

Morphology and thermal properties of polypropylene-montmorillonite nanocomposite using modified bentonite of Bener Meriah Aceh

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Abstract. Research on the use of modified bentonite from Bener Meriah Aceh to study the morphology and thermal properties of polypropylene-montmorillonite nanocomposite (PP-MMT) was carried out. Bentonite was isolated into nano-sized montmorillonite and modified with the addition of PP-g-MA as a compatibilizer and octadecylamine as a modifier of MMT. PP-MMT nanocomposite processing was carried out in an internal mixer at 180 °C with a time of 10 minutes, and a speed of 65 rpm. Based on the results of the TGA-DTA test, the modified bentonite from Bener Meriah Aceh with PP-g-MA and octadecylamine can improve the thermal properties of PP-MMT nanocomposite in a composition comparison of PP; PP-g-MA; MMT is 85; 10; 5. The SEM test results also showed that exfoliation and intercalation had occurred of MMT at PP-MMT nanocomposite.

Keywords: nanocomposite, polypropylene, bentonite of Aceh, montmorillonite, morphology properties, thermal properties

INTRODUCTION

Bentonite is natural clay whose main component is the mineral montmorillonite (85%), with the chemical formula of $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4 \cdot nH_2O$. In Aceh, natural bentonite can be found in the districts of North Aceh, Bener Meriah, Sabang, Central Aceh, and Simeulue [1,2] which reaches the amount of 2,618,224,030.20 tons [3]. To date, research on Aceh bentonite has been conducted only on several studies [4] 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.

Montmorillonite (MMT) is a filo-silicate 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 [5]. When an exfoliation occurs, the rheological and thermal properties of the nanocomposite increase dramatically when compared with the pure polymer [6]. 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 [7,8,9,10,11], thermal properties [12], fire retardancy properties [13], and increased degrees of degradation [14]. The use of MMT in the form of nanocomposite for various materials is very appropriate, because the MMT particles are mostly scattered in the form of separate platelets. It is expected that MMT from Bener Meriah can also be used to improve the

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morphology and thermal properties of nanocomposites. According to reports from futurologists, plastic consumption will continue to increase until 2020, with demand reaching 300 million tons, which shows a 16% increase compared to 2010 [15]. One of the most widely used plastics for various purposes is polypropylene (PP). In its application, PP has several disadvantages, including low strength and resistance to low temperatures. It is expected that with the addition of montmorillonite, the thermal properties of PP will increase.

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 [16]. 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 alkylammonium. The research was conducted several stages are characterizing of bentonite, isolation of the MMT nanoparticle, preparation and characterize of PP-MMT nanocomposites.

METHODOLOGY

The materials which were used in this research are polypropylene from Aldrich (density 0.896 gr/cm³, melting point 176 °C), PP-g-MA is polypropylene which has been grafted with maleic anhydride, density 0,934 g/cm³, melting point 156 °C, Mn 3,900 (GPC), Mw 9100 (GPC), oktadecylamine, (C₁₈H₃₉N, 90%) was obtained from Aldrich, CH₃Br (density 2,10 gr/ml), alcohol, montmorillonite K10 (standart) was obtained from Aldrich, montmorillonite was isolated from bentonite Bener Meriah of Aceh

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 and SEM.

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 below.

Table 1. Composition of material of polypropylene-montmorillonite (PP-MMT) nanocomposite

Code of sample	PP (%)	PP-g-MA (%)	Montmorillonite (%)	
			Bener Meriah	Commercial
A	10	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

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.

RESULTS AND DISCUSSION

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 $1031,20\text{ cm}^{-1}$, $538,15\text{ cm}^{-1}$ and $467,10\text{ cm}^{-1}$ respectively. The FTIR spectra of bentonite Bener Meriah showed similar absorption bands to those found in [17].

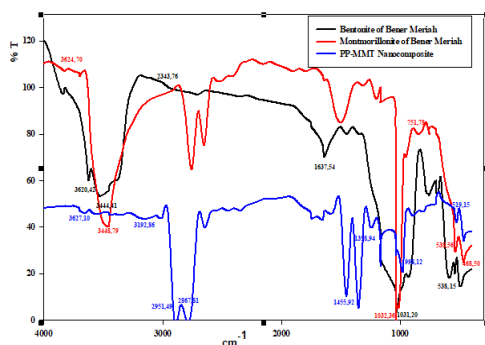


Figure 1. FTIR spectrum of bentonite Bener Meriah, montmorillonite of Bener Meriah and PP-MMT nanocomposite (PP/PP-g-MA/MMT: 85/10/5)

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 $468,50\text{ cm}^{-1}$, these spectra are similar to the standard montmorillonite [18]. Figure 1 also showed of FTIR spectra for PP-MMT nanocomposite (PP/ PP-g-MA/MMT: 85/10/5). Absorption bands at $3627,10 - 3192,86\text{ cm}^{-1}$ 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 $2951,49 - 2867,81\text{ cm}^{-1}$ correspond to alkane of PP and oktadecylamine, while absorption bands at $1455,92\text{-}1358,99\text{ cm}^{-1}$ and $998,12\text{-}519,15\text{ cm}^{-1}$ correspond to C-H of alkane of PP. Characteristic absorption of Si-O-Si from MMT can be observed at $1166,99\text{-}1041,88\text{ cm}^{-1}$. This indicates that MMT modified with octadecylamine has been intercalated into the galleries of PP.

