Effect of expanded organoclay by stearic acid to curing, mechanical and swelling properties of natural rubber nanocomposites

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Abstract. The interlayer basal spacing of organoclay (OC) could be increased with stearic acid (SA) added, thus OC changed into expanded organoclay by SA (OCSA). The effect of various loadings of OCSA on the curing, mechanical and swelling properties of natural rubber (NR) nanocomposites were studied. The natural rubber/expanded organoclay (NR/OCSA) nanocomposites were prepared by melt intercalation using a laboratory open mill. The curing characteristics of NR compounds were determined using a Moving Die Rheometer (MDR). The X-ray Diffraction (XRD), Attenuated Total Reflectance Infrared (ATR-IR) Spectroscopy and Field Emission Scanning Electron Microscopy (FESEM) were used to study the dispersion of OCSA in the NR matrix. The mechanical properties of NR/OCSA nanocomposites such as tensile strength, elongation at break and hardness were determined using ISO standard and swelling of NR/OCSA nanocomposites in toluene were determined using ISO 1817. The results showed that the SA intercalated into the gallery of OC and reacted with the hydroxyl groups in OC. It was indicated with the shifting of the negative peak 1,700 to 1,723 cm⁻¹ in the ATR-IR spectrum and increase the d-spacing of OC. The adding of various loadings of OCSA into NR could increase the torque and accelerate the curing of nanocomposites and it also could increase the mechanical and swelling properties of nanocomposites. The change in modulus at 100% elongation significantly increased with increasing the OCSA load until maximum loading at 10 phr. This trend was same with the hardness and modulus at 300% elongation. Meanwhile, the improvement of tensile strength and elongation at break was higher at 4 phr OCSA compared with the other loading. The increase of mechanical and swelling properties of NR/OCSA nanocomposites was due to intercalation/exfoliation of OCSA in NR matrix. It was revealed by appearing of the out-of-plane Si-O-(Al) stretch with peak value 1080 cm⁻¹ in the ATR-IR spectrum and the peaks of OCSA in the XRD pattern was disappeared until the loading of OCSA 8 phr and the thickness of morphology of OCSA below 100 nm.

1. Introduction

The rubber filler is used to improve the mechanical properties and reducing cost. There are several rubber fillers, though the rubber industry usually uses carbon black as reinforcing filler. But carbon black is made from petroleum and causes of pollution. In the last two decades, research was focused to develop the other reinforcing filler. Clay has been used as a filler for many years. Unfortunately, the hydrophilic nature of the clay made these materials incompatible with the hydrophobic rubber matrix, with resulted non reinforcing effects in the rubber matrix. Recently, clay
minerals could be used as a reinforcing rubber filler after modifying by intercalating quaternary ammonium compound into the interlayer space through ion exchange become organoclay (OC) [1].

The improvement of mechanical properties of rubber nanocomposite depends on the uniformly dispersed (exfoliated) and distribution of the clay in the rubber matrix. The fully exfoliated of clay within the rubber matrix is expected to enhance the mechanical properties of rubber composite [2]. The content of organoclay was below 6 wt% to get a completely exfoliated in the natural rubber (NR) matrix [3]. The high amount of clay due to the formation of agglomeration in rubber matrix as well as due to the cost factor. However, the small amount of organoclay did not improve the mechanical properties significantly. The tensile strength of NR-Styrene Butadiene Rubber (SBR) was not change in base rubber up to 2 wt% OC [4]. Therefore, the increase exfoliation of the OC with a sufficient amount in the rubber matrix is very important to improve mechanical properties.

The increase of exfoliation of OC in the rubber matrix can use expanded organoclay by using stearic acid (SA). From previous studies, SA had a beneficial effect on the intercalation/exfoliation on process of clay mineral in Nitrile rubber [5]. The adding OC 10 part hundred rubber (phr) and 10 phr SA could increase physical and mechanical properties of non polar rubber like NR, Ethylene Propylene Diene Monomer (EPDM), Butadiene Rubber (BR) and etc. [6]. The OC 10 phr and SA 2 phr could improve the tensile strength in polar and non-polar rubber [7]. SA intercalated in the gallery of OC, so that the d-spacing of OC increased with increasing SA concentration [8].

The present paper is aimed at studying the effect of various loadings of in-situ expanded organoclay by SA (OCSA) on the curing characteristic, mechanical and swelling properties of vulcanized NR/OCSA obtained by melt intercalation.

