



Article The Circular Economy Paradigm: Modification of Bagasse-Derived Lignin as a Precursor to Sustainable Hydrogel Production

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Abstract: There have been many efforts to valorise lignin to produce bio-based chemicals and advanced materials. In this study, alkaline delignification was initially employed to recover lignin from the rind, pulp, and whole bagasse fractions of Moroccan sugarcane. The lignin fractions were subsequently modified via silanization and acetylation reactions. The modified lignin and raw lignin were then characterised to assess changes in their physicochemical properties via Fourier transform infrared spectroscopy (FTIR), solubility and thermogravimetric assessment, with both salinization and acetylation modification shown to enhance the solubility properties of the raw lignin of both polar and non-polar solvents. Preliminary investigations into the suitability of employing the modified lignin in hydrogel preparation were also undertaken. The preliminary hydrogels were developed using heating and freeze-thawing methods, while polyvinyl alcohol (PVA) and epichlorohydrin (ECH) were used as the matrix and the crosslinking agents, respectively. Fourier transform infrared spectroscopy (FTIR), rheological analysis, scanning electron microscopy, and thermal analysis were then used to characterize the different lignin-PVA hydrogels. The study showed that the swelling behaviour of the hydrogels was mainly influenced by the nature of the lignin (i.e., modified or raw), and the morphology of the hydrogel surfaces varied depending on the preparation methods. The study showed that the hydrogel based on silanized lignin and PVA had superior mechanical performance and swelling capacity compared to the acetylated lignin-PVA and raw lignin-PVA hydrogels.

Keywords: lignin; acetylation; silanization; biomass; waste; circular economy; sustainability

1. Introduction

The increase in the global population has translated into an increase in the demand for polymers, leading to a progressive depletion of fossil resources. Such natural resource depletion has exacerbated the generation of greenhouse gases (i.e., NO_x, SO_x, etc.), which are considered to be responsible for climate change and global warming [1]. In response to these unfavorable environmental outcomes, researchers have recently sought to investigate alternative and sustainable pathways for polymer production [2,3]. In this regard, naturally sourced biopolymers were identified as possible alternatives to fossil-sourced polymers due to their sustainability and favorable characteristics, including biocompatibility, low toxicity, and degradability [4,5]. An example of such a notable biopolymer is lignin.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Lignin is a biopolymer with a molecular mass ranging from 1500–4000 Dalton [6,7]. It is composed of 4-hydroxyphenylpropanoid monomeric units of coumaryl alcohol, coniferyl alcohol, and synapilic alcohol [8] and has been reported to manifest improved mechanical strength, hydrophobicity, and thermal and chemical stability when subjected to silanization reactions [9,10]. The silanization reaction has also been proven to improve the dispersion and interfacial adhesion between polymers and fillers in composites via the introduction of silane groups [11]. Similarly, the literature highlights the potential of enhancing the solubility of lignin in organic solvents, via the conversion of hydrophilic hydroxyl groups to hydrophobic ester groups using acetylation reactions [12], thus making it a suitable candidate for the preparation of hydrogels [13]. Renewable hydrogel production is of interest in the present study due to its tissue engineering applications, which arise from its inherent matrices that can support cell proliferation [14,15].

The study will therefore apply silanization and acetylation reactions to modify lignin fractions sourced from Moroccan sugarcane. The modified lignin will then be characterized to assess changes in its physiochemical properties as a precursor to undertaking a preliminary assessment of its suitability in the production of lignin-based hydrogels. Ligninbased hydrogels will subsequently be prepared by using the modified lignin and PVA and epichlorohydrin (ECH) as the crosslinking agent, via epoxidation to prepare the modified lignin–PVA hydrogels by the freeze-thawing (F/T) method or the heating method, with or without using the crosslinking agent [16]. The properties of the modified lignin–PVA hydrogels will then be compared to the properties of the raw lignin–PVA hydrogels. The authors have employed PVA as the blending polymer since it is a water-soluble polymer that exhibits high reactivity with different types of functional groups and thus can readily form crosslinked hydrogels [17]. The novelty of the present work is demonstrated by the comparative exploration of the properties of the modified lignin via silanization and/or acetylation and the associated variation in the properties of the resultant hydrogel product. Indeed, the potential to improve lignin properties via the introduction of silane and/or acetyl groups as a precursor to hydrogel preparation will be investigated for the first time in the present study.

