International Journal of Chemistry Studies
ISSN: 2581-348X
www.chemistryjournal.in
Volume 1; Issue 1; June 2017; Page No. 61-67

Agro-filler: effect on mechanical and degradable properties of low density polyethylene composite

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Abstract

Agro- or bio-filler/low density polyethylene composite was studied to determine their properties in relation to the corresponding ratio by weight of the compounding agent. The polysaccharide used as bio-filler was isolated from corn kernel by steeping method, characterized and thoroughly mixed into the polyolefin matrix. The yield of 38.96 %, ash content of 9.40 %, insolubility in water and alcohol of the isolated filler were suitable for polymer composite formation. Injection moulding machine was used to extrude the plastic/bio-filler into sheets at the temperature of 250 0 C. The tensile and elongation at break properties of dump-bell shaped bio- filler/polyethylene sheets were determined using tensile strength machine of model (TTM2EL/0300/2005). There was zero water absorption for the pure low density polyethylene with no filler, as, against the bio- composite counterpart, with increased starch content. Other parameters determined confirmed that, bio-fillers are innovative, eco-friendly, degradable, renewable, and when compounded with daily-used plastic materials, will reduce cost, improve the properties and minimize environmental pollutions from plastic wastes.

Keywords: bio-filler, low density polyethylene, composites, tensile strength, water absorption

Introduction

Bio-filler/low density polyethylene (BF-LDPE) composites are formulated in order to improve the properties, reduce cost, increase bulk, improve degradability, and enhance processability of single-daily used non- degradable polyethylene. This plastic/bio-filler could be referred to as green composites, because, could be isolated from agricultural materials, and could be disposed without any environmental negative impact, (Fazeli, *et al*, 2018) [8]. Composites could be classified depending on the operational environment, cost, fibre type, and manufacturing method employed. The general purpose for having multiple components is either to soften, toughen a hard material, or to harden or strengthen a soft material.

Polymer composites can be classified based on the nature of polymer matrix, and reinforcing materials. The reinforcement materials are embedded into the matrix which holds them together.

The global challenges due to environmental pollution from non-degradable daily-used polymers and need for eco-friendly bio-filled polymeric composites for synthetic low density polyethylene, had initiated scientific interests, to investigate on sustainable counterpart. Most plastic-composites could be compounded with fibres, wood fillers, cellulose, starch, or other particles embedded in the polymer matrix, to improve their properties. The systematic combination of fillers could give the product efficient electrical conductivity than the respective single phase matrix system (Andreas *et al*, 2013). Styrene-Butadiene or volcanized rubber had been reported to give better mechanical properties when compounded with carbon black than the uncompounded or single phase rubber (Yiran and Geoff, 2018) [15]. They reported that, the improved properties was due to the incomplete combustion and presence of Carbon (iv) Oxides which increased the binding capability of the composite. They observed that the components generally remained separated and are distinct at the macroscopic or microscopic scale within the finished structure. However, combination of these two materials created a superior and unique interface within the composite. Research had been carried out on the multifunctional properties of polymer composites, such as poly (p-phenylene sulphide) using commercially available multiwall carbon nanotubes, in combination with micro-scale short carbon fibers and graphite as fillers (Rahmat and Hubert, 2011). Raghad, *et al* (2015) [12], also worked on reinforcing polyester matrix using beans-shell and observed that, beans-shell-filled polymer composite exhibited improved mechanical properties than the non-filler counterpart. The use of bio- fillers, such as starch, wood dust, etc, had been thought of as approach to managing polyethylene waste challenges in man’s environment.

