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Performance of UV weathered HDPE composites containing hull fiber from DDGS and corn grain

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ABSTRACT

The availability of distiller's dried grain with solubles (DDGS), the main co-product of corn ethanol production, exceeds its demand as feedstuff. A physical separation process named elusieve can separate the hull fiber from DDGS or corn flour to obtain DDGS with enhanced protein and oil content, or corn flour with higher starch content. This study was performed to investigate the potential of using the hull fiber separated with elusieve process on DDGS or corn flour as fillers in high density polyethylene (HDPE) composites at the commercial scale. Additionally, the degradation effects of UV accelerated weathering on this material were investigated. Commercial scale composite samples were made with six combinations of oak fiber, corn hull fiber and DDGS fiber, with the fiber loading maintained at 50%, and then the samples were subjected to UV accelerated weathering for 2000 h. The unexposed DDGS samples showed better resistance to moisture absorption (less than 5%) than the corn filler samples (18%). The specific gravity for all the filler composites was more than one for both unexposed and UV weathered composites. The DDGS fiber also showed higher flexural properties in oak25/DDGS25 than other filler composites. For all samples, the accelerated weathering resulted in a lightening during the first 1000 h of exposure, followed by a darkening at 2000 h of UV exposure. Overall, UV weathering resulted in a chain scission of the HDPE polymer increasing the crystallinity of the polymer in the weathered filler composites.

1. Introduction

Over the last few decades,natural fiber polymer composites have gained markets in building, landscaping and automobile applications because of their durability, low density, easy processing, high specific strength and stiffness, all at a low cost (Faruk et al., 2014; Pickering et al., 2016). These composites are generally considered for non-structural components for indoor applications as well as outdoor products such as fencing, decking, and pavements (Soccalingame et al., 2016; Stark et al., 2004). In addition, agricultural residues and cellulosic byproduct streams have been investigated as alternate fiber fillers in polymer composites (Georgopoulos et al., 2005; Nyambo et al., 2010). However, there is very limited research on the long-term performance of these polymer composites with agricultural byproduct as fillers under weathering agents such as UV light and moisture (Bajwa et al., 2015; Rahman et al., 2011).

The external factors such as UV light, heat, moisture, and humidity together affect the integrity of the fiber-matrix structures in a composite causing photodegradation. The weathering of natural fibers results in the degradation of lignin into water soluble products such as carboxylic acids, quinone, and hydroperoxy radicals (Li and Ragaukas, 2000). The polyolefins degrade due to the presence of chromophores such as catalyst residues, carbonyl groups, hydroperoxide group, and double bonds formed during the polymer manufacturing (Stark and Mueller, 2008). The degradation by carbonyl groups cause the most noticeable photodegradation through either of two reactions called as Norrish I or Norrish II reactions (Jabarin and Lofgren, 1994). These two reactions have unique mechanisms: Norrish I reaction generates free radicals which ultimately results into either cross linking between chains or chain scission whereas Norrish II leads to the formation of carbonyl and terminal vinyl groups with chain scission (Jabarin and Lofgren, 1994).

Distiller's dried grains with solubles (DDGS) is the main co-product of corn ethanol from the dry grind process. It is the unfermented portion of the corn grain remaining in the concentrated form after the starch is utilized. The expansion of corn ethanol industries in the US resulted in the dramatic increase in the production of DDGS from 9 million tons in 2005 to 40 million tons in 2015 (Dinneen, 2016). Currently, DDGS is mainly used as a feed supplement for livestock and

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poultry, as only low levels of DDGS are acceptable as a feed supplement for non-ruminants because of its high fiber content (Noll et al., 2001). A physical separation process named elusieve can separate hull fiber from both corn grain flour and DDGS to enhance the feed value by increasing the protein and oil content (Srinivasan and Singh, 2008; Srinivasan et al., 2009). The DDGS with higher protein and oil content attracts $5–20 more per ton because of the added nutritional value compared to the unprocessed DDGS containing hull fiber (Belyea et al., 2004). The benefits of DDGS without the hull fiber include increased weight gain in birds and a larger portion of the feed can be supplemented by elusieved DDGS (Kim et al., 2007; Martinez-Amezuca et al., 2007). The hull fibers extracted from DDGS and corn grain have shown good potential as a filler in polymer composites (Julson et al., 2004). However, the long-term performance of composite containing DDGS fiber filler under UV moisture weathering has not been evaluated.

This study investigated the impact of accelerated UV weathering on the physico-mechanical, surface color, and surface degradation properties of the HDPE composites containing hull fiber from DDGS and corn grain.

