

SYNTHESIS AND CHARACTERIZATION OF GREENER CERAMIC MATERIALS WITH LOWER THERMAL CONDUCTIVITY USING OLIVE MILL SOLID BYPRODUCT

*Xenofon Spiliotis*¹

Vayos Karayannis

*Department of Chemical Engineering
University of Western Macedonia
3 Ikaron str., Kozani, Greece, 50100
vkarayan62@gmail.com*

*Stylios Lamprakopoulos*¹

*Konstantinos Ntampeglitis*¹

*George Papapolymerou*¹

*¹Department of Environment
University of Thessaly
Gaiopolis Campus, Larissa, Greece, 41110*

Abstract

In the current research, the valorization of olive mill solid waste as beneficial admixture into clay bodies for developing greener ceramic materials with lower thermal conductivity, thus with increased thermal insulation capacity towards energy savings, is investigated. Various clay/waste mixtures were prepared. The raw material mixtures were characterized and subjected to thermal gravimetric analysis, in order to optimize the mineral composition and maintain calcium and magnesium oxides content to a minimum. Test specimens were formed employing extrusion and then sintering procedure at different peak temperatures. Apparent density, water absorption capability, mechanical strength, porosity and thermal conductivity were determined on sintered specimens and examined in relation to the waste percentage and sintering temperature. The experimental results showed that ceramic production from clay/olive-mill solid waste mixtures is feasible. In fact, the mechanical properties are not significantly impacted with the incorporation of the waste in the ceramic body. However, the thermal conductivity decreases significantly, which can be of particular interest for thermal insulating materials development. Furthermore, the shape of the produced ceramics does not appear to change with the sintering temperature increase.

Keywords: ceramics, green materials, circular economy, olive mill solid waste, porosity, thermal conductivity, thermal insulation.

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1. Introduction

Innovative technologies that incorporate different forms of biomass and other alternative solid products (produced from various waste treatments) into red ceramics seem to develop rapidly at a global level. Actually, biomass energy potential is addressed to be the most promising among the renewable energy sources, due to its spread and availability worldwide [1–3]. The interesting points in these technologies are that they:

- a) can act as an efficient disposal method;
- b) exploit the biomass energy content into clay bodies for fuel savings;
- c) use of materials with organic matter as pore-forming agents [4, 5].

Olive-mill solid waste is the main waste produced during the process of olive-pomace oil production. Particularly in Greece, approximately 250,000 tons of (olive stone wooden residue (OSWR) are produced annually [6, 7]. OSWR is mainly used as alternative fuel due to its high calorific value (18,828–20,577 MJ/Kg) [8, 9].

Introduction of olive-mill solid residue into clay-based ceramics can be considered as a promising alternative solution for the valorization of this solid residue. Effluent olive-mill wastewater sludge was already embedded into fired laboratory produced clay bricks by Hamza et al. [10]. Moreover, Cotes Palomino et al. [11, 12] have studied the influence of the amount of wet pomace (containing water, olive stone and pulp residue) into ceramics materials for optimization of their technological properties in order to meet the standards for use as structural construction bricks. Actually, the addition of olive-mill solid residue as a pore-forming agent into ceramic brick clays must be carefully controlled. High % addition into the ceramic body will liberate heat at an excessive rate and localized heating may cause defects in the products [13].

The aim of the present research is to provide broader insight into ceramic microstructures elaborated starting from standard industrial ceramic clays and OSWR powder, in the context of circular economy towards sustainable development. Emphasis is placed on the development of greener ceramic materials with lower thermal conductivity, thus focusing on the potential for improved thermal insulation capabilities with the beneficial utilization of this solid residue as admixture into ceramics. Particularly, the decomposition of OSWR in the ceramic body upon sintering is expected to influence the porosity and consequently the thermal conductivity of the produced ceramic material.

2. Materials and methods

2. 1. Raw Materials

2. 1. 1. Chemical Analysis

The ‘Viokeral’ clay mixture used in the present study is a blending at certain proportions of three clays collected from various locations of Central Greece and provided by “TERRA S.A.”. **Table 1** contains chemical analysis results of these clays.

