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The Effects of Alkalization to the Mechanical Properties of the Ijuk Fiber Reinforced PLA Biocomposites

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***Abstract*—**Today, the pollution due to non-degradable material such as plastics, has led to studies about the development of environmental-friendly material. Because of biodegradability obtained from natural sources, polylactid acid (PLA) and ijuk fiber are interesting to modify into a composite. This material is also expected to reduce the impact of environmental pollution. Surface modification of ijuk fiber through alkalinization with 0.25 M NaOH solution for 30 minutes was aimed to enhance its compatibility to PLA, in order to improve properties of the composite such as the mechanical properties. Alkalinization of the ijuk fibers annihilates some surface components such as lignin, wax and hemicelloluse, so the pore on the surface clearly appeared, decreasing of the density and diameter of the ijuk fibers. The change of the ijuk fiber properties leads to increase the mechanical properties of PLA composites reinforced the ijuk fibers through strengthening of *the mechanical interlocking* with the PLA matrix. An addition to enhance the distribution of the fibers in the PLA matrix, the stirring during DCM solvent evaporation from the mixture of the ijuk fibers and the dissolved-PLA can reduce amount of the trapped-voids and fibers pull-out phenomena, which can decrease the mechanical properties of the composite.

***Keywords*—**Polylactic acid, *Arenga pinnata*, alkalinization, compatibility, adhesion, morphology, mechanical properties, volume fraction, distributiom.

I. Introduction

NOWADAYS, composite is widely used for applications such as military, construction and automotive parts. Polymers have usually used as a matrix in composites due to low cost, low density, easily in processing and comparable mechanical properties with metal and ceramic. Unfortunately polymers in applications are generally still used petro-polymers which are originated from unrenewable sources and non-biodegradable polymers [1], [2]. Meanwhile reinforcement materials usually used are glass fibers which are non-biodegradable materials. Therefore development of environmental-friendly material has been an interesting researches area.

Biopolymers offer environmental advantages such as biodegradability, greenhouse gas emissions and renewability [3]. PLA or *polylactic acid* is one of biopolymers made up by lactic acid with sugar fermentation process from corn [4]; because, PLA is made up by lactid acid so PLA belonging to bio-derived polymer. Therefore it has degradable or decomposition ability so that can substitute petro-polymer product as a matrix in the material composite [5]. PLA has properties that are comparable with petro-polymers such as PP, PE, PVC, PS because of its high stiffness, strength, clarity, gloss and UV stability [6]. PLA commonly produced by two methods, through ring-opening polymerization of lactide and direct polycondensation of lactid acid [7]. However, its physical properties such as brittleness restrict the PLA application [8]. The mechanical and thermal properties of PLA can be improved by addition of fiber or filler materials [9]. There are many researches related with PLA such as combination of PLA with oil palm reported [10], combination of PLA with ramie and jute fiber reported [11], and combination of microfibrillated-cellulose with PLA reported [12]. Glass fibers are commonly fiber materials used for making composites, but have problem related with difficult degradation after post-comsumption. Recently, the use of glass fiber can be substituted by nature fibers due to their ability to degradation and decomposition. There are many types of natural fiber such as flax, hemp, jute, kenaf, sisal, abaca, ramie, coir pineapple leaf fiber, bamboo, rice husk, oil palm and bagasse [13]. The other natural fiber that still being developed is ijuk fiber or sugar palm fiber as one of the environmental-friendly materials obtained from *Arenga pinnata* plant. Other advantage of these fiber is corrosion resistance, lower density, lower cost, low processing methods, and also always available in the nature [14]. Researches about composite using the ijuk fiber was reported by [15] merging the ijuk fiber with unsatured polyester, the ijuk fiber with epoxy [16], [17], merging the ijuk fiber with HIPS [18], [19], merging the ijuk fiber with PE [20]. Because of good biodegradability and originated from renewable sources, polylactid acid (PLA) and ijuk fiber modified into a composite is an interesting study. Later on, application of this composite material will have a potency to reduce the impact of environmental pollution.

Unfortunately, the ijuk fiber has a bad compatibility with PLA because of hydrophilic PLA and hydrophobic ijuk fiber. Mohanty et al. reported that a surface modification through alkaline treatment also known as *mercerization* can increase the hydrophilicity of natural fibers such a bamboo fiber [21]. The alkalinization through addition of sodium hydroxide (NaOH) has been widely used to clean and to modify surface of the cellulose fibers. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall [21]. This treatment also disrupts the

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hydrogen bonding in the network structure, so that increasing the surface roughness [22], [23]. Therefore this method can be used to increase adhesivity of the natural fibers with the polymer matrix through enhancing an effective surface area of the fibers.

