Research Article

Lignocellulosic Composites Prepared Utilizing Aqueous Alkaline/Urea Solutions with Cold Temperatures

Brent Tisserat ¹, Zengshe Liu,² and Luke M. Haverhals³

¹Functional Foods Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University St., Peoria, IL 61604, USA

²Bio-Oils Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University St., Peoria, IL 61604, USA

³Mund-Lagowski Department of Chemistry and Biochemistry, Bradley University, Peoria, IL 61625, USA

Correspondence should be addressed to Brent Tisserat; brent.tisserat@ars.usda.gov

Received 12 September 2017; Revised 14 December 2017; Accepted 4 January 2018; Published 14 February 2018

Academic Editor: Penwisa Pisitsak

Copyright © 2018 Brent Tisserat et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Lignocellulosic composites (LCs) were fabricated by partially dissolving cotton to create a matrix that was reinforced with osage orange wood (OOW) particles and/or blue agave fibers (AF). LCs were composed of 15–35% cotton matrix and 65–85% OOW/AF reinforcement. The matrix was produced by soaking cotton wool in a cold aqueous alkaline/urea solvent and was stirred for 15 minutes at 350 rpm to create a viscous gel. The gel was then reinforced with lignocellulosic components, mixed, and then pressed into a panel mold. LC panels were soaked in water to remove the aqueous solvent and then oven dried to obtain the final LC product. Several factors involved in the preparation of these LCs were examined including reaction temperatures (−5 to −15°C), matrix concentration (15–35% cotton), aqueous solvent volume (45–105 ml/panel), and the effectiveness of employing various aqueous solvent formulations. The mechanical properties of LCs were determined and reported. Conversion of the cotton into a suitable viscous gel was critical in order to obtain LCs that exhibited high mechanical properties. LCs with the highest mechanical properties were obtained when the cotton wools were subjected to a 4.6% LiOH/15% urea solvent at −12.5°C using an aqueous solvent volume of 60 ml/panel. Cotton wool subjected to excessive cold alkaline solvents volumes resulted in irreversible cellulose breakdown and a resultant LC that exhibited poor mechanical properties.

1. Introduction

Lignocellulosic biomass is very resistant to being broken down (i.e., bioconverted) into carbohydrate components that could be used as intermediates to generate biobased fuels and products. This problem may be addressed by administering pretreatment methods [1, 2]. Lignocellulosic biomass is composed mainly of cellulose (β (1–4)-linked chains of glucose molecules), hemicellulose (heteropolymers composed of 5- and 6-carbon sugars such as arabinoxylan, xylan, glucuronoxylan, glucomannan, and xyloglucan) and lignin (polymer of three phenylpropanoid units: *p*-hydroxyphenyl, guaiacyl, and syringyl). The carbohydrate fraction (cellulose and hemicellulose) of lignocellulosic biomass is speculated to be covalently linked to lignin [1, 3]. One method used to break down the lignocellulosic bonds is to employ cold

alkaline solvents [1–11]. For example, cold sodium hydroxide (7% NaOH) or sodium hydroxide/urea solutions (≈7% NaOH/12% urea solution) cooled to −12°C is capable of breaking cellulose linkages to synthesis cellulose derivatives [1–3]. In other studies, some cold alkaline treatments (i.e., 5% NaOH solution cooled to −5°C) caused lignocellulosic fibers to swell but did not result in dissolution [1, 3]. An aqueous alkaline treatment of spruce wood with NaOH or NaOH/urea mixture solutions at similar low temperatures disrupts hemicellulose, cellulose, and lignin components making the cellulose more accessible to enzymatic hydrolysis [2]. Li et al. reported that aqueous alkaline/low temperatures treatments (≈7% NaOH/12% urea solution at −12°C) cleaved lignin ester groups in bamboo fibers but otherwise caused only minor changes in the overall lignin structure [1]. Cai and Zhang reported that LiOH·H₂O/urea was superior to

NaOH/urea or KOH/urea to dissolve cellulose [4]. Utilizing these techniques, dissolved cellulose could serve as a matrix and be reinforced with undissolved cellulose materials to generate novel all-cellulose composites (ACC) once the alkaline solution was removed [3–8, 10–12]. These novel ACCs are “environmentally friendly” and can be “recycled” since the composite is entirely composed of cellulose [1, 3, 6, 8, 10–12]. ACC films (0.25 mm thick) composed of cellulose nanowhiskers and a cellulose matrix has been produced using a cold aqueous alkaline solution (7% NaOH/12% urea at -12°C) [7, 8, 11]. Recently, a cold aqueous alkaline solution of $\text{LiOH}\cdot\text{H}_2\text{O}$ (4.6% $\text{LiOH}\cdot\text{H}_2\text{O}$: 15% urea at -12°C) was used to generate a nonporous cellulose gel from cotton fibers [7].

