

# Mechanical and Thermal Properties of High Density Polyethylene – Dried Distillers Grains with Solubles Composites

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Dried Distillers Grain with Solubles (DDGS) was evaluated as a bio-based fiber reinforcement. Composites of high density polyethylene (HDPE) composed of 25% by weight DDGS and either 0% or 5% by weight of maleated polyethylene (MAPE) were produced by twin screw compounding and injection molding. An improved DDGS bio-filler was produced by solvent treating DDGS (STDDGS). Injection-molded test specimens were evaluated for their tensile, flexural, impact, and thermal properties. Composite blends composed of STDDGS were superior to their DDSG counterparts. Composites made with STDDGS and MAPE had significantly improved tensile and flexural properties compared to neat HDPE. Impact strength of all composites was similar and lower than neat HDPE. Soaking of tensile bars of the various PE-DDGS blends in distilled water for 28 days altered their physical, color, and mechanical properties. Differential scanning calorimetry and thermogravimetric analysis were conducted on neat HDPE and DDGS composites to evaluate their thermal properties.

**Keywords:** Particle size; Adsorption tests; Mechanical properties; Flexural properties; Colorimetry; Differential scanning calorimetry; Thermal properties; Injection molding

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## INTRODUCTION

Resins used in the plastics industry consist primarily of petroleum-based thermoplastics and thermosets. Examples of thermoplastics include polyethylene (PE), polypropylene (PP), and polystyrene. Common thermosets include phenolic and unsaturated polyesters. Increasingly, the blending of eco-friendly, biodegradable fillers with thermoplastics can be performed to obtain unique composites (Carlborn and Matuana 2006; Lei *et al.* 2007; Clemons 2010). Bio-based lignocellulosic flour (LF) filler materials include wood flour (WF), natural fibers, dried distillers grain solubles (DDGS), and presscakes. Bio-based fillers have certain advantages over inorganic fillers (*e.g.*, clay, metals, glass, *etc.*) because they are renewable, relatively abundant, inexpensive, less abrasive to processing equipment, and are more environmental-friendly upon disposal

(Kalia *et al.* 2009; Onwulata 2009; Zabihzadeh 2010a; 2010b). WF is the most commonly used bio-filler, and it is used in the preparation of natural fiber reinforced decking and construction wood plastic composite (WPC) products (Febrianto *et al.* 2006; Clemons 2010). Most WPCs utilize PE or PP mixed with up to 50% of WF (w/w), depending on the desired mechanical and physical properties and industrial acceptance (Febrianto *et al.* 2006; Clemons 2010). Addition of fillers in composites sustainably reduces the cost of the final plastic product (Clemons 2010). PE and PP sell for  $\approx \$1.85$  to  $2.27/\text{kg}$  ( $\$0.91$  to  $1.12/\text{lb}$ ) and  $\approx \$2.23$  to  $2.47/\text{kg}$  ( $\$1.10$  to  $1.22/\text{lb}$ ), respectively (Anon 2012). Commercial hardwood flour blends are obtained from lumber milling byproducts (sawdust and shavings), composed of various tree species (maple, birch, ash) and sell for  $\approx \$0.04$  to  $0.10/\text{kg}$  ( $\$0.08$  to  $0.22/\text{lb}$ ) (Clemons 2010).

Several investigators have studied the uses of various LF fillers with various thermoplastic resins to obtain unique lignocellulosic plastic composites (LPC) (Hayes 1997; Lei *et al.* 2007; Kalia *et al.*, 2009; Li and Sun 2011; Rimdusit *et al.* 2011; Sutivisedsak *et al.* 2012). Each of these composites has its unique features; some advantages are low cost and environmental acceptance, while some disadvantages are a reduction in mechanical properties when compared to the neat PE. Nevertheless, these LF fillers potentially cost only a few cents a pound, making them very economically attractive to exploit (Onwulata *et al.* 2009). One common LF is DDGS that is generated during the distillation of alcohol to obtain bio-based ethanol fuel (Shurson 2012; Wisner 2010). Approximately 3.2 to 3.5 million metric tons of DDGSs are produced annually in North America, and this figure is expected to double in the next few years (Shurson 2012; Wisner 2010). Currently, DDGS is used almost entirely as an animal feed, although other uses of have been sought (Cheesbrough *et al.* 2008; Onwulata *et al.* 2009). DDGS sells for about  $\$0.06$  to  $0.10/\text{kg}$  ( $\$0.03$  to  $0.05/\text{lb}$ ), which makes it an attractive bio-filler to blend with thermoplastic resins.

The objective of this study is to perform an assessment of the mechanical and thermal properties of thermoplastic composites made with DDGS. Coupling agents have been used for wood fiber PE composites (Carlborn and Matuana 2006; Lei *et al.* 2007; Clemons 2010), so the use of a maleated PE was employed as part of the scope of the project. Further, because oils in DDGS may adversely affect the performance of DDGS composites due to their lubricating effect, a solvent extracted DDGS material was tested to assess the benefit of oil extraction. Finally, because DDGS is a bio-filler it is subject to degradation by water, water immersion tests were administered on these biocomposites to evaluate their environmental durability.

## EXPERIMENTAL

### Materials

The high-density polyethylene (HDPE) employed as the matrix material was Petrothene LS 5300-00 (Equistar Chemicals LP, Houston, TX). It had a melt-flow index of 40 g/10 min, a density of 0.950 g/cm<sup>3</sup>, and a melting point of 129 °C. The binding agent was a polyethylene-graft-maleic anhydride, or maleated polyethylene (MAPE), supplied by Equistar Chemicals LP (product code NE542013). The MAPE had a melting point of

104 to 138 °C with approximately 1% maleic anhydride by weight grafted on the polyethylene.

