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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-aminopropyltrimethoxsysilane, and finally it was modified with Kraft lignin earlier oxidised with sodium periodate (lignin bonded to SiO_2 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_2/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_2 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_2 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_2 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, thermoplaticity 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 it 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_2/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^3 of 95% of ethyl alcohol (Chempur®), 40 cm^3 of 25% ammonia water (Chempur®) and 28 cm^3 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^3 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^3 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^3 of cyclohexane. The mixture was dosed in portions to 132 cm^3 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_2 synthesis was precipitation in a polar medium. A reactor placed in a water bath of 85 °C was loaded with 100 cm^3 of a water solution of a hydrophobising agent (unsaturated fatty alcohol C_1—C_4 of an intermediate degree of oxyethylenation 7), to which 30 cm^3 of 5% sodium silicate (Vitrosilicon SA) and 9.8 g of sodium sulphate (Chempur®) were dosed. In the next stage of study, 370 cm^3 of sodium silicate was dosed at a constant rate of 8 cm^3/min and 210 cm^3 of 5% sulphuric acid (Champur®) was dosed at a rate of 4 cm^3/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 & Krysztafkiewicz, 2000; Jesionowski, Ciesielczyk, & Krysztafkiewicz, 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^3 solution of dioxane:water (9:1, v/v). Solution 2 (oxidising) was made of sodium periodate (Sigma–Aldrich®) dissolved in 30 cm^3 of water. Then solution 2 was dosed into solution 1 at the rate of 1.1 cm^3/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

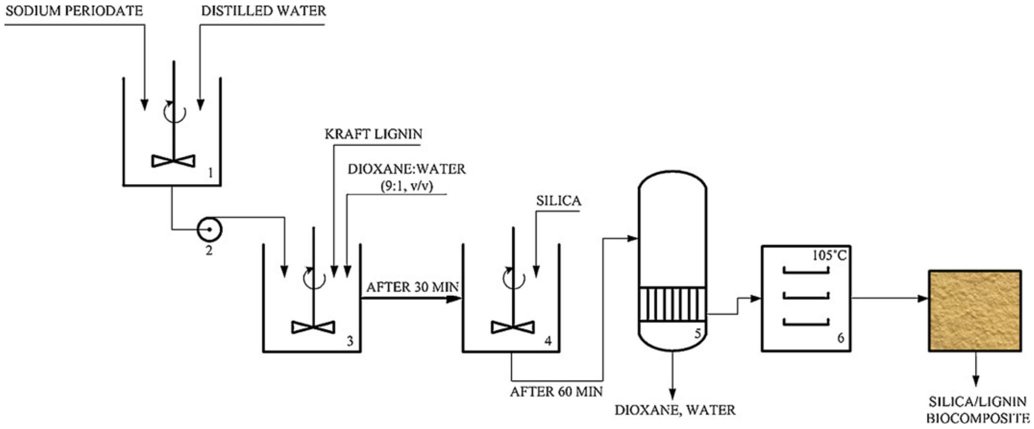

Fig. 1. Technological process for production of silica/lignin biocomposite (1–mixing device, 2–pump, 3,4–reactor, 5–vacuum evaporator, 6–convection dryer).

spectrometer Vacuum Systems Workshop Ltd. (UK) using non-monochromatised Al Kα radiation (1486.6 eV). The radiation source operated at 15 kV and 14 mA. The vacuum pressure was always kept around 3×10^{-8} mbar. The binding energy scale was corrected by referring to the aromatic peak of the C1s spectrum of 284.6 eV

The zeta potential was measured by a Zetasizer Nano ZS equipped with an autotitrator. The measurements were performed in a 0.001 M solution of NaCl. This instrument employs a combination of electrophoresis and laser measurement of particles mobility based on the Doppler phenomenon. The speed of particles moving in the liquid in an electric field, known as the electrophoretic mobility, is measured. Then, from the Henry's equation (1) the value of the zeta potential is obtained.

$$\mu_E = \frac{2\varepsilon\zeta f(\kappa a)}{3\eta} \qquad (1)$$

where: μ_E, electrophoretic mobility; ε, dielectric constant; ζ, electrokinetic (zeta) potential; η, viscosity; $f(\kappa a)$, the Henry function.

The Henry function $f(\kappa a)$ varies monotonically and increases from 1.0 at $\kappa a = 0$ to 1.5 at $\kappa a = \infty$. Obviously, at the lower limit we regain the Hückel equation ($\mu_E = 2\varepsilon\zeta/3\eta$) and the upper limit, the Smoluchowski equation ($\mu_E = \varepsilon\zeta/\eta$).

3. Results and discussion

3.1. SiO_2/lignin biocomposites obtained with unmodified silica

3.1.1. Dispersive and morphological properties

Table 1 presents results characterising dispersive properties of unmodified silica synthesised by three methods (sol–gel, precipitation in a nonpolar and polar medium) and silica/lignin biocomposites based on the three samples of unmodified silica.

The best dispersive properties were found for the unmodified silica synthesised by the modified Stöber method. Data from Mastersizer 2000 (Fig. 2a) indicate a homogeneous character of the product: 50% of the sample volume is taken by particles of diameters smaller than 12.1 μm, 90% of the sample volume is taken by particles smaller than 22.6 μm. The sample homogeneity is confirmed by the SEM image (Fig. 2b), which also shows spherical and regular shape of the particles (Plumieré, Ruff, & Spieser, 2012). The silica samples precipitated in nonpolar or polar media, do not show so high homogeneity, as follows from Table 1 and Fig. 2. The products contain primary particles of nanometric size and a much higher number of aggregates (to 1 μm) and agglomerates (above 1 μm) (Jesionowski, 2001; Żurawska et al., 2002). This conclusion is confirmed by SEM images, see Fig. 2c,d. There is a substantial difference between silicas (nonpolar medium and polar medium), the particles of the silica precipitated in a nonpolar medium are spherical, similarly as those of silica (sol–gel method), while the particles of the silica obtained in a polar medium have irregular shapes. The dispersive–morphological properties of biocomposites made of unmodified silica and Kraft lignin are comparable. The samples of biocomposites contain primary particles and larger agglomerate structures. With increasing content of lignin the amount of agglomerates increases, as shown by the data from both analysers, but mainly by those from Mastersizer 2000. The parameters d(0.5) and d(0.9) describing the percentage contribution of particles of certain diameters increase. It should be mentioned that the commercial Kraft lignin used in the study contains particles of sizes representing a wide range, which indicates a possibility of formation of large agglomerates. The particle size distribution according to volume contribution reveals the presence of three bands covering the following ranges of particle diameters 220–459 nm, 712–2670 nm and 3580–5560 nm.