Table 1
Chemical analysis of clays*

PARAMETER	CONSTITUENT CLAY (%)		
	A	B	C
L.O.I.**	11.95	9.87	16.54
SiO ₂	49.40	52.79	51.02
Al ₂ O ₃	12.89	13.53	8.55
Fe ₂ O ₃	7.10	7.57	4.66
CaO	8.58	6.29	11.62
MgO	4.86	4.31	3.89
K ₂ O	2.88	3.19	1.55
Na ₂ O	1.56	1.57	1.42
TiO ₂	0.818	0.855	0.621
CaCO ₃ (eq)	14.72	–	24.46
CO ₂	6.47	–	10.75

Note: * – source: TERRA S. A.; ** – L.O.I.=Loss on Ignition

OSWR is the main residue of olive-pomace oil production processes. The OSWR used in the present study was obtained from a local olive press treatment plant after dewatering. **Table 2** presents physicochemical analysis results for this OSWR while **Table 3** shows a typical physicochemical analysis of OSWR.

Table 2
Physicochemical Analysis of OSWR*

Physical characteristics	
Net Calorific Value	17,818 MJ/kg
Gross Calorific Value	19,269 MJ/kg
Chemical characteristics	
Carbon	48.68 % w/w
Hydrogen	6.84 % w/w

Note: * – source: TERRA S.A.

Table 3
Physicochemical Analysis of OSWR*

Physical characteristics	
Gross Calorific Value**	20,962 MJ/kg
Moisture	12.3 % w/w
Ash	1.9 % w/w
Combustibles***	85.8 % w/w
Chemical characteristics	
Carbon	48.59 % w/w
Hydrogen	5.73 % w/w
Oxygen	44.06 % w/w
Nitrogen	1.57 % w/w
Sulphur	0.05 % w/w

Note: * – Source: 1) Laboratory of Applied Thermodynamics; 2) Process design Laboratory, Aristotle University of Thessaloniki; ** – Dry basis; *** – Wet basis

An advantage of OSWR is that CO₂ emissions for this additive come from the biomass (free of calcium carbonate), which means that, regarding CO₂ emission trading, this is a way to reduce the assigned quantities of CO₂ and lower the carbon footprint, because biomass is weighed with a zero emission factor [14].

2. 1. 2. Thermal Analysis

Fig. 1 shows the thermal analysis results, specifically TGA/DTA curves (Setaram STA 1600), for the “Viokeral” clay mixture. In these curves, it is observed that up to 150 °C, release of hygroscopic water is taking place and the process is endothermic. From 155 °C to 425 °C, loss of molecular water takes place and the process is also endothermic. From 425 °C to 775 °C, several endothermic and exothermic peaks are noticed due to combined dehydroxylation of the silicate lattice, combustion of organic matter and decomposition reactions [15]. From 775 °C to 858 °C, the process is endothermic due to the dissociation of carbonates. According to these results, the “Viokeral” mixture does not belong to the Kaolinitic group, since the characteristic peak of the kaolinitic clays at about 980 °C is absent. The mass loss upon clay sintering at 1105 °C reaches 11.9 % w/w, which may be attributed to the elimination of organic matter by combustion, the elimination of water due to dehydroxylation, and the decomposition of carbonates.

In **Fig. 2**, the TGA/DTA curves for the OSWR used are presented. In these curves, the following endothermic and exothermic regions are noticed:

- 1) Up to 152.7 °C: Dehydration (endothermic);
- 2) 152.7–438 °C: Combustion of organic matter – Dehydration (endothermic);
- 3) 438–575 °C: Combustion of organic matter (exothermic);
- 4) 575–649 °C: Combustion of organic matter (endothermic);
- 5) 649–682.8 °C: Combustion of organic matter (strongly exothermic).