DDGS (corn-based meal) was obtained as the commercial animal feed pellet product (Archers Daniel Midland Co., Decatur, IL). DDGS were milled with a Thomas-Wiley mill grinder, Model 4 (Thomas Scientific, Swedesboro, NJ). DDGS particles exited through a 2 mm diameter stainless screen and were collected into a 1.81-L Mason jar. To examine what affect the oils in the DDGS may have on the mechanical properties of the composites, DDGS were extracted with hexane (to remove oils), then with dichloromethane (to remove polar extractables), employing a Soxhlet extractor. Throughout this paper, DDGS refers to the original DDGS, and STDDGS refers to the solvent treated DDGS. Particles were then reground and collected using a 1 mm screen and then sized through a Ro-Tap™ Shaker (Model RX-29, Tyler, Mentor OH) employing 203 mm diameter stainless steel screens. Sieve/Screens employed were #10, #30, and #40 US Standards (Newark Wire Cloth Company, Clifton, NJ). The DDGS mixtures consisted of particles obtained from the #40 mesh and finer ( $\leq$ #40) sieves.

### **Preparations**

To investigate the influence of the maleic anhydride coupling agent on the physical properties of the HDPE-DDGS blends, the following mixtures of HDPE-DDGS-MAPE by weight percent (%) were compounded, and their codes are summarized in Table 1.

**Table 1.** Weight Percentages in Test Formulations

Composition	DDGS	STDDGS	MAPE	HDPE
HDPE	--	--	--	100%
HDPE-MAPE	--	--	5%	95%
HDPE-DDGS	25%	--	--	75%
HDPE-DDGS-MAPE	25%	--	5%	70%
HDPE-STDDGS	--	25%	--	75%
HDPE-STDDGS-MAPE	--	25%	5%	70%

Composite blends were extruded with a Micro-18 30/1 L/D co-rotating twin-screw extruder (American Leistritz Extruder, Branchburg, NJ). The screw configuration was:

30/9020/30 15/60 10/30 KB30R/20 10/20 KB60L/20 15/30 10/30  
KB60L/20 20/60 KB60R/20 20/20 KB60L/20 15/30 10/30

where the first number is the pitch and the second the length in mm, except for the kneading blocks (KB), where the first number indicates the angle between blocks. The barrel had six different zones, each 90 mm long, which were controlled at the following temperatures (°C): 32, 60, 90, 125, 135, and 144, respectively. The cord die temperature was set at 120 °C. Premixed lignocellulosic flour (either DDGS or STDDGS) with MAPE fractions were fed into zone 1 at 4 to 4.8 g/min using a volumetric twin-screw gravimetric feeder (Accurate Model 106, Accurate, Whitewater, WI). At the same time, HDPE was fed with a second feeder (Accurate Model 106) in the same zone at the rate of 11.2 to 12 g/min. Screw speed was set at 100 rpm. Extruded strands were processed into pellets with Killion Strand pelletizer Model 4 (Killion, Cedar Grove, NJ). The pelletizer

was equipped with a 20 blade helical rotor of 10.16 cm diameter  $\times$  10.16 cm wide and driven by a speed-controlled 2 hp DC motor.

Pellets were fed into a reciprocating screw injection molder (Engel ES 30, 30-ton hydraulic clamp, Engel Machinery Inc., York, PA.). The set point temperatures ( $^{\circ}$ C) for the four zone injection molding barrel were feed: 160; compression: 166; metering: 177, and nozzle: 191. The mold temperature was 37  $^{\circ}$ C. An ASTM test specimen mold was used that included cavities for a ASTM D790 flexural tensile bar (12.7 mm W  $\times$  127 mm L  $\times$  3.2 mm thickness), a ASTM D638 Type I tensile bar (19 mm W grip area  $\times$  12.7 mm neck  $\times$  165 mm L  $\times$  3.2 mm thickness), and an ASTM D638 Type V tensile bar (9.53 mm W grip area  $\times$  3.18 mm neck  $\times$  63.5 mm L  $\times$  1.5 mm thickness). The Type I bars were used for the tensile strength property tests. The flexural bars were used to evaluate flexural properties and also used to make impact strength measurements. The Type V bars were used to evaluate changes due to prolonged exposure to water: weight change, color change, and changes in tensile mechanical properties of the composites.

### **Scanning Electron Microscopy (SEM)**

Fractured surfaces were created by freeze fracturing with liquid nitrogen. Materials were viewed under a JOEL 6400 V scanning electron microscope (Peabody, MA). Sample fragments were mounted with an adhesive to specimen stubs and the edge was painted with colloidal silver adhesive and sputter coated with a thin layer of gold. At this stage, tissues were mounted on aluminum SEM stubs with double stick tape (preferably conductive carbon). Stubs with mounted tissues are placed in sputter coater machine (SPI Supplies, West Chester, PA) to coat with gold. Fractured surfaces of HDPE, HDPE-MAPE blend, and DDGS composites samples were examined and digital images were collected at magnifications of 100, 200, 1000, and 2000 X.

### **Mechanical Property Measurements**

Injection-molded specimens, ASTM D638 Type I tensile bars, were tested for tensile modulus and strength using a universal testing machine (UTM), Instron Model 1122 (Instron Corporation, Norwood, MA). The speed of testing was 5 mm/min. Specimen thickness was measured with a digital micrometer, Model 49-63 (Testing Machines Inc., Amityville, NY). Initial samples (dry) were conditioned for approximately 240 hours at standard room temperature and humidity (23  $^{\circ}$ C and 50% RH) prior to any test evaluations.

Three-point flexural tests were carried out according to the ASTM-D790 specification on the Instron UTM Model 1122 device. The flexural tests were carried out using Procedure B with a crosshead rate of 13.5 mm/min. The flexural modulus of rupture (flexural strength) (MOR) and flexural modulus of elasticity (MOE) were calculated using the following formulas,

$$\text{MOR} = 3PL/2bd^2 \quad (1)$$

$$\text{MOE} = L^3m/4bd^3 \quad (2)$$

where  $P$  is the maximum applied load,  $L$  is the length of support span,  $m$  is the slope of the tangent, and  $b$  and  $d$  are the width and thickness of the specimen bars, respectively.

Five specimens of each formulation were tested. The average values and standard errors were reported.

