

Natural rubber (NR) • silica • carbonyl-terminated low molecular-weight NR (CLNR) • compatibility • silica-filled NR

Carbonyl-terminated low molecular-weight natural rubber (CLNR) was prepared by a scission reaction in the latex state. The compatibility of silica-filled natural rubber (NR) incorporated with various contents of the CLNR were investigated. In the presence of small amounts of the CLNR, the increase in filler-rubber interaction and decrease in filler-filler interaction of the silica-filled NR compounds could be observed. The SEM images revealed the good dispersion of silica in the rubber compound containing small amounts of CLNR. By adding an appropriate amount of the CLNR, the vulcanization time and cross-link density could be promoted. On the other hand, the excess amount of the CLNR showed detrimental effects.

Verbesserte Verträglichkeit zwischen Kieselsäure und Naturkautschuk durch den Einsatz von Carbonyl-terminierten Niedrigmolekulargewichts-Naturkautschuk

Naturkautschuk (NR) • Kieselsäure • Carbonyl-terminierter Niedrigmolekulargewichts-NR (CLNR) • Verträglichkeit • kieselsäuregefüllter NR

Carbonyl-terminierter Niedrigmolekulargewichts-Naturkautschuk (CLNR) wurde durch eine Kettenspaltungsreaktion im Latexzustand hergestellt. Es wurde die Verträglichkeit des kieselsäuregefüllten Naturkautschuks (NR) mit verschiedenen Anteilen an CLNR untersucht. Bei kleinen Anteilen von CLNR konnte die Zunahme der Füllstoff-Kautschuk Wechselwirkung und die Abnahme der Füllstoff-Füllstoff-Wechselwirkung für die mit Kieselsäure gefüllten NR-Mischungen beobachtet werden. Die REM-Bilder lassen die gute Dispersion der Kieselsäure in der Kautschukmischung bei kleinen Anteilen an CLNR erkennen. Bei Zugabe eines geeigneten Anteils von CLNR kann die Vulkanisationszeit und die Vernetzungsdichte gefördert werden. Andererseits zeigte ein Übermaß an CLNR gegenteilige Effekte.

Figures and Tables:  
By a kind approval of the authors.

# Improved Compatibility between Silica and natural Rubber by the use of Carbonyl-terminated low Molecular-Weight natural Rubber

## Introduction

Natural rubber (NR) is a very versatile raw material. It has been used in many industries such as tires, household, and medical products due to the high productivity of plant and its excellent properties, such as high green strength, high elasticity, good crack growth resistance and minimal heat build-up [1]. Although NR is known to exhibit numerous outstanding properties, fillers are necessarily added into NR in most cases in order to gain the appropriate properties for specific applications. A wide variety of particulate fillers is used in the rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs, and improvements in processing properties [2]. Silica and carbon black are reinforcing fillers that have been mostly used in tire compounds for the reason of the better overall performance of tires made thereof. Carbon black is mainly produced by the incomplete combustion of heavy petroleum products, whereas silica is generally found in nature such as sand and quartz [3]. The surface characteristics of both fillers are different, leading to a difference in agglomerate forms and dispersion ability in rubber matrix [4]. The filler-filler interaction of carbon black is mainly formed by *Van der Waal forces*, which can be broken easily during mixing. On the contrary, silica surface is composed of hydroxyl groups known as silanol groups. These make silica has the high polarity on its surface, leading to strong particle-particle interaction by hydrogen bonding, *Van der Waal forces* and other physical interactions. These factors are the reason for the incompatibility between silica and non-polar rubbers [5]. Therefore, this challenges researcher to improve dispersion and distribution of the silica-filled non-polar rubbers, particularly NR. The dispersion and distribution are the main factors affecting physical and mechanical properties of the vulcanizates such as modulus, tensile and tear strength, abrasion resistance,

and fatigue life [5-8]. Silane coupling agents are commonly used to improve the dispersion of silica in rubber matrix by chemical bonding with rubber, leading to an increase in the levels of the reinforcement [9]. However, the reaction between silanol group of silica and alkoxy groups of silane coupling agent releases some chemical or gas as by-products, resulting in negative effects on vulcanizates such as porous and blister on products [10]. The modification of rubber molecule as a polar rubber is an alternative method, which can be used as a compatibilizer for improving the interaction of silica-filled compounds. For example, epoxidized NR (ENR) has been modified to contain epoxide groups on the molecules [8, 11]. Grafting of hydrophilic chemicals such as maleic anhydride onto the NR molecule was also carried out [12]. Moreover, the transformation of NR into low molecular-weight NR (LNR) bearing active functional groups is an alternative way to improve the polarity of NR [13, 14].

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In this study, the so-called carbonyl terminated LNR (CLNR) was prepared by chain scission via an oxidative degradation reaction in the NR latex state, which is naturally available form of NR. The reaction in the latex state provides the benefits, i.e., the minimization of toxic solvent that has a good effect on the manufacturing costs and environment. However, it has been reported that reactions to NR latex are not efficient due to the obstruction by a protein layer on the rubber particles [9, 15, 16]. Therefore, the starting latex for the oxidative degradation reaction in this study is saponified latex, which is almost free from proteins. The aim of the present work is an attempt to utilize the CLNR as a modifier for enhancing the compatibility of silica-filled NR systems. The molecular structure of the CLNR was first characterized to confirm the reduction of molecular-weight and the presence of polar functional groups. The effect of the CLNR on the improvement of compatibility between NR and silica, as well as, the mechanical properties of the silica-filled NR was investigated.

