J Mater Sci (2008) 43:2693–2699
DOI 10.1007/s10853-007-2412-1

Mechanical properties of metakaolin-based geopolymers with molar ratios of Si/Al $\approx$ 2 and Na/Al $\approx$ 1

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Received: 5 September 2007 / Accepted: 18 December 2007 / Published online: 19 February 2008

Abstract The mechanical properties of four different types of geopolymers, but of the same composition (Na/Al $\approx$ 1, Si/Al $\approx$ 2 molar ratio), made using a combination of precursors, were determined. The four types were: (i) sodium aluminate ($NaAlO_2$/NaOH solution), Ludox (colloidal SiO_2 solution) and metakaolin (MK), (SAGP), (ii) NaOH, fumed silica and MK (FSGP), (iii) Ludox, NaOH and MK (LGP) and (iv) commercial sodium silicate and MK (SGP). The highest crushing strength (CCS) value obtained was for SGP (70 MPa) and the lowest value was for SAGP (16 MPa). The highest modulus of rupture (MOR) value obtained was for LGP (9 MPa) and the lowest value was for SAGP (3 MPa). The fracture toughness (K_{1c}) and Young's modulus (E) showed the same trend. The effect of adding sand (40 wt%) on their mechanical properties was also determined. The K_{1c} values increased up to 65% and E values increased up to 80% compared to samples free of sand. However, CCS and MOR values did not change much and gave mixed results. Overall, porosity is found to be the chief microstructural variable limiting the mechanical properties of the geopolymers. The properties of the geopolymers are compared with those of ordinary Portland cement.

Introduction

Geopolymers (GPs) with Si/Al molar ratios of $\approx$2 are alkali aluminosilicate materials [1, 2], which can be made at near ambient temperatures and are X-ray amorphous. They are composed of cross-linked AlO_4^- and SiO_4 tetrahedra, with charge balancing Na^+ or K^+ ions. GPs are made by exposing reactive aluminosilicate precursors such as fly ash, blast furnace slags or metakaolinite (MK) to caustic alkali solutions, with or without silicate, with minimum water addition to make a stiff paste. The mixtures polymerise and solidify upon curing at 20–90 °C, preferably in high humidity and sealed conditions. Their main potential applications are as building materials and some buildings have been constructed using GPs [3]. Their physical behaviour is similar to that of ordinary Portland cement (OPC), but their chemistry is different. Studies have demonstrated that GPs, which are brittle in nature, can attain reasonable compressive strengths [4–6]. Furthermore they have the added benefit of being used as adhesives to bond materials [7, 8] and as fire-resistant materials [9].

The most widely studied of the properties of GP compositions is the cold crushing strength (CCS) due to the ease of testing and as a direct comparison with OPC. The present study investigates the physical and mechanical properties of four types of GPs prepared from different precursors. GPs were made using these different precursors to examine differences in the mechanical properties and also because of the fact that these precursors occur in nuclear waste streams. For example $NaAlO_2$ is present in alkaline waste arising from radioisotope production of ^{99}Mo [10]. Ludox is a pure source of colloidal silica, and although it is expensive it is ideal for mixing. Likewise the influence of aggregates, in this case silica sand, on mechanical properties is also explored. In addition to CCS experiments, flexure tests were conducted to obtain bending strengths and fracture toughness of the materials. It is shown that the mechanical properties vary somewhat depending on the precursor composition and is influenced

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significantly by defects such as large pores and the level of open porosity. Furthermore the fracture toughness of the GPs is improved due to the addition of sand.

Experimental

Sample preparation

Geopolymers with same molar ratio Si/Al ≈ 2 and Na/Al ≈ 1 were prepared using different commercially available precursors and additives as listed in Table 1. Four types of GP were synthesised and designated as follows, based on the key precursors:

(i) SAGP: sodium aluminate ($NaAlO_2$), Ludox (SiO_2) and metakaolin (MK),
(ii) FSGP: NaOH, fumed silica and MK,
(iii) LGP: Ludox, NaOH and MK,
(iv) SGP: sodium silicate and MK.

