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Thermal evolution of the mechanical properties of calcareous earthenware

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Abstract

Calcareous earthenware is used very frequently for tableware, and fired twice between 980 °C and 1040 °C. Before firing it mostly consists in a kaolinitic clay accompanied by quartz and ≈7 wt% of carbonates (Ca and Mg) as fluxing fraction. In this article the firing temperature correlation with the textural, structural and mechanical properties was established in the 700–1100 °C firing range. Materials fired between 800 and 1050 °C presented an interesting correlation between the processing variable (temperature) and the evaluated properties. The porosity in this range was almost constant however the properties evolved exponentially with the temperature. A parallel behavior between flexural strength, diametral compression resistance and dynamic elastic modulus was observed. Furthermore within the technological temperature range the correlation was linear.

Finally the incorporation of the porosimetric analysis performed permitted to understand that the firing processes of calcareous earthenware below 1050 °C is not strictly a sintering process with a gradual densification and loss of porosity: it should be considered as a series of complex chemical processes accompanied by a textural evolution of pore size increase with no important porosity decrease. Only for higher temperature treatments (which exceed the technological ones) the porosity diminishes abruptly. When this reduction takes place, it is accompanied by an increment in the mechanical properties figures and a loss in the dimensional stability.

Keywords: C. Mechanical properties; Clay based ceramics; Earthenware; Processing

1. Introduction

The mechanical properties of porcelain bodies have been studied extensively for almost a century. During this period three theories have been presented to explain the strength of porcelains. These are the “mullite hypothesis”, the “dispersion strengthening hypothesis” and the “matrix reinforcement hypothesis” [1–5].

But in earthenware there are not a clear level of theoretical advances. In fact earthenware can be assumed to be an under fired porcelain, but this is only the case when strictly tri-axial (clay–quartz–feldspar) mixtures are being studied. Calcareous clay has little amount of feldspar in its starting mineralogic composition, and the fluxing part is formed by calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) hence it is wrong to assume this kind of material as an under fired triaxial ceramic [6,7].

The firing temperature is one of the most important processing variables in the manufacture of ceramic pieces. In fact, in some cases, it defines the final product cost.

Accurate measurement, prediction and predetermination of material properties are important for its posterior use, and undoubtedly the properties depend~~s~~ on both the phase (crystalline and non-crystalline) composition and microstructure of the final ceramic material [8–20].

Ceramic clays are one of the most complicated ceramic systems because of the non-simple relationship between the behavior of minerals during the ceramic processing and the transformations during heating. These new crystalline phases are sometimes grouped as neo-minerals [6]. A major challenge

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is to predict the phase transformations in silicate ceramics, since non-simple relationships occur between the structural characteristics of the fired products and the physical properties.

Upon firing, the minerals in the clay bodies undergo chemical and structural modifications deeply transforming the original materials. The high temperature, low-pressure mineral transformations are mainly influenced by the chemical and mineralogical composition of the original clay, its grain-size distribution, the maximum heating temperature, heating rate, duration of firing and kiln redox atmosphere [1].

Firing transformation inside traditional ceramic kilns was extensively reported in the literature, but usually this kind of evaluation is carried out qualitatively and not quantitatively.

During ceramic process, once the crystalline structures of minerals exceed their stability limits, they are partially (or completely) decomposed while simultaneously others are being formed. The destruction of the pre-existing structure does not occur instantly, the processes are governed by the system′s thermodynamic and kinetic properties. Moreover these transformations determine the final properties of the ceramic products [1–5].

The objective of this article is to elucidate the effect of the firing treatment in the mechanical properties: flexural strength, diametral compression and dynamic elastic modulus and to correlate them with the textural and structural properties of different ceramics processed from an important ceramic body fired in a wide range of temperatures that include the industrial employed conditions.

A second objective is to establish the temperature range where the studied mechanical properties are parallel.

The material studied in this work is a ceramic paste (body) for commercial white earthenware (“Pasta blanca lisa”, earthenware commercial formula from Argentina) and was previously studied in other aspects by the same group of authors. This kind of material is frequently used for tableware, and other small ceramic objects, usually fired at low temperatures in electric or gas kilns [21].

The present study complements the results obtained in a recent article [6]. In that work, the textural and crystalline thermal evolution of the calcareous clay were established by a complete thermal analysis (DTA-TG and dylatometric study accompanied by an XRD-Rietveld characterization of the samples fired in a wide range of temperatures (800–1100 °C).

