Influence of sand on the mechanical properties of metakaolin geopolymers

C. Kuenzel [a,b,*], L. Li [a], L. Vandeperre [b], A.R. Boccaccini [c], C.R. Cheeseman [a]

[a] Department of Civil and Environmental Engineering, Imperial College London, London SW7 2AZ, UK
[b] Department of Materials, Imperial College London, London SW7 2AZ, UK
[c] Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Cauerstr. 6, 91058 Erlangen, Germany

HIGHLIGHTS

- Metakaolin geopolymers need high water content to have appropriate rheology for some applications.
- Extensive drying shrinkage and cracking occurs in high water content metakaolin geopolymers.
- Geopolymer mortar samples with more than 10 vol% sand do not crack on heating to 110 °C.
- Sand particles limit linear shrinkage by forming a network.
- At higher additions micro-cracks form around non-shrinking sand particles.

ARTICLE INFO

ABSTRACT

Metakaolin geopolymers require a high water content to have appropriate rheology for use in some applications and these mixes exhibit extensive drying shrinkage and cracking. This work aimed to understand the effect of adding sand as inert filler to metakaolin geopolymers. It is found that the viscosity increases with sand addition and mortars become unworkable when more than 40 vol% sand is added. Linear drying shrinkage was reduced from about 8% in the absence of sand to less than 1% with 38 vol% sand addition. Moreover, geopolymer mortars containing more than 15 vol% sand can withstand drying at 110 °C without cracking. Because sand addition to metakaolin geopolymer mortars increases viscosity less than a reduction in water content it is possible to formulate mortars that flow but do not crack on drying and these materials have potential for use in a range of architectural and restoration applications.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Geopolymers are cementitious materials consisting of linked SiO_4 and AlO_4 tetrahedral groups where the negative charge on AlO_4 is balanced by alkali ions, typically Na^+ or K^+ [1–5]. The polymerisation is a geosynthesis reaction and a wide range of Al and Si containing materials can potentially be used to form geopolymers [6,7]. In general, the solid Al rich precursor is mixed with a strong alkali or alkali silicate activation solution. After mixing, the solid material dissolves, undergoes a polycondensation reaction and precipitates. During polycondensation, the aluminates and silicates form a polymeric Si–O–Al framework which is chemically and structurally similar to that of amorphous feldspar [5]. Several studies have reported that geopolymers have excellent mechanical properties, fire performance, acid resistance and durability. Therefore, they are being actively considered as replacements for a range of traditional structural materials and as potential matrix for nuclear waste encapsulation [8–11]. Further potential applications are restoration of buildings and sculptures and in art to produce new statues [12–15].

To produce geopolymers a wide range of solid precursors can be used. However, the main focus has been on metakaolin and pulverized fly ash (PFA) [4,16,17]. Metakaolin is generally preferred to PFA for geopolymers where a constant elemental composition is required [18–21]. This is because PFA is a by-product of coal combustion in power stations, while metakaolin is produced by heating white kaolin with a homogeneous chemical composition. PFA is an industrial by-product that is available at relatively low price and therefore it is a potential replacement for Portland cement in construction products. However, the dark appearance

* Corresponding author at: Department of Civil and Environmental Engineering, Imperial College London, London SW7 2AZ, UK.
E-mail address: c.kuenzel08@imperial.ac.uk (C. Kuenzel).

of PFA can be problematic when used for restoration of buildings and sculptures and for these applications metakaolin based geopolymers are of interest.

A disadvantage of metakaolin based geopolymers is extensive drying shrinkage and cracking. This is an issue when geopolymers are used for restoration. Recent work has shown that there are two types of water in geopolymers. Evaporable water can be removed without causing any shrinkage and structural water, independent of the initial water content, cannot be removed without causing significant shrinkage and cracking [22]. This drying cracking can be reduced by substituting metakaolin with low cost inert fillers such as sand [9,23–27]. These studies have not reported the influence of inert filler on the drying shrinkage and this is important to give mortar mixes that do not crack.

The aim of this study was to investigate the effect of sand addition on the shrinkage and cracking of metakaolin geopolymers and develop mixes with sufficient workability to be used in restoration and decorative applications. The influence of sand addition on the flow properties, mechanical properties, shrinkage and cracking of metakaolin derived geopolymer mortars is reported.

2. Experimental

2.1. Materials

Metakaolin (Metastar 501, Imerys, UK) with a mean particle size of 5.4 µm consisting of 59.5 mass% SiO_2 and 34.0 mass% Al_2O_3 was used to prepare geopolymer samples. The activating solution was formed using a sodium silicate solution (26% SiO_2/8% Na_2O, VWR International, Pennsylvania, USA) and NaOH pellets (Fischer Chemicals, New Hampshire, USA). Silica sand (Redhill 110, Sibelco, UK) with a particle size distribution as shown in Fig. 1 was used in the mortar samples.

2.2. Preparation of geopolymer mortar samples

The Al:Si:Na molar ratio in the geopolymer binder ratio was kept constant at 1:2:1 as this type of geopolymer has previously been extensively investigated [11,28–30]. The H_2O:Al molar ratio used in the literature is typically in the range from 5.5 to 7.2 [29–36]. However, preliminary experiments showed that the viscosity of the metakaolin/activation solution was too high for mixing when this ratio was below 7.5. Therefore, in this research, the molar water ratios used were 7.5, 8.5, 9.5 and 10.5.

