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Physical Properties Investigation of Natural Rubber Composites Using Cetyltrimethylammonium Bromide (CTAB) as Modifier of Local Clay Filler

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Abstract. Improved absorption of rubber backbone on filler surfaces is necessary to enhance the physical properties of rubber vulcanizate. One of the ways to repair the surface of the filler is through modifying using surfactant. Hence, this study aims to compare the physical properties of natural rubber vulcanizates using clay filler and modified clay with cetyltrimethylammonium bromide (CTAB). The processes that were followed to achieve the objectives of this research were the design of rubber formulas, mastication and milling of rubber, and testing of the physical properties of rubber vulcanization. The clay characterization and its modification using FTIR and XRD were also carried out. Characterization using FTIR and XRD showed that there was indeed a clay modification with CTAB. Natural rubber compounds were also analyzed using SEM. The torque on the rheometer for modified clay with CTAB is 12.34 kg-cm higher than for original clay, which is 7.05 kg-cm. Elongation at break and tensile strength for vulcanizate using CTAB-modified clay filler is lower than that using original clay, with 300% modulus and hardness increase. Thus, clay modification using CTAB as a filler has a good effect on the curing characteristics and physical properties of natural rubber vulcanization compared to only using local clay as a filler.

Keywords: Crosslink density, Local clay, Modified clay, Natural rubber, Surfactant

INTRODUCTION

Fillers are supporting materials in manufacturing finished rubber products (Morton, 1987). A variety of fillers have been used. Fillers are divided into reinforcing, semi-reinforcing, and non-reinforcing fillers. These three fillers each have their characteristics when used as a filler. Reinforcing filler, which is well known and cannot be replaced until now, is carbon black. Carbon black produces CO_2, so many researchers and practitioners have tried to reduce its use, for example, the use of a

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hybrid filler between carbon black and lignin (Bahl et al., 2014) and mixing carbon black with calcium carbonate, soy protein, and biochar (Peterson, 2022). Researchers have paid much attention to use natural materials, such as clay, as filler (Hasan et al., 2020). There are many clay deposits in nature, one of which is found in the Bukit Asam coal mine area, in Indonesia.

Clay cannot replace carbon black as a reinforcing filler in rubber, including natural rubber. Since clay is a non-reinforcing filler, many researchers modify the active surface of clay. Clay can be modified in different ways, for example, using surfactants. Surfactants consist of cationic (quattonary ammonium (quat)), anionic (sulfonic), and nonionic (polyethylene glycol (PEG)) surfactants, even amphoteric (Metin et al., 2012; Omurlu et al., 2016; Ni at al., 2018).

Many scientific articles related to the use of cationic surfactant have been published. For example, cetyltrimethylammonium bromide (CTAB) is used to modify the SiO_2 surface to expand the absorption on the SiO_2 surface and as an absorbent for dyes. The maximum absorption of CTAB on the SiO_2 surface took place well at pH 8.0. There is an ionic interaction between the positive and negative charges of CTAB and SiO_2 (Khan et al., 2019). A series of the cationic surfactants, dodecyl trimethylammonium bromide (DTAB), tetradecyltrimethyl-ammonium bromide (TTAB), and CTAB have been evaluated for its chain length effects of the cationic surfactant on the grain size of silica nanoparticles. The results of this modification are used to evaluate the physical properties of cement (Singh et al., 2011). The surface of silica nanoparticles was modified with CTAB, and the different experimental conditions, including the amount of surfactant as well as the modification temperature, have been studied (Ma et al., 2010). Solid adsorbent made by using CTAB for surface modification of silica was applied to absorb carbamate pesticides (Arnnok et al., 2014). Besides modified silica, organomodified kaolin is used for natural rubber filler where as the kaolin modifier is CTAB. Here, a variation of cation exchange capacity is carried out, and its effect on abrasion resistance, modulus, and hardness is observed (Ogbebor et al., 2015a). CTAB is also used as a kaolin modifier, whereas the organomodified kaolin is used as a filler in natural rubber latex. Variations in the concentration of organomodified kaolin were carried out in this study and observed through changes in the physical properties of modulus, elongation, abrasion, and tensile strength (Ogbebor et al., 2015b). Analysis of Mooney viscosity and psycho-mechanical properties of natural rubber using organomodified kaolin fillers with varying concentrations of organomodified kaolin has also been carried out. CTAB is used here as a clay modifier (Peter et al., 2016).

