Improvement in the properties of silica-reinforced natural rubber with the sustainable interfacial modifier: effect of molecular weight and content of interfacial modifier

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Abstract

Silica is the most reinforcing filler for enhancing the rubber properties. However, the incompatibility of silica with non-polar rubber is the main problem for application. Therefore, the researchers attempted to use the several methods in order to solve the problem. In this work, the appropriated hydroxyl telechelic natural rubber (HTNR) was determined by varying molecular weights in the range of 2,000-3,000 $g \cdot mol^{-1}$ and contents in the range of 4-16%w/w of silica content in order to enhance the rubber properties. It was found that the decrease in Payne effect and the improvement in cure characteristics of silica-reinforced NR were achieved by using HTNR. However, the incorporation of various molecular weights and contents of HTNR in rubber influenced C_1 (crosslink density determined by stress-strain measurement) in rubber, which related to rubber properties. The increasing in C_1 caused the increases in tensile strength and abrasion index and the decrease in heat build-up. The optimum properties of rubber with silica loading at 30 phr was achieved by adding 2,000 $g \cdot mol^{-1}$ HTNR at a loading of 8%w/w of silica content. However, for silica-reinforced NR, TESPT provided better properties than HTNRs.

1. Introduction

Natural rubber has been widely used in household and industries for a long time. The excellent elasticity and good mechanical properties of natural rubber are important factors which effect on selecting it to make products. In addition, chemical agents especially, reinforcing fillers are necessary to apply in rubber for improving its processing and mechanical properties [1]. Silica is one of the most important fillers for enhancing performance of rubbers. Nevertheless, silica has many silanol groups on its surface resulting in high polarity, which have an effect of poor interaction with non-polar rubber and undesirable cure characteristics of rubber [2,3]. Therefore, the several techniques have been attempted to improve silica surface such as admicellar polymerization [4], core-shell polymerization [5], plasma polymerization [6], silane treatment [7-9] and so on. Regarding the application of silane coupling agent, it is still a favorable method for modifying silica surface. The most efficient coupling agent is organosilane [10] (i.e. bis (3-triethoxy silylpropyl) tetrasulfide (TESPT) [11] because it has high efficiency to improve interaction between rubber and silica, and enhance the mechanical properties of rubbers [12]. However, the application of TESPT in silica- filled rubber has found the problems involving scorching of rubber [9] and releasing of

ethanol from the silanisation reaction [13]. This causes the defects in rubber matrix and then poor mechanical properties. Hence, the numerous researchers attempt to use the modified natural rubber with polar groups such as epoxidized natural rubber (ENR) [7,14], maleated natural rubber [15], and carboxy-terminated natural rubber [16] in order to improve rubber-filler interaction, and solve the problem which is occurred by using TESPT in silica- reinforced rubber. However, the utilization of modified natural rubber in silica-reinforced NR provides the limited improvement of the rubber properties (i.e. cure characteristics, mechanical and dynamic properties) when comparing with silica vulcanizates with TESPT due to higher molecular weight and lower functional groups of modified natural rubber.

Hydroxyl telechelic natural rubber (HTNR) is low molecular weight substance with bearing hydroxyl groups, which are subjected to further reaction and crosslink. HTNR is widely used in the production of polyurethane materials (i.e. adhesives [17], biomaterials [18], foams [19,20], and pressure sensitive adhesive [21]). In addition, it also has been used as compatibilizer for improving dispersion and compatibility of carbon black in polymer [22].

The aim of this study is to improve properties of silica-filled natural rubber by using HTNR as an interfacial modifier comparing with TESPT. The

expected mechanism to improve the properties of silica-reinforced NR with HTNR associates with hydrogen bonding between hydroxyl groups of HTNR and silanol groups of silica along with entanglement between isoprenic segments of HTNR with rubber molecules in the matrix resulting in improvement in compatibility between silica and rubber and hence enhancing mechanical properties of rubber. The influences of HTNR molecular weights in a range of 2,000-3,000 g·mol^{-1} and HTNR contents in a range of 4-16%w/w of silica content were investigated.

2. Experimental

2.1 Materials

For the synthesis of HTNR, high ammonia concentrated latex (60% DRC) was purchased from Yala latex industry Co., Ltd, Thailand. Formic acid and hydrogen peroxide were the products of Acros Organics, Belgium. Periodic acid was supplied by Merck, Germany. Sodium borohydride (NaBH$_4$) was procured from Loba Chemie Pvt. Ltd, India. For rubber compounding and vulcanization, natural rubber (STR 5L) was obtained from Yala latex industry Co., Ltd, Thailand. The precipitated silica (ULTRASIL®VN 3) used as a filler, and bis-(3-triethoxysilylpropyl) tetrasulfide silane (TESPT) used as a coupling agent were the products from Evonik, Germany. 2,2,4-Trimethyl-1,2-dihydroquinoline polymer (Flectol® TMQ), diphenyl guanidine (DPG), and N-tert-butyl-2-benzothiazole sulfonamide (TBBS) were supplied by Flexsys America L.P., U.S.A. Cure activators (zinc oxide and stearic acid) and sulfur were procured from Petch Thai Chemicals Co., Ltd., Thailand.

2.2 Preparation of HTNR

Hydroxyl telechelic natural rubbers (HTNRs) with various molecular weights were prepared by controlled epoxidation and cleavage of natural rubber, followed by reduction reaction of the obtained carbonyl telechelic natural rubber (CTNR). The epoxidation reaction was performed via *in-situ* generated performic acid at 60°C for 1.5 and 3 h to obtain the ENRs with the different degrees of epoxidation as 1.96 and 3.85%, respectively. Thereafter, the ENR was cleaved by periodic acid in solution (H$_5$IO$_6$/epoxide ratio = 1/1) in order to obtain CTNR, and finally it was reduced by 1.0 M NaBH$_4$ solution at 60°C for 6 h yielding HTNR. The procedure for reaction process of HTNR has been shown in Figure 1 and described elsewhere [19].

