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## Renewable Interfacial Modifier for Silica Filled Natural Rubber Compound

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### Abstract

A main problem of using silica as reinforcing filler in natural rubber (NR) compound is a poor dispersion of silica in the rubber matrix due to incompatibility between them. As silica contains high silanol groups on its surface, these polar groups promote strong filler-filler interactions leading to high degree of aggregation and agglomeration of silica particles. To overcome this drawback, many types of modifiers have been applied into silica filled recipes. In this work, a renewable and sustainable interfacial modifier, namely low molecular weight hydroxyl terminated natural rubber (HTNR). HTNR was prepared by controlled epoxidation and cleavage of natural rubber, following by reduction reaction of the obtained carbonyl telechelic natural rubber. Influence of the prepared interfacial modifier on enhancement of rubber-filler interaction was studied by focusing on the cure characteristics and the mechanical properties of silica filled natural rubber at a fixed silica content of 30 phr. In comparison with silica filled compound without silane coupling agent, shorter scorch and cure times, lower Payne effect and higher tensile strength of silica filled natural rubber were achieved with the presence of interfacial modifier at 2.4 parts per hundred parts of rubber (phr). This was attributed to an active reaction of silanol groups with interfacial modifier and compatibility between modifier and natural rubber. For HTNR-treated compound to obtain optimum properties, mixing should be carried out at initial mixing temperature of 30°C, mixing time of 12 minutes, and rotor speed of 60 rpm. However, TESPT is more effective than HTNR because it imposes better properties than HTNR.

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**Nomenclature**

2000HTNR	Hydroxyl telechelic natural rubber with molecular weight of 2000 g/mol
T30t12	Mixing temperature at 30 <sup>0</sup> C and mixing time of 12 min

**1. Introduction**

Natural rubber (NR) is a material widely used in various industries because of its excellent properties such as elasticity, low hysteresis, high resilience, toughness, and *etc.*<sup>1</sup>. Normally, NR is an amorphous material, however, when stretched it can crystallize. The strain induced crystallization contributes to good mechanical properties of NR such as tensile strength, tear resistance and abrasion resistance, etc. NR is highly elastic. It can recover almost completely to its original shape when the applied load is removed. Moreover, NR has a very good dynamic mechanical properties<sup>1</sup> and excellent tackiness. In general, rubber products are not made from pure rubbers. Many ingredients such as curing agents, fillers, antidegradants, processing aids etc., are added into rubbers to improve their processing characteristics and mechanical properties<sup>2</sup>. Modulus and strength of rubbers are greatly improved by incorporating reinforcing fillers such as carbon black and silica. Carbon black has been used as reinforcing material in tire industries for long times whereas the use of silica is only limited to coloured rubber products. In recent years, silica has been introduced to tire industries due to low rolling resistance and excellent wet traction and ice grip. The presence of silanol groups on silica surface induces strong particle–particle interaction, giving rise to a high tendency, for filler agglomeration, and low compatibility with non-polar rubbers, which leads to poor dispersion and processability. The structure of silica aggregates in rubbers can be tailored by modifying the filler surface in order to increase the compatibility of silica with hydrocarbon rubbers and to improve the filler dispersion, compound processability and various vulcanizate properties<sup>2</sup>. Surface modification of silica can be carried out by many methods such as admicellar polymerization<sup>3,4</sup>, core-shell polymerization<sup>5</sup>, plasma polymerization<sup>6-8</sup>, silane treatment<sup>9-11</sup>, and etc. However, silane treatment is more favourable method, TESPT is the most important silane coupling agent for silica reinforced non-polar rubber. Nevertheless, the use of TESPT in silica filled rubbers always encounters problems such as scorching of rubber compounds during the mixing stage and the release of ethanol during vulcanization etc<sup>10</sup>. In this study, hydroxyl telechelic natural rubber (HTNR) is used to improve interaction between NR and silica. Moreover, the mixing condition of silica reinforced NR with HTNR is studied in order to determine the optimum mixing condition for desired mechanical properties.

