

Degradation Studies During Water Absorption, Aerobic Biodegradation, and Soil Burial of Biobased Thermoplastic Starch from Agricultural Waste/Polypropylene Blends

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ABSTRACT: Thermoplastic starch (TPS) from agricultural waste consisting of different amylose/amylopectin ratios was blended with polypropylene (PP) for degradation studies. The agricultural waste material was obtained from seeds and tubers with low starch contents of ~50%. Non-Fickian behavior was observed for the water absorption test, and water uptake increased with increases in amylopectin content. The biodegradation was assessed based on the extent of carbon conversion, and was found to be dependent on the water absorption behavior and molecular structure of the starch component. Outdoor soil burial showed greater weight loss and deterioration in tensile properties compared to indoor soil burial. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Starch is a renewable polymer, inexpensive, and available year-round. Starch consists of linear amylose and highly branched amylopectin chains. The use of starch as a biodegradable polymer started as early as the 1960s, but the production of whole starch film has not achieved large-scale commercial success because the films are sensitive to moisture and become brittle after the plasticizer leaches out.^{1,2} Several attempts have been made to enhance the mechanical properties of starch and lessen its moisture sensitivity by blending thermoplastic starch (TPS) with other polymers such as polyolefins.^{3–5} The use of a compatibilizer, such as maleic anhydride grafted polypropylene (MA-g-PP), is common in TPS blends to improve the interfacial adhesion of the composite phases. The maleic anhydride functional group, which is grafted into PP, forms covalent bonds with the hydrophilic starch.⁶ Degradation studies of TPS-blend plastics have attracted much attention because degradation will limit the product service life-time.^{7–9} The addition of starch into PP has been promoted as a technique to increase its biodegradation. Biodegradation is a natural, complex process and the first stage is the attack by microorganisms on starch compo-

nent, which is located at the surface of the sample. Once the starch granules are removed, the cohesiveness of the material is reduced, and leaving behind a porous matrix.^{10,11} The increase in the surface/volume ratio makes the porous polymer more accessible for attack by both biotic and abiotic factors, subsequently enhancing other degradation mechanisms.^{12–14} A biobased product can be partially or fully made from renewable resources according to definition in ASTM D6852 and the biobased content can be determined via ASTM D6866. The TPS/PP blends prepared here are considered to be biobased materials.

In this work, the origin of the starch source is unique because it is obtained from agricultural waste, i.e., agricultural waste seed (AWS) and agricultural waste tuber (AWT), with a low starch content ≤50%. Previous studies on thermoplastic starch (TPS) typically used food crops starch sources such as potato, wheat, rice, and corn, which are generally higher in starch content >70%.^{15–18} The main reason behind the use of agricultural waste that can be converted into TPS is to avoid the food-feed debate and benefit from its low material cost. The challenge here is the agricultural waste contains a lower starch content

compared to a normal starch source, therefore, it may fail to attain the desired plasticity and degradability. The objective of this study is to utilize starch-containing agricultural waste for the preparation of biobased TPS/PP blends and to investigate the degradation behavior of these blends during water absorption, aerobic biodegradation and soil burial tests. Native tapioca starch (NTS) and commercially available biobased sample (CS) were also used for comparison. In addition, the effect of the amylose-to-amylopectin ratio in biodegradation studies and the comparison between the indoor and outdoor soil burial degradation performance were analyzed.

EXPERIMENTAL

Materials

Polypropylene (PP) was supplied by Texchem Material Sdn Bhd with melt flow index (MFI) of 3.16 g/10 min (190°C/2.16 kg) and density of 0.90 g/cm³. Maleic anhydride-grafted- polypropylene (MA-g-PP) was manufactured by Arkema (0.8 wt % maleic anhydride content, density of 0.91 g/cm³ and T_m of 161°C). Agricultural waste seed (AWS), average particle size 6.5 μm and agricultural waste tuber (AWT), average particle size 27.7 μm were obtained from Texchem Material Sdn Bhd and had starch contents of 43.2% and 50.4%, respectively. The remaining details of the waste products are as follows: moisture (8–14%), protein (2–19%), fat (1–8%), and fiber (1–14%). Native tapioca starch (NTS) (Fumakilla Malaysia Berhad) had an average particle size of 4.3 μm, a starch content of 85.4% and a moisture level of 11%. The amylose/amylopectin ratios for AWS, AWT, and NTS were 1 : 99, 26 : 74, and 29 : 71, respectively. Glycerol-based plasticizer, purchased from Texchem Material Sdn Bhd, had a density of 1.01 g/cm³, an acid value < 3 % and a moisture < 0.2%. Commercial biobased sample (CS) with a biobased content of 52% (~70% starch) per ASTM D6866 was obtained from Texchem Material Sdn Bhd. The MFI and density were 7.82 g/10 min (190°C/2.16 kg) and 1.19 g/cm³, respectively.

Sample Preparation

A compound of starch powder (AWS, AWT, or NTS), PP and plasticizer was prepared at a ratio of 4 : 4:2. MA-g-PP was added to the formulation 3% by weight. The single-step compounding was prepared in a Berstoff model twin-screw extruder with length-diameter (L/D) ratio of 54 : 1. The compounding was performed at temperatures in the 140–170°C range, and the screw speed was set at 200 rpm. Sheet extrusion was performed in a Berlyn model single-screw extruder with an L/D ratio of 31 : 1. The sheet extruder processing temperature range was 150–170°C, and the screw speed was 50 rpm. The chill rolls temperature range was 60–80°C with a speed of 1.0–1.2 rpm. Four types of sheets were extruded, i.e., AWS/PP, AWT/PP, NTS/PP, and CS to a thickness of 0.7 ± 0.1 mm.

