

## CHAPTER IV



### RESULTS AND DISCUSSION

The graft copolymerization of ST and ACN onto NR in this research was prepared by 2 techniques: solution method initiated by using BPO or AIBN and emulsion method initiated by redox initiator (CHPO/TEPA) or  $K_2S_2O_8$ . The mechanism of graft copolymerization is shown in Appendix B. The effect of initiator types, initiator concentration, reaction temperature and nitrogen pressure ( $P_{N_2}$ ) on the grafting properties was investigated. The ST/ACN (by wt) was kept constant at 3/1, which was close to the azeotropic point of copolymerization of ST with ACN. This was calculated from the reactivity ratios of ST (0.40) and ACN (0.04) (Qu, Shang, Liu and Zhang, 2002). These reactivity ratios indicated that ST and ACN are easily copolymerized. However, it was difficult to form a homopolymer unless conversion became too high even if the feed composition was far from the azeotropic point. For the present study, the graft copolymer of ST and ACN onto NR could be applied as the compatibilizers for blending consisting of elastomers having highly different polarity such as NR/NBR blends due to the highly polar function groups obtained from ACN in the graft product. Thus, this research also investigated the effect of the addition of grafted NR (GNR) obtained from graft copolymerization of ST and ACN onto NR on vulcanization characteristics, mechanical properties, oil resistance and morphology behaviour of NR/NBR vulcanizates.

#### 4.1 Preparation of Graft Copolymer of ST and ACN onto NR

##### 4.1.1 Emulsion Method

Emulsion method is used to produce commercial elastomers such as styrene-butadiene rubber (SBR) and NBR. Many of these polymers are used as solid form by isolating from the aqueous phase after polymerization. There are many ingredients in the emulsion polymerization. One of them is monomers that are poorly soluble in water. Both thermal and redox initiators generate free radicals for starting the polymerization process. Other ingredients found in emulsion polymerization are surfactant to promote the fast rate of polymerization and minimize coagulum or

fouling in the reactor, stabilizers to increase the colloidal stability and buffering agent. In this part, the graft copolymerization of ST and ACN onto NR was carried out by emulsion polymerization initiated by redox initiator CHPO/TEPA and  $K_2S_2O_8$ . The influence of the polymerization conditions such as the initiator concentration, reaction temperature and  $N_2$  pressure was investigated. The effect of initiator types was also studied. For CHPO/TEPA initiator, CHPO is normally dissolved in an oil phase, while TEPA is water-soluble (Kochthongrasamee, Prasassarakich, and Kiatkamjornwong, 2006). For graft copolymerization of ST and ACN onto NR, TEPA was used to promote CHPO which was rapidly decomposed at low temperature. The decomposition involved the formation of unstable ionic intermediates that could further react to give cumene hydroperoxyl radicals and radical cations (Malcolm, 1999). The CHPO then might interact with monomers or rubber molecules resulting to the formation of active sites for graft copolymerization. For  $K_2S_2O_8$  initiator, it is soluble in an aqueous phase. The persulphate ion has been known as a strong oxidizing agent that can be used either alone or with activators. The reaction proceeds via a free radical mechanism involving the decomposition of persulphate ions to form sulphate radical ions when it is heated alone or in the presence of a reducing agent (Chansook, 2001).

The effect of initiator concentration in the range of 1-3 phr on the grafting properties of GNR such as %monomer conversion, %grafting efficiency (%GE), %graft copolymer, %free NR and %free poly(ST-co-ACN) (SAN) was shown in Table 4.1. The reaction was carried out under 2 bar of  $N_2$  pressure at  $70^\circ C$  for 6 h. The ST/ACN wt ratio was kept constant at 3/1. The comparison of the grafting properties obtained from 2 types of initiator: CHPO/TEPA and  $K_2S_2O_8$  was also reported. The results indicated that the grafting properties of GNR product in terms of %monomer conversion, %GE and %graft copolymer increased with increasing the initiator concentration up to 2 phr for both initiator types. Above this point, these grafting properties tended to be significantly decreased, while, unreacted NR and free copolymer increased. It could be explained that the overload of initiator gave excess radicals which possibly reacted together resulting to a faster rate of termination or primary termination.

**Table 4.1** Effects of initiator concentration, reaction temperature and N<sub>2</sub> pressure on grafting properties of (ST-co-ACN) graft onto NR structure by using graft polymerization

Entry	Initiator Type	Initiator Conc. (phr)	T. (°C)	P <sub>N<sub>2</sub></sub> (bar)	%Monomer conversion	%GE	Grafting Properties		
							%Graft Copolymer	%Free SAN	%Free NR
1	CHOP/TEPA	1	70	2	74.8	93.9	66.0	2.59	31.4
2		2	70	2	90.9	96.4	78.6	1.73	19.7
3		3	70	2	76.5	91.8	67.8	3.56	28.6
4		2	60	2	82.4	95.2	71.5	2.19	26.3
5		2	80	2	90.6	92.0	78.7	3.80	17.5
6		2	70	1	66.7	95.1	63.3	1.96	34.8
7		2	70	4	88.1	91.9	77.8	3.82	18.4
8		2	70	6	91.6	89.2	82.5	5.18	12.3
9	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1	70	2	76.0	95.0	67.0	2.15	30.8
10		2	70	2	89.6	95.2	77.8	2.29	19.9
11		3	70	2	65.6	96.9	58.7	1.22	40.1
12		2	60	2	84.7	97.1	73.5	1.33	25.2
13		2	80	2	82.2	82.1	71.2	8.06	20.7
14		2	70	1	67.2	94.6	63.8	2.16	34.0
15		2	70	4	85.0	92.6	75.5	3.40	21.1
16		2	70	6	84.8	92.3	75.0	3.53	21.5

For the effect of reaction temperature on the grafting properties, the reaction temperature was varied in the range of 60-80°C under 2 bar of N<sub>2</sub> pressure with constant initiator concentration and ST/ACN at 2 phr and 3/1 (by wt), respectively. The results showed that the increase in the reaction temperature from 60 to 70°C gave the higher %monomer conversion, %GE and %graft copolymer with decreasing the amount of free NR and free SAN for both initiator types. It could be described that the rate of initiator decomposition enhanced with increasing the reaction temperature resulting to produce higher content of free radicals. This could promote the rate of graft copolymerization. However, the initiator efficiency for grafting decreased with increasing reaction temperature up to 80°C resulting to the reduction of grafting efficiency with promoting the free SAN content.

Due to the low boiling point of ACN (77 °C), it is easily evaporated into the vapor phase in the reactor during graft copolymerization. In this study the graft copolymerization of ST and ACN onto NR was carried out under various N<sub>2</sub> pressure in the range of 1-6 bar at 70°C for 6 h with a constant initiator concentration and ST/ACN at 2 phr and 3/1 (by wt), respectively. It could be seen that the increase in the N<sub>2</sub> pressure from 1 to 2 bar enhanced the %monomer conversion, %GE and %graft copolymer with low levels of %free NR and %free SAN for both initiators. It could be explained that the use of N<sub>2</sub> pressure higher than atmospheric pressure for both initiators induced the increment of acrylonitrile content in the liquid phase (Prasassarakich et al., 2001). This increased the chance of monomer diffusion to react with NR structure resulting to the higher grafting yield. However, it was found that the GNR obtained from higher 2 bar of N<sub>2</sub> pressure had slightly higher %monomer conversion, %graft copolymer and %free SAN with lower content of free NR and %GE for CHPO/TEPA initiator. On the other hand, it was found that the GNR obtained from the graft copolymerization process initiated by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> under N<sub>2</sub> pressure higher than 2 bar had slightly lower %monomer conversion, %GE and % graft copolymer with higher content of free NR and free SAN. It is possible that side reactions such as chain transfer to monomer might compete to the grafting reaction. This implied that the homopolymerization or copolymerization of monomers could be highly promoted than graft copolymerization at higher N<sub>2</sub> pressure.

From these experiments, it could be concluded that the optimum condition for emulsion graft copolymerization of ST and ACN onto NR was obtained at 70°C under 2 bar of N<sub>2</sub> pressure with 2 phr of initiators concentration for 6 h. The CHPO/TEPA initiator gave slightly higher %monomer conversion (90.9%), %GE (96.4%) and %graft copolymer (78.6%) than K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as an initiator (89.6%, 95.2%, 77.8%, respectively). For the similar experiment and similar reaction conditions, Prasassarakich et al., (2001) studied graft copolymerization (ST/ACN=3/2) of ST and ACN onto NR latex. It was found that the 1/1 by wt of NR/monomers, 1.5 phr of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> under 2.4 bar of N<sub>2</sub> pressure and 70°C for 8 h gave the maximum %GE (58.2%) with 63.1% graft copolymer which was lower than that found in this present experiment. It might be described that the use of ST/ACN at 3/1 by wt which was close to the azeotropic point of copolymerization of ST with ACN was the appropriate

condition for yielding the higher %GE and %graft copolymer to 95.2% and 77.8%, respectively.

