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Various Extraction Methods Influence the Adhesive Properties of Dried Distiller's Grains and Solubles, and Press Cakes of Pennycress (*Thlaspi arvense* L.) and Lesquerella [*Lesquerella fendleri* (A. Gary) S. Watson], in the Fabrication of Lignocellulosic Composites

Brent Tisserat [1,*], Fred Eller [1] and Rogers Harry-O'kuru [2]

[1] Functional Foods Research Unit, National Center for Agricultural Utilization, Agricultural Research Service, U.S. Department of Agriculture, 1815 N. University Street, Peoria, IL 61601, USA; fred.eller@ars.usda.gov

[2] Bio-Oils Research Unit, National Center for Agricultural Utilization, Agricultural Research Service, U.S. Department of Agriculture, 1815 N. University Street, Peoria, IL 61601, USA; rogers.harryokuru@ars.usda.gov

* Correspondence: brent.tisserat@ars.usda.gov; Tel.: +1-309-681-6289

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Abstract: Lignocellulosic composite (LC) panels were fabricated using an adhesive matrix prepared from three different agricultural by-products: dried distillers grains with solubles (DDGS), pennycress (*Thlaspi arvense* L.) press cake (PPC), or lesquerella [*Lesquerella fendleri* (A. Gary) S. Watson] press cake (LPC) reinforced with *Paulownia elongata* L. wood (PW) particles. The goal in this study was to assess the mechanical properties of composites utilizing these low-cost matrix materials, which were subjected to various oil extraction methods. Three types of oil extraction methods were utilized: ethanol, supercritical CO_2, and hexane, in order to generate matrix materials. These matrix materials were mixed with equal proportions of PW and hot pressed to generate panels. Overall, hexane extraction was the best method to enhance the mechanical properties of the matrices used to fabricate lignocellulosic composites. LPC's produced a matrix that gave the resulting composite superior flexural properties compared to composites generated from DDGS and PPC matrices. The mechanical properties of composites generated from soy products (soybean meal flour or soy protein isolate) were similar to those derived from DDGS, PPC, or LPC. The dimensional stability properties of LCs were improved when the hexane extraction method was employed, unlike with the other extraction methods that were used to generate matrices.

Keywords: flexural properties; panels; by-products; non-dietetic uses; modulus of rupture; modulus of elasticity

1. Introduction

The economic viability of a biorefinery is increasingly dependent on the efficient disposal of the residual seed meals to obtain a profitable revenue source [1,2]. Grain ethanol dry milling operations generally sell their solid seed meal residue by-product, i.e., dried distillers grains with solubles (DDGS), as an animal feed [3–6]. In 2016, 44.5 million tons of DDGS was projected to be generated in the USA, selling for \$0.06–0.07/lb (\$0.13–0.15/kg) [7,8]. Health concerns have arisen concerning DDGS nutritional safety due to the presence of toxins and genetic modifications [3,4,7–12]. DDGS revenues significantly aid in the profitability of biorefineries; however, DDGS prices fluctuate based on the price

of corn [1,13]. New product avenues to utilize DDGSs, which are not dependant on corn prices and nutritional health concerns, would benefit the ethanol industry.

Lesquerella [*Lesquerella fendleri* (A. Gary) S. Watson] and pennycress (*Thlaspi arvense* L.) are members of the family Brassicaceae and have been extensively studied as potential oil seed crops [2,14]. Lesquerella is native to southwestern USA, and its seeds contain ~30% oil and ~25% protein [2,15,16]. Lesquerella seeds contain high levels of the hydroxylated fatty acids, auricolic, and lesquereolic acids, which could compete with castor oil [2,14–16]. Pennycress is a winter annual grown in temperate North America and produces a seed that contains ~35% oil and ~30% protein [17,18]. The dominant fatty acid in pennycress is erucic acid, which could compete with rapeseed or canola oil [17]. However, neither plant is commercially harvested at this time due to their marginal profitability. In order to increase the revenues from these crops, other high-value products need to be identified from their seed meal residues [2,14]. Both plants have seed meals that contain high levels of glucosinolates, which precludes their use in human diets, as well as limits their use as an animal feed [18–20]. Two suggested non-dietary uses for pennycress press cake (PPC) are a soil biofumigant [20] or a filler/reinforcement material to be incorporated into plastic composites [21]. Non-dietary uses for lesquerella press cake (LPC) are a fertilizer [19], a tackifier adhesive [22,23], or a pre-cursor feed source to generate succinic acid via fermentation [24].

Engineered wood products are common building materials and are fabricated from sawmill scraps and wood wastes that are glued together by synthetic adhesives [25,26]. The majority of these adhesives is formaldehyde-based, which poses health and environmental problems [27–29]. As an alternative, bio-based adhesives using soybean meal flour (SBM), soy-protein hydrolysate, soy protein isolate (SPI), lignins, or tannins can partially or completely substitute for synthetic adhesives [27,30–32]. However, soy commercial products use as adhesives is minimal due to their high cost and higher value as a food additive [27]. Low cost and effective bio-based adhesives are needed by the engineered wood industry to replace synthetic adhesives. In this study, the adhesive properties of DDGS, LPC, and PPC in the fabrication of engineered panels were evaluated.

Our initial results revealed that non-defatted meals that retained residual oils were inferior adhesives compared to meals that were defatted [33]. This suggests that vegetable oil interferes with interfacial binding of the seed meal flour to the wood particles. Further, oil removal from meals increases protein concentration, which aids in adhesive bonding. Similarly, in other studies with plastic composites, DDGS and pennycress press cakes that were defatted prior to use made superior composites compared to those that were made with the non-defatted materials [21,34]. The focus of this study was to evaluate the mechanical properties of engineered panels fabricated with adhesive/resins derived from DDGSs and press cakes subjected to various solvent extraction techniques. Four distinct flours for each press cake or DDGS source were generated: no extraction/original material, ethanol extraction, hexane extraction, and supercritical CO_2 extraction. These methods of extraction are commonly used to extract vegetable oils from seed meal. Often, the industrial oil extraction process utilizes a mechanical extraction step whereby the oils are pressed out, producing a press cake or oilcake that contains some residual oil [35]. This press cake can be further treated with a solvent (typically *n*-hexane) to remove residual vegetable oils. Hexane solvent extraction is commonly used, but it has environmental and health issues [35]. Supercritical CO_2 and ethanol solvents are alternatives to hexane extraction [35–37]. Ethanol extraction has been found to remove sugars, oils, tocopherols, and phospholipids compared to using hexane extraction; fewer waxes were removed by ethanol extraction than by hexane extraction [35]. Supercritical CO_2 extraction utilizes the fluid state of CO_2 at or slightly above its critical temperature and critical pressure. Supercritical CO_2 is a common commercial industrial solvent because of its low toxicity and low environmental impact. The relatively low temperature employed in this process and the stability of CO_2 allows most compounds to be extracted with minimal denaturing of the original material [37]. Essentially, using the supercritical CO_2 solvent allows for removal of oils, which mimics hexane extraction.

