

## Fiberboard Created Using the Natural Adhesive Properties of Distillers Dried Grains with Solubles

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Distillers dried grains with solubles (DDGS) were employed as a bio-based resin/adhesive. DDGS were defatted with hexane, ball ground, and screened prior to use. DDGS flour was mixed dry with *Paulownia* wood (PW) to make composites using the following conditions: temperature of 150 to 195 °C, PW particle sizes of  $\leq 75$  to 1700  $\mu\text{m}$ , pressure of 2.1 to 5.6 MPa, and using DDGS dosages of 10 to 100%. Molded composites were evaluated for their flexural properties. Composites were examined with Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and X-ray diffraction. The best flexural properties were obtained from composites containing 50% DDGS and 50% PW, using 180 to 250  $\mu\text{m}$  PW particles, pressed at 5.6 MPa, and employing 185 °C. Flexural properties of DDGS-PW composites were similar to composites fabricated using soybean flour (Prolia) as the resin/adhesive. Dimensional stability properties (water absorbance and thickness swelling) of DDGS-PW and Prolia-PW composites were similar. DDGS-PW composite properties satisfied several European Committee Industry Standards for fiberboards in terms of flexural properties but were inferior in terms of thickness swelling properties.

*Keywords:* Medium density fiberboard; Particle board; Renewable resources; Paulownia; Flexural properties; Thermal properties; Dimensional stability

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### INTRODUCTION

It is estimated that by 2030, global consumption of industrial and solid wood will increase by 60% over currently consumed levels, and in addition, there will be a substantial demand for more paper and paperboard products (Elias and Boucher 2014). To satisfy wood needs, engineered wood products are employed such as fiberboard (FB), which includes particleboard (PB), medium density fiberboard (MDF), hardboard (HB), and oriented strand board (OSB) (Hemmilä *et al.* 2017). These products are composed of various sized cellulosic particles bonded together with synthetic resins or adhesives using heat and pressure. Engineered wood products are expected to grow 25 to 33% by 2020 (Elling 2015). Structural panels made in North America will increase 21% by 2020 (*i.e.*, from 31.5 billion square feet to 38 billion), largely in response to increased housing.

Currently, engineered wood products use petroleum-based thermosetting resins such as urea formaldehyde, phenol formaldehyde, melamine fortified urea formaldehyde, or polymeric diphenylmethane diisocyanate (Hemmilä *et al.* 2017). Using these resins to create engineered wood products has adverse environmental and health consequences because of the emission of volatile organic compounds (VOCs) such as formaldehyde (Hemmilä *et al.* 2017). New engineered wood products often employ isocyanate resins since they do not contain formaldehyde and are considered non-volatile when cured. In addition, other additives are incorporated into the FB such as borate compounds (to prevent termites, wood boring beetles, molds, and fungi) and waxes (to increase hydrophobicity) (Hemmilä *et al.* 2017). Engineered wood products are a major source of formaldehyde off-gassing in US homes and present a serious health problem (CPSC 2013). Formaldehyde is classified as a carcinogen, and its exposure levels are regulated in the USA to avoid health problems (CEPA-ARB 1997; EPA 2010; CPSC 2013; ClassAction.org 2015; Hemmilä *et al.* 2017). However, wood composite flooring made in China and exported to the US have formaldehyde emission levels that exceed current US safety emission standards, in some cases by as much as 350% (ClassAction.org 2015).

Soy protein-based adhesives derived from soya bean meal (SBM) have been employed to some extent over the last 80 years (Zhong *et al.* 2001). Soybean proteins are an alternative to petroleum polymers because of their abundance, renewability, biodegradability, and feasibility (Mo *et al.* 2001, 2003; Mohanty *et al.* 2002; Lodha and Netravali 2005a, 2005b; Liu and Li 2007; Frihart *et al.* 2014; Nasir *et al.* 2014; Xu *et al.* 2014). Soybean meal is inexpensive, abundant, and easy to handle because it can be cold or hot pressed (Zhong *et al.* 2001; Amaral-Labat *et al.* 2008; Jeon *et al.* 2011; Reddy and Yang, 2011; Gu *et al.* 2013; Xu *et al.* 2014). However, SBM was essentially replaced in the 1960s by less-expensive synthetic adhesives. In recent years, interest in their use as adhesives was renewed because they are biodegradable and free of VOCs. For example, Uniboard (Laval, Quebec, Canada) markets a “Nu Green SOYA” particle board utilizing a soy based adhesive (Uniboard Canada Inc. 2016). Soya protein isolate (SPI) has high adhesion strength but costs more than PF and UF (Mo *et al.* 2001; Zhong *et al.* 2001; Kumar *et al.* 2002; Lodha and Netravali 2005a, 2005b; Liu and Li 2007; Vnučec *et al.* 2015). Commercial products such as SPI (Pro-Fam 970) (ADM, Decatur, IL) containing 90% protein (dry basis) and defatted SBM such as Prolia (PRO) (Cargill, Cedar Rapids, IA) containing  $\geq 50\%$  protein are available. SBM currently sells for  $\approx$  \$0.45 to \$0.50/lb (\$0.99 to \$1.10/kg) (Alibaba.com 2016).

Other sources of bio-based adhesives have also been developed (Shukla and Cheryan 2001; Beg *et al.* 2005; Norström *et al.* 2014). Of particular interest is the employment of zein, which is derived from corn gluten meal and is highly effective as a resin/adhesive (Shukla and Cheryan 2001). Zein is a prominent storage protein (a prolamine protein) in corn and comprises  $\approx 35$  to 40% of the corn protein. It is extracted from corn gluten meal, which is obtained from the wet milling processing of corn seeds. Unfortunately, the cost of zein is prohibitive to most commercial enterprises such as bio-plastics and bio-composites. Zein sells for  $\approx$  \$4.54 to \$18.20/lb (\$10 to \$40/kg) (Shukla and Cheryan, 2001). Corn gluten meal itself contains 55 to 70% protein and is considerably less expensive, selling for  $\approx$  \$0.36 to \$0.45/lb (\$0.79 to \$0.90/kg) (Alibaba, 2016). Corn gluten meal has been employed in a myriad of products including livestock feed, plastic fillers, coatings, and bio-plastics (Beg *et al.* 2005; Samarasinghe *et al.* 2007).

Nevertheless, there is still a great need to develop even less expensive, abundant bio-based adhesives to be employed in the manufacture of engineered wood products.

The major feedstock used in ethanol production in North America is corn, with over 90% of the 226 operational ethanol plants utilizing corn exclusively (Liu 2011; Ethanolproducer.com 2017). Approximately 30% of the U.S. harvested corn acreage, representing 5,200 million bushels of corn, is used for ethanol production (Wisner 2015). Over 80% of the ethanol produced is derived from the dry-milling process (Kim *et al.* 2008). Distillers dried grains with solubles (DDGS) are the cereal by-product of the dry-milling process (Shukla and Cheryan 2001). Approximately 38 to 42 million metric tons of DDGSs are produced annually in North America (Clarizio and Tataro 2013). DDGS are a relatively low value by-product, are mainly used as an animal feed, and sell for about \$0.03 to \$0.05/lb (\$0.06 to \$0.10/kg) (Irwin 2017). Recently, DDGSs have been employed as a bio-filler blended with thermoplastic resin matrix (*e.g.* poly(lactic acid) (PLA)), high density polyethylene (HDPE), or thermoplastic starch to fabricate biocomposites (Tataro *et al.* 2009; Tisserat *et al.* 2013a; Clarizio and Tataro 2013; Lu *et al.* 2014a; 2014b; Madbouly *et al.* 2014; Ju *et al.* 2016). However, our interest was to utilize the DDGS, not as a filler/reinforcement material, but as the matrix itself in the fabrication of biocomposites. Both zein ( $\approx 96\%$  protein) and corn gluten ( $\approx 65\%$  protein) have been employed as matrix resin material to fabricate biocomposites (Shukla and Cheryan 2001; Beg *et al.* 2005; Samarasinghe *et al.* 2007). DDGS contains  $\approx 25$  to 35% protein, which suggests it could be employed as adhesive/resin to construct engineered wood products as a substitute for zein or corn gluten meal. This study investigated the possibility of developing a DDGS-wood biocomposite product. The filler material chosen in this study was *Paulownia* wood (PW) derived from trees of *Paulownia elongata* S.Y. Hu, (Paulowniaceae) grown at the Paulownia Demonstration Plot, Fort Valley State University. This tree is an extremely fast-growing coppicing hardwood that is native to China and cultivated in plantations in China and Japan. PW is highly valued in the construction and furniture industries (Chinese Academy of Forestry Staff 1986; Joshee 2012). *Paulownia* trees can be established on marginal lands and have deep tap roots, which make them drought tolerant (Joshee 2012). PW is light-weight, insect resistant, pale colored, and heat resistant (Chinese Academy of Forestry Staff 1986; Ashori and Nourbakhsh 2009; Joshee 2012). *Paulownia* trees offer an inexpensive source of woody biomass for both energy and lumber, and their wood wastes could be employed in the fabrication of engineered wood products (Ashori and Nourbakhsh 2009; Joshee 2012). Juvenile *Paulownia* trees could be a likely source of woody biomass needed in the future. Hence, this study utilized PW derived from juvenile tree biomass (*i.e.* 36-month-old).

The influence of processing temperatures, pressures, wood filler particle sizes, and DDGS-filler dosage ratios on the flexural properties of DDGS/PW biocomposites were assessed. The flexural properties of DDGS/PW biocomposites were compared to industry standards for commercial composites (*i.e.* PB, MDF, and HDF) to assess their potential commercial application. In addition, since SBM flour is commonly employed as a bio-adhesive in engineered wood products, the flexural properties of DDGS-PW composites to PRO-PW composites using various resin and wood dosages were also compared. As part of this study, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) were also employed to assess the bonding nature associated with DDGS and wood particles.

## EXPERIMENTAL

### Materials

DDGS were obtained as the commercial animal corn feed pellet product (Archers Daniel Midland Co., Decatur, IL, USA). Prolia™ (200/90) (PRO) containing 54% protein and 5% moisture was provided by Cargill Inc., Cedar Rapids, IA, USA and used as provided. *Paulownia elongata* wood material was obtained from 36-month-old trees grown in Fort Valley, GA. PW shavings were milled successively through 4-, 2-, and then 1-mm screens with a Thomas-Wiley mill grinder (Model 4, Thomas Scientific, Swedesboro, NJ, USA). Particles were then sized through a Ro-Tap™ Shaker (Model RX-29, Tyler, Mentor OH, USA) that employed 203 mm diameter stainless steel screen/sieves. The sieve/screens employed were #12, #30, #40, #80, #140, and #200 US Standards (Newark Wire Cloth Company, Clifton, NJ, USA). The shaker was operated for 60 min intervals at 278 rpm to obtain particle separation. Two PW mixtures composed of 50% ≤ 600 μm particle selection, obtained from particles passing through the #30 mesh sieve, and a 600 to 1700 μm particle selection, obtained from particles passing through the #12 mesh sieve and collected on the #30 mesh sieve, were used throughout this study. PW contained 6% moisture. DDGS were ground in a Wiley mill as described. DDGS were defatted with hexane as the solvent using a Soxhlet extractor to obtain a DDGS containing 30% crude protein and 5% moisture. DDGS were ball ground into a flour (< 425 μm particles) using a laboratory bench top ball mill (Model 801CVM, U.S. Stoneware, East Palestine, OH, USA) to obtain fine powder. DDGS was ground in Alumina mill jars containing Burundum cylindrical grinding media pellets (13 mm diam, ≈ 7.3 g wt.) (U.S. Stoneware) at a speed of 50 rpm for 60 h. DDGS flour was sieved through a #80 mesh to be obtained as ≤ 250 μm particles.