2.3 The influence of molecular weight and content of HTNR as an interfacial modifier in rubber

Different molecular weights (2,000 and 3,000 g·mol^{-1}) and amounts (4, 8, 12 and 16%w/w of silica content) of HTNR were investigated as an interfacial modifier on properties of silica-reinforced NR. The compound formulations for this study are shown in Table 1.
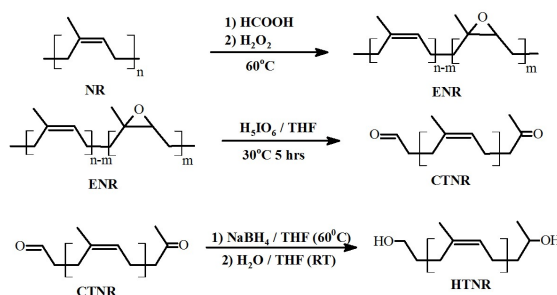

Figure 1. Preparation of HTNR.

All ingredients without curing agent were mixed in Brabender Plasticorder (Brabender 50®EHT) at a rotor speed of 60 rpm. The initial mixing temperature was set at 30°C for 8 min in order to protect thermal degradation of natural rubber and HTNR during mixing (This condition was found to be optimum in a preliminary study [23]) in the case of preparing silica-filled NR without silane coupling agent (Non-silane) and with HTNR. For silica-reinforced NR with TESPT, it was prepared by Brabender plasticorder at starting temperature of 90°C for 12 min in order to provide mixing temperature reaching to the high temperature which allowed silanization reaction taking place between TESPT and silica during mixing. Mixing procedure was started with mastication of NR for 1 min before HTNR was added and together mixed for 0.5 min. Zinc oxide, stearic acid, ½ silica, ½ DPG and ½ TESPT were added at 1.5 min. TMQ, ½ silica, ½ DPG and ½ TESPT were added at 4 min and mixed until the end of mixing time. The rubber compounds were left at ambient temperature for 24 h. Then, TBBS and sulfur were added into masterbatches on two roll mill for 5 min. The obtained NR compounds were fabricated by using hydraulic press at temperature of 160°C with the optimum cure time in order to prepare specimens.

2.4 Characterization

2.4.1 Characterization of HTNR

FTIR spectra of HTNR samples were recorded using an attenuated total reflection (ATR)–FTIR spectrometer (Tensor 27) in the range of 4000-400 cm^{-1}. The ^{1}H-NMR spectra of HTNR solution (0.02 g HTNR in 2 ml of deuterium chloroform) were obtained by using Varian Unity Inova 500 MHz at frequency of 500 MHz. Number-average molecular weights of HTNRs were determined using the following equation [24].

Table 1. Formulations of silica- reinforced NR compounds with HTNR as interfacial modifier.

Ingredient	Content (phr)			
	Non-silane	2000HTNR	3000HTNR	TESPT
Natural rubber	100.0	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0
Silica	30.0	30.0	30.0	30.0
2000 g/mol HTNR	0	4-16%w/w of silica	0	0
3000 g/mol HTNR	0	0	4-16%w/w of silica	0
TESPT	0	0	0	2.4
DPG	0	0	0	0.6
TMQ	1.0	1.0	1.0	1.0
TBBS	1.5	1.5	1.5	1.5
Sulphur	2.0	2.0	2.0	2.0

$$\overline{M}_n \ = \ \left[\frac{I_{5.10}}{I_{3.68}/2} \ x \ M_1 \right] + M_2 \qquad (1)$$

Where $I_{3.68}$ is the integrated area of peak at $\delta = 3.68$ corresponding to CH_2 adjacent to alcohol at the terminal chain, $I_{5.10}$ is the integrated area of peak at $\delta = 5.10$ which is the proton signal adjacent to carbon-carbon double bond units, M_1 and M_2 are molecular weights of the repeating unit of NR (68 $g \cdot mol^{-1}$), and the end groups of HTNR (-C_2H_4OH and -C_3H_6OH; 104 $g \cdot mol^{-1}$), respectively.

2.4.2 Rubber compound and vulcanizate testing

Payne effect of all silica-filled NR compounds (without curing agent) was studied by using rubber processing analyzer (RPA2000) at temperature of 100°C and a frequency of 0.5 Hz. The test was carried out at various strain amplitudes in the range of 0.56-100%. The difference between storage moduli at 0.56% strain and at 100% strain was considered to be Payne effect.

Cure characteristics of all rubber compounds (i.e. scorch time (t_{s1}), optimum cure time (t_{c90}), and cure rate index (CRI)) were determined by using oscillating disk rheometer (Rheometer ODR2000). The test was carried out at 160°C for 20 min.

The crosslink densities of vulcanized rubber were determined by swelling method in toluene. The vulcanized samples were cut in rectangular shape with dimension of $1.00 \times 1.00 \times 0.15$ cm and weighed before immersing in 30 ml of toluene at room temperature for 168 h. The weight of swollen samples was measured, and then crosslink density was calculated using the Flory-Rehner equation [25].

$$- \ln(1 - V_r) - V_r - \chi V_r^2 \ = \ 2V_s \eta_{swell} \left(V_r^{\frac{1}{3}} - \frac{2V_r}{f} \right) \qquad (2)$$

Where V_r is the volume fraction of rubber in the swollen gel.
V_s is the molar volume of toluene (106 $cm^3 \cdot mol^{-1}$).

χ is the rubber- solvent interaction parameter (0.3795 for NR).
η_{swell} is the crosslink density of the rubber (mol·cm^{-3}).
f is the functionality of the crosslinks (4 for the sulfur curing system).

Silica dispersion in rubber matrix was characterized by a scanning electron microscope (SEM FEI Quanta 400, FEI, Eindhoven, Netherlands) at an accelerating voltage of 20 kV. The specimens were cryogenically fractured and sputter coated with gold to prevent charging on the surfaces.

Tensile properties in terms of modulus and tensile strength of vulcanized rubbers were determined by using the dumbbell-shape specimens according to ISO 37. The tensile properties were measured by a universal testing machine (H10KS) at room temperature, with the extension speed of 500 mm·min^{-1}.

