International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2018): 7.426

Synthesis of Degradable Mulch Films from Bambara (Vigna Subterranean.L) Groundnut Starch/LDPE Composites

Gbemileke .S Ayedun

Department of Chemistry, Legacy University, Banjul, The Gambia

Abstract: ***Starch is a natural carbohydrate-based polymer that is globally available from various natural sources such as Bambara groundnut, wheat, rice, corn and potato with some inherent limitations to its industrial applications such as hydrophilicity, poor mechanical properties and dimensional instability. Biodegradable composites from Starch and Low-density Polyethylene were synthetically developed. The isolated native starch was modified by annealing at 50°C for 48 hr (BAS), and heat-moisture treated at 100°C for 16 hr at 25% moisture level (BHS).The crude protein of BG flour was 16.88%. The amylose content of the flour and native starch was 6.10% and 27.70%, respectively. Biodegradable composites were prepared by blending the native and modified starches with LDPE at 1%, 3% and 5% ww-1. Hydrothermal modification increased the gelatinization profile of the starch but reduces its pasting properties. Swelling and solubility of the flour and starches increased with increase in temperature. The tensile strength (T.S), enlongation at break percentage (EB%), water absorption test and 6 months soil burial test was carried out to determine the degradability. The tensile strength of the composite was lower than 6.37MPa for the 100% LDPE. BAC5 showed the highest level of degradability among other composites at the rate of 35.27%. Annealed starch and Heat moisture treated starch contributes better to starch degradability than the native starch.***

Keywords: Annealing; Bambara groundnut; Heat-moisture treatment; Low density polyethylene

1. Introduction

Polymers form a very important class of materials, with wide applications in various industries. They abound around us in everyday use; in rubber, in packaging materials, biomedicals, mulch films, in adhesives tapes etc. Polymers can be categorized as natural and synthetic types. The natural polymers include proteins, starch, cellulose etc, while synthetic types include polyethylene, polystyrene, phenol, formaldehyde resin, polypropylene, etc. The natural polymers can be easily purchased, relatively cheap and are renewable, while the synthetic polymers have better processing properties, improved mechanical strength, costly and they do not biodegrade easily in the environment (Halley, 2005). These qualities of synthetic polymers over the ages in various applications have contributed to its ubiquitous usage but the disposal and its accumulation in the environment are the major problems associated with it. One of the ways of addressing the problem associated with such polymers is to make them biodegradable.

Biodegradable polymers are the specific type of polymers that can easily be broken down by the action of microorganisms after its intended purpose which results in the release of natural by-products such as carbon dioxide and nitrogen; biomass, and inorganic salts. Biodegradable polymers are found both natural and synthetically made consisting of majorly esters, amide and ether functional groups. Their properties and breakdown mechanism are determined by molecular structure. They are synthesized by condensation reactions, ring opening polymerization and metal catalysts. Most of these materials are 'one use' which when disposed into the environment constitute a major environment hazard; hence, the necessity to develop a polymeric material that is economical and biodegradable. The modified natural polymers are the type, in which natural polymers are modified so that the environment acceptable polymer can be developed. The modification includes blends with other natural and synthetic polymers, grafting of other polymeric composition and chemical modification to introduce some desirable functional groups by oxidation or some other simple chemical reaction such as esterification or etherification.

Natural polymers have been reported to have more advantages over the synthetic polymer because they are comparatively economical, derived from renewable raw material and biodegradable (Lu and Sue, 2002). Among the naturally occurring renewable biopolymers, starch is one of the most abundant and low-cost biodegradable materials (Mohanty et al., 2000). Starch is a natural carbohydrate-based polymer that is globally available from various natural sources including Bambara groundnut, wheat, rice, corn and potato.

Starch, however have some inherent limitations such as hydrophilicity, poor mechanical properties and dimensional instability which limits its various use in industrial applications (Zhou et al., 2007). One of the ways of overcoming these limitations and consequentially increased the functional properties of starch for various industrial applications can be achieved by modifying the starch through physical and chemical method (Zhou et al., 2007). Physical modification of starch includes heat-moisture treatment, annealing, pre-gelatinisation, etc while chemical modification involves acidification, carboxylation, acification, etc (Lopez et al., 2002). The starch used in this research work is from Bambara ground nut (Vigna Subterranean. L) which is an underutilized legume with a very high content of carbohydrate and subjected to physical modification by heat-moisture and annealing.

