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ORIGINAL PAPER

Fabrication of Natural Fiber Composites Consisting of Osage Orange Seed flour Reinforced with Non-woven Hemp Mats

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Abstract
Natural fiber composites (NFC) were fabricated using a matrix consisting of an aqueous slurry of Osage orange (*Maclura pomifera* (Raf.) Schneid. family Moraceae) seed meal (OOSM) (50, 75 or 100 g L^{-1}) reinforced with non-woven hemp mats (450, 650, 800, 1000, 1200, or 1350 g m^{-2} surface densities). OOSM behaves as a thermoset adhesive/resin similar to soy flours. Non-woven mats of 7.6 cm W × 17.8 cm L of various surface densities were soaked in aqueous slurries for 30 min under vacuum and then directly hot pressed at 185 °C and 4.3 MPa for 4:30 min. NFCs matrix:reinforcement percentages varied depending on the surface density of the hemp mat employed. NFCs were evaluated for their mechanical, physical and dimensional stability properties. The OOSM slurry matrix was found to be as effective as matrices generated from soy flour or soy protein isolate slurries. The influence of various temperatures for processing was also evaluated.

Keywords Bio-based composites · Flexural properties · Tensile properties · Soy flour · Soy protein isolate · Surface roughness · Thermoset

Introduction

Composites consist of two components: a fiber portion that provides a discontinuous phase responsible for addressing load and a matrix that provides a continuous phase responsible for binding and transferring the load to the fibers [1]. Fibers employed in composites may be either synthetic (e.g., glass) or non-synthetic natural fibers (NF) (e.g., cotton, flax, hemp, jute, kenaf, or sisal). Advantages NFs have over synthetic fibers are cost, biodegradability and reduced density [2–8]. Typically, natural fiber composites (NFC) employ non-woven NFs arranged discontinuously and are imbedded in a continuous synthetic resin matrix such as thermoplastics (e.g., polypropylene or polyethylene) or thermosets (e.g., phenolic, polyester or epoxy resins) [1, 2, 9].

The NFCs industry was valued at $2.1 billion in 2010 [5]. NFCs are extensively employed in the automotive industry for non-structural applications [10]. NFCs may consist of a non-woven or woven (textile) mats. Non-woven mats cost considerably less than fabric textiles. Textiles are flexible woven materials composed of interlaced fibers which contribute to its uniform strength and properties. Non-woven materials are composed of disordered (isotropic), non-uniform fibers of varying lengths and thickness, and results in a product with varying densities occurring within the same mat [2]. The chemical and structural properties of the fibers greatly influence the mechanical properties of NFCs [1, 3, 5–7]. The interaction between the matrix and the fiber reinforcement is an important factor to obtain NFCs with high mechanical properties. Most matrices employed in NFCs are synthetic resins derived from petroleum sources [3, 6, 7]. NFCs containing synthetic resins do not biodegrade and are difficult to recycle; therefore they create environmental problems when disposed of.

In order to address the environmental problems associated with utilizing synthetic resins, bio-based resins such as polylactic acid (PLA) or polyhydroxyalkanoates (PHA) are increasingly being employed in NFCs [6, 7]. In addition, another potential adhesive/resin matrix that can be used in NFCs is soy flours [11–18]. Soy flour acts as a thermoset adhesive/resin [19, 20]. Thermosets cannot be re-melted once set and therefore are relatively heat resistant. Unfortunately, soy flours are expensive and are more profitable

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employed in food products than as adhesives [19, 20]. Soy flour and soy protein isolate (SPI) sell for ~$0.70/lb ($1.54/kg) and $1.70/lb ($3.96/kg), respectively [21, 22]. Further, PLA and PHA are also relatively expensive costing ~$1.00/lb ($2.20/kg). There is a great need to identify low cost bio-based adhesives/resins.

Osage orange (*Maclura pomifera* (Rafin.) Schneider, Family Moraceae) is a native tree from the southeastern portion of the United States but has established itself throughout the USA especially in the Midwest. Osage orange (OO) trees are invasive, fast-growing, capable of coppicing, and can be densely planted [23, 24]. These trees produce abundant large-sized fruits (10.2–12.7 cm in diam) that contain numerous seeds [23, 25]. OO trees have been recognized to have bio-energy applications through the production of fuels from their woody biomass and bio-diesel from their seed oil [23, 24]. OO seeds are composed of 34% protein, 6% moisture, 33% fat, and 7% ash [23, 25]. One hundred OO trees/ha could produce 1800 L oil/ha/year; thus making this tree oil yield very competitive to agricultural oil crops (e.g., oil yield (L)/ha/year for crops: 1340 for rapeseed, 560 for soybeans and 750 for sunflower, respectively). Commercial extraction of OO oil from seeds has recently been initiated by HTO LLC, Monmouth, Illinois [26]. The by-product of bio-diesel processing of oil seeds is the seed meal residue, which accounts for 60–75% of the seed weight. To maximize profits in the processing of OO seeds for industrial oils, a use for the residual OO seed meal (OOSM) needs to be developed. OOSM is not consumed as a food product and has no commercial or monetary value to date.

In this study, "novel" bio-based adhesives/resins were derived from OOSM that can be used to fabricate NFCs. OOSM binding mimics that of soy flours. The goal of this study was to develop a non-dietetic use for OOSM as adhesives/resins to product NFCs. Hemp mats served as the reinforcement portion of the NFC since they are commonly commercially employed in this function [27]. Emphasis will be placed on optimizing the conditions to obtain NFCs with high mechanical properties. The influence of the preparation procedure, mat surface density, matrix concentration, and temperature used in processing were studied. The mechanical, physical and dimensional stability properties of the NFCs generated were determined. Since soy flours are commonly employed as bio-based adhesives/resins they were incorporated as part of the scope of this project for comparative purposes.

