CEJOTER: Chelo Journal of Technology Development f Engineering
Vol. xx, No. xx, Month, 20xx, pp. xxx – xxx
ISSN (print) XXX ; ISSN (online) XXX

BIODEGRADABLE FIBER POLYMER COMPOSITES: POLYLACTIC ACID (PLA)/COIR USING BENTONITE

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ABSTRACT

Biodegradable fiber polymer composites: Polylactic acid (PLA)/coir using bentonite refers to a type of composite material that combines polylactic acid (PLA) as the polymer matrix, coir fibers as reinforcement, and bentonite as a filler material. The aim of this composite is to develop a sustainable and environmentally friendly material that can potentially replace traditional synthetic composites.Polylactic acid (PLA) is a biodegradable and renewable polymer derived from renewable resources such as corn starch or sugarcane. Hybrid fiber reinforced polymer nanocomposites were prepared from kenaf fiber, coir fiber, polypropylene and montmorillonite nanoclay through hot compression method. The study investigated the impact of fiber hybridization and montmorillonite on the physical, mechanical, and biodegradable properties of the composites. To increase adhesion and compatibility between the fiber and polymer matrix, both bentonite and coir fibers were treated with a 2% sodium hydroxide solution to reduce their hydrophilic nature before use. The mechanical properties of the composites, including tensile strength and Young's modulus, were measured using a universal tensile testing machine. Scanning electron microscopy analysis revealed that montmorillonite significantly improved the adhesion and compatibility between fibers and the polymer matrix. Hybridization improved the biodegradability and water absorption characteristics of the composites, while MMT addition had the opposite effect on these properties.

Keywords: Biodegradable, Polymer Composite, Polylactic Acid, Bentonite

INTRODUCTION

The depletion of fossil resources and non-degradable plastic waste causes environmental pollution and dangerous carbon dioxide to be trapped in the atmosphere [1]. Currently, around 50% of packaging products are made of plastic, mostly derived from fossil fuels. Developing biodegradable materials that can degrade in an environmentally friendly way in a relatively short time is important. Bio-based polymers can play a crucial role, unlike conventional plastics, in reducing greenhouse gas emissions (such as carbon dioxide). Additionally, the production and use of biodegradable polymers can also help increase the rate of depletion of fossil fuels [2].

The increasing demand for biodegradable materials is driven by the need to address environmental concerns. Biodegradable materials are perceived to be more environmentally friendly than non-biodegradable materials because they eventually break down and cause no lasting damage. The benefits of biodegradable materials are clear: they break down much faster and don't pollute the earth for centuries. Additionally, they often come from renewable resources 1 . However, there are also concerns about the environmental impact of biodegradable materials. For example, biodegradable plastics may release methane, a powerful greenhouse gas, as they break down in landfills. Additionally, if biodegradable materials are not managed properly once they become waste, they may not break down as intended. Despite these concerns, biodegradable fiber polymer composites are a promising alternative to traditional synthetic composites due to their potential advantages.

Advantages of biodegradable fiber polymer composites :

- Environmental friendliness: Biodegradable composites are made from natural fibers that are renewable, abundant and biodegradable, making them more environmentally friendly than synthetic composites.
- Low cost: Natural fibers are cheaper than synthetic fibers, making biodegradable composites more cost-effective.
- Lightweight: Plant fibers are lighter than glass, carbon, and aramid fibers, making biodegradable composites lighter and more suitable for certain applications.
- Sustainable: Biodegradable composites are sustainable and renewable, making them a viable alternative to non-renewable synthetic composites.

Disadvantages of biodegradable fiber polymer composites :

- Poor interfacial bonding: Natural fibers may have poor interfacial bonding with the polymer matrix, leading to reduced mechanical properties.
- Water absorption: Natural fibers may absorb water, leading to swelling and reduced mechanical properties.

- Limited applications: Biodegradable composites have been limited to certain applications such as the automotive and decking market.