### Preparations

To test the influence of mold temperature on DDGS-PW composites, a composite composed of 80 g of DDGS was mixed with 40 g of < 600 μm PW particles and 40 g of 600 to 1700 μm PW particles. DDGS and PW were mixed in a zip-lock bag and given 15 min of circular agitation using a 0.074 m<sup>3</sup> compact dryer (Model MCSDRY1S, Magic Chef, Chicago, IL, USA). An aluminum mold (outer dimensions: 15.2 cm width × 30.5 cm length × 5 cm depth and mold cavity: 12.7 cm width × 28 cm length × 5 cm depth) was employed. The mold interior was sprayed thoroughly with mold release (Paintable Dry Spray with Teflon, No. T212-A, IMS, Chagrin Falls, OH, USA). Pressings were conducted using manual hydraulic presses (Model 4126, Carver Press Inc., Wabash, IN, USA). The mold was then transferred to a preheated Carver press at 150, 170, 180, 185, or 190 °C. Initially, molds were given 2.8 MPa pressure for 4 min, and then pressure was released in order to remove internal air build-up within the composite. Then, molds were pressed to 4.2 MPa for 4 min and pressure was released again. Finally, molds were pressed to 5.6 MPa for an additional 4 min. Total heating/compression time was ~12 min. Mold composites were then held at 5.6 MPa pressure while the heating was terminated, and cooling process of the press platens commenced (*via* cold water). The mold was removed from the Carver press when the mold surface reached 27 °C.

The influence of PW particle size on the mechanical properties of DDGS-PW composites was determined by testing particles obtained from sieve/screens as previously described. Composites composed of 80 g of DDGS were mixed with 80 g of < 1700, <

600, 425 to 600, 180 to 250, 106 to 180, < 74, or 600 to 1700  $\mu\text{m}$  PW. DDGS-PW composites were subjected to 185 °C under 5.6 MPa pressure for 12 min. The influence of mold pressure on DDGS-PW composites was tested on composites composed of 80 g DDGS and 40 g of PW consisting of < 600  $\mu\text{m}$  particles and 40 g of PW consisting of 600 to 1700  $\mu\text{m}$  particles. DDGS-PW composites were fabricated at a temperature of 185°C for 12 min using a pressure of 2.1, 2.8, 4.2, or 5.6 MPa. To compare DDGS to PRO, 15, 25, 50, 75, and 100%, mixtures of DDGS or PRO were mixed with the balance of PW consisting of equal amounts of 74 to 600  $\mu\text{m}$  particles and 600 to 1700  $\mu\text{m}$  particles. DDGS-PW and PRO-PW composites were subjected to 185 °C temperature under 5.6 MPa pressure for 12 min.

### **FTIR**

FTIR spectra were measured on an ABB Arid Zone FT-IR spectrometer (ABB, Houston, TX, USA) equipped with a DTGS detector. Test samples were transparent discs that consisted of 1.00 mg solids homogenized with 300 mg of dry spectronic grade KBr, placed in a KBr die, and compressed at 24,000 psi using a Carver press. Absorbance spectra were acquired at 4  $\text{cm}^{-1}$  resolution and signal-averaged over 32 scans. Interferograms were Fourier transformed using cosine apodization for optimum linear response. Spectra were baseline corrected and adjusted for mass differences and normalized to the methylene peak at 2927  $\text{cm}^{-1}$ .

### **DSC and TGA**

DSC experiments were performed in duplicate on a TA Instruments DSC, Model Q2000 with refrigerated cooling system (New Castle, DE). Calibration was done without a pan for baseline and with indium for temperature. Samples (9 to 10 mg) were added in Tzero aluminum pans and press sealed (non-hermetic). The DSC was purged with dry nitrogen at 50 mL/min. The sample was equilibrated at -60 °C, then heated to 190 °C at 10 °C $\cdot\text{min}^{-1}$ , and this heating cycle was repeated twice. TGA experiments were conducted in duplicate with a Model Q50 TGA (TA instruments, New Castle, DE, USA) under nitrogen with 60 mL/min flow rate. An approximately 10 mg sample was placed on a platinum sample pan, and the pan was loaded with the autosampler. The sample was heated at 10 °C/min from 25 °C to 800 °C. TA Universal Analysis software was used to analyze the results.

### **XRD**

XRD analysis was employed to assess the morphological properties of ingredients and composites. X-ray diffraction spectra analyses were performed using a Bruker D2 Phaser (Bruker AXS Inc., Billerica, MA, USA) X-ray diffractometer. The X-ray source was Cu-K $\alpha$  radiation at a current of 10 mA and 30 kV, set up using  $\theta/\theta$  geometry. Samples were scanned at 10 to 90°,  $2\theta$ , step size 0.01°, 0.2 s/step, and stage rotation of 10 rpm. Initial divergence slit size was 0.6 mm and a 1 mm air scatter screen was used above the sample. A Lynxeye™ detector was used with a 2.5° Soller slit and a Ni-K $\beta$  filter.

### **SEM**

Scanning Electron Microscopy (SEM) was conducted at Fort Valley State University, Fort Valley, GA, USA. Samples were mounted on Hitachi aluminum specimen mounts M4,  $\phi 15 \times 6$  mm, (Ted Pella, Inc., Redding, CA, USA) using double

sided carbon tape. The samples were then dried at a room temperature ( $\sim 26$  °C) for 48 h to remove excess trapped moisture. After 48 h, the specimens were sputter coated with gold using Denton Vacuum Sputter Coater Desk V (Denton Vacuum, NJ, USA). The vacuum pressure was set at 0.05 torr for 60 sec of sputter coating with 50 Å thickness. A variable pressure SEM (Hitachi 3400 NII, Hitachi Technologies America, Inc., Pleasanton, CA, USA) was used to take pictures at various magnifications. Sample surfaces and edges were examined.

### Flexural and Physical Tests

Following pressings, composite panel boards were conditioned at 25 °C and 50% relative humidity (RH) for 72 h. A table saw was employed to cut specimen boards in order to conduct three-point bending tests (EN 310:1993). Specimen board thickness was measured according to the EN 310:1993 test. Specimen board dimensions were 127 mm long, 50 mm wide, and  $\approx 3.5$  to 5.5 mm thick, depending on the treatment. The specimen thickness dictated the free span length. Tests were performed on a universal testing machine [Instron Model 1122 (Instron Corp., Norwood, MA, USA)] using a crosshead speed of 5 mm/min. Densities of the composites were determined using the EN 323:1993 standard. Water absorbance (WA) and thickness swelling (TS) were conducted on 50 x 50 mm squares immersed in water for 24 h according to EN 317:1993 standards utilizing composite formulations of the various DDGS-PW dosages (EN 317:1993).

### Statistical Analysis

Five specimens of each formulation were tested. The average values and standard errors were reported. 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 ( $p \leq 0.05$ ) (Statistix 9, Analytical Software, Tallahassee, FL, USA).

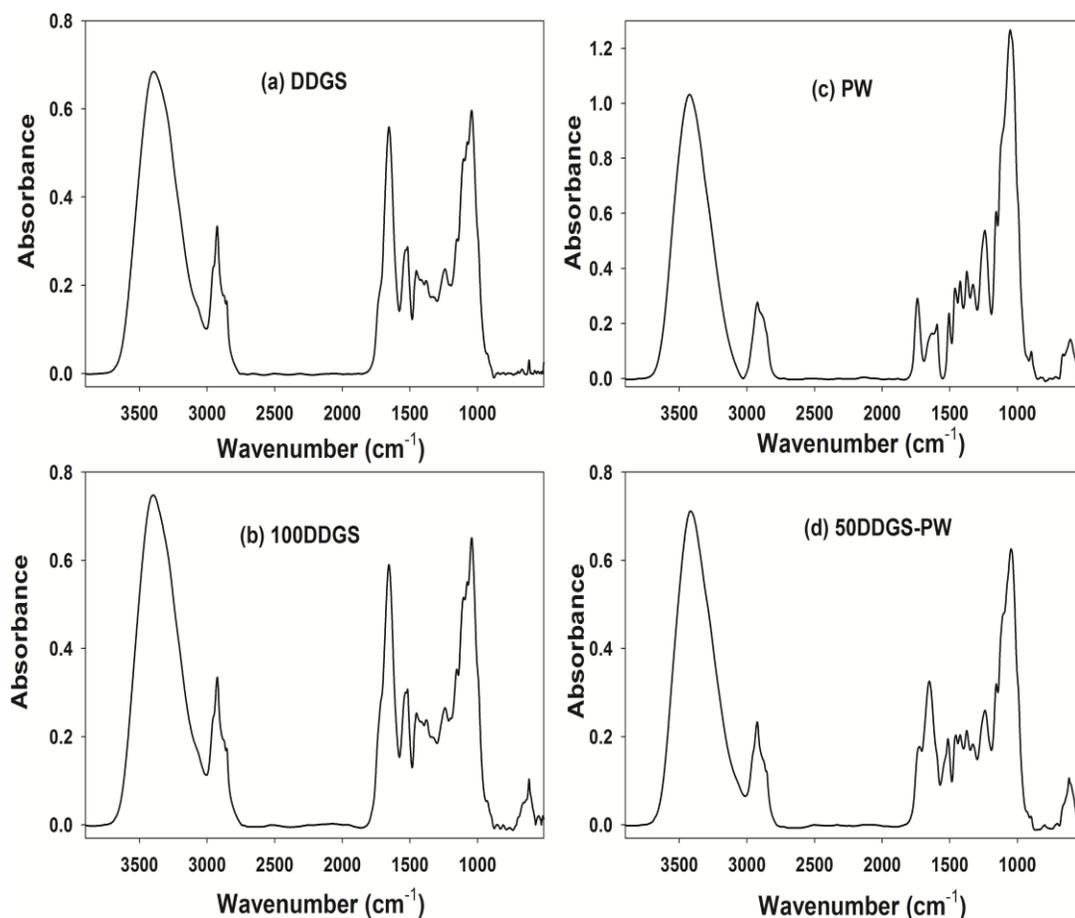
## RESULTS AND DISCUSSION

### FTIR Analysis

Figure 1 a-d shows the FTIR spectra of ingredients DDGS and PW and composite panels 100DDGS (100% DDGS wt.) and 50DDGS-PW (50% DDGS:50% PW wt.). There was no difference in the absorption bands between the original DDGS and 100DDGS composite panel except for a peak region occurring at  $625\text{ cm}^{-1}$  in the 100DDGS, which was absent in the DDGS ingredient spectra. The 600 to  $700\text{ cm}^{-1}$  region is characteristic of P-S and P=S stretching (Pretsch *et al.* 2000). That the region shows up in the 100DDGS suggests unfolding of the protein component so that a buried vibration could be observed.

