Effects of Hydrothermal treatments on the Physicochemical and biodegradability properties of starch-LDPE composite

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Abstract

Blending of Low density polyethylene (LDPE) with hydrothermally treated sorghum (*Sorghum bicolor*) starch was carried out with the aim of producing an ecological–friendly, economical, and biodegradable polymer for use as packaging materials. Native starch from sorghum was modified physically by heat-moisture treatment at 25% moisture level (100°C) for 16h; and by annealing in excess water for 24 h (50°C). The physicochemical properties of the starch were investigated. Biodegradable composites were prepared by blending the sorghum starches with LDPE at 1%, 3%, and 5% ww^{-1}, using 2% ww^{-1} ethylene-bis-stearamide as the binding agent, and the blends were thereafter extruded. The mechanical properties, water absorption, and thermal properties of the starch–LDPE composites were determined. Soil burial test was carried out for six months to evaluate the biodegradation rate of the composites. The mechanical properties of the starch–LDPE composites reduced progressively as the starch content increased The water absorption capacity of the starch–LDPE composite increased from 0.05% (in LDPE) to 2.85% (in 5% ASC). Thermal behavior of the composites showed two-stage degradation, the main stage occurring in the range 430 – 648°C. After the soil burial test, the extent of biodegradation (0.55%) for unmodified LDPE polymer was significantly increased in the starch–LDPE composites with 100% 5% ASC.

Key words: Starch, Annealing, Composites, Sorghum, Biodegradable

1. Introduction

Biodegradable polymers are defined as polymers that are degraded by the enzymatic action of living organisms such as bacteria, yeast, fungi, etc. and the ultimate end-product of the degradation process are carbon(iv)oxide (CO_2), water (H_2O) and biomass under aerobic condition and hydrocarbon (HX), methane (CH_4) and biomass under anaerobic conditions. Biodegradation through blending of natural biopolymers such as starch with the synthetic polymer to produce biodegradable polymer has received considerable attention in recent time (Ammala et al. 2011; Chanprateep, 2010). The reason behind the blending of starch with Low density polyethylene (LDPE) is that it is believed that if the biodegradable component (such as starch) is present in sufficient amounts in the polymer, it could be consumed or attacked by microorganisms such as bacteria and fungi in the soil or in the waste disposal environment, leading to increased porosity, void formation and loss of integrity by the polymer matrix, the plastic

containing the remaining inert component will fragment, disintegrate into smaller molecules, decompose and later disappear (Zavarexe et al., 2012; Pedroso and Rosa, 2005). Blending of starch with synthetic plastics has therefore become an economical and versatile route to obtain polymers with a wide range of desirable properties (Cerruti et al., 2011).

Starch is a natural renewable raw material with a wide range of versatility and usefulness, it is the basic source of energy for the majority of the world's population, it is consumed in various forms and products, it plays a major part in supplying the metabolic energy that enables the body to perform its different functions; it is also one of the most important raw materials for industrial use (Ammala et al., 2011).

However, previous studies had showed that addition of starch to LDPE drastically weakened the mechanical strength of the film, (Ratnayake and Jackson, 2009) and causes dimensional instability (Harinder *et al.,* 2011). Immiscibility of starch and polyethylene due to the differences in their polarity constitute another major obstacle to the blending (Pedroso and Rosa, 2005; Harinder et al., 2011; Tahira and Abid, 2014). Another major disadvantage of starch as a biopolymer is their dominant hydrophilic character, fast degradation rate and poor mechanical properties (Demirgoz et al, 2000).

From its chemistry, starch lends itself to various types of modifications that widen and enhance its industrial potential (Harinder *et al.,* 2011). Physicochemical modifications of starch such as annealing and heat-moisture treatment can yield diverse properties and improve the hydrophobicity of the starch (Meera and Lee, 2002). Starch modification has therefore proved to be capable of overcoming the problems of incompatibility of starch and LDPE. The objective of this work is to produce plastics that are environmentally degradable, affordable and environmentally friendly, to solve the environmental hazard caused by non-biodegradable polymer.

2.0 METHODOLOGY

2.1 Annealing and Heat moisture treatment of the starch

White sorghum starch was isolated following the methods of Adebowale *et al*. (2005). The native sorghum starch (NSS) was hydrothermally modified by annealing at 50°C for 48 h (ASS), while the heat-moisture treatment was carried out at 100°C for 16 h at 25% moisture level (HSS), following the method of Adebowale *et al.* (2005). All determinations were carried out in triplicate and results reported as mean ± standard deviation (at $p < 0.05$ confidence level). Data were assessed and analyzed using the procedure of SAS (Demirgoz et al., 2000).

