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Production of cement composites using alumina-lignin hybrid materials admixture

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Abstract: In the framework of this study, Al_2O_3-lignin hybrid materials differing in terms of the weight ratio of the inorganic and organic components were designed and obtained. The method of mechanical grinding of ingredients with simultaneous mixing using a mortar grinder and a high-performance ball mill was used in order to obtain the above-mentioned systems. The effectiveness of obtaining alumina-lignin materials was confirmed using Fourier transform infrared spectroscopy (FTIR) and, indirectly, by the colorimetric analysis. FTIR analysis allowed to confirm that hydrogen bonds formed between the components and classify the resulting systems as I^{st} class hybrid materials. In the course of the conducted research, the relatively high thermal stability of the hybrid materials was also confirmed and the dispersion and morphological character (SEM) of the obtained systems was determined. Favourable physicochemical and microstructural evaluation allowed to qualify the alumina-lignin hybrid systems as functional admixtures for cement mortars. As part of the tests, it was confirmed that the presence of lignin in the cement composites contributes to the increase of the plasticity of the mixture. In turn, the inorganic component allowed to preserve (and, in case of selected systems, improve) the mechanical properties of the final composites. The most favourable results of application tests were obtained for alumina-lignin hybrid systems with weight ratios equal to 5:1 and 2:1. The analysis of these systems indicated that there is a clear improvement of mechanical properties, whit a simultaneous enhancement of the plasticity of the mixture in comparison to the reference sample.

Keywords: alumina, lignin, hybrid materials, cement composites

1. Introduction

Materials based on Portland cement, such as concrete, mortar, fibre reinforced composites and others, are widely used as building materials (Mendes et al., 2015). Simply put, concrete is a mixture of only three materials: cement, aggregates and water (Neville, 2011). A paste consisting of Portland cement and water binds the aggregates (usually sand and gravel or crushed stone) in a rock-like mass when the paste hardens due to the chemical reaction between cement and water (Kosmatka et al., 2002). The quality of concrete depends on the quality of the paste and aggregate, and the bonds between them. In a properly prepared concrete, every aggregate particle and all spaces between the aggregate particles are completely filled with the paste (Kosmatka et al., 2003). In order to improve certain properties of concrete, either in the fresh state or in the hardened state, very small amounts of chemical products known as admixtures are introduced into the mixture (Neville, 2011). Based on their function, admixtures for cement mortars can be classified as: aerating, plasticizing, reducing the amount of water, retarding, accelerating, controlling the hydration process. Other admixtures contribute to shrinkage compensation, colouring and inhibition of corrosion or alkaline-silica reactivity. In addition to the admixtures mentioned above, others which improve workability, binding, reduce permeability or

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facilitate pumpability are also increasingly common (Kosmatka et al., 2003). Limestone powder is one of many examples of admixtures for cement mortars, which is introduced to accelerate the hydration process, to obtain the effect of activation or change the particle surface morphology (Li et al., 2018; Wang et al., 2018). Admixture in the form of titanium dioxide has a significant impact on the self-cleaning ability of concrete, allows to achieve the initial strength more rapidly and increases the resistance of concrete to abrasion (Norhasri, 2017). Silica is also often used in admixtures. The advantages of using silica fume include high early compressive strength, tensile strength, bending strength and modulus of elasticity; increased durability and resistance to abrasion as well as very low permeability for the penetration of chlorides and water (Siddique and Khan, 2011). The initial and final compressive strength of cement composites can be also improved by metallic oxides (Ślosarczyk et al., 2017). Natural materials are also increasingly used as admixtures. An example includes lignin materials and their derivatives, which are used as agents for reducing the amount of water and admixtures which increase the plasticity of the cement mixtures (Huang et al., 2018; Arel, 2017). Lignin porous microspheres are also used as specific sorbents due to their high porosity and presence of numerous surface functional groups (Goliszek et al., 2018; Podkościelna et al., 2017; Sobiesiak et al., 2017). Despite the high amount of already existing materials used in the form of admixtures for cement mortars, the design and production of new materials is still gaining increasing attention. The possibility to design materials with unique, desirable properties increases the interest in hybrid materials, which have recently gained numerous applications in many fields of science and industry, including in the role of effective sorbents of environmentally harmful metals ion (Klapiszewski et al., 2015; Klapiszewski et al., 2017a), eco-friendly polymer fillers (Bula et al., 2015; Goliszek et al., 2019; Kickelbick, 2014; Thakur et al., 2014) or functional additives for abrasive tools (Klapiszewski et al., 2017b; Klapiszewski et al., 2019).

Following the trends in innovation, the authors of this article decided to design, obtain and determine the most important physicochemical properties of inorganic-organic alumina-lignin hybrid materials as admixtures for cement mortars. The authors expect that an inorganic additive will contribute to a beneficial effect on the mechanical properties and that the organic part will allow for the increase of plasticity of the prepared cement composites. It should be noted that the use of alumina-lignin hybrid materials as functional admixtures for cement mortars has not been reported to date in the literature.

2. Materials and methods

2.1. Preparation of alumina-lignin hybrid materials

In the framework of the study, hybrid materials with alumina (Imerys Fused Minerals Villach GmbH, Austria) and kraft lignin (Sigma Aldrich, Germany) were designed. The method of mechanical grinding of components using a RM100 mortar grinder (Retsch GmbH, Germany) was used to obtain them - the grinding process lasted for 1 h, after which the system was transferred to a Pulverisette 6 Classic Line (Fritsch GmbH, Germany) ball mill, in which further fragmentation and product homogenisation (the process was continued for another 1 h) was carried out. As a result, the final hybrid admixtures with the following composition of alumina:lignin (in parts by weight) were obtained - 5:1; 2:1; 1:1; 1:2 and 1:5.

2.2. Physicochemical and dispersive-morphological characteristics of alumina-lignin systems and pristine components

In order to confirm the efficiency of obtaining alumina-lignin hybrid materials, infrared spectroscopy with Fourier transformation was used. The test was performed using a Vertex 70 spectrophotometer, manufactured by Bruker, Germany. To perform this analysis, an appropriate product was prepared in the form of a pellet. For this purpose, 1 mg of the analyzed substance was weighed and triturated in a mortar together with 0.1 g of KBr, and then the mixture was pressed using a steel ring for 15 min at 10 MPa and subsequently analysed.