Polyethylene mulch film is an important material used in agriculture farming to maintain water conservation in soil

and in the prevention of weed growth among other functions. The ubiquitious use of this material has caused a serious environmental hazard because it is one use product that is discarded hapharzardly into the environment. Degradable polymer developed by blending starch extracted from Bambara groundnut with Low-density Polyethylene (LDPE) for use as mulch films may go a long way to addressing the age long problem associated with the disposal of non biodegaradable polymeric mulch films since it readily decomposed and add nutrient to the soil. This decomposition also removes the man-hour associated with mulch removal after use, with a concomitant effect on the cost of production.

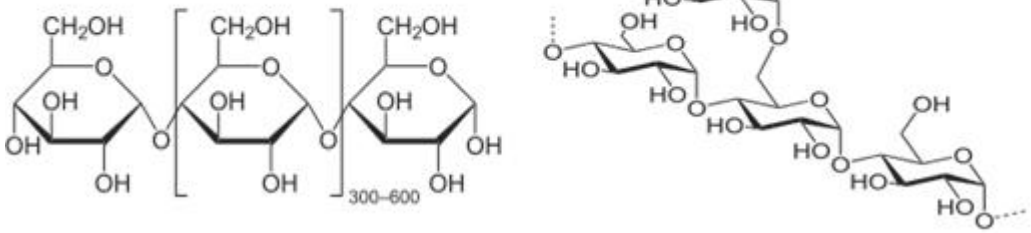
2. Materials and Methods

Low density Polyethylene (LDPE), Bambara groundnut sample was manually screened to eliminate defective ones and stones, dry milled to a fine powdered stored at 40C., Ethylene-bis-stearimide (EBS wax) and all chemicals used were of the analar grade.

2.1. Starch isolation

BG (*Vigna subterranean*) was purchased at Bodija market, Ibadan, Oyo State, Nigeria, BG bean was milled to produce the Bambara groundnut flour (BGF) used in the study. Its starch was isolated as described by Afolabi (2012)

Structure of starch



2.2. Hydrothermal modification

The native starch of BG starch (BNS) was hydrothermally modified by heat-moisture treatment at 100°C for 16 hr at 25% moisture level (BHS), while annealing was carried out at 50°C for 48 hr (BAS) following the method of Adebowale et al., (2005). The purity of the isolated starch was evaluated by determining their protein, fat, and ash content.

2.3. Proximate composition

The AOAC International (2005) method was used in determining the ash, moisture, fat, crude fiber, and protein contents of the starch sample. The carbohydrate content was determined by difference. The AACC (2003) method was employed for the determination of the amylose content of the starch and flour sample.

2.4. Swelling power and starch solubility

The effect of temperature on solubility and swelling power of the starch samples were investigated following the methods of Afolabi et al (2012).

2.5 Melt blending and film blowing

Prior to blending, all ingredients were dried in a vacuum oven at 80 ^{o}C for 24 hr. The prepared native and modified starch (1, 3 and 5 wt%) were pre-mixed with LDPE (3kg) and 2 wt% EBS wax (based on the blend weight). The polymer composites were developed on a twin screw extruder (model ZSK25, Germany). The extruder had screw diameter (d) of 25 mm and the length to diameter ratio (L/D) was 40. The temperature profile along the six heating zones of the extruder barrel was 115–120 ^{o}C (from feed zone to die) and the screw speed was set at 150 rpm. The prepared blends were merged in the form of continuous strands through the die. The pellets were then blown into 45 µm thick films.

Table 1: Formulations of starch/LDPE composites films with 2 wt% ethylene bisstearimide

Sample code	LDPE (wt/wt)	Starch (wt%)	EBS (wt%)
BNC1	99	1	2
BNC3	97	3	2
BNC5	95	5	2
BHC1	99	1	2
BHC3	97	3	2
BHC5	95	5	2
BAC1	99	1	2
BAC3	97	3	2
BAC5	95	5	2

BNC- Bambara native starch composite, BHC- Bambara heat-moisture starch, BAC- Bambara annealed starch composite.