The batch compositions of these four GPs are summarised in Table 2 along with the molar ratio of H_2O/Na. Although they all have the same nominal composition, the water content is dependent on the precursor used. It was not possible to use the same amount of water for different starting precursors because of either difficulty with mixing or the samples produced were not satisfactory for mechanical testing (see below). The batch sizes produced for all compositions were about 100 g mixed in the proportions given in Table 2. SAGP batches were prepared by intimately mixing the two solutions of sodium silicate and sodium aluminate and then adding MK powder and mixed by hand. The FSGP batch was prepared by dissolving NaOH in water and then adding fumed silica and then mixed thoroughly. The solution was kept at 75 °C for ≈15 h to dissolve the silica. A clear liquid was obtained with a residue at the bottom. MK was added to the decanted off clear liquid and mixed in a similar fashion to SAGP. The LGP batch was made by dissolving NaOH in Ludox and adding MK and then mixed as before. SGP batches were made by adding water to a sodium silicate solution followed by MK and then mixed. To most of the batch compositions 40 wt% sand was added and the slurries were blended thoroughly using an electric mixer. The sand used was ordinary washed beach sand of size fractions: 81 wt% 250–500 μm, 17 wt% 125–250 μm and 2 wt% <125 μm. For some SGP batches 60 wt% sand additions were also produced.

Table 2 Batch compositions (wt%) of geopolymers prepared

Precursors	SAGP	FSGP	LGP	SGP
Metakaolin	28.4	34.8	34.7	33.6
$NaAlO_2$	15.8			
Ludox			46.9	
NaOH		12.3	12.5	
Fumed silica		19.2		
Sodium silicate	55.8			63.1
Water		33.7	5.9	3.3
H_2O/Na[a]	9.4	4.5	5.5	7.2
Si/Al[a]	2	2	2	2
Na/Al[a]	1	1	1	1

[a] Molar ratio

To study the effect of water on the open porosity and bulk density, a series of water ratios were trailed for the LGP batch. For others this assessment was made on the observation of the product as to its suitability for mechanical testing.

The slurries produced in each instance were cast to required shapes in metal moulds for mechanical testing. The cast items were sealed to prevent the evaporation of moisture and kept at room temperature for 2 h before curing at 60 °C for 24 h in an oven. After removing the seals, the samples were left at ambient temperature for 4 days before demoulding. All density and porosity measurements of specimens were made after 7 days and mechanical properties were tested after 10 days.

Table 1 Precursors used in making geopolymers

Precursor	Description
Metakaolin	Kaolin clay (Kingwhite 80, Unimin, Australia Pty. Ltd.) heated at 750 °C for 15 h. Clay has a molar ratio of $SiO_2/Al_2O_3 = 2.01$ and also contains ≈ 1 wt% TiO_2, quartz and hematite
$NaAlO_2$	Solution consisting of ∼34 wt% $NaAlO_2$, 9 wt% NaOH and 57 wt% water. Supplied by Redox Ltd., Australia
Ludox	Solution consisting of 40 wt% silica and 60 wt% water, Ludox AS40, Sigma Aldrich, Australia
NaOH	Ajax Fine Chemicals Ltd., Australia
Fumed silica	Silica Fume SF 98, Australian Fused Materials Pty. Ltd., Australia. 93 wt% silica, 4 wt% ($ZrO_2 + HfO_2$)
Sodium silicate	Solution, consisting of 14.7 wt% Na_2O, 29.4 wt% SiO_2 and 55.9 wt% water, Grade D, PQ Corporation, Australia
Water	Deionised water
Sand	Washed beach sand, Australian Foundry Services Pty. Ltd., Australia

Two sets of OPC samples were made by mixing Aalborg cement with a water/cement ratio of 0.3, one set with 40 wt% sand and the other without. They were cast similar to the GPs (see above). They were cured at ambient for 28 days before testing.

Physical and mechanical properties

The bulk densities of all the materials were determined by measuring the mass and the volume with a Hg pycnometer. Open porosities were determined by immersing each specimen in octane (non-polar liquid) for 24 h and measuring the mass absorbed (density of octane = 0.703 g/cm^3). Saturation with water was considered unsuitable because of leaching in water, especially Na [11]. This method of determining open porosity is a comparative method and not an absolute determination as the open porosity may be higher because of incomplete permeation of the liquid into the pores.

CCS specimens of 25-mm diameter and 40-mm high, were cast for each batch. Each specimen was ground flat and parallel using silicon carbide paper prior to testing. The CCS tests were conducted at room temperature in a servo-electric universal mechanical testing machine (Instron 8562) with a 100 kN load cell. The specimens were tested in position control at a cross-head speed of 5 µm/s. A minimum of five specimens for each composition were tested.

