PROJECT COMPLETION REPORT

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SHORT TERM RESEARCH GRANT

EFFECT OF NANOCLAY LOADING ON NATURAL FIBER COMPOSITE

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ABSTRACT

EFFECT OF NANOCLAY LOADING ON NATURAL FIBER COMPOSITE

(*Keywors: Nanoclay, Bio-composite, PP/PLA, Kenaf Fiber*)

Kenaf fiber reinforced composite is prepared using the internal mixing technique in order to analyse the effect of nanoclay loading in the composite and improve the tensile properties of the conventional kenaf fiber reinforced. Composite is prepared by mixing constant composition of matrices PP/PLA and kenaf fibers at 97 wt%, 3 wt% and 40 wt% respectively but with different percentage of 0 wt%, 1 wt%, 3 wt% and 5 wt% nanoclay loading. Then, the hot press is done to produce the composite that undergoes tensile test. Result for tensile test shows increasing of nanoclay loading in the composite cause the decreasing tensile properties. However, 1 wt% nanoclay in the composite increases the Young Modulus of the composite. This is supported by the liquid immersion test results where the specimen with 1 wt% nanoclay has better result compared to other specimen that does not have nanoclay and specimens with 3 wt% and 5 wt% nanoclay. Based on the result, specimen KeN 1%-PP/PLA is the best specimen with average tensile strength of 30.59 MPa, average Young Modulus of 2.32 GPa while the average value liquid immersion is 1.78%.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Bast fibers have been grown for centuries throughout the world and can be characterized by long, strong fiber bundles that comprise the outer portion of the stalk. The word bast refers to the outer portion of the plant stem. Bast plants include flax, hemp, kenaf, sunn-hemp, ramie, and jute. Bast fiber plants provide a means for traditional forest products companies to maintain market share and even capture new markets through the use of alternative raw materials which possess unique and beneficial properties which are particularly fitting for certain applications. They also provide the perception of improved environmental stewardship of our resources [1].

The composite material however is defined as a combination of two or more different materials and creates one new material with better properties. Meanwhile, nanocomposite is defined as at least one dimension of the dispersed particles is in the nanometer range. In other word, materials with nanosize particle as the filler are nanocomposite. Nanocomposite became more widely studied in both academic and industrial laboratories when researchers from Toyota Central Research and Development Laboratories (CRDL) in Japan began a detailed examination of polymer/layered silicate clay mineral composites [2].

In this research, the matrix material will be polymer. Polymer will be added with nanoclay as the filler. Hence, polymer nanocomposite will be produced. The interest of combining natural fibers with polymers such as poly (lactic acid), poly (3-hydroxybutyrate), poly (caprolactone) and poly (butylene succinate) has been developed since 2008. This is due to the growing of environmental awareness and government regulations [3]. Depletion of petroleum resources and growing entrapment of non-biodegradable plastics in the food chain and environment has also fueled research of biocomposites or 'green composites' utilizing natural fibers and biodegradable plastics. These biocomposites are termed as next generation material because they are compatible with the environment and independent of fossil fuel [3].

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The advanced composite materials based on bast fibers and thermoplastic matrices have received great scientific attention especially in the area of lightweight, environmentally friendly, cost-effective composite materials. Special interest has been concentrated on kenaf fibers as potential reinforcing fillers for many thermoplastic composites [4].

