CHAPTER IV

RESULTS AND DISCUSSION

4.1 Modification of HNR via Addition of Thioacetate and Mercapto Functional Groups

The functionalization of thiols to olefinic double bonds has been known several decades. The thiol addition can be carried out in a solution or in latex form of unsaturated polymers. The free radical addition of thiol to olefin proceeds through a rather simple mechanism (Figure 4.1). Generally, reaction can be performed using azo compound, peroxides and photosensibilizers as initiators (Boileau, Henri and Blackborow, 2002). The free radical addition of thiols gives only the anti-Markovnikov isomer due to the prevalent formation of the more stable radical intermediate (Griesbaum, 1970). Several authors used the free radical addition reaction of thiols to olefinic double bonds in order to functionalize unsaturated elastomers. The addition of mercaptoacetic acid into rubber produced the carboxy-modified rubbers (Romani et al., 1999). Other thiol compound such as phosphonated thiols (Boutevin et al., 1998), fluorinated thiols (Ameduri et al., 1993), and mercapto propyl triethoxy silane (Schapman Couvercelle and Bunel, 1999) were reacted to the elastomer substrates to provide the better physical and mechanical properties of the resulting materials.

Oliveira et al. (1999) described the functionalization of EPDM with thioacetic acid in the presence of 2,2-azoisobutyronitrile (AIBN) that thioacetic acid content, initiator concentration and reaction time affected the extent of thioacetate
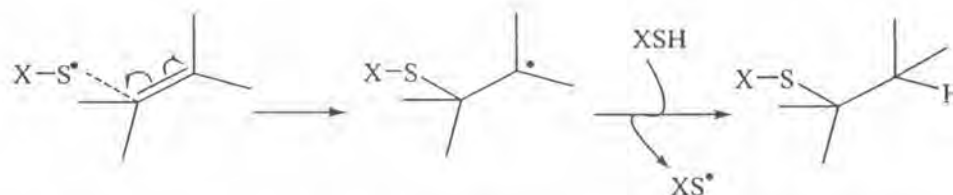

Figure 4.1 Mechanism of the free radical addition of thiols to olefins (Romani et al., 1999)

group in EPDM structure. The introduction of thiol derivatives containing ester functional group into NR was also investigated by Cunneen et al. (1960). Thus, the available literatures indicated that it is possible to functionalize unsaturated positions on the rubbers with thiol functional group via the free redical addition pathway.

This research work described the use of the free radical addition of thioacetate group for the functionalization of HNR. The functionaliaztion reactions were carried out using different conditions in order to get information about the effect of the reaction parameters on the reaction conversion. This approach can be used to design conditions to optimize the functionalization degree.

4.1.1 Thioacetate-Modified HNR (HNRTA)

4.1.1.1 Structure Characterization of the Resulting HNRTA

The structures of HNR and HNRTA were preliminarily characterized by FTIR spectroscopy as shown in Figure 4.2. The characteristic FTIR spectrum of HNR product (Figure 4.1a) showed that the absorption bands corresponding to the residual C=C stretching, $-CH_2-$, CH_3, olefinic C-H bending and $-(CH_2)_3-$ were located at 1660, 1449, 1376, 836 and 743 cm^{-1}, respectively (Hinchiranan et al., 2006). For thioacetate-modified HNR (Figure 4.2b), it was observed that the new absorption band was appeared at 1690 cm^{-1} related to the carbonyl groups ($-C=O$) of the thioester. This indicated the success of functionization of thioacetate group onto HNR structure.

The final degree of functionalization was determined by ^{1}H-NMR as shown in Figure 4.3. From Figure 4.3a, the spectrum of HNR presented a small peak at 5.1 ppm related to the proton of a carbon-carbon double bonds. The saturated aliphatic protons of $-CH_3$ and $-CH_2-$ appeared at 0.8 and 1.2 ppm, respectively. After functionalization using thioacetate, Figure 4.2b showed the reduction of peak area of the olefinic proton signal at 5.1 ppm and the new signals attributed to $-CH-S-$ at 3.6 ppm and methyl group of thioacetate at 2.3 ppm also appeared.
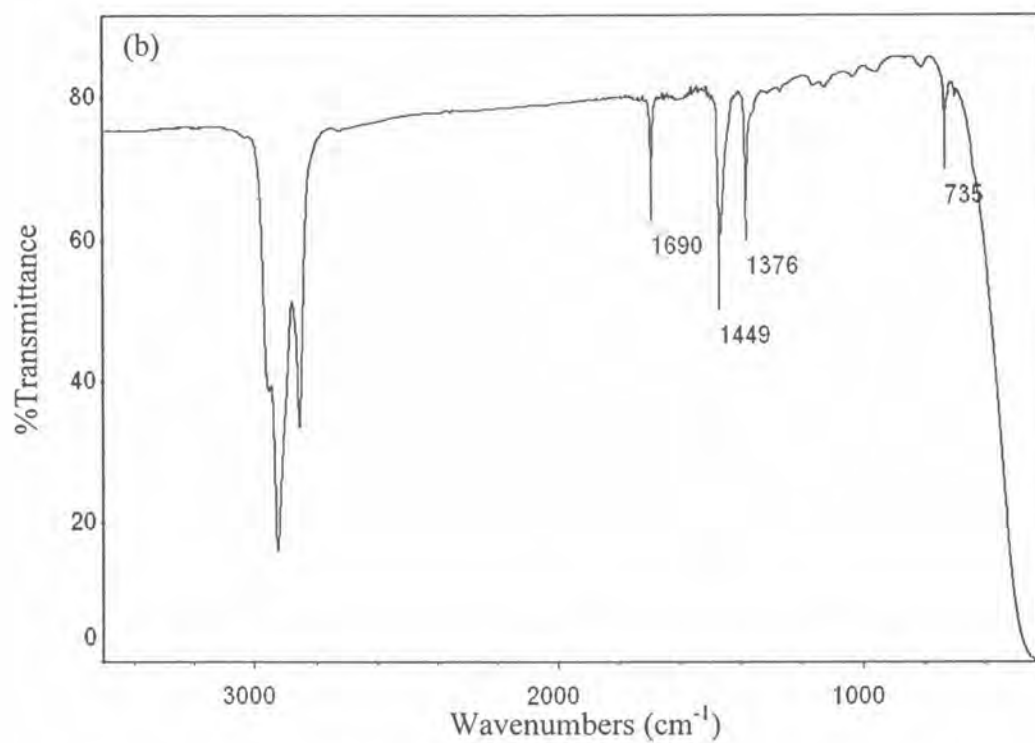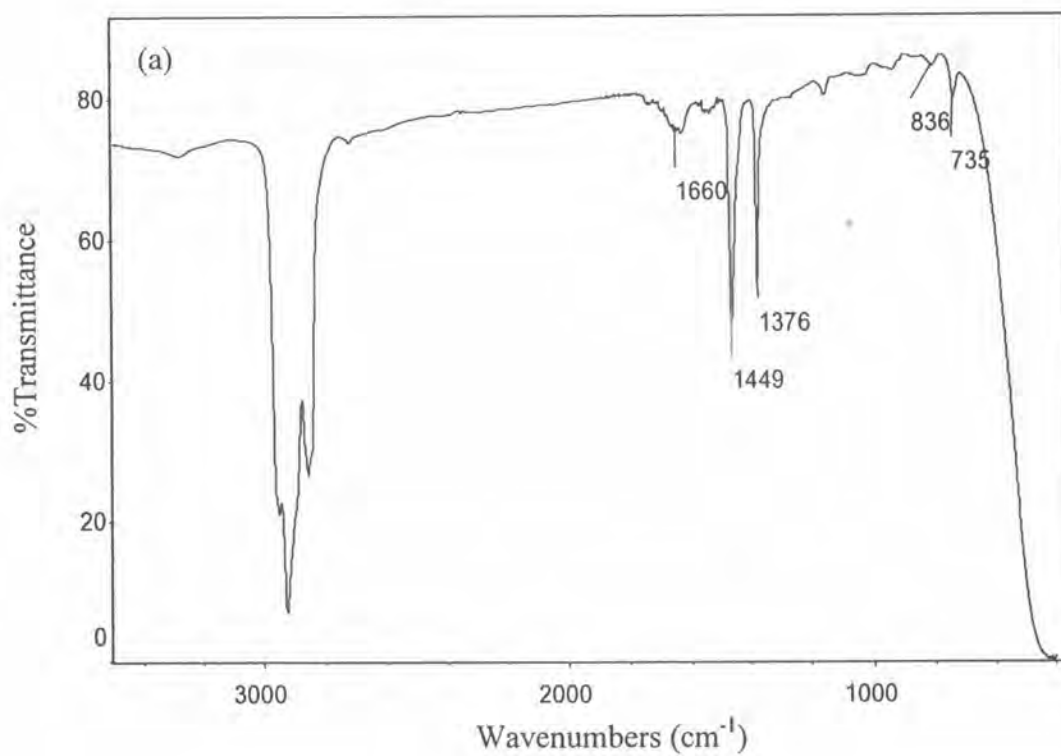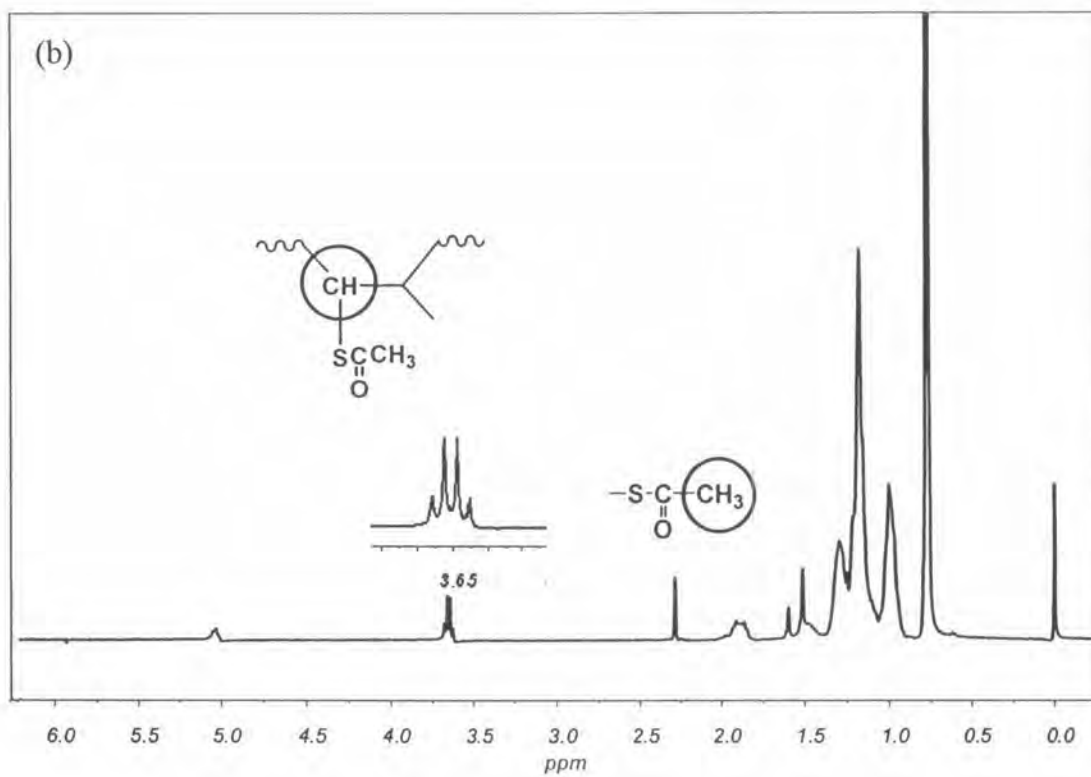
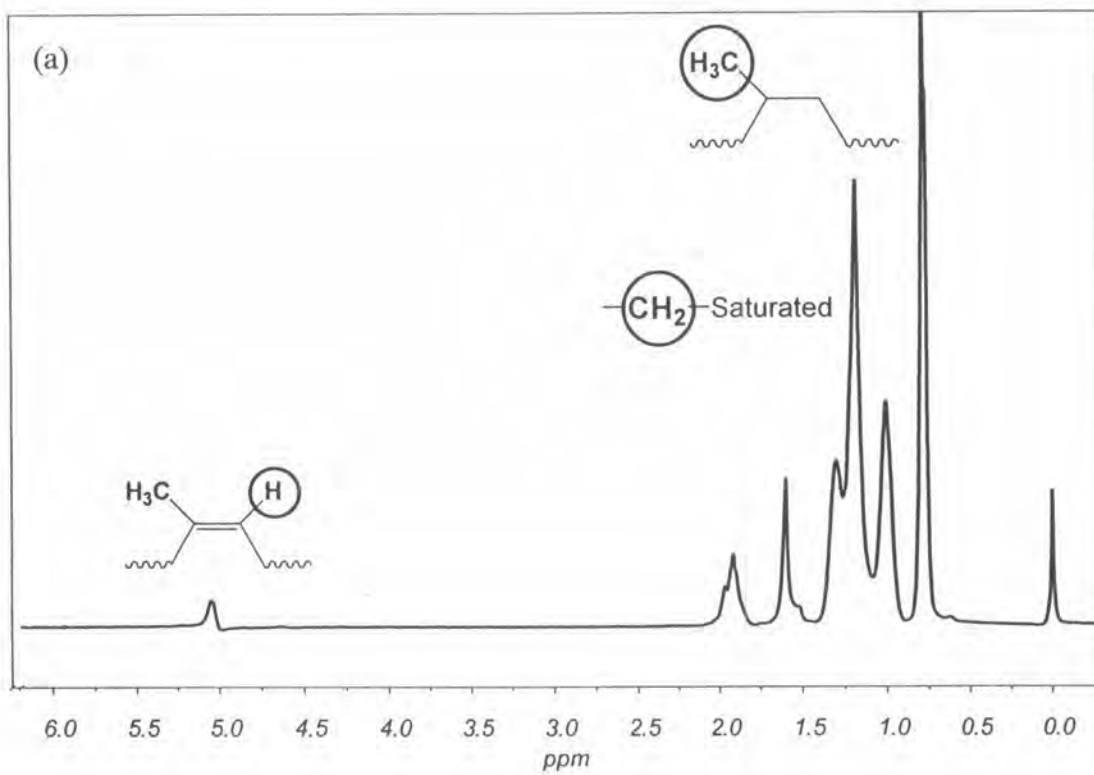**Figure 4.2** FTIR spectra of (a) HNR and (b) HNRTA.

