Biodegradation Behaviour of Thermoplastic Starch Films Derived from *Tacca leontopetaloides* Starch under Controlled Composting Condition

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Abstract. The biodegradation study of thermoplastic starch (TPS) films derived from *Tacca leontopetaloide*s starch; namely TPS/GLY, TPS/ACE and TPS/BCHR were investigated under controlled composting conditions. A manual set-up test rig in laboratory scale was built according to ISO 14855-1: 2012. The biodegradation percentage was determined by measuring the amount of CO_2 evolved using titration method and validated by automatic system (Arduino UNO System) that detected the CO_2 evolved. After 45 days under controlled composting condition, results indicated that TPS/GLY degraded the fastest, followed by TPS/BCHR and the TPS/ACE had the slowest degradation. The biodegradation process of TPS/GLY, TPS/ACE and TPS/BCHR also exhibited two stages with different degradation speeds. From these results, it indicated that chemical modification of the TPS films by adding acetic acid and rice husk bio-char to the thermoplastic starch can have a major impact on the biodegradation rate and final biodegradation percentage.

1. Introduction

The large use of synthetic non-degradable polymer and plastic materials produced from petrochemicals has led to serious environmental pollution. The solution to solve this problem is to use the biodegradable polymers (biopolymer); that is a renewable and can be the alternative material for replacement of many petroleum-based products. One type of the biodegradable biopolymer is thermoplastic starch that is produced from processed starch in the presence of plasticizers and under the influence of heat and shear [1]. Biodegradable polymer normally degrades into natural and harmless product results from the naturally occurring action of microorganism such as bacteria and fungi [2] such as carbon dioxide and water. In this study, the thermoplastic starch (TPS) was produced from *Tacca Leontopetaloides* starch. *T. leontopetaloides*, an annual herb of yam family contained starch in its tuber is a non-staple food readily available in Malaysia. The *T. leontopetaloides* starch was plasticised with glycerol in the present of heat to produce the TPS films with required properties. However, significant disadvantage of thermoplastic starch (TPS) is poor water resistance, making its application become limited. Thus, chemical modification was conducted to the TPS films by adding acetic acid and rice husk biochar in the formulation to improve its properties. However, the biodegradable properties of these TPS films after its end used or at ultimate disposal had not been investigated in detail. Therefore it is necessary to study the biodegradation behaviour of the TPS films in the natural environments.

2. Materials and Method

2.1. Materials

T. leontopetaloides starch used was collected from Mersing, Johor. Glycerol, acetic acid and sulphur were purchased from Merck (M) Sdn Bhd. Biochar of rice husk was supplied by Sendi Enterprise in Sekinchan, Selangor.

2.2. Preparation of TPS Films

Thermoplastic starch (TPS) films were prepared by dissolving *T. leontopetaloides* starch in distilled water to produce starch solution and heated under constant stirring for 30 min. Then, 10% (v/v) of glycerol was periodically added until solution completely gelatinized at 85°C to 90°C. The plasticized starch solution was then casted onto the polyacrylic plate and dried in ventilated oven at 45°C until constant weight was obtained. Then, the plasticized dried films were peeled off from the polyacrylic plate and milled using two-roll mill machine. 0.2% (w/v) sulphur was added during the milling process until even thickness was obtained. The curing temperature was set at 55°C to melt-blend the components and the speed of the roll-mill was adjusted at 5 rad/s. The sheet film obtained was denoted as TPS/GLY. Similar procedure was repeated to produce TPS/ACE where 5% (v/w) diluted acetic acid (10% v/v) was added to the plasticized starch solution. For TPS/BCHR film, the plasticized TPS/ACE film was supplemented with 5% rice husk biochar during melt-blend using two-roll machine until even thickness of film was obtained.

2.3. Compost Characterization

Mature compost was obtained from a plant nursery. The compost was screened using 10 mm sieve and large solids such as stone and wood were manually removed. The compost properties were determined according to the methods summarized in table 1.