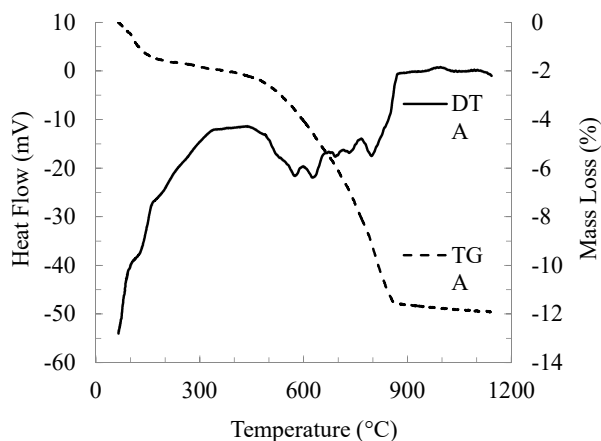


Fig. 1. DTA/TGA curves for the “Viokeral” clay mixture

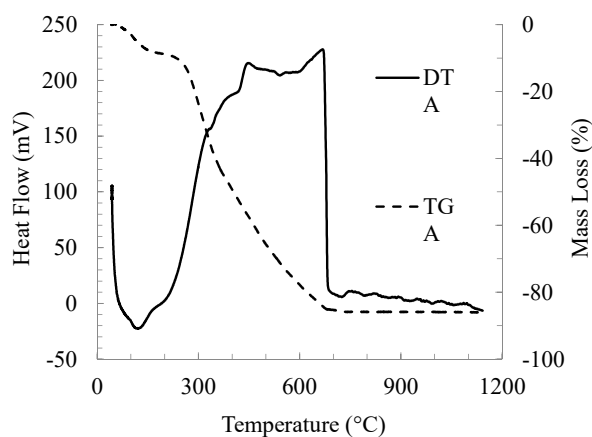


Fig. 2. TGA/DTA curves for OSWR

In **Fig. 3**, the TGA/DTA curves for the “Viokeral”/6 %w/w OSWR mixture are provided.

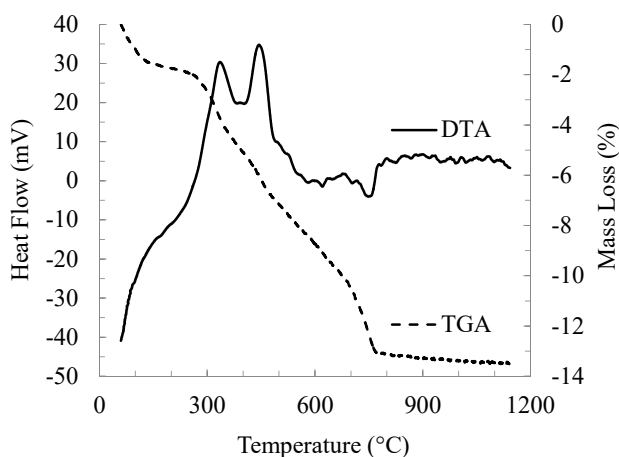


Fig. 3. TGA/DTA curves for “Viokeral”/6 %w/w OSWR mixture

In these curves (**Fig. 3**), the following endothermic and exothermic regions are noticed:

- 1) Up to 110 °C: Dehydration (endothermic);
- 2) 110–322.27 °C: Loss of molecular water (endothermic);
- 3) 322.3–383.6 °C: Loss of molecular water – Combustion of organic matter (exothermic);

- 4) 383.6–434.3 °C: Loss of molecular water – Combustion of organic matter (endothermic);
 5) 434.3–723.7 °C: Combustion of organic matter (exothermic);
 6) 723.69–774 °C: Dissociation of carbonates (endothermic).

2. 2. Synthesis of ceramic specimens

Ceramic bodies were produced using each time 0, 3, 6 and 9 % w/w OSWR powder as an additive in the clay mixture. The various clay/OSWR mixtures were ground to particle size <1 mm. Then, they were kneaded with water and shaped into specimens using a laboratory pilot-plant vacuum extruder provided with manual cutter. The rectangular specimen cross section bars were 80×43.5×18 mm. Extruded test pieces were optically checked and weighed for moisture determination using a thermos-balance. Subsequently, the specimens were first dried at room temperature for 12 hours and then in an oven at 110 °C for at least 24 hours, until reaching a constant weight. Finally, the dried specimens were sintered in a programmable electric furnace following a protocol of gradual heating up to a peak temperature (850, 950, 1050 or 1150 °C).