Abrasion resistance index was determined by using DIN abrasion test machine (GT-70120) according to DIN 53516. Abrasion resistance index of rubber was determined by abrading a cylindrically shaped specimen (thickness of 6 mm.) for an abrasion distance of 40 m with abrader paper (60 grit) at a constant force of 10 N and a constant speed of 0.32 m·s^{-1}. Abrasion resistance index was available to calculated by this equation.

$$\text{Abrasion resistance index (ARI)} = \frac{\Delta m_1 \cdot d_t}{\Delta m_t \cdot d_1} \ x \ 100 \qquad (3)$$

Where Δm_1 is mass loss of standard rubber (mg).
Δm_t is mass loss of test rubber (mg).
d_1 is density of standard rubber (g·cm^{-3}).
d_t is density of test rubber (g·cm^{-3}).

Heat build-up of rubber was investigated. The BF Goodrich Flexometer (FLEXOMETER) was used to measure the temperature rise of the cylindrical rubber specimens according to ASTM D 623. The specimens were cyclically deformed at 1,800 rpm and 100°C for 25 min.

3. Results and discussion

3.1 Characterization of chemical structure and molecular weight

The chemical structures of HTNR with different molecular weights were characterized by FTIR as shown in Figure 2. All infrared spectra showed the sharp peaks of C-H asymmetric stretching, C-H symmetric stretching and =CH- symmetric bending as the same as natural rubber structure at the wave number of 2925, 2869 and 835 cm^{-1}, respectively [19, 26]. Besides, the presence of the C=C *cis*- vinylene was appeared at the wave number of 1660 cm^{-1}. The stronger absorption peak of hydroxyl groups at wave number of 3355 cm^{-1} was observed with decreasing in molecular weight of HTNR due to the increment in the number of hydroxyl groups with decreasing molecular weight of HTNR when considering at the same HTNR content.

Figure 3. shows ^{1}H-NMR of HTNR with different molecular weights. The chemical shift of methyl protons next to the carbon-carbon double bond, methylene protons next to the carbon-carbon double bond and proton adjacent to carbon-carbon double bond of polyisoprenic structure appeared at 1.67, 2.09 and 5.10 ppm, respectively, for all HTNRs which were similar to natural rubber structure. Apparently, chemical shifts at 3.80 and 3.68 ppm of CH and CH$_2$ adjacent to terminal hydroxyl groups were appeared in HTNR. Moreover, chemical shift of methyl protons

adjacent secondary alcohol appeared at 1.20 ppm [19]. The increase of intensity ratio between CH$_2$ adjacent to terminal hydroxyl groups at 3.68 ppm compared with unsaturated methylene protons of isoprene units at 5.10 ppm indicating that decreasing molecular weight of HTNR. The number average molecular weights of 2,000 g·mol^{-1} HTNR and 3,000 g·mol^{-1} HTNR investigated and characterized by ^{1}H-NMR, are equal to 2,047 and 2,824 g·mol^{-1}, respectively. Moreover, the obtained HTNR consists of 2 hydroxyl functionality at chain end according to previous works [19].
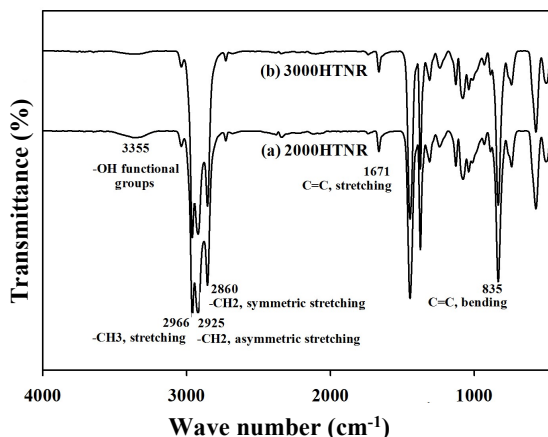
Figure 2. Infrared spectra of HTNR with molecular weight of (a) 2,000 g·mol^{-1} and (b) 3,000 g·mol^{-1}.

Figure 3. 1H-NMR spectra of (a) 2,000 g·mol^{-1} and (b) 3,000 g·mol^{-1}.

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3.2 Payne effect

Figure 4. shows high Payne effect of Non-silane system due to high polarity on silica surface and strong filler-filler interaction, whereas the decrease in Payne effect of silica-filled NR with increasing HTNR content was observed. It was attributed to increase in interaction between hydroxyl groups of HTNR and silanol groups on silica surface. At the similar content of HTNR, silica-filled NR with low molecular weight of 2,000 g·mol^{-1} HTNR showed lower Payne effect. This caused by higher functional groups of lower molecular weight HTNR resulting in the better interaction with silica. However, silica compound with 3,000 g·mol^{-1} HTNR showed the lowest Payne effect at its content of 16%w/w of silica loading owing to larger structure of 3,000 g·mol^{-1} HTNR causing larger shielding effect on silica surface. This phenomenon was also found in the case of the improvement of silanization efficiency and silica dispersion in silica-reinforced NR with the addition of the larger molecule of TESPT comparing with the lower molecule of vinyltriethoxysilane (VTES) [8]. It was found that less steric hindrance of VTES is a cause of better interaction with silica [8]. However, larger shielding effect on silica surface with addition TESPT caused better silanization efficiency and filler dispersion comparing with VTES [8]. In comparison with TESPT, Payne effect of silica- filled compound with HTNR was still larger than that of silica- filled compound with TESPT. This had been affected from the lower molecular weight (approximately 532.5 g·mol^{-1}) and the richer functional groups of TESPT.

