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All-lignin approach to prepare cationic colloidal lignin particles: Stabilization of durable Pickering emulsions

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Contents

I. Non-solvent precipitation of cationic lignin

The cationic lignin fraction soluble in neutral water (Catlig) was precipitated by pipetting 0.3 mL of Catlig into 1.2 mL of vigorously stirred non-solvent. Mainly water-miscible organic compounds were tested as non-solvents. Among them, 1-propanol appeared as the most promising non-solvent based on visual observation of the colloid number in the vial number 2 after 1 h, 18 h, and 288 h.

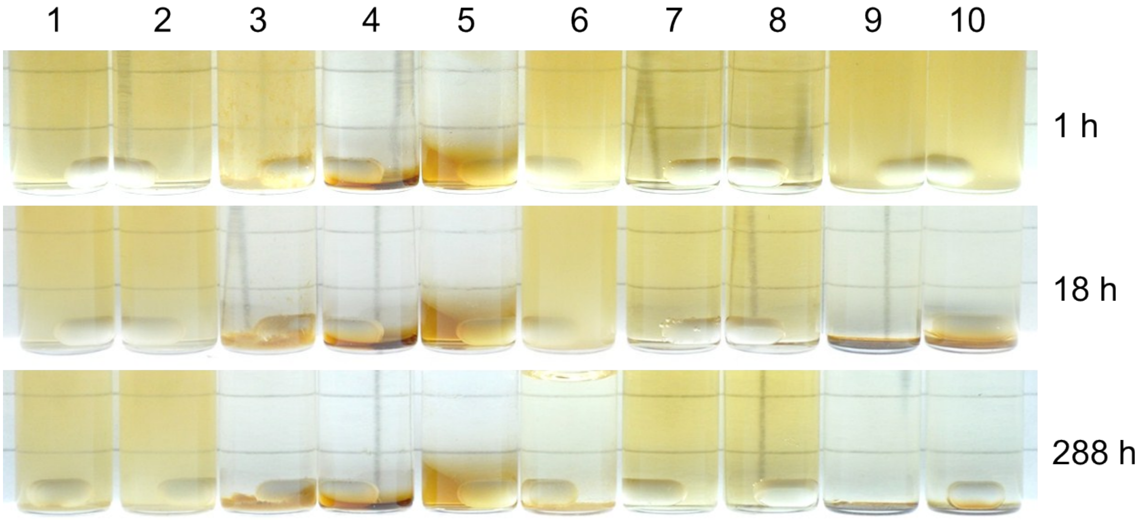


Figure S1. Observation of colloidal particle formation in bulk precipitation method of adding aqueous cationic lignin solution into various solvents: (1) ethanol, (2) 1-propanol, (3) 2-propanol, (4) 1-butanol, (5) ethyl acetate, (6) acetone, (7) ethylene glycol, (8) glycerol, (9) tetrahydrofuran, (10) 1,4-dioxane. The final proportion of water in the solvent mixtures was 20% by volume.

II. Lipase-catalyzed hydrolysis of emulsions

Lipase-catalyzed hydrolysis of olive oil-in-water emulsions (2:3 v/v) was carried out to assess suitability of CLPs and especially c-CLPs as emulsion stabilizers. The primary question challenged by these experiments was whether c-CLPS inhibit activity of Lipase M from *Mucor javanicus*. The emulsions used in the hydrolysis reactions were formed by vortex-mixing a mixture of olive oil (Sigma-Aldrich, 3 mL), aqueous 0.2 M Tris-HCl buffer (1 mL, pH 7), aqueous CLPs, c-CLPs or surfactant solution (2.5 mL, pH 7), and 1 mL of Lipase M (10 mg/mL, pH 7). Catlig, Tween 80, sodium dodecyl sulfate or didodecyldimethyl ammoniumbromide were used as emulsifiers in comparison to CLPs and c-CLPs (0.24 wt% relative to oil). Magnetically stirred reaction mixtures were transferred to ice after 30 min reaction at 40 °C (thermostatic water bath), and 3 mL of ethyl alcohol was added. The released fatty acids were titrated with 0.1 M sodium hydroxide in the presence of phenolphthalein as indicator (Fig. S2). As a summary of these experiments, CLPs, c-CLPs, and Catlig did not inhibit hydrolytic activity of Lipase M, unlike SDS.

