



Ionic Liquid Processing of Residual Wood Powder into Additive-Free Wood Composites

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Abstract

This work presents a novel process for production of additive-free wood composites by ionic liquid treatment of wood powder involving extraction of lignin followed by precipitation onto particle surfaces, and hot pressing to form a cellulose-reinforced lignin biocomposite. Physicochemical properties of lignin-coated wood powders, as well as their degree of fusion upon hot pressing, were evaluated with the aim of optimising ionic liquid treatment and hot-pressing conditions. Optimal conditions to achieve complete fusion while minimising process energy demand were determined using response surface methodology, and mechanisms of process parameter effects investigated using gas pycnometry, electron microscopy, image analysis, thermogravimetry, and calorimetry. These novel materials, derived solely from waste with only reusable reagents, represent a sustainable alternative to existing engineered wood products, which rely on petrochemical additives that release toxic volatile compounds, offering a means to reduce environmental and health hazards associated with production and use of composites from wood waste.

Keywords Biocomposite · Lignin · Fibreboard · Biomass · Structural · Pretreatment · Sawdust · Binder

Introduction

Approximately 300 million cubic metres of wood powder in the form of sawdust are produced globally each year [1]. Despite ample supply, sawdust typically makes up less than 20% of engineered wood products like fibreboard [2, 3], because manufacturers prefer the longer fibres of wood chips [2]. While nearly all remaining industrial sawdust in European Organisation of the Sawmill Industry member countries [4], and in North America [3], is used for alternative applications like bioenergy and animal bedding; open dumping, open-air burning, and landfilling are still widely

reported [5–10]. For example, an estimated 96% of sawdust produced in Nigeria is reportedly burnt in open air [6], and more than 60% of wood waste produced in Australia is estimated to be landfilled [10].

Most fibreboard products rely on the addition of up to 10% petroleum-derived binders (e.g. urea-formaldehyde, phenol-formaldehyde, asphaltite), which release toxic volatile compounds [11]. Lower binder contents can be used in wet-form manufacturing processes (typically <5%), which rely on lignin as a binder, the softening point of which is drastically reduced in the presence of water [2]. Though less reliant on additives, the thickness of wet-formed boards is limited by the necessity of water removal during forming [2]. Dry-formed boards avoid this limitation by forming pre-dried fibre–binder mixtures, requiring more added binder without the adhesive contribution of lignin.

This work describes production of a biocomposite material solely from wood powder—the first of its kind. Using the low-cost ($\sim \$1 \text{ kg}^{-1}$) [12] ionic liquid (IL) triethylammonium hydrogen sulphate ([TEA][HSO₄]), lignin and hemicellulose are extracted from wood powder by selective dissolution, followed by precipitation of the lignin with water to coat the surfaces of wood particles, and hot pressing to fuse coated particles together. Using this novel process,

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wood powders coated in lignins precipitated from IL solution can be dry formed into wood composites with no added binder because lignin is chemically modified by IL treatment to soften at low temperatures when dry. These additive-free wood composites offer a sustainable non-toxic alternative to conventional fibreboard. While it has been shown that [TEA][HSO₄] can effectively fractionate biomass [12, 13], this process has never before been used to coat particles of delignified wood in their own lignin, enabling production of additive-free wood composites by dry forming.

Previous work [12] has shown that the water used for lignin precipitation can be readily reclaimed by distillation, and the IL recovered at a rate of ~99% and reused indefinitely (because lignin remaining in solution is partially recovered on reuse). This work focuses on the one-pot process developed to coat wood powder in its own lignin, and on characterisation of the physical and chemical properties of resulting coated wood powders, as well as their propensity to fuse to form an additive-free wood composite upon hot pressing. The effects of IL treatment time and temperature, as well as hot-pressing time, temperature, and pressure, on these properties have been evaluated, and parameters optimised, using response surface methodology. This novel process enables production of additive-free fibreboards using only reusable reagents with high recovery rates.

Experimental Section

Materials

Beech dust (*Fagus sylvatica*) was purchased from HotSmoked.co.uk and milled until at least 80% w/w passed through a 125 µm sieve. This fraction (particle size < 125 µm) was termed beech/wood powder.

A 5 M aqueous solution of sulphuric acid (Product No. 11488962), 99% pure triethylamine (Product No. 10626362), and technical grade ethylene glycol (Product No. 13486369) were purchased from Fisher Scientific UK Ltd.

Ionic Liquid Synthesis

[TEA][HSO₄] was synthesised as follows: Triethylamine (75.9 g, 750 mmol) in a 500 mL round-bottom flask was cooled to ~0 °C in a circulating -8 °C 40% v/v ethylene glycol bath. Under stirring, 5 M sulphuric acid (150 mL, 750 mmol) was added dropwise. The rate of sulphuric acid addition was modulated to keep the solution temperature under 22 °C. The solution was then dried with a rotary evaporator at 60 °C and 72 mbar (condenser set to 20 °C). After 90 min, the temperature was raised to 80 °C and the vacuum

lowered to 40 mbar. After a further 60 min, the solution was transferred to a 250 mL wide-mouth glass bottle and dried at 103 °C overnight, at which point the bottle was closed, and the IL stored at room temperature.

Treatment Process and Yield Calculations

The IL treatment process used to coat wood powder in its own lignin is illustrated in Fig. 1. This one-pot process consists of extracting lignin from wood into an IL solution, followed by precipitating lignin with water such that it condenses onto the surface of delignified wood particles, and then separating this coated wood powder from the IL solution. Coated wood powder can then be hot pressed (as described in the 'Hot Pressing' section below) to form an additive-free wood composite by fusing the delignified wood particles in a lignin matrix; this process is also illustrated in Fig. 1.

Beech powder and [TEA][HSO₄] were dried at 105 °C overnight. An IL solution comprising 80 wt% IL and 20 wt% deionised (DI) water was prepared by mixing with a vortexer.

Extraction

1 g of beech powder and 5 mL of IL solution were then added to 15 mL front-sealed pressure tubes (Ace Glass Inc., Product No. 8648-04) and mixed with a vortexer at a speed of 2800 rpm for 30 s. Tubes were heated at temperatures between 150 and 170 °C for between 30 and 90 min, then cooled at room temperature for 45 min.

Precipitation

40 mL of DI water was then used to transfer the contents of each tube to a pre-weighed 50 mL centrifuge tube, using a vortexer as needed to minimise loss. Tube masses were then balanced, and tubes mixed with a vortexer at a speed of 2800 rpm for 60 s and left to settle overnight.

Separation

Tubes were then centrifuged with a force of 10,375 × g for 90 min. Supernatants were decanted (leaving behind a pellet of coated wood powder) and an additional 40 mL of DI water added to each tube. Tube masses were then balanced, and tubes mixed with a vortexer at a speed of 2800 rpm for 60 s and left to settle for 30 min. This process was repeated to wash the treated wood pellet of any residual IL, then tubes were centrifuged, and supernatants decanted one final time, after which the walls of centrifuge tubes were washed

