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The influence of temper shape on the mechanical properties of archaeological ceramics

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Abstract

The influence of tempering on the mechanical performance of pottery is assessed. Emphasis is placed on the examination of the impact of temper shape (low vs. high sphericity) and extent of vitrification on the strength and toughness of the ceramic material. Measurements on experimental briquettes show that the replacement of platy phyllitic temper with bulky granitic temper results in a reduction in strength but, at least at very high firing temperatures, in an increase in toughness. The observed differences in strength reduction with different temper shapes is semi-quantitatively assessed by adapting the damaged zone model, developed previously to disk-shaped particles. The effect of temper shape on toughness is particularly pronounced at high firing temperatures, where platy temper results in significantly lower fracture toughness of the corresponding material.

Keywords: Traditional ceramics; Mechanical properties; Strength; Toughness; Inclusions; Archaeological ceramics

1. Introduction

An argument that is frequently brought forward to explain changes in pottery manufacturing parameters, such as tempering practices, is the optimisation of performance characteristics. Within this context, the material properties usually discussed are strength, toughness or thermal properties. Although these material properties have long formed the core of discussions pertaining to functional requirements and the suitability of pottery for its varied uses in the past, our current understanding of them is still far from complete.[1]

Strength and toughness are important measures of the mechanical performance of archaeological ceramics. During manufacture and use-life, pottery is expected to withstand continuous exposure to various mechanical stresses without experiencing structural damage or losing functionality. The nature and the extent of these external stresses depend to a large part on the function of the vessel. Amphorae, for example, need to survive stacking during transportation (i.e. be able to bear the load of the overlying vessel layers), while any vessels used as containers should withstand the pressure exerted by their contents without fracture. For such sustained stresses it is strength which is a measure of survival. On the other hand, regularly manipulated pottery such as cooking vessels should be fit to endure frequent handling and activities such as cleaning or stirring. Any pottery product which is transported, be this by pack-animal or in a ship's hull, is exposed to impact stresses due to collisions with other objects or with the transportation means itself, caused by the movement of the carrier. For such short-term stresses, toughness can serve as a measure.

The *strength* of a material describes its ability to withstand the stresses it is subjected to without fracture initiation. For pottery, compressive strength is of very little importance since a pottery vessel is rarely subjected to pure compression; if it fractures, it usually does so in bending, under local tensile stresses. For this reason, it makes most sense to look at *bending strength* when studying the influence of different material parameters on the strength of pottery. The *transverse fracture* (*or rupture*) *strength* gives a measure of the amount of bending stress a material can be exposed to until cracks initiate on the surface under tension. In the case of very brittle materials, for example high-fired ceramics, the initiation of a crack is usually equivalent to the failure of

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the vessel, due to unstable crack growth. The stronger a vessel, the more energy is required to initiate a crack. For pottery, however, just assessing the strength of a vessel does not necessarily provide information on when it will lose structural integrity. For this, the *toughness* of the material has to be established. *Toughness* is a measure of the intrinsic fracture energy, required for crack initiation plus the energy that is absorbed by the material during crack propagation, through micromechanisms such as crack deflection, friction and crack arrest. It is therefore linked to the maintenance of structural integrity after crack initiation. Pre-existing flaws, ubiquitous in a material such as pottery, are potential origins of cracks. It is thus important that a crack, once initiated, is stopped quickly and effectively before leading to total fracture.

Fracture strength and toughness of traditional ceramics are known to be dependent on variables such as type of clay, temper and firing temperature. The determination of mechanical properties of clay ceramics in view of archaeological material has been reviewed recently.[1] Fracture strength has been determined in bending tests on archaeological material[2] or on replicates.[3–5] Since this testing method requires regularly shaped specimens and several measurements on different test bars cut from one sample, in many cases it cannot be employed for archaeological specimens. There are, however, alternative tests better suited for measurements on archaeological ceramics.[6,7] Toughness has been determined on replicates, in loading experiments of various designs.

A series of studies (e.g.,[4,5,8]) have contributed to our knowledge of the effect of technological choices on the performance of archaeological ceramics, especially regarding the influence of the volume fraction and grain size of temper on mechanical properties. Since the shape of aplastic inclusions is known to have an influence on the Young's modulus of a ceramic,[9] *temper shape* is also expected to influence mechanical properties. The effect of temper shape on the mechanical properties of archaeological ceramics is of interest since temper with different shapes was used widely in pottery production. Platy temper includes materials such as phyllite or shell, while typical bulky temper comprises quartz, granite or calcite, to name but a few. In this study the influence of temper shape on the strength and toughness of ceramic material is examined, comparing phyllite and granite as tempering materials. These two tempers, which usually display a platy or bulky shape respectively, were used widely in pottery production during the Aegean Bronze Age. Their selection for the present study reflects the particular archaeological case which gave the impetus for the assessment of temper shape, namely the cooking ware assemblage at Akrotiri, on Thera, Greece. Furthermore, it ensures comparability with an analogous study on quartz-tempered ceramics.[8] Sand and shell, another pair of platy and bulky temper frequently discussed in North American contexts,[2,3,10,11] are not suited for a systematical assessment of the influence of temper shape, as the stability range of shell temper is restricted to low firing temperatures.

For the present work, a range of briquettes was manufactured and tested to assess their mechanical properties. A calcareous clay was chosen as the base clay, due to the popularity of such clays in ancient pottery production in the Aegean. This paper presents the results of mechanical tests performed on these experimental briquettes. It discusses the influence of tempering on the mechanical properties of traditional ceramics, focusing on the effects of temper shape. Although strength and toughness are interdependent variables, as they both are based on changes in a ceramic's microstructure, for reasons of clarity, the strength and toughness experiments are presented and discussed separately. It is anticipated that this work, along with the existing literature, will provide a baseline for the discussion of tempering choices related to performance optimisation.