A schematic diagram of the proposed method is shown in **Fig. 4**.

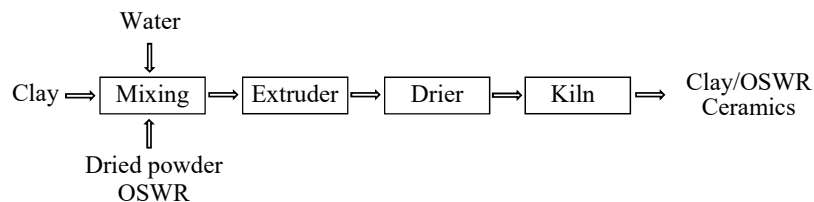


Fig. 4. Schematic diagram of the ceramic production process, using OSWR powder as admixture

2. 3. Characterization of ceramic specimens

2. 3. 1. Water absorption capacity & open porosity

The specimens were immersed in water (25–30 °C) for 24 hours. Water absorption (WA) capacity and open porosity (OP) are obtained from the following equations:

$$WA(\%) = 100 \frac{W_{wet} - W_{dry}}{W_{dry}}, \quad (1)$$

$$OP(\%) = 100 \frac{W_{wet} - W_{dry}}{\rho V_s}, \quad (2)$$

where W_{wet} – weight of saturated with water samples (g); W_{dry} – weight of dry samples (g); ρ – density of water (1 g/cm³); V_s – volume of the samples (cm³).

2. 3. 2. Three-point bending strength (Modulus of Rupture)

Strength of sintered specimens was determined upon three-point bending using a Universal Testing Machine (UTM) type INSTRON MTS 3382, and the Modulus of Rupture (MOR) was calculated from the following equation [16]:

$$MOR(\text{MPa}) = \frac{3PL}{2bw^2}, \quad (3)$$

where P – force (N); L – the opening width (36 mm); b – width of sample (mm); w – thickness of the sample (mm).

2. 3. 3. Thermal conductivity

Thermal conductivity coefficient (k) of sintered ceramics was measured at 25 °C by applying the guarded heat flow meter method using an Anter Unitherm Model 2022.

2. 3. 4. Scanning Electron Microscopy (SEM) characterization

SEM analysis of the ceramic specimens was conducted using a JEOL 6610LV microscope.

3. Results

3. 1. Mass loss on sintering and appearance color

Fig. 5 depicts the weight loss and the consequent change of the bulk density of the specimens, as a result of the sintering process.

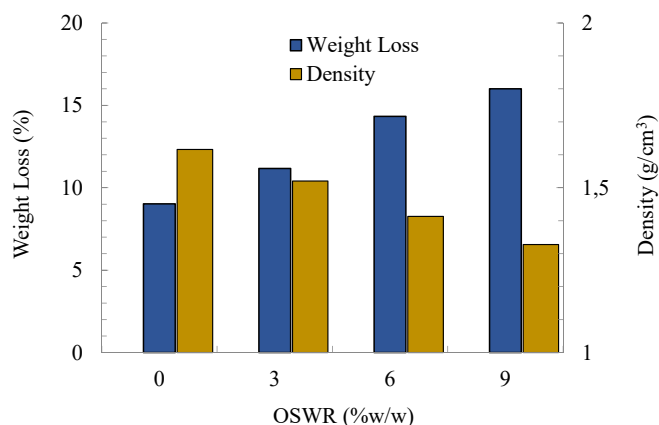


Fig. 5. Specimen weight loss and bulk density variation as a function of % OSWR content due to the sintering process ($T_{sint}=950$ °C)

3. 2. Water absorption capacity and open porosity

In Fig. 6, the influence of the OSWR proportion in the clay/OSWR mixtures on the water absorption (WA) capacity and open porosity (OP) is shown.

