Supporting information:

Improved Lignin Polyurethane Properties with Lewis Acid Treatment

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GPC analysis of unmodified/modified lignin

Molecular weight and molecular weight distribution of unmodified/modified lignin samples were analyzed by Waters GPC (Polymer Standards Services (PSS) columns (guard, 105, 103, and 102 Å)) using DMF as an eluent (flow rate 1.00 mL / min, 50 °C) with differential refractive index (RI) detector. The number average molecular weights (M_n) and molecular weight distribution (M_w/M_n) were determined with a calibration based on linear polystyrene standards using WinGPC 7.0 software from PSS. GPC trace is illustrated in Figure S1.

Gel permeation chromatography (GPC) was done to study molecular weight and molecular weight distribution of lignin. Two typical examples of pre- and post-HBr catalyzed lignin

modification is presented in figure S1. Molecular weight of modified lignin is higher than pre-modification and molecular weight distribution became slightly get broader after modification. Large molecular weight and molecular weight distribution changes were expected because Lewis acids can generate condensation reactions and cleavage reactions on lignin in various ways. The increase in hydroxyl group content of the lignin is originated from both demethylation of methoxy groups and cleavage of ether linkages such as β-O-4, α-O-4 and 4-O-5 in lignin. In such a case, substantial drop in molecular weight of modified lignin is expected. In contrast, condensation reactions under strong acidic condition such as ether-ether exchange reaction (transetherification)[1-4] can increase molecular weight of lignin after modification. In the present HBr-catalyzed lignin modification, the initial ether cleavage reaction may be followed by a condensation reaction that compensates decreased molecular weight from the ether cleavage reactions.[5] This is a possible reason for relatively unchanged molecular weight and molecular weight distribution. Both modified and unmodified GPC trace revealed relatively sharp signal at 31 mL. This kind of unexpected trace from lignin has been commonly observed by other researchers as well.[6-8] This particular trace is caused by non-size-exclusion effect which is attributed to ion exclusion between lignin samples and gel material in GPC column. Although because of this effect, GPC cannot detect actual hydrodynamic volume of the particular part of sample at 31 mL,[6-8], the overall molecular weight and PDI was determined as shown in figure S1.

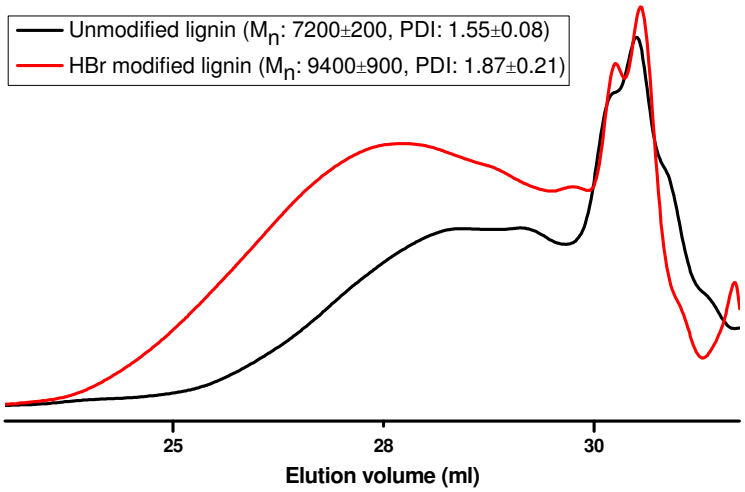

Figure S1. Gel permeation chromatography (GPC) trace for unmodified lignin (black) and HBr catalyzed modified lignin (red). Although molecular weight and molecular weight distribution of lignin were slightly increased after modification process, not significant hydrodynamic volume character change was observed.