Geopolymers were prepared by mixing Na_2SiO_3 solution with NaOH and deionised water. This solution was stirred for 24 h to reach equilibrium. The activating solution was then mixed with metakaolin and sand for 5 min using a rotary mixer (ELE International Ltd., UK). The amount of sand added was gradually increased and the homogeneous mix was cast into 8 mm × 8 mm × 50 mm ABS plastic moulds. Finally, the samples were vibrated for 15 min to remove entrapped air.
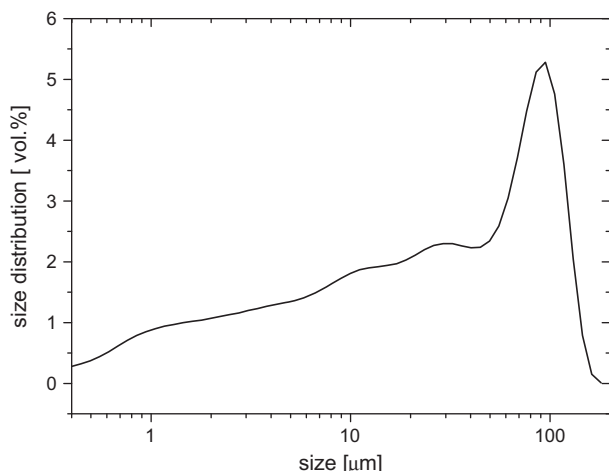

Fig. 1. Particle size distribution of sand used in this study obtained by laser diffraction.

At the lowest water content, the mix could no longer be used as it became dry and crumbly for 18 vol% sand, whereas for all other mixes up to 38 vol% sand could be used. Samples were removed from the moulds after 2 days and cured in sealed polyethylene bags at room temperature (22 ± 3 °C) for a further 75 days prior to testing.

2.3. Determination of the physical properties of metakaolin geopolymer mortars

The viscosity of the metakaolin geopolymer mortars was measured using a cone-plate rheometer (Anton PaarPhysica UDS200, Austria). The cone had a diameter of 50 mm and the shear rate was linearly increased from 0.1 to 75 s^{-1} at 25 °C. Geopolymer mortars were mixed with the activation solution and stirred by hand for 3 min before being placed in the rheometer. The cone was then lowered into the paste and left to stand for a period of 12 min before the test was initiated in order to minimise the shear thinning effects of the initial mixing.

Cured samples were dried and milled using a laboratory disc mill (TEMA mill, Germany) and the theoretical density was determined by pycnometry (AccuPyc II 1340 Helium pycnometer, Micromeritics, Georgia, USA). The compressive strength was measured using a Zwick/Roell Z010 (Germany) on five 8 mm × 8 mm × 8 mm cube samples using a crosshead speed of 0.2 mm/min. Vickers hardness (HV) was measured (Zwick/RoellIndentec ZHV instrument, Germany) using a 500 g load with a penetration time set to 10 s, with the average taken from seven measurements. The shrinkage during heating was measured using a dilatometer (Netzsch 402 E, Germany) in which 8 mm × 8 mm × 8 mm cubes were heated to a final temperature of 600 °C using a heating rate of 10 °C/min. To ascertain whether the material could survive drying, samples were heated to 110 °C in a circulating air furnace for 1 day and then, if possible, the compressive strength measured.

3. Results

The densities of the geopolymer matrix and of the sand were measured by pycnometry to allow the volume fractions to be determined. By using Eq. (1), the density of geopolymer and sand mixes can be predicted quite accurately assuming the geopolymer matrix density is independent of the amount of sand added, as shown in Table 1:

$$\rho_{total} = \rho_{geopolymer}(1 - f_{sand}) + f_{sand}\rho_{sand} \tag{1}$$

where ρ is the density and f is the volume fraction.

The fact that this prediction can be made indicates the sand only acts as inert filler because a change in density is expected during a chemical reaction.

To quantify the observations of ease of flow, the viscosity of the geopolymer mortars was measured. For shear rates 0.1 s^{-1} and 60 s^{-1}, shear thinning occurred (not shown), but at about 70 s^{-1}, the viscosity ceases to be dependent on the strain rate. The viscosity values taken from steady-state measurements at a shear rate of 70 s^{-1} are reported in Fig. 2, with greater sand additions corresponding to higher final viscosity and higher water contents giving rise to lower viscosity.

Fig. 3 shows compressive strength data for geopolymer mortar samples. In comparison with the viscosity, where even small additions of sand gave a noticeably rise in viscosity, the compressive strength does not increase strongly unless substantial amounts of sand are added. The observed strengths, σ_c, fit the rules of mixture (Eq. (2)):

$$\sigma_c = \left(\frac{1 - f_s}{\sigma_g} + \frac{f_s}{\sigma_s}\right)^{-1} \tag{2}$$

where f_s represents the volume fraction of sand with a strength, σ_s, of 1100 MPa for quartz (fused) [37] and σ_g is the strength of the geopolymer without sand.

Similar behaviour is observed for Vickers hardness, as presented in Fig. 4. Again a reasonable fit to all data can be obtained using the rule of mixtures as in Eq. (2) using an average Vickers hardness of 1000 kg mm^{-2} for sand [37].

After drying geopolymers mortars at 110 °C for 1 day, the compressive strength could only be measured for specimens containing more than 10 vol% sand, as samples with less sand had been extensively damaged during drying. As shown in Fig. 5, for those