Notched impact tests were conducted with an IZOD impact tester, Model Resil 5.5, P/N 6844.000 (CEAST, Pianezza, Italy), conforming to ASTM D256-84. Specimen bars were obtained by cutting the flexural specimens in half to 12.7 mm × 64 mm × 3.2 mm (width × length × thickness) and then notching them.

### Water Absorption

The Type V tensile bars injection molded for each composite were dried in an oven for 24 hours at  $100 \pm 2^\circ\text{C}$  and weighed. The thickness of each Type V tensile bar was measured at the gate, neck, and end portions using an electronic micrometer (Testing Machines Inc.). Tests were conducted in an incubator at  $25 \pm 2^\circ\text{C}$  under a photosynthetic photon flux density of  $180 \mu\text{mol.m}^2.\text{s}^{-1}$  using a photoperiod of 12 h light/12 h dark. Tensile bars were placed in distilled water at room temperature for 672 hours. At predetermined time intervals the specimens were removed from the distilled water, the surface water was blotted off with paper towels, and their wet mass and thickness were determined. Water absorption, measured as moisture content (MC) percentage, was computed using the following formula

$$\text{MC (\%)} = (m_t - m_o)/m_o \times 100 \quad (3)$$

where  $m_o$  denotes the oven-dried weight and  $m_t$  denotes the weight after soak time  $t$ .

### Spectrophotometric Evaluations

Tensile bar color values were measured using the Commission Internationale de l'Eclairage (CIE) Lab parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ) with a spectrophoto-colorimeter Chroma Meter CR-400 (Konica Minolta, Ramsey, NJ). The scanner was calibrated with a white tile. In this coordinate system,  $L^*$  value is a measure of lightness (brightness), ranging from 0 (black) to 100 (white);  $a^*$  value is a measure of redness, ranging from -100 (green) to +100 (red);  $b^*$  value is a measure of yellowness, ranging from -100 (blue) to +100 (yellow);  $C^*_{ab}$  value is a measure of Chromaticity (quality of color); and  $H^*_{ab}$  is a measure of Hue angle (the real color).  $C^*_{ab}$  and  $H^*_{ab}$  values are given as  $C^*_{ab} = \sqrt{(a^*)^2 + (b^*)^2}$  and  $H^*_{ab} = \arctan(b^*/a^*)$ , respectively.

### Thermal Properties

Differential scanning calorimetry (DSC) of molded specimens was conducted with an Auto DSC-7 calorimeter with a TAC/DX controller (TA Instruments, New Castle, DE). Samples of 5 to 7 mg were weighed and sealed hermetically in aluminum DSC pans. First, the calorimeter was programmed to increase the temperature from 0 to  $180^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  and kept isothermal for 3 min. Then, the samples were cooled to  $-50^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . Lastly, the samples were heated to  $180^\circ\text{C}$  from  $-50$  to  $180^\circ\text{C}$  at the same rate. Data from the second heating cycle were used to determine the melting temperature ( $T_m$ ) and enthalpy of melting ( $\Delta H_m$ ) for PE-PW blended samples. The heat flow rate corresponding to the crystallization of HDPE in composites was corrected for the content of the WF and MAPE. The value of crystallization heat was also corrected for the crystallization heat of MAPE. The crystallinity level ( $\chi_c$ ) of the HDPE matrix was evaluated from the following relationship (Lei *et al.* 2007),

$$\chi_c = \Delta H_{\text{exp}} / \Delta H \times 100 / W_f \quad (4)$$

where  $\Delta H_{\text{exp}}$  is the experimental heat of fusion ( $\Delta H_m$ ) or crystallization determined by DSC,  $\Delta H$  is the assumed heat of fusion or crystallization of fully crystalline HDPE (293 J/g), and  $W_f$  is the weight fraction of HDPE in the composites.

Thermogravimetric analysis (TGA) was performed to determine the thermal characteristics of the composites. TGA was conducted using a Model 2050 TGA (TA Instruments) under nitrogen at a scan rate of 10 °C/min from room temperature to 800 °C. A sample of  $\approx 7.5$  mg was used for each run. Data was analyzed using the TA Advantage Specialty Library software (TA Instruments). The derivative TGA (wt %/min) of each sample was obtained from the software.

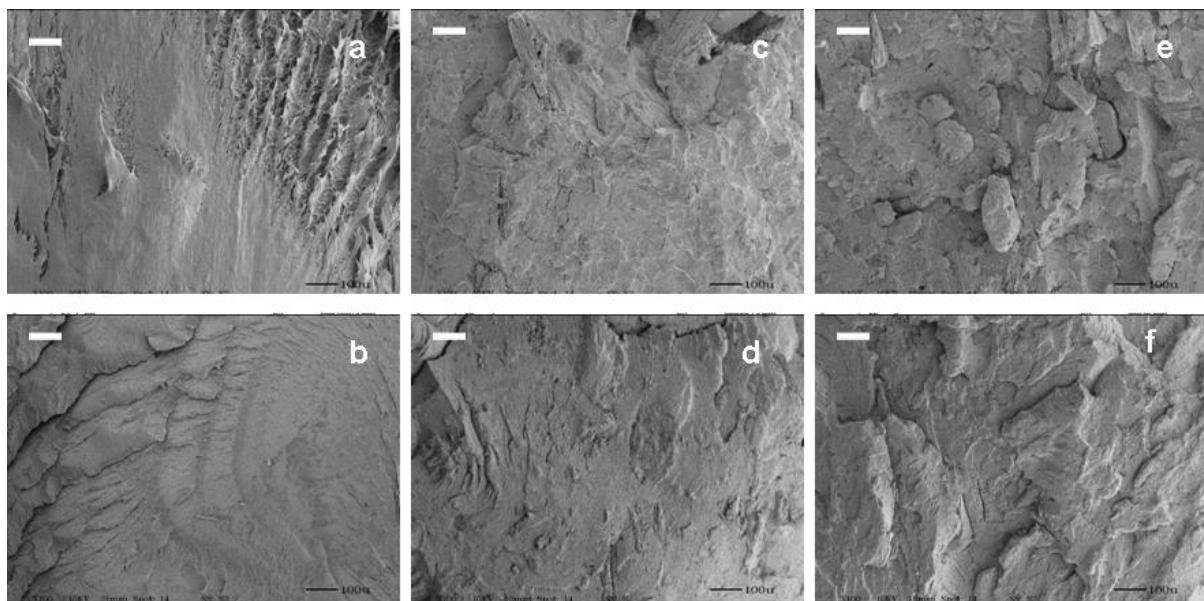
### Statistical Analysis

The experimental data obtained were analyzed statistically by analysis of variance for statistical significance and multiple comparisons of means were accomplished with Duncan's Multiple Range Test ( $p \leq 0.05$ ).