In order to understand this paper, some of the results are transcribed in the materials and methods of this paper in Sections 2.1–2.3. Furthermore in Section 2.4 we present the Hg porosimetry performed for this article, that complement the Archimedes textural characterization carried out in the former article. In Section 2.5 we present the mechanical characterization carried out. In Section 3 we present the results and discussion, finally we present the conclusions in Section 4.

2. Materials and methods

2.1. Materials processing

In a recent article the firing transformations of this material were presented [6]. The same material was employed for the mechanical characterization carried out in this article. Prismatic specimens of $8 \times 8 \times 70\ \text{mm}^3$ were elaborated by plastic forming and dried to constant weight in an oven at 100 °C. They were then fired at different temperatures between 700 and 1100 °C with a heating (and cooling) rate of 10 °C/min, and a 15 min soaking time was applied. The selected temperature range was chosen because the earthenware is usually fired at 980 °C (Orton standard cone 06) in the first firing usually known as biscuit fire, and the second glazing firing is usually carried out in the 1020–1040 °C range (cone 05).

Chemical analysis of a dried clay sample (clay) is shown in Table 1. In the same table, some properties of the unfired materials are shown: these values are typical for the kind of materials used in the local ceramic industry. It can be pointed out that the material present a high proportion of silica and that the alumina content is low. Furthermore the fluxing fraction is principally composed by calcium, magnesium and with small amounts of potassium and sodium. Finally, the iron content is 0.66%.

2.2. Textural properties of the calcareous earthenware

Fig. 1 shows the textural properties evolution with the firing temperature (porosity: P, water absorption: WA, and density: D). As a first glance P, WA and D remained stable up to 1000 °C; a slight variation after 900 °C could be detected, showing that before this temperature some mineralization started. Another remarkable result is the observed stability of the properties in this wide temperature range which make them unsuitable for quality control parameters. Instead, a mechanical characterization is suggested.

The dilatometric behavior of the material was presented and discussed in the mentioned previous work [6], but the most important result contraction started only at 1050 °C and was abrupt, up to 1100 °C (the end of the experiment).

2.3. Phase evolution, XRD-Rietveld analysis

Fig. 2 shows the thermal evolution in the crystalline phase of the original material. The material consists in a mixture of quartz, clays (caolinite and illite) and carbonates (calcite and dolomite) accompanied with a small amount of feldspars.

Table 1
Chemical composition and properties of the calcareous earthenware (unfired).

	As received dried clay (%wt)
SiO_2	70.85
Al_2O_3	12.81
Fe_2O_3	0.61
TiO_2	0.53
CaO	3.62
MgO	1.65
Na_2O	0.15
K_2O	2.00
LOI	7.80
Total	100
Properties	
Green density (gr/cm^3)	1.94
Green porosity (%)	28.3

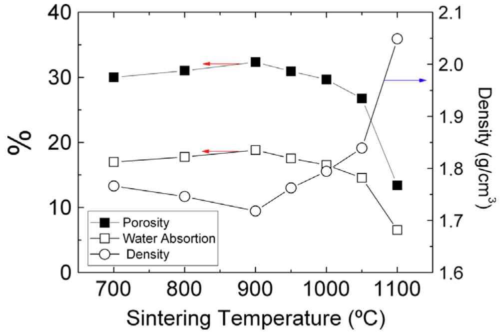

Fig. 1. Porosity, water absorption and density of the earthenware (P, WA and D) as a function of firing temperature [6].

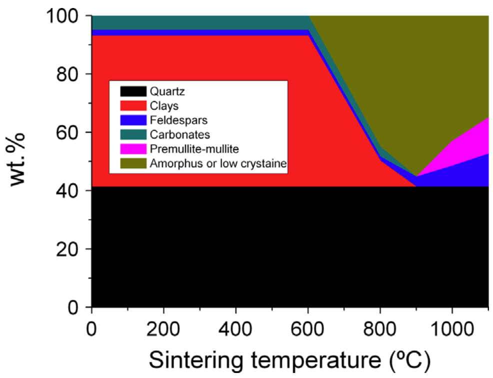

Fig. 2. Crystalline phase composition of the earthenware evaluated by the Rietveld method as function of the firing temperature.

A complete identification and quantification was shown in a previous work [6,22–24].

