Physical and mechanical of breadfruit leaves-polyethylene composites

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Abstract. A degradable polymeric composite was prepared from polyethylene (PE) and breadfruit leaves tree powders. Breadfruit leaves tree powders were mixed with PE in an internal mixer at a temperature above the glass transition of PE without additives. Formulations were based on PE/leaves ratio of 100/0, 90/10, 85/15, 80/20 and 75/25 on a dry weight basis. The effect of leaves powders of 140 and 100 meshon the composite mechanical properties was evaluated by means of universal testing machine (UTM) and hardness Rockwell tester. The results showed increases of elastic modulus and flexural modulus of the composites with increasing leaves powders. Tensile strength, yield strength, yield strain, and hardness decreased with increasing percentage of leaves powders in the composites. Flexural strength was slightly decreased with the presence of the leaves powders but independent on the percentage of the leaves powders. In general, the composite properties of 140 mesh leaves powders were more enhanced compare with that of 100 mesh. PE/leaves composites increased water absorption and caused the bulk composite surface more porous. Hence, oxo-biodegradation processes will more easily take place in the PE/leaves composites.

1. Introduction

Single-use articles and packaging waste materials such as food packaging, small container, wrap, shock absorberare produced every day. In municipal region, the quantity of packaging waste is increasing from day to day. Waste removal, using an incinerator may be a way to solve the problem on a long term, but it sometimes produces air pollution and it requires high investment and operational cost. Recycling is an environmentally attractive solution. However, only a minor portion of plastics is recyclable, and most plastics end up in municipal land fill sites. Natural decomposition and/ or natural degradation are believed the best way to solve the plastics waste problem. Packaging material should be designed appropriately to meet this purpose.A scientific solution can form a more significant contribution to this municipal problem.

Polylactic acid (PLA) is known as a biodegradable plastic with good mechanical properties [1-2]. The disadvantage of this plastic is too expensive as a packaging material as well as needs relative long time to be biodegraded. Pure PLA showed no weight and tensile strength change over 1 year in a soil buried treatment and looked like new or no discoloration, pitting [3].While blends of starch/PLA for the same treatment showed significant change in weightandtensile strength after 3 months.

The role of starch was very significant for degradation initiation of the starch/polycaprolactone composites [4]. In previous papers, starch/PEcomposites [5-20], lignin/PE [21-24], husk/PE [25-27], cellulose/PE [28-32], and wood flour/PE [33-34] showed that all of the biomass were being interest for research.Preparation of biodegradable films by acetylated acid modified rice starches and the thermal properties have been extensively studied [35].Thermoplastic starch could be an ideal matrix for packaging material or single-use articles, because it is a renewable resource material and biodegradable [36]. Since water is a plasticizer for starch, the performance of thermoplastic starch may be unstable and depending on the moisture contents, being in equilibrium with the ambient relative humidity [37]. A product made from thermoplastic starch is sensitive to water and inclined to retro-gradation which limits its application. A product composed from pure thermoplastic starch will become unstable in a moist environment and its mechanical performance will decrease strongly. For a practical extension of the utilization of starch-based products, reinforcement or modification of starch is essential. Efforts[38-39] have been made to provide suitable alternatives to upgrade starch-based product performance. However starch is consumed as food and still relatively expensive to be used for starter of degradability of the plastic composites.

Leaf-tree is one of biomass which has not been reported yet for producing polymer composites. A fall leaf treeis good availability and the lowest economically comparing to the starch, lignin, cellulose and wood. Besides, preparation of leaf flour needs the lowest energy compare to that of biomass flour in question.Since no reported data regarding leaf/plastic up to date, we would utilise the fall leaf as a degradable starter in our composites.

Biomass polymer and agricultural production are enviromentally easier degradable. In this context, polymers from biomass have been advocated as environmentally friendly alternatives to unmodified polyethylene. On a few practical application fields of packaging either blending or composites, it is strongly desired that these materials naturally degradable or at least compostable after their servises. As per standards [41-45], a minimum level of mineralization needs to be exhibited for the material to be classified as ‘‘compostable’’. Since during lifetime and after become waste packaging materials can be exposed to sunlight, heat, oxygen, moisture and micro organisms, it is of great importance to investigate the durability of these materials when exposed to these conditions. Firstly, only the effect of water on degradability will be investigated.