Starch $(C_6H_{12}O_5)_n$ is one of the commonest bio-filler, which is readily available, cheap, easily proccessable, renewable, and eco-friendly, due to it’s biodegradability. It could be compounded with most synthetic plastics, such as, low density polyethylene to improve its properties. The presence of amylose and amylopectin units in starch molecules is known to impact hydrophilic characteristic to starch molecule because of the presence of hydroxyl groups along the polymer chain (Doelker, 1993). The chains in amylose are more packed together, consisting of a linear or sparsely branched chains of α-D-glucopyranose units, and, are linked together by (1→4) bonds, through which bonding with other materials is made possible. Our target therefore is to formulate a bio- filer/polyethylene composite which could naturally decompose when no longer in use

Materials and Method

Extraction of the bio-filler (Corm starch)

The corn kernel from which the bio-filler used in this research was isolated was gotten from Department of Crop Science, College of Agriculture, Mgbakwu, Anambra State.

Isolation of the starch bio-filler

a. The Steeping Process

1000 g of cleaned corn kernel was transferred into a steeping plastic bucket containing hot water (100 0C) and covered tightly. 0.1 moles sodium hydrogen bisulphate was added to prevent detrimental action of bacteria, moulds, fungi or yeast, and allow only favourable ones like lactobacillus to catalyse the fermentation of the corn. Also, sulphur (1v) oxide gas was passed into the steeping system through a delivery tube. This was to aid the dissolution of the protein molecules embedded in the starch granules. The corn kernels were allowed to stand for 48 hours to soften and loosen the protein or gluten molecules in them. When some of the soluble substances seemed to have been separated, which was observed by the colour of the steeping liquor, softening, and swelling of the corn kernels to double of its original sizes, the fermentation process was completed. The steeped kernels were washed with clean water, and later subjected to the wet milling process.

1. The Wet Milling Process

The soaked corn seeds were ground in a machine to a slurry mixture, while adding water at intervals to ensure smooth milling. The corn slurry was kept for an hour after the milling operation to settle, while decanting the surface water at some intervals so as to reduce the milling liquor. The chaff was sieved out using a o.oo1 micro- sieve.

Fresh clean water was added to the crude corn starch slurry to extract the pure starch, and separate other contaminants using a white clean cloth. Distilled water was added to the corn starch slurry and decanted repeatedly until a clear water was obtained.

2. Dewatering and Drying of Corn Starch

The refined starch was separated from the water by pouring the milk into a draining white cotton bag and Compressed using a heavy stone to ensure proper dewatering. The dewatered pure starch was peeled from the bag, weighed and dried in a drying oven at 60 0C until a constant weight was obtained. The percentage yield of corn starch was calculated using the equation:

$$\text{Percentage yield (\%)} = \frac{M_1 - M_2}{M_1} \times \frac{100}{1}$$

Where:

M_1 is weight of dewatered pure corn-starch (g)
M_2 is weight of oven - dried pure corn starch (g)

Proximate Test on Corn Starch Iodine Test

This was carried out by adding few drops of iodine solution into 5g of the corn starch sample. The blue black coloration obtained confirmed the presence of starch molecule.

Particle Size Determination

The particle size of the corn starch was obtained by using SETHI Standard micro test sieve of 0.001 mm mesh.

Moisture Content

This was obtained by using the drying method according to the International Starch Institute (ISI 2006) and the percentage moisture content was calculated using the equation:

$$\text{Percentage moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times \frac{100}{1}$$

Where:

W_1 is Initial weight of corn-starch (g)
W_2 is Final weight of corn starch

Ash Content (ASTM D2584)

10 g of the oven-dried corn starch and porcelain crucible was placed inside a muffle furnace maintained at a temperature of 500 0C. The percentage ash content was determined after ashing, using the expression:

$$\text{Percentage ash content (\%)} = \frac{C_1 - C_2}{C_1} \times \frac{100}{1}$$

Where:

C_1 is Mass of oven-dried corn starch (g)
C_2 is Mass of ash (g)

Preparation of Bio- filler/LDPE Composite

The low density polyethylene (LDPE) was gotten from Cee-plastic Industries, Aba, Abia State, Nigeria. The bio-filler/polyethylene composite sheets were prepared respectively by mixing, different ratio by weight of polyethylene pellet to starch as given in table below: The mixture were blended using an injection moulding machine maintained at 250 to 300 oC, and extruded as sheets.