## RESULTS AND DISCUSSION

### SEM Surface Examination

Examination of DDGS composites under SEM magnifications revealed the occurrence of a heterogeneous matrix composed of areas of predominately HDPE and areas of DDGS particles embedded in the HDPE. DDGS particles were not uniformly spread throughout the HDPE matrix but could occur randomly or even in clumps, as shown in Fig. 1.



**Fig. 1.** Scanning electron microscope micrographs of fractured surfaces of DDGS composites. Neat HDPE (a), HDPE-MAPE blend (b), HDPE-DDGS (c), HDPE-DDGS-MAPE (d), HDPE-ST-DDGS (e), and HDPE-STDDGS-MAPE (f). Bar = 100  $\mu$ m

In contrast, the neat HDPE or HDPE-MAPE blend exhibited a smoother appearance. The fracturing of the composite surfaces resulted in no obvious pattern to suggest that DDGS particles were the cause of the fracture. However, more DDGS clumps were observed on the fractured surfaces of the DDGS composites without MAPE than in the blend of DDGS composites containing MAPE. This observation suggests that MAPE was responsible for greater adherence between the DDGS to the HDPE than composites without MAPE. However, it should be emphasized that regardless of the composite formulation, some portions of the specimens were relatively smooth, which typified the presence of fewer aggregates of the DDGS components while other portions were rougher and contained more of the DDGS aggregates. Further, when large clumps of DDGS particle clumps occurred, prominent fissures were generated between the DDGS and HDPE (Fig. 1). Cheesbrough *et al.* (2008) similarly noted this clumping and fracturing tendency in SEM micrographs of DDGS bound together with adhesive glues.

### Mechanical Properties

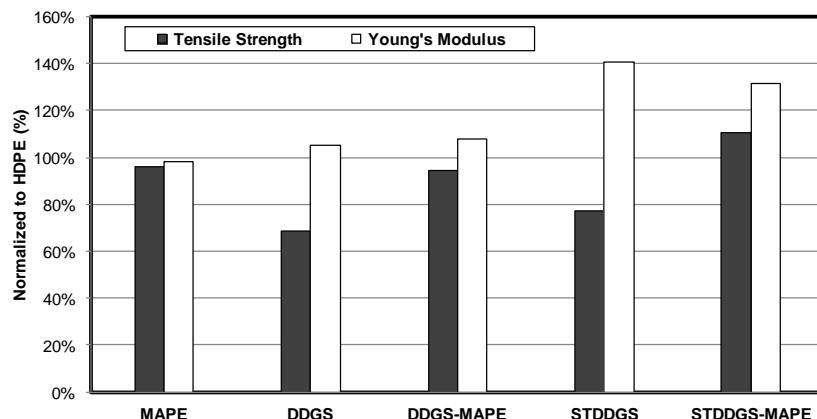
Every bio-filler is composed of unique anatomical, chemical, and physical attributes that greatly influence its performance to successfully integrate with thermoplastic resins. For example, although wood flour particles are commonly employed as bio-filler to produce WPC, the species source is a major factor toward usable composites. Pine and Red oak WF, for example, contain high concentrations of phenolic compounds, which may cause WPC to exhibit undesirable oxidization and staining when wet (Clemons 2010). DDGS contains high levels of crude protein ( $\approx 26\%$ ), water ( $\approx 5.5\%$ ), hexane extracted oils ( $\approx 14\%$ ), and dichloromethane extractables ( $\approx 3\%$ ). The solvent extraction treatments removed oils and polar extractables to obtain a modified DDGS composite (STDDGS) in order to obtain a potentially ‘improved DDGS composite’. The importance of removal of extractables to obtain superior filler has been previously documented (Clemons and Stark 2009; Kalia *et al.* 2009).

The mechanical properties of tensile strength (TS), Young’s modulus (YM), and elongation strain at breaking (ELO) of the HDPE-DDGS composites containing various DDGS formulations are shown in Table 2. The average for the five test specimens and their standard error is given for each property. Figure 2 graphically summarizes the data in Table 2 by normalizing the outcomes to the HDPE control material. For example, the TS of HDPE-MAPE is 96% of the neat HDPE thus the bar graph of the normalized TS for HDPE-MAPE is 96%. This rendering clearly illustrates the effect of additives.

**Table 2.** Mechanical Properties of DDGS Composites

Composition	TS (MPa)*	YM (Mpa)	ELO (%)
HDPE	$21.5 \pm 0.1a$	$339 \pm 10a$	$105 \pm 1a$
HDPE-MAPE	$20.6 \pm 0.2b$	$333 \pm 15a$	$103 \pm 13a$
HDPE-DDGS	$14.7 \pm 0.0c$	$356 \pm 9a$	$17.9 \pm 0.5b$
HDPE-DDGS-MAPE	$20.3 \pm 0.3b$	$366 \pm 6a$	$16.2 \pm 0.7b$
HDPE-STDDGS	$16.6 \pm 0.1d$	$478 \pm 68c$	$15.1 \pm 0.3b$
HDPE-STDDGS-MAPE	$23.8 \pm 0.2e$	$446 \pm 4d$	$14.5 \pm 0.4b$

\*Treatment values with different letters in the same column were significant ( $P \leq 0.05$ ). Means and standard errors derived from five different replicates are presented.



