

MODERN COMPOSITE MATERIALS BASED ON SILICA AND KRAFT LIGNIN

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Abstract

The study was undertaken to synthesise and characterise the silica/lignin biocomposite materials. Silica emulsion (composite matrix) was precipitated from an aqueous solution of sodium silicate as a SiO₂ precursor, hydrochloric acid as a precipitating factor, and cyclohexane as the organic phase. Silica was modified with a Kraft lignin (KL) solution. KL had been earlier oxidised with a solution of sodium periodate. The optimum conditions of the process, mainly the optimum ratio of the reagents used, were established. The influence of the amount of lignin introduced on the properties of the final product was tested. The biocomposites obtained were characterised by determination of their physicochemical, electrokinetic and dispersive–morphological properties.

1 Introduction

Attempts at obtaining organic/inorganic composites of high quality and wide range of applications have been undertaken at research centres all over the world for over a decade. An interesting proposition are the materials based on lignin as a biodegradable polymer and silica as an inorganic support. Very interesting properties of such composites have prompted us to synthesise a pro–ecological and biodegradable material based on SiO₂/lignin. Synthesis and characterisation of composites of this type have been covered in a few hitherto published reports [1–4].

The Swiss botanist A. P. Candolle used the term “lignin” for the first time, from the Latin word *lignum*, meaning “wood.” Being one of the most abundant natural polymers, together with cellulose and hemicellulose [5], lignin forms part of the secondary cell walls of plants and helps maintain the integrity of the cellulose/hemicellulose/pectin matrix. The composition and ratio of lignin in plants depends on the botanical species. In softwood lignin represents about 30% of the total mass, while in hardwood this share falls to 20–25% [6]. Herbaceous plants contain its variable, low amounts [7]. It is generally accepted that there are three basic phenol derivatives, the so–called monolignols, that make up almost all types of lignin found in nature [8]: p–coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [9]. Each monolignol produces p–hydroxyphenyl, guaiacyl, and syringyl residues in the polymer. The lignin polymer is synthesised by peroxidase–mediated dehydrogenation of monolignol units, giving a heterogeneous structure formed by basic units linked by C–C bonds and aryl–ether linkages with aryl–glycerol and β–aryl ether [10]. Many stereocenters are formed, but it is assumed

that the final polymer is an optically inactive form. The stereochemistry of simple lignin models has been studied elsewhere [11].

Several lignin preparations based on extraction and isolation procedures are commercially available [12] and because these have different chemical functionalisations, physical properties, and address a range of molecular masses, they are suitable for different purposes. Recently, large amounts of lignin has been produced as a side product in the so-called Kraft process [13, 14]. Lignin obtained in this process or isolated by some extraction methods has been used for instance to produce energy [15], in electrotechnology, electrochemistry [16, 17], pharmacy [18] and in production of modern functional biocomposites of specific properties [19].

A very popular material applied in many branches of science and industry is silica, which is characterised by a number of desirable properties such as chemical reactivity, good mechanical properties and highly developed surface area. SiO₂ can be obtained by the Stöber method or its modifications [20, 21] and in the process of precipitation from emulsion systems [22, 23] or water systems [24, 25]. Due to its specific and unique properties silica finds use as a polymer filler, sorbent of harmful organic compounds and in many other applications.

2 Experimental

2.1 Precipitation of silica

Silica was obtained from sodium silicate as a precursor of SiO₂, with the use of hydrochloric acid as a precipitating agent and cyclohexane as a solvent. At first two emulsions were made. The alkaline emulsion (E1) contained 20% solution of sodium silicate (Vitrosilicon SA), into which a mixture of two emulsifiers NP3 and NP6 (nonylphenylpolyoxyethyleneglycol ethers) and cyclohexane (Chempur[®]) was dosed. The emulsion was homogenised for about 15 minutes. The second acidic emulsion (E2) was made of organic phase (cyclohexane) and two emulsifiers NP3 and NP6 at appropriate proportions dosed in portions into a 5% solution of hydrochloric acid (Chempur[®]). Likewise emulsion E1, also emulsion E2 was subjected to homogenisation for about 15 minutes. The alkali emulsion (E1) was dosed at a constant rate to the acidic one (E2). After combination, the system of emulsions was homogenised for about 15 minutes and then destabilised at 85°C to separate the organic phase by vacuum distillation. The silica obtained was subjected to filtration under reduced pressure, washed with water and methanol (Chempur[®]). The precipitate was dried in a stationary drier at 105°C for about 24h.