#### 4.1.2 Solution Method

Solution and bulk method are homogeneous processes; whereas, the emulsion polymerization is heterogeneous process. The solution polymerization in the presence of solvent had an advantage when it is compared to bulk polymerization because the solvent acts as a diluent to transfer heat generated during polymerization. The solvent also allows easier stirring since the viscosity of the reaction mixture is decreased. Moreover, the thermal control is much easier in the solution polymerization compared to the bulk polymerization (Odian, 2004). In this work, the graft copolymerization of ST and ACN onto NR was carried out by solution polymerization initiated by using BPO and AIBN. The influence of the polymerization conditions such as the type and concentration of initiator, reaction temperature and  $N_2$  pressure on the grafting properties of GNR was also investigated. However, the %monomer conversion and %GE of GNR could not be reported according to the difficulty to remove some sticky product residue inside the reactor.

Effect of reaction temperature in the range of 70-90°C on the grafting properties of GNR was shown in Table 4.2. The 0.3 M of NR dissolved in toluene was grafted with ST/ACN at 3/1 (by wt) under 2 bar of  $N_2$  pressure for 6 h. The detail of all data and calculation are shown in Appendix C. The results indicated that the %graft copolymer of GNR initiated by 5 phr of BPO at 80°C under 2 bar of  $N_2$  pressure was 75.8% as high as one obtained from the grafting process initiated by AIBN (77.3%). However, it was observed that the %graft copolymer of GNR produced from the process using BPO decreased with increasing the reaction temperature from 70 to 90°C. It could be explained that the higher reaction temperature promoted the dissociation of initiator resulting to the large amount of free radicals. This had possibility to recombine or to enhance the copolymerization of monomer to decrease %graft copolymer with higher content of unreacted NR and ST-co-ACN. For the use of AIBN as the initiator (3phr), it was found that the appropriate reaction temperature to produce GNR having high %graft copolymer (81.1%) was 80°C. This was the effective condition of AIBN to promote the grafting reaction.

Below this point (70°C, entry 15), the amount of SAN increased to 40.3%. This means the graft copolymerization was more difficult to be occurred than copolymerization of ST and ACN by using AIBN as the initiator. Thus, the grafting reaction required the higher reaction temperature to increase the higher grafting properties. On the other hand, the graft copolymerization at 90°C (entry 16) indicated very low value of %graft copolymer (0.53%) and %free SAN (0.65%) with high content of unreacted NR (98.8%) possibly due to the decomposition of AIBN radicals.

**Table 4.2** Effects of initiator concentration, reaction temperature and N<sub>2</sub> pressure on grafting properties of (ST-co-ACN) graft onto NR structure by using emulsion graft polymerization

Entry	Initiator Type	Initiator Conc. (phr)	Temp (°C)	P <sub>N<sub>2</sub></sub> (bar)	Grafting Properties		
					% Graft Copolymer	%Free SAN	%Free NR
1	BPO	1	70	2	61.0	0.54	38.5
2		5	70	2	85.1	0.56	14.4
3		10	70	2	80.5	0.84	18.7
4		15	70	2	79.7	1.32	19.0
5		20	70	2	53.0	17.8	29.2
6		5	80	2	75.8	3.41	20.8
7		5	90	2	67.9	10.8	21.3
8		5	70	1	37.1	7.45	55.5
9		5	70	4	82.8	2.98	14.3
10		5	70	6	70.6	4.96	24.4
11	AIBN	1	80	2	67.4	0.62	32.0
12		3	80	2	81.1	1.23	17.7
13		5	80	2	77.3	2.26	20.4
14		10	80	2	60.8	3.85	35.3
15		3	70	2	1.91	40.3	57.8
16		3	90	2	0.53	0.65	98.8
17		3	80	1	28.1	2.03	69.9
18		3	80	4	7.95	5.84	86.2
19		3	80	6	1.07	5.48	93.5

Effect of initiator concentration in the range of 1-20 phr for BPO and 1-7 phr for AIBN on the grafting properties of GNR was shown in Table 4.2. The 0.3 M of NR solution was grafted by ST/ACN monomer mixture at 3/1 by wt at 70°C for BPO and 80°C for AIBN for 6 h under 2 bar of N<sub>2</sub> pressure. The %grafted copolymer of GNR increased with increasing initiator concentration to reach maximum value at 85.1% and 81.1% for BPO (5 phr) and AIBN (3 phr), respectively. The increase in the initiator concentration above this point caused the reduction of %graft copolymer. This could be explained that the large amount of initiator radicals was produced at the higher initiator concentration to increase the number of active sites for grafting. However, the recombination of two radical chains was possibly occurred. Therefore, when initiator concentration was higher than 5 phr for BPO and 3 phr for AIBN, %graft copolymer decreased and the contents of %free NR and %free SAN increased.

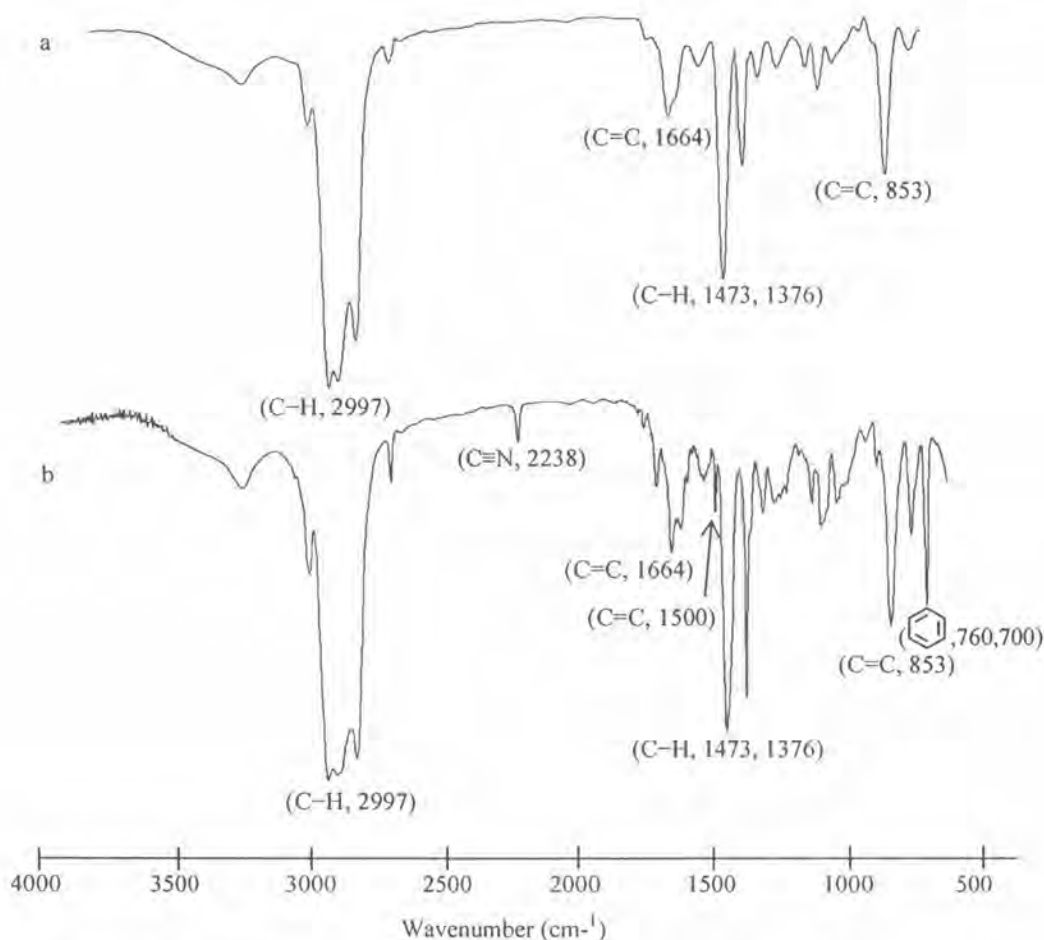
For the effect of N<sub>2</sub> pressure in the range of 1-6 bar at 70°C for BPO initiator and 80°C for AIBN with constant wt ratio ST/ACN at 3/1 for 6 h, the result showed that the increase in the N<sub>2</sub> pressure from 1 to 2 bar gave the higher %graft copolymer with lower content of free NR and free SAN for both initiator types. It could be explained that the solubility of ACN in the solution phase increased with increasing N<sub>2</sub> pressure because of the enhancement of boiling point of ACN phase. However, %graft copolymer decreased with higher %free NR and %free SAN when N<sub>2</sub> pressure was higher than 2 bar. It is possible that side reactions such as chain transfer to monomer might compete to the grafting reaction. This implied that the copolymerization of monomers could be highly promoted than graft copolymerization at higher N<sub>2</sub> pressure.

To compare the grafting potential between BPO and AIBN, the optimum condition of both initiators was carried out under 2 bar of N<sub>2</sub> pressure at 70 °C with 5 phr for BPO initiator and 80 °C with 3 phr for AIBN initiator. It can be seen that BPO gave the higher %graft copolymer (85.1%) than AIBN (81.1%) because BPO could generate the comparatively higher radical reactivity than AIBN (Huang and Sondberg, 1995).

