Fabrication and characterization of natural rubber composite (sir 5)/organo-montmorillonite using cetil trimetil ammonium bromide as a surface modifier

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Abstract. The research on fabrication and characterization of natural rubber composites (SIR 5)/organo-montmorillonite using cetil trimetil ammonium bromide (CTAB) as an organic modifier has been conducted. Natural rubber SIR-5 was masticated at 60 °C by applying the time variations of 0, 5, 10, 15, 20, and 25 minutes using two-roll mill. SIR-5 which has been masticated for 4 minutes as an optimum time with the smallest molecular weight was then grafted by glysidil methacrylate (GMA) in order to obtain natural rubber-grafted-glysidil methacrylate (natural rubber-g-GMA) which was used as a compatibilizer material. A 10 g of montmorillonite was modified by using CTAB with different concentrations of 0, 0.01, 0.03, 0.05, and 0.07 mole and then was added into rubber SIR-5 and natural rubber-g-GMA using internal mixer to obtain the composite. The prepared composite sample was examined using ASTM D-638 in order to perform a low speed tensile test (1 mm/minutes) and a thermal test using thermogravimetry analysis (TGA) operated at 30-80 °C. The surface morphology of composite was analyzed by using scanning electron microscopy (SEM) operated at 15 kV. The result of optimum elasticity which was achieved by adding montmorillonit produced using CTAB concentration of 0.03 mole was 1.57 MPa and had the value of the elongation at break of 2396%. Thermal degradation analysis using TGA showed that the most decomposed mass was 63.11% at 426 °C. The analysis of the morphology using SEM showed homogenous surface of the composite.

1. Introduction

The recent researches are focusing on the development of reinforcing materials for natural rubber in order to substitute carbon black in natural rubber compounds. Sepiolite, kaolin, and solid silica are commonly used as the reinforcing materials. However, these type of reinforcing materials have poorer mechanical properties in the product than that of carbon black.

Arroyo (2003) has used clay and clay minerals, such as montmorillonite, saponite, hecetonite, etc., which are widely used as fillers in rubber and plastic, in order to save the polymer consumption and reduce the cost of production. The clay minerals itself consists of a silicate layer (thickness ≈ 1 nm and lateral dimension of 200-300 nm). Internal and external cations can be changed by exposuring to inorganic ions or other organical compounds, such as alkyl quaternary ammonium ions. Organophilic modification causes the silicates become compatible with the polymer. The added molecules can increase the the distances between the still-parallel layers in an intercalation process or randomly disperse the separate layers in an exfoliation [1-2].
The modification of mechanical properties results better in natural rubber composites which are grafted by glycidil methacrylate (GMA) than that of natural rubber composites grafted by unmodified reinforcing fillers, as previously observed by Sari (2013) that used betonite as a reinforcing fillers. Wahyuni (2013) were also proved that the preferable mechanical properties and higher thermal stability existed in natural rubber composites which had been added with modified betonite compared to the natural rubber composites which used the unmodified fillers [3-4].

Based on the researches mentioned above, this study is aimed to compare the mechanical strength and thermal stability of natural rubber composite (SIR-5) using compatible natural rubber-grafted-GMA (natural rubber-g-GMA) and a fillers-montmorillonite-which have been modified by cetil trimetil ammonium bromide (CTAB). So that, the modified natural rubber can be properly mixed with organo-montmorillonite, in order to produce a composite that can enhance the strength of natural rubber.

2. Materials and Method

2.1. Materials
Natural rubber used in this experiment was SIR-5. Glysidil methacrylate (GMA) and cetil trimetil ammonium bromide (CTAB) were purchased from merck.

2.2. Procedure
The mastication process was performed to the natural rubber SIR-5 at a temperature of 60 °C with certain variation of time of 0, 5, 10, 20 and 25 minutes. The optimum masticated SIR-5 was then grafted with glysidil methacrylate (GMA) in order to produce a compatibilizer material; natural rubber-grafted-glysidil methacrylate (natural rubber-g-GMA). Separately, as many as 10 g montmorillonite was modified with CTAB by varying its concentration as 0, 0.01, 0.03, 0.05 and 0.07 mole. This mixture was then added into SIR-5 and natural rubber-grafted-glysidil methacrylate (natural rubber-g-GMA) by using internal mixture to produce the composite. Several characterizations were conducted towards the composite such as TGA, SEM and tensile strength test.