**Fig. 2.** Effect of additives on the Tensile Strength and Young's Modulus when compared to the control material HDPE

The YM of the STDDGS composite additive exceeded the YM of the DDGS composite regardless of whether MAPE was employed (Table 2, Fig. 2). This is likely due to the oils being removed in the STDDGS material. The oils present in the DDGS act as a plasticizer to lubricate relative molecular motion, hence lowering the modulus. Others have observed that the inclusion of WF or LF into thermoplastics such as PLA, PE, or PP generally results in a decrease in TS and ELO and an increase in YM (Febrianto *et al.* 2006; Li and Sun, 2011; Stark and Berger, 1997; Julson *et al.* 2004).

WPC are noted to be brittle (low strain) and have lower impact resistance than neat plastic products (Li and Matuana 2003). To address this situation, coupling agents are employed to improve the adhesion between the bio-based filler and plastic (Myers *et al.* 1991; Bengtsson and Oksman, 2006; Carlborn and Matuana, 2006; Li and Sun 2011; Rimdusit *et al.* 2011; Rodríguez-Llamazares *et al.* 2011). Coupling agents act as intermediates to bind hydrophobic polyolefins to hydrophilic LF materials (*e.g.*, wood or DDGS). The most common coupling agent to aid in the adherence of wood to plastic is maleated polyolefin (Carlborn and Matuana, 2006; Khalaf *et al.* 2008; Koo *et al.* 2003; Myers *et al.* 1991; Rimdusit *et al.* 2011; Rodríguez-Llamazares *et al.* 2011).

In this study, the HDPE-25% DDGS composite blends employed a maleated polyethylene, NE542013 MAPE (Equistar Chemicals LP), at a concentration of 5%. The addition of MAPE improved the TS in both variations of DDGS (Table 2 and Fig. 2). Likely the improved binding of the matrix polymer with the reinforcement material accounts for this improvement. Although the MAPE helped improve the TS, it is only in the case of the solvent treated DDGS did the addition of MAPE cause the TS to exceed the control material by a marginal amount of 11%.

The addition of DDGS additives significantly lowered the elongation to break as shown in Table 2. Apparently, the DDGS particles act as contaminants within the matrix thus interfering with the plastic flow of the polyethylene molecules.

### Flexural Behavior

The flexural strength (MOR) and modulus (MOE) of the composites and thermoplastic resins are given in Table 3. Figure 3 illustrates the effect of the additives compared to HDPE as done in Fig. 2. As with the tensile modulus, the flexural modulus greatly improved with the removal of oils. This is evident by comparing properties of

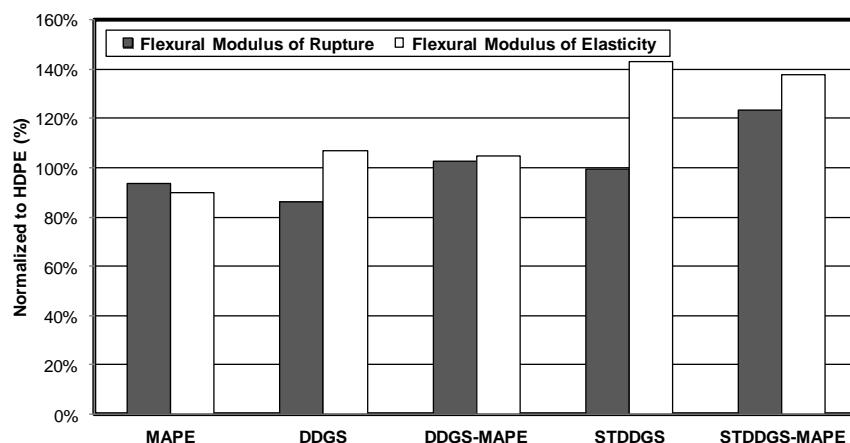
STDDGS composites to DDGS in Fig. 3. Others have shown that the flexural behavior of the composites can vary significantly with the type of filler and coupling agent employed (Myers *et al.* 1999; Clemons and Stark 2009). All composites had higher MOE values than the neat HDPE and HDPE-MAPE blends. However, the highest MOR and MOE values were obtained employing solvent treated DDGS. These results show that removal of oils and polar extractables by the solvent treatments resulted in an engineered composite with superior flexural properties compared to unextracted DDGS composites or neat HDPE. Similarly, Clemons and Stark (2009) noted that water-extracted pine- and saltcedar-WPC exhibited higher flexural values than unextracted pine- and saltcedar-WPC. Again, removal of a lubricant improves the modulus, as seen with the tensile data.

**Table 3.** Flexural and Impact Properties of HDPE and Composites

Composition	MOR (MPa)*	MOE (MPa)	Impact Energy (J/m)
HDPE	27.9 ± 0.1a	894 ± 15a	38.7 ± 0.1a
HDPE-MAPE	26.1 ± 0.1b	804 ± 8b	38.5 ± 0.5a
HDPE-DDGS	24.1 ± 0.1c	954 ± 6c	31.7 ± 1.2b
HDPE-DDGS-MAPE	28.6 ± 0.1d	937 ± 3d	28.7 ± 1.3b
HDPE-STDDGS	27.8 ± 0.1a	1280 ± 5e	30.4 ± 2.0b
HDPE-STDDGS-MAPE	34.4 ± 0.2e	1231 ± 14f	30.0 ± 1.7b

\*Treatment values with different letters in the same column were significant ( $P \leq 0.05$ ). Means and standard errors derived from five different replicates are presented.

Generally, those composites that exhibit high flexural strength (MOR) also will exhibit high flexural modulus (MOE) (Zabihzadeh, 2010a; 2010b). However, this was not the case for the DDGS composites (refer to Table 3 and Fig. 3). The flexural strength of the HDPE-STDDGS-MAPE blend was 23% higher than the neat HDPE. Without MAPE, flexural strength of the STDDGS composite was statistically identical to neat HDPE. However, the flexural modulus of elasticity (MOE) for composites made with STDDGS was greatly improved over the neat HDPE regardless of the addition of MAPE.