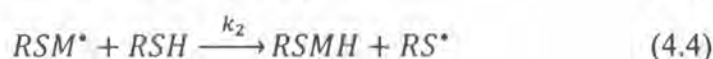**Figure 4.3** ¹H-NMR spectra of (a) HNR and (b) HNRTA.

4.1.1.2 Effect of Reaction Parameters on Functionalization Degree and Kinetics

The previous literatures reported the functionalization of polymers via free radical processes and the mechanism of the thiols addition to carbon-carbon double bonds initiated by free radicals (Ameduri et al., 1993 and Schapman et al., 1998). It is possible to describe the considering process of the involved reactions as shown below:
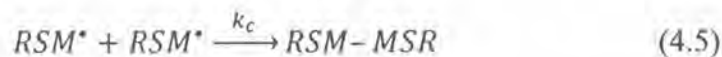
Initiation

$$A_2 \xrightarrow{k_d} 2A^{\bullet} \tag{4.1}$$

$$A^{\bullet} + RSH \xrightarrow{k_i} RS^{\bullet} \tag{4.2}$$

Propagation

$$RS^{\bullet} + M \xrightarrow{k_1} RSM^{\bullet} \tag{4.3}$$

$$RSM^{\bullet} + RSH \xrightarrow{k_2} RSMH + RS^{\bullet} \tag{4.4}$$

Termination

$$RSM^{\bullet} + RSM^{\bullet} \xrightarrow{k_c} RSM - MSR \tag{4.5}$$

where A_2, RSH and M represented the initiator, thiol and carbon-carbon double bond, respectively. When the initiation reactions (eq. 4.1–4.2) are concerned, it is likely that primary radicals ($A^{\bullet}$) formed through eq. 4.1 are preferably consumed by RSH to produce $RS^{\bullet}$ as shown in eq. 4.2. Then, the addition of $RS^{\bullet}$ into the carbon-carbon double bond of polymer is occurred as presented in eq. 4.3 and followed by transfer reaction (eq. 4.4) to allow a number of attached functional groups which are larger than that of primary radicals formed. The termination of reaction (eq. 4.5) is formed through to obtain the functionalized polymer product.

In this case, the general kinetic equation can be initially derived from the initiator disappearance rate (eq. 4.1) as shown in eq. 4.6 where k_d of ACCN is 6.5×10^{-6} s^{-1} at 80°C (Brandrup, Immergut and Grulke, 1999). After integration of eq. 4.6, an expression was shown in term of the reduction of initiator concentration as a function of time (eq. 4.7).

$$-\frac{d[A_2]}{dt} = k_d[A_2] \tag{4.6}$$

$$[A_2] = [A_2]_0 e^{-k_d t} \tag{4.7}$$

The rate of primary radicals production by thermal homolysis of the initiator (R_d) as shown in eq. 4.1 was given by eq. 4.8:

$$R_d = -2f\frac{d[A_2]}{dt} = 2fk_d[A_2] \tag{4.8}$$

where f was the initiator efficiency. The factor 2 represented two free radicals ($A^\bullet$) generated from initiator as shown in eq. 4.1 (Odian, 2004). In order to derive the kinetic equations, the assumption based on the rate of initiation (R_i) from eq. 4.2 which is equal to the rate of initiator decomposition (R_d) from eq. 4.2 as indicated in eq. 4.9.

$$R_i = R_d = 2fk_d[A_2] = k_i[A^\bullet][RSH] \tag{4.9}$$

The rate of termination (R_t) for eq. 4.5 could be kinetically expressed by eq. 4.10.

$$R_t = 2k_c[RSM^\bullet]^2 \tag{4.10}$$

The factor 2 was denoted as the combination of two radicals in the termination step. The next assumption implemented in this derivation assumed that the concentration of free radicals quickly reached a value which did not substantially change. This assumption was known as the steady state assumption. This can be expressed as shown in eq. 4.11a and 4.11b:

$$R_i = R_t \tag{4.11a}$$

$$2fk_d[A_2] = 2k_c[RSM^\bullet]^2 \tag{4.11b}$$

The thiol radical concentration could be expressed in terms of measurable quantities (eq. 4.12):

$$[RSM^\bullet] = \left(f\frac{k_d}{k_c}\right)^{1/2}[A_2]^{1/2} \tag{4.12}$$

The $[A_2]$ in eq. 4.12 was then replaced by eq. 4.7 as indicated in eq. 4.13.

$$[RSM^•] = \left(f\frac{k_d}{k_c}\right)^{1/2}[A_2]_0^{1/2}e^{-\frac{k_d}{2}t} \tag{4.13}$$

The rate of thiol consumption given by eq. 4.4 was shown in eq. 4.14.

$$-\frac{d[RSH]}{dt} = k_2[RSM^•][RSH] \tag{4.14}$$

The term of $[RSM^•]$ in eq. 4.14 was substituted by eq. 4.13. The final integral form of kinetic derivation could be expressed as shown in eq. 4.15 where $[RSH]$at to was presented as$[RSH]_0$.

$$\ln\frac{[RSH]_0}{[RSH]} = 2k_2\left(\frac{f}{k_dk_c}\right)[A_2]_0^{1/2}\left(1 - e^{-\frac{k_d}{2}t}\right) \tag{4.15}$$

4.1.1.2.1 Effect of Reaction Time

The effect of reaction time on the content of thioacetate functional group on the HNR structure with 80% and 90% hydrogenation containing 2.94 and 1.47 mmol/g of carbon-carbon double bond, respectively was presented in Figure 4.4. The reaction temperature was kept constant at 80°C under nitrogen atmosphere. The initial concentration of thioacetic acid (TAA) was equal to the total carbon-carbon double bond (C=C) concentration in the HNR sample and the mole ratio of carbon-carbon double bond to ACCN used as initiator was kept constent at 0.1. The results indicated that the content of thioacetate functional group on the HNR backbone increased with increasing the reaction time and reached a plateau after 48 and 64 h for HNR with 90% and 80% hydrogenation to obtain 0.96 and 1.87 mmol/g of thioacetate content on the HNR structure, respectively. Under similar conditions, the maximum thioacetate content was lower than the initial content of thioacetic acid in the feed. It is possible that the steric hindrance effect of thioacetate group on HNR structure could limit the increment of functionalization degree. These results are also similar to the functionalization of polybutadiene by free radical addition of thiols reported by Schapman et al. (1998).

Kinetic equation for the addition of thiol to C=C in HNR in the presence of radical initiator (A_2) is expressed in eq. 4.15. A plot of the experimental data as $\ln[RSH]_0/[RSH]$ versus $1 - e^{(-k_d/2)t}$ yielded a straight line which slope was $2k_2(f/k_dk_c)[A_2]_0^{1/2}$as presented in Figure 4.5. The results indicated that the slope
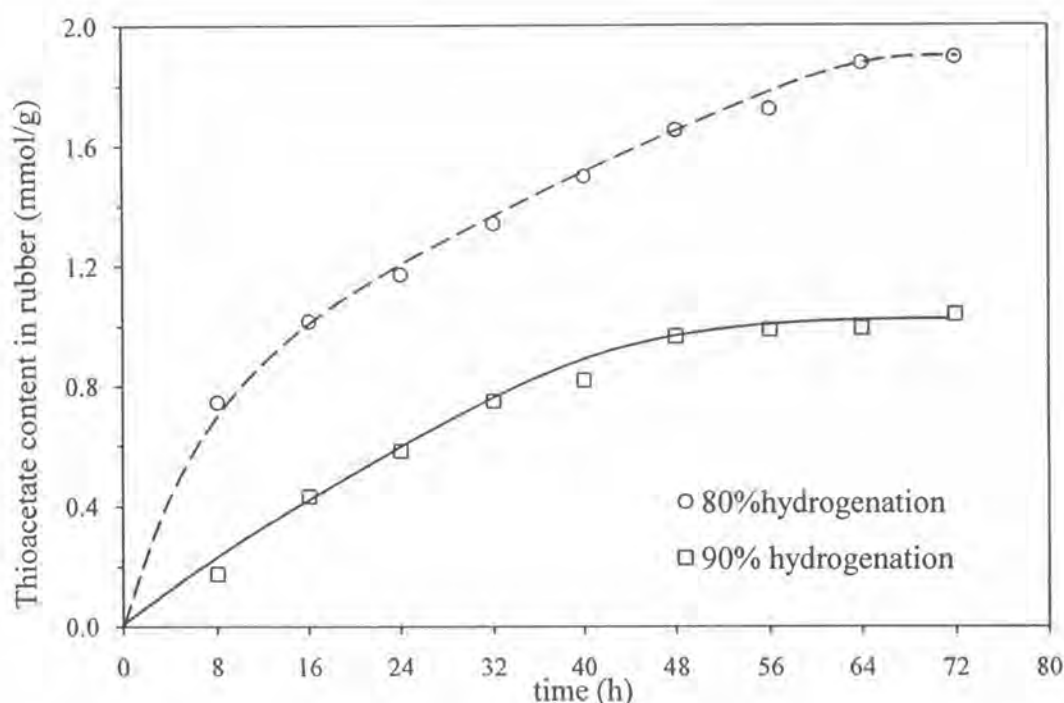
Figure 4.4 Effect of reaction time on thioacetate content in HNR at 80% (o) and 90% (□) hydrogenation: [C=C]/[TAA]/[initiator] = 1/1/0.1 by mole ratio at 80°C under N_2 atmosphere.

obtained from eq. 4.15 for HNR with 90% hydrogenation gave a quite straight line (R^2=0.98). These results also similar to the functionalization of fluorinated thiols onto the carbon-carbon double bonds of hydroxyl-terminated polybutadiene reported by Ameduri et al (1993). For HNR with 80% hydrogenation, two slopes for HNR with 80% hydrogenation was observed. In the initial period before 16 h of reaction time, HNR with 80% hydrogenation had higher slope value (2.65) than HNR with 90% hydrogenation. This means that the reaction rate of functionalization using thioacetic acid for modification of HNR with lower hydrogenation level was faster than that for HNR with higher hydrogenation level. This resulted to the high conversion of thioacetate when the reaction time was shorter than 24 h as shown in Figure 4.6. However, it can be seen that the second slope of HNR with 80% hydrogenation was lower (1.89) than that of HNR with 90% hydrogenation (2.23) when the reaction time was longer than 16 h. It might be due to the effect of steric hindrance resulting in the reduction of functionalization rate in HNR with 80% hydrogenation. In addition, the conversion of thioacetate for HNR with 80% hydrogenation was also lower than that with 90%hydrogenation after 24 h.
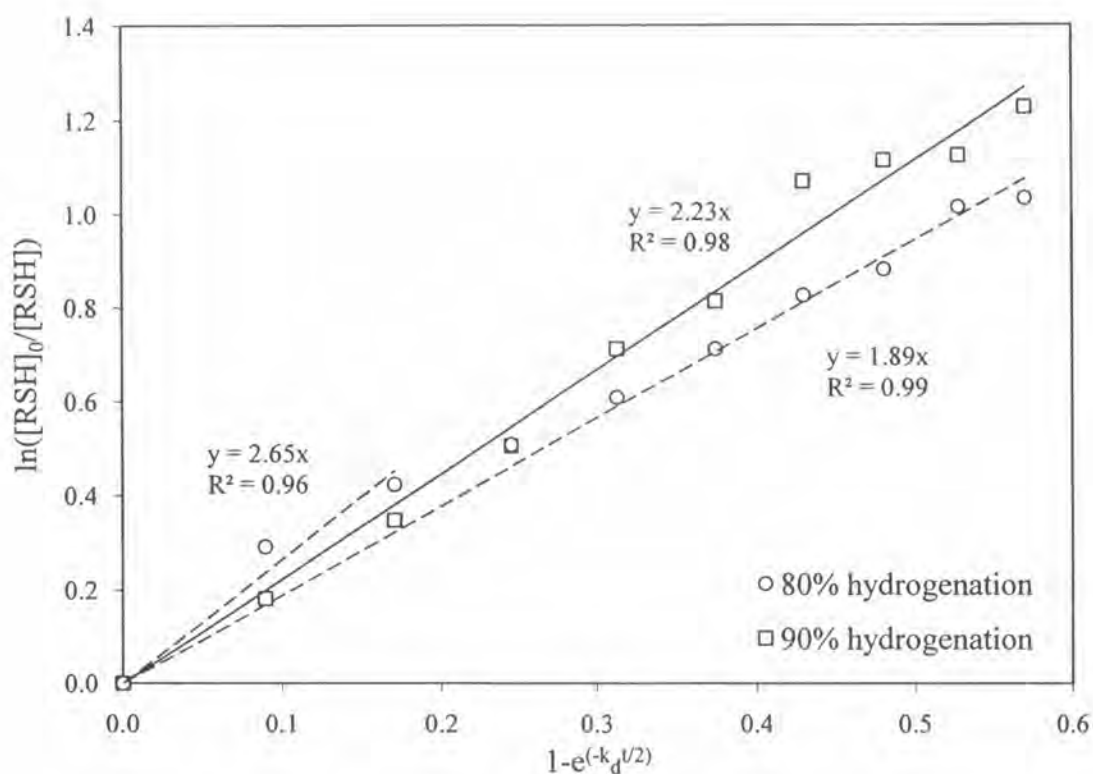
Figure 4.5 Effect of reaction time on the reaction rate of functionalization of HNR having 80% (○) and 90% (□) hydrogenation, according to eq. 4.15.

