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Supplementary Information

Closed Cycle Production of Concentrated and Dry Redispersible Colloidal Lignin Particles with a Three Solvent Polarity Exchange Method

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Materials

LignoBoost^{TM} lignin was obtained from UPM (BioPiva 100). The lignin had a 68.1 wt. % solid content, measured by TGA, of which 1.5 wt. % is THF insoluble inorganic ash. Table S1 reproduces the chemical structure of the lignin used in this work obtained by ^{31}P-NMR spectroscopy as presented in our previous publication.[1]

Table S1 Amounts of different hydroxyl group species in lignin samples according to 31P-NMR data

Aliphatic OH (mmol g^{-1})	Carboxylic (mmol g^{-1})	Phenolic OH (mmol g^{-1})	Total OH (mmol g^{-1})	Mw (g mol^{-1})	Sulfur (%)	−SH[a] (mmol g^{-1})
1.78	0.41	3.64	5.83	>4800	3.1	0.94

[a] Sulfur was assumed to be as thiol group

While the solvent exchange process is suitable for CLP formation of many types of lignin, we found that due to the excellent solubility of LignoBoost lignin in THF the solvent exchange process was especially suitable for it.[1] Thus the optimization of CLP production was conducted with LignoBoost lignin.

The THF used was obtained from CABB Chemicals (99.8 % purity), ethanol (EtOH) was obtained from Altia (Etax A7: 91.2 wt. % ethanol, 3.0 wt. % acetone, 5.8 wt. % water), water in small scale tests was deionized (Millipore) water and tap water (19 ppm Ca, 5.8 ppm Na, 39 ppm Fe) in large scale tests.

Dissolution of LignoBoost Lignin

In small concentrations, LignoBoost lignin can be dissolved in THF with ease. When the lignin concentration is raised to 20 wt. % or above the addition of THF to lignin causes the lignin to aggregate to ball that requires mechanical grinding to break and dissolve. With a proper stirrer, the dissolution of a 1 L solution can be accomplished in some minutes. When lignin is first dispersed in small amount of water, mechanical stirring can be used to produce a relatively homogenous slurry. The addition of EtOH and THF into the slurry causes an almost immediate dissolution of lignin. As the speed of lignin dissolution in to the solution decreases upon the increase of water content of the mixture, it is preferable to dissolve lignin into a solvent mixture with a low water content and only after lignin has dissolved to dilute the mixture to the desired water content. The ratio of solvents used in the experiment was 38:32:30 w:w of

THF:EtOH:water. The ratio of THF to EtOH is roughly 1:1 v:v and was not fully optimized for the maximum obtainable colloidal lignin particle (CLP) concentration. The water content could be raised higher than 30 wt. % of the solvents, but due to the low speed of lignin dissolution into a mixture with such a high water content, the addition of water would need to be conducted after the dissolution of lignin into the mixture. Additionally it was confirmed that lignin can be dissolved in recovered solvents. If lignin is added into a solution mixture with 38:32:30 w:w of THF:EtOH:water, lignin will ultimately dissolve. However lignin dissolves fast (within minutes) into a mixture with a low water content (83:8:9 w:w THF:EtOH:water) and can be further diluted with a mixture with a high water content to produce a solution with the desired concentration of lignin and solvent composition. Regardless of the way lignin is dissolved, the solutions produce CLPs identically. The removal of inorganic ash is preferably conducted with lignin dissolved into a THF solution, with as little water present as possible. While the ash precipitates from the THF solution and the ash-free solution is easily decanted off, the presence of water in the solution causes the precipitated ash to aggregate into moist flocs, which take longer to precipitate.

Effect of lignin concentration and solvent environment on CLP formation

Previously we showed that good quality 300 nm colloidal lignin particles (CLPs) can be formed from LignoBoost lignin upon dialysis of a 10 mg/ml THF solution against water.[1] At a concentration of 2.0 wt. % the lignin particles were already non-colloidal. If the particles were to be prepared with the time consuming dialysis step, the 1.0 wt. % concentration would be rather low. We tested the CLP size as a function of lignin concentration in THF when added into water in 24:76 w:w ratio (**Figure 2a,** blue dots). The solution (5.3 g in this case) was added into stirred water (16.9 g in this case) in a 100 ml round bottom flask and THF was removed immediately after CLP formation by rotary evaporation at 40 °C. With up to ca 0.8 wt. % of lignin in the mixture, all of the product was colloidal, with the average diameter raising from ca. 70 nm to ca. 200 nm. Beyond this concentration, the forming colloids seemed to aggregate and precipitate out. While the average particle size of the colloidal fraction remained around 500 nm from 1.1 wt. % lignin onwards, the fraction of non-colloidal precipitate increased rapidly as lignin concentration was increased.

