The use of bentonite of Bener Meriah Aceh to improve the mechanical properties of Polypropylene-Montmorillonite Nanocomposite

J Julinawati1,*, S Gea2, E Eddiyanto3, B Wirjosentono3, I Ichwana4

1Chemistry Department, Faculty of Mathematics and Natural Science, Universitas Syiah Kuala, Jalan Tgk. Tanoh Abe Nomor 3, Kopelma Darussalam, 23111 Banda Aceh, Indonesia
2Chemistry Department, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Jalan Bioteknologi No.1 Kampus USU, 20155 Medan, Indonesia
3Chemistry Department, Faculty of Mathematics and natural science, Universitas Negeri Medan, Jl. Willem Iskandar Psr. V Medan Estate, 20222 Sumatera Utara, Indonesia
4Department of Agricultural Engineering-Faculty of Agriculture, UniversitasSyiah Kuala. Jl. Tgk. Hasan KruengKalee No. 3 Kopelma Darussalam, 23111 Banda Aceh, Indonesia

E-mail: julinawati@unsyiah.ac.id

Abstract. The research on application of bentonite Bener Meriah of Aceh to improve the mechanical properties of polypropylene-montmorillonite nanocomposite has been conducted. Bentonite was isolated into the nano-sized montmorillonite and was used as a filler of polypropylene-montmorillonite nanocomposites with the addition of PP-g-MA as a compatibilizer and octadecylamine as a modifier of MMT. The results showed that bentonite of Bener Meriah Aceh contained montmorillonite with 70.6% content. Based on the result of mechanical properties test, it was discovered that montmorillonite isolated from Bentonite of Bener Meriah could improve the mechanical properties of PP-MMT nanocomposite in composition ratio of PP/PP-g-MA/MMT is 85/10/ 5.

1. Introduction
Bentonite is an abundant natural resource in Indonesia, such as in Java, Sumatra, and Sulawesi, which contain more than 380 million tons but has not been optimally utilized. In Aceh, natural bentonite can be found in the districts of North Aceh, Bener Meriah, Sabang, Central Aceh, and Simeulue [1,2,3] which reaches the amount of 2,618,224,030.20 tons [4]. To date, research on Aceh bentonite has been conducted only on several studies [5] and the bentonite that has been used only the one that found in North Aceh. Therefore, bentonite processing from other districts in Aceh is required. Bentonite that will be used in this research is bentonite from Bener Meriah, which is one of the areas in the Province of Aceh which has bentonite with a thickness of 1 m width of 20 Ha and its content reaches 520,000 tons [4] which has not been utilized.

*Corresponding authors julinawati@unsyiah.ac.id
Bentonite is natural clay whose main component is the mineral montmorillonite (85%), with the chemical formula of $\text{M}_x(\text{Al}_4\text{Mg}_2)\text{Si}_{8}\text{O}_{20}(\text{OH})_4\text{nH}_2\text{O}$. Montmorillonite (MMT) is a filo-siletic mineral that has the ability to expand and can be intercalated and exfoliated, thus it is widely used as filler of nanocomposite to enhance the properties of the nanocomposite [6]. When an exfoliation occurs, the mechanical and rheological properties of the nanocomposite increase dramatically when compared with the pure polymer [7]. Several researches on the addition of MMT in polypropylene (PP) nanocomposites has been conducted and indicated that MMT can improve some of these nanocomposite properties such as mechanical properties [8,9,10,11,12], thermal properties [13], fire retardancy properties [14], and increased degrees of degradation [16]. It is expected that MMT from Bener Meriah can also be used to improve the mechanical properties of nanocomposites.

Nanocomposites can be obtained by mixing the silicate layers of MMT with PP by melting intercalation method. Mixing of silicate layers from MMT in PP can be increased by using functional oligomers as compatibilizers. Several studies have reported using polypropylene-graft-maleic anhydride (PP-g-MA) as a compatibilizer [15]. MMT is also modified using a long organic alkyl chain, which is called a modified organo-silicate layer (OMLS) or organo-clay. The organic clay will change the hydrophilic into hydrophobic properties of MMT, which is allowing the MMT interface to interact with several different polymer matrix. The organic compounds commonly used to modify MMT are alkynammonium. The research was conducted several stages are characterizing of bentonite, isolation of the MMT nanoparticle, preparation and characterize of PP-MMT nanocomposites.