Table 1: Compositions of Low density Polyethylene/ Corn-starch filler

S/N	LDPE (Wt. %)	Corn Starch (wt. %)
1	100.00	0
2	97.50	2.50
3	95.00	5.00
4	92.50	7.50
5	90.00	10.00
6	87.50	12.50
7	85.00	15.00

Determination of Tensile Properties of Bio-filler/Low Density Polyethylene Composite.

Tensile Strength

The dumb-bell shaped low density polyethylene/bio-filler composite sheets were measured to determine the tensile strength, using ASTM D 638 specification. The machine (TTM2EL/0300/2005) was adjusted to the testing operational process. The test samples were labelled and carefully inserted at the upper jaw of the machine and tightened properly. The device was monitored carefully so as to stop the operation once the specimen breaks. The breaking force of three determinations were taken simultaneously, recorded respectively and the average taken to avoid error. The tensile strength were calculated using the expression;

Tensile strength= Breaking force/Cross-sectional area (10 x thickness);

$$\text{TS (N/mm}^2\text{)} = \frac{FORCE}{AREA}$$

Where: TS is tensile strength

Elongation at Break after Biodegradation

The elongation at break (EB) was also recorded along the meter rule pointer at 200–100 mm. The elongation at break of three samples were taken simultaneously in order to obtain the actual values, and calculated using the formula:

X_0
X_1

$$\text{Elongation (mm) in \%} = \frac{L_f - L_o}{L_o} \times \frac{100}{1}$$

where:
Lf = final length
Lo = Initial length (20 mm)

Water Absorption Properties of Various Low Density Polyethylene/Corn- Starch Composite

The low density polyethylene/corn starch bio-filler composite sheets were cut to a dimension of 2.50 × 2.50 cm, weighed, and recorded as (Xo). The samples were later placed in a clean beaker, and 100 cm3 of distilled water poured into the beaker which was immediately covered with filter paper, and placed in a safe place for 42 days.

During this period, the samples were removed from the water at one week intervals. The water adhering on the sample surfaces were carefully removed using filter paper, and weighed immediately to obtain the weight of the sample after immersion in water (X1). The weighed samples were put back in water after each measurement for the next measurement. The percentage (%) water absorbed by the samples were calculated as follows:

$$\text{\% water absorption} = \frac{X_1 - X_0}{1} \times \frac{100}{1}$$

where:
is the weight of the dried sample
is the weight of samples after water immersion.

Percentage Weight -Loss of LDPE/Bio-filler Composite

Weighed samples of LDPE/ starch composites were buried at a depth of 10 cm from the soil surface placed in perforated buckets and left for 180 days. The control sample (Pure low density polyethylene) was also buried in the soil under the same conditions. The weight loss was determined every 30 days from the starting days, and was calculated using:

$$\text{Weight-loss} = \frac{w_i - w_f}{w_i} \times \frac{100}{1}$$

where: Wf is the weight of the film after being washed with distilled water, and Wi is the initial dry weight of the film.

Results and Discussion

Results of proximate tests on the corn starch (bio- filler) is given in Table 1. The moisture content of the starch is 10 %, which is suitable to initiate any chemical reaction or combination. The percentage yield is good for any commercial purpose, whereas, the blue-black colouration with iodine solution, solubility in water and alcohol shows good starch properties.