2.2 Synthesis of composites

The precipitated silica was a support matrix for the final composites. The other precursor was commercial Kraft lignin (Sigma-Aldrich[®]). Two initial solutions were made: the first containing dioxane and water (9:1, v/v) and lignin, while the second was a water solution of sodium periodate (Sigma-Aldrich[®]). The solutions were combined by dosing the sodium periodate solution into the lignin solution, at ambient temperature and in the dark. To the combined solutions the earlier precipitated silica was added. The whole system was vigorously stirred for about 1 hour. The organic solvents were evaporated by vacuum distillation. The composite was dried for about 24 hours in a stationary drier at 105°C.

2.3 Characterisation of composites obtained

The final products of the above process of synthesis were subjected to thorough characterisation by determining their physicochemical, dispersive-morphological and electrokinetic properties. The particle size distributions according to the volume contribution were measured on Mastersizer 2000 analyser, Malvern Instruments Ltd., by laser diffraction

method. The result were confronted with morphological analysis performed on the basis of SEM images taken by a scanning electron microscope Zeiss EVO40. Electrokinetic stability was evaluated on the basis of zeta potential measurements made by Zetasizer Nano ZS equipped with an autotitrator. The instrument employs a combination of electrophoresis and laser measurement of particle mobility on the basis of Doppler phenomenon. The samples were also subjected to colorimetric analysis in the *CIE L*a*b** colour spece system on a spectrophotometer Specbos 4000. The success of functionalisation was verified by the FT-IR spectra on a spectrometer IFS 66v/S made by Bruker. The thermal stability of the samples was evaluated by determination of temperature changes in the sample weight, using an instrument Jupiter STA449F3 made by Netzsch.

3 Results and discussion

3.1 Dispersive and morphological properties

Table 1 presents the data characterising the dispersive properties of silica precipitated in the emulsion medium and silica/ lignin composites obtained. The particle size distributions of these samples, informing about their homogeneity, are shown in figure 1.

| Sample n° | Content of lignin in relation to the silica matrix [wt./wt.] | Particle diameter from Mastersizer 2000 [µm] | | | |
|-----------|--|--|--------|--------|--------|
| | | d(0.1) | d(0.5) | d(0.9) | D[4.3] |
| 1 | 0 (silica) | 4.1 | 17.3 | 39.8 | 19.9 |
| 2 | 3 | 4.1 | 16.1 | 39.2 | 19.4 |
| 3 | 5 | 4.4 | 16.4 | 41.2 | 20.4 |
| 4 | 10 | 4.2 | 22.1 | 50.4 | 25.5 |
| 5 | 20 | 4.5 | 22.6 | 54.6 | 26.6 |
| 6 | 30 | 5.3 | 25.2 | 52.5 | 27.5 |
| 7 | 40 | 6.4 | 27.3 | 55.6 | 29.7 |
| 8 | 50 | 6.7 | 28.5 | 56.1 | 30.2 |

Table 1. Dispersive characteristic of silica (sample 1) and silica/lignin biocomposites (samples 2–8)

The silica precipitated in nonpolar system is inhomogeneous and shows a tendency towards formation of larger agglomerate clusters (Mastersizer 2000) [24, 25]. According to the particle size distribution measurements, 50% of the silica sample volume is taken by particles of diameters below 17.3 µm, while 90% of the sample volume is occupied by particles of diameters smaller than 39.8 µm. The silica/lignin biocomposites are made of particles of nanometric size and reveal an increased tendency towards aggregate (up to 1 µm) and agglomerate (above 1 µm) formation, as evidenced by the particle size distributions according to volume contribution (figure 1). The tendency towards agglomeration is more pronounced with increasing content of lignin per 100 weight parts of silica, which is also a consequence of the fact that the Kraft lignin used has particles of micrometric size.

