



# A Comparative Analysis of Various Types of Modified Bentonite Clays Added to Poly Methyl Butadiene for Nanocomposite Preparation

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## Abstract

New Nano-composite of biopolymers was prepared for this analysis. The natural bentonite clay group forms Na-Bentonite (Na- BTT), K- Bentonite (K- BTt), and Ca- Bentonite (Ca-Btt) has been modified by the addition of synthesized fatty amide (FACO), namely Corn oil (CO). To achieve the modification the clay particles was mixed thoroughly in an aqueous (FACO) solution which increases the separation of the clay layer from 1.25 to 2.75 nm of BTT, 1.17 to 1.34 nm of BTt and 1.14 to 1.31nm of Btt due to the action exchange capacity of Na- BTT which is much greater than the low cation exchange capacity of K- BTt and Ca-Btt, respectively. The improved Na- BTT was then used in the preparation of poly methyl butadiene (PMB) Nano-composite. The modifiers interaction in the clay layer is described by X-ray diffraction (XRD). A conventional approach was used to synthesize the Nano-composite, in which the modified clay (FACO- BTT) was melt mixed with PMB. To classify the Nano-composite XRD, Transmission Electron Microscopy (TEM) and Thermogravimetric have been used. The results of XRD and TEM confirmed Nano-composite growth. In contrast to pure PMB, PMB modified BTT Nano-composite showed higher thermal stability. The use of FACO as a vegetable oil derivative to modify clay would minimize reliance on petroleum based surfactants. Moreover, such Nano-composites are considered environmentally friendly in addition to being renewable resources.

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**Key Words:** Poly Methyl Butadiene, Nanocomposite, Fatty Amides, Bentonite.

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## Introduction

A type of poly methyl butadiene (PMB) is thermoplastic elastomers –similar to polymers [1], but can be treated as thermoplastic polymer. The most promising results were obtained in the thermoplastic elastomers when mixing plastics with PMB. Out of several types of non-plastic rubbers, the best acceptable form of rubber for PMB producing countries is the thermoplastic PMB. In this area, several studies on processability and rheology have been conducted [2, 3]. Clay is one of the non- black rubber fillers that are most widely used. It is an inexpensive natural mineral that has become a significant part of the rubber industry; it is used as an economic filler to adjust the production and

efficiency of synthetic rubbers and PMB. Low surface activity and large particle size of clay cause its strengthening ability to be small despite being consisted of layers of silicate with planar structure of 1 nm thickness [4-6].

The clay particles in the PMB matrix could only be propagated on the microscale. Separation of layers is not possible by the general methods of polymer processing. The current approach to increase the clays capacity for enhancement is achieved by altering its shape from hydrophilic to organophilic by replacing clay interlayer cations with organic cations such as alkylammonium.

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Some researchers have been able to prepare polymer/clay nanocomposites by using the modified clay to intercalate different polymers in its interlayer [7, 8].

In the current work, three forms of bentonite were modified using mixed fatty amides (FA<sub>CO</sub>) synthesized with Corn oil. Modified Na- BTT has been used to prepare new Nano-composite (PMB/FA<sub>CO</sub>-BTT) while modified K- BTt and Ca-Btt were used to prepare new conventional composite [9-11], rubber / clay (PMB / FA<sub>CO</sub>-BTt and PMB / FA<sub>CO</sub>-Btt) [12, 13].

## Materials and Methods

### Materials

Na- Bentonite clay (Kunipia F) with a Na<sup>+</sup> capacity of 119 meq 100 g<sup>-1</sup> was purchased from Kunimine, Japan while corn oil was purchased from Ngo Chew Hong Oils and Fats(M) Sdn. The poly methyl butadiene (PMB) of SMR (CV60) grade was provided by the Malaysian MRB, Malaysia. Polymethyl butadiene (PMB), Urea, sodium hydroxide, and hexane were purchased from Merck, Germany. The two chemicals used were in the highest purity available.

### Preparation of FA<sub>CO</sub> - Clay

FA<sub>CO</sub> - **clay** was prepared by a cationic exchange method in which Na<sup>+</sup> in the BTT or K<sup>+</sup> in the BTt or Ca<sup>2+</sup> in the Btt was exchanged in an aqueous solution with the FA<sub>CO</sub> alkylammonium ion synthesized from triacyl glycerides, as reported in our previous paper [8]. A clay suspension has been formed by adding (4.00 g) of any type of bentonite to (600 mL) of hot distilled water and stirred vigorously for an hour. Next, FA<sub>CO</sub> (4.50 g) dissolved in 400 mL of hot water and concentrated HCL (16.00 mL) was applied to the FA<sub>CO</sub> clay suspension. The FA<sub>CO</sub> - **clay** suspension was filtered and washed with distilled water after being stirred vigorously for an hour at 80°C until no chloride was detected with a 1.0 M silver nitrate solution. It was then dried at 60°C for 72 hours. The dried FA<sub>CO</sub> - clay was ground until the particle size was less than 100 µm before the preparation of the Nano- PMB [8, 9].