All spectra (Fig. 1a-d) showed characteristic H-bonding and -OH stretching absorption around  $3300$  to  $3500\text{ cm}^{-1}$  and C-H asymmetric and symmetric stretching of methylene groups around  $2800$  to  $3000\text{ cm}^{-1}$  (Pretsch *et al.* 2000; Nagieb *et al.* 2011; Hemsri *et al.* 2012; Deka *et al.* 2015; Li *et al.* 2016). This region's band was centered at  $3384\text{ cm}^{-1}$  and is identified as -OH of carbohydrate overlapping the protein -NHs (Pretsch *et al.* 2000; Deka *et al.* 2015). A broad alkyl band occurs at  $2921\text{ cm}^{-1}$ , which was

resolved in the 2<sup>nd</sup> derivative spectrum into four bands: strong 2958 cm<sup>-1</sup> (-CH<sub>3</sub> asymmetrical stretching), very strong 2927 cm<sup>-1</sup> (-CH<sub>2</sub> asymmetrical stretching), 2876 cm<sup>-1</sup> (-CH<sub>3</sub> symmetrical stretching), and very strong 2858 cm<sup>-1</sup> (-CH<sub>2</sub> symmetrical stretching) (Pretsch *et al.* 2000; Deka *et al.* 2015). A residual ester or lignocellulosic carbonyl and protein bands occur at 1738 cm<sup>-1</sup> (-C=O, medium carbonyl band either from lignin or uronic esters), and 1656 cm<sup>-1</sup> (N-C=O, amide I). The 1543 and 1517 cm<sup>-1</sup> (H-N-CO) bands are the protein amide IIs (Pretsch *et al.* 2000; Deka *et al.* 2015). Bands 1470 cm<sup>-1</sup> and 1372 cm<sup>-1</sup> are identified as CH<sub>2</sub> and CH<sub>3</sub> deformations, respectively, and are commonly known as the alkyl deformation region of the spectrum (Pretsch *et al.* 2000). Other prominent bands are located at 1117 cm<sup>-1</sup> (O-C=O), 1081 cm<sup>-1</sup> (-CHO-), 1050 cm<sup>-1</sup> (-CH<sub>2</sub>O-), and 994 cm<sup>-1</sup> (unknown).



**Fig. 1.** FTIR spectra of ingredients (a) DDGS and (c) PW and bio-composites (b) 100DDGS and (d) 50DDGS-PW

Figure 1b 100DDGS spectrum is similar to Fig. 1a of the DDGS ingredient. As previously noted, a strong band occurs at 625 cm<sup>-1</sup> representing P-S and P=S stretching of protein. This band was inconspicuous in the spectrum of the folded DDGS protein (Fig. 1a) but now obvious in the unfolded matrix (Fig. 1b).

Figure 1c is the spectrum of PW. Like in many carbohydrates a broad and strong symmetric absorption band is observed at 3420 cm<sup>-1</sup> for the (H bonding and -OH stretching) with a moderate intensity alkyl band occurring at 2925 cm<sup>-1</sup> (Pretsch *et al.* 2000; Li *et al.* 2016). The broad band at 2925 cm<sup>-1</sup> is resolved into a sharp 2969 cm<sup>-1</sup> (-

CH<sub>3</sub> asymmetrical stretching), 2924 cm<sup>-1</sup> (-CH<sub>2</sub>- asymmetrical stretching), 2876 cm<sup>-1</sup> (-CH<sub>3</sub> symmetrical vibrations) and 2852 cm<sup>-1</sup> (-CH<sub>2</sub> symmetrical vibrations). The alkyl groups occurring between 2925 cm<sup>-1</sup> and 620 cm<sup>-1</sup> of the spectrum are easier to identify from its 2<sup>nd</sup> derivative spectrum because these bands are better defined. A medium carbonyl band either from lignin or uronic esters is also evident at 1739 cm<sup>-1</sup> followed by moderate protein absorbances at 1642 to 1505 cm<sup>-1</sup> (Pretsch *et al.* 2000; Li *et al.* 2016). Alkyl chain deformation bands (-CH<sub>2</sub>- and -CH<sub>3</sub>) trending toward the low frequency region ending at 620 cm<sup>-1</sup> (see previous paragraphs). The 620 cm<sup>-1</sup> band is analogous to that in processed 100DDGS. There is a single carbonyl band at 1738 cm<sup>-1</sup> assignable either to a uronic ester in the wood component or a lignin carbonyl moiety (Pretsch *et al.* 2000; Li *et al.* 2016). Next there is a low protein carbonyl absorption at 1656 cm<sup>-1</sup>, amide I and very intense peaks at 1597 and 1508 cm<sup>-1</sup> presumably represent the amide II mode. The -CH<sub>2</sub>- and -CH<sub>3</sub> deformation bands are shown at 1470 and 1372 cm<sup>-1</sup>, respectively. There is a sizable O-C=O band at 1246 cm<sup>-1</sup> followed by very intense -CHO-, and -CH<sub>2</sub>O- bands located at 1159, 1128, 1037, and 991 cm<sup>-1</sup>. Finally an anomalous P-S and P=S band is observed at 670 cm<sup>-1</sup> (Fig. 1c).

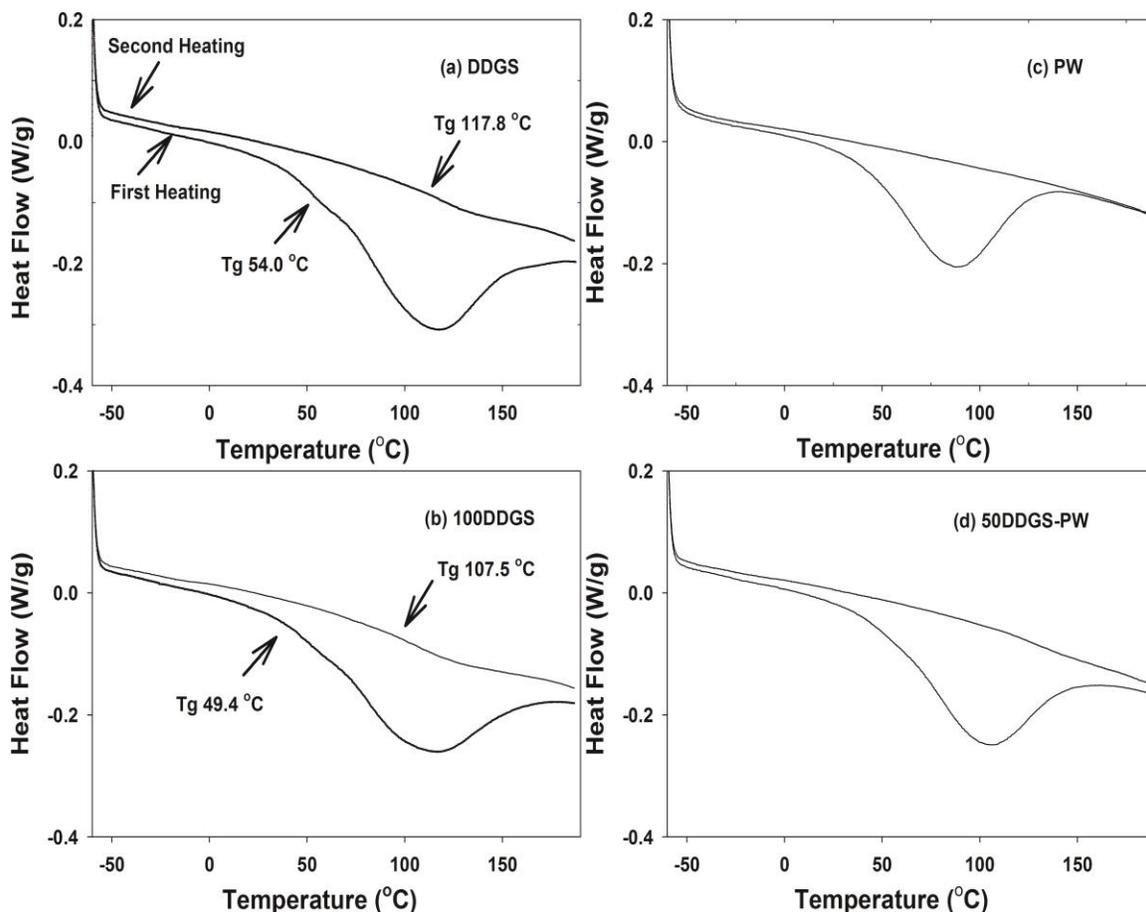
The 50DDGS-PW composite spectra ( Fig. 1d) is characterized by a strong 3410 cm<sup>-1</sup> band representing the overlapping -OHs of DDGS and PW together with the -NH stretching bands of the intrinsic protein content. A broad band at 2913 cm<sup>-1</sup> is resolved in the 2<sup>nd</sup> derivative of its FTIR spectrum into four discrete bands: 2959 cm<sup>-1</sup> (-CH<sub>3</sub> asymmetrical), 2923 cm<sup>-1</sup> (-CH<sub>2</sub> asymmetrical stretch), 2875 cm<sup>-1</sup> (-CH<sub>3</sub> symmetrical stretching) and 2854 cm<sup>-1</sup> (-CH<sub>2</sub> symmetrical stretching) absorption. The next absorption series of the spectrum comprise an ester carbonyl band at 1743 cm<sup>-1</sup> resulting from the PW, a single amide I absorbance at 1656 cm<sup>-1</sup> (probably the  $\alpha$ -helix of the DDGS), and prominent amide II peaks at 1596, 1546 and 1517 cm<sup>-1</sup>. These are followed by the deformation bands, 1470 and 1378 cm<sup>-1</sup> of the -CH<sub>2</sub>- and -CH<sub>3</sub> alkyl moieties, respectively. The latter bands are followed by the -O-C=O stretching of the ester at 1246 cm<sup>-1</sup> and the -COH- and -CH<sub>2</sub>O- at 1167, 1130, 1077, 1039 and 992 cm<sup>-1</sup> and finally by the P-S and P=S vibration at 621 cm<sup>-1</sup>.

## DSC and TGA Evaluations

Ganesan and Rosentrater (2007) observed glass transition temperatures ( $T_g$ ) at 20 to 50 °C with unmodified DDGS, defatted DDGS, or de-waxed DDGS using DSC. The defatted DDGS used in this study showed a somewhat higher  $T_g$  (54.0 °C) during the first heating cycle, which was shown as a small shoulder in the large water evaporation curve (Fig. 2a). The difference, presumably, resulted from slightly different compositions produced by different processes to obtain the DDGS. The second heating cycle, conducted after the first heating cycle, showed no water evaporation peak and a higher  $T_g$  (117.8 °C). The reason for this weak signal was that the DDGS is a mixture of many ingredients and some of them exhibit a “thermoplastic property”. The presence of water lowers the  $T_g$  and acts as a plasticizer in a material having glass transition, and thus removing the water increases the  $T_g$  (Frascareli *et al.* 2012). The DSC of PW did not show an obvious  $T_g$  during the first or the second heating cycles, indicating that the PW did not have ingredients undergoing glass transition (Fig. 2c). The DSC of 100DDGS showed a slightly lower  $T_g$  than that of DDGS in both the first and the second heating cycles, indicating that the materials showing glass transition underwent little change during the process of making this composite (Fig. 2b). In contrast, 50DDGS-PW showed no  $T_g$  (Fig. 2d). In the presence of wood, DDGS binds more completely to produce a

thermoset composite. This result indicated that in addition to the fact that 50DDGS-PW contained only 50% DDGS, there may have been physical changes in DDGS during the composite-making process.

The physical change such as the interface of DDGS molecules with PW particles may have been one of the possible reasons for the increased strength of 50DDGS-PW over 100DDGS (which will be discussed later), since there were no substantial chemical reactions evident between DDGS and PW as observed in FT-IR spectra.



**Fig. 2.** DSC of ingredients (a) DDGS and (c) PW and bio-composites (b) 100DDGS and (d) 50DDGS-PW

The TGA analysis confirmed water evaporation from both ingredients and composites was initiated around 100 °C (Fig. 3). DDGS further lost weight starting around 140 °C, while PW did not begin substantial weight loss until the temperature reached 210 °C. Beyond 210 °C, all four samples exhibited remarkable weight loss due to decomposition. This indicated that such process temperatures should have been avoided because of detrimental damage to the composites. However, there should be a certain temperature and enough incubation time for the physical changes required for interfacing of the DDGS molecules with PW particles to occur in order to obtain optimized strength of the composite. Process temperatures that are too high or process times that are too long could cause excessive thermal decomposition of the composite resulting in lower strength. This will be discussed further in a later section.