2.2 Blending and analysis of the composite

Mixing of the components of Low density polyethylene (LDPE) and Modified starch blends was done with a hand mixer at a speed of 300rpm for 30 min. LDPE was mixed with modified starch of 1, 3 and 5% ww^{-1} . 2% ww^{-1} of ethylene-bis-stearamide (EBS) wax was added to each of sample before mixing. The blending was done with a co-rotating screw extruder. Tensile strength, percent elongation at break, yield elongation and Young's modulus were determined according to the ASTM standard Thermogravimetric analysis was performed on a thermogravimetric analyzer, Water absorption test was carried out using method of (Gouhua et al., 2006)

2.3 Soil burial degradation test

Soil burial degradation test was performed as described by (Gouhua et al., 2006) with slight

modifications. The degradation of the specimen was determined at a regular interval of 15 days by taking the specimen carefully from the soil and washing it gently with distilled water to remove the soil, they were then dried under vacuum until a constant weight was obtained. Weight loss of the specimen with time was used to indicate degradation rate.

3.0 Results and Discussion

3.1 Mechanical properties of sorghum Starch-LDPE composites

The result of mechanical properties; Tensile strength (TS), Yield elongation (YE), Elongation percent (E %) and Young's modulus (YM) of the composites are presented in Table 1. The addition of starch granules to low density polyethylene (LDPE) produced starch-LDPE composites having Young's modulus which increased through stiffening of the granules and elongation which decreased as the starch content increased.

The Young's modulus of starch-LDPE composites are in the range 2.01 - 3.95 MPa for heat moisture treated sorghum starch composite (HSC). The values for annealed sorghum starch composite (ASC) ranges between 2.80 and 3.60 MPa. Both are higher than the values for native sorghum starch composite (NSC), indicating lower flexibility of HSC and ASC. The Young's modulus for all the composites increased with increase in sorghum starch content (Meera and Lee, 2002).

The values of yield elongation at break fell drastically in all starch composites when compared to 100% LDPE and slight variations among composites with different starch contents were not significant. There are remarkable improvements in the mechanical properties of modified starch-LDPE composite when compared with the native sorghum starch-LDPE composite.

The analysis of the TG thermograms showed that the degradation was composed of two weight loss steps. The main decomposition stage of the composites is between 361˚C and 628˚C.The highest T_o of 453˚C was reported for annealed sorghum composite (ASC). The thermal stability of the composites was reduced by the incorporation of the starch into the LDPE moiety. There was increased thermal stability for all the modified starch composites except HSC at 3% when compared with native starch composite (NSC). The decomposition processes can be attributed to weak interfacial combination between polyethylene and starch when the latter was not modified. (Cerruti et al., 2011; Wang et al., 1997). The initial decomposition temperatures (To) of the modified starch composites are lower than that of the native sorghum starch (NSC). However; the results showed that NSC rapidly decomposed as soon as it reached To unlike the modified starches composites; this can be accounted for by the homogeneity that occurs after modification of the starch. The main decomposition mechanism of the starch is the dehydration reaction between starch and hydroxyls; this suggests that the smaller the amount of hydroxyls groups left on the starch the more stable it will be.

The water absorption capacities (WAC) of modified sorghum starch-LDPE composites increased with increase in the starch contents. The values range between 0.05 and 2.85%. WAC for LDPE was 0.05% (Table 1).This shows that the inclusion of starch into the polymer matrix played significant roles in their water absorption capacities. Annealed sorghum starch-LDPE composite (ASC) however showed better absorption capacities than the heat-moisture treated sorghum starch-LDPE composites. Water absorption of the material allows microorganism such as bacteria and Fungi to grow and utilize the material as energy source thereby degrading and decomposing it (Zavareze et al., 2012).

Table 1: Mechanical properties and water absorption capacities (WAC) of native, annealed and heat-moisture treated sorghum starch and LDPE composites.

Starch-LDPE (% starch)	TS (MPa)	YE (MPa)	YM (MPa)	E (%)	WAC (%)
1% HSC	2.87 ±0.03	9.60 ±0.11	2.01 ±0.01	128.50 ±0.11	0.42 ±0.03
3% HSC	3.07 ±0.02	11.50 ±0.21	3.60 ±0.21	78.34 ±5.56	2.09 ±0.06
5% HSC	3.18 ±0.07	4.67 ±0.17	3.95 ±0.19	87.20 ±1.96	2.44 ±0.12
1% ASC	0.46 ±0.03	6.01 ±0.22	2.80 ±0.10	209.50 ±0.30	1.32 ±0.02
3% ASC	0.88 ±0.01	5.01 ±0.11	3.10 ±0.01	208.70 ±0.00	2.48 ±0.01
5% ASC	0.98 ±0.00	5.00 ±0.10	3.60 ±0.00	201.40 ±0.15	2.85 ±0.11
1% NSC	1.20 ±0.00	2.99 ±0.01	1.35 ±0.00	109.50 ±0.25	0.33 ±0.06
3% NSC	1.34 ±0.06	3.61 ±0.00	1.76 ±0.00	87.20 ±1.45	0.49 ±0.01
5% NSC	2.64 ±0.00	4.32 ±0.01	2.50 ±0.05	79.34 ±0.00	0.66 ±0.06
LDPE	3.78 ±0.01	13.44 ±0.00	2.55 ±0.00	210.01 ±0.01	0.05 ±0.06