## 4.2 Characterization of Structure and Composition of NR-g-(ST-co-ACN)

### 4.2.1 Structure Characterization

The structure of NR-g-(ST-co-ACN) obtained after soxhlet extraction of GNR was confirmed using FTIR spectroscopy. The FTIR spectra of NR and the NR-g-(ST-co-ACN) are shown in Figure 4.1. The FTIR spectra of NR exhibited the characteristic absorption bands of C=C stretching vibration at  $1664\text{ cm}^{-1}$ , C-H vibration at  $2997$ ,  $1473$  and  $1376\text{ cm}^{-1}$  and C=C bending vibration at  $853\text{ cm}^{-1}$ . The new signals of NR-g-(ST-co-ACN) appeared at  $2238\text{ cm}^{-1}$  attributed to the stretching vibration of C≡N group, C=C stretching vibration of the benzene ring of styrene at  $1500\text{ cm}^{-1}$  and characteristic peaks of monosubstituted benzyl ring were also observed at  $760$  and  $700\text{ cm}^{-1}$ . These confirmed that ST and ACN were grafted onto NR backbone. The similar results were also reported by Prasassarakich et al. (2001).



**Figure 4.1** FTIR spectra of (a) NR and (b) NR-g-(ST-co-ACN).



Figure 4.2 shows a comparison of NR and NR-*g*-(ST-*co*-ACN) structure evaluated by using  $^1\text{H-NMR}$  spectroscopy. Figure 4.2 (a) presents the  $^1\text{H-NMR}$  spectrum of NR which shows the important signals at 1.66 ppm ( $-\text{CH}_3$ ), 2.0 ppm ( $-\text{CH}_2-$ ) and 5.1 ppm (olefinic proton). After graft copolymerization, the new signals at 1.25-3.20 ppm defined as the overlap signals consisting of methylene and methane protons obtained from ST and ACN were appeared as shown in Figure 4.2 (b). It was also observed the peaks at 6.4-7.5 ppm which was noted as aromatic protons of ST in NR-*g*-(ST-*co*-ACN). To confirm FTIR and  $^1\text{H-NMR}$  results,  $^{13}\text{C-NMR}$  spectroscopic technique was also used to analyze the structure of NR and NR-*g*-(ST-*co*-ACN) as illustrated in Figure 4.3. Figure 4.3 (b) indicated the reduction of peak intensity of olefinic carbons (135.5 and 125.1 ppm) after graft copolymerization, while the new signals in NR-*g*-(ST-*co*-ACN) structure appeared at 119.5 ppm and 30.6 ppm which were attributed to  $-\text{CN}$  and carbon at polymer backbone bounded to  $-\text{CN}$ , respectively.

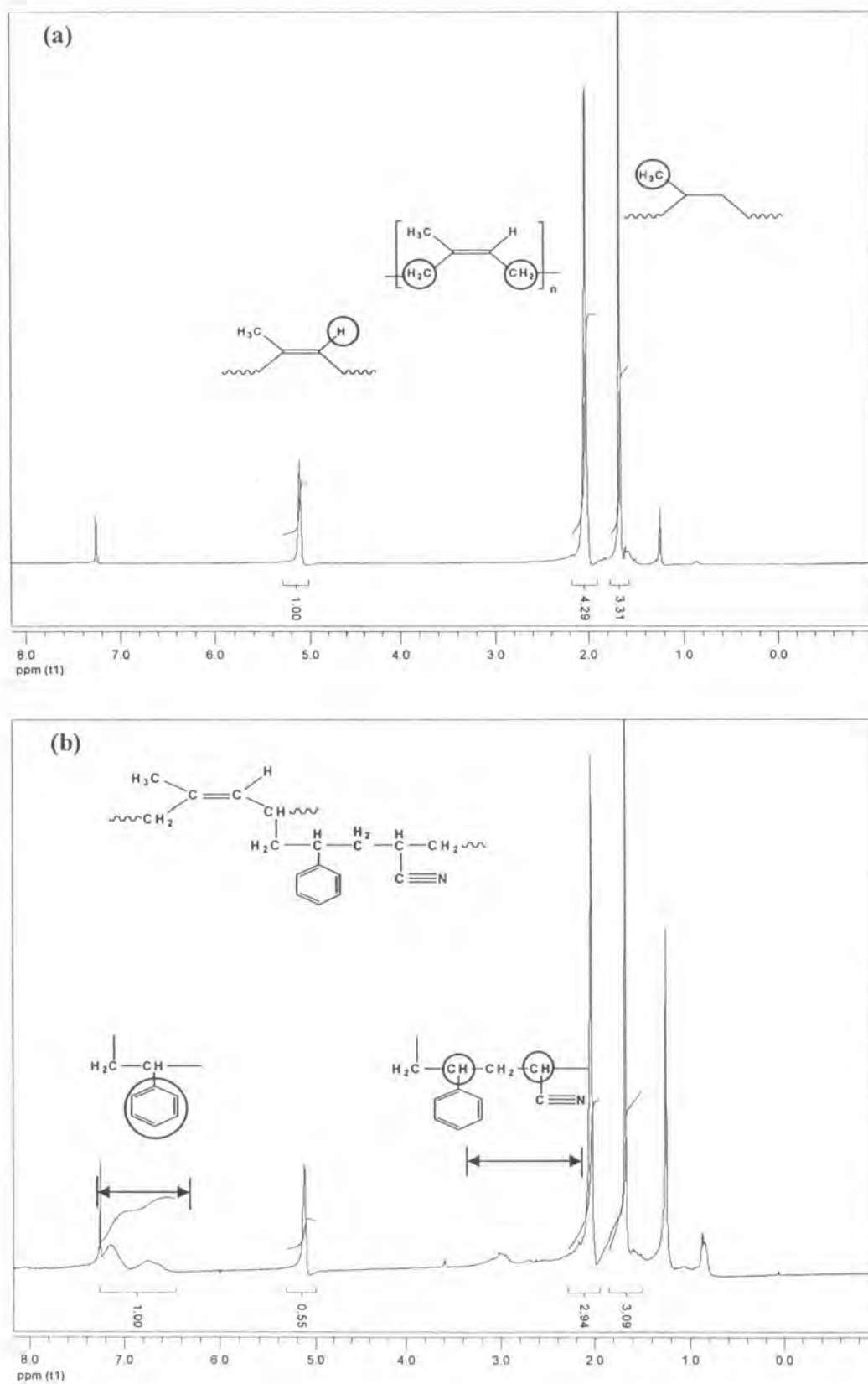


Figure 4.2  $^1\text{H-NMR}$  spectra of (a) NR and (b) NR-g-(ST-co-ACN).

