

Thermal Transformation of Aqueous Lignin Suspension into Nanoparticle Dispersion and Its Unique Associative Properties

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ABSTRACT

Lignin is the second most abundant biopolymer. Nanoparticle dispersions of lignin were obtained by simply heating in a controlled manner a partially neutralized lignin suspension in water. The lignin nanoparticles were found to form stable dispersions, to be associative with water soluble polymers and to have strong adsorption to common polymeric and inorganic solid surfaces, rendering the treated surfaces persistently more hydrophilic.

This widely available natural biopolymer, prepared in nanoparticle form, using a simple, environmentally friendly process, is now available for applications ranging from surface modification, polymer or actives delivery, and film property modification. Applicable markets may include hard surface cleaning, crop and surface protection, composite development, and others.

Keywords: lignin, nanoparticle, aqueous, dispersion, hydrophilic

INTRODUCTION

Wide industrial processing and application of lignin is often limited by its water-insolubility under neutral to mild alkaline conditions and by its chemical heterogeneity.

Lignin is a cross-linked polymeric material made of phenyl propanoid monomer units and it is integral to the secondary cell walls of plants and some algae. Lignin makes up approximately one third of the world's plant biomass, second only to cellulose. About 50 million tons per year of lignin are generated by the pulp and paper industry, mostly consisting of kraft lignin, most of which is burned to provide energy for mill operation, with only about 1.5 million tons, utilized in various commercial applications, the major part of which is water-soluble

lignosulfonates. Guided by Renewable Fuel Standard targets, it is anticipated that by year 2022, 150 million tons per year of lignin will be generated in the United States alone as byproduct from the production of 21 billion gallons of cellulosic derived fuels. While most of that additional lignin will be burned for energy, there is a growing interest in utilizing lignin as a sustainable raw material for new product developments [1-3].

While water-insoluble lignin is now industrially extracted from wheat straw or isolated from kraft black liquor through proprietary processes (e. g. LignoBoost [4] or LignoForce [5] processes), its large scale industrial utilization beyond burning, is often limited by its chemical heterogeneity and water-insolubility under mild pH conditions without further derivatization. A simple process to render industrially available lignin into a water dispersion with nanometer scale particles and at moderate pH would be useful for further processing of the lignin and for applications benefitting from nanoscale sizes.

PREPARING LIGNIN NANOPARTICLES

Generally, lignin nanoparticles could be obtained in the laboratory by sonication [6] or by solvent or other mechanical processes [7,8], but such processes are not economical for industrial practice. While experimenting for ways to disperse softwood kraft lignin in water at near neutral conditions, lignin in water mixture was heated to near reflux, and upon cooling produced a brownish aqueous dispersion, demonstrating that heating when combined with partial neutralization under specific condition in water forms a translucent-brown liquid dispersion at a pH where lignin is not known to be soluble. Subsequent analysis confirmed the presence of lignin nanoparticles using dynamic light scattering (100 – 200 nm) and Atomic Force Microscopic (AFM) analyses (Fig. 1).

CHARACTERISTICS OF LIGNIN NANOPARTICLES

We hypothesize that lignin molecules are thermally assembled into nanoparticles containing distinctive hydrophilic-hydrophobic domains. The lignin nanoparticles were found to be associative with water soluble polymers such as polyvinyl alcohol and polyvinyl pyrrolidone, as seen from the viscosity increase when combining their aqueous solutions. Such lignin nanoparticles also demonstrated strong adsorption to common polymeric and inorganic solid surfaces such as polyolefin, polyvinyl chloride, glass, ceramics, laminate and metals, rendering the treated surfaces evenly and persistently more hydrophilic, even after prolonged rinsing. This contrasts with traditional surfactants that wet surfaces evenly, but the effect is lost immediately after rinsing with water. These properties suggest that lignin nanoparticles, alone or in combination with functional water soluble polymers, may find use as tunable amphiphilic supramolecular structures, applicable in detergents, hard surface cleaning, polymeric composite materials, and other water-based processes.

In order to demonstrate the generality of the thermal process leading to the formation of lignin nanoparticle dispersions and to support our hypothesis of anisotropic properties of the particles, we further examined different sources of lignin and the interactions of the lignin nanoparticles with solution polymers and solid surfaces. As such, lignin from different sources and isolated using different processes was confirmed to undergo the transformation from a lignin suspension in water into a nanoparticle dispersion upon heating in the right pH window (e.g. Kraft softwood lignin isolated by the LignoForce^T, (FP Innovations) and LignoBoostTM (Domtar) processes, and lignin extracted from wheat straw e.g. ProbindTM 1000 and 2400 (GreenValue Enterprises LLC). The neutralizing base could be selected from mono-valent alkali hydroxides or carbonate, ammonia or organic amines such as triethanolamine. But the use of calcium hydroxide and other multivalent bases failed to yield stable nanoparticle dispersions. Di- and multi-valent cations could adversely affect the delicate balance of repulsive and attractive forces or contribute to inter particle crosslinking. Such balance of the two interactive forces is also demonstrated by the narrow range of conditions required, including a minimum solid content (~10 wt %), pH range (7 – 9), minimum temperature (~75 °C) for stable lignin nanoparticles to be assembled. Even the rate of temperature increase is a factor in the formation of stable nanoparticle dispersion, with faster rates leading to smaller particle size.