2. Experimental

In order to investigate the influence of tempering on mechanical properties, a series of experimental briquettes was fabricated and examined for strength and toughness. Specifically, bulky granitic and platy phyllitic tempers were chosen to assess the effect of temper shape. All measurements were carried out on replicates, since archaeological material is subject to alteration through use and subsequent burial. Furthermore, in order to assess the influence of individual parameters on mechanical performance, it is imperative to work under controlled conditions.

2.1. Materials and processing

Test specimens were fabricated with a calcareous (ca. >23% $CaCO_3$) clay from Pikermi (Attiki, Greece). This clay has been used in previous studies of mechanical and thermal properties and its chemical and mineralogical composition is described in detail elsewhere.[8,12] A fraction with a particle size of <30 μm was separated from the raw clay and mixed with bulky granite from the island of Naxos (Greece) and platy phyllite from the Northeast Peloponnese (Greece), respectively. Both materials were crushed and sieved to pass through a 1 mm mesh size, discarding the fraction which would pass through a 0.5 mm mesh size (in the case of the platy phyllite, the aspect ratio of the temper particles was approximately 1:5–1:10) (Fig. 1). Ceramic briquettes with 10 vol% and 40 vol% temper material were prepared in addition to untempered reference briquettes, resulting in a total of five different clay mixtures (Table 1). The briquettes were formed using a Perspex mould (*c*. 12 cm × 7 cm × 1 cm). For the preparation of the phyllite tempered briquettes, the paste mixture was repeatedly folded and flattened, in order to obtain a preferred orientation of the platy phyllite particles parallel to the largest surface of the briquettes, imitating common archaeological fabrics. The determination of the mechanical properties of the phyllite tempered fabrics was performed perpendicular to the alignment axis of the inclusions. The briquettes were dried for over 10 days at ambient temperature and humidity, covered by plates made of plaster of Paris to ensure homogenous drying. Briquettes of each composition were fired at 550 °C, 850 °C and 1050 °C. These temperatures were chosen since they were expected to lead to different microstructures: 550 °C is well below and 850 °C is around the onset of vitrification, while 1050 °C usually results in extensive vitrification.[13] Firing took place with a heating rate of 200 °C/h and a soaking time of 1 h in oxidizing atmosphere. The large surfaces of the fired briquettes

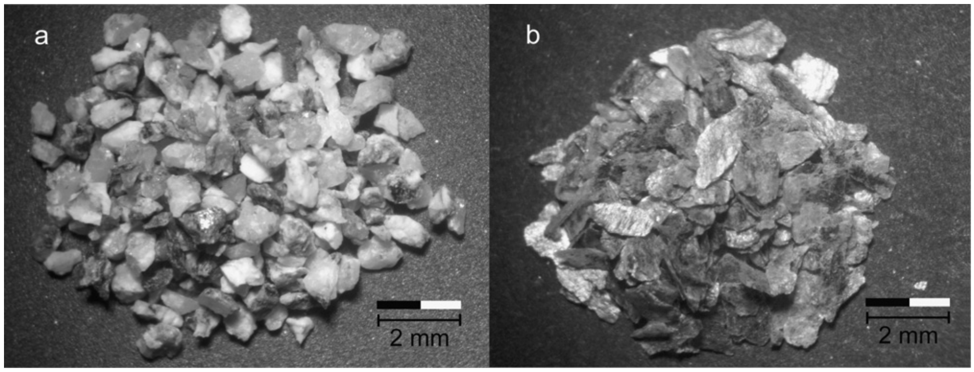

Fig. 1. Photograph of granitic (a) and phyllitic (b) temper material as used in the production of the experimental briquettes, fraction with particle size 0.5–1 mm. The difference in shape is clearly visible.

were ground parallel and cut into test bars of an approximate size of 1 cm × 1 cm × 7 cm for bending tests.

2.2. *Fracture strength*

The bending strength or transverse rupture strength (TRS), also known as the modulus of rupture in bending (MOR), was determined from three-point bending tests on bars of an approximate size of 1 cm × 1 cm × 7 cm on an INSTRON 1195 universal testing machine, at a constant loading rate of 109 μm/min. The load as a function of displacement was recorded for every specimen. For every ceramic type (corresponding to one set of parameters) TRS was measured on five bars. It is important to note that the strength of ceramics, which always contain a multitude of microstructural imperfections that can act as crack initiators (e.g., inclusions, pores, debonded zones, microcracks), is not an intrinsic material property but strongly dependent on those pre-existent flaws, on their distribution and concentration. After breakage, the fracture area was examined visually with the aid of a stereo microscope. Data from bars with clearly identifiable macroscopic flaws in the fracture surface were not included in the determination of the mean. TRS was then calculated according to standard methods.[14]

2.3. *Toughness*

The intrinsic toughness, G_{1c} is the energy that is needed for the onset of fracture, i.e. for the crack to initiate, and is mainly due to elastic deformation of the material, which, for brittle materials, is always small. For brittle materials that do not exhibit energy dissipation micromechanisms, the fracture energy is just the intrinsic part and can be determined by measuring the "fracture toughness" K_{1c} and Young's modulus E independently.[8] However, various ceramic materials exhibit micromechanisms that dissipate energy during crack propagation and accordingly show stable or quasi-stable fracture. In these cases, the so-called toughening component G_t, appears as a tail in the load–displacement curves and needs to be taken into account for the determination of the total toughness. To assess toughness, the fracture energy was determined from four-point bending tests on pre-notched bars of an approximate size of 1 cm × 1 cm × 7 cm, with a notch depth of 1 mm. The loading rate was held constant at 54 μm/min. For every ceramic type (corresponding to one set of parameters) three bars were tested. As with strength tests, load–displacement curves were recorded for every specimen. The results of the few test bars where breakage would not originate from the notch but from pre-existing macroscopic flaws were not included in the determination of the mean values. The total fracture energy (and the toughness) was calculated as described in the literature.[8]

2.4. *Young's modulus*

The Young's modulus (E) was obtained by determining $E_{bending}$[8] and by subsequent application of a correction factor that allows for the shear stress that contributes to the overall stress due to test geometry.