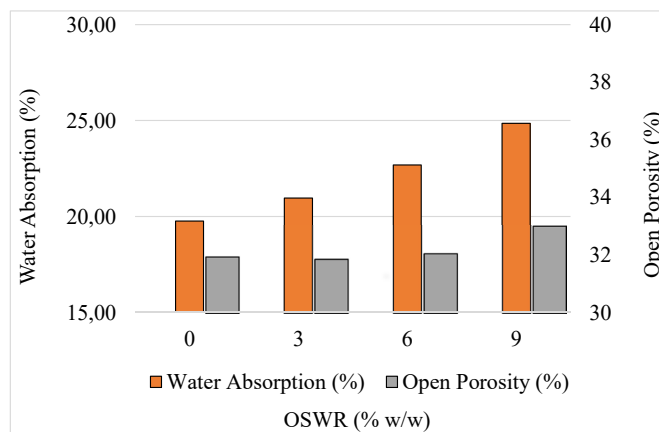


Fig. 6. Influence of the added OSWR percentage on Water Absorption (WA) and Open Porosity (OP) of sintered specimens ($T_{sint}=950$ °C)

3. 3. Mechanical Strength (Modulus of Rupture – MOR)

In Fig. 7, the dependence of mechanical strength calculated in terms of modulus of rupture (MOR) upon three-point bend testing of the specimens on the OSWR percentage in the clay/OSWR mixtures is presented.

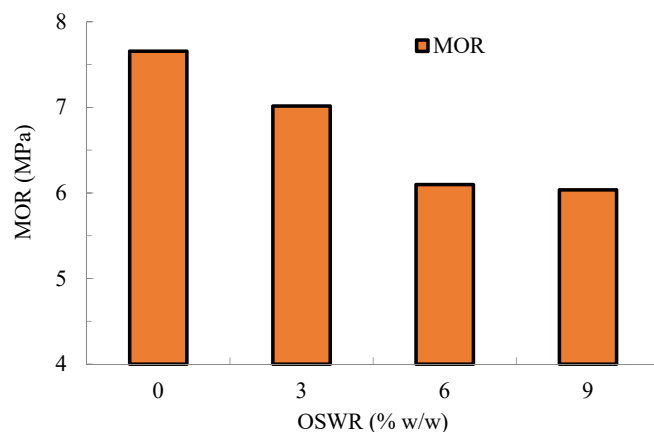


Fig. 7. Three-point bending strength (Modulus of Rupture – MOR) in relation to OSWR percentage in clay/OSWR mixtures, for sintered specimens ($T_{\text{sint}}=950\text{ °C}$)

In **Fig. 8**, the variation of MOR in relation to sintering temperature is shown.

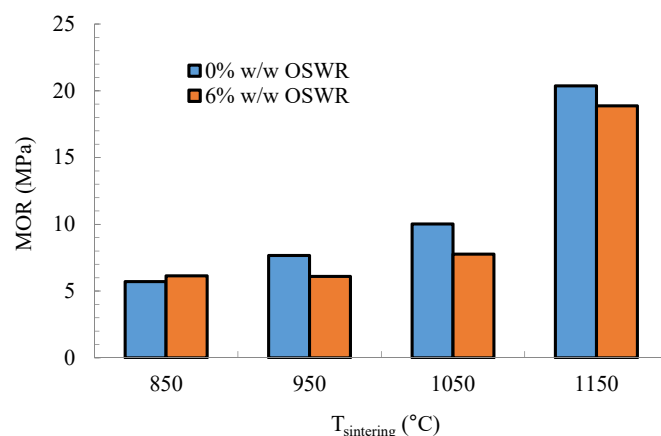


Fig. 8. MOR in relation to sintering temperature (6 % w/w OSWR content)

3. 4. Thermal conductivity

In **Fig. 9** the change in thermal conductivity coefficient in relation to % w/w OSWR in the clay/OSWR mixture is presented.