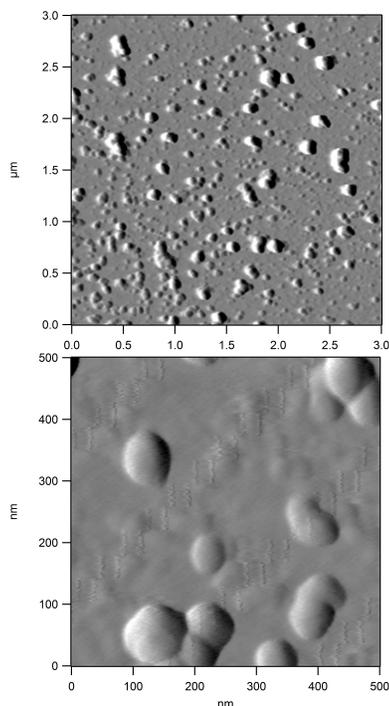


Figure 1. AFM Image of Lignin Nanoparticle Dispersion. The sample was cast on mica at 2000 ppm active lignin in water and air-dried (left and right).

The particle size was shown to be smaller upon drying on mica, with diameters of 40 – 100 nm along the x-y axis, but with a flattened structure with a height of less than 50 nm.

Membrane filtration combined with centrifugation, demonstrated that the nanoparticles were thermodynamically stable, as the particle size did not change as a result of the filtration-centrifugation process, with up to 99+ wt% of the lignin in nanoparticle form. While it previously had been demonstrated that aqueous polymer-grafted lignin combinations can assemble into nanoparticles with pH control [9], the thermal transformation of an *unmodified* lignin suspension into a nanoparticle dispersion is unprecedented.

Thus, we report here a new process to turn water insoluble lignin into unique nanoparticle dispersions by simply heating a partially neutralized lignin suspension in water. As such, isolated softwood kraft lignin or lignin extracted from wheat straw, resulted in nanoparticles of sizes from tens to hundreds of nanometers when partially neutralized to pH 7 - 9 in water, using monovalent alkali hydroxide and other organic bases for pH control combined with heating to 85 to 100 °C at up to 40 wt% solid content.

APPLICATIONS OF LIGNIN NANOPARTICLES

The presence of the anisotropic structure of the lignin nanoparticles was demonstrated through their associative interaction with polymers. As expected from the anionic nature of the particles, aqueous solutions of water soluble cationic polymers, such as commercially available poly(diallyldimethylammonium chloride), cationic polyacrylamide and polyamidoamine epichlorohydrin (PAE) wet strength resins, instantly flocculate the lignin nanoparticles. In contrast, solutions of neutral polymers, as represented by polyvinylpyrrolidone (PVP), show strong interactions through association, as demonstrated by the viscosity change when combining dilute dispersions of PVP and lignin nanoparticles (Fig. 2).

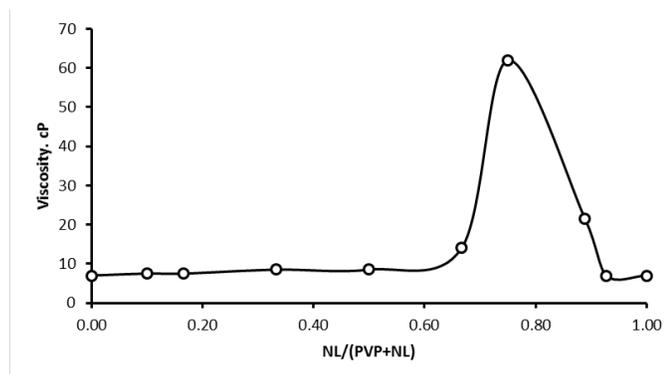


Figure 2. Association of PVP with Lignin Nanoparticles (NL) in Water. Viscosity was monitored by adding 2 wt% lignin nanoparticles to 2 wt% PVP (Plasdone K-90, Ashland Inc.)