Table 1. Compost characterization method

Properties	**Test method**
pH	pH was measured by mixing compost with water at weight ratio (inoculum: water = 1:5) according to ISO 10390:2005 [8]
Moisture content	Water (moisture) content by mass of compost was determined by ASTM D2216-98. [9]
Total solids	The compost was dried at about 105°C until constant mass was obtained.
Volatile solids	Compost was preheated, weighed and ignited at 550°C and reweight.
C/N Ratio	Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples according to ASTM D5373:2002.

2.4. Biodegradation Testing Rig

In this experiment, the test rig composed of three parts: I) a pressurized air control system which was to control aeration rate, to produce air saturated vapor and to remove carbon dioxide (CO_2) from the compressed air; II) a composting system consisted of 2L special vessel containing test materials and inoculum compost and III) CO_2 trap system to evaluate the carbon dioxide evolved from the biodegradation of the test materials in the composting system. The schematic diagram of the set-up is illustrated in Figure 1.

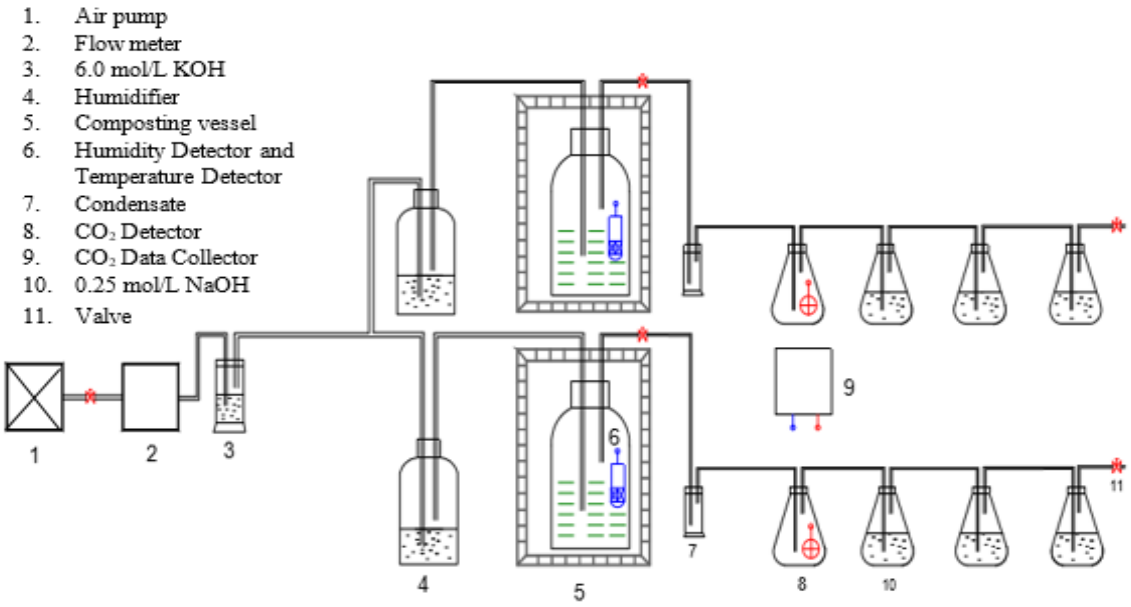

Figure 1. The test system of biodegradation for TPS films

2.5. Procedure

Compost with moisture content of 50 to 55% were mixed with test material (measurement 10mm x 10mm x 1mm) in 2L special vessel according to the ratio of 6:1 (w:w dry mass). Two special vessels were used; one containing compost with test materials and another one as background control containing compost only. Both vessels were aerated at 30 to 40 mL/min throughout the experiment to ensure adequate oxygen for biodegradation process and placed in the water bath for test environment of 58°C±2°C in dark condition. Humidity and temperature in the vessels were monitored using the humidity and temperature detector. The CO_2 evolved from the biodegradation vessels was measured twice daily to estimate the cumulative CO_2 production.