## Materials and methods

### Materials

Saponified NR (SPNR) latex was prepared by saponification of high ammonia NR (HANR) latex (Thai rubber latex Corp. Co., Ltd., Thailand). HANR latex was diluted to 30% dry rubber content (DRC) and then treated with 0.3% w/w NaOH in the presence of 0.5% w/w sodium dodecyl sulfate (SDS) (Kao industrial Co., Ltd, Thailand) at 70°C for 3 h, then separate cream fraction by centrifugation twice [17]. The nitrogen content of SPNR was less than 0.05%, as analyzed by a nitrogen analyzer (LECO-FP258). STR-CV60, a constant viscosity (CV) grade of NR, was kindly provided by Pan Star Co., Ltd., Thailand. Sodium hydroxide (Kao industrial Co., Ltd, Thailand), potassium peroxydisulfate (RCl Labscan Co., Ltd, Thailand) and propanal (A.C.S. Xenon Ltd., Thai-

### 1 Formulation of silica-filled NR compounds containing CLNR as a compatibilizer

Composition	Contents (phr)
NR (STR-CV60)	100
CLNR	0-15
Silica (Hi-Sil™ 233)	50
Zinc oxide	3
Stearic acid	2
TBBS	1
Sulfur	1.5
6PPD	1.5

land) were analytical grades. The compounding ingredients were zinc oxide (ZnO), stearic acid, sulfur (Chemmin Co., Ltd., Thailand), and *N-tert-butyl-2-Benzothiazol sulfonamide* (TBBS) (Flexsys Co., Ltd., Thailand). Silica was Hi-Sil™ 233, which has a surface area of 140 m<sup>2</sup>/g (PPG-Siam Silica Co., Ltd., Thailand). *N*-(1, 3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD) (Flexsys Co., Ltd., Thailand) was used as an antioxidant.

### Preparation of CLNR by oxidative degradation of SPNR latex

The SPNR latex (10% DRC) was treated with 1 parts per hundred rubber (phr) of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 15 phr of propanal [14]. The reaction was carried out in a shaking machine at 70°C with a shaking rate of 135 times/min for 7 h. The resulting latex was coagulated with acetone and purified by dissolving in toluene and reprecipitation twice with methanol and dried *in vacuo*. The mechanism of oxidative degradation reaction of NR by using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/propanal has been proposed as shown in Figure 1.

### Mixing process and vulcanization

The compounding formulation of silica-filled NR is shown in Table 1. In order to study the effect of the CLNR on the compatibility between NR and silica, the CLNR content was varied between 0 and 15 phr. Two-stage mixing procedure was employed to prevent the premature vul-

canization. The first stage, the rubber was compounded with fillers and other non-vulcanizing additives in a Brabender Plasti-Corder® at 40°C using the rotor speed of 40 rpm. STR-CV60 was first charged to the mixer and masticated for 3 min, followed by an addition of silica. The mixing was continued for 5 min and then the CLNR, ZnO, stearic acid, and 6PPD were subsequently added and mixed until 13 min of mixing time. After the compound was cooled down to the room temperature, it was mixed with vulcanizing agents, i.e., TBBS and sulfur using two roll mills at 40°C with rotor speed 40 rpm for 2 min. The optimum cure time (*t*<sub>90</sub>) used in a preparation of the vulcanized samples was the time required for the torque of the Rheometer to increase to 90% of the final torque at 150°C.

### Characterizations and properties measurement

The molecular structure of the obtained CLNR was characterized using Fourier transform infrared spectroscopy (FT-IR) by a JASCO-4100 FTIR spectrometer at a resolution of 4 cm<sup>-1</sup> with 300 scans. The rubber samples were dissolved in chloroform (1 %w/v) and cast on KBr disk.

The molecular-weight (MW) and MW distribution (MWD) of the rubber sample were determined by gel-permeation chromatography (GPC) using two columns packed with crosslinked polystyrene (PS). The CLNR was dissolved in tetrahydrofuran (THF) (HPLC grade) to make 0.01 %w/v solution and filtered through 0.45 μm nylon membrane (Millipore) to remove impurities and gel fraction. About 100 μl of the sample solution was injected in JASCO-Borwin GPC equipped with RI (RI2031) detector in THF at 35°C with a flow rate of 0.5 ml/min. Commercially obtained standard polyisoprenes (Polymer Standard Service GmbH, Germany) were used as standard for making calibration curve.

Bound rubber content was used to indicate the interaction between rubber and fillers [11, 18]. About 0.2 g of the silica-filled NR compound was cut into small pieces and immersed in 25 ml toluene without stirring for 7 days at room temperature in which the solvent was renewed after 3 days. The remaining sample, after extracting the unbound material, was dried at room temperature for 1 day and then at 105°C in an oven for 1 day. The bound rubber content (in per-

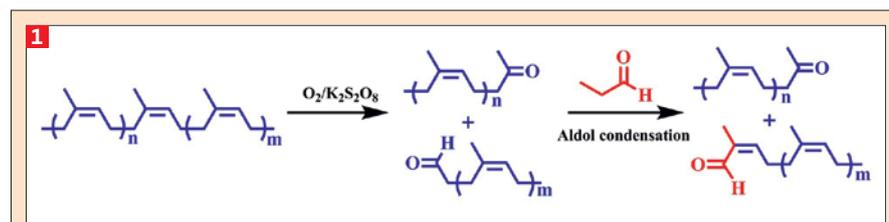


Fig. 1: Proposed mechanism of oxidative degradation reaction of NR in the presence of propanal and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

centage of initial rubber content of the compound) was calculated according to the equation (1) [18].

$$R_B(\%) = \frac{W_{fg} - W \left[ \frac{m_f}{m_f + m_p} \right]}{W \left[ \frac{m_p}{m_f + m_p} \right]} \times 100 \quad (1)$$

Where  $R_B$  is the bound rubber content,  $W_{fg}$  is the weight of filler and gel,  $W$  is the weight of the specimen, and  $m_f$  and  $m_p$  are the weights of filler and rubber in the compound, respectively.

