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M. Gajek[1], A. Rapacz-Kmita[1], M. Dudek[2], J. Partyka[1]

[1] *AGH University of Science and Technology, Faculty of Material Science and Ceramics, Department of Ceramics and Refractories, al. A. Mickiewicza 30, 30-059 Cracow, Poland mgajek@agh.edu.pl*

[2] *AGH University of Science and Technology, Faculty of Energy and Fuels, al. A. Mickiewicza 30, 30-059 Cracow, Poland*

MECHANICAL PROPERTIES AND MICROSTRUCTURE OF FAST – FIRED CLINKER TILES BASED ON WIERZBKA I RAW MATERIAL

ABSTRACT

The article presents results of research on microstructural and mechanical properties of floor tiles clinker manufactured on the basis of Wierzbka I raw material, which is part of the deposit Wierzbka, near Suchedniów. Wierzbka I clay was added in various volume fractions to the standard tile compositions used in industrial practice. The samples were pressed in a range of from 21 MPa to 42 MPa and fired in the laboratory furnace at 1130°C to 1190°C. Selected compositions were pressed at 28 MPa and fired in a standard industrial environment. The process of firing was conducted in an industrial kiln at temperature of 1160°C for 38 minutes, with holding for 4 minutes at maximum operating temperature. The samples, which were prepared in the laboratory and industrial conditions were evaluated for the effect of addition of the Wierzbka I clay on their microstructural and mechanical properties based on the measurement results of linear shrinkage, bulk density, open porosity, water absorption and flexural strength (б) of the tiles. Microstructural changes were observed with a scanning electron microscope (SEM). The results revealed that the tested tiles were characterized by a high degree of sintering, an apparent density of 2.5 g/cm^3, an open porosity and water absorption below 0.5%. The measurement results of mechanical bending strength showed that the tested samples had a high strength of 50 MPa.

***Keywords**: ceramic raw material, mechanical properties, clinker tiles, fast-firing*

INTRODUCTION

Ceramic tiles are among the basic construction materials used for building single-family houses and industrial and general access facilities, and are used for both interiors and exteriors. Mechanical properties, porosity, and (directly related) water absorption are basic properties of fired ceramic material, determining its potential for use [1-3]. This applies to both traditional and advanced ceramics [4-6]. These parameters are the result of using appropriately selected mineral materials and firing temperatures.

The process of manufacturing ceramic tile is similar to that of various other types of materials. Basic differences result from the composition of raw materials, firing process parameters and final decorative effects [7,8]. In the technology of manufacturing clinker tiles, brick-coloured clay materials are used; their composition includes Fe_2O_3, which promotes sintering processes and strongly influences the colour of the final product [9-14]. The raw materials used in this technology should be characterised by good sinterability, ensuring that a material with low water absorption as well as high chemical and mechanical resistance will be obtained.

The vast majority of manufacturing plants use raw materials provided by local and international suppliers. Due to exhaustion of the resources of a given raw material or geopolitical changes, manufacturers are constantly forced to search for new deposits, raw materials and formulations of ceramic masses. Ideally, a manufacturing plant can use raw materials from its own resources.

The main objective was the introduction of Wierzbka I clay to the composition of the clinker tiles and elimination of Clay 1 and Clay 2 from the composition. The study of essential properties of clinker tiles, such as mechanical strength, apparent density, water absorption and open porosity, indicate the high technological value of the clays from the deposit Wierzbka I.

MATERIALS AND METHODS

This paper concerns research on the potential for obtaining high-quality clinker tiles using raw materials from the Wierzbka I deposit. In June 2013, the ‘NEWMINE’ firm obtained a license to mine Triassic ceramic kaolin clays from the Wierzbka I deposit with balanced geological resources (equal to industrial resources) of 919,000 tonnes [15]. The Wierzbka I deposit, with a surface area of 1.9 ha according to the data in the Central Geological Database, constitutes part of the Wierzbka deposit. The Wierzbka I clay is to be mined for the purposes of Cerrad Sp. z o.o. which, among other things, manufactures pressed clinker products. The company’s manufacturing plant is situated approximately 20 km from the deposit.

Preliminary research conducted by the authors confirmed the suitability of clay materials from the Wierzbka I deposit for the production of clinker tiles [14]. Its suitability will be verified following inclusion in the composition for the production of clinker tiles.

