On the Design of Novel Biofoams Using Lignin, Wheat Straw, and Sugar Beet Pulp as Precursor Material

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ABSTRACT: In this paper, we report the synthesis and characterization of pyrolyzed lignin compacts reinforced with 50 wt % wheat straw (WS) or sugar beet pulp (SBP) fibers. The compacts were pyrolyzed at 300, 500, 700, and 900 °C in an Ar atmosphere. Detailed thermogravimetric analysis (TGA), thermo-mechanical analysis (TMA), Fourier transform infrared (FTIR) spectroscopy, and microstructure analysis were performed on these samples. FTIR analysis showed that pyrolysis of lignin–WS and lignin–SBP resulted in aromatic char. Scanning electron microscope (SEM) studies showed that foams obtained by pyrolyzing both lignin–50 wt % SBP and lignin–50 wt % WS composites have a cellular structure. X-ray tomography and energy-dispersive spectrometry (EDS) studies showed that pyrolysis of wheat straw caused the formation of mineral-rich nodules in the pyrolyzed lignin matrix, which was responsible for the denser and uniform microstructure of the lignin–WS composites. Due to this reason, the lignin–WS composites were denser and had a better mechanical strength as compared to the lignin–SBP composites. Both the compositions also showed temperature-dependent wettability behavior.

1. INTRODUCTION

Some examples of agricultural waste are sugar beet pulp (SBP) and wheat straw (WS).^{1–4} Due to the large-scale production, it is often difficult to manage the agricultural waste. Farmers use crop burning as a simpler method to manage these waste.⁵ The novel design paradigm of crop residue valorization can increase the farmer's income and reduce environmental pollution. Recently, lignocellulose-based biomass has emerged as an important source of precursor materials for producing engineered materials for sustainable components, biobased structures, surface engineering, and food protection.^{6,7} Material design by pyrolysis of biomass and innovative material structure like foams is an important pathway for commercialization of biomass.^{8–17} In general, the process is challenging as the biomass is composed of different constituents, namely, cellulose (40–60%), hemicellulose (15–30%), and lignin (10–25%), and the resultant combination is dependent on the source.⁹

As a background, cellulose is regarded as the most abundant linear polysaccharide in which long-chain glucose units are linked by β -1,4-glycosidic linkages.^{9,10} The sensitive glucosidic bonds are susceptible to perturbations like acid treatment and high-temperature processes and, consequently, degrade rapidly during high-temperature pyrolysis.^{9,10} Structurally, hemicellulose has an amorphous nature, which is distinguished by the short-chained and branched nature of the molecules.⁹ Scheller

and Ulvskov¹¹ have listed xyloglucan, xylans, mannans and glucomannans, and β -(1 $\rightarrow$ 3, 1 $\rightarrow$ 4)-glucans as the major constituents of hemicellulose. Due to the heterogeneous nature of hemicellulose, its pyrolysis behavior is dependent on the composition of the polysaccharides, which is further affected by the source of the biomass.⁹

Comparatively, lignin is a phenolic macromolecule with a complex and interlinked amorphous structure and is the main source of aromatic structures.¹² At the molecular level, lignin is composed of three main monolignols: *p*-coumaryl (4-hydroxycinnamyl, containing no methoxyl group), coniferyl (3-methoxy 4-hydroxycinnamyl, containing one methoxyl group), and sinapyl (3,5-dimethoxy 4-hydroxycinnamyl, containing two methoxyl group) alcohols. These monolignols are also referred to as *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units.^{9,12} Wang et al.⁹ have also pointed out these monolignols as phenylpropane units (ppu) as they also have a phenyl group and a propyl side chain. The content and relative

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Table 1.. Summary of Lignocellulose Data (All of the Data are Reported as % of Total Dry Matter)

fiber content	total sugars	glucan	xylan	mannan	arabinan	galactan	rhamnan	klason lignin	acid soluble lignin	extractives	ash
(−100 + 200 WS)	64.33	37.46	22.56	0.48	2.87	0.96	0.15	14.54	2.15	2.92	8.51
(indulin lignin)	3.31	1.04	1.05	0.07	0.30	0.85	x	58.40	1.01	31.59	3.13
(−100 + 200 SBP)	45.32	20.92	1.21	1.17	15.50	4.47	2.06	2.74	4.03	12.70	4.19

proportions of these units will be dependent on the type of the biomass.⁹ Due to these reasons, the chemistry of the lignin macromolecules is source-dependent, heterogeneous, and lacks stereoregularity, which make them difficult to valorize as compared to polysaccharides like cellulose.¹² In addition, as compared to cellulose and hemicellulose, which show weight loss in the temperature range of 315–400 and 220–315 °C, respectively, lignin is recalcitrant (tough molecular structure) and decomposes over a wide temperature range of 160–900 °C.¹³ From an environmental and commercial perspective, it is critical to find new avenues of commercialization of biomass from conventional resources like crop products and lignin.

Lignin-based foams have been fabricated by a combination of chemical reaction and foaming processes. Xue et al.¹⁴ have added 8.33–37.19% w/w lignin in lignin-based rigid polyurethane foam (LRPF) where di-*n*-butyltin dilaurate (DBTDL), silicone, and water were used as the catalyst, surfactant, and blowing agent, respectively.¹⁴ Stevens et al.¹⁵ replaced starch foams with 20% lignin without compromising the properties. Tondi et al.¹⁶ designed lignin-furanic-based biofoams by incorporating 24–37% lignin. They also used ethanol and H₂SO₄ as the blowing agent and catalyst, respectively. In a recent study, Gupta et al.¹⁷ demonstrated that 100% lignin-based foams with tailored wettability behavior can be designed by pyrolyzing lignin compacts at different temperatures to form carbonaceous foams. In other words, the pyrolysis behavior of lignin can be tailored to effectively utilize 100% lignin to fabricate biobased foams.