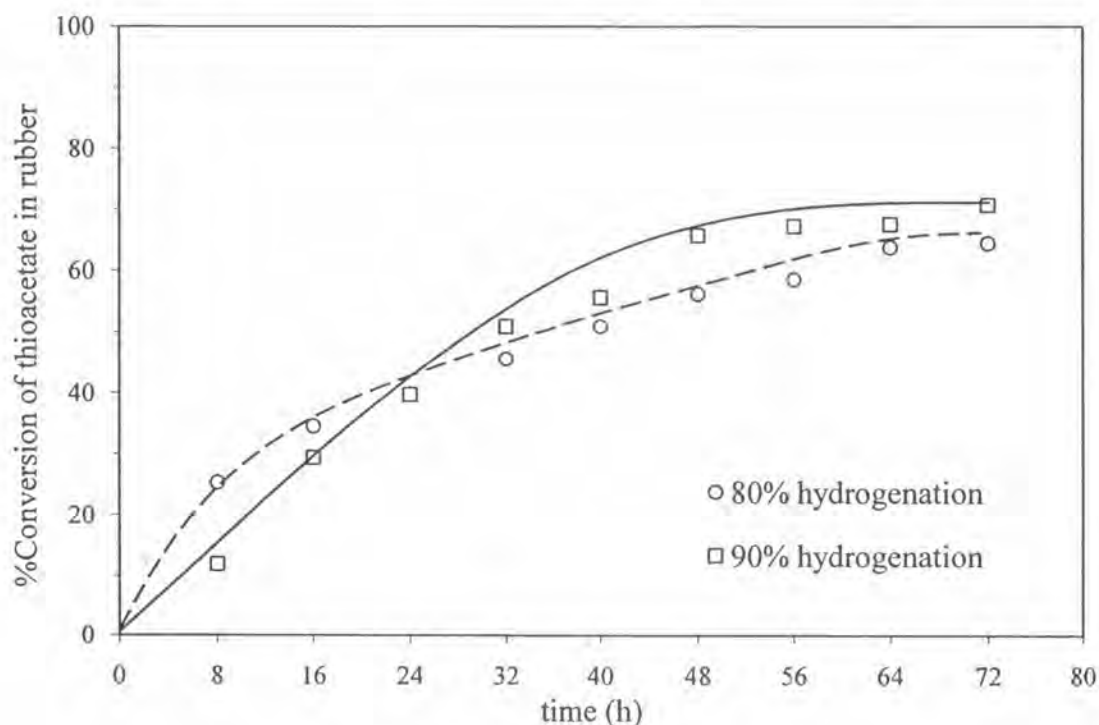**Figure 4.6** Effect of reaction time on thioacetate conversion in HNR at 80% (○) and 90% (□) hydrogenation: the mole ratio of [C=C]/[TAA]/[initiator] = 1/1/0.1 at 80°C for 48 h under N_2 atmosphere.

4.1.1.2.2 The Effect of Thioacetic Acid Concentration

The effect of TAA concentration on the thioacetate content on the HNR structure and its conversion was presented in Figure 4.7 and 4.8, respectively. The mole ratio of C=C to initiator concentration was 0.1. The reaction was carried out at 80 °C for 48 h under N_2 atmosphere. It was found that the amount of thioacetate in the HNR structure increased with increasing [TAA]/[C=C] from 0.5-1.0 (Figure 4.7). Nevertheless, the maximum thioacetate content in the HNR structure was lower than the content of thioacetic acid in the feed. This was not due to the effect of steric hindrance but it was also probably due to competitive reactions such as radical coupling reaction that could inhibit the increase in functionalization degree. Above 1.0 of [TAA]/[C=C], the thioacetate content in HNR slightly increased. Thus, the use of excess amount of thiol could not enhance the content of thioacetate function group on the HNR structure. Under similar condition, the conversion of thioacetate for HNR with 80% hydrogenation also lower than that with 90%hydrogenation (Figure 4.8). It might be due to the effect of steric hindrance from the higher content of thioacetate groups on HNR with 80% hydrogenation.

The effect of the thioacetic acid concentration on the reaction rate constant $(2k_2(f/k_dk_c)[A_2]_0^{1/2})$ of the addition of thiol to C=C of HNR as expressed in eq. 4.15 was shown in Figure 4.9. Generally, the increase in $[RSH]_0$ enhances the value of $2k_2(f/k_dk_c)[A_2]_0^{1/2}$. However, the experimental result indicated that the increase in $[RSH]_0$ decreased $2k_2(f/k_dk_c)[A_2]_0^{1/2}$ value as shown in Figure 4.9. It can be explained that the reaction rate constant (k_2) as shown in eq. 4.4 might be depended on a position for the addition of thioacetate group due to the effect of the local steric hindrance (Schapman et al., 1998). For the comparison of the effect of hydrogenation level on the rate of thioacetate addition onto HNR structure, it was found that the term of $(2k_2(f/k_dk_c)[A_2]_0^{1/2})$ for thioacetate-modified HNR with 90% hydrogenation was higher than that with 80% hydrogenation. This might cause from the higher global steric hindrance effect resulted from the higher content of thioacetate group on the HNR with 80% hydrogenation to yield the reduction of reaction rate constant.

Figure 4.7 Effect of thioacetic acid concentration on thioacetate content in HNR at 80% (o) and 90% (□) hydrogenation: the mole ratio of [C=C]/[initiator] = 1/0.1 at 80°C for 48 h under N_2 atmosphere.
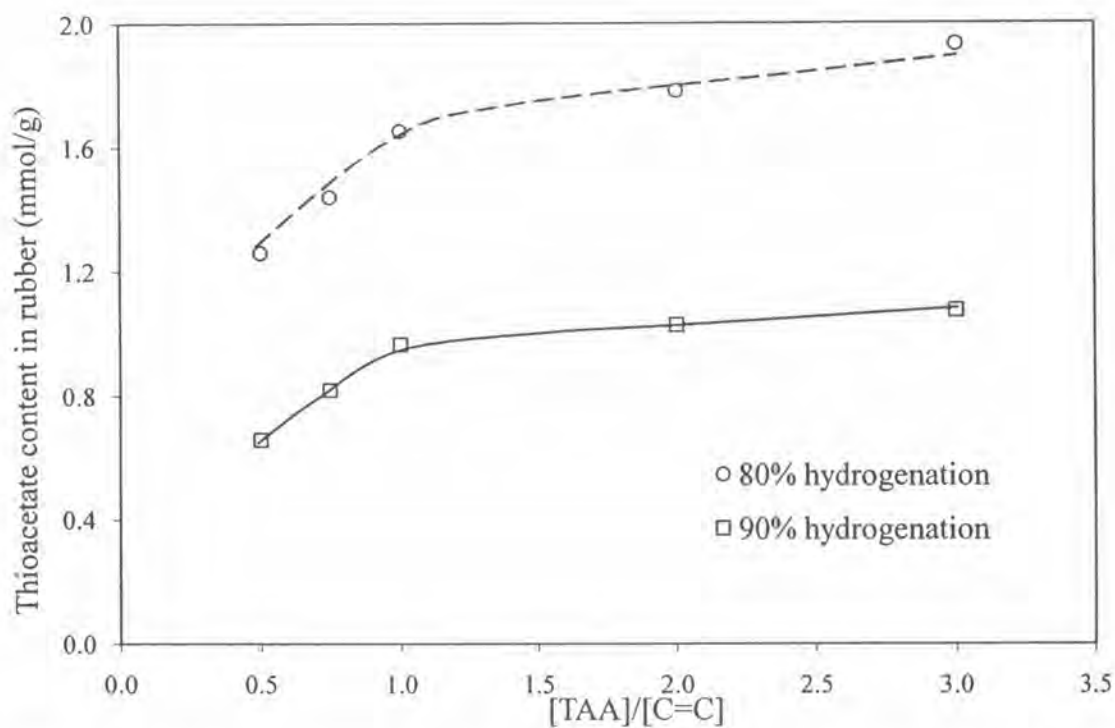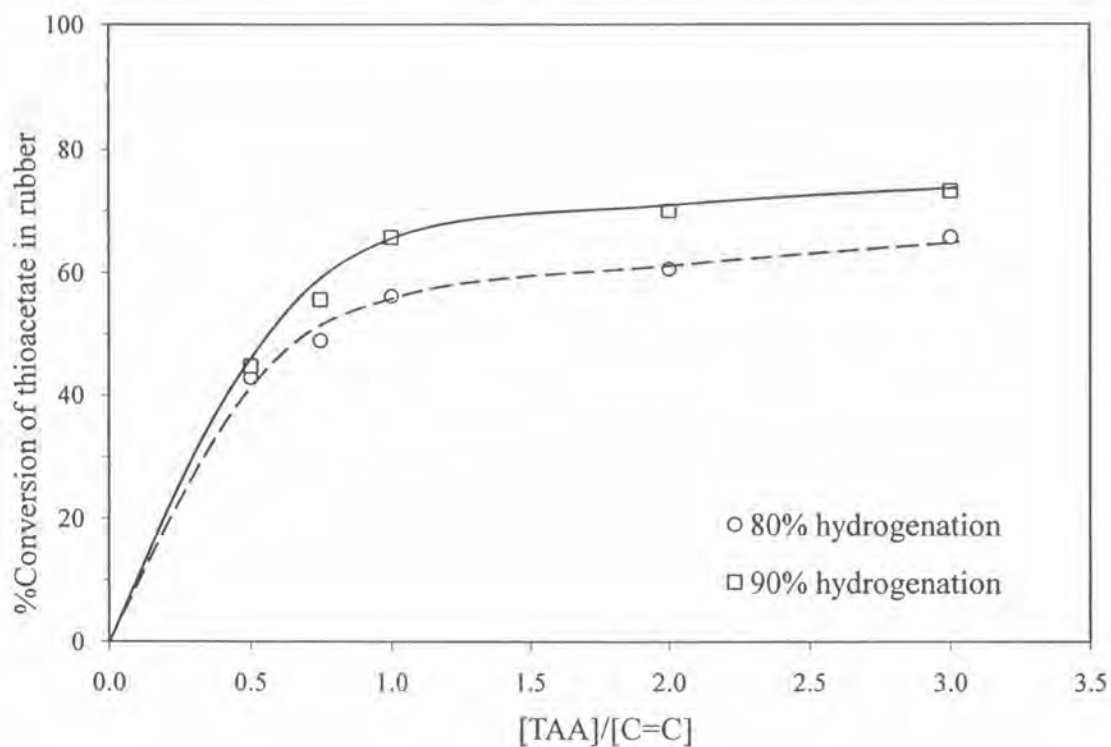

Figure 4.8 Effect of thioacetic acid concentration on thioacetate conversion in HNR at 80% (o) and 90% (□) hydrogenation: the mole ratio of [C=C]/[initiator] = 1/0.1 at 80°C for 48 h under N_2 atmosphere.
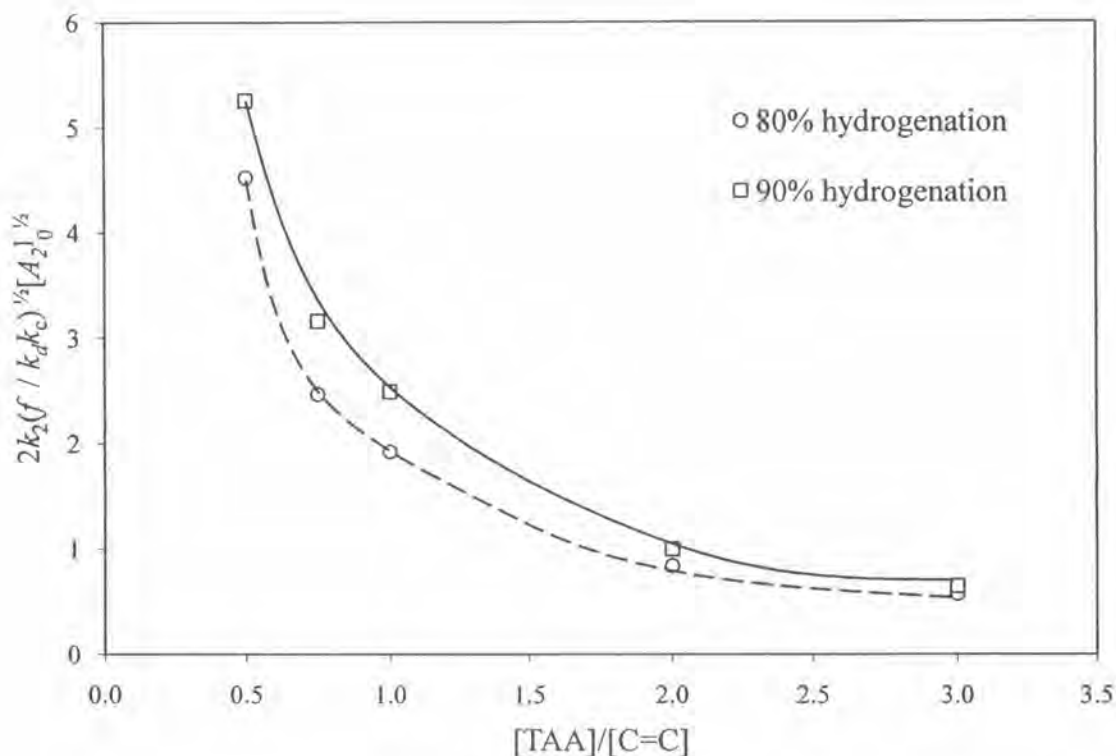
Figure 4.9 $2k_2(f/k_dk_c)[A_2]_0^{1/2}$ versus [TAA]/[C=C] for functionalization of HNR having 80% (○) and 90% (□) hydrogenation with TAA at 80°C for 48 h under N_2 atmosphere.