2. Materials and Methods

2.1. Materials
Polypropylene was obtained from Aldrich (density 0.896 gr/cm$^3$, melting point 176 °C), PP-g-MA is polypropylene which has been grafted with maleic anhydride, density 0.934 g/cm$^3$, melting point 156 °C, Mn 3,900 (GPC), Mw 9100 (GPC), oktadecylamine, ($C_{18}H_{37}N$, 90%) was obtained from Aldrich, CH$_3$Br (density 2,10 gr/ml), alcohol, montmorillonite K10 (standart) was obtained from Aldrich, montmorillonite isolated from bentonite of Pantanalah, Bener Meriah of Aceh.

2.2. Methods
2.2.1. Isolation nano montmorillonite from natural bentonite Bener Meriah.
Montmorillonite nanoparticles can be obtained by preparing 1 kg of bentonite sample and filtered with a 100 mesh sieves, then it was dried in oven at the temperature of 105 °C for 4 hours. Subsequently, the sample was fractionated. Fractionation was done with sedimentation by weighing 40 grams of 100 mesh bentonite and added with 2L aquades to form the suspension. Bentonite suspension was given ultrasonic waves for 15 minutes at 750 watts at room temperature. Furthermore, the suspension is left in a flat place and kept away from all vibrations. Precipitation that occur within 15 minutes are taken by pouring the suspension into another container and leaving the filtrate again. The precipitate formed in the next 3 days is filtered back and taken its filtrate. The floating fraction in the filtrate is stirred again, then the filtrate is left for a week and collected of precipitate is formed. This precipitate was dried in an oven at 105 °C for 3 hours, then crushed and sieved using 200 mesh sieve. This fraction is stored in a desiccator. The identification of the fraction (montmorillonite) was carried out using FT-IR, X-RD diffraction and SEM [16].

2.2.2. Preparation of polypropylene-montmorillonite nanocomposite (PP-MMT).
Variation of the composition materials of PP, PP-g-MA, and montmorillonite for preparing PP-MMT nanocomposite can be seen in Table 1. Materials of various compositions of PP, PP-g-MA and montmorillonite were compounded respectively in a Haake Rheomix 3000 internal laboratory mixer with high rotor intensity, operating at 180 °C at 65 rpm for 10 minutes. Samples for mechanical tests were made from the nanocomposite produced.
Table 1. Composition of material of polypropylene-montmorillonite nanocomposite

| Code of sample | PP (% wt) | PP-g-MA (% wt) | Montmorillonite (% wt) |
|---------------|-----------|----------------|------------------------|
|               |           |                | Bener Meriah | Commercial |
| A             | 100       | 0              | 0          |            |
| B             | 95        | 5              | 0          |            |
| C             | 95        | 0              | 5          |            |
| D             | 90        | 5              | 5          |            |
| E             | 85        | 5              | 10         |            |
| F             | 80        | 5              | 15         |            |
| G             | 85        | 10             | 5          |            |
| H             | 80        | 15             | 5          |            |
| I             | 85        | 10             | 5          |            |

2.3. Characterization

Samples of bentonite and nano montmorillonite were characterized by X-Ray Fluorecence (XRF) PANalytical, Axios Advance. The percentage of montmorillonite be calculated using the Meyer equation [17]. The functional group of bentonite, nano montmorillonite and nanocomposite specimen were analyzed by using FTIR of Perkin Elmer type spectrum 100 at wave numbers 400 to 4000 cm⁻¹. The X-Ray Diffraction scattering patterns of bentonite, nano montmorillonite and nanocomposite were recorded using XRD Shimadzu 6000, operating at Cu Kα radiation generated at 40kV and 30 mA. The sample were scanned in range of 3° to 50° with scan rate 5°(2θ)/minute. Surfaces morfologies of nano montmorillonite and nanocomposite was analyzed by Scanning Electron Microscopy (SEM) Merck Zeiss type EVO MA 10 at 20 kV. Mechanical tests was done using the equipment a Lloyd LR/10KN Universal, operation at room temperature and a speed of 50 mm min⁻¹, according to ASTM D638 and ASTM D256 standard. Nanoparticle was analyzed by Particle Size Analyzer (PSA) of LS 100 Q Coulter.

