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Transparent lignin nanoparticles for superhydrophilic antifogging coatings and photonic films

Karl Alexander Henn a, Sahar Babaeipour a, Susanna Forssell b, Paula Nousiainen a, Kristoffer Meinander a, Pekka Oinas b, Monika Österberg a,

a Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Kemistintie 1, 02150 Espoo, Finland
b Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Kemistintie 1, 02150 Espoo, Finland

Abstract
Lignin nanoparticles are useful in multiple applications, but their opaqueness remains an obstacle in optical applications. In this study, we present a method to prepare optically clear lignin nanoparticle dispersions from acetylated lignin. Thin lignin nanoparticle films remained transparent when deposited on glass and other smooth surfaces, and monolayered particle films provided effective antifogging properties. The particles could also be used to prepare multilayered films with bright structural colors that could be controlled via the film-thickness and were retained in dry conditions. We also developed an improved energy- and cost-efficient esterification method for controlled and quick lignin acetylation. The reaction could be selectively controlled to acetylate only aliphatic groups or to also include phenolic groups. We show here that stable nanoparticle dispersions can be produced from acetylated lignin at very high initial lignin concentrations without the formation of aggregates. Both the very short reaction time and high possible lignin concentration make the process industrially feasible as shown with a preliminary techno-economic assessment.

1. Introduction
During the last ten years, discussions on circular economy and climate change have sparked new interest in valorizing lignin to replace fossil-based materials. Known for being difficult to use and apply, lignin has largely been viewed as a side-stream material and merely a byproduct of the more highly valued cellulose fraction. Lignin is still underutilized, but academic research now demonstrates that even highly advanced inventions can be achieved. Lignin-based products could be commercially valuable and simultaneously act as carbon sinks, therefore contributing to relieving the current fossil-dependence and reducing carbon dioxide emissions.

Colloidal lignin nanoparticles (LNPs) emerged during 2014 – 2016 [1,2], a development that facilitated lignin’s use in rather sophisticated state-of-the-art applications by overcoming its poor water-solubility and heterogeneity. For a more detailed view on lignin utilization challenges, we refer to the review by Wang et al [3]. Although LNPs have performed well in multiple water-based applications [4–11], their heterogeneous light scattering can limit their applicability. LNPs would, for example, be a very interesting option for nanotextured antifogging coatings if the particles’ light scattering was more homogeneous and their appearance would be less opaque. Antifogging coatings are often hydrophilic and work by spreading water droplets into homogeneous films that do not scatter light [12–14]. Textured surfaces increase the total surface area, which for hydrophilic surfaces increases hydrophilicity further. LNPs are very suitable to create textures [4] and are hydrophilic [15], but minimizing their opaque appearance requires precise control over film thickness, which makes it impractical to use LNPs in optical applications.

Decreasing the particle size can potentially address lignin’s opaqueness, since small particles appear less turbid and scatter light more homogeneously [16–20]. The size of LNPs can be decreased to some extent by choosing a suitable solvent system [21] or by preparing particles at low lignin concentrations [22–25], but lignin’s molecular weight and hydrophilicity also play a role. The more hydrophilic the lignin is, that is, the more hydroxyl groups it has, the larger the particles become [26–29]. This is because as the hydroxyl groups interact with water (the anti-solvent), they counteract with and delay the aggregation process. In general, higher molecular weight also leads to smaller particles [29,30]. However, decoupling the effect of lignin chemistry and...
molecular weight is not always easy [31], as we further discuss in Section 3.1. It has been shown that different lignin fractions form particles of different sizes, and the particle size can be thus controlled by choosing a proper lignin fraction [24,29,32]. Fractionation has some drawbacks, such as reduced yields and the need for large amounts of solvents [33]. Because fractionation in itself is not a functionalization strategy, it does not necessarily remove the need for downstream processing and modification. Common among these previous methods is that they all require rather low initial lignin concentrations, and particle sizes below 80 nm are very rarely reported.

Chemical modification of the lignin to change its interaction with the solvents during particle formation could be a suitable strategy to achieve smaller particles [21,27]. Replacing lignin’s hydroxyl groups via esterification is commonly performed for analytical purposes [34], and could be one potential modification strategy. Interestingly, one of the first publications about spherical LNPs used acetylated alkali lignin to prepare the particles [35]. This strategy was most probably used to increase the lignin solubility in tetrahydrofuran (THF). The obtained particle size was around 100 nm [35]. This use of acetylated lignin for particles stopped when other studies showed that particles of a similar size and shape could be prepared from unmodified lignin [21,22]. Another main reason for avoiding acetylation is the chemicals used in the reaction [2]. Lignin esterification is most often done using halogenated carboxylic acids or acid anhydrides with pyridine as a catalyst [36,37]. These chemicals are relatively expensive to use on an industrial scale, and halogenated carboxylic acids and anhydrides are corrosive, which increases the wear and tear on the equipment. Pyridine is toxic and quickly migrates through soil into groundwater where it may not degrade [38], and its good water-miscibility and high boiling point makes it difficult to fully recycle from aqueous systems. Hence, for acetylated LNPs to be profitable and sustainable, the acetylation process needs to improve.

Although direct esterification and acetylation has achieved limited success, indirect esterification and acetylation (i.e., esterification using halogenated carboxylic acids or anhydrides) can be done successfully in many different ways. Lignin has been esterified with acetic anhydride using supercritical carbon dioxide as a solvent [39] or by mechanical activation-assisted solid-phase synthesis technology with acid or base catalysis [40]. Selective acetylation of aliphatic hydroxyl groups of kraft lignin has been obtained by reacting isopropanol acetate in ionic liquid both as solvent and catalyst [41]. Direct lignin esterification has some recent advances. For example, lignin has been acetylated directly with acetic acid at elevated temperatures using microwave reactors [42,43]. Microwave reactors are nevertheless expensive and are primarily designed for batch- or semi-batch operation [44,45]. Lignin has also been chemoselectively esterified using an excess of carboxylic acid, but elevated temperatures and long reaction times were needed [46].

