COMPARATIVE STUDY OF THE EFFECT OF POLY(LACTIC-ACID), STARCH, CHARCOAL ON PHYSICO-MECHANICAL PROPERTIES OF VIRGIN AND WASTE LOW DENSITY POLYETHYLENE COMPOSITES.

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ABSTRACT

A study was carried out to evaluate the effect of natural fillers on the mechanical properties of virgin and waste low density polyethylene. Samples of disposable sachet bags were obtained and blended with varying percentages of polylactic acid, starch, charcoal and maleic anhydride (M.A) in a 2 roll-mill mixer and compression molded to form composites using the two-roll mix and the compression molding machine for compounding. Samples were molded and cut according to ASTM for tensile strength, flexural strength, hardness and impact strength. From the results obtained, incorporation of the natural fillers reduced the tensile strength for the virgin composites more than the waste composites, similar results were observed with the flexural strength, hardness compared to the control sample. However, impact strength improved with increase with natural fillers.

Keywords: low density polyethylene, high density polyethylene, natural fillers, mechanical properties.

INTRODUCTION

The same durability properties which make plastics ideal for many applications such as in packaging, building materials and commodities, as well as in hygiene products, can lead to waste disposal problems in the case of traditional petroleum-derived plastics, as these materials are not readily biodegradable and because of their resistance to microbial degradation, they accumulate in the environment. In addition, in recent times oil prices have increased markedly. These facts have helped to stimulate interest in biodegradable polymers and in particular biodegradable biopolymers.[1]

Blending polymer is a simple technique to enhance the property of pure polymer. The benefits of blending are providing new materials with desired properties at the low price, quick formulation changes, plant flexibility and high productivity and reduction of the number of grades that need to be manufactured and stored [15]. From those advantages, polymer blending is widely used in polymer consumption such as packaging, textile, and engineering industries. Biodegradation rate of composite materials depends on the nature of components and on how strong they bond together, but also on the
environmental conditions (e.g., temperature, moisture and pH of soil, microbial population, and nutrient supply) to which the material is subjected [12]. Biological contact occurs at the material–environment interface, therefore the area and properties of the exposed surface play significant roles, a rough surface with a high number of polar hydrophilic functional groups is much more prone to biodegradation than a smooth, hydrophobic, and inert one. Natural fillers, being hydrophilic and more biodegradable, increase the adhesion of microorganisms to the composite material and favor biofouling [5].

PLA is a synthetic thermoplastic aliphatic polyester that is completely derived from renewable resources, such as corn starch or sugar cane, and has similar characteristics to classical PP, PE, and PS but is considered biodegradable. While of natural origin, PLA shares the common hydrophobicity of the fossil-based equivalent polyolefins. It has poor surface adhesion with natural fibers or fillers, which usually have high polar character, and requires compatibilizing agents to stabilize the interface in composites and decrease the glass transition, favoring biodegradation [12]. 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 [10]. Changes in properties of the material such as changes of the molecular mass and its distribution (determined by size exclusion chromatography—SEC); structural and compositional changes of chemical species in the material or its degradation products (determined by infrared spectroscopy—IR or nuclear magnetic resonance spectroscopy—NMR); changes in physical and morphology properties, such as surface features, mass loss, glass transition (Tg), melting temperature (Tm), crystallinity, thermal behavior (determined by differential scanning calorimetry—DSC or thermogravimetry—TG thermal analysis methods); or modification in mechanical properties, such as tensile strength or elongation at break, are useful parameters to evaluate the degradability of materials. The above-mentioned analysis and characterization methods are suitable to evaluate the evolution of degradation; however, they cannot be used for direct quantification of the processes [4].

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.

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 pellets (PLA) from Shanghai Huaiang Industries China, virgin LDPE pallets obtained from Albarka Plastic Company Kaduna, virgin HDPE pellets 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. The waste plastic samples were collected from dumpsites in Kaduna polytechnic, Albarka plastics Kaduna Metropolis Plastic Company in Kaduna State.

**Samples Preparation**

All samples will be 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 was 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 moulded using a compression moulding 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 high-density polyethylene/PLA/starch/charcoal samples using Table 1

**Mechanical tests.**

**Tensile tests**

Tensile test was carried out using Instron Universal testing machine (3369 model) as described in ASTM method D638. Each tensile specimen was positioned in the Instron Universal tester and then subjected to tensile load. As the specimen stretches, the computer generates the graph as well as all the desired parameters properties of the specimen fractures.

**Flexural test**

Three-point bending test was carried out in an UTM machine in accordance with ASTM
D790-03 to measure the flexural strength and flexural modulus of the composites. The specimens of dimensions 125 mm x 6 mm x 3 mm.