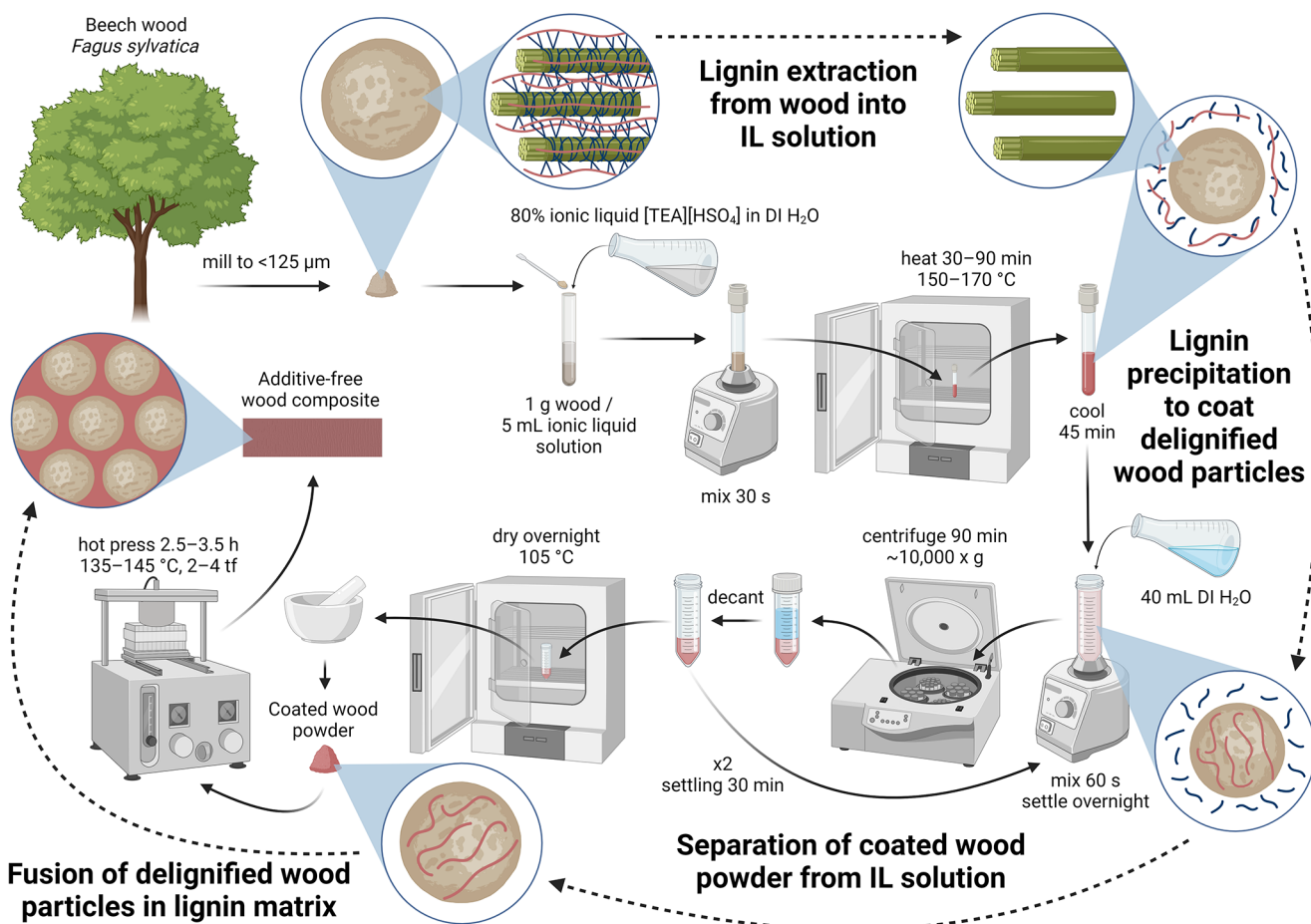


Fig. 1 Illustrated workflow of the additive-free wood composite production process. IL: ionic liquid; DI: deionised. Created with BioRender.com.

of debris with a DI water wash bottle, and the contents of tubes (treated wood pellets) dried at 105 °C overnight.

Tubes were then weighed to determine yields of coated wood powders as detailed in Eq. 1, where $M_{t,f}$ is the mass of the centrifuge tube containing the dried treated wood pellet, $M_{t,i}$ is the mass of the empty centrifuge tube, and M_d is the mass of untreated wood powder added to the pressure tube. Mean yields and associated standard errors are available in Supplementary Table 1.

$$\text{Yield [\% w/w]} = \frac{M_{t,f} - M_{t,i}}{M_d} \times 100\% \quad (1)$$

Gas Pycnometry

Gas pycnometry was used to evaluate effects of IL treatment conditions on true densities of lignin-coated wood powders, providing insight into structural changes to lignin resulting from IL treatment when considered alongside yield trends. An AccuPyc II 1340 (Micromeritics Instrument Corporation) was used for gas pycnometry volume measurements

and calibrated with iron spheres of known volumes. A 3.5 cm³ aluminium sample cup was used for all measurements, with coated wood powders filling at least 10% of its volume. Helium was applied to the sample chamber for three purges and three cycles with a fill pressure of 134.4 kPa and an equilibration rate of 0.575 Pa g s⁻¹. Sample masses measured with an analytical balance were used to estimate true densities from volumes measured with the pycnometer. Mean true densities and associated standard errors of measurements are available in Supplementary Table 2.

Colour Analysis

Colour analysis was used to evaluate effects of IL treatment conditions on the relative quantity, molecular weight, and quinone concentration of the lignin coating particles of delignified wood. Photographs of coated wood powders were taken at a standard distance (~9.8 cm) under standard lighting conditions at ISO 20, with an aperture of f/1.8, and shutter speeds between 1.8×10^{-3} and 2.1×10^{-3} s. Colours of each of 6.4×10^5 pixels in CIE 1976 L*a*b* colour space [14], as well as mean values, standard deviations, and

standard errors of each channel (see Supplementary Table 3) were determined in MATLAB (The MathWorks, Inc.).

Scanning Electron Microscopy

Scanning electron microscopy was used to evaluate effects of IL treatment conditions on the relative surface density of lignin coating particles of delignified wood. Samples of untreated and lignin-coated wood powders were mounted on aluminium stubs with adhesive carbon tabs and sputter coated with chromium at a current of 120 mA under a 10^{-3} mbar vacuum for between 3.5 and 7 min using a Quorum Q150T ES Plus Turbomolecular Pumped Coater (Quorum Technologies Limited). Samples were then imaged in a TESCAN MIRA scanning electron microscope (TESCAN ORSAY HOLDING, a.s.) using a field emission source with an accelerating voltage of 10 keV, a beam current of 1 nA, and a spot size of ~ 5.1 nm in 'DEPTH' observation mode. A secondary electron detector was used to acquire images at working distances between 9 and 13 mm with a dwell time of 320 ns per pixel as the average of 20 drift-corrected frames of 1280×960 pixels.

Thermogravimetric Analysis

Thermogravimetric analysis was used to evaluate effects of IL treatment on the thermal reactivity of lignin and cellulose, providing insight into both the location and chemistry of lignin in coated wood powders. Proximate analysis was used to compare compositions of coated wood powders by class of reactivity while differential thermogravimetry was used to compare rates and quantities of decomposition in different temperature regimes, one corresponding to lignin and the other to cellulose. Proximate analyses of untreated and coated wood powders were performed using a modified version of the TGA program described by ASTM D7582 [15] in a Discovery TGA (TA Instruments) thermogravimetric balance with a sample gas flowrate of 60 mL min^{-1} and a balance gas flowrate of 40 mL min^{-1} . A slower program was developed to ensure ample time for heat transfer both from the surrounding gas to the sample bed, as well as within sample particles; this program is detailed below.

1. **Drying:** Samples weighing between 1 and 3 mg in 100 μL high-temperature platinum sample pans (TA Instruments, Product No. 957571.901) were loaded into the furnace at $50 \text{ }^\circ\text{C}$ under N_2 sample gas. Once initial mass equilibration was detected, samples were heated to $105 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ and held at this temperature for 20 min. The mass of sample remaining after this program was termed the *dry mass*.

2. **Pyrolysis:** Dried samples were heated at a rate of $2 \text{ }^\circ\text{C min}^{-1}$ to $900 \text{ }^\circ\text{C}$ and held at this temperature for 7 min before

cooling at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $450 \text{ }^\circ\text{C}$. The mass of sample remaining after this program was termed the *pyrolysed mass*.

3. **Combustion:** Pyrolysed samples were heated to $750 \text{ }^\circ\text{C}$ in air at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ and held at this temperature for 15 min. The mass of sample remaining after this program was termed the *ash mass*, and the *daf mass* was determined as *dry mass* – *ash mass*.