In this work, we use acetylated lignin to prepare very small LNPs for transparent and colorless antifogging coatings, as well as brightly colored photonic coatings. We also seek to tackle prior challenges in lignin esterification using a new approach. We demonstrate an improved method to esterify lignin in a conventional Fischer system that solely relies on acetic acid as the organic solvent. The esterification could be done in minutes at only 60 °C with a high yield. Interestingly, we were able to prepare optically clear dispersions of spherical LNP at high concentrations after replacing some of the hydroxyl groups with acetyl groups. We then demonstrated the use of acetylated LNP dispersion as effective antifogging coatings as a high-value application. We also show a method of using the dispersions as photonic coatings by precisely controlling the coating thickness and thus the color and absorbance of light at different wavelengths. A preliminary techno-economic assessment was done for the use of the acetylated lignin as antifogging coatings, which determined that the scalability of the process would be economically feasible both as a stand-alone process and when integrated into a pulp mill.

2. Materials and methods

2.1. Materials

BiPiva 100 kraft LignoBoost® lignin, purchased from UPM (Finland) was used in this study. Dimethylformamide (99.8%), pyridine (99.0%), N-hydroxy-5-norbornene-2,3-dicarboxylic acid imine (97.0%), chromium(III) acetylacetonate (≥98.0%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), chloroform-D (99.8%), acetic acid (100%, Emparta®, ACS grade), sulfuric acid (95% – 97%, EMSURE® ISO), inhibitor-free tetrahydrofuran (≥99.9%), poly-L-lysine solution (0.1 % w/v in H2O), and polystyrene used for thin film preparation (Mw: 280,000 g/mol) was purchased from Sigma-Aldrich (Merck). Acetic anhydride (≥99%) was purchased from Riel-de Haen. Acetone (≥99%) and 1,4-dioxane (≥99.9%) was purchased from VWR Chemicals. Ethanol (≥99.5%, Etax Aa) was purchased from Alfa Aesar. The polystyrene standards used for GPC calibration were made by the following manufacturers: Mw 890 and 3470, g/mol. Fluka® Analytical; Mw 5010 g/mol, Supelco®; Mw 13 100 and 68 000 g/mol, Polymer Laboratories Ltd.

2.2. Lignin acetylation

Dry lignin was used for all experiments. The lignin was dried overnight in a vacuum oven at 40 °C at a pressure below 50 mbar. 3 ml glacial acetic acid or acetic anhydride was mixed with sulfuric acid while stirring. The evaluated sulfuric acid: acetic acid ratios were between 0.07:1 – 0.33:1 v:v, and the sulfuric acid: acetic anhydride ratio were between 0.004:1 – 0.025:1 v:v. We advise extreme caution when working with either of the above mentioned chemicals. The mixture’s temperature was adjusted on a heating plate with a thermometer with an accuracy of ±0.1 °C. When the temperature had stabilized, 0.3 g lignin was added to the mixture. To avoid the formation of clumps, the lignin was added evenly in small portions over a duration of 10 – 15 s. The reaction was allowed to take place for 5 – 20 min. The reaction was stopped by adding the solution to 10 ml of cool (10 °C) deionized water. The sample was allowed to precipitate for 2 – 3 min, with only slow agitation to ensure that the solvents were mixed. Then, the sample was transferred into an Eppendorf tube. The volume was diluted to 20 ml with deionized water, and the sample was centrifuged for 10 min at 10500 rpm with an Eppendorf 5804 centrifuge. The supernatant was removed, and the sample was diluted to 50 ml with deionized water. The sample was agitated and vortexed to redisperse the solids, and the centrifugation was then repeated. The supernatant was removed, and the sample was freeze-dried. The acetylated lignins that were used for thin film preparation (section 2.11) were centrifuged at 50 ml one additional time before freeze-drying.

For molecular weight comparison, the reference lignin was acetylated using the established pyridine – acetic anhydride method [34]. First, 1 ml of acetic anhydride was mixed with 1 ml pyridine. 5 mg lignin was added to the solution, and the reaction was allowed to take place for 16 h at room temperature. The reaction was quenched and precipitated by adding the solution to 10 ml ethanol. The solvents were removed by 5 cycles of rotary evaporation at 40 °C and 20 mbar. The cycle began by rotary evaporating the sample until it seemed dry. Then another 10 ml of ethanol was added, and the rotary evaporation was repeated.

For full acetylation of aliphatic hydroxyl groups and partial acetylation of phenolic hydroxyl groups, 200 – 500 µl acetic anhydride was added to 3 ml acetic acid and 0.5 ml sulfuric acid mixtures at 60 °C before 0.3 g lignin was added. The reaction time was 10 min, and the product was collected and washed as described previously.

The dimeric arylglycerol β-ether compounds the phenolic 1-(3-methoxy-4-hydroxy-phenyl)-2-(2-methoxy-phenoxy)-1,3-propanediol, and non-phenolic 1-(3,4-dimethoxyphenyl)-2-(2-methoxy- phenoxy)-1,3-propanediol were synthesized following the procedure of Nakatsu et al. [47]. Acetylation of phenolic dimer was done using pyridine – acetic anhydride method described above. All products were...
analyzed, and their purity was checked by NMR, with details below.

2.3. Preparation of lignin particles

The lignin used to prepare particles was dried either using a freeze dryer at a vacuum below 0.2 mbar or a vacuum oven at 40 °C at a pressure below 50 mbar for at least 16 h. The dried samples were weighed into beakers of appropriate size. Fully acetylated samples were dissolved in an aceton – deionized water mixture with a respective volumetric ratio of 10: 0.045 (v:v), while unmodified lignin and partially acetylated lignin were dissolved in an aceton – deionized water mixture with a respective volumetric ratio of 1: 0.33 (v:v). The concentration was adjusted to 10 – 200 µl/g. The samples were stirred for at least 3 h. Particles were prepared by adding 2.4 ml deionized water to 0.8 ml lignin solution under rapid stirring. After the addition of water, the dispersions were left stirring for 15 min. The acetone was removed by rotary evaporation at 40 °C and 100 mbar.

2.4. Dynamic light scattering (DLS)

A Zetasizer Nano-ZS90 (Malvern, U.K.) instrument was used to measure particle diameters and size distributions in water. A zeta dip cell was used to measure the surface charge and the Smoluchowski model was used to calculate the ζ-potential values from the obtained electrophoretic mobility data. The samples were diluted to 0.2 g/l with deionized water before analysis. A refractive index of 1.4 and an absorption of 0.9 was used for all samples. A scattering angle of 90° was used.

