Biodegradability of Cassava Starch/High Density Polyethylene Reactive Blend During Compost Burial

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Abstract. Starch is promising material to answer the environmental hot issues related to plastic wastes. Plasticized and gelatinized starch can behave as thermoplastic that completely biodegrade in nature. This study was aimed to investigate the biodegradability of cassava starch (CS) blended with high density polyethylene (HDPE). Simulated soil burial was applied using the compost. The blends were prepared by reactive mixing using Haake Rheomix internal mixer. The ratio of starch and HDPE was ranging from 30/70, 40/60, 50/50, 60/40, and 70/30. Dual hydrophobization was employed, i.e. addition acetic acid and polyethylene-grated maleic anhydride (PE-g-MA). Compost burial was performed indoor for 56 days. The surface appearance and morphology were investigated. Weight loss and change in tensile strength and elongation at break after burial also determined. Results findings showed that the increasing of cassava starch content and burial time decrease the tensile strength and elongation at break, however increased the weight loss of CS/HDPE reactive blend. In addition, evidence of biodegradation is shown by the appearance of some microorganism colonies on the surface of reactive blend and morphological changes in CS/HDPE reactive blend.

Keywords: Cassava starch, HDPE, reactive blend, biodegradability, compost burial

1. Introduction
A material is categorized as an ideal when stables during its service life but biodegrade rapidly in the environment [1]. By this definition, plastic is not an ideal even though it is relatively stable during service life but it hardly biodegrades when discarded into the environment. Conventional plastics, originate from petroleum such as polyolefin groups, degrade within decades or even hundreds year. Nowadays, large volumes application of plastics in most aspect of daily life has led to serious environmental problems. Therefore, there is a growing demand for environmentally friendly plastic that can compete with conventional plastic for both mechanical properties and cost-performance basis. Developing a fully biodegradable plastic, such as poly-lactic acid (PLA), from renewable resources could be one good solution. Unfortunately, this development needs high investment and is complicated production process involving large volumes of chemicals. Starch and starch-based polymer are promising for inducing biodegradability property. They are inexpensive, renewable resources and naturally biodegradable [2].

Plasticized and gelatinized starch (often called by thermoplastic starch/TPS) can behave similar to thermoplastic [2,3]. The application of TPS is limited by its hydrophilic nature [3] and low thermal
stability [5]. TPS fails to fulfill several essential requirements in general application because of its sensitivity to water that lead to brittleness [6]. The main point taken to improve these limitations is hydrophobization of starch, either through chemical modification or blending with other hydrophobic materials. One chemical modification is the addition the carboxylic acid into starch during processing. This addition has proven to increase the mechanical properties, thermal properties, aging and moisture resistivity of the resultant TPS [6]. TPS often blends with synthetic polymers such as polypropylene, polyethylene, poly-lactic acid and poly-glycolic acid [4] or polyesters to attain higher mechanical properties [7]. Many studies have been successfully blended starch with PE through reactive blending. Various types of starch such as corn starch [1,3,6,8], wheat starch [3] and cassava starch [7–9] were employed within these studies. High-density polyethylene (HDPE) is one of the polyethylene family and used in a variety of applications where excellent impact resistance, high tensile strength, low moisture absorption and chemical as well as corrosion resistance properties are required. However, the blend of starch and HDPE is immiscible with high interfacial tension. HDPE is highly hydrophobic, while on the other hand starch is hydrophilic. Thus, the blend of these materials is non-compatible that lead to inferior properties. The addition of compatibilizer could overcome this problem. The most common compatibilizer used for this purpose is PE grafted with maleic anhydride (PE-g-MA) [1–3]. PE-g-MA improve mechanical properties to some degree by improving the interfacial adhesion and reduces the dispersed phase [8].

The biodegradability term is related to how a material can be degrade biologically in nature. The key parameter of biodegradable material is the sensitivity to water and moisture. It becomes important because most microorganisms are likely to be active in high moisture atmosphere. On the other hand, material also must have sufficient strength to withstand the load during service life. Thus, comprehensive study should be taken in designing phase to obtain balanced properties. The study of biodegradation of a material usually describes in the term of low wettability, high water absorption and high weight loss after soil burial [2]. Soil burial, either natural or compost simulation, is probably the simplest way to investigate the biodegradability characteristic. Several studies have been attempted using this method [7,10–13]. They reported that weight loss dan reduction in mechanical properties of the starch/PE blends were observed after soil burial test.

In present work, the biodegradability of cassava starch/HDPE blends was investigated through simulated soil burial. Acetic acid was employed to improve starch hydrophobization and compatibilizer PE-g-MA was applied to enhance the interfacial interaction between starch and HDPE. By this dual modification, it was expected that the mechanical properties of starch/HDPE would increase, balanced with the biodegradation characteristic.