Proximate compositions of samples in terms of volatile matter and fixed carbon on a daf basis and ash content on a dry basis were determined as detailed in Eq. 2–Eq. 4.

$$\begin{aligned} & \text{volatile matter [\% w/w daf]} \\ &= \frac{\text{dry mass} - \text{pyrolysed mass}}{\text{daf mass}} \times 100\% \end{aligned} \quad (2)$$

$$\begin{aligned} & \text{fixed carbon [\% w/w daf]} \\ &= \frac{\text{pyrolysed mass} - \text{ash mass}}{\text{daf mass}} \times 100\% \end{aligned} \quad (3)$$

$$\begin{aligned} & \text{ash content [\% w/w dry basis]} \\ &= \frac{\text{ash mass}}{\text{dry mass}} \times 100\% \end{aligned} \quad (4)$$

Mean thermograms ($1 \leq n \leq 2$) of relative sample mass on a daf basis of the $2 \text{ }^\circ\text{C min}^{-1}$ ramp to $900 \text{ }^\circ\text{C}$ were calculated according to Eq. 5. Moving averages of mean thermograms (with a computation window of $\sim 0.4 \text{ }^\circ\text{C}$) were differentiated with respect to moving averages of measured temperatures (with a computation window of 12.5 s). Resulting differential thermograms were smoothed using a moving average filter (with a computation window of $\sim 33 \text{ }^\circ\text{C}$).

$$\begin{aligned} & \text{relative sample mass [\% w/w daf]} \\ &= \frac{\text{sample mass} - \text{ash mass}}{\text{daf mass}} \times 100\% \end{aligned} \quad (5)$$

The 105 to $500 \text{ }^\circ\text{C}$ range of differential thermograms calculated from unaveraged TGA thermograms were fitted with two variable-shape Pearson VII functions using a linear baseline correction with the MATLAB function 'peakfit.m' [16]. Mean peak positions & heights and model fit errors (percent root-mean-square differences between the data and the model) & coefficients of determination are reported.

Differential Scanning Calorimetry

Differential scanning calorimetry was used to evaluate effects of IL treatment conditions on lignin softening temperature and heats of reaction in different temperature regimes, one corresponding to lignin and the other to cellulose. Using a Discovery DSC (TA Instruments) with a sample gas flowrate

of $60 \text{ mL min}^{-1} \text{ N}_2$, 2.0 mg samples of untreated and coated wood powders in Tzero aluminium pans (TA instruments, Product No. 901683.901) with pierced lids (TA instruments, Product No. 901671.901) were loaded into the furnace at $25 \text{ }^\circ\text{C}$ and then heated to $105 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$. The samples were dried for 20 min at $105 \text{ }^\circ\text{C}$, then cooled to $10 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ and allowed to equilibrate at this temperature. Subsequently, samples were heated at a rate of $2 \text{ }^\circ\text{C min}^{-1}$ to $400 \text{ }^\circ\text{C}$, and then cooled to $25 \text{ }^\circ\text{C}$ before unloading. An identical empty pan was used as a reference for heat flow measurements normalised by temperature-resolved sample mass. Initial sample masses (2.0 mg) were adjusted according to mean TGA thermograms of relative sample mass, assuming that no mass was lost at temperatures less than $105 \text{ }^\circ\text{C}$. DSC thermograms were calculated as the average of between 1 and 3 individual measurements of the change in heat flow during the $20\text{--}350 \text{ }^\circ\text{C}$ range of the $2 \text{ }^\circ\text{C min}^{-1}$ ramp segment, and smoothed with a robust locally estimated scatterplot smoothing regression, using a computation window of $\sim 3.3 \text{ }^\circ\text{C}$.

Hot Pressing

Lignin-coated wood powders were hot pressed in a stainless steel mould in order to fuse delignified wood particles in a matrix of lignin to form an additive-free wood composite. Dried treated wood pellets, prepared as described in the ‘Treatment Process and Yield Calculations’ section, were removed from centrifuge tubes and homogenised using a mortar and pestle. Resulting coated wood powders were then stored in sealed centrifuge tubes. Polytetrafluoroethylene (PTFE) release film was applied with petrolatum to the bottom plate and underside of the plunger of a 1.5 by 7 cm stainless steel mould. 350 mg of coated wood powder was added to the mould and evened by spreading with a spatula and tapping the mould on a flat surface first without, then with the plunger. Moulds were then hot pressed at temperatures between 135 and 145°C for between 2.5 and 3.5 h with forces between 2 and 4 tf (pressures between ~ 26 and $\sim 52 \text{ MPa}$). Moulds were cooled at room temperature overnight, and hot-pressed samples (with thicknesses between 100 and $300 \text{ }\mu\text{m}$) demoulded and stored in closed petri dishes at room temperature.

Image Analysis

Image analysis was used to evaluate effects of IL treatment and hot-pressing conditions on the propensity of coated wood powders to fuse into an additive-free wood composite upon hot pressing. Photographs of one side of the largest plane of hot-pressed coated wood powder samples were taken at a standard distance ($\sim 12.5 \text{ cm}$) under standard

lighting conditions with an aperture of $f/1.8$ and a shutter speed of $1 \times 10^{-2} \text{ s}$ between ISO 32 and ISO 50. Images were processed using ‘Fiji’ software [17] (a distribution of ImageJ2 [18] from SciJava). They were segmented into fused composite, compressed powder, and background regions using the ‘Trainable Weka Segmentation’ plugin [19], and the fused fraction of sample surface area calculated as detailed in Eq. 6, where N_s is the number of pixels in the fused region and N_p is the number of pixels in the compressed powder region.

$$\text{fused fraction of sample} = \frac{N_s}{N_s + N_p} \quad (6)$$

Response Surface Methodology

A five-factor, three-level Box-Behnken experimental design comprising 41 distinct sets of conditions and two centre point replicates was used to evaluate effects and interactions of the factors ‘IL treatment time’, ‘IL treatment temperature’, ‘hot-pressing time’, ‘hot-pressing temperature’, and ‘hot-pressing force’ on the response ‘fused fraction of hot-pressed sample surface area’. Factor levels are detailed in Supplementary Table 4.

The experiment was designed, and the response modelled with a standard least squares personality using JMP Pro software (JMP Statistical Discovery LLC). The coefficient of determination associated with the model fit to the measured response data was 0.88. p -values for the test that the value of factors had no effect on the response, other factors’ effects on the response, or their own effect on the response against the two-sided alternative that they did have an effect were calculated, and effects with p -values less than 0.01 were determined to be significant. Calculated response surface contour plots represent the model response to each combination of two variable factors, while the remaining three factors are set to their respective centre values.

Optimisation was performed with the goal of achieving a fused fraction of 1 while minimising factors to reduce process energy demand. The fused fraction reaching the target value of 1 was attributed an importance of 3.82 times that of minimising the factors, which was found to be the minimum ratio at which a fused fraction of 1 was achieved. Desirability was maximised using 100 random starting points, each with a maximum of 100 cycles of 1000 iterations, with a convergence tolerance of 10^{-10} using the ‘Prediction Profiler’ function of JMP Pro. Relative influence of variables was assessed using the same function assuming inputs had independent uniform distributions.

Results and Discussion

Yields of Coated Wood Powders

Lignin and hemicellulose were extracted from wood particles at temperatures ranging from 150 to 170 °C for between 30 and 90 min. Lignins and pseudo-lignins (those incorporating hemicelluloses), as modified in solution, were then precipitated back onto the surfaces of particles with water. These coated particles were then separated from the IL solution, dried, and pulverised to yield lignin-coated wood powders. While the term ‘IL treatment’ refers to this entire process, ‘treatment conditions’ refers only to those varied in this study: the temperature at and time for which lignin and hemicellulose were extracted (dissolved and allowed to react in solution).

Yields of lignin-coated wood powders from beech powder were found to decrease with severity of IL treatment conditions (i.e. higher temperatures and longer treatment times) from ~92% w/w at 150 °C for 30 min, to ~63% w/w at 170 °C for 90 min (see Fig. 2a). A stronger effect of treatment time than treatment temperature was observed, as well as a greater magnitude of effect at higher temperatures and longer treatment times.

This decreasing trend indicates that more lignin and/or hemicellulose remained in solution after precipitation (with water) with increasing treatment severity. This is in part related to more lignin and hemicellulose being extracted under harsher treatment conditions, but also to increased hydrolysis of lignin in the IL solution [13] resulting in smaller, more soluble fragments [20]. Although Gschwend

et al. [13] showed near complete removal (upwards of 95%) of hemicellulose at IL treatment temperatures ≥ 160 °C and times ≥ 60 min, hemicellulose removal alone is unlikely to account for the entire 37% loss of mass observed upon IL treatment at 170 °C for 90 min. Therefore, it is believed that lignin hydrolysis contributed to the depressed yields observed under severe IL treatment conditions.

