Coco-yam and water-yam starches: As alternative dual purpose polymer ingredients.

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Increased elastic modulus and ultimate stress of low density polyethylene has been achieved by incorporating coco-yam, water-yam and guinea-corn starches into low density polyethylene using a standard hot-melt compounding technique. Some mechanical properties of compression moulded dumbbell shaped films of low density polyethylene containing up to a maximum of 20 wt% of each starch is reported. Evidence is offered using IR spectroscopy linking the degradation of the low density polyethylene/starch composites in a compost to an initial break down of the starch by micro-organism in the soil probably followed by diffusion of unsaturated lipids from the compost into the porous polymer which then leads to degradation by auto-oxidation.

Recent interest in starch as a filler in polymer industries is due to its high elastic modulus which is known to be at least twice that of low density polyethylene (LDPE), the potential in the elimination of blocking and static build-up and its biodegradable properties. The world's starch industry derives mainly from maize, wheat, potatoes, tapioca and rice to meet the needs of the food, paper, textile industries as well as many other miscellaneous uses. In the polymer industry, starch has long been used as a dusting powder to enable tacky materials to be handled much more easily. It has also been used as a transient filler in the manufacture of porous polymers as well as for battery separators. Recently, starch began to receive more serious attention for use in the polymer industry as a result of the use of chemically modified starches as reinforcing fillers for rubbers or as components of film forming compounds for cast films. It was first tried at the United States Department for Agriculture and commercially the process was not found to be attractive. However, based on the dominance of starch/polymer interface in determining the properties of starch/polymer composites, the idea of using starch grains directly as straight fillers for thermoplastics has opened up new interest in the area. The first commercial venture involving polymer and whole starch grains as fillers was as starch extended LDPE blown film for carrier bags.

Coco-yam (Dioscorea alata) and water-yam (Xanthesoma sagittifolium) grown in west tropical Africa and some parts of Asia are among the oldest food crops in these regions. In Nigeria for instance, they are used as food supplements in the months of March to June (cropping season). Diversified use such as gainful use of the starch from these crops in the polymer industry will not only encourage local farmers but also help in maintaining some balance in the world's starch market. These benefits will add to their anticipated role of improving some properties of the polymers into which they are incorporated. The work reported here is a preliminary work on the possible use of water-yam, coco-yam and guinea-corn (Sorghum bicolor) starches in LDPE as alternative, reinforcing a biodegradable fillers.

Experimental Procedure
The low density polyethylene (Standard Plastics, Kano, Nigeria) used as an ICI Q1388 grade of
Table 1—Some physical properties of coco-yam, water-yam, and guinea-corn starch grains.

<table>
<thead>
<tr>
<th>Property</th>
<th>Starch Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water-yam</td>
</tr>
<tr>
<td>Particle size range</td>
<td>12.5-41.8</td>
</tr>
<tr>
<td>Mean particle size</td>
<td>27.0</td>
</tr>
<tr>
<td>Refractive index (nD)</td>
<td>1.47</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Density 920 kg m⁻³ at 25°C and melt flow index 2 (105C, BSS, 2782). Coco-yam, water-yam, and guinea-corn were obtained from a local market.

Extraction of starch from water-yam and coco-yam were carried out by filtering grated mixtures of each with a cheese-cloth and a Griffin sweep net bag Silwood pattern VRF-780-T to obtain a filtrate free of fibres. Starch was collected from each filtrate after standing for 24 h and dried in an oven at 38–40°C. Guinea-corn starch was obtained by first milling grains that were previously soaked in water for three hours. The milled powder was put in water and starch was extracted following the procedure used for water and coco-yams.

Particle size of the extracted starch was determined using an Olympus laboratory microscope equipped with a graticule and an Olympus camera. Specimens prepared by adding 70% iodine solution in alcohol to a 1% starch were put on a glass slide covered with a glass cover-slip and viewed under the microscope. A 40X objective lens and a 10X eye-piece were employed. The size of the starch grains was recorded with the help of a microscope graticule. Densities and refractive indices of the starch were obtained using standard procedures.

LDPE supplied as granule were further chipped and mixed with each of the three starches (5, 7.5, 10, 12.5, 15, 17.5 and 20 wt %) using silicone oil as a processing aid. Dumb-bell shaped composites were obtained using 250 m thick aluminium sheet moulds filled with LDPE/starch mixture. The composites were made by compression moulding the mixtures between two steel blocks at 160–170%. The tensile properties were measured using an Instron tensile testing machine (Model 1026) with a weighing range of 0.001 -500 kg. A gauge length of 5cm was employed for all the samples. A chart speed of 10cm min⁻¹ and cross-head speed ratio of 4:1 were used. All measurements were carried out at 70% relative humidity and 20°C. The variation of stress with strain, ultimate tensile strength and elongation at yield were determined.

A modified compost similar to that employed by Griffin⁶ and described elsewhere was simulated⁷. Starch/polymer composites respectively containing 5, 7.5, 10, 12.5, 15, 17.5 and 20 wt % of each of the starches were buried for a total period of 16 weeks in a compost. After 16 weeks, the specimens were washed, dried and examined for carbonyl content by recording their IR spectra.