When adding a dilute dispersion of lignin nanoparticles (NL) to a dilute solution of PVP, the viscosity of the combination increases, and then peaks at a weight ratio of about 4:1 NL/PVP and then drops off. We assume that the viscosity change come from the association of PVP with NL. At a low ratio of NL to PVP the lignin nanoparticles are surrounded by PVP molecules. At a high ratio of NL to PVP, PVP would be expected to adsorb onto the lignin nanoparticles. At intermediate ratios, some inter-connecting of the nanoparticles by PVP to form network matrixes is expected, resulting in the viscosity peak and the formation of a weak three-dimensional structure.

The hydrophobic association of lignin nanoparticles with partially hydrolyzed (88%) polyvinyl alcohol (PVA) was demonstrated by monitoring the

viscosity increase of the blend when a 23 % by weight active aqueous lignin nanoparticle dispersion was mixed into a 10 % by weight aqueous solution of polyvinyl alcohol (Sandy PVA 88-50 from Sinopec). As it can be seen in Fig. 3, an exponential increase in viscosity was observed when the weight ratio of active lignin to active polyvinyl alcohol was increased. When a 5 % by weight solution of the polyvinyl alcohol (PVA 88-50) was used following the same procedure, a similar trend was also observed (Fig. 3).

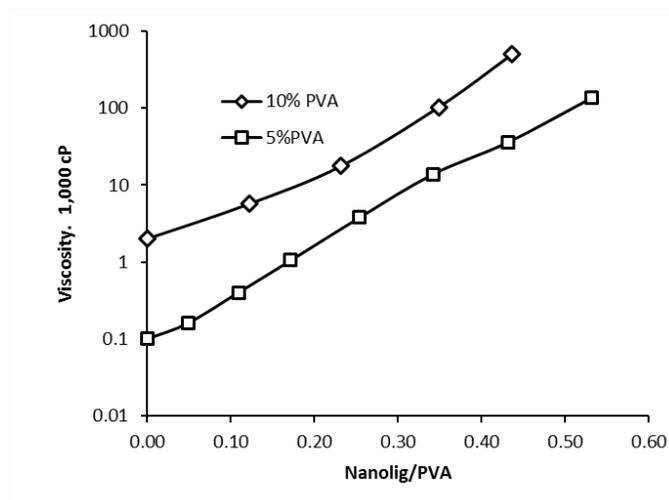


Figure 3. Interaction of Lignin Nanoparticles with PVA

This viscosity response is a further indication of the association of the lignin nanoparticles with polyvinyl alcohol. However, this exponential increase of viscosity was not observed when mixing a lignin nanoparticle dispersion into an aqueous solution of totally hydrolyzed polyvinyl alcohol (99%). We suggest that with the partially hydrolyzed PVA (88%) there exist hydrophobic associations between the hydrophobic vinyl acetate segments of polyvinyl alcohol with the hydrophobic domains of the lignin nanoparticles which results in the observed viscosity increase.

Not only were lignin nanoparticles observed to be associative to water soluble polymers, but also to solid surfaces. The water-rinse persistence of lignin nanoparticles to solid surfaces of metals (stainless steel, aluminum), polyvinyl chloride, polyolefin, laminate, ceramic and glass were observed through long-lasting hydrophilization of the treated surfaces. Generally, the surfaces were brought in contact with 0.2 to 5% (by weight) active lignin nanoparticle dispersions in water with gentle rubbing, until the surfaces were fully wetted, followed by rinsing with running tap water. Traditional surfactants will thoroughly wet these surfaces, but will be

rinsed off easily and rapidly. The lignin nanoparticle treated surfaces remain wetted over a long period of time, when rinsed repeatedly combined with gentle rubbing, as observed from the continued water-sheeting on the surfaces. Lignin nanoparticles were also observed by AFM to be retained on borosilicate glass cover slides after rinsing with running water.. The persistent hydrophilization of the solid surfaces by the lignin nanoparticles can be explained by association of the nanoparticles' hydrophobic domains with the more hydrophobic domains of the solid surfaces or by the simple entrapment of the nanoparticles in surface crevices. This in turn imparts an evenly distributed hydrophilic character to the surface through the hydrophilic functionalities present in the lignin nanoparticles' hydrophilic domains. (Figure 1).

CONCLUSION

It was demonstrated that aqueous lignin suspensions can thermally assemble into organic based nanoparticles dispersion under controlled conditions. Such lignin nanoparticles were found to be associative with polymers, presumably through hydrophobic association or/and electron donor-acceptor charge transfer. The lignin nanoparticles were also observed to have a strong affinity to solid inorganic or polymer surfaces. Such associative property could be useful in building supramolecular assemblies from lignin nanoparticles and polymers for various purposes, e.g. detergents, encapsulation and controlled delivery, surface treatment and emulsion stabilization. A wide array of applications for lignin nanoparticles and nanoparticle/polymer complexes that exploit their surface active properties is expected.

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