The formula for clinker tiles used in the manufacturing plant of Cerrad Sp. z o.o. was employed in the research. The main objective was the introduction of Wierzbka I clay to the composition of the product, whose detailed characteristics were presented in another paper. The potential use of Wierzbka I clay for the production of clinker tiles would mean the elimination of Clay 1 raw material and limited use of Clay 2 raw material. The research was conducted independently under laboratory conditions as well as at the manufacturing plant. The chemical composition of the Wierzbka I clay used are presented in Table 1.

***Table 1.** Chemical composition [wt. %] of the Wierzbka I clay*

	Wierzbka I Clay	Clay 1	Clay 2	Clay 3	RM A	RM B	RM C	RM D
LOI[a]	5.65	6.20	6.70	6.00	□	□	□	□
SiO_2	60.74	57.27	57.52	45.10	66.15	98.4	70.28	65.61
Al_2O_3	17.91	23.73	21.03	29.30	19.21	0.51	17.26	19.38
K_2O	3.20	2.52	2.86	1.80	3.94	0.04	4.67	3.02
Na_2O	0.17	0.25	0.65	0.20	7.71	0.1	4.92	3.81
CaO	0.25	0.24	0.38	0.54	0.65	0.03	0.91	0.73
MgO	2.64	1.09	2.65	0.92	0.36	0.02	0.37	1.19
Fe_2O_3	8.48	7.63	7.29	15.03	1.69	0.03	1.26	5.39
TiO_2	0.96	1.07	0.92	1.12	0.09	0.05	0.16	0.7

[a]loss on ignition

The compositions of the tested samples are presented in Table 2.

Table 2. *Composition of samples [wt. %]*

Sample	Wierzbka I Clay	Clay 1	Clay 2	Clay 3	RM A	RM B	RM C	RM D
C 0L[a]	□	24.0	25.0	10.0	25.0	6.0	5.0	7.0
C 24L	24.0	-	25.0	10.0	25.0	6.0	5.0	7.0
C 49L	49.0	-	-	10.0	25.0	6.0	5.0	7.0

[a]granulate production

The designed samples were wet-milled in high-energy mills for approximately 30 minutes until a degree of milling below 3% on a 63-µm sieve was obtained. The suspensions were then dried at 105°C until a solid mass was obtained. The milled and dried materials were granulated by adding 5% by weight of water, and the granules were then used to produce samples (10 samples 5 × 10 cm for each composition), which were pressed in a hydraulic press at pressures of 21, 28, 35 and 42 MPa. The samples were dried after pressing.

Next, the samples were subjected to a fast-cycle firing process for 1 hour in a Nabertherm LS 12/13 furnace at temperatures ranging from 1130°C to 1220°C with holding for 4 minutes at maximum operating temperature.

The remaining granules were pressed at the manufacturing plant at 28 MPa and fired in an industrial furnace in a fast cycle for 38 minutes at a maximum temperature of 1160°C with holding for 4 minutes at maximum operating temperature. The samples, which were pressed and fired at the manufacturing plant, were additionally marked with the *KIn* symbol (Industrial Kiln).

The microstructure of the samples obtained was observed using a Nova NanoSEM 200 scanning electron microscope (FEI Company); the chemical composition of the Wierzbka I clay was determined using a WDXRF Axios mAX spectrometer with an Rh lamp with a power of 4 kW (PANalytical). Open porosity, absorption and apparent density were determined using the hydrostatic weighing method for 15-g samples according to the PN-EN ISO 10545-3 standard [16].

Mechanical bending strength was determined using the samples prepared at the manufacturing plant; the measurements were performed in accordance with PN-EN ISO 10545-4 standard [17].

RESULTS AND DISCUSSION

Microstructural analysis

Microphotographs of polished sections of samples pressed at various pressure values are presented in Figs. 1 to 4. For microstructure observations, samples fired at 1160°C under laboratory conditions as well as samples fired at the manufacturing plant at the same temperature and pressed at a pressure of 28 MPa were selected.