The Mooney viscosities  $ML_{(1+4)}$  at 100°C of the compounds were determined using a TechPro Mooney viscometer based on ISO 289-1.

The “Payne effect” indicating the degree of filler–filler interaction was analyzed by strain sweep tests using a Rubber Process Analyzer (RPA) (RPA2000; Alpha Technologies, Ohio, USA). The rubber samples were measured for storage modulus ( $G'$ ) at 100°C by varying the strain from 0.5% to 1200% at a frequency of 1 rad/s. The different storage modulus at low and high strains ( $\Delta G'$ ) was ascribed to the “Payne effect” [19].

The morphologies of vulcanized NR samples were investigated by scanning electron microscope (SEM) (HITACHI S-2500) operating at an accelerating voltage of 15 kV. The samples were dipped into liquid nitrogen for 10 min, cryogenically fractured to create a new surface and coated with a thin layer of gold.

The optimum cure time ( $t_{c90}$ ) of each sample was determined using a moving die Rheometer (MDR) (TechPro MD+) at 150°C. After that, the rubber compound was vulcanized at 150°C according to its  $t_{90}$  by compression molding. In order to determine crosslink density of silica filled NR vulcanizates, approximately 0.7 g of vulcanized rubber compounds were cut into small pieces. The specimen was immersed in toluene (100 mL) for 7 days at room temperature in the dark. Then, the swollen samples were collected and excess liquid on the specimen surface removed using a filter paper. The specimens were weighed until the weight became constant. The crosslink density was calculated using the modified *Flory-Rehner* equation as shown in equation (2) [20–22].

$$v = \frac{1}{M_c} = \frac{-(\ln(1 - V_r) + V_r + \chi V_r^2)}{2\rho_r V_0 (V_r^{1/3} - \frac{V_r}{2})} \quad (2)$$

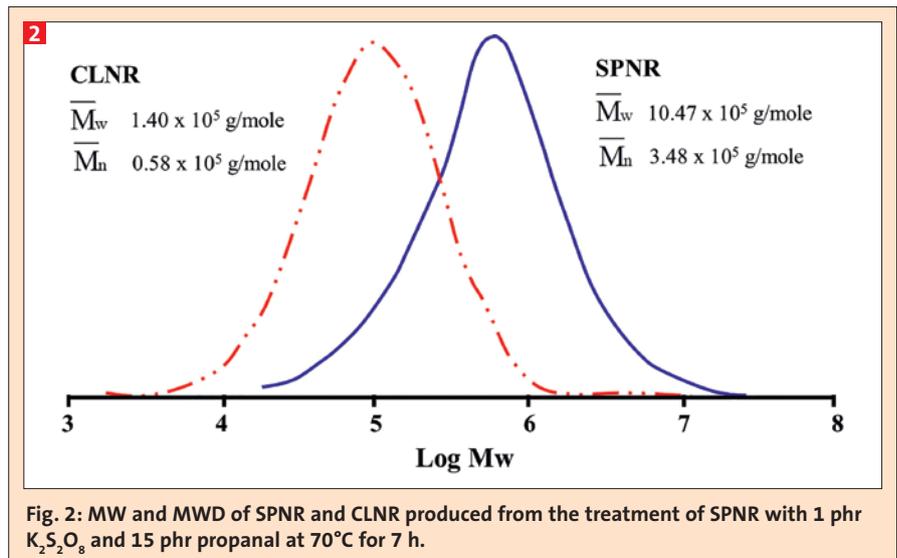


Fig. 2: MW and MWD of SPNR and CLNR produced from the treatment of SPNR with 1 phr  $K_2S_2O_8$  and 15 phr propanal at 70°C for 7 h.

Where  $v$  is the crosslink density,  $M_c$  is molecular-weight between crosslink,  $\chi$  is *Huggins* interaction constant (0.38 for silica-filled NR),  $V_0$  is molar volume of the solvent (106.9  $cm^3/mol$ ).  $V_r$  is volume fraction rubber for silica-filled rubber, was calculated as follows equation (3):

$$\frac{V_r^0}{V_r} = 1 - [3c(1 - V_r^{0/3}) + V_r^0 - 1] \frac{\theta}{1 - \theta} \quad (3)$$

where  $c$  is the parameter for silica-rubber interaction ( $c = 1.17$ ),  $\theta$  is the volume fraction of silica (0.2).  $V_r^0$  is volume fraction rubber obtained from the experiment, was calculated as follows equation (4):

$$V_r^0 = \left[ \left( \frac{\rho_r}{\rho_s} \right) \left( \frac{W_s - W_u}{W_u} \right) + 1 \right]^{-1} \quad (4)$$

Where  $\rho_r$  is the density of rubber (0.93  $g/m^3$ ),  $\rho_s$  is the density of the solvent (0.886  $g/m^3$ ),  $W_s$  is the weight of the specimen and  $W_u$  is the weight of the swollen rubber.