2.5. Fourier-transform infrared (FT-IR) spectroscopy

The FT-IR absorption measurements were done with a Spectrum Two™ FT-IR (Perkin-Elmer, Massachusetts, USA) device with an attenuated total reflectance (ATR) module. Only dry samples were used for the measurements, and the background measurement was done in air. The resolution was 1 cm⁻¹, and 10 scans were collected for each measurement between 4000 and 600 cm⁻¹. The samples were baseline-corrected using the Spectrum-Two software. Aromatic samples were normalized according to the smallest absorption signal throughout the spectra and the highest signal of the aromatic C-C stretch (1500 – 1515 cm⁻¹). Non-aromatic samples were min–max normalized according to the spectrum’s highest and lowest absorption values.

2.6. ¹H NMR and HSQC NMR

Acetylated lignin samples were prepared as follows. First, 50 – 70 mg of dried samples were weighed and dissolved. A solvent mixture of 500 µl dimethyl sulfoxide and 80 µl deuterium oxide was used for partially acetylated lignin and non-acetylated lignin, while the fully acetylated lignin samples were dissolved in pure deuterated chloroform. The spectra were referenced to the solvent signals. The measurements were performed using a Bruker Avance 400 MHz spectrometer equipped with a 5 mm BB probe. The standard pulse sequence zg with 16 scans, a pulse angle of 90°, an acquisition time of 5 s and a pulse delay of 5 s, and a spectral width of 16 ppm was used for ¹H NMR analyses. For HSQC measurements, the Bruker standard pulse sequence (hscqetgpsip,2) with 36 scans was used with spectral widths of 11 ppm in the F2 (¹H) dimension with 1024 data points and 215 ppm in the F1 (¹C) dimension with 256 data points. The measurements were done with a d1 of 2 s, and the total acquisition time was approximately 5.5 h. The spectra were analyzed with Bruker Topspin 4.1.4 Windows version using standard processing parameters.

2.7. ³¹P NMR

The samples were prepared as reported previously [4,48]. Samples were vacuum dried for at least 8 h at 40 °C prior to the preparation. 30 mg of the sample was weighed into separate glass vials. The samples were first dissolved in 150 µl dimethylformamide and 100 µl pyridine. An internal standard (N-hydroxy-5-norbornene-2,3-dicarboxylic acid imine) solution and a relaxation agent (chromium(III) acetylacetonate) solution with respective concentrations of 0.05 mol/l and 0.0326 mol/l were prepared in a solvent mixture of 1.6 parts pyridine and 1 part CDCl₃. Then, 200 µl and 50 µl of the respective solutions were added to the samples. 300 µl chloroform-d was added and the vials were stirred until the samples were fully dissolved. Last, 150 µl 2-chloro-4,4,5,5-tetraamethyl-1,3,2-dioxaphospholane, as phosphorylation agent, was added. The sample was allowed to react for at least 10 min and measured within 1 h of the addition of the phosphorylation agent.

A Bruker Avance 400 MHz spectrometer (Massachusetts, USA) equipped with a 5 mm broadband (BB) probe was used. A total of 128 scans were performed using the pulse sequence zg with a pulse angle of 90°, an acquisition time of 1 s, and a pulse relaxation delay of 5 s. The spectral width was 185 ppm. The chemical shifts were referenced to the phosphorylated water signal at 132.2 ppm in CDCl₃. Different regions were integrated according to literature and compared to internal standard (49) using the Bruker TopSpin 3.6.5 software. Some sharp peaks from residual acetic acid were observed at the carboxylic region (134.3 – 134.4 ppm). These peaks were subtracted from the carboxylic signal with automatic baseline correction.

2.8. Gel permeation chromatography (GPC)

An Agilent 1100 (Agilent Technologies, USA) high-performance liquid chromatography HPLC system with GPC-Add-on was used to analyze the molecular weight distributions. The samples were prepared by first dissolving 2 mg of dry sample in 2 ml inhibitor-free tetrahydrofuran. The samples were stirred at room temperature for at least 16 h and were then filtered with 0.2 µm syringe filters before the measurement. Two PSS MCX columns (Polymer Standards Service, Germany) with particle sizes of 5 µm and with porosities of 100 and 50 Å were used in that order, and both UV (at 280 nm) and RI detectors were used for monitoring. A series of polystyrene standards with molar masses 953, 3460, 5110, 13 100, 30 300, and 68 000 g mol⁻¹, as well as toluene, were used for calibration, and the standards were prepared and measured the same way as the other samples. A blank tetrahydrofuran sample was also used. A third-order polynomial fit was used for the calibration curve.

2.9. Evaluating lignin particle dispersions as antifogging coatings

Fully acetylated lignin was used. Particles were prepared with initial lignin concentrations of 10 g/l. Lignin dispersions prepared as described above were first diluted to 1.5 g/l with deionized water. Soda lime glass substrates were used for anti-fogging tests. The glass slides were cleaned by first being submerged in boiling water for 10 min and then submerged in 1 M NaOH for 5 min. The slides were further washed with deionized water and acetone, then rinsed thoroughly with deionized water once more, and finally dried using pressurized air. To deposit thin layers of nanoparticle dispersion, a small amount of dispersion was added to dry glass slides and spread out (spreads between 0.1 and 1.2 µl/cm²) using a non-absorbing rubber-latex film. The dispersion was spread evenly across the glass until the liquid had evaporated. This spreading method was used to simultaneously simulate field-use and allow control over the spread. A thicker spread of 20 µl/cm² was also deposited by spreading the liquid evenly once and then allowing the liquid to dry in ambient conditions.

The anti-fogging demonstration was done as follows. 100 µl deionized water was heated to 100 °C, and maintained boiling using a heating plate set to 110 °C. The glass slide was attached to a holder directly above the boiling water so that the steam hit the coated side at a 30° angle. The distance between the slide and the surface of the boiling
water was 15 cm. A photograph was taken 30 s after the sample had been attached above the boiling water. The steam’s effect on the coating could be examined by exposing coated silica wafers to steam and then examine the wafers using SEM. To do this, silica wafers were cut in the same sizes as the glass slides, whereafter they were cleaned, coated and exposed to steam in the exact same way as the glass. They were then dried in ambient conditions before being prepared for SEM.

The particle coating’s durability was evaluated with controlled practical tests on coatings with dispersions spreads of 0.4 µl/cm². The coatings resistance to water was evaluated by submerging a coated glass sample in 21 °C deionized water for 30 s, and then letting the sample dry in ambient conditions. Then, the sample was exposed to steam as previously described for 1 min. This procedure was repeated three times. The samples’ durability to abrasion and water was measured by exposing the particle coating to steam in the exact same way as the glass. They were then dried in ambient conditions. The droplet size was 4 μl, and 30 s after the drop had been placed on the substrate. MilliQ water was used for all tests.