2. Materials and Methods

2.1. Materials

The sugar cane bagasse used during the experiments was obtained from a local supplier (Beni Mellal, Morocco). Sodium hydroxide pellets (NaOH), sulfuric acid (H₂SO₄), pyridine anhydrous 99.8% (C₅H₅N), acetic anhydride ((CH₃CO)₂O), hydrochloric acid 37% (HCl), methyltrimethoxysilane (MTMOS), aluminum acetylacetonate (Al(acac)₃), dimethyl sulfoxide (DMSO), tetrahydrofuran 99% (THF), and acetic acid (AcOH) were purchased from Merck (Darmstadt, Germany). Ethanol 99% (EtOH) and acetone 99% (C₃H₆O) were purchased from VWR Chemicals (Lutterworth, UK). Polyvinyl alcohol (PVA) (MW 72KDa) was obtained from Chemlab, (Zedelgem, Belgium) and epichlorohydrin (ECH) were purchased from Sigma Aldrich (Hoeilaart, Belgium).

2.2. Sugar Cane Bagasse Preparation

The sugar cane bagasse was air dried at 22 $^{\circ}$ C to constant mass for a week and subsequently cut into small portions (1–2 cm), crushed, and sieved using a 0.1 mm sieve to obtain fine particles [18].

2.3. Lignin Extraction

Lignin extractions from the rind, pulp, and whole bagasse fractions were undertaken. Briefly, 50 g of each sample (i.e., rind, pulp, or whole bagasse) was weighed into a two-liter flask. The sample was treated with hot water at 70 °C for 2 h with a solid/liquid ratio of 1:10 w/v. After the hot water treatment, the pretreated sample was cooled to 25 °C and washed with water (a ratio of 1:10 w/w) prior to filtering to remove solubilized hemicelluloses. The solid residue was then recovered and dried to a constant mass for 24 h at 60 °C. The solid residue was then subjected to alkaline treatment using an aqueous alkaline solution (15% w/v of NaOH) at a solid/liquid ratio of 1:10 w/v and the mixture stirred for 4 h at 98 °C [19]. The black liquor obtained was then filtered, with the filtrate acidified using sulfuric acid (5 N), to attain a pH of 2. The mixture was then cooled to 25 °C to facilitate the lignin precipitation. The raw lignin (R-lignin) was subsequently collected and washed several times with distilled water until the pH of the wash water reached 7 and air-dried [19]. The lignin yield was then calculated as follows:

$$Y_L = \frac{W_1}{W_2} \tag{1}$$

where W_1 is the mass (g) of the recovered lignin and W_2 is the mass (g) of the sample used for the extraction.

2.4. Chemical Modification of Lignin

2.4.1. Lignin Acetylation

Lignin (200 mg) was dissolved in 4 mL of acetic anhydride and pyridine, 1:1 v/v, and stirred for 24 h at 90 °C. Then, 50 mL of hydrochloric acid (5 N) was added to the reaction mixture with the acetylated lignin, precipitated after 30 min, and then recovered using filtration. The precipitate was then washed with distilled water and the acetylated lignin (A-lignin) and dried in a vacuum oven at 40 °C overnight [20].

2.4.2. Lignin Silanization

To facilitate lignin silanization, the method reported by Siuda et al. was adapted [21]. Briefly, 1 g of lignin was added to the reaction mixture of MTMOS (10 mL) and ethanol (10 mL) with the catalysts of aluminum acetylacetonate (450 mg) and acetic acid (1 mL) also introduced to enhance the reaction rate. The mixture was stirred (500 rpm) for 24 h at 25 °C and subsequently centrifuged (20 min, 3000 rpm, 25 °C) using a Nuve NF-048 countertop centrifuge (Henderson Biomedical, London, United Kingdom). The supernatant of the centrifuged mixture containing silanized lignin (S-lignin) was then recovered by decantation. Samples were washed thrice using distilled water with the S-lignin recovered via filtration. The S-lignin was then dried to a constant mass at a temperature of 40 °C for 24 h.

The acetylated lignin was subsequently silanized with the method described in Section 2.4.1 above to obtain the acetylated-silanized lignin (A-S-lignin).

2.5. Preparation of Lignin Based Hydrogels

To facilitate a comparative assessment of the yield of hydrogel produced via alternative pathways, the heating methods and the freeze-thawing (F/T) method were employed and are described below.

2.5.1. Heating Method for Hydrogel Preparation

Briefly, 0.50 g of PVA was mixed with 10 mL of distilled water and placed in an oil bath at 90 °C for 10 min with continuous magnetic stirring at 400 rpm applied until the PVA was completely dissolved. Then, 0.25 g of lignin was dissolved in 10 mL of NaOH (1 M) at 22 °C. This mixture was subsequently added to the PVA solution and stirred at 22 °C to form a uniform solution. Finally, 0.15 mL of ECH was added, and the solution was subsequently heated at 90 °C for 20 min. A homogeneous and stable lignin–PVA hydrogel was obtained after washing with deionized water until the pH of the wash water was 7. Following that, the hydrogel was dried to constant mass [22].