Inagaki et al.¹⁸ classified the fabrication of carbon foams into five different categories: (I) expansion (blowing) of carbon precursors by mechanical or chemical methods and subsequent carbonization, (II) carbonization of resin-infiltrated and -templated porous carbon precursors, (III) preformed design by engineering the architectures of fully or partially exfoliated graphite via compression, etc., (IV) consolidation of graphene nanosheets by hydrothermal and chemical processes, and (V) other methods that do not fit the four categories mentioned earlier. For comparing with this research, it is instructive to compare the manufacturing process and properties of foams designed during this study with method (I) as it involves carbonization. During this manufacturing process, (a) the carbonaceous foams are produced by pyrolysis or chemical treatment and (b) then the foams are carbonized at the designated temperatures.¹⁸ By using the procedure outlined by Gupta et al.,¹⁷ porous carbonaceous foams from lignin can be synthesized in a single step where the gases produced during pyrolysis act as foaming agents, thus eliminating the need for foaming the agents proposed in previous research on lignin-based foams.^{14,16} In addition, 100% lignin compacts can undergo expansion and carbonization in a single step, thus eliminating the usage of multiple steps,¹⁸ which results in porous structures with >90% porosity.¹⁷

In this research, we will design lignin matrix porous biofoams by fabricating the composites with as-received biowaste fibers like sugar beet pulp (SBP) or wheat straw (WS). The objectives of this research study are to (a) design

and manufacture novel lignin matrix foams and (b) develop a fundamental understanding of the pyrolysis temperature-microstructure-property space using a tailored amount of biowaste fiber additives.

2. EXPERIMENTAL DETAILS

The WestBred wheat straw (WS) was procured from the National Renewable Energy Laboratory. Sugar beet pulp (SBP) was procured from the Crystal Sugar Plant of East Grand Forks. Table 1. shows the chemical composition of all of the precursors used during this study. The chemical information was determined by Celnis Analytical using their commercially available P-11 package (Celnis Biomass Analysis Laboratory, Plassey Technology Park, Limerick, Ireland).

All of the fibers were ball-milled (8000 M mixer Mill, SPEX SamplePrep, Metuchen, NJ) for 5 min. The pulverized powders were then sieved into a (−100 + 200) mesh by using a sieve shaker. Lignin (Indulin AT, MeadWestvaco, Richmond, VA) was mixed with 50 wt % WS or SBP for 5 min. Thereafter, it was mixed with 10 wt % deionized (DI) water for 5 min in a ball mill. The mixed powders were then poured and cold-pressed at a pressure of ~263 MPa in a ~12.7 mm steel die (Model EQ-Die-06D-B, MTI Corporation, Richmond, CA). The cold-pressed samples were then demolded to form compacts. The compacted samples were then pyrolyzed in a tube furnace for 1 h with flowing Ar at 300, 500, 700, and 900 °C.

The pyrolysis kinetics of WS and SBP was performed using a thermogravimetric analyzer (TGA Q500, TA Instruments, New Castle, DE) at a heating rate of 10 °C/min until 950 °C in N₂ atmosphere. The thermochemical changes of the pyrolyzed powders were studied by Fourier transform infrared (FTIR) spectroscopy (Thermo Scientific Nicolet 8700 instrument). During this process, (a) heat-treated or pyrolyzed powders were mixed with KBr powder and (b) the powders were consolidated into compacts. The spectra for each sample were then collected in the range of 400–4000 cm^{−1} with a spectral resolution of 4 cm^{−1}. Each sample was scanned 32 times. The peak positions were then designated in FTIR using an analysis software (OMNIC 802, company, Thermo Fisher Scientific, Waltham, MA).

The thermomechanical behavior of the cold-pressed samples was studied using a thermomechanical analyzer (TMA 60 H, Shimadzu Scientific Instruments, Columbia, MD) at a heating rate of 10 °C/min to 900 °C in an Ar atmosphere under a load of −0.01 N. During the measurement process, the samples were capped with alumina plates for uniformly distributing the stress over the samples.

The microstructures of all of the samples were characterized using a scanning electron microscope (SEM, JEOL JSM-6490LV, JEOL USA, Inc., Peabody, Massachusetts) in secondary electron (SE) and backscattered electron (BSE) mode. For chemical analysis of the samples, the samples were coated in a Balzers SCD 030 sputter coater (BAL-TEC RMC, Tucson, AZ) with Au/Pd. The chemical information on a

point of interest (PoI) was obtained using a thermo nanotracer energy-dispersive X-ray detector with NSS-300e acquisition in a point analysis mode. For every PoI, an average of three readings is reported in the text.

X-ray tomography was performed to evaluate the intrinsic structure of the foams, for example, morphology, interconnectivity, and distribution of the pores. During this process, the X-ray microcomputed tomography system (GE Phoenix vltomel x s, GE Sensing & Inspection Technologies GmbH, Niels Bohr Str 7, 31515 Wunstorf, Germany) was used to analyze the adhered sample on a glass rod. The main components of the equipment are a 180 kV high-power nanofocus X-ray tube (GE xsl180nf, GE Sensing & Inspection Technologies GmbH, Niels Bohr Str 7, 31515 Wunstorf, Germany) and a high-contrast flat panel detector (GE DXR250RT, GE Sensing & Inspection Technologies GmbH, Niels Bohr Str 7, 31515 Wunstorf, Germany). For each sample, 60 kV and 350 μ A were used for scanning and 1500 projections were acquired using a molybdenum target. The acquired images were reconstructed into a volume data set using GE datoslx 3D computer tomography software version 2.2 (GE Sensing & Inspection Technologies GmbH, Niels Bohr Str 7, 31515 Wunstorf, Germany). VGStudio Max version 3.3 (Volume Graphics, Inc., 415 Minuet Lane, Charlotte, NC) was used to view and extract the information from the reconstructed volume. During this analysis, a region of interest (ROI) was chosen from the sample volume. A surface determination (SD) was then applied to differentiate between the material surface and air, and the percentage material and percentage air were calculated for the extracted volume.¹⁷