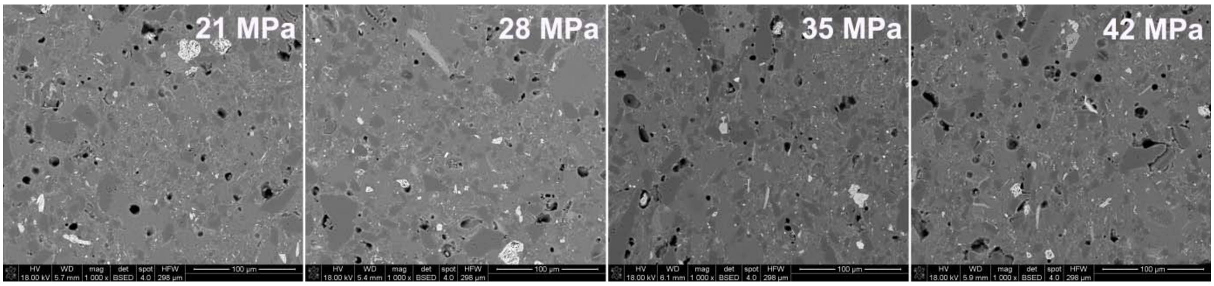

Fig. 1. SEM microphotographs of polished sections of the C 0L mass pressed at various pressure values

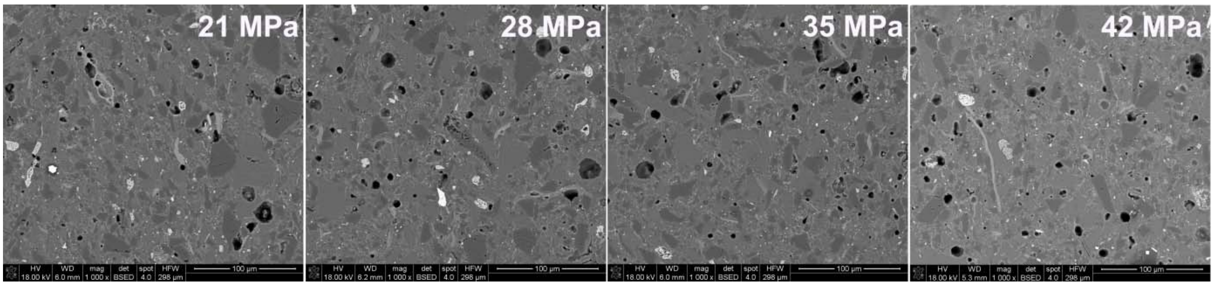

Fig. 2. SEM microphotographs of polished sections of the C 24L mass pressed at various pressure values

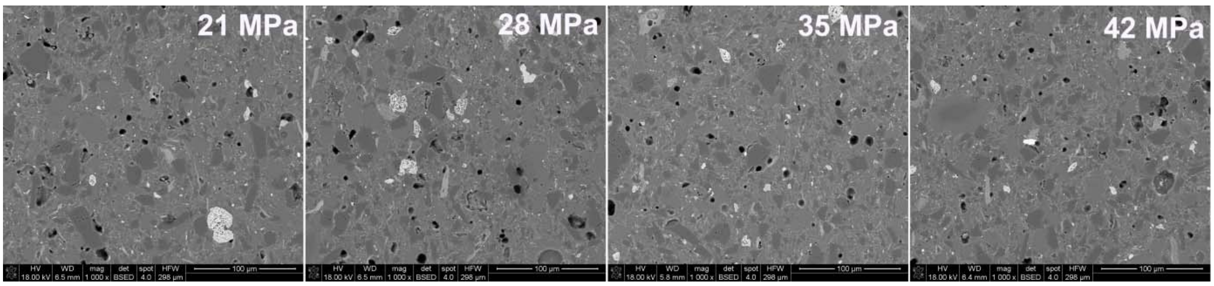

Fig. 3. SEM microphotographs of polished sections of the C 49L mass pressed at various pressure values

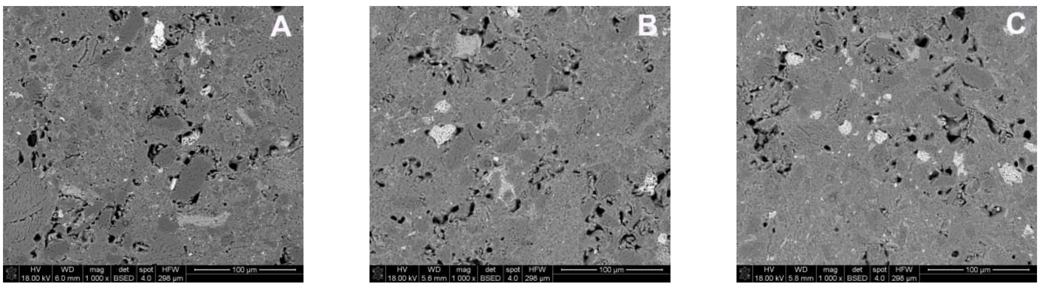

Fig. 4. SEM microphotographs of polished sections of the C 0L KIn (A), C 24L KIn (B), and C 49L KIn (C) masses pressed at 28 MPa and fired at 1160°C