This study aimed to investigate the optimal formula and operational conditions for preparing the leafs-plastics composites, to characterize the physical and mechanical properties of the composites. Blending leaf-tree and plastics is one of the alternatives to upgrade the natural degradability properties.

2. Experimental

2.1. Materials

The sample used in this experiment was Polyethylene (PE) produced by PT. Chandra Asri Petrochemical, Tbk. Indonesia. Lot number MI-LLD 45-12. It contained a conventional thermal stabilizer of undisclosed composition.The falled breadfruit leafs were washed and sun-dried, crushed and shaker sieved for 100 and 140 mesh. Powder violet leafs were dried in Nabertherm oven at 105^{o}C for at least 24 h. Water content was kept below 1% before melt blending.

2.2. Breadfruit leaf-based composites preparation

Variousleaf concentration of0, 10, 15, 20 and 25 wt% were melt blended with PE using an *Internal Mixer* (Labo Plastomill Model 30R150, Toyo Seiki Ltd. Japan, Capacity of 60 ml) at the set up temperature of 135^{o}C. The screw rotation was kept of 50 rpm. The mixing was stopped for mixing time of 8 min.

The composite sheets were prepared from the melt blended samples using a hand-press Gonno (ram stroke diameter 152 mm, capacity 37 ton). Pressing temperature was set at 130^{o}C. The melt blended samples were pressed in such a way till the end of the processing pressure of 50 kg/cm^2. After pressing for around 8 min, the sheets were dried quenching using a cold press.

2.3. Characterization techniques

Tensile properties were measured using Universal Testing Machine, Orientec Co. Ltd, Model UCT-5T. The composite sheet was cut into dumbbell according to ISO 572-2 type 5A. Dumbbell specimens were conditioned at 23^{o}C and 50% relative humidity for not less than 48 h before testing. The speed of testing was 50 mm/min.

Flexural properties were measured using the same machine with that of tensile properties. Loading *nose* and *supports* have cylindrical surfaces with radii of 5 mm. Conditioning before testing and measurement following ASTM D 790 – 02. Testing was performed by procedure B in ASTM D 790 – 02, since the samples did not break after the strain more than 5 %. The rate of crosshead motion was 13 mm/min.

In order to evaluate the hardness of the leaves composites,Rockwell Hardness Testing Machine, Matsuzawa Mrk-M was used to measure the hardness of samples. Testing procedure following ASTM D 785 – 98, using ball indenter of 12.7 mm diameter. The minor and major loads were 10 and 60 kg, respectively. The Rockwell hardness scale R (HRR) was determined 15 sec after releasing major load to minor load.

The rate of water absorption was measured by weighing the composites every day. The composites sample was cut into dumbbell ISO 527-2 type 1A, 7 specimens for each sample were prepared and weight before soaking in aquadest, then kept in room temperature. For water absorption measurement, samples were dried using absorbing toilet tissue paper. The relative weight increase (Wr) was determined with respect to the initial average weight according to equation (1).

$$Wr = ((Wd - Wi) / Wi) \times 100\% \quad (1)$$

whereas Wd and Wi were average weight at the soaking duration and the initial average weights, respectively.

Degradability of the leaves composites was investigated by measuring tensile properties after water absorption for 8 weeks, without conditioning at room temperature.

3. Results and discussion

To describe the mechanical properties of different PE composites, their elastic modulus, yield strength and yield strain were determined. Figure 1 shows the elastic modulus of 100 and 140 mesh PE composites. Elastic modulus is in general increased with increasing leaves addition, and they were higher than elastic modulus of pure PE. The elastic modulus of 140 mesh PE composites was lower than that of 100 mesh.