2.5.2. Freeze-Thawing Method for Hydrogel Preparation

Initially, 0.25 g of lignin was dissolved in 10 mL of NaOH (1M) solution at 22 °C. Secondly, 0.5 g of PVA was dissolved in 10 mL of distilled water and stirred at 90 °C for 10 min. Both solutions were then mixed at 1:1 v/v using magnetic stirring until a

homogeneous solution was achieved at 22 °C. A volume of 0.15 mL of ECH was added to the homogenous solution and the resulting mixture heated at 90 °C for 20 min. The mixture was then moved to petri dishes and allowed to 'stand' for 2 h under atmospheric pressure conditions and degassed. The degassed material was then frozen at -18 °C for 20 h, then allowed to thaw at 22 °C for 4 h. This freezing–thawing sequence constituted a complete cycle. The hydrogels were prepared by repeating the F/T cycle thrice. Finally, all the hydrogels were washed using deionized water and dried to constant mass [16]. The hydrogel yield Y_h was determined as follows:

$$Y_h = \frac{W_d}{W} \tag{2}$$

where W_d is the weight (g) of the dry hydrogel and W is the weight (g) of lignin and PVA used in the synthesis process.

2.6. Characterization Experiments

2.6.1. Fourier Transform Infrared Spectroscopy (FTIR)

To identify the characteristic functional groups, FT-IR measurements were performed using the JASCO FT/IR-4600 spectrometer (Easton, MD, USA) equipped with an attenuated total reflection (ATR) crystal surface. FT-IR measurements were performed by introducing the sample to the crystal surface, after which the mean spectrum was recorded after 80 scans in the range of 4000 to 200 cm⁻¹ with a resolution of 4 cm⁻¹.

2.6.2. Thermal Properties and Elemental Assessment

To measure the thermogravimetric properties of the samples, 10 mg of each sample was introduced to LabSys Evo TGA 1600 (Setaram KEP Technologies Caluire, France) and heated from 30 to 700 °C at a heating rate of 10 °C/min in a nitrogen atmosphere [19]. Further thermal assessments of samples were undertaken via differential scanning calorimetry (DSC) analysis and elemental analysis. The DSC analysis was performed by initially placing 5 mg of each sample in a hermetic pan that was then sealed in the TA Instruments DSC Q2000 (Paris, France) and heated in a temperature range from 30 to 400 °C with a heating rate of 5 °C/min. All DSC experiments were conducted in nitrogen gas at a flow rate of 60 mL/min [23]. Similarly, elemental analysis of samples was conducted using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SF-MS) using a Thermo Scientific Element 2.

2.6.3. Solubility Measurements

The solubility of each sample in aqueous and organic solvents was determined according to the method described by Sameni et al. [23]. The lignin samples were separately added to a basic solution of 1M NaOH, acidic aqueous solution of 5M HCl, and organic solvents of DMSO, ethanol, acetone, and tetrahydrofuran, while maintaining a concentration of 3 g/L in all solutions. For the R-lignin sample, a constant stirring of 500 rpm was imposed at different temperatures as follows: 10 °C for 40 min; 20 °C for 30 min; and 30, 40, 50, 60, and 70 °C for 20 min. For the modified lignin samples, the solubility tests were carried out at a fixed temperature of 25 °C for 20 min under constant stirring at 150–200 rpm. At the conclusion of the solubility tests, insoluble fractions were filtered using filter paper (Whatman paper no.4) and the filtrate dried at 60 °C in an oven for 2 h and then weighed, with the relative solubility of the samples subsequently calculated. All experiments were conducted in triplicate, with mean values reported with a standard deviation (\pm). Finally, the solubility results were analyzed and the main effect plot, highlighting the mean responses of sample solubility to variations in modification strategy determined.

2.6.4. Swelling Ratios of the Hydrogels

The prepared hydrogel discs (Section 2.5 above) of similar sizes were cut and weighed and their masses, W_d in g, recorded. The weighed discs were then incubated in 50 mL of

demineralized water at 25 °C for 24 h, after which the surface water of the hydrogel was removed using a filter paper to obtain the swollen weight (W_s in g). The swelling ratio (*SR*) of the hydrogels was determined as follows [24]:

$$SR = \frac{W_s - W_d}{W_d} \tag{3}$$

2.6.5. Scanning Electron Microscopy of Hydrogels

The surface morphologies of the prepared hydrogels were observed by SEM images (Hitachi SU-70, Tokyo, Japan). Briefly, the dried hydrogel samples were spread on a circular base with high conductivity double-sided tape and coated with a thin layer of carbon to promote conductivity prior to SEM observation.

