



## BIODEGRADATION AND MOISTURE UPTAKE MODIFIED STARCH-FILLED LINEAR LOW-DENSITY POLYETHYLENE (LLDPE) COMPOSITES

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### ABSTRACT

*Sixteen different modified-cassava starch-LLDPE blends containing starch in the range of 10-40% by weight were prepared. Calcium chloride, D-glucose, chloroform and alumina were differently used as modifying agents. The Moisture uptake and biodegradation of each of the composites were investigated. Both of these properties were found to increase with increase in the starch content, with remarkable change observed at 30% starch content. There is however no significant change observed with the change in modifying agent.*

**Key words:** Starch-LLDPE blends, Calcium chloride, D-glucose, Chloroform and Alumina.

### INTRODUCTION

Linear low-density polyethylene (LLDPE) is a substantially linear polymer (polyethylene) with significant number of short branches. It is made by co-polymerisation of ethylene with longer-chain olefins, using Ziegler-Natta catalysts. Recently, there has been great interest in metallocene catalysts, which perform the same functions as Ziegler-Natta catalyst, but produce superior quality polyethylene. (1).

Remarkably, because of the lack of long-chain branching, LLDPE has low viscosity at all strain rates. It however allows the chains to slide by one another upon elongation without becoming entangled. This property favours the production of LLDPE films that can be down gauged, while maintaining high strength and toughness. (2).

Generally speaking, LLDPE has higher tensile strength and higher impact and puncture resistance than Low-density Polyethylene (LDPE). It is very flexible and elongates under stress. It can be used to make thinner films much more than LDPE. It has good resistance to chemicals and to ultraviolet radiation. It has good electrical properties. (3).

LLDPE has percolated almost all polyethylene traditional markets. It is extensively used in the production of plastic bags and sheets of lower thickness than LDPE, plastic wrap, stretch wrap, pouches, toys, lids, pipes, buckets and containers covering of cables geomembranes and flexible tubing.

Starch has been considered as a useful material in polymer industry, because of its biodegradability, availability, non-toxicity, high purity and low cost. (4). Starch films possess low permeability and thus become attractive material for food packaging in plastic industry. Moreover, starch promotes biodegradability of non biodegradable plastics. In some industries, starch is used with fully biodegradable synthetic plastic, producing biodegradable blends of low costs. (2). Because of its

ability to remain in granular form in the plastic matrix, starch can effectively act as a filler. Moreover, its lower-specific gravity; 1.5, compared with that of an inorganic filler, such as clay, specific gravity, 2.6. is also an important factor. Degradable starch-plastics composites with good mechanical properties came into existence in the mid 1970. (5).

The incorporation of granular starch into plastics via melt mixing has become a common practice of great technological significance over the years. This is because it is the cheapest method for preparing starch-polymer composites. (4).

Plastics waste is now regarded as serious environment problems with polyethylene being the largest volume plastic used in packaging and is also the worst offender of our environment. It is also highly resistant to biodegradation. Because of the serious concern of environmentalist on the slow-degradation of polyethylene, starch is incorporated to serve as a biodegradant and use of other biodegradation aids, such as photo oxidants to accelerate the biodegradation process. For instance, Lee et al. (2) reported a degradation of polyethylene molecules by lignin degrading bacteria in those films containing starch and photo-oxidants. Sharma et al (6) found that the incorporation of photo-oxidant which consisted of metal salts and unsaturated elastomer enhanced the thermo-oxidative degradation rate of sago starch filled LLDPE composites. The use of glycerol plasticized starch has also been found to affect the degradability of the plastic blends.

### EXPERIMENTAL

#### SAMPLE PREPARATION

At temperature of 60°C, 10g each of the prepared starch powder were weighed into five (5) different beakers (20ml). To each beaker, 50cm<sup>3</sup> of distilled water was added to make a solution. After effective agitation and stirring, 5cm<sup>3</sup> of 2M NaOH was added to each beaker so as to make the pH alkaline.

Twenty gramme (20g) each of D-Glucose, CaCl<sub>2</sub>, alumina, and chloroform were then added respectively, to each of the four beakers containing the stalked solution. Another 20g, containing 5g each of D-glucose, chloroform, alumina and CaCl<sub>2</sub> was added to the fifth beaker of the solution.