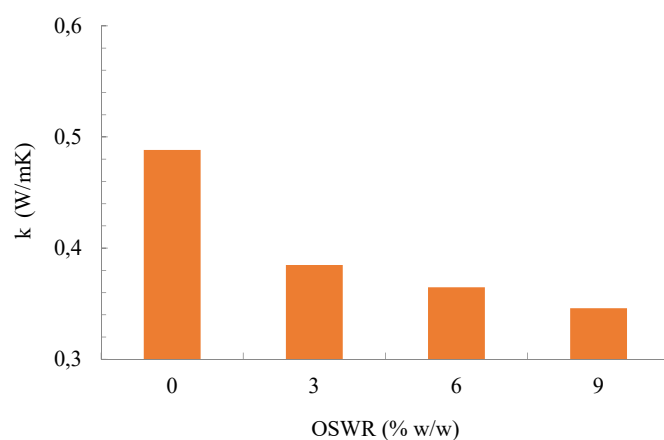


Fig. 9. Thermal conductivity coefficient (k) at 25 °C in relation to % OSWR addition, for sintered specimens ($T_{\text{sint}}=950\text{ °C}$)

Fig. 10 depicts the effect of sintering temperature on thermal conductivity.

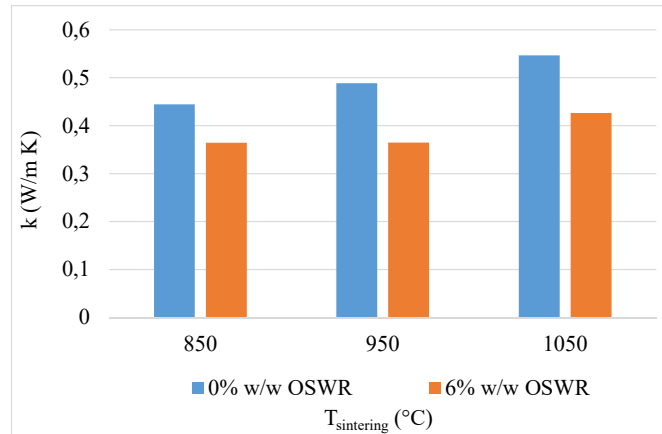
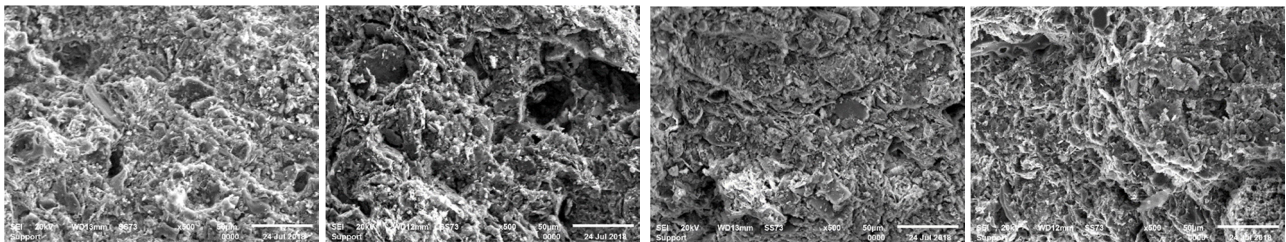


Fig. 10. Effect of sintering temperature on thermal conductivity coefficient (k) at 25 °C

3. 5. Microstructure

In Fig. 11, SEM micrographs of ceramic microstructures with 0–9 % w/w OSWR content, obtained at 950 °C, are presented. SEM micrographs of 6 % w/w OSWR content microstructures produced at 850–1,150 °C are given in Fig. 12 to provide broader insight in the densification process.