2.6.6. Rheological Properties of Hydrogels

The rheological properties of the prepared hydrogels were analyzed using an Anton Paar MCR302 Rheometer (Anton Paar MRC 302, Graz, Austria) equipped with a parallel plate geometry of 25 mm in diameter. The storage (G') and loss modulus (G") were determined using oscillatory tests at 25 °C. The amplitude sweep analysis, ranging from 0.01 to 1000%, was carried out at a constant frequency of 1 Hz to verify the linear viscoelastic region (LVR). The frequency sweep test was performed at frequencies ranging from 0.1 to 100 Hz with a constant strain of 0.5% [24].

3. Results

3.1. Yield and Thermochemical Characterization of Lignin Samples

The lignin yields were 11 wt.%, 14 wt.%, and 21 wt.% from the dry pulp, whole bagasse, and rind of the cane, respectively. The R-lignin was subjected to silanization, acetylation, and acetylation–silanization modifications to produce silanized lignin (S-lignin), acetylated lignin (A-lignin), and acetylated–silanized lignin (A-S lignin), respectively. These modified and raw lignin samples were subsequently used in the preparation of hydrogels.

3.1.1. Fourier Transform Infrared Spectroscopy Analysis of Lignin Samples

The infrared spectra of the lignin and the modified lignin samples are presented in Figure 1.



Figure 1. FT-IR absorption spectrum of raw/modified lignin extracted from Moroccan sugar cane bagasse: (**A**) R-lignin, (**B**) A-lignin, (**C**) S-lignin, and (**D**) A-S-lignin.

3.1.2. Thermal Properties of the Lignin

Based on the thermogravimetric assessment discussed in Section 2.6.2 above, thermograms were generated and presented in Figure 2.



Figure 2. Thermal analysis of R-lignin and A-lignin: (**A**) TGA thermogram, (**B**) DTG thermogram, and (**C**) DSC thermogram. S-lignin and A-S-lignin: (**D**) TGA thermogram, (**E**) DTG thermogram.

3.1.3. Elemental Analyses of the Lignin Samples

The elemental analyses were conducted according to the methods described in Section 2.6.2 above, with the results summarized in Table 1.

	Si	S	Na	Mg	К	Ca	Pb	Al	Cr	Mn	Fe	Со	Cu
Sample	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
S-lignin	125.39	0.40	0.20	0.09	0.03	0.42	0.21	4095	0.71	0.28	18.10	0.13	1.38
A-S-lignin	32.01	2.60	1.46	0.64	0.05	3.22	0.31	2077	0.75	0.53	32.20	1.23	10.58
R-lignin	3.76	51.55	73.89	0.24	0.60	0.61	0.02	124	1.24	1.16	48.70	0.06	4.06

Table 1. The composition of raw and modified lignin in different elements.

3.2. Solubility Assessments

The solubilities of the R-lignin in different solvents and temperature were determined and are presented in Figure 3. The solubility of each of the modified (S, A, and A-S) lignin in different solvents was also determined and is presented in Figure 4 at a constant temperature of 25 °C.



Figure 3. Solubility diagram of R-lignin in different solvents and different temperatures.



Figure 4. Solubility diagram of R-lignin and the chemically modified lignin in different solvents.



The statistical mean effects of the different lignin modification strategies were subsequently assessed and presented in Figure 5.

Figure 5. Statistical independent effects of the lignin modification strategies on the lignin solubility.

3.3. Yield, Swelling Ratio and Rheology of the Prepared Hydrogels

Employing the methods described earlier, the yields of the hydrogels are summarized in Table 2.

Table 2. Yield of the hydrogels using different preparation approaches and lignins. The ECH concentration is 3% (v/v) in all cases.

Preparation Methods	F/T	Heating	F/T	Heating	F/T	Heating	F/T	Heating
Type of lignin	R-lignin	R-lignin	A-lignin	A-lignin	S-lignin	S-lignin	A-S-lignin	A-S-lignin
Yield (wt. %)	67	54	75	55	92	70	88	64

The associated swelling ratios of the different hydrogels produced were also determined and summarized in Figure 6.

Table 3. Rheological properties of PVA-lignin hydrogels obtained from amplitude sweep analysis.