All of the process samples were ground into a cylindrical geometry. The height and width of the cylinders were measured by vernier calipers. The bulk density (ρ_b) was then calculated by normalizing the mass of the machined foam with the volume of the cylinders. The foams were further ground into powders using a mortar–pestle. The true density (ρ_t) of the foams was calculated from the crushed powders using He pycnometer Ultrapyc 1200e (Quantochrome Instruments, Boynton Beach, Florida). The total porosity (P_T) of the foams was determined using eq 1.¹⁷

$$P_T (\%) = (1 - \rho_b/\rho_t) \times 100 \quad (1)$$

The foams were then machined using a diamond saw into ~ 3 mm cubes for cold crushing strength (CCS) in compression using a mechanical testing unit (Shimadzu AD-IS UTM, Shimadzu Scientific Instruments Inc., Columbia, MD) at a deflection rate of 0.5 mm/min. For each composition, a set of at least 3 samples were tested (3 sets for lignin–50 wt % WS and 5 sets for lignin–50 wt % SBP-based compositions). In this paper, the ultimate compressive strength (UCS) is defined as the stress at which a sample attained maximum stress in the stress versus displacement plots. For each composition, an average of at least 3 UCS measurements is reported in the text.¹⁷

The contact angle analysis was performed on the polished samples. For each composition, a set of 3 tests were performed on randomly chosen spots using a contact angle analyzer (Data physics contact angle system, OCA 15Plus, Future Digital Scientific Corp, New York). During testing, a sessile drop of deionized (DI) water (10 μ L) was deposited on each spot using a needle (Gastight 1750, Hamilton-Bonaduz, Schweiz, Switzerland), and a snapshot was taken after 15 s. For each

drop, the baseline and the curve fitting were done manually. The contact angle was measured using the software SCA20.¹⁷

3. RESULTS AND DISCUSSION

3.1. Microstructure and Thermomechanical Analysis of Fibers. Table 1. summarizes the chemical composition of

Figure 1. SEM micrographs of wheat straw fibers (a) as-received in SE, (b) BSE at a higher magnification and treated at (c) 300 °C, (d) BSE at a higher magnification, (e) 500 °C, (f) BSE at a higher magnification, (g) 700 °C, (h) BSE at a higher magnification, (i) 900 °C, and (j) BSE at a higher magnification.

WS, SBP, and lignin. Both WS and SBP had higher sugar content (cellulose and hemicellulose) as compared to indulin lignin. WS had a higher amount of glucan, xylan, lignin, and ash content as compared to SBP, whereas SBP had a higher amount of arabinan, rhamnan, and galactan. Figure 1 shows the microstructure of the sieved WS fibers. In general, the fibers are anisotropic (Figure 1a,b) and retained similar morphology after pyrolysis at 300, 500, 700, and 900 °C (Figure 1c–j). Figure 2a,b shows the morphology of the SBP fibers, which had anisotropic morphology; however, the edges were rounded. Like the WS fibers, the SBP fibers retained similar morphology after pyrolysis treatment at higher temperatures (Figure 2c–j). In general, both the WS and SBP fibers had minerals composed of Na, K, Mg, Al, Si, and Cl. However, the Si content was higher in the WS fiber as compared to SBP

Figure 2. SEM micrographs of sugar beet pulp fibers, (a) as received in SE, (b) BSE of the same region and treated at (c) 300 °C, (d) BSE of the same region, (e) 500 °C, (f) BSE at a higher magnification, (g) 700 °C, (h) BSE at a higher magnification, (i) 900 °C, and (j) BSE at a higher magnification.

(Table 2). It is well known in the literature that WS is rich in SiO₂, which is undesirable, and can complicate its pulping, liquor recovery, and abrade factory installations.¹⁹

Figure 3a shows the TGA analysis of lignin, WS, and SBP. The solid char left after the pyrolysis of indulin lignin was ~45 wt % as compared to ~24.5 and ~19.5 wt % after the pyrolysis of WS and SBP, respectively. Yang et al.¹³ also similarly reported a solid residue content of ~45.7 wt % in kraft lignin and ~20 and ~6.5 wt % solid residues in hemicellulose and cellulose, respectively, after pyrolysis.

Lignin decomposes in the broad temperature range of 160–900 °C.^{13,20} Li et al.²⁰ divided the decomposition of organosolv lignin into mainly three stages: (I) removal of physically trapped water in the temperature range of 25–170 °C, (II) breakdown of various bonds in lignin, which resulted in products like coke, organic acid, and hydroxyl group-containing aromatic (phenols) compounds and gas products until 500 °C, and (III) finally pyrolytic degradation of lignin, where decomposition and condensation of the aromatic rings occurred at higher temperatures. Yang et al.¹³ observed that hemicellulose and cellulose degraded at much lower temperatures. From the structural perspective, hemicellulose is composed of branched and amorphous polysaccharides as compared to linear and long polymers of cellulose, which are

comparatively stronger.^{9–11,13} Due to this reason, hemicellulose decomposes in the lower-temperature range of 220–315 °C as compared to 315–400 °C in cellulose.