2. Experimental

Natural Rubber (NR) grade thin pale crepe was obtained from PTPN 8, West Java, Indonesia. Organoclay (OC) Cloisite® 20A was supplied by Southern Clay Products. Inc. Rockwood additives. Dimethyl dehydrogenated tallow quaternary ammonium was used as an organic modifier. The d-spacing of Cloisite® 20A was 2.42 nm. Zinc oxide (ZnO), stearic acid (SA), N-cyclohexylbenzothiazole-2-sulfenamide (CBS), and sulfur were purchased from local suppliers.

OC and SA were mixed together in-situ by using porcelain mortar with the weight ratio of OC:SA (1:0.2). The mix was put in an oven at 100 °C for 1 h. After cooling, the obtained product is called expanded organoclay by SA (OCSA). The crystallographic spacing (d) of OCSA was measured using XRD Rigaku, Japan in transmission mode using CuKα radiation (λ = 0.1542 nm), X-ray diffractometer (40 kV, 30 A). The interaction between SA and OC was studied by ATR-IR Thermo
Scientific Nicole iS5. ATR-IR spectrum was measured between 500-4,000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\).

Natural rubber/expanded organoclay (NR/OCSA) nanocomposites were prepared by melt intercalation method in an open two roll mill with a speed of slow roll (24 rpm) and friction ratio (1.4) maintained at 65 ± 5 °C. The rubber compounds were conditioned at room temperature for minimum 16 h. The formulation compounds are described in Table 1. The loading of OC were varied (0, 2, 4, 6, 8, and 10). Because the weight ratio OC:SA = (1:0.2), the loading of OCSA also varied (0, 2.4, 4.8, 7.2, 9.6, and 12.0) phr. The total amount of SA was adjusted same at each formulation of compound (2 phr) as the common dosage of normal rubber compound. The deficit of SA was added at two roll mill (2.0, 1.6, 1.2, 0.8, 0.4, and 0). The curing characteristics of the rubber compounds were determined using an MDR at 150 °C according to ISO 6502. The compounds were then molded at electrically heated hydraulic press at 150°C with the respective cure time (t\(_{90}\)), previously determined from MDR. The sample's thickness of 2 mm sheets was molded.

|                | NROCSA-0 | NROCSA-2 | NROCSA-4 | NROCSA-6 | NROCSA-8 | NROCSA-10 |
|----------------|----------|----------|----------|----------|----------|------------|
| NR             | 100      | 100      | 100      | 100      | 100      | 100        |
| OCSA           | 0        | 2.4      | 4.8      | 7.2      | 9.6      | 12.0       |
| ZnO            | 5        | 5        | 5        | 5        | 5        | 5          |
| SA             | 2        | 1.6      | 1.2      | 0.8      | 0.4      | 0          |
| CBS            | 1.5      | 1.5      | 1.5      | 1.5      | 1.5      | 1.5        |
| Sulfur         | 2.5      | 2.5      | 2.5      | 2.5      | 2.5      | 2.5        |

Tensile properties were measured according to ISO 37 by using universal testing machine Lloyd, with type 2 dumbbell test specimens. Hardness was measured by using Shore A durometer according to ISO 7619.

The improvement of mechanical properties of NR/OCSA nanocomposites with respect to the gum was calculated in the following [6]:

\[
\text{improvement} = \left( \frac{v(OCSA) - v(gum)}{v(gum)} \right) \times 100
\]  

(1)

The swelling of NR/OCSA nanocomposites in toluene was determined using ISO 1817 for 24 h at room temperature. The initial weight of the samples was taken, and then they were immersed into toluene. The samples were periodically removed from the test bottles, the surplus solvent was removed from the surface, and the samples were weighed immediately and then placed into the toluene again.
The swelling ratio, $Q_t$, was also determined from the weight of the sample in unswollen and swollen states. The equation as the following [9]:

$$Q_t = \frac{M_t - M_0}{M_0} \times 100$$ (2)

where $Q_t$ is the swelling ratio, $M_t$ the weight of the samples in the swollen states and $M_0$ the initial weight of the samples.

The intercalation/exfoliation of NR/OCSA nanocomposites was studied by XRD and ATR-IR. The morphology of NR/OCSA nanocomposites was characterized using FESEM INSPECT F50 (20 kV). Fractured surfaces of the vulcanizates NR/OCSA nanocomposites were obtained by tensile test. The surfaces were coated by gold/palladium to prevent electrostatic charging during examination.

