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Obtaining lignin nanoparticles by sonication

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ABSTRACT

Lignin, the main natural aromatic polymer was always aroused researchers interest. Currently around 90% of this biomaterial is burned for energy. It has a very complex and complicated structure which depends on the separation method and plant species, what determine difficulties to use as a raw material widely. This research presents a physical method to modify lignin by ultrasonic irradiation in order to obtain nanoparticles. The nanoparticles synthesized were dimensionally and morphologically characterized. At the same time the preoccupations were to determine the structural and compositional changes that occurred after sonication. To achieve this, two types of commercial lignins (wheat straw and Sarkanda grass) were used and the modifications were analyzed by FTIR-spectroscopy, GPC-chromatography, ^{31}P-NMR-spectroscopy and HSQC0. The results confirm that the compositional and structural changes of nanoparticles obtained are not significantly modified at the intensity applied but depend on the nature of lignin.

1. Introduction

Lignin was always attracted the interest of researchers being the second natural polymer as spreading after cellulose and categorized as a renewable resource. This made lignin a very interesting topic for researchers and companies. However, its complexity and unevenness has made it difficult until now to know its precise structure and also how it can be transformed into a widely used raw material. Due to the important modifications that occur in the native lignin structure during the extraction procedure, lignin can be mainly classified by separation methods [1]. Lignin is poorly understood in terms of chemistry and structure compared with other wood compounds such as cellulose. The knowledge of this complex biopolymer is still delayed due to its various covalent bonds, resistance to degradation, heterogeneous nature, the absence of selective and convenient analysis methods and the lack of efficient isolation methods [2,3]. The control and tailoring of lignin multifunctional nature is the basis for the exploitation of this fascinating still under exploration material. Depending on lignin modifications a wide array of different applications can be envisaged: fuels, binders, biocides, chemicals, paper additives, concrete additive, dispersants, cosmetics, lubricants, paints. Recently, with the aim to extend/develop special applications lignin was considered a possible starting material to obtain new nanostructured products. Wood cell wall is biosynthesized basically by self assembly principles of cell wall proteins, polysaccharides and lignin [4]. Fundamentally lignocellulosic materials are made up by a nanometer scale building. This confers important properties (mechanical, optical) for biomass [5]. More specifically lignin displays fractal structure and interesting aggregation behavior [6]. Aiming to conveying the above fundamental findings into new materials we decided to focus and exploit the lignin aggregation processes to synthesize nanoparticles. Nanotechnology allows the use of chemical, physical and biological effects that do not occur outside the nano scale which are environmental friendly in comparison with inorganic materials. Sonochemical synthesis solution is an effective method to prepare various nanomaterials [7]. Zimniewska et al. [8] prepared nanoparticles based on lignin by ultrasonication for textile fiber treatments. After treatments fiber acquired antistatic, antibacterial and ultraviolet radiation absorbing properties. In 1993 Schilling [9] obtained lignin nano/microparticles (~300 Å) by hydroxymethylation. These were integrated into the production of water-based ink. Another way to obtain lignin micro/nanoparticles is represented by epoxydation reaction. By the epoxydation of some commercial lignin (Protobind type), nanoparticles based on modified lignin were detected in liquid phase [10,11]. Both hydroxymethylated and epoxydated nano

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lignins were used in biocide systems in wood protection [12]. Preliminary results on obtaining nanoparticles based on lignin transformation by ultrasound were presented in a previous paper [13]. In this effort the authors carried out an extensive structural and morphological characterization of such interesting materials.

The development of a variety of chemical reactions due to the action of ultrasound is strongly related to the phenomenon of cavitation. Chemical processes induced by ultrasound field occur only when the ultrasound intensity met conditions to develop of cavities. Regardless, the duration of ultrasonic irradiation intensities that do not reach a certain threshold result in no chemical reactions occurring [14]. The parameters: pressure, temperature, ultrasound settings and type of liquid, influence the formation of the radicals in different ways. The amount of radicals formed due to sonication is a function of the number of cavities created and the number of radicals that are formed per cavitation bubble [15]. Cavitation is the phenomenon of sequential formation (increase and decrease) of millions of vapor bubbles in liquid. Collapse or implosion of these cavities creates local high temperatures and pressures in a very short period of time, forming hot spots in cold liquids. Cavitation is induced by high frequency sonic waves (16 kHz – 100 MHz) through the mass of liquid [16]. The transient state of the local high pressures and temperatures gives rise to the primary chemical reactions occurring during and after micro bubbles collapse [17]. Ultrasound treatments typically induce the formation of radical species. In aqueous solution and in the presence of air both hydroxyl and superoxy radical species are formed. In case of polymers, ultrasounds can lead to homolytic scission of the macromolecular chains resulting pair radicals or polymerization of monomers. Ultrasound energy was used to increase lignin extraction yield and purity or to remove the major inorganic load from the alkali lignin with no significant modifications observed in the properties (composition, structure; at 20 kH, 100 W) of the isolated lignin samples [18–20] or to polymerization for high molecular weight lignin [21]. Seino et al. [22] claim that the β-O-4 majority [23,24] bonds of lignin can be homolytically cleaved to some extent by sonication.

