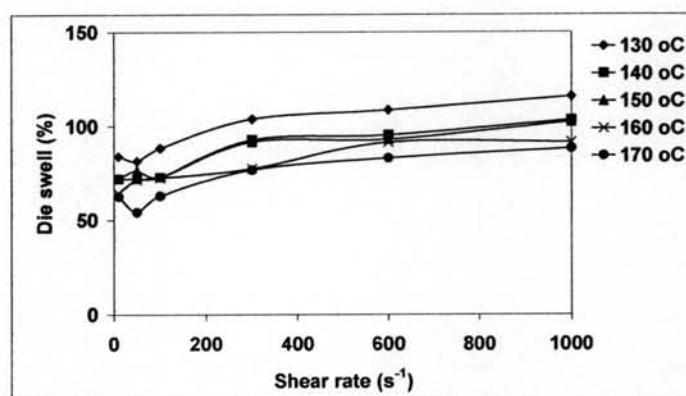
(a) NR

(b) 50 mM-styrene
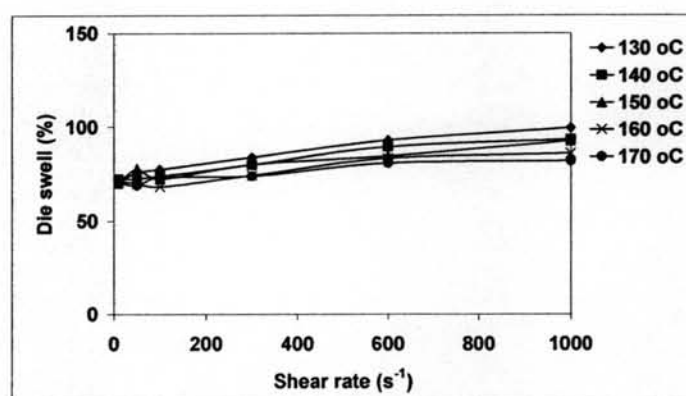

(c) 100 mM-styrene

Figure 4.11 Plots of die swell versus shear rate for admicelled PS-NR using L/D ratio of 5.

(a) NR

(b) 50 mM-styrene

(c) 100 mM-styrene

Figure 4.12 Plots of die swell versus shear rate for admicelled PS-NR using L/D ratio of 20.

4.3.1.2 *NR Blended Admicelled PS-NR*

The rheological behaviors of 50/50 NR/admicelled PS-NR blends were shown as Figures 4.13-4.14. It can be seen that the apparent shear stress of all cases increased as increase in apparent shear rate. The pure NR was higher in apparent shear stress and viscosity than those of blends. However, the NR blended admicelled PS-NR with 300 mM-styrene exhibited the higher apparent shear stress and viscosity when compared with the other admicelled PS-NR blends due to the increment of their rigidity and high MW. Figure 4.15 showed the die swell results of NR blended admicelled PS-NR. It could be seen that all case of NR blended admicelled PS-NR were higher in die swell than that of pure NR especially at shear rate of above $300s^{-1}$ due to the high molecular weight of NR in the blend. The swelling ratio of pure NR is about 58%, lower than that found in case of using 1 mm die diameter revealing a better chain relaxation in a bigger die. When NR was added to each admicelled PS-NR, the elasticity of the blend is ever stronger than pure NR, revealing better adhesion between two phases to resume elasticity of NR. This result was corresponded with Asaletha *et al.* (1998), that die swell decreased as increase the amount of NR in the system without compatibilizer. However, extrudate surface in all cases exhibited different degree of roughness (melt fracture) and found to be lower at higher content of styrene used. Therefore, the blends of admicelled PS-NR with pure NR could not be useful to improve the die swell properties.
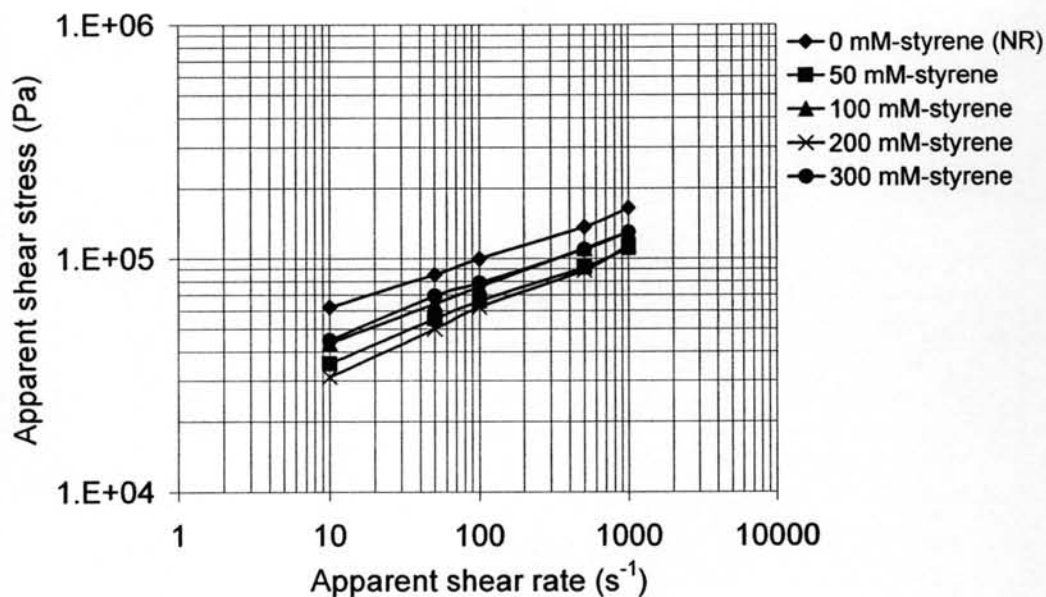
Figure 4.13 Logarithmic plots of apparent shear stress versus apparent shear rate for 50/50 NR/admicelled PS-NR blends at 150°C (L/D = 7.5, die length = 15 mm and die diameter = 2 mm).