4.1.1.2.3 The Effect of Initiator Concentration

The effect of initiator concentration (ACCN) on the thioacetate content on the HNR structure was studied when the mole ratio of C=C and TAA was kept constant at 1 (Figure 4.10). The reaction was performed at 80°C for 48 h under N_2 atmosphere. The amount of thioacetate functional group on HNR structure increased with increasing the [initiator]/[C=C]. This can be attributed to an increase in the amount of free radicals that are capable to generate sites for functionalization of thioacetate on the rubber main chain as described by Vikram and Nando (2007). However, it was found that the thioacetate content on HNR structure was independent on the initiator concentration when the [initiator]/[C=C] was higher than 0.1. This could be explained that the previous thioacetate groups, on the HNR structure might promote the steric to inhibit the addition reaction of radicals to C=C position (Ameduri et al., 1993). It was also found the insoluble rubber during the reaction when the mole ratio of [initiator]/[C=C] was 0.7. This phenomena was similar to the observation reported by Oliveira et al. (1999). They suggested that it might be due to

the effect of competitive crosslinking reactions which do not involve the thiol compound.

The effect of the initiator concentration in a term of $2k_2(f/k_dk_c)[A_2]_0^{1/2}$ for the addition of thiol to C=C as expressed in eq. 4.15 is shown in Figure 4.11. The increase in the thioacetate content in HNR structure depended on the initiator concentration but the rate reaction content $(2k_2(f/k_dk_c)[A_2]_0^{1/2})$ drastically increased when [initiator]/[C=C] was in the range of 0.5-1.0 (Figure 4.8). Schapman et al. (1993) also reported a similar behavior for the addition of mercapto propyl triethoxy silane on the polybutadiene structure. However, the value of reaction rate contant was independent on the initiator concentration when the [initiator]/[C=C] was higher than 0.1 because the steric hindrance effect of thioacetate group in HNR structure could limit the increment of functionalization degree as described in the previous work (Ameduri et al., 1993). In addition, the conversion of thioacetate for HNR with 80% hydrogenation also lower than that with 90%hydrogenation as shown in Figure 4.12. Similar result was also observed in the effect of thioacetic acid concentration as presented in the 4.1.1.2.2.

Figure 4.10 Effect of initiator concentration on thioacetate content in HNR at 80% (○) and 90% (□) hydrogenation: the mole ratio of [TAA]/[C=C] = 1/1 at 80°C for 48 h under N_2 atmosphere.

Figure 4.11 $2k_2(f/k_dk_c)[A_2]_0^{1/2}$ versus [initiator]/[C=C] for functionalization of HNR having 80% (○) and 90% (□) hydrogenation with TAA at 80°C for 48 h under N_2 atmosphere
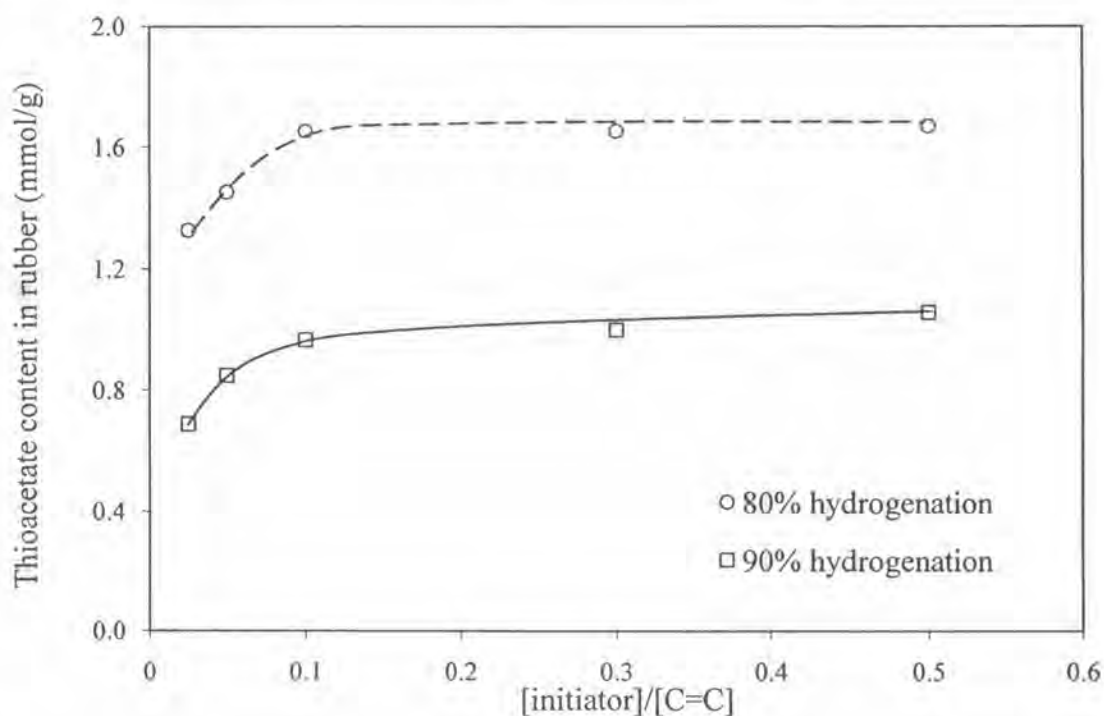

Figure 4.12 Effect of initiator concentration on thioacetate conversion in HNR at 80% (○) and 90% (□) hydrogenation: the mole ratio of [TAA]/[C=C] = 1/1 at 80°C for 48 h under N_2 atmosphere.

4.1.2 Mercapto-Modified HNR (HNRSH)
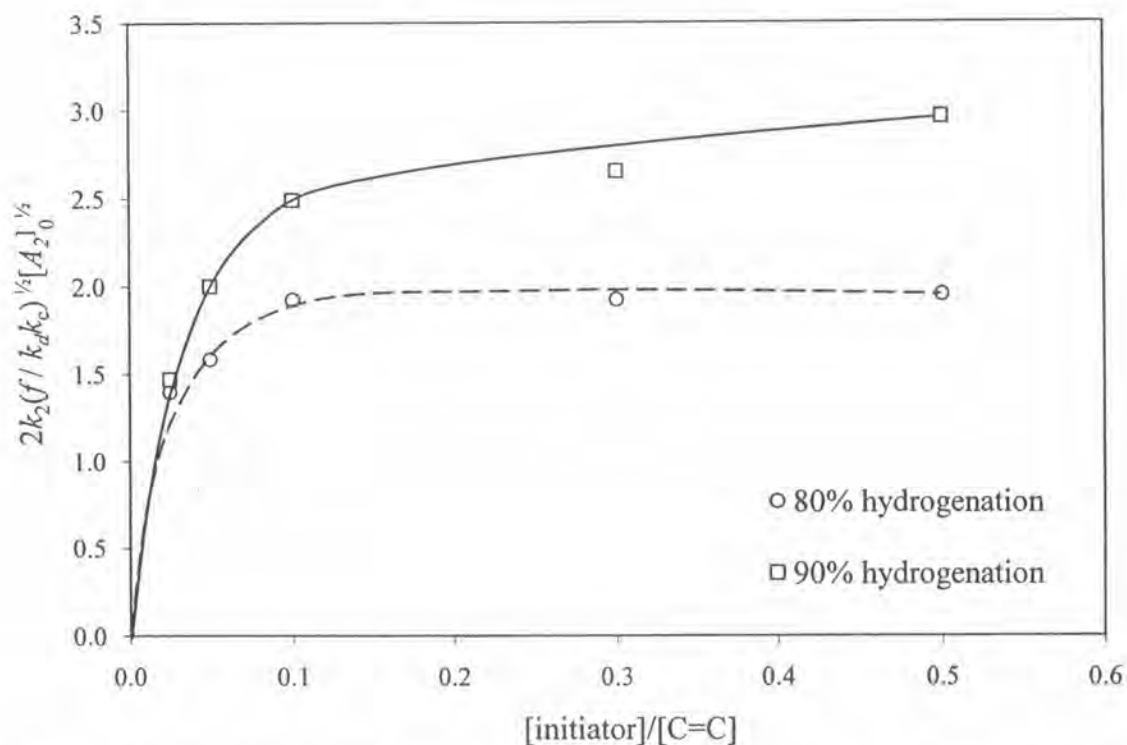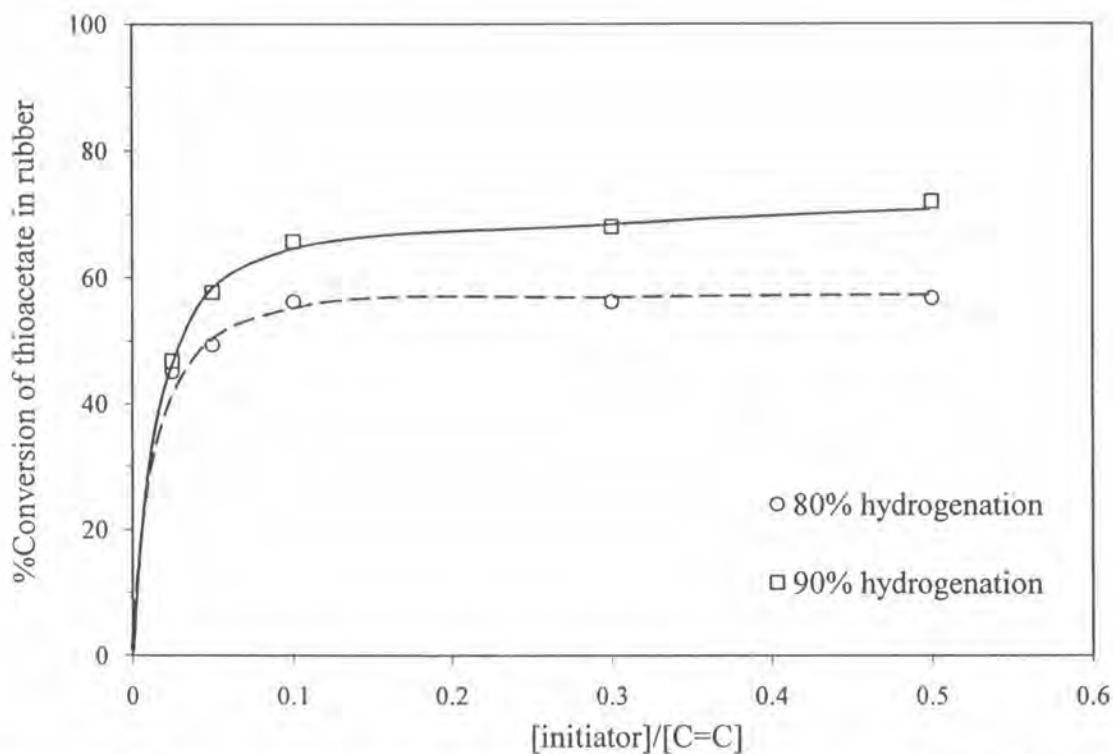
As described in a previous work (Sato et al., 1993), the thioacetate-modified poly (vinyl acetate) (CH$_3$COS-PVAc) was prepared via free radical addition of thioacetic acid. The resulting CH$_3$COS-PVAc was then methanolyzed to produce mercapto modified-PVAc (HS-PVAc). The synthesis of block copolymers containing PVAc as one constituent by the polymerization of several vinyl monomers such as acrylic acid and acrylamide in the presence of both functionalized PVAcs were used as chain transfer agents. From the experimental results, it was found that the number-average degree of polymerization (P_n) of HS-PVAc was larger than that of CH$_3$COS-PVAc. This indicated that the HS-PVAc was highly effective chain transfer agent.

Oliveira et al. (2001) also studied the effect of the EPDM functionalized with thioacetate (EPDMTA) or mercapto groups (EPDMSH) to be used as compatibilizers for NBR/EPDM blends. Both EPDMTA and EPDMSH increased tensile strength of the blends. EPDMSH exhibited the improvement of the properties of the blends probably due to the enchancement of crosslink density promoted by the reaction between mercapto groups and rubber matrix. On the other hand, the EPDMTA was not able to chemically react with carbon-carbon double bonds of the elastomer. This indicated that the chemical reactivity of mercapto group was higher than that of thioacetate group.

The major concern with *trans*-esterification of thioester group in the rubber structure was the crosslinking. The gel formation in the rubber resulted in the rubber hardening. Kihara et al. (1996) reported that aminolysis of a spherical microgel containing vinylbenzyl s-thioacetate, with an average diameter of 135 nm resulting from the removal of acetyl group gave a spherical microgel (MG-SH) bearing mercapto group. The average diameter of MG-SH increased to 165 nm indicating the gel formation during reaction.

This research work dealt with the methanolysis of HNRTA to produce mercapto modified-HNR (HNRSH). The gel formation occurred during the reaction was also investigated.

4.1.2.1 Structure Characterization of the Resulting HNRSH

The structure of HNRSH obtained from the methanolysis of
HNRTA was preliminarily characterized by FTIR spectroscopy (Figure 4.13). A
characteristic absorption peak at 1693 cm^{-1} related to a carbonyl group of thioester
was observed in the spectrum of the HNRTA sample. After methanolysis, this
absorption peak disappeared. The absorption related to the thiol group (at 2225 cm^{-1})
was not shown in the HNRSH spectrum because the amount of this group was too
small to be detected by FTIR spectroscopy.