All samples fired at 1160°C were characterised by a high degree of sintering. Closed pores (black areas) and areas with increased iron content (light areas) can be observed in the microphotographs. The lowest porosity of material was observed for C 49L sample. The materials pressed and fired at the manufacturing plant (Fig. 4) were characterised by slightly greater closed porosity compared to the samples produced at the laboratory. The lowest porosity of samples fired in the industrial conditions has also been observed for 49L sample.

Above dependence of the observed a lower number closed pores probably due to increased amounts of alkali oxides Na_2O and K_2O in Wierzbka I clay compared to Clay 1 and higher content of Fe_2O_3 as compared to Clay 1 and Clay 2. Higher presence of alkali oxides and

Fe_2O_3 increases quantity of the liquid phase and reduce its viscosity, which leads to better sintering process materials and the elimination of porosity during sintering process [18].

In addition Wierzbka I clay has a lower content of loss on ignition, which also leads to a reduction of the pores. In conclusion a higher content of alkali oxides and Fe_2O_3 as well as the smaller the value of loss on ignition leads to a reduction in numbers of pores and better sintering density during the firing process.

It is expected, that ceramic tiles with such a high degree of sintering should be characterized by low water absorption and high apparent density.

Analysis of the degree of sintering

The results of shrinkage determination for the samples pressed and fired at the manufacturing plant are presented in Table 3.

Table 3. *Shrinkage after firing for samples fired at the manufacturing plant*

Sample	C 0L KIn	C 24L Kin	C 49L KIn
Shrinkage %	7.82	8.24	7.72

The results for open porosity, absorption and apparent density of the tiles fired under laboratory conditions are presented in Figs. 5 to 7. For comparison, the graphs also show the results of measurements performed for the samples pressed and sintered at the manufacturing plant.