CHARACTERIZATION

Water Absorption Test

Water absorption tests were conducted according to ASTM D570. Extruded sheets specimens (76 mm × 25 mm) were dried in an oven at 50°C until constant weight and then

immersed in distilled water at room temperature. The test was conducted over 2 months, during which the weight gain was recorded by periodic removal of the specimen from the water. A cotton towel was used to wipe the wet surface before weighing. The percentage of weight change at any time, M_t , due to water absorption was calculated with eq. (1):

$$M_t(\%) = \left[\frac{W_w - W_d}{W_d} \right] \times 100 \quad (1)$$

where W_w is the weight of specimen immersed in water and, W_d is the initial weight of the dry specimen.

Aerobic Biodegradation Test

Biodegradation tests were performed according to ASTM D5988. NTS powder was used as the reference to check the biological activity of the soil. The test was regarded as invalid if the CO₂ evolved from the reference sample was less than 70% after 6 months.¹⁹ Specimens (20 mm × 20 mm) were buried in 120 g of soil at the bottom of the desiccator. 0.5N KOH (20 mL) and water (50 mL), each in a 100 mL beaker were placed on a perforated plate inside a desiccator. One desiccator containing only soil was prepared as a blank control. Vacuum sealant grease was applied to the rim of the desiccators to create an airtight seal, and the desiccator was kept inside of a cabinet at 23°C. Microorganisms inside the soil will assimilate the sample, and the CO₂ evolved from the microorganisms through the metabolic process was evaluated. The CO₂ evolved in each desiccator was trapped by a KOH solution. The unreacted KOH was titrated with 0.05N HCl, using phenolphthalein as indicator, and the amount of CO₂ evolved was calculated using the following formula:

$$\text{CO}_2 \text{ evolved (mg)} = 0.05 \times (B - V) \times 44 \quad (2)$$

where B is the volume (mL) of HCl used to titrate the KOH in the blank control and V is the volume (mL) of HCl used to titrate the KOH in the soil burial test.

The measurement of the CO₂ evolution using the titration method was performed every 3 days (d) for the first month, during which biodegradation was expected to be faster, and then every 1–3 weeks for 180 d. The percentage of biodegradation was calculated by determining the percentage of carbon (C) in the sample that had been converted into CO₂ (mineralization) as shown in eq. (3).

$$\% \text{ biodegradation} = \frac{\text{CO}_2 \text{ evolved (mg)}}{\text{theoretical CO}_2 \text{ (mg)}} \times 100 \quad (3)$$

The theoretical CO₂ content was determined using elemental analysis to measure the total organic C content in each sample.

Indoor Soil Burial Test

Indoor soil burial testing was performed under controlled conditions (temperature, water content, and pH), following ISO 846 method D. The moisture content was periodically monitored and maintained between 46 and 54%; it was raised using water when necessary. Normal gardening soil, pH 6.9, was used

as the medium. Extruded sheets were cut into dumbbell specimens, in both machine direction (MD) and transverse direction (TD), for the weight loss and tensile properties evaluations. The initial mass of the each specimen was recorded to the nearest 0.1 mg to prevent error caused by moisture absorption. All samples were subjected to vacuum oven drying before and after soil burial at 50°C for 24 hours. The specimens were buried in a gardening pot and covered by soil at a depth not greater than 12.5 cm. Each pot was placed inside the oven with temperature control at $29 \pm 1^\circ\text{C}$. The specimens were removed from the soil after 3 and 6 months. After removal, the specimens were cleaned, dried and allowed to equilibrate in desiccators prior to weighing.

Outdoor Soil Burial Test

The samples were buried in gardening pots and placed in an open outdoor area of the USM Engineering campus for a period of 6 months, i.e., from January to June 2011. The removal and weighing steps were similar to those of the indoor soil burial test.

Tensile Test

The tensile properties were determined with an Instron (model 3366) tester according to ASTM D638 at a cross-head speed of 50 mm/min. The specimens were conditioned at $24 \pm 1^\circ\text{C}$ and $50 \pm 5\%$ relative humidity for 2 d before the testing. The average tensile strength (TS), elongation at break (EB) and Young's modulus (YM) were collected from the stress-strain data. Tensile properties of the specimens before soil burial (control) were determined for comparison.

Scanning Electron Microscopy (SEM)

Field emission SEM (model LEO Supra 50VP) was used to observe the morphology of the various samples. All specimens were sputter-coated with a thin layer of gold to avoid electrical charging during examination.

RESULTS AND DISCUSSION

Water Absorption

Figure 1 shows water absorption plots for NTS/PP (native tapioca starch/polypropylene), AWS/PP (agricultural waste seed/polypropylene), AWT/PP (agricultural waste tuber/polypropyl-

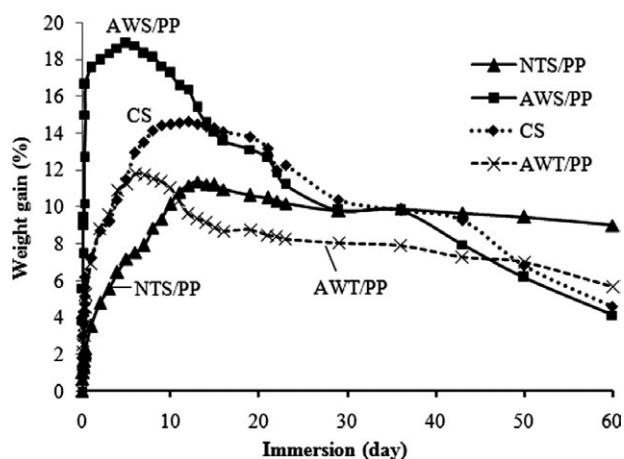


Figure 1. Water absorption for CS, AWS/PP, AWT/PP, and NTS/PP.

ene) and CS (commercial biobased sample). In all cases, an initial rapid weight gain was followed by a more gradual weight gain, and a subsequent slow or sharp weight reduction was observed. The curves show non-Fickian behavior because constant saturation was not observed. A previous study by Alain and Cavaille²⁰ found that for higher starch content compositions (>35%), the water uptake slightly decreased after reaching a plateau, most likely due to the partial dissolution or leaching of starch into water.