2.6. Biodegradation percentage determination

Titration method (Method A): The CO_2 gas produced from biodegradation of test material or inoculum compost was trapped in 0.25 mol/L NaOH. To evaluate the amount of CO_2 absorbed in the NaOH solution, 20 mL aliquots were removed from 500 mL of NaOH solutions. Then, acid-base titration was used to measure the amount of CO_2 evolved using 0.25M hydrochloric acid (HCl) with double indicator, Phenolphtalein and Methyl-Orange. The total amount of CO_2 evolved was calculated according to Du et al. [3] method by implementing equation (1).

$$CO_2(g) = V_2 \times C_{HCl} \times 44 \times \frac{500\ mL}{20\ mL} \quad (1)$$

Automatic method (*Method B*): The CO_2 gas evolved was detected by the CO_2 detector supported by microcontroller of Arduino UNO System. The board of microcontroller provide a real time clock module that capable to receive the data logging from CO_2 detector for each second. The raw data logging of CO_2 evolved was then collected using formatted Secure Digital (SD) Card that attached on the circuit of microcontroller board. Then, the raw data logging of CO_2 produced at 6 hours, 12 hours and 18 hours were averaged and used to calculate the quantity of CO_2 produced in gram from the biodegradation test using Eq. 2.

$$CO_2\ (g) = \frac{ppm\ CO_2}{10{,}000} \times liter\ of\ free\ air \times \frac{1\ m^3}{1000\ L} \times \frac{1.987\ kg}{m^3} \times \frac{1000g}{1kg} \times \frac{12}{44} \quad (2)$$

The theoretical amount of CO_2 ($ThCO_2$), g/flask was calculated using Eq. 3 and the biodegradation percentage (D_t) was calculated using Eq. 4 respectively.

$$ThCO_2 = M_{TOT} \times C_{TOT} \times \frac{44}{12} \quad (3)$$

$$D_T = 100\% \times \frac{(CO_2)_T - (CO_2)_B}{ThCO_2} \quad (4)$$

M_{TOT} is the total dry solids in test sample added into composting flask; C_{TOT} is the proportion of total organic carbon in the total dry solids in test sample; 44 and 12 are the CO_2 molecular mass and atomic mass of carbon, CO_{2_T} is the cumulative amount of CO_2 evolved in each composting flask containing test materials; CO_{2_B} is the mean cumulative amount of CO_2 evolved in blank flask.

3. Results and Discussion

3.1. Properties of compost.

Table 2 shows the properties of compost used in the controlled composting condition. As shown, the pH is slightly alkaline with the moisture content of 50.35%. The volatile solids indirectly indicating the organic matter and the % shown is on the total dry solids. The C:N ratio showing that the compost used is mature compost as it is ranged between 10 to 20 : 1 [4].

Table 2 The properties of compost

Chemical properties	**Value**
pH	7.94
Moisture (%)	50.35
Total dry solid (%)	49.38
Volatile dry solid (%)	24.22
C:N ratio	13.58

3.2. Biodegradation of TPS films.

The biodegradation curves of TPS/GLY, TPS/ACE and TPS/BCHR are shown in Figure 2 according to method A and Method B respectively. Two phases were observed in TPS/GLY AND TPS/BCHR biodegradation curves which can be defined as slow degrading phase which occurred during the first 20 days. The slopes were gradual at these days showing that the degradation rates were lower. The second phase, fast degradation phase occurred after 20 days as steeper slopes were observed. However, TPS/ACE showed linear curves throughout the 45 days of composting.

After 45 days of incubating the test materials with the compost mixture in the controlled composting condition, the degradation percentage TPS/GLY, TPS/ACE and TPS/BCHR were 70.1%, 23.89% and 54.04% respectively when determined using Method A. The percentages of degradation were validated as these values were similar when determined using Method B (69.8%, 24.1% and 50.1% respectively). Comparing the rate of degradation and degradation percentage for all types of test materials, TPS/ACE had the slowest values. These results indicating that chemical modification by adding acetic acid in the formulation affected the action of microorganisms in the compost to degrade the TPS/ACE film. The acetic acid was added as cross linking agent to improve the TPS/ACE film performance. It reacted with the hydroxyl group of starch creating new chemical bonds between molecular starch chains thus making its hydrophilic character reduced [5-7]. During the composting, the moisture content of the compost was kept constant at 50 to 55%. When moisture diffused into the test materials, it will cause the film to swell and stimulate the microbial growths thus enhancing biodegradation. However, the incorporation of the acetic acid reduced the moisture absorption and therefore resulting to slower the rate of degradation and degradation percentage. Similar observations also encountered by [5]. Among the three types of films, TPS/GLY had the highest degradation rate. This was predictable since moisture absorption expected to be higher which promoting higher microbial degradation compared to the other two films.