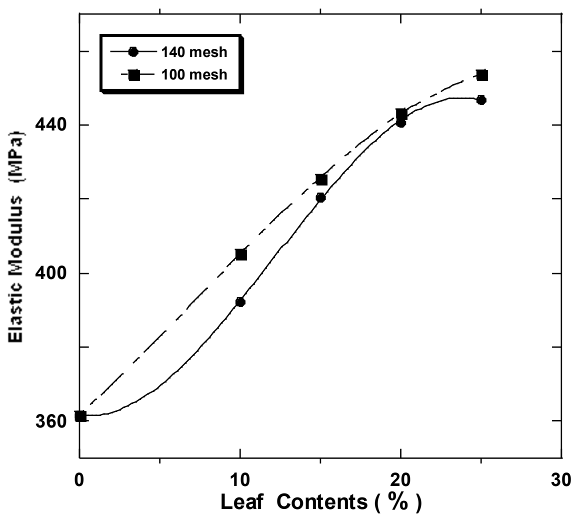

Figure 1.Tensile elastic modulus as a function of leaf contents.

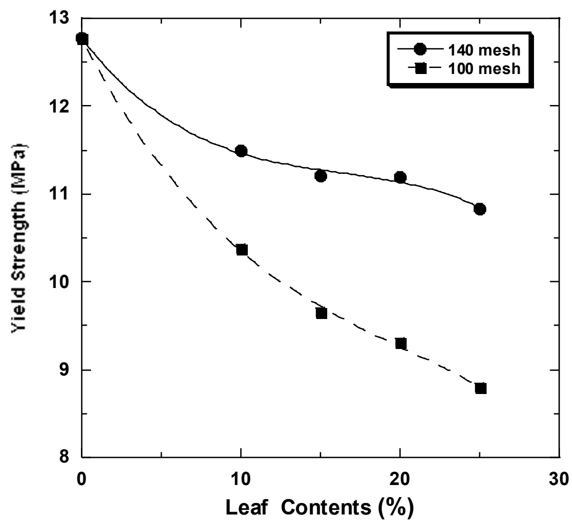

Figure 2. Yield strength as a function of leaf contents in tensile measurement.

Figure 2 shows the tensile strength of PE composites decreases with increasing leaves composition. The decreasing tensile strength was more severe in the PE composites of 100 mesh leaves. This can be explained by taking into account the adhesion of leaves powders-PE was smaller compared with the cohesion among PE molecules. For 100 and 140 mesh PE composites, tensile strength of PE composite with 10% leaves was of 84 and 90% of the tensile strength of pure PE, respectively. Composite with 100 mesh-25% leaves, shows the lowest tensile strength of 8.8 MPa.

These PE/leaves composites have the greater tensile strength compared with that of natural additive starch/ lignin LDPE blends prepared by others [46]. The tensile strength of the blends with natural additives is 6.8 – 7.2 MPa or 64% of the tensile strength of LDPE alone.

The elongation at breaking of PE/leaves composites was shown in Figue 3. Elongation at breaking for all composites was shorter than pure PE and decreased with increasing leaves content in the composites. The elongation at breaking of PE/leaves composites 100 mesh was lower than that of 140 mesh for all leaves composition. This suggests that characteristic of composites was more brittle with the higher leaves powders. The higher the leaves powders the less homogeneous composites/blends. The stress-strain curve of the PE/leaves composite did not show clear yield point.

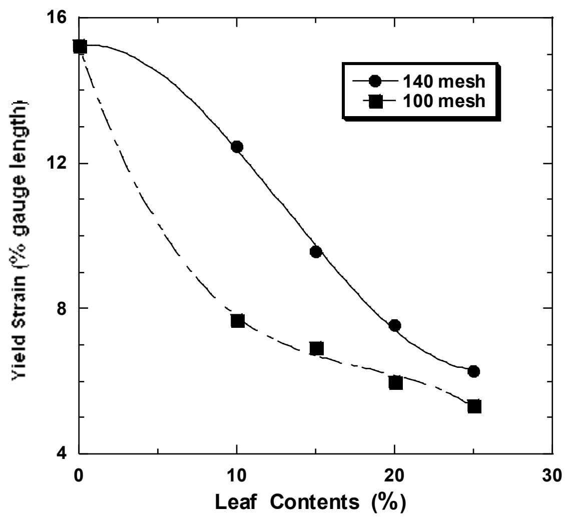

Figure 3. Yield Strain as a function of leaf contents in tensile test.

Figure 4 shows the flexural modulus of both PE/leaves composites of 100 and 140 mesh, obtained by the tangent at 0.4% of the strain. Their flexural modulus was higher than that of pure PE. The flexural modulus increased with increasing of leaves content in the composites. The highest flexural modulus was the 670 MPa, obtained from the composite with 25% leaves content of 140 mesh leaves powders. For all PE/leaves composites of 140 mesh showed slightly greater flexural modulus than that of 100 mesh for the same leaves powders content.