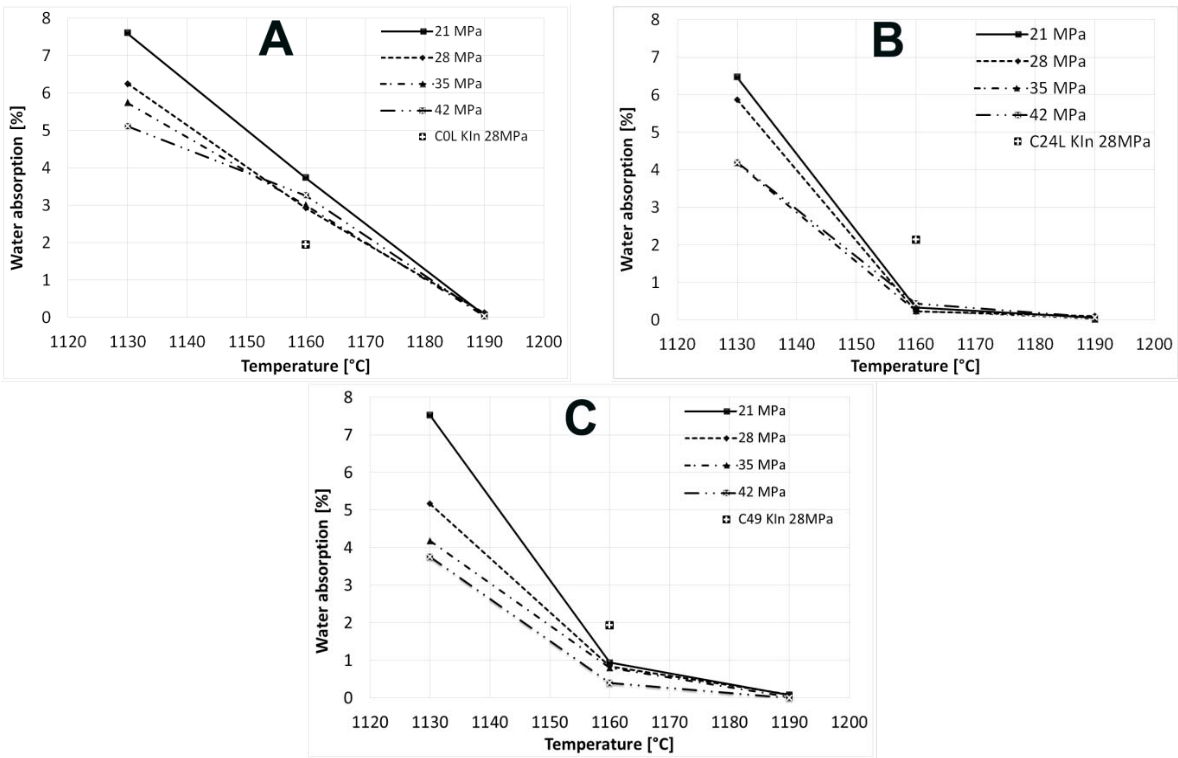

Fig. 5. Water absorption for laboratory samples and samples obtained via a standard industrial process (A - Series C 0L and sample C 0L KIn; B - Series C 24L and sample C 24L KIn, C - Series C 49L and sample C 49L KIn)

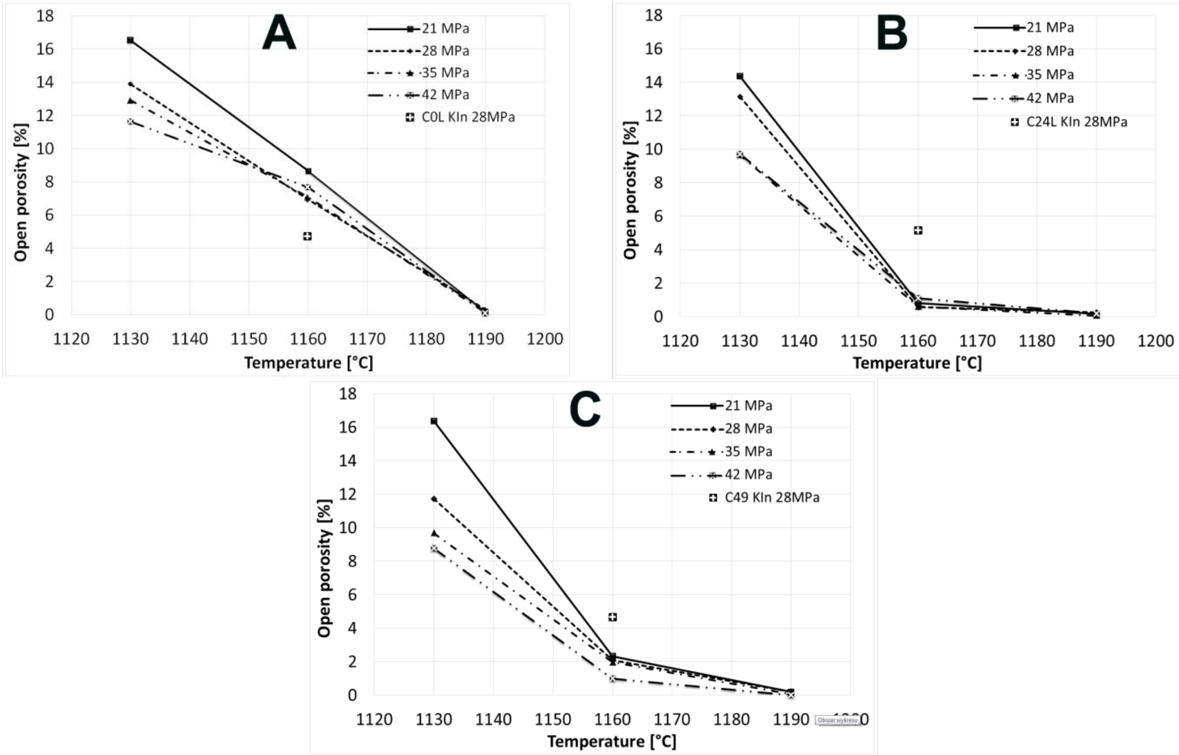

Fig. 6. Open porosity for laboratory samples and samples obtained via a standard industrial process(A - Series C 0L and sample C 0L KIn; B - Series C 24L and sample C 24L KIn, C - Series C 49L and sample C 49L KIn)