When lignin was dissolved into a THF:EtOH mixture with a 13:11 w:w ratio (roughly 1:1 v:v ratio) and this mixed solution was inserted into water with a final THF:EtOH:water ratio of 13:11:76 of w:w, the average size of the formed particles increased slightly slower up to 0.8 wt. % lignin in the final mixture (**Figure 2a,** yellow dots). However, whereas without ethanol the particle size started to increases rapidly after this point, the increase in size with the THF:EtOH solution was as moderate as up to this point. The particle size increased to ca. 200 nm at 2.8 wt. % lignin, after which the excess lignin would cause the aggregation and precipitation of the forming colloids.

The colloid formation was identical when lignin colloids were formed from lignin dissolved in a mixture of THF:EtOH:water with a 13:11:10 w:w ratio (30 wt. % water, **Figure 2a,** green dots). With up to 2.8 wt. % of lignin in the final dispersion, the majority of lignin formed into colloidal spheres, with less than 1 % of lignin forming non-colloidal aggregates. While the colloid size did not increase much after this point, clear aggregation of lignin was already visible at 3.2 wt. % lignin.

As in the case with the THF:EtOH:water mixture, when water was added (30 wt. % of solvents) to the solution of lignin in THF, the solution remained dissolved. The formation of the CLPs was identical from this solution compared to when CLPs were formed from a lignin dissolved in pure THF (**Figure 2a,** red dots). The curve is shown with lignin dissolved directly into a solvent mixture. An identical curve is obtained when a lignin solution in THF:EtOH is diluted with water and either used immediately for CLP formation or used after a day (curves not included in Figure 2a). This indicates that there seems to be no adverse aging effect relating to the presence of moderate amounts of water in the lignin solution.

Based on the experimental observations interpreted through the findings by Qian et al.,[2] we propose that lignin inhabits three states in the CLP formation (**Figure S1**). With sufficiently low water content, lignin remains dissolved in the solvent mixture. When the water content is increased, lignin is no longer soluble in the solvent mixture, but the solvent environment is still not conductive to rapid self-assembly (unstable region, the s-curve drawn only as a guideline and the borders of the region only roughly determined). In this region, lignin forms non-spherical aggregates. When the water content passes an experimentally observed threshold level, lignin apparently starts to behave much like an amphiphilic surfactant, with the curvature of the lignin being conducive to CLP self-assembly. In the small-scale experiments, where the mixing of the organic and aqueous phase occurs within second, the unstable region can be passed with no noticeable aggregation.

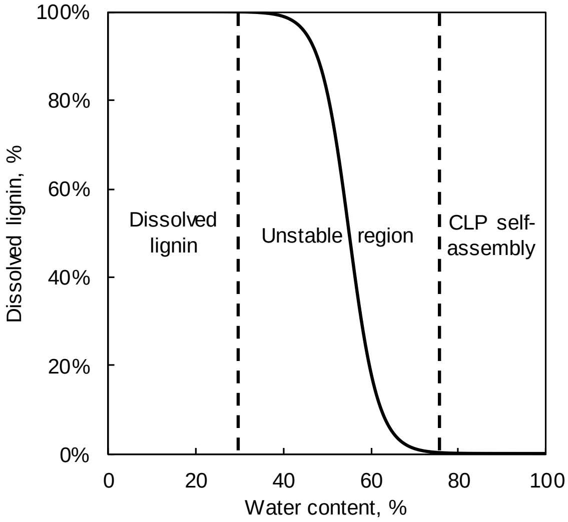

Figure S1. Proposed correlation between lignin solubility and CLP self-assembly based on experimental observations.

