Applied Clay Science 116–117 (2015) 220–230

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Strength of kaolinite-based ceramics: Comparison between limestone- and quartz-tempered bodies

Ignazio Allegretta *,[a], Giacomo Eramo [a], Daniela Pinto [a], Vassilis Kilikoglou [b]

[a] Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, 70125 Bari, Italy
[b] Department of Materials Science, N.C.S.R. "Demokritos", Aghia Paraskevi, 15310 Athens, Greece

ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form 17 March 2015
Accepted 21 March 2015
Available online 2 April 2015

Keywords:
Kaolinite-based ceramics
Transverse rupture strength
Young's modulus
Limestone ad quartz temper
Firing temperature
Grain size distribution

ABSTRACT

The addition of temper was a common practice in the fabrication of traditional ceramics. The present work shows the effects of limestone or quartz added as temper to a kaolinitic clay, on the strength of the ceramic body. With this purpose ceramic tests were prepared adding the 5, 15 and 25% of each temper to a kaolinitic clay. Unimodal skewed grain size distributions (GSDs) for temper were used instead on single grain sizes used in previous experimental works. Furthermore, samples were fired at 500, 750 and 1000 °C in order to analyse the effect of firing temperature on ceramic strength. A correlation between the strength and the porosity, the mineralogy and the microstructure of the samples is presented. Results shows that while temper improves the strength of 500 °C- and 750 °C-fired bodies, it worsens that of samples fired at 1000 °C. Moreover, while at 500 and 1000 °C limestone-tempered materials are less strong than quartz-tempered ones, at 750 °C the opposite occurs. For quartz-tempered bodies fired up to 750 °C, no difference in strength changing the temper GSD is observed, while in other cases the coarser the temper, the less strong the ceramic.

1. Introduction

Tempering, both by straightforward addition of non-plastics and by mixing clays, is a common practice in the manufacture of traditional ceramics since antiquity (Rye, 1976; Maggetti, 1982; Rice, 1987; Velde and Druc, 1998; Rye, 2002; Orton et al., 2008; Tite, 2008). Many different tempering materials have been used through time: natural materials, like rock and shell fragments, sand, seeds, bones or artificial ones, like grog and chamotte were often added to the clay kneading.

The presence of temper affects many physical properties that are crucial at the different stages of the ceramic production: it reduces the water absorbed by the kneading, producing a reduction of clay plasticity and drying time; moreover, it works as a skeleton enabling the withstanding of the object during drying and firing (Velde and Druc, 1998).

The two most common mineral phases present in temper are quartz and calcite (Rice, 1987; Rye, 2002; Broekmans et al., 2004; Eramo et al., 2004; Orton et al., 2008). According to the firing temperature used, these two materials face different mineralogical changes which affect the microstructure on the fired product and its physical properties (Allegretta et al., 2014). Quartz has a refractory behaviour and up to the metastable melting point (about 1450 °C) it undergoes a polymorphic reaction (α- to β-quartz) at 573 °C accompanied by a 5% increase in volume (Heaney, 1994) although there are also suggestions for 2% (Majumdar et al., 1964; Yao and Hatta, 1995).

On the contrary, calcite is not so stable at high temperatures. In fact, in the range between 700 and 850 °C calcium carbonate decomposes (Maggetti, 1982; Riccardi et al., 1999)

$$CaCO_3 \xrightarrow{700\text{–}850\,°C} CaO + CO_2(\uparrow)$$

producing hygroscopic CaO which then, in cases of ceramic bodies with a relevant open porosity, it reacts with the H_2O of the air forming $Ca(OH)_2$. This phase (portlandite) has greater volume than that of calcium carbonate and can cause the formation of cracks or failure of the ceramic body.

