Mechanical properties and biodegradability of Green composites based on polylactic-acid polymer

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1 General Introduction

Eco green composites are those that are made from degradable polymer (natural plastics) and natural fibers. They have no environmental impact. Natural plastics are produced from agricultural products. Natural fibers also come from agricultural products and are materially abundant. Both are environmental friendly and renewable.

Currently, the use of natural fibers in composite materials is increasing rapidly. The industry manufacturers choose these composites owing to their superior properties. The use of natural fibers as reinforcement polymer has several advantages over synthetic fibers such as light-weight, recyclability, biodegradability, renewability, and high strength to weight ratio. However, natural fibers have some weaknesses such as poor wetability, incompatibility with some hydrophobic polymeric matrices, low melting point and high moisture absorption. Nevertheless, these weaknesses can be overcome by some chemical treatments.

One kind of natural fibers is coconut filter (CF) fiber, which is from the coconut palm tree *(Cocos nucifera)*. Very few works discussed CF fiber. Satyanarayana *et al.* [1] studied the structural properties of fibers from various parts of the coconut tree, including CF fiber. Bilba *et al*. [2] studied chemical compositions of CF fiber. Reddy *et al*. [3] studied only the effect of alkali treatment on the properties of CF fibers. In the previous work, we studied the effects of some chemical treatment on the mechanical and flammability of thermoplastic polymer [4,5].

In designing materials we must consider durability and biodegradability which are two opposite properties. Durability refers to the length of time the material is still good for use while biodegradability refers to the ability of the material to decompose at the end of their useful life. A good material should possess both of these properties [6]. In the present work, the mechanical properties and biodegradability of untreated and treated fiber-reinforced polylactic acid (PLA) composites would be compared.

2 Experimental Procedures

2.1 Materials and treatments

Polylactic-acid (PLA) is produced by Cargill Dow LLC (USA). Coconut filter (CF) fibers are obtained from Indonesia, and the fiber is separated by combing.

CF fibers were cut to a length of 5-15 mm. The fibers were rinsed with water to remove dust and impurities and then boiled at 100^oC for 1h. After that, the fibers were rinsed in tap water and then dried in the oven at 70 ^oC for 24 h.

The fibers were then treated with 6 %(w/v) NaOH in distilled water at 95 ^oC for 3 h and then washed with tap water to eliminate any residual NaOH solution. Next, they were dried in the oven for 24 h at 70 ^oC and subsequently soaked in 0.5 % acrylic acid (AA) for 0.5 h followed by rinsing in tap water. Finally, the fibers were dried in the oven at 70 ^oC for 72 h.

2.2 Composite fabrication

Weight fraction of the fibers in the PLA composites was fixed at 35 %. The Composites fabrication process has been explained in our previous study [4].

2.3 Measurements
2.3.1 Mechanical tests of the composites

The determination of tensile and three-point bending (flexural) tests procedure was also explained in our previous study [4]. The Charpy impact unnotched specimens blown in both the edgewise and the flatwise direction were carried out according to the EN ISO 179.

2.3.2 Biodegradation of composites

The compost was made by mixing fertilized soil and dry sawdust at 1:1 ratio of 500g. Fertilized soil with an initial moisture content of 50-60 %, pH 5.8-6.8, and density 0.18-0.2 g/cc was supplied by Sanglim Co., Ltd., Korea. Water was supplemented on daily basis, and the weight of the compost, specimens and water contain were maintained at a minimum of 1000 g. The composites (30 mm x 20 mm) were weighed and buried under a 2 cm deep layer of the compost medium. Five replicas were prepared for each time interval, and all the samples were incubated at room temperature for 15 and 30 days. Each specimen was excavated from the compost, washed with tap water, and finally dried in an oven at 50 ^{o}C for 12 h. Biodegradability was determined by measuring weight loss of the specimens after burial in the compost. This method is similar to that used in a previous study by Naozumi Teramoto *et al.* [7] and Lifang Liu *et al.* [8]. The weight loss W_{loss} (%) was calculated using the formula [8]:

$$W_{loss}(\%) = \frac{W_o - W_t}{W_t} x100 \qquad (1)$$

where W_o and W_t are the weights of specimens before and after burial in compost respectively, which are measured by digital scale.