Materials and Methods

Materials Employed

Osage orange fruit were collected from trees grown in McLean, Peoria and Tazewell Counties, Illinois in 2015. OO fruits were soaked in water for 3 weeks to dislodge the seeds from the fruit portion. Extracted seeds were air dried. Seeds were milled using a Thomas-Wiley mill grinder (Model 4, Thomas Scientific, Swedesboro, NJ, USA) through a 2 mm screen mesh. The resultant OOSM was defatted in a Soxhlet extractor with hexane. OOSM were further finely ground with a laboratory bench top ball mill (Model 801 CVM, U.S. Stoneware, East Palestine, OH, USA) using milling jars containing grinding pellets. Ground OOSM was further sieved through a #80 screen to produce ≥ 177 µm particles to obtain the final matrix material. This defatted OOSM contains 44% protein, 6% moisture, and 3% ash. Defatted soybean meal flour, Prolia 200/90 (Mesh size screen thru/Protein index value) was obtained from Cargill Inc., Cedar Rapids, IA, USA. Prolia contains ≈54% protein and was factory sieved through a #200 screen. SPI (ProFam 974) was obtained from ADM Co., Decatur, IL, USA. SPI containing ≈90% protein, 6% moisture, 4% fat, and 5% ash and was factory sieved through a #100 screen. Prolia and SPI were used as provided. Hemp (*Cannabis sativa* L.) non-woven mats of various surface densities: 450, 650, 800, 1000, 1200, or 1350 g m^{-2} were obtained from HempFlax BV, Oude Pekela, Netherlands and employed as provided. Non-woven mats consist of 100% hemp fibers that were 40 µm in diam and 40–80 mm in length. The aspect ratio varied from 1000 to 2000. Hemp mats consisted of 66% cellulose, 16% hemicellulose, 4% pectin, 1% fat and wax, 12% moisture, and 2% minerals [27]. The physical properties of these mats are shown in Table 1.

NFC Preparations

The general method to prepare NFCs is described here. Slurries of OOSM were prepared by adding 10, 15 or 30 g of OOSM to 200 ml distilled water (50, 75 or 100 g L^{-1} OOSM-aqueous solution) in a beaker and mixed with a magnetic stirrer at 100 rpm for 30 min. The slurry was poured into an aluminum drip pan (13 cm W × 21 cm L × 3 cm H × 600 mm^3 cap.) (Webber-Stephne, Palatine, IL, USA). Hemp mats of 450, 650, 800, 1000, 1200, or 1350 g m^{-2} surface densities were cut into 7.6 cm W × 17.8 cm L pieces and submerged in this slurry while being pressed down with a clear acrylic Plexiglas weight predrilled with several openings to facilitate air bubble release. The pan containing the slurry and mat was then transferred to a Pyrex vacuum chamber (19 cm W × 24 cm L × 7 cm H × 2600 mm^3 cap.) (Best Value

Table 1 Physical properties of hemp reinforcement mats

Product code	Surface density (g m^{-2})	Thickness (mm)	Weight (g)	Density (kg m^{-3})	Void volume (%)
6000902	450	3.5	30	137.4	77
6000910	650	6	41.1	109.8	79
6000911	800	8	49.5	99.2	83
6000915	1000	8	62.4	125.1	81
6000921	1200	10	74.4	119.3	82
6000930	1350	12.5	80.7	103.5	83

Product codes and surface density specifications were provided by manufacturer: HempFlax BV, Oude Pekela, Netherlands. Area of original mats was 623.7 cm^2 (21 cm W × 29.7 cm L)

Vacs, Naperville, IL, USA). Mats were put under vacuum at -29 in Hg (−9.8 bar) for 30 min. Air bubbles were emitted from the mats under vacuum but they eventually ceased. Mats were then removed with a pair of forceps from the solution and the excess slurry was allowed to drain from the mat followed by lightly pressing with a spatula. Drained mats were transferred into an aluminum mold consisting of a frame (10.2 cm W × 20.3 cm L × 1.9 cm H) with a cavity (7.6 cm W × 17.8 cm L × 1.9 cm H) and a base plate (15.2 cm W × 22.2 cm L × 0.6 cm H) which was attached to the frame with 6 screws. An aluminum plunger (7.6 cm W × 17 .8 cm L × 1.9 cm H) was employed to press the treated mat. The treated mat was cold-pressed at room temperature by the application of the plunger to eliminate air and compress the composite materials. Excess slurry solution was emitted during this pressing which was wiped off the mold with a paper towel. Finally, the mold was put into Carver press pre-heated to 185 °C, unless otherwise indicated. Mold was initially pressed to 2.2 MPa and held for 1 min and pressure was released to remove air. The mold was pressed again to 3.3 MPa and held for 1 min and pressure released. The mold was pressed to 4.3 MPa and held for an additional 2:30 min and the pressure was again released. The total heating/compression time is 4:30 min. The mold was removed from the hot press to a laboratory bench to cool prior to opening in order to retrieve the dried NFC.

Dry and Wet Hemp Mat Preparation Methods

Hemp mats with a surface density of 450 g m^{-2} were soaked in a 50 g L^{-1} aqueous solution of OOSM for 30 min and then transferred to a convection oven set at 60 °C until dried. These dried OOSM mats were then hot pressed as previous discussed. As a control, hemp mats were prepared in the same solution but directly hot-pressed as previously described.

Influence of Mat Surface Density

Hemp mats of 450, 650, 800, 1000, 1200, or 1350 g m^{-2} surface densities were soaked in 50 g L^{-1} aqueous solution of OOSM for 30 min under vacuum and then directly hot pressed as previously described.

Influence of Slurry Concentration

Aqueous slurries were prepared using 50, 75 or 100 g L^{-1} concentrations of Prolia, SPI or OOSM. Hemp mats of 450 g m^{-2} were soaked in these various aqueous solutions under vacuum for 30 min. Treated mats were hot-pressed as previously described.

Influence of Hot-press Temperature

Hemp mats of 450 g m^{-2} were soaked in a 75 g L^{-1} aqueous solution of OOSM under vacuum for 30 min. Treated mats were then subjected to direct hot-pressing at 140, 150, 175, 185, or 200 °C as previously described.