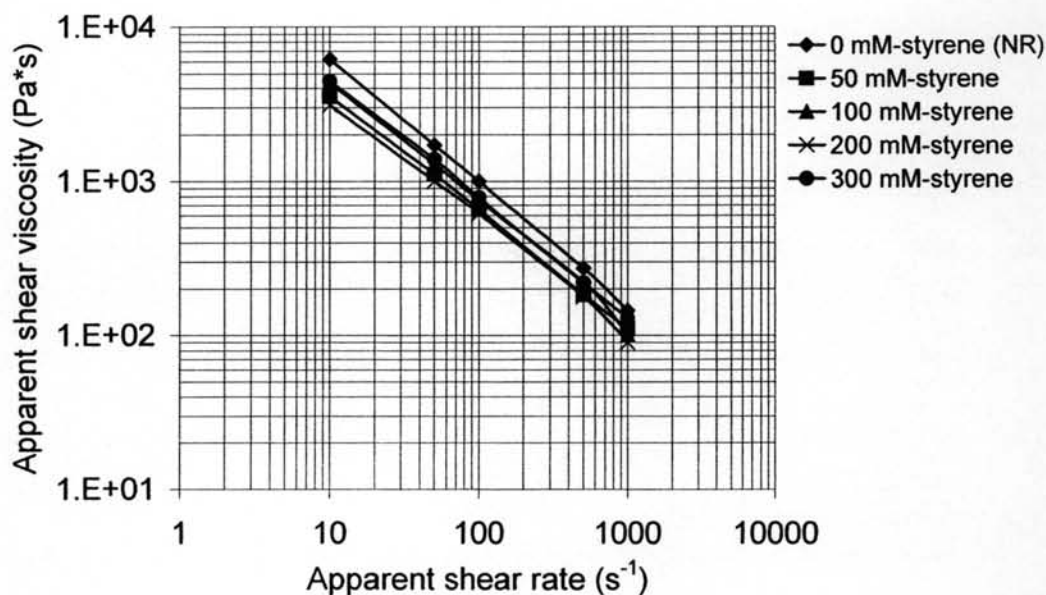**Figure 4.14** Logarithmic plots of apparent shear viscosity versus apparent shear rate for 50/50 NR/admicelled PS-NR blends at 150°C (L/D = 7.5, die length = 15 mm and die diameter = 2 mm).
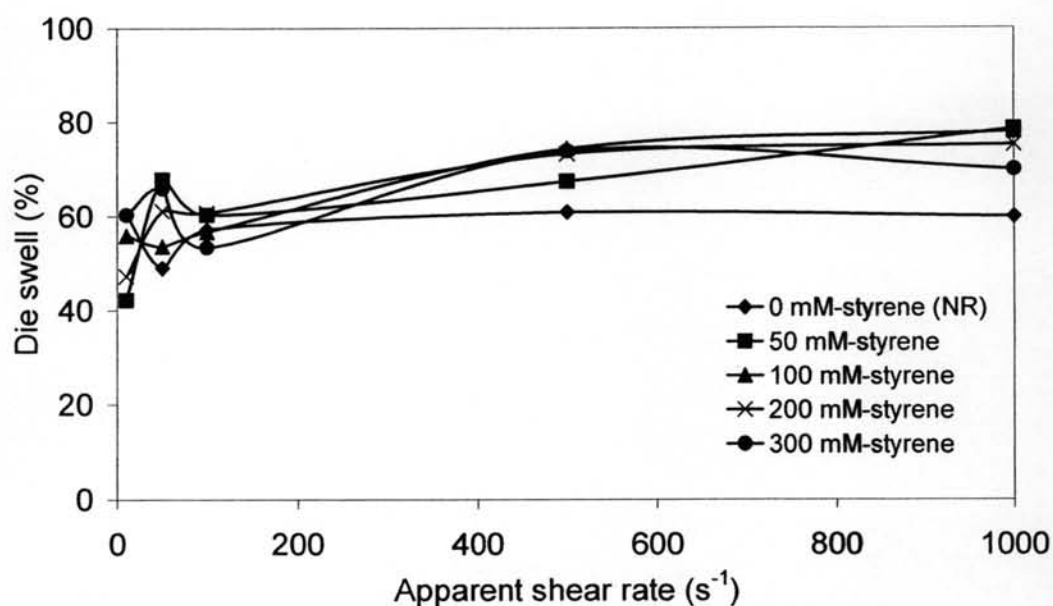
Figure 4.15 Plots of die swell versus apparent shear rate for 50/50 NR/admicelled PS-NR blends at 150°C (L/D = 7.5, die length = 15 mm and die diameter = 2 mm).

4.3.1.3 *Silica Filled Admicelled PS-NR*

Figures 4.16-4.18 showed the flow behavior of 30 phr-silica filled admicelled PS-NR compared with that of NR. It showed that the apparent shear stress and apparent shear viscosity of silica filled admicelled PS-NR samples were higher than that of NR blended admicelled PS-NR. Comparing the 30 phr-silica (BET=200 m^2/g) filled admicelled PS-NR and 20 phr-modified silica (BET=167 m^2/g) filled SBR from Bhowmick *et al.* (2004), the use of unmodified silica filled in admicelled PS-NR can increase about 10 times higher of shear stress and shear viscosity than that of modified silica filled SBR at particular shear rate. In addition, the measured results of the silica filled admicelled PS-NR with 50, 100 and 200 mM-styrene were not much different at any particular shear rate. However, all cases of admicelled PS-NR samples were significantly lower in shear stress and shear viscosity than that of pure NR. Normally the use of coupling agent can give rise to form the covalent bonding between silica and NR. In this case, even without silane coupling agent, but the smaller particles size of silica used (12 nm) can be brought about the reinforcement in NR (Leblanc, 2002). However, the interaction between

NR in admicelled PS-NR and silica may be interrupted by polystyrene which could result in lower the shear stress and shear viscosity. At higher content of styrene (300 mM-styrene), the rigidity may play an important role in increase of shear stress and shear viscosity. The measured die swell of silica filled admicelled PS-NR was significantly higher than that of silica filled NR at any particular shear rate due to the reason explained earlier. In other words, admicelled PS-NR can be adhere well to silica to create more networks and thus enhance elasticity of the chains.
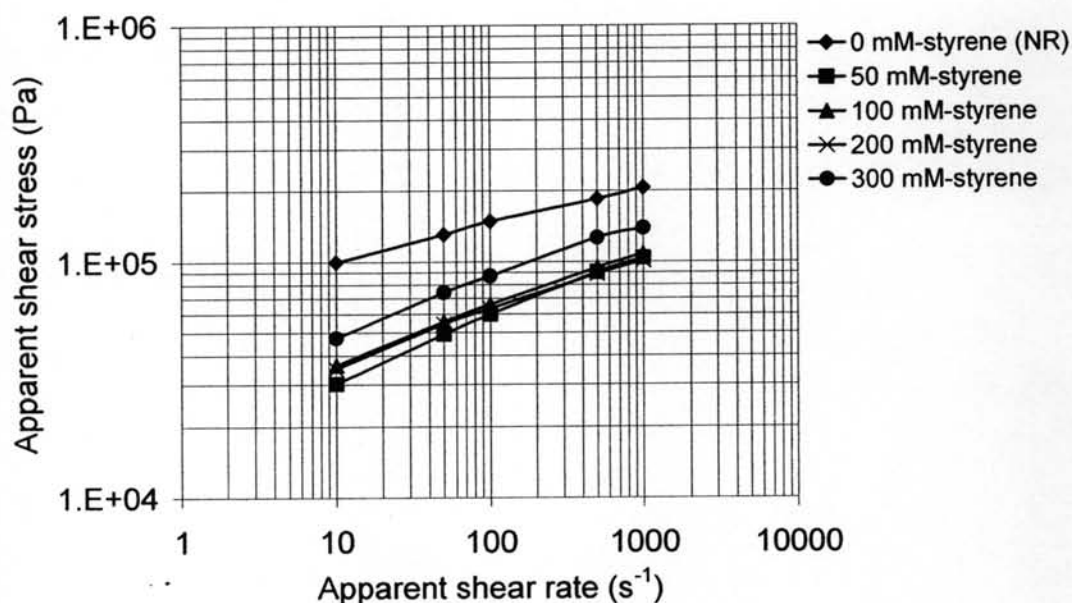