To confirm the FTIR results and to calculate the exact conversion of
methanolysis, Figure 4.14 shows a comparison of the ^{1}H-NMR spectra of HNRTA
and HNRSH. The results showed that the peak of the thiol group at 3.6 ppm still
remained after methanolysis. Whereas, the peak of methyl group of thioacetate
located at 2.4 ppm disappeared during methanolysis. This indicated the successful
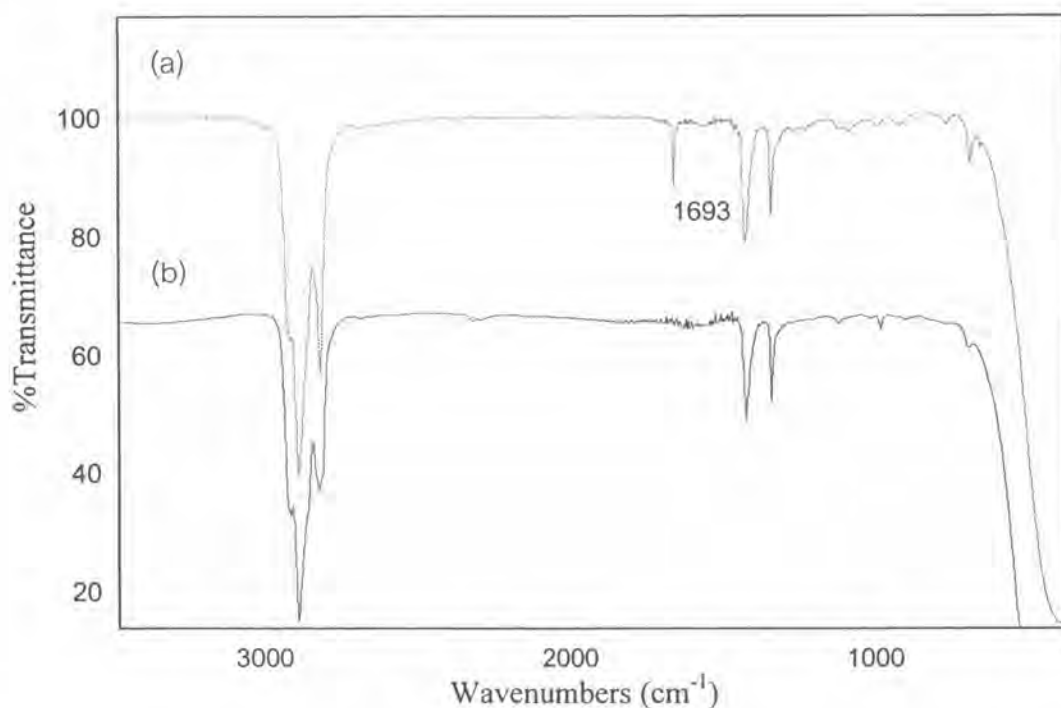transformation of thioacetate to be a mercapto functional group.

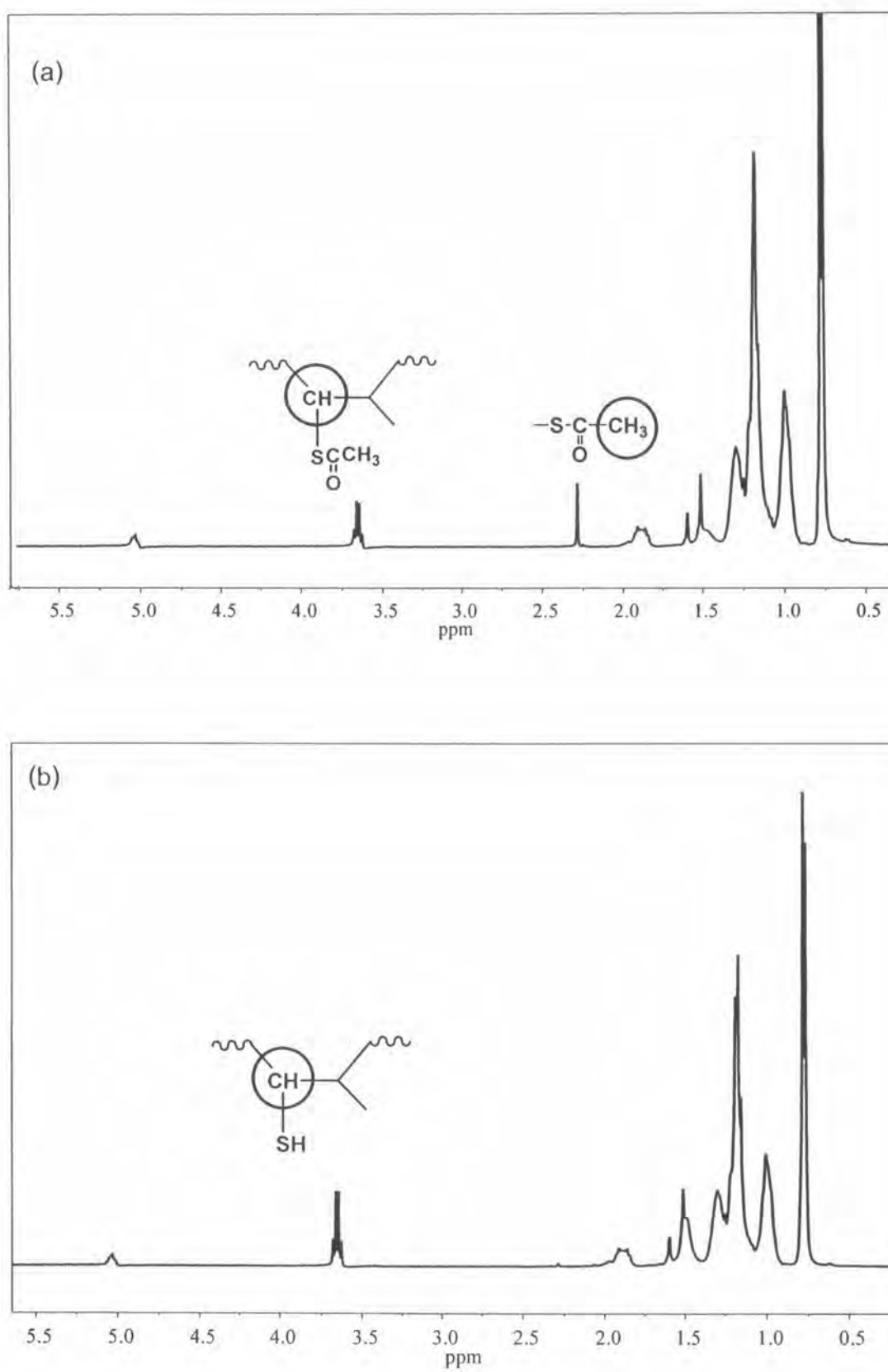**Figure 4.13** The comparison of the FTIR spectra of (a) HNRTA and (b) HNRSH.

Figure 4.14 The comparison of the ^{1}H-NMR spectra of (a) HNRTA and (b) HNRSH.

4.1.2.2 Mercapto-Modified HNRTA via Methanolysis

The effect of sodium hydroxide content on the degree of methanolysis and gel content during methanolysis of HNRTA was investigated as shown in Table 4.1. The HNRTA with 0.966 mmol/g of thioacetate content obtained from HNR with 90 %hydrogenation was used as a raw material for modification at various reaction time. The ratio of sodium hydroxide to methanol (NaOH/CH$_3$OH, %w/v) was varied from 3 to 10. It was found that the degree of methanolysis and gel content increased with increasing the NaOH/CH$_3$OH ratio and reaction time. This indicated that NaOH might act as the catalyst for methanolysis of HNRTA (Kihara et al. 1996). The level of methanolysis could reach 100% within 2 h when NaOH/CH$_3$OH was 10. However, the increasing NaOH/CH$_3$OH also increased the gel content. This indicated that the large amount of NaOH promoted the gel formation resulting in the crosslink within the polymer chain. Normally, the crosslink or gel formation increases the molecular weight and creates branched molecules with a broader molecular weight distribution (Hamed, 2001). This caused the difficulty for processing because the polymer with higher gel content is hard to be blended with other component resulting to poor physical and mechanical properties of the final product.

Table 4.1 Degree of methanolysis of and gel content during methanolysis of HNRTA at various NaOH concentrations.

NaOH/CH$_3$OH (%w/v)	Reaction time (h)	Methanolysis (%)	Gel (%)
3	1	56.0	10.5
	2	89.1	16.1
	3	99.1	19.8
5	1	90.5	25.0
	2	94.3	27.4
	3	100	28.1
10	1	97.9	74.9
	2	100	85.0

4.1.3 Thermal Characteristics of HNRTA and HNRSH

Thermal analysis is normally used to investigate the physical properties of materials as a function of temperature. A differential scanning calorimeter (DSC) and thermogravimetric analysis apparatus (TGA) are used to evaluate the glass transition temperature (T_g) and decomposition temperature, respectively. From Table 4.2, the experimental results showed that HNRTA and HNRSH had higher decomposition temperature compared to HNR. It is possible that the functionalization of HNR by using thioacetate and mercapto functional groups could promote the higher thermal resistance by reducing carbon-carbon double bond. In addition, it can be noticed that the HNRSH had slight higher decomposition temperature than the HNRTA. It was possible that the gel or crosslink occurred during the methanolysis of HNRTA to produce HNRSH enhanced the thermal resistance. However, the modification by using thioacetate- or mercapto- functionalization of HNR did not affect to T_g of HNR. It might be due to the presence of small amount of thioacetate (0.96 mmol/g) and mercapto (0.96 mmol/g) groups on the HNR structure after the modification. This result was different from the observation reported by Romani et al. (1998) that the functionalization with polar groups could shift T_g of polymer to be higher if these groups allowed intermolecular interaction such as hydrogen bond.

Table 4.2 Decomposition temperature, the glass transition temperature and gel values of the rubber samples

Rubber	decomposition temperature		$T_g(°C)$	Gel (%)
	$T_{id}(°C)$	$T_{max}(°C)$		
HNR (90%hydrogenation)	420.5	451.2	-61.9	7.44
HNRTA (0.966 mmol/g of thioacetate content)	422.3	463.1	-61.5	9.30
HNRSH (0.966 mmol/g of mercapto content)	425.1	465.8	-60.6	28.1

4.2 The Use of HNRTA and HNRSH as Compatibilizer for Rubber Blends

4.2.1 Vulcanization Characteristics

The modified HNR (90%hydrogenation) containing thioacetate (0.966 mmol/g) or mercapto (0.966 mmol/g) functional group was loaded into HNR/NR blends (50/50 %wt) in the range of 0-15 phr. The hydrogenation level of HNR in the blends was higher than 95% hydrogenation. The effect of the functionalized HNR on the vulcanization and mechanical properties of HNR/NR blends was investigated and compared to EPDM/NR vulcanizates at the same compositions. The effect of vulcanization systems such as conventional vulcanization (CV) and efficient vulcanization with peroxide (EPV) on the cure behavior of HNR/NR was also studied. The formulation of rubber blends was presented in Table 3.1. The accelerated sulfur vulcanization classified as CV is usually appropriate for unsaturated rubber such as NR to give the good mechanical properties. However, the blends containing highly different degree of unsaturation such as HNR/NR blends cured by CV system exhibited low tensile strength because of the cure-rate mismatch effect resulting from the imbalance of unsaturation of those rubbers. Hinchiranan et al. (2009) reported that the use of EPV system could improve the cure compatibility of the blend. It was believed that the addition of peroxide possibly retarded the reactivity of the sulfur donor in NR phase of the blends to reduce the cure-rate mismatch resulting in the improvement of tensile properties of the blends.

The effect of the addition of HNRTA and HNRSH and cure systems on the vulcanization properties of HNR/NR and EPDM/NR was summarized in Table 4.3 and Figure 4.15. The minimum and maximum torques of blends related to the crosslink density were increased by increasing the content of HNRTA and HNRSH in both HNR/NR and EPDM/NR blends obtained from EPV system. Moreover, the CV system also showed the same results in HNR/NR vulcanizates. This indicated that these functionalized HNRs could enhance the crosslink density in the blends containing different saturation level during curing process. This behavior was also confirmed from the swelling experiments for determining the amount of crosslink

Table 4.3 Effect of the addition of functionalized HNR and cure systems on vulcanization properties of HNR/NR and EPDM/NR at 50/50%wt

Rubber blends	Functionalized HNR (phr)		Minimum Torque (ML, dNm)	Maximum Torque (MH, dNm)	Scorch time (ts_2, min)	Optimum cure time (tc_{90}, min)
Conventional vulcanization						
HNR/NR	None	0	0.39	9.39	4.07	10.2
	HNRTA	5	0.43	9.73	4.01	10.1
	HNRSH	5	0.43	9.91	3.54	9.57
Efficient-peroxide vulcanization						
HNR/NR	None	0	0.31	5.28	5.12	16.4
	HNRTA	2	0.36	5.31	5.00	15.6
		3	0.35	5.33	4.57	15.2
		5	0.36	5.37	4.44	15.0
		10	0.35	5.41	4.43	15.0
		15	0.41	5.46	4.40	14.5
	HNRSH	2	0.40	5.60	4.57	15.6
		3	0.42	5.63	4.56	15.1
		5	0.45	5.65	4.55	15.1
		10	0.47	5.70	4.57	15.0
		15	0.50	5.73	4.40	15.0
EPDM/NR	None	0	0.17	3.00	10.4	19.2
	HNRTA	3	0.19	3.13	10.3	19.2
		5	0.26	3.24	10.3	19.0
		10	0.31	3.28	9.10	19.0
	HNRSH	3	0.24	3.18	9.50	18.5
		5	0.28	3.31	8.57	18.4
		10	0.30	3.41	8.33	18.3

density which would be explained in the section of mechanical properties (4.2.2). In addition, it can be noticed that the blends containing HNRSH had the higher minimum and maximum torque than the blends having HNRTA. This could be explained that the mercapto functional group had more effective participation than thioacetate resulting in the higher crosslink density in the blends (Sirqueira and Soarea, 2003).