Overall, biodegradable fiber polymer composites have the potential to be a sustainable and cost-effective alternative to traditional synthetic composites, but further research is needed to address their limitations and expand their applications [3]. Plastic materials produced from petrochemicals are widely used in packaging, automotive, healthcare applications, and communication or electronic industries. As these conventional synthetic polymers are not easily degraded because of their high molecular mass and hydrophobic character, they may accumulate in the environment and represent a significant source of environmental pollution potentially harmful to wildlife [3-6]. During the last few years, biodegradable polymers with suitable mechanical and physical properties have received particular attention to replace petroleum-based plastics.

A necessary prerequisite for extending their utilization is their biodegradability in natural environments, where they may serve as a source of carbon and energy for a variety of microorganisms [6]. Usually biodegradation studies are carried out in soil and/or compost, in particular, enhanced biodegradation of these materials may occur in the presence of compost, a complex biological environment, in which microbial diversity is relatively high and an increased degradation potential for polymeric compounds may results [7]. Moreover, it is commonly used in ISO standard test method.

Polylactic acid (PLA), classified as an aliphatic polyester because of the ester bonds that connect the monomer units, has gained a key role in the biomedical field for a wide range of applications: suture threads, bone fixation screws, devices for drug delivery, just to scratch the surface. PLA merges several interesting properties that make it an ideal candidate for biomedical applications. PLA naturally degrades in situ through hydrolysis mechanism: water molecules break the ester bonds that constitute the polymer backbone. This eliminates the necessity of additional surgeons in order to remove the device, improving patient recovery and optimizing health system costs.

The main phenomena involved in the degradation mechanisms and the most important factors that influence hydrolysis rate are currently well-established in scientific literature, thanks to a dedicated research activity that reached its peak between the 1980s and the 1990s. Consequently, the degradation kinetics and mechanical properties can be tailored by properly tuning some polymer properties (such as composition or molecular weight), thus leading to the development of biomedical devices optimized for each specific application. Degradation products (composed of lactic acid and its short oligomers) are recognized and metabolized by the body itself: this gives PLA an intrinsic biocompatibility that dampens the attainment of critical immune responses.

In addition, PLA can be processed with standard and established technologies, such as injection molding, polylactic acid (PLA) is a biopolymer matrix that has been widely used in the manufacture of biocomposites. Coir fibers have been used as a reinforcement material in biodegradable fiber polymer composites due to their low cost, high strength, and biodegradability. Bentonite, a natural clay material, has been used as a filler material in biodegradable fiber polymer composites to improve their thermal behavior.

- PLA is preferred among biopolymers due to its adequate compatibility with various natural reinforcements and comparable mechanical and physical properties.
- Coir fibers have been used as a reinforcement material in biodegradable fiber polymer composites due to their low cost, high strength, and biodegradability.
- Bentonite has been used as a filler material in biodegradable fiber polymer composites to improve their thermal behavior.
- The addition of bentonite fillers from North Aceh and Central Aceh to PLA/coir composites has been shown to improve their mechanical strength and thermal behavior [8,9].

PLA can be formed through the esterification process of lactic acid obtained by fermentation of bacteria using starch or simple sugars as substrate [9]. Another advantage of PLA is that it is transparent and safe to use in the medical field. Recent applications of PLA in other fields such as medicine include its use as artificial skin, surgical thread, drug capsules, and also for tissue engineering because it can be absorbed by the body. However, this biopolymer also has a weakness, which is that one of its melting points is lower than that of other plastic polymers, so its heat stability is not as good as other polymers [9].

Coir is a residue from coconut production in many areas, which produces coir fiber [10-12]. Coconut coir is a natural lignocellulosic fiber. It is a fruit fiber obtained from the outer shell or husk of the coconut. This fiber is widely used to make various types of flooring materials, furniture, yarn, rope, and others. Coconut coir almost reaches 1.7 million tons from the production of about 5.6 million tons of coconuts per year. The huge potential of coconut coir waste has not been fully utilized for production activities that have added economic value. Without optimal utilization, this waste will only cause environmental problems. Coconut coir contains fibers that are an alternative to natural fiber materials in composite manufacturing. Coconut fiber is being considered for use because it is not only easily obtained and cheap, but it can also reduce environmental pollution (biodegradability). Therefore, using coconut coir as a fiber in composites can address environmental issues that may arise from large amounts of unused coconut coir. This composite is environmentally friendly and does not pose a health hazard, so its use continues to be developed to produce more perfect and useful composites [12-14].