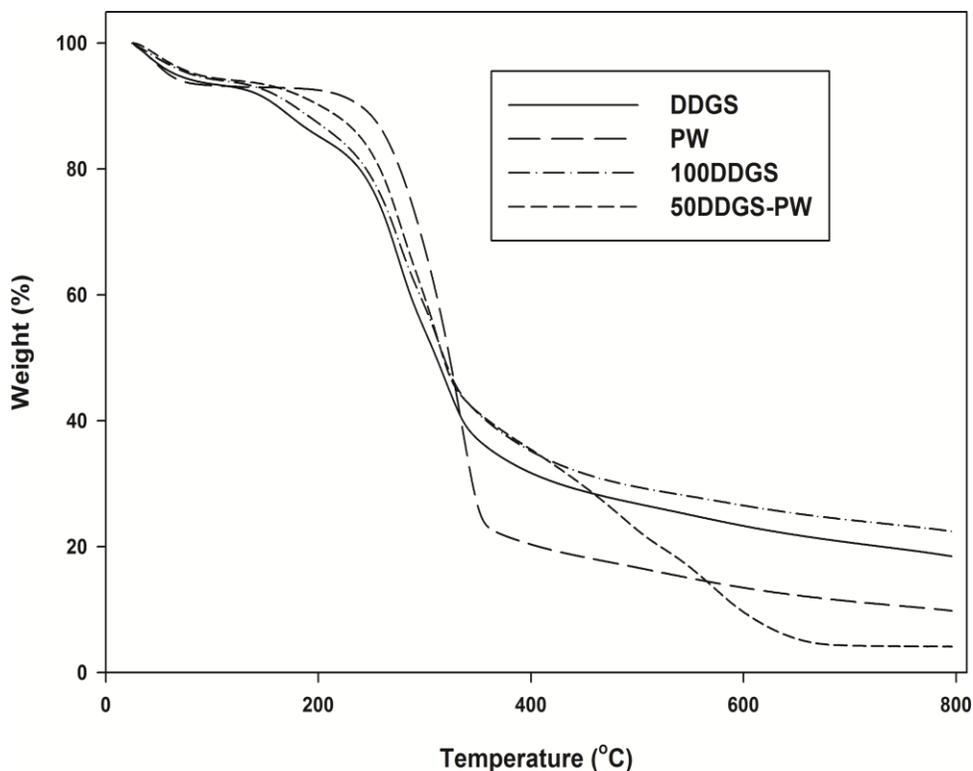


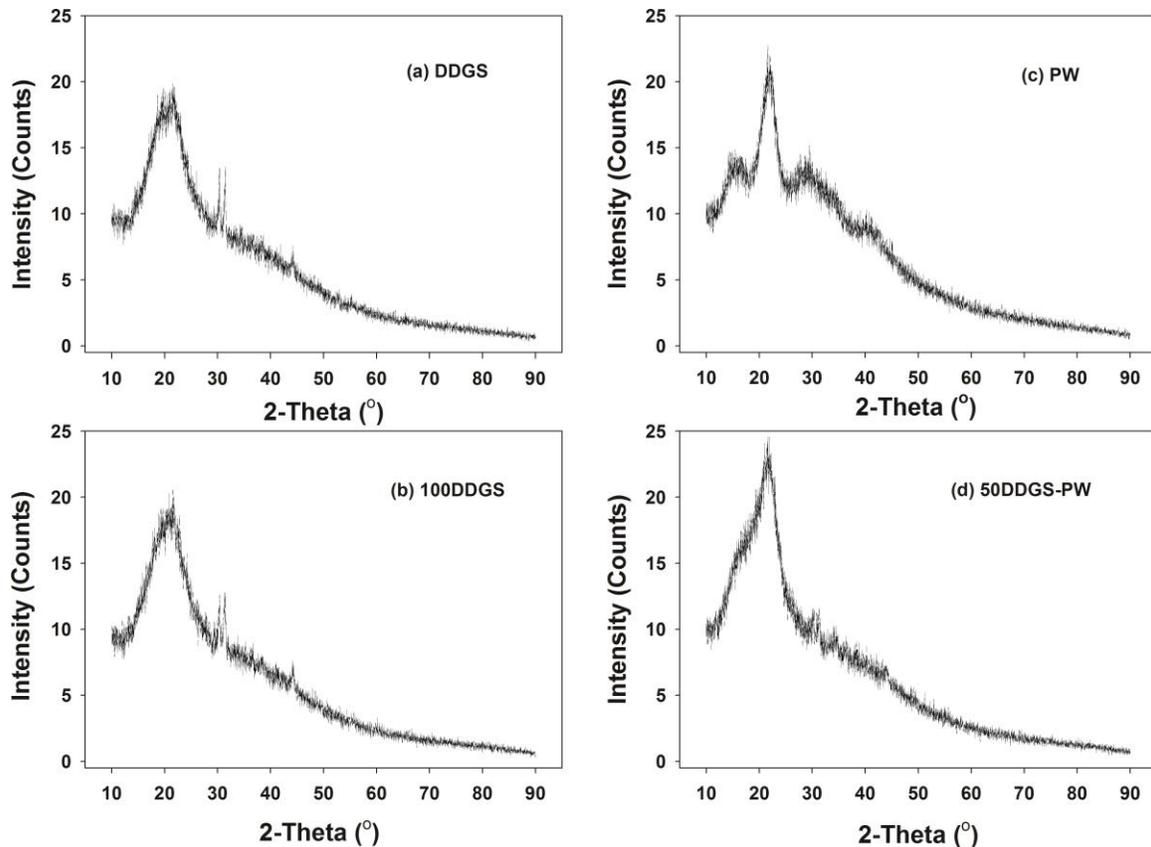
Fig. 3. TGAs of DDGS, PW, 50DDGS-PW, and 100 DDGS

### XRD Analysis

Figure 4 represents the X-Ray diffractograms of the native DDGS and PW versus the resulting bio-composites (100 DDGS and 50DDGS-PW). Both ingredients (DDGS and PW) are biological, amorphous solids that soften and semi-melt over a temperature range conducted in this study. In addition, it was noted that breaking of the 50DDGS-PW and 100DDGS panels results in curved or irregular faces, which are characteristic of amorphous solids.

The DDGS samples (DDGS, 100DDGS, and 50DDGS-PW) had a doublet peak occurring around 30 degree 2-theta. The occurrence of this doublet has been previously reported (Xu *et al.* 2008). The PW ingredient had a broad peak occurring around 22 degree 2-theta which is characteristic of amorphous materials such as wood (Devi and Maji 2013). In addition, PW diffractogram showed shoulder peaks occurring before and after the main peak at 22 degree 2-theta.

The 50DDGS-PW diffractogram represented a combination of the DDGS and PW ingredients without any new peaks occurring. The PW peaks of the 50DDGS-PW composite were somewhat masked by the broader DDGS peak. Overall, the composites did not show any additional peaks at higher degree 2-theta values, which would have indicated the occurrence of crystallization (Xu *et al.* 2008). It was concluded that little or no crystallization occurred in the preparation of the composites from the ingredients employed. This suggested that the interaction between the DDGS and PW is disordered and amorphous in nature.



**Fig. 4.** X-Ray diffractograms of ingredients (a) DDGS and (c) PW and bio-composites (b) 100DDGS and (d) 50DDGS-PW

### Effect of Temperature on Flexural Properties

It should be noted that all composites were found to have smooth tactile feel on their surface, resembling a commercial MDF or even thermoplastic or thermoset resin-wood composite. The temperature employed to hot-press composites was found to have remarkable influence on the flexural properties of the composites. The  $F_m$  obtained from specimens using 150, 170, and 180 °C as the hot-press temperatures were similar (Fig. 5). The DDGS-PW composites hot-pressed at 185 °C showed a remarkable increase in bending strength ( $F_m$ ), while the 190 °C hot-pressed specimens showed a decline. Likewise, the modulus of elasticity ( $E_m$ ) values followed the same pattern (Fig. 5).

Clearly, the mechanical properties of DDGS-PW composites hot-pressed at 185 °C were superior to other hot-press temperatures. This was attributed to the optimum plasticization of the DDGS matrix having occurred at this temperature. Below this temperature (185 °C) some plasticization of DDGS occurred, while above this temperature (190 °C) both plasticization and thermal degradation of the DDGS occurred. DDGS-PW composites hot-pressed at 185 °C had  $F_m$  and  $E_m$  values of  $41.4 \pm 0.7$  and  $6073 \pm 123$  MPa, respectively, while DDGS-PW composites hot-pressed at 150 °C had  $F_m$  and  $E_m$  values of  $22.8 \pm 2.0$  and  $3548 \pm 157$  MPa, respectively. This translated into DDGS-PW composites hot-pressed at 150 °C with  $F_m$  and  $E_m$  values being -45 and -42% less, respectively, than composites hot-pressed at 185 °C.

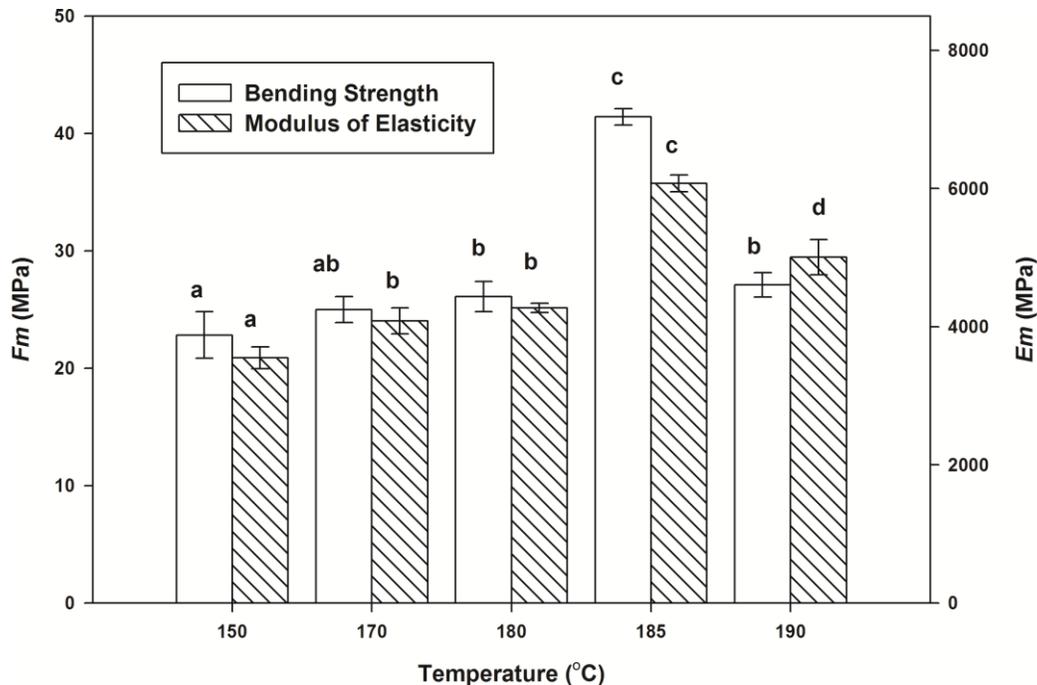
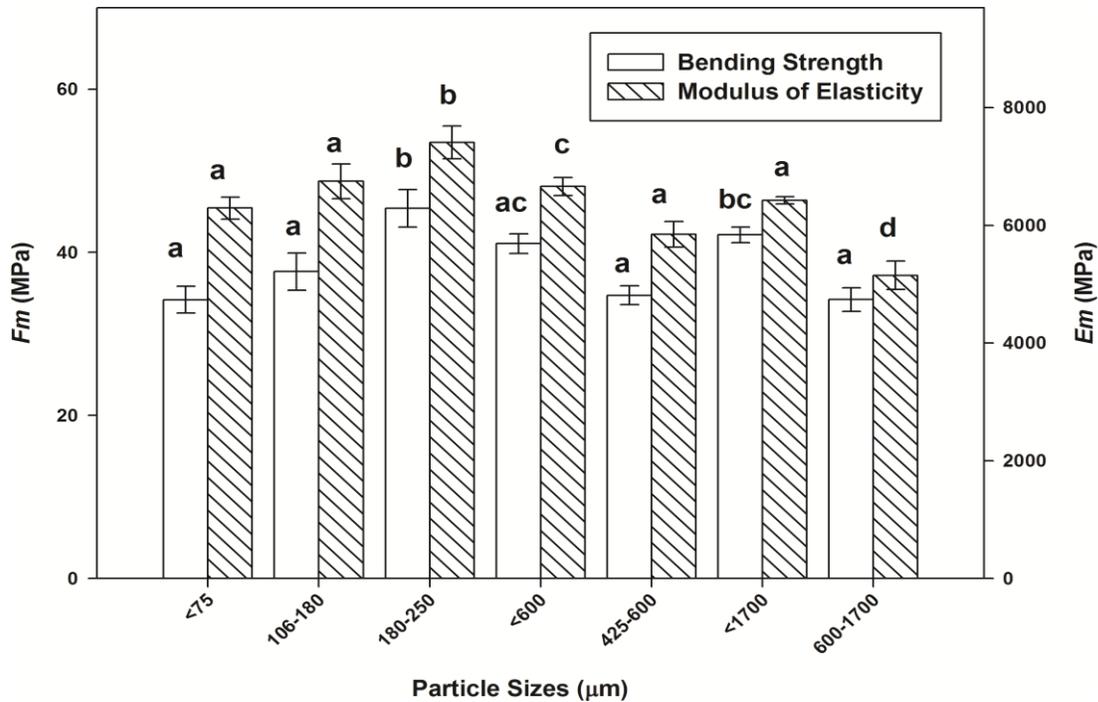