Hydrogel Preparation Method	Type of Lignin + PVA	Maximum G' with LVR at x = 10 rad/s, G'max (Pa)	G" with LVR at x = 10 rad/s, G" (Pa)	Flow Point (τ_f) (Pa)	Yield Point (τ_y) (Pa)	
	A-S-lignin	27,797.0	1196.8	4346.1	300.4	
BT E/T	S-lignin	11,127.0	605.9	2635.1	60.9	
By 17 1	A-lignin	8441.3	698.0	378.4	35.7	
	R-lignin	6062.6	557.1	47.5	11.2	
	A-S-lignin	47,959.0	3233.6	1843.7	262.2	
	S-lignin	31,115.0	1189.8	2598.4	166.0	
With ECH and F/ I	A-lignin	22,282.0	828.2	940.3	93.8	
	R-lignin	23,116.0	859.5	3486.9	155.3	
	A-S-lignin	280.8	12.7	0.4	0.2	
Pry Heating	S-lignin	330.6	27.0	13.4	1.8	
by nearing	A-lignin	6905.1	590.5	39.8	8.6	
	R-lignin	67,092.0	5293.9	548.6	86.8	
	A-S-lignin	6068.0	283.4	3372.5	336.5	
With ECH and	S-lignin	28,233.0	1563.8	1179.2	119.2	
heating	A-lignin	19,567.0	803.1	1149.3	52.6	
C	R-lignin	5435.1	367.9	671.6	671.6	



Figure 6. Effect of preparation methods on the swelling ratio of the lignin-PVA hydrogels.

The rheology of the prepared hydrogels was assessed by performing amplitude and frequency sweep tests of the hydrogels. They were performed to determine the impact of different hydrogel perpetration processes and various lignin modifications on the final rheological properties of the lignin–PVA hydrogels. The results are summarized in Table 3 and Figure 7.

3.4. Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy Analysis of Produced Hydrogels

The FT-IR spectra of the prepared hydrogels are presented in Figure 8.

The surface morphologies of the prepared hydrogels were subsequently determined via scanning electron microscopy (SEM) with the associated SEM images presented in Figure 9.



Figure 7. Frequency sweep test results for the PVA-lignin hydrogel samples made of (A) raw lignin, and different modified lignin, namely, (B) acetylation, (C) silanization, and (D) acetylation–silanization.



Figure 8. FTIR spectra of the hydrogels based on different types of lignin prepared by different methods: (**A**) with ECH and heating, (**B**) by heating, (**C**) with ECH, and F/T (**D**) By F/T.



Figure 9. SEM micrographs of prepared hydrogels: (**A**) R-lignin based hydrogel prepared by heating method with ECH; (**B**) R-lignin based hydrogel prepared by heating method; (**C**) R-lignin based hydrogel prepared by freeze-thawing method with ECH; (**D**) R-lignin based hydrogel prepared by freeze-thawing method; (**E**) A-lignin based hydrogel prepared by freeze-thawing method with ECH; (**F**) S-lignin based hydrogel prepared by freeze-thawing method with ECH;

4. Discussion

The assessment of the yield of lignin presented in Section 3.1 above shows that the yields are consistent with lignin yields reported in the literature and range from 15–17 wt.% (dry mass basis) [20,25]. The results also showed that the rind of the Moroccan sugar cane has the highest lignin fraction of all the sugarcane fractions investigated and was therefore specified as the representative fraction in subsequent investigations.

4.1. Fourier Transform Infrared of Lignin Samples

The FT-IR results of the R-lignin and the modified lignin are presented in Figure 1. The absorption peak at about 3412 cm^{-1} corresponds to a vibrational mode of the OH bond and indicates the presence of aliphatic hydroxyl OH and aromatic OH groups. The peak detected at 2916 cm⁻¹ is due to the stretching of C-H bonds in the lignin molecules, which indicates the presence of CH₃ and CH₂ functional groups [26,27]. The peaks at 1597, 1512, and 1490 cm⁻¹ correspond to the vibration bands of the aromatic skeleton, and the peaks at 1365 and 1329 cm⁻¹ correspond to the annular respiration bands. The characteristic bands of Guaiacyl (Ar-CH) units resonate at the wavenumbers of 1156 and 870 cm⁻¹, indicating a predominance of G units in the lignin fractions. The presence of guaiacyl-type (G) confirms that this type of lignin contains active sites for polymerization [28]. The presence of a peak at about 1103 cm⁻¹ is due to the deformation in the C–H plane of the syringyle unit. The syringyle (S) and guaiacyl (G) bands present in the lignin spectrum indicate that this lignin isolated from Moroccan sugar cane bagasse is similar to wood lignin.