3. Results and discussion

3.1. *Strength*

Generally, higher TRS was measured for the briquettes fired at higher temperatures (Fig. 2). The vitrification of the clay matrix during firing at high temperatures results in stronger bonding between particles than is the case with the only loosely connected clay particles in the low-fired specimen. It is therefore expected that changes in the degree of vitrification are reflected directly in the measured strength values. Indeed, after a

Table 1
Matrix table of the briquette types examined: five different clay mixtures were fired to three different temperatures each, resulting in a total of 15 different briquette types.

	Amount of temper		
	0 vol%	10 vol%	40 vol%
Granite temper	550 °C	550 °C	550 °C
	850 °C	850 °C	850 °C
	1050 °C	1050 °C	1050 °C
Phyllite temper	Same as above	550 °C	550 °C
		850 °C	850 °C
		1050 °C	1050 °C

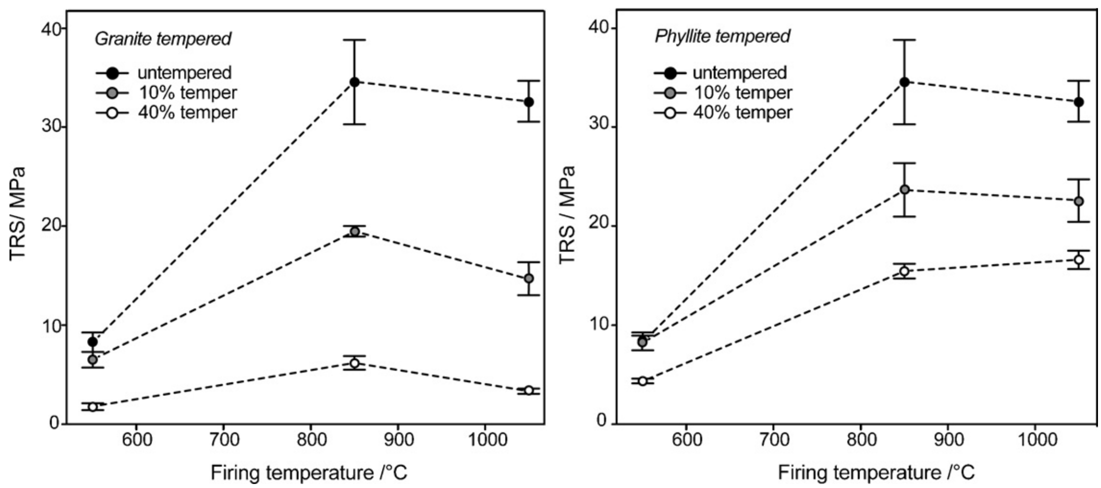

Fig. 2. Fracture strength as determined on three-point bending tests.

significant increase from 550 °C, the strength level of the untempered ceramics based on the Pikermi clay remains relatively stable between 850 °C and 1050 °C. This is expected, since vitrification remains practically constant in this temperature range, as corroborated by comparative previous microstructural studies.[13]

Addition of temper material led to a decrease in TRS which, for material containing either type of temper, is dependent on their volume fraction. As can be seen in Fig. 2, TRS values of vitrified briquettes fall from 35 MPa in the untempered state to around 10 MPa in briquettes with 40 vol% temper. This is expected due to flaws and imperfections which are introduced in the ceramics' matrix by the temper particles during all stages of manufacture. During mixing of clay with temper, cracks are created due to the incomplete wetting of the aplastic inclusions by the clay, resulting in weak bonding. Furthermore, during drying, damaged zones are formed around the rigid particles due to isostatic residual 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.[5] Ultimately, the observed decrease in fracture strength is a result of the consequential increase in overall flaw population.

Comparing the effect of the two different temper types, it is apparent that the addition of phyllite has a less detrimental impact on TRS than the addition of the same volume fraction of granitic temper. This effect becomes especially pronounced when adding high amounts of temper and at higher firing temperatures, since, for specimens fired to 550 °C, the differences between the two temper types are much less pronounced (Fig. 2). It can be argued that the reason for the different behaviour of the two temper types lies in the relative amount of flaws introduced by the respective temper particles. The different thermal expansion of the temper *material* does not appear to offer an explanation for the observed effect. Quartz, which at 573 °C undergoes a reversible phase transition accompanied by a 7 vol% change, is frequently cited in discussions of strength reduction.[1] However, the volume fractions of the quartz component in both temper types, as determined by XRD methods, are quite similar and reasonably low (0.26 for granite and 0.19 for phyllite) and cannot account on their own for the observed differences.

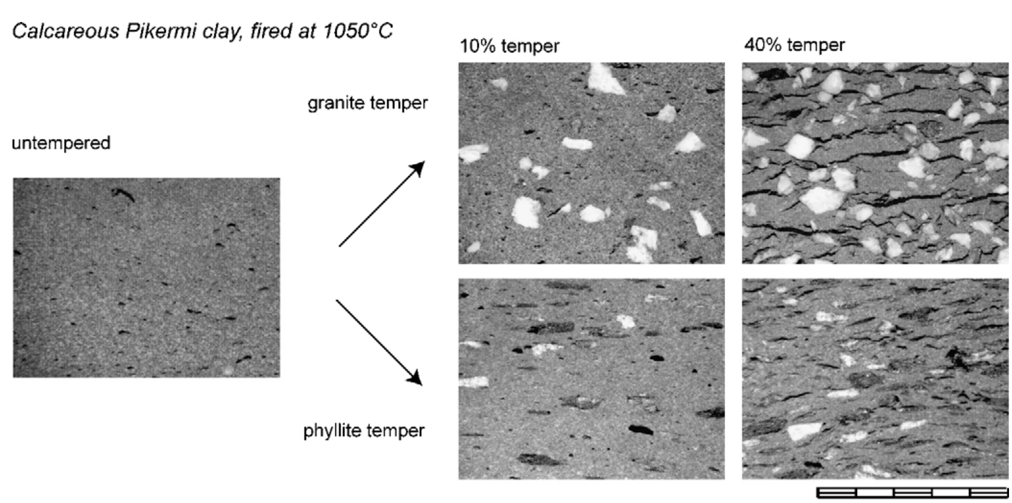

Fig. 3. Structure of high-fired fabrics. The emergence of large elongated voids due to restricted shrinkage of the matrix can be observed in the highly tempered fabrics, where the rigid inclusions act to "pin" the shrinking matrix, leading to the observed voids.