Following the extraction step, original or defatted materials were then pulverized and sieved to a flour and employed as adhesives/resins in the preparation of high density fiberboard (HDF) panels via hot-pressing. In this study, a HDF panel was fabricated containing 50% adhesive and 50% *Paulownia elongata* L. wood (PW) family Paulowniaceae. No other additives were included in the composition that could detract or alter the adhesive nature of the matrix materials. The mechanical properties of these HDF panels were compared to the mechanical properties of panels made with soybean meal flour (SBM) or soybean protein isolate (SPI). SBM and SPI are typically employed as bio-based adhesives/resins in engineered wood composite studies [29–32]. The ultimate goal of this study was to identify the conditions that would generate alternative matrix adhesive materials that compare favorably to soy flour products. The development of technology to employ inexpensive and abundant DDGS and press cakes as an adhesive/resin matrix would eliminate the use of formaldehyde-containing substances in engineered wood and provide product avenues for these abundant and inexpensive agricultural by-products.

2. Materials and Methods

2.1. Materials and Processing Employed

DDGS were obtained from a corn dry milling processing plant located in Peoria IL (Archer Daniels Midland, Decatur, IL, USA). Lesquerella seeds were obtained from a crop grown in Arizona, and pennycress seeds were obtained from a crop grown in Peoria County, IL. Lesquerella and pennycress seeds were initially milled between rollers (Model SP900-12 roller miller, Roskamp Champion, Waterloo, IA, USA) with a gap set at 0.25 mm. Milled seeds were preheated in a cooker to 93 °C for 75 min then screw pressed with a laboratory screw press (Model L-250, French Oil Mill Machinery Co., Piqua, OH, USA) to remove crude oil and generate press cakes [38]. Press cakes (LPC and PPC) and DDGS were then treated with hexane extraction via Soxhlet extractor, supercritical CO_2 extraction, or ethanol extraction. Hexane extractions (H) were performed with a Soxhlet apparatus with the condenser attached to a recirculating chiller (Merlin^{TM} Model M75 LR, ThermoFisher Scientific, Waltham, MA, USA). The 400 g of material was placed in a cellulose thimble (90 mm diam × 200 mm length × 1 mm thickness) (I.W. Tremont LabExact®, Hawthorne, NJ, USA). Extraction conditions were as follows: solvent temperature, 70 °C; condenser cooling temperature, 12 °C; solvent volume, 6 L; and extraction time 120 h. Supercritical CO_2 extractions (SC-CO_2) were performed in a modified Hewlett-Packard 7610A gas chromatograph oven (Hewlett-Packard, Avondale, PA, USA) with plumbing as described by Friedrich and List [39]. The material to be extracted was placed in a 100-mL stainless steel extraction vessel (Thar Technologies, Inc., Pittsburgh, PA, USA) with 30-mm diam Whatman glass microfiber filter circles (Fisher Scientific, Waltham, MA, USA) on each end. Extraction conditions were as follows: temperature, 80 °C; pressure, 55.2 MPa; the solvent to feed (S:F) ratio, 15:1 (g/g); and expanded CO_2 flow rate, ca. 3 L/min. A total of ca. 600 g of each material was extracted in 8–9 separate batches (i.e., individual batches of between 65 g and 80 g). Ethanol extractions (ETOH) were also performed in the modified gas chromatograph oven. The material for these extractions was placed in a 1-L stainless steel extraction vessel (Thar Technologies, Inc., Pittsburgh, PA, USA) with 7.62-cm diam Whatman paper filters (Fisher Scientific, Waltham, MA, USA) and glass microfiber filters on each end. Extraction conditions were as follows: temperature, 80 °C; pressure, 10.3 MPa; S:F ratio, 5:1 (g/g); and ethanol flow rate, ca. 10 mL/min. A total of ca. 700–800 g of each material was extracted.

After extractions, DDGS and press cake materials were ball ground into a flour (<74 μm particles) using a laboratory bench top ball mill (Model 801CVM, U.S. Stoneware, East Palestine, OH, USA). Materials were added to alumina mill jars containing grinding pellets (U.S. Stoneware) and ground at 50 rpm for 48 h. DDGS or press cake flours were sieved via a #80 screen and were composed of ≤250 μm particles. These were the matrix materials employed in this study.

Defatted Soybean meal (SBM) flour contained ~52% protein (Prolia (200/90, Cargill Inc., Cedar Rapids, IA, USA). Soy protein isolate (SPI) flour contained ~89% protein (PRO-Fam 974; ADM, Decatur, IL, USA). Soy materials were used as provided.

Wood reinforcements materials consisted of PW shavings procured from 3-year-old trees grown in Fort Valley, GA. Shavings were successively milled through 4-, 2-, and then 1-mm screens with a Thomas-Wiley mill grinder (Model 4, Thomas Scientific, Swedesboro, NJ, USA). Next, the particles were sized employing a Ro-Tap™ Shaker (Model RX-29, Tyler, Mentor, OH, USA) fitted with 203 mm diameter stainless steel screen/sieves of #10, #12, and #30 US Standards sizes (Newark Wire Cloth Company, Clifton, NJ, USA). Shaker was operated for 60 min intervals at 278 rpm. Two PW mixtures were used throughout this study composed of 50% ≤600 μm particle selection obtained from particles passed through the #30 mesh sieve and a >600–1700 μm particle fraction obtained from particles passed through the #12 mesh sieve, and were collected on the #30 mesh sieve. Moisture content of matrix materials was ~6–8%, and PW was ~8–9%.