3. Result and Discussion

3.1. Analysis of Molecular-Weight of masticated natural rubber (SIR-5) by Mooney Viscosity
Natural rubber, SIR-5 was masticated by using two roll mill. In this process the compression time was varied, i.e, 0, 2, 4, 6, 8, and 10 minutes. The optimum milling time is based on the lowest value of Monney viscosity in order to obtain a minimum molecular weight. The results of the determination of the molecular weights using mastication process are shown in Table 1.

| No. | Rotation Duration (Minutes) | \( \eta \) Mooney | Molecular Weight (g/mL) |
|-----|-----------------------------|-------------------|-------------------------|
| 1.  | 0                           | 61.94             | 1,016,622.34            |
| 2.  | 2                           | 33.24             | 432,440.15              |
| 3.  | 4                           | 27.70             | 338,168.30              |
| 4.  | 6                           | 31.88             | 402,372.40              |
| 5.  | 8                           | 28.96             | 351,551.70              |
| 6.  | 10                          | 30.33             | 376,669.45              |
Based on **Figure 1**, it can be seen that the optimum milling time is in 4 minutes, which is in accordance with the result of Monney viscosity value, i.e., 27.89. The conversion of this value using Mark-Houwink equation results in the molecular weight of 338,098.30 g/mL. Indicating that lowering the Mooney viscosity value results in an increased number of shortened molecular chain of rubber, so that molecular weight lowered.

### 3.2. The analysis of the modified montmorillonite

The Fourier transform infrared (FT-IR) spectrum of montmorillonite and montmorillonite modified using CTAB were performed to give the information about surface modification as well as to prove that the surface modification process have been applied to montmorillonite by using organic compound, CTAB. The surface modification process of montmorillonite might occur, where in the cations exchange takes place. The cations which are located in the interlayer of montmorillonite structure will be replaced by the cations from CTAB.

**Figure 2.** The FT-IR spectrum of montmorillonite and montmorillonite modified using different concentrations of CTAB
Figure 2 shows that the modification process of montmorillonite (cations exchange) which occurs in FT-IR spectroscopy measurement indicates the changes of functional groups. The modification using CTAB into montmorillonite causes the shift of the band and forms new functional groups, where the absorption band of OH-group, which comes from hydroxyl at the band of 3386.85 cm⁻¹ (specific features of montmorillonite), is altered by the absorption band of C-H group, which arises from CTAB at the band of 2925 cm⁻¹. These results indicate that the modification process have occured.

The data for the peaks of FT-IR spectrum of montmorillonite and montmorillonite modified using CTAB can be seen in table 2. The FT-IR spectrum of montmorillonite and modified montmorillonite shows that the absorbance peaks of the functional groups of compound have been changed, indicating the change of functional group as shown in Table 3.

Montmorillonite spectrum shows that there is an absorption band at 3388.85 cm⁻¹, indicating the absorption of H-O-H group. The absorption band in this case shows that H-O-H group arises from the water molecules which have a weak hydrogen bond on the surface of Si-O, wherein this absorption band is the result of H-O-H vibration which is easy to absorb the water. The spectrum of clay minerals shows the bending and strain in Si-O which is absorbed at OH bending in the range of the absorption bands of 1300-400 cm⁻¹. There are different structures among the layers (the character of 1:1 with 2:1 and/or di- with tri-octahedral), indicating the reflection of the sharp peak and position of the bond. In the clay mineral, montmorillonite, Si-O strain lies between the range of the band at 1030-1019 cm⁻¹, whereas the commercial montmorillonite shows the absorption band at 1038.27 cm⁻¹ [5]. The band at 1627.66 cm⁻¹ which is assigned to the vibration of bending overextend of H₂O in montmorillonite exists in the standard montmorillonite [6]. The absorption of OH group, which is bonded with the minerals arise from clay structure of montmorillonite having specific band, shows the informations of the composition of octahedral layers. Wherein the band at 795.60 cm⁻¹ is the absorption band of OH group bonded with aluminum (Al) in the form of Al₂OH [5].