1.2   BIO-COMPOSITE

In previous research, PLA pre-forms are molded by thermo compression in a closed mold. Various kinds of kenaf/PLA pre-forms with different thickness, specific weight and fiber/matrix ratios are molded. The composites have been constructed as multiple pre preg layers (2 or 4 layers) in the mold cavity, depending on the thickness of the starting kenaf/PLA performs and in accordance with the targeted thickness. The composites are cured at 175 ºC for 20 minutes, under pressure. The basic physical and mechanical properties of the composites are tested. Higher mechanical properties (flexural strength 21,7 MPa, modulus 1,22 GPa, impact resistance 60,3 kJ/m^2 and compression strength 6,5 MPa) are obtained for composites containing 60% fibers and 40% matrix, 20 mm thin and with specific weight of 40 kg/m³ indicate that the composites are superior to the most types of traditional building composites, such as wood boards, hardboards, thermo panels, plaster carton panels for walls and ceilings and systems for wall covering. From this point of view, it can be concluded that kenaf fibers/PLA composites are environmentally friendly and economically adjustable when compared to traditional building materials [4].

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Meanwhile from the experiment conducted in 2003, the nanocomposites of biodegradable polylactide/ C²C²18-mmt is successfully prepared by the simple melt extrusion, where the silicates of C²C²18-mmt are intercalated, stacked, flocculated, and well distributed in the PLA matrix. The C²C²18-mmt is supplied by the Hojun Yoka Co., Japan and the Na^+ in the montmorillonite is replaced with dimethyldioctadecylammonium cation by ion exchange reaction. Firstly, the C²C²18-mmt (powder form) and PLA (pellet form) are dry-mixed by shaking in the bad. Then, the mixture is melt extruded using twin-screw extruder at 210 ^{o}C at the screw speed of 100 rpm and feed rate of 120 g/min to yield the nanocomposite strands. There are four specimens prepared for the experiment; one is the neat PLA while the other three contain C²C²18-mmt with 4, 5 and 7 wt%, named PLACN4, PLACN5 and PLACN7 respectively. The result of the flexuCral properties of the neat PLA and the PLACNs are shown in Table 1.1 [5].

Table 1.1 Flexural properties of neat PLA and various PLACNs

Flexural properties	Neat PLA	PLACN4	PLACN5	PLACN7
Modulus (GPa)	4.84	5.43	5.38	5.39
Strength (MPa)	86	102	107	99
Distortion (%)	1.9	3.9	2.1	1.9

These flexural properties are measured at 25°C and by comparing the PLACNs data's measured compared to neat PLA, there is a significant increment of the flexural modulus between PLACN4 and the neat PLA but the C²C²18-mmt loading afterwards did not gave that much increment anymore. However, the flexural strength and the flexural distortion showed highly increment with PLACN4 and then gradually increased with PLACN5 and PLACN7. From the result, it summarized that high C²C²18-mmt loading may cause the material to be brittle. Therefore, by manipulating the C²C²18-mmt loading can control the flexural properties of the material for as far as it is known, 4 wt% of the C²C²18-mmt will make the material achieved high value of the flexural properties [5].