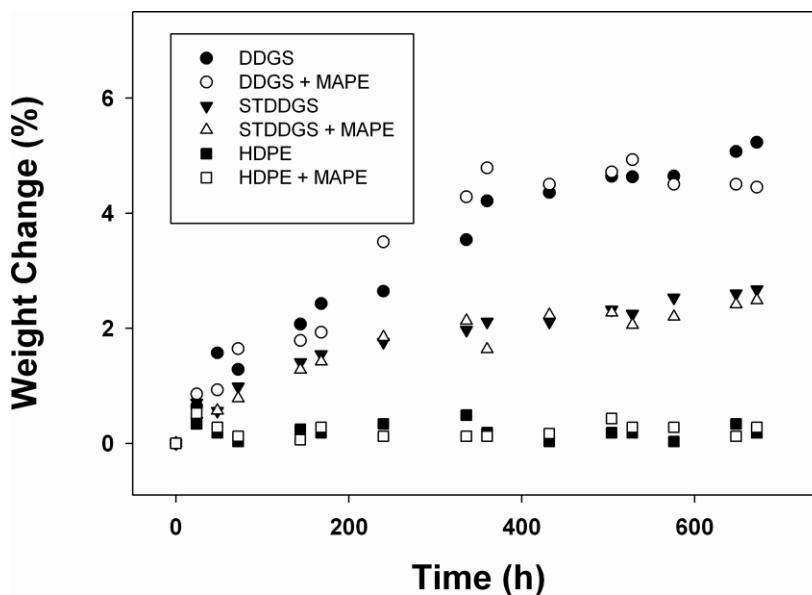
**Fig. 3.** Effect of additives on the Flexural Modulus of Rupture and Flexural Modulus of Elasticity when compared to the control material HDPE

## Impact Strength

The notched IZOD impact strengths for the various composites are listed in Table 3. The inclusion of a filler resulted in less energy required to initiate cracking, as shown in Table 3. Notched IZOD impact energy generally decreases with increasing filler content (Stark 1997). Further, the presence of MAPE made no significant difference in impact strength occurred among the DDGS composites, as can be seen in Table 3. In contrast, Myers *et al.* (1991) found that inclusion of MAPE had a negative effect on notched impact energy of pine WPC compared to specimens without MAPE.

## Water Absorption Response

Figure 4 shows the long-term water absorption plots of DDGS-based composites at room temperature, where weight change (%) (*i.e.*, water absorption) is plotted against immersion time. HDPE and HDPE-MAPE exhibited less than a 1% increase in weight after the immersion time. Both untreated DDGS treatments (DDGS and DDGS with coupling agent MAPE) exhibited higher weight changes than the solvent-treated DDGS treatments as seen in Fig. 4. For example, at the end of 672 hours the composite composed of HDPE-DDGS blends increased by 4.3% in weight, while the composite of HDPE-STDDGS-MAPE exhibited a 2.2% increase in weight ( $\approx 100\%$  less increase). The use of coupling agents, *i.e.*, MAPE, in the composite did not affect water absorption with DDGS composites. This observation contradicts others that found that inclusion of MAPE in the composite reduces water absorption when using bio-fillers of popular wood, loblolly pine wood, sisal fiber, or wheat straw (Joseph *et al.* 2002; Zabihzadeh, 2010a,b). The difference could be attributed to the chemical composition of DDGS, which contains more protein in comparison to these other fillers.



**Fig. 4.** Comparative water absorption plots for various DDGS composites over 672 hours of soaking

The response of biocomposites to water soaking is related to the bio-filler's chemical and lignocellulosic anatomical properties (Joseph *et al.* 2002; Kord 2011; Zabihzadeh 2010a; Segerholm 2012). Clearly, removal of oils and polar compounds by

the solvents resulted in a composite that was more resistant to water soaking, as evidenced by its ability to resist water absorption. Absorption of water by composites is a crucial factor in determination of the ability of biocomposite to be commercially utilized (Zabihzadeh 2010a,b).

Color is an important attribute of WPC and is associated with its commercial value (Clemons and Stark 2009; Fabiyi *et al.* 2008). Weathering causes color changes in WPC that are both undesirable and irreversible (Clemons and Stark 2009; Fabiyi *et al.* 2008). Water soaking is an important type of weathering test that is useful in determining the durable nature of a thermoplastic composite (Lopez *et al.* 2006; Clemons and Stark 2009; Zabihzadeh 2010a; Segerholm *et al.* 2012). Weathering causes PE-composites to undergo chemical reactions such as breakdown of lignins into water-soluble products, forming chromophoric functional groups such as carboxylic acids, quinones, and hydroperoxy radicals (Fabiyi *et al.* 2008).

Table 4 compares color values of the original composites to the soaked composites. All composites exhibited lightness ( $L^*$ ) following soaking. Water immersion tests with WPC show this same trend (Clemons and Stark 2009).