Figure 4.16 Logarithmic plots of apparent shear stress versus apparent shear rate for 30 phr-silica filled admicelled PS-NR at 150°C (L/D = 7.5, die length = 15 mm and die diameter = 2 mm).
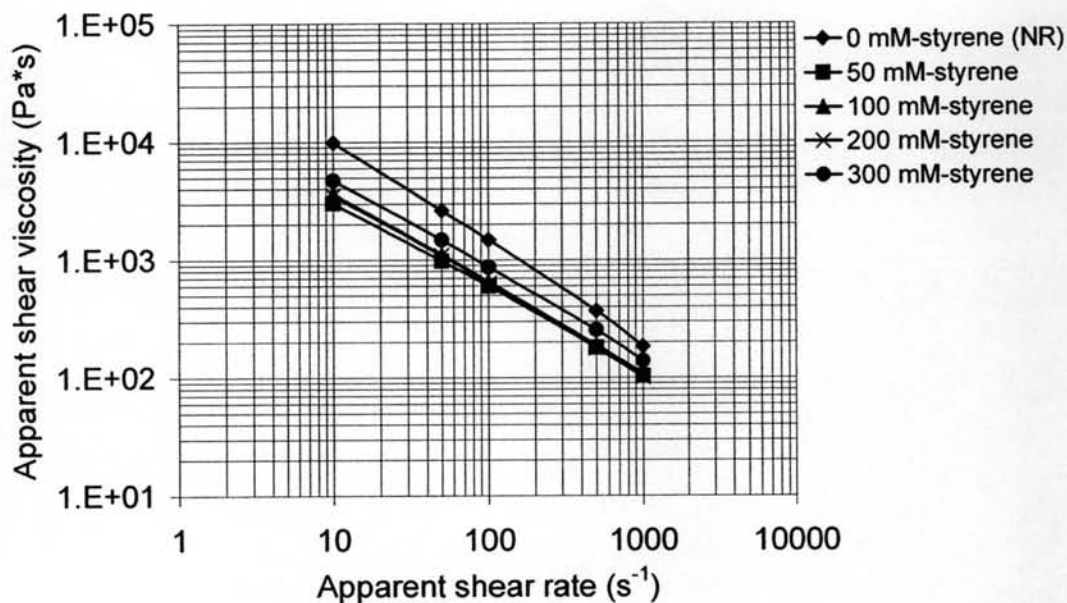
Figure 4.17 Logarithmic plots of apparent shear viscosity versus apparent shear rate for 30-phr silica filled admicelled PS-NR at 150°C (L/D = 7.5, die length = 15 mm and die diameter = 2 mm).
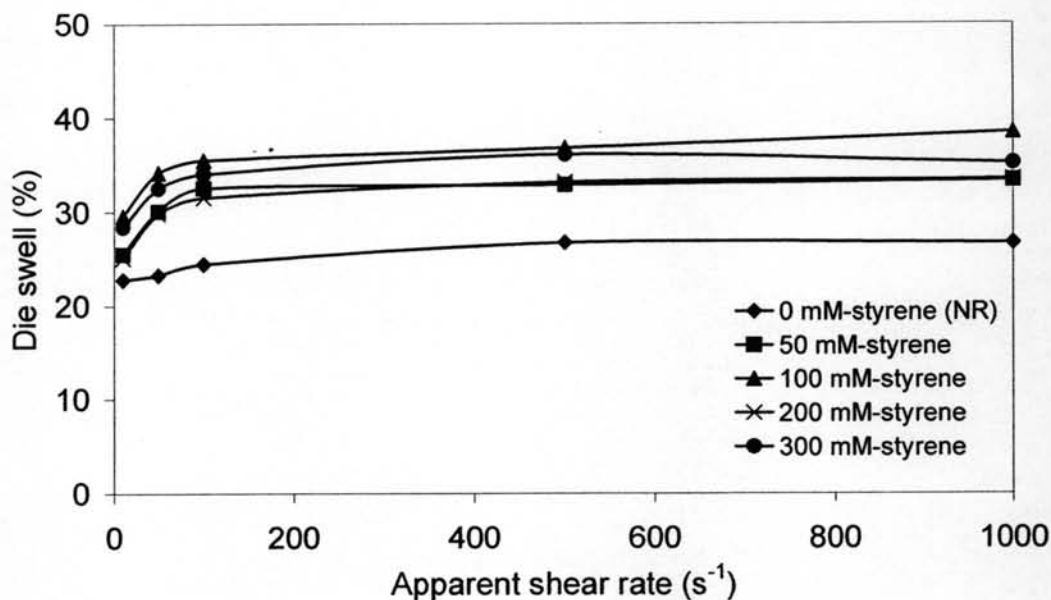

Figure 4.18 Plots of die swell versus apparent shear rate for 30-phr silica filled admicelled PS-NR at 150°C (L/D = 7.5, die length = 15 mm and die diameter = 2 mm).

4.3.2 <u>Rheological Behavior of Admicelled PS-NR Using Slit Die</u>

In this test, the admicelled PS-NR were blended with the 50 wt % of Natural rubber (NR) and filled with the 30 phr of silica to observe the processability of admicelled PS-NR in strip form. The slit die with dimension of 1 mm-thick and 10 mm-width was used to measure the flow behavior under shear rates of 10, 30, 60, 100, 200, 300 and 600s^{-1} at 150°C. The results were shown in the logarithmic plots as Figures 4.20-4.23.

- Flow Behavior of NR Blended Admicelled PS-NR

Figure 4.19 showed the measured real shear stress of NR blended admicelled PS-NR as increment of shear rate. It showed that the shear stress of all cases increased as increase in shear rate but the profile is less dependent on increasing shear rate than those found in circular die. In other words, the flow is more Newtonian like in the slit die. The pure NR showed the highest of real shear stress than that of all NR blended admicelled PS-NR at any particular shear rate, which are the same results as using circular die. It revealed that the blending with NR resulted in lowering the shear stress of admicelled PS-NR. In addition, the profile of capillary die used can affect the measured pressure of molten material which was higher in the slit die than that of circular die. Considering at higher content of styrene used, the NR blended admicelled PS-NR with 300 mM-styrene showed the lowest real shear stress at any particular shear rate. Those of real shear viscosity also exhibited the same tendency as shown in Figure 4.20. It could be seen that the die profile can affect the flow behavior of NR blended admicelled PS-NR, especially at higher content of polystyrene used.

- Flow Behavior of Silica Filled Admicelled PS-NR

The flow behaviors of silica filled admicelled PS-NR using slit die were shown as Figures 4.21-4.22. It can be seen that the silica containing admicelled NR especially at that with 300 mM-styrene results in increase the real shear stress and viscosity than that of the other silica filled admicelled PS-NR, which was different from previous result of blend products. Due to the reason explained earlier in circular die. However, the die profile did not affect the flow behavior of silica filled admicelled PS-NR at any styrene concentration used. This can be concluded that the silica filled in admicelled PS-NR showed the same tendency of flow

behavior either using circular or slit die. In summary, admicelled PS-NR can help to reduce molecular friction of rubber chains, enhance flow properties while keeping good adhesion between phases.
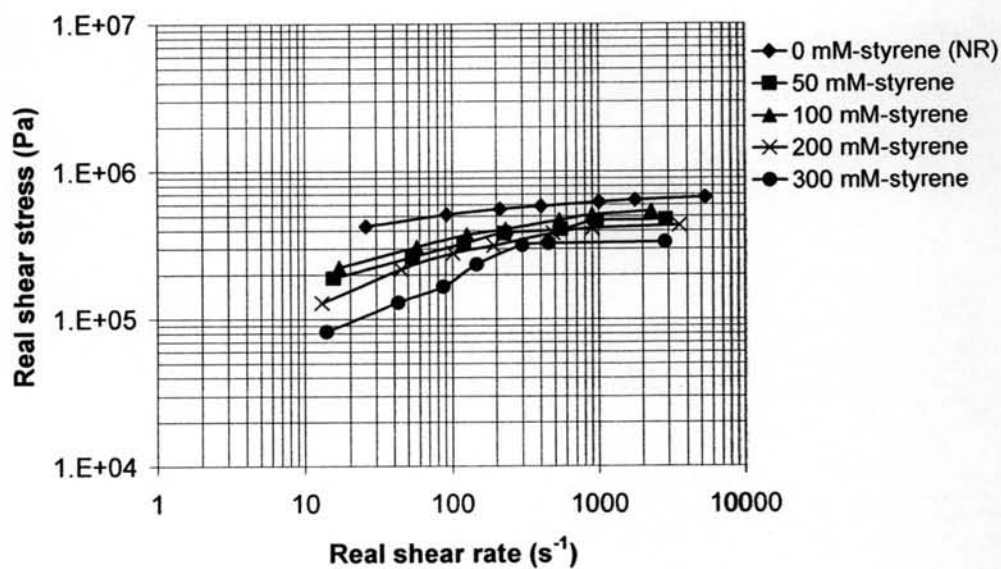