2. Experimental method

2.1 Materials
HDPE extrusion grade of Asrene SF 5007 were supplied from PT. Chandra Asri (density 0.950 g/cm³ and melt flow index 0.05 g/10 min (190 °C/2.16 kg)). Local tapioca starch with approximately 17.87% wt of amylose and 82.13% wt of amilopectin. Polyethylene-grafted-maleic anhydride (PE-g-MA) compatibilizer was purchased at Sigma-Aldrich with melting point and density of 156°C and 0.934g/cm³ respectively. Antioxidant Songnox 1010 was supplied by Songwon International. The commercial glycerol and aquadest as a plasticizer. Stearic acid and acetic acid were purchased from Bratacham. The compost was purchased from a flower nursery.

2.2 Preparation of CS/HDPE reactive blend Materials
Cassava starch (CS) was premixed with acetic acid, glycerol and water with a ratio of 70% of cassava starch, 1.3% of acetic acid, 20% glycerol, and 8.7% water. These materials were mixed thoroughly until attaining a homogeneous powdered for 15 min. The mixture then keep 2 days to allow the starch granules to swell. The CS/HDPE were prepared by reactive blending in a Haake Rheomix internal mixer at a temperature of 130°C and a rotor speed of 40 rpm for 15 minutes. The ratio CS/HDPE were
varied from 30/70; 40/60; 50/50; 60/40; and 70/30. PE-g-MA was employed 5% wt based on polymer blend. The amount of other additives (antioxidant, and stearic acid) were kept constant for all formulation.

2.3 Compost Burial Test

Compost burial test was carried out on a laboratory scale using the compost in accordance to Obasi et al. [14] with some modifications. The compost were purchased from local market that composed of manure, charcoal husk, sand, soil, and cocopeat. Therefore, the compost certainly contain microorganisms such as fungi and bacteria. Dumbbell shaped specimens of definite sizes were cutted from each of the blends and placed into plastic pot containing moist compost. The specimens were buried in the compost at a depth of 10 cm from the surface in order to be the subject of attacking microorganisms in compost. The test was carried outside the room and lasted for 56 days. After the test, the specimens were removed, gently cleaned to remove impurities, and conditioned at 23±2°C for 24 hours for further testing. The weight loss of the samples was calculated according to Equation (1),

\[
\text{weight loss} = \frac{W_0 - W_1}{W_0} \times 100\%
\]

where \(W_0\) is the initial weight of the samples before test, and \(W_1\) is the residual weight of the samples after test. Surface appearance also observed to investigate the changes after soil burial test.

2.4 Tensile Properties

Tensile tests for CS/HDPE blends were carried out with a universal testing machine Tinius Olsen-H25K according to ASTM D 882. A dumbbell shaped type was employed. Tensile strength and elongation at break were determined as the average of 5 replications. The tensile test was performed on the sample before and after soil burial.

2.5 Morphology Properties

The morphology of the CS/HDPE blends before and after soil burial was evaluated using a Scanning Electron Microscope SEC-SNE 3200M with 500x magnification.

3. Results and discussion

3.1. Surface appearance and morphology during compost burial test

HDPE is synthetic polymer with high hydrophobic level and high molecular weight, but is naturally non-biodegradable. Improvement of biodegradability of PE can be achieved by increasing its hydrophilicity level and/or reducing the polymer chain length by oxidation to be accessible for microbial degradation [9].

Figure 1 shows CS/HDPE reactive blend photos after compost burial test. It is visually observed that several black to gray and brown stains appear on the surface of the blends. These stains are assumed as the microorganism colonies. Water and moisture present in the compost during burial test facilitate the growth of microorganism. Further, these microorganism utilize starch as sole carbon source to support their life, resulting in partial degradation of the starch/HDPE blends [11]. Similar result is reported by Heydari et al. [15], in which black stains are observed on the surface of corn-starch nanocomposite film after soil burial associated with colonies of microorganisms. The higher starch content and the longest burial period, the more microorganisms present on the blend surface. It is related to the higher moisture absorption on higher starch content and longest burial period. This condition will accelerate the microorganism’s growth. These result show that the microorganisms initially attack starch in the blend, resulting in an increase in the porosity and consequent enhancement of its biodegradability as seen in Fig. 2b (i) to (iii).
Compost burial affect the morphology of CS/HDPE blend surface as shown in Figure 2. Initially, the CS/HDPE blends (2ai-iii) exhibit homogeneous and relatively smooth surface morphology. But they are slightly changed after 14 days burial (2bi-iii). The surface becomes rough and small holes and cracks on the surface are observed. The numbers of the hole and crack are more upon increasing starch content. Abd El-Rehim et al. [9] and Roy et al. [16] reported similar findings. It is presumably that the holes and crack are form as a result of microorganism activity during burial time. As they use starch as the food for their life, the blend starts to degrade. The holes and cracks formation also a sign that the CS/HDPE blend was degraded and decayed in the compost environment, but needed a time for a significant degradation.