3. Result and discussion

3.1. XRF analysis

XRF analysis was chosen as a method for the assessment of the quantitative results. The result of characterization of bentonite of Bener Meriah Aceh by XRF can be seen in Table 2. Table 2 shows the chemical composition of bentonite from Bener Meriah, the amount of Na₂O is greater than CaO, this indicates that the bentonite from Bener Meriah is Na-Bentonite as described in [18].

Table 2. Percentage of chemical composition of bentonite Bener Meriah

| Chemical composition of bentonite | Weight (%) |
|----------------------------------|------------|
| SiO₂                             | 65.39      |
| Al₂O₃                            | 16.6       |
| Fe₂O₃                            | 2.69       |
| CaO                              | 0.09       |
| MgO                              | 0.84       |
| Na₂O                             | 0.76       |
| K₂O                              | 0.84       |
3.2. Meyer test

The content of montmorillonite in Bener Meriah bentonite was analyzed using the Meyer equation, (1972) and the result was 70.6%. The percentage of montmorillonite is different for each region, it is also suspected to be influenced by the process of bentonite formation refer to [18]. Meyer equation:

\[
\text{Percentage of montmorillonite} = \frac{\text{dry weight of montmorillonite}}{\text{dry weight of bentonite}} \times 100
\] (1)

3.3. FTIR analysis

FTIR analysis was performed to determine the functional group of a sample. The FTIR spectra for bentonite of Bener Meriah are shown in Figure 1. The presence of absorption bands at 3620.42 cm\(^{-1}\) which can be attributed of Al-OH or Si-OH stretching, an absorption band at 3444.41 cm\(^{-1}\) and 1637.54 cm\(^{-1}\), attributed to OH stretching and OH bending respectively. Characteristic absorption of Si-O stretching, Al-O, Si-O bending and Si-O-Si can be observed at 1031.20 cm\(^{-1}\), 538.15 cm\(^{-1}\) and 467.10 cm\(^{-1}\) respectively. The FTIR spectra of bentonite Bener Meriah showed similar absorption bands to those found in [19].

![Figure 1. FTIR spectrum of bentonite Bener Meriah, montmorillonite of Bener Meriah and PP-MMT nanocomposite (PP/PP-g-MA/MMT: 85/10/5)](image)

The FTIR spectra for montmorillonite of Bener Meriah in Figure 1 showed absorption bands characteristic of montmorillonite in 3624.70, 3448.79, 1736.87, 1032.36, 751.78, 538.56, and 468.50 cm\(^{-1}\), these spectra are similar to the standard montmorillonite [20]. Figure 1 also showed of FTIR spectra for PP-MMT nanocomposite (PP/PP-g-MA/MMT: 85/10/5). Absorption bands at 3627.10 - 3192.86 cm\(^{-1}\) at FTIR spectra of PP-MMT nanocomposite can be attributed N-H of octadecylamine. Octadecylamine was used on the preparation of nanocomposites by mixing modified polypropylene with PP-g-MA and montmorillonite which have modified with octadecylamine. Absorption bands at 2951.49 - 2867.81 cm\(^{-1}\) correspond to alkane of PP and oktadecylamine, while absorption bands at 1455.92-1358.99 cm\(^{-1}\) and 998.12-519.15 cm\(^{-1}\) correspond to C-H of alkane of PP. Characteristic absorption of Si-O-Si from MMT can be observed at 1166.99-1041.88 cm\(^{-1}\). This indicates that MMT modified with octadecylamine has been intercalated into the galleries of PP.
3.4. XRD analysis

The characterization of the sample by X-Ray Diffraction (XRD) aimed to verify the existence minerals of Bentonite Bener Meriah and about exfoliation and intercalation of PP-MMT nanocomposite. The XRD patterns of bentonite Bener Meriah can be seen in Figure 2.

