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INVESTIGATIONS ON THE CORN-STARCH MODIFIED LOW DENSITY POLYETHYLENE BLENDS

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ABSTRACT

Investigations were carried out on the biodegradation properties of low density polyethylene, modified with different concentrations by mass of corn-starch. Convectional Low Density Polyethylene (LDPE) is widely used in all fields of life; therefore constitute the greatest municipal waste products, due to their inertness to biological attack, moisture, and weather conditions. Corn-starch which is a biofiller was characterized to ensure it's suitability in the blending of synthetic plastics like LDPE. The percentage yield, moisture content, ash content, iodine test, etc were carried out on the extracted starch. The blended polyethylene sheets were injection molded at 150 ^{0}C after mixing 0, 2.50, 5.00, 7.50, 10.00, 12.50, and 15.00 wt. % by mass of the starch with known weight of low density polyethylene pellets. Mechanical tests and percentage weight-loss properties of the corn-starch modified low density polyethylene were investigated before and after soil burial test. The evidence of biodegradation was exhibited on the reduced tensile strength, elongation at break, increased water absorption and other properties of the blended films as against the pure LDPE.

Keywords

Biodegradation, Blends, Mechanical tests, Low density polyethylene, Soil -burial

1. Introduction

Low Density Polyethylene (LDPE) is a synthetic plastic material due to their inertness to microbial, moisture, chemical or solvent attacks (Stevens, 2002). It is a unique material because of its outstanding mechanical, thermal and electrical conductivity properties which are the major factors for its application in all areas of life ranging from children's toys to sophisticated Engineering constructions. Innovation and advancement in Engineering and Technology had resulted into tremendous increase in the demand, production, consumption, and generation of polyethylene wastes, especially low density polyethylene (Okada, 2003; Wu, 2003). As a hydrocarbon LDPE consists of branched ethane monomer chains that are exothermically produced by free radical polymerization process (Deniss, 2011).

Reports had shown that millions of this inevitable plastic-based material is produced world-wide and pushed out to consumer's every-day (Bachelor, et al, 2013). Polyethylene are however engaged in routine applications for few minutes and are discarded off immediately as wastes, most especially, single-used products like bottles for water, milk, disposable plates or cups, sanitary materials, etc. These wastes can stay up to thousands of years without degradation, and therefore constitute the greatest municipal pollutants.

Non-biodegradability of polyethylene wastes had imposed serious threat to animals and birds who often mistaken them for prey, and are consequently shocked to death due to the non-degradability, or indigestibility of the polymer. Corn-starch which is a polysaccharide consisting of a large number of glucose units linked by the glycoside bonds are rich in amyl pectin chains. The amyl pectin is a polymer molecule with branching occurring at the-(1-6) glucosidal bonds. It has the tendency to form hydrogen bonds with another polymer chain, and as a result impact affinity towards water molecules due to the presence of many end points for enzymatic attack (Shrogen, et al, 2003). Corn starch consists of high amyl pectin molecules, had been considered in this research as a suitable material due to its inherent biodegradability, sustainability, low cost, non-toxic and easy of process ability properties.

Starch rich in amyl pectin had been reported to be higher in flexibility, elongation at break point, but exhibit lower tensile strength (Walenta, et al 2001). Aamer, et al (2003) reported that low density polyethylene can be modified to adjust their pH range, polymer structure, percentage of crystalline, water content and geometry of plastics chains to affect their biodegradation. Otey (2005) developed starch-plastic composite, although there was no acceptable laboratory method for determining their biodegradability. Shahzad (2012) reported that erosions observed on the surface of starch polyolefin blends were evidence of starch removal by starch-loving microorganisms which could initiate biodegradation process.

The incorporation of biodegradable biopolymers like starch into conventional low density polyethylene is receiving the attention of polymer scientists. There is a global call to development of an alternative plastic material which can easily decompose when no longer in use (Resist, et al 1997). As our contribution to answering this call, investigations were carried out on corn starch modified low density polyethylene blends to monitor its biodegradability.

2. Materials and Methods

2.1 Materials

Low Density Polyethylene (LDPE) pellets with specific density of 0.97 g /cm^3 and the injection molding machine used in this work were purchased from Cellist, Industries Aba. Corn (*zea Mays*) seed, from which the starch was extracted, was obtained from College of Agriculture Mgbakwu, Anambra State.