Thus, it can be concluded that the addition of ethanol into the solvent mixture increases the obtainable CLP concentration. It can also be seen that a significant amount of water can be left into the recovered solvents without any negative effect on the CLPs formed from the solution. The optimal ratio of THF to EtOH was not yet explored. However, the 76 wt. % water content seems to be very close to the lower limit of stability. When lignin dissolved in a mixture of THF:EtOH:water with a 13:11:10 w:w (the best mixture of the series) is inserted into water, with a final water content of 64 wt. % instead of 76 wt. % (3.3 wt. % of CLPs instead of 2.8 wt. %), the colloids fail to form and almost all of the lignin aggregates.

Formation of CLPs in a batch reactor

For the large-scale formation of CLPs, a 10 L batch reactor was used (**Figure S2**). The reactor has an overhead stirrer with a double impeller, which creates an efficient vortex into which the lignin solution is fed through a steel pipe. The steel pipe is connected into an addition funnel, from which the lignin solution is fed into the reactor in a controlled fashion. The lignin solution is fed into the reactor at a speed of 1.8 L/min within 2 minutes (see supplementary video 1). The colloids form within seconds of impact into the mixed water. This is seen by the black lignin solution turning opaque beige. It was found that a lignin concentration much above 2.0 wt. % was hard to obtain without significant precipitation in the batch reactor. We assume this to be somehow related to the fast formation of the colloids in relation to the addition speed of the lignin solution. Thus with high lignin concentrations, the addition of the final fraction of the solution is into a dispersion highly loaded with CLPs. Conversely, when the lignin solution is added to water in the smaller scale, the time for the solutions to mix (a few seconds at most) is shorter than it takes for the colloids to form (perhaps a few seconds more).

Thus, it can be considered that a continuous flow process, where both lignin and water are added at a continuous rate, would allow for the realization of the colloid formation at a higher concentration than a batch process. We are exploring this in a future publication.

The CLP formation is slightly exothermic (possibly mostly due to the exothermic dissolution of the THF:EtOH solution into water), but the temperature increase is just some degrees C for a 10 L batch of 1.7 wt. % CLPs.

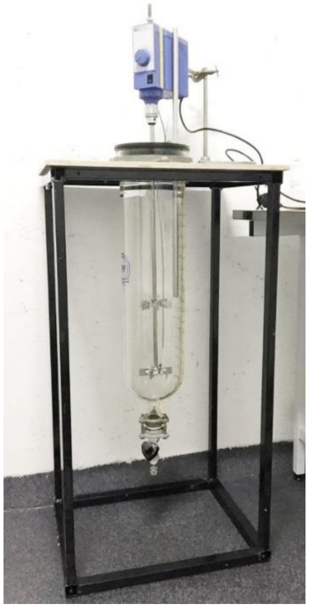

Figure S2. The reactor used in large scale CLP formation.

Organic Solvent Recovery by Rotary Evaporation

A 20 L rotary evaporator (Büchi R-220) was used for the recovery of organic solvents. A single CLP batch from the 10 L reactor could be distilled in one go. When the water bath temperature was set to 80 °C, and pressure gradually reduced to 120 mbar an azeotrope of THF, EtOH and water could be recovered with a vapor temperature of 50 °C. With these conditions, the presence of CLPs in the dispersion caused no foaming and the distillation could be conducted as if the dispersion were just a solvent mixture of water, THF and EtOH. The distillate was collected in two fractions: 1st fraction (2.7 L) had a solvent composition of 39:23:38 w:w of THF:EtOH:water (by GPC analysis, comparing the solution to a reference mixture); 2nd fraction (0.6 L) had a solvent composition of 1:7:92 w:w of THF:EtOH:water. The water content of the 1st recovered fraction is nearly low enough for its reuse in the process. While simulations (not shown here) suggest that a lower concentration of water in the distillate would be possible by rotary evaporation, the scaled up solvent recovery process would benefit from the constant flow nature of column distillation. Thus, the optimization of the solvent recovery was simulated primarily for distillation.

When organic solvents are removed from the aqueous phase by rotary evaporation, it can be questioned whether the solvents trapped into CLPs will be released. It can be assumed that the release of the solvents will not be instantaneous, but at least in the case of CLP formation by dialysis, the amount of THF detectable in CLPs was negligible.[1] While the study of the kinetics of THF release from the CLPs would be relevant for industrial applications, we were content with the knowledge that THF can be ultimately released from the CLPs.