2.2. Compositional Analysis Method

Crude protein content of untreated and extracted DDGS and press cake samples was derived through combustion using a Protein/Nitrogen Determinator (LECO FP-528 Model 601-500, St. Joseph, MI, USA). Moisture content of the untreated and extracted samples was determined using a Halogen Moisture balance/analyzer (Model HG63, Mettler-Toledo International Inc., Columbus, OH, USA).

2.3. Panel Preparations

Lignocellulosic panels were composed of 80 g of the adhesive matrix (i.e., DDGS, LPC, PPC, SBM, or SPI) respectively, mixed with 40 g of ≤600 μm PW particles and 40 g of 600–1700 μm PW particles (Table 1). Mixing of matrix and PW was performed in a zip-lock bag using circular agitation for 15 min in a compact dryer (Model MCSDRY1S, Magic Chef, Chicago, IL, USA). Materials were then transferred to an aluminum mold (outer dimensions: 15.2 cm W × 30.5 cm L × 5 cm D; mold cavity: 12.7 cm W × 28 cm L × 5 cm D). Pressings were conducted using manual hydraulic presses (Model 4126, Carver Press Inc., Wabash, IN, USA), preheated to 185 °C under 5.6 MPa pressure for 12 min, and then heating was discontinued and the platens cooled using cold water to room temperature while still under pressure.

Table 1. Weight percentage (wt. %) of tested composite formulations.

Formulation Code	Extraction Method [1]	Matrix (wt. %)	PW [2] (wt. %)
DDGS-PW	–	50	50
DDGS/E-PW	ETOH	50	50
DDGS/CO_2-PW	SC-CO_2	50	50
DDGS/H-PW	H	50	50
PPC-PW	–	50	50
PPC/E-PW	ETOH	50	50
PPC/CO_2-PW	SC-CO_2	50	50
PPC/H-PW	H	50	50
LPC-PW	–	50	50
LPC/E-PW	ETOH	50	50
LPC/CO_2-PW	SC-CO_2	50	50
LPC/H-PW	H	50	50
SPI-PW	–	50	50
SBM-PW	–	50	50

[1] Extraction method: ETOH = ethanol extraction; SC-CO_2 = supercritical CO_2 extraction; H = hexane extraction;
[2] PW fraction contains equal portions of ≤600 μm particles and 600–1700 μm particles.

2.4. Mechanical and Dimensional Property Measurements

Following pressing, composite panels were conditioned for 96 hs at 25 °C and 50% relative humidity. Specimen test board dimensions were then cut using a table saw as prescribed by EN

310:1993 procedures [40]. Panels were cut into test sample with dimensions of 50 mm W × 127 mm L × ≈ 3.5–5.5 mm thickness. The modulus of elasticity (MOE) and modulus of rupture (MOR) tests were conducted on five test samples for each formulation using a universal testing machine (Instron Model 1122 (Instron Corp., Norwood, MA, USA) with a crosshead speed of 5 mm/min equipped with a 1 kg load cell. Density of panels was measured using EN 323:1993 standard procedures, employing five samples for each formulation [41]. Following flexural analysis panels were photographed with a digital camera equipped with a 5× optical/2× digital zoom lense (Model # DSCF707 Cyber-shot 5 MP, Sony Corp., Tokyo, Japan). Surface and sawn cross sections of panels were examined and photographed.

Water absorption (WA) and thickness swelling (TS) of composite samples were conducted on samples cut into 50 mm^2 squares that were immersed into distilled water for 24 h following EN 317:1993 procedure [42].

For each composite formulation, five specimens were tested and their averages and standard errors reported. The experimental data was analyzed statistically by analysis of variance for statistical significance and multiple comparisons of means using Duncan's Multiple Range Test ($p \leq 0.05$).

3. Results and Discussion

3.1. Amino Acid, Moisture, Oil, and Protein Evaluation

As shown in Table 2 the protein, oils, and moisture content varied somewhat among the DDGS, LPC, and PPC matrices. The protein quality and quantity in various matrices is considered to be the major factor responsible for their adhesive properties [26–28,30–32]. For the DDGS matrix fractions, DDGS/E matrix exhibited the highest protein concentration (33.1%) while DDGS matrix had the lowest (26.6%). Since this study is interested in developing an adhesive product from these materials, we compared their protein contents to soybeans, which are the commercial standards for bio-adhesives. Protein adhesives (e.g., animal protein, caseins, and soy flours) have been employed to bond wood products for several years [30]. The DDGS and press cake materials have considerably less protein than soybean materials (Table 2). Prolia and SPI contain 52% and 89% protein, respectively. The final calculated amount of protein in the composite panels for the by-product matrices varied from 13.3 (DDGS) to 17.5% (PPC/E), while the composite panels employing SBM and SPI were calculated to contain 24.3% and 44.9%, respectively.

Table 2. Percent ingredients obtained from the chemical analysis of DDGS, press cakes, and soy products and the percent protein and lignocellulosic (LC)/panel.

Matrix	Protein (%)	Moisture (%)	Oil (%)	Other (%)	Protein/Panel (%)	LC/Panel (%)
DDGS	26.6	6.1	8.0	59.3	13.3	75.4
DDGS/E	33.1	5.8	n.d. [1]	61.1	16.6	76.3
DDGS/CO_2	28.5	5.9	n.d.	65.7	14.2	78.6
DDGS/H	31.2	5.8	n.d.	63.0	15.6	77.2
PPC	29.6	8.2	8.1	54.1	14.8	72.8
PPC/E	35.0	8.1	n.d.	56.9	17.5	74.2
PPC/CO_2	34.0	8.2	n.d.	57.9	17.0	74.7
PPC/H	30.1	8.2	n.d.	61.7	15.0	76.6
LPC	28.0	8.0	7.2	56.8	14.0	74.1
LPC/E	32.6	8.2	n.d.	59.2	16.3	75.4
LPC/CO_2	32.0	8.1	n.d.	59.9	16.0	75.7
LPC/H	31.3	8.2	n.d.	60.5	15.6	76.0
SBM	52.0	5.1	n.d.	44.4	24.3	69.0
SPI	89.0	3.2	0.0	6.8	44.9	49.3

[1] n.d. = not detected.

Moisture content in the ingredients is important, because excess water disrupts production speed and product quality [30]. Similarly, we found that employment of ingredients high in moisture

(25–30%) resulted in unsatisfactory panels that exhibited blistering and cracking. This was caused by excessive steam and water explusion during the molding process. Ingredients contained a relatively low moisture content of less than 9%. As shown in Table 2, the moisture content of DDGS, LPC, and PPC varied. The amino acid profiles of the various materials studied herein are presented in Table 3.