![Figure 2. XRD spectra of bentonite, montmorillonite of Bener Meriah and PP-MMT nanocomposite](image_url)

XRD spectra of bentonite Bener Meriah in Figure 2 shows the presence of montmorillonite (2θ: 5.86°, 16.29°, 21.93°, 23.65°, 26.64°, 27.83°, 35.14°) as majority phases. The patterns of diffraction peaks corresponding to planes (001) and (020), confirming the presence of montmorillonite in bentonite of Bener Meriah. The data also showed the presence of impurities such quartz (2θ: 20.87°), ilite (2θ: 8.9°), feldspar (2θ: 25.12°) and calcite (2θ: 29.78°) [16, 21]. In addition, the peak of 2θ at 5.86° and 16.29° in the Figure 2 showed that bentonite of Bener Meriah is Na-bentonite [22]. The XRD patterns of montmorillonite show only peak of 2θ: 5.47°; 14.54°; 25.25°; 35.04°, which is the result of isolation from bentonite of Bener Meriah [23]. The pattern XRD of the PP-MMT nanocomposite in the composition ratio of PP/PP-g-MA/ MMT is 85/10/5 showed peak of 2θ at 2.4 to 2.7°, that indicates PP chains insert into the interlayers of MMT and hence the polymer intercalated or exfoliated structure is achieved [24].

In addition, angular shifts from the top of MMT also explain the occurrence of intercalation and exfoliation in the silicate layer. The new peak are detected at 2θ: 15.3° and 17.6° corresponding to plane (110) and (040) of polypropylene(PP). Peak of 2θ at 18.9° and 22.8° shows the presence PP containing MMT modified. The reduced XRD peaks detected in PP-MMT nanocomposites can be ascribed to the irregular state of modified MMT distributed in the PP matrix [17, 23, 24].

3.5. SEM analysis

The Scanning Electron Microscopic (SEM) technique was used to explore the surface morphologies of the sample. Figure 3(A) shows the surface morphologies of montmorillonite which isolated from bentonite Bener Meriah. The figure showed that structure of MMT Bener Meriah has layered pores which randomly distributed with different sizes [25, 26]. The existence of these layered pores causes MMT to be used as a nanocomposite filler to enhance the properties of the nanocomposite. Figure 3 (B)
shows the surface morphologies of PP-MMT nanocomposite. The figure showed that montmorillonite Bener Meriah modified dispersed uniformly and homogenous in the PP matrix which is considered an indication of the successful preparation of the PP-MMT nanocomposite. The result indicates that exfoliation and intercalation of PP in MMT may occur so as to produce compatible nanocomposites [27].

Figure 3. SEM of montmorillonite(A) and PP-MMT nanocomposite of (PP/PP-g-MA/MMT: 85/10/5) (B)

3.6. PSA analysis
Montmorillonite which has isolated from bentonite was processed into nanoparticles by precipitation [16]. To analyze particle size of montmorillonite was used Particle Size Analyzer. The average result of particle size of montmorillonite Bener Meriah was 67.8 nm, can be seen in Figure 4. Then, this montmorillonite was used to preparation of nanocomposite.

Figure 4. Particle size of montmorillonite Bener Meriah

3.7. Mechanical properties of PP-MMT nanocomposite
Figure 5, 6 and 7 shows the mechanical properties of PP-MT nanocomposite, the figure showed that the addition of MMT Bener Meriah which has modified significantly increased the tensile strength, elastic modulus and elongation of PP-MMT nanocomposite [11,20,21]. The optimum of tensile strength, elastic modulus and elongation of PP/PP-g-MA/ MMT occurs when the ratio of composition of PP/PP-g-MA/MMT is 85/10/5. These values peak at 31.75 MPa for tensile strength, 374.41 Mpa for elastic
modulus and 8.48% for elongation. The value of mechanical properties of PP-MT nanocomposite which the addition of MMT Bener Meriah modified showed similar with mechanical properties of PP-MT nanocomposite which the addition of MMT commercial modified.

![Graph of the relationship between PP/PP-g-MA/MMT composition with tensile strength of PP-MMT nanocomposite](image1)

![Graph of the relationship between PP/PP-g-MA/MMT composition with elastic modulus of PP-MMT nanocomposite](image2)

![Graph of the relationship between PP/PP-g-MA/MMT composition with elongation of PP-MMT nanocomposite](image3)

4. Conclusion
It can be concluded that bentonite is Na-bentonit and has percentage of montmorillonite of 70.6%. Bentonite Bener Meriah was isolated into nano-sized montmorillonite and used as a filler of polypropylene-montmorillonite nanocomposites by the addition of PP-g-MA as a compatibilizer and octadecylamine as a modifier of MMT. The result indicates that exfoliation and intercalation of PP in MMT may occur to produce compatible nanocomposites. Based on mechanical properties test, it showed
that the addition of MMT Bener Meriah which has modified significantly increased the tensile strength, elastic modulus and elongation of PP-MMT nanocomposite in the composition ratio of PP/PP-g-MA/MMT is 85/10/5.

