

Green Synthesis, Mechanism, & Intrinsic Properties of Kraft Lignin Nanoparticles

Ahilan Manisekaran^{1,2,*}, Patrick Grysan¹, Benoît duez³, Damien Lenoble¹, and Jean-Sébastien Thomann¹

¹Department of Materials Research and Technology, Luxembourg Institute of Science and Technology,
L-4362, Esch-Sur-Alzette, Luxembourg

²Department of Physics and Materials Science, University of Luxembourg,
L-4365, Esch-sur-Alzette, Luxembourg

³Goodyear Innovation Center Luxembourg, Avenue Gordon Smith,
Colmar-Berg, L-7750, Luxembourg

*ahilan.manisekaran@list.lu

Extended Abstract

Lack of petroleum resources and sustainability concerns have led researchers to find green alternatives, such as Kraft Lignin (KL). KL is economical, eco-friendly, abundantly available, and usually obtained as a by-product from paper industries. KL is well known for its wide range of versatile applications such as, UV-absorber, antioxidant, anti-microbial, binder, dispersant, fillers, polymer, surfactant, a source of carbon and phenol, drug carrier, green composite, and 3D printing.^[1] Due to its recent demand, scientists are synthesizing nanoparticles out of KL. Solvent shifting is the greenest method to synthesize Kraft Lignin Nanoparticles (KLNPs). *State of the art:* Lignin is dissolved in a solvent, then the lignin solution is mixed with an excess amount of non-solvent. The formation of the nanoparticles takes place immediately due to the self-assembly of lignin. The secondary valency forces such as intermolecular π - π stacking, H-bonding, and van der Waals forces of lignin drive the self-assembly. The identification and understanding of all the synthesis parameters behind the solvent-shifting is the gap in the literature. We identified five main synthesis parameters to control nanoparticles' size, and stability. By optimizing the five synthesis parameters, we developed a one-pot, fast, eco-friendly synthesis to make stable smallest KLNPs (~9 - 55 nm) with narrow dispersity (< 0.2). The developed synthesis is scalable from lab to pilot scale and adaptable to an industrial scale. The challenge of increasing lignin's initial concentration without increasing the lignin nanoparticle's size is fulfilled by this research. The highest concentrations range of (20 – 60 g/L) were used to produce small-size nanoparticles with an excellent yield (95 %) in two different solvents. The two solvents were chosen depending on KL's Hansen Solubility Parameter (HSP). The HSP of KL was measured by examining its solubility in several solvents, thanks to HSPiP software. THF is one of the toxic solvents widely used in the solvent-shifting of lignin. Here, the amount of THF usage is significantly reduced. The water is the primary colloidal medium (non-solvent) that ensures safe synthesis, handling, and storage. All the solvents and non-solvents used in our technique are recycled and reused. Surprisingly, different solvents created nanoparticles with different sizes and unique morphologies, leading to the breakthrough identification of two distinct mechanisms governing the self-assembly of KLNPs. Such a difference in mechanisms may impact the intrinsic properties of KLNPs. The intrinsic properties of KLNPs synthesized with two different solvents were characterized using advanced tools such as Amplitude modulation-frequency modulation atomic force microscopy (AM-FM AFM), Helium ion microscopy (HIM), Scanning electron microscopy (SEM), UV visible spectroscopy, Dynamic light scattering (DLS) and Differential scanning calorimetry (DSC). The solvent and size-dependent structure-property relationship of KLNP is exclusively disclosed in our work. The size-tunable features of KLNPs provide even more remarkable chances for new performance discoveries in potential sustainable applications. The impact of this research will increase the vast usage of lignin in the design of circular economy. Further, I will present the results and discussions in detail.

Reference

[1] J. H. Lora and W. G. Glasser, "Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials," *J. Polym. Environ.*, vol. 10, no. 1, pp. 39-48, 2002.