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An experiment is done in 2008 to determine the tensile properties of kenaf bast fiber–plasticized PLA biocomposites by Mat T. R et al. PLA is firstly plasticized with 10% of PEG and referred as p-PLA. The fiber content varied from 10-40 wt%. The films of 1 mm thickness are prepared by compression molding and cut into the dumbbell shape to fulfill the specification of the tensile test standard.
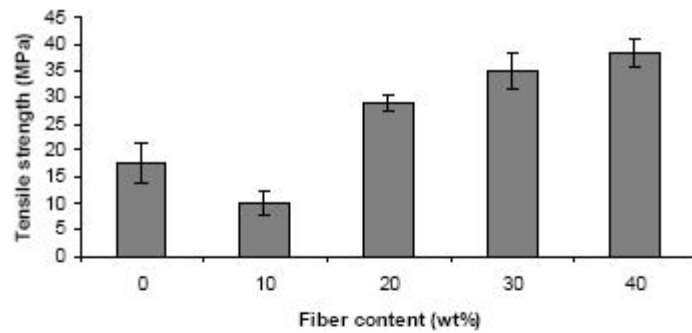
(a)
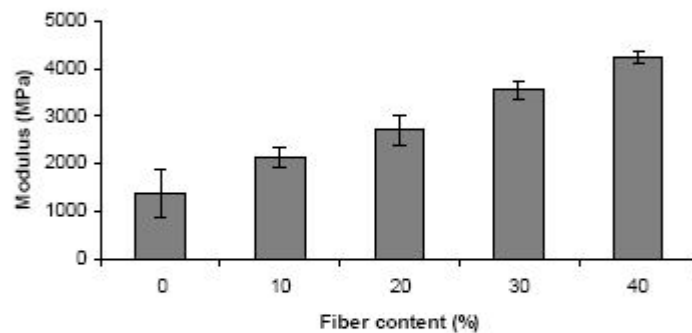
(b)
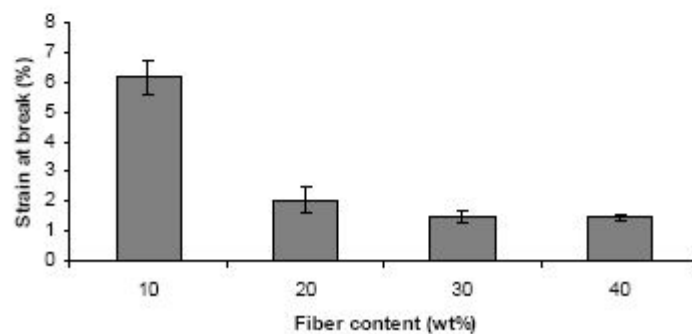
(c)

Figure 1.1 (a) tensile strength, (b) tensile modulus, and (c) strain at break results of p-PLA and p-PLA/KBF composites at various fiber contents [6].

Figure 1.1 shows that the tensile properties decrease at 10wt% of the KBF. However, starting from 20wt% to 40wt%, the properties begin to increase at the approximately 120% improvement. The modulus properties increased as the KBF content increase as shown in above. The strain however decreased with increased of KBF loading in the bio composites. Based on the result, the p-PLA/KBF composites are at its optimum properties when the composite is filled with 40wt% [6].

Nowadays, fiber reinforced plastic is extensively used in the aircraft, automotive, marine, leisure, electronic and medical industries. Composites are presently used to make available huge benefits with prominence on lower production and duration costs featuring notably. Enhancing the fiber stacking sequence is the potential of composites main characteristic [7].

1.3   NATURAL FIBER

As stated earlier, bast fibers have been grown for centuries throughout the world and the bast plants include flax, hemp, kenaf, sunn-hemp, ramie, and jute. The focus of our research has been on the species that can grow in temperate regions of the world, namely flax, hemp, and kenaf. These fibrous plants have long been noted for their exceptional strength in cordage and paper. The primary focus of our research will be from a North American perspective, although occasional references will be made to applicable international developments [8].

The remainder of the stem inside this bast layer is a different type of fibrous material, which has different names depending upon the species selected. This inner material is known as shives when referring to flax and sometimes hemp, as hurd in the context of hemp, and as core when from kenaf. For the purpose of simplicity and consistency, the word "core" is used when discussing this portion of the bast plant [3].

Bast fibers is well known for their low price, economical production with little requirements for equipment and low specific weight (low density), which results in a higher specific strength and stiffness when compared to glass reinforced composites. In addition, they are nonabrasive to mixing and molding equipment, which can contribute to significant equipment maintenance cost reductions. They also present safer handling and working conditions compared to synthetic reinforcements such as glass fibers. The processing atmosphere is friendly with better working conditions and therefore there will be reduced dermal and respiratory irritation compared to glass fibers [4].

The most interesting aspect about bast fibers is their positive environmental impact. These fibers are renewable resource with production requiring little energy and biodegradable. They are carbon dioxide neutral; therefore they do not return excess carbon dioxide into the atmosphere when they are composted or combusted.