Soil sample used for the biodegradation test was gotten from composite site at Anambra State University Uli. The Instron tensile strength testing machine was gotten from CUTIS cable Industries, Nnewi, Anambra State.

2.2 Methods

Extraction and Characterization of Corn Starch

Corn starch was extracted from the seeds by steeping process specification according to patent US 801226282(2011). The extracted starch was characterized by determining the percentage moisture content, particle size, ash content, iodine test, etc, to ascertain it's suitability in blending conventional LDPE.

2.3 Blending of LDPE/Corn Starch Samples

The blend films were prepared by thoroughly mixing weighed amount of LDPE pellets and corn starch, which were extruded as sheets using an injection molding machine at the operation temperature of 150^0 C. Compatibilized sheets were prepared by incorporating Malefic

Anhydride-g-Polyethylene. Pure LDPE to be used as control samples were also extruded under the same conditions.

2.4 Determination of the Mechanical Properties of Low Density Polyethylene /Corn Starch Blends

- **Tensile Strength (TS)**

The dumb-bell shapes of pure and blended LDPE sheets were clamped to the jaws of Instron Tensile Testing machine (TTM2EL/0300/2005). The breaking forces (TS) were determined according to ASTM D 638 standard.

- **Elongation at Break (%)** The elongation at break (EB) for the pure and corn starch blended LDPE were recorded along the meter rule pointer on the tensile testing machine and the average values calculated.

- **Weight-loss Determination**

Weighed samples of LDPE/Corn starch blend films were oven dried at 40^{0}C and later buried at a depth of 10 cm in a plastic bucket containing humus soil. Pure LDPE samples were also buried under the same condition and were left at the open for 180 days. The percentage weight–loss were determined according to ASTM D6003- 96 standard test and calculated using the formulary:

Weight- loss (%) $= \frac{x_1 - x_2}{x_1} \times \frac{100}{1}$ --------------- (i)

Where: x_1 **is weight of the oven dried sample or initial sample**
X2 is weight of samples after soil burial or final sample

- **Water Absorption Studies**

The blended and pure samples of LDPE were weighed and covered with filter paper in a beaker for a period of 30 days. The water absorption monitoring was carried out at 7 days' time interval. The percentage (%) water absorption of the samples was calculated accordingly using the formular:

Water Absorption (%) $= \frac{\square_{\square} - \square_{\square}}{\square_{\square}} \times \frac{\square\square\square}{\square}$ ……………… **(2)**

Where: w_{1} is **weight of sample before immersion in water**

W2 is weight of sample after immersion in water

3. Results and Discussion

3.1 Mechanical Properties of LDPE/Corn-Starch Blends

3.1.1 Tensile Strength

The tensile strength is the parameter used to determine the maximum load a material can support without fracture when stretched.

The results of the tensile properties of low density polyethylene/corn starch blends with, and without malefic anhydride-graft-polyethylene are illustrated graphically as shown in Figure 1.

The percentage increase in corn starch content from 0.00 to 15 wt. %, resulted into significant decrease in the tensile strength of the polymer blends from 12.17 N/m^2 to 2.86 N/m^2 before the soil burial tests. This is presumably, due to the incompatibility of the polyolefin with the incorporated corn starch granules. However, it is assumed that the inclusion of corn starch in low density polyethylene matrix caused a very significant stress concentration. In effect, fracture could be initiated from the weak interfacial bonding attraction between the molecules of the blends. Reports had shown that synthetic LDPE tends to exhibit poor interfacial adhesion with biopolymers like corn starch, thus resulting in reduced tensile properties. *Thakore et al (1999)* who investigated low density polyethylene/potato starch or starch acetate blends reported that the tensile strength of the blends decreased with increased starch acetate content. Similarly, *Lin et al (2003)* investigated low density polyethylene/corn starch blends and found his results similar to ours.