The spectrum of acetylated lignin in Figure 1B shows the complete disappearance of the hydroxyl functions at \sim 3412 cm⁻¹ and the appearance of a sharp peak at \sim 1760 cm⁻¹, which indicates the presence of carbonyl ester C=O bands [27]. This observation is due to esterification reactions that are reported to be responsible for the drastic reduction of the OH absorption band while promoting the formation of carbonyl ester bonds [29]. The two sharp peaks at 1240 cm⁻¹ and 1056 cm⁻¹ were also detected and correspond to the stretching C–O bonds that are present in aromatic and aliphatic esters, respectively [27]. The infrared spectra of the S-lignin are like those of the R-lignin, indicating that silane grafting on the lignin does not degrade the chemical structure of the biopolymer (Figure 1C). However, the spectra also show that S-lignin was characterized by a less intense peak at 3420 cm^{-1} compared to that of R-lignin, indicating increased interaction of the hydroxyl groups of lignin with silanols [30]. Figure 1D also shows that the stretching of the vibrational band of hydroxyl groups between 3200 and 3600 cm^{-1} decreases after stepwise acetylation and silanization reactions. The peaks observed at wavenumbers ranging from 1600-1800 cm⁻¹ and $1100-1300 \text{ cm}^{-1}$ indicate the presence of vibrational stretch absorptions of the ester groups of C=O and C-O, respectively [31,32]. These results also indicate the reduced presence of hydroxyl groups in the A-S-lignin.

4.2. Thermal Assessments of the Lignin Samples

Based on the thermogravimetric assessment discussed in Section 2.6.2. above, thermograms were generated and are presented in Figure 2. Figure 2A shows a progressive degradation of R-lignin as the temperature increases from 100-700 °C, with most of the R-lignin (80 wt.%) decomposing in the temperature range of 250–700 °C. An initial mass change of R-lignin of ~10 wt.%, observed as the temperature increases from 30 to 100 °C, is due to the evaporation of the absorbed water [19]. Notably, this stage is highlighted in Figure 2B by the first peak identified in the DSC thermogram. R-lignin degradation observed in the temperature range of 180–320 °C is attributed to the degradation of the carbohydrate components of lignin, which leads to the production of volatiles such as CO, CO₂, and CH₄ [33]. This degradation is also indicated by a second peak identified in the DSC thermogram in Figure 2B. The TGA curve shows that sustained heating leads to the thermal degradation of the R-lignin structure into non-volatile residues, which constitutes 20 wt.% of the R-lignin sample.

The TGA and DSC thermograms generated for A-lignin are also presented in Figure 2A,B. Figure 2A shows that the maximum rate of degradation (76 wt.%) of A-lignin occurs between 280 °C and 340 °C [34] with the TGA curve of A-lignin observed to be similar to the TGA curve of R-lignin. The TGA curve of A-lignin shows that the initial mass loss of 25 wt.% occurs between 60 and 110 °C and is due to water evaporation, after which a mass loss of 45 wt.% is observed at 270-340 °C and is due to the degradation of carbohydrate components and the acetyl groups of lignin [27]. The A-lignin DTG plot also shows that the degradation rate is maximum at \sim 340 °C (Figure 2B). The TGA and DTG plots for the S-lignin and A-S-lignin are presented in Figure 2D,E, respectively. At temperatures below 100 $^\circ$ C, S-lignin and A-S-lignin present negligible mass losses of ~4% due to minimal water evaporation. The thermal decomposition of S-lignin observed at 200 °C was due to pyrolysis reactions, which are responsible for the breakdown of aliphatic compounds such that significant degradation of ~ 60 wt.% is observed at temperatures between 250 and 450 °C. According to the TGA curves for S-lignin and A-S-lignin in Figure 2C,D, 30% of the sample is retained as non-volatile residues after the temperature of 700 °C is attained. The results obtained by thermogravimetric analysis (TGA) of A-S-lignin show that significant degradation occurs at 220 °C, unlike all other types of lignin, where mass loss begins at 80 °C (Figure 2). According to the results obtained, it can be hypothesized that ligning with a lower content of functional groups, such as hydroxyl and methoxy groups, give a higher number of carbonized residues. The results show some differences in the thermal behaviors for the different types of lignins. These differences were initially due to minor variations to the moisture retained by the different samples. It is also proposed that compositional differences in the presence of OH, acetyl, and silane groups will lead to different intramolecular bonding strengths and thus differences in thermal stability. The increase in decomposition temperature may also be due to secondary silane condensation or cross-linking reactions in the lignin macromolecule. The studies showed that, overall, the thermal stability was improved by silanization.

4.3. Elemental Analyses of the Lignin Samples

The elemental analyses were conducted according to the methods described in Section 2.6.2. above, with the results summarized in Table 1. Table 1 shows the results obtained for the content of different elements in R-, S-, and A-S- lignins. As expected, the S-lignin sample had the highest silicon content of 25.39 mg/g, thus indicating the high efficiency of silanization that is achieved in the presence of the Al(acac)₃ catalyst [17]. High Al contents of 4095 μ g/g and 2077 μ g/g were also observed for the S-lignin and A-S-lignin samples, respectively. Table 1 also shows that the S-lignin is characterized by a decrease in Na and S content.