Properties of a composite with fiber reinforcement, depend on some factors such as fiber dimension [24], direction and orientation fiber [24], void or pull-out content [25]-[29], compatibility [30]. Therefore the modification of the ijuk fiber with the PLA has to study the influence of the factors on the properties of the composite.

This research was performed to investigate alkalinization effect of the ijuk fiber to adhesivity between the ijuk and the PLA, and to study influence of the ijuk fiber and the PLA formulation and mixing technique on the mechanical properties of their composites. The experimental results were investigated by measuring FTIR to qualitatively characterize chemical content of ijuk fiber after and before alkalinization, UTM to investigate mechanical behavior of the composite, and FE-SEM to observe morphological behavior such as fracture and compatibility between the ijuk fiber and the PLA in their composites.

II. Experiments

A. Materials

Polylactic acid/PLA biopolymer type 7001D (Ingeo) was purchased from NatureWorks (Minnesota, USA). Natural fibre was purchased in local market in Depok, West Java, Indonesia. Sodium hydroxide/NaOH pellets (Merck) and the solvent dichloromethane/DCM (Merck) were purchased from PT. Sinar Bumi Nusantara (Jakarta, Indonesia). The materials were used directly without purification.

B. Experimental

The fibre was first cleaned with tap water, then cut repeatedly with a high-speed rotary cutter (2500 rpm, 1 minute) and finally sieved out to separate the long, uncut fibre from the short ones. Mesh screen (mesh No. 60) was used for this purpose. Only fibres that passed the sieve were collected and used to prepare composites. Afterwards, alkalinization was performed by immersing them in 0.25% NaOH solution for 30 minutes, then neutralised to pH 7, and finally dried at room temperature for 4 days.

Prior to composite preparation, the ijuk fiber without alkalinization (untreatment) and with alkalinization (treatment) were subjected to tensile test (UTM) using ASTM D 3379 with Chatillon LF Plus Universal Testing Machine (max. load 1 kN) fitted with tensile jig/grip. Measure of the density, observation of the morphology and qualitative analysis of compound content in the ijuk fiber were performed by using Archimedes Law, FE-SEM and FTIR, respectively.

The composition of the fiber (with and without alkalinization) in composite was set to 0, 10, 20, and 30% volume fraction. Preparation was performed by dissolving PLA in DCM and then adding the ijuk fibers in a closed system. The mixture was dried by keeping on the magnetic stirrer to evaporate DCM at room temperature for one night. Finally the composite was ready to be characterized by measuring tensile test (UTM) using ASTM D 1708 with Chatillon LF Plus Universal Testing Machine (max. load 1 kN) fitted with tensile jig/grip. Observation of the morphology and qualitative analysis of compound content in the composite were performed by using FE-SEM and FTIR, respectively.

III. Results and Discussions

A. The Ijuk Fiber Behaviours

Alkalinization of the ijuk fiber changed its surface appearance from dull into bright. This investigation was also performed by measuring dimension and density of the ijuk (see Table I). The table implies that the alkalinization leads to an annihilation of some surface components. Furthermore FTIR spectra of the ijuk fiber with and without alkalinization (Fig. 1) show an interesting comparison about some peaks. Fig. 1 implies some peaks related with C-O stretch part of hemicellulosa, pektin and lignin compound in range 1300-1000 cm^{-1} and some peaks related with C-C stretch part in ring of lignin in range 1500-1400 cm^{-1}. Comparison of transmission intensity on the FTIR spectra for the both ijuk fibers indicates that alkalinization leads to decreasing of lignin and hemicellulose content in the ijuk fibers. These results are confirmed by [31].