Table 3. Amino acid profiles expressed as percentage of dry matter of the crude protein for untreated DDGS, PPC, and LPC compared with SBM.

Amino Acid	Functional Group Characteristics	DDGS [43]	PPC [44]	LPC [45]	SBM [46]
Nonpolar:					
Alanine	hydrophobic	7.4	5.1	4.9	4.4
Isoleucine	hydrophobic	4.3	4.1	3.9	4.8
Leucine	hydrophobic	12.8	7.8	6.4	7.8
Methionine	hydrophobic	2.3	1.5	1.8	1.3
Phenylalanine	hydrophobic	5.5	4.8	4.6	5.0
Proline	hydrophobic	7.8	5.8	7.3	5.0
Trytophan	hydrophobic	0.8	1.3	0.9	1.0
Tyrosine	hydrophobic	4.7	3.3	3.1	3.6
Valine	hydrophobic	5.8	5.5	5.5	5.1
Total:		**51.4**	**39.2**	**38.5**	**37.9**
Polar:					
Arginine	positive charged/basic	5.5	7.7	8.0	7.3
Histidine	positive charged/basic	3.1	2.6	2.7	2.7
Lysine	positive charged/basic	3.9	5.4	6.6	6.6
Aspartic acid	negative charged/acidic	6.6	8.9	8.2	11.4
Glutamic acid	negative charged/acidic	12.8	17.1	15.3	17.2
Serine	uncharged	4.7	4.4	4.1	4.5
Threonine	uncharged	4.3	4.9	4.6	3.8
Total:		**40.9**	**51.0**	**49.5**	**53.5**
Other:					
Cystine	thiol	2.0	1.8	2.6	1.6
Glycine	hydrogen	4.3	6.9	6.6	4.3
Taurine	sulfonic acid	–	–	–	0.2
Hydroxy lysine		–	0.0	–	–
Hydroxyproline		0.4	1.1	2.8	–
Lanthionine		–	–	–	–
Ornithine		0.4	–	–	–
Total		**7.0**	**9.8**	**12.0**	**6.0**

The percentages of amino acid varied somewhat among the press cakes, DDGS, and SBM. The functional groups of amino acids of the proteins interact with reinforcement material (wood) and contribute toward adhesion [47]. Amino acids are often classified into general groups based on their polarity and charge [47,48]. DDGS were found to have a higher percentage of non-polar hydrophobic amino acids versus polar hydrophilic amino acids than PPC, LPC, or SBM. The individual amino acid profiles are given only for archival information, since we do not know how these amino acid functional groups are oriented in the protein types.

Essentially, there are four general protein types in plant seeds, and the specific type and quantity is distinct for each species (Table 4) [43–47]. Therefore, the bio-based adhesive composition is composed of a distinct protein profile (Table 4). For example, SBM consists of 80% globulins (glycinin and conglycinin) [30,47], while for DDGS 50% of the proteins were prolamins (specifically zein) [43]. The main protein types in PPC and LPC were albumins, globulins, and glutelins [44,45].

Table 4. Protein types in seed meals based on their percentage of crude protein.

Type	Extraction Solvent	DDGS [43]	PPC [44]	LPC [45]	SBM [47]
Albumin	Water	2	34	10	–
Globulin	0.5 M NaCl	8	13	24	80
Prolamin	70% ETOH	50	–	1	–
Glutelin	0.1 M NaOH	17	23	19	–
Other	Unextracted	24	30	45	20

Very little is actually known as to how these plant proteins manifest adhesive properties, although models have been proposed [30,47–52]. Seed proteins exist in quaternary structures that have little or no adhesive properties. Seed proteins are characterized as globular structures with a hydrophobic interior [48]. Denaturation of these proteins causes them to unfold into tertiary and secondary structures, allowing them to express interior amino acids. In this study, seed proteins subjected to high temperatures and pressure were able denature and express adhesive properties. As the proteins denature or unfold, the hydrophilic and hydrophobic groups of the amino acids interact with wood carbohydrate portion through hydrogen bonding, Van der Waal forces, and cross linking to create adhesion [47,48].

We attribute the majority of the extractables to residual oils. The type of extraction method affecting extraction yields (i.e., weight of material removed from the original seed meal) for each seed meal is shown in Table 5. The hexane extraction method (H) probably extracted primarily residual oils. When SC-CO_2 was employed, lesquerella exhibited the highest extraction yield, while DDGS exhibited the lowest yield. This suggests that lesquerella contains more non-polar material that is extracted by the non-polar SC-CO_2. However, when ETOH was employed, DDGS gave the highest yield, while pennycress gave the lowest yield. We can attribute this to the removal of the residual corn oil, proteins (zein), solubles, and carbohydrates from DDGS. Winkler et al. [53] similarly reported that ETOH extraction gave higher yields for DDGS than using hexane or SC-CO_2 extraction. DDGS apparently contain a higher amount of polar compounds that are removed by the relatively polar ethanol.

Table 5. Extraction yields (%) from DDGS, PPC, and LPC using various methods.

Extraction Method	DDGS	PPC	LPC
SC-CO_2	7.6%	9.5%	10.5%
ETOH	24.7%	17.4%	17.9%
H	8.0%	8.1%	7.2%

3.2. Adhesive Properties of Materials

The optical images of the flexural panels provide information concerning how the matrix and reinforcement materials interact (Figures 1 and 2). The surface portions of the panels had a smooth topography and did not exhibit any obvious imperfections. Visible differences between the composites were mainly those of color (Figures 1 and 2). The dark portions of the panels probably represent over-concentration of the matrix materials. Generally, composites containing the original untreated matrices were usually darker in color than the composites containing the treated matrices. The cross sections revealed color changes for the matrices. For example, the LPC-PW and LPC/H-PW composites were considerably darker than the LPC/E-PW and LPC/CO_2-PW composites (Figures 1 and 2). The sawn cross sections of composites also had a smooth topography (Figure 2). Wood particles were immersed in the matrices in a random manner. Clumping of wood particles was not observed, which indicates adequate distribution of the matrices and wood particles within the composites.