**2. Experiment****2.1. Materials**

High ammonia concentrated latex (60%DRC) was purchased from Yala latex industry Co.,LTD, Yala Thailand), Hydrogen peroxide and formic acid were supplied by Acros Organics, Belgium. Periodic acid is a product of Merck, Germany. Sodium borohydride (NaBH<sub>4</sub>) was purchased from LobaChemie Pvt. Ltd. All chemicals and solvents for HTNR preparation are of analytical grade. STR 5L was obtained from Yala latex industry Co.,LTD, Yala Thailand. ULTRASIL VN 3, precipitated silica, and bis-(3-triethoxysilylpropyl) tetrasulfide silane (TESPT) were obtained from Evonic, Germany. 2,2,4-Trimethyl-1,2-dihydroquinoline polymer, (TMQ), diphenylguanidine (DPG), N-tert-Butyl-2-benzothiazole sulfonamide (TBBS) are products of Flexsys America L.P., U.S.A. Zinc oxide (ZnO) stearic acid, and sulphur were supplied by Petchthai Chemicals.

**2.2. Preparation and structural characterization of HTNR.****2.2.1. Preparation of epoxidized natural rubber (ENR).**

Preparation of ENR was started with diluting concentrated NR latex (60% dried rubber content, DRC) to 20%DRC and preserving this latex with 3.0 phr of 10% non-ionic stabilizer (Teric N30) solution along with mechanical stirring at rotor speed of 75 rpm for 16 hrs. Then, 90% formic acid was introduced drop wise into the

latex for about 15 minutes along with constant stirring before 30% hydrogen peroxide was added. Epoxidation reaction was carried out at 60°C and reaction times depended on the desired degree of epoxidation. Then, saturated sodium bicarbonate solution was added into the latex for eliminating residual acid. After that, the latex was coagulated with methanol, sheeted out, washed and dried.

### 2.2.2. Preparation of carbonyl telechelic natural rubber (CTNR).

The 0.4M ENR solution was prepared by dissolving ENR in tetrahydrofuran (THF). Then, 0.4 M periodic acid ( $H_5IO_6$ ) solution in THF ( $H_5IO_6$ /Epoxide molar ratio = 1/1) was dropped into ENR solution together with constant stirring. The degradation reaction was carried out at 30°C for 5 hrs. Then, iodate salt from the reaction was filtered out before tetrahydrofuran evaporated. Dichloromethane was added into liquid CTNR before washing with saturated sodium bicarbonate and 20% sodium thiosulphate solutions to eliminate residual acid and iodate salt, respectively. The residual water in CTNR was removed by saturated sodium chloride solution and followed by magnesium sulphate anhydrous. Finally, dichloromethane was evaporated out from liquid CTNR.

### 2.2.3 Preparation of hydroxyl telechelic natural rubber (HTNR).

The 1.0 M sodium borohydride ( $NaBH_4$ ) solution of 1.5 L was introduced into 2.0 L reactor before 0.1 M CTNR solution in THF was added dropwise. Reduction reaction was carried out at 60°C for 6 hrs. The obtained HTNR solution was cooled down to room temperature before adding distilled water dropwise to eliminate residual sodium borohydride. Then, the solution was washed by saturated sodium chloride and dried with anhydrous magnesium sulphate. After that, THF was evaporated out from HTNR solution. Molecular weight and chemical structure of HTNRs were investigated using NMR spectroscopy. Their functional groups were also characterized by an attenuated total reflection (ATR)-FTIR spectroscopy.

### 2.2.4 Characterization of HTNR using $^1H$ -NMR spectroscopy and ATR-FTIR spectroscopy

The HTNR solution was prepared by dissolving 0.02 g. HTNR in 2 ml of deuterium chloroform ( $CDCl_3$ ). The  $^1H$ -NMR spectra of HTNR solution was recorded by using Varian Unity Inova 500MHz at 500 MHz. FTIR spectra of HTNR sample was recorded using an attenuated total reflection (ATR) -FTIR spectrometer (Tensor 27, Bruker) in the range of 4000-400  $cm^{-1}$ .

### 2.2.5 Conventional mixing in internal mixer.

Silica-reinforced NR compounds were prepared according to formulations given in Table 1. The amount of silica for each compound is 30 phr. The mixing procedure is shown in Table 2. All ingredients except for curing agent and accelerator were mixed using internal mixer for 12 min. The effects of initial mixing temperature (30, 60 and 90°C) on Payne effect and mechanical properties were studied. The masterbatch was kept at room temperature for 24 hrs before curing agent and accelerator being added and mixed on two roll mills for 5 min. The compounds were rested for 24 hrs before vulcanization and physical tests, i.e. tensile property test, dynamic property test, being carried out.