In some fabrics, differences are observed in the extent and amount of large elongated voids (Fig. 3): in the case of highly tempered granitic fabrics, the apparent length and amount of these voids appears more pronounced than in the corresponding phyllitic fabrics. Manufacturing (repeated folding and/or pressing into mould) results in an alignment of clay particles, so that shrinkage upon drying is more pronounced in a vertical direction, perpendicular to the clay particles.[15,16] This results in the observed horizontal alignment of the large pores. Due to temper shape and the alignment of the inclusions, the phyllitic fabrics can better accommodate perpendicular shrinkage and fewer voids open up. Overall porosity is approximately stable: all clay mixtures result in fabrics with a total (open) porosity of $32 \pm 2\%$, with no noticeable closed porosity.[12] Also differences in the extent and amount of the large elongated pores as observed in some fabrics, however, cannot solely be responsible for the strength differences: this phenomenon occurs only in highly tempered fabrics whereas strength differences are also observed at lower levels of tempering.

It is therefore necessary to consider the impact of the difference in temper *shape* on the integrity of the surrounding clay matrix. In the case of particles with a high sphericity, stresses develop all around the particles during drying and result in a damaged area that can be described as a sphere enclosing the whole particle.[5] By analogy, the damaged zone around the edges of a flake should have a toroidal shape (Fig. 4). The overall volume fraction of the ceramic that is susceptible to the development of microcracks during firing is thus much smaller, resulting in comparatively fewer flaws and higher TRS for the phyllite tempered ceramics. The small reduction in TRS for the tempered, very high-fired briquettes, as compared to the intermediate fired ones, is probably due to the fact that firing to higher temperatures results in increased shrinkage of the clay matrix and accordingly induces a more extensive damaged zone. This effect can be observed with the granite temper but appears negligible for phyllite, an observation which is in accordance with the different extents of damaged zones postulated for the different temper types. The influence of temper shape on damaged zones and accordingly on the mechanical properties of clay ceramics, both strength and toughness is discussed in more detail below. (The results of the toughness measurements will be presented later in the paper.)

3.2. Damaged zones: quantifying the influence of temper shape on damaged zones

Temper material induces damage to a ceramic matrix. Thermal expansion mismatches between temper particles and matrix, as well as phase transformations during firing result in internal stresses leading to the formation of microcracks around the temper particles upon cooling from firing.[17] Radial microcracks can easily link up to form extensive networks, which have a detrimental impact on strength levels. It has been postulated that the areas around quartz temper in clay ceramics experience microdamage already during drying.[5] When fired, these areas are highly susceptible to cracking ('damaged zone'). Furthermore, due to this microdamage, far more extensive radial microcrack-

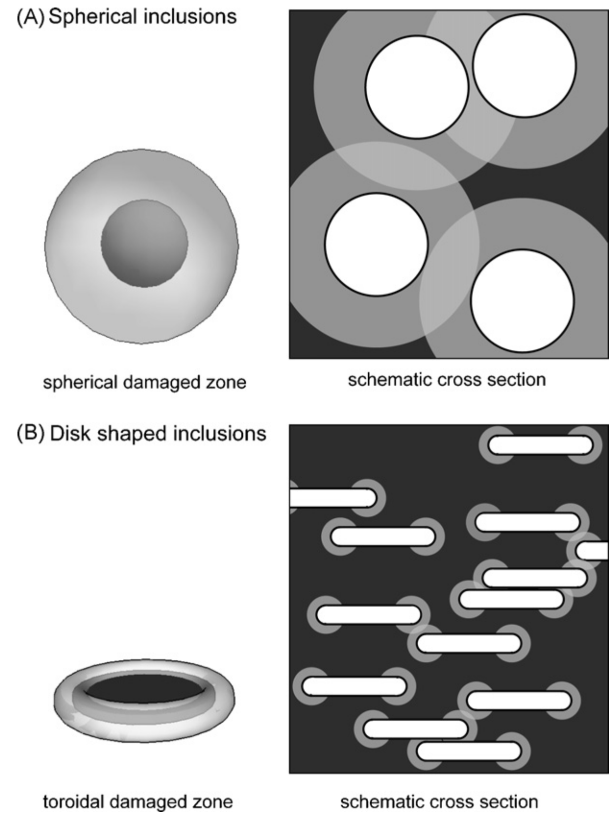

Fig. 4. Different geometries of damaged zones due to different temper shape, and resulting difference in amount of damaged matrix as illustrated by schematic cross-sections (damaged area in grey).

ing is induced upon firing even if the thermal expansion factors of temper and matrix fulfil the condition for circumferential cracking (i.e. $\alpha_{\text{matrix}} > \alpha_{\text{particle}}$).[17] Kilikoglou et al., using a stress-field mechanism, showed that for spherical inclusions, the effective radius of the damaged zone can be expressed as

$$r_{eff} = r_i \sqrt{\frac{\sigma_0}{\sigma_{gr}}} = r_i \sqrt{\frac{70(1 - V_f)}{\sigma_{gr}}} \quad (1)$$

with σ_0 the stress at the surface of a rigid inclusion, σ_{gr} the green strength of the material, V_f the volume fraction of temper added, r_i the radius of a spherical inclusion and r_{eff} the radius of the damaged zone around the particle.[5] The fraction of the area that is damaged is thus given by

$$\frac{A_{eff}}{A} = V_f \frac{\sigma_0}{\sigma_{gr}} = V_f \frac{70(1 - V_f)}{\sigma_{gr}} \quad (2)$$

with A_{eff} the extent of the damaged zone, and A the fracture area. In the model by Kilikoglou et al. the number of inclusions in the cross-section and the total damaged area are underestimated. A random cut will not go through the midpoint of an inclusion and the average cross-section of inclusions will therefore be smaller than πr_i^2. Additionally, damaged areas around non-meridian cuts are comparatively larger, and also damaged zones from particles not lying in the cross-section at all may contribute. To avoid these problems and to be able to compare different temper geometries, the existing two-dimensional model, which assesses