2.6 Thermal Properties Analysis of the Films.

Tensile and flexural specimens of dimensions 80 mm× 8 mm were prepared according to ASTMD5083-10 and kept in polyethylene bags at room temperature 20 ^{o}C and 50% RH for 3days before mechanical testing. A Saumya 3382 universal testing machine was used at room temperature. The machine capacity is 100 kN with 1:100 kN force ranges (it uses the load cell to 1% of its capacity with no loss of its accuracy). A tensile strain rate of 0.1 per min and a deflection rate of 2 mm/min were used for the tensile and flexural tests, respectively

2.7 Degradation Test

Samples of the polymer composites of dimensions 40 mm×8 mm×2 mm were buried at about 10 cm depth in a mixture of 50% sand and 50% soil. The temperature was maintained at 30 ± 2 ^{o}C. The water content of the soil and sand mixture were kept in range of 30–40% by adding 400 ml water to each 1250 g of mixture every 3 days, following the procedure outline by Maiti *et al*. (2010). After every predetermined period, samples were carefully cleaned with water before being dried at 40 $^{\circ}$C for 30 min and then weighed to determine the weight loss using the following equation:

$$\text{Weight loss } \% = \frac{Mi - Mf}{M_i} \times 100.$$

3. Results and Discussion

The proximate composition of Bambara groundnut native starch (BNS) was presented table 2. The protein content of BNS is 2.22% which is higher than the values 1.0% and 0.59% reported by Adebowale et al., (2002) and Mensah (2011) for Bambara starches respectively. These differences could be attributed to the method of isolation of the starch and probably the varietal diffrences of the legume. The 13.65% moisture content of the BNS was similar to the 14.80% reported by Adebowale et al. (2002) for BGS which can be attributed to the percolation of water into the Bambara groundnut starch soaking in the isolation process.

The 0.5% crude fiber content for BGS was at par with the values 0.5% and 0.6% reported by Mensah (2011) and Piyarat (2008) which was an indication that Bambara groundnut granule was mature. The 1.78% fat content content for BGS was found to be higher than 0.42% and 0.44% reported in the literature for Bambara groundnut(Mensah, 2011 and Piyarat, 2008). The 81.90% carbohydrate content in BGS was higher than 78.10% reported by Amara (2014).

Table 2: Proximate Composition of the Isolated Bambara Native Starch

Proximate	Composition (%)
Crude Protein	2.22± 0.00
Moisture content	13.65±0.01
Ash content	0.45±0.00
Crude Fat	1.78±0.02
Crude Fiber	0.50±0.03
Carbohydrate	81.90±0.07

Values are means of duplicate readings ±STD

3.1 Effect of Temperature on Swelling Power and Solubility of Native and Modified Starch

The effect of temperature on the swelling power of the native and modified Bambara groundnut starches is presented in Figure 4. The swelling capacity of the starch measured from the 55- 95 ^{o}C at 10^{o}C interval increased with increase in temperature, with Bambara Native Starch (BNS) - having the highest swelling power. Bambara Annealed Starch (BANN) and Bambara Heat Moisture Starch (BHT) also shows increment; BNS>BAS>BHT25.The reduction observed in annealed starch could be attributed to both crystalline perfection and interactions involving amylopectin chains which would decrease hydration of the amorphous regions, thereby decreasing granular swelling (Liu and Donner 2009).

While the lower swelling power of BHT compared to BAS could be attributed to restriction in percolation of water within starch matrices as a result of increased in starch crystalline after starch modifications. The reduction in swelling power of BHT could also be attributed to internal rearrangement of the starch granules, which causes further interaction amongst the starch functional groups (Hoover and Manuel, 1996), making it form more ordered double helical amylopectin side chain clusters.

The result obtained from the effect of temperature on solubility power of native and modified Bambara Groundnut Starch in Figure 1 reveals that the solubility of all the starch increased as temperature increases which is due to the fact that higher temperatures promote mobility of starch chains (Kittipongpatana and Kittipongpatana, 2011), thus increasing the dispersion of starch molecules, which improved the solubility, however a slight reduction was observed when the temperature was increased to 75^{o}C. There was a decrease in the solubility percentage both in the native and modified Bambara groundnut starches at 55^{o}C and 65^{o}C but a steady increase in the solubility percentage at temperature ranging from 75^{o}C and 85^{o}C. There is a slight reduction in both native and modified Bambara groundnut starch at 95^{o}C. The solubility percentage of both native and modified Bambara starch peaked at 85^{o}C with Bambara annealed starch having the highest value.