Figure 4.19 Logarithmic plots of real shear stress versus real shear rate for 50/50 NR/admicelled PS-NR blends using slit die at 150°C.
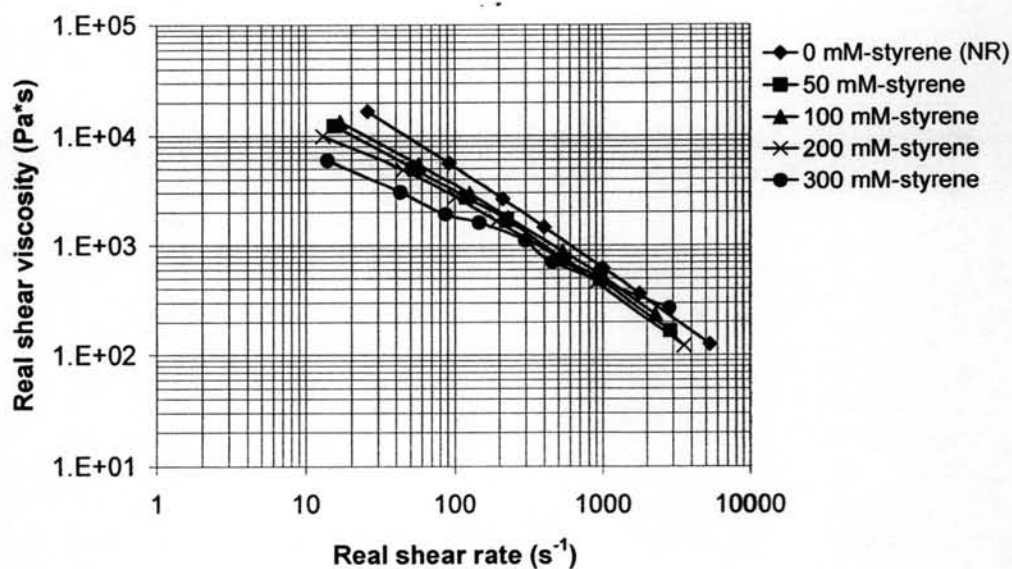

Figure 4.20 Logarithmic plots of real shear viscosity versus real shear rate for 50/50 NR/admicelled PS-NR blends using slit die at 150°C.
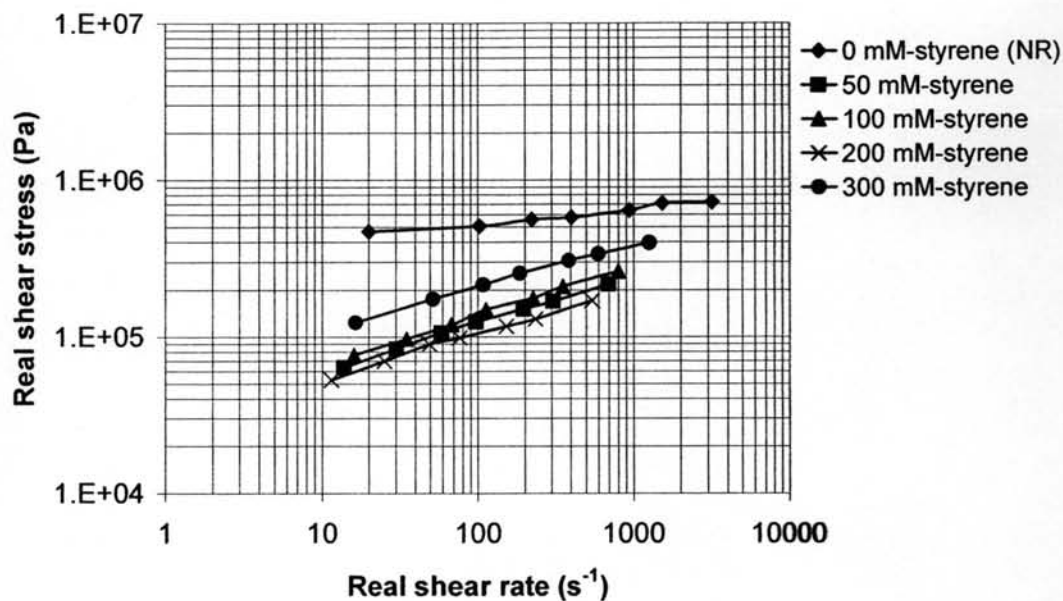
Figure 4.21 Logarithmic plots of real shear stress versus real shear rate for 30 phr-silica filled admicelled PS-NR using slit die at 150°C.
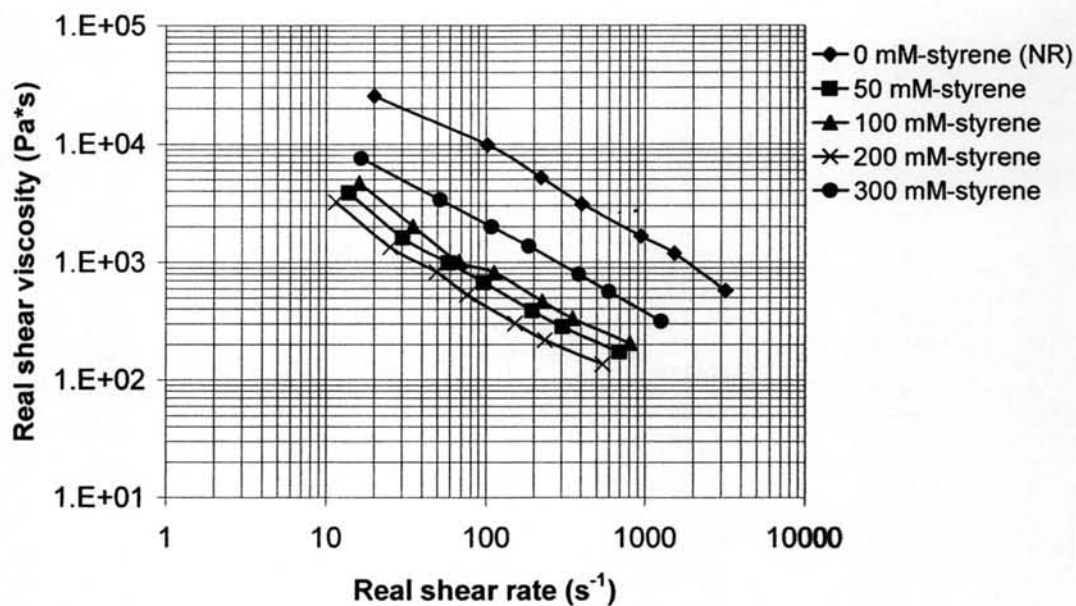

Figure 4.22 Logarithmic plots of real shear viscosity versus real shear rate for 30 phr-silica filled admicelled PS-NR using slit die at 150°C.