The complexity of the system from this perspective was clearly demonstrated. A group of clay minerals decomposed partially before 800 °C and completely before 900 °C.

The amorphous phases grouped in Fig. 2 are principally metakaolin, product of the thermal decomposition of the kaolinitic clay. In fact, this metakaolin is not strictly amorphous and can be understood as a low crystallinity phase [1,5].

The flux components (carbonates) also decomposed at around 800 °C, moreover dolomite (a Mg–Ca carbonate) resulted into a Ca carbonate at this temperature, and decomposed only at after higher thermal treatments [25–27]. The product of the decomposition is not crystalline and accompanies the metakaolin in Fig. 2 in the amorphous or low crystalline group.

A little amount of feldspars were present in the starting composition, the amount detected can be neglected [6]. On the other hand feldspars, particularly plagioclase and gehelenite, crystallized after 900–1000 °C thermal treatments becoming the first minerals that mineralize within the calcareous clay. However, after higher treatments they will decompose; gehlenite first (1000 °C) and plagioclase after higher (and out of range) temperatures (1150 °C) [28]. But a fring temperature of 1150 °C exceeds the one employed for these materials and is not observed in the performed tests.

The most important neo-mineral of triaxial ceramics is mullite, that starts its formation between 900 and 1000 °C [29] with high refractoriness being stable up to much higher temperatures (< 1600 °C), however this first mullite has low crystallinity and was well described before [29].

2.4. Hg porosimetry

Although a wide range of temperatures was studied, open porosity was almost constant (30%) up to 1050 °C (Fig. 1). The materials fired at 1100 °C presented a smaller porosity (≈15%). Mercury intrusion tests were performed by using a Pascal Porosimeter 140 Thermo Fisher and pressures ranging from 1 to 2000 kg/cm^2 (sizes equivalent radius of pores in the range of 37–75,000 Å). These results are complementary to the Archimedes analysis.

2.5. Mechanical properties characterization procedures

Three mechanical properties were chosen for this analysis: the dynamic elastic modulus (E), the flexural strength (σ_f) and the diametral compression resistance of short cylinders (σ_d). Fracture strength is one of the most common and widely used mechanical properties for structural ceramics because it is the most simple and important material reliability parameter. A number of methodologies and techniques have been developed for this purpose. Most of these techniques equate fracture strength to maximum stress (tensile, compressive or mixed) at fracture. Consequently, in order for a particular load and specimen geometry to be useful for determination of fracture strength stress distribution must be well established. Due to advantages including simple geometry, low cost specimen fabrication flexural tests are the most widely used for measuring ceramic materials strength.

The diametral compression test, also known as “splitting test” or “Brazilian Test”, has usually been employed in the mechanical evaluation due to several advantages: simpler piece preparation, simple geometry and quickness of testing, independent data with regard to surface finish and no edge effects [30–32].

The elastic modulus (E) is a measurement of the material stiffness, and is the slope of the stress strain plot. There are some dynamic methods for evaluating E; the impulse excitation technique is usually employed for ceramic materials [33,34]. When the object under test is subjected to an initial deformation by means of a light mechanical impulse, the object will immediately act as a spring-mass system and produce a transient mechanical vibration. The frequency of this vibration depends on the mass of the object and its stiffness, which is determined by its shape and dimensions and the modulus of elasticity of the material. The great advantage of this technique is the low operative cost, high repetitivity and the fact that it is nondestructive [33].

2.5.1. Dynamic elastic modulus (E)

The dynamic elastic modulus E of the composites were measured by the excitation technique with a GrindoSonic, MK5 “Industrial” Model [34]. In each case the test was carried out in prismatic bars. The actual expression of the dynamic elastic modulus can be found in literature [33].

2.5.2. Flexural Strength (σ_f)

The flexural strength (σ_f) was measured on 10 samples by a three points test on the bars with a 40 mm span and a displacing speed of 0.1 mm/min. Universal testing machine (Instron 4483). Ten samples were measured for each sample fired at different conditions.

The flexural strength was calculated from the following equation:

$$\sigma_f = \frac{3Ll}{2wh^2} \tag{1}$$

where L is the final maximum load of samples, l is the distance between the support points of the three point test, w is the width of the samples and h is the height of the prisms.