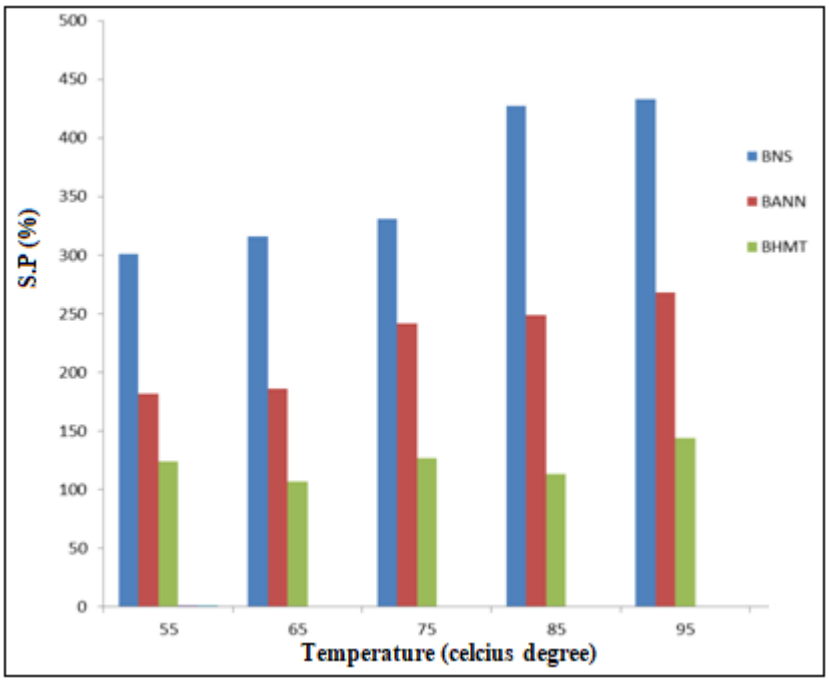


Figure 4: Effect of temperature on swelling of Bambara native(BNS), Annealed (BANN) and heat-moisture treated starch (BHMT).

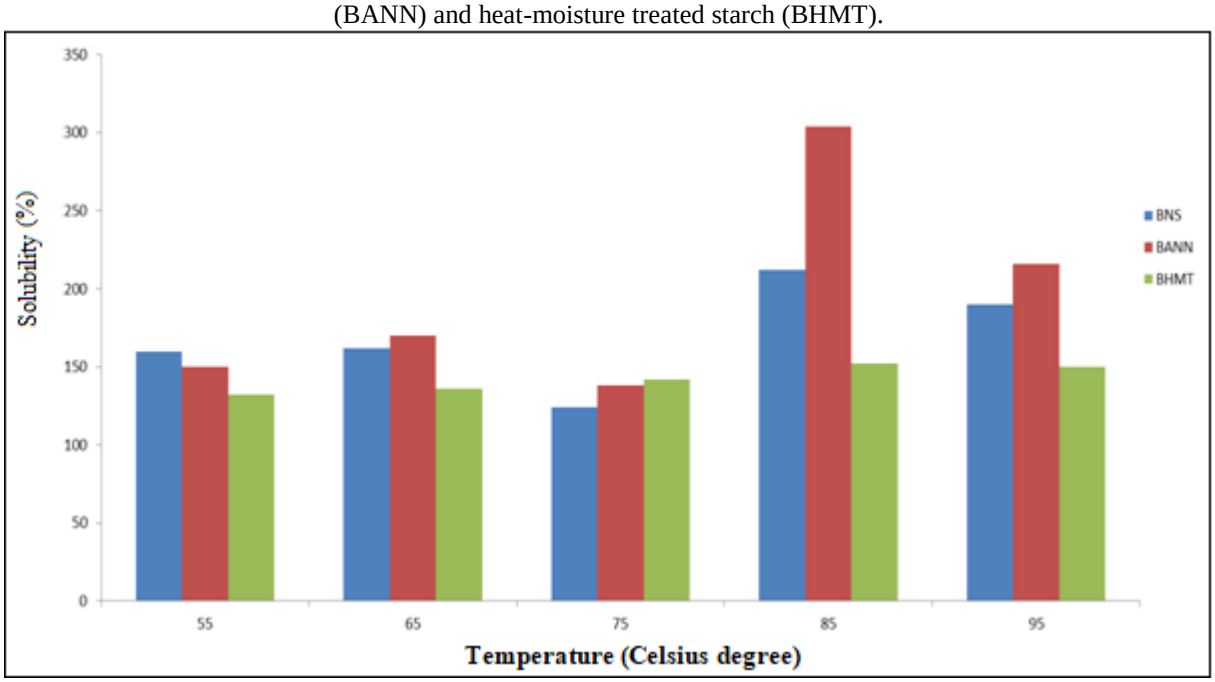


Figure 4: Effect of temperature on solubility of Bambara native (BNS), Annealed (BANN) and heat-moisture treated starch (BHMT)