From the description above, no researcher has compared CTAB-modified and unmodified clay's effect as a filler on the curing characteristics and the physical properties of natural rubber composites. Thus, this study aimed to compare the physical properties of natural rubber composites before and after aging with CTAB-modified and unmodified clay or local clay as a filler. CTAB characterization of modified and unmodified clay used FTIR, where the FTIR spectra were used to observe the bond between clay and clay modifier. In contrast, XRD was used to characterize changes in the crystallization of clay before and after modification. SEM analysis is only done on natural rubber compounds. Due to the influence of filler modification, the physical properties in question and macro properties of natural rubber composites are hardness, elongation at break, 300% modulus, and tensile strength.

MATERIALS AND METHODS

The methods used in this research included material used, procedure of local clay modification using CTAB surfactant, characterization of local clay and CTAB-modified clay filler, natural rubber compounding, and physical properties testing.

Materials

Local clay in the Bukit Asam coal mining area in South Sumatra, Indonesia, contained around 50.83–75.29% silica (Hasan et al., 2019), with the type of clay being kaolin clay (Hasan et al., 2020). A natural rubber RSS 1 (PTPN IX, Semarang, Indonesia) was used in this study. The rubber chemicals were Sulfur Midas SP-325 which was obtained from Miwon Chemicals Co., Ltd, Korea, TMTD Accelerator obtained from Qingdao Ever Century Trading Co., Ltd. China), ZnO Zinkoxyd Aktive UN 3077 and TMQ Vulkanox HS/LG from LANXESS Deutschland GmbH, Germany), stearic acid Aflux 52 obtained from Rhein Chemie Rheinau Mannheim GmbH, Germany), and processing oil provided from Minarex oil, Pertamina, Indonesia). Cetyltrimethylammonium bromide (CTAB) (Merck, Germany) was used as a clay modifier. All rubber chemicals and clay modifiers are not treated and used directly as received from suppliers.

The Procedure of Local Clay Modification using CTAB Surfactant

Modification of local clay using CTAB has been carried out according to previous researchers (Rittironga et al., 2015; Perera et al., 2020)

Clay was mixed with about 3 % wt distilled water and stirred at 40-50 °C for 30 minutes. About 18 mmol of CTAB was put into the formed clay suspension and stirred for 30 minutes. The suspense was left, and the product was filtered. The product is washed several times to remove bromine ions and tested with 0.1 M $AgNO_3$. The product, CTAB-modified clay, is dried for 2 days and crushed to become smooth.

After obtaining the CTAB-modified clay, characterization was carried out using FTIR, XRD, and SEM. This characterization was also carried out on the original clay or local clay.

Characterization of Local Clay and CTAB-modified Clay Filler

The clay and CTAB-modified clay samples were prepared using powder-pressed KBr pellets and analyzed with an FTIR Alpha instrument. The FTIR spectra were taken using Bruker, Germany and were recorded in the 500–4000 cm^{-1} range. The clay sample concentration in KBr was about 0.2 to 1 % (FT-IR sample preparation, 2007).

XRD were recorded using a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) with Cu kα radiation at λ = 1.54060, current of 20 mA, and voltage of 40 kV. XRD were determined at a scan rate of 0.02°/s in the 2θ range of 2–90°.

