THE STUDY OF USING NATURAL FILLERS ON THE BIODEGRADATION PROPERTIES OF VIRGIN/WASTE LOW DENSITY POLYETHYLENE AND VIRGIN/WASTE HIGH DENSITY POLYETHYLENE COMPOSITES.

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ABSTRACT

A study was carried out to check the effect of natural filler on the degradation properties of virgin and waste LDPE and virgin and waste HDPE. Samples were collected and compounded with Maleic Anhydride as a compatibilizer between the polymer matrix and PLA, starch and charcoal. Using the two-roll mix and the compression moulding machine for compounding, samples were moulded and cut according to specifications for the test. Tests carried out were done according to ASTM for water absorption, soil burial and QUV. Results showed as the amount of natural filler increased, it improved water absorption up to 42 days for both virgin LDPE and HDPE, while it took 180 days for samples with more percentage of natural fillers to record mass loss due to degradation. The SEM result confirmed a lot of cracks and holes as a result of immiscibility from the poly blends and which aided with high water absorption and degradation. The QUV results also showed degradation of all samples after exposure time in the accelerated weathering test.

Keywords: low density polyethylene, high density polyethylene, polylactic acid, degradation, soil burial, scanning electron microscopy

INTRODUCTION

Synthetic polymers (plastics) are deemed one of the most frequently used materials in everyday life. The production of oil-based plastics keeps growing every year [1]. An enormous amount of plastic waste is still landfilled or left in the environment and have become a serious environmental threat due to their contribution to the ever-increasing amount of solid waste [2]. Worldwide, plastic products and their components appear freely along roadsides, in parks, at beaches, in the oceans and so on [3]. The level of oil source reliance could be reduced by the advance of bioplastics, using biological sources or more specifically annually with renewable resources [4]. Biodegradable plastics appear to be a way of reducing the negative influence of plastic waste on the environment. A line of plastic materials that are degraded by microorganisms under certain environmental conditions (humidity, temperature and UV light) has been invented [5]. Now a day’s biodegradable materials are of prime interest for environmental reasons [6].

What is more, due to biological degradability, the production of bioplastics has received considerable attention. Therefore, study of the
biodegradability plays a significant role in development of biopolymers [7].

Few polymers such as polylactic acid (PLA) are derived from renewable natural resources. Hence, they can also be clarified under the category of biopolymers. Although they are derived from sources such as corn starch and cassava roots, they undergo chemical and enzymatic polymerization for large-scale production. However, a variety of biodegradable and biocompatible polymers are synthesized by chemical methods. Esters, anhydrides, diacids, and amides are few frameworks chemical compositions of these polymers. The weak hydrolyzable links forming the backbones of synthetic biopolymers are the prime source of biodegradability. They chemically or enzymatically break down into their monomer units, among which few are biologically acceptable by the human bodies, making their importance significant in various biomedical applications [8].

Many conventional techniques are adopted to dispose plastics which include incineration, pyrolysis, landfill, and recycling which involves many technical and economic problems. Synthetic plastics mixed with natural polymers including starch or alginate degrades when dumped in open environment. This degradation leads to changes in their physical and mechanical properties. This degradation can be enhanced by mild physico-chemical pretreatment including thermal or UV treatment. The biodegradability of high density polyethylene has been enhanced by introducing additives to it, including starch and pro-oxidants. Synthetic polymers (plastics) are deemed one of the most frequently used materials in everyday life. The production of oil-based plastics keeps growing every year [1]. An enormous amount of plastic waste is still landfilled or left in the environment and have become a serious environmental threat due to their contribution to the ever-increasing amount of solid waste [2]. Worldwide, plastic products and their components appear freely along roadsides, in parks, at beaches, in the oceans and so on [3]. The level of oil source reliance could be reduced by the advance of bioplastics, using biological sources or more specifically annually with renewable resources [4]. Biodegradable plastics appear to be a way of reducing the negative influence of plastic waste on the environment. A line of plastic materials that are degraded by microorganisms under certain environmental conditions (humidity, temperature and UV light) has been studied by [5]. Now a day’s biodegradable materials are of prime interest for environmental reasons [6]. What is more, due to biological degradability, the production of bioplastics has received considerable attention. Therefore, study of the biodegradability plays a significant role in development of biopolymers [7].