3.2 Mechanical Properties of the Starch-LDPE Composites

The Mechanical properties of the composites such as tensile strength (TS), elongation at break (EB%), Young Modulus(YM) of native and modified starch-LDPE composites are presented in Table 3. The 6.37MPa tensile strength in 100% LDPE film reduced as a level of starch in the composites due to the hydrophilic nature of starch, which is not compatible with hydrophobic polymers. The result showed that BHC of the same level of starch content with other composites had higher tensile strength than all the corresponding composites. It is observed that hydrothermally modified starch composites (BHC and BAC) had higher tensile strength than native starch composites films. This is observed trend could be attributed to the high amylose content in annealed and heat moisture treated starch than native starch which invariably contributes to bond strength. The values range from 0.49 to 6.37MPa for all the composites.

The percentage elongation at break (EB%) for the 100% LDPE was 52.38%. It was observed that increase in the starch content of the composite leads to corresponding decrease in the EB% as shown in Table 3. Hydrothermal modification also leads to increase in the EB% of the composites. BHC1 had the highest EB% of 50.00% while BAC5 had the lowest EB% value (13.50%). Starch fillers increase adhesion to one another through van der Waals forces and hydrogen bond which are similar to tensile

strength. However, decrease in the percentage elongation occurred because of the weakness of the interfacial adhesion between starch-LDPE (Danjaji et al., 2002). In synthetic polymer blends, the addition of the immiscible component to a ductile matrix generally decreased the elongation properties at break. The elongation will, therefore depend on the state of the interface (Rosa et al., 2004). Raymond and Charles (1980) also reported a reduction in EB% on sago starch-LDPE composite.

The Elastic modulus of LDPE was observed at 6540 which increased in almost all the composites. The 3%-level of starch in all the composites had higher value of modulus than other composites. The result showed that BHC3 had the highest value than other composites.

Table 3: Mechanical Properties of Starch-LDPE Composites.

Sample code	Tensile Strength (MPa)	EB%	Young modulus
LDPE	6.37± 0.00	52.38 ± 0.02	6540.85 ± 1.41
BNC1	1.71± 0.02	30.00 ± 0.71	109.85± 1.27
BNC3	1.69± 0.02	24.63 ± 0.07	69222.50 ± 1.41
BNC5	0.49± 0.02	13.50 ± 0.14	6131.20 ± 2.68
BHC1	4.41± 0.01	50.00 ± 0.35	8829.20 ± 2.33
BHC3	2.45± 0.01	27.13± 0.06	31882.50 ± 0.00
BHC5	0.61± 0.03	13.75 ± 0.14	560.50 ± 3.32
BAC1	2.94± 0.01	45.38 ± 0.14	26754.00 ± 2.12
BAC3	3.18± 0.01	38.50 ± 0.35	29328 ± 2.75
BAC5	0.51± 0.01	13.63 ± 0.21	20601.00 ± 2.82

Values are means of duplicate readings ± STD. BNS-Bambara native starch composites, BHC-Bambara heat-moisture treated starch, BAC-Bambara annealed starch composite. EB% = percentage elongation at break.

3.3 Determination of Water Absorption by the Composites.

The water absorption percentage of the composite consisting of both native and modified starch content and immersion time is depicted in Figure 6. The water absorption intake in the composites showed lower rate of absorption at the initial days of immersion which later increased as the immersion time increases with PAN5 having the highest value. The value ranges from 2% to 18%, in all the composites. The absorption value peaked at 9.0 %, 8.33 % and 8.0% for BAC5, BHC5 and BAC3 respectively. Water absorption capacity results shows that the composites absorption is highly dependent on increasing the starch content. It is observed that the annealed and heat-moisture starch-LDPE composites showed increased water uptake in the composites than native starch-LDPE composites.

Heat moisture starch-LDPE composites also had values increased from 1.15% to 8.33% during the 6 days of testing. It is widely accepted that the existence of materials such as starch and the ethylene-bis-stearamide could be responsible for water absorption sensitivity of the samples. Starch as a hydrophilic polymer can facilitate water uptake of the samples by forming hydrogen bonds between water and its hydroxyl groups (Oromiehie *et al*; 2013). Also, formation of branched and cross linked macromolecules as a consequence of reaction between PE-grafted-EBS and hydroxyl groups in modified starch may enhance the water absorption of the samples(Sabetzadeh et al., 2013).