There are many types of materials used as fillers, ranging from various types of plant fibers and other organic materials such as soil or clay (bentonite) [15]. Natural plant fibers such as bamboo, hemp, sisal, pineapple, oil palm empty fruit bunches, and coconut coir have been studied as reinforcements and fillers in composites. Bentonite is a natural colloid of hydrated aluminum silicate.

It has the ability to expand, ion exchange properties, a large surface area, and easy water absorption. In addition, the surface acidity of bentonite is related to Bronsted and Lewis acids, allowing it to be used as a catalyst. Bentonite is one of the minerals with various benefits in daily life. It can be used as a binding material in casting sand, raw material for making cement, ceramics, cosmetics, crayons, as an adsorbent, in the pharmaceutical field, and so on [. Bentonite itself consists of 2 groups, namely sodium bentonite (swelling bentonite) and calcium bentonite (non-swelling bentonite) [16-19].

One of the fillers that can be used is bentonite. Bentonite is generally used for refining cooking oil. Before being used as a filler, bentonite must be regenerated first. In addition, bentonite is generally activated using a surfactant first. This activation process aims to create a distance between the surfaces of bentonite (interlayer distance or basal spacing) so that bentonite can form various forms of nanocomposites with PLA [20].

Bentonite is a type of clay that is formed from volcanic ash. Unlike ordinary clay, bentonite contains ions which make it negatively charged so that it has the ability to absorb poisons containing positive ions, relieve inflammation and kill bacteria. Bentonite is an abundant mineral resource found in Indonesia. The mineral bentonite has a diameter of less than 2 micrometers and consists of various siliceous phyllosilicates, aluminum oxide and hydroxide which bind water. The bentonite structure consists of two layers (three layers) which are composed of two layers of tetrahedral silica and one central octahedral. The physical properties of the clay (bentonite) greatly influence its utilization, examining the qualitative properties and mineral composition that determine its good behavior.

Therefore, significant efforts have been made to improve the performance of this composite. Several different techniques have been used to optimize the composite interface properties, such as surface modification of fibers through physical or chemical routes and the use of appropriate additives such as Sodium Hydroxide (NaOH) as a bleaching agent [21]. NaOH has the ability to remove fiber color by eliminating lignin, hemicellulose and impurities on the surface. Therefore, it is interesting to investigate whether the use of fiber bleaching processes can improve composite properties in terms of appearance and performance. NaOH has the ability to remove fiber color by eliminating lignin, hemicellulose and impurities on the surface.

The use of alkali solution as a treatment step for fibers has been carried out. One example is done by Kuncoro, where polyester filled with hemp fibers was treated with an alkaline solution, namely sodium hydroxide (NaOH) solution. The resulting composite has a tensile strength of 190 MPa and an elastic modulus of 45,795 GPa (Diharjo & Kuncoro, 2006). Research conducted by Rohatgi stated that soaking coconut fibers in a 5% NaOH solution for 72 hours provides the best tensile strength (Rohatgi, 1983). In contrast, Mohanty stated that soaking in a 2% NaOH solution for 1 hour provides optimum tensile strength [21-23].

