Cassava Starch-Mixed Polypropylene Biodegradable Polymer: Preparation, Characterization and Effects of Biodegradation Products on Growth of Plants

Obasi, Henry C¹, Igwe, Isaac O²

¹²Department of Polymer and Textile Engineering, Federal University of Technology, Owerri, P.M.B. 1526, Imo State, Nigeria

Abstract: Blends of plasticized cassava starch (PCS) plasticized compatibilized cassava starch (PCCS) and polypropylenes (PP) were prepared using an injection molding process. Tensile, water absorption and biodegradable properties of the blends have been investigated. Here, variable amounts of cassava starch were processed in the presence of glycerol as plasticizer. The incorporation of PCS reduced the tensile strength and elongation at breaks but with an increase in Young's modulus of the blends. However, on addition of PP-g-MA to the blends, tensile properties were found to improve due to enhanced interfacial adhesion between PCS and PP, which can be proved by the scanning electron microscopy (SEM) observations. The percentage of water absorbed and weight loss of the PCS/PP were higher than the PCCS/PP blends due to poor interfacial adhesion. Biodegradation products of the various blends had no adverse effects on the growth of plants.

Keywords: Cassava starch, polypropylene, glycerol, PP-g-MA, Tensile properties, water absorption, weight loss.

1. Introduction

Plastics possess many desirable properties including water resistance and long life that make them suitable candidates for both consumer and industrial products. However, the attributes that make these products suitable for various applications are also the major cause of the waste disposal problems in the environment.

The desire for eco-friendly polymeric materials has given rise to increasing attention due to problems associated with the disposal of large volumes of plastic wastes. In the light of the above, most of the contemporary researches are focused on substitution of the synthetic plastics by biodegradable materials with similar properties and cheap in cost. The biodegradable materials upon disposal, are converted to natural compounds of water, carbon dioxide, methane and other biological components by microorganisms such as fungi, bacteria, algae and other natural agents [1].

Polypropylene (PP) is a thermoplastic polymer and plays a vital role in the industry of polyolefins due to its wide range of uses. Polypropylene has good properties such as high strength and flexibility, good processability, excellent resistance to acids, alcohols, bases and esters and dimensional stability [2]. However, PP wastes persist for many years after disposal causing environmental hazards. To overcome this non-degradability, the introduction of biodegradable polymers or natural fillers such as starch in PP based materials formulation maybe considered as a credible alternative in the development of eco-friendly material.

Starch is an important ingredient in food and non-food industries (such as paper, plastic, adhesive, textile and pharmaceutical industries) [3]. Starch is composed of amylose and amylopectin. The amount of amylose and amylopectin are different between various sources of starch and ratio of the two has an effect on product behavior. The widespread occurrence of starch with its biodegradable nature and low cost gave rise to exploitation of starch as a means of improving the biodegradability of inert polymers [4]. The use of starch as a filler is limited due to its hydrophilic nature and the hydrophilic nature of the synthetic polymer matrix. Neat starch is brittle and difficult to process into articles due to its relatively high glass transition and melting temperatures. Therefore, starch must be modified to breakdown the crystalline granules, decrease the glass transition and melting temperature either by incorporating plasticizers or blending with other polymers [5], [6], chemical modifications or contributions before they can be processed into plastics [7].

The addition of a plasticizer to a starch to obtain a thermoplastic starch (TPS) is required to overcome film brittleness, caused by high intermolecular forces. Plasticizers are mainly small molecules such as polyols like sorbitol, glycerol and polyethylene glycol (PEG) that intersperse and intercalate among and between polymer chains, disrupting hydrogen bonding and spreading the chains apart which not only increases flexibility, but also water vapour and gas permeabilities [8]-[10].

Biodegradable plastic from TPS/synthetic polymer blend has a poor interfacial adhesion due to incompatibility of the polar starch and non-polar synthetic polymer. To overcome this problem, a compatibilizer is introduced which will reduce the interfacial energy and homogenize the polar starch with the synthetic polymer [11]. Much work has been done on thermoplastic and biofiller blends, which have successfully proven satisfactory to various fields of technical applications. In fact, thermoplastics, such as polyethylene (PE) [12], [13], polypropylene (PP) [14]-[16], Polyvinyl
chloride (PVC) [17], and polystyrene (PS) [18], have been compounded with biofillers to obtain biodegradable products.