The FT-IR spectrum in the modified montmorillonite shows the change of the absorption band at 3388.85 cm⁻¹ (the absorption band of H-O-H group), wherein this absorption band indicates that H-O-H arises from water molecules having the weak hydrogen bond on the surface of Si-O. The absorption band, which is the result of the vibration of H-O-H, is replaced with the band at 2925 cm⁻¹ which is attributed to the metilen group (CH₂) asymmetric vibrations, as shown in the FT-IR spectrum of modified montmorillonite.

The analysis of functional groups in the modified montmorillonite is used as quantitative analysis to determine the optimum modification process by determining the width of the area of the peak of metilen group (CH₂) absorption of the modified montmorillonite having variation in the concentrations of CTAB. The results of the width of the area of the modified montmorillonite can be seen in the Table 2.

Table 2. Coverage area of C-H clock band in modified montmorillonite with variation of CTAB concentration

| Functional Group | Concentration of CTAB (mole) |
|------------------|-----------------------------|
|                  | 0.01 | 0.03 | 0.05 | 0.07 |
| large area on C-H group | 2,856 | 5,443 | 4,479 | 4,286 |
Table 3. The width of the area of absorption band of modified montmorillonite using different concentrations of CTAB

| Functional Group                  | Wave Number (cm⁻¹) | Standard Montmorillonite | Commercial Montmorillonite | Modified Montmorillonite |
|-----------------------------------|--------------------|--------------------------|---------------------------|--------------------------|
| O-H Relaxation of hydroxil (Al-OH) | 2923,31            | 3386,85                  | -                         |                          |
| C-H stretching                    | -                  | -                        | 2925,05                   |                          |
| O-H from H₂O                      | 1738,56            | 1629,66                  | -                         |                          |
| O-H Stretching from H₂O           | 1467,90 ; 1366,07  | 1039,25                  | 1039,25                   |                          |
| Si-O stretching                   | 1035,54            | 795,60                   | 795,60                    |                          |
| Si-O-Al                            | 798,12             |                          |                           |                          |

The width of area in the FT-IR spectrum of the modified montmorillonite is shown in Figure 2, in the shading part of the metilen peak, as well as in Table 2. It shows that the modification process of montmorillonite using different concentrations of CTAB has the optimum value at the concentration of 0.03 mole. This result also indicates that higher CTAB concentration results in a minimum cations exchange process.

3.3. The analysis of mechanical properties of natural rubber compound (SIR-5), of natural rubber composite/montmorillonite, and natural rubber/montmorillonite modified using CTAB

The analysis of mechanical properties were performed to measure the strength of the polymers, which is determined by the value of tensile strength. The tensile strength is determined by the maximum ability of the polymer to load bearing. The analysis result of natural rubber compound (SIR-5), of natural rubber composite/montmorillonite, and of natural rubber composite/montmorillonite modified using CTAB is given in the table 4.

Table 4. Mechanical properties of natural rubber composite/montmorillonite, and of natural rubber composite/montmorillonite modified using CTAB

| Sample                  | Tensile Strength (MPa) | Elongation Break (%) | Modulus Elasticity (MPa) |
|-------------------------|------------------------|----------------------|--------------------------|
| Natural Rubber          | 8.88                   | 3749                 | 1.04                     |
| NR/MMT                  | 5.86                   | 3296                 | 0.83                     |
| NR/MMT+CTAB 0.01 mole   | 6.42                   | 3215                 | 0.82                     |
| NR/MMT+CTAB 0.03 mole   | 5.59                   | 2394                 | 1.55                     |
| NR/MMT+CTAB 0.05 mole   | 5.05                   | 2173                 | 1.04                     |
| NR/MMT+CTAB 0.7 mole    | 8.77                   | 2725                 | 1.12                     |

