

THE INFLUENCE OF TEMPER ON PERFORMANCE CHARACTERISTICS OF COOKING WARE CERAMICS

^{1,2}N. S. Müller - ¹V. Kilikoglou - ²P. M. Day - ¹A. Hein - ¹G. Vekinis

¹Institute of Materials Science, NCSR Demokritos, nmueller@ims.demokritos.gr

²Department of Archaeology, University of Sheffield

Abstract: *The influence of temper on the performance characteristics of cooking ware pottery is assessed. Emphasis is placed on the examination of the impact of temper shape (platy vs. angular) on strength, toughness, thermal conductivity and thermal shock resistance. Mechanical and thermal tests performed on experimental briquettes tempered with phyllite or granite show that an improvement of those material properties thought to be relevant for cooking ware is achieved when replacing platy phyllitic with angular granitic temper.*

Keywords: *Cooking ware, thermal properties, mechanical properties, pottery*

INTRODUCTION

The present study is part of a larger project that investigates the technology of Bronze Age cooking vessels from Akrotiri, Thera, in Greece. The petrographic examination of the assemblage revealed a rich variety of fabrics, some of them clearly indicating imports from other islands, others representing different recipes within locally produced wares. An argument that is frequently used to explain changes in manufacturing parameters such as tempering practices, especially in the case of cooking ware, is the optimisation of performance characteristics. Those usually discussed are strength, toughness or thermal properties. However, although these material properties have long formed the core of discussions concerning issues of functional requirements and the suitability of pottery for its varied uses in the past, our current understanding of them is still far from complete (*Tite et al. 2001*). To provide a valid baseline for a discussion on topics related to performance optimisation, the influence of different temper materials identified in cooking ware from the Aegean Bronze Age, namely angular granite and platy phyllite, on a series of mechanical and thermal properties was assessed:

Transverse fracture strength, usually determined as modulus of rupture (MOR), gives a measure of the amount of stress a material can be exposed to until cracks initiate. In the case of very brittle materials, for example high fired ceramics, the initiation of a crack is usually equivalent to the failure of the vessel, due to unstable crack growth. In a tougher material the crack can be arrested by different mechanisms and stable fracture occurs. The stronger a vessel, the more energy is required to initiate a crack. However, only assessing the strength of a ceramic vessel does not necessarily provide information on when it will lose structural integrity.

To this end, the *toughness* of a material has to be established. Toughness is a measure of the intrinsic fracture energy, required for crack initiation, and of the

energy that is absorbed by the material during crack propagation, through mechanisms such as deflection and arrest.

Thermal shock resistance specifies whether a material is able to withstand repeated drastic changes in temperature.

Thermal conductivity, finally, is a measure of the heat transfer in a material under a particular temperature gradient.

The aim of the present paper is to discuss qualitative differences in the impact of granitic and phyllitic temper on those material properties, based on changes in the ceramics' microstructure, rather than giving an account of the quantitative results of the material tests that were performed on the experimental briquettes. For this reason numerical results are only given where they serve to illustrate the principles discussed.

EXPERIMENTAL

Based on the fabrics observed in the cooking ware assemblage of Bronze Age Akrotiri, granitic and phyllitic temper were chosen to assess the impact of temper shape on a series of performance characteristics. All measurements were carried out on experimental briquettes, as archaeological material is subject to alteration through use and subsequent burial. Additionally, to assess the influence of individual parameters on mechanical and thermal properties, it is imperative to work under controlled conditions.

Manufacture of briquettes

Two different base clays were selected for the fabrication of the replica briquettes: a calcareous (>20% CaCO₃) clay from Pikermi (Attiki, Greece) and a non-calcareous clay, from Kalami (Crete, Greece).

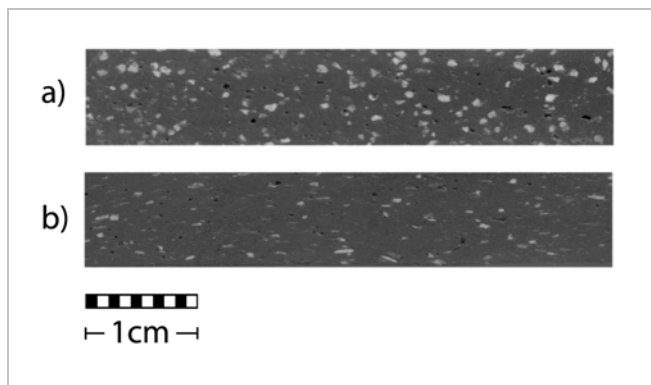


Fig. 1 Cross section of replicate briquettes, containing 10% of granite (a) and 10% of phyllite temper (b) respectively.