It is apparent then that temper affects drastically the performance characteristics of the fired ceramic bodies, something which attracted substantial attention in the last three decades. The studies have mainly reference to archaeological pottery, trying to explain changes of tempering traditions with time and use (Steponatis, 1984; Sabrah and Ebied, 1985; Bronitsky and Hamer, 1986; Okongwu, 1988; Hoard et al, 1995; Kilikoglou et al., 1995, 1998; Hein et al., 2008; Garcia-Ten et al, 2010a,b; Hein et al., 2013; Allegretta et al, 2014).

Regarding the mechanical properties of tempered ceramics, Kilikoglou et al. (1998, 1995) reported that the addition of quartz to

* Corresponding author. Tel.: +39 0805442608; fax: +39 0805442625.
E-mail addresses: ignazio.allegretta@uniba.it, ignazio.allegretta@libero.it (I. Allegretta), giacomo.eramo@uniba.it (G. Eramo), daniela.pinto@uniba.it (D. Pinto), kilikog@ims.demokritos.gr (V. Kilikoglou).

http://dx.doi.org/10.1016/j.clay.2015.03.018
0169-1317/

the clay mixture reduces Young's modulus and strength, while in volume fractions over 20% it improves the toughness of the fired product (950 °C). They also observed that the coarser the sand, the lower the ceramic strength. Other works deal with the comparison between the mechanical properties of ceramics tempered with different materials. In this field of the research, Hoard et al. (1995) observed that low-fired ceramics (600 °C) tempered with 35 wt.% of calcite are stronger than those tempered with the same amount of grog or grit. The same was found by Garcia-Ten et al. (2010b) for ceramics fired at 1000 °C, even if they used different grain sizes for quartz and calcite. In all the above mentioned works temper was added in specific grain sizes, although traditional potters usually use temper exhibiting a grain size distribution.

The effect of firing temperature on strength was systematically studied by Jordan et al. (2008). In fact, they observed that the increase in strength is relevant firing illite-based clay over 1050 °C because porosity and pore dimension reduce and new crystalline phase form from the decomposition of the illite. However, only non-tempered ceramics were tested. On the other hand, the effect of firing temperature on tempered materials was studied in deep by Müller et al. (2010), but the work was based on the study of granite and phyllite and no limestone was used in their experiments. Using a calcareous clay, they found that the greatest increase in strength is at 850 °C where the vitrification of the matrix enables a stronger bonding between particles. No further increase in bending strength was observed at higher temperatures. A decrease in strength was produced by adding aplastic material which produces cracks around it due to the thermal expansion mismatch between matrix and temper. Müller et al. (2010) found that also the shape of the temper affects this mechanical property since the addition of platy-shaped aplastic material led to a less reduction in strength than spherical ones. On the contrary, the fracture energy increases with the addition of temper whatever the firing temperature and, consequently, tempered ceramic can withstand load for a long time without failing immediately once the breaking point is reached. The shape of the added material influences this behaviour only at high temperature (1050 °C) where ceramic tempered spherical granite grains are tougher than phyllite-tempered bodies because in this last materials fracture propagates also through the temper grain resulting in a reduction of the toughness component.

Quartz is normally the most abundant phase present in clayey sediments. Its contribution to possible formation of secondary porosity, more than its reactivity to form new phases during firing, is a distinguishable feature compared to other silicates. Conversely, the presence of marine or continental calcite is critical for the firing process and functionality of the ceramic, since its reactivity may damage the ceramic body (Rye, 1976). However, Garcia-Ten et al. (2010b) found that when fine calcite and dolomite (particle size in the range of 14 to 24 μm) are added to the clay, the ceramics produced are stronger than those tempered with the same amount of quartz or feldspar.