- Extrudate Appearance of NR Blended Admicelled PS-NR and
Silica Filled Admicelled PS-NR

The appearance of NR blended admicelled PS-NR and silica filled admicelled PS-NR extrudates was shown as Figure 4.23. It showed that the silica filled admicelled PS-NR at any particular styrene concentrations and shear rate showed the better dimension stability compared to NR blended admicelled PS-NR. Most of the extrudates of silica filled admicelled PS-NR at any styrene concentrations have smooth surfaces at over wide range of shear rate used which was better than that of silica filled pure NR. In cases of NR blended admicelled PS-NR, at high shear rates, the extrudate surface exhibits different degree of roughness which was lower at higher content of styrene used. This is associated with the melt fracture occurs at high shear forces where the shear stress exceed the strength of the melt (Asaletha *et al.*, 1998). However, the higher rigidity of the higher styrene content resulted in the better shape stability of extrudate at any shear rate.
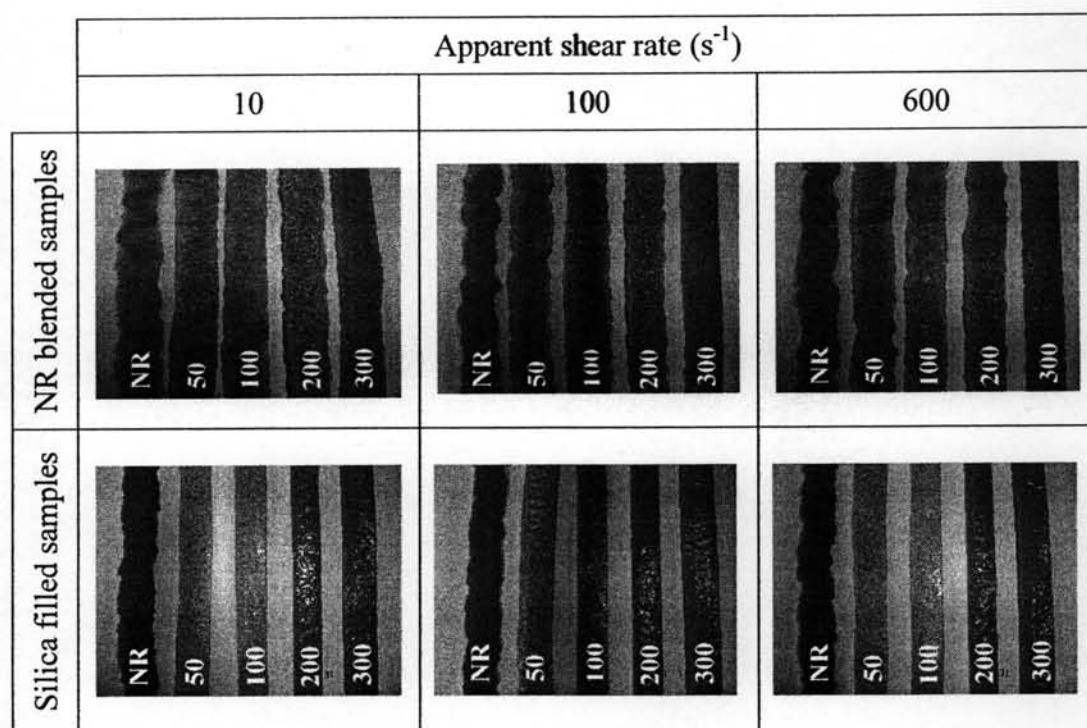

Figure 4.23 Extrudates appearance of admicelled PS-NR samples extruded by slit die (1 mm thickness and 10 mm width) at shear rates of 10, 100 and 600 s^{-1}.

4.4 Physical Properties

4.4.1 Crosslink Density

The average molecular weight between network crosslinks (M_c) of cured admicelled PS-NR with different styrene concentration that completely swelled in toluene solvent was shown as Figure 4.24. Normally, the M_c of NR is about 7000 g/mol (Chenal *et al.*, 2007). In this case, the lower M_c of pure NR is found, which might be caused by the different amount of vulcanizing agents used in the curing, e.g. sulfur and CBS. In all cases of cured admicelled PS-NR, the results is found to be lower the M_c (higher crosslink density, V_e) than that of pure NR, especially at 50 mM-styrene showed the best result. This might be from the presents of PS coated on a NR particle disturbed the expansion of NR chain inside a particle when it was acted by toluene solvent and then result in higher intra-crosslinking of NR chains in particle. However, the M_c trended to slightly increase as increase in the concentration of styrene monomer. This is because even the chain crosslinking in NR particle was higher, but the higher polystyrene contents coated on a NR particle could play important role to disturb the NR inter-crosslinking between particles resulting in higher the M_c which mean the lower crosslink density.
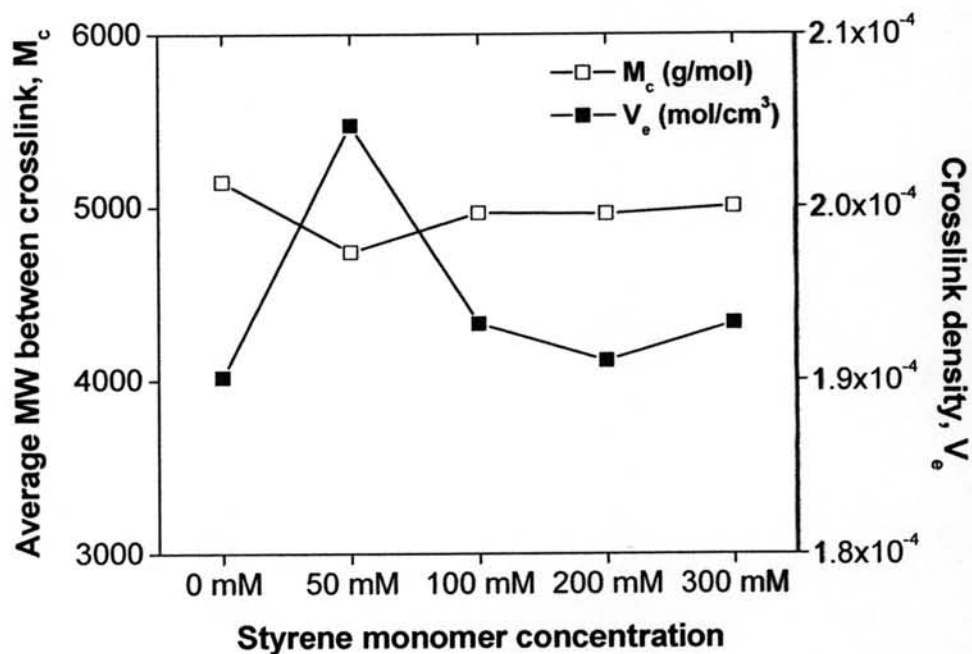
Figure 4.24 Average molecular weight between the network crosslinks (M_c) of cured admicelled PS-NR samples swelled in toluene solvent.

4.4.2 Tensile Testing

The results of tensile strength of admicelled PS-NR samples were shown as Figure 4.25. Normally, the tensile strength of cured NR was found to be about 25-30 MPa (Boochathum *et al.*, 2001). It could be seen that the cured samples of admicelled PS-NR were higher in tensile strength than that of cured samples with aging, silica filled samples and NR blended samples, respectively. In cured samples, the tensile strength increased as increasing the styrene monomer concentration, the cured sample of 300 mM-styrene was the highest. This is due to the synergistic advantage of the higher stiffness of polystyrene and higher crosslink density in admicelled PS-NR compared with cured pure NR, and then resulting in increasing the strength. In addition, the cured samples under aging condition gave the different results of tensile strength. The cured admicelled PS-NR with 100 mM-styrene showed the highest, this is due to the advantage of the higher chain crosslink that can withstand the thermal aging than the others. However, the strength trended to be lower as increasing the styrene monomer concentration. In addition, the silica filled