### Preparation of PMB / Organoclay

An internal mixer (Haake Poldrive) has been used to prepare the expected PMB output over a cycle of three minutes; it was softened in the first minute and mixed with the necessary amount of altered clay over the next two minutes. Next, the compounds

have been molded in an electrically heated hydraulic press at 130°C for 10 minutes with a pressure of 150 Kg / cm<sup>2</sup>.

Subsequently, the compounds were immediately cooled for 5 minutes [14, 15]. Table 1 shows the modified clay together with the amount of PMB prepared for this analysis.

**Table 1.** The weight in grams of PMB and types of modified clay

<u>Sample identity</u>	<u>PMB (gm)</u>	<u>modclay(gm)</u>
PMB mod.0	40.00	37.60
PMB mod.1	39.60	0.40
PMB mod.2	39.20	0.80
PMB mod.3	38.80	1.20
PMB mod.4	38.40	1.60
PMB mod.5	38.00	2.00
PMB mod.6	37.60	2.40

PMB mod.0, PMB mod.1, PMB mod.2, PMB mod.3, PMB mod.4, PMB mod.5 and PMB mod.6= 0,1,2,3,4,5 and 6 phr, respectively.

### Characterization

#### a. X-Ray Diffraction (XRD) Analysis

The analysis has been conducted using Shimadzu XRD 6000 diffractometer with CuK radiation (k = 0.15406 nm). A scanning rate of 1/minute and scanning range 2-10 was applied to scan the diffractogram.

#### b. Thermogravimetric Analysis (TGA)

The samples' thermal stability was examined by a Perkin Elmer model TGA 7 Thermogravimetry analyzer. The temperature of the samples was raised from 35 to 800°C with flow rate of 20 mL/min of nitrogen under nitrogen atmosphere at 10°C/min heating rate.

#### c. Transmission Electron Microscopy (TEM)

Using transmission electron microscopy (EFTEM) energy filtering, the dispersion of clay was examined. A LEO 912 AB EFTEM with an acceleration voltage of 120 keV was used to take TEM photographs. An Ultracut E (Reichert and Jung) cryomicrotome has been used to prepare the specimens. 100 nm slices were cut by a diamond knife at 120°C.

## Results and Discussion

### XRD Measurements

The space between the clay and layers of the silicate and that between the interlayer and the alkyl ammonium cations was measured by XRD technique. This technique has also been used to



quantify the scattering of FA<sub>CO</sub> - clays in the PMB matrix by the silicate layers. Table 2 indicates the alkyl ammonium (FA<sub>CO</sub> -BTT and poorly modified FA<sub>CO</sub> -BTt & FA<sub>CO</sub> -Btt ) interlayer gap of natural clays and modified clays [16, 17 ]. The interlayer gap of Na -BTT for FA<sub>CO</sub> -BTT, K- BTt for FA<sub>CO</sub> - BTt and Ca-Btt for FA<sub>CO</sub> - Btt has been extended from 1.25 nm to 2.75 nm, 1.17 nm to 1.34m and 1.14 nm to 1.31 nm respectively.

**Table 2.** Unmodified X-ray diffractometer types of clay and modified types of clay

Type of clay	Exchange cation	2θ (degree)	d-Spacing (nm)
Na-BTT	Na <sup>+</sup>	6.00	1.25
FA <sub>CO</sub> - BTT	RCO-NH <sub>3</sub> <sup>+</sup>	3.38	2.75
K-BTt	K <sup>+</sup>	7.70	1.17
FA <sub>CO</sub> - BTt	RCO-NH <sub>3</sub> <sup>+</sup>	6.43	1.34
Ca- Btt	Ca <sup>+2</sup>	8.00	1.14
FA <sub>CO</sub> - Btt	RCO-NH <sub>3</sub> <sup>+</sup>	6.90	1.31

The intercalated silicate layer in PMB / unmodified BTTand PMB / modified BTT nanocomposites obtained from the XRD analysis is summarized in table 3.