Maximum water absorption was observed in AWS/PP (18.9%), followed by CS (14.6%), AWT/PP (11.8%), and NTS/PP (11.4%). AWS/PP (~100% amylopectin) reached maximum water absorption after 5 days (d) of immersion. This result is supported by the work of Ke et al.,²¹ who reported the water absorption of high amylopectin content starch to be higher than that of blends made of high amylose content starch. The high water absorption of amylopectin is due to the increased degradation of amylopectin molecules during the extrusion process. Amylopectin is more susceptible to shear degradation and the destruction of starch granules allows water molecules to penetrate the starch.^{22–24} Moreover, the branched structure of amylopectin helps to retain more water.²⁵ A similar observation was reported by Van Soest and Essers,²⁶ who noted that materials rich in amylopectin were more hygroscopic than amylose-rich materials. It can be seen that the AWS/PP experienced a drastic drop in water uptake after 8 d of immersion. This drop may be attributed to the leaching of degraded starch component and desorption of low molecular compounds such as glycerol.²⁷ In this study, the glycerol based plasticizer acts as external plasticizer and forms hydrogen bonds with the starch.²⁸ The starch-plasticizer interaction through hydrogen bonding takes the place of the strong action between hydroxyl groups of starch molecules and makes the starch display plasticization.²⁹

CS had the second highest water absorption (14.6% after 12 d). The highest starch content was also found for CS and may have contributed to the large weight gain because there were more starch granules exposed at the surface. Starch granules at the surface absorb water faster than those encapsulated by the synthetic polymer in the core of the sample. After the sample surface is saturated with water (rapid process), then will penetrate throughout the porous structure.³⁰ The water uptake then decreased continuously with continued immersion. This decrease may be attributed to the leaching of starch granules, leaving cavities as shown by SEM (Figure 2).

Despite having similar maximum weight gain values (11–12%), AWT/PP reached the maximum weight gain in just 6 d, whereas NTS/PP required 13 d. This rapid weight gain could be attributed to the higher ratio of amylopectin in AWT/PP compared with NTS/PP. Amylopectin-rich material tends to show a faster rate of water uptake. Moreover, AWT powder, which had a larger particle size than NTS powder, showed poor adhesion with the polymer matrix and thus encouraged the penetration of water molecules, which could fill the void between the starch and matrix. A previous study by Sabetzadeh et al.,¹⁷ revealed that by decreasing the particle size of the dispersed phase, i.e., starch, a homogenous distribution can be achieved and provide better interfacial adhesion with the matrix.

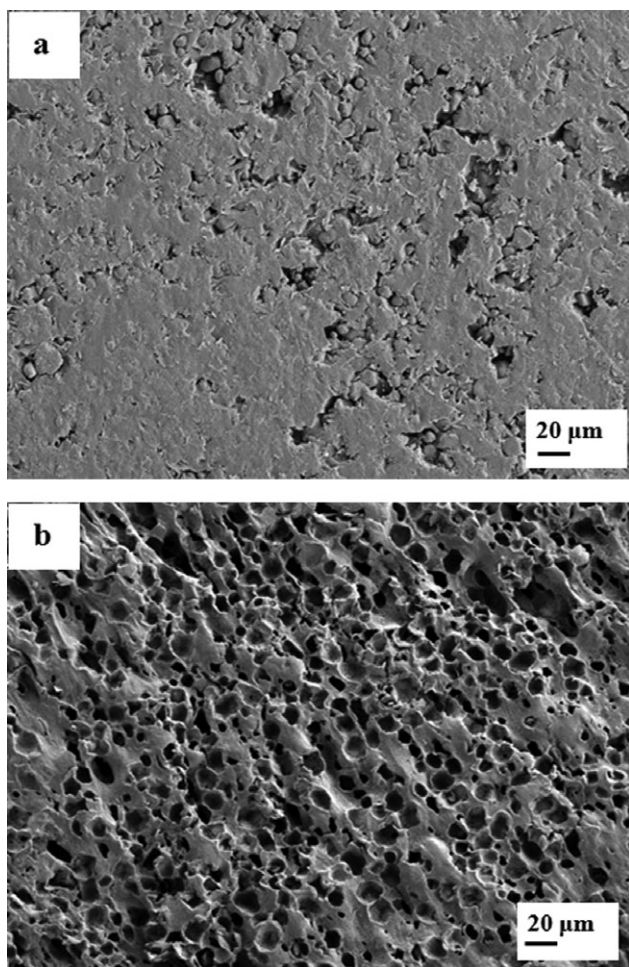


Figure 2. (a) SEM surface image of CS before water immersion. (b) SEM surface image of CS after 2 months of water immersion.

