Supporting information for

Lignin supracolloids synthesized from (W/O) microemulsions: use in the interfacial stabilization of Pickering systems and organic carriers for silver metal

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1

Stability of the lignin particles



Figure S1. SEM image of lignin particles after immersion for 24h in high pH solutions (pH 13). The dispersion was dried on a support for imaging.

FTIR analysis of the lignin particles

The FTIR spectrum of the neat lignin powder was compared to that of the (dry) synthesized lignin particles. Figure S2 presents the stacked spectra of the neat lignin (a), particles prepared using crosslinker-to-lignin ratio of 0.1:1 (b) and 1:1 (c) and lignin particles incorporated with silver at crosslinker to lignin ratio 5:1 in (d). Neat lignin revealed a peak at 3400 cm⁻¹ corresponding to hydroxyl stretching and at 2935 and 2842 cm⁻¹ for CH-stretch of the methyl groups. The symmetric and asymmetric ring stretching were detected at 1600 and at 1513 cm⁻¹, respectively. The spectra were normalized to the former signal. The peak at 1366 cm⁻¹ represents the bending vibrations of the phenolic OH groups. The peak at 1030 cm⁻¹ is assigned for aromatic C-H in-plane deformation and peaks at 854 and 816 cm⁻¹ correspond to C-H out of plane deformations and 742 cm⁻¹ to skeletal deformation of the aromatic rings and substituent groups. ¹⁻³

The scheme of crosslinking of lignin using epichlorohydrin is presented in Scheme S1. Depending on the reaction conditions the product is an epoxidised or cross-linked lignin. In general, a shift from crosslinking-dominated (Scheme S1d) to epoxidation-dominated (Scheme S1e) reaction occurred as the relative crosslinker content is increased. Several conclusions can be drawn from the FTIR spectra: First, the lignin particles exhibited the characteristic peaks for the aromatic skeletal vibration at 1510 and 1595 cm⁻¹ confirming their origin. Secondly, the main difference between the cross-linked particles and the neat lignin where found in the region of OH stretching, methoxyl group peaks, around 1082, 946 and 725 cm⁻¹. Thirdly, in all of the spectra the increased intensity of the methoxyl groups at 2935 and 2842 cm⁻¹ gives an indication of the methoxyl linkages formed within the cross-linked structure (Scheme S1d) but can also partly

originate from the surfactant used for the particle synthesis. As already discussed, the requisite for the cross-linked structure to form is a relatively low epichlorohydrin concentration. The crosslinker to lignin ratio of 0.1:1 indeed showed a more pronounced increase in the methoxyl group vibration compared to the ratio of 1:1. This supports the assumption of more cross-linked particles. With all the particle grades analyzed, a new peak arose after crosslinking at 1735 cm⁻¹ that can be assigned to carbonyl stretching indicating epoxidation.^{3, 4} However, a signal from the oxirane ring around 910 cm⁻¹ was not present. There was a strong peak at 1084 cm⁻¹ indicating C-O-C stretching of ethers, for all the particles. This peak had a shoulder reaching up to 1150 cm⁻¹ in the region of ether activity giving evidence of the crosslinking taking place. With the higher crosslinker concentration the shoulder was reduced also appearing around 1095 cm⁻¹. The peak at 1366 cm⁻¹ corresponds to the phenolic OH, shifted to 1350 cm⁻¹ with crosslinking.



Scheme S1. Scheme of crosslinking of lignin using epichlorohydrin.



Figure S2. FTIR spectra of (a) the neat lignin particles prepared using epichlorohydrin-to-lignin ratio of (b) 0.1:1 (c) 1:1 and (d) silver-functionalized lignin particles.



Stability of the Pickering emulsions stabilized by lignin particles

Figure S3. Light microscope images of hexadecane-in-water emulsions stabilized with 0.6 (a) and 0.2 (b) wt% of 320 nm lignin particles. Also included is the system with 0.2 wt% of lignin particles with a diameter of 600 nm in the aqueous phase observed 1 day after preparation (c). Images of the respective emulsions 3 (d, e and f) and 5 (g, h and i) days after preparation are also included.

References

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