Table 4: Water Absorption Capacity of the Starch-LDPE Composites

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
LDPE	0.00 ± 0.01	0.00 ± 0.02	0.01 ± 0.00	0.02± 0.01	0.03 ± 0.02	0.06 ± 0.03
BNC1	1.01 ± 0.01	1.40 ± 0.01	1.60 ± 0.14	1.70 ± 0.14	1.22 ± 0.02	2.35 ± 0.21
BNC3	1.48 ± 0.04	3.50 ± 0.42	4.35 ± 0.21	5.28 ± 0.41	6.10 ± 0.14	6.37 ± 0.52
BNC5	2.05 ± 0.04	2.60 ± 0.28	3.60 ± 0.14	5.20 ± 0.28	6.35 ± 0.35	6.85 ± 0.14
BHC1	1.15± 0.21	1.35 ± 0.21	16.69 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	2.30 ± 0.20
BHC3	1.10 ± 0.14	3.60 ± 0.14	5.43± 0.32	0.00 ± 0.01	0.00 ± 0.01	7.86 ± 0.60
BHC5	3.10 ± 0.14	4.23 ± 0.32	4.30 ± 0.28	0.00 ± 0.01	0.00 ± 0.01	8.33 ± 0.14
BAC1	1.10 ± 0.14	1.60 ± 0.14	2.65 ± 0.21	3.20 ± 0.28	4.35 ± 0.21	5.75 ± 0.07
BAC3	2.70 ± 0.28	4.30 ± 0.28	5.85 ± 0.51	6.55 ± 0.14	7.85 ± 0.35	8.00 ± 0.14
BAC5	4.07 ± 0.19	4.63 ± 0.27	6.25 ± 0.25	6.85 ± 0.35	8.10 ± 0.14	9.00 ± 0.28

Values are means of duplicate readings ± STD. BHC-Bambara heat moisture composites, BNC- Bambara native composites, BAC- Bambara annealed composites.

3.4 Degradation Test

Biodegradation of the starch-LDPE composites was determined by weight loss after burial in the soil for 6 months with periodic interval of fifteen (15) days as shown in Table 5. LDPE films made from 100% synthetic polymer degrade minimally(less than 0.35%) within six months with 0% degradation in the first five months during the soil burial test. However, an appreciable level of biodegradation commenced after 45 days in composites BHC3, BAC3, BNC5, and BAC5, while other composites degradation commenced from 60days.

It was observed that the rate of degradation of the composites increased with increase in the starch content of the composites over time. This implies that linkage of starch granules in the composites acts as an active site for microorganism attack and enzymatic susceptibility. Hydrothermal modification of starch also had effect on the composites by increasing the rate of biodegradation in the following order: BAC>BHC>BNC. The high biodegradation of BAC may be attributed to the higher water absorption capacity of acetylated starch as shown in Table 4 used in the composite, since this allows microorganism such as bacteria and fungi to grow and utilize the material as energy source leading to the degradation and decomposition of the composite.

Sample (%)	Days (months)											
	15	30 (1)	45	60 (2)	75	90 (3)	105	120 (4)	135	1500 (5)	165	180 (6)
BNC1	0	0	0	4.11	8.98	11.47	14.59	18.45	21.07	23.94	25.94	27.08
BHC1	0	0	0	4.23	12.35	15.57	15.2	18.72	23.46	24.04	26.45	27.56
BAC1	0	0	0	4.52	12	16.13	17.99	19.8	23.79	24.11	27.97	28.49
BNC3	0	0	0	4.81	12.5	17.72	19.89	20.98	24.13	25.86	29.48	31.62
BHC3	0	0	0.42	4.85	12.69	18.24	21.09	21.45	24.47	27.49	29.95	32.97
BAC3	0	0	1.16	4.98	12.88	19.99	21.96	21.81	24.94	27.85	30.28	33.24
BNC5	0	0	0.16	5.05	12.97	20.56	22.13	23.92	25.51	21.49	30.38	33.81
BHC5	0	0	0	5.22	13.04	21.21	22.59	24.63	25.74	27.67	31.16	35.12
BAC5	0	0	0.33	5.43	13.48	21.6	22.8	25.05	26.22	28.21	31.73	35.27
LDPE	0	0	0	0	0	0	0	0	0	0	0.13	0.24

4. Conclusion

Mulch films synthesized using LDPE with native and modified Bambara groundnut starch degrade progressively with time while the 100% LDPE exhibited little biodegradation(less than 0.3% in 6months). The physically modified starches (HMT and ANN) - LDPE composite biodegradation was about 35% within 6months. Also composites produced from physically modified Bambara groundnut starch-LDPE have good mechanical, biodegradation and physical properties that will make it suitable for application in the industries