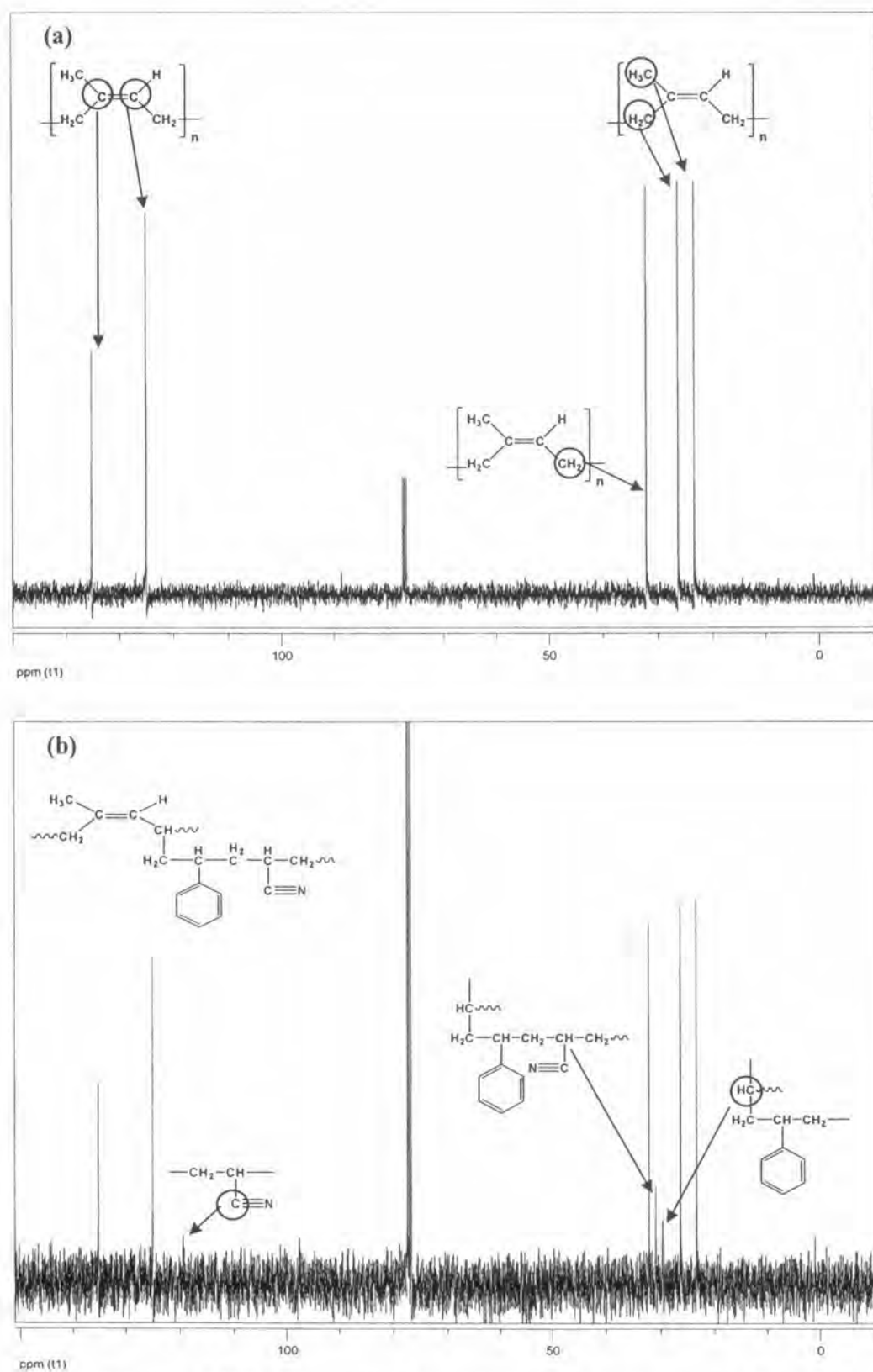


Figure 4.3  $^{13}\text{C}$ -NMR spectra of (a) NR and (b) NR-g-(ST-co-ACN).

#### 4.2.2 Determination of Composition of graft copolymer

The composition of NR-*g*-(ST-*co*-ACN) could be reported as the percentage of ST, ACN and isoprene by using CHN analyzer. The ratio of ST, ACN and isoprene monomers (ST/ACN/isoprene) were calculated by using the number of mole according to C, H and N in NR-*g*-(ST-*co*-ACN) obtained after soxhlet extraction. The effects of initiator concentration, reaction temperature and N<sub>2</sub> pressure on the amount of composition in NR-*g*-(ST-*co*-ACN) obtained from the solution graft copolymerization initiated by BPO were shown in Table 4.3. The details of all data and calculation were indicated in Appendix D.

It was found that contents of ST and ACN were maximum at 4.44 and 14.3 mole%, respectively when the graft copolymerization was initiated by 5 phr of BPO at 70°C under 2 bar of N<sub>2</sub> pressure for 6 h. When initiator concentration increased higher than 5 phr, the contents of ST and ACN tended to be decreased with higher amount of isoprene in the resulting graft copolymer due to the recombination effect of free radicals. This could inhibit the production of graft product as previously described in the section 4.1.2.

For the effect of reaction temperature when the initiator concentration was kept at 5 phr under 2 bar of N<sub>2</sub> pressure for 6 h, the amount of ACN increased from 4.44 mole% to 4.85 mole% when the reaction temperature was risen from 70 to 90°C. However, it was observed that ST content in NR-*g*-(ST-*co*-ACN) decreased from 14.3 mole% to 3.30 mole%. This was possible that ACN had more difficulty to graft onto NR structure compared to ST due to the highly different polarity between ACN and NR. Thus, the operating condition with higher reaction temperature was required to achieve the higher amount of ACN in NR-*g*-(ST-*co*-ACN). However, the increase in the reaction temperature decreased the grafting efficiency which could be observed from the enhancement of isoprene content related to unreacted NR and the reduction of ST content in NR-*g*-(ST-*co*-ACN). This could be explained that the higher reaction temperature could promote the decomposition of initiator. The free radicals underwent either recombination or other side reactions such as chain transfer reaction; the initiator efficiency for grafting was reduced at higher temperature as described in the previous section 4.1.2.

For the effect of N<sub>2</sub> pressure at 5 phr of initiator concentration and 70°C for 6 h, the results indicated that the increase in N<sub>2</sub> pressure from 1 to 2 bar gave the higher contents of ACN (4.44 mole%) and ST (14.3 mole%) with lowest value of isoprene (81.2 mole%). This might be described that the higher N<sub>2</sub> pressure could inhibit the evaporation rate of monomer at a given reaction temperature. However, the use of higher N<sub>2</sub> pressure than 2 bar caused the reduction of ACN and ST contents in the GNR structure. This indicated that the copolymerization of monomer could be highly promoted than graft polymerization at high pressure.

**Table 4.3** Effect of reaction parameters on the content of ACN, ST and isoprene in NR-g-(ST-co-ACN) obtained from solution method initiated by BPO

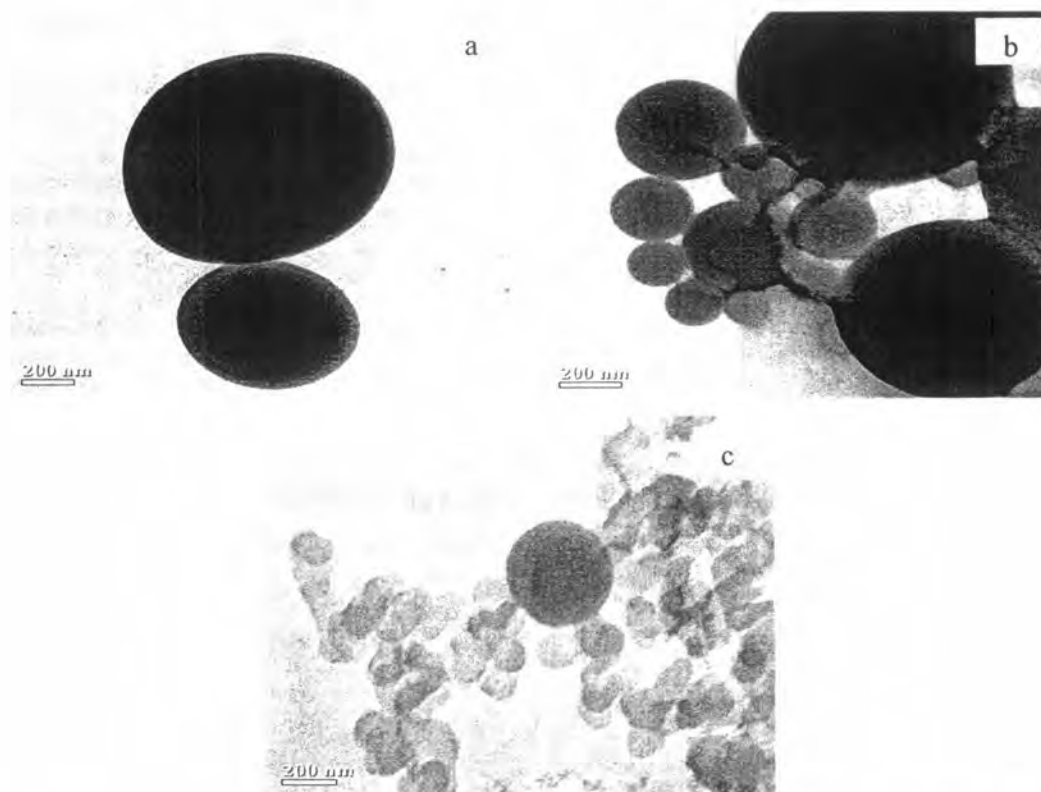
Entry	BPO concentration (phr)	Temp. (°C)	N <sub>2</sub> Pressure (bar)	ACN (mole%)	ST (mole%)	Isoprene (mole%)
1	1	70	2	1.62 (0.35)*	3.83 (0.43)	94.6(0.08)
2	5	70	2	4.44 (0.08)	14.3 (0.01)	81.2(0.06)
3	10	70	2	3.33 (0.19)	13.0 (0.69)	83.7(0.49)
4	15	70	2	3.52 (0.07)	7.66 (0.38)	88.8(0.31)
5	20	70	2	3.51 (0.00)	6.54 (0.08)	90.0(0.08)
6	5	80	2	3.96 (0.13)	8.50 (0.16)	87.5(0.28)
7	5	90	2	4.85 (1.59)	3.30 (0.91)	91.9(2.50)
8	5	70	1	1.97 (0.31)	1.57 (1.35)	96.5(1.05)
9	5	70	4	2.80 (0.97)	6.10 (0.52)	91.1(1.48)
10	5	70	6	2.45 (0.11)	6.18 (0.33)	91.4(0.22)

\*The standard deviation is in a parenthesis

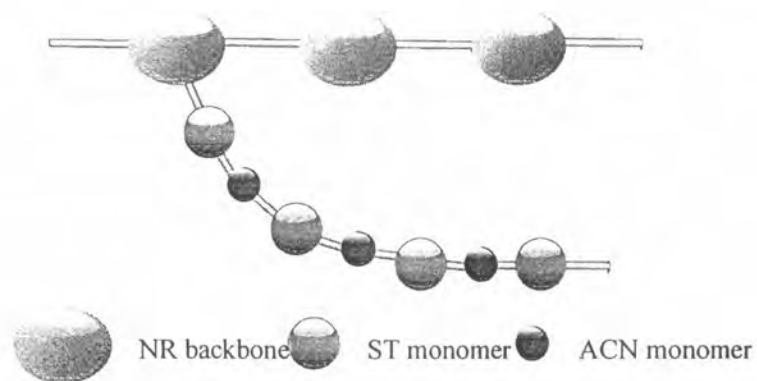
### 4.2.3 Transmission Electron Micrographs (TEM)