Fractions with a particle size of $<30\ \mu\text{m}$ were separated from the raw clays and mixed with two different types of temper materials: granite from the island of Naxos (Greece) and phyllite from the northeast Peloponnese (Greece). Both rock types were crushed and fractions with a particle size of $0.5\text{--}1.0\ \text{mm}$ were separated to be used for tempering.

Mixtures with 10 wt% and 40 wt% temper material were prepared, in addition to untempered reference pastes. For the preparation of the phyllite tempered briquettes, the paste was repeatedly folded and flattened, in order to obtain a preferred orientation of the platy phyllite particles parallel to the largest surface (**Fig. 1**). The different pastes were fired to 550, 850 and 1050°C with a heating rate of 200°C/h and soaking times of 1 hour in oxidizing atmosphere.

Measurement of mechanical and thermal properties

Fracture strength was measured in three point bending tests on bars of approximately $10 \times 10 \times 60\ \text{mm}$ using an INSTRON universal tester, with a loading rate of $104\ \mu\text{m}/\text{min}$. The modulus of rupture was determined on 5 specimens per paste/temperature combination. Samples with clearly identifiable macroscopic flaws were not included in the calculation of the mean value. *Fracture toughness* was established on pre-notched test bars of the same size, from four point bending tests, at a loading rate of $52\ \mu\text{m}/\text{min}$. For all experiments load displacement curves were recorded. MOR and fracture energy were calculated as described in *Kilikoglou et al. (1998)*. *Thermal shock resistance* was assessed as reduction in fracture strength after thermal shocking by quenching. Thermal shocking consisted of subjecting the test bars to five cycles of sudden temperature changes in the range of 400°C, by alternately placing them in a furnace maintained at 430°C and in a waterbath (30°C). *Thermal conductivity* was assessed with a modified Lees' disk set-up as described in *Hein et al. (2008)*. With the phyllite tempered fabrics, all measurements were performed perpendicular to the alignment axis of the inclusions.

RESULTS

Fracture strength

Any addition of temper material led to a decrease of fracture strength compared to the untempered reference briquettes. The more temper added, the greater the loss in strength. This observation seems to be a consequence of the fact that temper particles damage the ceramics' matrix during firing and drying. During drying, damaged zones are formed around the rigid particles due to hydrostatic tensile stresses. These zones are highly susceptible to cracking when fired: the different thermal expansion factors of temper and matrix result in the formation of microcracks (*Kilikoglou et al. 1995*). A consequence of the increase in overall flaw population is the observed decrease in fracture strength.

The impact of phyllitic temper on strength reduction is less severe than of the same amount of granitic temper. The reason for this lies in the relative amount of flaws introduced by the two temper types. It might be argued that different thermal expansion of the temper *material* is responsible for this behaviour; here especially the impact of quartz is frequently referred to (*Tite et al. 2001*). However, the volume fractions of quartz in both temper types used in this study are quite similar and do not account, on their own, for the observed differences. It is therefore necessary to take a look at the impact of the difference in temper *shape*. In the case of rather globular particles, stresses during drying result in a damaged area that can be described as a sphere around the whole particle (*Kilikoglou et al. 1995*). Accordingly, it can be argued that in the case of platy particles, the damaged zone around the edges of a flake is of toroidal shape. The overall volume fraction of the ceramic that is susceptible to develop microcracks during firing is thus much smaller and fewer flaws are introduced into the material (**Fig. 2**). As a consequence, higher fracture strength is observed for the phyllite tempered fabrics.

Toughness

The addition of temper to a base clay results in an increase in toughness at all firing temperatures. The more temper added, the higher the increase. This behaviour is expected, as the temper particles provide the ceramics with additional means of deflecting and arresting cracks. For the ceramics fired at 850°C, both types of temper result in fabrics with similar toughness. Only when the briquettes are fired to 1050°C does the toughness of the phyllite tempered fabrics decrease in comparison to the lower fired pastes, while the toughness of the granitic tempered ceramics remains stable at a high level. The high fired phyllitic fabrics are significantly less tough than the corresponding granitic ones. The intrinsic toughness, i.e. the amount of energy that is needed to start crack propagation, is actually greater in the case of phyllitic tempered fabrics, but the energy that is absorbed during crack *propagation* accounts for the