References

[1] Adebowale, K.O. and Lawal, O.S. 2000. Effect of Annealing and Heat-moisture conditioning on the Physicochemical Characteristics of Bambara Groundnut (Voandzeia subterranean) starch. Nahrung / Food. 46: 311-316
[2] Adebowale, K.O., Afolabi, T.A. and Lawal, O.S. 2002.Isolation, Chemical Modification and Physicochemical Characterization of Bambara Groundnut (Voandzeia subterranean) Starch.
[3] Anchirina, V.M., Yiridoe, E.K. and Bennett-Lartey, S.O. 2001 Enhancing sustainable production and genetic resource conservation of Bambara groundnut. A survey of indigenous agricultural knowledge systems: Outlook in Agriculture 30(4):281-288
[4] AOAC. 1990. Official methods of analysis (15th edition). Washington, DC: Association of Official Analytical Chemists.
[5] Averous, L. 2004. Biodegradable multiphase systems based on plasticized starch A review. Journal of Macromolecular Science, Part C: Polymers Reviews, 44(3), 231–274.
[6] Begemann, F.1986.Bambara Groundnut Background Information .International Institute of Tropical Agriculture (IITA), Genetic Resources Unit, Ibadan, Nigeria.pp 17
[7] BeMiller, J.N. and Whistler, R.L.2009.Starch Chemistry and technology (3rd edition).
[8] Brough, S.H., Azam-Ali, S.N. and Taylor, A.J. 1993.The Potential of Bambara Groundnut In vegetable milk production and basic protein functionality systems. Journal of Food Chemistry.47: 277-283.
[9] Carioca, J. O., H. L., Pamir, P.V., Selvan, Tavares, Kennedy, L. F and Knill, C. J 1996. Industrial Utilization of starch and its derived products in Brazil. Starch/starke48(9):121-130
[10] Djuric, D.2008.Continuous Granulation with a Twin-screw Extruder. CuvillierVerlag
[11] Eknayake, S., Jansz, E. R. and Nair, B. M. 1999. Proximate Composition, Mineral and Amino acid content of Mature Canavalia gladiata seeds. Journal of Food Chemistry, 66, 115–119
[12] Flores, S. K., Costa, D., Yamashita, F., Gerschenson, L. N. and Grossmann, M. E.V. 2010. Mixture Design for Evaluation of potassium sorbate and Xanthan gum effect on properties of tapioca starch films obtained by extrusion. Materials Science and Engineering, Vol. 30, 196–202
[13] Gidley, M.J. 1987. Factors affecting the Crystalline type (‘A’-‘C’) of native starches and model compounds: A rationalization of the Observed Effect in terms of Polymorphic Structure. Carbohydrate Research, 161, 301- 304
[14] Goli, A.E. 1997. Bibliographical review. In: Bambara groundnut. Vigna subterranea (L.)Verdc. Proceedings of the workshop on Conservation and Improvement of Bambara Groundnut (Vignasubterranea (L.)Verd).
[15] Hoover, R and Vasanthan, T. 1994 Effects of heat-moisture treatments on the structure and Physicochemical Properties of Cereal, Legume and Tuber starches. Carbohydrate Research 252: 33-53
[16] Hoover, R. and Manuel, H. 1996. The effect of annealing on the physicochemical properties of legume starches.In G. R. Fenwick, C. Hedley, R. L. Richards, and S.
[17] Hoover, R. and Vasanthan, T.1994.Effects of Heat Moisture Treatments on the Structure and Physicochemical Properties of Cereal, Legume and Tuber Starches.Carbohydrate Research 252: 33-53.
[18] Jacobs, H. and Delcour, J. A. 1998. Hydrothermal modifications of granular starch, with retention of the granular structure: A review. Journal of Agricultural and Food Chemistry, 46, 2895–2905.
[19] Jacobs, H., and Delcour, J. 1998.Hydrothermal Modifications ofGranular Starch with Retention oftheGranular StructureA review. Journal of Agriculture and Food Chemistry. 46:2895–2905.
[20] Janssen, L and Moscicki, L.2009.Thermoplastic Starch: A Green Material For Various Industries. Wiley, Weinheim.
[21] Karikari, S.K. 1971. Economic importance of Bambara Groundnut. World Crops. 3(4):195-196.
[22] Kerr, R. W. 1950. Polymer chemistry. In: Chemistry and industry of starch, 2nd edition, Academic Press, New York, Pp. 3–25.