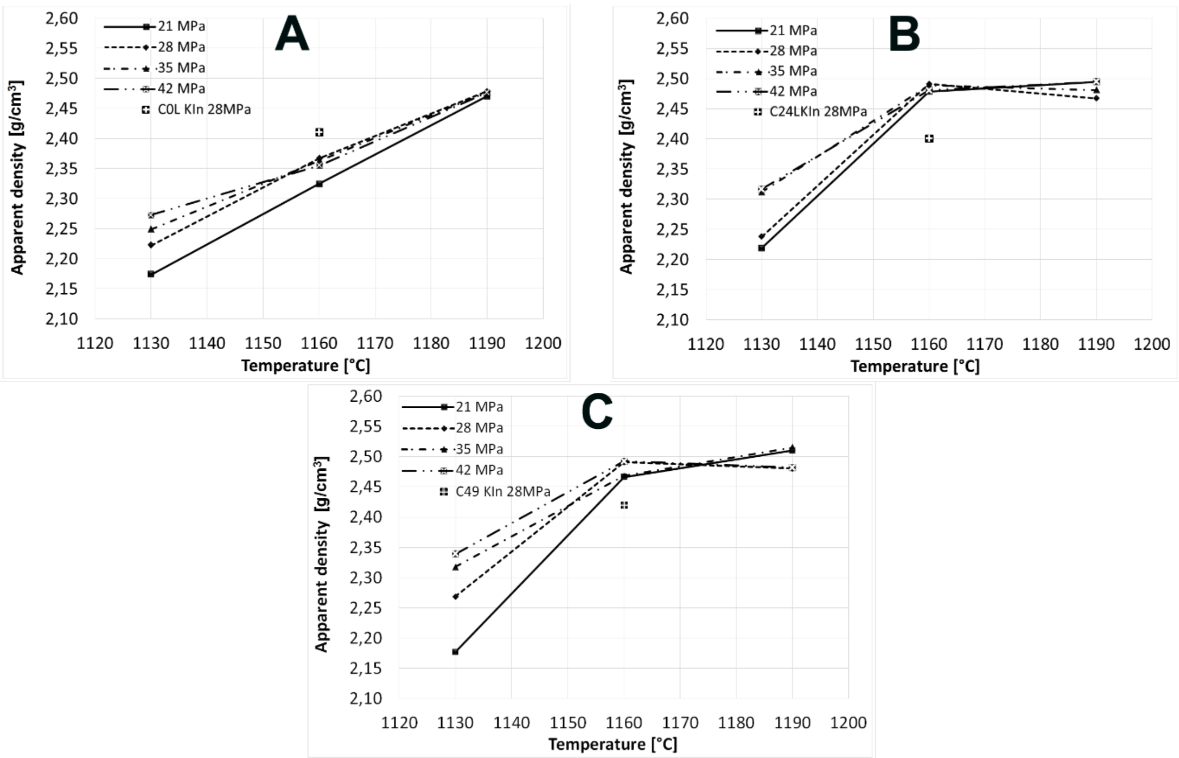

Fig. 7. Apparent density for laboratory samples and samples obtained via a standard industrial process(A - Series C 0L and sample C 0L KIn; B - Series C 24L and sample C 24L KIn, C - Series C 49L and sample C 49L KIn)

Shrinkage of the samples pressed and sintered at the manufacturing plant, namely C 24L KIn and C 49L KIn, ranged from 7.7 to 8.2%. For the C 49L KIn sample, the value of the firing shrinkage was almost the same as for the C 0L KIn.

Absorption measurements of the tested samples showed, in accord with expectations, that the water absorption of materials decreases as the pressing temperature and the firing temperature increase. Analysis of the results enabled the observation of the following relationships:

- for the C 0L sample with the composition of industrial granules, pressed at 42 MPa and fired at 1190°C, water absorption at a level of 0.04% was obtained;
- for the C 24L sample with 24% content of the Wierzbka I raw material, pressed at 35 MPa, water absorption of 0.02% was obtained at 1190°C;
- for the C 49L sample pressed at 42 MPa, at 1190°C, water absorption of 0.0% was obtained, the lowest value among the tested materials.

Open porosity tests conducted on the samples showed a relationship similar to that obtained for the water absorption determination, as follows:

- for the C 0L sample, pressed at 35 MPa and 42 MPa, open porosity of 0.10% was obtained at 1190°C;
- for the C 24L sample, pressed at 35 MPa, open porosity of 0.05% was obtained at 1190°C;
- for the C 49L sample, pressed at 42 MPa at a temperature of 1190°C, the lowest open porosity value was measured, i.e. 0.0%.