In this study, an attempt is made to produce a biodegradable polymer from a polypropylene (PP) and plasticized Cassava Starch (PCS) at different filler content in order to investigate the effect of maleic anhydride-graft-polypropylene addition on some mechanical properties, fracture surface morphology, water absorption and biodegradable behavior of the PP/PCS blends.

2. Materials and methods

2.1 Materials

Polypropylene granules with melting temperature of 165°C and Melt Flow Index (MFI) of 70g/10min were purchased from CeePlast Industries Ltd, Aba, Nigeria. Maleic anhydride-graft-polypropylene (MA-g-PP), compatibilizer was obtained from Sigma-Aldrich Corporation with melting point and density of 156°C and 0.934g/cm³ respectively. Glycerol, plasticizer was obtained from Ajax chemicals. Cassava starch extracted from cassava tubers (Manihot esculenta) which were purchase from local market in Ehime Mbano, Imo State, Nigeria. It has a particle size of 0.075mm.

2.2 Preparations of plasticized cassava starch

Plasticized cassava starch (PCS) was obtained from the extracted cassava starch according to the method of St-Pierre et al. [19]s using a high speed laboratory mixer. Good mix of starch, water and glycerol was obtained at 70°C and 50 rpm. The PCS obtained was then dried in an oven at 90°C for 12h to reduce moisture content.

2.3 Preparation of PCS/PP blends

Mixtures of plasticized Cassava starch and polypropylene were melt-blended in an injection machine at a temperature of 169-190°C and a screw speed of 50 rpm to obtained PCS/PP compositions. The PCS contents range from 0-50 wt. % in the blends. Maleic anhydride-graft-polypropylene (MA-g-PP) was used as a compatibilizer at 10 wt. % based on the starch loading. The liquid melt was injected into a mould to obtain sample sheets. These sheets were oven dried over night at 70°C to reduce moisture content and then stored in a desiccator.

2.4 Tensile Properties

Tensile tests for the PCS/PP blend samples were conducted using universal tensile testing machine, Instron 3366 according to ASTM D 638. The test on dumb bell shaped specimens of 3mm thickness was performed at a cross-head speed of 5mm/min at 23 ± 5°C. Five specimens were used to obtain the average values of the tensile properties.

2.5 Water Absorption Test

Water absorption by the various PCS/PP Blends were carried out using cut samples of dimensions, 20 mm x 20 mm. Prior to the absorption test, the cut samples were carefully washed with tap water, oven-dried at 50°C for 12 h, cooled in desiccators and immediately weighed (W₀). Thereafter, the samples were immersed in distilled water at room temperature range 32-36°C. Samples were removed from the water at definite intervals (10 days) and weigh using electronic balance to obtain the weight after immersion in water (Wᵢ). The percent (%) water absorbed by the samples was calculated using,

\[
\text{% water absorbed} = \left( \frac{Wᵢ - W₀}{W₀} \right) \times 100
\]

(1)

2.6 Soil Burial Test

The soil burial test was carried out using blend samples of dimensions, 20 mm x 20 mm at room temperature to determine the biodegradability of the PCS/PP blends. The samples were buried 100 mm below the surface of alluvial soil placed in performed boxes which was regularly moistened with water. The samples were taken out at regular time intervals (10 days), washed with distilled water, dried at room temperature to a constant weight before weighing. The percent weight losses of the sample measured after every 10 days and that obtained after every tenth day were determined respectively as follows;

\[
\% \text{ weight loss} = \left( \frac{W₀ - Wₙ}{W₀} \right) \times 100
\]

(2)

Where W₀ and Wₙ are initial mass before and after degradation in the soil respectively.

\[
\% \text{ weight loss (After every 10 days)} = \left( \frac{\text{Initial wt. before 10 days} - \text{final wt. after 10 days}}{\text{Initial wt. at the beginning}} \right) \times 100
\]

(3)

2.7 Growth of Plants

The growth of soya bean, and wheat plants was checked from the germination stage to find out whether or not the degradation products from the PCS/PP samples would affect their growth. The soya bean and wheat seeds were placed uniformly in different containers containing the already removed PCS/PP blends, and were allowed to grow in the open for 30 days. The length and height of the roots and shoot of the growing plants were measured respectively.

2.8 Morphology Test

The Scanning Electron Microscopy (SEM) was used to evaluate the samples microstructure. The samples were first dried in an oven to remove moisture and then sputter coated with a thin layer of gold to avoid electrical charging.