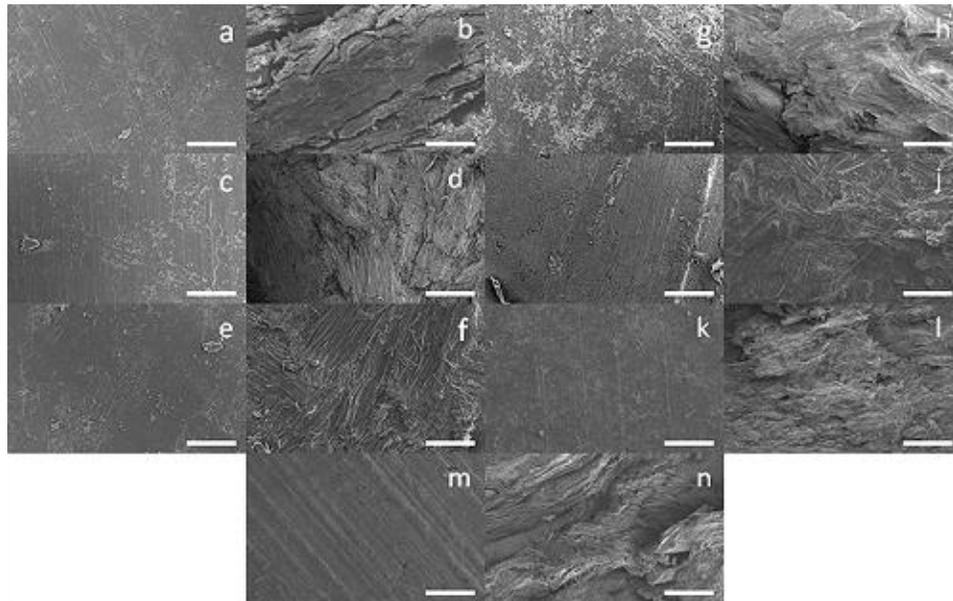
Fig. 5. Effect of press temperatures on the flexural properties of biocomposites

### Effect of Particle Size on Flexural Properties

The size of wood particles plays an important role in the fabrication and overall characteristics of engineered wood (Korosten MDF manufacture 2013; Lias *et al.* 2014). Particleboard usually consists of large wood particles obtained from inexpensive wood sources, which are hot-pressed with a petroleum based binding agent (*i.e.*, formaldehyde resins) (Korosten MDF manufacture 2013). MDF in contrast is made of finer wood particles and typically are much denser and thinner than particleboard. MDF may be glued together with lignin and wax (paraffin), and these are therefore more eco-friendly than particleboard (Korosten MDF manufacture 2013; Lias *et al.* 2014). In this study a variety of wood particles were employed in the DDGS-PW composites (Fig. 6). It was found that the bending strength ( $F_m$ ) and modulus of elasticity ( $E_m$ ) values of DDGS-PW composites were influenced by the particle size of the wood employed. For example, composites composed of the largest wood particles (600 to 1700  $\mu\text{m}$ ) had the lowest flexural values when compared to the other composites tested,  $F_m$  and  $E_m$  values were  $34.2 \pm 1.4$  and  $5151 \pm 244$ , respectively. The composite that contained 425 to 600  $\mu\text{m}$  particles selection also exhibited lower flexural properties. Composites containing 180 to 250  $\mu\text{m}$  particles had the highest  $F_m$  and  $E_m$  values that were  $45.4 \pm 2.3$  and  $7409 \pm 276$ , respectively. This suggested that this particle size was optimum for producing high quality composites. Composites that contained a mixture of wood particles composed of  $< 1700 \mu\text{m}$  or  $< 600 \mu\text{m}$  exhibited higher flexural properties that rivaled the 180 to 250  $\mu\text{m}$  composite. Interestingly, composites containing the smallest particle ( $< 74 \mu\text{m}$ ) exhibited lower  $F_m$  values but had  $E_m$  values in par with the other composites. Other researchers have noted the importance of wood particle size on the mechanical properties using thermoplastic resin-wood blends (Stark and Berger 1997; Tisserat *et al.* 2013b).



**Fig. 6.** Effect of the Paulownia wood (PW) particle size on the flexural properties of DDGS-PW composites



**Fig. 7.** SEM micrographs of DDGS-PW composites composed of various particles sizes: (a) < 74 to 1700  $\mu\text{m}$  particles-surface, (b) < 74 to 1700  $\mu\text{m}$  particles-edge, (c) < 74 to 600  $\mu\text{m}$  particles-surface, (d) < 74 to 600  $\mu\text{m}$  particles-edge, (e) 425 to 600  $\mu\text{m}$  particles-surface, (f) 425 to 600  $\mu\text{m}$  particles-edge, (g) 180 to 250  $\mu\text{m}$  particles-surface, (h) 180 to 250  $\mu\text{m}$  particles-edge, (i) 106 to 180  $\mu\text{m}$  particles-surface, (j) 106 to 180  $\mu\text{m}$  particles-edge, (k) < 75  $\mu\text{m}$  particles-surface, (l) < 75  $\mu\text{m}$  particles-edge, (m) 600 to 1700  $\mu\text{m}$  particles-surface, (n) 600 to 1700  $\mu\text{m}$  particles-edge; scale bar = 200  $\mu\text{m}$

SEM examination of the various composites showed little differences in their surface topography (Fig. 7). However, the cut edges showed the outlines of the particles sizes employed in the composition of the panels (Fig. 7). DDGS coating of the particles often obscured the wood particles (Fig. 7). Deeper fissures occurred in the micrographs of the DDGS-PW composites containing the larger particles sizes compared to that found in the other composites (Fig. 7 b and n). These fissures were often associated with poor interfacial adhesion between ingredients and resulted in lower flexural properties (Fig 6).

The interaction between the DDGS and wood particle size was responsible for flexural properties of the composite. The DDGS matrix somewhat resembled a thermoset matrix, which mimics SBM74 matrix/adhesives. The mode of bio-based adhesion is unclear and complex (Frihart *et al.* 2010; Frihart 2011; Frihart and Birkeland 2014; Frihart *et al.* 2014). The adhesive nature of SBM is believed to be attributable to the protein composition (Frihart *et al.* 2010; Frihart 2011; Frihart and Birkeland 2014; Frihart *et al.* 2014). Soya seed proteins represent 30 to 50% of the seed mass with storage proteins accounting for 65 to 80% of the total proteins. The main storage proteins in SBM are quaternary globulins, glycinin, and conglycinin (Frihart and Birkeland 2014; Wolf 1970). DDGS is chemically dissimilar from SBM. In addition, yeast contributes 5.3% of the protein content of DDGS (Lim and Yildirim-Aksoy 2008). Corn meal proteins consist of 14% albumin/globulin, 35 to 40% zein (a prolamine protein), and 30% glutelin. It is conjectured that soy protein adhesive properties occur through the denaturation of the quaternary globulins into tertiary structures and crystalline secondary structures,  $\alpha$ -helices, and  $\beta$ -sheets (Frihart 2010; Frihart and Birkeland 2014; Frihart *et al.* 2014). These crystalline secondary protein structures are suspected to provide the optimum adhesive properties that bind protein to wood (Frihart 2010; Frihart and Birkeland 2014). No crystalline structures in the XRD studies with DDGS were observed which suggested a different method of protein adhesion may occur.

Denaturation of proteins can be achieved through a variety of methods such as heat, alkali, or chemical modification (Frihart and Birkeland 2014; Frihart *et al.* 2014). DDGS powder contained 30% protein and was originally a solid and through the application of heat and pressure undergoes a “phase change or transition” and becomes a “liquid-gel” that binds with wood. These events are recognized as typical in the adhesive process (Adhesives.org 2017). Apparently, the DDGS proteins are denatured under pressure and heat to a state that can then bind to wood. Upon cooling, DDGSs transitions back into a solid, which cannot be melted again.

It should be noted that employing a high moisture DDGS-PW formulation results in explosive steam generation and ultimately an unacceptable composite exhibiting excessive blistering. Therefore, a relatively dry DDGS-PW formulation was employed which was prepared by mixing the ingredients dry and not pre-stirring DDGS in any liquids as commonly reported in the fabrication of SBM biocomposites (Zhong *et al.* 2001; Amaral-Labat *et al.* 2008; Jeon *et al.* 2011; Reddy and Yang, 2011; Gu *et al.* 2013). In addition, in the preparation method steam was allowed to escape during the molding process by short releases of the molding pressure. Further, it was found that rapid cooling resulted in blistering and internal cracking of the DDGS-PW composites, while slow cooling the composite produced a non-blistered composite (Fig. 8). Blistering is a common problem in thermoset materials (Plenco 2015). Thermoset materials cure as a result of a chemical reaction and are affected by temperature and pressure (Plenco 2015). Blistering is often due to areas of gas trapped beneath the surface. One of the methods commonly employed to address this problem in injection molding is to decrease

mold temperature by cooling after molding (Plenco 2015; IDI Composites International 2017). Reddy and Yang (2011) employed prolonged slow cooling to molds to obtain soy-wood composites. Likewise, this problem was recognized and was addressed similarly.