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

Ingredient	Content (phr)		
	non- silane coupling agent (non-silane)	silane coupling agent (si69-DPG)	2000HTNR
Natural rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	1	1	1
Silica (Ultrasil VN3)	30	30	30
TESPT (Si-69)	0	2.4	0
2000HTNR	0	0	2.4
DPG	0	0.6	0
TMQ	1	1	1
TBBS	1.5	1.5	1.5
Sulfur	2	2	2
total	140.5	143.5	142.9

Table 2. Mixing procedure.

Time (min)	Action
Step 1	
0.0	Add natural rubber (mastication)
1.0	Add hydroxyltelechelic natural rubber (HTNR)
1.5	Add zinc oxide, stearic acid, ½ silica, ½ DPG and ½ si-69
4.0	Add TMQ, ½ silica, ½ DPG and ½ si-69
12.0	Dump
Step 2	
After 24 hrs the curatives (TBBS and sulphur) were added into rubber compound on two roll mill at mixing time of 5 min	

### 2.3. The determination of cure characteristics

The cure characteristics of silica-filled compounds such as minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), torque difference ( $M_H - M_L$ ), scorch time ( $t_{s1}$ ), cure time ( $t_{c,90}$ ) and cure rate index ( $CRI$ ), were determined by using oscillating disk rheometer (ODR) according to ASTM D2084 method. About 10 g of rubber compound was used. The test was carried out at 160°C and oscillating frequency of 100 cpm for 20 minutes. The cure rate index of rubber was calculated by this equation as followed.

$$CRI = \frac{100}{t_{c,90} - t_{s1}} \quad (1)$$

### 2.4. The determination of tensile properties

The tensile properties of rubber vulcanizates were investigated according to ISO 37 using universal testing machine (Hounsfield H10KS). The extension rate is of 500 mm/min. Reinforcement index ( $RI$ ) was calculated according to equation (2)

$$RI = \frac{M_{300}}{M_{100}} \times 100 \quad (2)$$

Where,  $M_{100}$  and  $M_{300}$  are stresses at 100% and 300% strain, respectively.

### 2.5. The determination of dynamic properties

The Payne effect or filler-filler interaction of filled rubbers without curing agent and accelerator was investigated using rubber process analyzer (RPA). The rubber sample of about 5-6 g was tested in strain sweep mode at 100°C and a frequency of 0.5 Hz. The strain was in the range of 0.56-100%. The difference between storage modulus at 0.56% strain ( $G'_{0.56}$ ) and at 100% strain ( $G'_{100}$ ),  $\Delta G'$ , is an implication of the Payne effect.

## 3. Results and discussion

### 3.1 Chemical structure of HTNR.

Chemical structure of HTNR was characterized by NMR spectroscopy and ATR-FTIR spectroscopy. NMR spectrum of HTNR is shown in Fig.1(a). The chemical shifts at 1.67, 2.09 and 5.10 ppm correspond to 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, which are similar to those of NR described in previous works.<sup>12</sup> The chemical shift at 1.20 ppm corresponds to methyl protons adjacent to secondary alcohol. Chemical shifts of CH and CH<sub>2</sub> adjacent to terminal hydroxyl group appear at 3.80 and 3.68 ppm<sup>12</sup> respectively.

Fig.1(b) is FTIR spectra of HTNR. The sharp peaks at the wavenumber of 2925, 2869 and 835 cm<sup>-1</sup> are assigned to the C-H asymmetric stretching, the C-H symmetric stretching and the =CH- symmetric bending in NR structure, respectively. The peak at 3355 cm<sup>-1</sup> corresponds to the presence of the hydroxyl groups in HTNR.<sup>12</sup> However, the small peak at wavenumber of 1683 cm<sup>-1</sup> represents the residual carbonyl groups.