2.5.3. Diametral compression (σ_d)

The diametral compression of cylinders was performed in ten samples of 15.0 mm diameter (d) and 7.0 mm of thickness (t) with the same Universal testing mechanical machine, with the same load speed. In this case MoS_2 lubricant paste was applied on the platen surfaces in contact with the disk to reduce the effect of friction; white and carbon papers were placed together between each platen and the disk for load distribution (padding material). L was employed for the final maximum load of samples.

For this method the mechanical strength can be calculated with the following equation (Eq. 2) effects [30–32].

$$\sigma_d = \frac{2L}{\pi dt} \tag{2}$$

3. Results and discussion

3.1. Hg porosimetry

Pore size distributions (Hg intrusion) are shown in Fig. 3. Accumulative pore size curves are not similar for group of materials studied, showing an important change when achieving 1100 °C. The starting asymptote of the materials behavior is concordant with the Archimedes results (Fig. 1), the under fired samples present higher and constant value. And the sample fired at 1100 °C presented the lowest value.

However same difference could be evaluated: small pores (between 50 and 100 nm) proportion in the samples fired at low temperature (800–900 °C) are important and null for the samples fired at 1000 and 1100 °C.

Finally, the mean pore diameter was plotted as a function of the firing temperature, inset in Fig. 3. The average pore size is clearly correlated with the firing. Remembering that the porosity was constant and ≈30% for samples fired below 1050 °C, the evaluated progression is remarkable. Showing that the firing processes of earthenware below 1050 °C is not strictly a sintering process with a gradual densification instead it is a complex chemical processes described in Section 2.3 accompanied by a textural evolution of pore size increase.

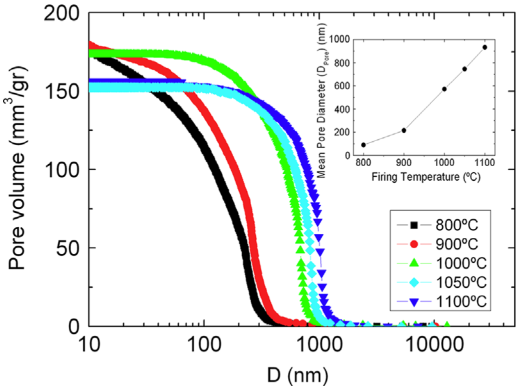

Fig. 3. Hg porosimetry curves of the earthenware fired at different temperatures. The mean pore diameter as a function of the firing temperature is shown as a inset.

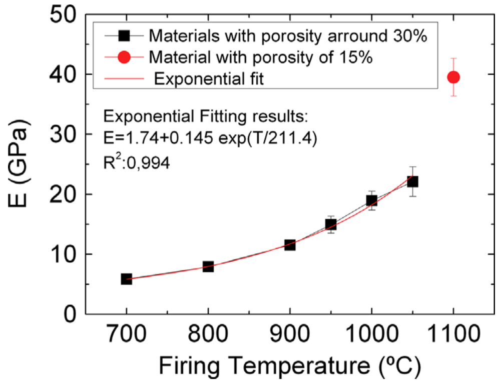

Fig. 4. Dynamic elastic modulus (E) of the calcareous earthenware as a function of the firing temperature (materials with ≈30% of porosity in squares and the material with 15% of porosity as a circle); the exponential growth fitting is shown as well.

3.2. Dynamic elastic modulus (E) of the calcareous earthenware

The obtained values are comparable to the ones that can be found in literature [21]. The dispersion values are low for this property. Fig. 4 shows the evolution of the dynamic elastic modulus of the material as a function of the maximum firing temperature employed in the 700–1100 °C range. The results were grouped in two groups in terms of the porosity evaluated by the Archimedes method (Fig. 1), materials fired between 700 and 1050 °C presented porosities near to 30% and the material fired at 1100 °C presented a 15% porosity value.

An exponential growth is evident in the first group (squares); in the graph the exponential growth fitting results are also shown. The fitting results (measured in the value of R^2) are adequate. This exponential growth has been reported for different ceramic materials. And is usually related to the sintering (densification and decrease in the porosity) of the

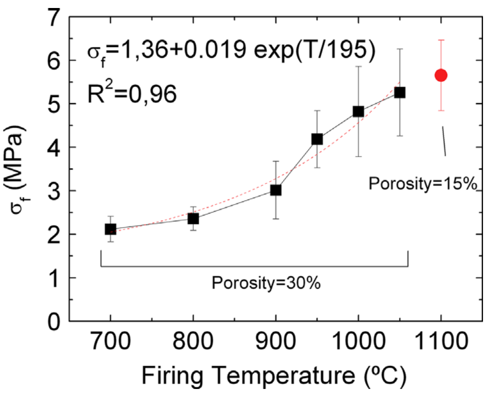

Fig. 5. Flexural strength (σ_f) of the calcareous earthenware as a function of the firing temperature (materials with ≈30% of porosity in squares and the material with 15% of porosity as a circle); the exponential growth fitting is shown as well.