TABLE I
Physical Properties of the Ijuk Fiber

The Ijuk Fiber	Diameter,µm	Density,g/cm^3	Appearence
With Alk. (TR)	376	1.29	Dull
Without Alk. (UT)	344	1.26	Brigtht

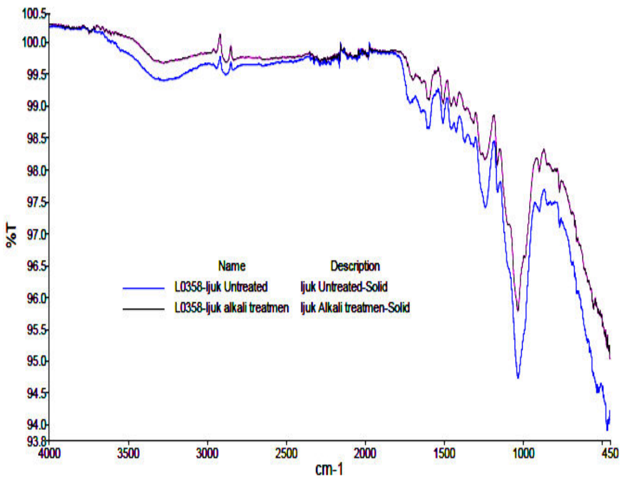


Fig. 1 FTIR Spectra of The Ijuk Fiber with and without alkalinization

To compare in detail the surfaces of the ijuk fiber with and without alkalinization, morphologies of the ijuk fibers were observed by measuring FE-SEM. Fig. 2 confirms that the alkalinization leads to an annihilation of some components on fiber surface so the pores on the surface clearly appeared. Condition of this pores then may enhance the mechanical properties of PLA/ijuk fibers composite through *the mechanical interlocking mechanism* [32] with the matrix.

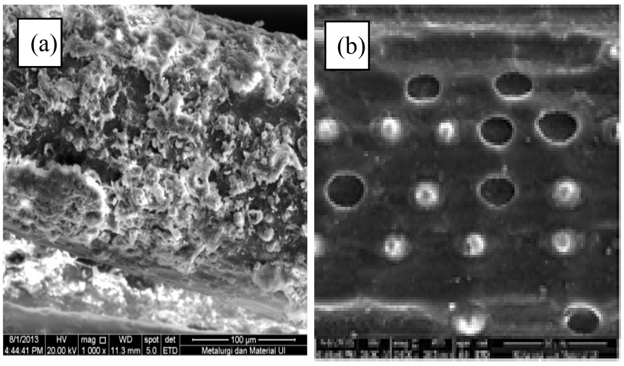


Fig. 2 FE-SEM images of morphology of (a) ijuk fiber without (UT) (b) ijuk fiber with (TR) alkalinization

TABLE II
MECHANICAL PROPERTIES OF THE IJUK FIBER

The Ijuk Fiber	Tensile strength, MPa	Modulus Young, GPa
With Alk. (TR)	187.44	1.83
Without Alk. (UT)	182.21	1.23

Further study was performed to investigate influence of the alkanization on mechanical properties of the ijuk fibers. Table II indicates that alkalization decreased the mechanical properties of ijuk fiber. This tendency may be caused by decreasing content of hemicelulosa, lignin and pectin after the treatment. Furthermore [31], [33] reported that combination between lignin and pectin have a role to bind celulose-hemicelulose network in fiber where the network is responsible to the mechanical properties. The results indicate that alkalinization in order to enhance compatibility of the ijuk fiber to PLA has a restriction due to decreasing of the mechanical properties of the fiber.

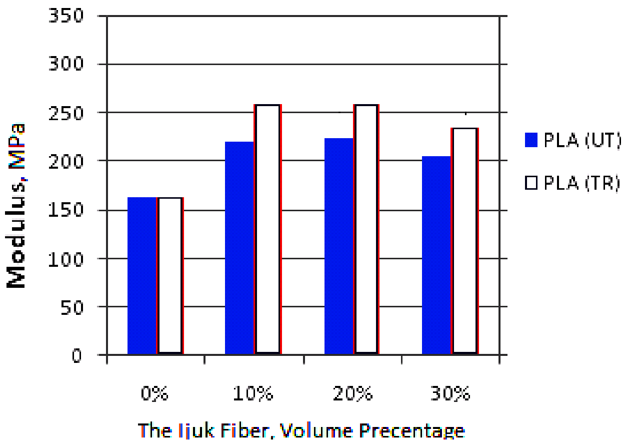
B. Mechanical Behaviors of PLA/the Ijuk Fibers Composite

Influence of the ijuk fiber alkalinization on its compatibility to PLA matrix, is studied by investigation of mechanical properties of PLA/the ijuk fiber composites. The mechanical behavior analysis is then supported by observing morphology of the studied composites.