Composites that contained predominately large wood particles formed an interfacial complex with the “melted” DDGS, which formed a biocomposite that was weaker than the DDGS composite matrix that interacted with smaller wood particles. It was speculated that smaller wood particles interacted better with the DDGS matrix because of the ability of the DDGS to obtain a more fluid molten state that could penetrate the wood of smaller particles. Composites consisting of various particle sizes exhibited different flexural properties, suggesting that two types of interactions were occurring: (1) the wood particles were providing a support role based on their size, which contributed to the composite strength, and (2) the DDGS was interacting differently with the wood particles depending on their size. The  $< 1700 \mu\text{m}$  blend produced a composite that exhibited high flexural properties and was the simplest to prepare when compared to the other composites. This PW composite blend was adopted in all further studies (Fig. 8).



**Fig. 8.** Comparison of composite panels. Top panel consists of 50:50 mixture of DDGS: PW subjected to fast cooling. Note blistering and internal cracking. Middle panel consists of 50:50 mixtures of DDGS:PW subjected to slow cooling. Note absence of disruptive blemishes. Bottom panel is commercial PB locally purchased

### Effect of Pressure on Flexural Properties

The effect of pressure applications on the flexural properties of composites is presented in Fig. 9. Best flexural properties were obtained using the highest pressure tested. The equipment used did not permit higher pressures to be administered. Composites subjected to 5.6 MPa had  $F_m$  and  $E_m$  values of  $41.4 \pm 0.7$  and  $6073 \pm 123$ , respectively. Composites subjected to 2.1 MPa had  $F_m$  and  $E_m$  values of  $12.6 \pm 1.0$  and  $2354 \pm 286$ , respectively.  $F_m$  and  $E_m$  values of composites subjected to 5.6 MPa were 228% and 158% greater than  $F_m$  and  $E_m$  values of composites subjected to 2.1 MPa, respectively. Similar results have been reported by other investigators (Li *et al.* 2011). Applied pressure had a profound influence on the flexural properties and affected their physical properties, thickness and density. This phenomenon was attributed to the increased densification of the DDGS-PW composite, which resulted in an enhancement in the interfacial binding between particles and thus improving the flexural properties of

the composites. Density of composites treated with 2.1, 2.8, 4.2, or 5.6 MPa were 929, 1,052, 1,212, or 1,275 kgm<sup>3</sup>, respectively. Conversely, thickness of the composites decreased when treated with 2.1, 2.8, 4.2, or 5.6 MPa to 0.470, 0.430, 0.361, or 0.358 mm, respectively.

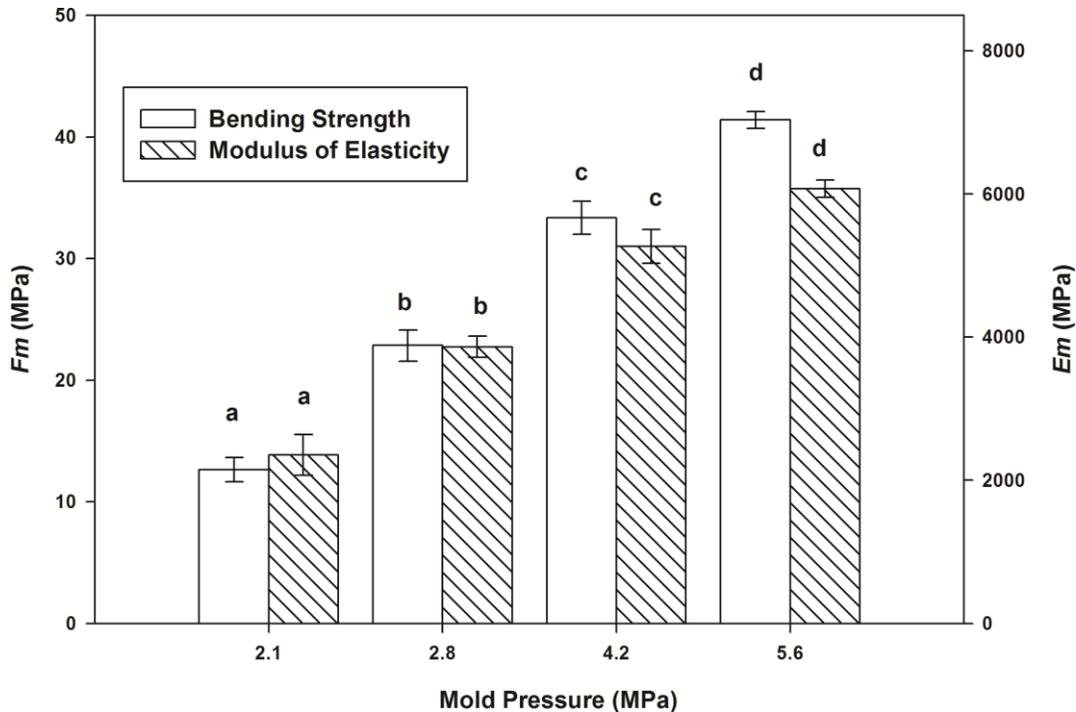


Fig. 9. Effect of various mold pressures on the flexural properties of composites

### Influence of PW dosage on the Flexural Properties of Composites

The influence of DDGS-PW and PRO-PW dosages on the flexural properties of composites is presented in Table 1. Neat DDGS (100%) produced a panel that had the highest density and lowest thickness of all DDGS-PW composites tested but exhibited the lowest flexural values of all the DDGS-PW composites tested (Table 1). Increasing PW content increased the flexural values of all the DDGS-PW composites compared to neat DDGS. The highest flexural properties were obtained from composites containing 50:50 DDGS-PW (% wt.). Increasing the concentration of PW in the 10:90, 15:85, and 25:75 DDGS-PW (% wt.) composites resulted in a reduction of flexural properties compared to other DDGS-PW composites (*i.e.* 50:50 and 75:25 % wt.). DDGS-PW composites had flexural properties comparable to PRO-PW composites for the 50:50 formulations (Table 1). However, the flexural properties of PRO-PW composites to DDGS-PW composites differed depending on the concentrations tested. For example, neat 100% PRO produced a panel that cracked and shattered within 24 h after removal from the mold and therefore could not be tested. Composite formulations of 10PRO-PW, 15PRO-PW, and 25PRO-PW had superior flexural properties compared to 10DDGS-PW, 15DDGS-PW, and 25DDGS-PW. Soy flours (*e.g.* SBM, Prolia, Prosante, and SPI) have been employed in numerous studies to fabricate fiberboards (Zhong *et al.* 2001; Mo *et al.* 2001; Amaral-Labat *et al.* 2008; Frihart *et al.* 2010; 2014; United (USA) Soybean 2010; Jeon *et al.* 2011; Gu *et al.* 2013; Vnućec *et al.* 2015). SBM and DDGS have different protein compositions and concentrations. Nevertheless, the adhesive properties of DDGSs were

similar to PRO. That observation suggested that DDGS may have merit as a potential substitute for soybean flour as a bio-based adhesive.

**Table 1.** Comparison of the Flexural Properties of Biocomposites Using Soybean and DDGS Flours\*

	Thickness	Density	$F_m$	$E_m$	WA	TS
Composition	(mm)	(kg·m <sup>3</sup> )	(MPa)	(MPa)	(%)	(%)
10DDGS-PW	3.8 ± 0.05a	1065 ± 24a	20.8 ± 2.7a	3640 ± 276a	133 ± 7a	141 ± 18a
15DDGS-PW	3.7 ± 0.03a	1092 ± 24a	28.3 ± 3.1ac	4169 ± 248a	101 ± 7b	116 ± 6b
25DDGS-PW	4.1 ± 0.12b	1069 ± 46a	25.4 ± 1.2a	4027 ± 142a	78 ± 7c	104 ± 3c
50DDGS-PW	3.4 ± 0.24c	1288 ± 39b	41.4 ± 0.7b	6073 ± 123b	38 ± 7de	49 ± 9e
75DDGS-PW	3.1 ± 0.04c	1408 ± 14c	31.5 ± 1.0c	5309 ± 90c	37 ± 4d	40 ± 1e
100DDGS	2.6 ± 0.1d	1401 ± 6c	21.5 ± 1.0a	2840 ± 73d	29 ± 1e	44 ± 5e
10PRO-PW	3.8 ± 0.05a	1065 ± 25a	30.5 ± 1.7c	4665 ± 423a	94 ± 14b	84 ± 5f
15PRO-PW	3.8 ± 0.04a	1059 ± 22a	34.3 ± 2.7c	4511 ± 334a	75 ± 6c	78 ± 6g
25PRO-PW	3.8 ± 0.04a	1098 ± 51a	36.6 ± 5.6cf	5179 ± 731c	51 ± 3f	54 ± 5e
50PRO-PW	3.3 ± 0.04c	1262 ± 12b	41.8 ± 0.8bf	7575 ± 589e	49 ± 5f	51 ± 2e
75PRO-PW	3.2 ± 0.05c	1304 ± 14e	26.8 ± 0.6c	5699 ± 155c	54 ± 0f	62 ± 1h
100PRO	--	--	--	--	--	--

\*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.

### Water Absorption and Thickness Swelling of Composites

Water absorption and thickness swelling of DDGS-PW composites were compared to PRO-PW composites (Table 1). Regardless of the adhesive matrix employed, as the concentration of wood flour increased, the amount of water absorbed by the composite increased proportionally. This situation occurred because of the decreasing cohesion that occurs within the composites between the wood and the adhesive (Pan *et al.* 2006). Higher adhesive contents within the 50DDGS-PW and 75DDGS-PW composites exhibited substantially less water absorption and thickness swelling. TS and WA properties vary with the type of raw materials (*i.e.* bonding agents, additives, and fillers/reinforcements) employed during manufacturing (Mendes *et al.* 2012; Melo *et al.* 2014). Bio-based adhesives have a hygroscopic nature compared to synthetic adhesives derived from petroleum sources which are more hydrophobic. WA and TS for the two different types of adhesive composites were somewhat comparable (Table 1).

### Comparison of DDGS-PW Composites Properties with European Committee for Standards

As shown in Table 1, the DDGS-PW composites produced in this study compared well with the nominal flexural requirements for PB, MDF, and HDF established by the European Committee for Standards presented in Table 2 (EN 662-2:1997; EN 622-5:2006; EN 312:2003). However, the non-conventional DDGS-PW composites prepared in this work were often inferior in terms of TS compared to that adopted by the European Committee for Standards (EN 662-2:1997; EN 622-5:2006; EN 312:2003). Clearly, additional research is necessary to improve water resistance properties.