2.3.3 Scanning electron microscopy (SEM)

The fracture and biodegradation surfaces of composite samples were coated with gold and then examined using a scanning electron microscope (SEM) (JEOL JSM-6400 Japan).

3 Results and Discussions
3.1 Tensile Properties of Composites

In Fig. 1, alkali and AA treatment significantly improve the tensile strength and modulus. As shown in Fig. 2b and c, the interfacial bonding between alkali-treated fiber and AA-treated fiber with PLA, respectively, reveal compatibility without debonding and fibers pullout. Meanwhile, Fig. 2a clearly shows the fiber debonding and pullout for untreated fiber composite. Particularly, the AA treatment resulted in the best tensile strengths, due to the absence of hemicellulose in CF fiber which allows a better esterification of the hydroxyl groups of cellulose, thereby leading to a stronger interface contact between the fibers and polymer [9].

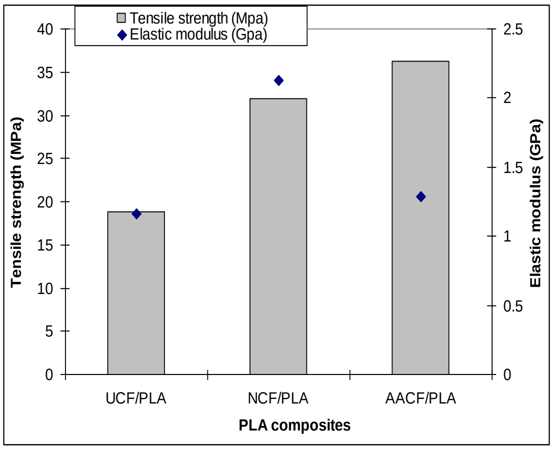

Fig. 1 Tensile strength of composites
Remark: UCF= untreated, NCF=NaOH-treated, AACF=NaOH+acrylic acid-treated of coconut filter fiber

3.2 Flexural Properties of Composites.

Fig.3 shows that alkali and AA-treatments significantly improve the flexural strengths of the PLA composites. Both flexural strength as well as tensile strength of AACF/PLA are highest.

Flexural moduli of all composites reinforced with treated fibers are also higher than those of untreated-fiber reinforced composites. This may be due to the chemical treatments having a lasting effect on the mechanical behavior of natural fibers, especially on fiber stiffness (10).

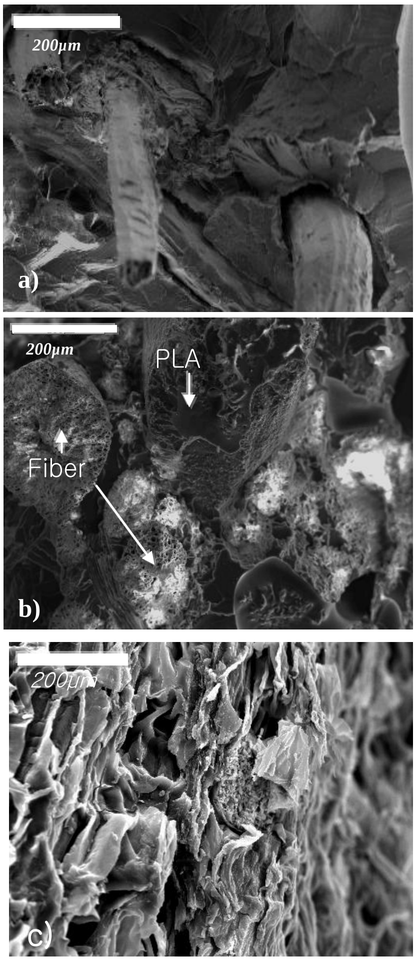

Fig. 2 Tensile fracture surfaces of: a). UCF/PLA b). NCF/PLA, c) AACF/PLA composites.

Our composites had better flexural properties than coir-polyester composites, which had been studied by S.N. Monteiro *et. al* [11].

Fig. 4a illustrates the fracture surface of UCF/PLA composite. It shows fiber pullout from the matrices. AACF/PP has the strongest interaction between fiber and matrix, as indicated in Fig. 4c. Its fracture surface seems to be uniform and has failed simultaneously [12].