The information on dispersive properties obtained by measurements on a Mastersizer 2000 is confirmed by SEM images analysis (figure 2). The images illustrate the increasing size of particles and the tendency towards formation of aggregates and then secondary agglomerates, with increasing content of lignin. The particles of biocomposites have regular, spherical shapes.

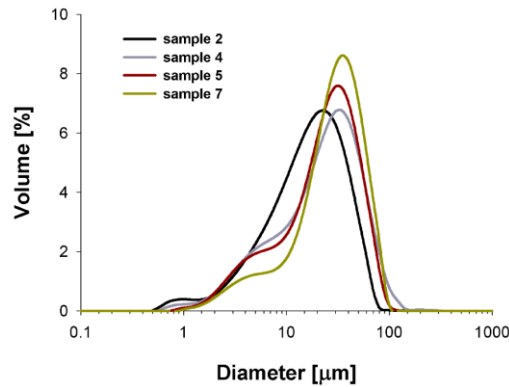


Figure 1. Particle size distribution by volume of silica/lignin biocomposites (Mastersizer 2000)

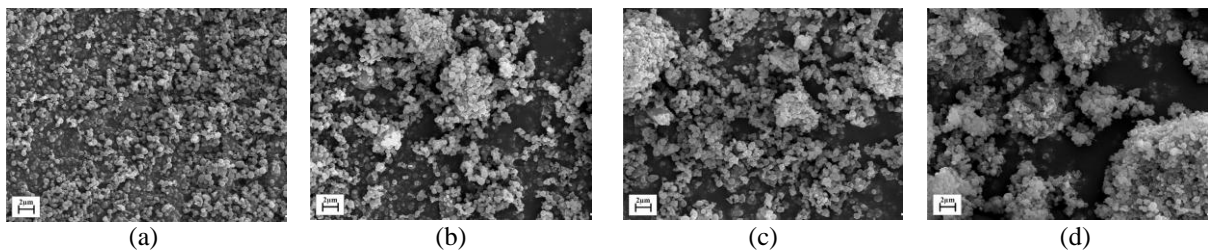


Figure 2. SEM images of silica/lignin biocomposites containing (a) 3 wt./wt. (b) 10 wt./wt. (c) 20 wt./wt. and (d) 40 wt./wt. of lignin in hybrid matrix

3.2 Electrokinetic characteristics

The effect of pH on the surface charge and stability of silica/lignin biocomposites was characterised by determination of zeta potential. The measurements were made in a 0.001M NaCl solution for pH varied from 1.5 to 11. Figure 3 presents the electrokinetic curves of silica (sample 1), Kraft lignin and the silica/lignin biocomposites containing 3, 10 or 40 wt./wt. Kraft lignin.

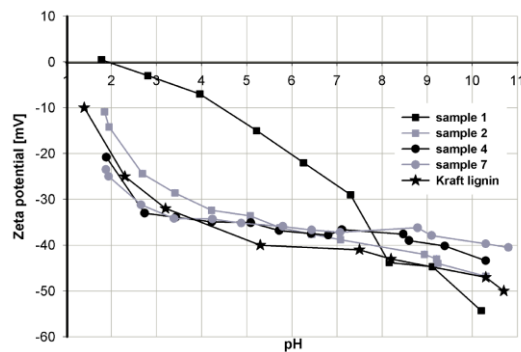


Figure 3. Zeta potential versus pH for silica, Kraft lignin and selected SiO₂/lignin biocomposites

As follows from the results, silica makes highly stable dispersions. It shows the isoelectric point (i.e.p.) for pH ranging from 1.7 to 2. The small differences in i.e.p. are related to the method of silica synthesis, conditions of its storage and its surface properties [26, 27], which has been confirmed by the results obtained in this study. The shape of the electrokinetic curve recorded for Kraft lignin suggests that it tends to an i.e.p. at pH of 1, which means that the surface charge density of lignin gradually decreases with decreasing pH. The surface charge of Kraft lignin is negative almost in the entire pH range studied, which is a consequence of

ionisation of the hydroxyl and acidic groups because of their dispersion in water solution [28]. The values of zeta potential of silica/lignin biocomposites are negative and indicate high stability of their water dispersions. With increasing content of lignin the electrokinetic curves are shifted towards lower values of zeta potential, which additionally confirms the effectiveness of the applied method of silica functionalisation.