Aerobic Biodegradation

NTS was used as a reference to test the activity of the soil and it fulfilled the standard requirement of achieving a 79% biodegradation in 50 days (d). Figure 3 shows the biodegradation rates for CS, AWS/PP, AWT/PP, and NTS/PP. In an aerobic reaction, microorganisms oxidise carbon (C) to CO_2 as one of the

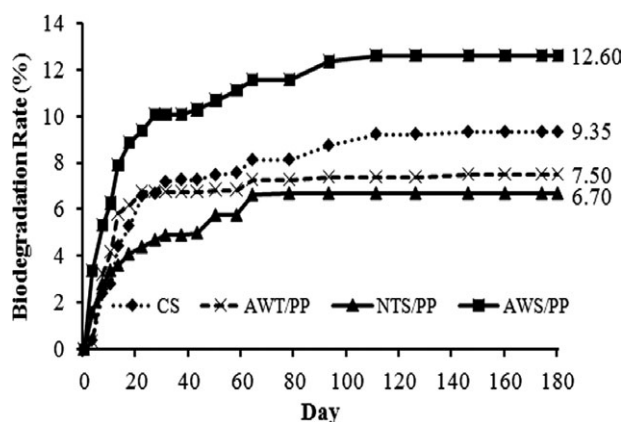


Figure 3. Biodegradation rate for CS, AWT/PP, AWS/PP, and NTS/PP.

metabolic end products.³¹ The biodegradation rate was faster in the first 30 d, then slowed down and plateaued after 100 d when all of the accessible C had been oxidized. AWS/PP showed the highest biodegradation rate (12.6% at 180 d) and that C was already mineralized into CO_2 . After 180 d, NTS/PP displayed the lowest biodegradability (6.7%) whereas values of 7.5% and 9.35% were obtained for AWT/PP and CS, respectively. A previous study revealed that blending wheat based-TPS with LDPE in a co-continuous phase (50/50) could achieve a 25% biodegradation rate in 98 d.⁸ However, in this blend, starch granules do not form a continuous phase (Figure 4). This discontinuity would slow the biodegradation rate because starch granules were encapsulated by the plastic and were not accessible to soil microorganisms.³² Ramis et al.⁵ reported that biodegradation occurs in starch and not the PP matrix. A similar observation was reported for the starch/PLA system, where the degradation in soil over a 1-year period did not affect the PLA.³³ Amylases hydrolyze starches and these enzymes can be easily found in most organisms (bacteria, fungi, animals, and in some plants).¹⁵

The highest biodegradation rate, achieved by AWS/PP, could be affected by the structure of the amylopectin. The branched amylopectin structure is more easily hydrolyzed by enzymes than amylose.³⁴ As discussed earlier, AWS/PP showed the highest water absorption rate and subsequently encouraged the growth of microorganisms. The lower water absorption rates of CS, AWT/PP, and NTS/PP tend to reduce the susceptibility to microorganisms. Fungi, for instance, require at least 70% relative humidity for growth, whereas bacteria require a liquid aqueous environment.³⁵

Indoor Soil Burial

Table I shows the weight loss over time for samples in machine direction (MD) and transverse direction (TD) after indoor soil burial and the degree of weight loss in descending order is $\text{CS} > \text{AWS/PP} > \text{NTS/PP} > \text{AWT/PP}$. The sample orientation (MD or TD) does not significantly affect the weight loss. CS with the highest starch content showed the greatest weight loss at 52.8%

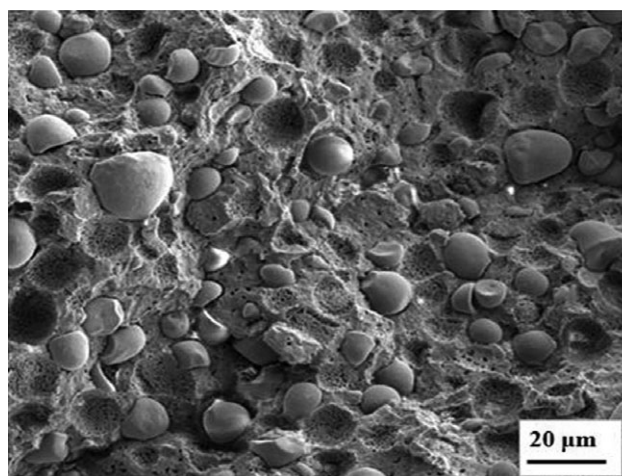


Figure 4. SEM cross-section image of NTS granules dispersed in PP matrix.

Table I. Indoor and Outdoor Soil Burial Weight Loss (%)

| Weight loss (%) | Months | CS | AWS/PP | NTS/PP | AWT/PP | |
|-----------------|--------|----|--------|--------|--------|------|
| Indoor | MD | 3 | 38.8 | 37.7 | 29.2 | 25.1 |
| | | 6 | 52.8 | 48.0 | 35.1 | 32.9 |
| | TD | 3 | 39.6 | 36.7 | 28.0 | 27.3 |
| | | 6 | 50.6 | 44.8 | 36.5 | 35.8 |
| Outdoor | MD | 3 | 36.6 | 37.7 | 16.5 | 20.1 |
| | | 6 | 61.4 | 48.9 | 40.9 | 35.6 |
| | TD | 3 | 37.0 | 38.0 | 15.7 | 22.8 |
| | | 6 | 58.6 | 49.1 | 40.5 | 38.2 |

(MD) and 50.6% (TD). The high water uptake behavior in AWS/PP facilitates the entrance of soil microorganisms and ranked second in weight loss. AWT/PP, which had lower starch content than NTS/PP, showed the least weight loss. Zuchowska et al.⁷ reported a 40% weight loss for PP-potato starch blends (50/50) during 3 months of soil burial and suggested that the continuity of the starch phase had significantly enhanced the rate of weight loss.