3.1.2. Elemental analysis

According to the results of elemental analysis, there are very small differences in composition of the silica samples (Table 2). The elemental contents of carbon and hydrogen are as expected, only in the sample precipitated in a nonpolar medium they are a bit higher (biocomposite 4–6), which can be related to the type of solvent used and not to the presence of unreacted lignin in molecular form. The theory has been confirmed by the results from XPS and FT–IR spectroscopy studies. The elemental compositions of silica/lignin biocomposites some what greater differences depending on the silica used. The greatest increase in the percentage content of the elements analysed is noted for the products obtained with silica precipitated in a nonpolar or polar medium. The presence of lignin having carbon and hydrogen in its composition is bound to be reflected in increased percentage contents of these elements in biocomposites so the results are as expected and confirm effectiveness of the biocomposites formation. The biocomposites were found to contain some small amounts of sulphur, increasing with growing concentration of lignin, which is explained by the presence of trace amounts of this element in the commercial Kraft lignin used in the study.

3.1.3. FT–IR and XPS spectroscopy

Measurements made by FT–IR and XPS methods confirmed the effective mode of binding between silica and lignin leading to formation of the final silica/lignin biocomposite. Detail investigation was performed for each type of silica obtained in this study and Kraft lignin. Moreover, the measurements were performed for silica/lignin composites containing 20 weight parts of lignin per 100 weight parts of SiO_2 samples obtained by each of the methods

Table 1
Dispersive characteristic of unmodified silicas and silica/lignin biocomposites.

Sample name	Type of SiO$_2$ synthesis	Content of Kraft lignin in relation to the unmodified silica matrix (wt./wt.)	Dispersive properties				
			Particle size distribution from Zetasizer NanoZS (nm)	Particle diameter from Mastersizer 2000 (μm)			
				d(0.1)	d(0.5)	d(0.9)	D[4.3]
Unmodified silica	Sol–gel method	–	190–615 4800–5560	5.7	12.1	22.6	13.3
Biocomposite 1		3	295–342 1110–5560	4.0	11.4	20.3	11.2
Biocomposite 2		20	220–459 2670–5560	3.9	9.2	19.3	10.1
Biocomposite 3		50	164–459 2300–5560	4.1	11.7	30.7	14.8
Unmodified silica	Nonpolar medium	–	122–220 2300–5560	4.1	17.3	39.8	19.9
Biocomposite 4		3	79–106 1280–4150	4.1	16.1	39.2	19.4
Biocomposite 5		20	79–106 955–4800	4.5	22.6	54.7	26.6
Biocomposite 6		50	79–142 825–4150	6.4	27.3	55.6	29.7
Unmodified silica	Polar medium	–	44–59 1110–5560	4.6	19.4	43.3	22.1
Biocomposite 7		3	91–122 220–295 1480–5560	4.6	16.9	37.3	19.2
Biocomposite 8		20	79–122 1720–4150	4.5	19.4	42.2	21.7
Biocomposite 9		50	79–142 1280–4150	5.2	23.1	48.4	25.4

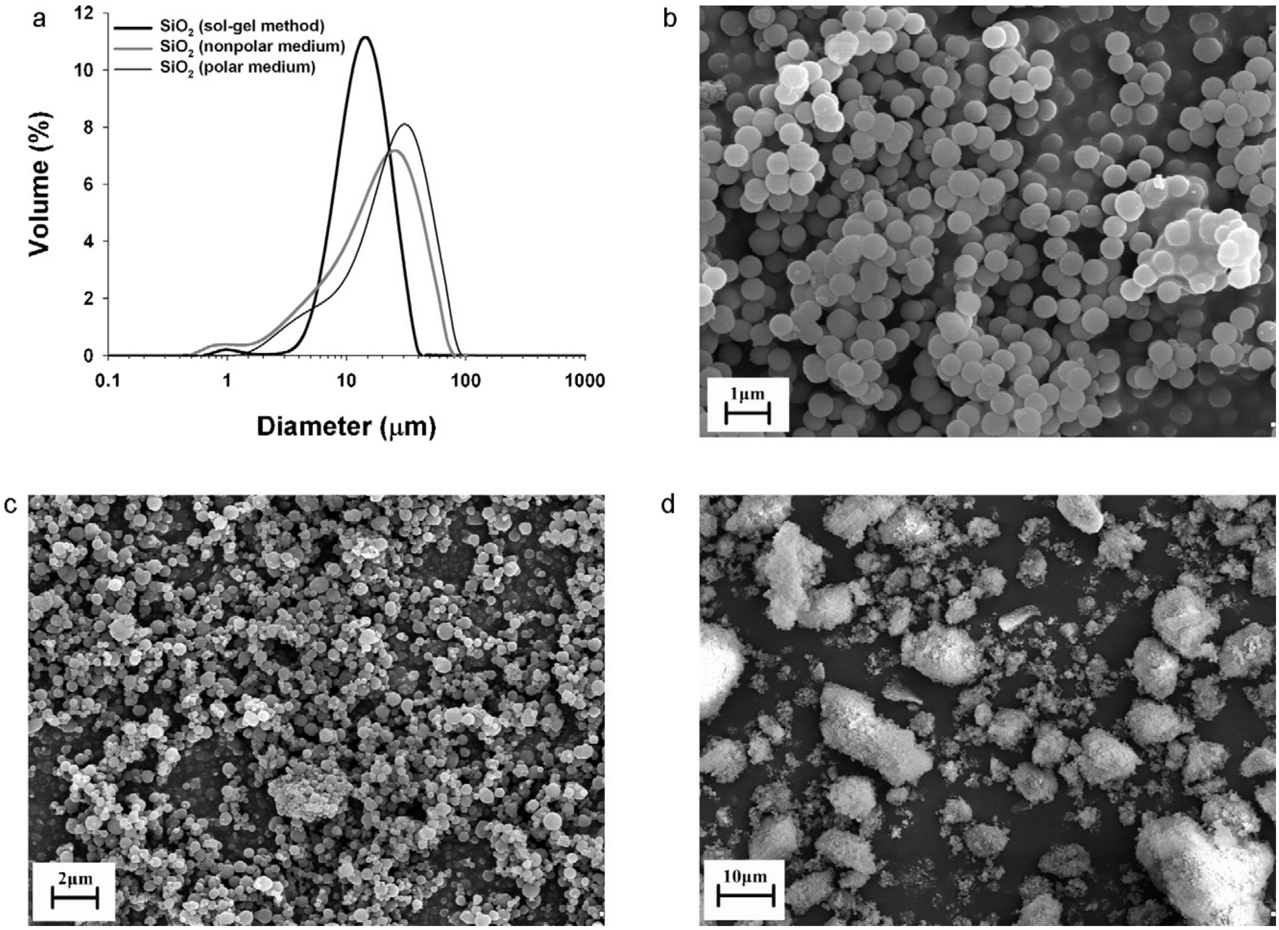

Fig. 2. (a) Particle size distributions by volume and SEM images of unmodified silicas obtained by (b) sol–gel method, (c) in nonpolar medium and (d) in polar medium.