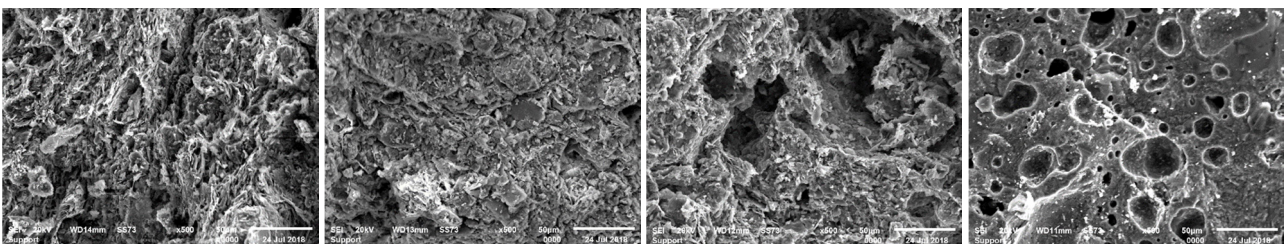
a

b

c

d

Fig. 11. Representative SEM micrographs of ceramic microstructures obtained at 950 °C, incorporated with OSWR:
 $a - 0\%$ w/w; $b - 3\%$ w/w; $c - 6\%$ w/w; $d - 9\%$ w/w



a

b

c

d

Fig. 12. Representative SEM micrographs of 6 % w/w OSWR content ceramic microstructures obtained at:
 $a - 850\text{ }^{\circ}\text{C}$; $b - 950\text{ }^{\circ}\text{C}$; $c - 1050\text{ }^{\circ}\text{C}$; $d - 1150\text{ }^{\circ}\text{C}$

In addition, photographs of real ceramic specimens, with OSWR (6 % w/w) and without OSWR (prototype) are provided in Fig. 13.

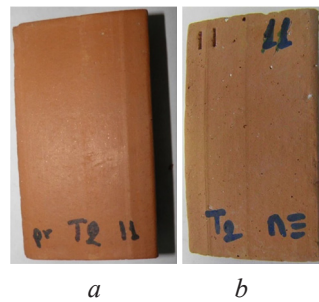


Fig. 13. Representative photographs of ceramic specimens obtained at 950 °C, incorporated with OSWR: *a* – 0 % w/w (prototype); *b* – 6 % w/w

4. Discussion

The experimental results (**Fig. 5**) showed that the sintering process causes significant weight loss, without significant change of the volume of the specimens. This results in an almost linear depletion of density with OSWR content increase. Raising the sintering temperature (T_{sint}) from 850 °C up to 1050 °C does not affect either the outlook or the geometry of the specimens. At $T_{\text{sint}}=1150$ °C however, significant changes are observed: the color becomes dark brown, the texture vitreous and the samples almost waterproof (water absorption measurements confirm this observation), and also intense sample shrinkage occurs. Nevertheless, the specimen geometry is kept without any distortion, despite the large ratios of width/thickness (>2.3) and length/thickness (>4.3). The observed weight loss is attributed to the loss of the added OSWR. In particular, for clay/OSWR (6 % w/w) mixtures, the weight loss corresponds to more the 97 % of the OSWR mass ($950\text{ °C} < T_{\text{sint}} < 1050\text{ °C}$) or more than 80 % of the OSWR mass ($T_{\text{sint}} > 1050\text{ °C}$ or $T_{\text{sint}} < 950\text{ °C}$). The above observations confirm that OSWR can act as pore-forming agent. Moreover, increasing the OSWR content in the clay mixtures results in the weakening of the terracotta color of the specimens, which become paler.

Water absorption capacity (WA) and open porosity (OP) of the ceramic specimens obtained (**Fig. 6**) do not change significantly as far as the OSWR percentage in clay/OSWR mixture is up to 6 % w/w. A noteworthy increase in the parameters under study seems to occur for 9 % w/w OSWR use. It can, therefore, be assumed that, for clay/ OSWR mixtures with up to 6 % w/w OSWR content, formation of closed pores is possibly favored (significant weight loss but stable water absorption).