It was observed that soil burial samples showed higher % weight loss (>30% in 6 months) compared to aerobic biodegradation (6.7–12.6% in 6 months) as displayed in Figure 3. The difference in these values is that weight loss is gravimetrically determined while the biodegradation rate is based on yield of CO₂. Furthermore, a small amount of starch-based C is converted into microbial biomass or dissolved organic carbon,^{8,36} which results in a low biodegradation rate.

Table II shows that all specimens had lower tensile strength (TS) values after 6 months of indoor soil burial. A similar result was reported by Wu,³⁷ where after soil burial, the mechanical properties of the starch composites deteriorated. Here, the MD TS were significantly higher than those of the TD ($P < 0.05$), which is likely because the polymer chains are highly oriented in MD. This finding is consistent with the work of Selling and Sessa³⁸ for the properties of plasticized zein.

In this work, there was a positive correlation ($R = 0.93$) between the TS loss values and weight loss. For example, CS had the highest TS loss, 28–32%, after 6 months of soil burial (Table II) and had the highest weight loss (Table I). AWT/PP showed the least change in TS (0.7–4%), and it experienced the lowest weight loss (32.9–35.8%). This finding is in agreement with that of Bikiaris et al.¹⁵ The weight loss and deterioration in physical properties are attributed to the starch consumption by microorganisms, resulting in the formation of voids, thus weakening the polymer and disintegrated under mild stress.^{29,39}

Elongation at break (EB) was also affected after 6 months of indoor soil burial (Table II). Surprisingly, there were samples that showed an increase in EB despite experiencing weight loss. NTS/PP and AWS/PP experienced similar values of EB loss in MD and TD after 6 months of soil burial. However, both CS and AWT/PP showed an increase in EB for the first 3 months; then, EB started to decrease after 6 months but remained rela-

tively high compared to the control. An increase in EB for CS and AWT/PP could be attributed to the slow structural changes in the starch phase (e.g., moisture absorption) and an improvement of phase adhesion due to diffusion processes within the phase boundary over time.⁷ Stading et al.⁴⁰ reported that a higher relative humidity surrounding the starch film can lead to plasticization and increased mobility in the network. A previous study by Lluch et al.⁴¹ also revealed that the increase in moisture content produced a plasticizing effect and reduce the interaction. In this work, the plasticizing effect was more pronounced in CS than in AWT/PP. This finding could be attributed not only to the high starch content of CS, which has strong affinity for moisture, but also its surface, which has a large number of holes, as shown by SEM [Figure 5(a)], and this facilitates the moisture penetration. The micrographs in Figure 5(a,b) show rough heterogeneous surfaces and the presence of holes and gaps for CS and AWT/PP. On the contrary, AWS/PP and NTS/PP with smaller starch particle size (~4.3–6.5 μm) display good adhesion with matrix, smooth, and more homogeneous appearances can be observed [Figure 5(c,d)].

All samples showed a decrease in Young's modulus (YM) of 23–75% (Table II) after 6 months of soil burial and this is consistent with the work of Hanafi et al.³⁹ CS showed the greatest YM loss of 72–75%, consistent with the greatest weight loss reported. Similar findings were observed for AWS/PP and NTS/PP; a greater weight loss for AWS/PP compared with NTS/PP resulted in a greater YM loss for AWS/PP. However, a different trend was observed for AWT/PP. AWT/PP had a greater YM loss (30–31%) than AWS/PP (27–29%) and NTS/PP (23–24%), although it showed the lowest weight loss after 6 months of soil burial. This behavior may be attributed to the plasticizing effect of water in AWT/PP, as discussed earlier; thus, there was an increase in flexibility but a reduction in material stiffness.

Outdoor Soil Burial

Table I shows the % weight loss during outdoor soil burial. It showed a trend similar to that of indoor soil burial for both machine direction (MD) and transverse direction (TD) samples. The outdoor soil burial samples showed higher weight loss values (1–9%) than indoor soil burial. For example, CS (MD) showed the higher weight loss (61.4%) during outdoor burial compared with indoor burial (52.8%) after 6 months. The outdoor environment is more aggressive in promoting degradation in soil. On the basis of the climate data supplied by the Malaysia Meteorological Department, the UV radiation amount reported from Jan to June 2011 was in the range of 2598–3877 J/m², average temperature of 28°C, humidity of 80% and average total rainfall of 160 mm each month. This warm and humid climate encourages the microbial growth.

Outdoor soil burial tensile strength (TS) data are presented in Table II. All the samples showed deterioration in TS after 6 months of outdoor soil burial, with a loss of 8.9–29.3%. Danjaji et al.⁴² reported a 17% and 19% loss in TS and EB, respectively, for 15 wt % sago starch-filled LLDPE after 6 months of outdoor soil burial. The average loss of TS after 6 months of indoor soil burial was 15% (for both MD and TD), while the loss for outdoor soil burial was 18.8%. This finding shows that degradation