2.13. Atomic force microscopy (AFM)

A MultiMode 8 AFM with a Nanoscope V controller (Bruker, Santa Barbara, CA, USA) was used with NCHV-A probes (antimony-doped silicon with a tip radius of 8 nm). All images were collected using tapping mode in air. A scan rate of 0.5 Hz, and a resolution of 512 samples per line was used for all collected images. Silica wafers were used as a substrate for all samples. The height differences of particle films were evaluated as follows. One line was carefully drawn in the sample using a smooth metal tip with minimal pressure to remove the particle film while avoiding denting the silica. A measurement was conducted across the line so that the cantilever crossed it once for each scanned line at an approximately perpendicular angle. The layers’ thicknesses were calculated using the height difference between the drawn line and the top of the film. The tilt was adjusted according to Fig. S17.

2.14. Transmission electron microscopy for electron tomography reconstruction

First, hexagonal 300 mesh Cu grids with ultrathin carbon support film (Electron Microscopy Sciences, Pennsylvania, USA) were plasma-cleaned using a Model 1070 NanoClean plasma cleaner (Fischione Instruments Inc., Pennsylvania, USA) for 30 s. The grids were then loaded with 10 nm fiducial gold nanoparticles as markers. The LNP dispersions to be analyzed were diluted ten times with deionized water (to a concentration of approximately 0.25 g/l), and 3 µl of the diluted dispersions were pipetted onto the grids and allowed to sink into the mesh. The excess water was blotted using filter paper, and the samples were dried in ambient conditions. The measurements were done using a JEOL (Japan) JEM-3200FSC cryo transmission electron microscope operated at 300 kV in bright-field mode with an Omega-type zero-loss energy filter. The sample temperature was maintained at −187 °C during imaging, and the electron tomography data was acquired using the SerialEM software package with a Gatan Ultrascan 4000 camera, following previously reported procedures [21]. The possible tilt-range depended on the sample’s position. The non-acetylated LNPs were tilted between −65.5°–60.5°, the partially acetylated LNPs were tilted between −70.6°–56.9°, and the fully acetylated LNPs were tilted between −65.5°–64.5° with increments steps of 2° in low dose mode. IMOD was used to pre- and fine-align and to crop the obtained tilt series. To reduce noise and computation times, the images were binned two times. USCF Chimera was used to generate the volumetric graphics and perform image analysis.

2.15. Scanning electron microscopy (SEM)

A Mir3 scanning electron microscope (Tescan, The Czech Republic) was used for all SEM images in the main text, and for the images indicated in Fig. S7. In Fig. S5, a Zeiss (Germany) Sigma VP was used. The images were obtained under vacuum using an accelerated voltage of 2 kV. All samples were coated with a gold–palladium mixture (Au80Pd20) with a Q150R S plus rotary-pumped coater (Quorum Technologies, U.K.). The used sputter current, sputter time, and coating factor was 20 mA, 1 min, and 1.0, respectively.

2.16. Ultraviolet–visible (UV–vis) spectroscopy

Light transmittance for dispersions were measured using a Shimadzu (Japan) UV-1800 UV–vis spectrometer. A high precision quartz cell (Hellma Analytics, Germany) with a 10 mm light path was used. The transmittance spectrum was measured on medium scan speed, and with a data interval of 1 nm.
Fig. 1. Formation of water-dispersible lignin nanoparticles (LNPs) with fully and partially acetylated lignin compared to unmodified lignin. (a-c) Atomic force microscopy images of fully-, partially- and non-acetylated LNPs made with an initial lignin concentration of 10 g/l. The sizes marked in the figures are the particle heights and were obtained with the NanoScope Analysis 3.0 software. (d-f) The appearance of the dispersions 2 h after preparation. In case of aggregate formation, the height of the aggregated mass is indicated. (g) The zeta potential (h) and hydrodynamic diameter of particles as a function of initial lignin concentration. The initial lignin concentrations between 10 and 200 g/l result in lignin particle concentrations between 2.5 and 50 g/l after anti-solvent addition and consequent particle-formation. The asterisk (*) is used next to measurement points where significant sedimentation of large aggregates skew results towards smaller particle sizes.
Low lignin concentrations of 10 g/l produced particles with hydrodynamic diameters as high as 200 g/l when using fully acetylated lignin. These findings can help to solve many challenges in LNP research. The research on how structural factors affect LNP size has increased, but some of the most important parameters correlate with each other. For example, high molecular weight is believed to lead to small particles, but lignin with high molecular weight tends to have less phenolic end groups and more aliphatic hydroxyl groups [26,27,29,51,52]. The fully acetylated lignin had a much lower molecular weight than non-acetylated lignin, which suggests that reduced hydroxyl group content is more important than molecular weight. Zou et al. suggested that good solvent-lignin interactions lead to small particle size [21]. The fully acetylated lignin’s solubility in acetone tremendously increased, which indicates that the addition of acetyl groups does indeed improve the lignin’s solvent-interactions. To obtain a more direct measure of the acetylation’s effect on hydrophobicity, water contact angles were measured on thin films of acetylated and non-acetylated lignin. Thin films were prepared by spin coating lignin solutions with concentrations of 0.5 wt% onto polystyrene-coated silica wafers. The polystyrene-coated wafers without any lignin had contact angles of around 98°. Fully acetylated and partially acetylated lignin films both had contact angles of around 66°, while non-acetylated lignin films had contact angles of 62° as has been previously also seen for nonparticulate unmodified lignin films (Fig. S5a) [15]. Interestingly, by using thicker lignin films prepared from 5 wt% lignin solutions, we observed a significant difference in water absorption rate. The fully acetylated lignin
films did not absorb water during the 30 s the water drop was monitored (Fig. S6). Minor absorption was noticed for the partially acetylated lignin films, and in contrast, the non-acetylated lignin films absorbed water so quickly that the droplets nearly disappeared completely within 30 s. The water absorption naturally led to significantly reduced contact angles (Fig. S5b). These results indicate that both partial and full acetylation significantly reduce the lignin’s hydrophilicity and water interactions. Taking our results and previous research into consideration, we suggest that water-solubility and solvent interactions are the most important parameters to control particle size in solvent shifting processes.

Small particle sizes are beneficial in many applications, such as particulate reinforcing agents in composites [9,53,54], surface coating applications [4,36], and cosmetics and medicinal applications [31,55,56]. With unmodified lignin, it is difficult to make concentrated dispersions of particles below 200 nm in diameter with the popular solvent shifting process. Small particles can be produced but usually only at very low concentrations [21,23–25,30,31,57,58]. However, a low initial lignin concentration also means a greater need for concentrating the dispersion, adding to the energy consumption of the process.