Natural rubber compound samples with lateral dimensions of approximately 10 mm × 10 mm and a thickness of 3 mm were used to examine the dispersion of the fillers in the natural rubber composites using an SEM SU3500 instrument (Hitachi, Japan).

Natural Rubber Compounding

General processes for natural rubber composites are listed in Figure 1.

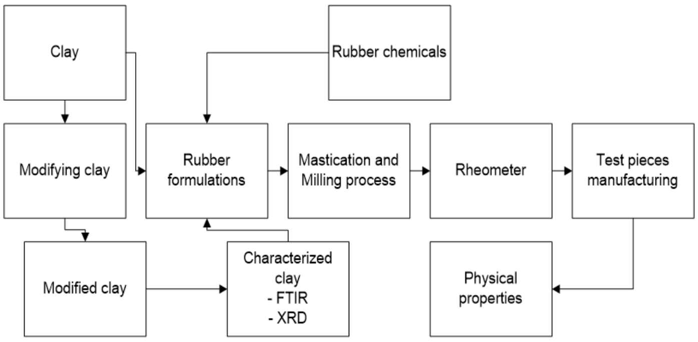


Fig. 1: General processes for natural rubber compounding until natural rubber vulcanizates and its characteristics

Table 1. Natural rubber formula with local clay filler and CTAB-modified clay.

Ingredients	Compounds, phr	
	Local clay filler	CTAB-modified clay
Natural rubber RSS 1	100	100
Stearic acid	2	2
ZnO	5	5
TMQ	2	2
TMTD	0.5	0.5
Sulfur	3	3
Processing Oil	3	3
Local clay fillers	15	-
CTAB-modified clay	-	15

The natural rubber formula (see Table 1), which includes original clay filler and CTAB-modified clay, rubber chemicals, and rubber, is then weighted according to their respective contents in phr (parts per hundred rubber), then ground with an open two roll mill 1 kg capacity (Berstorff, Germany) and the resulting compound was tested for its curing properties using a moving die rheometer MDR 2000 (Alfa Tehcnology, United State).

Physical Properties Testing of Natural Rubber Vulcanizates

The rheometer of the MDR 2000 was used for making rubber vulcanization test samples, which were then tested for the physical properties of natural rubber vulcanization using the standard ASTM test method. The physical properties of vulcanized natural rubber, including hardness, were tested using ASTM D 2240-15, while elongation at break, tensile strength, and modulus 300% were analyzed using ASTM D 412-16. All of these physical properties' tests were also tested after aging.

RESULTS AND DISCUSSION

FTIR Spectra Analysis

The characterization of clay and CTAB-Modified clay using FTIR spectra analysis can be seen in Figure 2. According to Madejova (Madejova et al., 2003), kaolinite, mostly Al in an octahedral position has four absorption bands in 3 OH stretching. This OH group is located between the tetrahedral and octahedral sheets, with absorptions of about 3620 cm^{-1} and 3625 cm^{-1} in this study. Another OH group is on the octahedral surface and forms weak hydrogen bonds with the Si–O–Si bonded oxygen on the lower surface of the next layer. Absorption at 3695 cm^{-1} is associated with phase symmetric stretching vibration, which in this observation is at 3697 cm^{-1}; two weak absorptions at 3669 and 3653 cm^{-1} are associated with plane stretching vibration. Figure 2 also shows the spectra of the FTIR characterization results with patterns and absorption peaks that are almost identical to those of Madejova's characterization. The results of another study published by Belachew and Hinsene showed that for kaolin, the absorption peaks were at 3700, 3670, 3650, and 3620 cm^{-1} due to the inner OH attached to Al or O (Belachew and Hinsene, 2020).