Flexural strength of PE/leaves composites was shown in Figure 5. For these composites samples did not yield or break within the strain limit when tested by procedure A of ASTM D 790 – 02, the testing were performed by increasing the strain rate to 0.1 mm/mm/min. However, the samples did not yield or broken within the required 5% strain limit. According to the standard, the flexural strength should be determined as the flexural stress at the strain of 5%, and the testing or loading specimen were terminated. The flexural strength of PE/leaves composites for all leaves composition was lower than that of pure PE, but seemed to be independent of the leaves contents. The flexural strength of PE/leaves composites of 140 mesh were greater than that of 100 mesh for the same leaves contents. These flexural data show that the composite are still flexible. Even though the yield strain of the tensile test show significant decreased (Figure 3), the composite was not brittle.

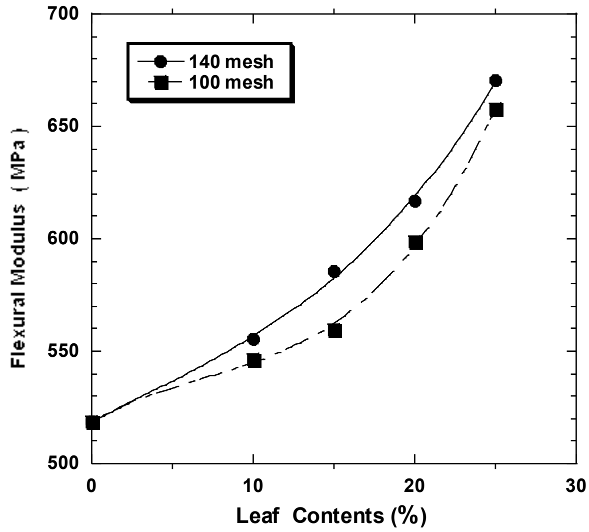

Figure 4. Flexural modulus as a function of leaf contents.

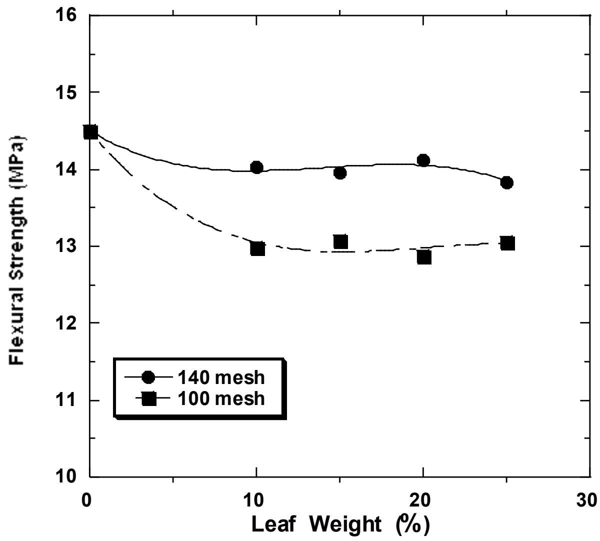

Figure 5. Flexural strength as a function of leaf contents.

Figure 6 shows the average hardness of the leaves composites as a function of leaves contents. The average hardness decreased with increasing of leaves contents. The average hardness of leaves composites of 140 mesh is higher than that of 100 mesh for the same leaves contents. The finer powder