**Table 2.** European Standards for the Nominal Properties for Particleboard, Medium Density Fiberboard, and Hard Density Fiberboard

Specifications	$F_m$	$E_m$	TS
(Description, thickness)	(MPa)	(MPa)	(%)
Particleboard (PB): <sup>1</sup>			
General Purpose boards/dry conditions (P1), 3 to 6 mm	14	--	--
Boards for interior fitments (including furniture)/dry conditions (P2), 3 to 4 mm	13	1800	--
Boards for interior fitments (including furniture)/dry conditions (P2), >4 to 6 mm	14	1950	--
Non-load-bearing boards/humid conditions (P3), 3 to 4 mm	13	1800	17
Non-load-bearing boards/humid conditions (P3), >4 to 6 mm	14	1950	16
Non-load-bearing boards/humid conditions, 3 to 4 mm	--	--	15
Non-load-bearing boards/humid conditions, >4 to 6 mm	--	--	14
Load-bearing boards/dry conditions (P4), 3 to 4 mm	15	1950	23
Load-bearing boards/dry conditions (P4), >4 to 6 mm	16	2200	19
Load-bearing boards/humid conditions (P5), 3 to 4 mm	20	2550	13
Load-bearing boards/humid conditions (P5), >4 to 6 mm	19	2550	12
Medium Density Fiberboards (MDF): <sup>2</sup>			
General Purpose boards/dry conditions (MDF), >2.5 to 4 mm	23	--	35
General Purpose boards/dry conditions (MDF), >4 to 6 mm	23	2700	30
General Purpose boards/humid conditions (MDF.H), >2.5 to 4 mm	27	2700	30
General Purpose boards/humid conditions (MDF.H), >4 to 6 mm	27	2700	18
Load-bearing boards/dry conditions (MDF.LA), >2.5 to 4 mm	29	3000	35
Load-bearing boards/dry conditions (MDF.LA), >4 to 6 mm	29	3000	30
Load-bearing boards/humid conditions (MDF.HLS), >2.5 to 4 mm	34	3000	30
Load-bearing boards/humid conditions (MDF.HLS), >4 to 6 mm	34	3000	18
Hardboard Fiberboard (HB): <sup>3</sup>			
General Purpose boards/dry conditions, ≤3.5 mm	30	--	35
General Purpose boards/dry conditions, >3.5 to 5.5 mm	30	--	30
General Purpose boards/humid conditions, ≤3.5 mm	35	--	25
General Purpose boards/humid conditions, >3.5 to 5.5 mm	32	--	20
General Purpose boards/exterior (HB.E), ≤3.5	40	3600	12
General Purpose boards/exterior (HB.E), >3.5 to 5.5 mm	35	3200	10
Load-bearing boards/dry conditions (HB.LA), ≤3.5	33	2700	35
Load-bearing boards/dry conditions (HB.LA), >3.5 to 5.5	32	2500	30
Load-bearing boards/humid conditions (HB.HLA1), ≤3.5 to 5.5	38	3800	15
Load-bearing boards/humid conditions (HB.HLA1), >3.5 to 5.5	36	3600	13
Heavy-duty load-bearing boards/humid conditions (HB.HLA2), ≤3.5 to 5.5	44	4500	15

<sup>1</sup>EN 312:2003, <sup>2</sup>EN 622-5:2006, <sup>3</sup>EN 622-2:1997.

## CONCLUSIONS

1. Novel DDGS-PW composites were fabricated containing 25 to 75% distillers dried grains with solubles (DDGS): 75 to 25% paulownia wood (PW) through a phase-change process whereby the DDGS flour powder reacts with PW particles under high pressure and temperature to become a “liquid-gel” matrix to interfacially bond to the PW. Upon slow cooling, the DDGS liquid-gel transforms back into a solid to create panel boards exhibiting relatively high flexural properties.
2. FTIR analysis failed to show esterification; similarly, thermal analysis using DSC and TGA suggested that plasticization of DDGS occurs around 117 °C. XRD analysis failed to show evidence of crystallization, suggesting the DDGS and PW interaction is associated with the generation of a composite in which the binding material is amorphous in nature.
3. Pressure, temperature, PW particle size, and DDGS dosages were found to be important factors in the fabrication of DDGS-PW composite panels in terms of its flexural properties.
4. DDGS-PW composite panels were found to have similar flexural properties when compared to PRO-PW panels.
5. DDGS-PW composite panels exhibited similar water resistance properties as PRO-PW panels.
6. DDGS-PW composite panels were found to be comparable or superior to flexural properties required by Industry Standards (EN 312:2003). However, DDGS-PW composite panels were often found to be inferior in terms of water resistance (*i.e.* thickness swelling) compared to Industry Standards.

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## REFERENCES CITED

- Adhesives.org. (2017). “Science of adhesion – What is bonding?,” (<http://www.adhesives.org/adhesives-sealants/science-of-adhesion>), Accessed 01 November 2017.
- Alibaba.com. (2016). “Bulk crop commodity prices,” (<http://www.alibaba.com/>), Accessed 01 July 2017.
- Amaral-Labat, G. A., Pizzi, A., Goncalves, A. R., Celzard, A., Rigolet, S., and Rocha, G. J. M. (2008). “Environment-friendly soy flour-based resins without formaldehyde,” *J. Appl. Polym. Sci.* 108(1), 624-632. DOI: 10.1002/app.27692

- Ashori, A., and Nourbakhsh, A. (2009). "Studies on Iranian cultivated paulownia – A potential source of fibrous raw material for paper industry," *Eur. J. Wood Wood Prod.* 67(3), 323-327. DOI: 10.1007/s00107-009-0326-0
- Beg, M. D. H., Pickering, K. L., and Weal, S. J. (2005). "Corn gluten meal as a biodegradable matrix material in wood fibre reinforced composites," *Mat. Sci. Engin.* 412(1-2), 7-11. DOI: 10.1016/j.msea.2005.08.015
- California Environmental Protection Agency-Air Resources Board (CEPA-ARB) (1997). *Research Note 97-9: Topic = Indoor Emissions, Formaldehyde, Toluene* (No. 97-9), (<http://www.arb.ca.gov/research/resnotes/notes/97-9.htm>), Accessed 01 July 2017.
- Chinese Academy of Forestry Staff (1986). *Paulownia in China: Cultivation and Utilization*, Asian Network for Biological Sciences and International Development Research Centre, Singapore.
- Clarizio, S. C., and Tatara, R. A. (2013). "Tensile strength, elongation, hardness, and tensile and flexural moduli of injection-molded TPS filled with glycerol-plasticized DDGS," *J. Polym. Environ.* 21(3), 623-630. DOI: 10.1007/s10924-013-0607-x
- ClassAction.org. (2015). "Lumber liquidators class action lawsuit investigation over formaldehyde levels," (<http://www.classaction.org/lumber-liquidators>), Accessed 01 July 2017.
- U.S. Consumer Product Safety Commission (CPSC) (2013). *An Update on Formaldehyde* (Publication 725. 2013 Revision 012013), (<http://www.cpsc.gov/PageFiles/121919/AN%20UPDATE%20ON%20FORMALDEHYDE%20final%200113.pdf>), Accessed 01 July 2017.
- Deka, H., Wang, T., Monhanty, A. K., and Misra, M. (2015). "Novel biocomposites from biobased epoxy and corn-based distillers dried grains (DDG)," *J. Polym. Environ.* 23, 425-436. DOI: 10.1007/s10924-015-0739-2
- Devi, R. R., and Maji, T. K. (2013). "In situ polymerized wood polymer composite: effect of additives and nanoclay on the thermal and mechanical properties," *Mat. Res.* 16(4), 954-963. DOI: 10.1590/s1516-14392013005000071
- Elias, P., and Boucher, D. (2014). "Planting for the future," (<http://www.ucsusa.org/sites/default/files/attach/2014/10/planting-for-the-future.pdf>), Accessed 01 July 2017.
- Elling, J. (2015). "Demand for EWP products to growth through 2020," (<http://www.lbmjournal.com/demand-for-ewp-products-to-grow-through-2020/2/>), Accessed 12 July 2017.
- EN 310 (1993). "Wood-based panels—Determination of modulus of elasticity in bending and of bending strength," European Committee for Standardization, Brussels. DOI: 10.3403/00299457u
- EN 317 (1993). "Particleboards and fibreboards—Determination of swelling in thickness after immersion in water," European Committee for Standardization, Brussels. DOI: 10.3403/00299500u
- EN 323 (1993). "Wood-based panels—Determination of density" European Committee for Standardization, Brussels. DOI: 10.3403/00299563
- EN 622-2 (1997). "Fibreboards—Specifications—Part 2: Requirements for hardboards," European Committee for Standardization, Brussels. DOI: 10.3403/30101404
- EN 312 (2003). "Particleboard—specifications," European Committee for Standardization, Brussels.

- EN 622-5 (2006). “Fibreboards—Specifications—Part 5: Requirements for dry process boards (MDF),” European Committee for Standardization, Brussels. DOI: 10.3403/30112440
- Ethanolproducer.com (2017). “U.S. ethanol plants,” (<http://ethanolproducer.com/plants/listplants/US/Operational/All>), Accessed 26 October 2017.
- Frascareli, E. C., Silva, V. M., Tonon, R. V., and Hubinger, M. D. (2012). “Determination of critical storage conditions of coffee oil microcapsules by coupling water sorption isotherms and glass transition temperature,” *Intern. J. Food Sci. Technol.* 47(5), 1044-1054. DOI: 10.1111/j.1365-2621.2012.02939.x
- Frihart, C. R., Birkeland, M. J., Allen, A. J., and Wescott, J. M. (2010). “Soy adhesives that can form durable bonds for plywood, laminated wood flooring, and particleboard,” in: *Proceedings of the International Convention of Society of Wood Science and Technology and United Nations Economic Commission for Europe, Timber Committee*, Geneva, Switzerland.
- Frihart, C. R. (2011). “Influence of soy type on wood bonding performance,” in: *34<sup>th</sup> Annual Meeting of the Adhesion Society*, Savannah, GA.
- Frihart, C. R. and Birkeland, M. J. (2014). “Chapter 8: Soy properties and soy wood adhesives,” in: *Soy-based Chemicals and Materials, ACS Symposium Series*, American Chemical Society, Washington D.C., pp. 167-192.
- Frihart, C. R., Hunt, C. G., and Birkeland, M. J. (2014). “Soy proteins as wood adhesives,” in: *Recent Advances in Adhesion Science and Technology in Honor of Dr. Kash Mittal*, W. Gutowski, and H. Dodiuk (ed.), Taylor & Francis Inc., Boca Raton, FL, pp. 277-292.
- Ganesan, V., and Rosentrater, K. A. (2007). “Characterization of DDGS using differential scanning calorimetry,” in: *2007 ASABE/CSBE North Central Intersectional Conference, RRV07147*, pp. 1-10. DOI: 10.13031/2013.24188
- Gu, K., Huang, J., and Li, K. (2013). “Preparation and evaluation of particleboard bonded with a soy flour-based adhesive with a new curing agent,” *J. Adhes. Sci. Technol.* 27(18-19), 2053-2064. DOI: 10.1080/01694243.2012.696950
- Hemmilä, V., S. Adamopoulos, S., Karlsson, O., and Kumar, A. (2017). “Development of sustainable bio-adhesives for engineered wood panels—A review,” *RSC Adv.* 7, 38604-48630. DOI: 10.1039/c7ra06598a
- Hemsri, S., Grieco, K., Asandei, A. D., and Parnas, R. S. (2012). “Wheat gluten composites reinforced with coconut fibers,” *Comp.: Part A* 43(7), 1160-1168. DOI: 10.1016/j.compositesa.2012.02.011
- IDI Composites International (2017). “Troubleshooting molding problems,” ([www.idicomposites.com/pdfs/idi-molding-troubleshooting-guide.pdf](http://www.idicomposites.com/pdfs/idi-molding-troubleshooting-guide.pdf)), Accessed 01 November 2017.
- Irwin, S. (2017). “What’s up with ethanol production profits?,” *Farmdoc Daily* 7, 118. (<http://farmdocdaily.illinois.edu/2017/06/whats-up-with-ethanol-production-profits.html>), Accessed 02 February 2018.
- Jeon, J., Lee, J. H., and Kim, S. (2011). “Soybean-based green adhesive for environment-friendly furniture material,” *J. Korea Furn. Soc.* 22(3), 173-182.
- Joshee, N. (2012). “Paulownia: A multipurpose tree for rapid lignocellulosic biomass production,” in: *Handbook of Bioenergy Crop Plants*, C. Kole, C. P. Joshi, and D. Shonnard (eds.), Taylor & Francis Inc., Boca Raton, FL, USA, pp. 671-686. DOI: 10.1201/b11711-31