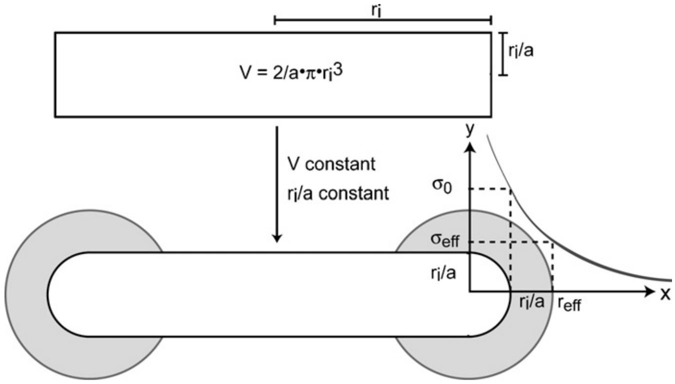

Fig. 5. Cross-section: damaged zones around the edges of a disk-shaped particle with blunt edges, platyness factor $a=5$.

the extent of damaged area for spherical inclusions, is extended here to three dimensions and platy particles.

3.2.1. Three-dimensional model

The volume occupied by inclusions in a cube with volume B is $B_{\text{incl}}=BV_f$ and the total number of *spherical* inclusions in B can be calculated as $N_{\text{incl}}=B_{\text{incl}}/(4/3\pi r_i^3)$. The amount of the total damaged volume B_{eff} can be calculated by multiplying the number of inclusions with the volume of one damaged zone $4/3\pi r_{eff}^3$. In the same way as in the two-dimensional case we obtain for the damaged volume fraction

$$\frac{B_{eff}}{B}=V_f\left(\frac{\sigma_0}{\sigma_{gr}}\right)^{3/2}=V_f\left(\frac{70(1-V_f)}{\sigma_{gr}}\right)^{3/2} \tag{3}$$

As in the two-dimensional case, overlap is not taken into account, and the calculated values are therefore too high. They provide, however, a measure for the extent of the crack network. Importantly, the three-dimensional model allows a qualitative comparison of spherical with platy particles.

Stress concentration factors become increasingly important with increasing sharpness of a particle. As a first step therefore, the influence of increasing "platyness" is assessed for the case of a *blunt flat inclusion* where the stress concentration at its edges is minimal, allowing for a simplified stress-field approach. This condition is fulfilled for a disk-shaped inclusion with rounded edges (Fig. 5).

The volume of such a blunt disc is given by $2/a\pi r_i^3$, where r_i is the radius of the disk, $2r_i/a$ is the disk's thickness and a is the quotient of disc diameter to thickness, and a measure of the platyness. Keeping the volume and height constant and adjusting the edges so that stress concentration is minimal (i.e. smallest possible curvature), results in a disk whose edges can be described in cross-section as half circles with radius r_i/a (Fig. 5). This procedure entails changes in the radius of the disk, but they are small enough so that they can be neglected for the further calculations. The effective radius of the damaged zone, which for $a>2$ forms a torus around the disks, can then be expressed in analogy to the spherical case as

$$r_{eff}=\frac{r_i}{a}\sqrt{\frac{\sigma_0}{\sigma_{gr}}}=\frac{r_i}{a}\sqrt{\frac{70(1-V_f)}{\sigma_{gr}}} \tag{4}$$

Table 2
Extent of damaged zones expressed as volume fractions B_{eff}/B for particles of different geometries. The values have been calculated for a nominal volume fraction of 10% temper material, with a grain size diameter of 750 μm, for a material with a green strength of 8.4 MPa.

	Sphere	Disk	
		$a=5$	$a=10$
r_{eff}	1027 μm	205 μm	103 μm
N_{incl}	453	1510	3018
B_{eff}/B	2.1	0.4	0.2

For $a>2$, the damaged volume caused by one particle is described by a torus around the edges of the platy inclusions with $B_{eff,inc}=2\pi^2 r_{eff}^2 r_i$. The volume occupied by inclusions in a volume B is: $B_{\text{incl}}=BV_f$, the number of inclusions $N_{\text{incl}}=B_{\text{incl}}/(2/a\pi r_i^3)$, so that the fraction of the damaged volume B_{eff}/B can be calculated as

$$\frac{B_{eff}}{B}=\frac{\pi}{a}V_f\left(\frac{\sigma_0}{\sigma_{gr}}\right)=\frac{\pi}{a}V_f\left(\frac{70(1-V_f)}{\sigma_{gr}}\right) \tag{5}$$

Applying Eqs. (3) and (5), for spherical and platy temper respectively, allows a comparison of the extent of damaged zones for different geometries. Table 2 lists the extent of damaged zones expressed as volume fractions B_{eff}/B for particles of different geometries. The number of inclusions N_{inc} is calculated for a nominal volume of 1 cm^3. r_{eff} corresponds for a spherical inclusion to the radius of the resulting spherical damaged zone, and in the case of a platy inclusion to the minor radius of the torus shaped damaged zone. The results indicate that for a nominal amount of 10 vol% inclusions, an average grain diameter of 750 μm and a green strength of 8.4 MPa (*cf.* calculations for two-dimensional model with spherical inclusions[8]), an ideally blunt platy particle with moderate platyness ($a=5$) should induce five times *less* damage to the ceramic than the same amount of spherical temper.