As part of the performed physicochemical analysis, the thermal stability of hybrid systems and pristine components was also determined. The tests were carried out using the Jupiter STA 449F3 device, from Netzsch GmbH, Germany. Measurement with the Jupiter device consisted of heating the appropriate sample mass in the temperature range of 30-1000 °C, with a step of 10 °C/min, under a nitrogen atmosphere.

The surface morphology as well as the shape and size of individual grains were examined using scanning electron microscopy. An EVO40 microscope, from Zeiss AG (Germany), was used for the study. The particle size analysis was carried out using Zetasizer Nano ZS and Mastersizer 2000, by Malvern Instruments Ltd. (UK), enabling particle size measurements in the range of 0.6-6000 nm and 0.2-2000 μm, respectively, using the non-invasive backscattering method of measurement of intensities of scattered light and laser diffraction.

The Specbos 4000 colorimeter (JETI Technische Instrumente GmbH, Germany) was used to measure the color of the materials. This apparatus determines the basic colors in the 0°/45° surface geometry and differentiates the tested powder materials in terms of even slight discrepancies occurring in the shades of color. In order to determine the basic color parameters, *CIE L*a*b**, system was used, which determines the coordinates of color in a very simple and understandable manner, as discussed in greater detail in the results section.

2.3. Preparation of cement composites with the use of Al_2O_3-lignin hybrid systems

Preparation of cement mortar composites included the preparation and addition of the following components of cement mortar to the Hobart mixer: 450 g cement (Portland CEM I 42.5R cement, (Gorażdże Cement SA, Poland), which included Portland clinker (95%) as the main component and setting time regulator (up to 5%)), 225 mL of water and properly designed hybrid admixtures or pristine components (in the amount of 0.5 wt.% and 1 wt.% in relation to the cement mass). The system was subjected to mixing at 140 rpm for 30 seconds, then 1350 g of standard quartz sand (Kwarcmix, Poland) designed for laboratory tests of cement strength was added, and the mixing rate was increased to 285 rpm for another 90 seconds. The finished mortar was transferred to standardized molds and performed mechanical tests. The curing time of the samples was equal to 28 days.

2.4. Properties of cement composites

2.4.1. Determination of the plasticity of the cement mortar

The test consisted of measuring and determining the spreading diameter of the tested samples and was carried out in accordance with the PN-EN 1015-3 standard. A flow table, a truncated cone shape and a steel rammer were used to perform the test. To determine the plasticity of cement mortars, the following course of action was used: (*i*) before the test, the surface of the tile was wetted; (*ii*) the mold was placed in the center of the plate; (*iii*) the test mortar was introduced into the mold in two layers - each layer was compacted as a result of a tenfold impact; (*iv*) the excess material was cut with a knife and the surface was smoothed (*v*) the mold was lifted vertically and the sample was shaken by turning a special crank at 1 rpm; (*vi*) after completion of this process, two diameters of plasticized grout and/or mortar were immediately measured (with an accuracy of 0.2 cm).

2.4.2. Determination of bending strength

The test was based on subjecting cement mortar samples with a rectangular shape and a size of 40 mm x 40 mm x 160 mm to bending with a loading force evenly increased by 50 ± 10 N/s until the sample was destroyed. The result of the test was the quotient of the maximum bending moment and the strength index of the cross-section of the beam, assuming that the linear elasticity of the concrete during the test is maintained. The bending strength of cement mortars was calculated based on formula (1):

$$R_f = \frac{1.5 \cdot F_f \cdot l}{b^3} \ (MPa) \tag{1}$$

where F_f is breaking load in the middle of the beam (N), l is distance between supports (mm) and b is side length of the beam section (mm).

The result of the bending strength test was given as the arithmetic mean of three measurements, rounded to 0.1 MPa.

2.4.3. Determination of compressive strength

The test was carried out using halves of the beams previously tested during bending strength tests. The half of the beam was placed in a special insert equipped with hardened steel square compressive plates, with a side of 40.0 ± 0.1 mm. The plates pressed the central part of the test beam. The load was evenly increased at a rate of 2.4 ± 0.2 kN/s until the sample was crushed. Compressive strength was calculated according based on formula (2):

$$R_c = \frac{F_c}{1600}\ (MPa) \tag{2}$$

where F_c is compressive force (N) and 1600 is surface of compression plates (40 mm x 40 mm).

The result of the compressive strength test was given as the arithmetic mean of three measurements, rounded to 0.1 MPa. Bending and compression strength tests were carried out using the Servo Plus Evolution testing machine from Matest®, Italy.

3. Results and discussion

3.1. Physicochemical and dispersive-morphological characteristics of alumina-lignin hybrid systems and pristine components

Fourier transform infrared spectroscopy analysis was conducted in order to confirm the efficiency of obtaining alumina-lignin hybrid materials (see Fig. 1). The spectra of the pristine components – alumina and lignin are presented in Fig. 1a, in turn, the spectra of the obtained inorganic-organic systems are presented in Fig. 1b.

In the spectrum obtained for pristine alumina, the following bands characteristic for this compound appear: the O-H stretching band in the wavelength range of 3600-3200 cm^{-1}, the O-H bending oscillation band originating from the water physically bound to the surface of the oxide with the maximum wavelength at 1618 cm^{-1} and bands, with wavenumbers below 1000 cm^{-1}, mainly 755 cm^{-1}, 695 cm^{-1}, 560 cm^{-1} and 483 cm^{-1} which were attributed to vibrations of Al-OH and Al-O groups, in which aluminium ions occupy both tetrahedral and octahedral sites (Klapiszewski et al., 2017b; Naskar, 2009).