New evolved acidification processes have emerged to solve these issues [59,60]. For example, soft LNPs can be produced at high concentration using acidification, but this process uses mostly lignosulfonates [60]. Here we demonstrate a way to overcome the limitations of the solvent shifting process, attaining small and spherical particles from kraft lignin at high concentrations. The higher concentration that the use of acetylated lignin allows can in some cases completely remove the need for concentrating the dispersions. For example, 0.1 – 0.6 wt% (roughly 1 – 6 g/l) of unmodified LNPs are needed for efficient emulsion stabilization depending on the oil phase [61]. In our work, the concentration immediately after particle formation was 50 g/l when using an initial lignin concentration of 200 g/l, which means that no water would have to be removed to use the dispersion for Pickering emulsion stabilization.

Because of the difference in nanoparticle size and self-assembly behavior at high initial lignin concentration, we were curious whether there were internal morphological differences between the acetylated and non-acetylated LNPs. Electron tomography was used to construct 3D images of the particles’ structures (Fig. 2). We observed only small differences in electron density patterns between unmodified and acetylated LNPs. All particles seemed to be built of small building blocks, in
hydroxyl groups may furthermore increase the molecular packing density of lignin within the particles, which cause it to pack denser. The loss of hydrophilicity is therefore curious to evaluate whether the LNPs’ carboxylic hydroxyl groups, on the particles with assembles the most hydrophilic structures, in this case the carboxylic hydroxyl groups on the particles because the solvent shifting process that the LNPs were prepared interconnections have not been studied extensively. One explanation could be that the lignin on the particles’ surfaces is less shielded from water than the lignin within the particles, which cause it to pack denser. The loss of hydroxyl groups may furthermore increase the molecular packing density at the surface for the acetylated lignins compared to the non-acetylated lignin because of reduced water-interactions. However, the structure of LNPs has not yet been extensively studied, and more research would therefore be needed to draw definitive conclusions.

3.2. Transparent antifogging coatings

As water vapor condenses on hard surfaces, it forms small droplets that scatter and refract light and reduces or completely disable transparency. Foggation can easily occur on the windshields of vehicles or on the inside of protective masks and other protective goggles, which is potentially dangerous. Superhydrophilic surfaces can achieve antifogging properties by spreading condensing water into thin homogeneous films, rather than allowing it to form light-scattering droplets [64–67]. Surface roughness increases the total surface area and thus total surface interactions, which is why textured hydrophilic surfaces easily achieve antifogging properties [12,64,66]. LNPs are more hydrophilic than bulk lignin because the solvent shifting process that the LNPs were prepared with assembles the most hydrophilic structures, in this case the carboxylic hydroxyl groups, on the particles’ surfaces [15,58]. We were therefore curious to evaluate whether the LNPs’ hydrophilicity combined with the roughness caused by a thin layer of particles would lead to antifogging properties. We chose fully acetylated particles for these tests, and compared their properties with those of non-acetylated LNPs.

The acetylated LNP dispersions effectively hydrophilized glass slides in our tests, and only 0.1 µl/cm² of a dispersion with a concentration of 1.5 g/l was needed to reduce the water contact angle from 29 ± 6° (uncoated glass) to 9 ± 4° (Fig. 3, Fig. S4). The contact angle for these samples was so low that the angles were difficult to accurately measure. These results are in striking contrast to the much higher water contact angles for smooth, non-particulate acetylated lignin films (S5 and S6), illustrating the influence on the particle structure on wetting properties. Scanning electron microscopy (SEM) images indicated that the particles formed a very smooth layer on the substrate (Fig. 4a). The antifogging effect was observed for dispersion spreads between 0.1 and 1.6 µl/cm². SEM of samples coated with various spreads indicate that spreads between 0.1 and 0.8 µl/cm² formed sub-monolayers, while the dispersion spreads beyond 0.8 µl/cm² resulted in saturated monolayers, with intermittent multilayer regions of approximately 2 – 3 layers (Fig. S7). These layers were invisible and excellently retained their transparency when exposed to steam from boiling water at close range. Water vapor can also condense on freezing cold substrates in humid conditions. Such situations were also simulated with the acetylated LNPs, and the coated slides retained their transparency significantly better compared to the uncoated glass. The contact-angles of non-acetylated LNP films were between 27 and 22° (Fig. S4). These results are in rather good agreement with the results obtained by Farooq et al. [15], but the films did not provide antifogging properties (Fig. S8 h). The non-acetylated LNP films could also be seen on the glass slides when spreads of more than 0.8 µl/cm² formed sub-monolayers, while the dispersion spreads beyond 0.8 µl/cm² resulted in saturated monolayers, with intermittent multilayer regions of approximately 2 – 3 layers (Fig. S7). These layers were invisible and excellently retained their transparency when exposed to steam from boiling water at close range. Water vapor can also condense on freezing cold substrates in humid conditions. Such situations were also simulated with the acetylated LNPs, and the coated slides retained their transparency significantly better compared to the uncoated glass. The contact-angles of non-acetylated LNP films were between 27 and 22° (Fig. S4). These results are in rather good agreement with the results obtained by Farooq et al. [15], but the films did not provide antifogging properties (Fig. S8 h). The non-acetylated LNP films could also be seen on the glass slides when spreads of more than 0.8 µl/cm² dispersion was deposited (Fig. S3).

To evaluate the durability of acetylated LNP films, we tested whether the antifogging effect would last after several exposures to fog followed by drying at ambient conditions, but no significant reduction in antifogging effect was observed after five cycles. The films’ resistance to water was investigated by submerging a coated glass slide in water for
30 s, followed by exposure to steam for 1 min. The antifogging property was reduced by each submersion, and lost after three submersions. The film was also sensitive to dry wiping, as the antifogging effect was completely lost after three controlled wipes with a dust-free paper cloth. These results are promising for the feasibility of the coating but more research would be needed to enable washing or cleaning of the coating.