Lazdovica et al.²⁶ studied the pyrolysis of WS and have documented three main stages: (a) removal of H₂O until 100 °C by (b) decomposition and breakdown of various derivatives, hemicelluloses, cellulose, and lignin components of WS in the temperature range of 200–450 °C, and (c) pyrolytic degradation of lignin and charring of the residue in the temperature range of 450–700 °C. The higher amount of lignin and ash content in WS as compared to SBP can explain the higher wt % of char observed in WS as compared to SBP. By comparing refs 20 and 26, we have also divided Figure 3 into three regimes as proposed by Li et al.²⁰ as the decomposition regimes of lignocellulosic materials are well established in the literature.

Figure 3b shows the thermomechanical behavior of lignin–50 wt % WS and lignin–50 wt % SBP. As a comparison, using in situ high-temperature rheology, Shrestha et al.²¹ established that lignin undergoes softening in the temperature range of 140–250 °C; thereafter, it undergoes a hardening process in the temperature range of 250–370 °C. In a previous study, we showed that lignin showed the onset of viscous deformation at ~200 °C (the compact is not able to withstand the marginal load of ~0.01 N during thermomechanical analysis), and by 300 °C, it slumped to ~86% of its original length. Thereafter, at higher temperatures, the compact gradually stopped collapsing, which further indicates that the compact had become rigid.¹⁷ Both the lignin–50 wt % SBP and lignin–50 wt % WS composites started to deform at ~220 °C, and lignin–50 wt % SBP deformed to ~75% of its original height by 275 °C. Comparatively, lignin–50 wt % WS deformed by ~47% by 275 °C; thereafter, it deformed gradually to ~67% by 450 °C. This result shows that the WS fibers can marginally support the lignin matrix at higher temperatures as compared to SBP.

3.2. FTIR Analysis. **3.2.1. FTIR Analysis of Lignin.** Figure 4a–c and d–f shows FTIR analysis of the lignin–WS and lignin–SBP composites pyrolyzed at different temperatures, respectively. FTIR is a well-established technique for analyzing biomass, and several excellent references have summarized the results of the FTIR of biomass.^{13,21–26} Table 3 summarizes the peak assigned to different wave numbers and corresponding to different fractions of biomass. As a summary, the peaks in the 3400 cm^{−1} range belong to O–H stretching.^{13,21–23} The peak at 1735 cm^{−1} is the characteristic peak of hemicellulose (xylans);²⁵ peaks in the range of 1459–1600 cm^{−1} are the characteristic peaks of lignin;^{21,22} and 667, 898, and 1322 cm^{−1} peaks can be correlated with cellulose.^{24,25} For a fundamental understanding, the peaks corresponding to the CH aromatic band/wag in the range of 900–700 cm^{−1} are used for studying the changes in the aromatic structures during pyrolysis.²² In general, FTIR analysis of the WS and SBP fibers pyrolyzed at higher temperatures showed that the intensity of peaks is decreased at higher temperatures due to the breakdown of lignocellulose molecules (Figure 4). Due to this reason, Figure 4c,f shows the FTIR results obtained between 500 and 900 °C superimposed on each other for better visualization of the data. WS and SBP are composed of cellulose, hemicellulose, and lignin (Table 1.), and hence, it is fundamental to review the pyrolysis behavior of these constituents individually.

Wu et al.¹⁰ reported the presence of levoglucosan due to depolymerization of cellulose at 300 °C; however, at 500 °C,