The main selection of bast fiber in this study is kenaf as shown in Figure 1.2 which can be describe as a woody herbaceous annual low-cost natural fiber with a deep penetrating taproot, believed to be native to India. It is mostly unbranched and rapidly reaches maturity, in only 4 to 5 months the plants can grow to 2 to 5 meters tall. The leaves are individually stalked and lobed to some degree while the flowers are yellow or white with a red centre and can be up to 10 cm in diameter. The kenaf also have fruits those are fleshy and in the fruits contain seed capsules with 1 cm long containing many seeds. The seeds are brown and wedge shaped, 5 mm long with a 1000 grain weight of 25 g.

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Figure 1.2 Kenaf Plant

Kenaf has some promising characteristics along with certain limitations. Nutrient requirements are low, with no significant improvement in yield at nitrogen levels above 33.5 pounds per acre, (USDA, ARS, 1970). The length of the vegetative phase is determined by daily length of the dark period. A growing period of 90 -150 days is needed, with fastest growth at temperatures of 20 – 22 °C, (68 – 72 °F), and approximately 6000 m³ water per hectare, [3]. Growth becomes quite minimal when temperatures reach below 50 °F [3].

Kenaf contains a bast fiber portion comprising 26 - 35% (by dry weight) of its stem. This bast crop shows potential as a substitute for hardwood species as shortages may become more pronounced in various locales of the Southeast and Mid-South. Bast fibers average 2.5 mm in length, very similar to southern pine species, while the core, with lengths of 0.5 mm closely matches that of hardwoods. This composition provides a desirable blend for many pulp and paper applications, spurring continued interest and development.

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1.4   NANOCLAY (NANOCOMPOSITE)

Nanoclay is one of the most affordable materials that have shown promising results in polymers. It is made from montmorillonite mineral deposits known to have "platelet" structure with average dimension of 1 nm thick and 70 to 150nm wide. Nanoclays are known to enhance properties of many polymers such as nylon 6, EVA, epoxy, PET, PE and PP [9].

An enormous amount of interest is focused in the field of clay-polymer nanocomposite technology. The essential nanoclay raw material is montmorillonite, a 2-to-1 layered smectite clay mineral with a platy structure. Individual platelet thicknesses are just one nanometer (one-billionth of a meter), but surface dimensions are generally 300 to more than 600 nanometers, resulting in an unusually high aspect ratio. Naturally occurring montmorillonite is hydrophilic. Since polymers are generally organophilic, unmodified nanoclay disperses in polymers with great difficulty. Therefore through clay surface modification, montmorillonite can be made organophilic and, therefore, compatible with conventional organic polymers. Surface compatibilization is also known as "intercalation" is used to compatibilize nanoclays disperse readily in polymers [10].

Nanoclay is also known as hydrated sodium calcium aluminum silicate. The nominal physical properties of nanoclay are shown in Table 1.2.

Table 1.2 Nominal Properties of Nanoclay

Molecular Weight (g/mol)	540.46
Average Density (g/cm³/	2.35
Crystal System	Monoclinic
Group	Smectite group
Fracture	Uneven to lamellar
Luster	Earthy (dull)
Average Specific Gravity (g/cc)	2.3-3

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Color	White, yellow
Cleavage	Perfect in one direction, basal
Characteristic	Crystal Expand to mani times of the volume when added to water
Field indicators	Softness and soapy feel

Nanoclay, on the other hand, are a new class of composites, for which at least one dimensions of the dispersed particles, is in the nanometer range. Nanocomposite based on clay and layered silicates have been most widely investigated, probably because the starting clay materials are easily available and because their intercalation chemistry has been studied for a long time [11]. Layered silicates used in the synthesis of nanocomposites are natural or synthetic minerals, consisting of very thin layers that are usually bound together with counter-ions. Figure 1.3 shows nanoclay molecule [12]. Their basic building blocks are tetrahedral sheets in which silicon is surrounded by four oxygen atoms and octahedral sheets in which a metal like aluminum is surrounded by eight oxygen atoms.