Densities of Coated Wood Powders

True densities of lignin-coated wood powders (as approximated using a gas pycnometer) were found to primarily increase with severity of IL treatment conditions, with the exception of the harshest set of conditions tested (170 °C for 90 min). Figure 2b shows that estimated true densities were found to increase from ~ 1.49 g cm $^{-3}$ to ~ 1.54 – 1.55 g cm $^{-3}$ relatively similarly with increasing treatment time and temperature at 150–160 °C and 30–60 min. However, moving from 60 to 90 min at 170 °C, and from 160 to 170 °C for 90 min, density was found to decrease back to ~ 1.50 g cm $^{-3}$. Measurement errors were over an order of magnitude smaller than these trends (see Supplementary Table 2).

The increasing density trend moving from mild to moderate treatment conditions can be explained by two factors: (1) increased loss of lignin (~ 1.40 g cm $^{-3}$) and hemicellulose (~ 1.52 g cm $^{-3}$), which are less dense than cellulose (~ 1.56 g cm $^{-3}$) [21], to solution; and (2) increasing hydrolysis of lignin to lower molecular weight fragments [13], resulting in decreased free volume of the amorphous polymer [22]. This lower free volume allows for denser molecular packing, and thereby greater true density as measured

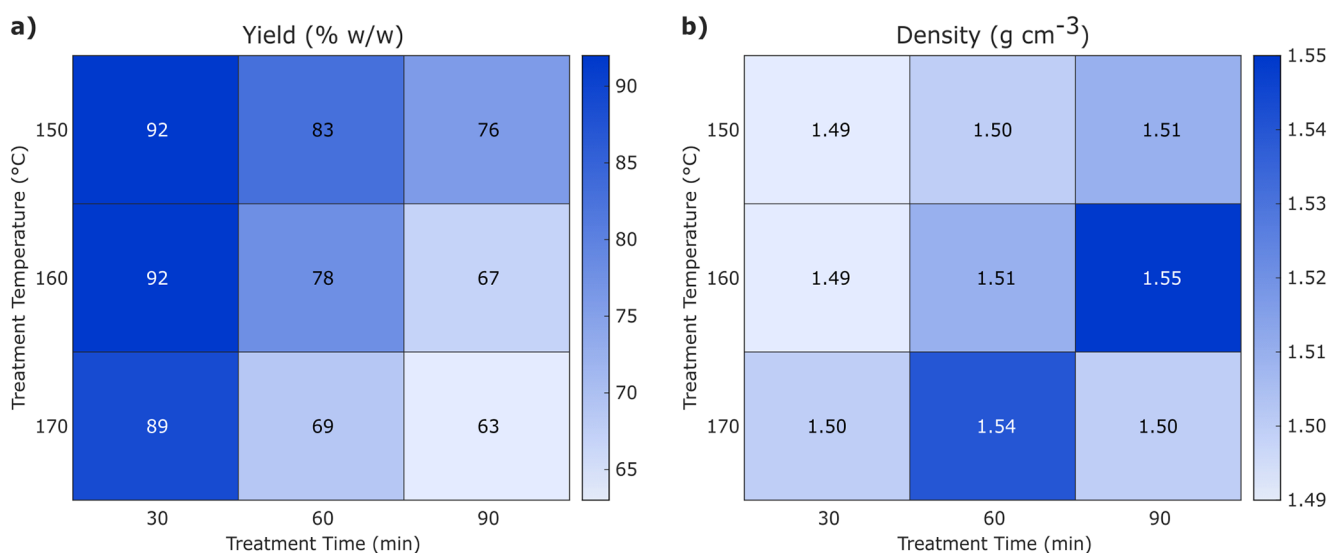


Fig. 2 Yields and true densities of lignin-coated wood powders by ionic liquid treatment time and temperature. **(a)** Mean yields ($1 \leq n \leq 17$) of coated wood powders from beech powder by ionic liquid treatment time and temperature. Standard errors are provided in Supplementary

Table 1. (b) Mean true densities ($n = 3$ measurements of pooled samples) of coated wood powders approximated using a gas pycnometer by ionic liquid treatment time and temperature. Standard errors are provided in Supplementary Table 2

by pycnometer. The decreasing density trend moving from moderate to harsh treatment conditions can be explained by condensation of lignin and hemicellulose to higher molecular weight lignin fragments and pseudolignins [13], resulting in increased free volume of these amorphous polymers [22], and thereby less dense molecular packing and lower true density.

Morphology of Coated Wood Powders

The surface of wood particles was observed to roughen with increasing severity of IL treatment conditions; Fig. 3 shows electron micrographs of wood cells (fibres or rays) of untreated and lignin-coated wood particles by IL treatment time and temperature. These show an increasing concentration of rough lignin/pseudolignin precipitate deposited on the surfaces of wood particles with both IL treatment time

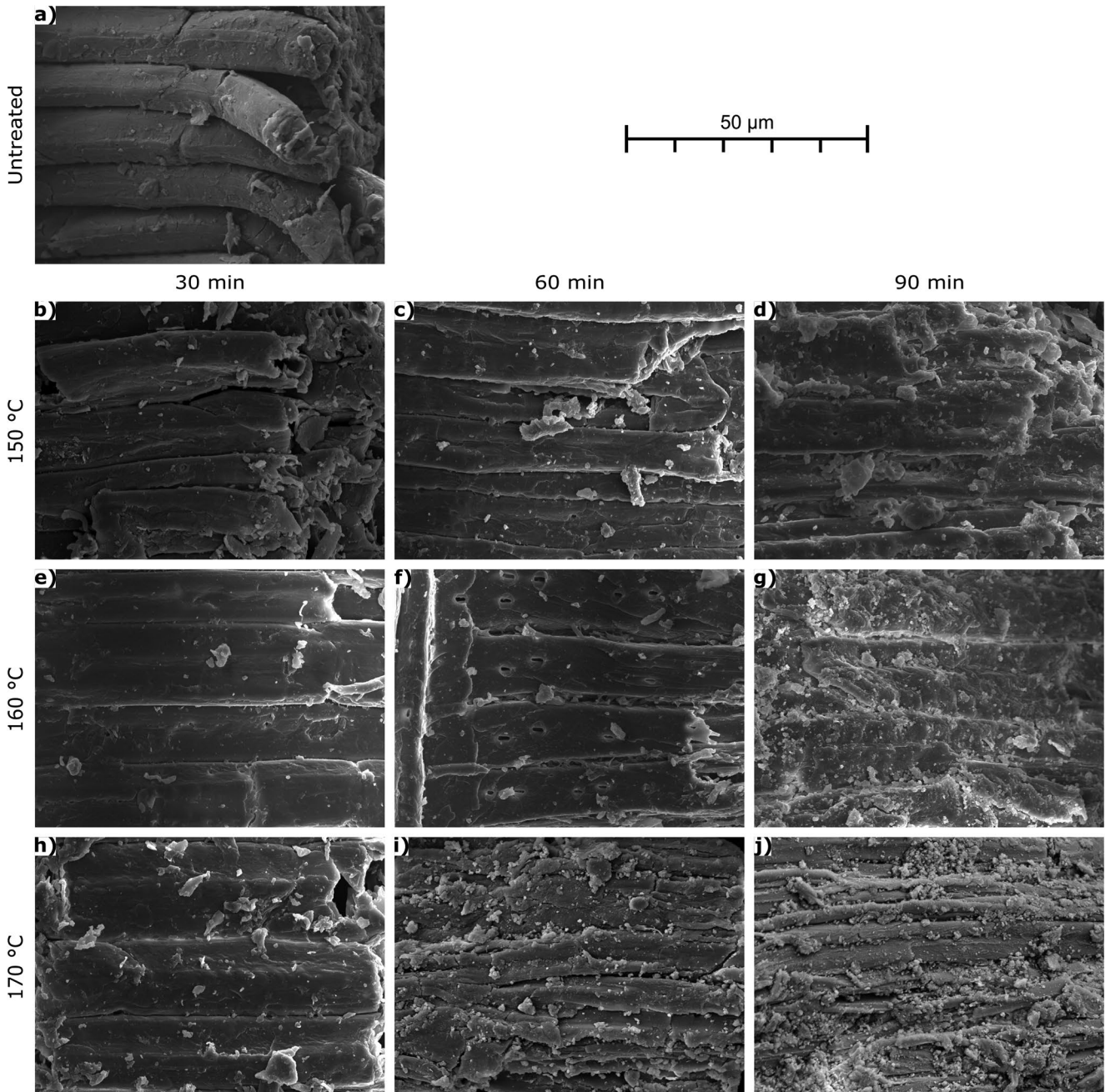


Fig. 3 Scanning electron micrographs of untreated and lignin-coated wood powders by ionic liquid treatment time and temperature. **(a)** Scanning electron micrograph of untreated beech (*Fagus sylvatica*)