Heat-moisture treated sorghum starch-LDPE composite (HSC); Annealed sorghum starch-LDPE composite (ASC); Native sorghum starch-LDPE composite (NSC); Low density polyethylene (LDPE) Tensile strength (TS); Percent elongation (E); Young's modulus (YM) and Yield elongation (YE)

Table 2: Percent weight losses for Starch-LDPE composites after their burial in soils

Starch-LDPE (% Starch)	Percent weight loss (%)						
	90 days	105 days	120 days	135 days	150 days	165 days	180 days
1% HSC	0.54 ±0.02	1.04 ±0.01	1.30 ±0.00	1.80 ±0.00	2.60 ±0.03	3.40± 0.03	8.65 ±0.06
3% HSC	0.51 ±0.01	1.22 ±0.21	1.31 ±0.02	2.05 ±0.01	2.80 ±0.02	3.87 ±0.05	10.75 ±0.00
5% HSC	0.97 ±0.01	0.98 ±0.03	2.58 ±0.00	3.05 ±0.01	4.65 ±0.00	5.59 ±0.03	10.35 ±0.02
1% ASC	0.35 ±0.04	3.46 ±0.19	6.90 ±0.00	12.60 ±0.01	20.65 ±0.08	46.25 ±0.08	63.50 ±0.00
3% ASC	0.67 ±0.05	1.36 ±0.02	11.68 ±0.03	15.09 ±0.01	26.50 ±1.95	48.75 ±2.95	71.50 ±0.00
5%ASC	0.50 ±0.11	10.75 ±0.05	11.19 ±0.05	16.53 ±0.00	37.87 ±0.02	69.05 ±0.02	98.89 ±3.87
1% NSC	1.20 ±0.06	1.39 ±0.03	1.66 ±0.02	4.35 ±0.03	6.50 ±0.01	8.38 ±0.03	10.56 ±0.06
3% NSC	0.73 ±0.03	0.75 ±0.03	0.80 ±0.02	2.16 ±0.06	4.10 ±0.03	14.35 ±0.03	18.66 ±0.03
5% NSC	0.30 ±0.16	0.40 ±0.14	1.20 ±0.02	1.91±0.11	6.53 ±0.03	10.26 ±0.14	22.26 ±0.16
LDPE	NIL	NIL	NIL	NIL	0.13 ±0.01	0.24 ±0.01	0.55 ±0.12

Heat-moisture treated sorghum starch-LDPE composite (HSC); Annealed sorghum starch-LDPE composite (ASC); Native sorghum starch-LDPE composite (NSC); Low density polyethylene (LDPE)

3.2 Biodegradation of sorghum Starch-LDPE composites

The biodegradability of starch-LDPE composite was studied by evaluating their weight losses over a period of six months (180 days), Table 2 shows the results of biodegradation of the composites after burial in soils for various times. Soil burial test is an outdoor experiment which provides a natural environment where parameters such as soil humidity, temperature and microbiological activities are in less control.

All the tested specimens had relatively same shape and size to avoid the effects of the composites shape on the biodegradation. All the composites except 100% low density polyethylene (LDPE) showed slight increase in weight few days after soil burial due to water uptake from the soil. Evidence of microbial attack was noticed after 45days of burial in the soil.

All the samples decreased in weight within 90 days. Annealed sorghum starch composites (ASC) however showed the highest level of weight loss while the heat moisture treated sorghum starch composite (HSC) recorded the least. According to Serrano and Franco (2005), starch annealing increases the starch enzymatic susceptibility. The 5% annealed sorghum starch composite (5% ASC) was completely biodegraded within six months of burial while 3% annealed sorghum starch composite (3% ASC) was 71.50% biodegraded.

It was observed that the rate of degradation increased with time in all the starch-LDPE

composites and the increase is proportional to the quantity of the starch in the composite.

Diffusion of water into the polymer matrix resulted in the swelling of the composite and allowed the growth of microorganism on the film. The faster degradation rate of the composite could be attributed to the increased ability of the film to absorb higher amount of water. This is because enzymatic activities occur in the aqueous medium. The water absorbed by the film caused the microorganism to attach and grow on the composite and since the composite films have become the main source of energy for the microbial growth the polymer structure is broken, thereby reducing the molecular weight of the polymer for further decomposition. The result is consistent with those of water absorption properties of the composite which increased with incorporation of the starch into the polymer matrix (Table 2). Lan *et al.* (2014) observed similar report for Poly vinyl acetate-Starch composites and the water absorption capacities of the composites was also reported to have increased with increase in the starch content of the composite.

However the degradation of pure LDPE was negligible when compared with the sorghum starch-LDPE composite, which confirm that incorporation of the sorghum starch into the composite greatly enhanced the biodegradation process. Similar results were reported by (Ali and Hasnain, 2014) for rice starch-LDPE and potato starch-LDPE blends (Suda et al., 2001) for cassava starch-LDPE composite.

4.0 Conclusion

Blending of sorghum starch with LDPE enhanced the biodegradation of the composites; Hydrolysis of the starch occurred and makes the LDPE structure porous increasing the surface of composites assessable for the attack by microorganisms and thereby accelerating the degradation process.

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