In turn, analysis of the spectrum of pristine lignin confirmed the presence of the following vibrations of characteristic groups: stretching vibrations of O-H groups (3600-3200 cm^{-1}), stretching vibrations of C-H groups (CH_3 + CH_2 – 2960-2910 cm^{-1} and O-CH_3 – 2850-2835 cm^{-1}), stretching vibrations of carbonyl groups (1720-1565 cm^{-1}). The bands of C-C and C=C groups related to the aromatic structure of the biopolymer and the bands associated with the presence of C-O(H) and C-O(Ar) stretching vibrations (at the maximum at wavenumbers of 1375 cm^{-1}, 1270 cm^{-1}, 1210 cm^{-1}) appear subsequently in the spectrum. Furthermore, the band at 1040 cm^{-1} corresponds to the stretching vibration of the C-O-C groups. An important role in the lignin structure is also played by the vibrations of C-H groups, which are mainly visible at the wavenumbers below 1000 cm^{-1}. The obtained spectra coincide with data published in previously published papers (Klapiszewski et al., 2013; Klapiszewski et al., 2015; Wysokowski et al., 2014).

Based on the spectral analysis of inorganic-organic hybrid materials (see Fig. 1b) it can be concluded that the components are permanently bound, which is mainly related to the presence of characteristic functional groups derived from particular compounds in all spectra. The small shifts in the absorption maxima of the respective bands of functional groups in relation to the spectrum obtained for pristine precursors (alumina and lignin – Fig. 1a) are an additional confirmation of this fact. This clearly indicates the effective binding of the components and the formation of unstable hydrogen bonds between them and thus the creation of a class I hybrid material. When the materials are used as admixtures for cement mortars, unstable hydrogen bonds are sufficient, and the lack of strong chemical interactions affects the final properties of the final cementitious composites. The proposed mechanism of interactions in the alumina-lignin hybrid material is presented in Fig. 2.

Very important data were provided by the analysis of the thermal stability of the obtained hybrid systems and pristine components (for comparison). Thermogravimetric curves for all products are presented in Fig. 3.

The TGA curve for alumina indicates a low (2%) loss of product mass in a wide temperature range, which was mainly associated with the presence of water physically bound to the oxide surface

(Klapiszewski et al., 2017b). Lignin, on the other hand, has significantly lower thermal stability, which was confirmed by a relatively high loss, equal to 51%, of biopolymer mass in the analysed temperature range. In the first temperature range of 25-220 °C, elimination of water physically bound to the surface of the material (mass loss of ~10%) occurs, the next stage of significant mass loss (~35%) in the temperature range of 220-600 °C is concerns the complex thermal decomposition of the biopolymer related to the fragmentation of its structure as a result of unclear and uncontrollable reactions. Subsequently, beyond the temperature of 600 °C, the lignin is completely depolymerized, resulting in low molecular weight compounds (mass loss of ~6%). The previously published reports regarding the thermal stability of lignin are a confirmation of the above-mentioned dependencies (Bula et al., 2015; Klapiszewski et al., 2017b).

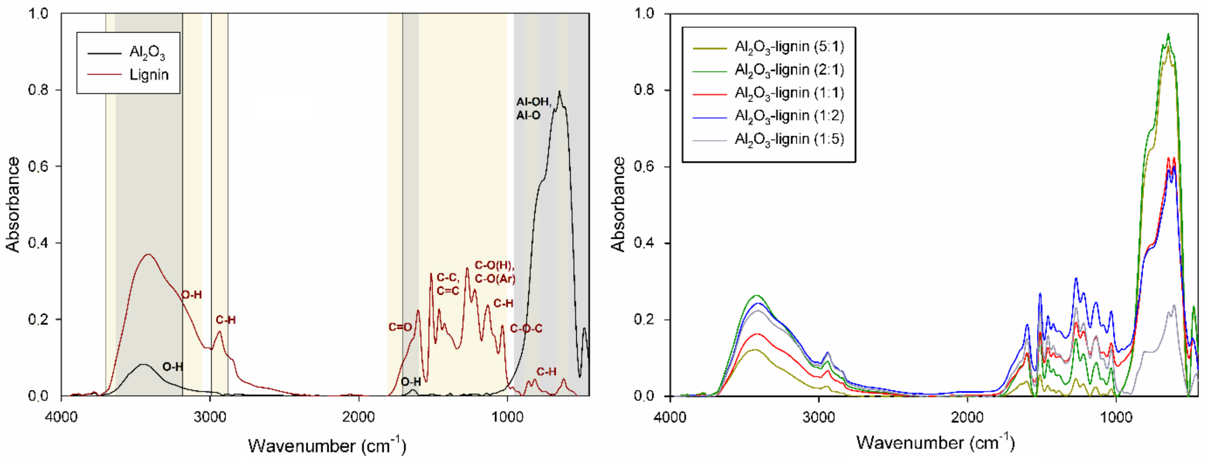


Fig. 1. FTIR spectra of alumina and lignin (a) and alumina-lignin hybrid materials (b)

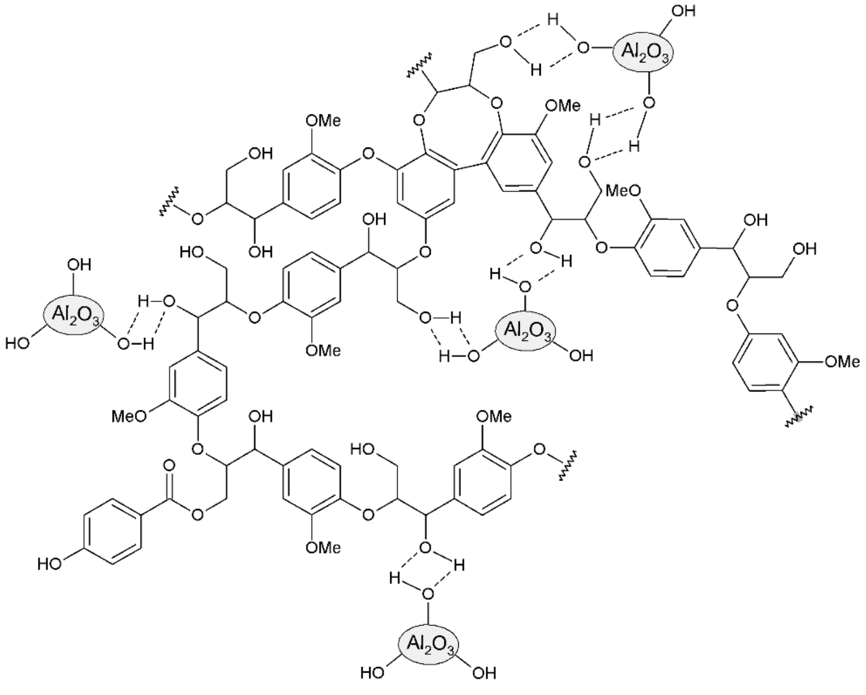


Fig. 2. The proposed mechanism of interactions in the alumina-lignin hybrid material