Table 2: Showing the Proximate values of Corn Starch

Determinations on the Corn Starch	Values
Moisture Contents (%)	10
% Yield	38.96 %
Ash Content (%)	9.40 %
Iodine test	Blue black
Solubility in Water and Alcohol	insoluble

Tensile Strength of LDPE/ Bio-filler Composites

The capability of the plastic/bio-filler composite to endure stress and resist maximum load without fracture was represented graphically in Figures 1. It was observed, that increasing the corn-starch (bio-filler) content, decreases the tensile strength. This may be as a result of uneven stress concentration in the polyethylene matrices. Poor interfacial adhesion can as well cause fractures, weak the bonds and reduce the tensile strength. Our findings conformed with that of Thakore *et al* (1999) [14], who discovered that, low density polyethylene/potato starch exhibited reduced tensile strength with increased starch or starch acetate content.

Table 3: Tensile Strength values of Low Density Polyethylene/starch bio-composite

Corn-starch content (wt.%)	LDPE contents (wt.%)	Tensile-strength (N/m2)
0.00	100.00	12.17
2.50	97.50	11.61
5.00	95.00	10.88
7.50	92.50	10.67
10.00	90.00	10.48
12.50	87.50	9.49
15.00	85.00	8.95

Sanadi *et al* (2001) [13], suggested that trans-crystallization and changes in the apparent strength of the bulk matrix can result to changes in the composites mechanical strength.

However, Boryniec, *et al* (2004) [4] concluded that, the non-polar interaction between the natural or bio-filler and the synthetic polymer can affect their tensile properties, although incorporation of compatibilizing agents, could improve this property. Matzinos, *et al* (2001) [11] characterized LDPE/starch blends and reported an increased tensile strength at bio- filler (starch) contents of up to 50 wt. %, which later dropped with further increase in starch content. We can then conclude that, tensile strength of most plastics could be affected with increased bio-fillers.

Elongation at Break

The values obtained for elongation at break (EB) as shown graphically in Figure 2, all the starch-filled LDPE composite exhibited reduced elongation at break than the pure LDPE.

The more the starch contained in the blend, the more the reduction in elongation at break, and vice versa. The decrease in elongation at break with starch content as observed in this study is in agreement with the reported works of Martins *et al* (2001) [10], and Kang *et al* (1998) [9].

Similarly, Obasi (2013) who investigated the biodegradation of cassava, and sweet potato starch blended polypropylene (PP) using the soil burial test found that all the starch blended PP exhibited lower elongation at break than pure PP.

Table 4: Elongation at Break (%) for Low Density Polyethylene/corn-starch composite.

Corn-starch content (wt. %)	LDPE content (wt. %)	Elongation at break (%)
0.00	100.00	444.65
2.50	97.50	206.65
5.00	95.00	206.65
7.50	92.50	136.65
10.00	90.00	61.65
12.50	87.50	50.20
15.00	85.00	29.30

