MODELLING OF THERMO-MECHANICAL BEHAVIOUR OF PRE-INDUSTRIAL CERAMICS: FUNCTIONAL ANALYSIS VIA AN EXPERIMENTAL AND A NUMERICAL APPROACH

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Ceramics are the most abundant materials found in archaeological sites and they are often the only evidence of a productive area or of a settlement. Archaeological data suggest that ceramics could be divided into different classes and types on the base of function and on fabric (Rice, 1987). It could be deduced that each object has a particular “affordance”, which depends on its shape, raw material and production cycle (Kilikoglou & Vekinis, 2002).

While scientific research is at the base of the new composite materials and of the ceramics development, the production and the evolution of traditional ceramics was governed by empiricism and so by the good or bad outcomes of tests made by craftsmen, who produced objects suitable for a particular use without very proper materials (Hein *et al.*, 2007; Tite *et al.*, 2001).

Although industrial and academic research has already given a great contribution to the understanding of thermodynamical processes, mineralogical evolution and thermo-mechanical properties of new materials (*e.g.*, Coble, 1961; German & Munir, 1976; Tsvelikh *et al.*, 1995; Kuang *et al.*, 1997; Lee & Moore, 1998; Suzdal’tsev, 2003; Evans, 2008), the study of traditional and archaeological ceramics has not been given the same attention. Both the characterisation and the modelling of artefacts made of natural raw materials is more complicated than that of new composites, generally made of one or two phases.

However, in these last twenty years more attention has been paid to traditional and archaeological materials and in particular to technical ceramics (*e.g.*, Freestone, 1982; Pollard & Hatcher, 1994; Adriaens *et al.*, 1999; Eramo, 2006; Martinòn-Torres *et al.*, 2006; Hein *et al.*, 2007; Martinòn-Torres & Rehren, 2009). These works are focused on technological and functional analysis.

The functional analysis of a pre-industrial ceramic is one of the key steps of the archaeological and archaeometrical research. Several strategies and approaches have been used by scholars to identify the function of artefacts dug up from archaeological sites (Rice, 1987). While the early studies on this field tried to find a solution to function characterisation by comparing the object with other artefacts or ancient iconographies and written sources (Rice 1987; Orton *et al.*, 1993), in the recent twenty years the application of material science approaches has given a great help in the functional analysis. With this purpose, some works (Hoard *et al.*, 1995; Kilikoglou *et al.*, 1995, 1998; Kilikoglou & Vekinis, 2002; Hein & Kilikoglou, 2007; Hein *et al.*, 2008;) tried to analyze the function of archaeological ceramics, studying their physical properties by experimental and numerical approaches. However, while some technological aspects have been widely studied (*e.g.*, the effect of quartz addition on mechanical properties or the effect of pore shape on thermal conductivity), other aspects should be deeply investigated. For example, even if some works on the effect of the limestone addition on ceramics strength have been done (Hoard *et al.*, 1995), the effect of its granulometry and quantity has never been studied. Moreover, the effect of the temperature on mechanical properties of limestone-tempered bodies has never been analysed. Even if Garcìa-Ten *et al.* (2010) analysed the effect of both calcite and quartz on the thermal conductivity of the ceramic body, no information about granulometry is provided. The studies carried out till now have been led using a material science point of view and, hence, using temper with a specific grain size, not sand belonging to a granulometric distribution, which, on the contrary, occurs in archaeological artefacts (Rye, 1981; Rice, 1987; Orton *et al.*, 1993). While the phase evolution with firing temperature has been widely studied, the effect of mineralogy and microstructures developed in fired ceramic bodies, have been correlated with ceramics physical properties only in some cases (Hein *et al.*, 2008, 2013).

In this context, this work of thesis wants to contribute to deepen the knowledge on the effect of raw materials on the physical performances of traditional ceramics, as a tool for functional analysis. In particular, the effect of the nature, percentage and granulometry of the temper and firing temperature on the mineralogy, the microstructure and the thermo-mechanical properties of pre-industrial ceramics is investigated. Moreover, this thesis aims to model the behaviour of ancient ceramics and combine both experimental and numerical results in order to identify the possible “affordance” of an archaeological artefact and, in this way, give a contribution to the improvement of the functional analysis of ceramics.

With this purpose, ceramics briquettes were prepared using a kaolinitic clay tempered with 5, 15 and 25 vol.% of limestone and quartz, two of the most used non plastic elements added by ancient potters (Rice, 1987; Orton *et al.*, 1993; Velde & Druc, 1999). Contrary to previous works (Kilikoglou *et al.*, 1995, 1998), temper belonging to two granulometric distributions (a 1 mm- and a 0.125 mm- mode curves), and not with a specific grain size, is used in order to better represent the archaeological datum. Five percent of water was added to the mixture and briquettes were prepared by uniaxial pressing using a pressure of 25 MPa. Finally, samples were fired at 500, 750 and 1000 °C with a soaking time of 1 h.

For the determination of strength, toughness and Young’s modulus of the ceramics, three- and four-point bending tests were led, while for the measurement of their thermal conductivity a modified Lee’s disks apparatus was employed. Moreover, the porosity, the mineralogy and the microstructure of the ceramic samples were characterised using respectively water immersion, X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM).

The modelling of mechanical and thermal ceramic properties followed two different paths: for the forecasting of material strength a new model (Geometrical Siering Model) based on the ceramic sintering process was developed, while for the understanding of thermal behaviour of quartz-tempered ceramics a finite element model (FEM) was compared with a Marxwell-Litovsky approach (Kingery *et al.*, 1976; Litovsky *et al.*, 1992).

Results show that technological parameters highly affect the physical properties, the mineralogy and the microstructure of ceramics.

Temper addition reduces the strength of 1000 °C-fired ceramics but increases their toughness. At these temperatures, limestone-tempered materials are less resistant than quartz-tempered ones and the coarser the temper granulometry, the less strong the ceramic.

On the contrary, in samples fired at 500 and 750 °C, it produces an increase in material strength. There is not a great difference between limestone-tempered and quartz-tempered bodies, even if in samples fired at 500 °C the former are a little bit less strong than the latter ones and in ceramics fired at 750 °C the opposite occurs. At these two temperatures, granulometry does not affect the behaviour of quartz-tempered ceramics, while in limestone-tempered bodies the finer the sand, the stronger the material.

The increase in firing temperature improves the material strength due to the formation of new phases (amorphous phases, mullite and a spinel-type phase), which are more resistant than raw materials, and to the higher sintering level.

As to ceramic thermal behaviour, while the addition of quartz improves the thermal conductivity of ceramics, limestone reduces it. Moreover, in ceramics fired at 500 °C, the higher the quartz content, the higher the thermal conductivity, while at 750 and 1000 °C the maximum conductivity is measured with the 15% of quartz. SEM micrographs suggests that this is due to the α-β quartz phase transition which forms a detachment zone around quartz grains which behaves as a heat barrier reducing the thermal conductivity of samples tempered with 25% of quartz (Allegretta *et al.*, 2014). Granulometry does not affect the thermal conductivity of the body.

Numerical results were compared with experimental data and the Geometrical Sintering Model can describe the mechanical behaviour of medium-high sintered bodies using, as input, raw material characteristics.

Finite element model can describe better than previous methods the thermal behaviour of quartz-tempered ceramics and, via this approach, the influence of α-β quartz phase transition on ceramics thermal conductivity is explained.

Finally, technological and functional considerations were carried out and “recipes” for the production of storage and transport vessels, building ceramics, ware for internal and external heating were suggested.

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