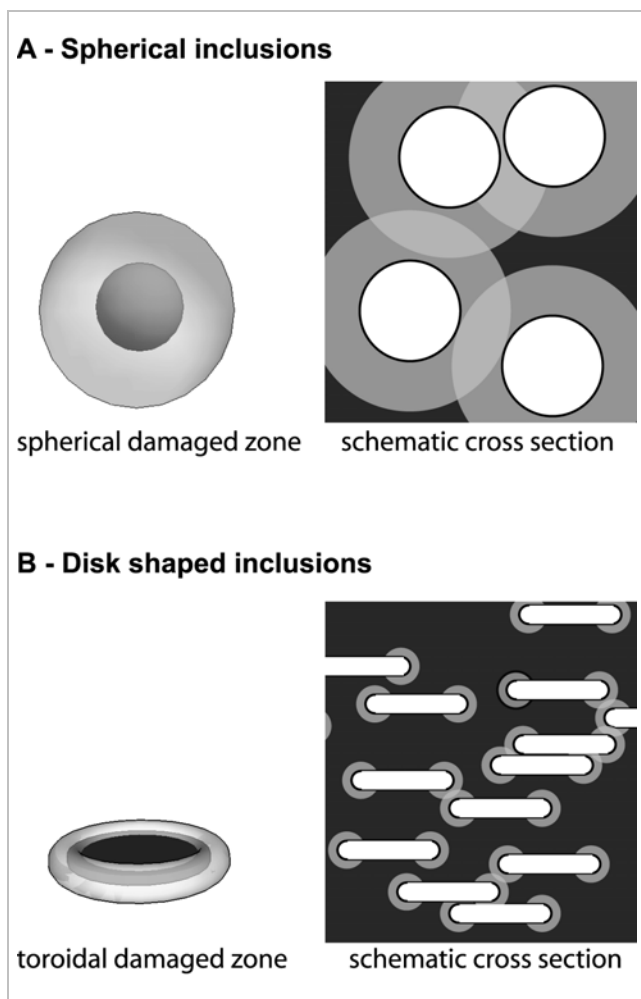


Fig. 2 Different geometries of damaged zones due to different temper shape and resulting difference in amount of damaged matrix as illustrated by schematic cross sections (damaged area in light grey).

difference. In the case of granitic temper, a significant amount of energy is needed to propagate the crack through the ceramic. This is not the case for phyllite temper; here semi-stable to brittle fracture is observed. Due to increasing strength of the matrix, crack propagation starts at higher loads and the stored energy is great enough for the crack to propagate through the particles, breaking the thin plates along the short axis.

This happens to a much lower extent in the high fired granitic fabric, as the amount of energy required to break a granitic grain is much greater. The observation that at lower firing temperatures both types of temper result in fabrics with comparable toughness is due to the fact that the phyllite temper still exhibits toughening properties in ceramics fired up to 850°C. The crack propagation starts at lower fracture loads, the stored energy is lower and can be absorbed by crack deflection and through pull-out mechanisms of the particles (**Fig. 3**).

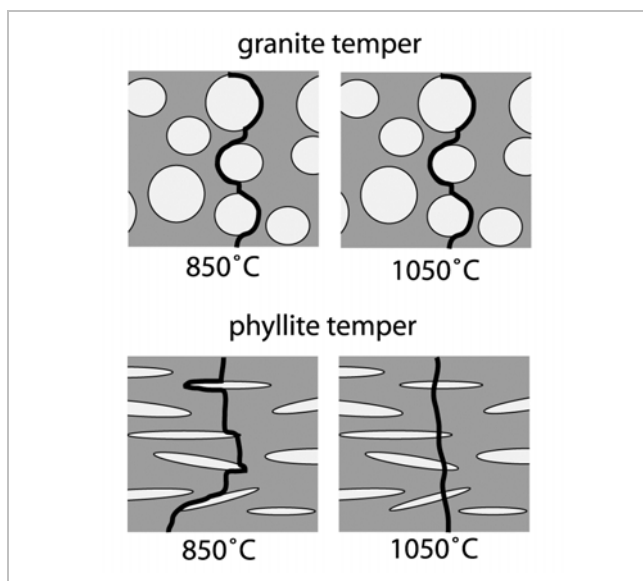


Fig. 3 Schematic crack paths for phyllite and granite tempered fabrics fired to 850°C and 1050°C respectively.

Thermal properties

Thermal shock resistance as assessed here is a measure of the stability of the strength level of a material that is exposed to sudden changes in temperature. Thermal shock resistance improved with increasing amounts of temper material. As discussed above, the addition of temper introduces flaws to a ceramic. A structure with a high number of flaws and cracks can better accommodate the tensions that arise from differing thermal expansion due to a temperature gradient within a material. As a result, fewer new cracks form and the reduction in fracture strength is less severe. Accordingly, low fired, highly tempered fabrics showed the highest thermal shock resistance. Phyllite tempered fabrics lost relatively more strength than their granitic tempered counterparts, an observation that is in-line with the reasoning above: i.e. the platy shaped temper particles induce fewer flaws and the resulting fabrics are thus more susceptible to microcracking.