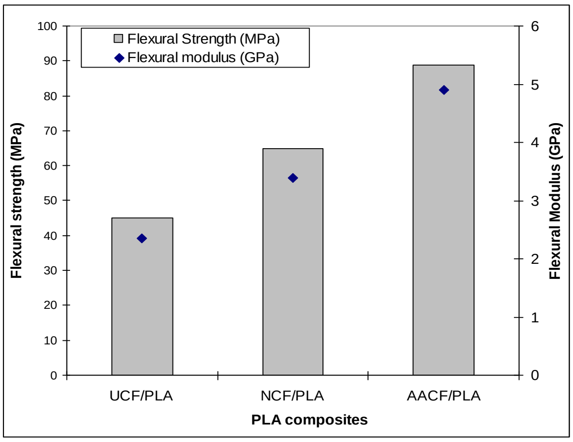

Fig. 3 Flexural strength of composites

3.3 Impact strength of composites

The incorporation of the 35 wt.% CF fibers in PLA causes a decrease on impact strength compared to that of neat polymer. This is because the ductile behavior of the matrix was reduced in the reinforcement process. Fig. 5 shows that the impact strength of composites in flatwise test is higher than in edgewise test. This higher impact strength in flatwise samples could be due to the additional energy required for the crack initiation in the flatwise specimens compared to the edgewise specimens. It can be observed from the fracture form that flatwise specimens do not have completely fractured, but only hinge break.

The composites with AA-treated fiber yield the highest impact strength. It appears that AA treatment provide effective resistance to crack propagation during impact test because of improvement of interfacial adhesion between AA-treated fiber and PLA matrix.

3.4 Biodegradation

Fig. 6 shows that after 30 days, the composites were degraded more than it were in 15 days. The magnitudes of weight loss decreased in the following order: alkali-treated, untreated, and AA-treated fibers. The weight losses for all composites may occur due to the combined effects of leaching and biological attack [13]. The weight loss of the NCF/PLA (1.56%) compared to AACF/PLA (0.41 %) was four times.

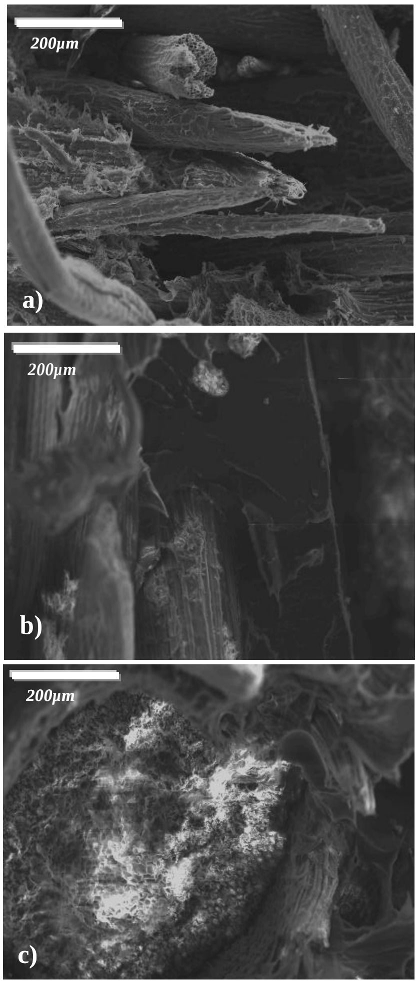

Fig. 4 Flexural fracture surfaces of: a). UCF/PLA b). NCF/PLA, c) AACF/PLA composites.