The obtained hybrid materials were characterized by relatively good thermal stability, depending on the ratio of the components used. The systems which contained higher ratio of the inorganic component were definitely more stable. As a result, the total mass loss of such products was equal to 11% (alumina-lignin 5:1 wt./wt.) and 21% (alumina-lignin 2:1 wt./wt.). The higher ratio of lignin in the system results in a deterioration of the thermal stability of final products, which can be observed in Fig. 3 - the total mass loss of such materials was equal to 38% (alumina-lignin 1:2 wt./wt.) and 47% (alumina -lignin 1:5 wt./wt.).

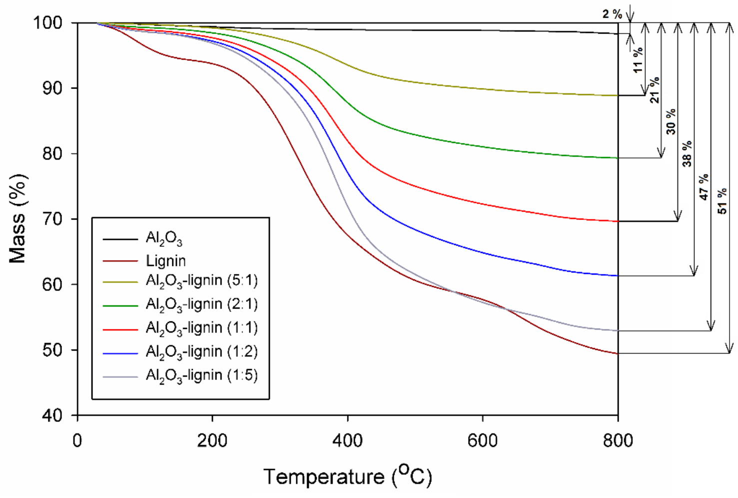


Fig. 3. TGA curves of pristine components and alumina-lignin hybrid materials

In the framework of the studies, the evaluation of dispersion and morphological characteristics of the hybrid materials was also carried out. The SEM images of alumina-lignin hybrid materials are presented in Fig. 4, which clearly confirm that as the ratio of the biopolymer relative to the inorganic component increases, the products tend to aggregate and agglomerate, and thus become less homogeneous. In case of alumina-lignin products with 1:2 and 1:5 weight ratios (Fig. 4e and 4f), the presence of a larger lignin structures is clearly visible, with smaller alumina particles building up on their surface, which are bound together by weak hydrogen bonds as demonstrated based on FTIR spectroscopy.

The data presented in Table 1, which include the particle size ranges obtained using the Zetasizer Nano ZS analyser and the most important dispersive parameters derived from the Mastersizer 2000 analysis, confirm these conclusions. Based on the analysis of the data presented in Table 1, an important conclusion emerges, which indicates that the increase of the ratio of lignin to alumina results in an increased occurrence of larger structures in the final product. According to the dispersion data, the pristine alumina was characterized by the highest homogeneity, with a particle size ranging from 342-2670 nm (data from the Zetasizer Nano ZS analyser), and the average particle size equal to 1.8 μm (data from Mastersizer 2000). In turn, lignin possesses a very wide particle size range, which is equal to

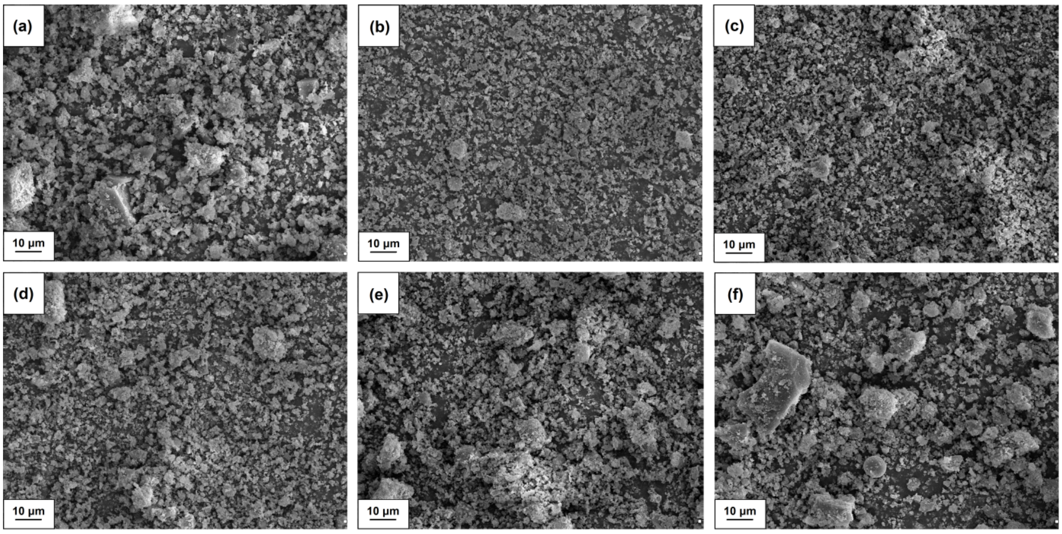


Fig. 4. SEM images of lignin (a) and alumina-lignin hybrid materials with the following weight ratios of the components: 5:1 (b), 2:1 (c), 1:1 (d), 1:2 (e) and 1:5 (f)

Table 1. Dispersive properties of alumina, lignin and alumina-lignin hybrid materials