Incorporation of the compatibilizer (Malefic anhydride-graft-Polyethylene; MA-g-PE) to the polyolefin blends increased the tensile properties of the blends. Two types of behaviors can be observed; **(i)** the tensile strength of the uncompatibilized low density polyethylene/corn starch blends was smaller than that of the compatibilized LDPE within the MA-g-PE content investigated. It is believed that MA-g-PE increased the adhesion between the polyolefin matrices and corn starch. This improved interfacial adhesion between the polyolefin's and corn starch has a positive impact on stress transfer, thus reducing the chance of interfacial deboning, leading to improved tensile strength properties (Ramkumar and Bhattacharya, 1997). **(ii)** The tensile strength value of 11.61 N/m^2 for the uncompatibilized LDPE at the lower corn starch content of 2.5 wt. % is equal to that of compatibilized blends. The results obtained above support the assumption that the interaction between starch and MA-g-PE molecules was a chemical reaction between the hydroxyl groups in the corn starch and anhydride groups in MA-g-PE. According to the studies of (Boryniec et al, 2004) polar interaction between starch and MA-g-PE cannot improve their interfacial adhesion properties to any significant extent. In contrast to our results, *Matzinos et al (2001)* who characterized LDPE/starch blends reported an increase in the strength of the blends with starch contents of up to 50 wt. % after which the tensile strength of the blends decreased with any increase in starch content.

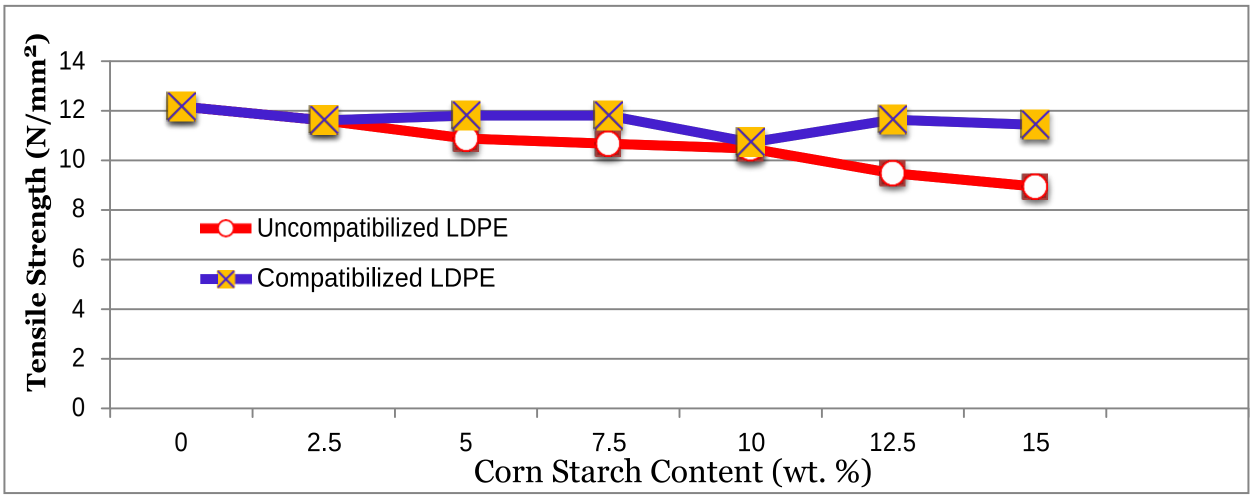

Figure 1: *Plots of Tensile Strength of Uncompatibilized and Compatibilized LDPE and Corn –Starch Blends*

3.1.2. Elongation at Break

Results obtained for elongation at break (EB) for the various starch and polyolefin blends are illustrated graphically in **Figure 2**. The pure LDPE films exhibited greatest value (444.65 %) of elongation at break than the starch blended LDPE, showing 206.65 % at starch content of 2.5 wt. %. 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) and Kang et al (1998). 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.

It is generally observed that compatibilized blends exhibited higher EB than uncompatibilized ones. The decrease in elongation at break of LDPE/corn starch blends with increased corn starch content could be attributed to, **(i)** the heterogeneous dispersion of starch in the polyolefin matrices, and thus, the incompatibility of polyolefin's and starch. **(ii)** 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 polyolefin chains, strain cracks could be generated, and the propagation of these cracks could result into fracture.

According to Enamel et al (2013), 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 blend 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).