It is important to note here that a material with high thermal shock resistance does not necessarily have a higher residual strength after quenching than a material with a lower resistance to thermal shocking. When comparing the absolute strength values after thermal shocking, it is important to note that the phyllitic tempered ceramics are still stronger than the corresponding granitic ones, although their thermal shock resistance is inferior (**Fig. 4**). Another point worth mentioning is that a decrease in strength upon thermal shocking can be accompanied by an increase in fracture toughness. For some fabrics this was observed to be associated with a change in fracture mode, so that considerably more energy was required to propagate a crack through the thermally shocked material.

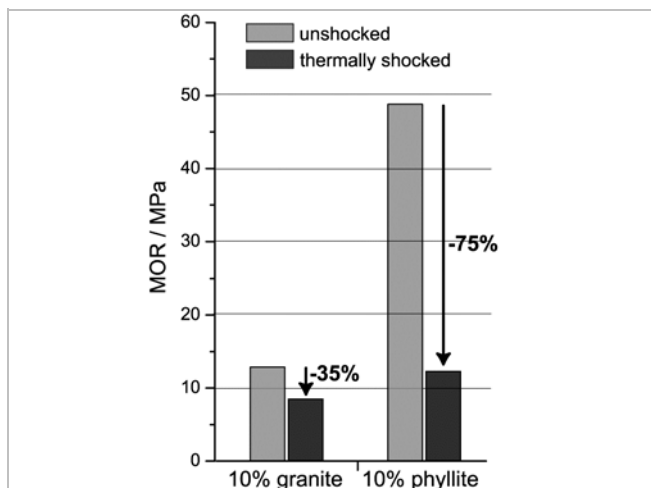


Fig. 4 Transverse fracture strength before and after thermal shocking of ceramics tempered with 10 wt% granite and phyllite, made from non calcareous clay, fired at 1050°C. Tempering with granite results in a more stable strength level, however, the residual strength after thermal shocking is higher for the phyllitic tempered fabrics.

As described in detail elsewhere (Hein *et al.* 2008), phyllitic temper has been found to reduce the *thermal conductivity* of the replica briquettes significantly; this reduction is less pronounced with granitic temper.

DISCUSSION

To summarise the influence of the different temper types on the measured mechanical and thermal material properties we can state the following (**Table 1**): any addition of temper reduces fracture strength, although this effect is less pronounced with platy temper. On the other hand, when aiming for a tough material, the addition of temper is beneficial. The kind of temper does not play an important role unless the ceramics are fired to high temperatures. In this case it is preferable to add angular granitic temper. The thermal shock resistance of material tempered with granite is improved compared to a phyllite tempered one, but the residual strength of the latter is higher. And, finally, to ensure high thermal conductivity, granitic temper proved to be a better choice than phyllite. We can theorise that, for cooking pottery, toughness, thermal shock resistance and thermal conductivity are more important parameters than strength. Apart from the obvious fact that cooking is intrinsically tied to heat, cooking ware as a utilitarian product is used on a daily basis and has to deal with frequent impacts due to stirring and handling, suggesting the relative importance of toughness over strength. On these grounds, we could argue that the use of granitic temper instead of phyllitic temper results in ware better adapted to cooking purposes. However, this statement is subject to restrictions. All the above is valid for *materials*, without consideration of the influence of vessel shape.

	Phyllite (platy)	Granitic (angular)
Strength	+	
Toughness		
- Low- intermediate fired	no influence	no influence
- High fired		+
Thermal shock resistance		
- Relative loss in strength		+
- Residual strength	+	
Thermal conductivity		+

Table 1 Influence of temper on performance characteristics.

To assess the performance of an object such as a cooking vessel, it is imperative to take its geometry into account, as mechanical and thermal properties are sensitive to such factors as wall thickness or curvature. This can be achieved with computer modelling, based on material properties such as those assessed herein (e.g. Kilikoglou & Vekinis 2002; Hein & Kilikoglou 2007). Furthermore, it is essential to consider which of these properties are behaviourally relevant in which context, i.e. can possibly be discerned by the potter or the user.

CONCLUSIONS

It seems, for the demands commonly made on cooking ware, that angular granitic temper results in ware that is better suited for cooking purposes than a platy, phyllitic one. However, as discussed above, this can only be a preliminary statement, as it is based solely on the properties of the material. Further work, taking vessel shape into account is necessary to confirm this hypothesis. Also, it has been highlighted that strength, toughness, thermal shock resistance and thermal conductivity cannot be considered as independent properties, as they all are dependent on the microstructure of a material. Improving one property usually occurs at the expense of another. Therefore, changes observed in manufacturing techniques must always be viewed considering this complex interplay, i.e. by carefully evaluating their effects on an array of potentially significant material properties, rather than basing a discussion on an isolated variable.

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