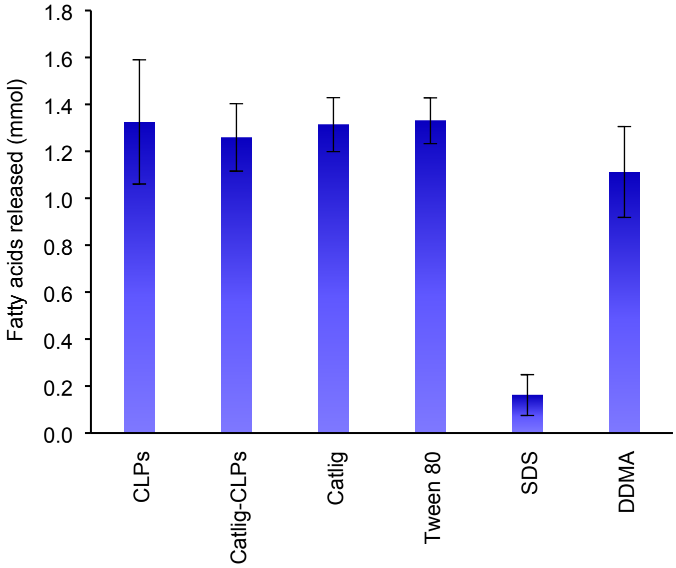
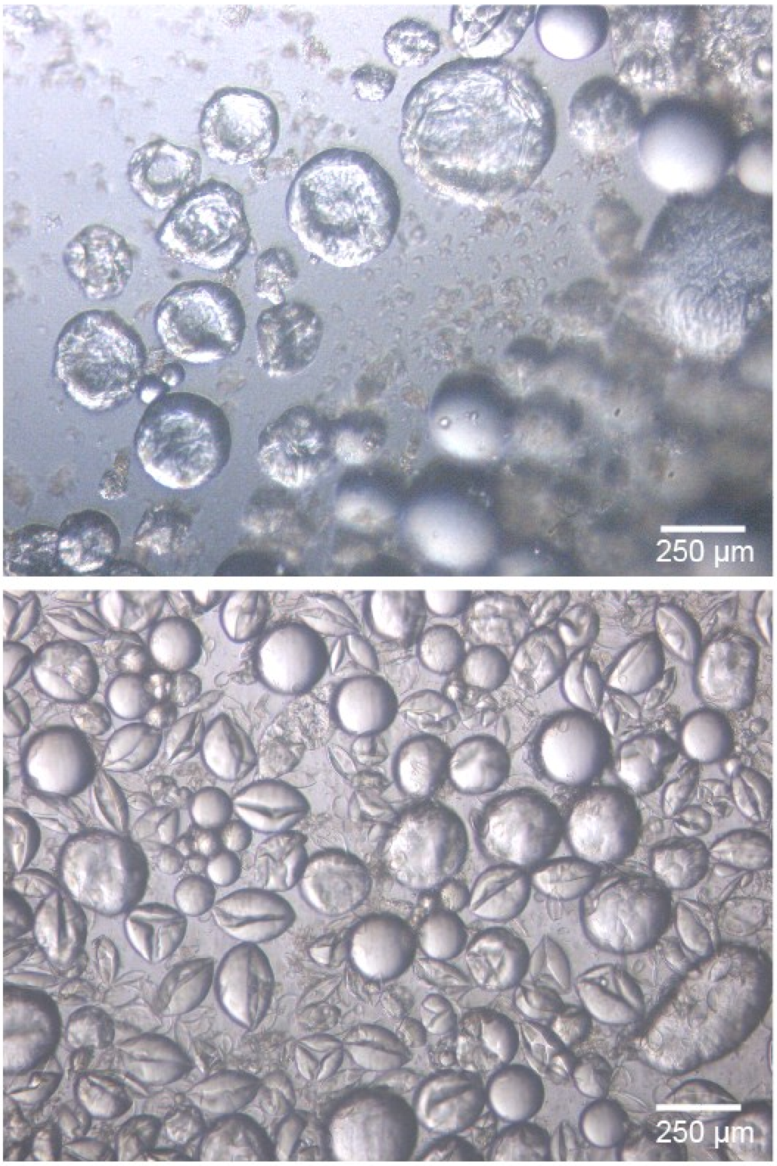