Next, we investigated the effect of layer thickness with a dispersion spread of $20 \mu l/cm^2$. Layers this thick partially lost their invisibility, as a faint yellow hue was noticeable. This thicker film still reduced droplet formation, but its structure collapsed and the film partially lost its transparency upon wetting and drying. SEM images of the layers confirmed their different structure (Fig. 4 & Fig. S9). Low spreads resulted in monolayers that retain their structure upon exposure to steam. In contrast, higher spreads resulted in a compact multilayer film. After exposure to steam, cracks and tears were observed in the multilayered coating. This suggests that the film swells slightly when becoming moist and shrinks when dried. While swelling, some larger flakes could detach upwards from the substrate to give the film space to swell. When drying again, the film is likely torn, resulting in the tears observed for the multilayer coatings in Fig. 4. Although the particles are not expected to swell by themselves, unmodified LNPs have been shown to bind water, which then results in the swelling of LNP films [15]. In sub-monolayers, the swelling does not disrupt the film structure, because there is space between the particles. Control over the layer-thickness is consequently a deciding factor to achieve both transparency and antifogging properties.

Many current nanotextured antifogging surfaces are prepared by constructing textures onto or into the material as it is prepared [13,68,69], which limits their applicability. Coatings, on the other hand, are versatile and can be applied almost anywhere. There are very few antifogging coatings that are explicitly bio-based, which makes lignin’s good performance in this application a welcome development.

### 3.3. Photonic color-adjustable film

While preparing multilayers for the antifogging tests, we observed that thick layers of LNP dispersion caused faint structural colors via thin film interference, but the colors shifted almost randomly in blue, green, and red. We were interested in the eventual possibility to better control the multilayers’ thickness and thus selectively choose the film’s color. We chose to use layer-by-layer deposition of partially acetylated LNPs and poly-L-lysine to control the coating’s thickness on silicon wafers as substrate. Poly-L-lysine was chosen as cationic anchor because of its good performance for the preparation of LNP monolayers in previous studies [15]. Partially acetylated LNPs where chosen for these tests because of the possibilities to modify them via their phenolic hydroxyl groups, which could allow for more potential benefits and applications in future studies.

When a few layers had been added, lignin’s typical brown color started to appear. The color nevertheless shifted as more layers were added, and a cycle of rainbow colors in the order of blue, yellow, and purple were obtained when the number of layers reached 20, 30 and 40, respectively (Fig. 5). The films’ thicknesses were then analyzed in AFM to better understand how the color and film thickness correlated. The blue color was achieved with layer thicknesses of ca. 115 nm, the yellow color with ca. 155 nm, and the purple color with ca. 250 nm thick layers. The colors shifted when observed from different angles. For example, when looking at the film from smaller angles, the yellow film shifted to blue, and the purple film shifted to yellow (Fig. 5d). These results show that LNP multilayers can be used to achieve specific colors that are
sensitive to the angle of incidence via thin film interference [70].

Being able to produce photonic films and coatings from LNPs provides a few notable benefits to the field of photonic materials. Similar photonic thin films have been prepared from polystyrene-methyl methacrylate particle dispersions [71], but our approach provides a bio-based alternative that is technically less challenging to prepare, since there are no long polymerization reactions needed. Non-particulate lignin films prepared by spin-coating lignin-solutions can cause thin film interference [72], but our approach removes the need for volatile solvents when preparing the film, which increases their applicability and user safety. Lignin in the form of nanoparticles has been demonstrated as a photonic material in recent studies, but previous approaches have relied on precise control over particle size, either through lignin fractionation or centrifugation, and the color is activated via moisture [24,32]. In contrast, our method provides an alternative where the colors are retained when the surfaces are fully dry. Although photonic properties have been reported for LNPs of specific sizes, this is the first time that thin films of LNPs have shown structural colors, which creates new possibilities for their use specifically as coatings.
stimuli-responsive sensor materials [74,75], or perhaps even for cars and other vehicles.

We proceeded to examine how well the colors could be predicted by thin film interference theory. The phenomenon occurs due to the superposition of light reflected from the top and bottom interfaces of a thin film (Fig. 5b) [71,76]. Either constructive or destructive interference will occur for specific wavelengths of light, and the resulting color will depend on which of the dominant wavelengths in the transmission spectrum undergoes the most constructive interference. Constructive interference for a direction normal to the surface can be expressed as 

\[ \tan(\theta) = \frac{2n_d d}{\lambda} \],

where \( d \) is the thickness and \( n_d \) is the refractive index of the film. When the thickness of the film is increased, the different spectral components will be enhanced until the optical path difference is more than twice the length of the shortest wavelength. If the sample is tilted with respect to the direction of the incoming light, the optical path difference will decrease with a factor of \( \cos^2 \theta \), where \( \theta \) is the angle of refraction. When the thickest film with 40 layers was tilted, the color changed from the original purple, presumably caused by a mixture of red and blue wavelengths, to the same yellow as was seen for a thinner film, and finally to the blue color seen for the thinnest film. This suggests that only first order interference occurs with the two thinnest films, where the maximum thickness of each film results in an optical path difference equal to one wavelength of the reflected light. The wavelengths for blue and red light differ by approximately a factor or two, suggesting that constructive interference occurs for both of these colors with the thickest film.

The optical path for light traveling through the film is also affected by the film’s refractive index. The enhanced colors of blue, yellow, and red that were seen for these films have wavelengths of about 380 nm, 550 nm, and 750 nm, respectively. Together with the film heights measured by AFM, considering that the maximum film thickness will vary with the roughness of the films, this would indicate that the refractive index of the lignin film has a value in the range of 1.3–1.6. However, the substrate’s refractive index must also be considered. An additional phase shift of 180° (corresponding to an extra optical path difference of a half wavelength) can occur if light strikes a surface with a refractive index greater than that of the medium it is traveling through. This phase shift occurs for the light reflected at the air-lignin interface, and it can occur at the lignin-silicon interface if the film’s refractive index is smaller than the silicon’s, which has a refractive index of approximately 1.45–1.50 [77]. Phase shifts seem to occur at both interfaces, because otherwise interference would be expected to occur at less than 20 bilayers. Therefore, a refractive index for the acetylated LNP film will likely be close to the lower boundary of 1.3, which fits well with previously reported values of 1.37 for lignin-containing coatings [77].

3.4. Design of acetylation reaction conditions

The antifogging and photonic films that were presented and discussed in the previous sections are interesting and valuable, but their preparation must also be considered. The acetylation process’ feasibility is key, and we therefore decided to explore options to the traditional acetylation process. Acetic anhydride or halogenated carboxylic acids are currently the most frequently used acetylation reagents for lignin. These reagents are more expensive than regular carboxylic acids, and acetylation reactions with these acetylation agents are often catalyzed by pyridine, which is toxic, harmful to the environment, and expensive to be used at industrial scale [78]. Here, we sought to find a functioning acid-catalyzed system to directly acetylate lignin with acetic acid and get a general overview of how varying certain reaction parameters would affect the resulting acetylated lignin.