3. Results and Discussion

3.1. Characterization of Expanded Organoclay (OCSA).

Figure 1 shows the XRD pattern of OC, SA and OCSA. The spectrum of OC presents two quite broad peaks. The first peak ($d_{001} = 2.52$ nm) was related to intercalated ions with a paraffin-like structure [10], whereas the small second peak ($d_{001} = 1.25$ nm) was a portion of the clay layers has not been intercalated after chemical modification. The interlayer distance of OCSA was shifted from 2.52 nm of OC to 3.83 nm. It was indicated that the expanding space should be attributed to SA intercalation into a gallery of OC. The intercalation of SA were due to the van der Walls forces between SA and the alkylammonium ions [6] and the esterification between SA and OC [7]. The second peak ($d_{001} = 2.01$ nm) of OCSA shows that some SA molecules recrystallize during the cooling process. The second peak of OC was shifted from 1.25 to 1.33 nm. It was indicated that SA also intercalating into the clay layer which has not been intercalated by alkylammonium ions.

![Figure 1. XRD pattern of OC, SA and OCSA](image-url)
ATR-IR spectrums of OC, SA and OCSA are shown in Figure 2. There was no peak of carboxylic structure (1695.27 cm\(^{-1}\)) at spectrum ATR-IR of OC. Spectrum OCSA revealed that the peak at 1695.27 cm\(^{-1}\) is shifted to 1723.55 cm\(^{-1}\), which means that carboxylic group were esterified by hydroxy groups of OC layers. The esterification could be the driving force for SA intercalating into OC and expand the spacing of OC [7].

![Figure 2. ATR-IR spectrums of OC, SA and OCSA](image)

3.2. Curing Characteristic of NR/OCSA

The curing characteristics, expressed in terms of the scorch time (\(t_s\)), optimum cure time (\(t_90\)), cure rate index (CRI) and torque value (\(S'\)) of NR and NR/OCSA compounds are compiled in Table 2. The increase of loading of OCSA could decrease the scorch time and optimum cure time of NR compound and increased the cure rate index. From these results it can be assumed that OCSA can act as accelerators for the sulfur vulcanization system. The amine groups present in the OC facilitate the curing reaction of NR and it was a synergy with CBS accelerator that could accelerate the vulcanization [11].

| Samples | \(S'_{max}\) (dN m) | \(S'_{min}\) (dN m) | \(t_s\) (min) | \(t_90\) (min) | \(\Delta S'\) (dN m) | CRI \(^a\) (min\(^{-1}\)) |
|---------|---------------------|---------------------|---------------|---------------|----------------|---------------------|
| NROCSA-0 | 7.13                | 0.36                | 5.22          | 7.32          | 6.77             | 47.62                |
| NROCSA-2 | 7.59                | 0.12                | 2.13          | 4.35          | 7.47             | 45.05                |
| NROCSA-4 | 8.25                | 0.13                | 1.36          | 4.22          | 8.12             | 34.97                |
| NROCSA-6 | 8.69                | 0.33                | 1.29          | 4.22          | 8.47             | 34.13                |
| NROCSA-8 | 9.02                | 0.24                | 1.19          | 3.55          | 8.78             | 42.37                |
| NROCSA-10| 9.04                | 0.30                | 1.15          | 3.59          | 8.74             | 40.98                |

\(^a\)CRI = Cure rate index = 100/(\(t_90\)-\(t_s\))

The increase of OCSA loading of the NR compound could improve the value of torque maximum and delta torque (\(\Delta S' = S'_{max} - S'_{min}\)). The delta torque (\(\Delta S'\)) value was related to crosslink
density, it could be concluded that OCSA increases the crosslink density of NR. The increasing of $\Delta S'$ was attributed to the intercalation/exfoliation of OCAS in the NR matrix.

3.3. Mechanical and Swelling Properties of NR/OCSA

Figure 3 describes the improvement of mechanical properties of NR/OCSA nanocomposites. The improvement of all mechanical properties of all NR/OCSA nanocomposites always higher compared with NR containing only OC. The change in modulus at 100% elongation significantly increased with increasing the OCSA load. This trend was same with the hardness and modulus at 300% elongation, because the modulus at 100%, hardness and modulus at 300% was related to crosslink density of NR/OCSA compounds [12]. The improvement of tensile strength and elongation at break was higher at 4 phr OCSA compared with the other loading. The improvement of tensile strength in case of rubber/organoclay nanocomposites was given by some researcher [9,13,14]. Their studies suggested that the increase of tensile strength was related to the degree of dispersion (intercalation/exfoliation) of OC in the NR matrix. The exfoliation of OC causes an increase in surface area. Hence, the tensile strength of NR/OCSA at 4 phr OCSA recorded high tensile strength.