With regard to bending strength (**Fig. 7**), for OSWR up to 6 % w/w in the clay/OSWR mixture, the modulus of rupture (MOR) of the sintered specimens is reduced by approximately 20 % compared to those produced from clay (0 % w/w OSWR). This trend seems to decelerate significantly for OSWR percentages higher than 6 % w/w. Moreover, raising firing temperature from 850 °C to 950 °C (**Fig. 8**), the MOR remains stable. However, from 950 °C to 1050 °C, the MOR increases by approximately 27 %, while for sintering temperatures above 1050 °C, the MOR strongly increases (by approx. 140 % up to 1150 °C). For comparison, laboratory prepared samples of clay-bricks with as much as 6 % olive-mill wastewater sludge were also reported to successfully undergo mechanical and environmental tests [10]. Savings of raw materials into ceramic samples incorporated with wet pomace from olive oil industry are further referenced in the scientific literature, with the best results obtained for 3 wt % addition [11, 12].

In the present research, especially the reduction of thermal conductivity by approx. 20 % achieved for only 3 % w/w OSWR addition in the clay mixture (**Fig. 9**) should be underlined. Indeed, for more than 3 % w/w of OSWR, thermal conductivity is further decreased even to 30 % for 9 % w/w OSWR. This means that even small quantities of OSWR in the clay mixture lead to increased porosity thus improving considerably the heat transfer resistance of the ceramic material produced. For 6 % w/w OSWR in the clay mixture, ceramic specimen thermal conductivity is reduced (**Fig. 10**) by 18.1 % at $T_{\text{sint}}=850$ °C and by 25.3 % at $T_{\text{sint}}=950$ °C, while, at 1,050 °C, a more pronounced reduction in specimen thermal conductivity is observed. This means that the incorporation of the pore-making agent OSWR into ceramic bricks promotes the

insulating properties even at lower sintering temperatures and much more at higher temperatures. These findings can be of particular importance for the development of thermal insulating ceramic materials.

Beyond the beneficial effect of OSWR acting as pore-former in the bulk of the ceramic bodies, any possible impact on ceramics properties by using different sources and years of harvest of OSWR are rather considered negligible, given the limited residue percentages incorporated. In fact, the SEM examination of the specimens indicates a relatively limited effect of the incorporation of OSWR in the ceramic microstructures obtained, except of desirable increased porosity (Fig. 11). On the other hand, the microstructure becomes more compact by increasing the firing temperature from 850 °C to 1025 °C (Fig. 12, a–c). Indeed, by further raising the sintering temperature up to 1150 °C (Fig. 12, d) an extended diffusion involving viscous flow in the ceramic matrices produced is clearly shown, resulting in a certain decrease in porosity, thus, at least partially, explaining the above stated increase in modulus of rupture (MOR).

5. Conclusions

Adding OSWR (the main solid residue of olive-pomace oil production processes) into clay mixtures typically used by the ceramic industry for brick manufacturing does not hinder neither the extrusion, nor the drying and firing processes.

A decrease in the fired bulk density from approximately 1.62 g/cm³ to 1.33 g/cm³ is attained for an OSWR addition of 9 % at 950 °C. Mechanical (bending) strength is not modified significantly, when OSWR content does not exceed 3 %, while MOR is reduced by 20 % when OSWR percentage attains 6 %, and this trend seems to decelerate furthermore at higher % OSWR contents. Nevertheless, by sintering at 850 °C or 950 °C, the brick bending strength remains stable, while, at 1050 °C, it increases by approximately 27 %, and much more at 1150 °C.

Particularly, thermal conductivity of the produced ceramic bricks is reduced by as much as 21.2 % for only 3 % addition of OSWR into the clay mixture (0.385 Wm⁻¹K⁻¹), while the three point bending strength (M.O.R.) remains around 7 MPa.

In conclusion, beneficial utilization of OSWR can be attained in two ways:

- a) production of high density bricks, at low % addition of OSWR as a body fuel;
- b) production of lower density bricks at OSWR percentages greater than 3 %, both as a body fuel and pore-former agent.

Hence, the valorization of an olive-oil industry by-product can be achieved, while the fired clay brick industry can benefit from lower fuel consumption during the manufacturing process. The novel and greener ceramics so-produced are almost equivalent to the traditional ones, while also exhibiting lower thermal conductivity thus increased thermal insulation capability.

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