Table 2. Elemental Analysis of Pyrolyzed SBP and WS Composites

code	C*	O	Mg	Al	Si	P	S	Cl	K	Ca	Na
A1	54.1 ± 1.39	37.5 ± 2.26	x		1.93 ± 1.29	x			3.63 ± 0.19	0.83 ± 0.16	x
A2	62 ± 5.22	37.2 ± 5.36			0.71 ± 0.13				0.21 ± 0.04		
B1	51.4 ± 0.78	34.3 ± 0.68	0.20 ± 0.01	0.10 ± 0.01	13.3 ± 0.17				0.43 ± 0.06	0.20 ± 0.05	
B2	63.3 ± 1.30	33.0 ± 1.74	0.16	0.51 ± 0.11	1.15 ± 0.20				1.33 ± 0.13	0.63 ± 0.06	
C1	67.4 ± 1.46	18.3 ± 0.37	0.59 ± 0.09	0.23 ± 0.05	2.48 ± 0.09				x		
C2	78.8 ± 0.39	14.5 ± 0.76	0.19 ± 0.02	x	1.42 ± 0.19	0.37	0.35 ± 0.03	1.62 ± 0.07	3.11 ± 0.23		
D	78.3 ± 0.19	18.6 ± 0.27	0.31 ± 0.05		4.57 ± 0.20	x		0.49 ± 0.01	x	0.42	
E2	21.4 ± 0.27	55 ± 0.34	x		21.1 ± 0.21			0.16 ± 0.03			0.21
E1	25.3 ± 0.53	55.3 ± 0.17			17.41 ± 0.16			0.15	1.82 ± 0.05		0.18
SBP1	28.6 ± 2.26	50.9 ± 3.73	0.58 ± 0.07	5.58 ± 2.88	7.61 ± 3.99	x		x	2.71 ± 0.29	4.30 ± 1.93	x
SBP2	45.9 ± 6.44	42.1 ± 6.64	0.38 ± 0.10	0.19 ± 0.045	2.34 ± 1.00		0.38		0.47 ± 0.06	2.78 ± 0.70	
SBP3	43.3 ± 3.40	44.5 ± 4.96	0.80 ± 0.20	x	x				0.92 ± 0.18	6.46 ± 1.17	
F1	64.8 ± 1.67	30.4 ± 1.95	1.02 ± 0.12			0.1	0.61 ± 0.03		1.07 ± 0.05	1.48 ± 0.11	
G1	71.3 ± 0.84	15.8 ± 2.91	1.7 ± 0.25		0.93 ± 0.16	x	0.93 ± 0.17		3.34 ± 1.27	5.85 ± 1.97	1.13 ± 0.12
G2	63.2 ± 0.40	23.6 ± 0.10	1.75 ± 0.13	0.13 ± 0.22			1.76 ± 0.16		2.74 ± 0.23	6.63 ± 0.17	0.4
H1	33.5 ± 1.61	29.4 ± 3.08	0.34 ± 0.02	0	0		10.7 ± 0.28		0.45 ± 0.03	25.5 ± 1.29	0.38
H2	88.8 ± 0.49	x	0.93 ± 0.15	0.243 ± 0.03	0.45 ± 0.02		1.55 ± 0.04		1.09 ± 0.01	6.48 ± 0.3	0.40 ± 0.08
I1	65 ± 0.4	14.5 ± 0.46	0.86 ± 0.04	0.22 ± 0.05	0.53 ± 0.03		7.34 ± 0.10		0.93 ± 0.05	9.97 ± 0.15	0.56 ± 0.04
I2	95 ± 0.04	x	1.11 ± 0.03	x	x	0.2	0.26 ± 0.05		1.47 ± 0.16	1.43 ± 0.07	0.67 ± 0.09
J	95.9 ± 0.06		x			x	5.96 ± 0.54		0.74 ± 0.12	3.41 ± 0.08	x
L1	51.9 ± 0.63	39.6 ± 0.33		0.61 ± 0.01	2.40 ± 0.29				5.43 ± 0.33		
L2	54.5 ± 3.55	25.1 ± 5.94		3.44 ± 0.96	x				13.0 ± 1.03		
M1	79.8 ± 14.8	25.2 ± 0.39		0.18 ± 0.01	1.37 ± 0.20				0.68 ± 0.14		1.16 ± 0.07
M2	96.8 ± 0.23	x		0.18	x				1.14 ± 0.07		1.93 ± 0.06
N1	97.2 ± 0.16		0.39	0.12					1.43 ± 0.10	0.55	0.97 ± 0.05
N2	97.9 ± 0.27		x	0.17				0.26	x	x	0.78 ± 0.06
N3	55.5 ± 0.26	24.9 ± 0.13		1.3					11.98 ± 0.23		1.18 ± 0.04
K1	86.6 ± 0.55	8.98 ± 0.47	0.11 ± 0.08	x	6.43 ± 0.45		0.41		0.38 ± 0.03		x
K2	97.7 ± 0.01		x		2.55 ± 0.08		0.70 ± 0.01		1 ± 0.01

Figure 3. Plot of (a) TGA of lignin, wheat straw (WS), and sugar beet pulp (SBP) and (b) thermal strain (%) versus temperature of lignin–50 wt % SBP and lignin–50 wt % WS.

Figure 4. FTIR of pyrolyzed WS between (a) 400 and 2000 cm⁻¹, (b) 2000 and 4000 cm⁻¹, and (c) 400 and 2000 cm⁻¹ (the superimposed data of WS treated at 500, 700, and 900 °C) and pyrolyzed SBP between (d) 400 and 2000 cm⁻¹, (e) 2000 and 4000 cm⁻¹, and (f) 400 and 2000 cm⁻¹ (the superimposed data of SBP treated at 500, 700, and 900 °C).

different products like C₂–C₃ carbonyls, furans, pyrans, cyclo-C₅, and anhydrosugars were detected. Wu et al.¹⁰ also reported that the char became aromatic in nature after cellulose was pyrolyzed at 900 °C due to (a) furans undergoing reforming and combinatorial reactions (cycloadditions) between different

Table 3. FTIR Analysis of Lignin, WS, and SBP

peak assignment	lignin	WS	SBP
O–H stretching ^{21,22,25}	3424	3417	3409
aromatic C–H stretch ²²	3000	x	x
aromatic, ¹³ aliphatic ^{13,21,22}	2934	2918	2927
methoxy ^{21,22}	2850	x	x
C=O stretching in unconjugated ketones, carboxyls, and ester groups ²¹	1707		
stretching of unconjugated CO groups ²⁵	x	1735	1741
aromatic skeletal vibrations ²⁴		x	1640
aromatic skeletal or ring vibrations ^{21,22}	1596	1604	x
aromatic skeletal or ring vibrations ^{21,22}	1513	1509	1521
CH deformation ^{21,22} and vibration of aromatic rings ²²	1463	1459	x
asymmetric C–H (O–CH ₃) deformation [21] or C=C stretching in aromatic groups ²⁵	1426	1425	1436
C–H deformation ^{21,22,25} or OH in-plane bending ²²	1371	1374	1374
C–O aromatic ring ^{21,25}	x	1322	1326
aryl ring breathing with C=O stretch ²¹	1269	x	
C–C, ^{21,23} C–O (phenol) ^{13,21,23} and C=O ²¹ stretching	1218	1245	1246
C–O–C stretching vibration, ^{13,25} aromatic C–H ^{21,23}	1151	1162	x
aromatic C–H ^{21,23}	1128	1103	1109
deformation and stretching of C–O ¹³	1082	1055	1061
aromatic C–H in-plane deformation ²¹	1032	x	
symmetric glycosidic bonds ^{24,25}	x	898	x
single aryl CH vibration ²²	856	x	
two adjacent aryl CH vibration ²²	817		
C–OH out-of-plane bending ^{22,25}	x	667	667
C–C and C–H stretching ¹³	625	608	602
C–C and C–H stretching ¹³	560	562, 463	515

constituents and (b) further decomposition and chemical evolution of char obtained at lower temperatures.