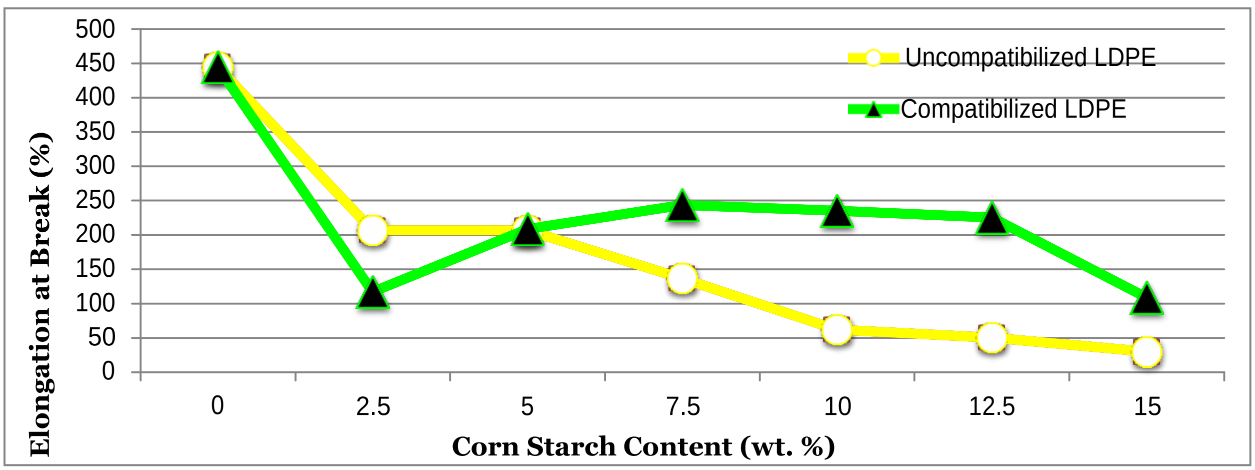

Figure 2: *Plot of Elongation at Break (%) of Uncompatibilized and Compatibilized Low Density Polyethylene / Corn Starch Blends*

3.1.3 Weight - Loss after Soil Burial Tests

The results of weight changes of the polyolefin /corn starch blend samples after soil burial are presented in Figures 3 and 4. The plots revealed that there was a continuous increase in weight-loss for the samples undergoing biodegradation tests in soil with increase in corn starch content, and period of biodegradation. There was no apparent weight-loss change for the pure

LDPE which was used as control sample in this study. This was attributed to the inertness (or resistance) of polyethylene to air, moisture, and microbial attack. The reduction in the weight of corn starch blended 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. Albertson (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.

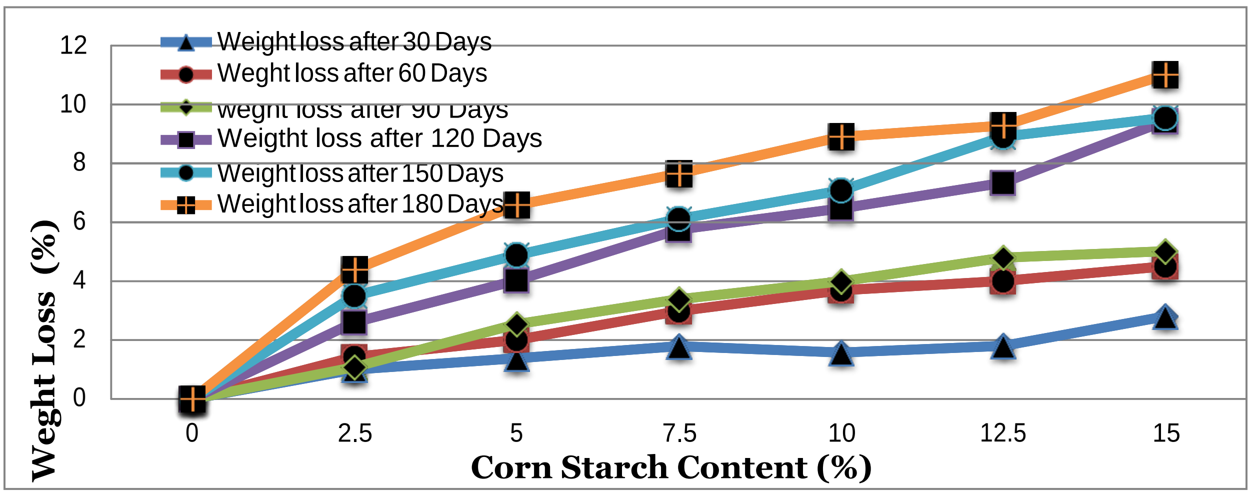

Figure 3: *Plots of Weight loss of Compatibilized Low Density Polyethylene and Corn Starch Blends*