In this study, we expanded on the use of cold aqueous alkaline solvents to prepare lignocellulosic composites (LCs). In prior studies, ACCs were entirely composed of cellulose (~100%). Herein we employed a semidissolved cellulose matrix that was mixed with nondissolved lignocellulose reinforcement to produce a LC composed of 15% to 35% cellulose and 65 to 85% reinforcement. These LCs have several unique characteristics: (1) their composition consists of readily abundant and inexpensive biomass materials, (2) they do not contain any adhesives or resins unlike commercial composites, and (3) since they are entirely biological in nature they are completely biodegradable and compostable. Several factors associated with the fabrication of these LCs were studied herein including the influence of reaction temperatures, matrix composition, alkaline mixture volumes, and a comparison of the effectiveness of various alkaline solvent formulations. To evaluate the effectiveness of each study, the mechanical properties of the resultant LCs were tested. It would be premature to identify a specific use for the LCs generated in this study as a commercial product. Our goal was to examine the factors that give LCs high mechanical properties since this could translate into a potential product. Therefore, at the conclusion of this study we compared the LCs mechanical properties with various commercial products.

The reason for employing the ingredients used in this study was based on their effectiveness, cost, and availability. Cotton (*Gossypium sp.*, family Malvaceae) is a soft, fluffy staple fiber that grows in a protective capsule or boll. Its fiber is almost pure cellulose. Global cotton production amounts to 25 million tons and its acreage accounts for 2.5% of the world's arable land [13]. Its selection in this study as the matrix material was due to its availability and excellent cellulose characteristics. Cotton currently cost \$0.58–0.69/lb [14]. Blue agave (*Agave tequilana* F.A.C. Weber, family Asparagaceae) is a succulent plant grown in Mexico for the extraction of tequila liquor from its stem; in this process sisal fibers or agave fibers (AF) (bagasse) are generated as a by-product [15]. Blue agave bagasse accounts for 40% of the wet weight of the plant and is an underutilized by-product although several studies have suggested possible uses for it [15–19]. Sisal fibers derived from *Agave* species are well known for their fibrous strength and are sold as a textile commodity [20]. Osage orange (*Maclura pomifera* (Raf.) Scheid., family Moraceae) trees are considered an invasive species and are common to the mid-western US states [21, 22]. Although a number of

TABLE 1: Alkaline aqueous solvent test formulations.

Alkaline aqueous formulations (w/w)	References
4.7% NaOH/12% urea	[3, 5, 7]
4.2% $\text{LiOH}\cdot\text{H}_2\text{O}$ /12% urea	[3]
8% NaOH/6.5% thiourea/8% urea	[4]
4.6% $\text{LiOH}\cdot\text{H}_2\text{O}$ /15% urea	[6]
8% $\text{LiOH}\cdot\text{H}_2\text{O}$ /6.5% thiourea/8% urea	—
4.2% $\text{LiOH}\cdot\text{H}_2\text{O}$ /6.5% thiourea/8% urea	—

uses have been previously proposed for osage orange wood (OOW) its current value is insubstantial since there is no large commercial use of this wood [21]. One of our long term research project goals is to identify new uses for biomass materials which are abundant, inexpensive, and derived from plants common to the Midwest region of the US. Therefore, in this research study, two currently underutilized biomass materials were employed as reinforcements to be mixed with a cotton matrix to produce LCs.

2. Experimental

2.1. Materials and Preparations. Cotton wool (absorbent medical) was obtained from U.S. Cotton Company, Lachine, Quebec, Canada. Agave fibers were obtained from leaves of 12-year-old plants grown in Jalisco, Mexico. Leaves were air dried and the fibrous portion shipped to Peoria, IL. Agave fibers (AFs) were loosely separated by hand and sieved through #5 and #12 sieves and then cut into individual fibers varying from 15 mm to 30 mm in length $\times$ 0.1–0.2 mm in thickness. Osage orange wood (OOW) particles were obtained from 20-year-old trees grown in Missouri, USA. OOW was chipped and shredded and then milled successively through 4-, 2-, and 1-mm diameter stainless screens. Particles were then sized through a Ro-Tap™ shaker (Model RX-29, Tyler, Mentor, OH, USA) employing 203 mm diameter steel screens. OOW particles that were screened through a #30 US Standards mesh (Newark Wire Cloth Company, Clifton, NJ, USA) were employed in further operations. These particles varied in size from 600 to 75 μm in diam. The chemical compositions of materials used in this study were cotton (94% cellulose), OOW (33% cellulose, 17% hemicellulose, and 40% lignin) and AF (43% cellulose, 19% hemicellulose, 15% lignin) [15, 23, 24]. Materials were dried for 48 hr at 60°C prior to use.