Our kraft lignin possesses some typical side-chain structures, including \( \beta-O-4 \), \( \beta-5 \), and \( \beta-\) structures that are visible in the unmodified lignin HSQC NMR spectrum (Fig. S12). Lignin is prone to condensing in strongly acidic environments by dehydration reactions followed by the formation of covalent bonds between aromatic carbons and the dehydrated side chain [79,80]. \( \beta-O-4 \) structures are particularly prone to acidolysis reactions cleaving the side-chain, which leads to the formation of reactive carbocations and promotes condensation reactions with neighboring aromatic groups. To outcompete dehydration and thus reduce possibilities for condensation, the acetylation reaction was designed to occur rapidly. We started with a reaction time of 10 min and a temperature of 60 °C, and the lignin: acetic acid ratio was kept constant at 100 g/1. A volumetric sulfuric acid: acetic acid ratio of 0.1: 1 was chosen as a starting point. As signs of successful esterification were observed in FT-IR spectral analysis in these conditions, we continued to screen the sulfuric acid: acetic acid ratio, the reaction time, and the reaction temperature (Fig. S10). Increasing the sulfuric acid: acetic acid ratio to 0.17: 1 v:v led to small improvements in the degree of acetylation according to FT-IR analysis, but no significant benefits were observed by increasing the ratio beyond that. Gel permeation chromatography (GPC) was used to determine whether increasing the amount of acid catalyst would lead to condensation. Surprisingly all samples, regardless of sulfuric acid: acetic acid ratio, had slightly smaller number- and weight-average molecular weights compared to unmodified kraft lignin (Fig. S14b, Table S3).

These results suggest that even though dehydration reactions occur [80], the follow-up elimination to enol ether with final acidolysis reactions seems to be prevalent over carboxylation condensation with other electron-rich lignin macromolecules. The lignin is consequently slightly depolymerized while being acetylated. The reaction time’s effect was also examined, but no significant differences were obtained when increasing the reaction time above 10 min. Changes in the amount of hydroxyl groups were determined by quantitative \( ^{31} \)P NMR, and structural changes in the acetylated lignin were examined with 2D heteronuclear single quantum coherence (HSQC). \( ^{31} \)P NMR analysis showed a reduced number of aliphatic hydroxyl groups but mostly retained phenolic hydroxyl groups (Fig. 5d). Only 8 – 19% of the aliphatic hydroxyl groups remain non-acetylated, while 75 – 85% of the phenolic hydroxyl groups are non-acetylated (Table S4). Here we observed a slight increase in degree of acetylation at higher temperatures. The quantity of non-acetylated phenolic hydroxyl groups decreased as the reaction temperature increased, suggesting that under more severe reaction conditions, condensation of the molecular backbone increases. HSQC NMR showed that partial acetylation reactions modify the side-chain structures, evidenced by the disappearance of side-chain signals together with changes in the aromatic signal area (Fig. S12). However, we also observed a clear increase in the chemical shifts of the correlation signals originating from lignin acetylated γ-carbons, with a chemical shift of unmodified signals at 60–62/3.3–3.9 ppm moved to 63–65/3.8–4.2 ppm. This in combination with the reduced molecular weight indicates that the lignin is to some extent re-arranged, undergoing cleaving and condensation side-reactions during the acetylation process.

Selectivity can be desirable in many cases, but it can also limit applications where high degrees of acetylation are needed. Acetylation using acetic anhydride is commonly used to acetylate cellulose and lignin, but lignin has typically been acetylated using bases, like pyridine, as catalyst [34,81–84]. We were curious whether acetic anhydride would be effective in an acid-catalyzed system for full lignin-acetylation, without having to use pyridine. A similar optimization as was done for acetylation with acetic acid was performed for acetic anhydride, starting from a reaction time of 10 min, a volumetric sulfuric acid: acetic anhydride ratio of 0.025: 1, and a reaction temperature of 30 °C. FT-IR analysis indicated that these conditions were enough to achieve complete acetylation within 5 – 10 min. \( ^{31} \)P NMR analysis indicated that only carboxylic hydroxyl groups remained, while nearly all aliphatic and phenolic hydroxyl groups were acetylated (Table S3). \(^1\)H NMR and HSQC NMR analysis revealed strong signals from both aliphatic and phenolic acetyl groups and reduced signals from aliphatic hydroxyl groups (Fig. 5d-g and Fig. S11). However, the lignin side-chain structures remain present, with the most significant difference being the shift of the acetylated \( \beta-O-4 \) α-signals (from 6C/6H 71/4.8 ppm to 73/5.9–6.0 ppm).
In the FT-IR spectra, the fully and partially acetylated lignins differed unproporionately in absorption intensity, and some ester-derived bands had shifted in position. To get a better understanding of how the type of ester group (aliphatic versus phenolic) affected the FT-IR spectra, we examined a set of model compounds (Fig. 7). Comparing phenyl acetate (only phenolic esters) and an acetylated β-O-4 dimer (one phenolic ester and two aliphatic esters per molecule) provided a few important insights. In phenyl acetate, all ester-derived bands were more intense compared to those of the acetylated β-O-4 dimer. Similar differences in the band positions as observed when comparing fully- and partially-acetylated lignins were also observed when comparing the model compounds, especially for signals derived from the ester’s α-carbon. For example, the C-O stretching band for phenyl acetate was found at 1183 cm⁻¹ and at 1201 cm⁻¹ for the acetylated β-O-4 dimer. The comparison between non-acetylated phenolic- and non-phenolic β-O-4 dimers provided insights about how the presence of aliphatic and phenolic hydroxyl groups affect the band at 3600 – 3100 cm⁻¹. The non-phenolic dimer contained only one rather sharp band at 3489 cm⁻¹, likely due to dimeric intermolecular hydrogen bonding [85]. In the phenolic dimer, the position of this band was slightly less intense and had shifted to 3444 cm⁻¹, and an additional broad band was present at 3600 – 3100 cm⁻¹. The hydroxyl bands’ broadness hence seems to be more strongly affected by lignin’s phenolic groups compared to its aliphatic groups, which explains why the absorption bands of partially acetylated and non-acetylated lignins have similar shapes.