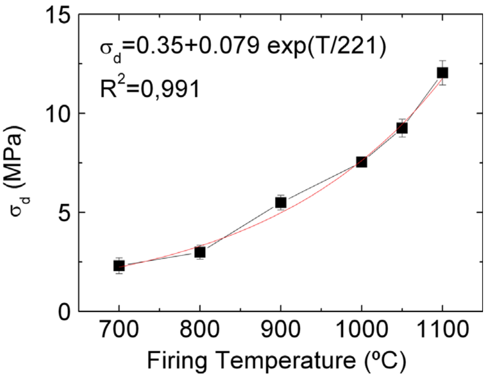

Fig. 6. Diametral compression resistance (σ_d) of the calcareous earthenware as a function of the firing temperature; the exponential growth fitting is shown as well.

ceramic material. As described in former sections this is not the case in the present earthenware, but the increase is still exponential. In this case the behavior occurs with nearly constant porosity and might be related with the pore size that grows with the firing temperature as shown in Fig. 3, instead of pore fraction in the 700–1050 °C range. Finally, for the material fired at 1100 °C the abrupt increase is related to the important porosity difference.

3.3. Flexural strength (σ_f) of the calcareous earthenware

Only after 1000 °C treatments the mechanical properties achieved were adequate for the application [21] the actual industrial cycles are of 1040 °C. Fig. 5 shows the evolution of the flexural strength (σ_f) with the firing temperature. The same aggrupation was carried out (Section 3.2). In the first group (porosity ≈30%) the exponential growth can be observed. As expected the relative error is higher for σ_f than E. The result of the mean square fitting is also shown in Fig. 5 and adequate. The achieved values are comparable to the one reported [1,7,21] for similar materials. The value for the over fired material with lower porosity is relatively lower than the one achieved for E, the flexural strength value depends on the weakest defects and the elastic modulus is more related to the bulk property. Again the observed exponential behavior is remarkable taking into account that the firing processes are not a strict sintering process in the 700–1050 °C temperature range. For a nearly constant porosity group of ceramics the mechanical property obtained was not constant.

3.4. Diametral compression (σ_d) of the calcareous earthenware

The evolution of the diametral compression resistance can be observed in Fig. 5, the achieved values are greater than the flexural strength (almost doubles). The exponential behavior was corroborated by the mean square fitting. The results are shown in Fig. 5 also. The exponential behavior was accomplished in the whole range (700–1100 °C). The fact that the standard deviation values are much smaller than the ones obtained for the flexural strength, together with the higher values shows the benefits of this technique for this kind of materials. When the material is plastic the employed disc shapes can be easily obtained by extrusion (Fig. 6).

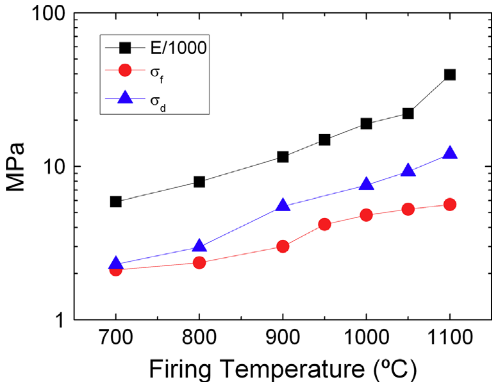

Fig. 7. Mechanical properties of the studied materials (log graph).

3.5. Comparison of the three mechanical properties studied

The three mechanical properties chosen present an exponential growth. The logarithms of the three properties are plotted as a function of the firing temperature in Fig. 7. Instead of E, $E/1000$ is plotted in order to compare easily. Evidently the three properties grow in a parallel way. Nevertheless in a more accurate analysis the exponential parameter follows the $E < \sigma_f < \sigma_d$ progression. And the pre-exponential parameter follows the same progression.