cells. **(b–j)** Scanning electron micrographs of beech (*Fagus sylvatica*) cells coated in their own lignin by ionic liquid treatment time and temperature

and temperature. Qualitatively, there appears to be a somewhat stronger effect of treatment time than temperature on this concentration (e.g., compare Fig. 3c vs. e, d vs. f/h).

Gschwend et al. [13] (cf. Figure 3) showed that under the same IL treatment conditions used here, 51–78% of native lignin was extracted resulting in a 35–76% yield of precipitate on addition of excess water. Delignification was shown to peak under moderate treatment conditions (170 °C for 30 min and 160 °C for 60 min), while precipitate yield was shown to increase with IL treatment severity. Hemicellulose fragments (on their own, largely soluble in water) are thought to join this precipitate when relatively harsh IL treatment conditions are used, as lignin and hemicellulose fragments condense to form pseudolignins under such conditions [13].

Colour Analysis of Coated Wood Powders

The colour of lignin-coated wood powders was found to vary with IL treatment conditions (see Fig. 4a). Coated powders were darker, as determined using the CIE 1976 L*a*b* colour space [14] lightness parameter (L*), when treated under harsher conditions (see Fig. 4b). As was observed of yields, a stronger effect on lightness of treatment time than treatment temperature was observed, as well as a greater magnitude of effect at higher temperatures and longer treatment times.

The increased darkness (decreased L*) of coated wood powders with severity of IL treatment conditions is likely due primarily to the increased concentration of lignin/pseudolignin precipitate deposited on the surfaces of treated wood particles (see Fig. 3). Greater concentration of this precipitate would result in a higher density of chromophores, and therefore darker colour [23]. During IL treatment under relatively harsh conditions, condensation of lignin and hemicellulose fragments to condensed lignins and pseudolignins occurs in solution [13]. These condensed lignins and pseudolignins may also contribute to the darker colour of precipitates due to their greater degrees of conjugation and unsaturation [23]. Zhang et al. [23] have shown both that lignin condensation drives darkness and that darker lignins are less dense (cf. Figure 6), meaning the exceptional darkness of the sample prepared at 170 °C for 90 min further supports the theory of lignin condensation driving the lower density observed under these conditions.

‘Redness’ of coated powders, as measured by the CIE 1976 L*a*b* colour space [14] a* (green–red axis) chromaticity parameter, was maximised under moderate IL treatment conditions (150 °C for 60 min and 170 °C for 30 min—see Fig. 4b). Redness increased with treatment temperature at a treatment time of 30 min, but decreased with treatment temperature at treatment times of 60 and

90 min. At a treatment temperature of 150 °C, redness was maximised at a treatment time of 60 min, while it decreased with treatment time at treatment temperatures of 160 and 170 °C. Trends in ‘yellowness’ of coated powders, as measured by the CIE 1976 L*a*b* colour space [14] b* (blue–yellow axis) chromaticity parameter, opposed those of redness (see Fig. 4b).

Redness of precipitates is primarily driven by the presence of quinones [24–26]. These are produced by demethylation and oxidation of lignin fragments, for which the presence of phenoxy radicals is necessary [24]. During IL treatment under moderate conditions, hydrolysis of *b*-aryl ether (*b*-O-4) and phenylcoumaran (*b*-5) linkages of extracted lignin fragments occurs in solution, increasing the abundance of phenolic hydroxy groups [13], which are necessary for the formation of phenoxy radicals. Conversely, available hydroxy groups can be consumed by condensation reactions under harsher IL treatment conditions. This may explain the observed maximisation of redness under moderate IL treatment conditions.

Thermal Analyses of Coated Wood Powders

Thermostability of lignin-coated wood powders was evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), with the aim of determining effects of IL treatment conditions on reactivities of the lignin and cellulose fractions of coated powders. While thermostability was evaluated in an inert atmosphere (N₂), air was used to determine ash contents of samples, as to normalise by only the potentially reactive (ash-free) fraction.

Thermogravimetric Analysis

Onset temperature is defined here as the temperature intercept of the tangent line to the mass loss thermogram (Fig. 5a–c) at its first peak rate of mass loss, and not the temperature at which measurable mass loss first occurs. While potentially misleading in the case of particularly slow transitions to peak rates of mass loss [27], it is useful here as a comparative metric due to the similar shapes of the onset of mass loss among treatment conditions.

Thermogravimetric analysis revealed lower onset temperatures with increasing severity of IL treatment conditions, ranging from 247 °C in untreated beech powder to 206 °C in beech powder treated at 170 °C for 90 min (see Fig. 5c). Onset temperature decreased with both treatment time and temperature, with the greatest difference (23 °C) being that between 30 and 60 min treatment times at 150 °C (see Table 1).

Earlier onset of degradation with increasing treatment severity can be partially attributed to greater exposure of

Fig. 4 Photographs and colour analysis of lignin-coated wood powders by ionic liquid treatment time and temperature. **(a)** Photographs of pooled coated wood powder samples by ionic liquid treatment time and temperature. **(b)** Mean pixel colours ($n = 6.4 \times 10^5$ pixels) of photographs of coated wood powders in CIE 1976 $L^*a^*b^*$ colour space [14] by ionic liquid treatment time and temperature. L^* is an index of lightness ranging from 0 (black) to 100 (white); a^* is a measure of chromaticity on a green–red axis, with positive values indicating more red than green; b^* is a measure of chromaticity on a blue–yellow axis, with positive values indicating more yellow than blue. Error bars represent standard deviation