Table 2
Elemental content of carbon, hydrogen and sulphur in unmodified silicas and silica/lignin biocomposities.

Sample name	Type of SiO_2 synthesis	Content of Kraft lignin in relation to the unmodified silica matrix (wt./wt.)	Elemental content (%)		
			C	H	S
Unmodified silica	Sol–gel method	–	0.15	1.30	–
Biocomposite 1		3	2.13	1.35	0.09
Biocomposite 2		20	5.94	1.49	0.40
Biocomposite 3		50	6.75	1.63	0.58
Unmodified silica	Nonpolar medium	–	2.62	1.89	–
Biocomposite 4		3	4.85	2.09	0.14
Biocomposite 5		20	7.95	2.24	0.50
Biocomposite 6		50	12.58	2.29	0.90
Unmodified silica	Polar medium	–	0.31	1.28	–
Biocomposite 7		3	1.56	1.37	0.14
Biocomposite 8		20	5.01	1.53	0.50
Biocomposite 9		50	10.56	1.86	1.03

proposed. As the results obtained for the products based on different types of silica were very similar, we decided to present only those for the silica obtained by the sol–gel method.

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. Fig. 3 presents the FT–IR spectrum of silica obtained by the sol–gel method and Kraft lignin (precursors of biocomposites) and SiO_2/lignin biocomposites containing 20 weight parts of lignin per 100 weight parts of silica (sol–gel method). The spectrum of SiO_2 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 (Hou et al., 2010). The other bands, that is the one corresponding to stretching vibration O—H (3600–3200 cm^{-1}) and a low-intensity one at ~1630 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 (3600–3200 cm^{-1}), stretching vibrations C—H (2960–2835 cm^{-1}), stretching vibrations of ketone group C=O (1710–1550 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 (González Alriols, Garcia, Llano-ponte, & Labidi, 2010; Tejado, Peña, Labidi, Echeverria, & Mondragon, 2007).

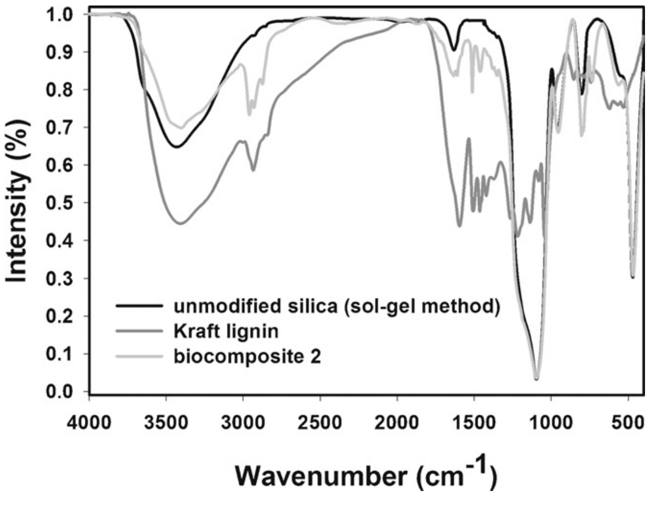

Fig. 3. FT–IR spectra of unmodified silica (sol–gel method), Kraft lignin and selected silica/lignin biocomposite.

The FT–IR spectrum of SiO_2/lignin biocomposites confirms the effectiveness of the proposed method of synthesis. It is associated with an increase in the intensity of the bands assigned to the appropriate functional group compared to the unmodified silica spectrum.

Chemical structure of unmodified silica, Kraft lignin and silica/lignin biocomposite were also studied by XPS spectroscopy (Fig. 4). XPS can yield information on the chemical structure of surface and the presence of defects and has been routinely used to follow different modification procedures. Basically, the information obtained is consistent with the results of elementary analysis and FT–IR spectroscopy.

It is rather obvious that unmodified SiO_2 consist mostly of silicon as evidenced by the sharp Si2p peak at binding energy (BE) of ca. 103 eV and Si2s peak at BE of ca. 150 eV, with a large amount of oxygen (the O1s peak at BE of ca. 533 eV). Analysis of the XPS spectra of Kraft lignin revealed a peak at C1s at BE close to 285 eV and a characteristic peak O1s at BE of 533 eV (Milczarek & Ciszewski, 2012). Next, the formation of a biocomposite with lignin results in a remarkable enhancement of the carbon signal as expected (compared to the unmodified silica). Analysis of XPS spectra of the precursors (silica and Kraft lignin) evidenced unambiguously a chemical bonding between SiO_2 and lignin leading to composite formation and confirmed the absence of molecular forms of the starting components. Fig. 4b presents a high-resolution XPS spectrum of an exemplary silica/lignin biocomposite (biocomposite 2), which is a magnified part of the spectrum presented in Fig. 4a in the fragment corresponding to the binding energy of C1s. Table 3 presents results of a quantitative analysis of elements composition and relative percent content of different types of carbon atom bonds. The results refer not only to the final composite but also to the unmodified precursors (unmodified silica and lignin). In the biocomposite the number of C=O, O—C—O and O=C—O bonds was greater than in Kraft lignin. This result was a subsequent proof for the chemical affinity of lignin to silica surface, consistent with the results obtained by FT–IR spectroscopy and elemental analysis.

3.1.4. Electrokinetic properties

The influence of pH on the surface charge and stability of the silica/lignin composites obtained was determined on the basis of zeta potential measurements. The measurements were performed in a 0.001 M solution of NaCl of pH varied from 1.7 to 11. Fig. 5 presents the electrokinetic curves of the unmodified silica samples, Kraft

Table 3
Surface composition and relative concentration of different bonds of carbon atoms obtained by the XPS analysis of unmodified silica, lignin and selected biocomposite.

Sample name	C (%)	O (%)	Si (%)	C1 (%) C—C/C—H	C2 (%) C—O—	C3 (%) C=O, O—C—O	C4 (%) O=C—O
Unmodified silica (sol–gel method)	1.19	49.36	49.45	Minimum content			
Kraft lignin	58.48	34.54	–	60.85	35.55	2.03	1.57
Biocomposite 2	28.83	33.22	26.88	56.50	23.03	9.56	10.91

lignin and the biocomposites obtained by surface functionalisation of SiO_2 with 3, 20 and 50 wt./wt. of Kraft lignin.