These results describe the situation for ideally blunt inclusions. In reality, the difference between platy and spherical particles is far less pronounced since they are never blunt but always exhibit sharp edges. This is reflected in the relative strength loss observed in the experimental briquettes tempered with bulky granite and platy phyllite, when compared to the untempered specimens (Fig. 2). From microscopic observations, it is clear that the edges of the temper particles are not blunt but display significant sharpness, resulting in the concentration of stresses around the edges. Stress concentration depends on the curvature of the particle, the corresponding equation for elliptical geometry with radius c is known as Inglis' law:

$$\sigma_{\max}=2\sigma\sqrt{\frac{c}{\rho}} \tag{6}$$

With increasing curvature, the local stress $\sigma_{\max}$ induced at the edge of a sharp inclusion increases for the same external stress σ applied. Fracture initiation will occur when this local stresses $\sigma_{\max}$ at a particle edge exceed the local fracture strength of the ceramic (critical particle).

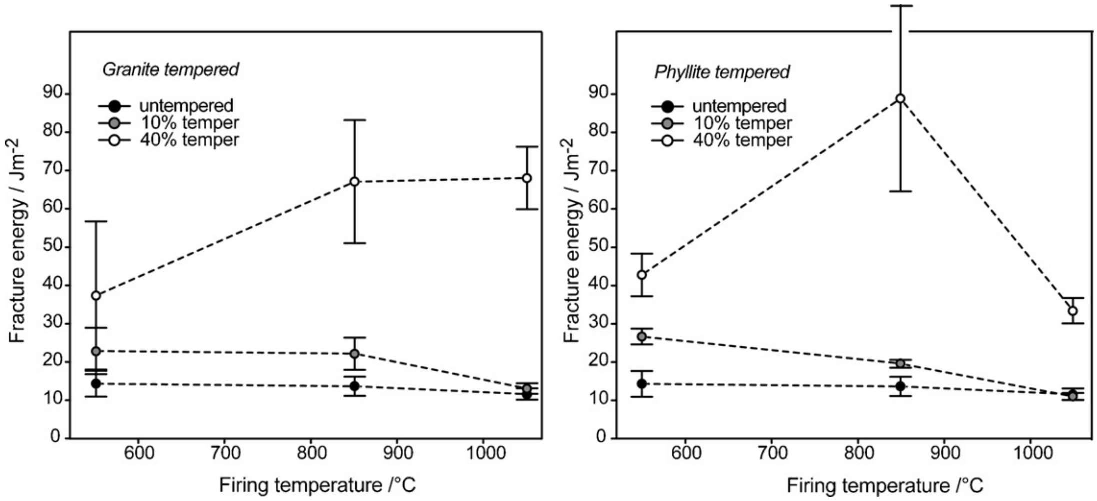

Fig. 6. Fracture energy as determined in four-point bending tests.

The above model allows for the rationalisation of the observed differences in the reduction of fracture strength with spherical and platy temper in high-fired specimens, by revealing that the extent of the damaged zone which develops in a ceramic with platy temper particles is substantially smaller than for a corresponding material which contains spherical particles. In the low-fired specimens the strength reduction is lower (Fig. 3) since the ceramic bodies are not vitrified and even the untempered briquettes contain high amounts of flaws and cracks.

It must be emphasised that the orientation of the platy particles plays an important role in fracture strength. The effects of aligned elongated flaws on strength can be substantial: even one poorly bonded elongated particle, lying approximately parallel to an applied tensile stress, can cause premature failure. The method of manufacture of the experimental briquettes containing phyllite ensured that the platy particles were all aligned perpendicular to the test direction, so that no such detrimental flaws in direction of the testing would have occurred.

In terms of toughness (the results of the toughness measurements on the experimental briquettes will be discussed in detail below) elongated particles might offer additional energy dissipation due to frictional pull-out. The above model, however, has been developed mainly to explain the strength differences between high-fired granite and phyllite tempered samples (see Fig. 2). In these cases, fracture goes through the phyllite particles so that pull-out mechanisms do not contribute. This is reflected in the lower toughness values for high-fired phyllite tempered samples than corresponding granitic ones (Fig. 6).

3.3. Toughness

Generally, the results of the measurements show that the addition of temper increases the toughness of a material (Fig. 6). The higher the volume fraction of inclusions, the higher is the toughness of the corresponding material. This behaviour is expected, as the rigid inclusions provide the ceramics with additional means of energy dissipation through crack deflection, bifurcation and arrest. With platy particles, pull-out processes are also expected. At low and intermediate firing temperatures, the nature of the temper material does not have a discernible influence on the toughness of the ceramics, both types of temper result in fabrics with similar toughness. Only when fired to 1050 °C, do the fabrics containing high amounts of phyllitic temper behave distinctively differently from their granitic counterparts: their toughness decreases in comparison to the lower fired pastes, while the toughness of the granitic tempered ceramics remains stable at a high level. Thus, for high firing temperatures, the addition of phyllitic temper results in significantly less tough material than with granitic temper.

It has been observed for quartz-tempered ceramics made of Pikermi clay that a change in the mode of fracture from brittle to stable occurs at around 20 vol% of temper material.[5] The granite tempered samples in this study seem to follow this pattern; fabrics with 10% temper exhibit brittle to semi-stable fracture, while the ones containing 40% temper material break in a stable manner. Accordingly, the ceramics containing 10% temper do not show any considerable energy dissipation during crack propagation and overall toughness is largely determined by intrinsic toughness. Only at 40% temper does the contribution of G_t become significant (Fig. 7).