While we did not study this specifically in the case of rotary evaporation, it can be assumed the loss of THF by this means should be at least economically insignificant. Whether the minute trace of THF in CLPs has any influence will depend on the application they are used for. At least when used for drug loading the produced CLPs were non-cytotoxic in clinically relevant concentrations.[3]

Simulation of solvent recovery by distillation

As was noted in the previous chapter, the constant flow recovery of solvents is easier to realize with a distillation column that with rotary evaporation. Especially for industrial processes, the use of a rotary evaporator is impractical in most cases. Based on the dissolution experiment, the dissolution of lignin can be realized with a THF with a small fraction of water (the EtOH content did not seem to be as crucial). Based on the CLP formation experiment, the lignin solution can be diluted with water at least up to 30 wt. % of the solvent. We simulated a condition where 38.7 kg/h of solvent mixture (having 1.11 kg of CLPs, with a 2.8 wt. % solid content), with a mass ratio of 13:11:76 w:w THF:EtOH:water was fed in to the 3rd stage of a 5 stage distillation column with the reflux rate set to a minimum of 0.01 (a setting of zero not possible in the ASPEN simulation program). By varying the heating power of the bottom stage, we could vary both the fraction of solvents in the distillate and in the bottom fraction. Additionally the data reveals the fraction of solvent collected in the distillate fraction as a function of the temperature of the bottom stage and the energy consumption of the distillation. The energy consumption per kg of CLP dry mass was calculated according to the maximum CLP concentration of 2.8 wt. % obtained from the CLP formation experiments, which translates to 1.11 kg of CLPs in the mixture.

Figure 2b shows the water content of the distillate as a function of the recovered solvents. It can be seen that the separation of THF from water is quite effective up to 90 % recovery, after which the water content is moderately increased up to 18 wt. % at 100 % THF recovery. At this point only 40 % of ethanol is recovered. The water content of the distillate increases steadily as a function of ethanol recovered up to 30 wt. % water in the distillate, when 94 % of the EtOH is recovered. After this, the water content increases rapidly up to 46 wt. %, with 100 % ethanol recovery. **Figure 2c** shows the energy consumption of the process for each simulation. It can be seen that the first simulation with a 100 % THF recovery has an energy consumption of just 21.4 MJ/kg CLP. The first simulation with a 100 % EtOH recovery has an energy consumption of 53.2 MJ/kg CLP. The large difference in energy consumption between the two cases reflects the large quantity of water being evaporated as an azeotrope, especially alongside EtOH. Thus it can be seen that even though the use of EtOH increases the maximum obtainable concentration of CLPs, its use will incur an added cost in solvent recovery. However, as the process is designed so that all of the solvents are reused, we can assume that some of the EtOH can be left in the bottom fraction and reused in the aqueous phase in CLP formation. Considering this, a distillation with a 100 % THF recovery and 94 % EtOH recovery, which contains 30 wt. % of water in the distillate, can be considered enough for the full reuse of the solvent. The energy consumption of this distillation is 35.7 MJ/kg CLP. When this distillation is conducted in two columns, the requirements of near full solvent recovery can be realized. In the first column, with the distillate at 65 °C and the bottom fraction at 85 °C, the distillate contains 81 % of the THF, and 9 % of the EtOH (82:8:9 w:w of THF:EtOH:water). Experiments confirm that this mixture can dissolve lignin at a concentration that enables the full reuse of solvents. When the bottom fraction of the first column is fed into a second column, with the distillate at 79 °C and the bottom fraction at 100 °C, the distillate contains 19 % of the THF, and 85 % of the EtOH (12:45:43 w:w of THF:EtOH:water). When the fractions are combined the THF recovery is 100 %, EtOH recovery is 94 % and the water content in the mixture is 30 wt. %.