Physical Properties Measurements

NFC and mat thickness were measured using a Precision micrometer, Model No. 49–63 (Testing Machine Inc., Amityville, NY). The void volume percentage within the mats was determined by using the following equation:

$$\text{Void volume}(\%) = \frac{\text{Orginal mat density (kg m}^{-3})}{\text{Hot pressed mat density (kg m}^{-3})} \times 100$$

Hot pressed mat density was determined by pressing the original mat devoid of the OOSM slurry matrix as previously described in the NFC preparation section. Porosity of the NFC was determined using the following equation [28]:

$$\text{NFC porosity}(\%) = \frac{1 - \text{NFC density (kg m}^{-3})}{\text{Hot pressed mat density (kg m}^{-3})} \times 100.$$

Hot pressed OOSM density was determined by pressing the defatted OOSM flour as previously described in the NFC preparation section.

Surface roughness properties of the NFCs and mats were obtained using a portable Surface Roughness Measuring Tester, Model SJ-210 (Mitutoyo Corp., Kanagawa, Japan) equipped with a stylus profile detector. Average roughness (R_a), mean peak-to-valley height (R_z) and maximum roughness (maximum peak-to-valley height) (R_y) were characterized according to ISO 4287:1997. NFCs were subjected to five surface roughness readings. Tester specifications were: speed: 0.5 mm/s, pin diameter: 10 µm and pin angle: 90°. Tracing line (L_t) length was 12.5 mm and cut-off (λ_x) was 2.5 µm. Measuring force of the scanning arm was 4 mN. The detector was calibrated prior to tests and all tests were conducted at room temperature (25 ± 2 °C). Dimensional stability tests [percent water absorbance (WA) and percent thickness swelling (TS)] were determined for NFCs containing 450, 650, 800, 1000, or 1200 g m^{-2} hemp mats. Specimen bars from NFCs of varying surface densities were incubated at 100% R.H. for 24 h prior to recording WA and TS values. To evaluate the dispersion of fibers and matrix in the NFCs and mats specimens were examined and photographed using a Wild Heerbrugg M5 Stereo dissecting microscope (Leica Microsystems GMbH, Wetzlar, Germany).

Mechanical Property Measurements

NFC test specimen bars were cut with a clipper press to obtain 1.27 cm W × 6.4 cm L × ~ 0.2 cm thick samples. All samples were conditioned at room temperature (25 ± 2 °C) under 50% relative humidity for 10 d prior to evaluations. A modified ASTM D638 test using a universal testing machine (UTM), Instron Model 1122 (Instron Corporation, Norwood, MA) was employed to obtain the tensile strength (σ_u), Young's modulus (E) and elongation at break (%El). Test speed was 5 mm/min. ASTM-D790 test was conducted on the Instron UTM. Flexural strength or modulus of rupture (σ_{fm}) and flexural modulus of elasticity (E_b) were determined using Procedure B with a test crosshead speed of 13.5 mm/min.

Statistical Analysis

Significant differences between the average values for groups were determined using Duncan's multiply range test. Where applicable, Pearson correlations coefficients were determined comparing various recorded variables (Statistix 9, Analytical Software, Tallahassee, FL, USA).

Results and Discussion

Influence of Pressing Procedures

Most work conducted with plant seed meal (e.g., soy and cottonseed meal) adhesives is concerned with its effectiveness to bind to wood [19, 20, 29]. Soy and cottonseed meal flour adhesives/resins behave as thermosets whereby they are converted from a solid to a molten form (gel point) via high temperature. In this form they become a viscous liquid state that intimately interacts with the reinforcement material and then solidifies (sets) to create the final bonding matrix. The active component in seed meal bio-based adhesives is considered to be uncoiled protein polymers that occur in irregular, unpredictable patterns that are capable of binding with wood or reinforcement materials [19, 20]. A quick method to evaluate the effectiveness of seed meal bio-based adhesives is to prepare a seed meal aqueous slurry and apply it using a brush to wood strips that are then hot-pressed [19, 20, 29]. These bonded strips are subsequently tested with a UTM for their adhesive properties. OOSM bonding activity probably behaves similarly as the soy and cottonseed meal adhesives. OOSM when mixed with water readily produces a slurry that can sufficiently penetrate and coat hemp fiber mats. The direct hot-pressing process removes excess solution and induces the remaining OOSM to gel into an adhesive that binds to the hemp mat fibers to create a NFC. This procedure is termed the direct-press method. Alternatively, a procedure of slowly drying the slurry-hemp mat NFC in an oven at 60 °C prior to a final hot pressing was also employed and is termed the oven dried-press method.

NFCs produced from the oven dried-press method versus NFCs derived from the direct-press method exhibited substantial differences in their mechanical properties (Fig. 1). NFCs that were oven dried prior to hot pressing exhibited significantly lower mechanical properties compared to NFCs that were direct-pressed wet. NFCs generated by the direct-press method had E, σ_u, %El, σ_{fm}, and E_b values that were 159, 108, 12, 160, and 537% greater respectively, than of NFCs generated by the oven dried-press method. The oven dried-pressed NFC had higher matrix values than direct-pressed NFCs. This indicates that less matrix was lost using this procedure. However, the oven dried-pressed NFCs exhibited a much higher porosity (void volume) percentage, ~ 40% higher, than direct-pressed NFCs. As noted in Table 2, the oven dried-pressed composites were 26% thicker than the direct-pressed composites although the weights of both composites were similar. This resulted in oven dried-pressed composites having less density, ~ 36% less, than the direct-pressed composites. These physical factors contributed toward poor interfacial binding between the OOSM proteins and hemp fibers which in turn were responsible for