4.4. Solubility Characteristics of the Lignin Samples

As expected, the solubility of each lignin sample was negligible in the aqueous solution of HCl (5M) due to significant differences in the polarity and solubility parameters of the lignin and the acid solution. Figure 3 shows the solubility of R-lignin in different organic solvents and basic NaOH solution (1 M or 0.1 M) at different temperatures when the fixed mass concentration of 3 g/L was imposed. It is observed that DMSO constitutes the best organic solvent for lignin dissolution compared to other solvents, since R-lignin begins to dissolve at a low temperature of 10 °C, and is completely dissolved at 30 °C. Figure 4 also shows that aqueous 1 M NaOH solution represents the second most favorable solvent for R-lignin dissolution after total dissolution at 40 °C. However, the results obtained in the 0.1M NaOH solution showed that lignin is moderately soluble in temperatures above 50 °C and slightly soluble in temperatures below 30 °C, which may be due to the low concentration of the NaOH solution [23]. Figure 4 shows the solubility of R-lignin compared to A-lignin, S-lignin, and A-S lignin in different organic solvents and basic NaOH solution (1 M or 0.1 M) at different temperatures when the fixed mass concentration of 3 g/L is imposed. It is observed that the A-lignin samples were almost completely soluble in DMSO and

the aqueous NaOH solution (1 M). Figure 4 also shows a lower solubility of the modified lignin samples in the aqueous NaOH (1 M) solution compared to R-lignin. This observation may be due to the hydrophobic character of A-lignin, S-lignin, and A-S-lignin. DMSO, a polar protic solvent with a high dielectric constant [35], was shown to be the most suitable solvent for A-lignin, S-lignin, and A-S-lignin. This observation was because of DMSO's capacity to interact with large hydrophobic molecules [35].

The results also showed that while R-lignin is almost insoluble in THF, A-lignin is more soluble than S-lignin and A-S-lignin in the THF solvent. The poor solubility of R-lignin in ethanol is expected since, according to Shukry et al. [36], ethanol is not efficient for dissolving A-lignin due to there being a high value of hydrogen bonding required, which is limited in all forms of lignin. Figure 5 shows that, on average, in all solvents considered, A-lignin presented the highest solubility and may be attributed to the high levels of hydroxyl groups in its structure [36]. The solubility of A-S-lignin was also observed to be higher than the solubility of S-lignin, on average, when all solvents investigated in this study are considered. This is because the A-S-lignin contains higher concentrations of hydroxyl groups compared to the S-lignin. Figure 5 also shows that all modifications led to improvements in lignin solubility in relation to R-lignin.

4.5. Hydrogel Yields and Swelling Ratios

Table 2 shows that for all lignin types, the F/T hydrogel preparation approach facilitated the production of the highest hydrogel yields ranging from 67 wt.% to 92 wt.%, highlighting the improved performance of the F/T process. Furthermore, the S-lignin and the A-S lignin resulted in high and comparable hydrogel yields of 92 wt.% and 88 wt.% respectively.

With respect to the swelling ratio assessments, Figure 6 shows that in all cases, the swelling ratio is higher for hydrogels synthesized via the F/T process in the presence of the crosslinking agent (ECH) than the swelling ratios measured for hydrogels produced via other methods. It is possible that the presence of the crosslinking agent gives compactness to the network of the hydrogel and its ability to 'hold' more water within the network, leading to an improved swelling compared to that of the hydrogel prepared without the crosslinking agent. Furthermore, Figure 6 shows that the swelling ratio of the hydrogel based on the A-S lignin and prepared via the heating process is higher than the swelling ratio of the hydrogels based on R-lignin, A-lignin, and S-lignin and prepared via the heating process. This observation may be due to the presence of the acetyl groups and the silane network in the hydrogel structure, which enhances the hydrophilic nature of the hydrogel.

4.6. Rheological Properties of the Prepared Hydrogels

As shown in Table 3, the weakest elasticity is presented by the hydrogel that was made using A-S-lignin after heating treatment (Max G' = 280 Pa and Max G' = 12.7 Pa). For such hydrogel samples, the 'cross point' for the hydrogels occurs at the lowest shear stress ($\tau_{f} = 0.4$ Pa) compared to other groups. Notably, the non-modified lignin or R-lignin facilitated the production of a stable hydrogel, when prepared only via the heating process. The F/T process was also observed to favor the production of stable hydrogel when A-S lignin is employed, with stability enhanced by the presence of ECH. The improved stability in the presence of ECH could be due to the introduction of functional groups in the lignin polymer chain awakening stronger intermolecular bonds. The obtained data also shows that the use of A-S lignin in the preparation of hydrogel via the F/T process and in the presence of ECH constitutes the most favorable approach for the preparation of elastic and stable hydrogels. Figure 7 also shows the changes in G' and G'' due to the variation in angular frequency. It is observed that the effect of frequency on the moduli curves is insignificant in most cases, with minor changes in the curves observed in Figure 7D (for hydrogels produced via the heating method using A-S-lignin). This suggests that the hydrogels are largely characterized by a robust, well-structured network [37]. Additionally, as illustrated, there is no cross-point of G' and G'' in this frequency range, proving the typical solid-like characteristics of the hydrogels in all cases [38-40].