Table II. Indoor and Outdoor Soil Burial Test Tensile Properties

| Months | | | CS | AWS/PP | NTS/PP | AWT/PP | |
|---------|----|----------|------------|-------------|-------------|-------------|-------------|
| Control | MD | 0 | TS (MPa) | 7.5 ± 0.9 | 19.9 ± 1.7 | 16.0 ± 1.2 | 17.7 ± 1.9 |
| | | | EB (%) | 15.7 ± 3.9 | 489 ± 35 | 383 ± 36 | 76.6 ± 12.3 |
| | | | YM (MPa) | 660 ± 19 | 547 ± 16 | 535 ± 22 | 677 ± 27 |
| | TD | 0 | TS (MPa) | 5.3 ± 0.7 | 15.6 ± 2.3 | 13.5 ± 1.1 | 13.6 ± 0.7 |
| | | | EB (%) | 5.9 ± 1.6 | 371 ± 47 | 344 ± 32 | 10.5 ± 1.1 |
| | | | YM (MPa) | 547 ± 15 | 456 ± 36 | 563 ± 10 | 622 ± 22 |
| Indoor | MD | 3 | TS (MPa) | 5.8 ± 1.9 | 18.9 ± 1.1 | 14.9 ± 1.9 | 15.9 ± 3.4 |
| | | | | [-22.7] | [-5.0] | [-6.9] | [-10.2] |
| | | | EB (%) | 36.6 ± 11.5 | 395 ± 28 | 145 ± 28 | 104 ± 11 |
| | | | | [+133] | [-19.3] | [-62.1] | [+35.8] |
| | | | YM (MPa) | 227 ± 9 | 405 ± 78 | 385 ± 32 | 360 ± 38 |
| | | | | [-65.6] | [-26.0] | [-28.0] | [-46.8] |
| | 6 | 3 | TS (MPa) | 5.1 ± 1.7 | 17.9 ± 1.3 | 13.0 ± 2.3 | 17.0 ± 0.2 |
| | | | | [-32.0] | [-10.1] | [-18.8] | [-4.1] |
| | | | EB (%) | 27.2 ± 6.0 | 148 ± 37 | 95.0 ± 30 | 92.9 ± 16.9 |
| | | | | [+73.2] | [-69.7] | [-75.2] | [+21.3] |
| | | | YM (MPa) | 185 ± 7 | 385 ± 32 | 405 ± 22 | 472 ± 7 |
| | | | | [-72.0] | [-29.6] | [-24.3] | [-30.3] |
| | TD | 3 | TS (MPa) | 4.5 ± 0.8 | 12.8 ± 3.8 | 11.4 ± 0.9 | 12.8 ± 3.2 |
| | | | | [-15.1] | [-17.9] | [-15.6] | [-5.9] |
| | | | EB (%) | 26.0 ± 7.0 | 32.9 ± 10.1 | 58.0 ± 21.2 | 24.8 ± 6.1 |
| | | | | [+341] | [-91.1] | [-83.1] | [+136] |
| | | | YM (MPa) | 135 ± 27 | 426 ± 40 | 413 ± 33 | 402 ± 8 |
| | | | | [-75.3] | [-6.6] | [-26.7] | [-35.4] |
| 6 | 3 | TS (MPa) | 3.8 ± 0.9 | 12.2 ± 0.2 | 12.9 ± 0.2 | 13.5 ± 0.3 | |
| | | | [-28.3] | [-21.8] | [-4.4] | [-0.7] | |
| | | EB (%) | 15.9 ± 8.0 | 30.1 ± 10.1 | 30.1 ± 7.8 | 21.8 ± 8.2 | |
| | | | [+169] | [-91.9] | [-91.3] | [+108] | |
| | | YM (MPa) | 136 ± 2 | 332 ± 8 | 431 ± 43 | 428 ± 16 | |
| | | | [-75.1] | [-27.2] | [-23.4] | [-31.2] | |
| Outdoor | MD | 3 | TS (MPa) | 6.1 ± 0.2 | 18.5 ± 2.5 | 12.6 ± 1.2 | 17.7 ± 2.1 |
| | | | | [-18.7] | [-7.0] | [-21.3] | [0.0] |
| | | | EB (%) | 25.1 ± 4.7 | 122 ± 39 | 92.4 ± 24.1 | 67.0 ± 17.7 |
| | | | | [+59.9] | [-75.1] | [-75.9] | [-12.5] |
| | | | YM (MPa) | 204 ± 40 | 420 ± 32 | 500 ± 7 | 572 ± 33 |
| | | | | [-69.1] | [-23.2] | [-6.5] | [-15.5] |
| | 6 | 3 | TS (MPa) | 5.3 ± 0.2 | 16.5 ± 2.2 | 13.5 ± 1.4 | 14.8 ± 2.9 |
| | | | | [-29.3] | [-17.1] | [-15.6] | [-16.4] |
| | | | EB (%) | 21.2 ± 3.6 | 15.3 ± 5.1 | 13.8 ± 3.0 | 50.4 ± 8.0 |
| | | | | [+35.0] | [-96.9] | [-96.4] | [-34.2] |
| | | | YM (MPa) | 123 ± 4 | 427 ± 23 | 425 ± 19 | 588 ± 18 |
| | | | | [-81.4] | [-21.9] | [-20.6] | [-13.1] |
| | TD | 3 | TS (MPa) | 5.1 ± 0.4 | 11.0 ± 3.4 | 13.1 ± 0.9 | 12.5 ± 3.2 |
| | | | | [-3.8] | [-29.5] | [-3.0] | [-8.1] |
| | | | EB (%) | 20.7 ± 4.0 | 61.8 ± 15.4 | 85.7 ± 23.6 | 16.1 ± 2.7 |
| | | | | [+251] | [-83.3] | [-75.1] | [+53.3] |
| | | | YM (MPa) | 163 ± 21 | 302 ± 20 | 530 ± 28 | 548 ± 33 |
| | | | | | | | |