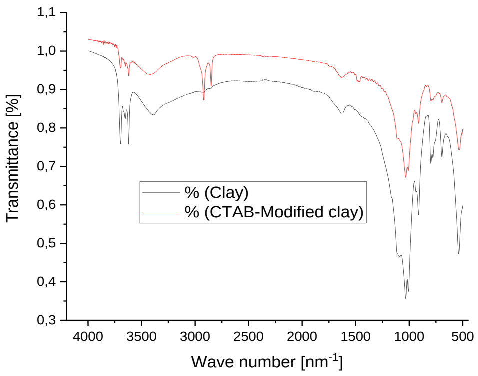
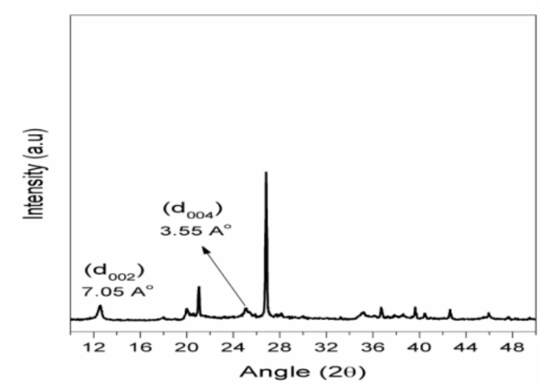


Fig. 2: FTIR spectra analysis of clay and CTAB-modified clay (kaolin clay). The blue line shows the FTIR spectra of original clay and the red line is the FTIR spectra of CTAB-modified clay

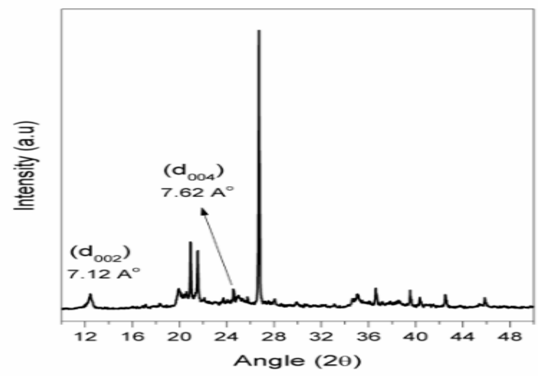
These peaks are contained in the curve in Figure 2. In Figure 2, precisely on the CTAB-Modified clay (kaolin) curve, a new peak was detected around the wave number of 3010 cm^{-1} caused by the CH_3-N stretching vibration. This peak was also analyzed by Zenasni (Zenasni et al., 2014). Symmetrical and asymmetrical strain vibrations of the aliphatic chain methyl (CH_3) and methylene (CH_2) of the surfactant showed stronger absorption at wave numbers 2850 cm^{-1} and 2920 cm^{-1} (Nojavan and Gharbani, 2017; Vieyres et al., 2013; Ikeda 2014). Observations in this study were at the absorption of 2851 cm^{-1} and 2953 cm^{-1}. The absorption peak at wave number 1396 cm^{-1} or 1404 cm^{-1} in Figure 2 appears from the C-N bond of the organic modifier, which is a feature of the surfactant molecular bond between silicates (Vieyres et al., 2013).

XRD Pattern Characterization

The diffraction pattern of local clay filler and CTAB-modified clay is shown in Figure 3. From this image, there are changes in d-spacing clay and CTAB-modified clay. d_{002} for clay is 7.05 A° and d_{004} is 3.55 A° while d_{002} for CTAB-modified clay is 7.12 A° and d_{004} is 7.62 A°. The lattice parameter for clay is a= 5.19, b= 8.83, and c= 14.48, while for CTAB-modified clay, the lattice parameter value is a= 5.21, b= 8.87, and c= 14.59. d-spacing shows a distance between atomic planes produced by X-ray diffraction peaks. This atomic plane has 3-dimensional coordinates. This coordinate results in D Spacing, calculated by the formula d_{hkl}. Clay modification causes a change in the hkl dimension of the atom; this means that the modification complies with the FTIR test.