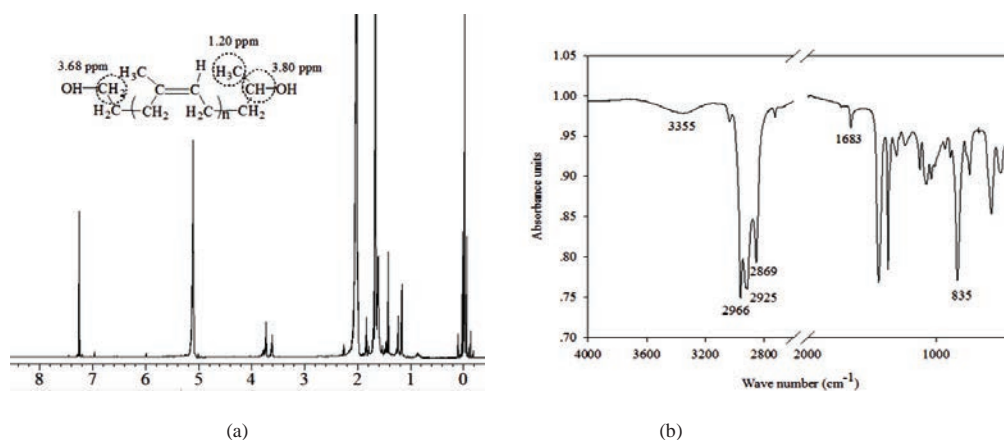


Fig. 1. (a) <sup>1</sup>H-NMR spectra; (b) FTIR spectra of HTNR.

### 3.2 Filler-filler interactions or the Payne effect

The effects of mixing conditions on storage modulus at different strains and the Payne effect ( $\Delta G'$ ) of silica filled compounds are shown in Fig.2 (a) and 2(b), respectively. From Fig.2 (a), it can be seen that the storage modulus is high at small strain, gradually decreases with increasing strain, and sharply drops at strains greater than 10%. This is caused by the breakdown of filler-filler networks in silica formed by strong interactions among silica aggregates. This phenomenon is called the Payne effect.<sup>13</sup> The difference between  $G'$  at very low and high strains is always used as an indication of the Payne effect. The larger Payne effect (a larger different in storage modulus at 0.56 and 100%) suggests the larger degrees of filler-filler interactions.

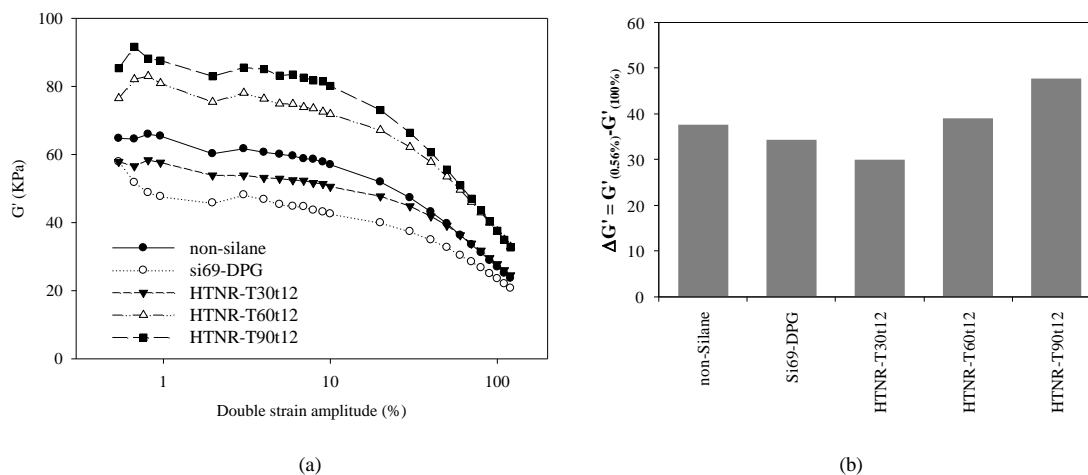


Fig. 2. (a) Storage modulus of silica-filled NR as a function of strain; (b)  $\Delta G'$  ( $G'_{(0.56\%)} - G'_{(100\%)}$ ) of silica-reinforced natural rubber with various interfacial modifiers.