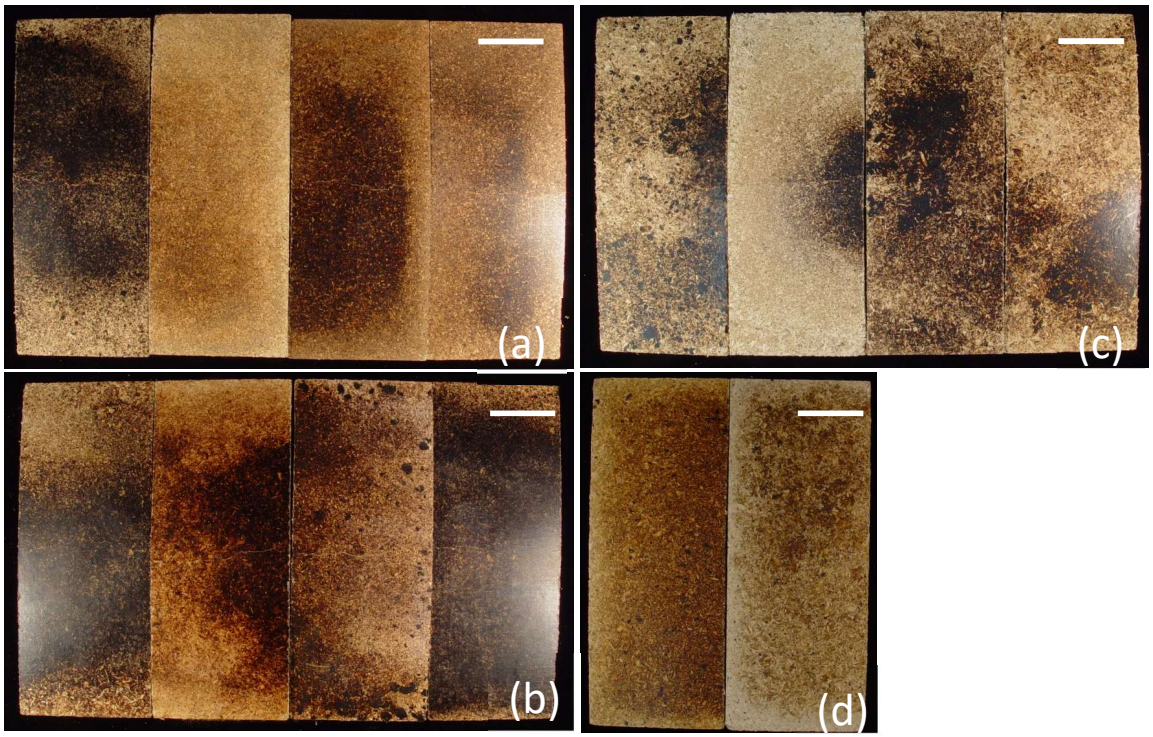

Figure 1. Examples of composite panels employed in flexural testing. (**a**) from left to right: DDGS-PW, DDGS/E-PW, DDGS/CO_2-PW, and DDGS/H-PW; (**b**) from left to right: LPC-PW, LPC/E-PW, LPC/CO_2-PW, and LPC/H-PW; (**c**) from left to right: PPC-PW, PPC/E-PW, PPC/CO_2-PW, and PPC/H-PW; (**d**) from left to right: SBM-PW and SPI-PW. Bar = 25 mm.

Figure 3 shows the flexural properties of panels fabricated in this study. The method of extraction employed on the matrix material had significant effects on the resulting panels' flexural properties. Generally, superior flexural properties were obtained from composites when the matrix material was subjected to extraction methods versus the untreated original matrix materials. For example, DDGS-PW panels exhibited modulus of rupture (MOR) and modulus of elasticity (MOE) values of 21.7 $\pm$ 1.9 MPa and 3365 $\pm$ 300 MPa, respectively, while DDGS/H-PW composite panels exhibited MOR and MOE values of 28.9 $\pm$ 2.2 MPa and 4965 $\pm$ 460 MPa, respectively. This translates in into percent increase in MOR and MOE values of +32% and +22%, respectively. For DDGS composites, no difference in flexural properties occurred comparing DDGS-PW to DDGS/E-PW, while significantly higher flexural properties were obtained from DDGS/CO_2-PW and DDGS/H-PW composites (Figure 3). In the case of DDGS/E-PW, the ethanol extraction appeared to be considerably less effective, probably due to the inadvertent removal of both carbohydrates and prolamin (zein) proteins. It is interesting to note that although this treatment (DDGS/E-PW) increased overall protein content, it still did not enhance the flexural properties over the untreated DDGS-PW composite. It is well documented that ethanol solvent is notable for removing prolamins in plant seeds [43–47]. The H and SC-CO_2 extraction generated a DDGS matrix material that had greater interfacial adhesion to the wood materials. We attribute this result to the effective removal of residual oils by these treatments. This situation is somewhat similar to that observed in hexane extraction of the DDGS results in a superior plastic composite when compared to plastic composites containing untreated DDGS [34].