samples and NR blended samples were significantly lower in the strength because there is no molecular chain crosslinking.
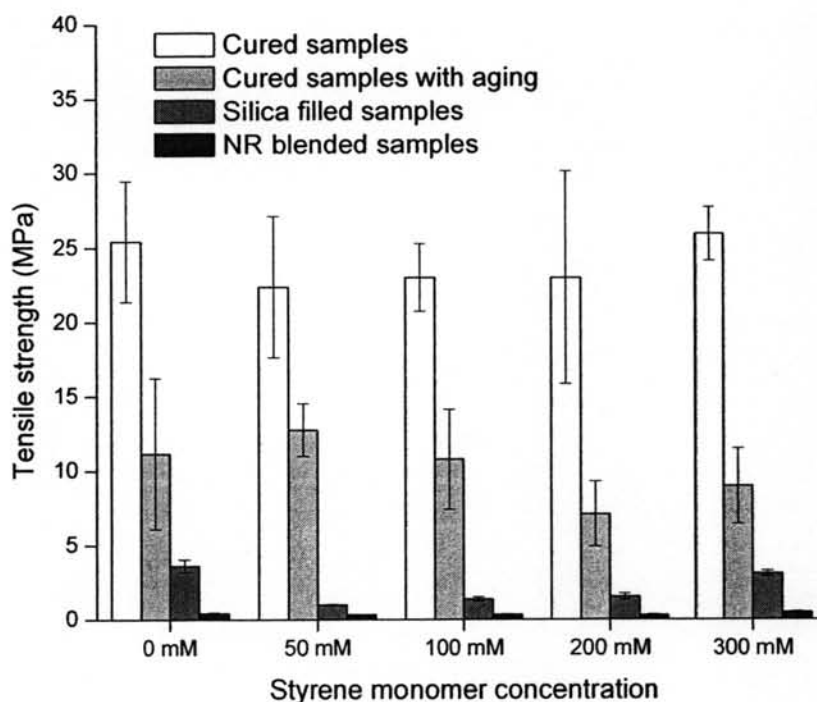

Figure 4.25 Tensile strength of admicelled PS-NR samples.

Elongation at break of admicelled PS-NR samples were shown as Figure 4.26. In all cases of samples, the elongation results trended to decrease as increase in concentration of styrene monomer. It can be seen that the cured samples were higher in elongation at break than the others at any particular concentration of styrene monomer. The higher content of styrene in cured samples could have been synergistic advantages as explained earlier to lower their elasticity. However, in most cases, samples with using 50 mM-styrene showed the higher elasticity than the others corresponding to lower in tensile. In addition, the presence of silica filler in all cases of admicelled PS-NR can increase the elasticity, especially at higher content of styrene used when compared to cured cases under thermal aging. However, all cases of blend samples showed the lowest elongation at break when compared to the others. Therefore, it could be concluded that the silica filler can give us the better strength of admicelled PS-NR than blending method with pure NR.
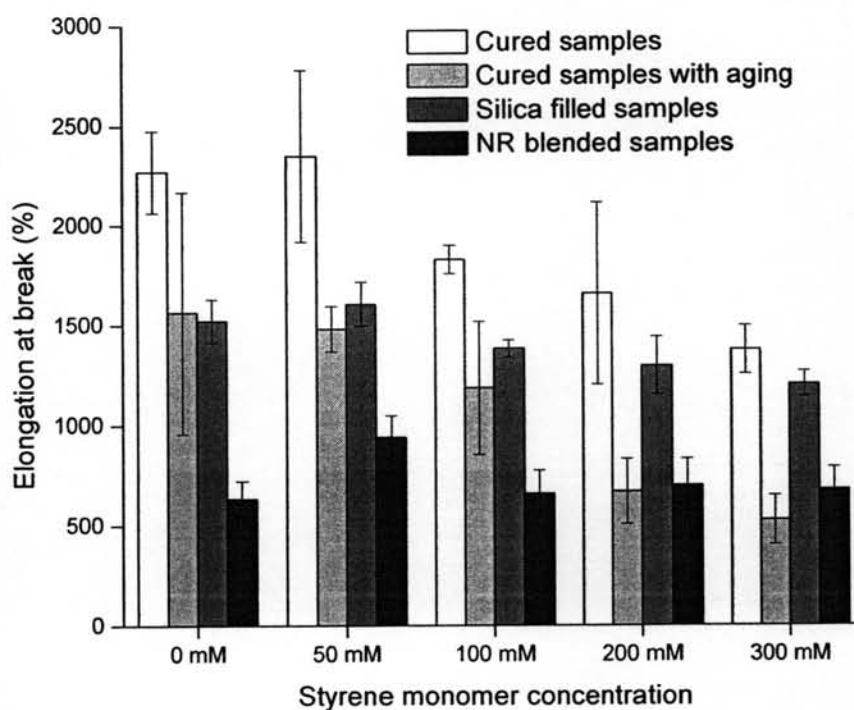
Figure 4.26 Elongation at break of admicelled PS-NR samples.

Young's modulus of admicelled PS-NR samples was showed as Figure 4.27. It was clearly observed that the cured samples were significantly higher in Young's modulus than other cases and also increased as increase in concentration of styrene monomer. Thus, it could be presumed that the stiffness of NR can be improved when composed with polystyrene by using this technique under system of the curing. Under thermal aging, Young's modulus of cured samples was affected to be lower. However, the result of silica filled and NR blended admicelled PS-NR showed the same tendency as tensile strength but give us the lower value.
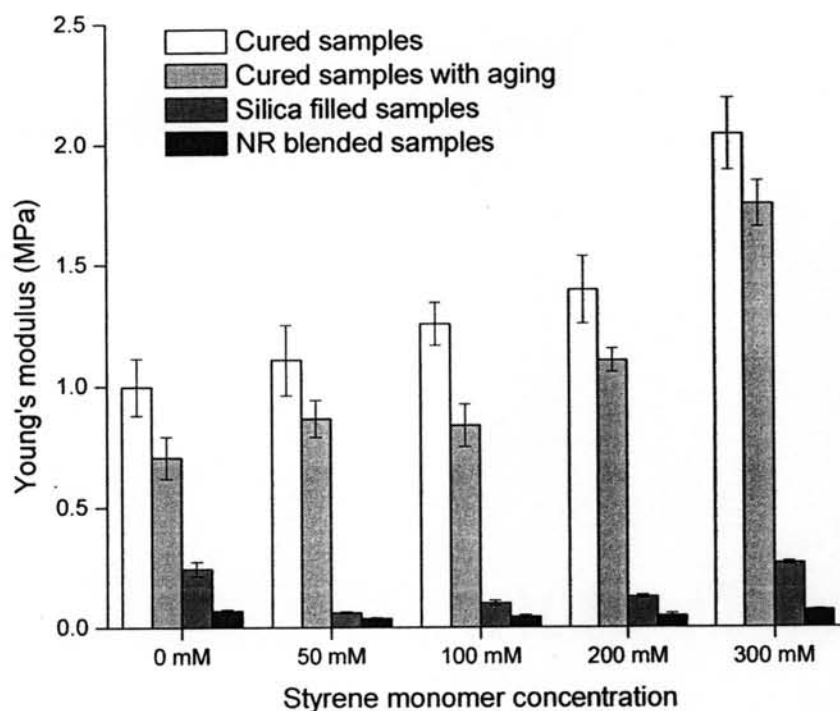
Figure 4.27 Young's modulus (at break) of admicelled PS-NR samples.