2.2. Fabrication of LC Panels. Alkaline hydroxides ($\text{LiOH}\cdot\text{H}_2\text{O}$ and NaOH), thiourea, and urea were of analytical grade (Aldrich-Sigma, St. Louis, MO, USA) and used as received without further purification. Alkali hydroxide, thiourea, urea, and distilled water solvent formulations are shown in Table 1. Unless indicated elsewhere the following procedure was employed to fabricate LC panels. Alkaline solvents (45 ml) were precooled (-5 to -12.5°C) in a stainless steel vessel (75 mm diam $\times$ 105 mm length $\times$ 450 ml capacity) in the reservoir of a recirculating refrigerated chiller. Once the desired solvent temperature was obtained 2.5 g of cotton

TABLE 2: Parameters for experiments conducted*.

Experiment	Matrix (%)	Reinforcement (%)	Matrix stirring (rpm : min)	Reinforcement stirring (rpm : min)	Reaction temperature (°C)	Solvent volume (ml/panel)
Temperature	25	75 OOW	350 : 15	350 : 10	-5, -7.5, -10, -12.5, or -15	45
Matrix concentration	15, 25, 30, or 35	85, 75, 70, or 65 OOW/AF	350 : 15	350 : 10	-12.5	45
Solvent volume	25	75 OOW/AF	350 : 15	350 : 10	-12.5	45, 60, 75, 90, or 105
Alkaline treatments**	25	75 OOW/AF	350 : 15	350 : 10	-12.5	60

* All experiments unless noted otherwise were conducted using a 4.6% LiOH·H₂O/15% urea alkaline aqueous formulation. ** See Table 1 for the alkaline aqueous formulations employed.

was immersed in the precooled solvent and stirred for approximately 15 min employing a mixer (Model 1750, Arrow Engineering, and Hillside, NJ, USA) fitted with a three-blade propeller at 350 rpm. This resulted in the partial dissolution of the cotton cellulose generating a white translucent cellulose gel. OOW particles (3.75 g) and AFs (3.75 g) were added to the vessel and stirred for an additional 10 min at 350 rpm. The resultant composite was transferred to a polyethylene foam molds of 105 mm W × 130 mm L × 5 mm D O.D. with 80 mm W × 100 mm L × 5 mm D I.D. Two polyethylene meshes with 2 mm² openings were used to sandwich the panel. The molds were then subjected to several solvent-water exchange treatments consisting of submergence in tap water under vacuum for 15 min followed by continuous submergence in water for 24 hrs punctuated with 6 water replacements. After the first hour of soaking the composite panels were firm enough to be removed from the molds to facilitate greater diffusion of the solutes into the water. At end of the soaking treatment, panels were damp dried on paper towels and then placed between two steel plates under 0.5 psi (0.0034 MPa) pressure and dried in a vacuum oven at 60°C and 25 inches Hg for 24 hr. Panels were subsequently densified by subjection to 8 tons pressure for 10 min at 180°C.

2.3. Test Preparations. The summary of experiments conducted in this study is presented in Table 2. The following studies employed 4.6% LiOH·H₂O/15% urea as the solvent [7]. Following each preparation test, the mechanical properties of the resultant LC panels were evaluated. To study the influence of reaction temperatures on the mechanical properties of LCs, a LC formulation consisting of 25% cotton and 75% OOW was prepared using -5, -7.5, -10, -12.5, or -15°C temperatures. Based on the resultant mechanical properties obtained from this study, a -12.5°C reaction temperature was employed hereafter. The influences of various cotton matrix concentrations (15, 25, 30, or 35% cotton) were tested with a 50/50 OOW/AF reinforcement. The influences of various alkaline solvent volumes (45, 60, 75, 90, or 105 ml/panel) were tested on the LC formulation of 25% cotton and 75% OOW/AF reinforcement. Comparisons of several alkaline aqueous solvents using 60 ml/panel were tested on the 25% cotton: 75% OOW/AF formulation (Table 1). Using 60 ml of

the 4.6% LiOH·H₂O/15% urea alkaline solvent the mechanical properties of panels composed of 100% cotton, 25% cotton: 75% OOW, 25% cotton: 75% AF, or 25% cotton: 75% OOW/AF were determined.

2.4. Mechanical Tests. LC panels were punched with a clicker press fitted with specimen cutting dies to obtain ASTM test specimen sample bars: ASTM D790 flexural testing bar (12.7 mm W × 63.5 mm L × 1.5 mm thickness) and ASTM D638 Type V tensile testing bar (9.5 W mm grip area × 3.2 mm neck × 63.5 mm L × 1.5 mm thickness × 7.6 mm gage L). Dry LCs were conditioned for approximately 240 hours at standard room temperature and humidity (23°C and 50% relative humidity) prior to any test evaluations. ASTM D638 Type V tensile bars were tested for Young's modulus (E) and tensile strength (σ_u) using a universal testing machine (UTM), Instron Model 1122 (Instron Corporation, Norwood, MA). The speed of testing was 5 mm/min. Three-point flexural tests were conducted according to ASTM-D790 specification on the Instron UTM Model 1122 using flexural bars. The flexural tests were carried out using Procedure B with a crosshead rate of 13.5 mm/min to determine the flexural strength (σ_{fm}) and flexural modulus of elasticity (E_b). Five specimens of each formulation were tested. The average values and standard errors were reported. The results were subjected to analysis of variance for statistical significance, and multiple comparisons of means were conducted using Duncan's Multiple Range Test ($p \leq 0.05$).