Concentration of CLPs by ultrafiltration

While CLPs can be concentrated with methods involving the evaporation of water, this will always be energy intensive and should be avoided when possible. When the particles are concentrated by ultrafiltration, no evaporation of water is required. While filtration is often used in the separation of unwanted solids from a solution, it can also be used to concentrate particles of value. Especially when the feed solution has a high concentration of particles and the aim is to increase the concentration of the particles to a maximum, the fouling of the ultrafiltration membranes is an issue. We used a Valmet OptiFilter CR250/2 membrane filtration module to concentrate the CLPs. In the unit, a pump generates a pressure differential over a separation membrane and a rotor adjacent to the membrane produces a turbulent flow that prevents the membranes from clogging. In this unit, the power consumption of the pressure generation is minimal in comparison with the power required by the rotor. The unit that we used takes in a maximum power of 1 kW and has a membrane area of 0.09 m^2.

In our test cycle, we passed an aqueous CLP dispersion through an OptiFilter unit with a single rotor and two membranes. Three membrane materials were tested: Polyether sulfone (PES), polystyrene (PS) and regenerated cellulose (RC).

Figure S4 shows that the highest permeate flux (100 $Lm^{-2}h^{-1}$) was obtained with an RC membrane. The flux stabilized from 160 $Lm^{-2}h^{-1}$ to 100 $Lm^{-2}h^{-1}$ within 20 minutes after which it remained constant for the rest of the 3 h filtration test. The PS membrane achieved a flux of 50 $Lm^{-2}h^{-1}$. The flux of the PES membrane dropped to 40 $Lm^{-2}h^{-1}$ within an hour but the flux did not seem to stabilize. Without cooling, the temperature of the system increases slightly. In this case from ca. 20 °C to below 30°C within five hours. The increase of temperature increases the permeation speed and improves the ultrafiltration efficiency. We observed a small fraction (less than 0.1 wt. %, estimated by the color of the permeate and its DLS signal intensity) of CLPs passing through the membrane. When undiluted filtrates were characterized by DLS, only ca. 300 nm particles were detectable by the instrument. It can be assumed that a minute number of the CLPs can penetrate the membranes and the larger pores of the membranes are clogged with CLPs, until the permeate becomes clear and the flux stabilizes. As the permeate can be reused in the CLP formation, this loss will not affect the efficiency of the process.

To obtain the highest possible concentration, the concentrate was recirculated through the OptiFilter unit. When a concentration of 14.3 wt. % was reached the volume of the concentrate reached the internal volume of the system, at which point the filtration was stopped. At this point there was still no sign of the reduction of flux speed caused by the viscosity increase of the concentrate. It is difficult to say exactly how high a concentration could be obtained with the system. A conservative estimate based on similar dispersions filtered with the system would be around 25 to 30 wt. %.

For the power consumption calculation, we use the data of existing industrial OptiFilter units to evaluate to power consumption of the ultrafiltration. An industrial unit with 101 rotors running at 1 kW, with a total membrane area of 144 m^2 consumes 0.7 MJ/kg CLP of energy, when concentrating a 4.2 wt. % (concentrated from 2.8 wt. % in solvent recovery) dispersion to 14.3 wt. %, with a permeate flux of 100 $Lm^{-2}h^{-1}$.

This is roughly one hundredth of the power consumption of the same amount of water removal by spray drying (51 MJ/kg). In actuality the higher investment costs of the construction of the OptiFilter unit brings the cost of ultrafiltration roughly to 1/10th of the cost of distillation.

A relevant point for the scale-up of the process is the order of ultrafiltration and solvent recovery. If solvents are to be recovered with distillation, the solvent feed into the distillation column should preferably not have any CLPs, as the particles can easily foul the column. In this case, it is preferable that CLPs are concentrated with ultrafiltration before solvent recovery.

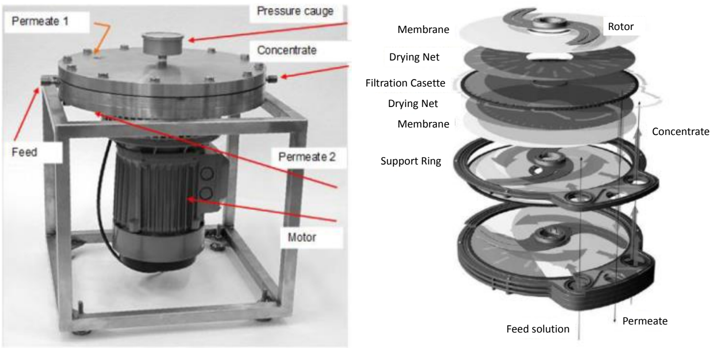

Figure S3. Valmet OptiFilter CR250/2 membrane filtration module.