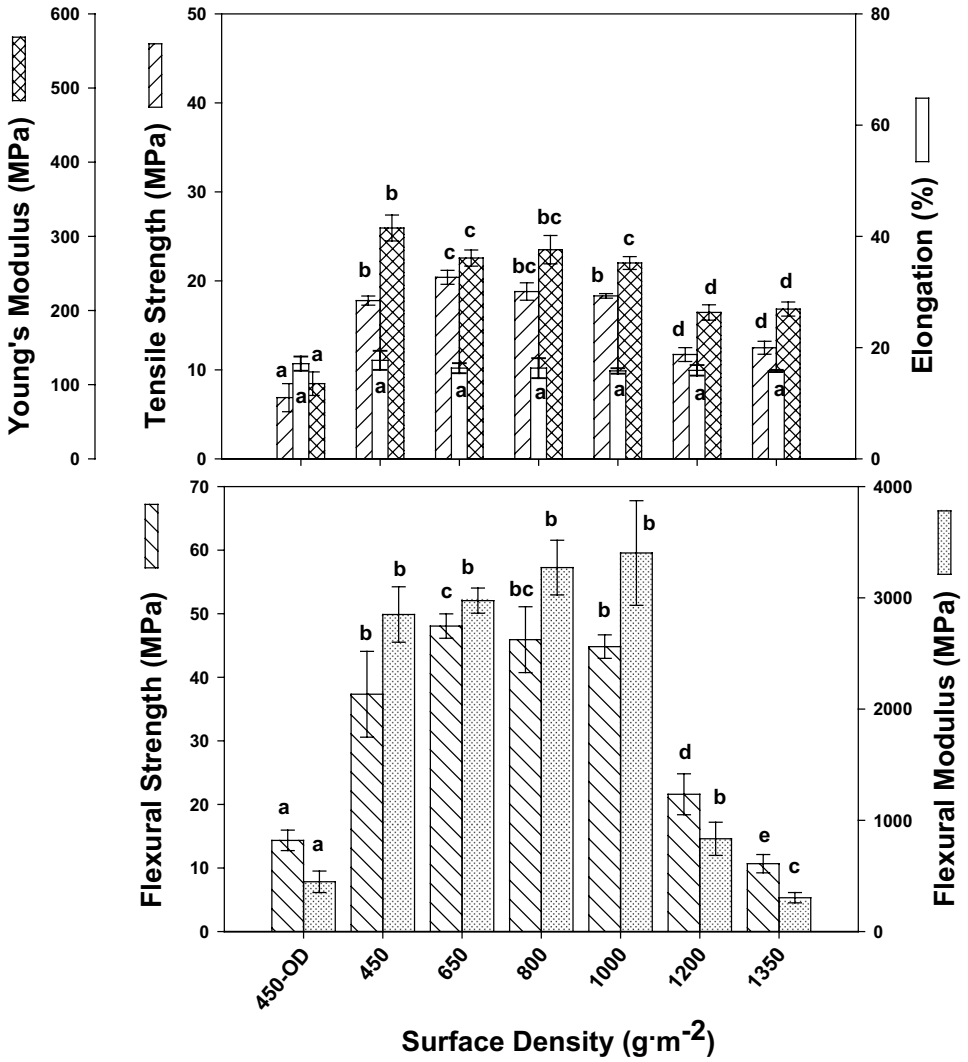

Fig. 1 Comparison of the mechanical properties of NFCs derived from oven dried-pressed (OD) and direct-pressed methods fabricated with hemp mats of various surface densities. Matrix material consisted of a 50 g L^{-1} OOSM slurry. Means with standard errors derived from five different replicates are presented. Mechanical values with different letters were significantly different ($P < 0.05$) according to Duncan's multiple range tests

Table 2 Physical properties of NFCs derived from oven dried-pressed (OD) and direct-pressed methods fabricated with various hemp mats

Mat surface density (g m^{-2})	Composition (Matrix:Mat) (%)	Thickness (mm)	NFC density (kg m^{-3})	Porosity (%)	R*a* (μm)	R*z* (μm)	Ry (μm)
450-OD	33:67	1.03 ± 0.02a	674 ± 21a	48	4.3 ± 1.0a	23.0 ± 2.2a	37.5 ± 8.3a
450	25:75	0.76 ± 0.01b	916 ± 8b	29	3.2 ± 0.7b	16.5 ± 2.2b	25.6 ± 4.1b
650	12:88	0.85 ± 0.03c	981 ± 10b	24	5.2 ± 0.7c	28.4 ± 3.6c	44.4 ± 5.6a
800	12:88	0.75 ± 0.02b	1022 ± 30b	21	6.9 ± 2.1c	33.2 ± 5.4c	49.7 ± 8.1ac
1000	14:86	0.93 ± 0.03d	940 ± 19b	27	8.3 ± 1.3d	34.0 ± 3.7c	55.8 ± 5.3c
1200	8:92	1.45 ± 0.02e	891 ± 15b	31	9.2 ± 1.5d	36.4 ± 3.7c	58.4 ± 6.9c
1350	8:92	1.41 ± 0.04e	792 ± 9c	39	9.3 ± 1.1c	45.1 ± 8.5c	71.4 ± 9.7d

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

the poor mechanical properties of oven dried-pressed composites (Fig. 1; Table 2). Surface roughness properties of the composites are attributed to a variety of factors including: material characteristics, species, particle sizes, distribution of ingredients, fabrication variables, pressing parameters, and surface densification [30–32]. Surface irregularities of the composites detected by a surface roughness tester represent the degree of compaction and bonding of the

ingredients of the composite [30, 32]. Oven dried-pressed composites exhibited higher surface roughness values compared to direct-pressed composites. R_a, R_z and R_y values of oven dried-composites were 26, 28 and 32% greater, respectively, than that of direct-pressed composites (Table 2). High surface roughness values reflects poor interfacial binding between the OOSM matrix to the hemp fibers causing surface irregularities and thus contributing to weaker mechanical properties. Based on these results, only the direct-pressed method was used hereafter.