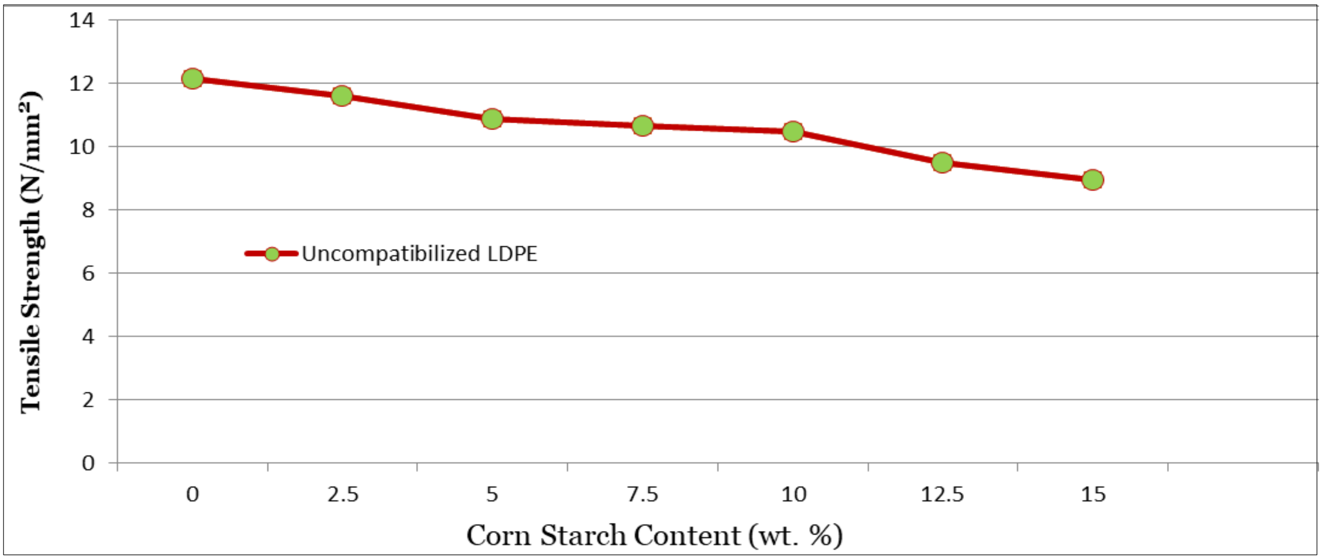
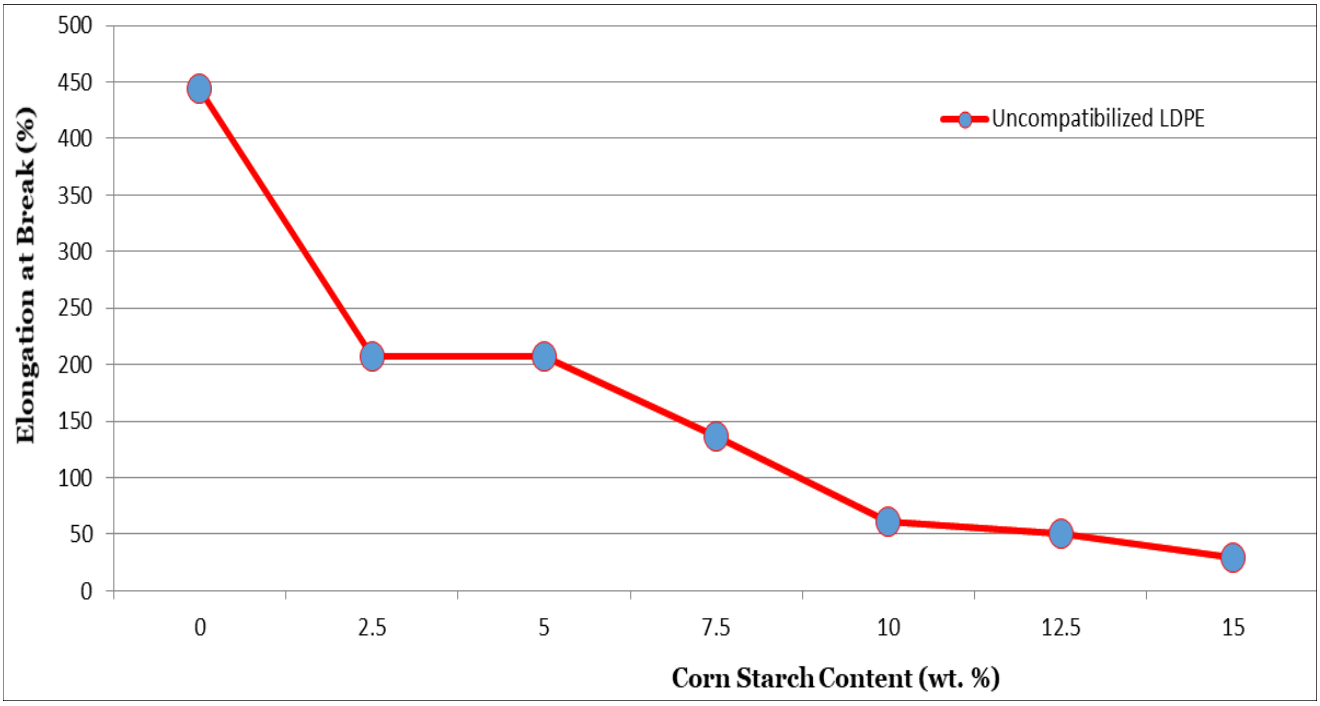


Fig 1: Plot of Tensile Strength of LDPE-Bio-filler Composite



Elongation at Break of Low Density Polyethylene after 60 Days of Soil Burial.