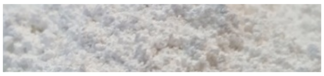
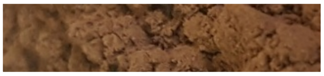
Sample	**Particle size distribution from Zetasizer Nano ZS (nm)**	**Particle diameters from Mastersizer 2000 (μm)**			
		d(0.1)*	**d(0.5)****	**d(0.9)*****	**D[4.3]******
Alumina	342-2670	0.9	1.6	2.3	1.8
Lignin	68-142; 712-1720; 2670-5560	2.0	5.6	8.5	7.0
Alumina-lignin (5:1)	106-615; 955-4800	1.8	4.7	7.9	6.2
Alumina-lignin (2:1)	122-712; 1110-5560	2.2	5.0	8.6	6.9
Alumina-lignin (1:1)	122-615; 1484-5560	2.2	5.4	8.8	7.2
Alumina-lignin (1:2)	164-712; 1110-5560	2.3	5.8	9.2	7.5
Alumina-lignin (1:5)	220-955; 1720-5560	2.6	6.0	9.5	7.9

*d(0.1) – 10% of the volume distribution is below this diameter value; **d(0.5) – 50% of the volume distribution below this diameter value; ***d(0.9) – 90% of the volume distribution is below this diameter value; ****D[4.3] – average particle size in examined system.

68-142 nm; 712-1720 nm and 2670-5560 nm according to data obtained from Zetasizer Nano ZS. The average particle size estimated with the Mastersizer 2000 was equal to 7.0 μm. Therefore, it is reasonable that with the increase of the ratio of lignin to alumina, the samples will exhibit a less homogeneous character, and larger agglomerate structures will be present in their structure. Similar conclusions can already be found in the literature reports in case of using other hybrid materials, such as silica-lignin (Bula et al., 2015; Klapiszewski et al., 2013; Klapiszewski et al., 2015; Klapiszewski et al., 2017b). The presence of larger aggregate and agglomerate structures, however, does not disqualify the use of the above-mentioned products as admixtures for cement mortars in any way.

The study also included colorimetric evaluation of the resulting products and original components (see Table 2). This analysis indirectly allowed to confirm the effectiveness of obtaining the final products

Table 2. Colorimetric analysis of alumina, lignin and alumina-lignin hybrid materials

Sample	**Digital photo**	**Colorimetric data**			
		L^*	a^*	b^*	ΔE
Alumina		90.8	0.3	1.8	2.5
Lignin		46.7	12.7	23.8	45.2
Alumina-lignin (5:1)		76.6	4.1	12.1	18.0
Alumina-lignin (2:1)		70.2	6.3	13.6	22.5
Alumina-lignin (1:1)		65.4	8.1	17.1	29.2
Alumina-lignin (1:2)		60.5	9.4	19.7	34.9
Alumina-lignin (1:5)		56.2	10.6	21.4	39.8

L^* – the lightness, a^* and b^* – color coordinates ($+a^*$ is the red direction, $-a^*$ the green direction, $+b^*$ the yellow direction, and $-b^*$ the blue direction), ΔE – the total change in color and additionally provided important conclusions which may be relevant during the development of targeted cement mortars. The data presented in Table 2 indicate that the highest value of the lightness parameter was assumed for pristine alumina (L^* = 90.8). The other colorimetric parameters (a^* and b^*) were very low and can be omitted during the analysis of the inorganic component. Based on the tests carried out for lignin, the lightness value was equal to L^* = 46.7 for this compound, while the a^* and b^* parameters were equal to 12.7 and 23.8, respectively, as confirmed by the target lignin color, which can be observed on the basis of analysis of the digital image (see Table 2). The total color change of the analyzed product was equal to ΔE = 45.2. As expected, the values of colorimetric data, estimated for hybrid materials, assume intermediate values in relation to those obtained for pristine components. Detailed data along with digital images of hybrid materials are presented in Table 2.

3.2. Determination of plasticity and assessment of mechanical strength of cementitious composites

In order to determine the plasticity of the mortars, the flow table test was carried out. The obtained results are presented in Fig. 5.

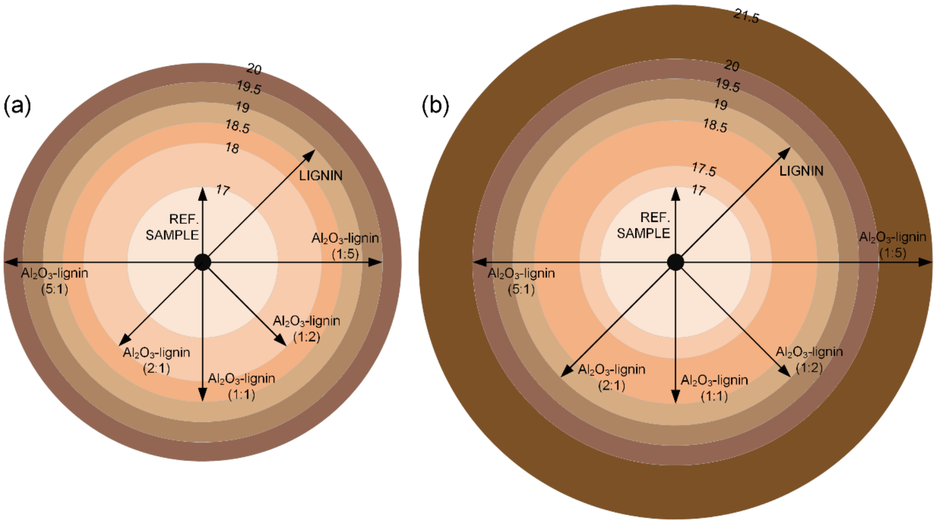


Fig. 5. Flow test results of cement mortars with 0.5 wt.% (a) and with 1.0 wt.% (b) of admixture

Cementitious mortar without any admixture with a diameter of 17 cm was used as the reference sample. After analysing the obtained data, a beneficial effect of admixtures on the plasticity of the cement mixture was observed. The highest value of the flow was obtained for the sample containing 1.0 wt.% admixture of alumina-lignin hybrid material (1:5 wt./wt.). The lowest size of the flow, equal to 16 cm, was obtained for alumina doped samples, both for 0.5 wt.% and 1.0 wt.%, (data not presented). Samples containing lignin and the Al_2O_3-lignin hybrid system (5:1 wt./wt.) were characterized by the same flow size regardless of the amount of admixture. In the case of other hybrid materials, a more beneficial effect was noted for 1.0 wt.% addition of admixtures.