3.3 Colorimetric analysis

Colorimetric analysis has provided indirect proof of the successful and effective functionalisation. Figure 4 presents the colorimetric data lightness (L^*), contribution of red (a), yellow (b) and the total change in colour (dE) measured for the products obtained. For pure silica (sample 1), L^* is 93.8, the addition of lignin results in a decrease in this parameter to 87.5 for sample 2 and to 49.3 for sample 7. Similarly, the total change in colour dE increases with increasing content of Kraft lignin.

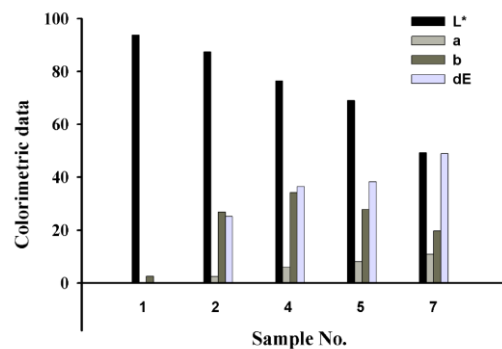


Figure 4. Colorimetric data of silica (sample 1) and selected silica/lignin biocomposites (samples 2, 4, 5, 7)

3.4 FT-IR spectra analysis

To confirm the effectiveness of the method of silica/lignin biocomposite synthesis, the FT-IR spectra of the products were taken to check for the presence of characteristic functional groups. Figure 5a presents the FT-IR spectrum of silica precipitated from the emulsion system and Kraft lignin (precursors of biocomposites), while Figure 5b shows the FT-IR spectra of SiO₂/lignin biocomposites.

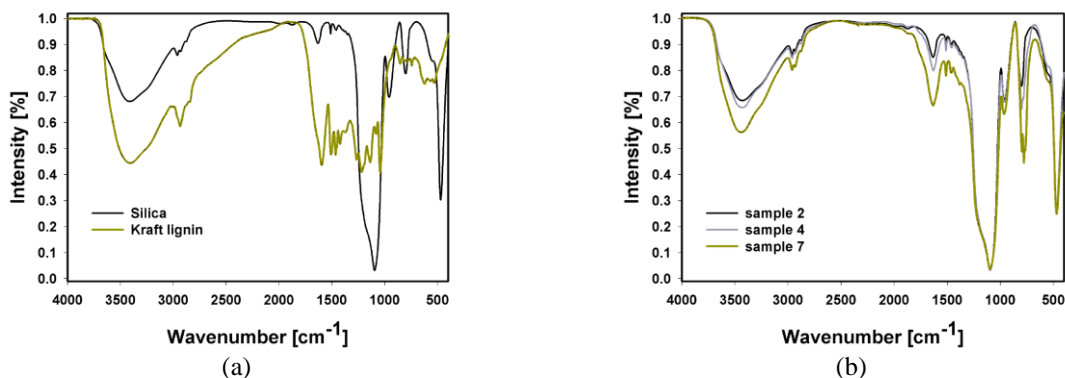


Figure 5. FT-IR spectra of (a) unmodified silica and Kraft lignin, (b) selected samples of biocomposites obtained

The spectrum of SiO₂ reveals the presence of the characteristic bonds Si-O-Si (ν_s : 1096 cm⁻¹, ν_{as} : 805 cm⁻¹), Si-OH (ν_s : 960 cm⁻¹) and Si-O (δ : 470 cm⁻¹), where ν_s and ν_{as}

stand for the symmetric and asymmetric stretching vibrations, while δ are the bending vibrations, their presence is in agreement with [29]. The other bands, that is the one corresponding to stretching vibration O–H ($3600\text{--}3200\text{ cm}^{-1}$) and a low-intensity one at $\sim 1630\text{ cm}^{-1}$ are assigned to water physically bound in silica. The FT-IR spectrum of Kraft lignin shows the bands assigned to the stretching vibrations O–H ($3600\text{--}3200\text{ cm}^{-1}$), stretching vibrations C–H ($2960\text{--}2835\text{ cm}^{-1}$), stretching vibrations of ketone group C=O ($1710\text{--}1550\text{ cm}^{-1}$) and the ones at 1600 cm^{-1} , 1510 cm^{-1} and 1420 cm^{-1} assigned to the stretching vibrations of the C–C bonds in the aromatic skeleton. There is another group of bands at 1375 cm^{-1} , 1265 cm^{-1} , 1220 cm^{-1} and 1045 cm^{-1} corresponding to the stretching vibrations of C–O and ether bonds C–O–C. The spectrum also shows a group of bands below 1000 cm^{-1} assigned to the in-plane and out-of-plane vibrations of aromatic C–H bonds. All these data are in agreement with literature [30, 31]. Figure 5b presents the spectra of biocomposites. The bands appearing in the spectra and the increasing intensity of the bands assigned to particular functional groups with increasing content of lignin, confirm that the above mode of functionalisation has been successful.