2.5. Physical Measurements. To access the distribution of the OOW, AF, and cotton matrix in the composites, surface and fractured cross sections of specimen bars were optically examined and photographed with a Wild Heerbrugg M5 Stereo dissecting microscope (Leica Microsystems GmbH, Wetzlar, Germany). FTIR spectra were recorded at room temperature with a FTIR spectrometer (Thermo Nicolet Nexus 470, Thermo Fisher Scientific, Inc., MA). Sample spectra consisted of 32 scans recorded from 4000 to 400 cm⁻¹ using a 2 cm⁻¹ resolution. Thermogravimetric analysis (TGA) was performed on the cotton, OOW, and AF ingredients and the resultant 25% cotton: 75% OOW/AF composite panels. TGA was conducted using a Model 2050 TGA (TA Instruments,

FIGURE 1: Preparation of LC panels. (a) Cotton gel first prepared by stirring cotton in cold alkaline solvent, (b) cotton gel combined with OOW and AF ingredients and stirred, (c) the resultant LC gel transferred to foam panel and then transferred to water to remove alkaline solvent, and (d) representation of the final composite and the original ingredients (cotton, OOW, and AF) employed.

New Castle, DE) at a scan rate of $10^{\circ}\text{C}/\text{min}$ from 25°C to 600°C . Samples of ~ 7.5 mg were employed. Dimensional stability tests (i.e., water absorbance and thickness swelling) were conducted on the LC (25% cotton: 75% OOW/AF) flexural bars by water immersion for 24 hrs.

3. Results and Discussion

Cai and Zhang employed a 4% cotton/cellulose concentration with a 96% aqueous alkaline solution volume of 4.2% $\text{LiOH}\cdot\text{H}_2\text{O}/12\%$ urea, 7% $\text{NaOH}/12\%$ urea, or 9.8% $\text{KOH}/12\%$ urea to dissolve the cotton [4]. Several investigators have employed these same compositions as their cold alkaline solvents to prepare their ACCs [3, 8, 11, 12]. Li et al. employed a 94% aqueous solution volume of 4.6% $\text{LiOH}\cdot\text{H}_2\text{O}/12\%$ urea solution to dissolve 6% cotton/cellulose [7]. Initially, we chose to employ this aqueous alkaline formulation in our first LC

studies, since this solution was identified to be very effective [7]. In contrast to other studies, we initially employed a 22% cellulose/lignocellulose mass in a 78% alkaline aqueous solution volume of 4.6% $\text{LiOH}\cdot\text{H}_2\text{O}/12\%$ urea solution at -10°C . Rather than attempting to dissolve the entire cotton (cellulose) portion in the alkaline aqueous solvent as other investigators did [3, 6–10], our aim was to only partially dissolve the cotton/cellulose portion in order to obtain an “adhesive” or “plastic-like” gel matrix that could then be mixed with lignocellulosic reinforcement agents (e.g., OOW and/or AF). Initially, we prepared construct formulations of 100% cotton, 100% OOW, 100% AF, 25% cotton: 75% OOW, 25% cotton: 75% AF, or 25% cotton: 75% OOW/AF. It was not possible to prepare a panel composed entirely of 100% OOW or 100% AF; but all the other composite formulations produced panels. Figure 1 illustrates the steps employed to fabricate LC panels. These steps were employed throughout this study. Successful panels composed of a combination

FIGURE 2: Influence of temperature on the mechanical properties of biocomposite composed of 25% cotton: 75% OOW. Treatment values with different letters for the same mechanical test are significantly different ($p \leq 0.05$) following Duncan's Multiple Range Test analysis.

of 25% cotton and 75% OOW and/or 75% AF were also obtainable but both were found to be relatively weak in structure. However, these results suggested that further investigations into improving the parameters involved in LC panel preparations (reaction temperature, matrix concentration, aqueous alkaline volume, and alkaline treatments) could aid in obtaining an improved LC with greater mechanical properties. With this purpose in mind, the following studies were performed.

The mechanical properties of LCs composed of 25% cotton and 75% OOW prepared using various incubation temperatures are shown in Figure 2. It was noted that cotton gel matrices formed a viscous gel at temperatures of -10°C and lower (i.e., -12.5°C or -15°C), while the higher temperatures (i.e., -5°C or -7.5°C) were less effective in dissolving the cotton to produce a gel. The creation of this gel matrix was subsequently found to be conducive to the adhesive qualities of the matrix to bind with lignocellulosic reinforcements. Both -12.5°C and -15°C temperature preparation regimes produced a

FIGURE 3: Influence of cotton matrix concentration on the mechanical properties of biocomposites composed of 25% cotton: 75% OOW/AF. Treatment values with different letters for the same mechanical test are significantly different ($p \leq 0.05$) following Duncan's Multiple Range Test analysis.

resultant LC that exhibited higher σ_u , E , σ_{fm} , and E_b values compared to LCs produced obtained from using higher temperatures (i.e., -5°C and -7.5°C) (Figure 2). For example, the LCs prepared using -12.5°C exhibited σ_u , E , σ_{fm} , and E_b values that were 108%, 151%, 183% and 203% higher than LCs prepared using -5°C .