The tests have indicated that, as predicted, the addition of lignin increases the plasticity of the cement mixture, which was also indicated by other reports (Gupta et al., 2017; Kalliola et al., 2015). As a result, samples of cement mortars with an admixture of hybrid alumina-lignin materials also exhibited higher flow values compared to the reference sample.

Mechanical tests are among the most important studies regarding the use of cement composites. In the framework of this study, the bending and compression strength tests were carried out. The obtained test results for bending strength tests are presented in Fig. 6.

The reference sample possessed an average bending strength of 7.1 MPa. For the inorganic component, the values of 8.0 MPa and 9.2 MPa were obtained, respectively, for 0.5 wt.% and 1.0 wt.% admixture. The result equal to 9.2 MPa is the highest among the analysed data. Lignin, as an organic precursor, was characterized by lower bending strength, i.e. 4.9 MPa for samples with 0.5 wt.%, while for 1.0 wt.% this value was equal to 4.4 MPa. In case of samples containing admixtures of hybrid materials (Fig. 6b), a more beneficial effect of 0.5 wt.% admixture was observed. It was also observed that the average bending strength increases with the increase of alumina content in the hybrid materials. The most favourable results were obtained for 0.5 wt.% admixture of Al_2O_3-lignin (5:1 wt./wt.) – 8.1 MPa and Al_2O_3-lignin (2:1 wt./wt.) – 7.8 MPa while comparable in case of Al_2O_3-lignin (1:1 wt./wt.) the results were comparable to the reference sample (7.1 MPa). Additionally, digital images of the samples after the bending strength test are presented in Fig. 7.

The results of compressive strength tests are presented in Fig. 8 and, additionally, digital images of the samples after the test shown in Fig. 9. After analysis of the obtained results of average compressive

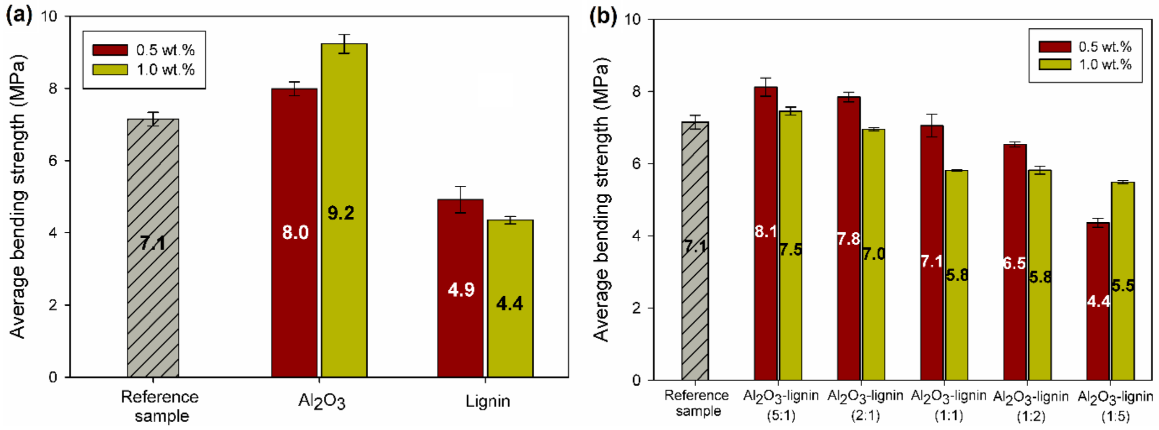


Fig. 6. Cement mortars average bending strength results for reference sample and samples with admixture of Al_2O_3 and lignin (a) and for samples containing alumina-lignin hybrid materials (b)