4.4.3 Hardness

The hardness (Shore A) results were shown as Figure 4.28. The hardness of cured NR was found to be about 49 Shore A corresponding to Boochathum *et al.* (2001) which was about 40-50 shore A. In all cases of cured admicelled PS-NR under aging and unaging conditions, the hardness increased as increasing the concentration of styrene monomer caused by higher in rigidity. The hardness of cured admicelled PS-NR was found to be higher than that of SBR which was about 42 IRHD (Poh *et al.*, 2001). This result can be generally consistent with Shore A results of admicelled PS-NR within about five hardness. In addition, under thermal aging condition of cured samples, the hardness could be improved, especially cured admicelled PS-NR with 100 mM-styrene. The silica filled samples were dramatically higher in hardness especially when it was filled in pure NR and admicelled PS-NR at 300 mM-styrene due to its high reinforcement property (Dick, 2001). Therefore, it could be concluded that the technique of admicellar

polymerization can achieve the desired hardness of natural rubber with the use of appropriate concentration of styrene monomer.
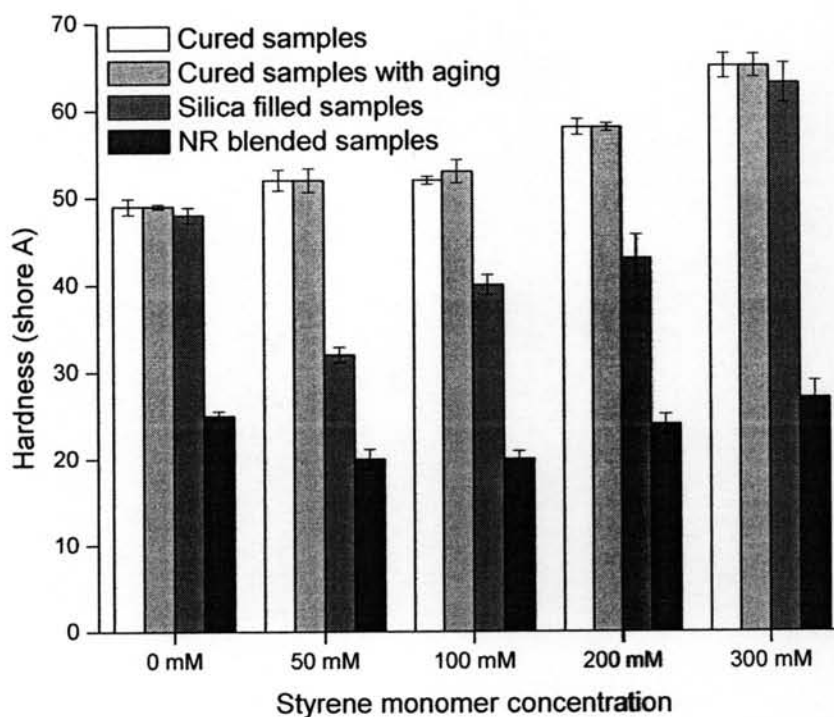

Figure 4.28 Hardness of admicelled PS-NR samples.

4.4.4 Cure Characteristics

The cure curves in conventional system of admicelled PS-NR were shown as in Figure 4.29. Practically, the rubber manufacturers always prefer a vulcanization systems that can give low cure time (t_{90}), high scorch time (t_2) and high cure rate as a result of processing advantages in time gained and cost reduction (Akinlabi *et al.*, 2006). The admicelled PS-NR at any different of styrene content can achieve that advantage in lowering the curing time as seen in Table 4.2. This might be caused by the effect of amine group in CTAB surfactant located between PS and NR particle, which behave as accelerator (all slopes are similar shape) to increase the rubber crosslinking. However, it was observed that the admicelled PS-NR at any particular styrene concentration were lower in minimum torque as a result of lower

viscosity, scorch time and cure rate but gained in higher maximum torque when compared with pure NR as listed in Table 4.2. However, those results were not much different at which concentration of styrene monomer was increased. Therefore, it could be concluded that the present of styrene in NR by using this technique is available to reduce the processing time.
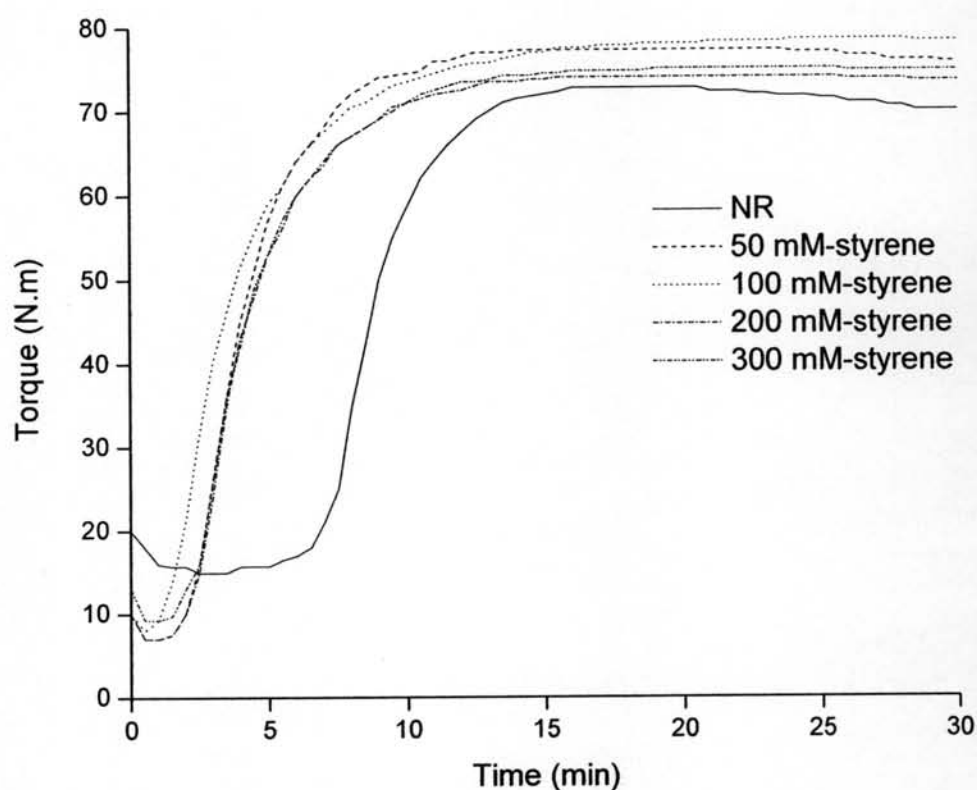

**Figure 4.29** Cure curves in conventional system of admicelled PS-NR with various styrene monomer concentrations.

Table 4.2 Cure characteristics of admicelled PS-NR

Products	Torqe (N.m)		Scorch time		Cure time	Cure rate	
	M_H	M_L	t_1	t_2	t_{90}	t_{s1}	t_{s2}
NR	72.98	15.24	5.78	6.29	11.88	16.39	17.89
50 mM-styrene	77.52	6.47	1.60	1.88	7.71	16.37	17.15
100 mM-styrene	78.93	7.73	1.00	1.17	9.08	12.38	12.64
200 mM-styrene	74.32	6.69	1.63	1.88	8.25	15.11	15.70
300 mM-styrene	75.29	8.99	1.63	1.88	8.75	14.04	14.56

*Note that $\triangle$Torque of NR is lower than $\triangle$Torque of admicelled PS-NR.

where;

- M_H and M_L are the maximum and minimum torque, respectively.

- t_1 is the time in minute to an increase of 1 unit of torque above M_L.

- t_2 is the time in minute to an increase of 2 unit of torque above M_L.