In the highly tempered fabrics fired at 850 °C, both temper types exhibit similar toughening properties and the toughening component G_t that accounts for the energy that is absorbed during crack propagation is comparable for both temper materials. When the briquettes tempered with 40% phyllite are fired to 1050 °C, however, G_t becomes much smaller, resulting in an overall smaller toughness, compared to the lower fired phyllitic fabric but also to the granitic counterpart. Since the *intrinsic* toughness G_{1c} is actually greater in the case of phyllitic temper, the decisive factor is the toughening component G_t. In the case of granitic temper, a significant amount of energy is needed to propagate the crack through the ceramic. In the case of phyllitic temper in a high-fired matrix, a crack propagates in a more unstable way and the contribution of the toughening component G_t to the overall toughness G_{tot} is small. The observed decrease in fracture toughness, as compared to the lower fired phyllitic tem-

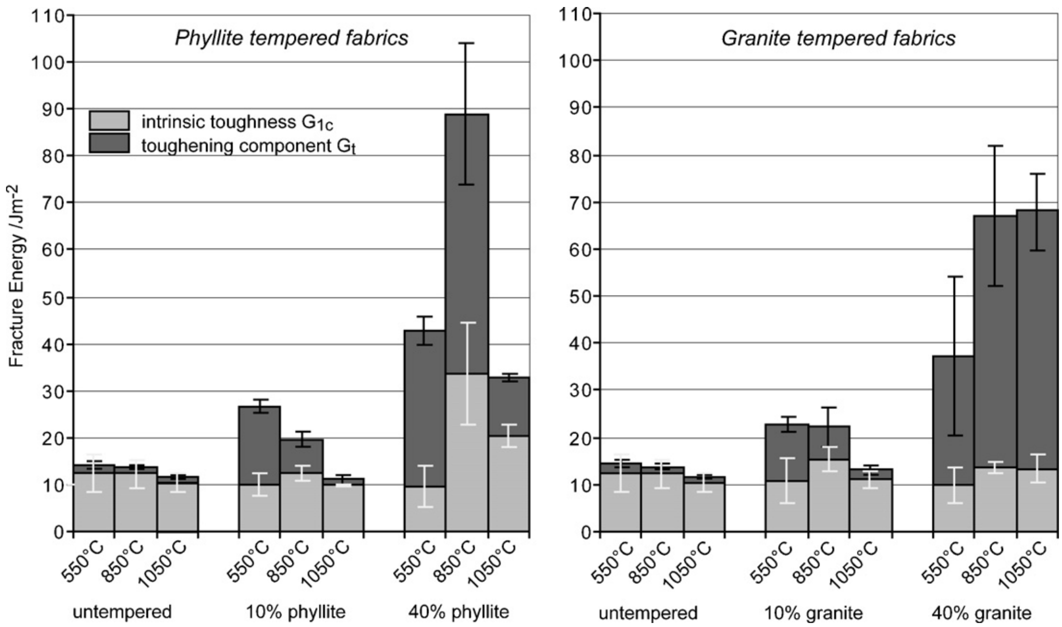

Fig. 7. Contribution of intrinsic toughness G_{1c} and energy dissipation part G_t to total fracture toughness of granite and phyllite tempered fabrics.

pered material, may be due to differences in the Young's moduli. While the onset of fracture occurs at roughly the same loads for material fired at 850 °C and 1050 °C, the Young's modulus of the higher fired briquettes with 40% phyllite temper is nearly twice (8.7 GPa) that of their lower fired counterpart (4.8 GPa). The increased stiffness of the material results in a fabric which is less able to absorb energy during fracture. Indeed, when examining the fracture surfaces, it is observed that in the highly fired samples the crack often propagates through the phyllite particles, breaking the thin plates in half, eliminating any contribution they may have had on the toughening. Breakage of temper plates is seen to a much lesser amount in samples fired to 850 °C. The reason for this preferential phyllite cracking is probably the weakening effect of high-temperature processing on the phyllite itself (caused by dehydroxylation and subsequent structural breakdown of the phyllosilicate component at very high temperatures), combined with enhanced bonding expected between the matrix and the particles at such temperatures. In this regard, it may be instructive to measure the effect of tempering clays with a type of platy particles that retain their strength at high temperatures.

For ceramics fired at very low temperatures, higher toughness for platy temper material as compared to more equant inclusions has also been reported in the literature,[11] a phenomenon which has been explained by higher energy dissipation during crack propagation through additional mechanisms such as pull-out mechanisms. The means of the toughness values of the lower fired samples in the present study show a similar trend: before the onset of vitrification (i.e. in samples fired to 550 °C), phyllitic temper seems to result in marginaly higher values for fracture toughness than granitic temper. In these cases fracture initiates at very low loads, and with 40% temper, a stable fracture mode is observed for both temper types. Briquettes with 10% granite exhibit a mean fracture energy of 23 J/m^2, while the mean fracture energy of their phyllitic counterpart is 27 J/m^2. However, this finding is obscured by the rather broad spread of the measurements and the resulting high standard deviations (especially for the briquettes containing 40% temper).

In the fabrics containing 40% granite temper, which already show a considerable toughening component, additionally an indentation mechanism is observed. Even after complete division of the test bars into separate pieces, the two fracture surfaces still hold together, due to interlocking that is comparable to Lego™ bricks. The protruding granitic grains act as studs while their impressions provide the sockets. As a result, the materials are able to undergo significant bending without losing structural integrity (Fig. 8). This effect seems especially effective with the relatively large size of temper employed in the present study, and is related to the "pull-out" mechanism for inclusions.