The results presented in Fig. 5 imply that colloidal silica forms highly stable dispersions. SiO_2 has the isoelectric point (i.e.p.) at pH from the range 1.7 to 2. The i.e.p. value can show small differences depending on the method of silica synthesis, conditions of its storage or its surface properties (Jesionowski, 2005; Xu, Zhang, & Shong, 2003), which was confirmed by the results obtained in this study. The silicas obtained by precipitation in a nonpolar medium ($pH_{i.e.p.}$~2) (Fig. 5b) or polar medium ($pH_{i.e.p.}$~1.7) (Fig. 5c) have similar electrokinetic properties described by negative zeta potential in the whole pH range analysed. This character of electrokinetic curves follows from the fact that silica dispersed in water solutions has positive charge in a strongly acidic environment (pH < 1), while at pH higher than i.e.p it has high negative values of zeta potential, which is caused by increased dissociation of silanol groups on the SiO_2 surface. The reactions of dissociation can be written as (Binner & Zhang, 2001):

$$\text{pH} > \text{i.e.p.} \quad \text{Si—OH} = \text{Si—O}^- + \text{H}^+ \tag{2}$$

$$\text{pH} < \text{i.e.p.} \quad \text{Si—OH} + \text{H}^+ = \text{Si—OH}_2{}^+ \tag{3}$$

The pH range of high resistance against aggregation, that is high stability for silica is from 7 to 11, although the silica precipitated in a nonpolar medium shows a better stability and is characterised by zeta potential from 1 to -55 mV in the entire pH range considered. For pH higher than 11, the zeta potential decreases again because of the compression of the double electric layer. The electrokinetic curve recorded for the silica obtained by the modified Stöber method is significantly different (Fig. 5a). As the value of i.e.p. almost always coincides with the point of zero charge (pzc) found by potentiometric titration, the surface charge of SiO_2 changed from negative to positive at pH close to 4.5, which has also been observed in (Szekeres, Dékány, & De Keizer, 1998; Kosmulski, 2009). The positive charge of SiO_2 surface below $pH_{i.e.p.}$~4.5 is not typical of silica surface but is a consequence of the presence of some small amount of $—NH_3{}^+$ incorporated into the silica network, which is related to this particular method of synthesis.

The electrokinetic curve estimated for Kraft lignin suggests its tendency to reach i.e.p. at pH of 1, which means that the density of lignin surface charge gradually decreases with decreasing pH. Kraft lignin has negative surface charge almost in the entire pH range studied. The charge appears as a consequence of ionisation of the surface hydroxyl and acidic groups as a result of their dispersion in water solution. In Kraft lignin H^+ and OH^- ions contribute to potential appearance. Dong, Fricke, Moudgil, & Johnson, 1996, have proposed a simple mechanism leading to the appearance of the initial surface charge on Kraft lignin *(4)*:

$$R(OH)_x + {}_xH_2O \rightarrow (O^-)_xR(OH)_{n-x} + x(H_3O^+) \tag{4}$$

and they have described the influence of pH on zeta potential (5,6):

$$[O^-]_x[R][OH]_{n-x} + yOH^- \rightarrow [O^-]_{x+y}[R][OH]_{n-(x+y)} + yH_2O \tag{5}$$

$$[O^-]_x[R][OH]_{n-x} + zH^+ \rightarrow [O^-]_{x-z}[R][OH]_{n-x+z} \tag{6}$$

where: R, the main chain of lignin molecule; OH, hydroxyl group; n, total number of OH groups; x, y, z, total interactions between the hydroxyl groups on the lignin surface and the H^+ and OH^- ions in water.

Kraft lignin is highly stable for pH from 3 to 11. The electrokinetic properties of lignin are similar to those of unmodified silicas (nonpolar and polar medium), but lignin is characterised by much higher negative values of zeta potential so also by a greater pH range of stability (Dong et al., 1996).

According to the electrokinetic curves of silica/lignin biocomposites based on unmodified silica, these samples are characterised by negative values of zeta potential. With increasing content of lignin the electrokinetic curve is shifted towards lower zeta potential, which additionally confirms the effectiveness of the method of silica functionalisation with lignin. All silica/lignin biocomposites, irrespective of the type of silica used, show high stability for pH

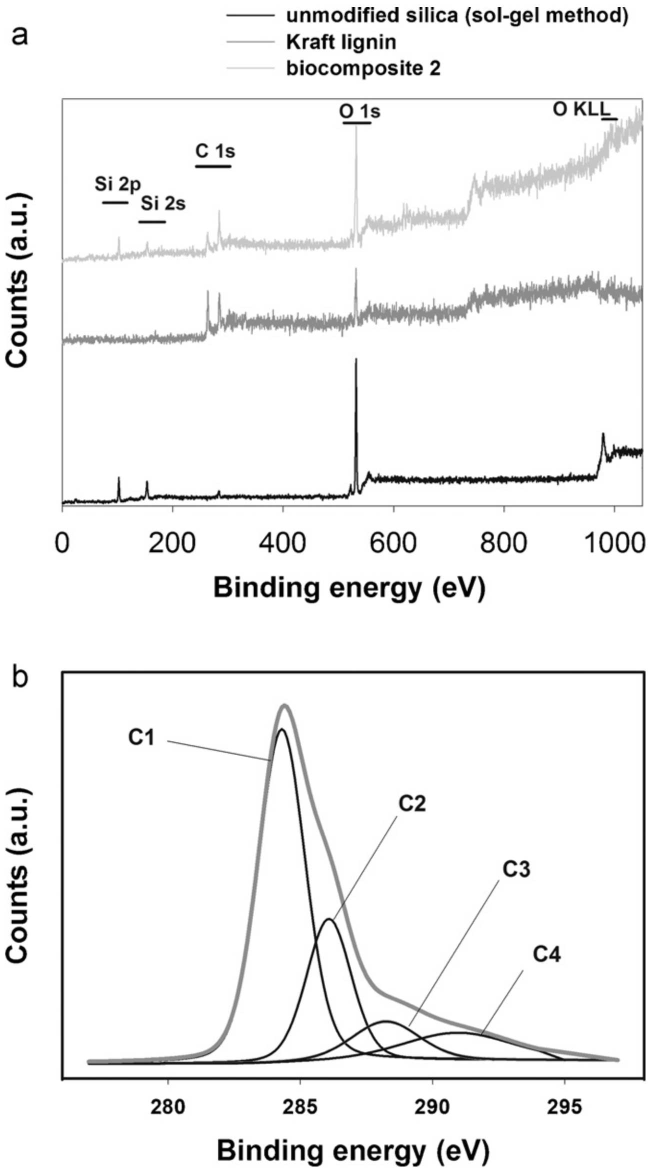

Fig. 4. (a) XPS survey spectra of unmodified silica (sol–gel method), Kraft lignin and selected SiO_2/lignin biocomposite; (b) C1s band deconvoluted into components in biocomposite.

from 1 to 11. This observation means that increase in the content of lignin per 100 weight parts of SiO_2 has beneficial effect on the biocomposite stability, which extends the application range of the final products.