These results are similar to those of Cai and Zhang who tested a range of temperatures varying from -5°C to -20°C with a 7% NaOH/12% urea solvent and found that -10°C produced the most stable solvent conditions in order to dissolve a 4% concentration of cotton (cellulose) to generate an AAC composed of 100% cotton (cellulose) [4]. In contrast, our LCs composed of final matrix composition of 25% cotton generated by a partially dissolvment of the cotton forming a viscous gel construct that when mixed with 75% OOW readily formed a solid LC construct. We selected the temperature regime of -12.5°C for further studies since it produced a LC with high mechanical properties (Figure 2).

The percent of the cotton matrix greatly influenced the mechanical properties of the resultant LCs (Figure 3). LCs

TABLE 3: Dimensional and weight changes of LC panels during processing.

Panel treatment	Residual panel volume (mm ³)	Residual wt. (g)*	Panel volume (%)	Residual wt. (%)**
Original	40000	72	100	100
Soaked	40000	40	100	56
Oven dry	16800	8.3	42	12
Compression	8400	8.2	21	11

*Original panel contained 2.5 g cotton, 3.75 g agave fiber, and 3.75 g OOW = 10 g total materials. Loss of materials is due to handling and water loss during drying. **Residual Wt. (%) indicates the change in weight of the original LC material weight (72 g) during processing to the final weight (8.2 g).

prepared with lower concentrations of cotton (e.g., 15 or 25%) exhibited lower mechanical values than LCs prepared by using higher concentrations of cotton (e.g., 30 and 35%) (Figure 3). For example, LCs of 35% cotton: 65% OOW/AF exhibited σ_u , E , σ_{fm} , and E_b values that were 135%, 343%, 153%, and 109% higher, respectively, versus LCs prepared of 15% cotton: 85% OOW/AF (Figure 3). Mechanical properties of LCs employing 30 or 35% cotton matrix were essentially the same. This suggests that optimum concentration of cotton matrix for the LC to achieve the highest mechanical properties was obtained. The presence of high cotton matrix concentrations in the LC increases interfacial binding between the matrix and the reinforcement which translates into higher mechanical properties. An overall goal of this study was to prepare LCs inexpensively and since the cost of cotton was the major cost of the final LCs price, it was decided that further work would be conducted employing LCs utilizing lower cotton concentrations (i.e., 25%). Hereafter, we attempted to improve on the preparation methods to attain LCs with higher mechanical properties.

Solvent volume employed to prepare LCs greatly affected the mechanical values of the LCs as shown in Figure 4. The optimum solvent volume used to prepare a LC panel was 60 ml/panel based on its mechanical values. LCs prepared using either 45 or 75 ml/panel usually had diminished mechanical properties compared to LCs prepared using 60 ml/panel. Use of 90 or 105 ml aqueous alkaline solvent per panel resulted in a LC panel that had substantially lower mechanical properties than the 60 ml/panel (Figure 4). We can speculate that higher volumes of solvent/panel diluted the LC ingredients resulting in a weakened panel with poor mechanical properties. Essentially, too much alkaline solvent for the same amount of ingredients results in “runny” matrix mixture indicating a greater breakdown of the cellulose structure than that obtained using less alkaline solvent. For example, LCs prepared using 60 ml/panel exhibited the σ_u , E , σ_{fm} , and E_b values that were 58%, 45%, 55%, and 58% greater, respectively, than the LCs mechanical values obtained using 105 ml/panel (Figure 4).

The effectiveness of employing different published and nonpublished solvent formulations on the mechanical properties of resultant LCs was evaluated (Table 1; Figure 5). All solvent formulations produced LCs; however their mechanical properties varied considerably (Figure 5). The results suggest that further research to optimize the alkaline solvent formulation is necessary in order to increase the mechanical properties from the LCs. However, this test showed that

FIGURE 4: Effect of $\text{LiOH}\cdot\text{H}_2\text{O}$ /urea solvent volume on mechanical properties of panels composed of 10 g 25% cotton: 75% OOW/AF. Treatment values with different letters for the same mechanical test are significantly different ($p \leq 0.05$) following Duncan's Multiple Range Test analysis.