**Table 4.** Influence of Soaking on Color Analysis of DDGS Composites

Composition	Colors	Original <sup>*</sup>	Soaked	Change (%)
HDPE-DDGS	$L^*$	$30.1 \pm 1.8$	$33.9 \pm 0.4$	12.6
	$a^*$	$1.3 \pm 0.1$	$2.0 \pm 0.2$	59.3
	$b^*$	$3.0 \pm 0.3$	$4.7 \pm 0.2$	54.9
	$C^*_{ab}$	$3.3 \pm 0.1$	$5.1 \pm 0.2$	55.4
	$H^*_{ab}$	$1.2 \pm 0.0$	$1.2 \pm 0.0$	-0.6
HDPE-DDGS-MAPE	$L^*$	$24.3 \pm 0.8$	$31.7 \pm 0.7$	30.8
	$a^*$	$1.5 \pm 0.1$	$1.6 \pm 0.2$	10.8
	$b^*$	$2.6 \pm 0.7$	$3.6 \pm 0.2$	40.4
	$C^*_{ab}$	$3.0 \pm 0.1$	$4.0 \pm 0.1$	33.7
	$H^*_{ab}$	$1.1 \pm 0.0$	$1.2 \pm 0.0$	9.0
HDPE-STDDGS	$L^*$	$34.3 \pm 0.4$	$36.4 \pm 0.5$	6.2
	$a^*$	$2.7 \pm 0.0$	$3.2 \pm 0.0$	18.3
	$b^*$	$5.9 \pm 0.4$	$5.3 \pm 0.2$	-9.5
	$C^*_{ab}$	$6.5 \pm 0.2$	$6.2 \pm 0.1$	-4.2
	$H^*_{ab}$	$1.1 \pm 0.0$	$1.0 \pm 0.0$	-9.6
HDPE-STDDGS-MAPE	$L^*$	$28.1 \pm 1.1$	$34.1 \pm 0.8$	21.4
	$a^*$	$2.5 \pm 0.1$	$2.4 \pm 0.1$	-2.1
	$b^*$	$4.9 \pm 0.6$	$3.6 \pm 0.7$	-25.2
	$C^*_{ab}$	$5.5 \pm 0.4$	$4.4 \pm 0.1$	-19.9
	$H^*_{ab}$	$1.1 \pm 0.0$	$1.0 \pm 0.0$	-10.0

\* Means and standard errors for five different replicates are presented.

Interestingly, the most pronounced lightness value changes occurred in those composites containing the coupling agent MAPE. This observation appears counterintuitive, since coupling agents are included in the biocomposites to improve bio-filler binding to the thermoplastic resin (Koo *et al.* 2003; Myers *et al.* 1991; Stark *et al.* 2004). Changes in the color values  $a^*$  (redness),  $b^*$  (yellowness),  $C^*_{ab}$  (chromaticity,

color quality), and  $H^*_{ab}$  (hue) also occurred when comparing the original and soaked composites (Table 4). These color changes are associated with chemical and physical alterations occurring from the composites in response to the presence of water.

Mechanical properties of WPC after exposure to environmental stress of water soaking have been measured by others to assess the potential commercial value of a composite (Thwe and Liao 2002; Lopez *et al.* 2006; Clemons and Stark 2009; Kord 2011; Zabihzadeh 2010a,b). Flexural properties (MOR and MOE) have been shown to decrease when LPC are weathered (Thwe and Liao, 2002; Lopez *et al.* 2006; Clemons and Stark 2009). In this work, the Type V tensile bars that were not soaked and Type V bars that were soaked in water for 672 hours were tested for TS and YM, as shown in Table 5. The mechanical properties of composites as well as neat HDPE and HDPE-MAPE may be affected by water soaking. HDPE and HDPE-MAPE blends exhibited reductions in ELO values, while their TS and YM values increased. TS values increased about 5 to 9% for the HDPE and HDPE-MAPE, respectively. Generally, the TS and YM values for soaked composites (except HDPE-DDGS) were retained, while the ELO values decreased when compared to untreated controls (Table 5). The largest change in TS values occurred in the HDPE-DDGS-MAPE composite, which declined 12%. The HDPE-STDDGS-MAPE composite still retained the highest TS and YM values when compared to the other HDPE, HDPE-MAPE, or composite formulations (Table 5). However, ELO values were significantly lower in the soaked HDPE-STDDGS-MAPE composite than the unsoaked composite.

**Table 5.** Mechanical Properties of Original and Soaked Type V Tensile Bars

Composition	TS (MPa)*	YM (MPa)*	ELO (%)*
HDPE	18, 19a	152, 160a	1716, 1014a
HDPE-MAPE	17, 18a	149, 158a	1605, 1161a
HDPE-DDGS	14, 14	124, 110	37. 44a
HDPE-DDGS-MAPE	17, 15a	147, 113a	40, 36
HDPE-STDDGS	16, 16	208, 202	30, 24a
HDPE-STDDGS-MAPE	21, 21	210, 213	30, 25a

\*Properties are given as unsoaked separated by a comma from soaked treatment. The presence the letter "a" after a value indicates significant difference between treatments ( $P < 0.05$ ).

### Thermal Analysis

Due to the unique chemical properties associated with each species, every bio-filler affects the thermal properties of the composite differently (Kalia *et al.* 2009; Onwulata *et al.* 2009; Sutivisedsak *et al.* 2011). DDGS contains a higher concentration of protein ( $\approx 26\%$ ) than found in most LF ( $\approx 1.5$  to 7 %). The thermal properties measured by DSC of the DDGS composite blends containing different concentrations of MAPE and DDGS preparations are shown in Table 6. All composites regardless of the concentration of MAPE invariably exhibited a slightly lower  $T_m$  compared to the  $T_m$  of neat HDPE. This observation is common in LPC (Lei *et al.* 2007; Pilla *et al.* 2007; Khalaf 2010; Li and Sun 2011; López *et al.* 2012; Sutivisedsak *et al.* 2012), but not always (Kalia *et al.* 2009; Onwulata *et al.* 2009). We can attribute the reduction in  $T_m$  in the composites due to disruption of the HDPE crystal lattice network by the presence of DDGS particles.

The addition of DDGS to HDPE resulted in composite with lower crystallization levels than neat HDPE, as can be seen in Table 6.