Influence of the Various Mat Surface Densities

Commercial needle punched non-woven mats contain fibers arranged in a semi-isotropic manner and are produced with various surface densities (Table 1). Table 2 shows the physical properties of the NFCs that contained mats of various surface densities that were immersed in a 50 g L^{-1} OOSM slurry and then subjected to a direct hot pressing. It should be noted that the mechanical properties of the original hemp mats, regardless of their composition (e.g., 450–1350 g m^{-2} mat surface densities), were negligible and therefore are not reported. The original hemp mats were found to consist of high void volumes (77–83%) (Table 1). In contrast, NFCs contained low porosity percentages (29–39%) which was attributed to the hot pressing procedure which caused binding between the matrix and the reinforcement mats. The surface roughness properties of the original mats could not be accurately accessed without compressing the mats and thus creating artificial results; therefore they are not reported. This situation was due to the irregular topographic characteristics of the mats. In contrast, NFCs created by immersion of mats in the OOSM slurry and direct hot-pressing had easily detectable surface roughness values (Table 3). As shown in Table 2, NFCs made with mats with high surface densities generally have greater thickness, weights, and surface roughness values versus NFCs reinforced with mats of low surface densities. It is of interest that NFCs composed of the lower surface density mats (i.e., 450–1000 g m^{-2}) had higher densities than NFCs composed of higher surface density mats (i.e., 1200 and 1350 g m^{-2}) (Table 2). As shown in Table 2 the percentage of matrix versus percentage of mat (reinforcement) varies considerably among the NFCs depending on the surface density of the hemp mat employed. The highest percentage of matrix retained in the NFC was obtained by employing the 450 g m^{-2} hemp mat. The least percentage of matrix retained in the NFCs occurred when the 1200 or 1350 g m^{-2} hemp mats were employed. Essentially, NFCs composed of higher surface density mats had more fibers than NFCs composed of lower surface density mats. The slurry employed could not adequately coat these additional fibers which resulted in inferior mechanical properties.

Table 3 Pearson correlation coefficient values for the physical properties of the NFCs fabricated by direct-pressing various mat types with a 50 g L^{-1} OOSM aqueous slurry

Correlations	Mat surface density (g m^{-2})	Thickness (mm)	NFC density (kg m^{-3})	R_a (μm)	R_z (μm)	R_y (μm)
Mat surface density (g m^{-2})	–	0.897*	⁻0.619	0.974*	0.923*	0.943*
Thickness (mm)	0.897*	–	⁻0.799*	0.780*	0.718*	0.765*
NFC density (kg m^{-3})	⁻0.619	⁻0.799*	–	⁻0.445	⁻0.477	⁻0.514
R_a (μm)	0.974*	0.780*	⁻0.445	–	0.936*	0.952*
R_z (μm)	0.923*	0.718*	⁻0.477	0.947*	–	0.995*
R_y (μm)	0.943*	0.765*	⁻0.514	0.952*	0.995*	–

*Values with asterisks were significant at P = 0.05 employing 5 observations

Table 4 Pearson correlation coefficient values for the mechanical properties of the NFCs fabricated by direct-pressing various mat types with a 50 g L^{-1} OOSM aqueous slurry

Correlations	Mat surface density (g m^{-2})	σ_u (MPa)	E (MPa)	%El (%)	σ_{fm} (MPa)	E_b (MPa)
Mat surface density (g.m^{-2})	–	⁻0.808*	⁻0.945*	⁻0.745*	⁻0.733*	⁻0.756
σ_u (MPa)	⁻0.808*	–	0.858*	0.250	0.946*	0.937*
E (MPa)	⁻0.945*	⁻0.858*	–	0.676*	0.802*	0.876*
%El (%)	⁻0.745*	0.250	0.676*	–	0.168	0.279
σ_{fm} (MPa)	⁻0.733*	0.946*	0.802*	0.168	–	0.972*
E_b (MPa)	⁻0.756	0.937*	0.876*	0.279	0.972*	--

*Values with asterisks were significant at P = 0.05 employing 5 observations

Pearson correlation coefficients comparing the physical properties of the various NFCs prepared in this study are shown in Table 4. Correlation is an important test to determine the linear association between two continuous variables. Several of the physical properties had high correlations with each other (Table 3). For example, very high positive correlations occurred between surface density and surface roughness (R_a, R_z and R_y) values. High positive correlations occurred between the thickness and surface roughness values. Very high correlations occurred between all the surface roughness values. These correlations suggest strong associations occurred between the surface densities of the mats and the physical values of the NFCs. However, there was low correlation between surface density and density values (Table 3).

Figure 1 shows the mechanical properties of NFCs as influenced by the hemp mat employed. Higher mechanical values occurred in the composites utilizing mats with surface densities of 1000 g m^{-2} or less (Fig. 1). For example, σ_u, E, %El, σ_{fm}, and E_b values of NFCs utilizing mats with a surface density of 450 g m^{-2} were 30, 52, 22, 71, and 89% greater, respectively, than NFCs utilizing 1350 g m^{-2} mats. We attribute this situation to greater interfacial bonding occurs between the OOSM matrix and hemp fibers using the less surface dense mats than between OOSM matrix and high surface dense mats. NFCs composed of the higher surface denser mats (i.e., 1200 and 1350 g m^{-2}) apparently prevented the slurry solutions from adequately penetrating sufficiently and affected the interfacial bonding between the matrix and the fibers. Based on these results, we employed the 450 g m^{-2} non-woven mats for the rest of this study.

Table 4 shows the Pearson correlation coefficients comparing the mechanical properties of the various composites conducted in this study. Several mechanical properties values (σ_u, E, σ_{fm}, and E_b) had high correlations with each other (Table 4). In addition, high positive correlations occurred between surface density and σ_u, E, %El, and σ_{fm} values.