Silica-filled rubber without silane coupling agent (non-silane) shows greater Payne effect than rubber compounds containing TESPT (si-69-DPG) and HTNR (initial mixing temperature 30<sup>0</sup>C; HTNR-T30t12). These results indicate that the agglomeration of silica was decreased with addition of TESPT and HTNR. This is due to the TESPT contains large amount of functional groups which can react with silanol groups on silica surface, resulting in less filler-filler interactions or Payne effect. HTNR contains hydroxyl groups which can form hydrogen bond with silanol groups on silica surface leading to reduction in filler-filler interactions and agglomeration of silica. However, for HTNR treated samples, the Payne effect is strongly affected by the initial mixing temperature. Apparently, the Payne effect increased with increasing initial mixing temperature (Fig 2(b)). During mixing, shear stress is transferred through the rubber matrix to break down silica agglomerates. If the viscosity of the rubber is high, the stress will be effectively transferred causing the breakdown of silica agglomerates and, hence the agglomerate size is decreased, resulting in smaller Payne effect. When the initial mixing temperature is high, the viscosity of rubber is low so that the shear stress will not be effectively transferred through the rubber medium to break down silica agglomerates. Therefore, the Payne effect increased with increasing initial mixing temperature (HTNR-T60t12 and HTNR-T90t12, initial mixing temperature of 60 and 90<sup>0</sup>C, respectively).

### 3.3 Cure characteristics

Cure curves of silica-filled NR with and without interfacial modifiers are shown in Fig.3(a). Silane-treated silica-filled NR has shorter scorch time and cure time than non-silane sample. It has been known that for silica-filled compounds, silanol groups on silica surface can interact with polar materials such as accelerators resulting in longer scorch and cure times, and lower cure rate. For the silane-treated rubber, the ethoxy groups of silane are first hydrolysed to form a hydroxyl group which undergoes condensation reaction with silanol groups on silica surface<sup>14-16</sup>, resulting in less adsorption of accelerator. Therefore, shorter scorch and cure times (Fig. (a)), and greater cure rate index result (Fig. 3 (b)). For HTNR- treated samples, cure properties depend on initial mixing temperature. With increasing initial mixing temperature, the increase in scorch time and cure time (Fig.3(a)), and the decrease in cure rate index (Fig.3(b)) are observed. At high initial mixing temperature, the size of silica agglomerates is large, HTNR may interact less with silanol groups, resulting in the increase in adsorption of accelerators on silica surface, hence, deactivating cure reaction. The torque difference of silane-treated silica-filled NR is greater than non-silane and HTNR-treated samples (Fig. (c)) because silane can react with both silica and rubber to form strong chemical bonds, resulting in the increase in crosslink density of rubber and filler-rubber interactions. However, for HTNR-treated compounds the torque difference decreases with increasing the initial mixing temperature because at high initial mixing temperature the agglomerate size of silica is large and HTNR interacts less with silica leading to less silica-NR interactions. Apparently, HTNR is effective at low initial mixing temperature which is 30<sup>0</sup>C in this case.