[23] Khokhar (Eds.), An interdisciplinary approach (pp. 157–161).Cambridge UK: Cambridge: Royal Society of Chemistry
[24] Kim, B.S. and Lim, S.T. 1999.Removal of Heavy Metal ions from Water by Cross linked Carboxymethyl corn starch. Carbohydrate Polymer, 39, 217–223
[25] Kittipongpatana, O.S. and Kittipongpatana, N. 2011.Preparation and physicochemical properties of modified jackfruit starches. Food Science and Technology, 44, 1766–1773.
[26] Lee, C. J., Kim, Y., Choi, S. J. and Moon, T. W. 2012 .Slowly digestible starch from heat moisture treated waxy potato starch: Preparation, structural characteristics, and glucose response in mice. Food Chemistry, 133(4), 1222–1229.
[27] Light, J.M. 1989. Modified Food Starches National Starch and Chemical Cooperation Bridgewater, NT08807.
[28] Mali, S., Sakanaka, L., Yamashita, F. and Grossmann Eiras, M., 2005. Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. Carbohydrate Polymer. 60, 283–289
[29] Mohanty, A. K., Misra, M. and Hinrichsen, G. 2000. Biofibers, Biodegradable polymers andbiocomposites: An overview. Macromolecular Materials and Engineering, 276–277(1), 1–24.
[30] Ning, W., Jiugao, Y., Xiaofei, M. and Ying, W. 2007. The influence of citric acid on the properties of thermoplastic starch/linear low-density polyethylene blends. Carbohydrate Polymers, 67(3), 446–453.
[31] Oromiehie, A.R., Lari, T.T. and Rabiee, A. 2013.Physical and Thermal Mechanical Properties of corn starch/LDPE composites. Journal of Applied Polymer Science, 127(2), 1128–1134.
[32] Otey, F.H., Westhof, R.P. and Doane, W.M. 1987. Starch-based blown films. Industrial. Engineering chemical production. 26(8), 1659–1663.
[33] Perez, S. and Imberty, A. 1996. Structural Features of Starch.Carbohydrates in Europe 15:17.
[34] Pilpel, N. 1971. Advances in Pharmaceutical Science.New York Academic Press.
[35] Radley, J.A., 1953. Analysis of the Derivatives of Different Flour Types in Starch and its Derivatives, 3rd Edition, Volume. I Chapman and Hall, London, pp. 58–80.
[36] Sabetzadeh, M., Bagheri, R. and Masoomi, M. 2012. Effect of Corn starch content in Thermoplastic Starch/Low-density polyethylene blends on their mechanical and flow properties. Journal of Applied Polymer Science, 126(S1), E63–E69.
[37] Satyanarayana, K. G. and Wypych, F. 2007. Characterization of Natural fibers. In D.Bhattacharyya, and S. Fakirov (Eds.), Engineering biopolymers: Homopolymers, blends and composites (pp. 3–48). Munich: Hanser Publishers.
[38] Satyanarayana, K.G., Arizaga, G. G. C. and Wypych, F. 2009. Biodegradable composites based on Lignocellulosic fibers—An overview. Progress in Polymer Science, 34(9), 982–1021.
[39] Shieldneck, P. and Smith, C. E. 1971.Production and Uses of Acid modifiedstarch. In R. L. Whistler, & E. F. Paschall (Eds.), Starch: Chemistry and Technology (pp. 173–215). New York: Academic Press.
[40] Shujun, W., Jiugao, Y. and Jinglin, Y. 2006. Preparation and characterization of Compatible and Degradable Thermoplastic Starch/Polyethylene film. Journal of Polymers and the Environment, 14(1), 65–70.
[41] Shujun, W., Jiugao, Y. and Jinglin, Y. 2006. Preparation and characterization of compatible and degradable thermoplastic starch/polyethylene film. Journal of Polymers and the Environment, 14(1), 65–70
[42] Smith, A. M. 1982.The biosynthesis of the starch granule.Biomacromolecules.2: 335–341
[43] Takaya, T., Sano, C. and Nishinari, K.2000.Thermal Studies on the Gelatinization and Retrogradation of Heat-Moisture treated Starch. Carbohydrate Polymer 41, 97-100.
[44] Yamaguchi, M. 1983. World Vegetables. New York: Van Nostr and Reinhold
[45] Zhang, Y., Zeng, H., Wang, Y., Zeng, S. and Zheng, B. 2014. Structural characteristics and crystalline properties of lotus seed resistant starch and its prebiotic effects. Food Chemistry, 155, 311–318