The emulsion graft copolymerization of ST and ACN onto NR was a core-shell type emulsion polymerization. The GNR particles consist of NR core and the compatibilized ST/ACN shell. During polymerization, backbone of polymer molecules would be encapsulated with applied polymer molecules. Figure 4.4 show TEM micrographs of GNR latex particles from different initiator types. The darker area represented the NR core regions, while the lighter area was ST/ACN films as shell. Figure 4.4(a) shows the surface of NR latex and Figure 4.4(b) shows the surface of the GNR latex particles initiated by CHPO/TEPM. This exhibited the presence of modules of many poly(ST-*co*-ACN) particles on the surface of the NR particles. This was due to the growing macroradical chains, which were grafted onto the surface of the NR particles and then propagated to form the shell layer. The large amount of grafting polymer molecules appeared on the surface of the rubber particle. On the other hand, Figure 4.4(c) shows the surfaces of GNR latex initiated by  $K_2S_2O_8$  bounded to the ST-*co*-ACN polymer chain. Most of ST and ACN monomers were polymerized on the microdomain at the surface layer of NR particles because the physical partitioning of the initiator radicals between the polymer (NR) and aqueous phase may contribute a significant difference to the surface morphology as previously described in the Kochthongrasamee, et al., 2006.

The graft of the second monomer onto polyisoprene may be induced in two ways. The first method is through a graft-site initiation, where the radicals derived from initiator either add to the double bond or abstract hydrogen atom from the polyisoprene backbone (Kochthongrasamee et al., 2006). For the comparison of the reactivity ratio between ST and ACN ( $r_{ST} = 0.4$  and  $r_{ACN} = 0.04$ ) (Immergutand and Brandrup, 1989), the styryl radicals have higher reactivity than ACN radicals. Moreover, ACN had more difficulty to graft onto NR structure compared to ST due to the highly different polarity between ACN and NR. Thus, ST was expected to react first with NR macroradicals and then the resulting styryl radicals copolymerized with ACN. The model of NR-*g*-(ST-*co*-ACN) is presented in Figure 4.5.



**Figure 4.4** TEM micrographs of (a) NR latex particles; (b) GNR latex particle (78.7% graft copolymer) initiated by CHPO/TEPA and (c) GNR latex particles (77.8 % graft copolymer) initiated by  $K_2S_2O_8$ .



**Figure 4.5** Model of graft copolymer of ST and ACN on NR backbone.

### 4.3 Utilization of GNR as Compatibilizer for NR/NBR Blends

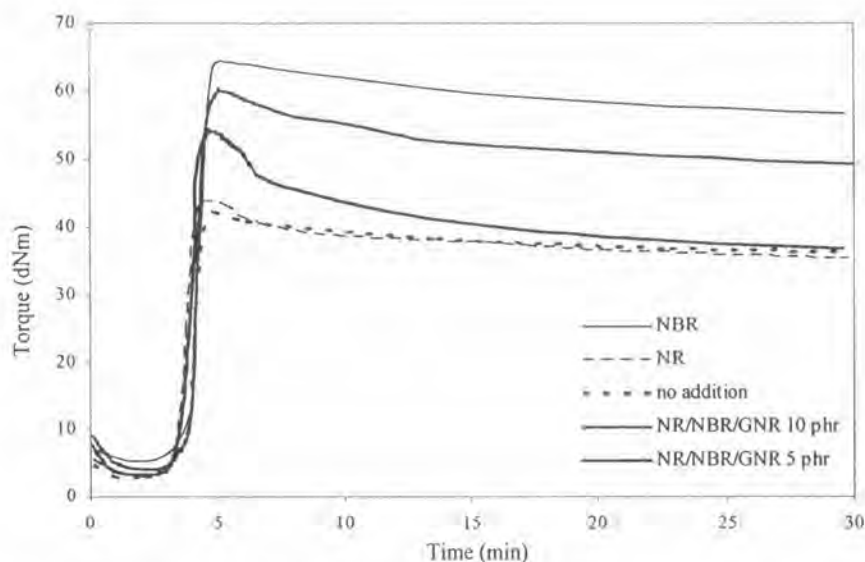
#### 4.3.1 Cure Characteristics

The effect of the addition of GNR (53-85% graft copolymer) obtained from solution graft copolymerization of ST and ACN onto NR initiated by BPO on vulcanization properties of NR/NBR blends was investigated. The GNR was loaded into NR/NBR blends at 50/50 wt% in the range of 0-20 phr. The vulcanization characteristics of the blends are summarized in Table 4.4 and Figure 4.6.

**Table 4.4** Effect of the addition of GNR on vulcanization properties of NR/NBR blends (50/50 wt%)

Sample	Content of GNR (phr)	% Graft copolymer	Minimum torque (ML,dNm)	Maximum torque (MH, dNm)	Scorch time (t <sub>s2</sub> ,min)	Optimum cure time (t <sub>c90</sub> ,min)
NR	-	-	3.34	42.1	3.21	4.21
NBR	-	-	5.13	64.3	3.42	4.75
NR/NBR	-	-	2.90	42.7	3.42	4.50
	10	53	2.38	41.5	3.50	4.38
	10	70	3.20	42.9	3.54	4.63
	10	76	3.27	44.1	3.29	4.33
	10	85	4.38	59.8	3.67	4.75
NR/NBR	-	-	2.90	42.7	3.43	4.50
	5	85	3.49	54.3	3.30	4.38
	10	85	4.38	59.8	3.67	4.75
	15	85	3.90	51.4	3.04	4.21
	20	85	3.86	43.6	3.17	4.17





**Figure 4.6** Effect of the addition of GNR (85% graft copolymer) on the rheographic profiles of vulcanized NR/NBR blends at 50/50 wt% obtained from ODR at 150°C.

The results showed that the NR blend had the minimum (3.34 dNm) and maximum torques (42.1dNm) lower than NBR blend due to the faster vulcanization rate of NR than that of NBR. This was caused from the reactivity difference between isoprene and butadiene units as well as the degree of unsaturation (Ismail et al., 1999). For NR/NBR blends, it could be observed that the minimum and maximum torques of the blends containing GNR were higher than that of ones without the addition of GNR. The minimum and maximum torques of the blends with GNR also increased with increasing %graft copolymer in the GNR when the content of GNR added into the blends was kept constant at 10 phr. This indicated that the GNR possibly enhanced the compatibility between NR and NBR in the blends. Thus, the main role of the graft copolymer is to act as an interfacial agent for reducing the interfacial tension between the different rubber phases and it may facilitate the interaction of the rubbers (Paul, 1987 cited in Oommen et al., 2000). However, it was found that the minimum and maximum torques of the blends tended to be decreased with increasing the content of GNR (85% graft copolymer) higher than 10 phr in the blends. It could be explained that the higher content of GNR with high level of %graft copolymer could promote the phase separation of the blends containing elastomers with highly different polarity since the GNR with the large amount of ACN was more compatible to the highly polar rubber phase.

For the scorch time and optimum cure time of NR/NBR blends, the results showed that the scorch time and optimum cure time of NR blend were slightly shorter than that of NBR. This could be implied that NR had slightly faster vulcanization rate than NBR. This was possible to promote the incompatibility in NR/NBR blends as high as the effect of dissimilar polarity of these rubbers. However, the results obtained from ODR indicated that the addition of GNR in the NR/NBR did not significantly affected the scorch time and optimum cure time of NR/NBR blends.

#### **4.3.2 Mechanical Properties of NR/NBR Vulcanizates Containing GNR**

Mechanical properties of NR/NBR vulcanizates at 50/50 wt% compatibilized by the addition of GNR (5-20 phr) with various %graft copolymer in the range of 53-85% were investigated. The mechanical properties of the blends are shown in Table 4.5.

It was found that the NR vulcanizate exhibited the higher tensile strength (19.9 MPa) and ultimate elongation (730%) than NBR vulcanizate due to the strain-induced crystallization property of NR. Thus, it was expected that the blend of NBR with NR could enhance the mechanical properties of NBR with increasing the oil resistance property of NR phase. However, the NR/NBR vulcanizate showed the low value of tensile strength (4.70 MPa) and ultimate elongation (364%) due to the dissimilarity of polarity of both rubbers. NBR is the rubber with higher polarity than NR which is defined as a non-polar elastomer. Therefore, the rubber phase separation could be occurred during vulcanization. The materials produced from NR functionalized by polar functional groups via graft copolymerization have been well known to be used as compatibilizers for the blends containing elastomers with highly different polarity. The experimental results from Table 4.5 showed that the addition of GNR synthesized from graft copolymerization of ST and ACN onto NR was effective compatibilizers for improving the mechanical properties of NR/NBR vulcanizates. It indicated that the blends containing the same content of the GNR with higher %graft copolymer had the greater mechanical properties.