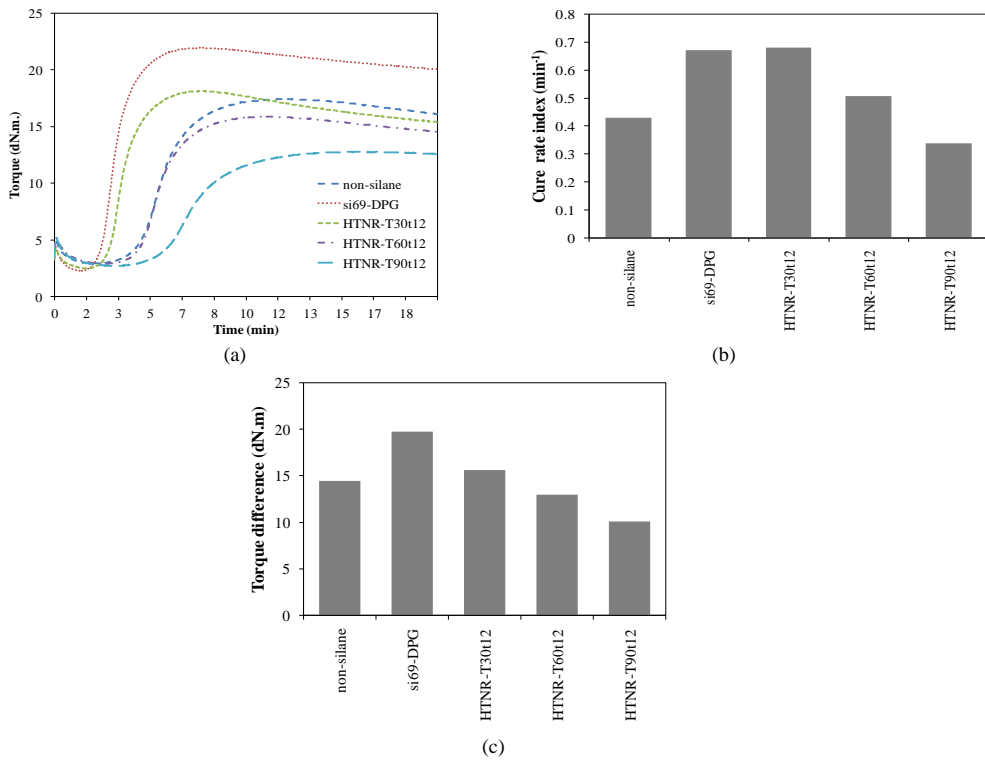


Fig. 3. (a) Cure curves; (b) cure rate index, and (c) torque difference of silica-filled NR with and without interfacial modifiers.

### 3.4 Tensile properties

Reinforcement index, tensile strength and elongation at break of silica-reinforced NR with and without various interfacial modifiers are shown in Fig. 4(a) and 4(b), respectively. Reinforcement index and tensile strength of TESPT-treated rubber are greater than non-silane and HTNR-treated samples because of higher crosslink density and rubber-filler interactions. Initial mixing temperature slightly affects reinforcement index and tensile strength of HTNR-treated rubbers, but not elongation at break. Reinforcement index and tensile strength slightly decrease with increasing initial mixing temperature. This may be due to the degradation of rubber molecules caused by heat.

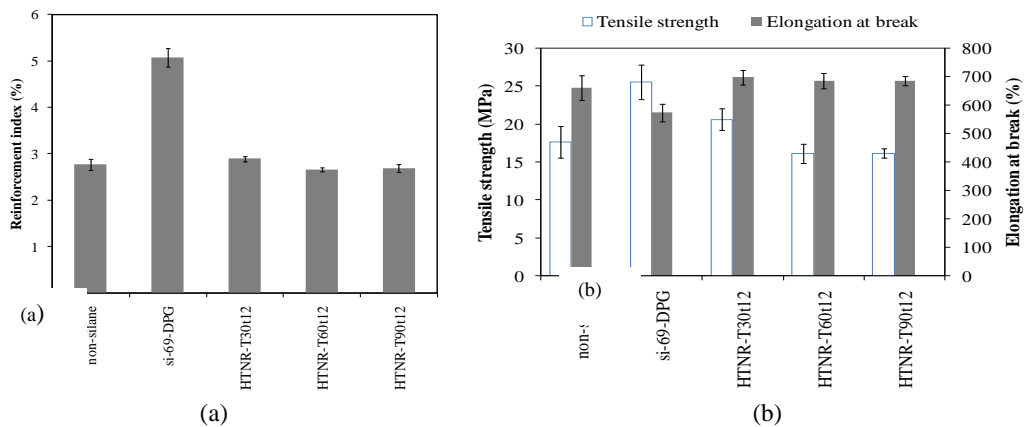


Fig. 4 (a) Reinforcement index; (b) tensile strength and elongation at break of silica- reinforced NR with and without various interfacial modifiers.



#### 4. Conclusion

TESPT and HTNR can be used as interfacial modifiers for silica –filled rubber compounds, because they provide better cure characteristic, tensile properties and lesser Payne effect than non-treated compound. However, TESPT is more effective than HTNR because it imposes better properties than HTNR. For HTNR-treated samples, cure characteristics, tensile properties, and Payne effect are affected by initial mixing temperature. Scorch and cure times increase with increasing initial mixing temperature in contrast to cure rate index and torque difference. Reinforcement index and tensile strength slightly decrease with increasing initial mixing temperature possibly due to degradation of rubber molecules caused by heat. The Payne effect increases with increasing initial mixing temperature because low viscosity of rubber results in less effective transfer of the shear stress through the rubber matrix to breakdown silica agglomerates. For HTNR-treated compound to obtain optimum properties, mixing should be carried out at initial mixing temperature of 30<sup>0</sup>C, mixing time of 12 minutes, and rotor speed of 60 rpm.