- Cure time is calculated using the formula: $[90(M_H-M_L)/100]+M_L$

- Cure rate is calculated using the formula: 100/(cure time-scorch time)
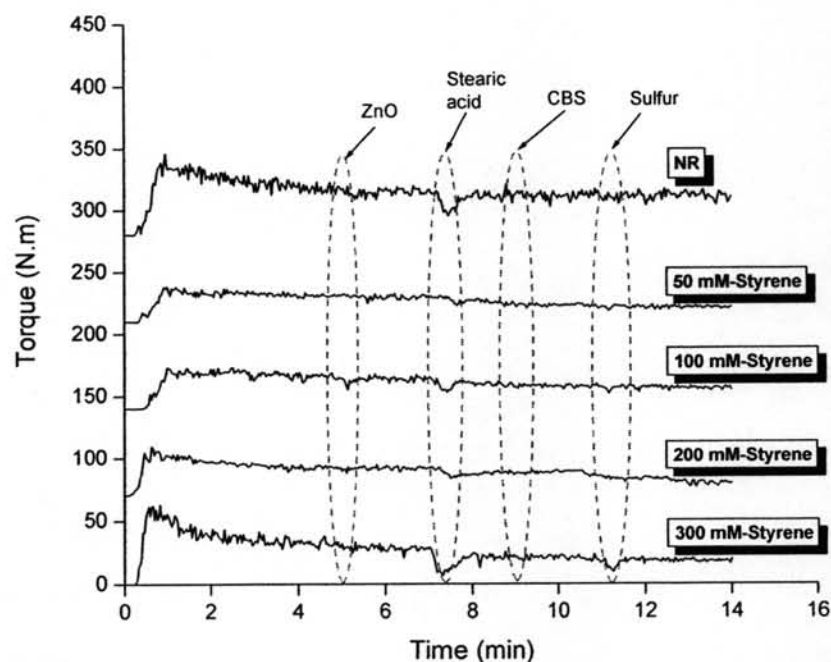
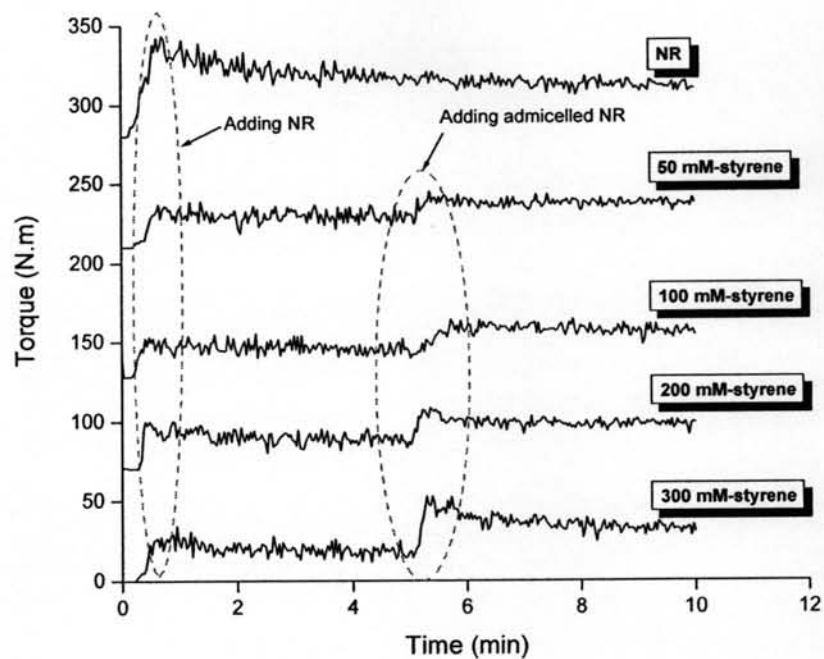**Figure 4.30** Torque of mixing for admicelled PS-NR compounds.

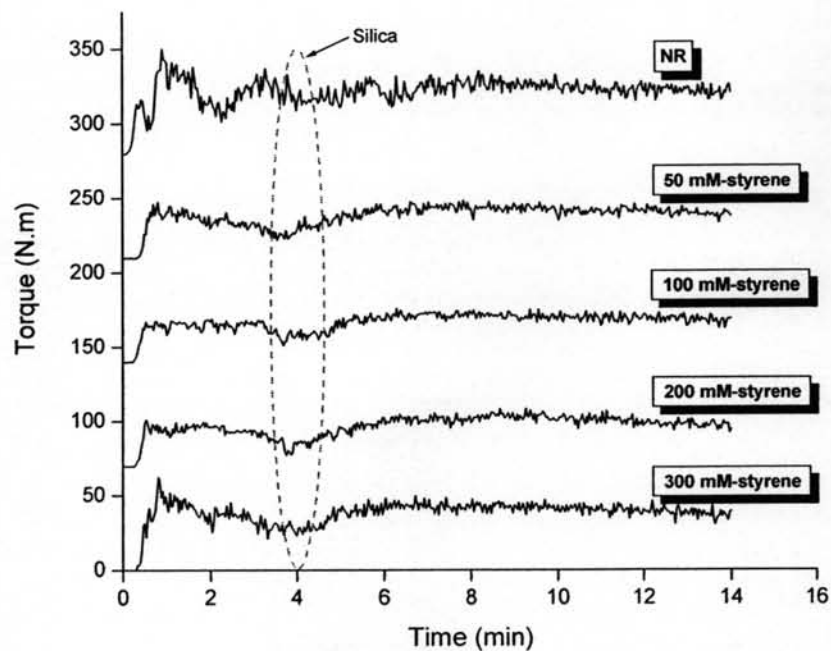**Figure 4.31** Torque of mixing for NR blended admicelled PS-NR.

Figure 4.32 Torque of mixing for silica filled admicelled PS-NR.

4.4.5 Torque of Mixing

Torque results of admicelled PS-NR compounds were shown as in Figure 4.30. In period of mixing, the torque trended to decrease slowly until finish the mixing due to the reduction of molecular chain entanglement (chain scission) causing by mastication. However, it could be seen that the reduction of mixing torque was clearly observed when the stearic acid was added at minute 7th before increasing again after that time. In the Figure 4.31, the result of mixing torque of 50/50 NR/admicelled PS-NR blends was observed. It was found that the blending NR with admicelled PS-NR can increase the torque of mixing in blend products. Moreover, the increment of mixing torque was proportional to the content of styrene used in admicelled PS-NR. Figure 4.32 showed the torque results in all cases of silica filled admicelled PS-NR. In this case, it showed that the addition of reinforcing silica filler resulted in slightly increase in torque, especially when adding in admicelled PS-NR. Thus, in all cases products, it could be concluded that the incorporation of styrene in NR result in increase the torque of mixing and it was found to be higher when the higher content of styrene was used due to the higher rigidity.

4.4.6 Ozone Resistance

The result of ozone resistance for cured admicelled PS-NR was investigated as presented in Table 4.3. It can be seen that the nature intensity of cracks due to ozone attack was different. The crackings on surface were clearly observed in all cases of cured samples and it trends to propagate perpendicular to the direction of stress applied. However, the cracks of admicelled PS-NR samples are small and discontinuous whereas continuous and deep cracks are observed in the cured pure NR. This may be due to the higher extent of cross-links formed in these admicelled PS-NR as suggested by Varghese et al. (2002). In addition, those crack sizes were smaller at the higher content of styrene in admicelled PS-NR. From the picture, it was clear that incorporation of polystyrene in NR will show the better ozone resistance compared to other cured pure NR.

Table 4.3 Ozone resistance of cured admicelled PS-NR without antiozonant

Conditions	Cured admicelled PS-NR				
	0 Mm-styrene (NR)	50 mM-styrene	100 mM-styrene	200 mM-styrene	300 mM-styrene
Unstretched samples before exposing in O_3 atmosphere					
Stretched samples after exposing in O_3 atmosphere ([O_3] = 50 pphm) for 72 h. at 20% strain stretching with the crosshead speed of 500 mm/min.					