Low absorption and open porosity values obtained for the C 24L and C 49L materials affected their apparent density value. Materials with a content of 24% and 49% of the Wierzbka I material, pressed at pressures ranging from 21 MPa to 42 MPa and fired at 1160°C, were characterised by the highest apparent density value of 2.5 g/cm^3.

The materials pressed and sintered (at 28 MPa and 1160°C) at the manufacturing plant were characterised by slightly lower parameters compared to those pressed and fired at the laboratory under the same conditions. Water absorption of the fired samples fell within a range from 1.9% to 2.5%; the lowest absorption values were obtained for C 24L KIn (2.1%) and C 49L KIn (1.9%) with an open porosity value of < 6% in all cases. The lowest open porosity value was obtained for the C 49L KIn sample: 4.7%. The apparent density of all pressed and fired materials was 2.4 g/cm^3. These slightly lower values may result from the fact that the firing time at the industrial plant was 38 minutes, as compared to 60-minute firing in the laboratory furnace, and thus the time for the completion of all firing and concentration processes was shorter by 22 minutes.

Samples with the addition of Wierzbka I clay were characterized by significantly improved degree of sintering. The results are consistent with the microstructure observations. The enhancement noted above can be explained by the higher content of alkali oxide Na_2O, K_2O and Fe_2O_3 as well as smaller loss on ignition in relation to the withdrawn Clay 1 and Clay 2. This eventually leads to the improvement of sinterability and consequently reduces the number of open and closed pores.

The degree of sintering close to maximum, which was evaluated based on measurements of apparent density, open porosity and water absorption was achieved at a temperature of 1160ºC for two samples containing Wierzbka I raw material 24% and 49% respectively.

It appeared, that pressure value used for pressing the samples had a significant impact only at a lower temperature, i.e. 1130ºC, and better parameters were obtained along with an increase in pressure. The results obtained at the other two temperatures 1160ºC and 1190ºC and the pressure of 28, 35 and 42 MPa were comparable.

Bending strength

Table 4 presents the results of the bending strength and shrinkage of the tested samples, which were pressed and fired at 1160°C at the manufacturing facility.

Table 4. *Bending strength of the samples pressed and fired at the manufacturing plant*

Sample	C 0L KIn	C 24L KIn	C 49L KIn
б [MPa]	50.72 ± 2.6	47.84 ± 1.7	49.35 ± 1.9

The results of the bending strength measurements revealed that all tested samples were characterised by a high strength of 50 MPa, which greatly exceeds the 30 MPa requirements for this type of material [17]. There was no reported increase in strength for the samples with a higher content of the Wierzbka I clay, as expected, and no significant differences in the strength were also noticed for the subsequent test samples. Eventually, it may be concluded that, the observed microstructural changes in the degree of sintering and porosity did not significantly affect mechanical strength.

CONCLUSIONS

The conducted research enabled detailed analysis of process-related properties of the materials obtained from the Wierzbka I clay. The results of this study indicate a high technological value of raw materials from the deposit Wierzbka I. Favorable results for the samples have been already obtained at the firing temperature of 1160°C. This is due to larger contents of alkali oxides (K_2O and Na_2O) and Fe_2O_3 in the Wierzbka I clay which improved sinterability. Positively influenced on reducing the porosity also had a smaller loss on ignition of the Wierzbka I clay in relation to Clay 1 and Clay 2. The results showed that Wierzbka I clay can be used in the clinker tiles.

The microstructure of the clinker materials obtained both under laboratory and industrial conditions showed a high degree of sintering with a small number of closed pores.

1. The C 24L and C 49L samples containing 24% and 49%, respectively, of the Wierzbka I clay, pressed at 28 MPa and fired at 1160°C, were characterised by water absorption below 1.0% and open porosity below 2%, which, in accordance with PN-EN standard [19], is the reason for their classification in the group of BIb tiles with water absorption below 3%.
2. The C 24L KIn and C 49L KIn samples fired at the industrial plant (pressure 28 MPa, firing temperature 1160°C) showed nearly the same properties as the C 0L KIn mass used in current production. The samples were characterised by water absorption below 2.5% and open porosity below 6%.
3. The bending strength of the samples containing the Wierzbka I clay which were fired at the manufacturing plant considerably exceeded standard requirements for this type of material, i.e. 30 MPa [19]. For C 24L KIn and C 49L KIn, the measured mechanical strengths were 47.7 MPa and 49.3 MPa, respectively.

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