3. Results and Discussion

3.1 Tensile Properties

The tensile strength (TS), elongation at break (EB) and Young’s modulus (YM) graphs of PCS/PP and PCCS/PP blends are presented in Figures 1 and 2. The addition of cassava starch filler to PP matrix followed the general trend of the effects of non-reinforcing filler on polymer properties. The tensile strength and elongation at break showed an inverse relationship with starch content. This indicates that
the tensile strength and elongation at break decrease with increase in starch content. The reduction of tensile strength and elongation at break became more pronounced when the concentration of starch loading was increased. It is clear that the tensile strength and elongation at break of PCS blends decreased from 38.902 N/mm² to 11.751 N/mm² and 17.2% to 4.8% respectively (Fig. 1). This may be attributed to the filler-filler interaction, which becomes more significant than that of the filler-matrix interaction. Another reason could be the lack of the formation of strong interfacial bonds like hydrogen bonds between starch filler and PP matrix. These results are in agreement with the works of Wahab and Mottaleb [20], Danjaji [21], and Rosa et al. [22]. The Young’s modulus increases with the incorporation of cassava starch into PP matrix. The Young’s modulus increased from 226.174 N/mm² to 273.297 N/mm² when starch content was increased from 0% to 50%. This may be due to the stiffening effect that the starch granules are stiffer than that of the PP. The hydrogen bonding in starch gives higher modulus than that of a semi-crystalline polymer like PP, with no hydrogen bonding. Young’s modulus exhibited direct relationship with the starch content in the blends. These results are similar to the works of Willet [23], Danjaji [21], and Cinelli et al. [24]. Figure 2 shows the effect of PP-g-MA on tensile strength, elongation at break and Young’s modulus of cassava starch/blend. It was then clear that the PP-g-MA contained blends showed higher increase in tensile strength and elongation at break compared with uncompatibilized blends, and that the difference increases with increasing starch content. The tensile strength of the blends increased by 40.4 % and 38.1 % whereas elongation at break improved by 29.2 % and 59.6 %, relative to the uncompatibilized blends at 10 wt.% and 50 wt.% starch content respectively. However, the tensile strength and elongation at-break of both blends decreased with increasing starch content compared with the neat PP. From Fig. 2 also, it was observed that the Young’s modulus experienced a higher increase on addition of compatibilizer. The Young’s modulus of the blends increased by 8.2 % and 8.9 %, relative to the untreated blends at 10 wt.% and 50 wt.% starch content respectively. The improvement in the tensile properties of blends could be linked to the improved interfacial adhesion between the hydrophilic starch and hydrophobic PP matrix. These findings are similar to the works of Bikians et al. [25], and Wu [26].

3.2 Water Absorption Test

Figure 3 shows the percentage of water absorbed by PCS/PP and PCS/PP blends as a function of time. Water absorption increased with increasing immersion time and starch content. This observation is due to the hydrophilic nature of cassava starch, which is responsible for the water absorption in the blends. Hence, at higher starch content, a higher amount of water is being absorbed [27]. The PCS/PP blend showed higher water resistance capability than the PCS/PP blends. The increment of water absorption for PCS/PP blends compared with PCS/PP blends was about 28.3 % and 15.7 % at 10 wt. % and 50 wt. % filler content respectively. The low percentage water absorption increment at 50 wt. % may be attributed to the leaching away of starch particles from the samples at high filler content with increasing time. The blends did not equilibrate even up to 90 days immersion in water. These findings were similar to the result of Willet [23] demonstrating that the equilibration time for starch-PE blend is the period of months even when immersed in water. In this study, the comparatively lower water absorption of PCS/PP blend was caused by the formation of ester linkage groups on the blend.
3.3 Soil Burial Test

Figure 4 shows the changes in weight with time for the PCS/PP and PCCS/PP blends burial in the soil. It is expected that the water present in the soil diffuse into the blend samples, causing swelling and increase in biodegradation.

In the figure, the biodegradability of the blend increased up to 26 % as the burial time increased for 90 days. The weight loss of PCS/PP and PCCS/PP blends increased with increase in starch content as well as burial time indicating the extent of biodegradation. Furthermore, PCS/PP blend had a higher weight loss percent than PCCS/PP, with an increment of about 18.5 % at 10 wt. % and 35.6 % at 50 wt. %. This behavior may be caused by the same factors that led to its high water absorption.