Table II. (Continued)

| Months | | CS | AWS/PP | NTS/PP | AWT/PP |
|--------|----------|------------|------------|------------|------------|
| 6 | TS (MPa) | [−70.2] | [−33.8] | [−5.9] | [−11.9] |
| | | 4.3 ± 1.7 | 11.1 ± 2.3 | 12.3 ± 1.0 | 11.5 ± 2.7 |
| | EB (%) | [−18.9] | [−28.8] | [−8.9] | [−15.4] |
| | | 18.6 ± 7.4 | 4.0 ± 2.3 | 11.7 ± 6.0 | 10.1 ± 1.1 |
| | YM (MPa) | [+215] | [−98.9] | [−96.6] | [−3.8] |
| | | 188 ± 16 | 331 ± 19 | 446 ± 27 | 512 ± 44 |
| | | [−65.6] | [−27.4] | [−20.8] | [−17.7] |

[] square bracket indicates % of change in the tensile properties.

occurred faster in an outdoor environment. The outdoor soil burial samples are also subjected to attack by small insects (i.e., ants), weed growth, climate changes, and other factors that can affect the tensile properties. A good correlation between the weight loss and the loss in TS ($R = 0.85$) was also reported for outdoor soil burial. CS showed the greatest loss in TS (19–29%), and this finding is consistent with CS displaying the greatest weight loss after 6 months of outdoor soil burial. The only exception is AWT/PP, which showed a slightly higher TS loss compared to NTS/PP, even though its weight loss was 2–5% lower. This result could be attributed to the more severe surface erosion of AWT/PP than NTS/PP, as shown by SEM micrographs [Figure 6(b,d)]. NTS/PP showed a pitted surface after the removal of starch granules by microbial attack, while

AWT/PP showed the formation of larger gaps, cracks, and peeling on the surface.

Table II shows the changes in elongation at break (EB) over time for outdoor soil burial in MD and TD. NTS/PP, AWS/PP, and AWT/PP showed a decrease in the EB, ranging from 3.8 to 98.9%, after 6 months of soil burial. However, the EB of CS increased after 6 months of outdoor soil burial compared to control sample, displaying the same trend as the indoor soil burial. The increase in EB may be due to the absorption of moisture, which provided a plasticization effect. Nonetheless, once degradation has begun, the EB dropped, as shown in the AWT/PP (TD) sample, where at the beginning stage (first 3 months), it gained 53.3% but eventually lost 3.8% after

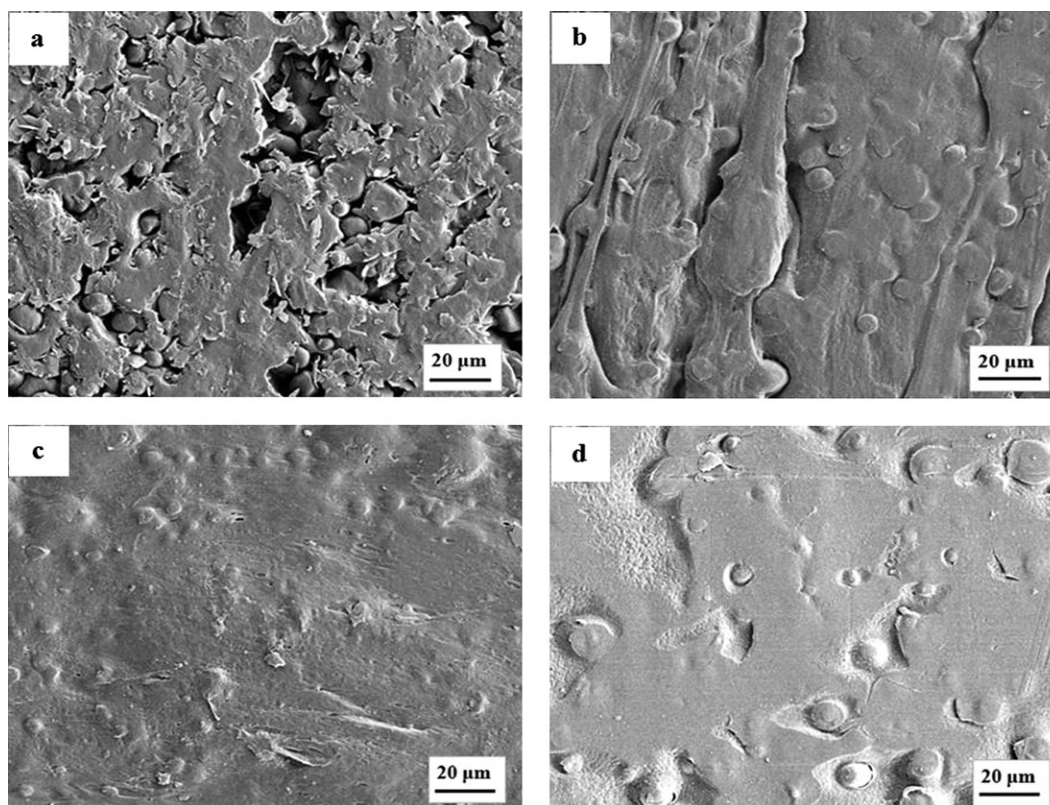


Figure 5. (a) SEM surface image of CS before soil burial. (b) SEM surface image of AWT/PP before soil burial. (c) SEM surface image of AWS/PP before soil burial. (d) SEM surface image of NTS/PP before soil burial.