#### BIODEGRADATION STUDIES

Biodegradation studies of the polymer films have been carried out by investigating the action of micro-organism in activated compost soil mixtures after three (3) months of soil burial. The soil mixture composing of soil; 50%, sand; 30% and composted manure; 20%, at pH 7.5 were maintained at 60±5% water holding capacity. The films were buried in each of four soil boxes in the incubator. The temperature of the experiment was monitored at 60°C. At intervals of four (4) weeks, polymer specimens were removed from the soil mixtures. They were cleaned by 100:0%, 50:50% and 0:100% buffer: ethanol solution followed by drying

in an oven. Dried films were weighed to calculate the weight loss (1).

#### MOISTURE ABSORPTION

The moisture absorption is evaluated in accordance with the ASTM D 570 test. The blends were conditioned in an oven at 50°C for 24 hours, placed inside a desiccator for another 24 hours and weighed. The samples were then placed inside a container containing sufficient quantity of water, so that they were completely immersed. After 48 hours the samples were removed and weighed again.

The decrease in weight (from degradation) of the blends was studied after three months of soil burial. This is done to allow a reasonable loss in weight as a result of microbial degradation, as investigated earlier; the weight loss in starch-polyethylene composites during soil burial was rapid during the first 30 days; thereafter it proceeded slowly. (8). The results obtained is as shown in Table 1.

#### RESULTS AND DISCUSSION

##### BIODEGRADATION STUDIES

**Table I: Observed loss-in weight of different LLDPE composites buried on activated compost sort.**

S/No	Sample	Weight before burial W1 (g)	Weight of Sample after removal W2 (g)	Loss of weight W1-W2(g)
	A <sub>0</sub>	0.0514	0.0512	0.0002
	A <sub>1</sub>	0.0524	0.0502	0.0022
	A <sub>2</sub>	0.0529	0.0501	0.0028
	A <sub>3</sub>	0.0541	0.0491	0.0500
	A <sub>4</sub>	0.0548	0.0497	0.0051
	B <sub>0</sub>	0.0518	0.0517	0.0001
	B <sub>1</sub>	0.0525	0.0506	0.0019
	B <sub>2</sub>	0.0528	0.0507	0.0021
	B <sub>3</sub>	0.0543	0.0503	0.0040
	B <sub>4</sub>	0.0547	0.0497	0.0050
	C <sub>0</sub>	0.0520	0.0520	0.0000
	C <sub>1</sub>	0.0532	0.0510	0.0022
	C <sub>2</sub>	0.0532	0.0512	0.0030
	C <sub>3</sub>	0.0548	0.0501	0.0048
	C <sub>4</sub>	0.0548	0.0497	0.0051
	D <sub>0</sub>	0.0528	0.0527	0.0001
	D <sub>1</sub>	0.0525	0.0503	0.0022
	D <sub>2</sub>	0.0526	0.0503	0.0023
	D <sub>3</sub>	0.0548	0.0503	0.0045
	D <sub>4</sub>	0.0552	0.0501	0.0051

A <sub>0</sub>	=	glucose-modified starch; 0% weight in the blend
A <sub>1</sub>	=	glucose-modified starch; 10% weight in the blend
A <sub>2</sub>	=	glucose-modified starch; 20% weight in the blend
A <sub>3</sub>	=	glucose-modified starch; 30% weight in the blend
A <sub>4</sub>	=	glucose-modified starch; 40% weight in the blend
B <sub>0</sub>	=	Alumina modified starch; 0% weight in the blend
B <sub>1</sub>	=	Alumina modified starch; 10% weight in the blend
B <sub>2</sub>	=	Alumina modified starch; 20% weight in the blend
B <sub>3</sub>	=	Alumina modified starch; 30% weight in the blend
B <sub>4</sub>	=	Alumina modified starch; 40% weight in the blend
C <sub>0</sub>	=	Chloroform modified starch; 0% weight in the blend
C <sub>1</sub>	=	Chloroform modified starch; 10% weight in the blend
C <sub>2</sub>	=	Chloroform modified starch; 20% weight in the blend
C <sub>3</sub>	=	Chloroform modified starch; 30% weight in the blend
C <sub>4</sub>	=	Chloroform modified starch; 40% weight in the blend
D <sub>0</sub>	=	Calcium chloride modified starch; 0% weight in the blend
D <sub>1</sub>	=	Calcium chloride modified starch; 10% weight in the blend
D <sub>2</sub>	=	Calcium chloride modified starch; 20% weight in the blend
D <sub>3</sub>	=	Calcium chloride modified starch; 30% weight in the blend
D <sub>4</sub>	=	Calcium chloride modified starch; 40% weight in the blend

When one looks at the impact of microbial attack on the starch-filled blends, it would be observed that the action is highest with more starch content. This is because starch is usually utilized in the form of granules, and is actually formed by one branched and one linear polymer. Amylase, the linear polymer, comprises approximately 20% of starch, while Amylopectin, the branched polymer, constitutes the remaining 80%. (9)

Biodegradation of materials occurs in various steps. Initially, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, leading to a progressive enzymatic dissimulation of the macromolecule from the chain ends (10).