**Table 3.** XRD analysis of composites of PMB / unmodified types of clay and PMB / modified types of clay

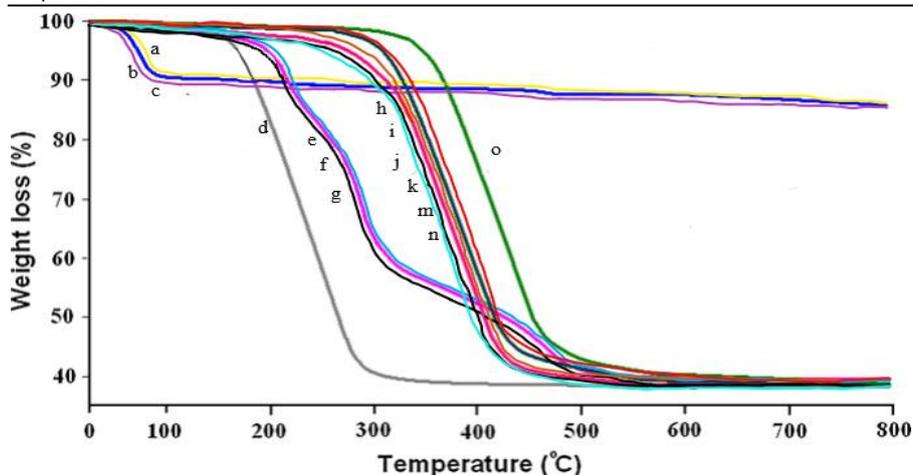
PMB/clay	d- Spacing, (nm)					
	1 phr	2 phr	3 phr	4 phr	5 phr	6phr
PMB /Na-BTT	1.33	1.35	1.32	1.30	1.29	1.27
PMB /FA <sub>CO</sub> - BTT	3.01	3.14	3.28	3.15	2.93	2.81
PMB /K-BTt	1.21	1.23	1.25	1.21	1.20	1.19
PMB /FA <sub>CO</sub> - BTt	1.34	1.36	1.38	1.39	1.36	1.32
PMB /Ca-Btt	1.19	1.21	1.22	1.24	1.19	1.17
PMB /FA <sub>CO</sub> -Btt	1.30	1.32	1.35	1.36	1.37	1.29

**Thermogravimetric Analysis (TGA)**

Figure 1 displays curves for the weight loss of Ca-Btt, K-BTt, Na-BTT, FA<sub>CO</sub>, FA<sub>CO</sub>- Btt, FA<sub>CO</sub>- BTt, FA<sub>CO</sub>- BTT, PMB, PMB/ 4 phr Ca-Btt, PMB/ 3 phr K-BTt, PMB/ 2 phr Na-BTT and PMB/ 5 phr FA<sub>CO</sub>- Btt, PMB/ 4 phr FA<sub>CO</sub>- BTt micro-composite, PMB/ 3 phr FA<sub>CO</sub>- BTT

nanocomposite containing water caused by hydrated sodium cation (Na<sup>+</sup>) intercalated within the clay layers. The presence within the BTT interlayer spacing of vegetable based surfactant alkyl ammonium group reduces the surface energy of inorganic structures and transforms organophobic material into organophilic materials. The primary distinction between the thermogram of unmodified clay and the organoclay is that the decomposition temperature of the organic components in the organoclay is between temperatures 195 and 495°C. The FA<sub>CO</sub> decomposes as temperature rose from 160 to 605°C (Fig. 1d). (Fig. 1g) shows that the decomposition temperatures of FA<sub>CO</sub> - BTT are greater than Ca-Btt (Fig. 1a), K-BTt (Fig. 1b), Na-BTT (Fig. 1c), pure FA<sub>CO</sub>(Fig. 1d), FA<sub>CO</sub> - Btt (Fig. 1e) and FA<sub>CO</sub> - BTt (Fig. 1f) temperatures. The increase in temperature of FA<sub>CO</sub> in organoclays implies that the clay and the alkyl ammonium cations have strong intermolecular interaction. That is, their decomposition temperature increases due to the intercalation and bonding of FA<sub>CO</sub> ion to the clay silicate layers. In order to evaluate the impact of unmodified nanocomposites, thermogravimetric analysis was also performed on the microcomposite PMB/ 4 phr Ca-Btt (Fig. 1i ), PMB/ 3 phr K-BTt (Fig. 1j), PMB/ 2 phr Na-BTT (Fig. 1k), PMB/ 5 phr FA<sub>CO</sub>- Btt (Fig. 1m), PMB/ 4 phr FA<sub>CO</sub>- BTt(Fig.1n) and PMB/ 3 phr FA<sub>CO</sub>- BTT (Fig. 1o) nanocomposites. Poorly altered clay (poor organoclay FA<sub>CO</sub>- Btt then FA<sub>CO</sub>- BTt, respectively) and altered clay content (organoclay FA<sub>CO</sub>- BTT) in the thermal properties of rubber matrix.(Fig.1: h, i, j, k, m, n, o) display the results of the TGA. For PMB containing FA<sub>CO</sub> - PMB ( Fig. 1o ) at 370°C compared to pure PMB (Fig. 1h), PMB/ 4 phr Ca-Btt (Fig. 1i), PMB/ 3 phr K-BTt (Fig. 1j), PMB/ 2 phr Na-BTT (Fig. 1k), PMB/ 5 phr FA<sub>CO</sub>- Btt (Fig. 1m) and PMB/ 4 phrFA<sub>CO</sub>- BTt (Fig.1n) micro-composite, at 255, 260, 265, 270, 280 and 285°C, respectively. The results show that with the addition ofFA<sub>CO</sub>- BTT the thermal stability increases in (Fig. 1o) up to 3 phr loading. It also indicates that the thermal stability cannot be enhanced by increasing of this percentage. The presence of homogeneously dispersed silicate on the polymer surface obstructs the permeability of substrate’s volatile degradation products and helps to prolong the degradation of nanocomposite [18].