According to Yuan Xu (2007), clay-containing nanocomposites (CPNC) has advantages over the matrix polymer where it will improve the modulus, impact strength, barrier properties and even the plane-strain fracture toughness epoxy matrix [13]. The experiment conducted by Hosur M. V. et al. (2006), there are three types of foam cores prepared to be tested energy levels of 15, 30 and 45 J, those are the neat polyurethane, 0.5% nanoclay reinforced polyurethane and 1% nanoclay reinforced polyurethane. The damage analysis showed that the foams with nanoclay had smaller damage is compare to the neat polyurethane. Therefore, by using nanoclay in the sandwich construction structure will not only sustain higher load, reduce the damage size during impact but will also lower the reduction in mechanical properties [14].
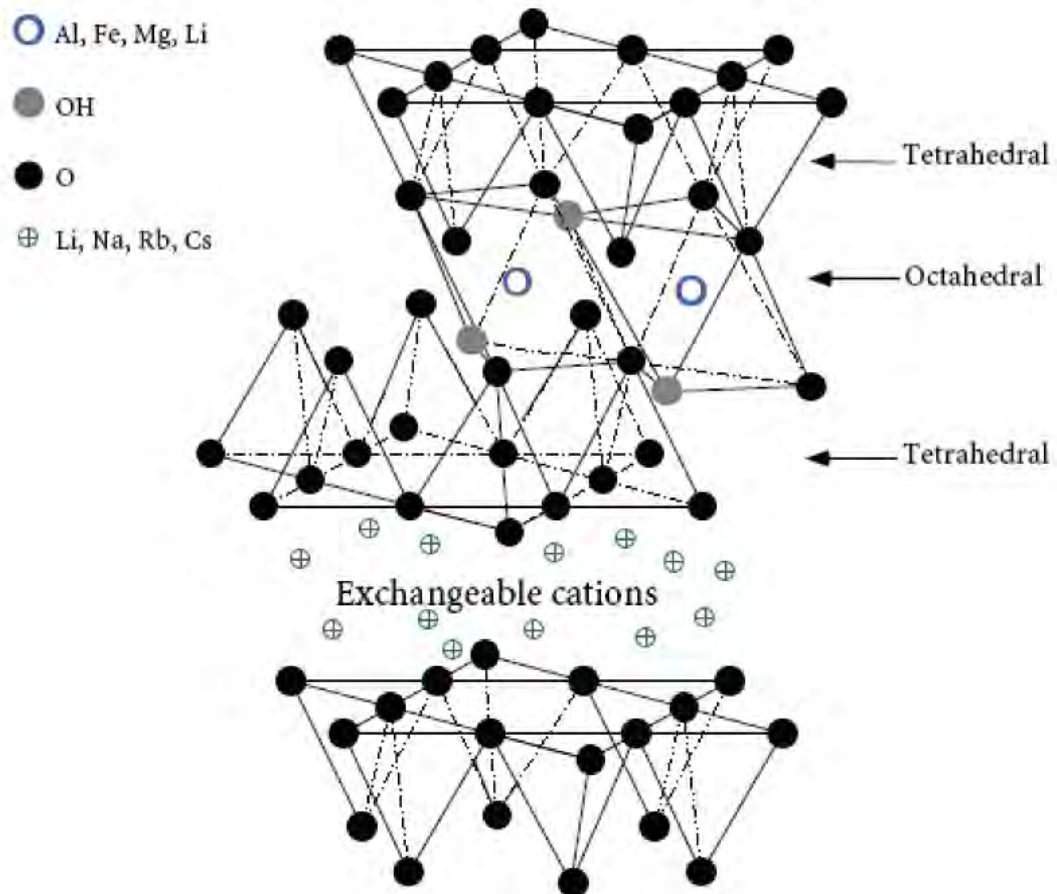
Figure 1.3 Nanoclay Molecules [12]

1.5   OBJECTIVES

The aim of this study is to improve the conventional biocomposites of Kenaf Bast Fiber, thermoplastic polymer, Polypropylene and the biodegradable polymer, Polylactic Acid by using the nanoclay. The main objectives of this project are:

1. To investigate the effect of nanoclay loading in order to improve the matrix of the kenaf fiber composite properties. The weight percentage of the nanoclay will be varied to study tensile propeties based on the nanoclay loading (1, 3 and 5 wt% respectively).