Fig 2: Elongation at Break (%) for LDPE/Corn-starch Composite.

The elongation at break for LDPE/Bio-filler composite was observed to decrease drastically with increase in starch content from 2.50 wt. % up to 7.50 wt. % and tend to level off with further increase in corn starch content. The decrease in elongation at break of LDPE/corn starch blends with increased corn starch content could be attributed to the heterogeneous dispersion of starch granules in the polyolefin matrices, and thus, the incompatibility of polyolefins and starch. Furthermore, the absorption of moisture by the starch at the polyolefin/starch interface had the capability to weaken the interfacial adhesion. Since the starch granules cannot stretch or elongate along with the LDPE chains, strain cracks could be generated, and the propagation of these cracks could result into fracture.

According to Enamul *et al* (2013) [7], at high starch contents, filler-filler interaction became more pronounced than filler-matrix interaction, and this could reduce the effective cross-sectional area of the polymer sample due to the presence of starch particles. Because of the reduction in the composite cross-sectional area, an applied stress could not be transferred accordingly from the polymer matrix to the rigid starch particles, and hence, the effective stress experienced by the matrix was essentially higher, and tended to lower the EB or other mechanical properties (Chandra, 1998).

The water absorption property for polyethylene/corn starch composite are illustrated in Figures 3. The figures show progressive increase in the amount of water absorbed by LDPE/starch composite with increase in the amount of starch incorporated and duration of immersion in water.

Figures 3, shows that pure LDPE absorbed negligible amount of water which tended to remain fairly constant throughout the duration of the experiment. Polyolefin generally are hydrophobic. The water absorbed by the composite is due to the presence of hydrophilic starch particles in the composite sheets. Starch particles possess abundant hydroxyl groups in their molecules, and which are available for interaction with water molecules. Thus, water molecules can saturate the surface of the polyethylene/corn starch blends easily, and penetrate into the composites through voids which result in higher water absorption in a short immersion period (Sanadi *et al*, 2001; Danjija *et al*, 2001) [13]. LDPE has a high degree of short chain branching in its molecule (*Katchy, 2000)* and which has the capacity to loosen up the main chain structure thereby allowing the water molecules to penetrate more easily. This property could be improved by incorporating compatibilizers, which, could Improved adhesion between starch and polyethylene and reduced the water penetration into the plastic/bio-filler sheets.