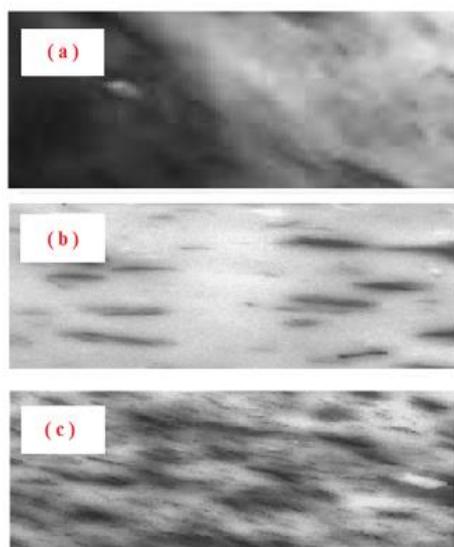




**Figure 1.** TGA thermograms of a : Ca-Btt, b: K-BTt, c: Na-BTT, d: FACO, e: FACO- Btt, f: FACO- BTt : g : FACO- BTT : h: PMB, i: PMB/ 4 phr Ca-Btt, j: PMB/ 3 phr K-BTt, k: PMB/ 2 phr Na-BTT, m: PMB/ 5 phr FACO- Btt, n : PMB/ 4 phr FACO- BTt, o : PMB/ 3 phr FACO- BTT

### Transmission Electron Microscopy (TEM)

Fig. 2 displays transmission electron microscopy micrographs of PMB composites assisted by 5 phr  $FA_{CO}$ -Btt, 4 phr  $FA_{CO}$ -BTt and 3 phr  $FA_{CO}$ -BTT. Due to the incompatibility of both parts, the  $FA_{CO}$ -Btt and  $FA_{CO}$ -BTt micrograph of PMB /5 phr and PMB /4 phr respectively, reveals that the PMB matrix has fully maintained its stack morphology (Fig. 2a, 2b). Dark bundles are the thickness of each clay or agglomerate layer, but there are less agglomerates in (Fig. 2b) than (Fig. 2a) image, Fig. 2c displays TEM images of PMB / 3 phr  $FA_{CO}$ -BTT nanocomposites demonstrating strong properties and composite effects. The images clearly show the scattering of the altered clay dark bundles within the matrix of PMB with an intercalated state.



**Figure 2.** TEM micrographs of a: PMB /5 phr  $FA_{CO}$ -Btt, PMB /4 phr  $FA_{CO}$ -BTt microcomposite and b: PMB /3 phr  $FA_{CO}$ -BTT nano-composite

### Conclusions

Synthesized fatty amides ( $FA_{CO}$ ) of corn oil have been used as an  $FA_{CO}$  to modify the natural mineral clay group (Na- BTT, K-BTt and Ca- Btt). The existence of fatty acids long chain in  $FA_{CO}$  indicates that they could only be useful for modifying Na- BTT as surfactants. New PMB/BTT nanocomposites (Nano- PMB) have been prepared using modified BTT. The analysis indicates that PMB nanocomposites developed by using  $FA_{CO}$  as a modifier display more thermal stability compared to microcomposites produced on the basis of poorly configured Btt or BTt with PMB respectively, these are considered environmentally friendly nanocomposites.

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