**Impact test (Charpy Impact test)**

Pendulum-type hammers testing machine model IMPACT TESTER were used. At first, the requirements of Charpy impact test is to adjust the level of the machine in both directions, the transverse location at centre of the pendulum arm for straightness, the pointer friction and finally measured the vertical distance of fall of the pendulum striking edge from the trip height to its lowest point.

**Hardness test**

Hardness is the resistance of a material to deformation, indentations or scratching. The tests were carried out to determine the hardness of all samples using the shore hardness (Muver Fransisco, Munoz). The tests were done according to ASTM E2240. Each sample will be tested on the hardness tester (Muver) while in the compressed molds form of 100mm x 100mm (3mm thick) and subjected to seven hardness reading at different positions on the 3. The average was calculated using the mean of the seven reading for each sample and was recorded.

**RESULTS AND DISCUSSIONS**

**Tensile strength**

![Figure 1: Effect of natural fillers on the tensile strength of virgin LDPE/PLA/charcoal/starch composite.](image)
Results from Figure 3.1 showed that the composite A (100% LDPE) had the highest tensile strength of 20.30 MPa and sample F had a tensile strength of 16.66 MPa. Sample B has a tensile strength of 21.53 MPa, sample C and D showed a slight decrease in the tensile strength as the amount of natural filler increased as compared to sample A. Results showed that as the amount of natural fillers (PLA and starch) increased in samples E (16.93 MPa) and F (16.66 MPa) there was an increase in the tensile strength, this may be attributed to the fact that more polylactic acid was added as seen from the formulation table above. The result is expected because of the difference in polarity between the matrix and the natural filler (PLA and starch, charcoal) which are hydrophilic. Also, the non compatibility between the polymer blends may result to a decrease in the tensile strength as reported by Anour 2018. Results from the tensile modulus of the virgin LDPE composites sample A had the highest tensile modulus at 93.06 MPa. It can be seen that all samples showed a decrease in the tensile modulus as the amount of natural filler increased. Sample B had a tensile modulus of 107.95 MPa, sample C had a tensile modulus of 83.06 MPa while sample D 82.06 MPa while sample E was 67.85 MPa showed a slight increase in the tensile modulus. Sample A tensile modulus is more ductile than samples C, D, E and F. The virgin LDPE composites C, D, E and F showed a general decrease in the elongation at break compared to 100% LDPE. The natural fillers did not improve the elongation at break hence, there was a decrease in the tensile modulus as the amount of natural fillers increased and it reduced the ductility, making them more brittle in nature and have poor thermal stability [13].

**Tensile test results for waste LDPE composites**

![Figure 2: Effect of natural fillers on the tensile strength for waste LDPE/PLA/charcoal/starch composite.](image-url)
Figure 2 showed that sample S (waste LDPE) had a tensile strength of 19.94 MPa. Sample T had no starch in the formulation and had a tensile strength of 20.65 MPa while sample U showed a slight reduction in the tensile strength as seen in Figure 3.2. Sample U showed a slight decrease in the tensile strength with a value of 20.13 MPa and was with samples V (13.50 MPa) and W (9.10 MPa). From the results obtained there is a slight increase as the amount of natural filler content (PLA, starch and charcoal) increased in sample T. A decrease in the tensile strength of samples U, V, W and X. [6] reported similar findings that incorporating starch films into polyethylene exhibited similar physical characteristics as in conventional packaging plastics in terms of transparency, tensile strength and non-toxicity. Also reported by [7] that the tensile strength was observed to decrease with time of exposure to the natural environment, probably because of increasing cross-linking or change in the crystal structure, it was observed during field visits that the material actually shrinks over time. It was, therefore, concluded that the observed phenomena were the result of chemical activity associated with aging. This may be reinforced by the fact that the material was observed to have increased brittleness over time.

The tensile modulus of the waste LDPE where sample S had the highest tensile modulus of 41.05MPa while sample T had a value of 43.70MPa which is an increase in the tensile modulus from sample S. Sample T had no starch in the formulation and this account for the higher tensile modulus compared to sample S and all other samples (T, U, V, W). The waste LDPE composites show a decrease in the tensile modulus of all composites within the range between (41.05 – 9.10Mpa). The reduction of tensile strength in the blends, compared to the pure polymers is due to the incompatibility between nonpolar PE and polar PLA. Non-compatible polymer blend eventuating in sharp boundaries between the two polymeric phases, which the applied stress could not be efficiently transferred through the interface of blended component [8]. This kind of results that the tensile strength values of the blend are lower than pure polymer could be seen in typical immiscible polymer blend [4].