The dimensional stability properties (WA and TS) of NFCs were similar regardless of the reinforcement mat employed (Table 5). These results suggest that the matrix coating and bonding of the reinforcement mats were relatively similar and uniform for these NFCs. NFCs prepared with the OOSM matrix were inferior to that of NFCs prepared with polyethylene or PLA [17, 33]. For example, a NFC consisting of a matrix of 60% polyethylene and a reinforcement of 40% walnuts soaked in water for 24 h exhibited 0.3% WA and 0.2% TS [33]. A NFC consisting of a matrix composed of matrix of an 85% mixture of 40%PLA:60% soy flour and a reinforcement of 15% bagasse soaked in water for 24 h exhibited 37.9% WA [17]. In contrast, a NFC consisting of a matrix of 25% OOSM and a reinforcement of 75% hemp fibers consisting of a 450 g m^{-2} surface density mat soaked in water for 24 h exhibited 64.3% WA and 32.4% TS. Clearly, a hydrophobic coating should be administered to improve the dimensional stability properties of the OOSM-hemp NFCs.

Table 5 Dimensional stability properties of NFCs composed of various surface density hemp mats after being soaked in water for 24 h

Mat surface density (g m^{-2})	WA (%)	TS (%)
450	64.3 ± 5.5a	32.4 ± 6.7a
650	58.5 ± 2.5a	42.9 ± 0.7b
800	62.1 ± 3.4a	37.4 ± 8.4ab
1000	62.6 ± 2.4a	48.0 ± 4.9b
1200	64.3 ± 4.4a	33.3 ± 3.5a

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

Influence of Slurry Types and Concentration

Soy flour and SPI are common bio-based adhesives employed to fabricate veneer panels and fiberboards [19, 20, 34]. An adhesive comparison between NFCs using OOSM and soy matrices reinforced with hemp mats was conducted. The influence of slurry concentrations employing various concentrations of OOSM, Prolia or SPI on the mechanical properties of their respective hemp composites is shown in Fig. 2. OOSM containing NFCs exhibited mechanical properties that were similar to NFCs produced with Prolia or SPI. These results suggest that OOSM could be a useful bio-based adhesive. Figure 3 shows the surfaces of NFCs generated using the 75 g L^{-1} slurry of OOSM, Prolia or SPI reinforced with a 450 g m^{-2} mat. The mat fibers coated with the various matrices were obscured (Fig. 3b–d) when compared to the original mat (Fig. 3a). This observation indicates good interfacial bonding between the matrices and hemp fibers.

Influence of Hot-Press Temperatures

Soybean meal adheres to wood using pressure temperatures varying from 110 to 180 °C [20]. A broad range of temperatures were employed to determine their bonding effect on OOSM-hemp mat interaction. As shown in Table 6 the pressing temperatures administered to the OOSM slurry-mats did not result in any clear trends concerning their physical properties. Thickness, densities and surface roughness values were relatively similar among the specimens regardless of the hot-pressed temperature. The surface roughness values of the NFCs were similar regardless of the temperature administered. High surface roughness values represent poor bonding between the ingredients employed in the composite while lower surface roughness values indicate better interfacial bonding [31]. During the hot-pressing operation,

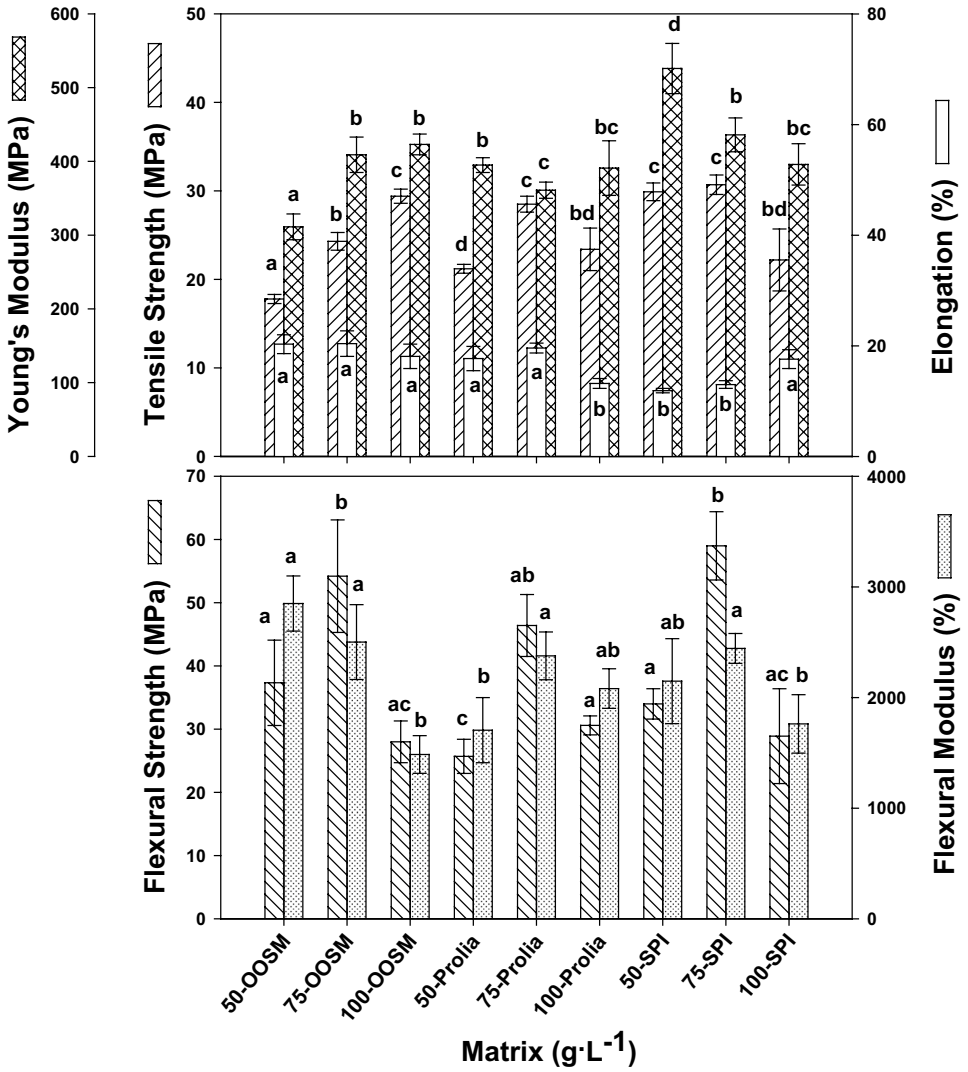

Fig. 2 Comparison of the mechanical properties of NFCs utilizing matrices consisting of 50, 75 and 100 g L^{-1} aqueous solutions of OOSM, Prolia and SPI fabricated with hemp mats of 450 g m^{-2} surface densities. Means with standard errors derived from five different replicates are presented. Mechanical values with different letters were significantly different ($P < 0.05$) according to Duncan's multiple range test