Tensile strength measurement was determined by an Instron Model 5566 at room temperature. The testing cross-head speed of 500 mm/min was applied with a load cell of 1 kN. The vulcanized samples were cut into a dumbbell-like shape (type C) according to ASTM D6746. This device allowed symmetric deformation of the sample and monitoring the

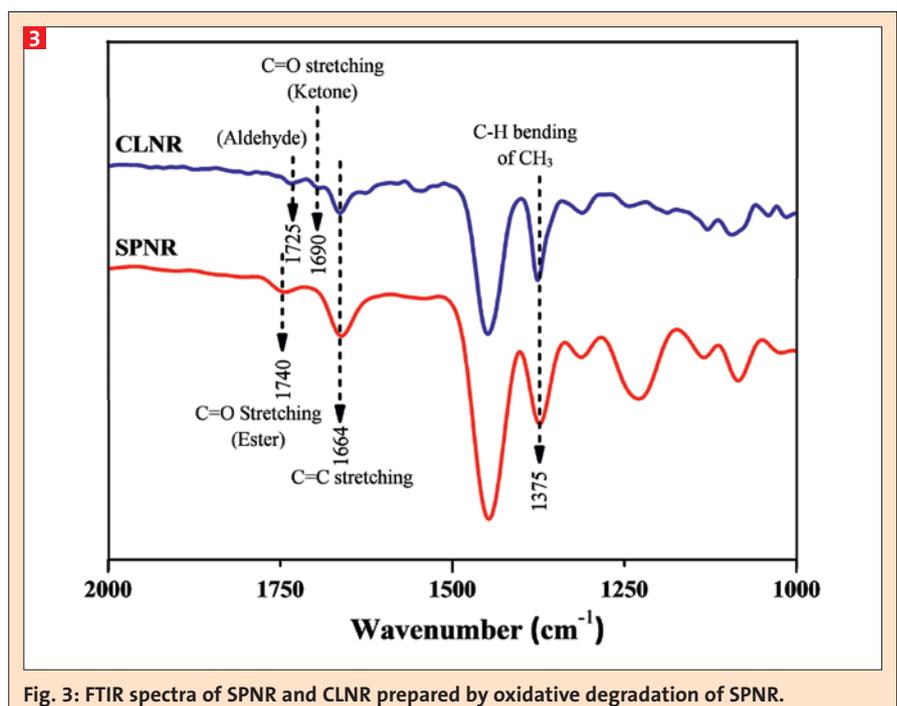


Fig. 3: FTIR spectra of SPNR and CLNR prepared by oxidative degradation of SPNR.

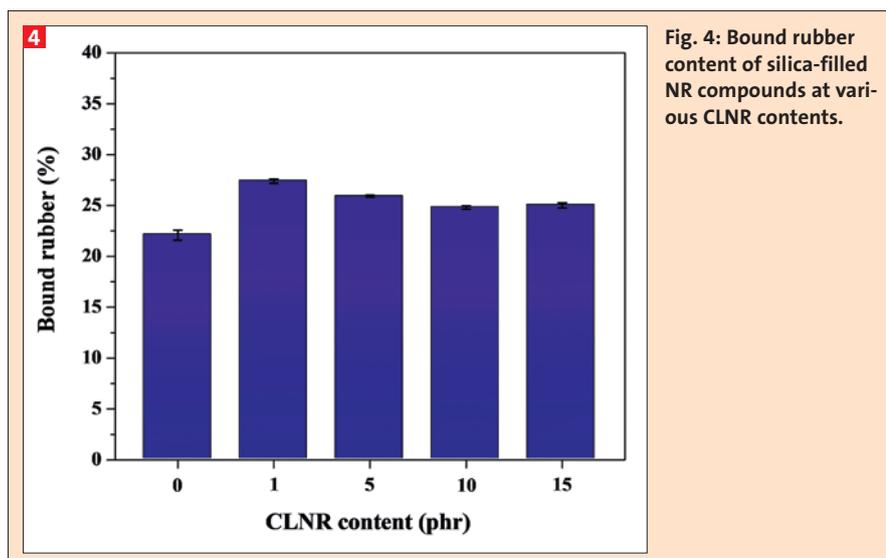


Fig. 4: Bound rubber content of silica-filled NR compounds at various CLNR contents.

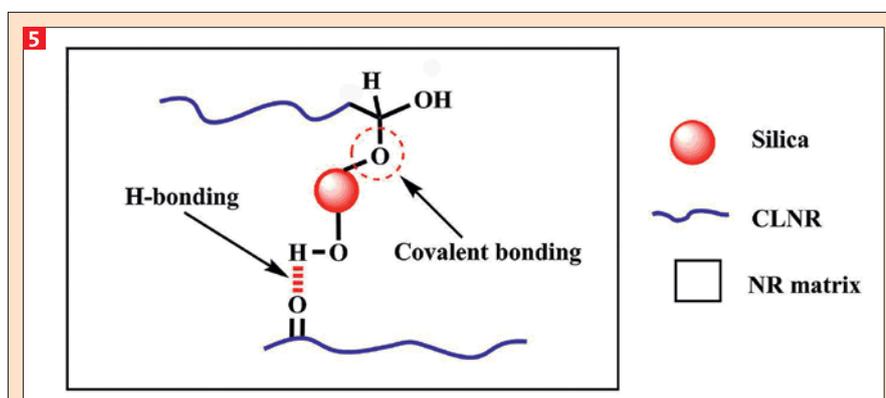


Fig. 5: Postulated interactions between the carbonyl groups of the CLNR and the hydroxyl group on silica surface.