(a)



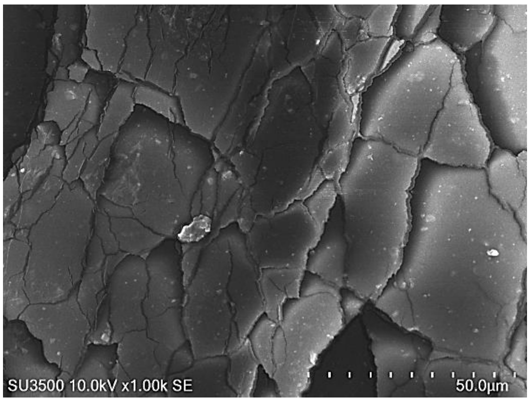
(b)

Fig. 3: XRD patterns for original clay and CTAB-modified clay, (a) shows the diffraction pattern of clay filler, and (b) is the diffraction pattern of CTAB-modified clay

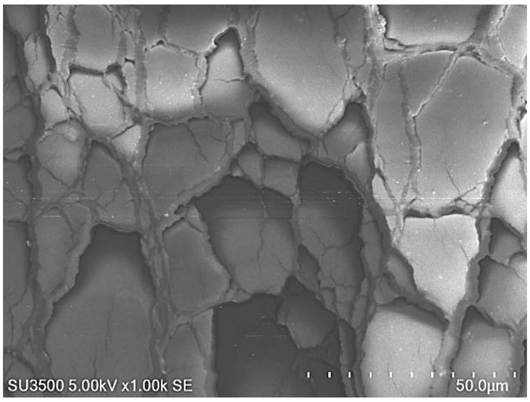
Belachew and Hinsene, in 2020, reported that two samples of kaolin clay and CTAB-modified kaolin clay did not produce different diffraction patterns. There is a slight difference in the d spacing of kaolin clay, which changes from d_{001} = 7.14531A° to d_{001}= 7.14763 A° for CTAB-modified kalin clay at an angle of 2θ = 12.3735 (Belachew and Hinsene, 2020).

SEM Investigation

The results of the SEM characterization of the natural rubber compound utilizing local clay and CTAB-modified clay filler can be seen in Figure 4.



(a). Compound with clay filler



(b). Compound with CTAB-modified clay

Fig. 4: SEM analysis of natural rubber compounds for local clay filler. Local clay filler image (a) and CTAB-modified clay (b)

In Figure 4(a), the clay filler grains are still clearly visible. In contrast, in Figure 4(b), the CTAB-modified clay filler is better dispersed inside the natural rubber compound and is no longer visible in real terms compared to (a) at the same magnification. This good CTAB-modified clay dispersion can affect the curing characteristics of natural rubber compounds and their vulcanized rubber physical properties. A good filler dispersion greatly affects several natural rubber molecules that can be absorbed on the surface of CTAB-modified clay filler. Of course, bound rubber can be improved, and in the end, physical properties can also be influenced (Hasan et al., 2019).

Curing Characteristics of Natural Rubber Compound

The curves in Figure 5 reveal that the vulcanization reaction that occurs in the compound using CTAB-modified clay filler increases sharply compared to using filler unmodified clay. The absorption of CTAB on the clay surface causes the clay surface to be more active so that the modified clay can become a better filler than the original clay. Filler can also cause stiffness in rubber vulcanization in addition to the vulcanization reaction. The movement of the rubber molecules cannot be free and is restrained by the filler surface, so the flexibility of the rubber vulcanization decreases and causes an increase in stiffness. This stiffness results in high torque on the vulcanized rubber (Vieyres et al., 2013).

In contrast to the compound that uses unmodified clay filler, the stiffness that occurs in rubber vulcanization is only caused by the vulcanization reaction and is less affected by the presence of filler. Here, unmodified clay cannot function well as a filler. The intermolecular network of rubber or a three-dimensional network between sulfur rubber molecules of rubber molecules formed only due to the vulcanization reaction causes the stiffness of the rubber vulcanization to increase (Ikeda, 2014).