excess moisture and steam ejection occurred during the first few minutes of pressing. However, after this period the mold ceased to emit any liquids or gases indicating that a final phase change occurred where the solid material was converted to a gel then solidification was achieved. In other words, the proteins and binding components of the OOSM slurry were now bonded to the hemp fibers.

Table 7 shows the influence of the hot-pressing temperature on the mechanical properties of NFCs. Little differences in mechanical properties occurred among the NFCs occurred employing the various temperatures. This study was conducted to determine if a certain temperature was superior to others in the fabrication of NFCs. To this end, no particular temperature was ascertained as superior for tensile properties. However, the 185 °C hot pressing produced an OOSM-NFC that had higher flexural properties than NFCs generated using other temperatures. Similarly, Frihart *et al.* reported that best bonding of SPI to maple wood veneer strips occurred at 180 °C versus 120 or 150 °C [20].

Conclusions

These results show that a non-dietary application of OOSM is feasible whereby OOSM can be employed as a thermoset adhesive/resin. OOSM served as an adhesive/matrix matrix that was reinforced with non-woven hemp mats to fabricate NFCs. NFCs were produced from hemp non-woven mats immersed in an OOSM slurry (50, 75 or 100 g L^{-1}) under vacuum and then hot pressed within a mold. Direct hot-pressing of wet hemp mats produced a NFC that had higher mechanical properties than hemp mats that were allowed to oven dry prior to hot pressing. Direct hot-pressing of hemp mats with different surface densities (450, 650, 800, 1000, 1200, or 1350 g m^{-2}) in a OOSM slurry showed that NFCs consisting of lower surface densities ($\leq$1000 g m^{-2}) yield NFCs with superior mechanical properties compared to NFCs employed mats of higher surface densities ($\geq$1200 g m^{-2}). NFC utilizing the OOSM matrix (50, 75 or 100 g L^{-1}) reinforced with 450 g m^{-2} hemp mats were

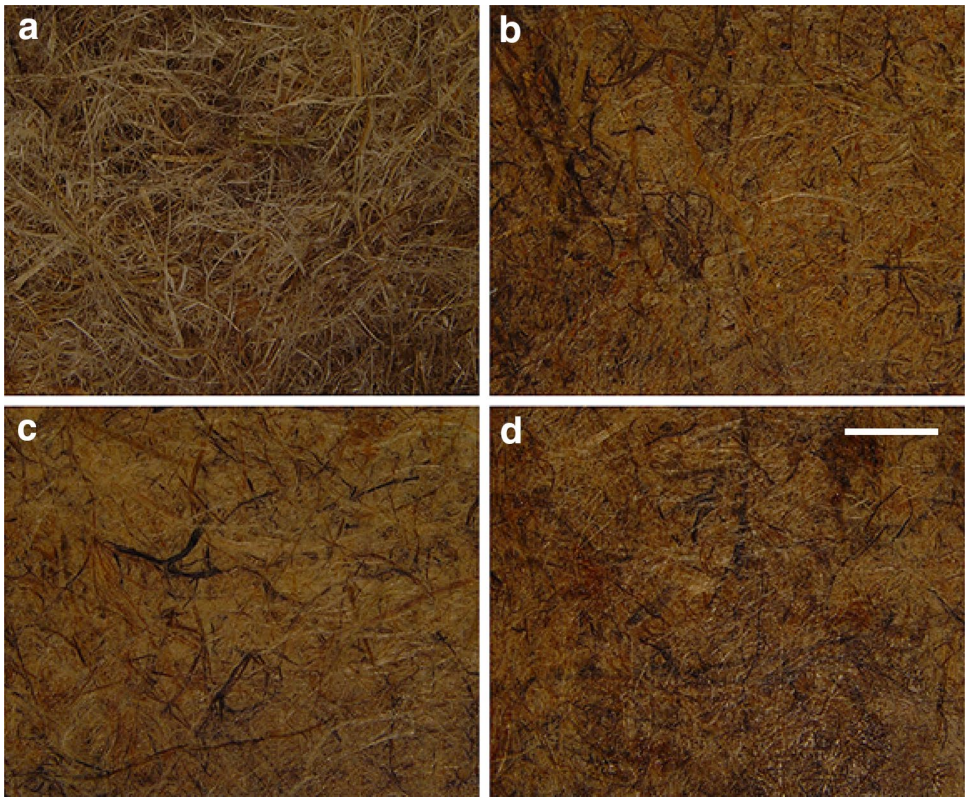

Fig. 3 Optical microscope images of NFCs prepared using 75 g L^{-1} slurry solutions. **a** original 450 g m^{-2} hemp mat, **b** OOSM-mat composite, **c** Prolia-mat composite, and **d** SPI-mat composite. Bar represents 5 mm

Table 6 Physical properties of NFCs fabricated from a 75 g L^{-1} OOSM slurry reinforced with 450 g m^{-2} mat and subjected to different temperature hot pressings