adsorption of accelerator and zinc stearate on silica surface resulting in retardation of vulcanization reaction. Apparently, scorch time increased with increasing amount of HTNR due to dilution effect from the addition of HTNR resulting in retardation of vulcanization reaction at the initial stage. Cure time of silica compounds tended to decrease with HTNR content up to 8%w/w of silica content, and then increase again at HTNR content of 12%w/w of silica content. Meanwhile, CRI of silica-reinforced NR with HTNR increased with increasing HTNR content, and reached the maximum value at 8%w/w of silica content. The decrease in cure time, and increase in CRI at low HTNR content were due to the enhancement of the interaction between HTNR and silica resulting in the less absorption of accelerator and zinc stearate on silica surface. However, the further addition of HTNR in silica-reinforced NR over the optimum content which provided the lowest cure time and the highest CRI, resulted in increment in cure time and reduction of CRI due to the formation of an undesirable interaction between the remaining hydroxyl groups of HTNR and chemical agents (i.e. zinc stearate and accelerator) in rubber matrix leading to delay in vulcanization reaction. The similar behavior was observed in silica-reinforced NR with ENR as compatibilizer where scorch and cure time increased with increasing ENR contents due to interaction between free epoxide groups of ENR with accelerator resulting in retardation of vulcanization reaction [14]. However, scorch and cure time, and CRI of silica-reinforced NR with the various molecular weights of HTNR were not significantly different. The presence of TESPT in rubber compounds resulted in the reduction of scorch and cure time, and the increment in CRI of silica-reinforced rubber due to interaction of ethoxy groups of TESPT with silanol groups on silica surface resulting in reduction of adsorption of accelerator and zinc stearate on silica surface. Moreover, the sulfur atom of TESPT was an important parameter for the improvement of cure characteristic [7, 27].
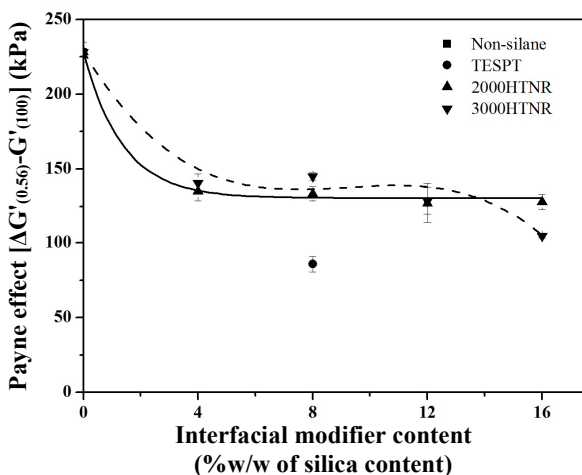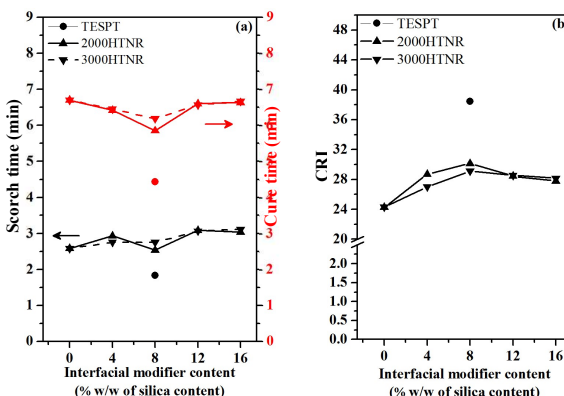

Figure 4. Payne effect of silica-reinforced NR as a function of HTNR contents.

3.3 Cure characteristic

Scorch time, cure time, and CRI of silica-reinforced NR are shown in Figure 5(a) and 5(b). The long scorch and cure time, and the lowest CRI of Non-silane system were caused by the high polarity and

Figure 5. Cure behavior based on (a) scorch and cure time, and (b) CRI of silica-reinforced NR as a function of HTNR contents.

3.4 Crosslink density

Figure 6. represents crosslink density of silica-reinforced NR with the various HTNR contents determined by swelling test and calculated by Flory-Rehner equation. The low crosslink density of Non-silane was caused by high polarity and adsorption of accelerator on silica surface resulting in retardation of vulcanization reaction. Moreover, it was found that crosslink density of silica compounds increased with increasing HTNR content up to 8%w/w of silica content, and then decreased. The increase of crosslink density involved with the improvement of true sulfur crosslink and rubber-filler interaction [3,28] by HTNR as interfacial modifier. However, crosslink density decreased when HTNR was added more than 8%w/w of silica content due to the interaction of free hydroxyl groups of HTNR with curing agents. The similar behavior was found in silica-reinforced NR with alkonolamide (ALK) when crosslink density of vulcanizate increased to the optimum value at 5.0 phr of ALK content and then decreased with further increase in ALK content [29]. However, crosslink density of silica-reinforced NR was not significantly affected by varying molecular weight of HTNR. However, TESPT provided the highest crosslink density of silica-reinforced NR due to the release of sulphur atoms from dissociation of TESPT which further reacted with rubber molecules resulting in more bonding between rubber and silica [27].
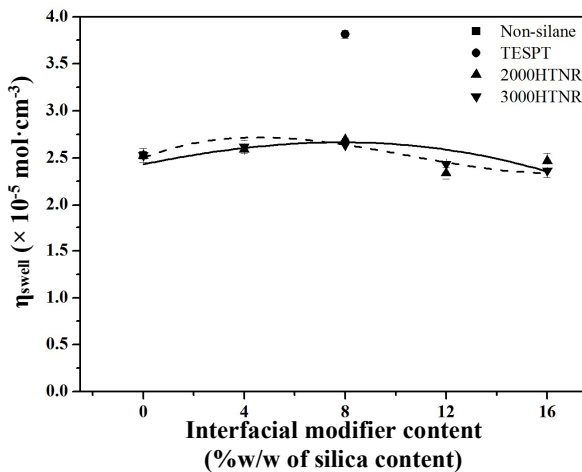

Figure 6. Crosslink density of silica-reinforced NR as a function of content of HTNR.

