



## Physicochemical and electrokinetic properties of silica/lignin biocomposites

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### ABSTRACT

A new method of synthesis of novel composites obtained from silica and Kraft lignin has been proposed. Silica used in the study was obtained by three methods (hydrolysis and condensation of tetraethoxysilane, precipitation in a nonpolar and polar medium with the use of sodium silicate). To extend the possible range of applications, the silica was preliminary modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, and finally it was modified with Kraft lignin earlier oxidised with sodium periodate (lignin bonded to SiO<sub>2</sub> by covalent interactions). The products physicochemical and electrokinetic properties were thoroughly analysed. The dispersive properties and surface morphology were evaluated on the basis of particle size distributions and SEM images. The stability of dispersion in inorganic-organic systems were characterised on the basis of the zeta potential, whose value also permitted concluding on the interactions between colloidal molecules dispersed in water solutions. The products were subjected to elemental analysis to get percentage contents of N, C, H, S elements and were also characterised by XPS and FT-IR spectroscopy. Results of the study are of practical importance in prospective applications of SiO<sub>2</sub>/lignin biocomposites.

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### 1. Introduction

Dynamic development of technologies of synthesis of new materials has been driven by the need to obtain products of specific unique properties. The majority of the new products have been based on silica and show a variety of different morphologies. Because of its particular structure and properties, including large surface area and high mechanical strength, silica is attractive for many applications. An additional advantage of SiO<sub>2</sub> is the possibility of its surface modification because of the presence of surface functional groups capable of reactions with many substances. By silica surface modification it is possible to change its chemical and physical properties to meet particular demands (Jesionowski, Żurawska, & Krysztafkiewicz, 2003). SiO<sub>2</sub> can be obtained by precipitation in a polar or nonpolar medium (Jesionowski, 2001; Żurawska, Krysztafkiewicz, & Jesionowski, 2002), by hydrolysis and condensation of tetraalkoxysilanes according to the Stöber method or its modifications (Ibrahim, Zikry, & Sharaf, 2010; Stöber, Fink, & Bohn, 1968).

Recently much attention is paid to production of SiO<sub>2</sub> composites with a biopolymer of organic origin such as e.g. lignin. It is a high-molecular natural compound formed as a result of enzyme-induced polymerisation of three main precursors (monolignols): coniferyl, *p*-coumaryl and sinapyl alcohols

(Collinson & Thielemans, 2010). It has been estimated that lignin makes about 30% of global organic carbon resources. Besides cellulose, it is the second most abundant natural polymer on the earth (Lora & Glasser, 2002). It shows attractive chemical properties such as reactivity, thermoplasticity and incomplete solubility, which makes it an excellent substrate for synthesis of hybrid materials for removal of biological and organic pollutants, in the soil and water (Jawaid & Abdul Khalil, 2011; Telysheva et al., 2009). The use of lignin as a biodegradable polymer in an inorganic matrix permits obtaining a highly functional material of a new generation and can become important for general economic development. So far rare attempts at obtaining such inorganic-organic products have been made. The presence of many functional oxygen groups on silica surface enables its modification with lignin, accompanied by formation of more active sites, which increases its ability to adsorb heavy metal ions, organic compounds and many other pollutants (Hayashi, Shoji, Watada, & Muroyama, 1997; Kajiwara & Chujo, 2011; Qu et al., 2010). High abundance and natural character of lignin in combination with silica makes this material an excellent polymer filler permitting getting products of desired properties at low cost (Ignat, Ignat, Ciobanu, Doroftei, & Popa, 2011; Stiubianu, Cazacu, Cristea, & Vla, 2009). In view of the potential uses of silica/lignin biocomposites is important to determine in the zeta potential, which provides important information about surface chemistry and the electrokinetic stability (Hunter, 1981; Kosmulski, 2001; Saha, Manna, Sen, Roy, & Adhikari, 2012). It is one of the most important parameters permitting indication of application possibilities of materials in novel industrial

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technologies. Zeta potential permits quantitative description of electrostatic interactions between particles dispersed in colloidal systems, which determine the behaviour and physical stability of disperse systems. Zeta potential is important to qualify material for the use in pharmaceutical, cosmetic, food or paint industries, for biomedicine, protection of the natural environment, waste purification, water treatment, production of paints and lacquers or for production of chemical substances for agriculture. Besides, zeta potential measurements are used for optimisation of various processes (Bernsamann, Frisch, Ringwaldand, & Ball, 2010; Kuzniatsova, Kim, Shaqau, Dutta, & Verweij, 2007).

The aim of the study was physicochemical and electrokinetic characterisation of the silica/lignin biocomposites obtained. As the electrokinetic properties of materials depend significantly on the surface character of given materials, it was highly relevant to check the effect of the method of silica synthesis and the amount of lignin used for modification of the inorganic support on the zeta potential values. Moreover, the influence of the preliminary surface functionalisation of silica with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D) on the electrokinetic curves characterising the composite systems studied. Indirectly, also the stability of water dispersions of SiO<sub>2</sub>/lignin was evaluated on the basis of zeta potential.

## 2. Experimental

### 2.1. Silica/lignin biocomposites synthesis

#### 2.1.1. Synthesis of silica

Silica obtained for this study was synthesised by three methods. The first was the sol-gel method based on a simultaneous hydrolysis and condensation of tetraethoxysilane (TEOS) in the environment of alcohol and basic catalyst. The reagents were 200 cm<sup>3</sup> of 95% of ethyl alcohol (Chempur®), 40 cm<sup>3</sup> of 25% ammonia water (Chempur®) and 28 cm<sup>3</sup> of tetraethoxysilane (Sigma-Aldrich®). They were placed in a reactor and vigorously stirred for 1 h. The product was subjected to sonification and three times washed with ethanol and finally with water. To remove moisture, silica was subjected to convectional drying at 105 °C for 24 h.