$\text{LiOH}\cdot\text{H}_2\text{O}$ is superior to NaOH as the alkaline ingredient to produce a LC with higher mechanical properties (Figure 5). We speculate that the size of the alkaline molecule may have a roll in the gel formation from cotton since $\text{LiOH}\cdot\text{H}_2\text{O}$ is a smaller molecule than NaOH. A formation of a viscous cellulose gel was critical to the binding of cellulose to the lignocellulose reinforcement ingredients. Undoubtedly good interfacial binding of ingredients results in a LC with higher mechanical properties. Table 3 shows the change in the LCs

FIGURE 5: Effect of various alkaline aqueous solvent formulations on the mechanical properties of panels composed of 25% cotton: 75% OOW/AF. Treatment values with different letters for the same mechanical test are significantly different ($p \leq 0.05$) following Duncan's Multiple Range Test analysis.

FIGURE 6: The influence of various reinforcements of composites on their mechanical properties. Treatment values with different letters for the same mechanical test are significantly different ($p \leq 0.05$) following Duncan's Multiple Range Test analysis.

volume and weight during processing. Considerable volume and weight changes occurred in the LC panel materials during the processing steps. One of the most interesting features about these LC panels is their weight. Originally, panels consisted of 10 g of cotton, OOW, and AF and through processing the resultant dried panel consisted of only 8.2 g. The weight loss could be attributed to handling.

The influence of various reinforcement ingredients used to prepare biocomposites formulations on their mechanical properties is shown in Figure 6. The 100% cotton formulation was the most expensive panel to prepare and had similar mechanical properties to the LC panels containing 25% cotton: 75% OOW or 25% cotton: 75% OOW/AF which were considerably less expensive to prepare. The LC containing

FIGURE 7: Optical microscope images of the composite consisting of 25% cotton : 75% OOW/AF: (a) surface view of panel and (b) side view of panel. Bar = 0.5 mm.

FIGURE 8: FTIR spectra of (a) cotton, (b) OOW, (c) agave fibers, and (d) 25% cotton : 75% OOW/AF composite.

25% cotton : 75% AF yielded the poorest mechanical properties. We can speculate that this was due to the absence of smaller particles provided by the OOW particles that aid in interfacial binding with the matrix material. Based on these results, inexpensive LCs with acceptable mechanical properties (when compared to the 100% cotton panel) can be procured without the employment of high percentages of cotton.

The close-up optical images of the 25% cotton : 75% OOW/AF panels are shown in Figure 7. The surface of the composite was found to be relatively smooth consisting of a layer of cotton matrix. The cotton matrix was light colored and punctuated with dark agave fibers. OOW particles were not evident on the surface but were coated with the cotton matrix and subepidermal in placement (Figure 7(a)). This situation occurs because the smaller OOW particles

were more easily coated by the matrix while the agave fibers being larger and longer were less likely to be coated uniformly by the cotton matrix and could protrude on the surface uncoated. Examination of the cross section of the LC revealed a very heterogeneous mixture of ingredients. As shown in Figure 7(b) the cotton matrix consists of stringy fibers coating the lighter OOW particles and darker agave fibers. The composite appears to consist of numerous layers separated with air crevices. This suggests that considerable air spaces occurred between the matrix and the reinforcement. Undoubtedly, the hot-pressing compression of the panels contributed to this situation.

Figure 8 shows the FTIR spectra for the ingredients and the final composite obtained by treating with cold 4.6% LiOH·H₂O/15% urea solvent. The cotton ingredient does not exhibit a hemicellulose peak which would occur

TABLE 4: Comparison of various commercial composites and plastics mechanical properties used for packaging*.

Item	σ_u (MPa)	E (MPa)	σ_{fm} (MPa)	E_b (MPa)
25% cotton: 75% OOW/AF	12.6 ± 1.5	1029 ± 76	42 ± 10	3338 ± 710
High density polyethylene	21.5 ± 0.1	339 ± 10	28 ± 0.1	894 ± 15
Poly(lactic acid)	52.2 ± 0.5	397 ± 30	122 ± 0.3	3914 ± 4
Polypropylene	25.2 ± 0.1	576 ± 5	44 ± 0.1	1387 ± 8
Egg carton	4.0 ± 0.3	227 ± 19	4 ± 0.4	326 ± 50
Keyboard box packaging	7.6 ± 0.5	390 ± 35	4 ± 0.9	772 ± 204
"Jimmy Dean" sandwich box	21.4 ± 0.5	864 ± 18	19 ± 0.6	2313 ± 133
Milk carton	25.6 ± 4.7	1098 ± 156	36 ± 0.5	5840 ± 90
Computer mouse packaging	37.1 ± 2.2	1833 ± 63	30 ± 4.4	5201 ± 1008

*Mechanical properties determined by the authors.

FIGURE 9: Thermogravimetric analysis (TGA) curves of ingredients and LC.

around 1742 cm^{-1} . Similarly, the 25% cotton: 75% OOW/AF composite did not exhibit a prominent hemicellulose peak. This suggests that the cold alkaline solution extracts the hemicellulose from the ingredients during the preparation processes. This observation has been similarly observed by other investigators who have employed an alkaline solution [25]. Cellulose bands occur around $1000\text{--}1200\text{ cm}^{-1}$ correlated to the alcoholic C-O stretching vibration. These peaks were prominent in all the ingredients and LC. Lignin absorbance bands typically occur around 1500 cm^{-1} and are attributed to the aromatic ring framework vibrations. Cotton linter lacked this peak but lignin was prominent in the other ingredients and the composite.