Table 4.3 also indicates the reduction of scorch time (ts_2) and optimum cure time (tc_{90}) of the blends when both functionalized HNRs were added. This means that the thioacetate and mercapto functional groups in the modified HNR acted as the accelerator during vulcanization process. This result was similar to the report of Poh and Ng (1998) who observed the catalytic effect of thiol groups which could enhance the rate of NR vulcanization.
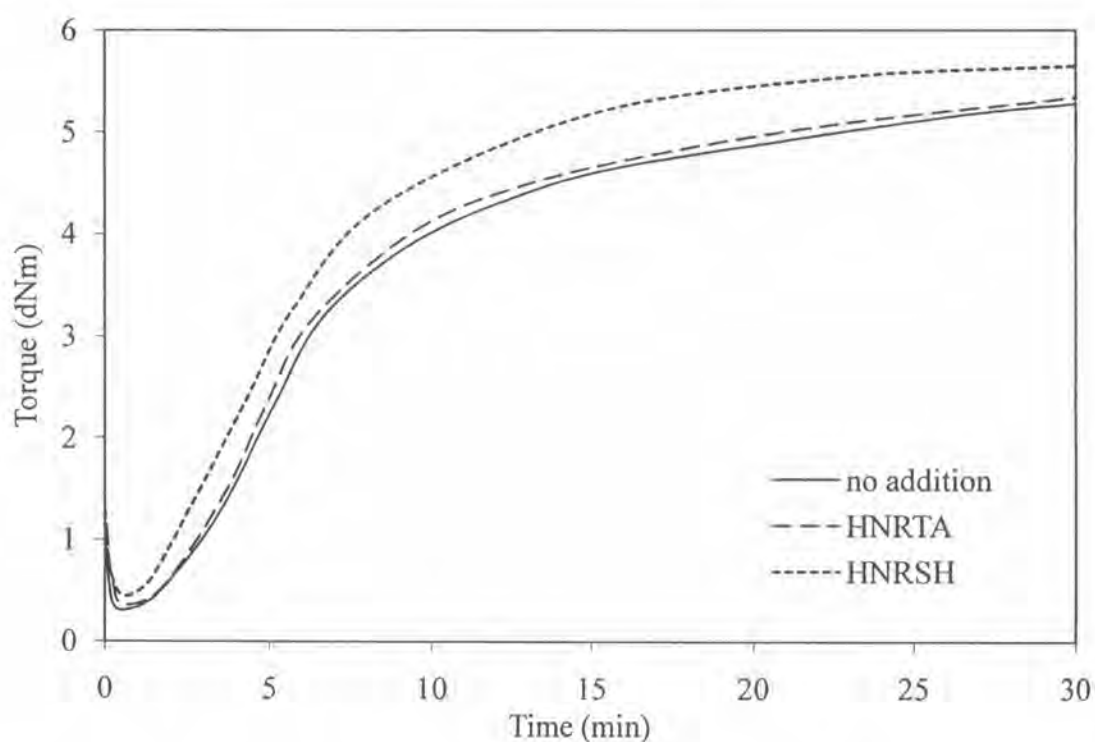

Figure 4.15 Effect of the addition of HNRTA and HNRSH on the rheograph profiles of HNR/NR vulcanizates (50/50 %wt) at 150°C: no addition (—), HNRTA addition (– –) and HNRSH addition (----).

4.2.2 Mechanical Properties

The effect of the vulcanization system and the addition of HNRTA and HNRSH on the mechanical properties and crosslink density of HNR/NR and EPDM/NR blends was shown in Table 4.4. The HNR/NR vulcanizates at 50/50 %wt obtained from the EPV system had the higher tensile strength than that cured by CV system. It can be explained that the cure-rate mismatch effect resulting from the imbalance of unsaturation of these rubbers could decrease the mechanical properties of the blends cured by sulfur vulcanization system as described in the previous work (Ghosh et al., 2001). The addition of peroxide in efficient vulcanization using sulfur donor agent such as TMTD was found to be the effective system for vulcanization of blends containing elastomers with highly different saturation level such as EPDM/NR or HNR/NR blends. It was believed that peroxide could retard the reactivity of TMTD for curing unsaturated elastomer phase resulting in the reduction of cure-rate mismatch effect to improve the mechanical properties of the blends (Hinchiranan et al., 2009).

From Table 4.4, the addition of HNRTA in to the HNR/NR blends at 50/50 %wt vulcanized by CV system did not affect the crosslink density of the vulcanizates when compared to the HNR/NR blends without the addition of HNRTA. It is possible that HNRTA was not able to chemically react with the carbon-carbon double bonds of the elastomer during the mixing process (Oliveira and Soares, 2001). However, it could be seen that the tensile strength of vulcanizates slightly increased from 3.86 MPa to 3.93 MPa and it also showed the reduction of elongation at break value of HNRTA-modified blends. This means that HNRTA may act as the compatibilizer to give the better reactive compatibilization in the blends containing the elastomers with highly different unsaturation levels (Sirqueire and Soares, 2003). For the addition of HNRSH into the blends, it was found that the crosslink density of HNR-modified blends was higher than that of the vulcanization containing HNRTA resulting in the better tensile strength. This indicated that HNRSH enhanced the compatibilization of HNR and NR in the blends due to the reaction between mercapto functional groups and carbon-carbon double bonds (Sirqueira and Soares, 2002).

Table 4.4 Mechanical properties and crosslink density of HNR/NR and EPDM/NR blends as functions of HNRTA and HNRSH content.

Rubber blends	Functionalized HNR	(phr)	Tensile strength (MPa)	Elongation at break (%)	Crosslink density $\times 10^4$ (mol/cm^3)	Hardness
Conventional vulcanization						
HNR/NR	None	0	3.86 ± 0.75	593 ± 20	1.98 ± 0.50	49.5 ± 0.5
	HNRTA	5	3.93 ± 0.37	451 ± 42	1.98 ± 0.35	50.2 ± 0.3
	HNRSH	5	4.49 ± 1.00	387 ± 23	2.17 ± 0.30	50.5 ± 0.5
Efficient-peroxide vulcanization						
HNR/NR	None	0	6.98 ± 0.31	829 ± 31	0.52 ± 0.00	40.3 ± 0.6
	HNRTA	2	8.46 ± 0.21	798 ± 21	0.60 ± 0.01	41.5 ± 0.5
		3	8.90 ± 0.87	752 ± 25	0.61 ± 0.01	41.5 ± 0.5
		5	9.27 ± 0.10	719 ± 34	0.64 ± 0.03	41.7 ± 0.3
		10	9.57 ± 0.90	703 ± 57	0.67 ± 0.02	42.3 ± 0.6
		15	9.35 ± 0.19	700 ± 24	0.70 ± 0.02	42.6 ± 0.2
	HNRSH	2	8.49 ± 1.27	763 ± 15	0.65 ± 0.06	41.2 ± 0.5
		3	9.11 ± 0.13	711 ± 23	0.77 ± 0.02	41.8 ± 0.3
		5	9.42 ± 0.24	664 ± 26	0.90 ± 0.04	42.2 ± 0.3
		10	9.95 ± 0.71	644 ± 19	1.03 ± 0.13	42.5 ± 0.5
		15	9.83 ± 1.04	639 ± 20	1.10 ± 0.04	43.2 ± 0.2
EPDM/NR	None	0	5.42 ± 0.30	800 ± 30	0.32 ± 0.06	33.8 ± 0.8
	HNRTA	3	5.43 ± 0.31	767 ± 23	0.34 ± 0.05	34.2 ± 0.3
		5	5.63 ± 0.34	755 ± 45	0.44 ± 0.02	34.7 ± 0.3
		10	6.10 ± 1.45	698 ± 63	1.07 ± 0.12	35.2 ± 1.0
	HNRSH	3	5.54 ± 0.60	766 ± 19	0.44 ± 0.03	34.2 ± 0.3
		5	5.90 ± 0.20	751 ± 30	0.47 ± 0.02	35.2 ± 0.3
		10	6.83 ± 0.03	686 ± 54	1.36 ± 0.00	35.8 ± 0.8

In EPV system using TMTD as the sulfur donor, the increase in the amount of both HNRTA and HNRSH increased the crosslink density and tensile strength with reduction of elongation at break. In the case of HNRTA, it could be explained for the increase in the mechanical properties of the blends containing HNRTA that the dicumyl peroxide (DCP) used as the co-crosslinking agent in EPV system might react with the thioacetate groups on the HNR structure to give the mercapto radical species that was responsible for the increase in the crosslink density.

For the addition of HNRSH into the blends cured by EPV system, the presence of DCP increased the compatibility of HNRSH due to its catalytic efficiency in abstracting a hydrogen atom of –SH group functionalized along the HNR backbone. It could promote a faster reaction between mercapto group situated on HNRSH and the NR phase (Jansen, Gomes and Soares, 1996). However, it was found that the addition of HNRTA and HNRSH higher than 10 phr gradually decreased the tensile strength of HNR/NR vulcanizates due to a loss of the interfacial activity. Similar phenomenon has been reported by George et al. (1996) during the addition of phenolic modification polypropylene (Ph-PP) as a compatibilizer into the PP/nitrile rubber (NBR). They suggested that the decrease in the tensile strength was due to the saturation of the interface. The decrease in the elongation at break and the slight increase in the hardness of the blends containing HNRTA or HNRSH resulted from the increase in the crosslink density. For the effect of the addition of HNRTA and HNRSH into EPDM/NR blends, it showed the similar results as exhibited in HNR/NR blends. However, the addition of HNRTA and HNRSH into EPDM/NR blends showed the lower improvement of their mechanical properties when compared to HNR/NR blends. It was possible that both HNRTA and HNRSH were more compatible to HNR than EPDM phase.

4.2.3 Morphology of Rubber Vulcanizates

The effect of the addition of HNRTA and HNRSH on the tensile fracture surfaces of both HNR/NR and EPDM/NR vulcanizates at 50/50 %wt obtained from EPV system was tested by using Scanning Electron Microscope (SEM) as illustrated in Figure 4.16 and 4.17, respectively. For the non-compatibilized HNR/NR blend
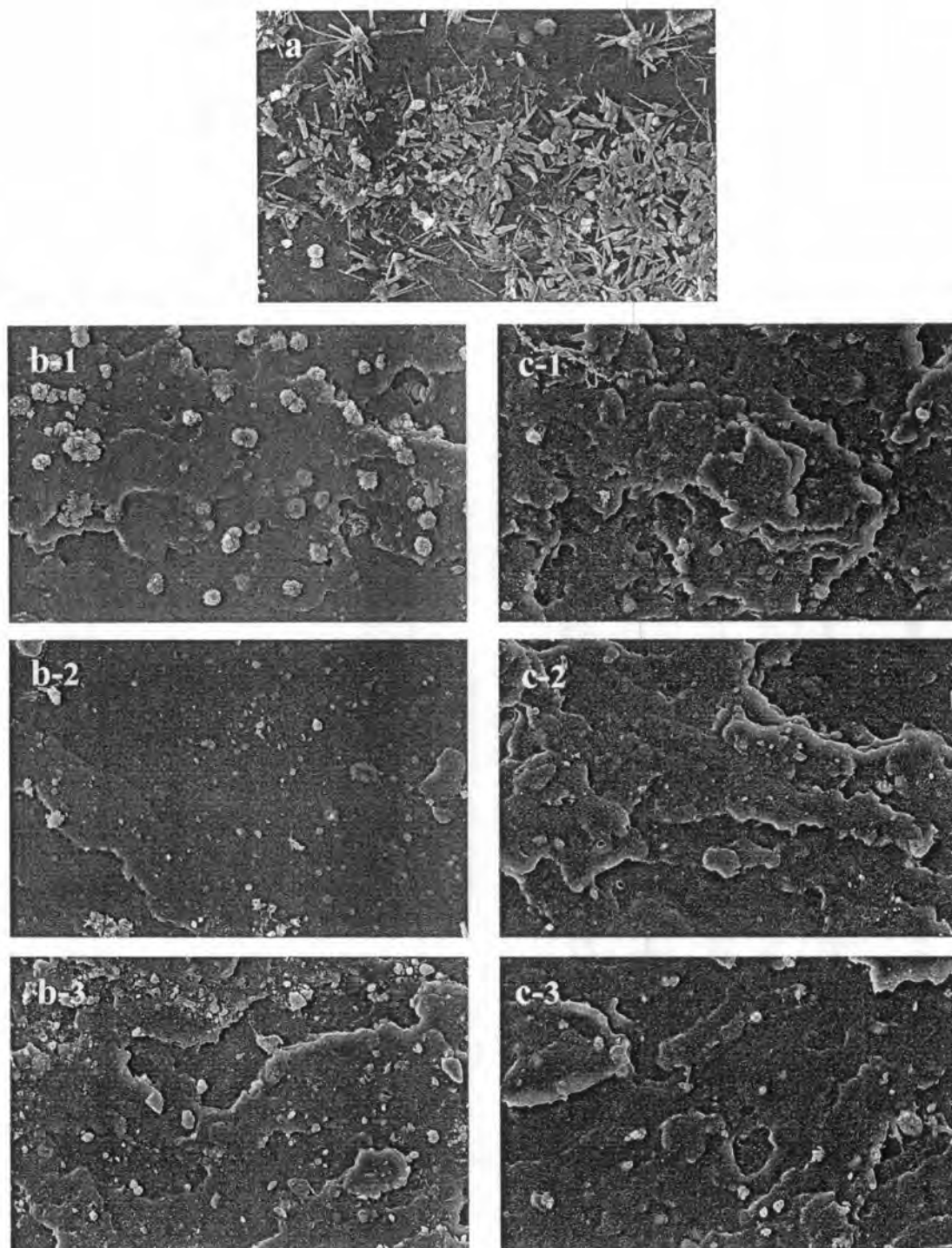
Figure 4.16 Scanning electron micrographs of the tensile fracture surface of HNR/NR
vulcanizates at 50:50 %wt obtained from EPV system: (a) without the
compatibilizers, (b-1) with 3 phr of HNRTA; (b-2) with 5 phr of HNRTA;
(b-3) with 15 phr of HNRTA; (c-1) with 3 phr of HNRSH; (c-2) with 5 phr
of HNRSH and(c-3) with 15 phr of HNRSH (×500 magnitude).