3.5 Morphological properties

The morphology of silica-reinforced NR with the various HTNR contents is represented in Figure 7. The poor dispersion of the larger silica agglomerates in rubber matrix is appeared in Non-silane. It is attributed to poor rubber-filler interaction and strong filler-filler interaction. However, the addition of HTNRs (both in 2,000 g·mol^{-1} and 3,000 g·mol^{-1} HTNRs) and TESPT

in silica-reinforced NR provided smaller silica agglomerates and better silica dispersion in rubber matrix due to the interaction of hydroxyl groups of HTNR or alkoxyl groups of TESPT with silanol groups on silica surface. This resulted in an improvement in the compatibility between rubber and silica together with decrease the strong filler-filler interaction. Moreover, the size of silica agglomerates decreased with an increase in HTNR content. It is a reason of increasing the interaction between silica and HTNR resulting in reduction of silica agglomeration. However, the incorporation of the different molecular weights of HTNR is not significant difference in silica dispersion and size of silica agglomerates.
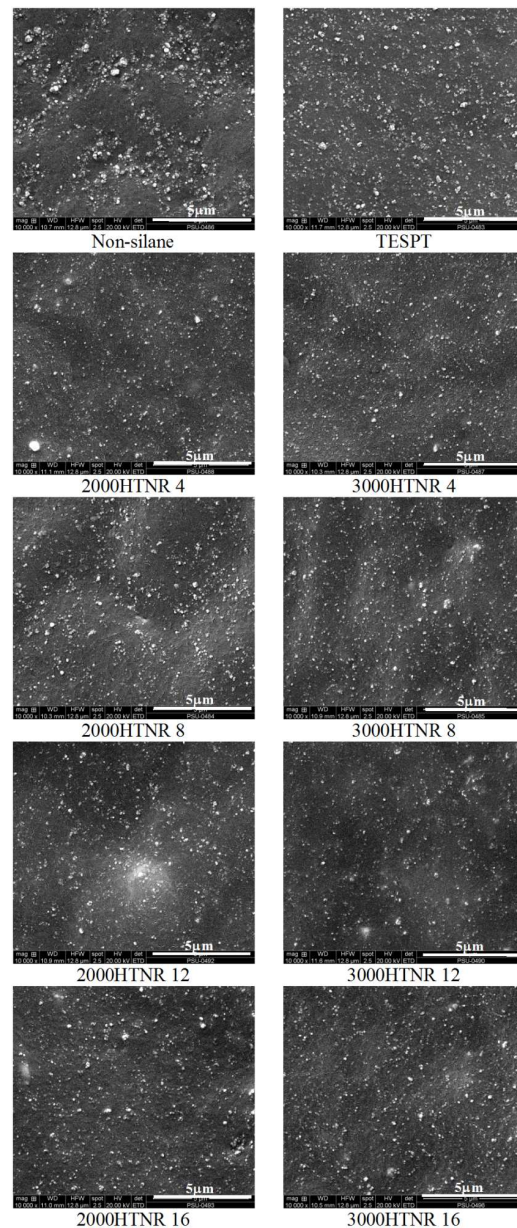

Figure 7. SEM photographs of silica-reinforced NR as a function of HTNR contents.

3.6 Mechanical properties

Stress-strain curves of silica-reinforced NR with the various HTNR contents were shown in Figure 8. The low stress of Non-silane was due to poor rubber-filler interaction. At low strain, the introduction of HTNR in silica-reinforced NR caused decreasing stress due to the interaction between HTNR and silica leading to the reduction in silica agglomerates and rubber viscosity. Moreover, low molecular weight and plasticizing effect of HTNR were important factors for facilitating rubber molecular movement during stretching, especially rubber vulcanizates with higher HTNR content as shown in Figure 8(a), and 8(b). Stress of silica-reinforced NR with higher HTNR content was lower than that with the lower HTNR content, especially at high strain due to increasing interaction between HTNR and curing agents (i.e. accelerator, zinc stearate and sulfur) and plasticizing effect of HTNR. The increase of the interaction between HTNR and curing agents can be confirmed by increase in cure time and decrease in CRI with increase HTNR content. However, the incorporation of 2,000 g·mol^{-1} HTNR (at 8%w/w of silica content) and 3,000 g·mol^{-1} HTNR (at 4%w/w of silica content) in silica-reinforced NR provided higher stress at high strain than Non-silane. It was due to the suitable interaction between HTNR and silica resulting in the reduction in silica agglomeration and the adsorption of accelerator and zinc stearate on silica surface. Besides, the HTNR-silica interaction caused the increment in hydrophobic behavior on silica surface and then the improvement in the compatibility between silica and rubber. However, silica-reinforced NR with TESPT provided the highest stress. It was attributed to greater interaction between TESPT and silica, and bonding between TESPT and rubber molecules [13,27].

The stress-strain curves were converted into Mooney Rivlin according to equation.

$$\sigma^* = \frac{\sigma}{\lambda - \lambda^{-2}} = 2C_1 + 2C_2\lambda^{-1} \qquad (4)$$

Where σ is the applied stress, λ is the extension ratio, and C_1 and C_2 are the Mooney-Rivlin constants related to the network and flexibility of the network chains, respectively. The plot of reduced stress (σ^*) against the reciprocal of extension ratio (λ) is shown in Figure 9.

The presence of sharply stress upturn at low the reciprocal of extension ratio ($\lambda^{-1}<0.5$) was due to finite extension of polymer chains [30,31] and strain induced crystallization [32]. The C_1 in the Mooney Rivlin curve was used to determine crosslink density of rubber in the range of 30-150% ($\lambda^{-1} \approx 0.4$-0.7). The low intercept ($2C_1$) and reduced stress of Non-silane was related to low crosslink density. It is attributed to high polarity and adsorption of accelerator on silica surface resulting in retardation of vulcanization reaction and then producing lower crosslink formation. Even though, the incorporation of HTNR in silica-reinforced NR is a cause of the reduction in