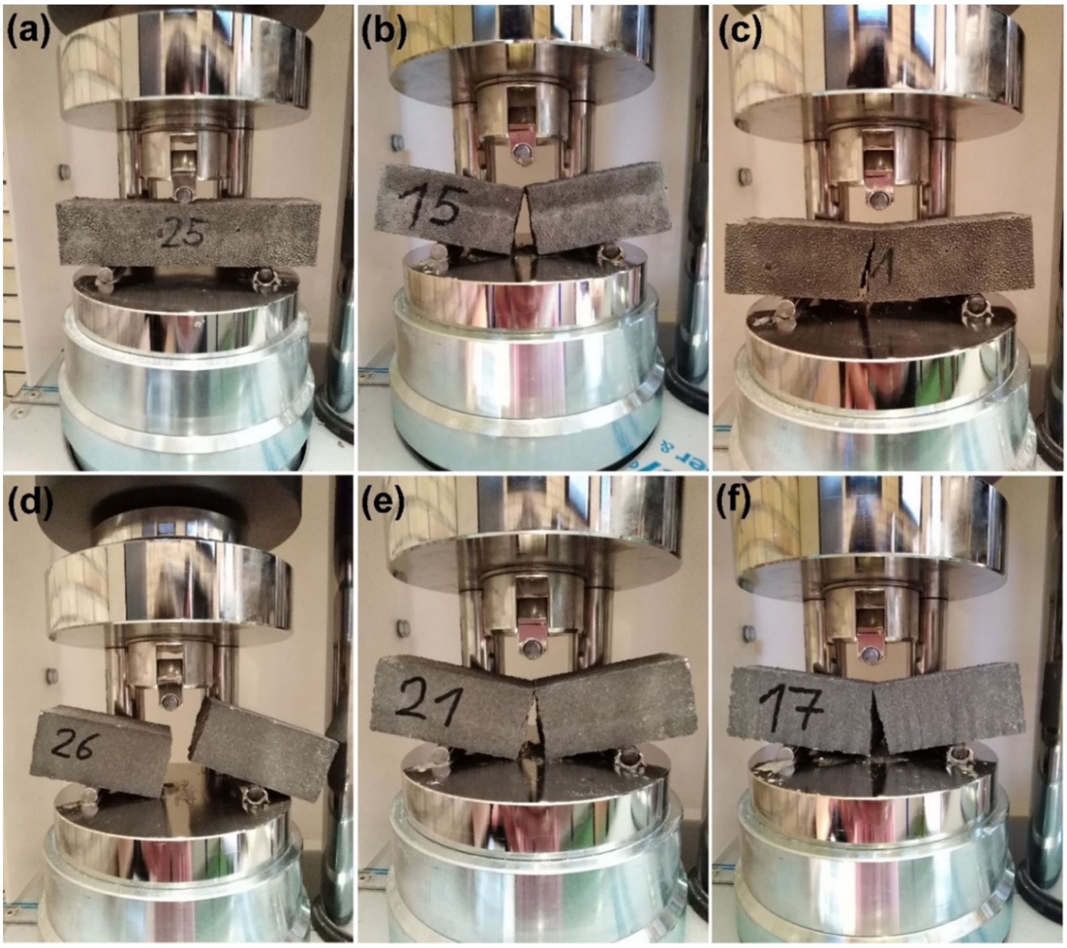


Fig. 7. Digital images obtained after bending strength tests for reference sample (a) and samples with 0.5 wt.% admixture of Al_2O_3 (b), lignin (c) and for samples containing 0.5 wt.% alumina-lignin hybrid materials 5:1 (d), 2:1 (e) and 1:1 (f)

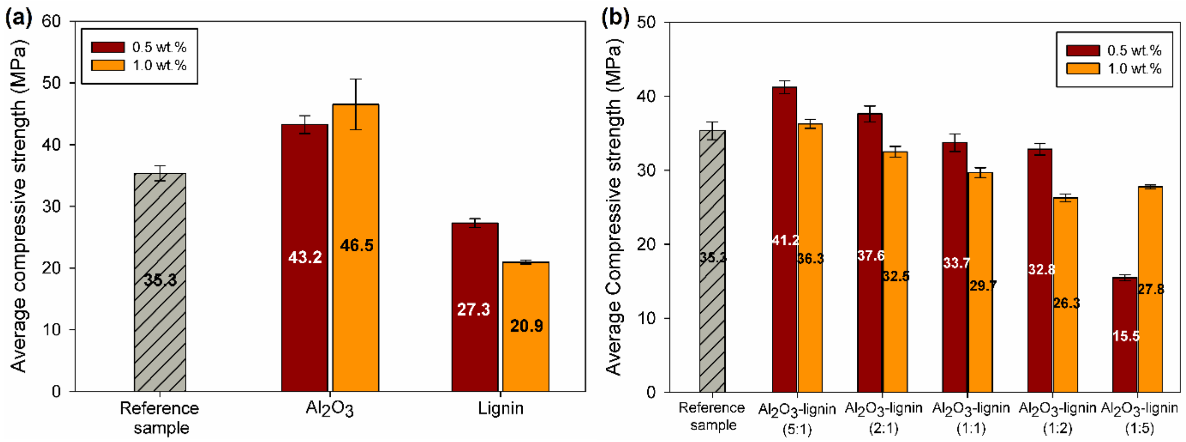


Fig. 8. Cement mortars average compressive strength results for reference sample and samples with admixture of Al_2O_3 and lignin (a) and for samples containing alumina-lignin hybrid materials (b)

Fig. 9. Digital images obtained after compressive strength tests for reference sample (a) and samples with 0.5 wt.% admixture of Al_2O_3 (b), lignin (c) and for samples containing 0.5 wt.% alumina-lignin hybrid materials 5:1 (d), 2:1 (e) and 1:1 (f)

strength, analogous relations were observed as in the case of bending strength tests. Again, the sample with a 1.0 wt.% admixture of alumina was characterized by the highest strength – 46.5 MPa, which is higher by 11.2 MPa as compared to the reference sample (35.3 MPa). Samples containing 0.5 wt.% and 1.0 wt.% admixture of lignin reached the values of 27.3 MPa and 20.9 MPa, respectively. In case of hybrid materials, the highest average compressive strength results were again achieved for samples with 0.5 wt.% of Al_2O_3-lignin (5:1 wt./wt.) – 41.2 MPa, then for Al_2O_3-lignin (2:1 wt./wt.) – 37.6 MPa, while the results obtained for Al_2O_3-lignina (1:1 wt./wt.) were slightly lower compared to the reference sample – 33.7 MPa.

The presented relationships clearly indicate the beneficial effect of an inorganic component, in the form of alumina, on the mechanical properties of cementitious composites, which was also confirmed by numerous reports (Norhasri et. al, 2017; Liu and Chen, 2016). The research allowed to confirm the assumptions that the combination of an inorganic component with an organic material allows to achieve both favourable mechanical properties of cementitious composites and improve their plasticizing properties.

4. Conclusions

Alumina-lignin hybrid materials were used as admixtures for cementitious composites. The inorganic-organic systems were designed and obtained using the method of mechanical grinding of ingredients with simultaneous mixing using a mortar grind and a ball mill. Fourier transform infrared spectroscopy allowed to confirm that the components were bound by means of hydrogen bonds, which indicates the formation of the I^{st} class hybrid materials. The formation of bonds may also be indirectly inferred based on the colorimetric analysis. Based on thermogravimetric analysis, it was confirmed that the prepared hybrid systems were characterized by relatively good thermal stability over a wide temperature range, which is mainly associated with the contribution of the inorganic component.

Alumina-lignin hybrid materials have also been used as functional admixtures for cement mortars. On the basis of the carried out tests, it was confirmed that the addition of lignin improves the plasticity of the cement mortars, which is very important when it is used for construction. Additionally, the inorganic component improved the mechanical properties, including bending strength and compression strength, compared to the reference sample without any admixture. The most favourable results were obtained for cement mortars in which alumina-lignin hybrid materials were introduced at the 5:1 and 2:1 weight ratios. These systems are characterized by the best mechanical properties with simultaneously more favorable plasticity in relation to the reference sample and other composites containing hybrid admixtures with different weight ratios.

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References

AREL, H.S., 2017. *The effect of lignosulfonates on concretes produced with cements of variable fineness and calcium aluminate content.* Constr. Build. Mater. 131, 347-360.

BULA, K., KLAPISZEWSKI, Ł., JESIONOWSKI, T., 2015. *A novel functional silica/lignin hybrid material as a potential bio-based polypropylene filler.* Polym. Compos. 36, 913-922.