Hemicellulose (xylan and glucomannan are the main components in angiosperms and gymnosperms, respectively) undergoes depolymerization at >240 °C for xylan or >270 °C for glucomannan due to rapid deterioration of glycosidic linkages, which produces anhydrosugars during the process. During the charring process at 300 °C and higher temperatures, the char became aromatic.⁸ Similarly, detailed FTIR studies have shown that the aromatic structure in lignin transitions to closed-ring structures like naphthalene, substituted naphthalene, and anthracene at higher temperatures.²²

For both WS and SBP, the peaks corresponding to xylenes (1735 cm⁻¹, Table 3) were not observed after pyrolysis at 300 °C (Figure 4c,f). Similarly, the peak corresponding to cellulose (1322 cm⁻¹, Table 3) disappeared after 500 °C for both WS and SBP (Figure 4c,f). This further supports our initial analysis that the pyrolysis regime during TGA can be divided into three regions (Figure 3). The peaks corresponding to aromatic vibrations were observed for both WS and SBP in the range of 1490–1600 cm⁻¹ after pyrolysis at 300 °C. More particularly, the peaks corresponding to 1596 cm⁻¹ (Table 3) were observed at 1583, 1551, and 1578 cm⁻¹ for WS treated at 500, 700, and 900 °C, respectively (Figure 4c). Similarly, for SBP, the peaks corresponding to 1596 cm⁻¹ (Table 3) were observed at 1577, 1544, and 1553 cm⁻¹ for SBP treated at 500, 700, and 900 °C, respectively (Figure 4f). The peak corresponding to 1513 cm⁻¹ (Table 3), a characteristic peak of lignin and well-established marker for phenyl ring skeletal

Figure 5. SEM micrographs of the lignin–sugar beet pulp composites after pyrolysis at (a) 300 °C, (b) BSE of the same region, (c) 500 °C, (d) BSE of the same region, (e) 700 °C, (f) BSE at a higher magnification, (g) 900 °C, and (h) BSE of the same region.

vibrations,^{21,22} was observed at 1512 and 1515 cm^{-1} after pyrolysis of WS and SBP at 300 °C, respectively, but disappeared completely after pyrolysis at higher temperatures. An additional peak in the range of 1218–1240 cm^{-1} also disappeared at higher temperatures, which indicates delignification.²⁷ These observations also support the results of previous studies that the aromatic nature of the char increases at high temperatures due to the breakdown of lignocellulosic molecules.^{8,10,17,22,27}

To understand the chemical nature of the aromatic pyrolyzed char, as discussed earlier, the peaks in the range of 900–700 cm^{-1} are used for understanding the aromatic characteristics of the char.²² The peak corresponding to the single aryl CH vibration was observed at 856 cm^{-1} for lignin but was not observed for WS or SBP (Figure 4a,d). Comparatively, after pyrolysis treatment of WS at 500 and 700 °C, this peak shifted to 876 and 878 cm^{-1} , respectively (Figure 4c). Similarly, after pyrolysis treatment of SBP at 500 and 700 °C, this peak shifted to 872 and 877 cm^{-1} , respectively (Figure 4f). Fused ring compounds like naphthalene, substituted naphthalene, and anthracene have this band in the range of 875–823, 905–835, and 900–875 cm^{-1} .²² For WS, initially no peaks were detected at 817 cm^{-1} ; however, after pyrolysis of WS at 300, 500, 700, and 900 °C, the corresponding peaks were observed at 799, 806, 799, and 799 cm^{-1} . Similarly, during the pyrolysis of SBP, initially no peaks were detected at 817 cm^{-1} , but after pyrolysis at 300, 500, 700, and 900 °C, the new peaks were detected at 782, 799, 796, and 727 cm^{-1} , respectively (Figure 4c,f). Like previous studies,^{10,12} this study also shows that the char formed during the pyrolysis

Figure 6. SEM micrographs of the lignin–wheat straw composites after pyrolysis at (a) 300 °C, (b) BSE at higher magnifications, (c) 500 °C, (d) BSE at higher magnification, (e) 700 °C, (f) BSE of the same region, (g) 900 °C, and (h) BSE at higher magnification.

of WS and SBP has aromatic nature after pyrolysis at higher temperatures and is composed of fused rings due to the breakdown of oxygen-containing functional groups.²² Lupoi et al.²⁷ reviewed different analytical techniques for analyzing biomass-based products. They summarized that there is no stand-alone technique that can be used as a “superlative analytical method” for understanding the lignin-based products. Thus, further studies are recommended using nuclear magnetic resonance (NMR) and Raman spectroscopy to understand the detailed chemistry of closed-ring structures derived from the pyrolysis of lignin.

3.3. Microstructure Analysis of Foams. Figure 5 shows the SEM images of the lignin–50 wt % SBP foams fabricated at different temperatures; for example, Figure 5a–b, c–d, e–f, and g–h shows foams fabricated at 300, 500, 700, and 900 °C, respectively. On closer examinations of these micrographs (for example, Figure 5a,b), cells (pores, which are encircled by thin layers), cell wall (boundaries or interface, where individual cells meet), windows (pathways or corridors, which connect a cell wall to neighboring cells), and struts (junction between neighboring cell walls, which supports the load) were observed. These features are the typical characteristics of a porous foam structure.¹⁸

Figure 6 shows the SEM images of the lignin–50 wt % WS foams fabricated at different temperatures, for example, Figure 6a–b, c–d, e–f, and g–h shows foams fabricated at 300, 500, 700, and 900 °C, respectively. Unlike the lignin–SBP composites, the lignin–WS composites have a denser microstructure and mineral-rich nodules were observed (L1, M1, N1, N3, and K1; Table 2). Figure 7 shows the chemical

Figure 7. (a) SE SEM lignin–WS composites pyrolyzed at 500 °C and corresponding chemical maps of (b) C, (c) O, (d) Si, (e) Na, (f) Al, (g) Mg, (h) K, and (i) Ca.