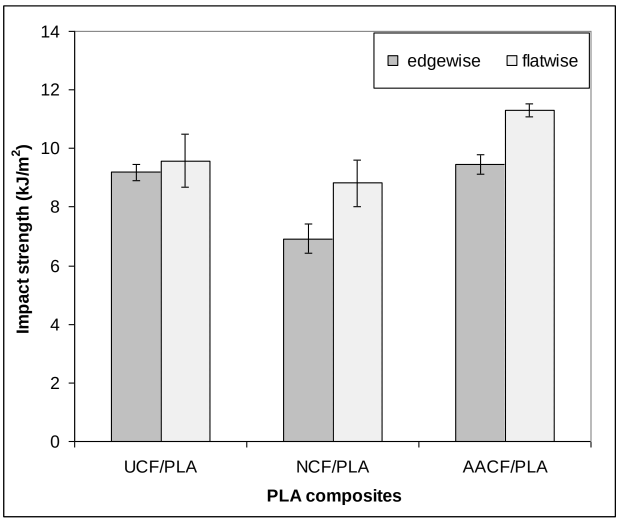

Fig. 5 Impact strength composites

In this study, the weight loss of untreated fiber PLA composite was also high, indicating that there was significant contribution of organic degradation during these tests. A low degradation rate of the composites sample with AA-treated fiber may indicate that CF fibers treated with alkali followed by AA treatment conferred significant decay protection to the natural fibers. These results were supported by the observation in SEM of degraded surfaces. Significant fragmentation was observed, randomly dispersed all along the surface of the PLA composite with alkali-treated fibers after 30 day burial (Fig. 7a). Fewer areas of fragmentation were noted on the PLA composite reinforced with AA-treated fibers for the same burial time (Fig. 7b), suggesting that the fibers in the NCF/PLA were less protected than in the AACF/PLA composite, so the fibers decay more easily. More specifically, biodegradation of NCF/PLA composite proceeds from both external and interface surfaces. The surface of composites near the fiber is more susceptible to breakage. SEM (Fig. 8a-c) images support the NCF/PLA composite analysis, as the composite surfaces appeared increasingly cracked and broken with increasing burial time in the compost. After buried for 15 days, fragmentation growth on the surface was observed (Fig. 8b). After 30 days, fragmentation and some destruction became apparent (Fig. 8c), which may have been due to biodegradation by bacteria.

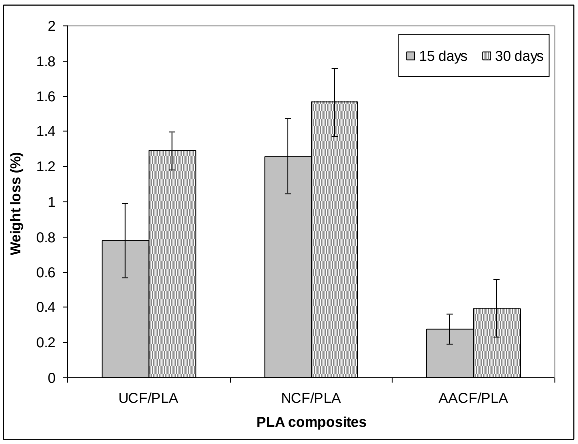

Fig. 6 Biodegradation of composites

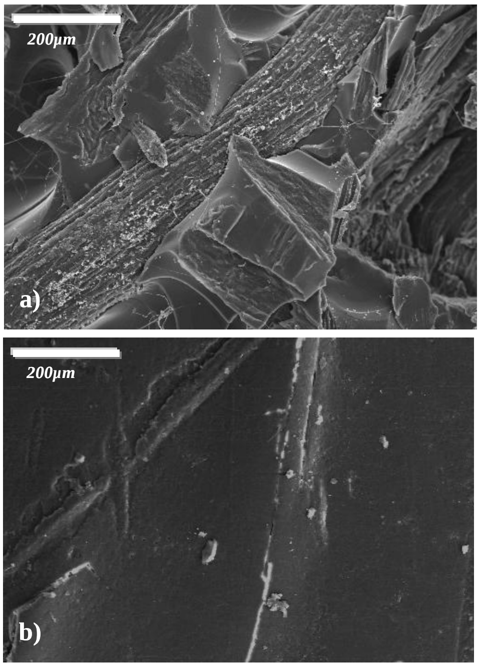

Fig. 7 SEM of: a). NCF/PLA and b). AACF/PLA composites after burial time 30 days.

3.5 Effect of biodegradation on flexural properties

Flexural properties of composites after burial in compost were determined and the results are presented in Fig. 9. The flexural strengths of composites decrease with increase in burial time. The decrease of flexural properties is about 20 – 60 % after being buried 30 days in the compost. This may be due to the swelling and degradation of the fibers and also degradation of PLA, resulting in fiber-matrix debonding [13]. Fracture surfaces of PLA composites after flexural testing showed that debris of the PLA increased with increasing burial time, especially for the NCF/PLA composite (Fig. 10).