**Table 4.5** Effect of % grafted copolymer and GNR content (phr) on the mechanical properties and volume fraction of NR/NBR (50/50 by wt) blends

Rubber blends	GNR content (phr)	% Graft copolymer	Tensile strength (MPa)	Ultimate elongation (%)	Hardness	Volume fraction ( $V_r$ )
NR	-	-	19.9(1.5)*	730 (17)	45.3 (0.8)	0.24(0.0)
NBR	-	-	2.82 (0.2)	326 (10)	55.1 (0.4)	0.32(0.01)
NR/NBR	-	-	4.70 (0.5)	364 (21)	41.0 (0.9)	0.25(0.01)
	10	53	10.2 (0.2)	641 (22)	41.5 (0.0)	0.26(0.01)
	10	70	11.4 (0.9)	610 (12)	41.9 (0.3)	0.28(0.01)
	10	76	12.1 (0.1)	604 (37)	42.3 (0.3)	0.29(0.01)
	10	85	12.1 (1.6)	540 (27)	42.5 (0.4)	0.30(0.01)
NR/NBR	-	-	4.70 (0.5)	364 (21)	41.0 (0.9)	0.25(0.01)
	5	85	12.0 (0.3)	590 (7.3)	42.0(0.4)	0.29(0.0)
	10	85	12.1 (1.6)	540 (27)	42.5 (0.4)	0.30(0.01)
	15	85	11.0 (0.3)	668 (28)	41.5(0.8)	0.28(0.01)
	20	85	10.6 (0.1)	666 (27)	40.5 (0.3)	0.26(0.01)

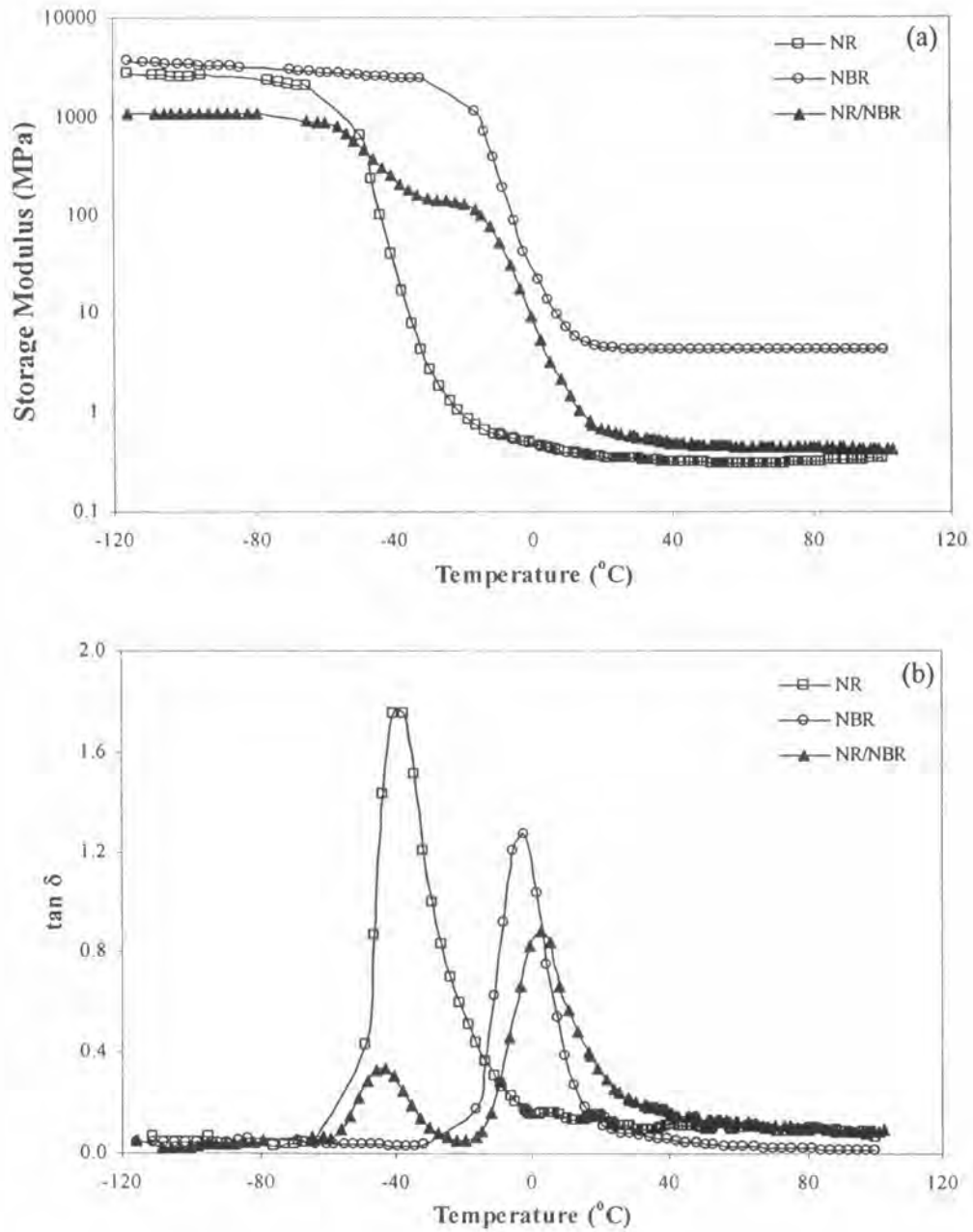
\*The standard deviation is in a parenthesis

The tensile strength of the vulcanizates increased from 4.70 MPa to 12.1MPa when %graft copolymer in GNR was in the range of 76-85%. The ultimate elongation of NR/NBR vulcanizates compatilized by GNR was also higher than that of ones without the addition of compatibilizers due to the higher compatibility of NR/NBR blends by the adding GNR. When the %graft copolymer in GNR was kept constant at 85%, the increase in the content of GNR decreased the tensile strength and hardness with increasing the ultimate elongation of the NR/NBR vulcanizates. This might be due to the effect of the excessive crosslink density of the blends or the effect of interfacial saturation. The similar results were also reported by Thomas et al. (1992, cited in Suriyachai et al., 2004).

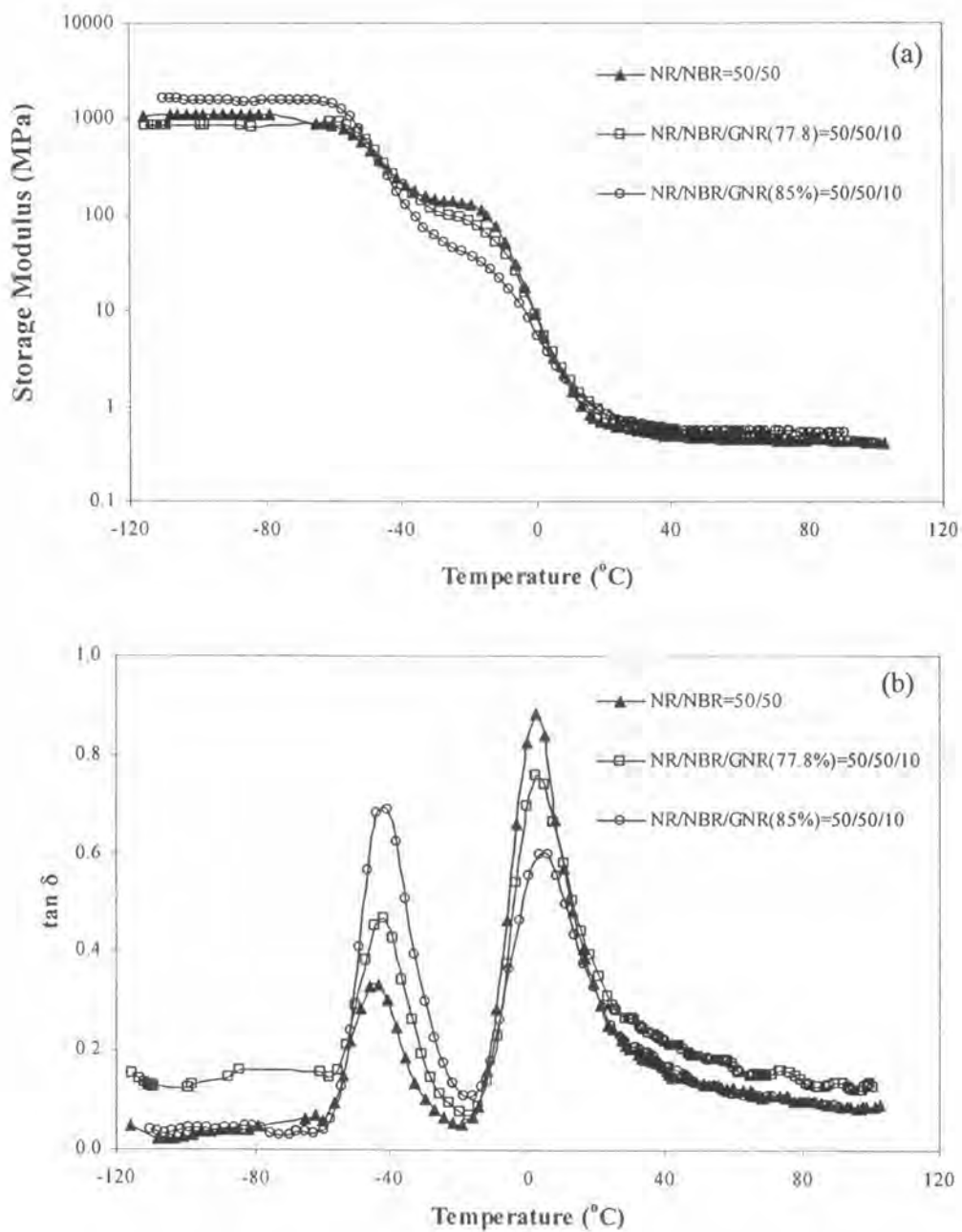
### 4.3.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) is a measurement to determine the elastic modulus of a material and its mechanical damping or energy dissipation characteristics as a function of frequency and temperature (Stuart, 2002). A specimen is subjected to some kind of cyclic deformation over a temperature or time scan. Various deformations can be used such as compressive, flexure, tension, torsion or bending. A sinusoidal stress introduced into the materials results in a sinusoidal deformation response which refers to dynamic storage or elastic modulus ( $E'$ ) and dynamic loss or viscous modulus ( $E''$ ).  $E'$  means the energy stored and recovered during each cycle and it also indicates the stiffness of the material.  $E''$  or damping factor or loss factor is related to energy dissipation in the system per cycle. It indicates the impact strength or ability of the system to absorb energy. Another factor called the loss angle is  $\tan \delta$  determined from  $E''/E'$  (Cheremisinoff, ed., 1993).