linked to NR chain, respectively. On the other hand, the CLNR spectrum exhibited the characteristic bands of C=O stretching of  $\alpha$ ,  $\beta$ -unsaturated aldehyde at  $1690\text{ cm}^{-1}$  and ketone at  $1725\text{ cm}^{-1}$ . This suggests that the obtained CLNR molecule was composed of aldehyde and ketone groups, which is consistent with the previous report on the presence of these groups at both terminals [14]. Accordingly, it can be proposed that the obtained CLNR was a telechelic polymer having polar functional groups that could be a promising compatibilizer for the silica-filled NR compounds [14].

#### Filler-rubber and filler-filler interactions of unvulcanized compounds

To improve the compatibility between rubber and silica particles, various contents, i.e., 0 to 15 phr, of the prepared CLNR was added to the silica filled NR compound containing 50 phr silica filler and other additives. Figure 4 shows the result of bound rubber of the compound in the presence of different CLNR contents, which the degree of rubber-filler interaction was measured by bound rubber content. It was found that bound rubber content of the compound increased after the addition of the CLNR. This result signifies the improvement of the interaction between fillers and NR chains by adding the CLNR. This might be due to the crosslink ability of the carbonyl groups on the CLNR chains that linked together between silica surfaces and NR matrix generating more insoluble portion that cannot be extracted by good solvent of the rubber [7, 11]. Postulated interactions between the carbonyl groups of the CLNR and the polar groups on silica surfaces are shown in Figure 5. The CLNR possibly forms both chemical and physical bonds with silica. Moreover, based on the same main structure as NR matrix, the CLNR should be well compatible with NR matrix and hence provides the good rubber-filler interaction.

Viscosity is one of the parameters that can give the information of rubber-filler interaction. The viscosity of filler-filled rubber compound arises from their heterogeneous nature and the strong interactions that develop between their various ingredients [3]. Mooney viscosity ( $ML_{1+4}$ ) of the silica-filled NR compounds at various contents of the CLNR is given in Figure 6. It was observed that Mooney viscosity of the compounds in the presence of the CLNR increased with increasing the CLNR content from 0 to 5 phr and remar-

structure change of the sample by illuminating the same sample position during deformation.

## Results and discussion

### MW, MWD and functional groups of CLNR

Previously, we have achieved the preparation of the well-defined structural degraded rubber in the latex state by a combination of a radical initiator and carbonyl compound [14]. Herewith, the CLNR was prepared by treating the SPNR latex in the presence of 1 phr  $K_2S_2O_8$  and 15 phr propanal as initiator and carbonyl compound, respectively at  $70^\circ\text{C}$  for 7 h. Figure 2 shows MW and MWD of the SPNR and the obtained CLNR. The apparent shift from high to low molecular-weight peaks in the MWD chromatogram could be observed for the preparation of the CLNR from SPNR latex. This result indicates the effectiveness of  $K_2S_2O_8$  and propanal for the chain scis-

sion of the rubber chains in the latex state. This might be due the good solubility of  $K_2S_2O_8$  in the rubber latex and the more stable terminal groups after the chain scission as a result of propanal. The number-average molecular-weight ( $\bar{M}_n$ ) and the weight-average molecular-weight ( $\bar{M}_w$ ) of the obtained CLNR were  $0.58 \times 10^5$  and  $1.40 \times 10^5$  g/mole, respectively. Based on the low range of molecular weight, the CLNR appears to be a liquid-like material, which might assist to improve the processability of the rubber compound.

The molecular structure of the CLNR was characterized by FT-IR to confirm the presence of carbonyl groups as the polar functionality. FT-IR spectra of SPNR and CLNR are presented in Figure 3. It was found that the spectrum of SPNR as a starting material for preparing the CLNR showed only the characteristic bands of NR at  $1375$ ,  $1664$  and  $1740\text{ cm}^{-1}$ , corresponding to C-H bending of  $\text{CH}_2$ , C=C stretching and C=O of phospholipid

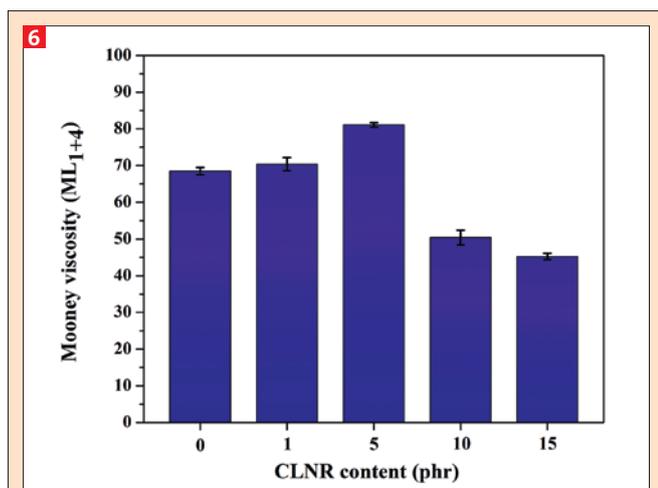


Fig. 6: Mooney viscosity (ML<sub>1+4</sub>) of silica-filled NR compounds at various CLNR contents.