(Figure 4.16a), it could be seen that the HNR phase was separated from the NR phase in the blend due to the incompatibilization effect. The addition of 3 phr of both HNRTA (Figure 4.16b-1) and HNRSH (Figure 4.16c-1) resulted in a substantial decrease in the size of HNR dispersed phase. However, the morphology still exhibited the heterogeneity. At 5 phr of HNRTA (Figure 4.16b-2) and HNRSH (Figure 4.16c-2), the SEM micrographs showed the morphology of the continuous phase with higher homogeneity. These morphologies suggested a reduction of the interfacial tension with the compatibilization resulting in co-vulcanization state of the blends to increase the tensile strength and the crosslink density of the blends (George et al., 1995). Moreover, it could be observed that the presence of HNRSH promotes a higher uniform morphology than HNRTA because the mercapto groups was more effective to react with NR at the interface thioacetate group. Thus, this indicated that the mercapto functional group could increase the chance of phase coalescence (Oliveira and Soares, 2003). Figure 4.16b-3 and 4.16c-3 showed the addition of 15 phr of HNRTA or HNRSH into HNR/NR blends. It is interesting to note that the homogeneity of the matrix decreased and the size of the dispersed phase became larger. Several authors (Noolandi and Hong, 1984 and George et al., 1995) suggested that there was maximum quantity of compatibilizer that could saturate the interface. Addition of a compatibilizer beyond this point might not satisfy the improvement. Moreover, the addition of overload of HNRTA or HNRSH into HNR/NR blends resulted in the higher incompatibilization similar to the behavior observed when the HNR content was increased to HNR/NR blends as described by Napida Hinchiranan et al. (2009). For the EPDM/NR blend without using any compatibilizer, a rubber phase separation was also observed (Figure 4.17a). The addition of 5 phr of both HNRTA (Figure 4.17b) and HNRSH (Figure 4.17c) into EPDM/NR blends could improve the compatbilization. However, it showed the lower compatibility when compared to HNR/NR blends. This indicated that HNRTA and HNRSH were more compatible to HNR than EPDM phase resulting in higher tensile properties of HNR/NR vulcanizates (Table 4.4).
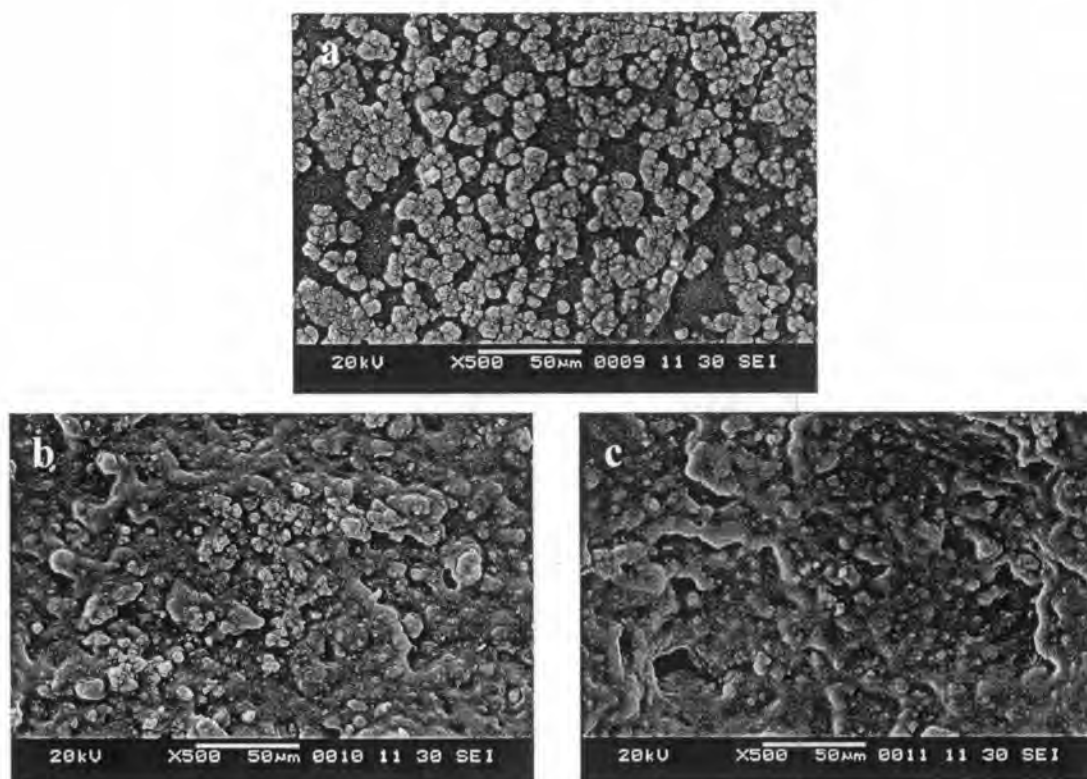
Figure 4.17 Scanning electron micrographs of the tensile fracture surface of EPDM/NR (50:50 %wt) vulcanizates obtained from EPV system (a) without compatibilizers, (b) with 5 phr of HNRTA and (c) with 5phr of HNRSH (×500 magnitude).

4.2.4 Thermal Properties of Rubber Vulcanizates

The effect of the addition of HNRTA and HNRSH on the thermal properties of HNR/NR vulcanizates (50/50 %wt) cured by EPV system was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC is normally used to determine the glass transition temperature (T_g) of polymers. It is also used to study the miscibility of compositions in the polymer blends by monitoring the shift of T_g. In the totally miscible polymer blends, one T_g depending on the blend composition is appeared. The two T_g shifted to the direction of their average is typical for the partially miscible polymer blends. For pure HNR vulcanizates, the T_g of HNR was the same as that of NR vulcanizate (Inouse and Nishio, 2007). Therefore, it is difficult to determine the miscibility of the blends. However, Table 4.5 showed that the T_g of HNR/NR vulcanizates containing 5 phr of HNRTA and HNRSH slightly increased compared to the blend without the addition of

the compatibilizers. Moreover, the T_g of HNR/NR vulcanizate with HNRSH addition had higher T_g (-62.6°C) than the one containing HNRTA (-63.2°C) due to the more crosslink density to decrease the mobility of the polymer chain.

From the TGA results, Figure 4.18 exhibits the TGA thermograms of HNR/NR vulcanizates with and without the addition of HNRTA or HNRSH at 5 phr. It indicated the two-stage decomposition pattern. Table 4.5 showed that the initial (T_{id}) and maximum (T_p) decomposition temperatures of the first stage of thermal decomposition appeared around 350-354°C and 376-379°C, respectively. This corresponded to the decomposition of the NR phase in the blends. The second stage of decomposition occurred at the peak temperature around 453-461°C which indicated to the maximum decomposition temperature of HNR phase. This means that the addition of HNRTA or HNRSH into the blends did not affect the thermal stability of the vulcanizates.

Table 4.5 Thermal properties of HNR/NR vulcanizates obtained from EPV system containing 5 phr of compatibilizers.

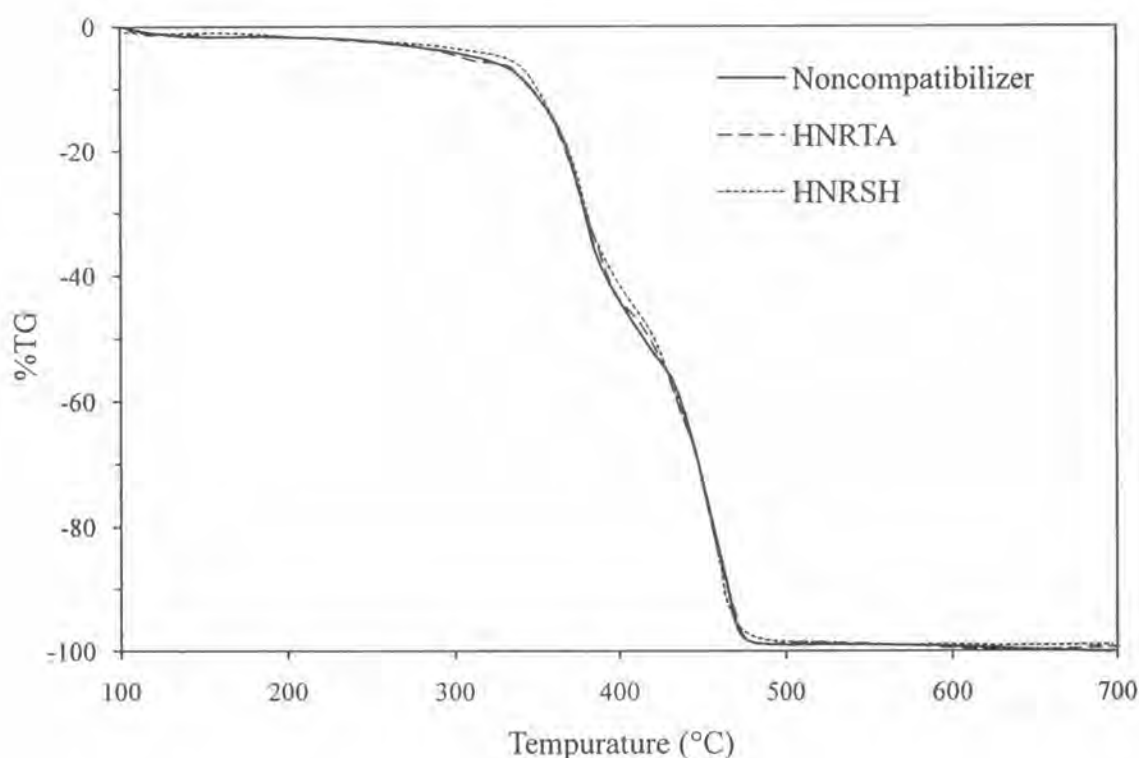| Compatibilizer	T_g(°C)	Decomposition Temperature (°C)			
		NR phase		HNR phase	
		$T_{id,NR}$	$T_{p,NR}$	$T_{id,HNR}$	$T_{p,HNR}$
non	-63.6	353.5	377.1	438.8	460.5
HNRTA	-63.2	350.1	376.3	442.9	456.3
HNRSH	-62.6	352.9	378.6	436.1	453.6

Figure 4.18 TGA curves of HNR/NR vulcanizates (50:50 %wt) obtained at a heating rate 10°C/min: noncompatibilized blend (—), compatibilized with 5 phr of HNRTA (– –) and compatibilized with 5 phr of HNRSH (----) under N_2 atmosphere.

4.2.5 Dynamic Mechanical Properties

The effect of the addition of HNRTA and HNRSH on the dynamic mechanical properties such as storage modulus (E') and tan δ of HNR/NR vulcanizates at 50/50 %wt cured by EPV system is shown in Figure 4.19 and Table 4.6. The results indicated that the addition of HNRTA and HNRSH slightly decreased the T_g of the blends. This is possible that the crosslink chain generated from HNRTA and HNRSH might be more flexible under applied stress. The plateau region of E' curve after transition zone exhibits the crosslink density of polymer (Soni, 1991, cited in Cheremisinoff, ed., 1993: 176). The storage modulus in the plateau region at 30°C of HNR/NR vulcanizates without the compatibilizers as reported in Table 4.6 was higher than that of the blends with the compatibilizers. It means that the presence of compatibilizer in HNR/NR blends had a higher crosslink density than that without the compatibilizers. The HNR/NR vulcanizates containing HNRSH had a higher storage modulus than the one having HNRTA probably due to the higher amount of crosslink