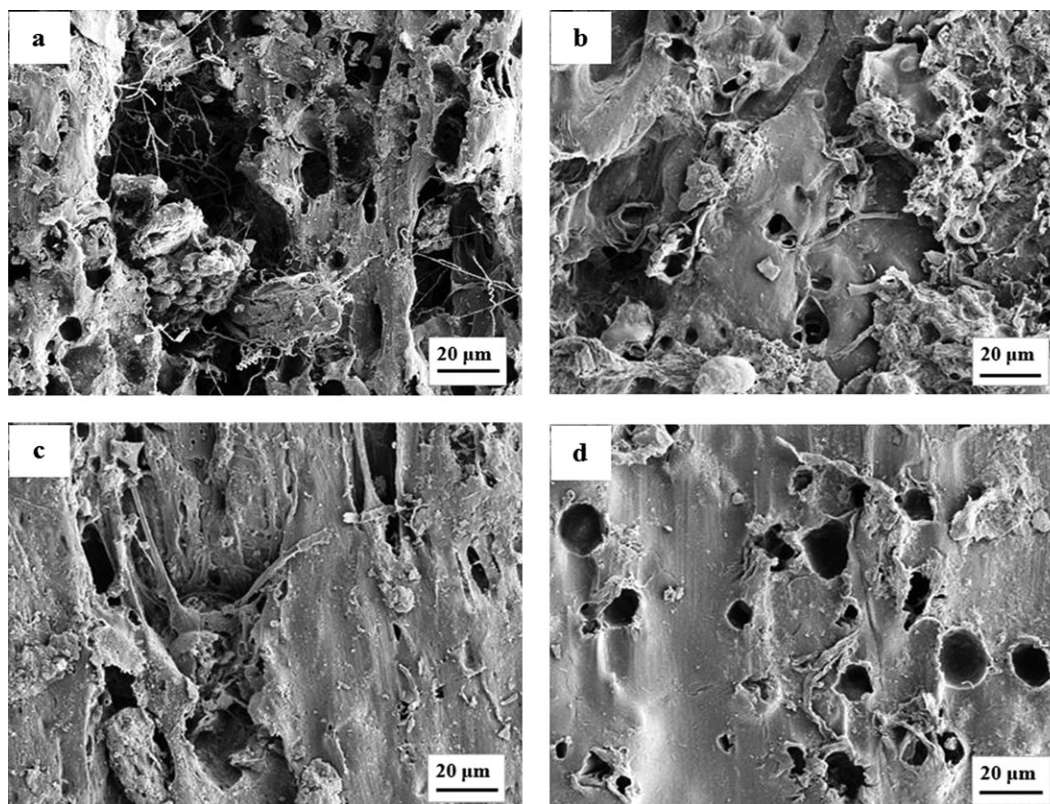


Figure 6. (a) SEM surface image of CS after 6 months of outdoor soil burial. (b) SEM surface image of AWT/PP after 6 months of outdoor soil burial. (c) SEM surface image of AWS/PP after 6 months of outdoor soil burial. (d) SEM surface image of NTS/PP after 6 months of outdoor soil burial.

6 months. After a certain point, the moisture absorbed from the surrounding no longer acted as a plasticizer because most of the starches had been consumed and there was an increase porosity that then weakened the matrix. When compared to the indoor soil burial, this outdoor soil burial displayed overall greater EB loss. AWS/PP (MD) showed 69.8% EB loss for indoor burial but 96.9% EB loss after outdoor burial. A similar trend was observed for NTS/PP (MD), with 75.2% EB loss for indoor soil burial compared with 96.4% loss for outdoor soil burial after a 6-months period of exposure.

The Young's modulus (YM) of the outdoor soil burial specimens decreased over time (Table II). The reduction in YM was 13.1–81.4% after 6 months. The CS specimen, which had the greatest weight loss, suffered the greatest loss in YM as well. AWT/PP, which had the least weight loss, showed the least reduction in the YM. This finding again shows modulus drop corresponding to a decrease in weight loss.

SEM Micrographs of Soil Burial Samples

SEM micrographs of samples before and after 6 months of outdoor soil burial are shown in Figure 5(a–d) and Figure 6(a–d), respectively. The micrographs show the presence of microorganisms on buried specimens, which, along with the formation of voids, a sign of degradation. This finding is consistent with those of previous studies.^{15,43} Alvarez et al.⁴⁴ reported that the surfaces of sisal fibers/Mater Bi-Y biocomposites were colonized by bacteria, actinomycetes, and fungi after burial. In this study, the PP matrix was not affected by the microorganism attack;

however, it became porous after the loss of starch granules. A similar observation was reported by Ratanakamnuan and Aht-Ong⁴⁵ for buried LDPE/banana starch films.

CONCLUSIONS

The degradation behavior of agricultural waste based-TPS/PP is found to be similar to that of native tapioca starch blend (NTS/PP) and commercial grade sample (CS). The deterioration in properties depends on the starch compositions (e.g., amylose-to-amylopectin ratio), particle size, dispersion, and interfacial adhesion with matrix. The highest weight gain due to water absorption was observed for high-amylopectin starch blends (i.e., AWS/PP) compare to blends made with high-amylose starch (i.e., NTS/PP). Amylopectin molecules are more susceptible to shear degradation, and the destruction of starch granules allows the easy penetration and retention of water molecules. The biodegradation rate of the blends was found to depend on the water absorption behavior and starch structure. Amylopectin is more easily broken down by the microorganism than amylose. Extensive water uptake behavior encouraged the growth of soil microorganisms and conversion of C into CO₂. Biodegradation occurred in the starch phase and not PP. In general, TPS/PP experienced greater weight loss and deterioration in tensile properties during outdoor soil burial compared to indoor soil burial. The outdoor soil burial was more aggressive in promoting degradation. The deterioration in tensile

properties was attributable to starch depletion, which yielded a porous matrix with a loss of structural integrity.

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