SEM analysis

The Scanning Electron Microscopic (SEM) technique was used to explore the surface morphologies of the sample. Figure 2(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 [19,20]. The existence of these layered pores

causes MMT to be used as a nanocomposite filler to enhance the properties of the nanocomposite. Figure 2 (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 [21].

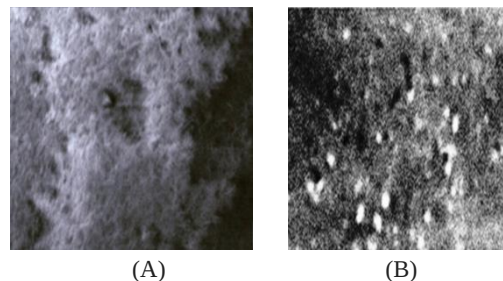


Figure 2. SEM of montmorillonite (A) and PP-MMT nanocomposite of (PP/PP-g-MA/MMT: 85/10/5) (B)

Thermal properties of PP-MMT nanocomposite

The thermal properties of nanocomposites were analyzed using TGA-DTA. Based on the results of the TGA thermogram in Figure 3, it was found that the degradation of pure polypropylene occurred at $382\text{ }^{\circ}\text{C}$ and the degradation of the nanocomposite PP-MMT occurred at $430\text{ }^{\circ}\text{C}$. These results indicate that PP has been added with montmorillonite of Bener Meriah with the composition of PP/PP-g-MA/MMT; 85/10/5 have increased thermal stability. Previous research also used MMT modified with dimethyl dihydrogenated thallow, quarterly ammonium, indicating that the degradation of nanocomposite PP occurred at $442\text{ }^{\circ}\text{C}$ with the composition of PP/PP-g-MA/MMT; 82/15/3. Stability thermal of nanocomposite can be increased due to the addition of MMT. At high temperatures, MMT in nanocomposites is able to form a carbonaceous-silicate layer and this can inhibit the release of volatile products produced during decomposition. Other studies have also explained that the MMT structure of multi-layer silica can prevent the diffusion of volatile decomposition products. The silica content in MMT will affect the number of carbonaceous silicates formed. In addition to the increase in thermal stability of PP-MMT nanocomposite can be caused by the catalytic effect of the silica layer from MMT.

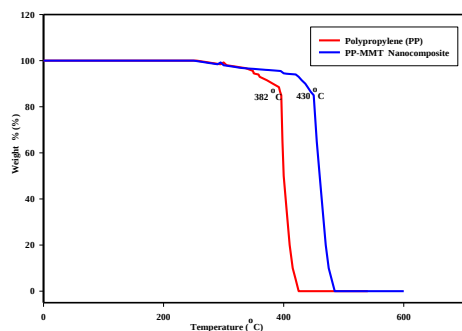


Figure 3. Thermogram of Polypropylene and PP-MMT nanocomposite (PP/PP-g-MA/MMT; 85/10/5)

Stability thermal of nanocomposite can be increased due to the addition of MMT. At high temperatures, MMT in nanocomposites is able to form a carbonaceous-silicate layer and this can inhibit the release of volatile products produced during decomposition [22]. Other studies have also explained that the MMT structure of multi-layer silica can prevent the diffusion of volatile decomposition products. The silica content in MMT will affect the number of carbonaceous silicates formed [23]. In addition to the increase in thermal stability of PP-MMT nanocomposite can be caused by the catalytic effect of the silica layer from MMT [24].

CONCLUSION

Bentonite of Bener Meriah was isolated into nano-sized montmorillonite and was used as a filler of polypropylene-montmorillonite nanocomposite with the addition of PP-g-MA as a compatibilizer and octadecylamine as a modifier of MMT. The morphology of polypropylene-montmorillonite nanocomposite indicates that exfoliation and intercalation of MMT in PP-MMT nanocomposite may occur to produce compatible nanocomposites. Based on the results of the thermal properties test it was found that the addition MMT of Bener Meriah can improve the thermal stability of PP-MMT nanocomposite with the composition of PP/PP-g-MA/MMT; 85/10/5.

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