In this study, an attempt was made to modify the combination of PLA (Poly Lactid Acid) polymer with coconut coir fiber and bentonite fillers. By varying the filler volume fraction: filler at 80%:20%, 70%:30%, 60%:40%, and 50%:50%. The coconut coir fiber used as a filler is first modified using NaOH with variations in concentrations of 30% and 40% as a preliminary step before being mixed with PLA polymer. The PLA-coir-bentonite composite is formed by mixing through a melting method with an extruder and hot press. The type of natural fiber (coconut coir) and bentonite used affects the increase in biodegradability, mechanical properties, and thermal properties, showing the presence of increasing molecules based on the results of tensile tests, TGA (thermal) tests and morphology using scanning electron microscopy (SEM)

EXPERIMENTAL

2.1 Material

Coirfibers and bentonite were collected from North Aceh. Sodium hydroxide (NaOH) and Poly Lactic Acid were obtained from Nature Works LLC Company, USA.

2.2 Methodology

2.2.1 Chemical treatment of fibers

The chopped and dried raw fibers were immersed in a 2% NaOH solution in a beaker at room temperature for 5 h. The fibers were then removed and thoroughly washed in distilled water until the pH of the fibers became neutral. Finally, the washed treated fibers were open-air dried under direct sunlight for 10 days.

2.2.2 Treatment of bentonite

Bentonite is weighed and pounded using a hammer. Sieve with a size of 250 mesh. Bentonite from the sieve was put into 1200 ml of distilled water and then dispersed by stirring for 6 hours using a magnetic stirrer with moderate rotation (scale 2). The dispersion results were then allowed to stand until a bentonite precipitate formed and was separated from water containing impurities. Clean bentonite was put back into 1250 ml of distilled water and then redispersed with a magnetic stirrer for 2 hours. The dispersion results were then centrifuged for 2 minutes at a speed of 700 rpm to be separated from the liquid. Bentonite is dried in an oven at ±105 ^{o}C until dry.

2.3 Sample Preparation

2.3.1 Preparation of nanocomposites

The fibers and bentonite were mixed with PLA granules using an extruder to ensure thorough and homogeneous mixing. Different weight fractions of fibers, bentonite and PP matrix were mixed for the fabrication of composites. The mixture was then introduced into a mold inside a hot compression machine (Model no. D.28033, HSIN-CHI Machinery Co. Ltd.) designed according to ASTM 638 and ASTM 790 standards for the desired composite thickness. The mold was pressed using a manual hydraulic press until the pressure reached 1000 psi, and the temperature of both upper and lower heaters was set at 200 ◦C for 15 minutes. The mold was cooled to room temperature without opening it to prevent any shrinkage during the extraction of the composite.

2.4 Characterization

2.4.1 Tensile test

Mechanical properties were tested through an Instron universal testing machine (Model 4032) following ASTM D638. The sample was clamped at both ends with one end fixed to the machine and the other end at the removable clamp. Loads were applied until the samples were broken. Five tests were conducted for each type of specimen and the average values were reported.

2.4.2 Analysis of thermal properties by thermogravimetric analysis (TGA)

The process of mass loss in the thermal test occurs due to the decomposition process, which is the breaking of chemical bonds. The TGA test results graph for samples with various results. In principle, this method measures the reduction in material mass when heated from room temperature to a high temperature, usually around 900°C. TGA is equipped with a microbalance inside so that the sample weight can be recorded automatically at any time and presented in a graphical display.

2.4.3 Scanning Electron Microscopy (SEM)

The surface morphology of the manufactured nanocomposites was examined under a Scanning Electron Microscope (JSM5510, JEOL Company Limited, Japan). The tensile fracture and cross-sectional micrographs were taken to study the fracture mechanisms and interface adhesion of the composites. The samples were sputter-coated with platinum before observation under the SEM. The micrographs are presented and described in Section.

RESULTS AND DISCUSSION

3.1 Tensile Test

Figure 3.1 below shows the results of the tensile strength test of the PLA/Coir/bentonite composite. Where in this study the filler from the composite was varied, the filler was coir and bentonite. It varies from 80% : 20% meaning that the composite contains 80% coir and 20% bentonite, and so on for the next variation. From Figure 3.1 below it can be seen that the tensile strength test has increased as the filler variation has decreased. The highest tensile strength value was obtained for the composite with a filler variation of 50%: 50%, this means that the filler in the 50/50 ratio is suitable for improving the properties of the composite.