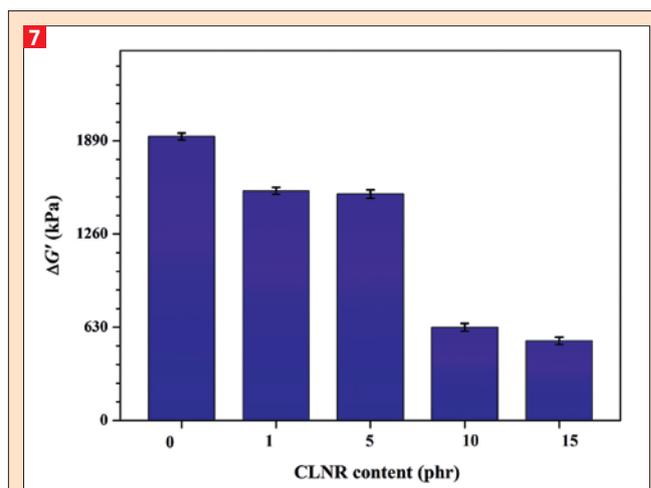


Fig. 7: ΔG' of silica-filled NR compounds at various CLNR contents.

kably decreased when CLNR content increased from 10 to 15 phr. The maximum Mooney viscosity of rubber compound at 5 phr of the CLNR might be attributed to an increase of filler–rubber interaction improved by carbonyl functional groups of the CLNR resulting in the low mobility of rubber molecules. In contrast, owing to the low molecular-weight nature of the CLNR, it can act as a good plasticizer as well. At high content (10–15 phr), the excess CLNR could be localized between the rubber molecules as a plasticizer to obviously reduce Mooney viscosity of the rubber compounds.

Considering strain-dependent modulus testing, as shown in Figure 7, where ΔG' indicates the “Payne effect” whereby the lower ΔG' infers a decrease in filler–filler interaction and better filler dispersion, it can be seen that ΔG' of the rubber compounds decreased when CLNR content increased to 5 phr and remarkably decreased when CLNR content increased up to 10 and further to 15 phr. The decrease in ΔG' of the rubber compound at low amount of the CLNR (1–5 phr) signifies the effectiveness of the CLNR to reduce filler–filler interaction of the rubber compound as a result of the interaction of carbonyl groups on the CLNR and hydroxyl group on silica surfaces. However, the dramatic decrease in ΔG' of the rubber compound at high amount of the CLNR (10–15 phr) is attributed to not only the reduction of filler–filler interaction but also the very low modulus in nature caused by the plasticizing effect of CLNR that takes place at high quantity of the CLNR. This result was supported by Mooney viscosity of the rubber compounds as above results.

It should be noted that such the low viscosity of rubber could lead to the poor dispersion of fillers due to the low shear force during mixing [23, 24]. Therefore, the effect of the CLNR on the dispersion of silica should be further clarified. The degree of silica dispersion could be visualized by the morphology of the cryogenic fracture surfaces of vulcanizates, as displayed by SEM images in Figure 8. Silica aggregates can be clearly seen in the NR without the CLNR. The aggregates became lower after the addition of 1 phr of the CLNR and disappeared after the addition of 5 phr of the CLNR. In contrast, the aggregates appeared again after the addition of 10 and 15 phr of the CLNR. These findings confirm the potential of

the CLNR as a good compatibilizer between NR and silica when the CLNR was used at a small amount, while at high amount of the CLNR, the poor dispersion of silica could be observed due to the plasticizing effect of the CLNR.

#### Cure characteristic and crosslink density of silica-filled NR

The optimum cure time of the compounds is shown in Figure 9. It can be seen that the optimum cure time which is referred to the time completion of vulcanization of the samples decreased with increasing CLNR content from 0 to 5 phr and then increased at higher content of the CLNR (10–15 phr). These results can be explained that at a small

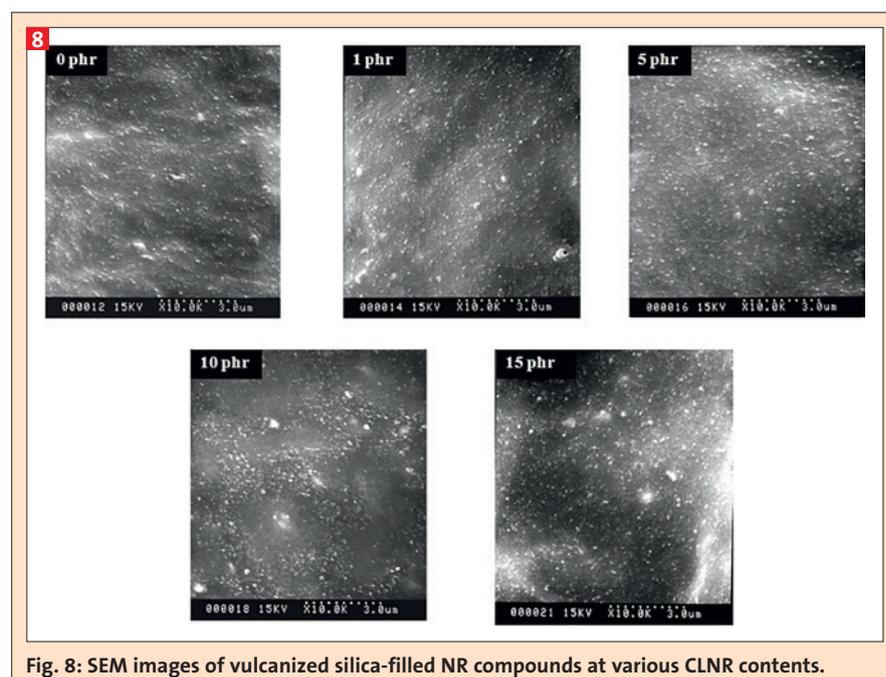


Fig. 8: SEM images of vulcanized silica-filled NR compounds at various CLNR contents.