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2. To improve the tensile properties of conventional kenaf fiber composite. This is because the fiber tends to break when the matrix of the composite has a low stiffness property. Therefore, by adding nanoclay, there is a possibility that the properties of the composite can be maintained even if the fiber breaks.

1.6   PROBLEM STATEMENT

There is not much information that well understood about the failure and fracture behaviors of nanoclay-filled polymers. The most particular interest to fracture behavior is the role played by the clay particles in nucleating or enhancing the localized crack tip strength fields. Therefore, this study will identify the effectiveness of having the nanoclay particle in the composite.

It is known that there is always fiber breakage in the composite due to the low stiffness properties of the matrix. The initial start of the fiber breakage will lead to the other fiber breakage when the force is applied upon the composite. This is because the load transfer is no longer possible due to the fiber breakage that broke the bond between the matrix and reinforcement in the composite. Eventually, the composite will break.

In order to make the load transfer in the composite is possible even when there is fiber breakage; the nanoclay particle is added to increase the stiffness of the matrix. When the stiffness of the matrix is increased, the composite will have higher tendency to be fractured at higher applied force. This is because nanoclay particle helps the matrix to hold up the bond even if there is fiber breakage.

CHAPTER 2

EXPERIMENTAL SETUP

2.1   MATERIAL

There are four types of raw materials used in this study during the speciment preparation process. The material was kenaf bast fiber, PLA, PP and modified montmorillonite.

The kenaf fibers used in this study were purchased from Innovative Pultrusion Sdn Bhd. These fibers already have been harvested, retted, dried, and mechanically separated. The fibers were crush into short and random fibers within range of 1mm to 3 mm by using the crusher machine in *Fakulti Kejuruteraan Pembuatan, UTeM*.

In this study the organo-modified montmorillonite used are the Nanomer I.28E$^{®}$Nanoclay, it were design for easy dispersion and enhanced at low loading. The nanoclay was also purchased from the Innovative Pultrusion Sdn Bdn. First, the nanoclay was dispersed and stir in water for 2 hours. Then, the nanoclay was left in the water for 48 hours to fully disperse it. After that, mechanical stirrer with heat of 130°C was use for water evaporation process. Time consume for this process were 8 hours.

Another two raw materials used in this study were pellet type PP and emulsion type PLA. The pellet type PP supplied by Polypropylene Malaysia Sdn. Bhd. and this homopolymer PP grades also known as Propelinas SHAC320. This grade of PP produced by using Super High Activity Catalyst 320 technology under license from Dow Chemical,USA. This grade of PP offers up to 10-15% increases in mechanical properties and give higher transparency than conventional homopolymer PP. Emulsion type PLA was supplied by Innovative Pultrusion Sdn. Bhd. The properties of PP and PLA are shown **in Table 2.1.**

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Table 2.1 Properties of PP and PLA

Polymers	Density (g/cm^3)	Glass Transition Temperature, T_g(°C)	Melting Temperature, T_m(°C)
Polypropylene	1.25	-18	165
Poly lactic acid	0.85	55-60	175

2.2   SPECIMEN PREPARATION

Generally, there were two types of specimen compound need to be prepared which are composite materials with and without nanoclay.

2.2.1 Specimen preparation for composite material without nanoclay compound.

In this study the composition used to produce composite material without nanoclay composite were kenaf bast fiber, PLA and PP. There was only one specimen need to be prepared and the specimen compound composition was as shown in Table 2.2.