Before burial

**Figure 1.** Surface appearance during compost burial of various CS/HDPE ratio a) 30/70, b) 40/60, c) 50/50; d) 60/400 and e) 70/30
After 14 days burial

Figure 2. Scanning electron micrograph of the blend containing various CS/HDPE ratio a) before burial test b) after 14 days burial test. Note: nomenclature i, ii and iii associated to CS/HDPE ratio of 30/70, 50/50, 70/30, respectively.

3.2. Weight loss

The weight loss of CS/HDPE reactive blends at different CS/HDPE ratio after compost burial test shown in Figure 5.

Figure 3. Weight loss of CS/HDPE blends during burial time.

Figure 3 shows the weight lost of CS/HDPE reactive blend at different CS/HDPE ratio content generally increase with increase in CS content and burial time. This weight loss may be due to the invasion of microorganisms into the reactive blends sample due to reactive blends absorpt moisture from the compost during the burial. Reactive blends with higher moisture absorption is usually more prone to microorganism attack. According to Maran et al. [4], Sahari et al. [16] increase in hygroscopic characteristics of material will promote the growth of microorganisms during degradation and increases the weight loss of material. The reactive blend samples with highest CS content in compost degraded rapidly in the first 14 days. Over the next 56 days a gradual decrease of starch occurred. In the 14 days burial test period, weight reductions of reactive blend containing CS 30 phr, 40 phr, 50 phr, 60 phr and 70 phr were 1.75%, 2.19%, 4.97%, 23.77% and 37.75% respectively. In the longest burial test period (56 days) weight reduction of reactive blend containing CS 30 phr, 40 phr, 50 phr, 60 phr and 70 phr were 11.2%. 11.68%, 40.42%, 51.64% and 62.08% respectively.
3.3. The change of tensile properties

Structural degradation as a result of microorganism activity in compost burial consequently affect the mechanical properties. Effect of compost burial test on the tensile strength and elongation at break are shown in Figures 4 and Figure 5 respectively.

![Tensile strength change as a function of number of burial days.](image1)

Figure 4. Tensile strength change as a function of number of burial days.

Tensile strength tends to decrease by increasing burial time. It confirms the structural changes occurred during burial. Figure 4 clearly depicts that the reduction of tensile strength runs little bit slow up to 50% starch in the blend. In the other hand, fast reduction is observed when starch content is 60 and 70% the first 14 days of burial, then the reduction rate is slower. Similar to tensile strength, elongation at break of the blends also reduces upon increasing burial times. This reduction probably related to water absorption capability of the starch. As mentioned earlier, high water absorption of starch will stiffen the starch. Thus, the blend becomes more brittle and will fails at low elongation. The severe effect is found on higher starch content (70%). Details data related to loss tensile strength and elongation at break is listed on Table 1.

![Elongation at break as a function of number of burial times.](image2)

Figure 5. Elongation at break as a function of number of burial times.
Table 1. Percent decrease in tensile strength and elongation at break.

| CS/HDPE ratio | % loss in tensile strength | % loss in elongation at break |
|---------------|-----------------------------|-------------------------------|
|               | burial time                 | burial time                  |                               |
|               | 14 days | 28 days | 42 days | 56 days | 14 days | 28 days | 42 days | 56 days |
| 30/70         | 6.02   | 7.23    | 9.64    | 13.85   | 4.17    | 5.74    | 5.97    | 27.93   |
| 40/60         | 2.05   | 6.16    | 10.96   | 10.96   | 18.11   | 18.32   | 29.74   | 42.20   |
| 50/50         | 1.64   | 3.28    | 17.21   | 18.03   | 18.09   | 20.95   | 20.95   | 66.38   |
| 60/40         | 30.48  | 31.05   | 35.14   | 38.76   | 17.56   | 25.27   | 25.95   | 43.97   |
| 70/30         | 34.2   | 38.41   | 42.13   | 58.74   | 34.01   | 35.91   | 38.69   | 61.09   |

The reduced value of tensile strength and elongation at break are caused by the deterioration of the sample that occurs more and more due to the breaking of polymer bonds by microorganisms in the compost which ultimately leads to a decrease in tensile strength and elongation at break of the reactive blend samples. These results are in agreement with Obasi et al. [14], and Ali et al. [17].

4. Conclusion

Compost burial test result showed that the increasing of cassava starch content and burial time reduced the tensile strength and the elongation at break, however increased weight reduction of CS/HDPE reactive blends. At the 56 days of burial test, the highest drop of tensile strength (58.74%) was indicated by a reactive blend with 70/30 of CS/HDPE ratio, whereas the highest percent decrease of elongation at break (61.09%) indicated by reactive blend with 50/50 of CS/HDPE ratio. The physical appearance of the reactive blend surface shows that some black and red stains are formed. The morphology test result showed that voids cracks, and damages on the surface are formed after burial in compost.

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