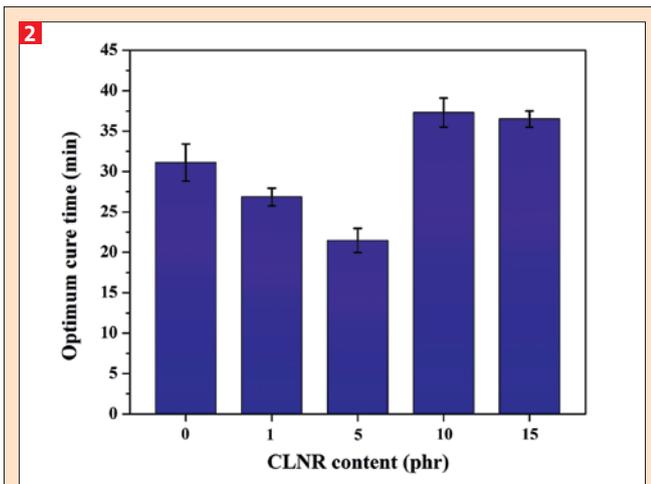


Fig. 9: Optimum cure time of silica-filled NR compounds at various CLNR contents.

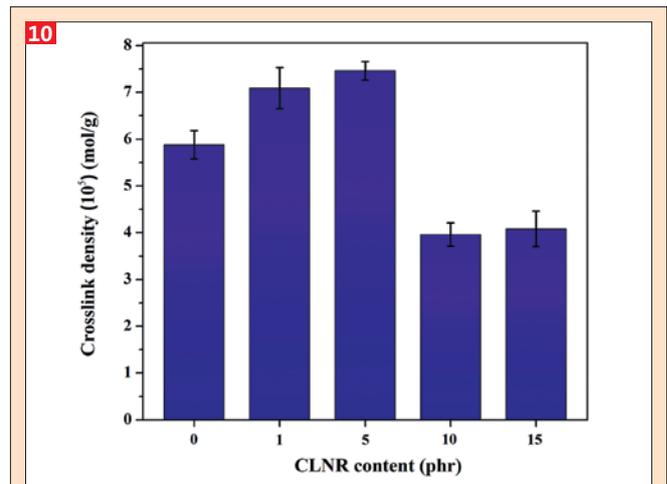


Fig. 10: Crosslink density of silica-filled NR compounds at various CLNR contents.

portion of the CLNR (1 and 5 phr), silica had a good interaction with CLNR chain by physical and chemical bondings. Therefore, a number of free silanol groups on the silica surfaces that can probably react with some polar curatives were reduced, so high crosslink efficiency could be promoted. On the other hand, at high content of the CLNR (> 5 phr), the numerous carbonyl groups of the CLNR could interfere the vulcanization. Since polar curatives could form physical bonding with carbonyl groups of CLNR as well, the polar curatives could be adsorbed and migrated into the CLNR phase. Furthermore, the addition of high amount of CLNR results in the significant increase of rubber phase in the compounds, while the amount of curatives is fixed. This leads to the dilution of the curatives in the compounds and hence the curatives were insufficient in

the vulcanization system. Consequently, the prolonged vulcanization occurred when the high amounts of the CLNR were added to the rubber compounds [11, 25].

Figure 10 shows crosslink density of silica-filled compounds with various contents of the CLNR. It is apparent that the crosslink density of vulcanizates increased after the addition of the CLNR from 1 to 5 phr, whereas the reverse result could be observed when 10 and 15 phr of the CLNR were added to the rubber compounds. These can be explained by the efficiency of vulcanization as described in the results of optimum cure time that low content of the CLNR promoted crosslinking reaction, while high content of the CLNR suppressed crosslinking reaction. Moreover, the strong interaction of rubber molecules to the surface of silica particles caused by the addition of small

amount of the CLNR could resist swelling and enhance the degree of crosslink density [26]. On the contrary, the decreased crosslink density of vulcanizates containing 10 and 15 phr of the CLNR might be due to the poor dispersion of the silica in these vulcanizates.

#### Tensile properties of silica filled NR vulcanizates

The modulus at 100% strain, tensile strength and elongation at break of silica-filled NR vulcanizates are shown in Figures 11-13, respectively. It was clearly found that the CLNR influenced the modulus at 100% strain and tensile strength, but the elongation at break was not affected by the CLNR. Figures 11 and 12 reveal that both the modulus at 100% strain and tensile strength increased with increasing CLNR content up to 5 phr and subsequently decreased after the

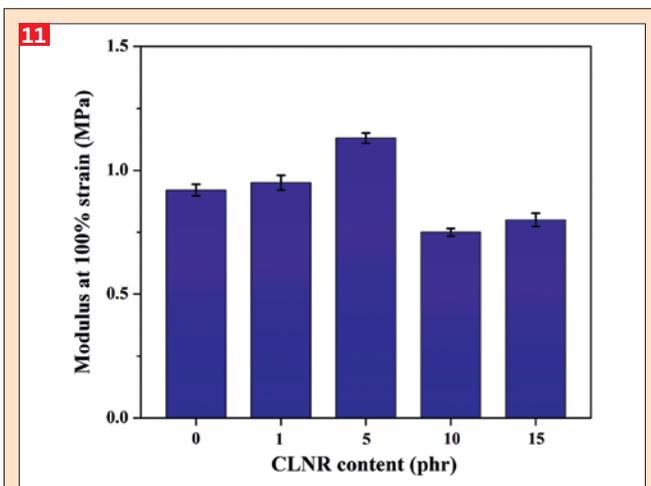


Fig. 11: Modulus at 100 % strain of vulcanized silica-filled NR at various CLNR contents.