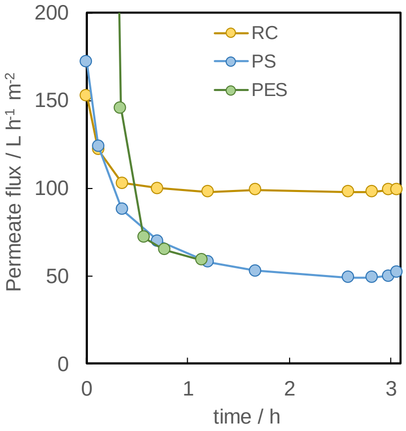

Figure S4. Permeate flux during the ultrafiltration of a CLP dispersion with a Valmet OptiFilter CR250/2 membrane filtration module. ● Regenerated cellulose (RC) membrane (MWCO 500 000 gmol^{-1}); ● Polysulfone (PS) membrane (MWCO 100 000 gmol^{-1}); ● Polyethersulfone (PES) membrane (MWCO 150 000 gmol^{-1}).

Spray drying of CLPs

Spray drying is the second most energy intensive step of the process alongside solvent recovery by distillation. Thus, the solid content of the concentrate going into the spray drier should be maximized. In the industry, water suspensions are concentrated by vapor-compression evaporators and falling film evaporators, which have a significantly lower energy consumption than spray drying.[4] However as these methods are not readily available for laboratory testing we omitted these concentrations steps from our analysis. It can be noted, though, that with these methods the solid content can be raised to over 50 wt. %.

While a fully optimized industrial process of CLP formation would also include these energy saving processes, for our purposes we were satisfied with showing that spray drying is both possible and does not consume an excessive amount of energy. Laboratory scale spray dryers are not designed for optimal energy efficiency, but the results of the spray drying experiments should be translatable to industrial processes with an energy consumption as low as 3.0 GJ/t evaporated water.[5]

The Spray drier used in the process was GEA Mobile Minor™ spray dryer (evaporation capacity 0.5 – 6 kg/h). The concentrated CLP dispersion was introduced into the spray drier, where finely sprayed colloidal particles were passed through a stream of 180 °C air, producing dry CLPs (**Figure S5**) and steam. The typical particle size produced by the device is 5 to 80 µm, which matches well with the spherical microclusters visible in **Figure 3g**. These clusters comprise of individual CLPs (**Figure 3g**). It can be seen that most CLPs are ca. 200 nm diameter, but a fraction of the particles are up to 1 µm in size. Redispersion experiments (**Figure 3b**) show that mechanical mixing is sufficient to redisperse most of the CLPs from these microclusters, but the redispersion can be further enhanced by sonication.

Figure 2d shows the calculated heat of evaporation of the spray drying as a function of the CLP concentration. The specific energy consumption, E_s, of modern industrial spray dryers is quite low, ranging between 3.0-3.5 GJ/t of water for the most efficient models. With an E_s value of 3.0 GJ/t, the spray drying of a 4.2 wt. % dispersion, obtained after solvent recovery consumes 69 MJ/kg CLP, whereas the spray drying of a 14.3 wt. % dispersion, obtained after the ultrafiltration experiment, consumes 18 MJ/kg CLP. As noted before, the concentration of CLPs could be further increased by either ultrafiltration or other methods described above. Thus, the energy consumption of the spray drying step could be further reduced.

Figure S5. Spray dried CLP powder.