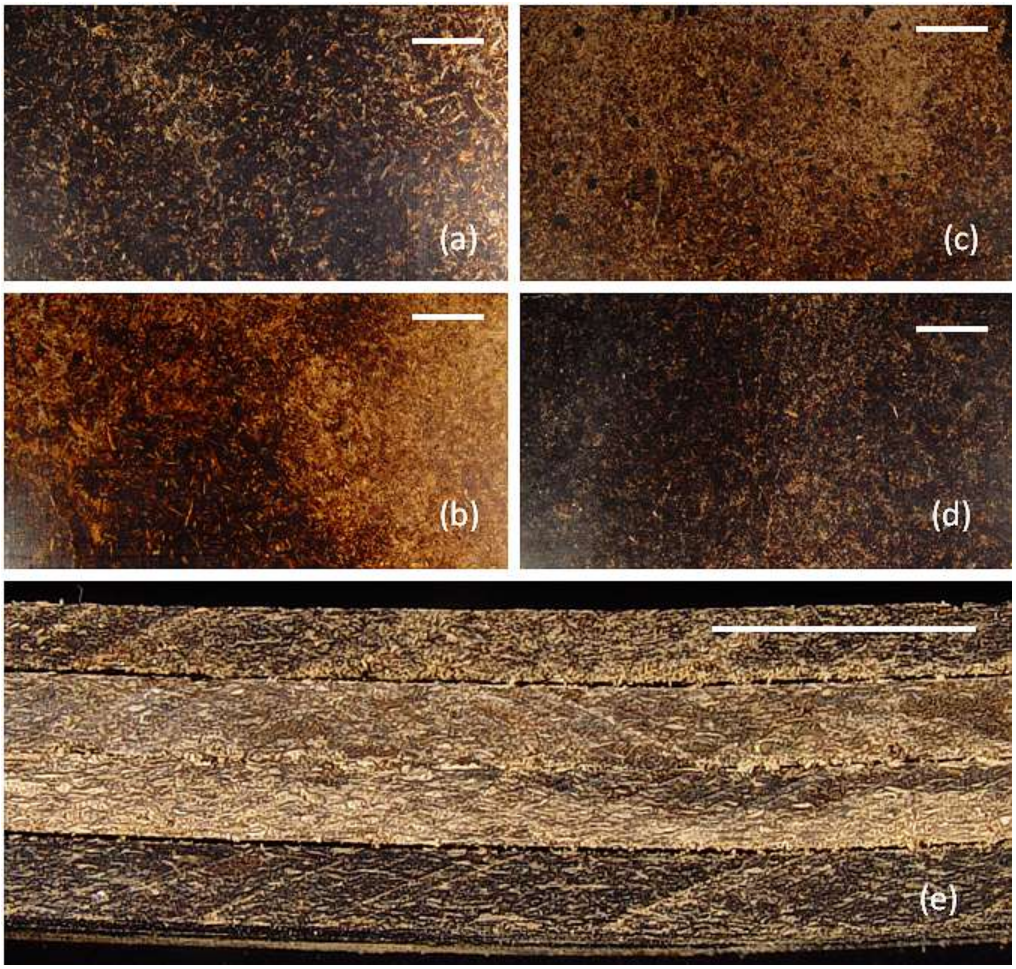

Figure 2. Optical images of surface and sawn cross sections of lesquerella composites. (**a**) LPC-PW surface; (**b**) LPC/E-PW surface; (**c**) LPC/CO_2-PW surface; (**d**) LPC/H-PW surface; and (**e**) cross sections of biocomposites, from top to bottom: LPC-PW, LPC/E-PW, LPC/CO_2-PW, and LPC/H-PW. Bar = 10 mm.

For the pennycress composites, the untreated control (PPC-PW) exhibited the lowest flexural properties compared to the composites resulting from treated substrates (Figure 3). For example, the MOR and MOE of PPC/E-PW, PPC/CO_2-PW, and PPC/H-PW composites were +101% and +114%, +149% and +140%, and +155% and +148% greater, respectively, than the MOR and MOE values of PPC-PW composite. However, the PPC/E-PW composite exhibited lower flexural values compared to the flexural properties exhibited by PPC/CO_2-PW and PPC/H-PW composites. We attribute this situation to the type of extraction method employed. Reifschneider et al. [21] reported superior mechanical performance of PPC-plastic composites if the oils were removed by hexane compared to composites prepared with PPC containing oils. Clearly, removal of oils from the agriculture by-products improves the resultant composite's performance (Figure 3).

The highest MOE and MOR values were obtained from the LPC compared to the DDGS and PPC composites. For example, MOR and MOE values of LCP-PW were +85% and +163% greater than MOR and MOE values of DDGS-PW. This suggests that LCP may have some additional adhesive properties over those of the other two materials tested that not attributed to the protein content. This observed characteristic of the LPC matrix can be rationalized from earlier reported composition of the seed polysaccharide, namely, the seed surface gum, an arabinogalactan comprising some 15% galacturonic acid residues that enhance viscosity [45,54–59]. It has been suggested that the polysaccharide gums

found in lesquerella could be employed as an adhesive [22,23]. Apparently, these results confirm these earlier observations. The combination of the proteins (30–36%) with polysaccharide gums (15–20%) results in superior adhesive properties exhibited by LPC when compared to DDGS or PPC. Extraction of LPC by ethanol and hexane extraction resulted in composites (LPC/E-PW and LPC/H-PW) that had the highest flexural properties obtained in this study (Figure 1). The MOR and MOE of LPC/E and LPC/H were +31% and +29% and +31 and +25% greater than the MOR and MOE values of LPC-PW composite. Interestingly, the supercritical fluid extraction method resulted in a composite (LPC/CO_2-PW) that had inferior flexural properties to all other LPC composites. Further research would be necessary to clarify why this particular method failed to improve the adhesive properties of LPC.

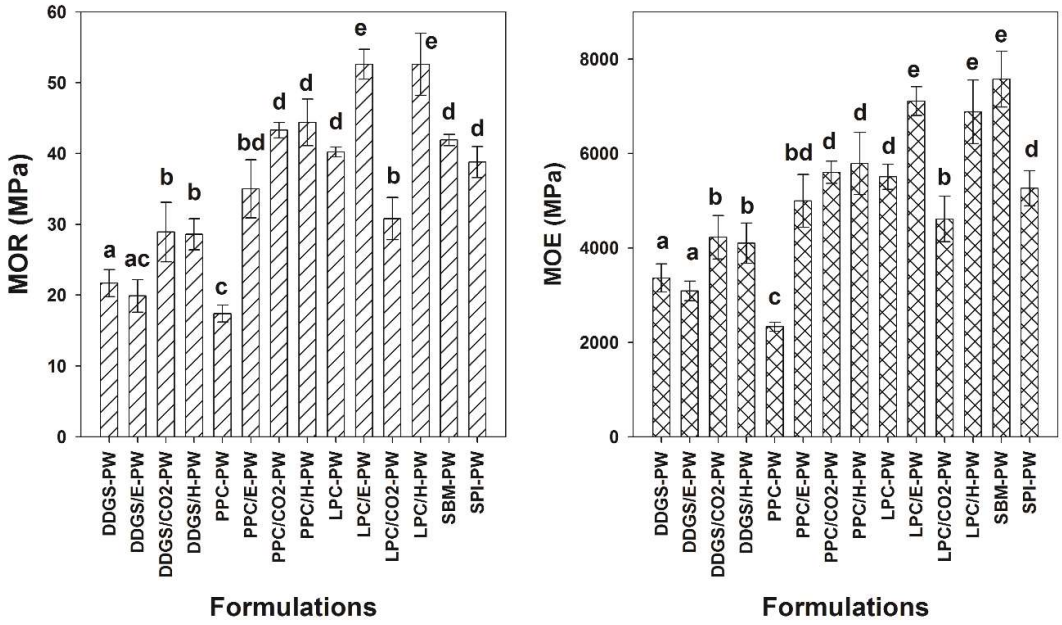

Figure 3. Mechanical properties of various panel formulations Means and standard errors are presented; treatment having different letters were significant ($P \leq 0.05$).