Figure 8. X-ray tomography of samples pyrolyzed at: 300 °C: (a) three-dimensional (3D) view, (b) cross-section, and side-views (c) and (d); 500 °C: (e) 3D view, (f) cross-section, and side-views (g) and (h); 700 °C, (i) 3D view, (j) cross-section, and side views (k) and (l); and 900 °C, (m) 3D view, (n) cross-section, and side-views (o) and (p) of lignin–50 wt % SBP composites.

mapping of lignin–50 wt % WS pyrolyzed at 500 °C. This result also supports the SEM results that the carbonaceous

lignin matrix is reinforced with in situ formed mineral-rich constituents. The presence of mineral-rich nodules can also

Figure 9. X-ray tomography of samples pyrolyzed at: 300 °C, (a) 3D view, (b) cross-section, and side-views (c) and (d); 500 °C, (e) 3D view, (f) cross-section, and side-views (g) and (h); 700 °C, (i) 3D view, (j) cross-section, and side views (k) and (l); and 900 °C, (m) 3D view, (n) and (o) side views, and (p) cross-section.

account for the gradual deformation of the lignin–50 wt % WS composites during the TMA studies (Figure 3b).

Figure 8 shows the microCT scan of the foams fabricated at different temperatures of the lignin–50 wt % SBP composites. In all of the cases, the pores are interconnected. In addition, a large cavity (macropore-I, Figure 8b,j) or a few large pores (macropore-II, Figure 8f) were observed at the center. These pores were surrounded by finer macropores, which were further encapsulated with cellular walls. In a previous study, we had also observed similar microporous structures in pyrolyzed lignin.¹⁷ The presence of pores or space in these foams can be further used for introducing different materials for enhancing the functionalities of these pores.

Figure 9 shows the microCT scan of the foams fabricated at different temperatures of the lignin–50 wt % WS composites. Compared to the lignin–50 wt % SBP composites, the microstructures of the samples fabricated were uniform. In other words, mineral-rich nodules were able to control the foaming nature of the pyrolyzed lignin. Table 4 summarizes the porosity of different lignin–SBP and lignin–WS foams. In general, the pyrolyzed lignin foams had porosity in the range of 93–94%;¹⁷ the addition of SPB decreased the porosity to 69, 75, 79, and 79% after pyrolysis at 300, 500, 700, and 900 °C, respectively. Comparatively, lignin–50 wt % WS was denser and had a porosity of 42, 56, 56, and 57% after pyrolysis at 300, 500, 700, and 900 °C, respectively. It is also important to note that microCT was not able to accurately determine the

porosity of the samples (Table 4). Based on these results, it is recommended that microCT is an important tool for inspecting the morphology and connectivity of macropores; however, for understanding the finer nature of the pore structures, a detailed SEM analysis is needed.

3.4. Mechanical Behavior and Wettability. Figure 10a plots the compressive stress versus displacement behavior of a lignin–50 wt % SBP fabricated at different temperatures. In these foams, gradual recovery from failure during compressive stress due to the gradual failure of the individual cells of the pyrolytic foam can be observed. As defined earlier, the maximum stress reached by a pyrolytic foam is defined as the ultimate compressive strength (UCS). The average UCS of the foams fabricated at 300 °C is 1.31 ± 0.59 MPa, which decreased to 1.03 ± 0.52 MPa for the foams fabricated at 500 °C, thereafter increased to 1.14 ± 0.35 MPa at 700 °C, and then increased to 2.03 ± 1.23 MPa at 900 °C (Table 4).

Figure 10b shows the compressive stress versus displacement behavior of a lignin–50 wt % WS fabricated at different temperatures. These foams also showed signs of damage recovery, but their strength was higher than that of the lignin–SBP foams. For example, the UCS of lignin–50 wt % WS was 20.4 ± 13 MPa at 300 °C, which decreased to 13.1 ± 3.68 and 14.9 ± 7.26 MPa after pyrolysis at 500 and 700 °C, respectively, and then increased to 27.6 ± 10.08 MPa after pyrolysis at 900 °C (Table 4).

Table 4. Summary of the Porosity and Mechanical Properties

composition	temperature (°C)	bulk density (g/cc)	total porosity (TP) (%)	porosity by microCT (%)	ultimate compressive strength (UCS) (MPa)	refs
lignin	300	0.14 ± 0.02	93.3 ± 0.95	80.3	0.77 ± 0.21	17
	500	0.13 ± 0.02	94.5 ± 0.76	90.7	0.49 ± 0.16	
	700	0.13 ± 0.05	93.3 ± 1.98	82.9	0.95 ± 0.60	
	900	0.15 ± 0.02	93.4 ± 0.67	87.6	0.95 ± 0.24	
lignin-SBP	300	0.44 ± 0.03	68.9 ± 2.23	59	1.31 ± 0.59	this work
	500	0.38 ± 0.02	75.4 ± 1.07	70.2	1.03 ± 0.52	
	700	0.38 ± 0.01	79.0 ± 0.56	61.8	1.14 ± 0.35	
	900	0.42 ± 0.03	79.2 ± 1.52	66	2.03 ± 1.23	
WS-SBP	300	0.84 ± 0.02	41.8 ± 1.76	3.95	20.4 ± 13	
	500	0.81 ± 0.07	56.1 ± 3.62	31.8	13.1 ± 3.68	
	700	0.80 ± 0.06	56.2 ± 3.62	12.9	14.9 ± 7.26	
	900	0.88 ± 0.13	57.3 ± 6.31	28.8	27.6 ± 10.08	
waste polyurethane-based carbon foam	1200 °C, 4 h	0.57	68.2 ± 0.3	x	21.6 ± 1.2	28
		0.57	71.9 ± 0.4		24.7 ± 1.5	
phenolic foams (base sample - NP)	microwave curing	1.167	94.4		0.11	29
CP 0.5 (0.5 wt % MWCNT)		1.079	95.3		0.14	
CP 1 (1 wt % MWCNT)		1.052	93.8		0.13	
CP 2 (2 wt % MWCNT)		1.002	89.7		0.24	
GP 0.5 (0.5 wt % graphene)		1.123	93.5		0.14	
GP 1 (1 wt % graphene)		1.057	95.4		0.17	
GP2 (2 wt % graphene)		0.945	92.3		0.17	
carbon foam from poly(arylacetylene) resin	carbonized at 1000 °C	0.6	x		25.8	30
carbon foam from modified coal tar pitch	carbonized at 800 °C	0.61			17.79	31
		0.65			19.63	
		0.76			21.27	
		0.69			20.71	
		0.64			18.83	
Kingwood Coal	calcined at 1000 °C	0.32	84.1		2.9	32
Lower War Eagle Coal		0.33	82.7		5.5	
Bakerstown coal - 01		0.38	80.3		8	
Bakerstown coal - 02		0.4	79.3		9.9	
Powelton extract - 01		0.25	87		2.5	
coal tar pitch-based - I (QI containing)		0.67	64.8		18.2	
powelton extract - 02		0.31	83.6		18.7	
petroleum pitch-based		0.34	82.9		3.9	