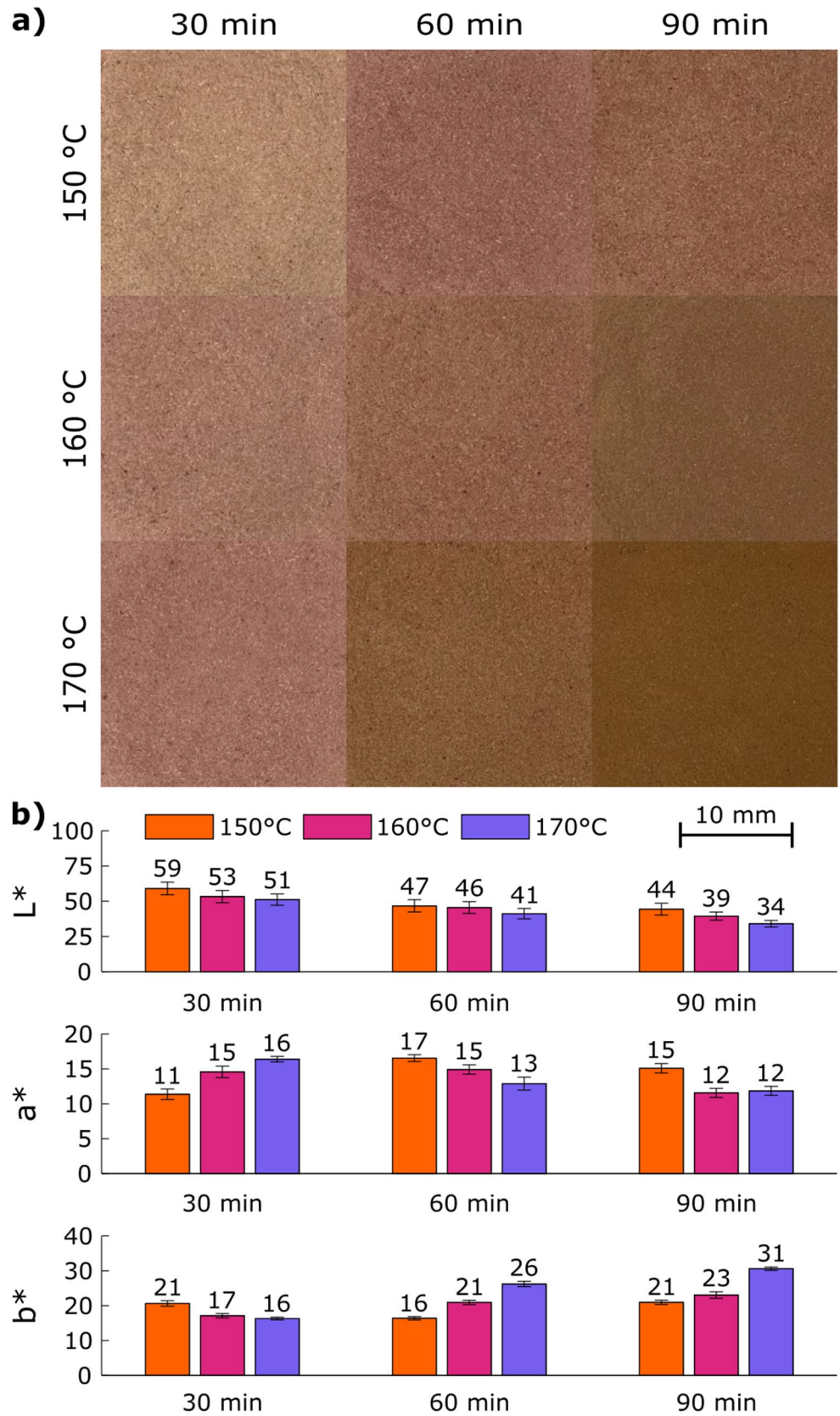


Table 1 Key thermogravimetric analysis data. Mean onset temperatures and proximate compositions ($1 \leq n \leq 2$) of untreated and coated wood powders by ionic liquid treatment time and temperature

Treatment time (min)	Treatment temperature (°C)	Onset temperature (°C)		Proximate composition (% w/w daf)			Ash content (% w/w dry basis)	
		Mean	SE	Volatile matter	Fixed carbon	SE (p.p.)	Mean	SE (p.p.)
Untreated		247	0.162	100	n.d.		3.20	1.64
30	150	238		100	n.d.		n.d.	
	160	225	1.48	99.6	n.d.	0.362	1.61	1.61
	170	222	1.35	99.6	n.d.	0.332	1.92	1.92
60	150	215	1.03	98.2	1.81	0.278	2.83	2.32
	160	214		97.2	2.84		3.60	
	170	214	0.0175	94.3	5.74	0.992	2.92	1.15
90	150	212	1.08	97.2	2.80	0.227	2.59	2.59
	160	210	1.81	91.7	8.26	1.48	1.98	1.08
	170	206		89.7	10.3		n.d.	

Standard errors are based on two sample analyses. daf: dry ash-free basis; SE: standard error; p.p.: percentage points; n.d.: not detected (less than instrument baseline drift)

lignin (which begins to degrade at a lower temperature than cellulose) [28] as it is extracted from wood particles and deposited on their surfaces. The concentration of precipitate deposited on particle surfaces was shown to increase with treatment severity by SEM micrographs of treated wood particles (see Fig. 3). When lignin is distributed throughout particles along with cellulose (which has not yet begun to react), loss of lignin mass from particles is limited by the rate of heat transfer into, and mass transfer out of, particles. Onset of mass loss therefore appears to begin at a higher temperature during a steady temperature ramp than does that of lignin in isolation. This trend may also be in part related to the relative instability of smaller fragments in precipitates, especially given that the greatest changes in onset temperature were seen at the lowest treatment temperatures and times (compare Fig. 5a–c), where hydrolysis dominates reactions of lignin in IL solution [13].

Furthermore, total dry ash-free (daf) mass loss (i.e. volatile matter in terms of proximate analysis) was found to decrease with increasing severity of IL treatment conditions, ranging from complete extinction in untreated beech powder, and that treated at 150 °C for 30 min, to ~90% w/w in beech powder treated at 170 °C for 90 min (see Table 1). Mass loss decreased with both treatment temperature and time, with the greatest differences occurring at the highest treatment temperatures and times (compare Fig. 5a–c). This is likely due to condensation of lignin fragments to more stable highly-conjugated high-molecular-weight lignins and pseudolignins in IL solution under harsher treatment conditions [13].

Differential Thermogravimetry

Differential thermogravimetry (DTG) revealed two overlapping regimes of mass loss (see Fig. 5d–f).

1. Low temperature lignin degradation (peaking between 254 and 271 °C).

2. Degradation of cellulose (peaking between 313 and 357 °C).

The peak rate of low temperature lignin degradation was found to follow similar trends with respect to IL treatment conditions as was density (compare Table 2 and Supplementary Table 2). This implies that the small lignin fragment size driving higher densities also results in more rapid degradation of lignin, and vice versa.

The temperature at which the peak rate of low temperature lignin degradation occurs also follows similar trends (see Table 2), implying that those lignin fragments that degraded faster did so at higher temperatures than did those that degraded slower. This can be explained by kinetics: degradation and volatilisation reactions are faster at higher temperatures. The most substantial change observed in this metric was that between untreated (289 °C) and treated (254–271 °C) wood powders.

Higher peak rate temperatures occurred due either to later onset of lignin degradation (compare Tables 1 and 2), to wider peak morphology (mass loss over a greater range of temperatures), or to a combination of the two. Where onset temperature correlates with peak rate temperature (at treatment times of 30 and 90 min), increasing exposure of lignin on particle surfaces is thought to drive decreases in peak rate temperature with IL treatment temperature. Where peak width plays a role (at treatment times ≥ 60 min), peak rate temperature is likely influenced by lignin fragment size, with more stable larger fragments ceasing to react at lower temperatures assuming the same onset temperature (e.g. Figure 5f).

The peak rate of cellulose degradation was found primarily to decrease, and to occur at increasing temperatures, with IL treatment severity (see Table 2), indicating delayed slower degradation of cellulose due to physical shielding by