3.5 Thermal characteristic

Selected samples were also subjected to thermogravimetric study based on the record of mass changes as a function of temperature. To be able to compare the character of temperature changes in the sample mass for samples of different contents of lignin, the measurements were made for sample 4 containing 10 wt./wt. of lignin and sample 7 containing 40 wt./wt. of lignin. The DTA curves also permit observation of transformations taking place upon heating in the range $20\text{--}1000^\circ\text{C}$. They revealed exo- and endothermic effects. The exothermic effect appeared in the range $25\text{--}320^\circ\text{C}$ and was assigned to elimination of crystallisation water. TG curves were also recorded and their character was in agreement with that of DTA curves. The effects on the TG curves in the above temperature range corresponded to the loss of mass by 9.8% for sample 4 and by 18.1% for sample 7. Another significant effect corresponding to the loss of mass was observed in the range $650\text{--}850^\circ\text{C}$ and interpreted as corresponding to decomposition of lignin and fragmentation of its macromolecule. In this temperature range for sample 4 the TG curve shows a jump change corresponding to mass loss by 4.0%, while for sample 7 the mass loss reaches 18.7%.

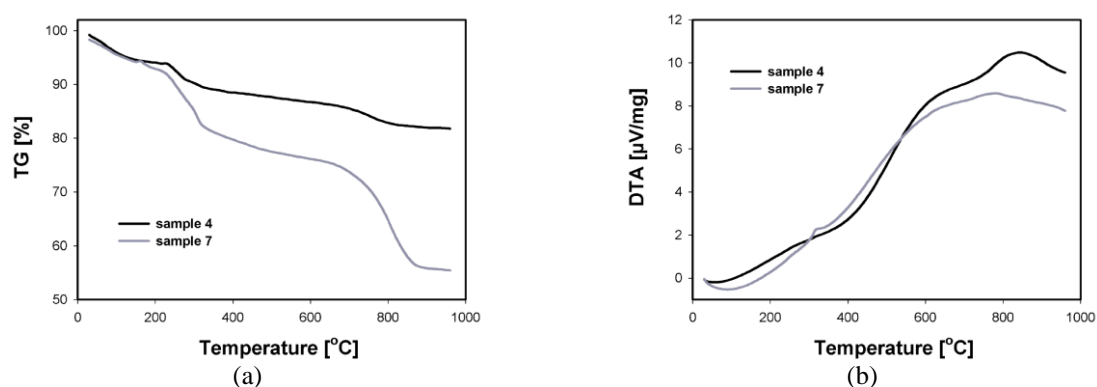


Figure 6. Thermal analysis (a) TG and (b) DTA of composites containing 10 wt./wt. (sample 4) and 40 wt./wt. (sample 7) of lignin in hybrid matrix

4 Conclusions

The proposed method for the synthesis of silica/lignin biocomposites permits obtaining products of specific target physicochemical, dispersive and morphological properties. The results have proved a significant dependence of the above properties on the content of lignin used for silica modification. As evidenced by electrokinetic analysis, the biocomposites obtained show dispersive stability almost in the entire pH range considered. The success and effectiveness of the modification performed have been confirmed by results of the colorimetric analysis and FT-IR spectra. Moreover silica/lignin biocomposites have been found to be characterised by higher thermal stability than that of pure lignin. In general, the silica/lignin biocomposites have been shown to be suitable for the use as polymer fillers, adsorbents of harmful organic compounds and in other applications in electrochemistry, pharmacy, production of paints and lacquers.

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