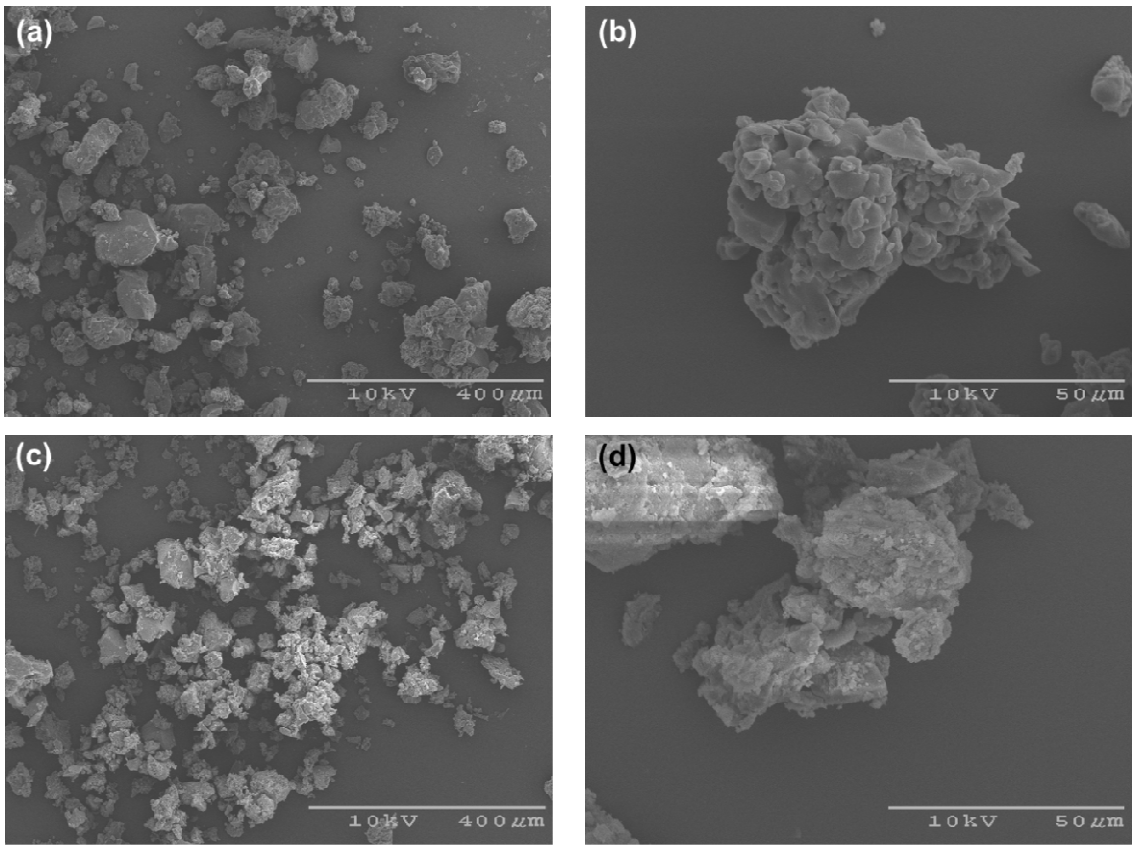

Figure S2. Scanning electron microscope (SEM) images of (a) overall view of unmodified lignin with 400 μm scale bar, (b) high magnification image of unmodified lignin with 50 μm scale bar, (c) overall view of Lewis acid catalyzed hydroxylated lignin with 400 μm scale bar (d) high magnification image of Lewis acid catalyzed hydroxylated lignin with 50 μm scale bar.

A morphological analysis of lignin pre- and post-HBr-catalyzed modification was conducted with a Hitachi 2460N SEM as shown in figure S2. Particle size distribution was very broad and actual sizes did not significantly change after modification, with the particle sizes varying from 10 μm to 100 μm. High magnification SEM images demonstrated slight particle

morphology differences after modification. Figure S2 (b) is high magnification view of (a) and (d) is high magnification of (c). Particles after HBr-catalyzed modification appeared to have a finer texture with many smaller cracks on the surface of the particles than unmodified particles according to a comparison of Figure S2 (b) and (d). Therefore, the resulted SEM images demonstrated that HBr catalyzed modification changes morphology of fine surface structure of lignin particles.

References

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