3.2. SiO_2/lignin biocomposites obtained with preliminary modified silica

3.2.1. Dispersive and morphological properties

The relevant data characterising dispersive and morphological properties of biocomposites based on preliminary modified silica and determined by measurements with Zetasizer Nano ZS and Mastersizer 2000 are presented in Table 4.

The results do not differ significantly from those obtained for the composites based on unmodified silica (Table 1). Modification of silica with aminosilane enhanced the surface activity of the support leading to increased affinity with the preliminary oxidised lignin. It is important that with increasing content of lignin in the silica matrix, formation of secondary agglomerates takes place, deteriorating the homogeneity of the samples. Good dispersive–morphological properties were shown by the composites containing 20 wt./wt. of lignin in the matrix. A detail comparison of the biocomposites made of silica obtained by the three methods mentioned above modified with 20 wt./wt. of lignin is given in Fig. 6. As follows from the data, biocomposite 11 is the most homogeneous. The particle size distributions for biocomposite 14 and 17 show two bands, indicating increasing tendency towards agglomerate formation. Mastersizer 2000 results showed that 50% of biocomposite 11 volume is taken by particles of diameters below 9.9 μm, 50% of sample biocomposite 14-by particles of diameters to 20.1 μm, and 50% of biocomposite 17 volume by particles of diameters to 21.4 μm. Analysis of SEM images confirmed the presence of separate primary particles that are gradually joined to form aggregates (to 1 μm) and agglomerates (above 1 μm). The above observations are confirmed by the results obtained by Zetasizer Nano ZS (Table 4).

No significant changes were noted in the dispersive–morphological properties of the composites based on unmodified silica and that preliminary modified with aminosilane. The best properties were obtained for the products based on silica modified with aminosilane and lignin in the amount of 3 wt./wt. and 20 wt./wt.

3.2.2. Elemental analysis

Table 5 presents results of elemental composition of silicas preliminary modified with aminosilane and composites based on these silica samples and lignin.

Preliminary functionalisation of the silica surface with aminosilane brought the appearance of nitrogen at a level of 0.44–0.61%, depending on the method of SiO_2 synthesis, which is related to the presence of this element in the aminosilane. Besides the appearance of nitrogen, no significant differences were noted in the percentage content of the other elements in all samples of modified silica. The elemental analysis of silica/lignin biocomposites, irrespective of the method of silica synthesis, an increase in the content of carbon, hydrogen and sulphur was noted with increasing wt./wt. amount of lignin. The highest percentage content of these three elements was found in samples biocomposite 12 (C = 7.11%, H = 1.78%, S = 0.65%), biocomposite 15 (C = 13.05%, H = 2.39%, S = 1.05%) and biocomposite 18 (C = 11.33%, H = 1.93%, S = 1.03%), so in the samples containing the greatest amounts of lignin. The results obtained are in agreement with expectations. Moreover, much higher content of these elements in products in comparison to their presence in the analogous products based on unmodified silicas (Table 2) confirms the effectiveness of preliminary modification with aminosilane. The increase in the content of sulphur is related to its presence in Kraft

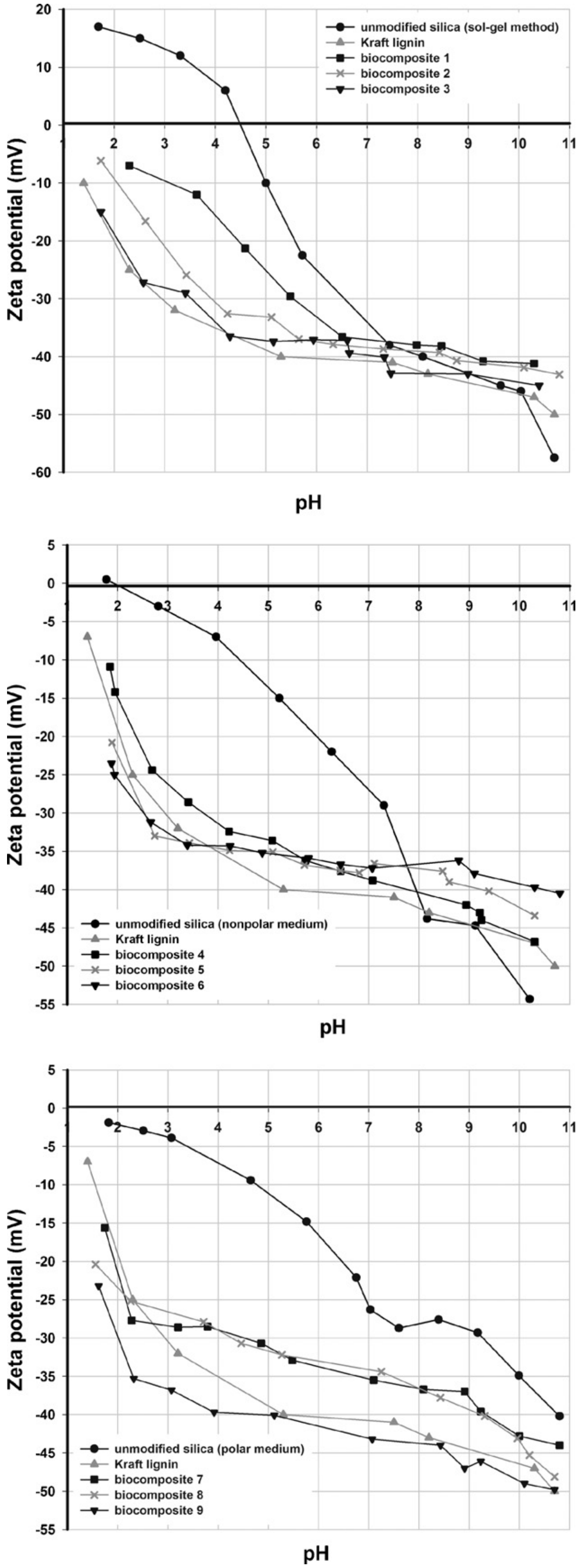

Fig. 5. Zeta potential vs. pH of the unmodified silica samples, Kraft lignin and SiO_2/lignin biocomposites.

Table 4
Dispersive characteristic of modified silicas and silica/lignin biocomposites prepared on the basis of silicas modified with 5 weight parts by mass of aminosilane.