4. Summary and conclusions

In agreement with earlier experiments[2,5] a reduction of fracture strength and an increase in toughness was observed with increasing amounts of aplastic inclusions in a ceramic fabric. The strength decrease is less pronounced with platy temper material, while toughness at low and intermediate firing temperatures is comparable for the two temper types. The observed differences in strength reduction with different temper shape could be accounted for qualitatively by adapting the damaged zone model developed by Kilikoglou et al. to disk-shaped particles and is confirmed by reported measurements on low-fired specimens.[3] The single most important parameter for obtaining high fracture toughness is the presence of relatively high amounts of temper material, as has been shown by the present work. The kind of temper does not play an important role unless the ceramics are fired to temperatures in excess of about 1000 °C where the

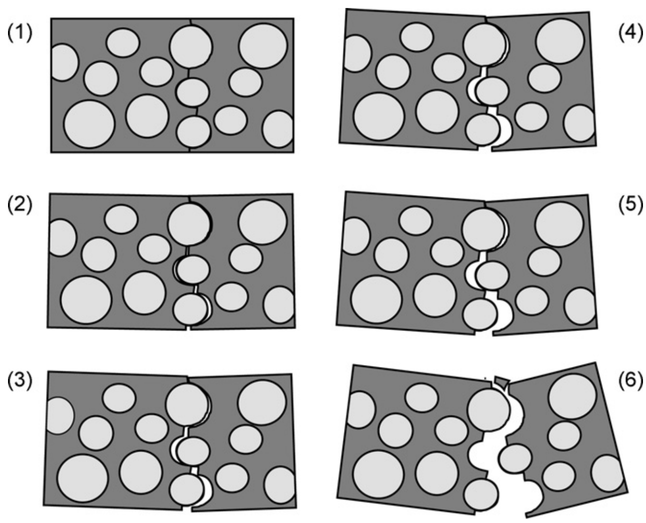

Fig. 8. Indentation mechanism observed in highly tempered granitic ceramics. Even after complete fracture (1) the two pieces still hold together due to interlocking. Complete separation (6), usually by breakage of the 'weakest link' part of the matrix occurs only after significant bending (2–5).

addition of granite temper appears preferable over phyllite temper. It is clear therefore that, when aiming for a tough material, the addition of temper or the selection of coarse clays seems beneficial.

These findings have important implications when assessing technological choices observed in archaeological material. It can be argued that for the mechanical properties of the usually relatively coarse utilitarian vessels, such as cooking pots which are not subjected to significant bending stresses, fracture toughness rather than strength is the more significant performance characteristic. As coarse materials will have low strength levels due to high flaw levels introduced by aplastic inclusions, it is the *propagation* of a crack which needs to be avoided rather then its initiation. High fracture toughness is obtained by adding substantial amounts of temper material. In the case of granitic fabrics, toughness remains stable at higher firing temperatures, while care has to be taken with phyllitic fabrics not to fire the pottery too high, as otherwise fracture toughness decreases again. Another example would be transport amphorae used in maritime trade. Here, one could argue that strength would play a bigger role. Accordingly, higher firing temperatures and finer fabrics containing less temper material would be advantageous and platy temper preferable over bulky one. However, as impact stresses are very likely to occur also in these types of vessels, especially during transportation, the toughness of the material must still be satisfactory and should also be considered.

While the above is an important contribution to discussions of technological choices observed in archaeological material, it should be emphasised that such studies must take into account the interrelated nature of material properties, carefully balancing several potentially significant material properties. Further, any discussion relating to the performance of archaeological material needs to be placed in the socio-cultural context of production and consumption.

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References

1. Tite MS, Kilikoglou V, Vekinis G. Strength, toughness and thermal shock resistance of ancient ceramics, and their influence on technological choice. *Archaeometry* 2001;**43**(3):301–24.
2. Steponaitis VP. Technological studies of prehistoric pottery from Alabama: physical properties and vessel function. In: van der Leeuw SE, Pritchard AC, editors. *The many dimensions of pottery*, 1984. Amsterdam: University of Amsterdam; 1984. p. 79–127.
3. Feathers JK. Effects of temper on strength of ceramics: response to Bronitsky and Hamer. *Am Antiquity* 1989;**54**:579–88.
4. Hoard RJ, O'Brien MJ, Khorasgany MG, Gopalaratnam VS. A materials-science approach to understanding limestone-tempered pottery from the midwestern United States. *J Archaeol Sci* 1995;**22**(6):823–32.
5. Kilikoglou V, Vekinis G, Maniatis Y. Toughening of ceramic earthenwares by quartz inclusions: an ancient art revisited. *Acta Metall Mater* 1995;**43**:2959–65.
6. Neupert MA. Strength testing archaeological ceramics: a new perspective. *Am Antiquity* 1994;**59**:709–33.
7. Vekinis G, Kilikoglou V. Mechanical performance of quartz-tempered ceramics: part II. Hertzian strength, wear resistance and applications to ancient ceramics. *Archaeometry* 1998;**40**(2):281–92.
8. Kilikoglou V, Vekinis G, Maniatis Y, Day PM. Mechanical performance of quartz-tempered ceramics: part I, strength and toughness. *Archaeometry* 1998;**40**(2):261–79.
9. Rossi RC, Cost JR, Janowski KR. Influence of the shape of dispersed particles on the elastic behaviour of composite materials. *J Am Ceram Soc* 1972;**55**(5):234–7.
10. Bronitsky G, Hamer R. Experiments in ceramic technology: the effects of various tempering materials on impact and thermal shock resistance. *Am Antiquity* 1986;**51**:89–101.
11. Feathers JK, Scott WD. Prehistoric ceramic composite from the Mississippi Valley. *Am Ceram Soc Bull* 1989;**68**(3):554–7.
12. Hein A, Müller NS, Kilikoglou V, Day PM. Thermal conductivity of archaeological ceramics: the effect of inclusions, porosity and firing temperature. *Thermochim Acta* 2008;**480**:35–42.
13. Tite MS, Maniatis Y. Scanning electron microscopy of fired calcareous clays. *Br Ceram Trans J* 1975;**74**(1):19–22.
14. BSI British Standards. *Advanced technical ceramics, mechanical properties of ceramics composites at room temperature, part 3: determination of flexural strength*. British Standard BS EN 658-3:2002; 2002.
15. Lawrence WG, West RR. *Ceramic science for the potter*. second ed. Pennsilvania: Chilton, Radnor; 1982. pp. 86.
16. Rice PM. *Pottery analysis, a sourcebook*. Chicago: The University of Chicago Press; 1987. pp. 68.
17. Davidge RW. *Mechanical behaviour of ceramics*. Cambridge: Cambridge University Press; 1986. pp. 86–87.