In this paper the results obtained in the modification of two types of commercial alkali lignins (from wheat straw and Sarkanda grass) using ultrasounds which were analyzed by FTIR-spectroscopy, GPC-chromatography, ^{31}P-NMR-spectroscopy and HSQC0 are presented.

2. Materials and methods

2.1. Materials

Wheat straw lignin (L1) and Sarkanda grass lignin (L2) were kindly supplied by Granit Recherché Development Company Switzerland. Their characteristics have been previously reported [25].

2.2. Lignin nanoparticles synthesis

Aqueous suspensions of lignin (0.7%) were used. The lignin suspensions were sonicated for 60 min. Finally, a homogeneous stable nanodispersion was obtained. The samples resulted in sonication of lignin were dried in mild conditions to be used in further analysis. Ultrasonication was performed by using an ultrasonic horn (Sonics & Materials VC600/CV17) at 20 KHz frequency, 600 W power [13].

2.3. Characterization

2.3.1. Light scattering

Particle size distribution analysis of nanoparticles was done with Shimadzu SALD 7001 instrument. This device allows the determination of the size of particles in a range of 15 nm to 500 μm by laser diffraction method.

2.3.2. TEM

Transmission electron microscopy investigations were performed on a HT7700 type Transmission Electron Microscope operating at 100 KV.

2.3.3. Gel permeation analysis

Gel permeation chromatograms were recorded by a Shimadzu LC 20AT liquid chromatograph equipped with a SPD M20A ultraviolet diode array (UV) detector set at 280 nm. Two columns in series: Agilent PL gel MIXED-D 5 μm, 1–40 K and PL gel 5 μm, MW range 500 Da – 20 kDa were connected for measurements. Calibration was achieved with polystyrene standards produced by Fluka. Tetrahydrofuran (THF) was used as eluent [26,27]. The lignin samples were acetylated with acetyl bromide before the injection, following the procedure described by Asikkala et al. [28].

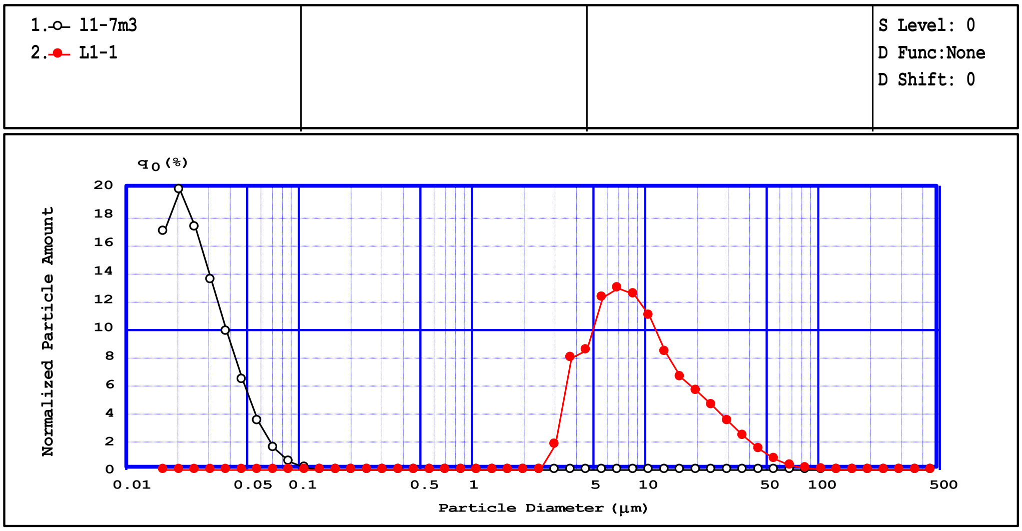

Fig. 1. Average particle size distribution analysis for wheat straw lignin (L1-1 L1) and for sonicated wheat straw lignin (l1-7m3).

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