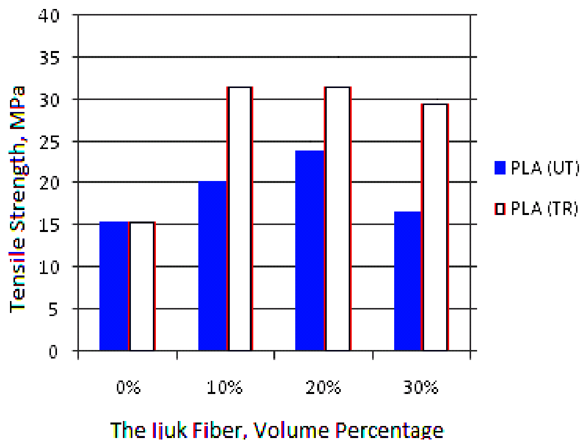
Fig. 3 implies that addition of the both ijuk fibers with and without alkalinization in PLA leads to enhancement of mechanical properties such as modulus Young and tensile strength of the composites. This tendency may be caused by reinforcement of the ijuk fibers in PLA which is suitable with the mixture equation for a composite.

Comparing the elastic modulus and the tensile strength values for composites reinforced the ijuk fibers with and without alkalinization, Fig. 3 also reveals that the alkalization is able to enhance the compatibility of the ijuk fibers to PLA. Further investigation was performed by observing morphology on the PLA composites reinforced the ijuk fiber with (TR) and without alkalinization (UT), as shown in Fig. 4. The figure shows that alkalization, because the compatibility between matrix and fiber improved. It can be checked by surface adhesion.

Surface adhesion between PLA matrix and the ijuk fiber without alkalization is low indicated by some small gaps between them. Meanwhile morphology of the PLA composite reinforced the ijuk fiber with alkalization reveals no small gap. It indicates that alkalization has been able to enhance the compatibility of the ijuk fibers.



(a)



(b)

Fig. 3 (a) the Young modulus and (b) tensile strength of the PLA composites reinforced the ijuk fiber with (TR) and without alkalinization (UT)

Fig. 3 also shows a significant decrease of both elastic modulus and tensile strength value after 20% of the ijuk fiber volume fraction. This decreasing may be caused by voids and fibers pull-out in the composite. The reasons are confirmed by morphology observations on the composites, as shown in Fig. 5. Voids may be resulted from volatile substances [26] such a dichloromethane (DCM) solvent that was trapped in bulk area after drying composite. Voids and fiber pull-out phenomena can cause a decrease of the mechanical properties of the composites [34]. Void causes no compensation to stress concentration and then initiates a cracking that triggering the failure of composites. Besides that, fiber pull-out phenomenon causes a bad surface adhesion due to fiber length below critical fiber length [29]. This behaviors can be reasons to a decreasing of both elastic modulus and tensile strength after 20% of the ijuk fiber volume fraction.

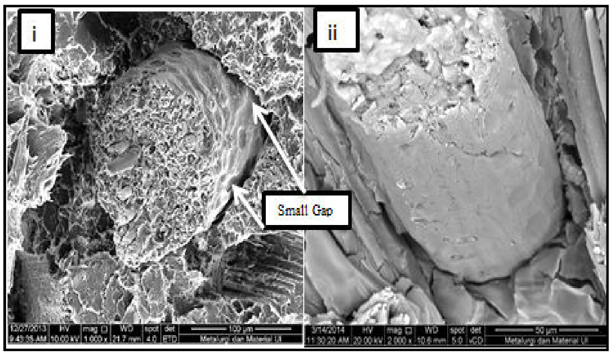


Fig. 4 Morphology on the PLA composites reinforced the ijuk fiber (i) without alkalinization (UT) and (ii) with (TR)

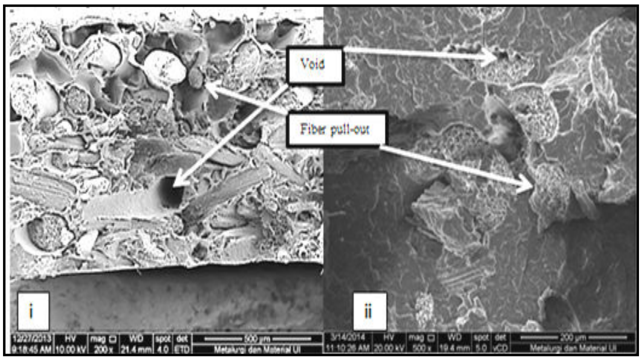
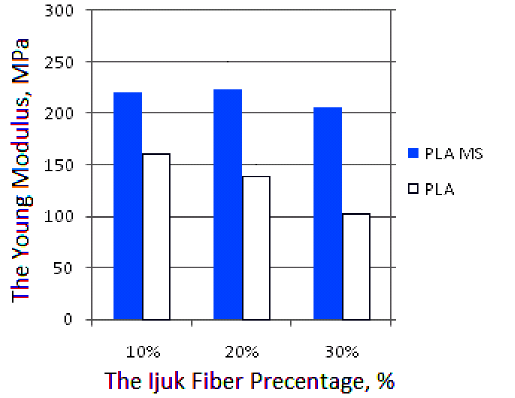