- Ju, Y., Liao, F., Dai, X., Cao, Y., Li, J., and Wang, X. (2016). "Flame-retarded biocomposites of poly(lactic acid), distiller's dried grains with soluble and resorcinol di(phenyl phosphate)," *Comp.: Part A* 81(1), 52-60. DOI: 10.1016/j.compositesa.2015.10.039
- Kim, Y., Mosier, N. S., Hendrickson, R., Ezeji, T., Blaschek, H., Dien, B., Cotta, M., Dale, B., and Ladisch, M. R. (2008). "Composition of corn dry-grind ethanol by-products: DDGS, wet cake, and thin stillage," *Bioresource Technol.* 99, 5165-5176. DOI: 10.1016/j.biotech.2007.09.028
- Korosten MDF Manufacture (2013). "Difference between MDF, woodfiber board and particleboard," (<http://www.kmm.ua/en/technology/the-difference-mdf-of-dsp-and-dvp>), Accessed 14 July 2017.
- Kumar, R., Choudhary, V., Mishra, S., Varma, I. K., and Mattiason, B. (2002). "Adhesives and plastics based on soy protein product," *Ind. Crops Prod.* 16(3), 155-172. DOI: 10.1016/s0926-6690(02)00007-9
- Li, J., Li, S., Wang, H., Yang, Y., and Guo, G. (2011). "Preparation of a lignin-based composite and its properties," *BioResources* 6(2), 1532-1542. DOI: 10.15376/biores.6.2.1532-1542
- Lias, H., Kasim, J., Johari, N. A. N., and Mokhtar, I. L. M. (2014). "Influence of board density and particle sizes on the homogenous particleboard properties from kelepayan (*Neolamarckia cadamba*)," *Int. J. Latest Res. Sci. Technology* 3(6), 173-176.
- Lim, C. and Yildirim-Aksoy, M. (2008). "Distillers dried grains with solubles as an alternative protein source in fish feeds," in: *8<sup>th</sup> International Symp. Tilapia Aquaculture*, Cairo, Egypt, pp. 67-82.
- Liu, Y., and Li, K. (2007). "Development and characterization of adhesives from soy protein for bonding wood," *Internat. J. Adhes. Adhes.* 27(1), 59-67. DOI: 10.1016/j.ijadhadh.2005.12.004
- Liu, K. (2011). "Chemical composition of distillers grains: A review," *J. Agric. Food Chem.* 59, 1508-1526. DOI: 10.1021/jf103512z
- Li, X. Y., Timar, M. C., Varodi, A. M., and Yi, S. L. (2016). "Effects of ageing on the color and surface chemistry of Paulownia wood (*P. elongata*) from fast growing crops," *BioResources* 11(4), 9400-9420. DOI: 10.15376/biores.11.4.9400-9420
- Lodha, P., and Netravali, A. N. (2005a). "Characterization of stearic acid modified soy protein isolate resin and ramine fiber reinforced 'green' composites," *Comp. Sci. Technol.* 65(7-8), 1211-1225. DOI: 10.1016/j.compscitech.2004.12.036
- Lodha, P., and Netravali, A. N. (2005b). "Thermal and mechanical properties of environment-friendly 'green' plastics from stearic acid modified-soy protein isolate," *Ind. Crops Prod.* 21(1), 49-64. DOI: 10.1016/j.indcrop.2003.12.006
- Lu, H., Madbouly, S. A., Schrader, J. A., Kessler, M. R., Grewell, D., and Graves, W. R. (2014a). "Novel bio-based composites of polyhydroxylaklanoate (PHA)/distillers dried grains with soluble (DDGS)," *RSC Adv.* 4(75), 39802-39808. DOI: 10.1039/c4ra04455j
- Lu, H., Madbouly, S. A., Schrader, J. A., Srinivasan, G., McCabe, K. G., Grewell, D., Kessler, M. R., and Graves, W. R. (2014b). "Biodegradation of behavior of poly(lactic acid) (PLA)/distillers dried grains with soluble (DDGS) composites," *ACS Sustainable Chem. Eng.* 2(12), 2699-2706. DOI: 10.1021/sc500440q
- Madbouly, S. A., Schrader, J. A., Srinivasan, G., Liu, K., McCabe, K. G., Grewell, D., Graves, W. R., and Kessler, M. R. (2014). "Biodegradation behavior of bacterial-

- based polyhydroxyalkanoate (PHA) and DDGS composites,” *RSC*. 16(4), 1911-1920. DOI: 10.1039/c3gc41503a
- Melo, R. R., Stangerlin, D. M., Santana, R. R. C., and Pedrosa, T. D. (2014). “Physical and mechanical properties of particleboard manufactured from wood, bamboo and rice husk.” *Mat. Res.* 17(3), 682-686. DOI: 10.1590/s1516-14392014005000052
- Mendes, L. M., Mendes, R. F., Tonoli, G. H. D., Bufalino, L., Mori, F. A., and Guimarães, J. B. (2012). “Lignocellulosic composites made from agricultural and forestry wastes in Brazil,” *Key Engin. Mat.* 517, 556-563. DOI: 10.4028/www.scientific.net/kem.517.556
- Mo, X., Cheng, E., Wang, D., and Sun, X. S. (2003). “Physical properties of medium-density wheat straw particleboard using different adhesives,” *Ind. Crops Prod.* 18(1), 47-53. DOI: 10.1016/s0926-6690(03)00032-3
- Mo, X., Hu, J., Sun, X. S., and Ratto, J. A. (2001). “Compression and tensile strength of low-density straw-protein particleboard,” *Ind. Crop Prod.* 14(1), 1-9. DOI: 10.1016/s0926-6690(00)00083-2
- Mohanty, A. K., Misra, M. and Drzal, L. T. (2002). “Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world,” *J. Polym. Environ.* 10(1/2), 19-26. DOI: 10.1023/A:1021013921916
- Nagieb, Z. A., Nassar, M. A., and El-Meligy, M. G. (2011). “Effect of addition of boric acid and borax on fire-retardant and mechanical properties of urea formaldehyde saw dust composites,” *Int J. Carb. Chem.* 2011, 1-6. DOI: 10.1155/2011/146763
- Nasir, M., Gupta, A., Beg, M. D. H., Chua, G. K., and Kumar, A. (2014). “Physical and mechanical properties of medium-density fibreboards using soy-lignin adhesives,” *J. Trop. For. Sci.* 26, (1), 41-49.
- Norström, E., Fogelström, L., Nordquist, P., Khabbaz, F., and Malmström, E. (2014). “Gum dispersions as environmentally friendly wood adhesives,” *Ind. Crops Prod.* 52, 736-744. DOI: 10.1016/j.indcrop.2013.12.001
- Pan, Z., Cathcart, A., and Wang, D. (2006). “Properties of particleboard bond with rice bran and polymeric methylene diphenyl diisocyanate adhesives,” *Ind. Crop Prod.* 23(1), 40-45. DOI: 10.1016/j.indcrop.2005.03.004
- Plastic Engineering Company (Plenco) (2015). “Philosophy of troubleshooting compression molding problems,” ([https://www.plenco.com/plenco\\_processing\\_guide/Sect%2018%20Compression%20Troubleshooting%20Guide.pdf](https://www.plenco.com/plenco_processing_guide/Sect%2018%20Compression%20Troubleshooting%20Guide.pdf)), Accessed 01 November, 2017.
- Pretsch, E., Bühlmann, P., and Affolter C. (2000). *Structure Determination of Organic Compounds--Tables of Spectral Data*, Springer-Verlag, Berlin.
- Reddy, N., and Yang, Y. (2011). “Completely biodegradable soyprotein-jute biocomposites developed using water without any chemicals as plasticizer,” *Ind. Crop Prod.* 3(1), 35-41. DOI: 10.1016/j.indcrop.2010.08.007.
- Samarasinghe, S., Easteal, A. J., and Lin, A. P. Y. (2007). “Corn gluten meal-based blends and composites,” in: *Handbook of Engineering Biopolymers, Homopolymers, Blends, and Composites*, S. Fakirov, and D. Bhattacharyya (ed.), Carl Hanser Verlag GmbH & Co. Kg, Munich, Germany, pp. 537-577.
- Shukla, R., and Cheryan, M. (2001). “Zein: The industrial protein from corn,” *Ind. Crop Prod.* 13(3), 171-192. DOI: 10.1016/s0926-6690(00)00064-9
- Stark, N. M., and Berger, M. J. (1997). “Effect of particle size on properties of wood-flour reinforced polypropylene composites,” 4<sup>th</sup> Intern. Conf. Wood fiber-plastic Comp. May 12-14, Forest Products Socl, Madison, WI, pp. 134-143.

- Tatara, R. A., Rosentrater, K. A., and Suraparaju, S. (2009). "Design properties for molded, corn-based DDGS-filled phenolic resin," *Ind. Crops Prod.* 29(1), 9-15. DOI: 10.1016/j.indcrop.2008.03.002
- Tisserat, B., Reifschneider, L., Harry O'Kuru, Rogers, and Finkenstadt, V. L. (2013a). "Mechanical and thermal properties of high density polyethylene-dried distilled grains with soluble composites," *BioResources* 8(1), 59-75. DOI: 10.15376/biores.8.1.59-75
- Tisserat, B., Reifschneider, L., Joshee, N., and Finkenstadt, V. L. (2013b). "Evaluation of *Paulownia elongata* wood polyethylene composites," *J. Thermplast. Comp. Mat.* 28(9), 1301-1320. DOI: 10.1177/0892705713505856
- U.S. Environmental Protection Agency (EPA) (2010). *Toxicological Review of Formaldehyde (Inhalation) (External Review Draft 2010)* (EPA/635/R-10/002A) Washington, D.C., ([http://cfpub.epa.gov/ncea/iris\\_drafts/recordisplay.cfm?deid=223614](http://cfpub.epa.gov/ncea/iris_drafts/recordisplay.cfm?deid=223614)), Accessed 01 July 2017.
- Uniboard Canada Inc. (2016). "Particleboard," (<http://uniboard.com/particleboard>), Accessed 14 July 2017.
- United Soybean (USB) (2010). "Advantages of soy-based adhesives," (<http://www.adhesivesmag.com/blogs/14-adhesives-blog/post/88951-advantages-of-soy-based-adhesives/>), Accessed 14 July 2017.
- Vnučec, D., Goršek, A., Kutnar, A., and Mikuljan, M. (2015). "Thermal modification of soy proteins in the vacuum chamber and wood adhesion," *Wood Sci. Technol.* 49(2), 225-239. DOI: 10.1007/s00226-014-0685-5
- Wisner, R. (2015). "Estimated U.S. dried distillers grains with solubles (DDGS) production and use," *AgMRC.*, ([www.extension.iastate.edu/agdm/crops/outlook/dgsbalancesheet.pdf](http://www.extension.iastate.edu/agdm/crops/outlook/dgsbalancesheet.pdf)), Accessed 10 July, 2017.
- Wolf, W. J. (1970). "Soybean proteins: Their functional, chemical and physical properties," *J. Agr. Food Chem.* 18(6), 969-976. DOI: 10.1021/jf60172a025
- Xu, C., Su, H., and Cang, D. (2008). "Liquefaction of corn distillers dried grains with solubles (DDGS) in hot-compressed phenol," *BioResources* 3(2), 363-382. DOI: 10.15376/biores.3.2.363-382
- Xu, H., Luo, J., Gao, Q., Zhang, S., and Li, J. (2014). "Improved water resistance of soybean meal-based adhesive with SDS and PAM," *BioResources* 9(3), 4667-4678. DOI: 10.15376/biores.9.3.4667-4678
- Zhong, Z., Sun, X. S., Fang, X., and Ratto, J. A. (2001). "Adhesion properties of soy protein with fiber cardboard," *JAOCs* 78(1), 37-41. DOI: 10.1007/s11746-001-0216-0

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