Sample name	Type of SiO_2 synthesis	Content of Kraft lignin in relation to the silica matrix modified with aminosilane (wt./wt.)	Dispersive properties: Particle size distribution from Zetasizer Nano ZS (nm)	Particle diameter from Mastersizer 2000 (μm)			
				d(0.1)	d(0.5)	d(0.9)	D[4.3]
Modified silica	Sol–gel method	–	164–712 4150–5560	7.2	14.2	25.8	15.4
Biocomposite 10		3	220–396 825–1110 4800–5560	6.1	12.3	22.2	13.2
Biocomposite 11		20	142–295 3090–5560	4.0	9.9	21.9	11.7
Biocomposite 12		50	106–342 615–1280 1990–5560	4.7	13.7	35.6	17.5
Modified silica	Nonpolar medium	–	79–122 295–459 1110–3580	4.7	19.8	40.4	21.7
Biocomposite 13		3	79–122 825–4150	4.2	16.8	35.7	18.7
Biocomposite 14		20	79–142 531–712 1110–3580	3.2	20.1	47.0	22.8
Biocomposite 15		50	68–122 531–2670	4.7	24.6	53.3	27.5
Modified silica	Polar medium	–	59–105 1480–5560	5.7	22.7	47.8	25.1
Biocomposite 16		3	44–79 1280–4800	4.4	16.1	34.2	18.0
Biocomposite 17		20	68–122 712–1480 2670–5560	4.9	21.4	44.2	23.4
Biocomposite 18		50	68–106 459–4150	5.0	22.8	48.1	26.1

lignin used in the study and does not cause deterioration of the final products quality.

3.2.3. FT–IR and XPS spectroscopy

At the second stage of the study, the unmodified silica was subjected to preliminary functionalisation and then in the modified form it was used for the synthesis of final composites. The modification was performed to increase the surface activity of SiO_2 to facilitate the binding with lignin, which was evidenced by FT–IR and XPS results. The presence of certain functional groups in the samples studied was concluded on the basis of the FT–IR spectra. Fig. 7 presents the FT–IR spectra of silica modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, pure Kraft lignin and silica/lignin biocomposites containing 20 weight parts of lignin per 100 weight parts of SiO_2 (Stöber method) modified with aminosilane. In the spectrum of silica modified with aminosilane, the intensity of O—H band insignificantly increases (compared to that recorded for unmodified silica). This increase could be a result of overlapping of the stretching vibrations of N—H groups coming from the modifier used. The appearance of a low-intensity band at 1650–1560 cm^{-1}, assigned to the bending vibration of N—H, confirms the success of the surface modification with aminosilane.

In the range 2965–2850 cm^{-1} there is a band assigned to the stretching vibrations of C—H bond. The intensity of this band increased in comparison with that recorded for unmodified silica (Fig. 3) and then gradually increased with increasing content of lignin content in the biocomposite evidencing the chemisorption and/or physisorption of lignin on the surface of silica. Increase in the intensity of the other bands and the appearance of new ones confirm the effectiveness of the method proposed for the synthesis of silica/lignin biocomposite.

Fig. 8 presents the XPS results for selected samples. For modified silica the N1s spectrum show an intense peak at 398.7 eV and a weak shoulder peak at 399.9 eV. The low binding energy originates from the free amines ($—NH^{-}$ and $—NH_2$) and the high

Table 5
Elemental content of nitrogen, carbon, hydrogen and sulphur in silicas modified with aminosilane and silica/lignin biocomposities.

Sample name	Type of SiO_2 synthesis	Content of Kraft lignin in relation to the silica matrix modified with aminosilane (wt./wt.)	Elemental content (%): N	C	H	S
Modified silica	Sol–gel method	–	0.44	1.46	1.59	–
Biocomposite 10		3	0.37	2.53	1.49	0.11
Biocomposite 11		20	0.34	6.23	1.67	0.46
Biocomposite 12		50	0.26	7.11	1.78	0.65
Modified silica	Nonpolar medium	–	0.57	2.87	2.02	–
Biocomposite 13		3	0.41	5.01	2.19	0.16
Biocomposite 14		20	0.33	8.20	2.31	0.54
Biocomposite 15		50	0.29	13.05	2.39	1.05
Modified silica	Polar medium	–	0.61	1.44	1.48	–
Biocomposite 16		3	0.44	2.60	1.47	0.18
Biocomposite 17		20	0.40	6.70	1.75	0.57
Biocomposite 18		50	0.31	11.33	1.93	1.03