the intercept ($2C_1$) and reduced stress at high the reciprocal of extension ratio, but the addition of 2,000 g·mol^{-1} HTNR at 8%w/w of silica content and 3,000 g·mol^{-1} HTNR at 4%w/w of silica content in silica-reinforced NR provided higher intercept ($2C_1$) and reduced stress at low the reciprocal of extension ratio than Non-silane. The lower intercept ($2C_1$) and reduced stress at high the reciprocal of extension ratio of silica-reinforced NR is a cause of plasticizing effect of addition of HTNR and reduction of filler-filler interaction with interaction between HTNR and silica.
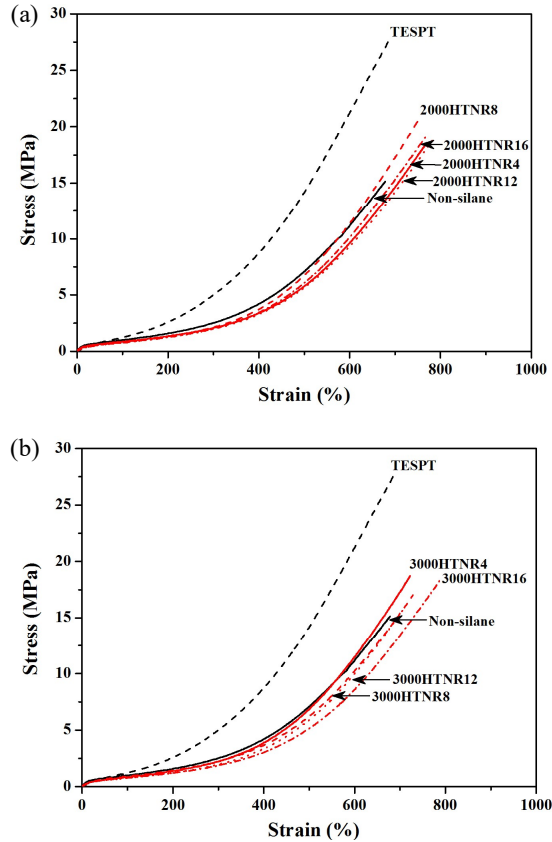

Figure 8. Stress-strain curves of silica-reinforced NR with the various HTNR contents (a) 2,000 g·mol^{-1} HTNR, and (b) 3,000 g·mol^{-1} HTNR.

However, higher intercept ($2C_1$) and reduced stress at low the reciprocal of extension ratio of silica-reinforced NR with the addition of 2,000 g·mol^{-1} HTNR (at 8%w/w of silica content) and 3,000 g·mol^{-1} HTNR (at 4%w/w of silica content) was due to increase hydrophobic behavior on silica surface with HTNR-silica interaction resulting in the reduction of the accelerator adsorption on silica surface and the improvement in the compatibility between silica with rubber. Among, the different molecular weights and contents of HTNR, vulcanizates with 2,000 g·mol^{-1} HTNR at 8%w/w of silica content showed the highest intercept ($2C_1$) compared with all of the silica-reinforced NRs with HTNR. It was attributed to the

greater reduction of silica agglomerates with higher hydroxyl groups of 2,000 g·mol⁻¹ HTNR compared with 3,000 g·mol⁻¹ HTNR. Meanwhile, the further addition of HTNR over the optimum loading at 8%w/w of silica content could increase the adsorption of accelerator and vulcanizing agents in rubber matrix. This result, therefore, affected the reduction crosslink density. However, the highest intercept $(2C_1)$ was achieved by using TESPT. It was attributed to the exceptional interaction between TESPT and silica during mixing, and interaction of TESPT with natural rubber during vulcanization resulting in the excellent rubber-filler interaction and crosslink density [13,27].
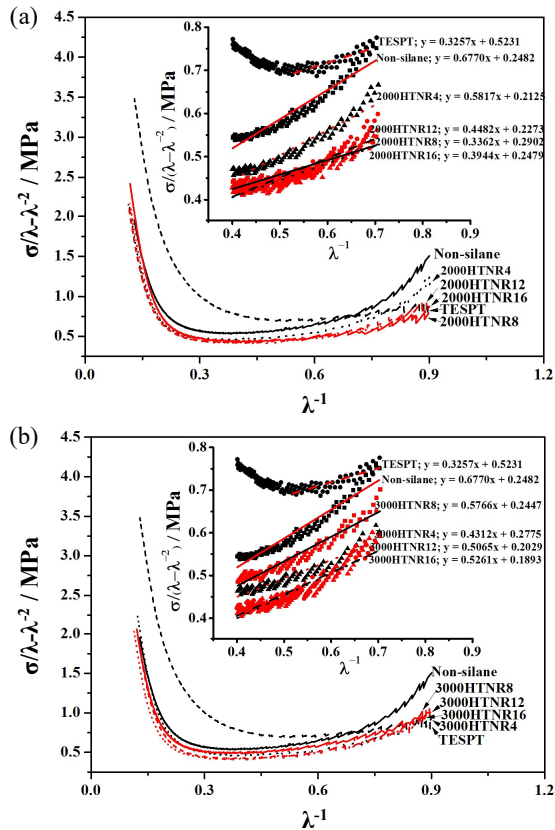

Figure 9. Mooney- Rivlin curves of silica-reinforced NR with the various HTNR contents (a) 2,000 g·mol⁻¹ HTNR, and (b) 3,000 g·mol⁻¹ HTNR.

From Figure 10, C_1 of Non-silane gave the low value due to the agglomerations of silica and the adsorption of chemicals (e.g., zinc stearate and accelerator) on silica surface by the presence of silanol groups on silica surface, and then decreased the crosslink density [2,3]. In addition, the highly different polarity between natural rubber and silica was a cause of a poor compatibility between rubber and silica [2]. Even though the introduction of HTNR in silica-reinforced NR tended to decrease in C_1, but the addition of 4%w/w of silica content for 3,000 g·mol⁻¹ HTNR and 8%w/w of silica content for 2,000 g·mol⁻¹ HTNR in silica-reinforced NR tended to increase in