Starch is fundamentally employed as filler in LLDPE, because of its unique properties, which are

explained earlier in this work. Moreover, LLDPE composites containing higher starch content (in this work, 30 and 40% starch weight) were found to undergo more degradation process than the blends with low or no starch content. Earlier works of Nikazar M. *et al.*, (2005) describe the process as the microbes initially attack starch in the blend, resulting in an increase in the porosity and surface to volume ratio of the polymer blend and consequent enhancement of its biodegradability. In order to attack the starch, the microbes, should first adhere to the surface of the polymer, so polymers that have a rougher surface finish are more prone to microbial attack. Scanning electron microscopy (SEM) analysis has shown that starch based polymers have textured surface, whereas polyethylene has a smooth surface (1). There is no remarkable change however, observed with the change in modifying agent.

### Water Absorption

The Percentage moisture uptake was calculated according to the relation: -

$$\% \text{ Mt} = \frac{W_2 - W_1}{W_1} \times 100$$

Where Mt = the total moisture uptake  
 $W_1$  = the weight of the sample before immersion in water  
 $W_2$  = the weight of the sample after immersion in water

And the result obtained is as shown in table II below

**Table 2: Observed moisture uptake of different LLDPE composites.**

Blends	Sample	Weight immersion ( $W_1$ )	Weight immersion ( $W_2$ )	Moisture uptake %Mt
	A <sub>0</sub>	0.0514	0.0514	0.0
	A <sub>1</sub>	0.0524	0.0539	2.9
	A <sub>2</sub>	0.0523	0.0538	2.9
	A <sub>3</sub>	0.0541	0.0570	5.4
	A <sub>4</sub>	0.0548	0.0579	5.7
	B <sub>0</sub>	0.0518	0.0518	0.0
	B <sub>1</sub>	0.0525	0.0542	3.2
	B <sub>2</sub>	0.0525	0.0542	3.2
	B <sub>3</sub>	0.0543	0.0571	5.2
	B <sub>4</sub>	0.0547	0.0579	5.9
	C <sub>0</sub>	0.0520	0.0520	0.0
	C <sub>1</sub>	0.0532	0.0548	3.0
	C <sub>2</sub>	0.0532	0.0548	3.0
	C <sub>3</sub>	0.0549	0.0578	5.3
	C <sub>4</sub>	0.0548	0.0581	6.0
	D <sub>0</sub>	0.0528	0.0528	0.0
	D <sub>1</sub>	0.0525	0.0539	2.7
	D <sub>2</sub>	0.0525	0.0539	2.7
	D <sub>3</sub>	0.0548	0.0584	5.5
	D <sub>4</sub>	0.0552	0.0533	5.8

From the result above, it can be observed that the moisture uptake of the blends, generally increase with increasing starch content as filler. A rapid moisture uptake was observed in the first few days of immersion, which later decreased with time. Moreover, this is well observed in all the blends with higher starch content, regardless of the modifying agent employed. The water absorption is related to its rate of diffusion into the composites this is because moisture uptakes in starch-LLDPE composites is

mainly due to the starch particles; exposed starch granules or those at near the surface absorb moisture faster than those in the interior. The decrease in the rate of moisture uptake with immersion time could be due to a concentration gradient across the two materials. Initially, water molecules added to starch particles have been found to be strongly bonded as in hydrates. When all of the available hydroxyl groups are used-up in this way, subsequent water absorbed is held less firmly (11).

**CONCLUSION**

From the result obtained it is observed that LLDPE blends containing modified starch as filler show relatively, some reasonable changes in the biodegradation and moisture uptake of the polymer. However, the effect of the starch on the moisture

uptake is found to be significantly better than the biodegradation of the composites. On the other hand, the higher the starch contents the more the observed moisture uptake and the degradation up to an optimum level.

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