As we can see on the 80% : 20% where the composite has the highest coir content makes the composite have weak mechanical properties. Coir fiber has a lower cellulose content compared to other natural fibers, which affects the strength of natural fiber reinforced polymer composites. However, in variations that continue to show a balance between coir and bentonite it also shows good tensile strength results. This means it is a good collaboration between coir and bentonite. Coir bentonite composite has better mechanical properties than other natural composites.

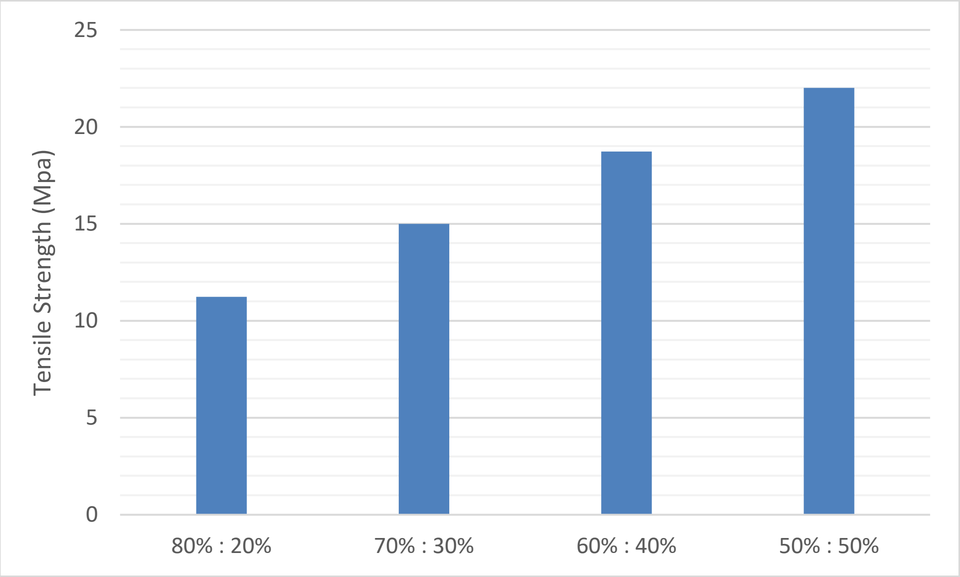

Figure 3.1 Tensile strength of PLA/coir/bentonite composites

3.2 Analysis of thermal properties by thermogravimetric analysis (TGA)

Hotthe changing reactions affect changes in the bioplastic mass, these mass changes occur because of a reaction process in the form of changes in the structure and phase of the bioplastic.Based on the graphs in Figure 3.2 and Figure 3.3 showing the results of the analysis, the composites obtained underwent decomposition up to a temperature of 600. From the graphs it can be seen that at a temperature of 200 the biocomposites began to decompose. Changes in the TGA thermogram are caused by changes in heat of reaction which are not only influenced by the mass change reaction of the biocomposite but also by the structural change (reaction) process and phase change of the biocomposite.