![Figure 3. Improvement of mechanical properties: (a) tensile strength, (b) 100% modulus, (c) 300% modulus, (d) elongation at break, (e) hardness](image)

The swelling curves of NR/OCSA nanocomposites with various loadings of OCSA are shown in Figure 4. The swelling curve was obtained by plotting between $Q_t$ and time ($t^{1/2}$). Figure 4 shows that the swelling ratio decreased with increasing the loading of OCSA. It was due to the dispersion impermeable clay layers in the NR matrix which obtained the “Tortuous Path Model” [15]. Hence, the platelet structure of layered silicate in NR matrix could improve the swelling properties of NR vulcanizates.
3.4. Morphology Analysis of OCSA

The morphology of OCSA was analyzed in order to study the intercalation/exfoliation of OCSA in the NR matrix. XRD patterns of NR/OCSA nanocomposites with various loadings of OCSA are shown in Figure 5. For NR without OCSA, there were no peaks in the NR vulcanizates XRD pattern. The XRD pattern of OCSA shows that the distance of spacing is 3.83 nm (2Theta = 2.3°). This peak disappeared after OCSA was added into NR compound. However, for 10 phr OCSA in the NR compound, the peak appeared and shifted to 3.99 nm (2Theta = 2.2°).
It means that the OCSA exfoliated in the NR matrix until 8 phr and for 10 phr of OCSA, there were partially intercalated and exfoliated of OCSA in NR matrix. The peak intensity of SA in the NR/OCSA vulcanizates at 2Theta 4.8° increased with increasing loading of OCSA in NR compounds. It was indicated that the SA molecules in the clay gallery were not reacting with zinc oxide and recrystallize after cooling process [16].

![Figure 6. ATR-IR spectra of NR and NR/OCSA nanocomposites with various loadings of OCSA](image)

![Figure 7. Morphology of NR/OCSA nanocomposite with various loadings of OCSA: (a) 0 phr; (b) 2 phr; (c) 4 phr; (d) 6 phr; (e) 8 phr and (f) 10 phr.](image)

The degree of exfoliation of OC could be characterized by using ATR-IR spectra from 1140 to 900 cm⁻¹. Ijdo et al., (2006) [17] studied the degree of OC delamination and orientation in nanocomposites materials using infrared and observed appeared the absorption band around 1080 cm⁻¹. The increase of this absorption band revealed the degree of exfoliation increased [18]. The spectrum ATR-IR of NR and NR/OCSA nanocomposites with various loadings of OCSA are shown in Figure 6. The transmission band of Si – O at 1000 – 1100 cm⁻¹ increased with increasing the OCSA in the NR
compounds. This result was same with Diez et al., (2011) used SBR nanocomposites [18]. The increasing of OCSA loading could increase the transmission band of Si – O – (Al) around 1080 cm$^{-1}$. It was revealed that the degree of exfoliation of OCSA in NR matrix increased with increasing the OCSA loading in NR compounds.

The morphology of NR and NR/OCSA nanocomposites are shown in Figure 7. The fractured surface of samples from tensile test revealed that there were some OCSA agglomerated particles appeared with increasing OCSA in the NR compound. The platelet structure of organoclay could be analyzed at NR/OCSA that containing 4 phr of OCSA as shows in Figure 8. The thickness of platelet structure was below 100 nm. We were difficult to analyze the thickness of others platelet because the platelet position on the fractured surfaces (Figure 8).

4. Conclusion
Curing characteristics, mechanical and swelling properties of NR/OCSA nanocomposites with various loadings of OCSA were studied. The results showed that the increasing of OCSA loading into natural rubber could increase the torque and accelerate the curing of NR/OCSA compounds and also increased the mechanical and swelling properties of nanocomposites. The change in modulus at 100% elongation significantly increased with increasing the OCSA load until maximum loading at 10 phr. This trend was same with the hardness and modulus at 300% elongation. Meanwhile, the improvement of tensile strength and elongation at break was higher at 4 phr OCSA compared with the other loading. The increase of delta torque, mechanical and swelling properties of NR/OCSA nanocomposites was due to better dispersion (intercalation/exfoliation) of OCSA in the NR matrix. The degree of intercalation/exfoliation of OCSA increased in the NR matrix was revealed by the band Si-O-(Al) with peak value 1080 cm$^{-1}$ in the ATR-IR spectrum increased with increasing the loading of OCSA in the
NR compounds. The peaks of OCSA in the XRD pattern is disappeared until the loading of OCSA 8 phr and the thickness of morphology of platelet structure of OCSA below 100 nm.

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