Thermal decomposition of the ingredients and resultant composite (25% cotton: 75% AF/OOW) are shown in Figure 9. Thermal degradation between room temperature to 100°C shows the mass loss due to the loss of moisture. The thermal degradation of the cotton ingredient occurred in a single stage, beginning at 239.5°C with a maximum decomposition rate occurring at 368.9°C . The cotton matrix material

consisted of 96% cellulose and generated the least amount of ash residue (8.5%) when compared to the composite or other ingredients (OOW and AF). The OOW, AF, and LC samples exhibit a 33.7, 21.2, and 16.1% ash residue, respectively, at 600°C . There are a number of degradation peaks associated with the thermal degradation of the LC and the AF and OOW ingredients. The lower degradation peak is associated with the decomposition of hemicellulose and lignin which degrades between 165 and 300°C , followed by a higher degradation peak which is associated with the decomposition of cellulose and lignin which degrades between 230 and 450°C . Lignin degrades around $200\text{--}450^\circ\text{C}$ and its peaks are obscured by the hemicellulose and cellulose degradation peaks [26].

Mechanical properties are important in order to evaluate the potential use of composites. Table 4 compares the mechanical properties of the final LC generated in this study to common plastics and commercial packaging materials. This comparison shows that LCs are compared favorably to several of these materials in terms of its mechanical properties. It is the authors' opinion that emphasis should be placed on comparing the mechanical properties of LCs with common commercial products in order to determine a replacement potential. The dimensional stability of LCs is very poor. For example, soaking the final 25% cotton: 75% OOW/AF composite in water for 24 hrs caused a water absorbance and thickness increase of $202 \pm 16\%$ and $81 \pm 18\%$, respectively. This suggests that a coating is necessary for LCs to improve the dimensional stability values. However, more studies are needed to improve the LCs mechanical properties but the results obtained thus far appear encouraging.

4. Conclusions

LCs were fabricated using a formulation containing 15–35% cotton/cellulose matrix and 65–85% reinforcement materials of OOW and/or AF using cold aqueous alkaline solvents. LCs consisted of low-cost, raw materials that were employed without any prior chemical pretreatments. Because no adhesives or resins are employed in the LC fabrication process the panels are remarkably light weight and yet have relatively strong mechanical properties. Several variables such as reaction

temperature, matrix concentration, solvent volumes, solvent types, and compositional ingredients were been found to significantly influence the mechanical properties of generated LCs.

Disclosure

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture. USDA is an equal opportunity provider and employer.

Conflicts of Interest

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

Acknowledgments

The authors acknowledge the faculty and students of Chemistry Department, Bradley University, Peoria, IL, for technical assistance. They are grateful to Hedgeapple Biotech, Bloomington, IL, for providing the osage orange wood sawdust, and Gen2 Energy Company Inc., Ames, IA, for providing blue agave bagasse.