For TPS/BCHR, the degradation rate was in between TPS/GLY and TPS/ACE. Table 3 shows the physical and chemical properties of the rice husk biochar used. From Table 3, the ash content was almost 50% of the content making the biochar relatively inert. Addition of acetic acid also made the film had lower water absorption, and yet the degradation rate was higher compare to TPS/ACE. Possible explanation could be due to the pH of the biochar. As it was slightly alkaline, it altered the pH of films. Furthermore, the biochar also has source of carbon and nitrogen that may had gave the microorganism source of nutrients.

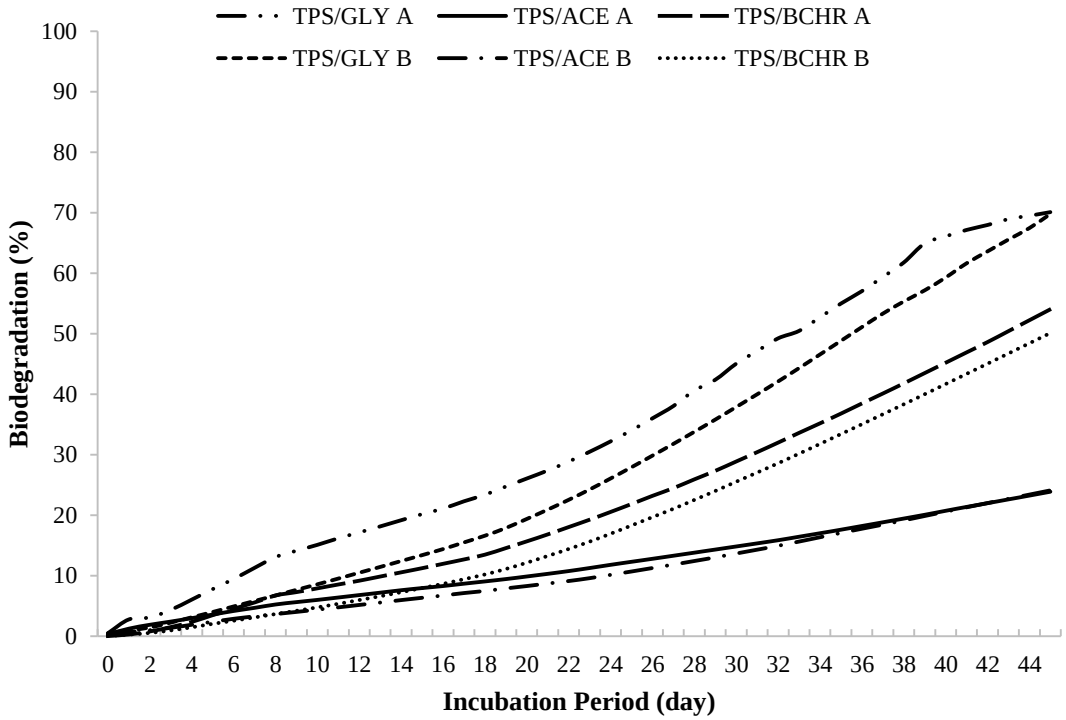

Figure 2 Biodegradation curve of TPS/GLY, TPS/ACE and TPS/BCHR under controlled composting condition (A – Method A, B – Method B).

Table 3. Physical and Chemical Properties of Rice Husk Biochar

Moisture % (w/w)	pH	Volatile Matter (%)	Ash (%)	C (%)	H (%)	N (%)	BET Surface Area (m^2/g)
8.15	8.20	13.64	48.20	26.23	6.88	0.28	186.99

4. Conclusion

The biodegradability of three types of TPS samples namely TPS/GLY, TPS/ACE and TPS/BCHR were investigated. It was observed that, TPS/GLY had the highest percentage of degradation followed by TPS/BCHR and TPS/ACE had the slower degradation rate. Chemical modification by the addition of acetic acid and biochar significantly affected the degradation percentage. The microorganisms that were responsible for the degradation of these films could be isolated and identified in future work.

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