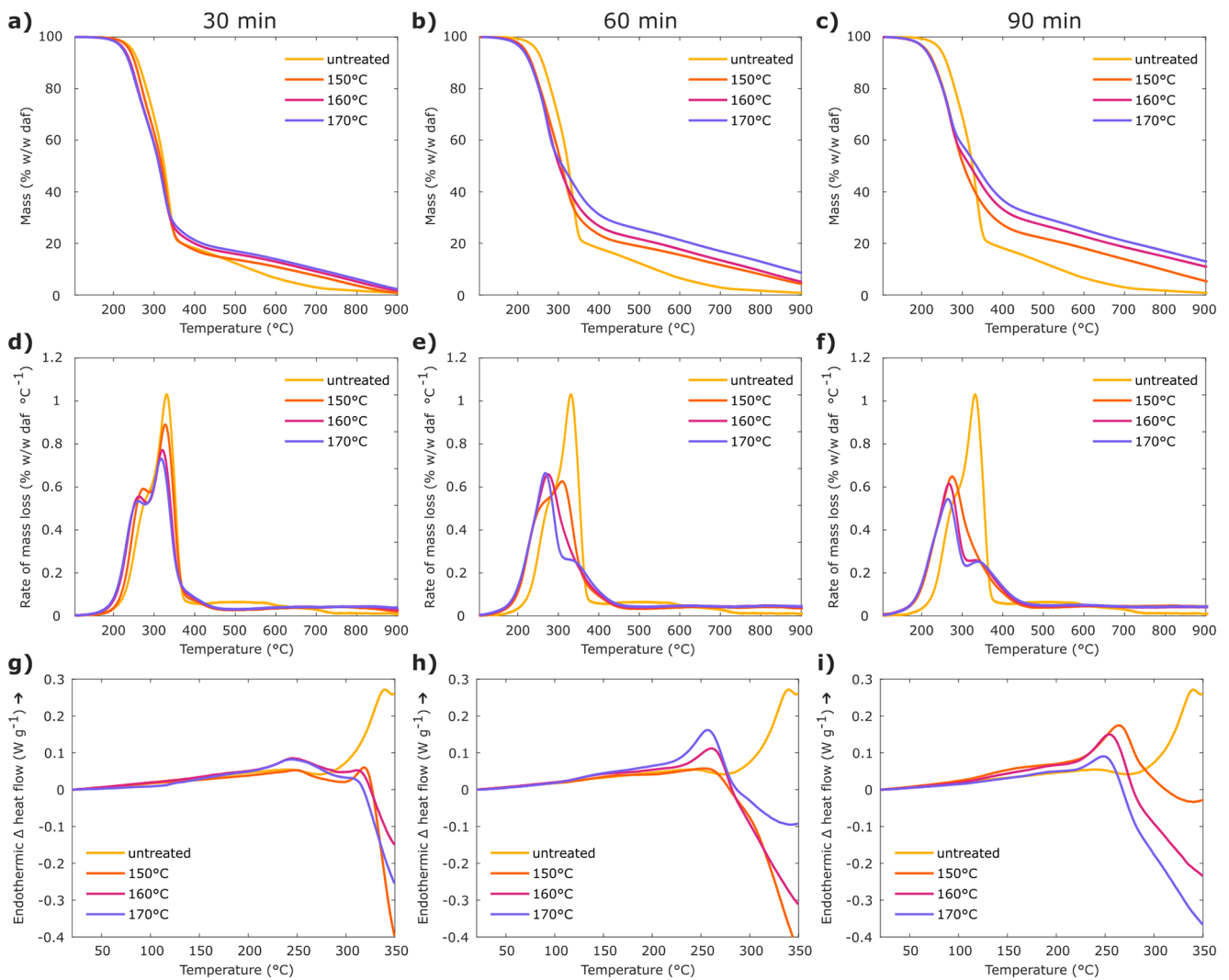


Fig. 5 Thermograms of untreated and lignin-coated wood powders by ionic liquid treatment time and temperature. **(a–c)** Mean thermogravimetric analysis thermograms ($1 \leq n \leq 2$) of untreated and coated wood powders by ionic liquid treatment time and temperature. **(d–f)** Differential thermogravimetry thermograms calculated from mean thermogravimetric analysis thermograms ($1 \leq n \leq 2$) of untreated and

coated wood powders by ionic liquid treatment time and temperature. **(g–i)** Mean differential scanning calorimetry thermograms ($1 \leq n \leq 3$) of untreated and coated wood powders by ionic liquid treatment time and temperature. daf: dry ash-free basis; D: change in metric from initial value

precipitated lignin. Relatively small opposing trends with IL treatment severity (seen at both extremes of tested conditions) may be due to increased isolation of cellulose from lignin resulting in earlier and faster degradation. Compared to the intimate intermeshing of lignin and cellulose in native biomass, mixtures of isolated components have been shown to result in faster and lower temperature cellulose depolymerization [28]. All of these trends can be explained by more lignin being extracted and precipitated onto particle surfaces under harsher IL treatment conditions.

Differential Scanning Calorimetry

Two reaction regimes very similar to those revealed by DTG were observed *via* DSC, the first peaking between 241 and 265 °C, and the second between 315 and 340 °C (see Fig. 5g–i). In the first regime, both the peak endothermic heat flow and the temperature at which this was achieved were maximised under moderate conditions (150 °C for 90 min, see Table 3). This is once again attributable to the instability of smaller lignin fragments produced by hydrolysis in IL solution under moderate treatment conditions [13], as the higher peak rate temperature appears related to wider peak morphology as opposed to later onset of degradation (see Fig. 5i).

Table 2 Key differential thermogravimetry peak data. Mean positions & heights ($1 \leq n \leq 2$) of peaks fitted to differential thermograms of untreated and coated wood powders by ionic liquid treatment time & temperature and associated mean fit errors (percent root-mean-square differences between the data and the model) & coefficients of determination (R^2)

Treatment time (min)	Treatment temperature (°C)	Low-temperature peak		High-temperature peak		Fit error (%)	Fit R^2
		Position (°C)	Height (% w/w daf °C ⁻¹)	Position (°C)	Height (% w/w daf °C ⁻¹)		
Untreated		289	0.546	334	0.783	0.844	0.999
30	150	271	0.527	329	0.827	1.36	0.998
	160	260	0.470	322	0.724	1.32	0.998
	170	257	0.435	319	0.685	1.25	0.999
60	150	254	0.379	313	0.547	1.21	0.999
	160	271	0.607	354	0.114	1.05	0.999
	170	264	0.610	353	0.162	2.32	0.993
90	150	271	0.594	357	0.115	1.35	0.998
	160	262	0.565	355	0.161	2.49	0.992
	170	257	0.491	355	0.180	2.57	0.992

daf: dry ash-free basis

Table 3 Key differential scanning calorimetry data. Mean inflection point temperatures and temperatures & magnitudes of local maxima by ionic liquid treatment time & temperature

Treatment time (min)	Treatment temperature (°C)	Inflection point temp. (°C)		Low-temperature local maximum				High-temperature local maximum			
		Mean	SE	Temperature (°C)	SE	Mean	SE	Temperature (°C)	SE	Mean	SE
Untreated				241		0.0561		340		0.275	
30	150			249	1.13	0.0548	1.99×10^{-2}	319	1.35	0.0634	0.0748
	160	151	4.93	245	1.42	0.0866	1.48×10^{-2}	315	0.685	0.0521	0.0478
	170	139	0.965	247	3.23	0.0838	9.36×10^{-3}				
60	150	135	5.14	261		0.0556	6.21×10^{-2}				
	160	128	1.80	261	0.557	0.113	2.10×10^{-2}				
	170	133	0.982	257	0.601	0.163	2.00×10^{-2}				
90	150	135	0.585	265	0.421	0.176	1.91×10^{-2}				
	160	137	3.13	254	0.249	0.152	1.07×10^{-2}				
	170	161	2.33	248	1.13	0.0924	2.76×10^{-2}				

Standard errors are based on two to three sample analyses. SE: standard error

An endothermic peak in the higher-temperature regime corresponding to cellulose depolymerisation was only observed in untreated samples, and in those treated for 30 min at 150 and 160 °C (see Fig. 5g). Both the amplitude and temperature of this peak were observed to decrease with IL treatment severity, indicating an influence of both lignin shielding cellulose and isolation of cellulose, respectively, as discussed above. A particularly large difference in both metrics (up to 25 °C and a > 80% decrease in heat flow) was observed between untreated and treated wood powders (see Table 3).

Finally, an inflection point indicative of lignin softening was observed at temperatures between 128 and 161 °C in treated powders under all but the mildest conditions tested (150 °C for 30 min, see Fig. 5g–i). While there was no discernible trend in softening temperature with IL treatment

conditions, most were less than 145 °C (see Table 3), which was the maximum temperature used to fuse coated wood powders into cellulose-reinforced lignin composites by hot pressing.

The lack of inflection point in the untreated wood powder thermogram shows that IL treatment was necessary to induce the low-temperature softening of lignin (absent water) needed to dry-form composites without added binder. While water decreases the softening point of lignin [2], allowing wet-formed fibreboards to use little to no added binder, contaminated process water must be removed from these boards during hot pressing, limiting their thickness. Dry-formed boards avoid this by adding binders that cure at lower temperatures than lignin in the absence of water. By modifying lignin to soften at low temperatures when dry, this IL treatment process avoids the pitfalls of

both conventional forming processes to enable production of potentially thicker fibreboards without additives.