The second method was precipitation in a nonpolar medium. Two emulsions were prepared E1 (alkaline one) and E2 (acidic one). E1 was prepared of 100 cm<sup>3</sup> of 20% solution of sodium silicate (Vitrosilicon SA), a mixture of emulsifiers (nonylphenylpolyoxyethylene-glycol ethers) NP3 in the amount of 6.0 g and NP6 in the amount of 4.0 g and 340 cm<sup>3</sup> of cyclohexane (Champur®). The mixture of cyclohexane and surfactants were introduced in portions to sodium silicate. The contents were subjected to homogenisation for 15 min. Emulsion E2 was prepared in a similar way as E1. In another vessel a mixture of emulsifiers: 2.0 g of NP3 and 1.2 g of NP6, were made and flooded with 140 cm<sup>3</sup> of cyclohexane. The mixture was dosed in portions to 132 cm<sup>3</sup> of 5% hydrochloric acid (Chempur®). The contents were homogenised for 15 min. The emulsions were combined and the system was destabilised at 80 °C, then cyclohexane was separated and the sample was filtered off under reduced pressure. The precipitate was dried at 105 °C for 24 h.

The third method of SiO<sub>2</sub> synthesis was precipitation in a polar medium. A reactor placed in a water bath of 85 °C was loaded with 100 cm<sup>3</sup> of a water solution of a hydrophobising agent (unsaturated fatty alcohol C<sub>1</sub>–C<sub>4</sub> of an intermediate degree of oxyethylenation 7), to which 30 cm<sup>3</sup> of 5% sodium silicate (Vitrosilicon SA) and 9.8 g of sodium sulphate (Chempur®) were dosed. In the next stage of study, 370 cm<sup>3</sup> of sodium silicate was dosed at a constant rate of 8 cm<sup>3</sup>/min and 210 cm<sup>3</sup> of 5% sulphuric acid (Champur®) was dosed at a rate of 4 cm<sup>3</sup>/min. The contents were vigorously stirred.

Silica was filtered off under reduced pressure, washed a few times with water and then dried by the convection method at 105 °C for 24 h.

#### 2.1.2. Functionalisation of silica surface

Silica surface was modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (Sigma-Aldrich®). An appropriate amount of the silane was hydrolysed in a system of methanol: water (4:1, v/v) and then applied on the silica surface by the method described in detail in (Jesionowski & Krysztalkiewicz, 2000; Jesionowski, Ciesielczyk, & Krysztalkiewicz, 2010).

Subsequently, the preliminary modified and unmodified silica was subjected to proper modification with a solution of Kraft lignin (Sigma-Aldrich®). A technological scheme of this process is shown in Fig. 1. First, two solutions were made. Solution 1 was made of lignin dissolved in a 75 cm<sup>3</sup> solution of dioxane:water (9:1, v/v). Solution 2 (oxidising) was made of sodium periodate (Sigma-Aldrich®) dissolved in 30 cm<sup>3</sup> of water. Then solution 2 was dosed into solution 1 at the rate of 1.1 cm<sup>3</sup>/min, in the dark. To the mixture of the two solutions 5 g of modified or unmodified silica was added and the whole content was stirred for 1 h. Finally the solvent was removed in a vacuum evaporator and the product was subjected to convection drying at 105 °C for 24 h.

### 2.2. Physicochemical and electrokinetic characteristics

Dispersive properties of the products were characterised with the use of Zetasizer Nano ZS (0.6–6000 nm) and Mastersizer 2000 (0.2–2000 μm) instruments both made by Malvern Instruments Ltd. (UK), employing the method of dynamic light scattering (DLS) and laser diffraction technique, respectively. Dynamic light scattering is a non-invasive, well-established technique for measuring the size and size distribution of molecules and particles typically in the submicron region, and with the latest technology even lower than 1 nm. Typical applications of DLS are the characterisation of particles, which have been dispersed or dissolved in a liquid. The Brownian motion of particles or molecules in suspension causes laser light to be scattered different intensities. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes-Einstein relationship.

The laser diffraction method is based on two physical phenomena: diffraction and interference of light waves. In laser diffractometers the component waves have the same amplitudes and depending on the angle of intersection the resultant wave is alternately quenched or enhanced, which is observed as a series of alternate bright and dark lines. The results are obtained as a relation between the volume (in %) and the diameter of particles, in fact of a fraction of particles. The limiting diameters of particle fractions are the equivalent diameters of the spherical balls which would give the same diffraction pattern as the sample studied. The control unit (a PC) converts the pulses recorded into the diameters of particles, which is performed according to the MIE theory. This method assumes that the particles are spheres and are arranged randomly in the suspension, and that there is no interaction between them and there is no shielding of smaller particles by larger ones.

On the basis of scanning electron microscope, Zeiss EVO40 (Germany) images the grain morphology, type of agglomeration and dispersion degree were analysed. Elemental composition of the products was established with the use of Vario El Cube instrument made by Elementar Analysensysteme (Germany), which gave the percentage contents of carbon, hydrogen, nitrogen and sulphur after high-temperature combustion of the samples analysed. The presence of desired functional groups were confirmed by Fourier transform infrared spectra (FT-IR), recorded on an EQUINOX 55 spectrophotometer made by Bruker (Germany). XPS spectra of the biocomposites were obtained with a VSW photoelectron

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