Temperature (°C)	Thickness (mm)	NFC density (kg m^{-3})	R_a (µm)	R_z (µm)	R_y (µm)
140	0.74 ± 0.02a	995 ± 29a	10.5 ± 1.5a	43.1 ± 6.8a	62.3 ± 10.9a
150	0.53 ± 0.02b	941 ± 23a	12.4 ± 2.1a	53.7 ± 6.5a	67.9 ± 11.6a
175	0.55 ± 0.03b	980 ± 25a	9.4 ± 1.7a	43.5 ± 7.3a	50.8 ± 4.0a
185	0.61 ± 0.02c	993 ± 38a	11.3 ± 1.9a	43.8 ± 7.0a	67.7 ± 12.2a
200	0.6 ± 0.01c	1006 ± 14a	10.6 ± 1.5a	46.1 ± 6.8a	61.5 ± 7.3a

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

Table 7 Mechanical properties of NFCs fabricated from a 75 g L^{-1} OOSM slurry reinforced with 450 g m^{-2} mat and subjected to different temperature hot pressings

Temperature (°C)	σ_u (MPa)	E (MPa)	%El (%)	σ_{fm} (MPa)	E_b (MPa)
140	22.2 ± 1.6a	349 ± 31a	24 ± 2a	33.9 ± 1.4a	1700 ± 71a
150	21.7 ± 2.7a	441 ± 20b	16 ± 1b	29.2 ± 4.6a	1833 ± 136a
175	20.3 ± 5.2a	388 ± 29a	18 ± 4ab	33.0 ± 2.6a	2185 ± 184b
185	20.5 ± 1.9a	384 ± 32a	21 ± 2a	54.2 ± 4.5b	2501 ± 169c
200	17.9 ± 1.9a	410 ± 12ab	17 ± 1b	33.1 ± 3.1a	2119 ± 176ab

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

found to exhibit similar mechanical properties as NFC generated using commercial soy flour Prolia or SPI as the matrix. A wide range of temperatures (140–200 °C) could be employed to fabricate NFCs that exhibited similar mechanical properties.

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Compliance with Ethical Standards

Conflict of interest The authors declare that there are no conflicts of interest regarding the publication of this paper.

References

1. Jauhari N, Mishra R, Thakur H (2015) Mat Today Proc 2:2868
2. Yu ZC, Alcock M, Rothwell E, McKay S (2009) Proc 12th ICCM, Jul 27–31, 2009
3. Faruk O, Bledzki AK, Fink H-P, Sain M (2012) Prog Polym Sci 37:1552
4. Scarponi C, Schiavoni E, Sánchez-Sácz S, Barbero E, Sarasini F (2012) J Biobased Mat Bioen 6:361
5. Mohammed L, Ansari MNM, Pua G, Jawaid M, Islam MS (2015) Int J Polym Sci 2015:243947
6. Al-Oqla FM, Sapuan SM, Anwer T, Jawaid M, Hoque ME (2015) Synth Met 206:42
7. Pickering KL, Aruan Efendy MG, Le TM (2016) Comp Part A 83:98
8. Westman MP, Fifield LS, Simmons KL, Laddha SG, Kafentzis T (2010) Natural fiber composites: a review. USDE, PNNL-19220, Mar 2010
9. Ratim S, Bonnia NN, Surip SN (2012) 2nd APCTP Work Adv Mat Nanotech. AIP Conf Proc 1455:131
10. Martin N, Davis P, Baley C (2016) Ind Crop Prod 83:194
11. Saenghirunwattana P, Noomhorm A, Rungsardthong V (2014) Ind Crop Prod 60:144
12. Chabba S, Matthews GF, Netravali AN (2005) Roy Soc Chem 7:576
13. Drzal LT, Mohanty AK, Liu W, Thayer K, Misra M (2009) US Patent No:US 7576147:B2
14. Kelley MD, Manna J (2009) US Patent No:US 2009/0232953 A
15. Iman M, Banja KK, Maji TK (2013) Ind Eng Chem Res 52:6969
16. Sreekumar PA, Thomas SP, Saiter JM, Kuruvilla J, Unnikrishnan G, Thomas S (2009) Comp Part A 40:1777
17. Boontima B, Noomhorm A, Puttanlek C, Uttapap D, Rungsardthong V (2015) J Polym Environ 23:97
18. Deepmala C, Singh VK, Chauhan S, Jain N (2017) RRJOMS 5:66
19. Coolidge T, Mock C, Valle E (2016) Polymers 8:394
20. Frihart CR, Hunt CG, Birkeland MJ (2014) In: Recent Adv Adh Sci Technol CRC Press, Boca Raton
21. Alibaba.com (2018) https://www.alibaba.com/showroom/defatted-soy-flour.html
22. Alibaba.com (2018) https://www.alibaba.com/showroom/price-soy-protein-isolates.html
23. Moser BR, Eller FJ, Tisserat BH, Gravett A (2011) Energy Fuels 25:1869
24. Tisserat B, Reifschneider L, Gravett A, Peterson SC (2017) Bioresources 12:7898
25. Saloua F, Eddine NE, Hedi Z (2009) Ind Crop Prod 29:1
26. Mitchell L (2017) http://www.thenewmix.com/2017/10/25/hedge-apples-are-valuable/
27. Realhemp (2018) Indiana Hemp Ind Assoc http://www.realhemp.com/hemp-industries/hemp-biocomposites/
28. He W, Ma W, Young T, Teo WE, Ramakrishna S (2005) Biomat 26:7606
29. He Z, Chapital DC, Cheng HN (2016) J Appl Polym Sci 133:43637
30. Tabarsa T, Ashori A, Gholamzadeh M (2011) Comp Part B 42:1330
31. Ayrilmis N (2011) Bioresources 6:3178
32. Akgül M, Korkut S, Çamlibel O, Candan Z, Akbulut T (2012) Maderas Cien Techol 14:185
33. Salasinska K, Ryszkowska J (2012) ECCM15-15th Venice, Italy, 24–28 June, 2012
34. Mo X, Sun XS (2013) Adhes Sci Technol 27:2014