Figure 2.1 shows the Haake Internal Mixer used in this study to mix up the materials. The mixing process was under the condition of 175°C for 12 minutes with 50 rpm rotor speed. Pour pellet type PP in the mixer for the first 4 minutes. After that, mix together Emulsion type PLA with PP in the mixer and melt compound mixture will be produce from this process. Next, put in together nanoclay into the mixer. Divide evenly kenaf fiber into 3 portion and finally, poured kenaf fibers in the mixer at the 6th, 8th and 10th minutes. The product of this proceses was as shown in Figure 2.2.

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Table 2.2 Composition of 1, 3, 5 wt% of nanoclay loading KeN-PP/PLA specimen

Specimen	PP [wt%]	PLA wt%]	Kenaf [wt%]	Nanoclay [wt%]
KeN 0%	97	3	40	0

**Please refer Appendix A for composition sample calculation.
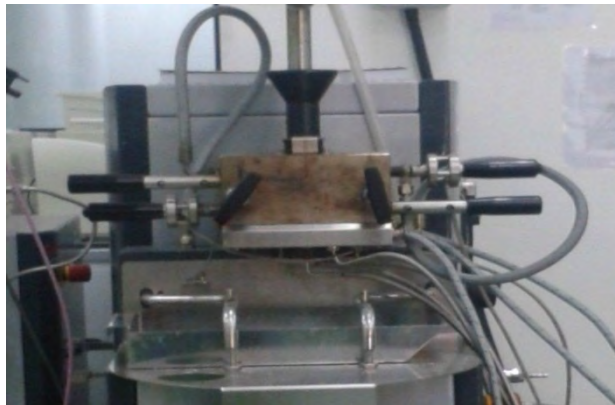

Figure 2.1 Haake International Mixer

Figure 2.2 Composite material with nanoclay compound blends

2.2.2 Specimen preparation for composite material with nanoclay compound.

The composition used to produce these composite are the kenaf bast fiber, PLA, PP and nanoclay. There are three type of specimen used in this study and those four specimens were prepare with different composition of nanoclay according to the specified requirement. These specimens are labeled as KeN 1%, KeN 3% and KeN 5%.

KeN 1% contains 1% of nanoclay and the composition mixture of kenaf bast fiber and PLA is 99%. Moreover, KeN 3% and KeN 5% contain 3 wt% and 5wt% of organo-modified montmorillonite and the mixture of kenaf bast fiber and PP/PLA of 97wt% and 95wt% respectively. All of the specimen composition were as shown in Table 2.3.

By using the same machine as shown in Figure 2.1, the mixing process was under the condition of $175^{o}C$ for 12 minutes with 50 rpm rotor speed. Pour pellet type PP in the mixer for the first 3 minutes. Then, mix together Emulsion type PLA with PP in the mixer for the next 2 minutes and melt compound mixture will be produce from this process. Next, put in together nanoclay into the mixer, the nanoclay composition were base on the specimen type and nanoclay weight percentage as shown in Table 2.3. Finally, poured kenaf fibers in the mixer at the 6th, 8th and 10th minutes.

Table 2.3 Composition of 1, 3, 5 wt% of nanoclay loading on composite material specimen

Specimen	PP [wt%]	PLA [wt%]	Kenaf [wt%]	Nanoclay [wt%]
KeN 1%	97	3	40	1
KeN 3%	97	3	40	3
KeN 5%	97	3	40	5

**Please refer Appendix A for composition sample calculation.

2.2.3 Standard specimen preparation.

After the mixing process or compound preparation process, the melt compound mixtures of composite material with or without nanoclay undergo crushing process. Crusher machines used to crash the compound (Figure 2.3) into the pellet size for about approximately 3 mm in length as shown in Figure 2.4.

Figure 2.3 Crusher Machine

Figure 2.4 Pellet size of composite material polymer blends

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