**Flexural Test.**

Result from Figure 3 showed that as the amount of natural filler increased in the virgin LDPE composite, it decreased the flexural strength. Sample A had the highest flexural strength of 65.74N/mm², Sample B had a flexural strength of 56.62N/mm², sample C was 54.78N/mm², sample D was 54.90N/mm², sample E showed an increase in the flexural strength as PLA content was increased in samples E and F 65.58 N/mm².
Figure 3: Effect of natural fillers on the flexural strength for virgin LDPE/PLA/charcoal/starch composite.

Similar pattern was observed in the flexural modulus which is an indication of stiffness and more resistance to bend. As the amount of PLA and starch increased, the flexural modulus increased, this indicates that the higher the flexural modulus of a material, the harder it was to bend under an applied force. The brittle nature of starch affected the flexural modulus by making it stiffer.

Figure 4: Effect of natural fillers on the flexural strength for waste LDPE/PLA/charcoal/starch composite.
Result from Figure 3.4 showed sample S had a flexural strength of 65.42N/mm$^2$, sample T does not contain any starch and had a flexural strength of 66.06 N/mm$^2$ which is higher than sample S. samples U was 62.03N/mm$^2$, sample V was 60.01N/mm$^2$, sample W had the least flexural strength at 60.00N/mm$^2$. Samples X had a flexural strength of 62.00N/mm$^2$ which was higher than sample W which had the highest amount of PLA from the formulation table. Similar results was reported by [2], who studied biodegrading of waste low density polyethylene (LDPE) disposable bags using natural fillers (starch, charcoal) that as the amount of natural filler (starch and charcoal) increased in waste LDPE composites, it affected the flexural modulus by making it weaker and harder to bend under applied force. Waste LDPE collected from Kaduna polytechnic may have suffered some form of degradation from the sun and out door weathering before being collected as this may contribute to the decrease in the flexural strength and modulus to bend due to out weathering of the waste LDPE.

**Hardness test**

It can be seen that the waste samples S which is 100% waste low density polyethylene has a higher hardness value (95.00) than sample A of (94.00) which is 100% virgin LDPE. A similar trend is seen in samples T (93.00) and B (92.00), U (94.50) and C (91.00), W (92.00) and E (92.00) and sample X (92.00) and F (90.00).

The hardness results showed a trend of decrease in the hardness property for both the virgin and waste low density polyethylene composite as seen in Figures 5 and 6. The waste LDPE composites had higher tensile strength values and hardness values than the virgin LDPE composites.

![Figure 5: Effect of natural fillers on the hardness test of virgin LDPE/PLA/charcoal/starch composite.](image-url)
From the results obtained both starch and PLA affected the hardness property by decreasing the hardness strength. All waste samples have higher values than the virgin counterpart this can be due to the fact that the waste collected from the industries have a lot of additives that were added to the resin before manufacture to improve property such as color, UV stabilizers etc. whereas the virgin resin is 100% without any additives as reported by [3].

![Figure 6: Effect of natural fillers on the hardness test of waste LDPE/PLA/charcoal/starch composite.](image)

It can be seen that the waste samples S which is 100% waste low density polyethylene has a higher hardness value (95.00) than sample A of (94.00) which is 100% virgin LDPE. A similar trend is seen in samples T (93.00) and B (92.00), U (94.50) and C (91.00), W (92.00) and E (92.00) and sample X (92.00) and F (90.00).

The hardness results showed a decrease in the hardness property for both the virgin and waste low density polyethylene composite as seen in Figures 5 and 6. The waste LDPE composites have higher tensile strength values and hardness values than the virgin LDPE composites. The high-density polyethylene virgin and waste composites will have higher hardness, tensile strength values and rigidity than LDPE due to crystallinity content, crystallinity has a direct influence on the tensile strength and hardness [11]. These findings are also in agreement with some mechanical results such as the tensile strength and hardness as studied by [10] where he studied that hardness value varies inversely with ductility and the deformation caused by the hardness indenter are of similar magnitude to those occurring at the ultimate strength in the tensile strength test.
**Impact strength.**

Figures 7 and 8 revealed the impact strength of the virgin LDPE composites increased from the control sample A at 152.50J/mm$^2$ to 164.50J/mm$^2$ for sample B, 174.00J/mm$^2$ for sample C. Sample D had an impact strength of 181.80J/mm$^2$ while sample E had an impact strength of 182.40J/mm$^2$. Sample F showed a decrease in the impact strength 149.00J/mm$^2$ which is the lower than the control sample.