3.6. Linear temperature dependence range

For a technological propose a linear range was seeked. Fig. 8 shows the linear evolution of E and σ_f in the 900–1050 °C range. This range includes both technological temperatures (980 °C and 1040 °C). Also in this range a linear fit

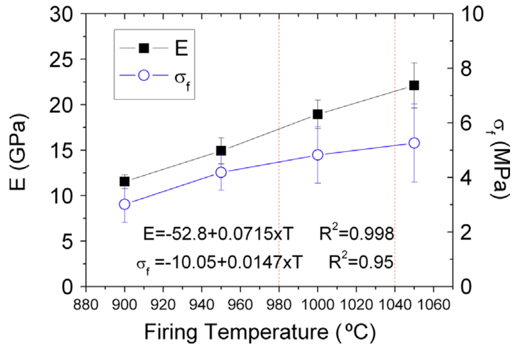

Fig. 8. Dynamic elastic modulus (E) and flexural strength (σ_f) as a function of the firing temperature (intermediate range). The results of the linear fitting are shown. The vertical lines represent the manufacturing temperatures.

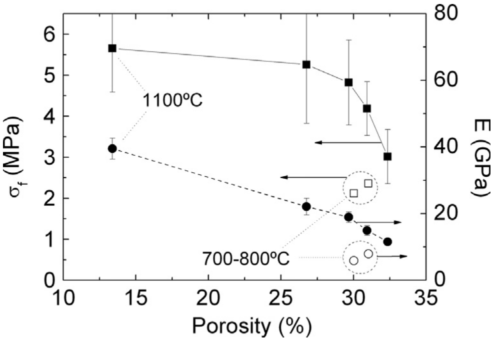

Fig. 9. Dynamic elastic modulus (E) and flexural strength (σ_f) of the earthenware as a function of the porosity.

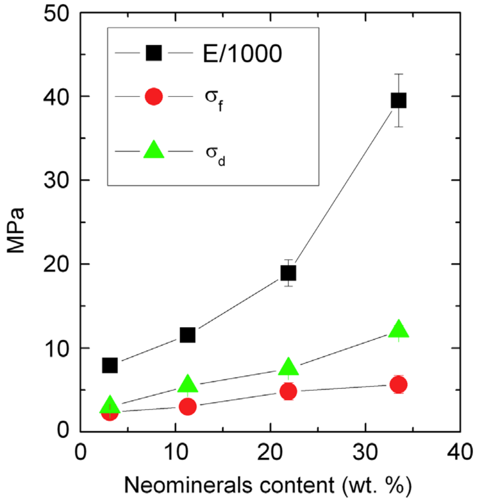

Fig. 10. Mechanical properties of the studied calcareous earthenware as a function of the neominerals content (sum of all the crystalline phases).

was carried out satisfactorily showing that the E slope is five times the flexural strength slope. An interesting result is that within this temperature range both technological properties are bonded. This fact could represent an important operative saving in production control ($E=4.1+4.86\sigma_f$) and ($\sigma_f=-0.84+0.206E$).

3.7. Correlation between the mechanical properties. And different important properties of the calcareous earthenware

3.7.1. Porosity and density correlation

There are several empirical or semi empirical models for the relationship between the mechanical properties and the porosity of ceramic materials [35–37]. All of them can be grouped in exponential (or hyperbolic) decreases of the mechanical properties as a function of the porous fraction P. Fig. 8 shows the relation between the porosity, the dynamic modulus (E) and the flexural strength (σ_f). The behavior is far away from the exponential decay generally observed in ceramic materials [35–37]. Undoubtedly this fact is related with the crystalline transformations that occur in parallel with the sintering processes during the thermal treatments. All the empirical models are based in stable materials that only differ in the porosity.

Particularly, the behavior can be described as following. Presenting two ranges, one dependent range (900–1100 °C) and one independent range (700–900 °C). For E, the decrease is gradual (almost linear) with porosity in 30–10%. The decrease in the 1100–900 °C is not linear, in fact it is abrupt in the 900–1050 °C range. These ranges correspond to the ones observed in the sintering processes (Fig. 1).

3.7.2. Crystalline phases correlation

Once the porosity correlation is discarded, the crystallographic correlation is proposed. Fig. 9 shows the value of the mechanical properties as a function of the amount of neominerals that crystalized in the ceramic material (Fig. 2).

Fig. 10 shows the correlation between the amount of crystalized minerals (neominerals) and the three mechanical properties studied in the 800–1100 °C firing temperature range. While the correlation is linear for the flexural and diametral compression strength it is exponential for the dynamic elastic modulus. It is important to point out that these correlations occur in the range that includes the evaluated porosity step (30–15%) (Fig. 1).