5. References

[1] Syuhada, Rachmat W, Jayatin and Saeful R 2009 Jurnal Nanosains & Nanoteknologi 2 8-51
[2] Zulfikar, Adrian Z, Djadja T and Irwan M 2006 Proceeding Pemaparan Hasil-Hasil Kegiatan Lapangan dan Non Lapangan Tahun 2006 Pusat Sumber Daya Geologi 1 1
[3] Kaelani M S, Iwan A H, Irwan M, Asep S, Jubbel B, Abdul F and Yeni A 2007 Proceeding Pemaparan Hasil Kegiatan Lapangan dan Non Lapangan Tahun 2007 Pusat Sumber Daya Geologi 1 1
[4] Wastoni C P and Martua R P. 2009 Proceeding Pemaparan Hasil-Hasil Kegiatan Lapangan dan Non Lapangan tahun 2009 Pusat Sumber Daya Geologi, 1 1
[5] Lubis S 2007 Jurnal Rekayasa Kimia dan Lingkungan, 6 77
[6] Qina H, Shimin Z, Chungui Z, Meng F, Mingshu Y, Zhongjun S, Shousheng Y 2004 Polymer Degradation and Stability 85 807
[7] Cipriano B H, Kashiwagi T, Zhang X, Raghavan S R 2009 ACS Applied Material and Interface 1 130
[8] Ding C, Demin J, Hui H, Baocun G, Haoqun H 2005 Polymer Testing 24 94
[9] Castel C D, Pelegreti T Jr, Barbosa R V, Liberman S A, Mauler R S 2010 Composites Part A 41 185
[10] Kord B 2012 Turk. J. Agric. 36 510
[11] Barleany D R, Rudi H and Santoso 2011 Prosiding Seminar Nasional Teknik Kimia “Kejuangan” 1 DO3-1- DO3-6
[12] Leszczyńska A, Njuguna J, Pielichowski K, Banerjee J R 2007 Thermochimica Acta 453 75
[13] Wang Z M, Nakajima H, Manias E and Chung T C 2003 Macromolecules 36 8919
[14] Shi D, Robert K Y L, Wei Y, Jinghua L 2007 European Polymer Journal 43 3250
[15] Liu, Lim S H, Zhao J H, Juay M S, Yong and Lu X H 2005 SIMTech Technical Reports 6 33
[16] Fisli A, 2008 Indonesian Journal of Materials Science 10 12
[17] Meyer W A 1972 AFS Cast Metals Res. J. 8 161
[18] Tekmira 2008 Bentonit http://www.tekmira.esdm.go.id/
[19] Rahardjo A K, Maria J J S, Alfink K, Nani I, Suryadi I 2011 Journal of Hazardous Materials 190 1001
[20] Ulfah F, Irwan N 2014 Molekul 9 155
[21] Lumingkawas S 2006 Eugenia 12 242
[22] Manias E, Touny A, Wu L, Strawhecker K, Lu B and Chung T C 2001 Chem. Mater. 13 3516
[23] Zhihong Y, Minghu W, Gang C, Shengjuan L, Panpan P and Qiaolian Z 2016 Polymers & Polymer Composites 24 331
[24] Nejad S J, Ahmadi S, Abolghasemi H, Mohaddespour 2007 e-Polymer 7 1
[25] Lee S Y, Kang I A, Doh G H, Kim W J, Kim J S, Yoon H G, and Wu Q 2008 EXPRESS Polymer Letters 2 78
[26] Bharadwaj R K, Mehrabi A R, Hamilton C, Trujillo C, Murga M, Fan R, Chavira A and Thompson A K 2002 Avery Research Center 43 3699
[27] Bahrami S H, Mirzaie Z 2011 World Applied Sciences Journal 13 493