In another set up, the weight loss percent of the PCS/PP and PCCS/PP blends measured after every 10 days were presented in Figure 5. This was taken as the weight of the sample on each 10th day minus the preceding weight of the sample prior to 10 days. It is evident that the rate of weight loss was low at lower starch content (≤ 20 wt. %) for both blends. Afterwards, the rate of weight loss increased with PCS/PP blends having a higher weight loss percent. It is observed again that at 90 days of soil burial, the PCCS/PP blends had weight loss percent of about 2.06 %, at 50 wt. % starch content which almost corresponds to that PCS/PP at 30 wt. % starch content. This phenomenon may be linked to the improved interfacial adhesion between the starch filler and polymer matrix in PCCS/PP blends.

3.4 Growth of Plants

Wheat and soya bean plants were planted in the containers where PCS/PP and PCCS/PP blends were soil buried in order to determine the effects of biodegradation products on the lives of the plants. The plants were monitored from germination stage, and the shoots of the plants were measured every 10 days for the period of 30 days. The average lengths of the shoots measured are illustrated graphically as shown in Figures 6 and 7. It is observed that all the plants germinated as planted, and with different growth rates and independent of starch content. The growth rate was rapid at early stages and later slowed down. This later situation could be because the plants were approaching maturity.

The behavior of the plants roots was also observed since they were directly in contact with the sample soil, even though the root was not an edible part of the plants under study. The average determined length of the roots is presented in Table 1 for both PCS/PP and PCCS/PP blends. These observations showed that the degradation products are not harmful to the growth of the plants.
Figure 7: Average length of wheat and soybean plants for compatibilized PP/PCS blends after 30 days.

Table 1: Average length of plants roots for PP/PCS and PP/PCCS blends.

<table>
<thead>
<tr>
<th>Starch content, wt.%</th>
<th>Uncompatibilized PP/PCS blends</th>
<th>Compatibilized PP/PCCS blends</th>
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<tbody>
<tr>
<td></td>
<td>Wheat plants, cm</td>
<td>Soy bean plants, cm</td>
</tr>
<tr>
<td>10</td>
<td>15.40</td>
<td>22.20</td>
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<tr>
<td>20</td>
<td>14.60</td>
<td>20.30</td>
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<tr>
<td>30</td>
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<tr>
<td>40</td>
<td>12.80</td>
<td>20.20</td>
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<tr>
<td>50</td>
<td>13.60</td>
<td>19.80</td>
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3.5 Morphology Test

SEM micrographs of fracture surfaces of PCS/PP and PCCS/PP blends at 10 and 50 wt. % starch content before and after soil burial are shown in Figures 8 and 9, which revealed the dispersion of starch granules in PP matrix and extent of degradation in the soil. Rough surface of the glycerol plasticized cassava starch could be observed as presented in the figures. Figures 8(a) and 9(a) represent starch content at 10 wt. % in which starch is less visible due to poor dispersion of the filler within the matrix, however, with minimal effect in Fig. 9(a) because of the presence of compatibilizer. Figures 8(b) and 9(b) represent starch content at 50 wt. %, in Fig. 8(b), starch granules are clearly visible; an evidence that the starch granules are not all covered by the matrix. However, Fig. 9(b) shows a better distribution of starch in PP matrix. The agglomeration at higher starch content can be minimized with the incorporation of PP-g-MA. This buttressed the improvement of tensile properties of PP/PCS blends on an addition of compatibilizer.

4. Conclusions

1. Incorporation of plasticized cassava starch (PCS) enhanced the Young’s modulus of PCS/PP blends at the expense of tensile strength and elongation-at-break. The addition of PP-g-MA to the PCS/PP blends is necessary to improve the tensile properties.
2. In the water absorption behaviour, water uptake by the uncompatibilized PCS/PP blends increased with the increase in starch content because of the inherent hydrophilic nature of PCS in addition to the presence of voids at the filler-matrix interfacial.
3. As for the compatibilized PCS/PP blends, a lower weight loss percent than the uncompatibilized PCS/PP blends is observed, suggesting good interfacial adhesion.
4. The growth of plants reveals that biodegradation products of the various blends had no adverse effects on them.
5. SEM micrographs of the fracture surfaces show better presence of PP-g-MA as a compatibilizer.

References


Author Profile

Henry C. Obasi received the M. Sc. and Ph. D degrees in Polymer Science and Engineering from Federal University of Technology, Owerri. He is currently with the Department of Polymer and Textile Engineering of the same institution. His research interest has been in the areas of polymer blends and composites, synthesis, testing and characterization.

Isaue O. Igwe, is a university Professor of Polymer Science and Engineering, Federal University of Technology, Owerri. He is currently the Head of Department, Polymer and Textile Engineering. His research interests include (but not limited to) polymeric materials synthesis and characterization, polymer blends and composites.