In this work, the dynamic mechanical properties of NR/NBR vulcanizates (50/50 by wt) with and without the addition of GNR prepared from graft copolymerization of ST and ACN onto NR were evaluated using tension mode of deformation over a temperature range of -100 to 100 °C at a heating rate of 5 °C/min and a frequency of 1 Hz. Figure 4.7(a) and 4.8(1) show the temperature dependence of storage modulus of NR, NBR and NR/NBR vulcanizates with and without the addition of GNR, respectively. The results indicated that the storage modulus of all samples decreased with increasing temperature. This phenomenon appeared around the transition region because of the increasing mobility of polymer chain when the temperature increased (Da Costa et al., 2002). From the storage modulus curve in Figure 4.7(a), it was also observed that the storage of NBR was greater than that of NR at high temperature due to high stiffness of NBR on account of high  $T_g$ .



**Figure 4.7** Temperature dependence of (a) the storage modulus ( $E'$ ) and (b) the loss tangent ( $\tan \delta$ ) for NR, NBR and NR/NBR vulcanizates without the addition of GNR as the compatibilizers.



**Figure 4.8** Temperature dependence of (a) the storage modulus ( $E'$ ) and (b) the loss tangent ( $\tan \delta$ ) for NR/NBR blends at a ratio of 50/50 wt% with and without the addition of 10 phr of GNR.

The exact value of glass transition temperature ( $T_g$ ) obtained from DMA technique can be evaluated from the onset of a sharp reduction in storage modulus if a plateau in the storage modulus before  $T_g$  is well defined. However, it is difficult to determine for some materials which have a broad region of storage modulus decline. Alternatively, the peak of either the loss modulus or  $\tan \delta$  may be used to evaluate  $T_g$  of polymers; especially, the onset in the increase in the  $\tan \delta$  is a good representative for the beginning of the change in the viscoelastic balance within the polymer system (Morrison cited in Cheremisinoff, ed., 1993). Figure 4.7(b) and 4.8(b) show the dependence of the damping characteristics, measured from the  $\tan \delta$  as a function of temperature. It can be seen that  $\tan \delta$  is very low at sufficiently low temperature because the viscosity of rubbers is so high; thus, the movement of the polymer segment and the adjustment of their relative position can hardly take place during the dynamic experiment. When the temperature increased, the damping curve goes through a maximum and then decreased. The maximum point of damping or  $\tan \delta$  indicates  $T_g$ , where the viscosity of the polymer rapidly decreases and molecular adjustments take place more easily so that elastic modulus is decreased (Da Costa et al., 2002). The  $\tan \delta$  curve of NR (Figure 4.7(b)) shows a peak at  $-40^\circ\text{C}$  due to the a transition arising from the segmental motion. This corresponded to the  $T_g$  of NR, while NBR showed  $T_g$  at  $-3.1^\circ\text{C}$ . The  $\tan \delta$  uncompatibilized at 50/50 wt% NR/NBR blends shown in Figure 4.7(b) indicated two distinct transitions to support the strongly incompatible nature of these.

Figure 4.8(a) represents the storage modulus of NR/NBR vulcanizates at 50/50 wt%, the addition of 10 phr of 77.8 and 85.0% graft copolymer at 10 phr as a function of temperature at a frequency of 1 Hz. At the plateau region ( $> 40^\circ\text{C}$ )  $E'$  curves after the transition zone exhibits the crosslink density of polymers (Soni 1991, cited in Cheremisinoff, ed., 1993). The storage modulus in the plateau region at  $80^\circ\text{C}$  of NBR as reported in Table 4.6 was higher than that of NR. It means that NBR has a higher crosslink density than NR and NR/NBR blends.  $E'$  of NR/NBR vulcanizates compatibilized by GNR was also higher than that of one without the addition of GNR. This was due to the formation of higher crosslink density in the blends by using GNR. From Figure 4.8(b), it clearly showed the separated peaks resulted from NR and NBR phased. This means that the addition of the compatibilizers could not promote the reactive compatibilization or molecular level miscibility to generate the single phase of

**Table 4.6** Glass transition temperature and  $\tan \delta$  of NR/NBR vulcanizates with addition of 10 phr of GNR.

Materials	$T_g$ (°C)		Tan $\delta$ at $T_g$		$E'$ at 80°C (MPa)
	NR	NBR	NR	NBR	
NR	-40.0	-	1.77	-	0.32
NBR	-	-3.10	-	1.27	4.34
NR/NBR	-45.2	1.70	0.34	0.88	0.44
NR/NBR (77.8% graft copolymer)	-42.7	2.90	0.47	0.76	0.45
NR/NBR (85% graft copolymer)	-42.3	3.70	0.69	0.60	0.55

rubber blends. This agrees with the conclusions made by Paul (1987 cited in Oommen et al., 2000) who suggested that if two polymers are far from being miscible, then, no copolymer is likely to make the system in single phase. In a completely immiscible system, the main role of the graft copolymer is the interfacial agent to decrease the interfacial tension between the rubbers. With the addition of the GNR, the  $T_g$  values of both rubbers slightly shifted to higher temperature. It was possible that GNR induce more physical crosslink. Due to the balance of properties in the blends, it caused the increase in the loss modulus of NR phase with increasing %graft copolymer whereas the loss modulus of NBR decreased. Thus, the  $\tan \delta$  values of NR increased with increasing in %graft copolymer; while, the  $\tan \delta$  values of NBR decreased. This could be implied that the compatibility of NR/NBR blends increased via the addition of GNR.

#### 4.3.4 Oil Resistance of NR/NBR Vulcanizates Compatibilized by GNR

Swelling measurements in the presence of IRM 903 oil was applied to NR/NBR vulcanizates with and without the addition of GNR. The %change in mass of the vulcanizates after immersion in IRM 903 oil at room temperature for 70 h was presented in Table 4.7.



**Table 4.7** Effect of %graft copolymer and GNR content on oil resistance of NR/NBR vulcanizates at 50/50 wt%

Sample	GNR Content (phr)	% Graft copolymer	% Swelling
NR	-	-	152.2 (5.9)*
NBR	-	-	3.520 (0.1)
NR/NBR	-	-	114.7 (8.7)
	10	53	93.23 (23)
	10	70	84.08 (18)
	10	76	72.23 (2.2)
	10	85	69.45 (6.2)
NR/NBR	-	-	114.7 (8.7)
	5	85	80.59 (0.0)
	10	85	69.45 (6.2)
	15	85	90.17 (13)
	20	85	96.26 (1.1)