C_1. The increase of C_1 of silica-reinforced NR with HTNR was due to the reduction of the adsorption of accelerator and zinc stearate on its surface and the improvement of rubber-filler interaction with addition of HTNR. Regarding HTNR content at 4%w/w of silica content, the addition of 3,000 g·mol⁻¹ HTNR in silica-reinforced NR provided higher C_1 than that with 2,000 g·mol⁻¹ HTNR, even 2,000 g·mol⁻¹ HTNR consisted of higher functional groups than 3,000 g·mol⁻¹ HTNR at the same HTNR content. It can be explained by larger shielding effect of 3,000 g·mol⁻¹ HTNR on silica surface resulting in the increase of hydrophobic behavior on silica surface and hence the improvement in the compatibility between silica and rubber. This phenomenon was found by Sengloyluan and co-worker that a better silanization efficiency and filler dispersion in silica-reinforced NR with the addition of the larger molecule was found when compared with the lower molecule, as previously mentioned in Payne effect [8]. However, the further addition of HTNR over the optimum content of HTNR provided the inferior mechanical properties of rubber. It may be attributed to the increase of undesired interaction between free HTNR and curing agent. Meanwhile, TESPT showed the highest C_1 which was contributed to increasing crosslink density as well as providing excellent rubber-filler interaction from its chemically silanization efficiency between silica and NR [12].
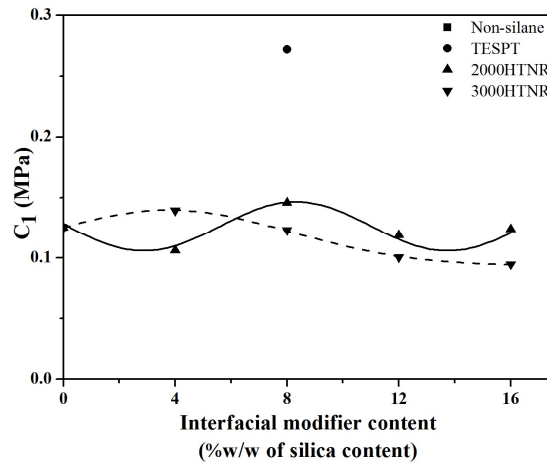

Figure 10. C_1 from Mooney-Rivlin curves of silica-reinforced NR with the various HTNR contents.

3.7 Relationship between C_1 and mechanical properties

Figure 11 shows tensile strength of silica-reinforced NR as a function of C_1. The lesser C_1 of Non-silane was a cause of low tensile strength. Meanwhile, the increment in C_1 of silica-reinforced NR with addition of 2,000 and 3,000 g·mol⁻¹ HTNR caused the improvement in tensile strength. Moreover, it was found that tensile strength of silica-reinforced NR was

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not only depended on C_1, but also depended on HTNR contents. By considering tensile strength at a given C_1, tensile strength of silica-reinforced NR with 2,000 $g \cdot mol^{-1}$ showed higher than that of a higher molecular weight of 3,000 $g \cdot mol^{-1}$ HTNR, especially at low C_1. It was attributed to the stronger prominence of plasticizing effect at a higher loading of 3,000 $g \cdot mol^{-1}$ HTNR. However, tensile strength at high C_1 of silica-reinforced NR with addition of 3,000 $g \cdot mol^{-1}$ HTNR increased to almost the same level that obtained by adding 2,000 $g \cdot mol^{-1}$ HTNR. It was due to the increase in crosslink density and rubber-filler interaction of silica-reinforced NR with the addition of 3,000 $g \cdot mol^{-1}$ HTNR reaching almost the same level as providing from 2,000 $g \cdot mol^{-1}$ HTNR. However, the highest C_1 of silica-reinforced NR with TESPT caused the highest tensile strength.
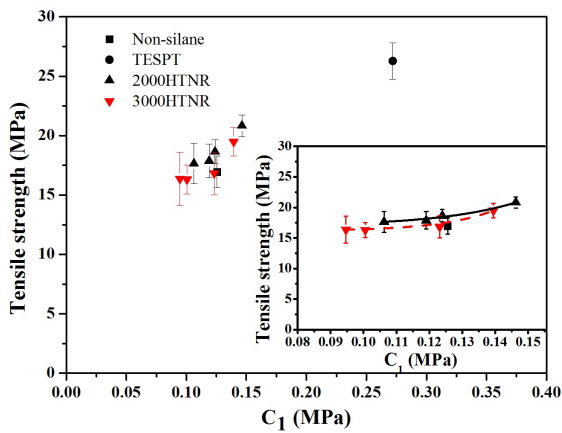

Figure 11. Tensile strength of silica-reinforced NR as a function of C_1.

Abrasion resistance of silica-reinforced NR as a function of C_1 is shown in Figure 12. The poor C_1 of Non-silane was a cause of low abrasion index. The increase C_1 was remarkable enhancement in abrasion index of silica-reinforced NR with addition of HTNR. In regard to C_1 at low value, the incorporation of 2,000 $g \cdot mol^{-1}$ HTNR in silica-reinforced NR provided higher abrasion index than that with 3,000 $g \cdot mol^{-1}$ HTNR. It was attributed to plasticizing effect when 3,000 $g \cdot mol^{-1}$ HTNR was added at high content in silica-reinforced NR. However, abrasion index of silica-reinforced NR with addition of 3,000 $g \cdot mol^{-1}$ HTNR reached almost the same level of 2,000 $g \cdot mol^{-1}$ HTNR, and provided higher than Non-silane at high C_1. It was attributed to an effective interaction between HTNR and silica together with good compatibility of rubber matrix with HTNR coated on silica surface. However, the highest C_1 of silica-reinforced NR, which was a cause of the greatest abrasion index, was obtained by adding TESPT.

Heat build-up of silica-reinforced NR as a function of C_1 is shown in Figure 13. Non-silane exhibited the inferior in high heat build-up due to low value of C_1.