![Figure 7: Effect of natural fillers on impact strength of virgin LDPE/PLA/ starch/charcoal composite](image1)

![Figure 8: Effect of natural fillers on impact strength of waste LDPE/PLA/ starch/charcoal composite](image2)
Figure 8 showed a decrease in the impact strength as the amount of natural fillers was cooperated into the waste LDPE composites. Samples S had an impact strength of 376.33 J/mm² which had the highest impact strength than all other samples. Sample T had an impact strength of 310.50 J/mm², sample U 306.00 J/mm². Sample V had an impact strength of 306.00 J/mm², sample X had the lowest impact strength of 145.00 J/mm².

As the amount of natural fillers increase in the HDPE composites, it showed a decrease in the impact strength, this could be attributed to incompatibility and slight degradation from factors such as sun, rain, wind and weathering which also affects some of the mechanical properties as seen in the tensile strength.

Results from Sample G had the highest impact strength of 260 J/mm² and other samples showed a decrease in the impact strength as the amount of natural fillers increase as seen in samples H 226.00 J/mm², sample I with 216 J/mm², sample J had an impact strength of 206.00 J/mm², sample K 199.00 J/mm² and sample I was 175.00 J/mm² with the lowest impact strength. Similar finding was observed with the waste LDPE composites where there a general decrease in impact strength as the amount of natural fillers increased. The samples became easier to break and more brittle as natural filler content increased as compared with the control sample (sample G).

Figure 9: Effect of natural fillers on impact strength of virgin HDPE/PLA/ starch/charcoal composite
Figure 10: Effect of natural fillers on impact strength of waste HDPE/PLA/ starch/charcoal composite.

Waste HDPE results also showed a decrease in the impact strength. Sample M had an impact strength of 464J/mm² and sample N had an impact strength of 480J/mm², which is higher than the control. This sample contains no starch, and this may be why the impact is higher than the control. As the natural filler content increases, the impact strength further decreased as seen with samples O 426J/mm², sample P 412J/mm², sample Q 402.50J/mm² and the lowest Impact strength was sample R 337.00J/mm². As the amount of natural fillers increase in the HDPE composites, it showed a decrease in the impact strength, this could be attributed to incompatibility and slight degradation from factors such as sun, rain, wind and weathering which also affects some of the mechanical properties as the tensile strength [3]. The results obtained in the virgin HDPE, samples G, H, I and waste HDPE samples M, N, O and P are within the range from the control sample. Waste HDPE results also had a decrease in the impact strength. Sample M had an impact strength of 464J/mm², and sample N had an impact strength of 480J/mm², which is higher than the control. This sample contains no starch, and this may be why the impact is higher than the control. As the natural filler content increases, the impact strength further decreased as seen with samples O was 426J/mm², sample was P 412J/mm², sample was Q 402.50J/mm² and the lowest Impact strength was sample R was 337.00J/mm². From the results obtained in the virgin HDPE, samples G, H, I and waste HDPE samples M, N, O and P are within the range from the control sample.
CONCLUSION

The result of the work suggested that using virgin low-density polyethylene for making disposable bags are preferred to use for manufacture than the waste low density polyethylene this can be seen from the mechanical tests.

1. Tensile strength of the virgin LDPE/pla/starch/charcoal composites showed a decrease in both the tensile strength and modulus from sample A to sample F. Most of the samples made from virgin LDPE and compounded with natural fillers had a decrease in the tensile strength but still showed a promising tensile strength of 84.08% with sample D and 82.00% for sample F having the highest PLA content in it. The waste LDPE compounds showed a decrease in the tensile strength and modulus with significant loss in the tensile strength of up to 45%.

2. The flexural strength of the virgin LDPE composites showed a slight decrease within the range from the control sample A to sample F from (100- 97.00%). The flexural strength was not really affected by the addition of natural fillers similar results was seen in the flexural modulus. An increase in the flexural modulus was seen as the amount of natural filler increased hence, making the samples move from flexible to stiffer samples and more resistance to bending from external forces while the waste LDPE composites showed a decrease of 94% in the flexural strength and flexural modulus.

3. The hardness result for the virgin LDPE composites showed a slight decrease in terms of hardness from the control sample A as the amount of natural fillers were in cooperated into the virgin LDPE. From samples A to F showed of up to 95%. Similar decrease in the hardness result was seen in the waste LDPE composites.

4. The impact results for virgin LDPE composites showed an increase in the impact strength as the amount of natural fillers were incorporated from samples A to sample E. While the waste LDPE samples showed a decrease in the impact strength from samples S to X with sample X having 38.50% which showed significant loss of strength as compared to the control waste sample S.

The samples of the virgin LDPE composites showed better mechanical properties for use in the manufacture of disposal leather bags with up to 21.50% PLA content and 7% starch content in the virgin low density polyethylene mix.
REFERENCES