Figure S2. Lipase-catalyzed hydrolysis of aqueous olive oil o/w emulsions. Comparison of quantities of fatty acids released from emulsions formed in the presence of colloidal lignin particles (CLPs), cationic CLPs (c-CLPs), cationic lignin (Catlig), Tween 80, sodium dodecyl sulfate (SDS), and didodecyldimethylammonium bromide (DDMA) at 0.24% dosing relative to the weight of olive oil.

III. Comparison of drying behavior of toluene-in-water emulsions stabilized with CLPs or c-CLPs

Toluene-in-water Pickering emulsions stabilized by CLPs and c-CLPs were observed under an optical light microscope. The rapid evaporation of toluene from the two Pickering emulsions former distinct morphological structures from the collapsed droplets (Fig. S3). Droplets with regular CLPs collapsed into crumpled circular structures, while droplets with c-CLPs formed smooth sickle shaped structures, with distinct dent at the centre.



Toluene-in-water
Pickering emulsion
stabilized by CLPs

Toluene-in-water
Pickering emulsion
stabilized by Catlig/CLPs

Figure S3. Comparison of the drying behavior of toluene droplets from Pickering emulsions (toluene:water 1:1 v/v) stabilized by CLPs or Catlig/CLPs.

IV. Lignin characterization

Nuclear magnetic resonance (NMR) spectroscopy analysis of lignin was carried out to reveal various structural moieties in the starting softwood lignin. Quantitative 31P and 13C NMR experiments revealed detailed structural information as shown in Table S1. In addition, X-ray photoelectron spectroscopy (XPS) analysis of thin films formed from softwood kraft lignin, two fractions of cationic softwood kraft lignin, and c-CLPs provided atomic concentrations of C 1s, O 1s, N 1s, and Si 2p (Table S2).

Table S1. Analysis of various moieties of softwood kraft lignin by quantitative ^{13}C and ^{31}P NMR spectroscopy experiments.

Moiety	^{31}P	^{13}C	
	mmol/g	mmol/g	Per 100Ar
Aliphatic OH	1.92	2.79	49.9
Total phenolic OH	4.11	3.73	62.0
5-free guaiacyl OH	2.10	1.73	28.7
5-substituted guaiacyl OH	1.74	2.01	33.3
OMe	na	4.66	81.0
Pinoresinol	na	0.12	2.0
Phenylcoumaran	na	0.13	2.2
β-O-4	na	0.18	4.0
β-5	na	0.13	2.2
β-β	na	0.06	1.0
G_2+cond-$G_{2,6}$	na	3.00	49.9
Degree of condensation	45.4%[a]	-	79.7
Non-conjugated COOR	na	0.60	10.9
Conjugated COOR	na	0.02	0.3
Conjugated CO	na	0.21	3.6
Non-conjugated CO	na	0.35	6.2
Sugars	na	0.02	0.3

[a]: Calculated as the ratio of condensed guaiacyl hydroxyl units to the total number of guaiacyl phenolic hydroxyls. na, not available from the data.

Table S2. Atomic concentrations calculated from XPS data recorded on silicon wafer surfaces coated with softwood kraft lignin, the corresponding cationic lignin (pH 7 soluble and insoluble fractions), and cationic colloidal lignin particles (c-CLPs).

	Wide atomic concentrations (AC, in atomic %)			
Sample	C 1s	O 1s	N 1s	Si 2p
kraft lignin[a]	65.3	20.4	0.08	14.2
Catlig[b]	63.8	20.1	1.5	14.5
Catlig[c]	74.5	19.0	1.3	5.3
c-CLPs	42.0	27.5	0.5	30.0

[a] Softwood kraft lignin. [b] pH 7 soluble fraction of cationic softwood kraft lignin. [c] pH 7 insoluble fraction of cationic kraft lignin.