However, the enhancement in C_1 with the addition of 2,000 and 3,000 $g \cdot mol^{-1}$ HTNR resulted in an improving ability to resist heat and cyclic deformation during the test corresponding to the reduction of heat build-up. On the other hand, the increase of heat build-up of silica-reinforced NR with the addition of 2,000 $g \cdot mol^{-1}$ HTNR, which were occurred at C_1 of 0.1191 and 0.1239 MPa, were attributed to plasticizing effect at high loading of 2,000 $g \cdot mol^{-1}$ HTNR. The lowest heat build-up was found in the silica-reinforced NR with TESPT. This was an evident by the highest C_1 relating to the highest crosslink density and rubber-filler interaction of the rubber, and represented by the highest C_1.
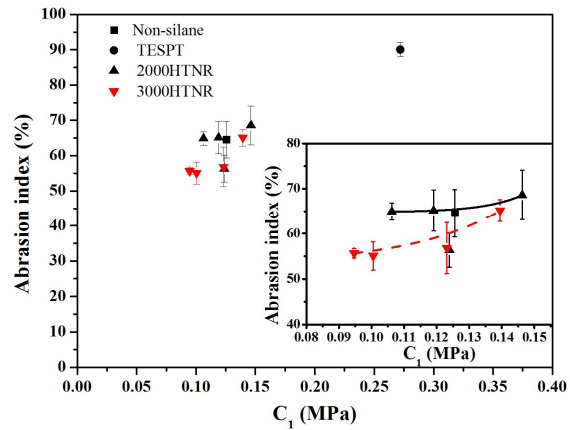

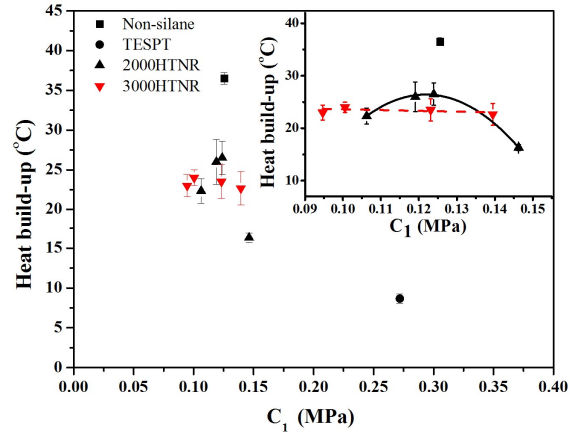**Figure 12.** Abrasion resistance of silica-reinforced NR as a function of C_1.

Figure 13. Heat build-up of silica-reinforced NR as a function of C_1.

3.8 Efficiency of HTNR in silica-reinforced NR

From the results mentioned in this study, the appropriated hydroxyl telechelic natural rubber (HTNR) was determined by varying molecular weights in the range of 2,000-3,000 $g \cdot mol^{-1}$ and contents in the range of 4-16%w/w of silica content in order to enhance the

rubber properties. It was found that the optimum properties of rubber with silica loading at 30 phr was achieved by using 2,000 g·mol^{-1} HTNR at a loading of 8%w/w of silica content. Thus, the efficiency of the use of 2,000 g·mol^{-1} HTNR at a loading of 8%w/w of silica content as interfacial modifier in silica-reinforced NR is comparatively studied with silica-reinforced NR without silane coupling agent (Non-silane) and with a commercialized silane coupling agent (TESPT). The poorest efficiency in Payne effect and mechanical properties of Non-silane involved strong filler-filler interaction and poor rubber-filler interaction. Meanwhile, the efficiency in Payne effect, crosslink density, tensile strength, heat build-up and abrasion index of silica-reinforced NR are significantly improved by adding HTNR. They are attributed to the good interaction between HTNR and silica resulting in increase the hydrophobic behavior on silica surface and reduction of filler-filler interaction. Moreover, this resulted in an improvement in the compatibility between rubber and silica, and the mechanical properties. However, silica-reinforced NR with TESPT provided the highest efficiency in the properties. It was attributed to greater interaction between TESPT and silica, and bonding between TESPT and rubber molecules [13,27]
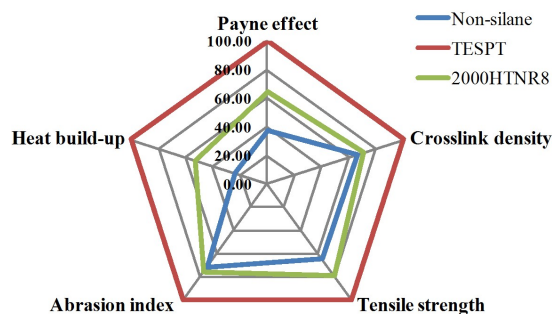

Figure 14. Efficiency of 2,000 g·mol^{-1} HTNR at a loading of 8%w/w of silica content in silica-reinforced NR.

4. Conclusions

The cure characteristics and mechanical properties of silica-reinforced NR have been affected by molecular weight (i.e., 2,000 and 3,000 g·mol^{-1}) and content (i.e., 4, 8, 12 and 16%w/w of silica content) of HTNR. The increasing HTNR content decreased Payne effect while scorch time increased. The reduction of Payne effect might be attributed to the interaction between hydroxyl groups of HTNR and silanol groups of silica. Meanwhile, the increase of scorch time was caused by the dilution effect from the addition of HTNR. Moreover, increasing scorch time and decreasing C_1 (crosslink density determined by stress-strain measurement) with increasing in HTNR content were due to the undesirable interaction of hydroxyl groups of HTNR with zinc stearate, and

accelerator in rubber matrix. Among silica-reinforced NR with HTNR, the shortest cure time, and the highest cure rate index (CRI) and crosslink density of the rubber were achieved by using HTNR loading of 8%w/w of silica content. The improvements of these properties had been involved by the interaction between hydroxyl groups of HTNR and silanol groups of silica. However, these properties tended to decrease with increasing HTNR content more than 8%w/w of silica content due to interaction of free HTNR with zinc stearate and accelerator in rubber matrix. Moreover, the cure characteristics and mechanical properties of silica-reinforced NR still depended on molecular weight of HTNR. The increase of Payne effect with increasing molecular weight of HTNR was due to lower functional groups. However, scorch time, cure time, CRI and crosslink density were not significantly affected by varying molecular weights of HTNR. Moreover, we found that the variation of C_1 of rubber which influenced rubber properties, were caused by the application of the various molecular weights and contents of HTNR in the rubber. The increasing in C_1 caused the increases in tensile strength and abrasion index, and decrease in heat build-up. As the results, it could be concluded that the change in C_1 in rubber matrix was an important factor for controlling the properties of silica-reinforced NR with HTNR. The optimum properties of rubber with silica loading at 30 phr was achieved by using 2,000 g·mol^{-1} HTNR at a loading of 8%w/w of silica content. However, cure and mechanical properties of silica-reinforced NR with HTNR was lesser than those with TESPT.

5. Acknowledgements

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