The present work aims to analyse in a systematic manner the effect of both limestone and quartz on the strength of traditional ceramics in relation to the temperature they have been fired. Such types of temper were added to three different clays, (1) kaolinitic clay poor in iron, (2) kaolinitic clay rich in iron and (3) illitic calcareous clay, taking into account their firing characteristics as reported in several publications (e.g. Maggetti and Rosmanith, 1981; Maggetti, 1982; Riccardi et al., 1999; Cultrone et al., 2001; Eramo et al., 2004). In this paper, we report the results obtained from ceramic tests prepared with a clay of the first type, which could be assimilated to earthenwares produced by primary clays (e.g. Smith, 2000; Buxeda I Garrigòs et al., 2003; Eramo and Maggetti, 2013).

The goal is to conduct a comparative study of these two important temper materials, using the same clay paste, in order to understand how these materials can affect the mechanical behaviour of a kaolitic-based ceramic. Another important aspect in the present work is that the specific temping materials used unimodal and skewed GSD imitating the ones found in archaeological and traditional pottery. These results could be also used in ceramic studies aiming to relate raw materials with the affordance of archaeological ceramic finds.

Table 1
GSD of the temper used the production of the ceramic briquettes.

ϕ	d (mm)	1 mm-granulometry	125 μm-granulometry
		wt.%	wt.%
−1	2.000	5	0
−0.5	1.414	20	1
0	1.000	35	2
0.5	0.707	17	3
1	0.500	8	4
1.5	0.354	5	5
2	0.250	4	8
2.5	0.177	3	17
3	0.125	2	35
3.5	0.088	1	20
4	0.063	0	5

2. Materials and methods

The base clay used in this work is a kaolinitic one poor in iron (1.2 of Fe_2O_3) with the following mineralogical composition: kaolinite = 58%, illite = 18%, smectite = 2%, quartz = 22%, rutile and anatase in traces (Bellanova, 2009). With this clay thirteen mixtures were produced containing 5, 15 and 25 vol.% of quartz or limestone. Temper belonged to two distinct GSD (Table 1): a fine sand with a mode at 125 μm (positive-skewed curve) and a coarse sand having a mode at 1 mm (negative-skewed curve). The positive-skewed curve has a mean, median, standard deviation and skewness respectively at 2.7, 1.5, 1.7 and 0.7 (in ϕ values). In the negative-skewed curve, only the mean and the skewness change and they are set respectively at 0.3 and −0.7 (in ϕ values). In all mixtures, 5 vol.% of water was added and three bars (10 × 10 × 55 mm) per mixture were fabricated by applying uniaxial pressure of 25 MPa. After a drying time of 24 h at a temperature of 100 °C, samples were fired at 500, 750 and 1000 °C at a rate of 150 °C/h and a soaking time of 1 h. The briquettes were tested one month after their formation in order to enable the hydration reaction of CaO in limestone-tempered specimens. In this way, also the effect of portlandite and at the extent at which limestone is deleterious for the strength of the ceramics could also be studied. A total of 117 samples were prepared.

Specimens were labelled according to the type, amount and granulometry of temper they contain and the temperature that they were fired, as follows:

1. for non-tempered ceramics the prefix NT is followed by the firing temperature (500, 750 and 1000 °C);
2. for the other material the label is composed by the percentage (5, 15 and 25), the granulometry (F for fine and C for coarse) and the nature of the temper (L for limestone and Q for quartz) followed by the

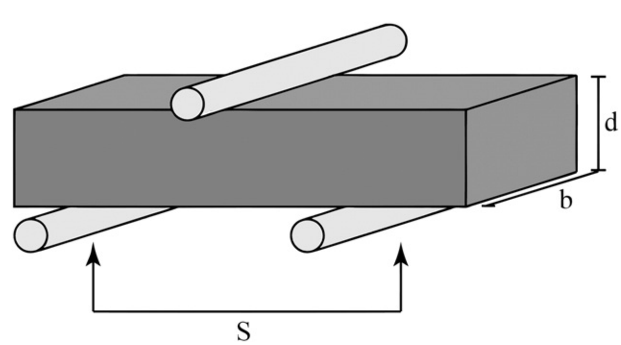

Fig. 1. Diagram of the experimental setup used for three-point bending tests.