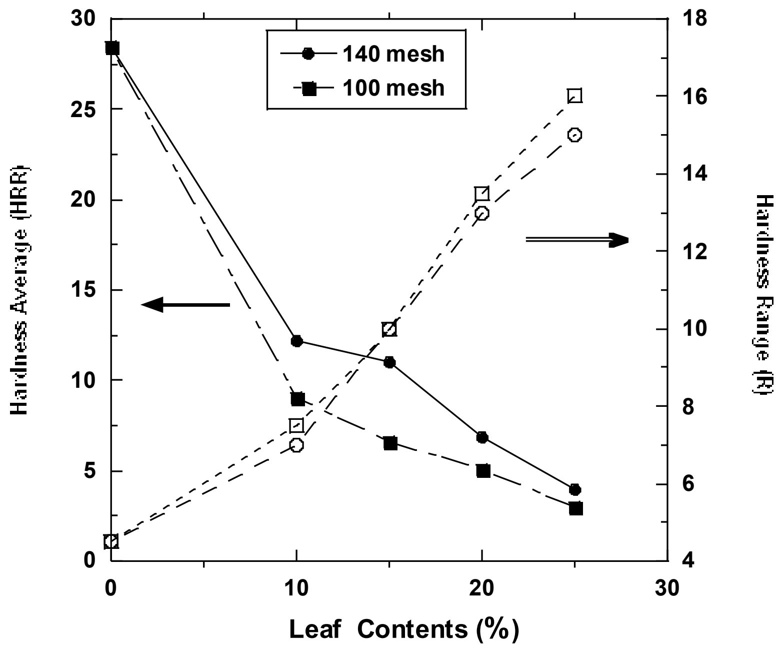

Figure 6. Rockwell hardness average and hardness range as a function of leaf contents.

leaves may resulting composites mixture more homogeneous. In hardness measurement, the indentation applied in small area, so that inhomogenity of compound was easily identified from each hardness value in a set of measurement. The range of hardness was determined from the difference of the highest and lowest hardness in a set measuring hardness for n =17, according to ASTM E18-2011. Figure 6 shows the hardness range (R) increased significantly with the increasing of leaves content in both 100 and 140 mesh composites. These facts may be attributed to less homogeneity in mixing the compounding by increasing the leaves content. To get a homogeneous mixture, the mixing time should be longer for higher leaves content.

The relative weight increased during water absorption is shown in Figure 7. For each composite shows a significant absorption after 3 days.

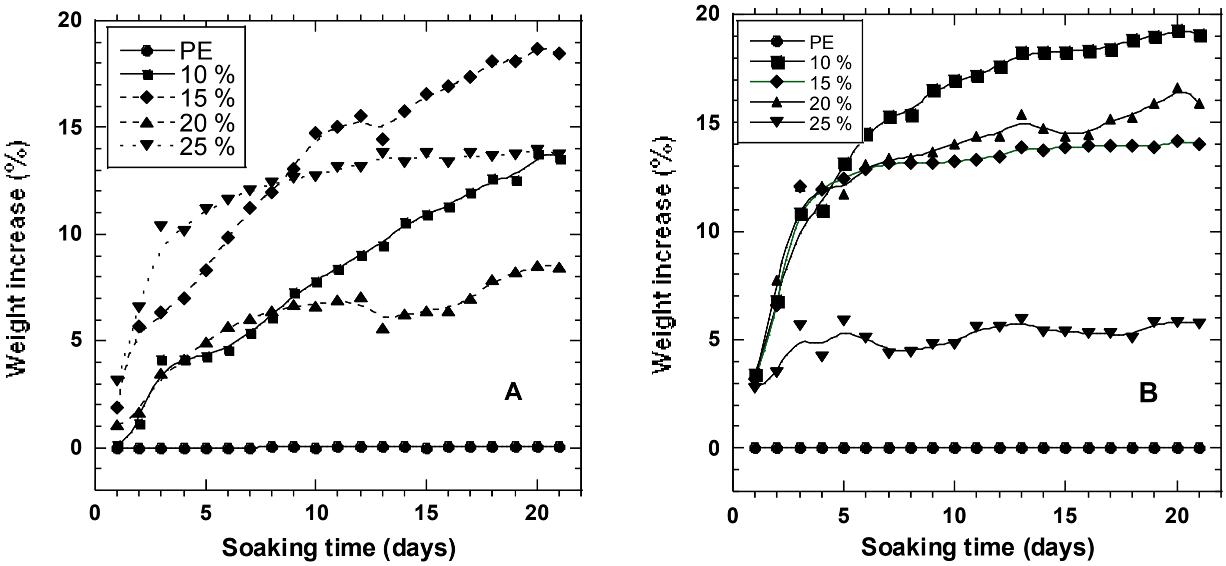

Figure 7. Relative weight increse during soaking in aquadest at room temperature.
A: 140 mesh and B: 100 mesh.