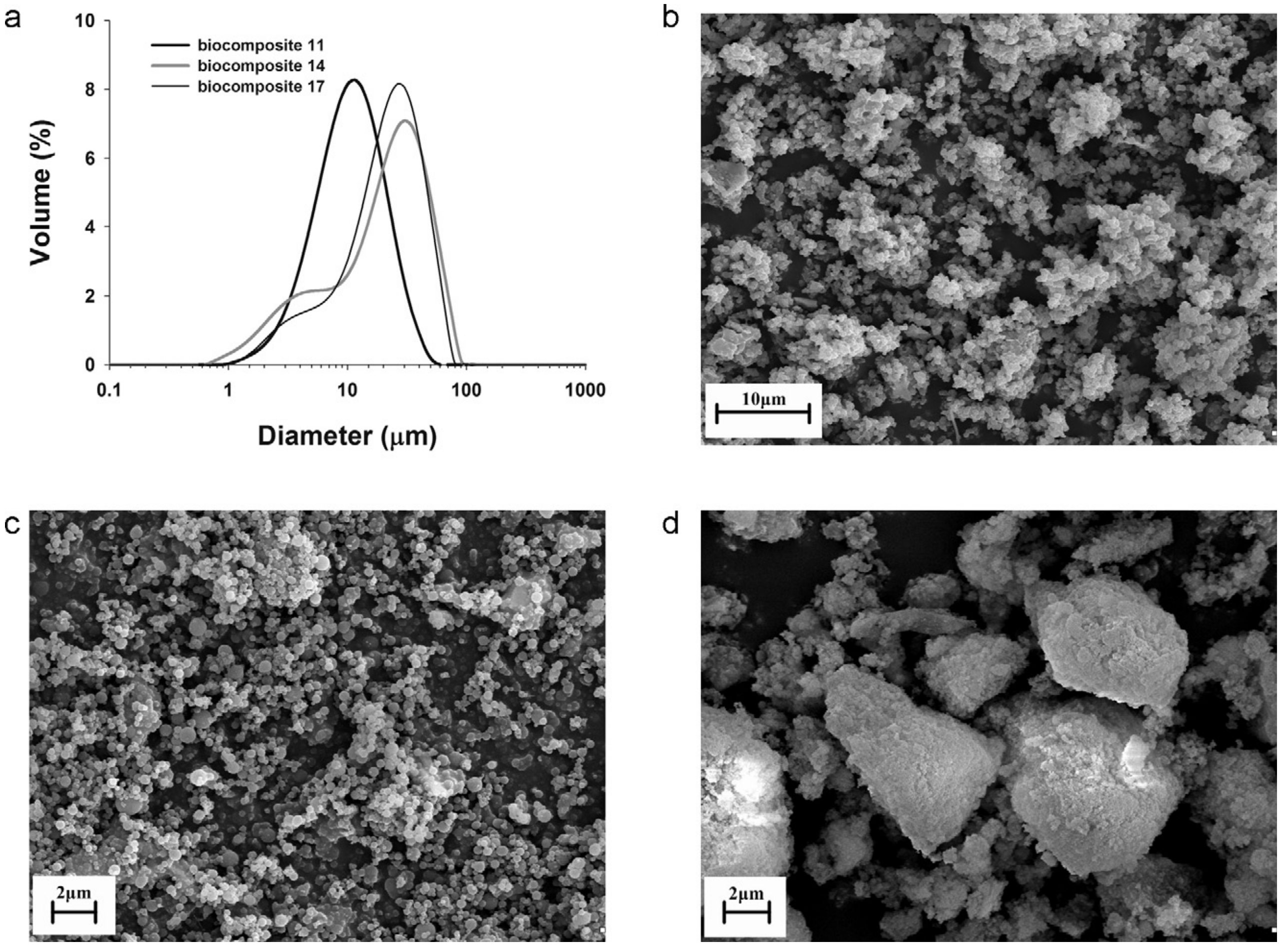

Fig. 6. (a) Particle size distributions by volume and SEM images of silica/lignin biocomposites containing 20 weight parts of lignin per 100 weight parts of appropriate silicas matrix.

Table 6
Surface composition and relative concentration of different bonds of carbon atoms obtained by the XPS analysis of modified silica, lignin and selected biocomposite.

Sample name	C (%)	O (%)	N (%)	Si (%)	C1 (%) C—C/C—H	C2 (%) C—O—	C3 (%) C=O, O—C—O	C4 (%) O=C—O
Modified silica (sol–gel method)	27.70	30.59	9.85	31.86	90.50	9.50	–	–
Kraft lignin	58.48	34.54	–	–	60.85	35.55	2.03	1.57
Biocomposite 11	58.34	34.78	1.33	5.54	63.52	27.13	5.83	3.53

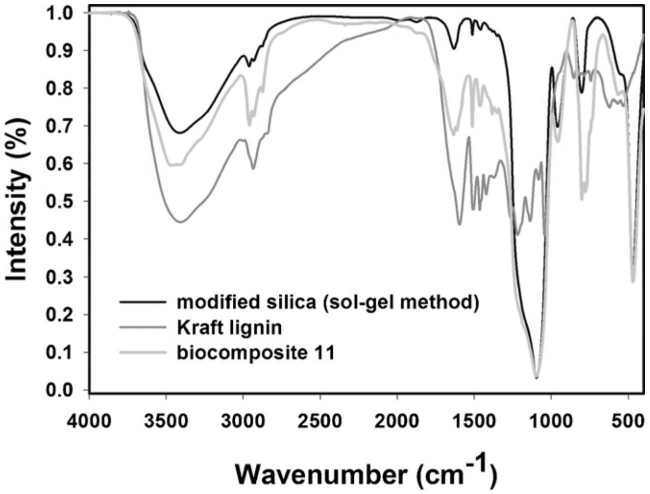

Fig. 7. FT–IR spectra of aminosilane–grafted silica (sol–gel method), Kraft lignin and selected silica/lignin biocomposite.

binding energy comes from the protonated amines (—NH_3^+). The XPS results further confirmed that the reactive precursor was chemically immobilized onto the surface of silica particles through the —NH_2 groups of aminosilane anchored to silica, which has been also observed by the authors of (Gao et al., 2007). The XPS spectrum of the biocomposite confirmed the effectiveness of the synthesis performed, first of all evidenced by the enhancement of the peak C1s at BE close to 285 eV. From the point of view of the aim of this analysis it is important to consider the XPS spectrum of the biocomposite in the BE range of C1s bonds (Fig. 8b), the detail bond composition and relative percentage content of carbon bonds, presented in Table 6. These data imply that in the biocomposite the percentage content of carbon–oxygen bonds increases, which points to a chemical bonding of lignin with the modified silica. This bonding is realised directly through amine groups form the modifier applied.

The data presented in Table 6 also confirm the effectiveness of the process of silica modification with aminosilane by showing an increase in the percentage content of nitrogen with respect to that established for unmodified silica. This result is consistent with those of FT–IR spectroscopy and elemental composition. Similar

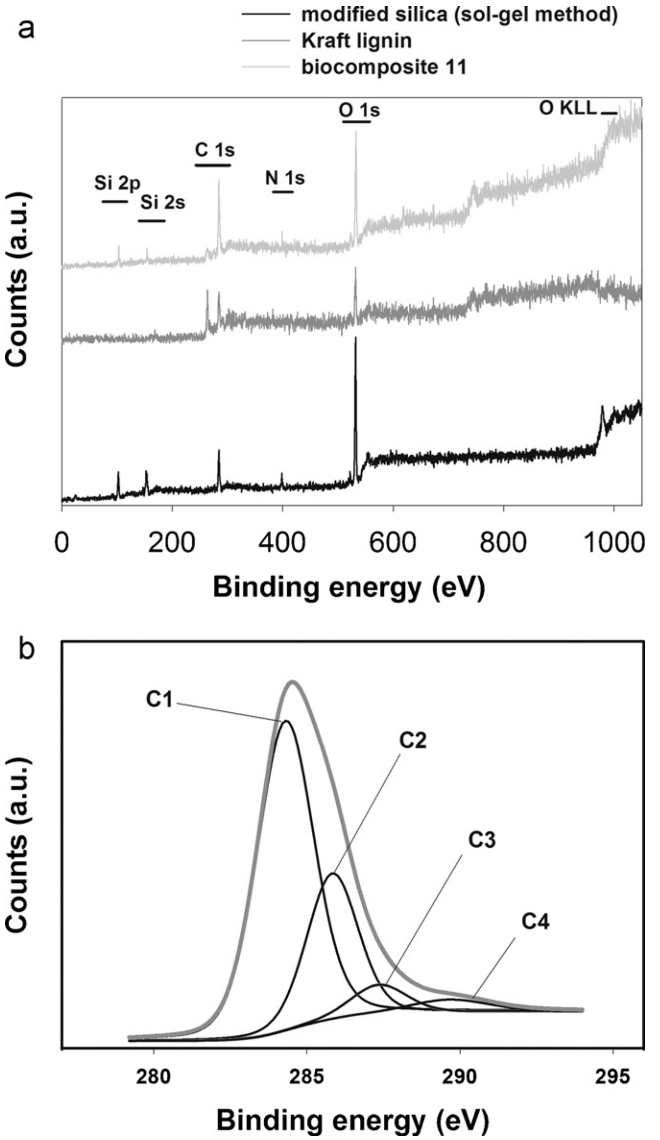

Fig. 8. (a) XPS survey spectra of aminosilane–functionalised silica (sol–gel method), Kraft lignin and selected SiO_2/lignin biocomposite; (b) C1s band deconvoluted into components in biocomposite.

results were obtained for the other two types of silica and for the biocomposites based on them. The above analysis was described for the silica obtained by the sol–gel method (Stöber silica) just to illustrate the way of proving the effective bonding between silica and lignin to get a final biocomposite.