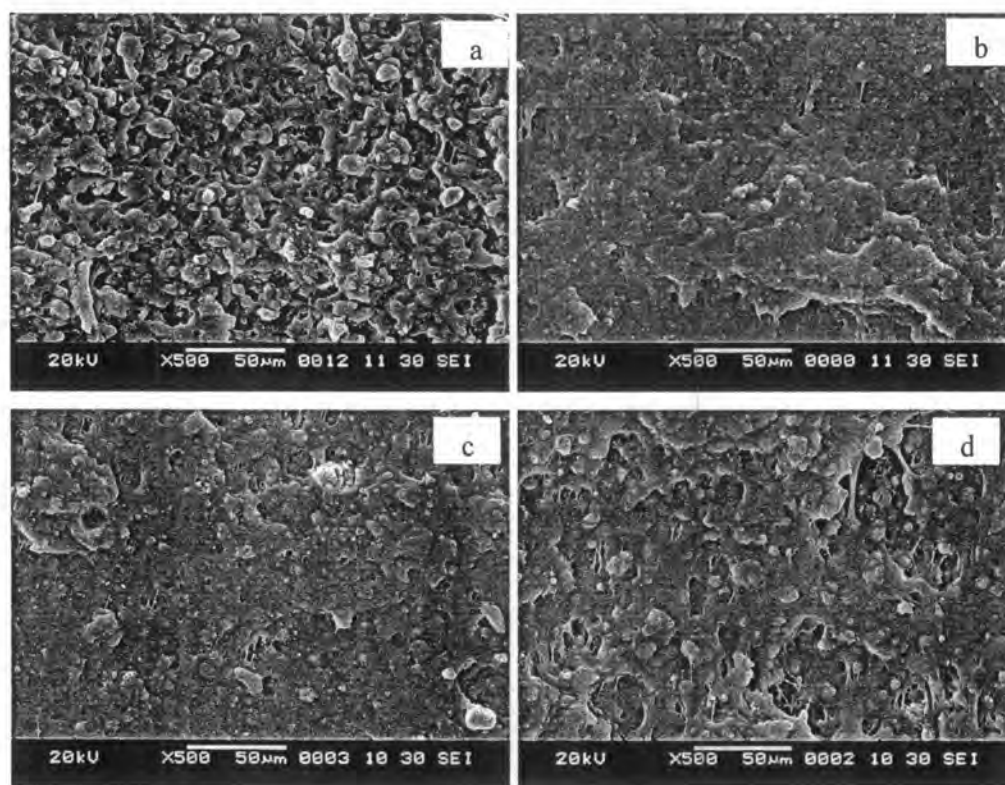
\*The standard deviation is in a parenthesis.

The oil resistance of special rubbers mainly originates from their polarity. Thus, the oil resistance of rubbers is expected to increase with increasing the polarity of them (Ismail et al., 2002). In this experiment, NBR had an excellent oil resistance property due to the presence of nitrile group in its structure. Conversely, NR is a non-polar rubber which is easily dissolved in oil or non-polar solvents. Thus, the % swelling of NR vulcanizate (152.2%) was greater than that of NBR vulcanizate (3.60%). For NR/NBR vulcanizates at 50/50 wt%, the % swelling of the vulcanizate without the addition of the GNR was still high (114.7%). This means that this blend could not stand in the presence of oil; although, it contained the amount of NBR which is the polar rubber. The addition of 10 phr of GNR into the blend exhibited the higher oil resistance with increasing %graft copolymer in the GNR. This indicated that the addition of the GNR not only enhanced the mechanical properties of the NR/NBR vulcanizates by increasing the crosslink as shown in Table 4.7, it also acts as the oil resistance improver for these blends. However, it was found that the addition of the GNR at 85 %graft copolymer higher than 10 phr caused the reduction

of oil resistance of the vulcanizates due to the higher NR content in the GNR and the loss of the compatibility.

#### 4.3.5 Scanning Electron Microscope (SEM)

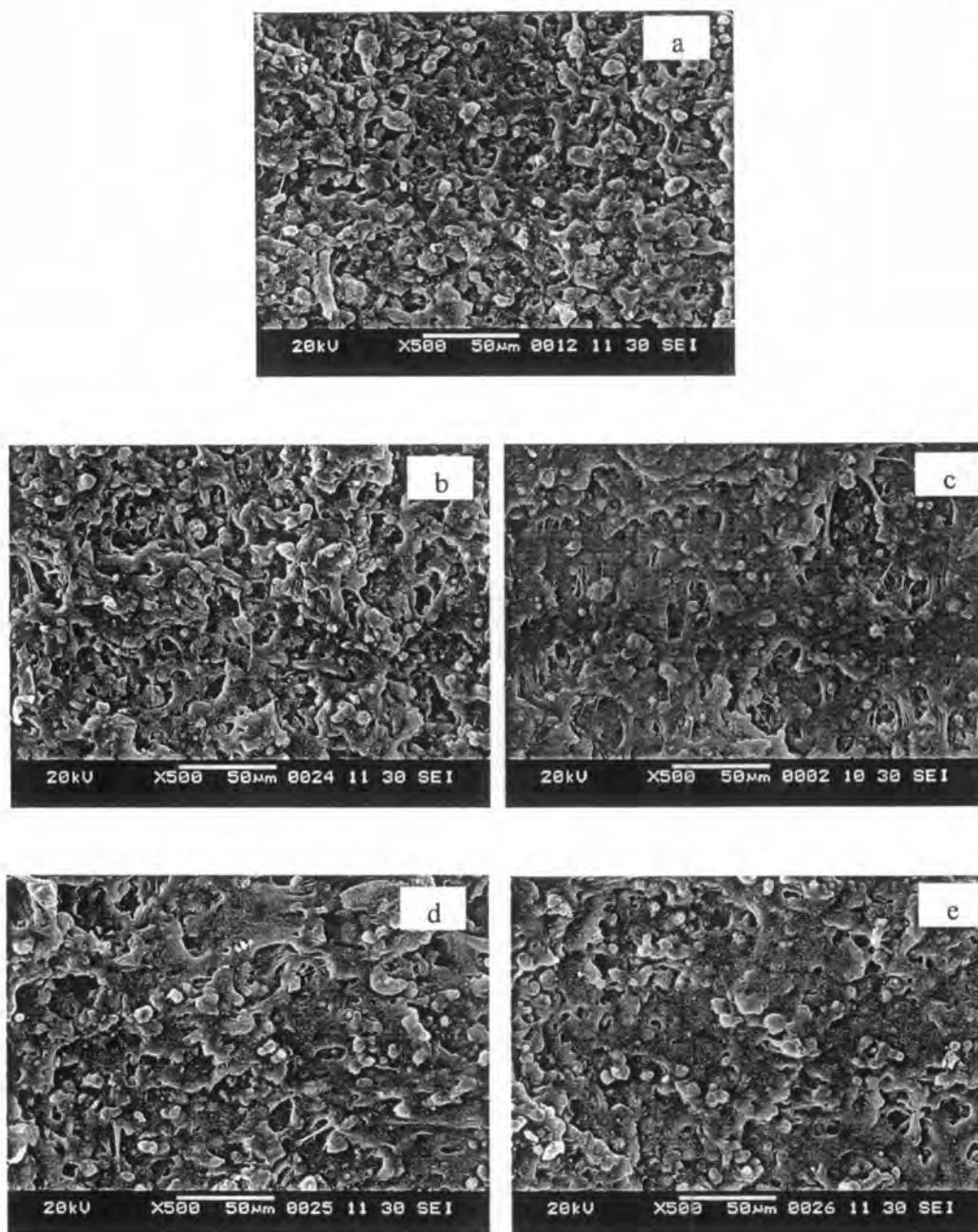
The SEM was used to investigate the fracture surface of NR/NBR specimens at 50/50 wt% obtained from the tensile properties test. The morphology of the blend surfaces with and without the addition of GNR as the compatibilizers was shown in Figure 4.9. It indicated that the NR/NBR vulcanizates without the addition of GNR compatibilizers showed a rubber phase separation (Figure 4.9a).



**Figure 4.9** SEM micrographs of the tensile fracture surface of NR/NBR vulcanizates at 50/50 wt% (a) without the addition of the GNR compared to the blends containing 10 phr of the GNR with various % graft copolymer : (b) 53%; (c) 76% and (d) 85%.

This behavior refers to the poor interfacial adhesion between NR and NBR phase due to the dissimilar polarity resulting to the incompatibilization. Generally, the polymer showing a lower viscosity tends to be the continuous phase in rubber blends. Therefore, NR possibly acted as the continuous phase, whereas NBR became the dispersed phase because of the lower viscosity of NR during mastication in mixing process (Nah et al., 2002). After blending with the GNR containing 53% and 75% graft copolymer, there were no phase separation appeared on the tensile fracture surfaces of NR/NBR vulcanizates as presented in Figure 4.9(b) and 4.9(c). It could be concluded that the GNR having CN groups was the effective compatibilizer for NR/NBR blends to improve the interfacial adhesion and permit the finer dispersion resulting the better mechanical properties as described in the previous section. However, it was noticed that the addition of GNR with 85% graft copolymer at 10 phr showed the reduction of homogeneity of the rubber matrix possibly due to the imbalance of polarity in the blends to cause the formation of rubber phase separation (Figure 4.9d).

At the constant 85% graft copolymer in the GNR, it was found that the tensile fracture surface of NR/NBR vulcanizates became more homogenous when the amount of GNR increased from 5-15 phr due to the higher compatibility as shown in Figure 4.10 (b)-(d). However, the increase in the content of GNR above 15 phr caused the higher heterogeneity of the rubber matrix (Figure 4.10 (e)) to decrease the mechanical properties of the NR/NBR vulcanizates.



**Figure 4.10** SEM micrographs of the tensile fracture surface of NR/NBR vulcanizates at 50/50 wt% (a) without the addition of the GNR compared to the blends containing the GNR with 85% graft copolymer at : (b) 5 phr; (c) 10 phr; (d) 15 phr and (e) 20 phr.