2. Materials and methods

2.1. Materials

An experiment was conducted at commercial scale to compare hull fibers from DDGS, corn grain and oak wood fiber as full or partial filler in HDPE composites The DDGS was obtained from Midwest Ag Energy Group (ND, USA), and elusieved at Mississippi State University (MS, USA); the DDGS fiber had 46.9% neutral detergent fiber (NDF), 21.1% protein, 3.3% starch, and 8.1% fat by dry weight. The elusieved corn grain fiber was also obtained from Mississippi State University (MS, USA); the corn grain fiber had 49.2% NDF, 7.9% protein, 31.9% starch, and 3.1% fat by dry weight. The oak wood fiber was obtained from Southern Wood Services LLC (GA, USA); the oak wood fiber consisted of cellulose (45.7%), hemicellulose (24.8%), and lignin (27.6%) by dry weight. The HDPE polymer (Petrothene LB 010000 (melt flow index: 0.50 g/10 min, density 0.953 g/cm^3, tensile yield strength 27.3 MPa, and flexural modulus of elasticity 1275 MPa) was obtained from Equistar Chemicals (TX, USA). Zinc stearate (ZnSt) was used in some formulations to act as a lubricant during extrusion, and talc was used as an inorganic filler.

2.2. Composite manufacturing

The fibers from DDGS, corn, and oak were ground in a Wiley mill (Model 4, Thomas Scientific, NJ, USA) with a 1 mm sieve, and subsequently sieved through a 30–60 mesh (0.250 mm-0.595 mm) with a Ro-tap shaker (W.S. Tyler® Ro-Tap® 8in Sieve Shaker, 230 V/50 Hz, USA). The sized fibers were then oven dried at 105 °C until the moisture content was less than 1%. Prior to extrusion, all the components were mixed in the exact proportions specified for each formulation (Table 1). The mixture was then compounded and extruded with a counter rotating twin screw (L/D ratio of 28) Cincinnati extruder (Milacron, OH, USA) with five heating zone temperatures set between 160 and 180 °C. The sample material was extruded into bars with a rectangular profile of 35 mm wide and 10 mm thick.

Table 1
Formulation of the HDPE composite samples containing six different combinations of fiber fillers. All weight (wt) percentages are computed on dry basis.

Sample Name	Fiber Loading, % wt	Polymer % wt	Lubricant % wt	Talc % wt
Oak50	50	42	4	4
Corn50	50	42	4	4
DDGS50	50	46	–	4
Oak25/Corn25	25/25[a]	42	4	4
Oak25/DDGS25	25/25[a]	46	–	4
Corn25/DDGS25	25/25[a]	46	–	4

[a] Denotes 25% by weight of each fiber in the mixed fiber composite.

2.3. UV weathering

To simulate natural weathering conditions, the composite samples were placed in a QUV accelerated weathering tester (QUV/Spray, Q-Lab Co., USA) for a duration of 2000 h according to ASTM Standard G154 (2016). The weathering cycle consisted of 8 h of UV exposure (UV-A lamps) at 60 °C, followed by a 4 h condensation cycle without UV lights at 50 °C. The UV irradiance used was 0.89 W/m^2 at 340 nm wavelength. The surface color of the samples was recorded three times: prior to UV weathering, at 1000 h of weathering and at 2000 h. The lightness (L) and chromaticity coordinates (a, b) were recorded with an X-rite color checker (X-Rite, Grand rapids, MI, USA). The weathered samples were conditioned at room condition for 30 days before performing the following physico-mechanical and characterization techniques on composite materials.

2.4. Composite material testing

Composite samples before and after weathering were tested for water absorption, specific gravity, flexural, compression, and impact strength. Five samples were tested from each formulation before and after weathering to avoid potential biases due to homogeneity of material and testing conditions.

2.4.1. Water absorption

The water absorption of both unexposed and weathered composite samples was recorded according to the ASTM Standard D570-98 (2010). Sample coupons in the size of 75 mm × 35 mm × 10 mm were cut, and dried at 50 °C for 24 h before immersing them in a water bath set at 23 °C. The weight gain by each sample was recorded every 24 h for 18 days for the unexposed samples and every 24 h for 15 days for the weathered samples. The reported results are the average of five samples.

2.4.2. Specific gravity

The specific gravity of the composite material was tested in accordance with Method A of ASTM Standard D792 (2013). The test was performed to measure the specific gravity as the ratio of the mass of a given volume of a sample measured at 23 °C to the same volume of tap water at the same temperature withan analytical balance, a wire, a wooden block, and a small bucket as immersion vessel. The mass of the samples was first recorded in air before immersing it in the water with the wire cage to measure the weight loss of the sample in water. Five samples were used for the test.

2.4.3. Flexural properties

The flexural properties of both unexposed and weathered samples were tested according to the ASTM Standard D7264 (2015), a three-point bending test method for polymer composites. The weathered samples were first dried in an oven at 105 °C for 24 h to ensure the moisture content was same as those of the unexposed samples. The UV exposed surface of the weathered samples was used on the compression side for the test the test samples had a span to depth ratio of 20:1. The crosshead motion rate was calculated based on the depth of the samples used in the test and a universal testing machine (Test Resources Inc, MN, USA) was used for testing the materials. Five samples were tested for each formulation.

2.4.4. Compression properties

The compression properties of the unexposed and UV weathered composite samples were measured in accordance with ASTM Standard