The highest MOE and MOR values were obtained from the LPC compared to the DDGS and PPC composites. For example, MOR and MOE values of LCP-PW were +85% and +163% greater than MOR and MOE values of DDGS-PW. This suggests that LCP may have some additional adhesive properties over those of the other two materials tested that not attributed to the protein content. This observed characteristic of the LPC matrix can be rationalized from earlier reported composition of the seed polysaccharide, namely, the seed surface gum, an arabinogalactan comprising some 15% galacturonic acid residues that enhance viscosity [45,54–59]. It has been suggested that the polysaccharide gums found in lesquerella could be employed as an adhesive [22,23]. Apparently, these results confirm these earlier observations. The combination of the proteins (30–36%) with polysaccharide gums (15–20%) results in superior adhesive properties exhibited by LPC when compared to DDGS or PPC. Extraction of LPC by ethanol and hexane extraction resulted in composites (LPC/E-PW and LPC/H-PW) that had the highest flexural properties obtained in this study (Figure 1). The MOR and MOE of LPC/E and LPC/H were +31% and +29% and +31 and +25% greater than the MOR and MOE values of LPC-PW composite. Interestingly, the supercritical fluid extraction method resulted in a composite (LPC/CO_2-PW) that had inferior flexural properties to all other LPC composites. Further research would be necessary to clarify why this particular method failed to improve the adhesive properties of LPC.

The extraction method employed to remove oils was found to profoundly affect the adhesive properties of DDGS and press cakes in the composites (Figure 3). For DDGS, supercritical fluid extraction and hexane extraction produced superior composites, compared composites employing matrices obtained from no extraction, or ethanol extraction. In the case of Pennycress, supercritical fluid extraction and hexane again gave rise to superior composites compared to unextracted matrix or ethanol extraction. However, PPC/E-PW composites obtained from ethanol extraction were clearly superior to untreated controls (PPC-PW). Superior mechanical properties were obtained in Lesquerella composites that were derived from press cakes subjected to ethanol and hexane extraction compared to untreated control composites. Extraction of LPC by supercritical fluid extraction resulted in an inferior composite (LPC/CO_2-PW) compared to composites derived from the other treatments. These results suggest hexane extraction overall appears to be the most reliable method to treat DDGS and press cakes, while CO_2 and ethanol extraction may result in an inferior composite depending on the starting material employed.

A comparison between MOR and MOE values of composites produced from a matrix of DDGS, PPC, or LPC and composites of a matrix using SBM or SPI is shown in Figure 3. The flexural properties of the SBM-PW composite were similar to several composites (e.g., PPC/CO_2-PW, PPC/H-PW, and LPC-PW). SBM and SPI matrix composites were superior to all DDGS composites (Figure 3). For example, MOR and MOE MPa values of SBM-PW were 41.8 $\pm$ 0.8 and 7.575 $\pm$ 578, respectively, compared to MOR and MOE MPa values of DDGS/H-PW, which exhibited 28.6 $\pm$ 2.2 and 4.228 $\pm$ 427, respectively. It should be noted that SBM contains ~50% protein, while the hexane extracted DDGS, PPC, and LPC contained 29%, 31%, and 36% protein, respectively (Table 2). This suggests that protein content may not be the only factor involved in the adhesive properties of these matrix materials. The SPI-PW composite contained ~45% proteins but did not exhibit greater flexural properties than the SBM-PW composite, which contained 24% protein or several other press cake composites (Figure 3). Several PPC and LPC composites (i.e., PPC/CO_2-PW and LPC/E-PW) were found to exceed the SPI-PW composite in terms of flexural properties. Several investigators have demonstrated the adhesive properties of various commercially available soy flours and products [30,32,48]. It is the contention of the authors that alternative agriculture by-products—namely, DDGS, PPC, and LPC—also have adhesive properties that may compete with soy flours.

It should be noted that those composite panels that exhibited higher densities and were thinner also exhibited higher mechanical properties compared to composite panels that had lower densities and were thicker (Figure 3, Table 6). All composite materials contained the same amount of materials and were fabricated in the same manner. The matrix material and method of extraction were responsible for the physical properties of the composite panel, which in turn influenced its mechanical properties. The panels employed in this study were unique in that they contained a high proportion of matrix material versus wood, i.e., 50:50 mixture. The matrix itself also contains a considerable amount of lignocellulosic material (~43–52%); thus, the the composite is composed of 73–79% lignocellulose and 13.3–17.5% protein (Table 2). Our lignocellulosic panels had a density between 986 to 1.256 kg/m^3. Commercial panels usually contain 85–90% wood, with the remaining components being adhesives and additives. High density fiber boards (HDF) panels have a density (900–1000 kg/m^3), and medium density fiberboards (MDF) have a density of (600–1000 kg/m^3). HDF and MDF are generally marketed in thickness varying from 3 to 12 mm in thickness. The panels employed in this study roughly correspond to HDF boards.

3.3. Dimensional Stability

It is important to ascertain the dimensional stability of our engineered panels and compare them to panels employing recognized adhesives [60,61]. The water absorption (WA) and thickness swelling (TS) of the various composites are shown in Table 6. Following 24 h of soaking composites, TS increased from 29 to 83%, while WA increased from 28 to 84% depending on the composite composition. Generally, there was a close association between the thickness and density of the TS and

WA values (Tables 6 and 7). However, the extraction method and matrix type also were contributing factors (Table 6). For example, comparing some DDGS composites, DDGS/H-PW had a thickness of 3.55 ± 0.10 mm, and a density of 1.188 ± 47 kg/m^3 exhibited TS of 42 ± 4% and WA of 37 ± 3%, while DDGS/E-PW had a thickness of 4.28 ± 0.28 mm, and a density of 986 ± 280 kg/m^3 exhibited 83 ± 4% TS and 84 ± 12% WA. Interestingly, the soy flour composites, SPI-PW and SBM-PW, exhibited relatively high TS and WA comparable to other composites tested. These results suggest that high protein content in these composites imbibes water, which adversely affects the dimensional stability. The employment of hexane extraction was found to be the most effective treatment for the various composites to improve the mechanical, physical, and dimensional stability properties (Figure 3, Table 6). Soy flour adhesives are noted to be effective in terms of their strength when compared to synthetic adhesives but exhibit poor durability, since they are susceptible to water damage [30,32,48,49].