Results and Discussion

Reichard⁸ has given comprehensive treatments to general starch properties and technology. Starch grains are either near spherical as in rice or ellipsoidal as in potato. The range of particle size of the starches studied is shown in Table 1 and fit into the particle size range of 3-100 μm cited in the literature for various other starches.

Sample histograms from direct microscopic reading for the three starches studied are shown in Figs 1-3. The size of these starches clearly do vary as can be seen from these figures. Generally, very little information on the mechanical properties of starch grains is published. The densities and refractive indices of the starches studied in the present work are given in Table 1.
The stress-strain curves for LDPE/starch composites obtained by a tensile deformation of duplicate samples of dumb-bell shaped specimens are shown in Figs 4-6. For coco-yam LDPE/starch composites, there is a reinforcing effect between 5-10 wt % of starch. For water-yam LDPE/starch composites, there is a reinforcing effect up to 15 wt % of starch. These are significant results because up to 10 wt % of coco-yam starch and 15 wt % of water-yam starch can respectively be added to LDPE (with a reduction by the same amount in virgin polymer) without impairing the properties of the material. The strain at yield, modulus and ultimate tensile stress of the composite specimens compared to weight % starch in the specimen are shown in Figs 7-9. Fig. 7 shows that water-yam starch down-grades the yield strength of LDPE at 5 wt % of starch composition and that there is only a marginal improvement between 5-10 wt % of starch composition. The figure also shows that coco-yam starch down-grades the yield strength of LDPE at all coco-yam starch compositions. This is particularly not surprising judging from the high reinforcing characteristic of this starch at about 5 wt % starch composition. In Fig. 8, it is seen that all the three starches up-grade the modulus of LDPE in the range 5-20 wt % starch composition. The modulus of the composites is positively synergistic for coco-yam and guinea-corn starches at 5 wt % and at 10 wt % for water-yam starch. Guinea-corn starch as can be seen from Fig. 7 showed no significant effect on the yield strength of its composites with LDPE. Guinea-corn and coco-yam increased the ultimate stresses of their composites with LDPE between 0-5 wt % starch while water-yam increased the ultimate stress of LDPE between 0-10 wt % of starch.

The changes in the densities of the composites with compositing time are shown in Fig. 10 for LDPE/coco-yam starch composites and Fig. 11 for LDPE/water-yam starch composites. There is an increase in density with compositing time in each case at both 5 and 10 wt % of starch compositions which reaches a maximum after 14 weeks in the compost in the 10 wt % of the composite. 10 wt % of water-yam starch composition enhances both mechanical and soil degradation properties. This is a significant advantage judging by the concern being shown on the environmental problems posed...
OGBOBE et al.: COCO-YAM AND WATER-YAM STARCHES

Fig. 5—Stress-strain curve of water yam starch/LDPE composite.

Fig. 6—Stress-strain curve of guinea corn starch/LDPE composite.

Fig. 7—Strain at yield as a function of % starch composition. 
〇 coca-yam, ◇ water yam, △ guinea corn.

Fig. 8—Modulus as a function of starch composition: □ water yam, ○ coco yam, △ Guinea corn.

Fig. 9—Ultimate stress as a function of % starch composition. 
□ water yam, ○ coco yam, △ Guinea corn.

Fig. 10—Density of LDPE / X. Sagittifolium starch composite after exposure in a warm compost for 16 weeks. 
〇 LDPE/10%: X. Sagittifolium starch composite 
△ LDPE/5%: X. Sagittifolium starch composite.
by polyolefin films disposal. Figs. 12 and 13 show the IR recordings of the LDPE starch composites after 16 weeks in the compost. It is easily seen that the spectra are considerably modified from the usual LDPE IR spectrum. Three peaks (at 1710 cm\(^{-1}\), 1600 cm\(^{-1}\), and 1000 cm\(^{-1}\)) not usually associated with the polyethylene spectrum are clearly discernible, one of which at 1710 cm\(^{-1}\) is associated with the carbonyl group. This observation coupled with the increase in density with composting time indicate a break down in the structure\(^9\) of LDPE. The mechanism through which this happened is not clear but it is thought that this happened through an initial break down of the starch molecules by micro-organisms in the soil. This gives rise to a porous material which then easily allowed access of unsaturated lipids from the compost that leads to degradation by auto-oxidation.

**Conclusions**

It has been shown that coco-yam and water-yam starches increase both elastic modulus and ultimate tensile strength of LDPE between 5-10 wt \% of starch compositions. Densities of the composites increase with time in a composting environment. IR studies also showed presence of carbonyl content over time in a compost indicating that the starches can be used as biodegradable fillers in polyolefins. This is of significant technological importance as polyolefins disposal have posed serious environmental problems. Coco-yam and water-yam starches have therefore been shown to be dual purpose fillers for LDPE plastic.

**References**