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Starch-based bioplastics constitute a new generation of materials able to significantly reduce the environmental impact in terms of energy consumption and greenhouse effect in specific applications, to perform as traditional plastics when in use, and to completely biodegrade within a composting cycle through the action of living organisms when engineered to be biodegradable. They offer a possible alternative to traditional materials when recycling is unpractical or not economical or when environmental impact has to be minimised [19].

Blends of Polyesters and Starch Blending of synthetic polymers with starch provides cost and performance advantages because starch is renewable, cheaper and is available throughout the year. It has been observed that blends of PCL and granular starch exhibit biodegradation to greater extent [2]. PLA and starch are preferred for obtaining polymer blends as both are biodegradable and are derived from renewable resources. In their blends, starch improves the biodegradability and lowers the cost of the polymer whereas PLA can regulate the mechanical properties of the blend [9].

MATERIALS AND METHODS

Ultrafine corn starch gotten locally from Kaduna market, Maleic Anhydride (MA) Shanghai Huaiang Industries China, distilled water (Kaduna Polytechnic), Charcoal (Panteka, Kaduna), Polylactic acid pallets (PLA) from Shanghai Huaiang Industries China, virgin LDPE pallets obtained from Albarka Plastic Company Kaduna, virgin HDPE pallets collected from Albarka Plastic Company Kaduna, waste LDPE waste bags from Malali and Kaduna Polytechnic waste dump sites, waste HDPE bottles from Kaduna Polytechnic waste dump sites Kaduna, the virgin plastic samples gotten from Albarka plastic company.

Samples Preparation

All samples were weighed with the Digital analytical weighing balance according to Table 1.
Table 1. Material formulations in blends preparation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>LDPE (g)</th>
<th>PLA (g)</th>
<th>Starch (g)</th>
<th>M/A (g)</th>
<th>Charcoal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>250</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>225</td>
<td>0</td>
<td>0</td>
<td>12.50</td>
<td>12.50</td>
</tr>
<tr>
<td>C</td>
<td>200</td>
<td>12.50</td>
<td>12.50</td>
<td>12.50</td>
<td>12.50</td>
</tr>
<tr>
<td>D</td>
<td>175</td>
<td>37.50</td>
<td>12.50</td>
<td>12.50</td>
<td>12.50</td>
</tr>
<tr>
<td>E</td>
<td>150</td>
<td>50.00</td>
<td>25.00</td>
<td>12.50</td>
<td>12.50</td>
</tr>
<tr>
<td>F</td>
<td>125</td>
<td>75.00</td>
<td>25.00</td>
<td>12.50</td>
<td>12.50</td>
</tr>
</tbody>
</table>

The two-roll mill will be used to mix and compound the composite according to Table 3.1, (low density polyethylene/PLA/starch/charcoal) for 175°C for 15 minutes after which each uniformly blended samples was labelled and allowed to cool at room temperature. The samples were molded using a compression molding machine at 180°C for 15 minutes and shaped into square shapes with dimension about 100 mm x 100mm x 3 cm and thickness using a mold and allowed to cool before further testing was carried out. Same procedure was carried out for all virgin and waste high density polyethylene/PLA/starch/charcoal samples using Table 1.

**Degradation test.**

*Soil burial (Determination of biodegradability)*

Biodegradability of the two sets of natural starch PLA/LDPE and starch/PLA/HDPE will be carried out by soil burial method to degrade PLA/LDPE/starch/MA and PLA/HDPE/starch/MA/charcoal composites. Biodegradation as previously reported by [7] rectangular samples with 25 mm x 25 mm x 3mm dimensions will be oven dried until their weights become constant (W1). The samples were then buried in the soil at a depth of 20 cm from the surface of the soil for 180 days. One set of samples will be carefully taken out of the soil for testing every 14 days and then washed with distilled water to remove the sand from the surface of the samples and oven dried at 55 °C until their weights become constant (W2). The percentage of weight loss (% WL) was calculated using equation 1

\[
% \text{ WL} = \left[\frac{(W1 - W2)}{W1}\right] \times 100 \quad \ldots \ldots \quad 1
\]

**Water Absorption**

The ASTM -570 method was used for all the water absorption test, the 24 sets of molded samples (charcoal/starch/PLA/LDPE and charcoal/starch/PLA/HDPE composites samples) with dimensions 90 mm x 25 mm x 3mm will be dried in an oven at 50°C for 24 hours and then
placed in a desiccator to cool. Immediately upon cooling, the specimen will be weighed, and the weight recorded.

The composite will be immersed in distilled water at ambient temperature for 32 days (the water level will be changed after every 7 days).