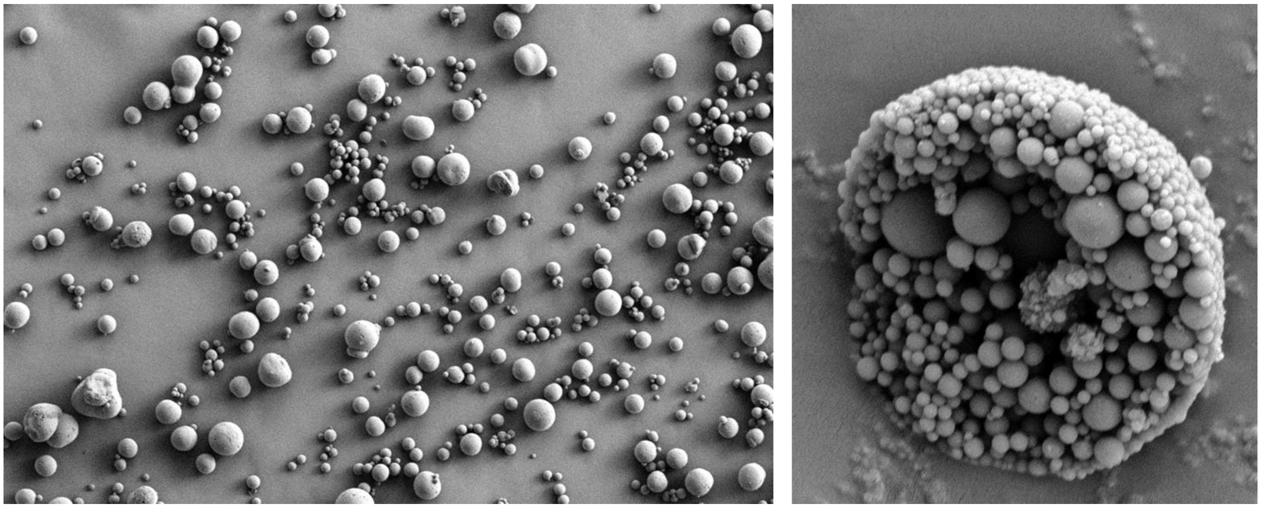

Figure S6. Original non-colored images of spray dried CLP powder.

CLPs in Pickering emulsions and CLP:PLA composites

While the focus of this work is in the design of a process to produce CLPs, we consider it relevant to show how they function in large-scale applications. Already known application with lignin colloids and lignin nanoparticles range from antimicrobials,[6] drug release,[3789] Pickering emulsions[10] and composites[1112]. While value-added antimicrobial and drug release applications could be conceived with less energy efficient methods for CLP production, the use of lignin in Pickering emulsions would require a truly cost-effective method for their production for them to be competitive against existing materials. Polylactide (PLA):lignin composites have already been studied before.[1213] Theoretically the properties of these composites would be improved if the inherently heterogeneous lignin could be introduces into the composite blend as spherical nanoparticles (dried colloids). However, without an efficient means to obtain CLPs in at least the scale of hundreds of grams, even the mechanical testing of such blends would be difficult. Thus we chose a CLP Pickering emulsion to demonstrate an application with the concentrated CLPs and a CLP:PLA composite to demonstrate an application with the dried CLPs.

An aqueous CLP dispersion produces Pickering emulsions with 1:1 volume ratio of rapeseed oil and water, with emulsion stability increasing as the initial aqueous concentration of CLPs increases from 0.1 to 1 wt. % CLPs. The lowest CLP concentration produced a heterogeneous emulsion system with distinct double emulsion droplets (**Figure 3b**), whereas at 1% CLP concentration, free and clustered oil droplets were observed (**Figure 3c**).

The spray dried CLPs were used in the preparation of CLP:PLA composites as they were. 1:2 w:w ratio of CLPs were blended with PLA at 200 °C, forming a uniform mixture. Films pressed from this mixture were visually uniform (**Figure 3h**), but closer observation by SEM showed that the film held air pockets of some µm in diameter (**Figure 3i**). When the CLP:PLA was tested against a neat PLA film (**Figure 3j**), it was found that it’s Young’s modulus remained unchanged (or increased slightly). However, the Ultimate load and Tensile strength are slightly lower than the PLA reference, which could be due to the small number of air pockets in the film. For a more comprehensive analysis of CLP:PLA composites, more testing would be required. However it can be deduced that CLP:PLA composites can be prepared with a high CLP loading, without significant reduction in the mechanical properties of the films. As the potential cost of CLPs is significantly lower than that of PLA, even the retaining of the composite qualities can be considered good enough for commercial applications of CLP:PLA composites.

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