density indicated by the swelling experiment as shown in Table 4.4. In addition, the strong interaction between the functional groups along the HNR backbone and the NR phase decreased the mobility of the polymer chain giving a decrease in the damping from 1.32 to 1.28 as shown in Table 4.6 (Sirqueira and Soares, 2002).
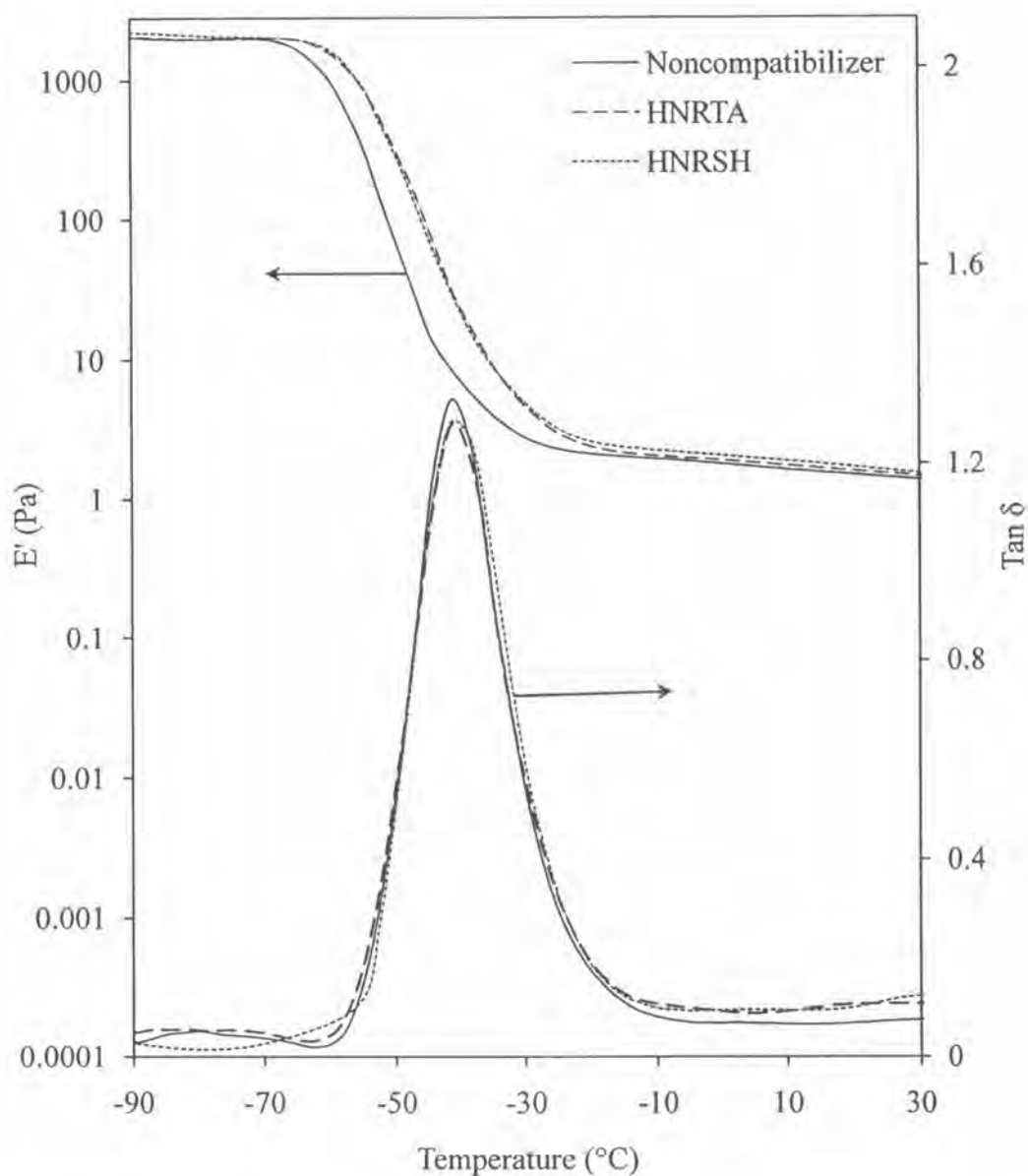

Figure 4.19 Dynamic mechanical properties of HNR/NR vulcanizates (50:50 %wt): noncompatibilized blend (—), compatibilized with 5 phr of HNRTA (– –) and compatibilized with 5 phr of HNRSH (----).

Table 4.6 T_g, tan δ at T_g and E' at 30°C of HNR/NR vulcanizates with and without the compatibilizers

Compatibilizer	T_g(°C)	tan δ at T_g	E' at 30°C (MPa)
non	-40.1	1.32	1.42
HNRTA	-40.6	1.28	1.47
HNRSH	-41.3	1.28	1.60

4.2.6 Ageing Resistance

4.2.6.1 Effect of Thermal Ageing on the Mechanical Properties

The effect of the compatibilizers (HNRTA and HNRSH) on the mechanical properties after thermal ageing at 100°C for 22±2 h of HNR/NR and EPDM/NR blends vulcanized by using CV and EPV systems was investigated as presented in Table 4.7. It can be seen that the HNR/NR vulcanizates obtained from EPV system had higher retention properties than ones cured by CV system. It could be explained in that the thermal resistance of C-C linkages generated by peroxide in EPV system was higher than that of polysulfidic linkage produced by sulfur in CV system (Diego, 1978). Moreover, the TMTD in EPV system possibly reacted to zinc oxide to produce zinc-dimethyldithiocarbamate (ZDMDC) which is an efficient antioxidant (Morrell, 1982)

For the EPV system, the non-compatibilized HNR/NR and EPDM/NR vulcanizates after heat ageing had lower mechanical properties due to the partial rubber degradation. The increase in the amount of HNRTA and HNRSH in the blends resulted in the higher retention of tensile strength and lower retention of elongation at break of the vulcanizates. This indicated that the addition of HNRTA and HNRSH could promote the formation of crosslink during heat ageing (Olivera and Soares, 2001). The similar results were found in the EPDM/NR vulcanizates. The tensile strength retention of HNRTA-compatiblized blends was better than that of HNRSH-compatiblized blends. It might be explained that the residue of thioacetate group in the blends after vulcanization was higher than that of mercapto group which

Table 4.7 Effect of compatibilizer on the mechanical properties of HNR/NR and EPDM/NR blends at 50/50 %wt before and after thermal ageing at 100°C for 22 h.

Rubber blends	Compatibilizer Content (phr)		Tensile strength (MPa)		Elongation at break (%)	
			After ageing	%Retention	After ageing	%Retention
Conventional vulcanization						
HNR/NR	None	0	1.76 ± 0.54	45.4	206 ± 86	34.7
	HNRTA	5	2.46 ± 1.01	62.5	348 ± 42	77.3
	HNRSH	5	3.53 ± 0.63	78.7	248 ± 44	64.3
Efficient-peroxide vulcanization						
HNR/NR	None	0	6.98 ± 0.31	89.3	739 ± 49	89.2
	HNRTA	2	8.49 ± 1.27	93.8	716 ± 37	89.8
		3	9.11 ± 0.13	94.4	654 ± 72	87.0
		5	9.42 ± 0.24	95.6	585 ± 70	81.3
		10	9.95 ± 0.71	100.3	526 ± 50	74.8
		15	9.83 ± 1.04	103.2	420 ± 66	60.0
	HNRSH	2	7.65 ± 1.66	90.0	678 ± 64	88.8
		3	8.33 ± 0.67	91.5	621 ± 50	87.4
		5	8.51 ± 0.99	90.4	580 ± 79	87.4
		10	9.55 ± 0.90	96.0	560 ± 63	87.0
		15	9.57 ± 1.08	97.4	514 ± 70	80.4
EPDM/NR	None	0	4.35 ± 0.68	80.0	770 ± 9	96.3
	HNRTA	3	4.56 ± 0.81	84.0	720 ± 24	93.9
		5	5.51 ± 1.18	97.8	687 ± 28	91.0
		10	7.03 ± 0.73	115.3	634 ± 11	90.9
	HNRSH	3	4.53 ± 1.06	81.8	729 ± 39	95.2
		5	5.49 ± 1.82	93.1	741 ± 45	91.5
		10	6.96 ± 0.86	101.9	683 ± 31	92.4

enhanced the crosslink density during the ageing process. These results indicate that both HNRTA and HNRSH could increase the thermal stability of these blends. As reported in the previous literature (Olivera and Soares, 2001), antioxidants containing mercapto group are normally employed to protect rubber vulcanizates against heat aging.

4.2.5.2 Ozone Resistance

Ozone at only a few parts per hundred million readily cleaves carbon-carbon double bonds in elastomers. NR exposed to ozone under strained state quickly develops surface cracks (Hamed, 2001). The blending of NR with a highly saturated elastomer such as HNR was effective to reduce the ozone cracking on the surface of vulcanizates NR (Hinchiranan et al., DOI 10.1002/app.30034).

The effect of the addition of HNRTA and HNRSH on the ozone resistance of HNR/NR vulcanizates was investigated. The HNR/NR samples with and without the addition of HNRTA and HNRSH were exposed in a HAMPDEN ozone cabinet at 40°C in an atmosphere containing 50 pphm by volume of ozone concentration for 6, 24 and 48 h. Before exposure to the ozone atmosphere, the specimens were stretched by 20% in the absence of light for 48 h. The test method followed the ISO 1431 Part 1 and The Physical Testing Standards of Rubbers by Nishi and Nagno (1983). A lens of magnification of about 7 times was used to detect the appearance of cracking on the surface of specimens. A type of ozone cracking on the rubber surface was classified according to Table 4.8. After exposure to the ozone atmosphere at the same condition, the cracking of HNR/NR vulcanizates cured by EPV system with and without the addition of compatibilizers was compared as shown in Table 4.9 and Figure 4.20.

The ozone cracking of non-compatibilized HNR/NR vulcanizate at 50/50 %wt was initially attacked by ozone after 6 h exposure time as shown in Figure 4.20(a-1). Hinchiranan et al. (DOI 10.1002/app.30034) reported that antioxidant of ZDMDC obtained from the reaction of zinc oxide and TMTD in EPV system enhanced the resistance to ozonolysis for vulcanizates. The length of cracking

traces on the surface of non-compatibilized HNR/NR vulcanizate was expanded and became longer than 3 mm with an increasing exposure time to 24 and 48 h as shown in Figure 4.20(a-2) and 4.20(a-3), respectively. For the effect of compaibilizer of HNR/NR blends, the presence of HNRTA and HNRSH in the blends could retard the initiation of surface cracking by ozone, but it could not retard propagation of surface cracking after 24 h of exposure as shown in Figure 4.20 (b-1)-(b-3) and Figure 4.20 (c-1)-(c-3). It is possibly due to both functionalized HNRs employed as antioxidants to protect rubber vulcanizates against the ozone cracking at the initiation of surface cracking. For the comparison of HNRTA and HNRSH, the use of small amount (3 phr) of HNRTA did not show the ozone cracking traces on the surface of HNR/NR vulcanizate after exposure in ozone atmosphere for 6 h, but for the vulcanizates compatibilized by HNRSH, the ozone cracking traces were found when HNRSH content in the blends was lower than 10 phr. It might be explained that the residue of thioacetate group in the blends after vulcanization was higher than that of mercapto group which retard the initiation of surface cracking caused by ozone.

Table 4.8 Classification of cracking on rubber surface (Nishi and Nagano, 1983)

Number of Cracking	Size and Depth of Cracking
A: a small number of cracking	1. That which cannot be seen with eyes but can be confirmed with 10 times magnifying glass.
	2. That which can be confirmed with naked eyes.
B: a large number of cracking	3. That which is deep and comparatively long (below 1 mm).
	4. That which is deep and long (above 1 mm and below 3mm).
C: numberless cracking	5. That which is about to crack more than 3 mm or about to sever.

Table 4.9 Effect of compatibilizer on ozone resistance of HNR/NR vulcanizates cured by EPV system

Compatibilizer	Content (phr)	Type of cracking at a specific exposure time		
		6 h	24 h	48 h
None	0	C-4	C-4	C-5
HNRTA	3	nc[1]	C-4	C-5
	5	nc	C-4	C-5
	10	nc	C-4	C-5
HNRSH	3	C-4	C-4	C-5
	5	B-4	C-4	C-5
	10	nc	C-4	C-5

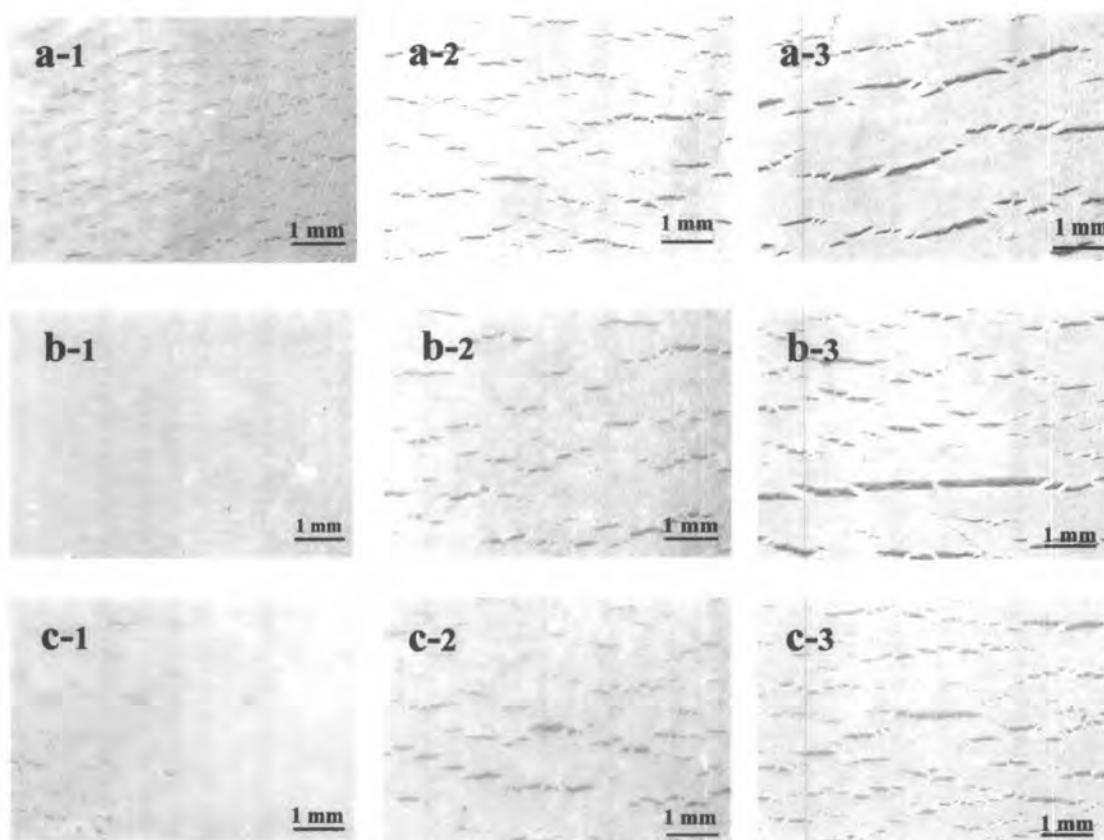[1]nc = The cracking did not appeared on the surface of specimens.

Figure 4.20 Stretched surface of vulcanized HNR/NR (50:50 wt%) blends : (a) non-compatibilized blend, (b) compatibilized with 5 phr of HNRTA and (c) compatibilized with 5 phr of HNRSH after exposure to ozone (50 pphm) at 40°C for (1) 6 h, (2) 24 h and (3) 48 h.