4 Conclusions

Based on the discussions, the following conclusions can be drawn:

1. Treated-fiber reinforced PLA composites exhibit higher tensile and flexural properties than those of untreated-fiber reinforced composites, with AA-treated possesses the highest tensile, flexural and impact strengths compared to other treatments.
2. The lowest degradation rate (the highest durability) of the green composites with AA-treated fiber may indicate that CF fibers treated with alkali followed by AA conferred significant decay protection to the natural fibers. Therefore, the extent of reduction of flexural properties of this composite is less than those of untreated and alkali-treated composites.

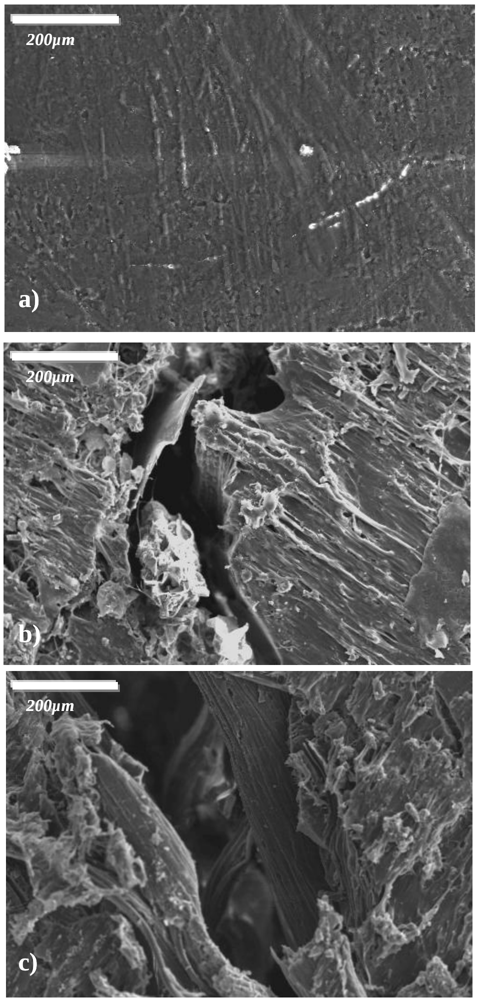

Fig. 8 SEM of NCF/PLA after burial time: a). 0, b). 15, and c). 30 days in the compost.

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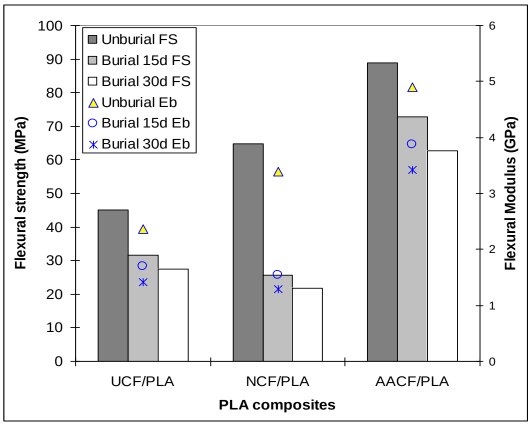

Fig. 9 Flexural properties of PLA composites.

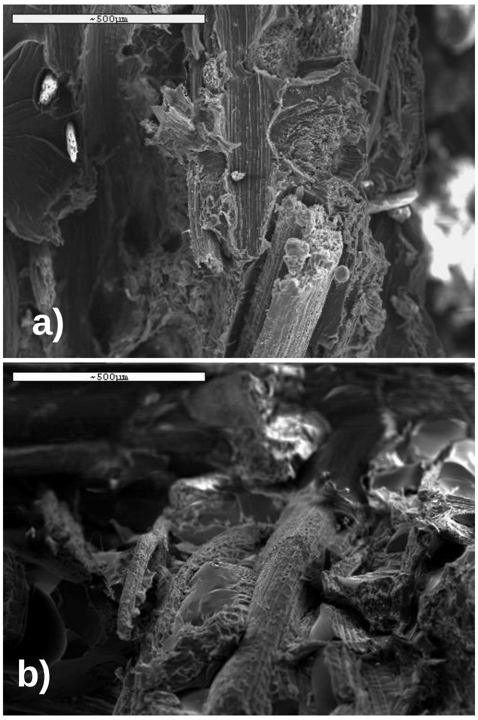

Fig.10 SEM of flexural fracture surfaces of NCF/PLA: a). without and b). 30 days burial in compost.

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