Water Absorption Properties

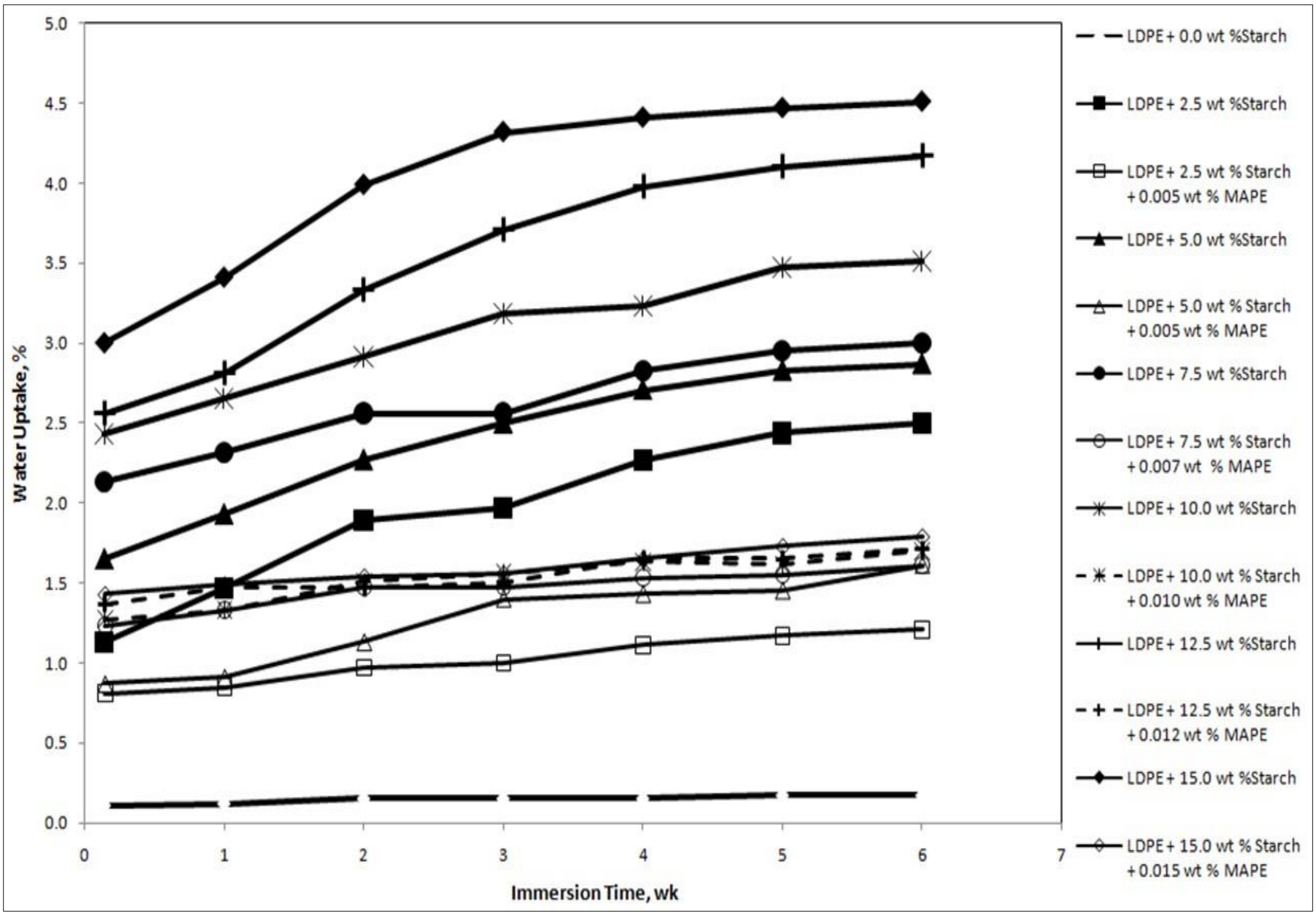


Fig 3: Plots of water absorption verses immersion time for Pure and LDPE /Corn Starch Composite.