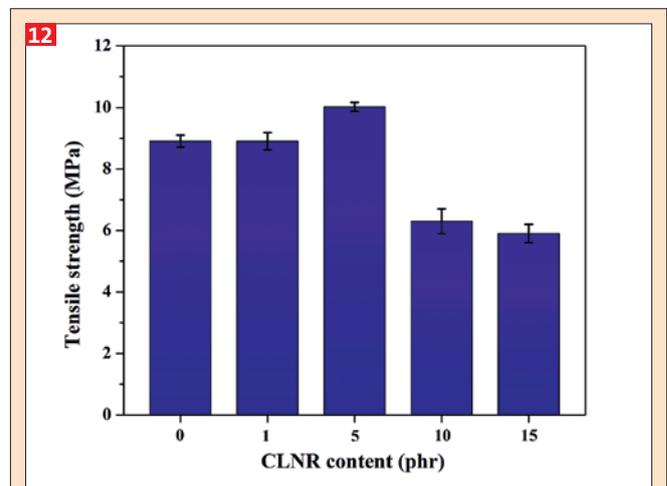


Fig. 12: Tensile strength of vulcanized silica-filled NR at various CLNR contents.

addition of 10 and 15 phr of the CLNR. The increase in the modulus at 100% strain and tensile strength was ascribed to the good dispersion of silica and high crosslink density caused by the improvement of compatibility between NR and silica, based on the utilization of a small amount of the CLNR. On the other hand, the decrement of the modulus at 100% strain and tensile strength was due to the poor dispersion of silica and low crosslink density as a result of plasticizing effect of the CLNR when the high amount of the CLNR was added to the rubber compound.

Based on the above findings, it can be deduced that the suitable amount of the CLNR can raise silica-NR interaction and reduce silica-silica interaction, leading to the improvement of tensile properties of the rubber vulcanizates. Therefore, the CLNR could be a promising compatibilizer for silica-filled rubber compounds.

### Conclusions

The CLNR containing carbonyl groups as a polar functional group could be prepared by the oxidative degradation of the saponified NR latex in the presence of  $K_2S_2O_8$  and propanal. The addition of small portion of CLNR (1-5 phr) could increase filler-rubber interaction and decrease filler-rubber interaction of the rubber compounds, as evidenced by an increase in the bound rubber and Mooney viscosity, as well as a reduction of "Payne effect". However, the plasticizing effect of the CLNR was appeared at high amount of the CLNR (10-15 phr), indicated by the remarkable decrease in Mooney viscosity and "Payne effect" of the rubber compounds. The degree of silica dispersion visualized by SEM demonstrated that the good dispersion of silica in the rubber compounds could be observed when the CLNR was used at a small amount, while the poor dispersion of silica in the rubber compounds caused by the plasticizing effect of the CLNR could be found when adding high amount of the CLNR. The vulcanization time and crosslink density could be promoted by adding small amount of the LNR, whereas the high amount of the CLNR contributed to the prolonged vulcanization and low crosslink density. The compatibilizing effect of the CLNR at a proper amount provided the good dispersion of silica and high crosslink density, leading to the improvement in tensile properties. Therefore, the CLNR could

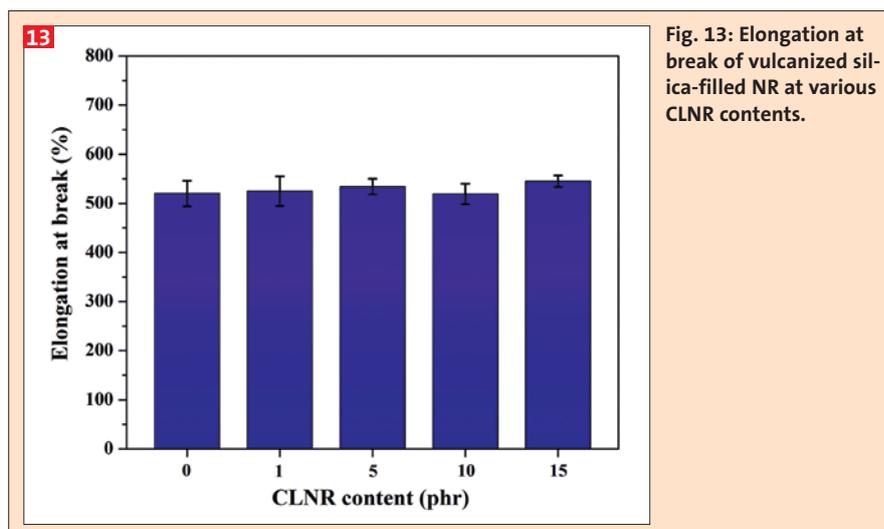


Fig. 13: Elongation at break of vulcanized silica-filled NR at various CLNR contents.

be an attractive compatibilizer to enhance the compatibility between silica and NR.

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