Direct acetylation using acetic acid is much less complicated compared to acetic anhydride from an industrial perspective. When acetic anhydride reacts with sulfuric acid, acetic acid is formed as a byproduct. This consumes some of the acetic anhydride and leads to higher makeup costs. It also creates the need to separate and purify the non-reacted acetic anhydride from the mixture to be able to recycle it. Acetic anhydride is furthermore more expensive than acetic acid. However, since the two methods functioned in such similar conditions, we investigated if the selectivity could be controlled by adding small amounts of acetic anhydride to the acetic acid and sulfuric acid mixture. As expected, the addition of acetic anhydride increased infrared absorption signals from phenolic acetyl structures (Fig. S15). Using this approach, only small amounts of acetic acid would be needed, and hence, the acetic anhydride would not necessarily have to be recycled. This would allow the degree of substitution to be controlled without adding significant expenses to the process cost. The increase in cost nevertheless has to be motivated by demand and utility. Herein, we focused on novel, high-value applications of acetylated LNPs from kraft lignin. However, acetylated lignin has shown good compatibility in plastic blends [87,88], and the impact in that segment is immense. In future studies, it may be interesting to evaluate if this process is suitable for other amphiphilic lignin types, such as organosolv or milled wood lignins. Lignin’s with high hydroxyl group contents can be too hydrophilic to form spherical and stable particles, and this issue may be addressable via acetylation. Overall, the simple and rapid acetylation reaction described here could broad benefits on lignin valorization, and we were thus curious to see if the reaction could be feasible at a large scale.

3.5 Industrial scale process design

To get an overview of the acetylation procedure’s feasibility in commercial scale, an industrial scale process was developed for the production of acetylated lignin based on the experimental results presented above. The capacity of the production was designed to be 2 kt/a, with a lignin content of 30 wt%. The acetylated lignin can be processed...
into lignin nanoparticles (LNPs) and further diluted to produce 300000 m$^{-3}$ antifog coatings. The possibility to scale up the production of unmodified LNPs has been examined in our previous studies, and the same approach can be used for acetylated lignin with the major difference that higher lignin concentrations can be used [22,57,89]. The production facility would preferably be integrated into an existing biorefinery or pulp mill. The production capacity was designed to be rather low for an industrial plant because of the high value of the product and the high energy needed for the recycling of solvent. The main steps in the process are illustrated in Fig. 8 and described below.

The sulfuric acid catalyst is mixed with acetic acid in a static mixer. Thereafter, dry lignin is fed to the heated mixture of sulfuric acid catalyst and acetic acid. The lignin-rich phase and the acid-rich phase are separated in three steps by using clarifier-decanters, with water washing between each centrifugation. The acetylated lignin is concentrated slightly by drying before the LNP formation.

The first acid-rich phase can be recycled back into the acetylation reactor by separating the acids and the water. Due to the close boiling points of acetic acid and water, they cannot be fully separated by distillation. However, ethyl acetate forms an azetrop with water and can thus be used as an entrainer to separate the acetic acid from water [90], resulting in a recycled stream with the sulfuric acid and the acetic acid. Another distillation column is needed to separate the ethyl acetate and water to enable the recycling of ethyl acetate.

Based on mass balances generated, a pre-feasibility techno-economic assessment (TEA) for the process was carried out. The raw material costs for LNPs manufacturing from acetylated lignin with 30 wt% lignin concentration were calculated to be €1200 t$^{-1}$ (assuming 1) integration of the plant to an existing biorefinery or pulp mill and 2) approximately 80 wt% recycling of the sulfuric acid and acetic acid. The distribution of raw materials costs [89,91–93] are presented in the supplementary material in Fig. S16. The LNPs can be further diluted to antifog coatings with a dry lignin concentration of 0.15 wt%. Antifog coatings have a global market size of approximately €1.7 billion [94], with a product price of €1300 m$^{-3}$ [95]. A plant producing 2 kt/a of acetylated lignin and LNPs would result in a notable revenue of approximately €430 million. Hence, the designed production plant would be profitable.

Quite conventional types of processing equipment can be used in this process, though there is room for further innovation. Novel designs may be necessary to mitigate the equipment expenses due to corrosive acids that are used in the process, for example. However, raw material costs are acceptable, and with a CAGR of 7.1% from 2022 to 2030 for antifog coatings [94], there is a market for the high-value product also in the future. Thus, it can be concluded that the scalability of the process is favorable. The full, detailed techno-economic assessment of the production of acetylated lignin is planned for a future publication. To increase the accuracy of this pre-feasibility assessment, and consequently the technology readiness level (TRL) of the process for scale-up and full-scale product launch, further experimental and computational research is required.

4. Conclusions

In this work, we present a quick and simple lignin acetylation method that selectively acetylates only aliphatic hydroxyl groups, or both aliphatic and phenolic hydroxyl groups, without causing polymerization. We demonstrated the use of partially and fully acetylated lignin for the synthesis of stable dispersions from ultra-small LNPs at exceptionally high concentrations. The small size of these particles enabled excellent control of layer thickness and appearance, from transparent sub-monolayers to multilayered films with a range of bright structural colors. The ultrathin transparent coatings reduced droplet-induced light scattering on glass and are thus excellently suitable for antifogging coatings for transparent surfaces. By applying thicker layers, the film’s color could be controlled using thin film interference, which allowed bright hues of yellow, blue and purple to be achieved. We established a rapid, efficient and tunable acetylation procedure that is applicable both for the production of LNPs as well as to increase the compatibility of lignin in polymer blends, advancing the field of chemical lignin modification. New insights into factors that affect the dispersion stability and size of LNPs were also achieved. A pre-feasibility techno-economic assessment showed that the industrial scale production plant would be profitable and scalability of the process favorable. With this work, we aim to advance lignin’s current position as a waste side stream into a useful raw material for diverse, economically and technologically valuable applications, and thus encourage its valorization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supplementary data

The supporting information document contains UV–visible spectroscopy transmittance results, water contact angles of monolayers coated with lignin particles, additional SEM images of LNP films, including images with lower magnification of coatings before and after being exposed to steam, FT-IR, HSOQC, 1H NMR spectra andGPC molecular weight distributions of differently acetylated lignins, a cost distribution of raw materials for large-scaled acetylated lignin production, and finally, AFM images showing how the height of the colored LNP-PLL bilayers were obtained and how the tilt was corrected.

Supplementary videos showing the reconstructed ET TEM models of the particles are also included. Supplementary data to this article can be found online at https://doi.org/10.1016/j.cj.2023.145965.

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