As can be seen from table 4, that the natural rubber composite/montmorillonite modified using CTAB with concentration of 0.03 mole has larger value of elastic modulus or Young modulus than that of other composites, i.e., 1.57 MPa. It can be said that the natural rubber compound/montmorillonite modified using CTAB with concentration of 0.03 mole is the optimum compound. It can increase the elasticity of the natural rubber without fillers, from 1.05 MPa to 1.57 MPa. It also has larger elasticity value that of both natural rubber composite/montmorillonite and natural rubber compound/montmorillonite modified using CTAB with other concentrations. These results are shown in figure 3.
3.4. **The analysis of thermal properties of natural rubber compound (SIR-5), natural rubber composite/montmorillonite, and natural rubber composite/montmorillonite modified using CTAB**

The analysis of thermal endurance was performed by using TGA. TGA is a test to measure the change of weight-loss due to the change of temperature. The data presents the information about the significant value of weight-loss due to the change of temperature, thus this data can be used to predict the thermal stability.

![Graph showing mechanical properties](image)

**Figure 3.** Mechanical properties of natural rubber/montmorillonite and natural rubber/montmorillonite modified using CTAB

![Graph showing weight-temperature curves](image)

**Figure 4.** The weight-temperature curves of natural rubber compound (SIR-5), natural rubber composite/montmorillonite, and natural rubber composite/montmorillonite modified using CTAB
It can be seen from figure 4 that the rubber composite is stable thermally at 502 °C as indicated by the data of decomposition temperature, that is of 302 – 404 °C. As can be seen that at 42 -302 °C the composite lose the weight due to the loss of water absorption resulting from the surface of clay, whereas at 502 – 804 °C the composite lose the weight due to the loss of water resulting from decomposition of OH group structure [5]. The natural rubber composite without fillers, the natural rubber composite/montmorillonite and the natural rubber composite/montmorillonite modified using CTAB at 0.03 mole did not undergo the change of decomposition significantly. It can be explained as these three compounds have been crosslinked so that they have similar thermal stability.

3.5. The morphology analysis using scanning electron microscopy (SEM) images

SEM images were used to analyze the morphology structures of the surface of natural rubber compound (SIR-5), of natural rubber composite/montmorillonite, and of natural rubber composite/montmorillonite modified using CTAB. The SEM images are shown in figure 5.

![SEM images](a) (b) (c)

**Figure 5** SEM images of: a) natural rubber compound, b) natural rubber composite modified using MMT and c) NR Compound/MMT + CTAB

As can be seen in the figure 5(a), the rubber compound blended nonuniformly, indicating that the composition of the ingredients did not blend evenly. It is showed by the existence of the white powder of ZnO in the surface. While figure 5(b) shows that natural rubber composite/montmorillonite did not blend uniformly as indicated by the presence of white powder of montmorillonite in the surface of composite. It is attributed to the difference of polarity level of natural rubber and of montmorillonite, resulted in a weak interaction between the compounds. Finally, figure 5(c) shows that natural rubber/montmorillonite modified using CTAB has roughly uniform blend as indicated by the small number of the white powder in the surface of compound, indicating a strong interaction between the natural rubber and montmorillonite modified using CTAB, resulted in uniform dispersion of fillers into the matrix of rubber.
4. Conclusion
The analysis of mechanical and thermal properties shows that the natural rubber composite/modified montmorillonite is able to enhance the strength of natural rubber as indicated by the increase of modulus of elasticity, from 1.05 MPa to 1.57 Mpa, and by the increase of decomposition temperature of the modified natural rubber composite. The natural rubber composite/montmorillonite compound has uniform blend, as explained from the morphology of the compound shown by SEM images. It can be concluded that the graft using GMA in the natural rubber composite/montmorillonite is able to improve the quality of the dispersion of fillers into the matrix of rubber. Thus, the maximal result can be obtained by modifying montmorillonite as a fillers.

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