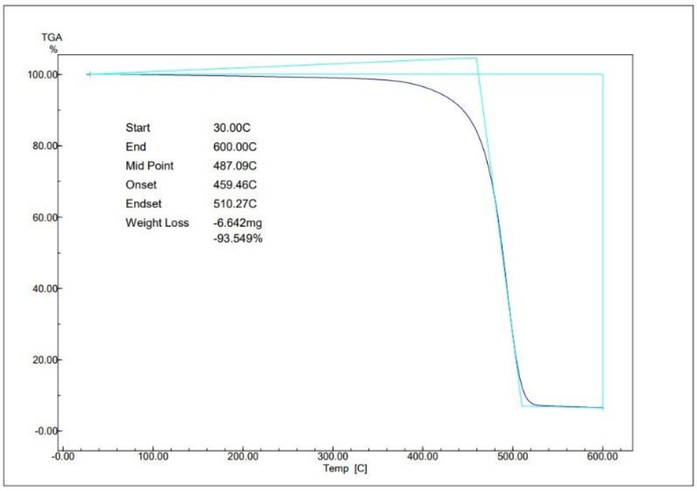

Figure 3.2 TGA 50% : 50% thermogram

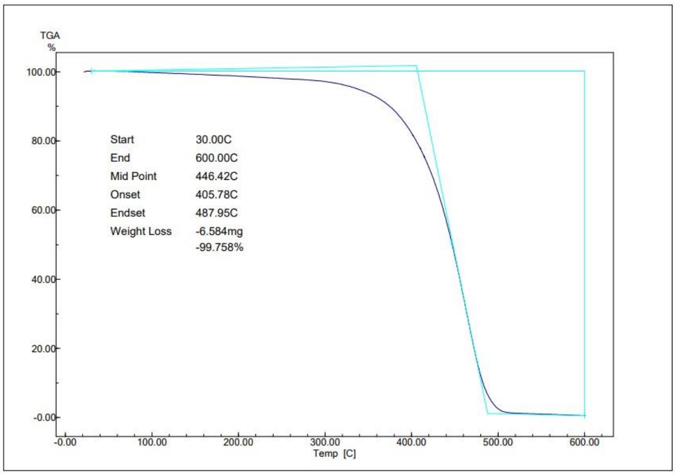

Figure 3.3 DTA thermogram 80% : 20%

These results indicate that the increase in degradation temperature is caused by the stronger bonding of the polymer and filler which makes it difficult to break and the decomposition of the material becomes slower. In samples with the addition of bentonite coir where the best tensile strength test results with a variation of 50%: 50% also show good thermal properties when compared with a variation of 80%: 20% where it can be seen that the largest mass loss is owned by the composite with a filler ratio of 50/50. This shows that the composite with a coir content of 50% and 50% bentonite can improve the thermal properties of the composite. This mass loss also affects the ability of the composite to be degraded, this means that the composite will be more easily degraded if the filler content between coir and bentonite is balanced.°C°C

3.3 Morphology Analysis usingScanning Electron Microscopy (SEM)

Tensile fracture surface morphology of typical composites was investigated through scanning electron microscopy (SEM). SEM micrographs taken at low and high magnifications are shown in Figs. 3.4 respectively. From Figs. 3.4 (a), it can be observed that there are a number of pullout traces of fiber with rough surfaces and micro-voids as well as agglomeration of the fiber in the composite. This result indicates that the dispersion and interfacial bonding between fiber/bentonite and polymer matrix was very poor. Similar results were also obtained for some composites indicating interfacial interaction and adhesion were not much improved. However, it was found from Figs. 3.4 the fiber pullout were significantly reduced from the surfaces for composites samples.

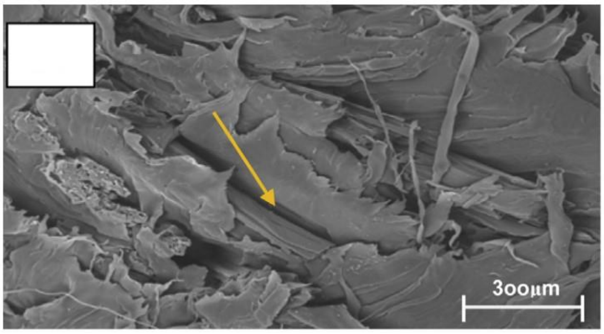

Figure 3.4 Typical SEM micrographs of tensile surfaces

CONCLUSION

The study found that natural fiber reinforced polymer composites had successfully improved their physical and mechanical properties. The interaction and adhesion between the fiber and polymer matrix were enhanced in the hybrid composites, as confirmed by TGA and SEM results. However, there were fig changes that were observed when bentonite and coir fibers were used differently. From the various comparisons made, it was found that the 50/50 composite showed good mechanical properties and thermal properties.

ACKNOWLEDGEMENTS

The authors express their gratitude and thanks to Politeknik Negeri Lhokseumawe for the educational support.

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