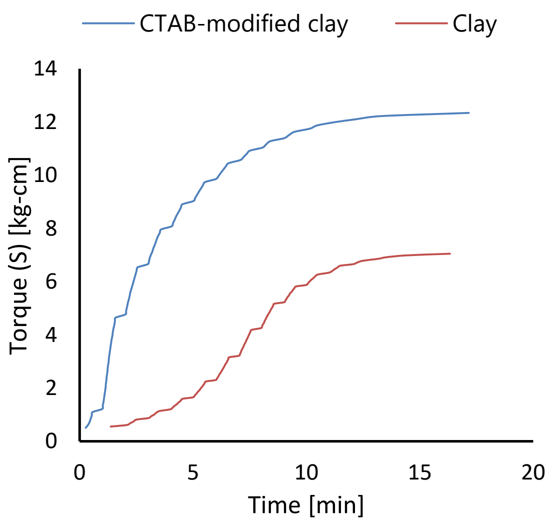


Fig 5: Comparison of the stiffness properties of natural rubber vulcanizates observed through torsion between natural rubber composites using CTAB-modified clay and original clay fillers using rheometer

The Effect of Filler on the Physical Properties of Natural Rubber Vulcanizates

Hardness and Elongation at Break

The relationship between hardness and elongation at the break of natural rubber vulcanization with filler clay and modified clay is shown in Figure 6. Figure 6 shows that the hardness of natural rubber vulcanization increased after the aging process was carried out either using CTAB-modified clay, unmodified clay filler, or original clay filler. This result shows that the vulcanization reaction is still occurring. The formation of a three-dimensional network between sulfur rubber molecules that occurs due to the vulcanization reaction causes an increase in stiffness. This rigidity contributes to an increase in hardness. Hardness for rubber vulcanization using CTAB-modified clay also showed higher hardness than unmodified clay filler. The success of surface modification of clay filler using CTAB as a modifier can be identified through the absorption of rubber molecules on its surface. The more rubber molecules adsorbed on the surface of the filler, the more the bound rubber (Hasan et al., 2019). The increase in inbound rubber affects the physical properties of rubber vulcanization, including hardness. High rubber bound can cause increased hardness. The elongation at break in Figure 6 decreases after aging using CTAB-Modified clay or unmodified clay as a filler. An Increase in hardness causes this change in elongation at break. This increase results in a decrease in elongation at break. The elongation at the break that uses unmodified clay filler is higher than at the break of vulcanized rubber that uses CTAB-modified clay as a filler.

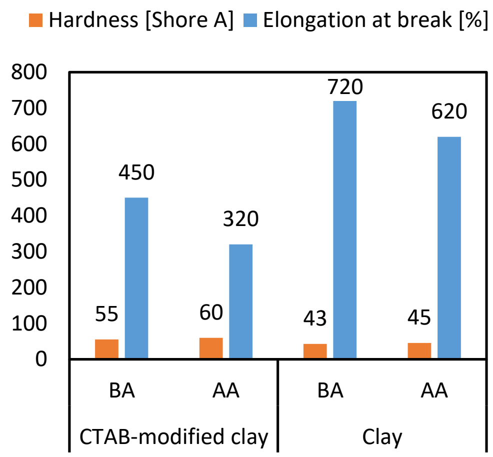


Fig 6: Comparison between hardness and elongation at break of natural rubber vulcanizates observed before and after aging using CTAB modified clay and clay filler. AA : after aging and BA : before aging

This impact is the opposite of hardness. CTAB-modified clay resulted in high hardness with low elongation at break and vice versa. Here, unmodified clay does not function well as a filler compared to CTAB-modified clay. Ionic interaction between the positive charge of CTAB and the negative charge of clay (Khan et al., 2019), the surface of CTAB-modified clay filler to be able to absorb rubber molecules on its surface, and this means that CTAB-modified clay filler functions as a better filler than the original clay.