The water uptake was measured after 7, 14, 21, 28, 35, 42, 49, 56, 63, 70 and 75 days. Water absorption of the composites will be determined using ASTM D570-95 specification. The experimental results obtained will be analysed for statistical significance.

Water absorption (%) \[= \frac{\text{(Wet weight} - \text{Dry weight}) \times 100}{\text{Dry weight}} \tag{2} \]

**Accelerated Weathering test.**

The Accelerated Weathering Tester model QUV spray method using (ASTM G154-QUV) will be used to observe and monitor the changes that UV can enact and would be far too slow of a process in real time. The samples will be cut into 2mm x 2mm by 2mm and subjected to accelerated UV testing to simulate the effects of long-term environmental exposure on samples to UV radiation for longer periods and more intense level than it would naturally encounter.

Test Cycle consists of 8 hours UVA-340 light at 0.89W/m² at 60°C BP, followed by 4 hours condensation at 50°C BP. These tests will speed up the simulations to render results from years of actual exposure to matter of weeks.

**Scanning Electron Microscopy (SEM)**

Scanning electron microscopy images was obtained using an SF-3700 microscope (Hitachi Co Ltd) Japan. Operated in secondary electron mode at a beam current of 100MA and an accelerating voltage of 10KV sample will previously be coated with gold for 150 seconds. The test was carried out on all samples before the soil burial test.
RESULTS AND DISCUSSIONS

Water Absorption

Figure 1: Result for water absorption test for virgin and waste LDPE composites.
Figure 2: Result for water absorption test for virgin and waste LDPE composites.
Results from water absorption shows that all virgin LDPA composites and virgin HDPE samples absorb water except for the control samples A (100% LDPE) and G (100% HDPE). The result showed the percentage degradation of the polyblends by the soil environment on all 24 samples by weighing the mass(g) before immersing in water and one week interval to check any change in mass(g). Results from the samples showed as the amount of natural fillers increased in the polymer matrix, all samples absorbed water up to 42 days for both virgin LDPE and HDPE composite samples after which the samples did not absorb any further water. Water absorption increased weekly up to about 42 days after which the rate of water absorption started to decrease as the amount of natural fillers increased because of the inherent hydrophilic nature of starch and charcoal in addition to the presence of voids at the filler-matrix interfacial.

Majority of reports concluded that PLA degradation occurred strictly through hydrolysis with no enzymatic involvement. Other reports suggest that enzymes have a significant role in the degradation of PLA [20]. Recently, several microorganisms that are capable of degrading PLA have been discovered [18].

The waste LDPE and HDPE samples absorbed maximum absorption up to 35 days after which loss in mass was recorded. This process can be affected by non-living (e.g. ultraviolet light, heat, water) or living factors (enzymes properties, such as tensile strength, toughness and flexural strength. [17] reported that there was an increase in the water absorption for all polyblends as the percentage PLA increased. He explained that PLA has good biodegradable property which is able to be broken down by water thus, affecting their degradation properties.

It can be concluded that generally, the more PLA added to the formulation of LDPE/LDPE-g-MAH/PLA will increase the percentage of water absorption. This can be explained since PLA has a good biodegradable property which able to be broken down by the water, thus affecting to their degradation properties. as reported by [12].

**Soil Burial test (Biodegradability test)**

![Soil Burial test graph](image)
After 2 weeks of soil burial there was no change in mass recorded in all samples as seen in the result. After 28 days there was an increase in the weight of samples except the control samples which did not show any change in weight, 100% virgin LDPE (A) and 100% waste (S) and 100% virgin HDPE (G) and 100% waste HDPE (M) as seen in Figures 3 and 4.
As the amount of natural filler increased in the polymer matrix, it affected the degradation by first absorbing water and impurities from the soil up to 130 days for both virgin LDPE and HDPE samples after which loss in mass was recorded with samples that contained 50 to 70 grams of PLA and 25g of starch. The virgin LDPE samples revealed that samples D, E and F recorded weight loss of 5.45% (13.50g), 7.23% (18.09g) and 13.6% (31g) respectively after 180 days. It may there is the biotic components such as microorganisms decomposers in the soil which able to degradable the polyblend. As reported by [15] that when PLA was buried in the soil, it can be mineralized into CO$_2$, water, and other simple biomass perfectly after 4-6 weeks. Samples from both virgin and waste LDPE and HDPE showed maximum absorption from the soil at about 98 days after which there was loss in mass due to fact that the waste LDPE and HDPE samples collected could have suffered a small amount of degradation from weather, soil and other natural factors

natural fillers, being hydrophilic and more biodegradable, increase the adhesion of microorganisms to the composite material and favor biofouling. PLA degradation starts by abiotic chemical hydrolysis and continues by enzymatic hydrolysis under microbial attack, which occurs preferably in the amorphous regions, and by biotic assimilation of degradation products [3].