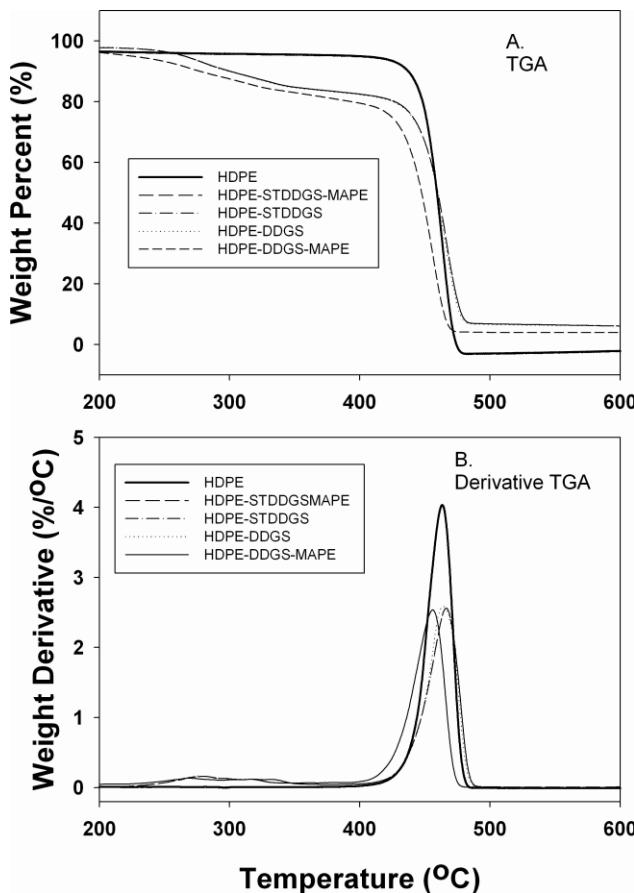
**Table 6.** DSC Thermal Data for HDPE-DDGS Composites

Composition	$T_m$ (°C)	$\Delta H_m$ (J/g)	$\chi_c$ (%)
HDPE	128.4	186.9	63.8
HDPE-MAPE	128.1	204.4	69.8
HDPE-DDGS	126.6	118.7	40.5
HDPE-DDGS-MAPE	126.5	119.3	40.7
HDPE-STDDGS	126.5, 129.15	111.6	38.1
HDPE-STDDGS-MAPE	126.8	114.4	39.0

The lowered crystallization levels in composite blends roughly corresponded to the concentration of DDGS filler employed. For example, a blend containing 25% DDGS and 75% HDPE exhibited a crystallinity level 36% lower than neat HDPE; and blend containing 25% STDDGS and 75% HDPE exhibited a crystallinity level 40% lower than neat HDPE. Other investigators have also observed a decrease in the crystallinity values associated with various LPC (Kalia *et al.* 2009; Sutivisedsak *et al.* 2011). The presence of MAPE in the composite did not affect the crystallinity level of the composites. For example, a blend containing 25% DDGS and 75% HDPE exhibited a crystallinity level 36% lower than neat HDPE; and a blend containing 25% DDGS, 5% MAPE, and 70% HDPE also exhibited a crystallinity level 36% lower than neat HDPE.

It is important to determine the thermal stability of DDGS fillers because the temperatures employed in their processing (injection molding) may exceed 200 °C. The thermogravimetric curves are plotted in Fig. 5, and these results are summarized in Table 7. The degradation of neat HDPE occurs in a single stage that begins at 448.7 °C, with a maximum decomposition rate occurring at 463.3 °C. HDPE degradation was 99.1% complete at end of this stage. Similarly, the HDPE-MAPE blend mimics these parameters. In contrast, there are several degradation peaks for the DDGS composites. The initial degradation temperature ( $T_d$ ) of the DDGS flour was 242.4 °C, and the decomposition peak occurs at 269.3 °C. This degradation peak is associated with the decomposition of low molecular weight components such as hemicellulose, which degrades between 225 to 325 °C (Lee and Wang 2006; Clemons and Stark 2009). A second higher degradation peak occurs with a maximum at 316.2 °C. This degradation peak is associated with decomposition of cellulose, which degrades in the 300 to 400 °C (Lee and Wang 2006). A third degradation peak that corresponds to lignin decomposition is often reported occurring near 420 °C; however it is not readily seen in this study (Lee and Wang 2006). This peak was obscured by the decomposition of the HDPE. The DDGS composite has a residual weight 6.9% due to the heterogeneous ingredients in the flour. Differences among the DDGS composite  $T_d$ s is due to the association of the filler material and the plastic resin. Higher  $T_d$ s and peak temperatures occurred for STDDGS composites compared to the DDGS composites; this can be attributed to the occurrence of higher levels of low-molecular-weight organic compounds in DDGS composites compared to STDDGS composites. Similarly, other investigators have reported that addition of extractables (e.g., clay) cause decreases in  $T_d$  values (Lei *et. al.*, 2007). The

addition of the coupling agent MAPE had little influence on the decomposing behavior of the DDDG composites. Based on the TGA analysis and since the injection molding temperatures did not exceed 200 °C, the DDSG composites were relatively thermally stable for the temperatures to which they were subjected in this study.



**Fig. 5.** TGA analysis of HDPE and HDPE-DDGS composites. A. TGA profile of HDPE and HDPE-DDGS composites. B. TGA derivative of HDPE and HDPE-DDGS composites. Note that overlapping of the thermograms obscures the composites data

**Table 7.** TGA Data for DDGS Composites

Composition	1st	2nd	Peak temp. (°C)**			Residual (%)
	T <sub>d</sub> (°C)*	T <sub>d</sub> (°C)	Peak 1	Peak 2	Peak 3	
HDPE		448.7			463.4	0.9
HDPE-MAPE		443.5			460.6	4.4
HDPE-DDGS	242.4	437.9	269.3	316.2	456.1	6.9
HDPE-DDGS-MAPE	235.5	441.3	274.7	314.3	459.4	7.0
HDPE-STDDGS	254.7	449.6	280.1	334.2	466.7	8.8
HDPE-STDDGS-MAPE	253.1	448.0	276.2	329.9	464.1	8.5

\* Initial thermal degradation temperature (T<sub>d</sub>).

\*\* Maximum degradation temperature.

## CONCLUSIONS

1. DDGS subjected to solvent extraction generates an improved DDGS filler material that was superior to the original DDGS filler material when blended with HDPE.
2. Solvent extracted DDGS with the addition of a MAPE coupling agent creates a HDPE bio-based composite with tensile and flexural properties that exceed neat HDPE.
3. All HDPE-DDGS composite blends exhibited lower impact energy properties than neat HDPE.
4. All DDGS composites soaked in water for 28 days exhibited an increase in weight gain, color changes, and an alteration of their mechanical properties, especially ELO.

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