Tensile Strength and Modulus 300%

Figure 7 shows the relationship curve between tensile strength and modulus of 300% observed for aging and before aging.

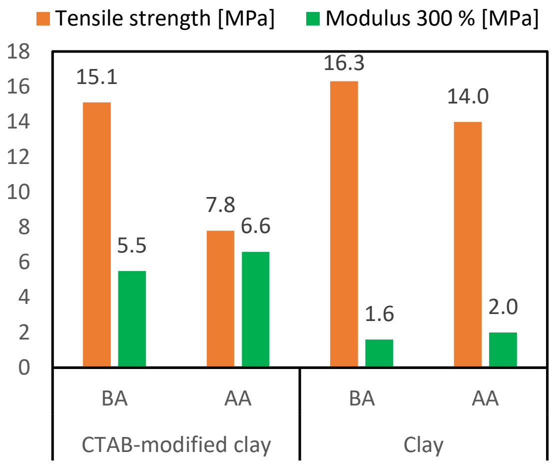


Fig 7: Comparison between tensile strength and modulus of 300% natural rubber vulcanizates observed before and after aging using CTAB-modified clay and clay filler. AA : after aging and BA : before aging

Figure 7 shows that the tensile strength decreased considerably for both vulcanizates using CTAB-modified clay and unmodified clay filler from before to after aging. The greatest decrease in tensile strength occurred in rubber vulcanization using CTAB-modified clay compared to unmodified clay filler. This is because CTAB-modified clay is better able to function as a filler. Stiffness increases due to better filler function (Vieyres et al., 2013). Besides the effect of the filler, the vulcanization reaction still occurs when the aging process is carried out. The vulcanization reaction also contributes to the stiffness of rubber vulcanization (Ikeda, 2014).

Something else happens where the modulus increases by 300% with the aging process. This occurred in both rubber vulcanizations using CTAB-modified clay and clay fillers. The 300% modulus is directly proportional to tensile strength and inversely related to elongation at break. Figure 6 shows that the elongation at break of vulcanization using unmodified clay filler is higher than vulcanization using CTAB-modified clay filler.

As shown in Figures 6 and 7, changes in physical properties can also be explained through the formation of bound rubber and crosslink density. The more active surface of the CTAB-modified clay filler compared to the clay filler, the more rubber molecules are absorbed on the filler surface. As a result, bound rubber increases, and the physical properties of natural rubber are affected (Hasan et al., 2017). When the filler is functioning properly, the vulcanization reaction that contributes to the stiffness of the rubber vulcanisate (Ikeda, 2014), crosslink density also rises and affects the physical properties of the rubber vulcanisate (Hasan et al., 2017; Hasan et al., 2013).

CONCLUSIONS

Modification of clay using CTAB as a modifier has been successfully carried out and proven by the results of FTIR spectra analysis and diffraction pattern of XRD. SEM analysis also distinguishes the surface contours of natural rubber compounds. The curing characteristics of the two natural rubber compounds using CTAB-modified clay as filler resulted in a much higher torque of 12.34 kg-cm compared to 7.05 kg-cm of original clay.

A comparison of the physical properties between natural rubber vulcanized filled with original clay and CTAB-modified clay shows very different properties. Elongation at break and tensile strength for natural rubber vulcanized using CTAB-modified clay as filler is lower than that using original clay. Still, the modulus is 300%, and hardness is increased.

Elongation at break dropped from 720% to 450% for aging, and after aging, it dropped from 620% to 320%. Tensile strength before aging also dropped from 16.3 to 15.1 MPa, while after aging, tensile strength dropped from 14 to 7.8 MPa. The 300% modulus increases from 1.6 to 5.5 MPa before aging and from 2.0 to 6.6 MPa after aging. Hardness rises from 43 to 55 Shore A before aging and after aging goes up from 45 to 60 Shore A.

SECTION 5 ACKNOWLEDGEMENT

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