Fig. 5 Morphology on the PLA composites reinforced with (i) 30% and (ii) 20% of the alkalized

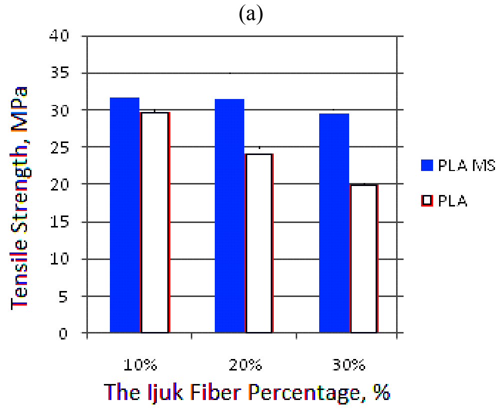
C. Distribution of the Ijuk Fibers in the Composites

The mechanical behavior of the fiber reinforced composite depends on distribution of the fibers in the PLA matrix. The distribution of the ijuk fibers can be controlled by stirring at DCM solvent evaporation from the mixture of the ijuk fibers and the dissolved-PLA. This investigation was performed by comparing the mechanical properties of the PLA composites which are dried with stirring (MS) and without stirring.

Fig. 6 indicates that stirring at drying leads to enhancement of the mechanical properties such as the Young modulus and the tensile strength (comparison of the PLA MS and the PLA diagrams). This tendency is confirmed by morphology observation of the related composites, as shown in Fig. 7. The figure reveals that the PLA composite which was dried with stirring has a better distribution of the ijuk fibers than without stirring. The fibers that well distributed cause a strengthening mechanism whole part of the composites [29].



(a)



(b)

Fig. 6 (a) the Young modulus and (b) tensile strength of the PLA composites which was dried with stirring (MS) and without stirring

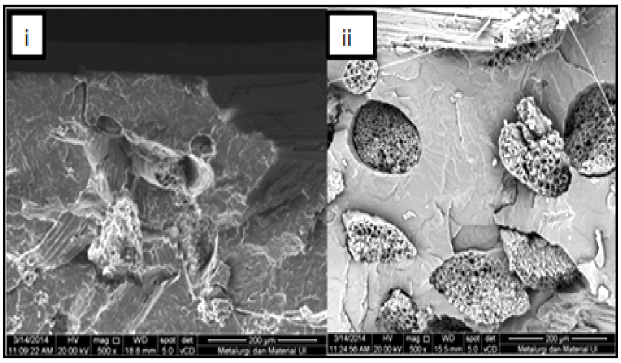


Fig. 7 Morphology of the PLA composites which was dried (i) without stirring and (ii) with stirring (MS)

Fig. 6 also implies that a decreasing of the mechanical properties with increasing of the ijuk fibers volume fraction in the composites. This tendency may be caused by increasing probability amount of trapped-voids and fibers pull-out in the composites. This results lead to a conclusion that the stirring may be able to reduce amount of trapped-voids and fibers pull-out in the PLA matrix.

IV. Conclusions

Alkalinization of the ijuk fibers annihilates some surface components such as lignin and hemicelloluse, so the pore on the surface clearly appeared, decreasing of the density and diameter of the ijuk fibers. The change of the ijuk fiber properties leads to increase the mechanical properties of PLA composites reinforced the ijuk fibers through strengthening of *the mechanical interlocking* with the PLA matrix. Therefore the alkalinization can enhance the compatibility of the ijuk fibers to PLA. Addition of the alkalinized-ijuk fibers into PLA should consider the trapped-voids and fibers pull-out phenomena. Those phenomena may be minimized by stirring during DCM solvent evaporation from the mixture of the ijuk fibers and the dissolved-PLA. The stirring during the evaporation can also enhance the distribution of the fibers in the PLA matrix, which lead to enhancement of the composite mechanical properties.

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