GOLISZEK, M., PODKOŚCIELNA, B., FILA, K., RIAZANOVA, A.V., AMINZADEH, S., SEVASTYANOVA, O., GUN'KO, V.M., 2018. *Synthesis and structure characterization of polymeric nanoporous microspheres with lignin.* Cellulose 25, 5843-5862.

GOLISZEK, M., PODKOŚCIELNA, B., SEVASTYANOVA, O., FILA, K., CHABROS, A., PĄCZKOWSKI, P., 2019. *Investigation of accelerated aging of lignin-containing polymer materials.* Int. J. Biol. Macromol. 123, 910-922.

GUPTA, C., NADELMAN, E., WASHBURN, N.R., KURTIS, K.E., 2017. *Lignopolymer superplasticizer for low-CO_2 cements.* ACS Sustain. Chem. Eng. 5, 4041-4049.

HUANG, C., MA, J., ZHANG, W., HUANG, G., YONG, Q., 2018. *Preparation of lignosulfonates from biorefinery lignins by sulfomethylation and their application as a water reducer for concrete.* Polymers 10, 841-853.

KALLIOLA, A., VEHMAS, T., LIITIA, T., TAMMINEN, T., 2015. *Alkali-O_2 oxidized lignin – a bio-based concrete plasticizer.* Ind. Crops Prod. 74, 150-157.

KICKELBICK, G., 2014. *Hybrid materials – past, present and future.* Hybrid Mater. 1, 39-51.

KLAPISZEWSKI, Ł., NOWACKA, M., MILCZAREK, G., JESIONOWSKI T., 2013. *Physicochemical and electrokinetic properties of silica/lignin biocomposites*. Carbohydr. Polym. 94, 345-355.

KLAPISZEWSKI, Ł., BARTCZAK, P., WYSOKOWSKI, M., JANKOWSKA, M., KABAT, K., JESIONOWSKI, T., 2015. *Silica conjugated with kraft lignin and its use as a novel 'green' sorbent for hazardous metal ions removal.* Chem. Eng. J. 260, 684-693.

KLAPISZEWSKI, Ł., SIWIŃSKA-STEFAŃSKA, K., KOŁODYŃSKA, D., 2017a. *Preparation and characterization of novel TiO_2/lignin and TiO_2-SiO_2/lignin hybrids and their use as functional biosorbents for Pb(II).* Chem. Eng. J. 314, 169-181.

KLAPISZEWSKI, Ł., JAMROZIK, A., STRZEMIECKA, B., KOLTSOV, I., BOREK, B., MATYKIEWICZ, D., VOELKEL, A., JESIONOWSKI, T., 2017b. *Characteristics of multifunctional, eco-friendly lignin-Al_2O_3 hybrid fillers and their influence on the properties of composites for the abrasive tools.* Molecules 22, 1920-1939.

KLAPISZEWSKI, Ł., JAMROZIK, A., STRZEMIECKA, B., JAKUBOWSKA, P., SZALATY, T.J., SZEWCZYŃSKA, M., VOELKEL, A., JESIONOWSKI, T., 2019. *Kraft lignin/cubic boron nitride hybrid materials as functional components for abrasive tools.* Int. J. Biol. Macromol. 122, 88-94.

KOSMATKA, S.H., KERKHOFF, B., PANARESE, W.C., 2003. *Design and Control of Concrete Mixtures EB001. 14th edition.* Portland Cement Association, Skokie, Illinois, USA.

LI, C., JIANG, L., XU, N., JIANG, S., 2018. *Pore structure and permeability of concrete with high volume of limestone powder addition.* Powder Technol. 338, 416-424.

LIU, N., CHEN, B., 2016. *Experimental research on magnesium phosphate cements containing alumina.* Constr. Build. Mater. 121, 354-360.

MENDES, T.M., HOTZA, D., REPETTE, W.L., 2015. *Nanoparticles in cement based materials: A review.* Rev. Adv. Mater. Sci. 40, 89-96.

NEVILLE, A.M., 2011. *Properties of concrete.* 5th edition, Pearson Education Limited, London.

NORHASRI, M.S.M., HAMIDAH, M.S., FADZIL, A.M., 2017. *Applications of using nano material in concrete: A review.* Constr. Build. Mater. 133, 91-97.

PODKOŚCIELNA, B., GOLISZEK, M., SEVASTYANOVA, O., 2017. *New approach in the application of lignin for the synthesis of hybrid materials.* Pure Appl. Chem. 89, 161-171.

SIDDIQUE, R., KHAN, M.I., 2011. *Supplementary Cementing Materials.* Springer-Verlag, Berlin, Heidelberg.

SOBIESIAK, M., PODKOŚCIELNA, B., SEVASTYANOWA, O., 2017. *Thermal degradation behavior of lignin-modified porous styrene-divinylbenzene and styrene-bisphenol A glycerolate diacrylate copolymer microspheres.* J. Anal. Appl. Pyrol. 123, 364-375.

ŚLOSARCZYK, A., KWIECIŃSKA, A., PEŁSZYK, E., 2017. *Influence on selected metal oxides in micro and nanoscale on the mechanical and physical properties of the cement mortars.* Procedia Eng. 172, 1031-1038.

THAKUR, V.K., THAKUR, M.K., RAGHAVAN, P., KESSLER, M.R., 2014. *Progress in green polymer composites from lignin for multifunctional applications: A review.* ACS Sustain. Chem. Eng. 2, 1072-1092.

WANG, D., SHI, C., FARZADNIA, N., SHI, Z., JIA, H., 2018. *A review on effects of limestone powder on the properties of concrete.* Constr. Build. Mater. 192, 153-166.

WYSOKOWSKI, M., KLAPISZEWSKI, Ł., MOSZYŃSKI, D., BARTCZAK, P., SZATKOWSKI, T., MAJCHRZAK, I., SIWIŃSKA-STEFAŃSKA, K., BAZHENOV, V.V., JESIONOWSKI, T., 2014. *Modification of chitin with kraft lignin and development of new biosorbents for removal of cadmium(II) and nickel(II) ions.* Mar. Drugs 12, 2245-2268.