Reduction in weight of LDPE/Bio-filler Composite after 180 Days of Soil Burial

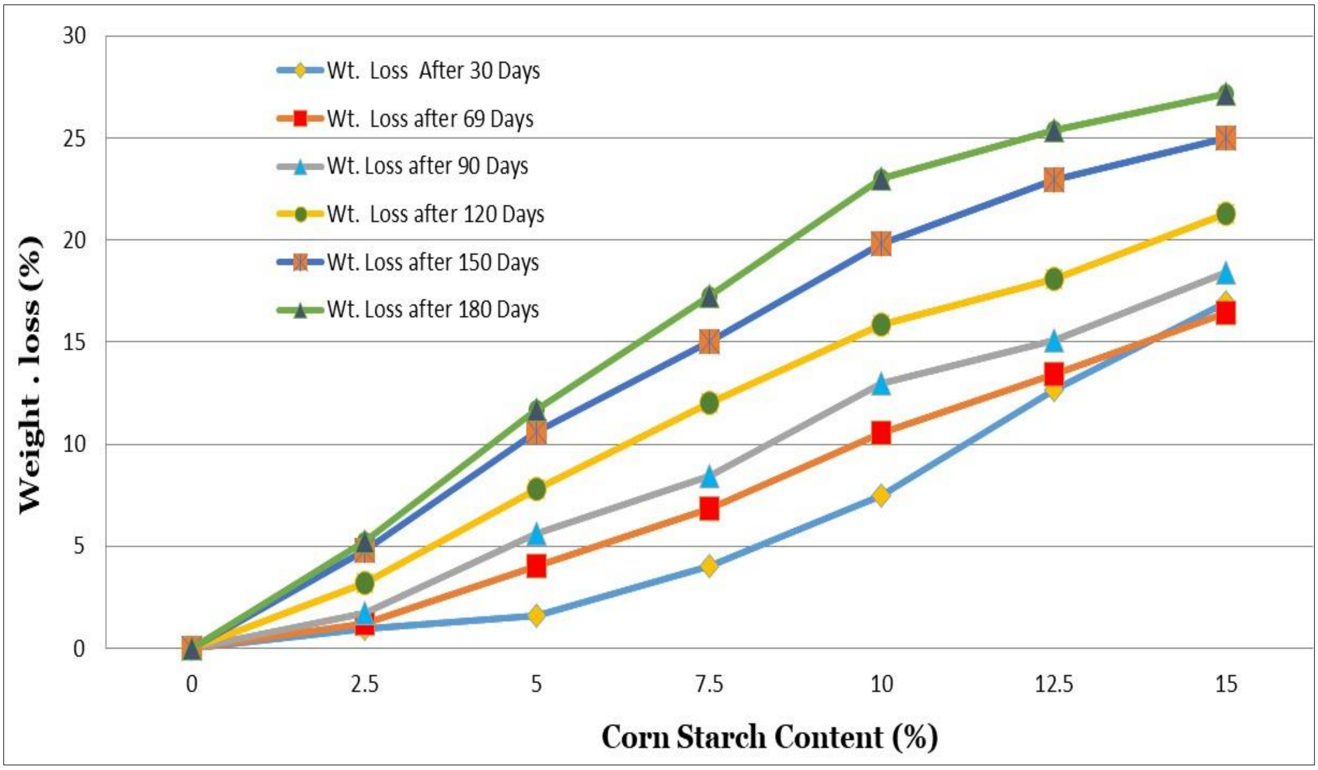


Fig 4: Weight-loss of LDPE/ Corn Starch Composites.

Figure 3.5 represents the results of weight loss of LDPE /Corn-starch composite samples after 180 days of soil burial. There was no weight-loss for the pure polyethylene which was used as a control sample. This could be attributed to the inertness (or resistance) of polyethylene to air, moisture, and microbial attack. The reduction in weight of corn starch filled polyethylene samples subjected to biodegradation tests is attributed to the removal of the corn starch granules by soil microorganisms, and this resulted in the decrease in the weight of blended polyethylene samples.

It is to be expected that the extension of the degradation period could result into complete degradation of the polyolefin fragments, since the weight loss increased with increase in the number of soil burial days (i.e from 30 to 180 days).

Albertsson (1998) had reported that the penetration of small amount of solar radiation reaching the film under soil surface might initiate oxidation process in the polyolefin blend films. This was supposed to affect the degradation process by speeding up the microbial consumption of surface/volume ratio in the polyethylene matrix. The hydrophilic nature of starch, it is envisaged, allowed for moisture absorption, and retention that contributed to biodegradation and consequently reduction in weight of the composite. Our findings are same to that of Borghei *et al* (2010) [2], and Danjaji *et al* (2002) [6] who discovered weight reduction in the biodegradation of poly-composite incorporated with bio-filler.

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