When chain scissoring occurs and as the degradation progresses further, the geomembrane will become increasingly brittle, and the tensile properties change to the point that cracking occurs in stressed areas. Once sufficient cracks have developed to significantly increase flow through the geomembrane, the geomembrane may be considered to have reached the end of its service life [13]. It can be concluded that generally, the more PLA added to the formulation of LDPE/LDPE-g-MAH/PLA will increase the percentage of water absorption. This can be explained since PLA has a good biodegradable property which able to be broken down by the water, thus affecting to their degradation properties as reported by [12].
Decomposition generally begins with fragmentation, i.e. the material that is exposed to living or non-living factors undergoes a chemical decomposition of the polymer and therefore decomposes mechanically (fragments). In the next phase, the products of this decomposition are mineralized by microorganisms. This second phase is a necessary step that characterizes this process as biodegradation, because the partially degraded polymers (fragments) are hereby metabolized into end products. There are other cases (oxo-degradable materials) where the material undergoes a quick fragmentation under the influence of heat and UV light but the mineralization stage is very slow, which means that the relatively inert micro particles of the plastic material remain that have a poor susceptibility to biodegradation [16].

Accelerated ultraviolet test (QUV) Visual examination.

All samples were subjected to 8 hours UVA-340 light at 0.89 W/m² at 60°C BP followed by 4 hours of condensation at 50°C BP. On visual examination The control samples A (100% virgin LDPE) and G (100% HDPE) showed no cracks continuously break down into smaller particles, known as micro plastics. Sample and yellowing light colour. Under normal environmental factors such as sunlight, temperature, humidity, oxygen, and mechanical stress, plastic materials lose physical integrity and A showed no cracks was observed and had severe yellowing due to degradation and severe damage. Sample B showed no cracking, no change in colour and no chalking. Sample C showed no cracking, no colour change and no chalking. Sample D and E showed similar results to samples B and C with no cracking, no colour change, and no chalking. Sample F showed extreme discoloration and slight cracking with a release of a sticky substance at the back of the sample. From the results obtained from the QUV samples containing higher amount of natural filler suffered some damages due to degradation. Results showed as the amount of natural filler content increased, a lot of chalking and minor cracks was observed due to degradation. In environmental conditions, solar radiation with air as an oxidizing agent, to start chemical reactions
that cause changes in colour (e.g. yellowing or discoloration) and appearance of materials, which can continue up to embrittlement and loss of physical integrity. UV radiation (100-400um) represents only 6.8% of the spectral range of solar radiation (100=3000um) but it has significantly high energy to break chemical bonds, thus damaging the outdoor exposed material [11].

Plate 1: Results of samples after QUV exposure.

**Scanning Electron Microscopy**
Results from the SEM revealed that all control samples A and G had a smooth surface with little to no cracks or any irregular pattern as seen in plate 2. As the amount of natural filler content increased in the compounding, other samples had cracks, small holes and irregularity as seen in a typical immiscible blend. The result from the SEM analysis accounted for some of the reason for reduction in mechanical properties (tensile and impact test) and a high rate of water absorption and degradation during soil burial in a polyblend with natural fillers.

To compare SEM micrographs of pure polymer film with that of PP/PLA blend films, the surface of the blends become rougher after blending. The multilayer system, physically phase separation between PE phase and PLA phase, was clearly shown in SEM micrographs of longitudinal fractured surface that is a typical behaviour of immiscible polymer blends [10] that the blend composition has a significant effect on the nucleation density.
Plate 2: Result of the SEM scanning of LPE and HDPE composites.
CONCLUSION

The work results suggested that using virgin low density polyethylene for making disposable bags was recommended compared to the virgin high density polyethylene this can be seen from some of the test carried out in terms of the water absorption, soil burial biodegradability test, QUV and SEM result.

The water absorption results showed that all samples absorbed water as the amount of natural filler increased up to 42 days. The soil burial result revealed as the amount of natural fillers increased in the polymer matrix, it aided biodegradability with loss in mass after 180 days for virgin samples of LDPE and HDPE samples having 30% PLA and 20% starch content in the poly blend.

REFERENCES