For lignin, the average UCS of the foams fabricated at 300 °C is 0.77 ± 0.21 MPa, which decreases to 0.49 ± 0.16 MPa for the foams fabricated at 500 °C, and thereafter it increases to 0.95 ± 0.60 MPa at 700 °C; a similar strength is retained for the foams fabricated at 900 °C¹⁷ (Table 4).

Table 4 shows the summary of carbon foams derived from polyurethane,²⁸ phenolic foams,²⁹ polyarylacetylene resin,³⁰ coal tar pitch,^{31,32} and petroleum-based precursors.³² By comparing the mechanical performance data based on a brief review, it is observed that the lignin-WS samples pyrolyzed at 900 °C showed comparable mechanical performance to different types of carbon foams although they had a higher density. The carbon foams have been reinforced with carbon nanotubes and graphene,²⁹ but comparatively, in situ-formed mainly silica-rich minerals are effective in strengthening the foams.

In a previous study,¹⁷ we showed that lignin foams fabricated at 300 and 500 °C were hydrophobic with contact angles of (111 ± 10) and $(107 \pm 3)^\circ$, respectively. Comparatively, the foams fabricated at 700 and 900 °C were hydrophilic as the water was absorbed into the surface within a

few seconds. Lignin-50 wt % SBP fabricated at 300 and 500 °C had a wetting angle of (73 ± 5) and $(94 \pm 46)^\circ$, respectively, and became hydrophilic at higher temperatures where water diffused into the sample rapidly. Lignin-50 wt % WS fabricated at 300 °C had a wetting angle of $(114 \pm 44)^\circ$ and it became hydrophilic at higher temperatures; for example, water diffused into the sample at 500 and 900 °C and the wetting angle was $(72 \pm 20)^\circ$ at 700 °C, respectively. In summary, after pyrolysis, WS fibers naturally form mineral-rich nodules that are effective in reinforcing the porous matrix and controlling the pore size formation during pyrolysis. Comparatively, SBP fibers are ineffective in reinforcing the pyrolyzed lignin matrix. By analyzing these results, it can be argued that lignin-based foams offer us a unique material system where the porosity, mechanical strength, and wettability of foams can be functionalized by incorporating different biobased agricultural fibers.

Carbon-based foams are used for a multitude of applications like absorption, catalysis, energy storage, and batteries, among others.¹⁸ An important outcome of this research is that lignin-biomass-based pyrolyzed foams provide us with a unique

Figure 10. Plot of compressive stress versus displacement behavior of the (a) lignin–50 wt % SBP and (b) lignin–50 wt % WS composites pyrolyzed at different temperatures.

platform for tailoring the wettability of the carbonaceous foams using 50% lignin. The hydrophobic foams can be potentially used for difficult operations like oil spill cleaning.³³ Closed-ring structures like anthracene are being studied for solar applications, luminescence, and energy harvesting, among others.^{34,35} Further studies are recommended to determine the exact chemical composition of the hydrophilic closed-ring aromatic structure-based foams derived at 500 °C or higher temperatures, which can then be used for finding the niche applications for these novel foams.

4. CONCLUSIONS

Lignin-based foams reinforced with WS and SBP were fabricated at 300, 500, 700, and 900 °C by pyrolysis in an Ar atmosphere. FTIR analysis showed that the foams are aromatic in nature. Detailed SEM studies showed that the lignin–SBP foams were more porous than the lignin–WS foams although both the foams showed a cellular structure. Energy-dispersive spectrometry (EDS) studies showed that pyrolysis of wheat straw caused the formation of mineral-rich nodules in the pyrolyzed lignin matrix, which was responsible for the denser and uniform microstructure of the lignin–WS composites. This observation was further confirmed by the microCT results. The average UCS of the lignin–SBP foams fabricated at 300 °C is ~1.31 MPa, which decreased to ~1.03 MPa for the foams fabricated at 500 °C, and thereafter increased to ~1.14 and ~2.03 MPa at 700 and 900 °C, respectively. Comparatively, the UCS of lignin–50 wt % WS was ~20.4 MPa at 300 °C, which decreased to ~13.1 and ~14.9 MPa after pyrolysis at 500 and 700 °C, respectively, and then increased to ~27.6 MPa after pyrolysis at 900 °C. Both the foams showed temperature-dependent wettability.

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Notes

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