Fusion of Coated Wood Powders upon Hot Pressing

When lignin-coated wood powders were hot pressed, up to 100% of the sample fused into a composite material, while any remaining powder was simply compressed. The fraction of each sample that fused was found to depend significantly ($p < 10^{-5}$) on IL treatment time, IL treatment temperature, and hot-pressing force (see Fig. 6). Increasing each of these significant parameters had a positive influence on the fused fraction achieved, but effects were not necessarily uniform over the range of values tested; effects of IL treatment time and hot-pressing force were found to be significantly nonlinear ($p < 0.007$). The relative influence of significant parameters on the fused fraction achieved was found to be: IL treatment time \gg hot-pressing force $>$ IL treatment temperature, with treatment time being approximately twice as influential as the other two parameters.

Minimum values of production parameters to achieve complete fusion of coated powders on hot pressing were determined to be IL treatment at ~ 163 °C for ~ 73 min, followed by hot pressing at 135 °C and ~ 2.9 tf for 2.5 h. The optimal hot-pressing temperature and time were found to be the lowest values tested (given the statistical insignificance of these factors in the tested range, and the desirability of minimisation to reduce process energy demand), meaning it is possible that even lower values of these parameters could be used to achieve complete fusion.

Fusion of coated wood powders during hot pressing is thought to be dependent on the softening phenomenon visible in Fig. 5g–i. Should softening occur at lower temperatures under greater pressure, this could explain the greater degree of fusion when more force is used for hot pressing. However, softening temperatures do not appear dependent on IL treatment conditions beyond the lack of observable softening under the mildest conditions tested, and therefore cannot fully explain the dependence of fusion on IL treatment severity. The greater concentration of precipitate on particle surfaces with increasing treatment severity observable in Fig. 3 could instead explain this dependence.

Conclusions

Using a novel one-pot IL treatment process, it is possible not only to coat sawdust in its own lignin, but to control the extent of this coating and the physicochemical properties of precipitated lignins by modulating process parameters. These properties have also been shown to affect the conversion of coated wood powders to fused biocomposite upon

hot pressing. In general, harsher treatment conditions appear to result in a greater concentration of precipitate on particle surfaces, leading to greater fusion of particles. Meanwhile, the thermal reactivity (instability) of lignin appears to be maximised, and that of cellulose minimised under moderate treatment conditions, indicating simultaneously increasing isolation of the two biopolymers, shielding of cellulose by lignin, quantity of surface precipitate, condensation of lignin fragments, and incorporation of hemicelluloses into precipitates with increasing treatment severity. Condensation of lignin and hemicellulose fragments to higher-molecular-weight lignins and pseudolignins under harsher treatment conditions is also supported by trends in the density and colour of coated wood powders with respect to IL treatment conditions.

Although increasing IL treatment time & temperature and hot-pressing force were found to significantly increase conversion of coated powders to fused composite, moderate values of these parameters were determined to be sufficient for complete conversion. Therefore, to minimise process energy demand, moderate values of these parameters, and mild values of the parameters not found to have a statistically significant effect on fusion (hot-pressing time and temperature) are suggested (see ‘Fusion of Coated Wood Powders upon Hot Pressing’), and even lower hot-pressing times and temperatures should be investigated to further optimise process efficiency.

Future work will focus on characterisation and optimisation of mechanical and physical properties (including density, hydrophobicity, translucency, and morphology) of produced biocomposites, as well as identification of suitable structural applications for these materials, which represent a sustainable alternative to existing engineered wood products. Production of wood composites using the novel method introduced here has the potential to displace the use of approximately 14 Mt year⁻¹ of toxic petrochemical binders [11], resulting in reduction of greenhouse gas emissions and non-renewable resource demand, as well as elimination of the health hazard associated with production and use of composites from by-products of the sawmill industry.

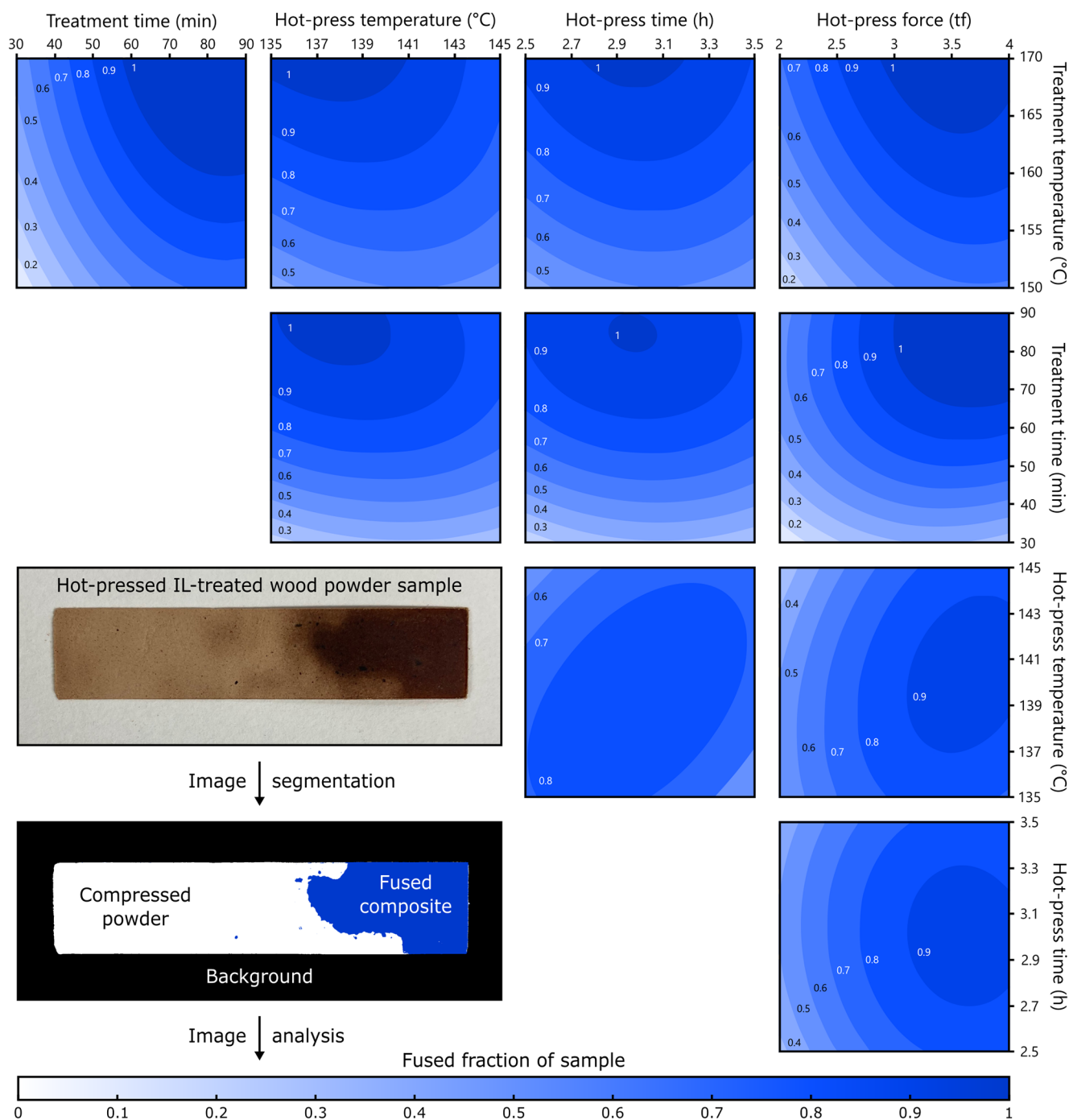


Fig. 6 Response surfaces of the fused fraction of hot-pressed lignin-coated wood powder samples to ionic liquid treatment and hot-pressing conditions. Response surface contour plots of the fused fraction of hot-pressed samples (as determined by image analysis) to ionic liquid treatment time & temperature, and hot-pressing time, temperature, & force. Contour lines represent estimated fused fractions at values of two parameters defined by plot coordinates (the other three parameters

being set to their respective centre values) based on a standard least squares model of a five-factor Box-Behnken experimental design with three centre points. Ionic liquid treatment time & temperature, and hot-pressing force, were found to significantly influence the fused fraction of samples by a *t* test with p -values $< 10^{-5}$. Influences of ionic liquid treatment time and hot-pressing force were found to be nonlinear by a *t* test with p -values < 0.007 . IL: ionic liquid

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Data Availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing Interests The authors have no relevant financial or non-financial interests to disclose.

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