Table 6. Dimensional Stability properties of composites soaked in distilled water for 24 h. Means and standard errors are presented; treatment having different letters in the same columns were significant ($p \leq 0.05$).

Formulations	Thickness (mm)	Density (kg/m^3)	TS (%)	WA (%)
DDGS-PW	3.84 ± 0.09 a	1.133 ± 65 a	57 ± 8 a	48 ± 5 a
DDGS/E-PW	4.24 ± 0.28 ab	986 ± 280 a	83 ± 4 b	84 ± 12 b
DDGS/CO_2-PW	3.67 ± 0.10 ac	1.156 ± 39 a	60 ± 4 a	54 ± 4 a
DDGS/H-PW	3.55 ± 0.07 c	1.188 ± 47 a	42 ± 4 c	37 ± 3 c
PPC-PW	3.44 ± 0.08 c	1.256 ± 19 a	61 ± 4 a	51 ± 3 a
PPC/E-PW	3.67 ± 0.18 ac	1.182 ± 43 a	61 ± 9 a	59 ± 11 a
PPC/CO_2-PW	3.39 ± 0.05 c	1.290 ± 18 b	31 ± 3 d	30 ± 3 d
PPC/H-PW	3.28 ± 0.03 d	1.312 ± 28 b	29 ± 4 d	28 ± 3 d
LPC-PW	3.38 ± 0.03 cd	1.296 ± 14 b	55 ± 4 a	45 ± 7 a
LPC/E-PW	3.50 ± 0.05 ac	1.239 ± 28 ab	56 ± 7 a	48 ± 6 a
LPC/CO_2-PW	4.11 ± 0.07 b	1.088 ± 117 a	62 ± 4 a	81 ± 15 b
LPC/H-PW	3.35 ± 0.04 cd	1.266 ± 19 ab	44 ± 6 ac	40 ± 3 c
SBM-PW	3.29 ± 0.04 d	1.262 ± 12 a	51 ± 2 a	49 ± 5 e
SPI-PW	3.70 ± 0.01 a	1.201 ± 18 a	73 ± 4 a	68 ± 5 e

Pearson correlation coefficients comparing the physical properties (thickness and density) of composites with their response to water (TS and WA) are presented in Table 7. There were high correlations between composite panel thickness and TS (0.775) and thickness and WA (0.898). The thicker the panel, the greater the TS and WA values. High negative correlations occur between panel density and TS (−0.753) and density and WA (−0.849). These correlations indicate a close relationship between the thickness and density of the panel and its dimensional stability.

Table 7. Pearson correlation coefficient values for the physical dimensions and dimensional stability [1].

Correlations	Thickness (mm)	Density (kg·m^{-3})	TS (%)	WA (%)
Thickness (mm)	–	−0.959	0.775	0.898
Density (kg·m^{-3})	−0.959	–	−0.753	−0.849
TS (%)	0.775	−0.753	–	0.892
WA (%)	0.898	−0.849	0.892	–

[1] All values were significant at p = 0.05 employing 5 observations.

Frihart et al. [48] noted that for a new adhesive to be accepted commercially, it must satisfy several requirements: (1) it must be abundant and have consistent properties; (2) it should be used with the typical industrial processing conditions and equipment; (3) it must have a similar viscosity compatible with existing equipment for specific processes; (4) it must not alter with the moisture content of the wood product during processing; and (5) it must provide a finished product of adequate strength and stiffness as defined by industry standards. In the wood industry, three main classes of fiberboard material classification are: interior non-structural, exterior non-structural, and structural [62–64]. In our

case, the lignocellulosic panels produced from various agricultural by-products satisfy some of these commercial requirements, especially in terms of their flexural properties, and as such are comparable to soybean flours. However, the dimensional stability of the composite panels presented in this study precludes their use in exterior applications. According to the European standards for the nominal properties of PB, MDF, and HDF, TS values are 35% and less (typically 10–25%). Only two composites (PPC/CO_2-PW and PPC/H-PW) were able to achieve TS values that were of these dimensional stability standards. European standards for HDF nominal MOR and MOE properties vary from 30–44 MPa to 2500–4500 MPa, respectively [62]. Several of the LC panels fabricated in this study satisfy these property requirements (Figure 3). In addition, these agricultural by-product adhesives are abundant (or could be if commercialized), can be employed as a powder (as soy flour often is), and confer strength/stiffness in composite panels. The dimensional stability results suggest that these agricultural adhesives should be restricted to interior non-structural uses. More research is necessary to enhance the use of these agricultural by-products to make them commercially acceptable. However, these results are a promising beginning.

4. Conclusions

Seed meal by-products generated from dry milling (DDGS) and mechanical pressing of oil seeds (PPC and LPC) have been found to have adhesive properties. Using DDGS, PPC, and LPC as an adhesive/resin with wood lignocellulosic, composites panels were fabricated that exhibited high mechanical properties. Further, the extraction of residual oils enhanced the adhesive properties of these by-products. The type of extraction method to remove oils from DDGS, PPC, or LPC profoundly affected the mechanical, physical, and dimensional stability of subsequent composites generated. Overall, the Soxhlet extraction method using hexane was most effective at removing oil, giving rise to a matrix material that produced composites with higher mechanical properties compared to the other extraction methods. Composites containing the LPC matrix had greater mechanical properties than DDGS and PPC. Several DDGS, PPC, or LPC composites were found to have more similar mechanical properties than they were when using soy flour matrix materials. There was a close relationship between composite panel thickness and density and mechanical properties. Composite panels that were thinner with higher densities usually exhibited higher mechanical properties. Dimensional stability (i.e., thickness swelling and water absorbance) was found to be correlated with panel thickness and density. Overall, composite panels from hexane-treated matrix materials exhibited better dimensional stability than composite panels that were not. Further, several composite panels employing DDGS, PPC, or LPC exhibited better dimensional stability than composite panels employing soy flours.

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