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#### References

1. Abraham J, Thomas S, George SC. Micro and Nano TiO<sub>2</sub> Reinforced Natural rubber Composites. In: Thomas S, Chan CH, Pothen L, Joy J, Maria H, editors. *Natural Rubber Materials*, Cambridge 2014; 2: p. 290-306.
2. Ciesielski A. An Introduction to Rubber Technology, Southampton: Hobbs the Printers 1999; **16**: 31-37.
3. Pongprayoon T, Yooprasert N, Suwanmala P Hemvichian K. Rubber products prepared from silica modified by radiation-induced admicellar polymerization. *Radiation Physics and Chemistry* 2012; **81**: 541-546.
4. Nontasorn P, Chavadej S, Rangsunvigit P, Haver, JHO, Chaisirimahamorakot S, Na-Ranong N. Admicellar polymerization modified silica via a continuous stirred-tank reactor system: Comparative properties of rubber compounding. *Chem Eng J* 2005; **108**: 213–218.
5. Marini M, Pourabbas B, Pilati F, Fabbri P. Functionally modified core-shell silica nanoparticles by one-pot synthesis. *Colloids and Surfaces A: Physicochem Eng Aspects* 2008; **317**: 473-481.
6. Akhavan B, Jarvis K, Majewski P. Hydrophobic Plasma Polymer Coated Silica Particles for Petroleum Hydrocarbon Removal. *ACS Appl Mater Interfaces* 2013; **5**: 8563–8571.
7. Mathew T, Datta RN, Dierkes WK, Noordermeer JWM, van Ooij WJ. Mechanistic Investigations of Surface Modification of Carbon Black and Silica by Plasma Polymerisation. *Plasma Chem Plasma Process.* 2008; **28**: 273–287.
8. Tiwari M, Noordermeer JWM, Ooij WJ, Dierkes WK. Plasma polymerization of acetylene onto silica: An approach to control the distribution of silica in single elastomers and immiscible blends. *Polym Adv Technol* 2008; **19**(11): 1672–1683.
9. Chonkaew W, Mingvanish W, Kungliean U, Rochanawipart N, Brostow W. Vulcanization Characteristics and Dynamic Mechanical Behavior of Natural Rubber Reinforced with Silane Modified Silica. *J Nanosci and Nanotechnol* 2011; **11**: 2018-2024.
10. Seo G, Park SM, Ha K, Choi KT, Hong CK, Kaang S. Effectively reinforcing roles of the networked silica prepared using 3, 3'-bis(triethoxysilylpropyl) tetrasulfide in the physical properties of SBR compounds. *J Mat Sci* 2010; **45**(7): 1897–1903.
11. Thongpin C, Sangnil C, Suerkong P, Pongpilaipreerti A, Sombatsompop N. The Effect of Excess Silane-69 used for Surface Modification on Cure Characteristic and Mechanical Properties of Precipitated Silica filled Natural Rubber (PSi/NR). *Adv Mat Research* 2009; **79-82**: 2171-2174.
12. Controlled Degradation of Natural Rubber and Modification of the Obtained Telechelic Oligoisoprenes: Preliminary Study of Their Potentiality as Polyurethane Foam Precursors. *J App Polym Sci* 2010; **117**: 1279-1289.
13. Payne AR. *Rubber Chem. Technol.* 1971; **44**: 440.
14. Gauthier S, Aime JP, Bouhacina T, Attias AJ, Desbat B. Study of grafted silane molecules on silica surface with an atomic force microscope. *Langmuir* 1996; **12**: 5126-5137.
15. Li Y, Han B, Wen S, Lu Y, Yang H, Zhang L, Liu L. Effect of the temperature on surface modification of silica and properties of modified silica filled rubber composites. *Composites: Part A* 2014; **62**: 52-59.
16. Ten Brinke JW, Debnath SC, Reuvekamp LAEM, Noordermeer JWM. Mechanistic aspects of the role of coupling agents in silica–rubber composites. *Compos Sci Technol* 2003; **63**: 1165–1174.