The compatibilized LDPE as represented on figure **4**, showed reduced weight-loss when compared to the uncompatibilized blends throughout the soil burial periods. This could be attributed to the increased adhesion, and bonding effect of MA-g-PE to the polyolefin matrix/corn starch blends. The weight-loss for compatibilized LDPE blended with 2.5 wt. %, and 5.0 wt. % corn starch after 30 to 90 days of soil burial tests were low when compared to the uncompatibilized blends. This could be attributed to **(i)** the short time for biodegradation; (**ii)** low content of corn starch to render biodegradation.

The hydrophilic nature of starch, it is envisaged, allowed for moisture absorption, and retention that contributed to biodegradation. Borghei et al (2010), and Danjaji et al (2002) had also reported that increased starch content resulted to increased weight reduction and increased in biodegradation of polyolefin/starch blends.

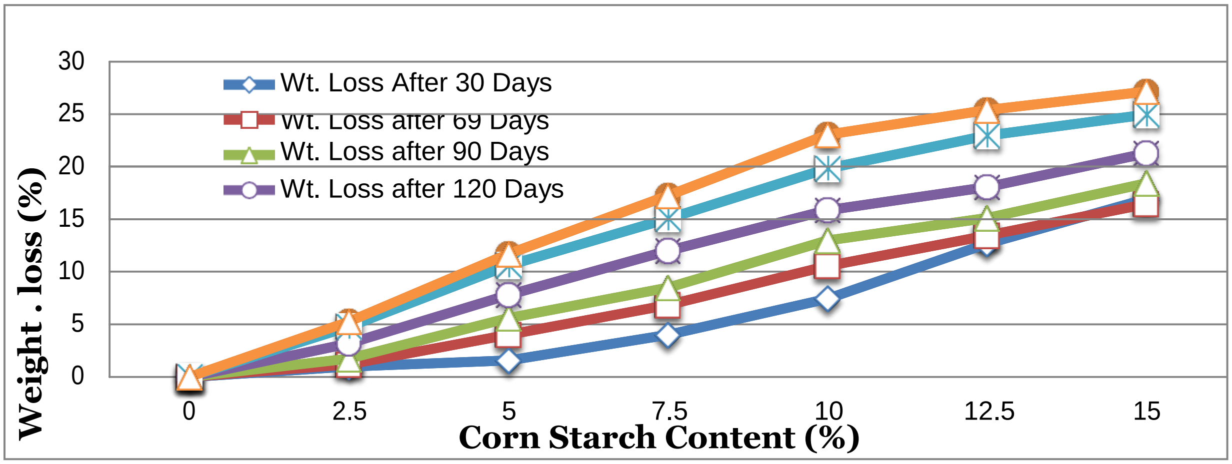

Figure 4: *Plots of Weight-loss of Uncompatibilized Low Density Polyethylene/corn Starch Blends*

4. Conclusion

This research had proved a method of militating against the dilemma of plastic waste through biodegradation.

The incorporation of corn starch to the plastic matrix resulted into reduction in the tensile strength and elongation at break of the blends but, addition of MA-g-PE was observed to improve these properties.

The present study has demonstrated that corn starch would be used in making varieties of biodegradable polyethylene–based plastics for packaging, medicine, agricultural purposes, etc. The cost of corn starch is less than that of the plastic matrix in the polyethylene blends, and small starch content led to a significant biodegradation of polyethylene blends. The improved biodegradation of hitherto inert/resistant polyethylene on incorporation of corn starch is definitely a factor that needs to be considered by the plastic industries when evaluating polyethylene/corn starch blends.

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