3.7.3. Mullite correlation

Fig. 11 shows the correlation of the three mechanical properties studied and the mullite content in the final materials evaluated by the Rietveld method. The mechanical properties increase with the mullite content. The mullite hypothesis is corroborated to this group of materials. It can be clearly shown although the mullite reinforcement method is not the only acting mechanism that undoubtedly this mechanism contributes to the increment in the mechanical properties. It is difficult to separate the mullite contribution to the other crystalline phases contribution (Section 3.7.2).

3.7.4. Mean pore size correlation

Finally Fig. 12 shows the values of the three mechanical properties studied as function of the mean pore size evaluated by porosimetry (Section 3.1). In the above sections the mechanical properties porosity relation could not be observed moreover the porosity was almost constant between 800 and

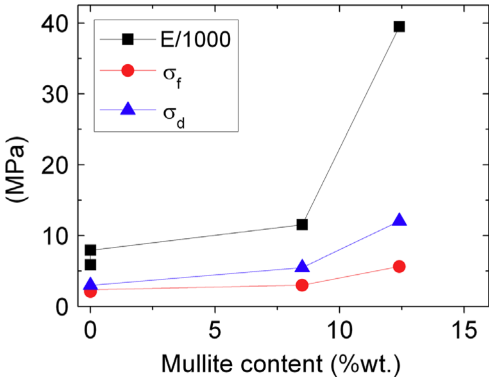

Fig. 11. Mechanical properties (flexural strength, diametral compression and dynamic elastic modulus) of the calcareous earthenware as a function of the mullite content.

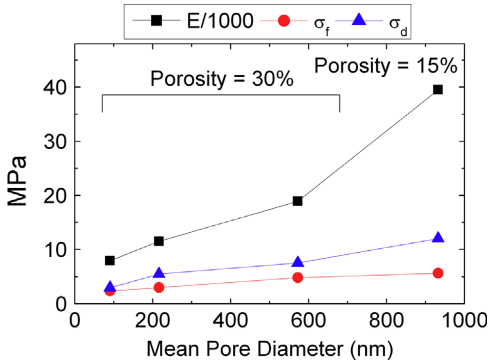

Fig. 12. Mechanical properties (flexural strength, diametral compression and dynamic elastic modulus) of the calcareous earthenware as a function of the mean pore diameter.

1050 °C firing treatments. However the mechanical properties are clearly correlated with the mean pore size in the sintering temperature range studied, this correlation must be taken into account together with the crystalline phase (neominerals and mullite correlation) revealed in Sections 3.7.2 and 3.7.3.

4. Conclusions

The effect of the firing temperature on the structural and textural properties of calcareous clay body was established in a previous work. This material is frequently employed for tableware, fired between 980 °C and 1040 °C. In this article the firing temperature correlation with the textural, structural and mechanical properties was established in the 700–1100 °C firing range. Materials fired between 800 °C and 1050 °C presented an interesting correlation between the processing variable (temperature) and the evaluated properties. The porosity in this range was almost constant however the properties evolved exponentially with the temperature.

The three mechanical properties evaluated increased in a parallel way showing that in this temperature range, with the accurate evaluation of one of them, the other two could be calculated. Furthermore a linear parallel correlation was found in the technological temperature range (800–1050 °C). Only after 1000 °C treatments the mechanical properties achieved were adequate for the application.

In fact, in this temperature range (800–1050 °C) the mechanical properties increase with the crystallization of the neominerals product of the described chemical processes. These neominerals are feldspars (plagioclase and gehelenite) and the spinel-type pre-mullite alumino silicate. Also during this range the pore sized increased exponentially with no densification.

The parallel growth of these mechanical properties was established. Moreover it was shown to be exponential in the wide range (700–1050 °C) and linear in a more technological range (900–1050 °C).

Finally the performed porosimetric analysis permitted to understand that the firing process of calcareous earthenware below 1050 °C is not strictly a sintering process with a gradual densification and loss of porosity instead it is a complex chemical processes accompanied by a textural evolution of pore size increase with no important porosity decrease. Only for higher temperature treatments (exceeding the technological ones) the porosity diminishes abruptly. This fact is accompanied by an increase in the mechanical properties figures and a loss in the dimensional stability.

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