3.2.4. Electrokinetic characteristics

The–OH groups present on the silica surface permit attachment of trialkoxysilanes functionalised with such functional groups as amine ($-NH_2$) or mercaptan ($-SH$) via covalent bonding. Besides organosilanes, also individual atoms or polymers can be used as modifiers (Jankiewicz, Jamioła, Choma, & Jaroniec, 2012). Different functional groups present in the modifying substance significantly influence the zeta potential of modified samples, extending the range of their applications. Fig. 9 presents the electrokinetic curves recorded for silicas modified with 5 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane and for SiO_2/lignin biocomposites based on the preliminary modified silica supports.

Modification of the silica surface results in a clear shift of the electrokinetic curve of SiO_2 towards higher pH values relative to

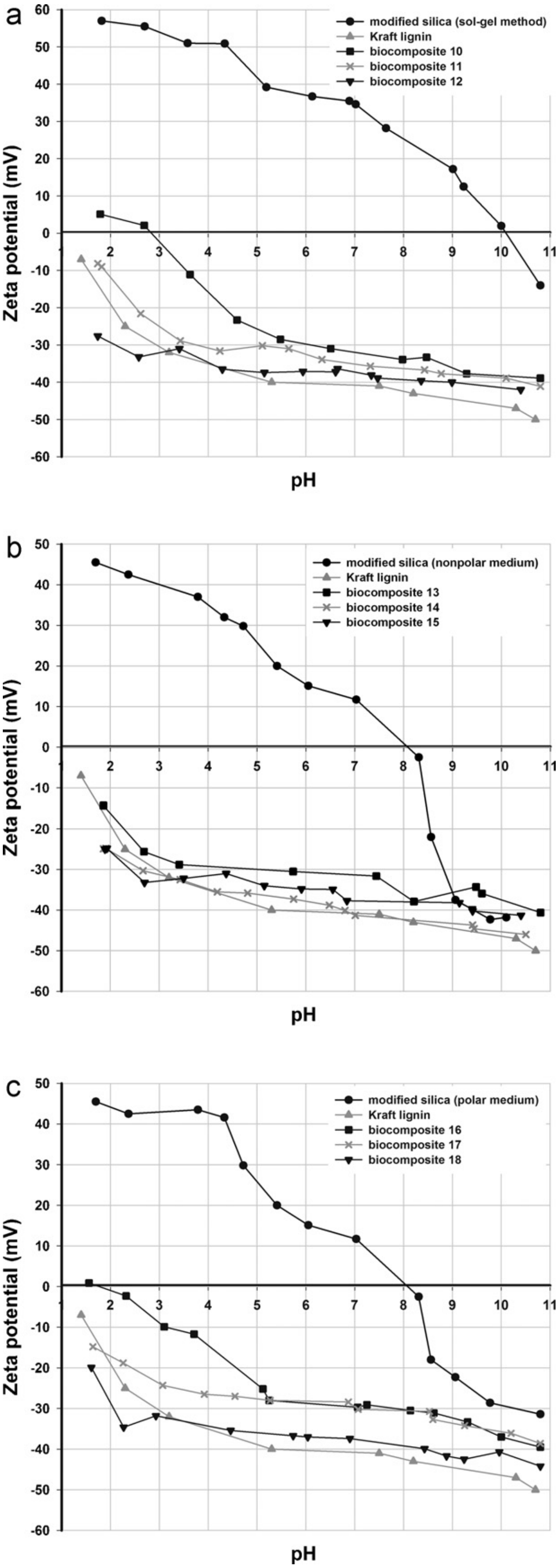

Fig. 9. Zeta potential vs. pH for silicas preliminary modified with aminosilane, Kraft lignin and SiO_2/lignin biocomposites.

those recorded for unmodified silica. This fact can be explained by ionisation of $-NH_2$ groups coming from the modifier molecules, important for changes in the surface charge. High density of H^+ ions generates $-NH_3^+$ groups so that the surface of modified silica has positive charge (protonisation effect). With increasing concentration of H^+ ions the process of ionisation is restricted and the surface charge is reduced (Jesionowski et al., 2010). The mechanism of SiO_2 surface modification with aminosilane has been proposed in earlier works (Jesionowski, Nowacka, & Ciesielczyk, 2012). Modification with amine compounds leads to high i.e.p. values of functionalised SiO_2, which is related to the basic properties of its surface. SiO_2 obtained by the sol–gel method shows positive values of zeta potential almost in the entire pH range analysed, reaching i.e.p. at pH close to 10 (Fig. 9a). Similar electrokinetic curves are obtained for the aminosilane modified silica obtained in the nonpolar and polar media, for which $pH_{i.e.p.} \sim 8$ (Fig. 9b, c). Additional functionalisation of the silica surface with 3, 20 or 50 wt./wt. of lignin leads to decreasing zeta potential (the decrease is more pronounced for increasing content of lignin), which is most probably caused by a high content of hydroxyl groups present in the lignin molecule. From the viewpoint of applications, the best pH range of stability was found for biocomposites obtained on silica synthesised in a polar medium (Fig. 9c). The products show zeta potential ranging from -30 to -45 mV for pH ranging from 3 to 11. In general, as follows from the results obtained for biocomposites, preliminary modification of silica with aminosilane has no significant effect on stability and electrokinetic properties of the final products when compared to those obtained for biocomposites based on unmodified silica.

4. Conclusions

Advanced composite materials consisting of silica and Kraft lignin may be novel biomaterials of important practical significance. Their particularly attractive feature for practical use its their stability, especially electrokinetic stability. The zeta potential values were found to be influenced by the character of surface of a given material. Modification of the SiO_2 surface with aminosilane significantly changed the pH range of stability of dispersed silica. Biocomposites obtained by the three methods of synthesis used were characterised by good electrokinetic properties, showing high negative values of zeta potential almost in the entire pH range studied. Preliminary functionalisation of silica with aminosilane had no significant effect on the character of electrokinetic curves of the final biocomposites. The effectiveness of the proposed method of silica surface modification was confirmed by results of elemental analysis (N, C, H, S), XPS and FT–IR spectroscopy. As evidenced by dispersive and morphological analysis, the amount of lignin used for obtaining the final biocomposites was found to significantly affect the homogeneity of the products. A general conclusion is that the results have confirmed the need for working on biocomposites of this type because of their potential use in science and industry.

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