4.7. Fourier Transform Infrared Scanning Electron Microscopy Analysis of Prepared Hydrogels

Figure 8 shows the effects of the different lignin treatments on the hydrogen bonding between lignin and PVA in the prepared hydrogels. The region shown in the range of ~ 3000–3700 cm⁻¹ represents the phenolic and alcoholic hydroxyl groups involved in the hydrogen bonds [41], while a deformation of the band shape or intensity indicates a change in the hydrogen bonding [42]. The band at ~2920 cm⁻¹ represents C-H stretching of methyl groups of lignin, and the ECH treated samples are shown to have an enhanced peak. Notably, in the spectra of ECH treated samples, new peaks around 840 and 920 cm⁻¹ were observed and are representative of epichlorohydrin's epoxy groups [43]. The peaks observed at ~916 and 850 cm⁻¹ represent the CH₂ and C–C stretching vibrations of PVA, respectively [24,44].

For the SEM images generated, it is clear from Figure 9 that surface morphology of hydrogels largely varies with the method of preparation. Figure 9 shows the pore size distribution for the differently prepared hydrogels. The ones prepared via the F/T process and in the absence of the crosslinking agent (ECH) have a wider pore size distribution than hydrogels prepared in the presence of ECH. The wider pore sizes are due to the absence of the crosslinking effects and an intermittent formation of ice crystals during the F/T process. In other words, during each F/T cycle, ice crystals are formed in the freezing stage and then melt during the thawing stage, which translates to numerous pores being present in the structure [45]. Thus, due to the higher porosity of the hydrogels produced via the F/T process, it is expected that the increased surface area will aid water absorption, with the water-holding capability enhanced in the presence of ECH. The hydrogels produced using the S-lignin (Figure 9F) and A-lignin (Figure 9E) also showed homogeneously distributed pores with larger pores due to the presence of ECH as a crosslinking agent. Moreover, the results displayed that the prepared hydrogels have a tight, dense, rough, and wavy surface, which indicates their high toughness and dense crosslinking.

4.8. Notable Considerations

The approach employed in lignin recovery from the bagasse (i.e., use of alkaline), in the present study, may lead to high extraction costs as well as the generation of unwanted masses of wastewater. This situation can significantly inhibit the sustainability of future lignin-based hydrogel production. In this regard, the alternative approach of lignin recovery using the organosolv method may be considered in future studies since the method has been reported to facilitate the isolation of high-quality lignins while simultaneously reducing water pollution [8]. Indeed, the use of organic solvents such as ethanol and acetone for lignin extraction presents the opportunity for solvent recovery for possible reuse since such organic solvents typically have low boiling temperatures. The potential for solvent reuse and limited wastewater production will greatly enhance process sustainability and is worthy of future investigations.

5. Conclusions

In recognition of the existing underutilization of lignin as a renewable biopolymer and the need to explore more sustainable hydrogel production strategies, the present study investigated the modification of lignin as a precursor to the use of a hydrogel. In this regard, lignin extracts were modified via acetylation and silanization reactions, with their physicochemical properties initially assessed as a precursor to being employed in hydrogel production. The study was able to establish that acetylation reactions enhanced lignin solubility in both the A-lignin and A-S-lignin samples and was attributed to the introduction of higher levels of hydroxyl groups in its structure. Consideration of the hydrogel products showed that the swelling ratio of the hydrogel based on the A-S lignin was higher than the swelling ratio of other lignin hydrogels with the observation attributed to the highly porous structure of the network of acetyl groups and the silane groups in the hydrogel structure. As expected, the introduction of the crosslinking agent was shown to further enhance swelling performance and mechanical properties by enabling a more homogeneous distribution of pores. Overall, the study was able to show that bagassesourced lignin has the potential to serve as a next-generation sustainable platform for hydrogel production. However, the authors emphasize that future studies of the biological activity (i.e., antibacterial, antioxidant properties) of these lignin-based hydrogels will be crucial to reinforce its future applicability in biomedical engineering.

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