Water absorption increased with the increasing time, although the increasing fluctuation was not clear correlation with the leaves contents. The water absorption for composite 100 mesh-25% leaves increased from the 1^{st}- 5^{th} days, then almost stable until the following 3 weeks. A consequence of the water absorption was preferable by wild microorganism [47] and certain microorganism in the nature [48]. Further, biodegradation could be expected.

Figure 8 shows the elastic modulusof the leaf composites after 10 weeks soaking in destiled water. The elastic modulus of all the composites drops to around 160 MPa, whereas the elastic madulus of pure PE remain unchanged (360 MPa). Water absorption of pure PE was almost zero percent for 10 weeks (Fig. 7), so that its modulus was not affected. Upon the soaking of the composites, water absorption occured in the leaf powders. The water absorption affects interfacial adhesion between grain leaf powder and PE. The absorbed water in the leaf composite plastics deteriorated the elastic modulus of the composites and independent of the leaf contents.

Figure 9 shows the yield strength of the leaf composites after soaking in destiled water for 10 weeks. As shown in this figure, the yield strength of PE remained unchanged. The yield strength of composites decreased with increasing leaves contents. For the same leaves contents, yield strength of 140 mesh was slight greater than that of 100 mesh composites. This fact indicated that leaf composites are easy to deteriorated even only in water. The absorbed water will induces stress to PE molecules and may stimulate the PE matrix cleavage. Water molecules also disturbed the micro-structure of the PE

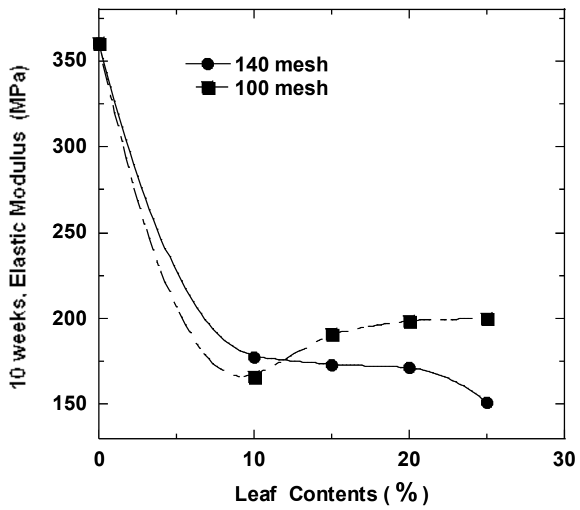

Figure 8. Tensile elastic modulus as a function of leaf contents after 10 weeks in water.

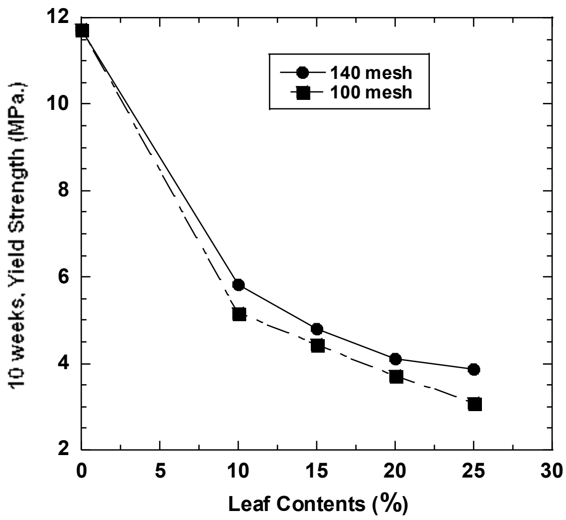

Figure 9. Yield Strength as a function of leaf contents after 10 weeks in water.

and oxo- biodegradation being started. So that the PE is further fractioned. In shortly, the absorbed water accelerate oxo-biodegradation processes [48].

4. Conclusion

Results of current work allow the comparation of PE and bio-composites characteristic. The mechanical and physical properties of the bio-composites are different fairly. Modulus elastic and the flexural modulus of the composites increased compare with that of pure PE. Whereas tensile strength, yield strength, yield strain and hardness were deceased compare to that of pure PE. The mechanical properties of the composite are changed by every kind of the leaves composition and the powder size. Leaves composites absorbed water quickly and raised stress or tension on PE molecules of which stimulated fragmentation.

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