References

- [1] M.-F. Li, Y.-M. Fan, R.-C. Sun, and F. Xu, "Characterization of extracted lignin of bamboo (*Neosinocalamus affinis*) pretreated with sodium hydroxide/urea solution at low temperature," *Bioresources*, vol. 5, no. 3, pp. 1762–1778, 2010.
- [2] Y. Zhao, Y. Wang, J. Y. Zhu, A. Ragauskas, and Y. Deng, "Enhanced enzymatic hydrolysis of spruce by alkaline pretreatment at low temperature," *Biotechnology and Bioengineering*, vol. 99, no. 6, pp. 1320–1328, 2008.
- [3] T. Budtova and P. Navard, "Cellulose in NaOH–water based solvents: a review," *Cellulose*, vol. 23, no. 1, pp. 5–55, 2016.
- [4] J. Cai and L. Zhang, "Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions," *Macromolecular Bioscience*, vol. 5, no. 6, pp. 539–548, 2005.
- [5] S. Zhang, F. Li, J. Yu, and L. Gu, "Novel fibers prepared from cellulose in NaOH/thiourea/urea aqueous solution," *Fibers and Polymers*, vol. 10, no. 1, pp. 34–39, 2009.
- [6] J. Cai, L. Zhang, J. Zhou, H. Li, H. Chen, and H. Jin, "Novel fibers prepared from cellulose in NaOH/urea aqueous solution," *Macromolecular Rapid Communications*, vol. 25, no. 17, pp. 1558–1562, 2004.
- [7] K. Li, J. Song, M. Xu, S. Kuga, L. Zhang, and J. Cai, "Extraordinary reinforcement effect of three-dimensionally nanoporous cellulose gels in poly(ϵ -caprolactone) bionanocomposites," *ACS Applied Materials & Interfaces*, vol. 6, no. 10, pp. 7204–7213, 2014.
- [8] B. Duchemin, D. Le Corre, N. Leray, A. Dufresne, and M. P. Staiger, "All-cellulose composites based on microfibrillated cellulose and filter paper via a NaOH-urea solvent system," *Cellulose*, vol. 23, no. 1, pp. 593–609, 2016.
- [9] B. Xiong, P. Zhao, K. Hu, L. Zhang, and G. Cheng, "Dissolution of cellulose in aqueous NaOH/urea solution: role of urea," *Cellulose*, vol. 21, no. 3, pp. 1183–1192, 2014.
- [10] H. Qi, J. Cai, L. Zhang, and S. Kuga, "Properties of films composed of cellulose nanowhiskers and a cellulose matrix regenerated from alkali/urea solution," *Biomacromolecules*, vol. 10, no. 6, pp. 1597–1602, 2009.
- [11] P. Piltanen, N. C. Hildebrandt, B. Westerlind, J.-P. Valkama, T. Tervahartala, and M. Illikainen, "Green and efficient method for preparing all-cellulose composites with NaOH/urea solvent," *Composites Science and Technology*, vol. 135, pp. 153–158, 2016.
- [12] J. W. Dormanns, J. Schuermann, J. Müssig, B. J. C. Duchemin, and M. P. Staiger, "Solvent infusion processing of all-cellulose composite laminates using an aqueous NaOH/urea solvent system," *Composites Part A: Applied Science and Manufacturing*, vol. 82, pp. 130–140, 2016.
- [13] Cotton, "Wikipedia, the free encyclopedia," 2017, <http://en.wikipedia.org/wiki/Cotton>.
- [14] National Cotton Council of America, *Cotton Futures*, 2015, <http://www.cotton.org/>.
- [15] E. Tronc, C. A. Hernández-Escobar, R. Ibarra-Gómez, A. Estrada-Monje, J. Navarrete-Bolaños, and E. A. Zaragoza-Contreras, "Blue agave fiber esterification for the reinforcement of thermoplastic composites," *Carbohydrate Polymers*, vol. 67, no. 2, pp. 245–255, 2007.
- [16] S. C. Davis, F. G. Dohleman, and S. P. Long, "The global potential for Agave as a biofuel feedstock," *GCB Bioenergy*, vol. 3, no. 1, pp. 68–78, 2011.
- [17] S. Kestur G., T. H. S. Flores-Sahagun, L. P. Dos Santos, J. Dos Santos, I. Mazzaro, and A. Mikowski, "Characterization of blue agave bagasse fibers of Mexico," *Composites Part A: Applied Science and Manufacturing*, vol. 45, pp. 153–161, 2013.
- [18] J. A. Perez-Pimienta, M. G. Lopez-Ortega, P. Varanasi et al., "Comparison of the impact of ionic liquid pretreatment on recalcitrance of agave bagasse and switchgrass," *Bioresource Technology*, vol. 127, pp. 18–24, 2013.
- [19] C. G. Iñiguez, C. J. Bernal, M. W. Ramírez, and N. J. Villalvazo, "Recycling agave bagasse of the tequila industry," *Advances in Chemical Engineering and Science*, vol. 4, no. 2, pp. 135–142, 2014.
- [20] Alibaba.com, "Natural raw sisal fiber," 2017, https://www.alibaba.com/product-detail/Natural-raw-sisal-fiber-sisal-fibre_50032858093.html.
- [21] J. L. Smith and J. V. Perino, "Osage orange (*Maclura pomifera*): history and economic uses," *Economic Botany*, vol. 35, no. 1, pp. 24–41, 1981.
- [22] R. Wynia, *Plant Guide for Osage orange* (*Maclura pomifera*), USDA-Natural Resources Conservation Service, Manhattan Plant Materials Center, Manhattan, NY, USA, 2001, http://plants.usda.gov/plantguide/pdf/pg_mapo.pdf.
- [23] M. Z. M. Salem and N. H. Mohamed, "Physico-chemical characterization of wood from *Maclura pomifera* (Raf.) C.K. Schneid. Adapted to the Egyptian environmental conditions," *Journal of Forest Products and Industries*, vol. 2, no. 2, pp. 53–57, 2013.
- [24] Textile Technologist, "What is cotton fiber. Chemical composition of cotton fiber," 2012, <http://textilefashionstudy.com/what-is-cotton-fiber-chemical-composition-of-cotton-fiber/>.
- [25] S. Hemsri, K. Grieco, A. D. Asandei, and R. S. Parnas, "Wheat gluten composites reinforced with coconut fiber," *Composites*

Part A: Applied Science and Manufacturing, vol. 43, no. 7, pp. 1160–1168, 2012.

- [26] D. Theng, N.-E. El Mansouri, G. Arbat et al., “Fiberboards made from corn stalk thermomechanical pulp and kraft lignin as a green adhesive,” *Bioresources*, vol. 12, no. 2, pp. 2379–2393, 2017.