Flexure specimens were prepared as bars 6 × 10 × 50 mm, for elastic modulus and strength evaluation. Five specimens were obtained from each batch composition. Young's modulus of each specimen was measured using a non-destructive impulse excitation technique. The long edges of each specimen were then chamfered on the prospective tensile face to avoid edge failures. The strength or modulus of rupture (MOR) was determined using three-point bending with a support span $S = 40$ mm on the testing machine at a cross-head speed of 5 µm/s. The MOR values, σ_F, were calculated from the failure load and the specimen dimensions using the formula [12]:

$$\sigma_F = \frac{3PS}{2bw^2}, \tag{1}$$

where P is the fracture load, b is the specimen width and w is the specimen thickness.

Specimens for toughness evaluation were the same size (but now with thickness = 10 mm and width = 6 mm) to those used for MOR except that a notch was made at the centre of each bar on the tensile face using a thin diamond blade. The notch depth was measured using an optical measuring device (MicroVu, Model 9050A). The notched specimens were then tested in three-point bending as before, with all failures occurring from the notch. The fracture toughness, K_{IC}, of each specimen was then calculated [13]:

$$K_{IC} = \frac{3PS}{2bw^2}\sqrt{\pi a} f\left(\frac{a}{w}\right) \tag{2}$$

with:

$$f\left(\frac{a}{w}\right) = \frac{1.99 - \frac{a}{w}\left(1 - \frac{a}{w}\right)\left(2.15 - 3.93\frac{a}{w} + 2.7\left(\frac{a}{w}\right)^2\right)}{\left(1 + 2\frac{a}{w}\right)\left(1 - \frac{a}{w}\right)^{3/2}}, \tag{3}$$

where P is the fracture load, b is the specimen width, w is the specimen thickness, a is the notch length and S is the span length. Equations 2 and 3 are valid for $S = 4w$ as used in this work ($S = 40$ mm and $w \approx 10$ mm).

All the GPs were analysed by X-ray diffraction (XRD: Model D500, Siemens, Karlsruhe, Germany) using CoKα radiation on crushed portions of material. Selected samples were sectioned, mounted in epoxy resin and polished to a 0.25-µm diamond finish and examined by a scanning electron microscope (SEM: Model 6400, JEOL, Tokyo, Japan) operated at 15 kV and fitted with an X-ray micro-analysis system (EDS: Model: Voyager IV, Tracor Northern, Middleton, WI, USA). Some polished samples were also examined using optical microscopy.

Results and discussion

Physical and mechanical properties of GPs with 40 wt% sand are listed in Table 3. The mechanical property values of the SAGP are the lowest of the lot. More water was used to make this geopolymer, and this is believed to have resulted in SAGP having the highest open porosity. It is important to note that the water used (Table 2) to make a geopolymer varied widely depending on the precursor used. The highest CCS was obtained for LGP and SGP, and these also exhibited the highest Young's modulus. Using different mixing techniques should reduce the water requirement, thus making the porosity lower.

Table 3 Physical and mechanical properties of GPs with 40 wt% sand

	SAGP	FSGP	LGP	SGP
Bulk density (g/cm^3)	1.45	1.48	1.57	1.60
Open porosity (%)	32	28	20	20
CCS (MPa)	16 (2)	28 (5)	69 (5)	70 (6)
MOR (MPa)	3.2 (1.0)	7.4 (0.8)	8.8 (0.5)	7.2 (0.4)
K_{Ic} (MPa · m$^{1/2}$)	0.25 (0.04)	0.43 (0.04)	0.49 (0.03)	0.56 (0.02)
E (GPa)	5.5 (0.2)	9.6 (0.4)	14.0 (0.6)	14.0 (0.6)

Standard deviations are given in parentheses

Table 4 Variation of porosity and density of LGP with water content

H_2O/Na molar ratio	Open porosity (%)	Bulk density (g/cm^3)
2	6	1.85
4	12	1.64
4.5	16	1.55
5.5	20	1.57
6	30	1.30

Notes: 1. Porosity and density determined on the seventh day after making. 2. First three samples developed cracks after 10 days

Table 4 lists the variation of open porosity and bulk density for LGP samples made by varying the amount of water. It is seen that by using less water, the open porosity can be reduced. However, the samples developed cracks after about 10 days for those with less water than for H_2O/Na molar ratio of <5.5. The sample with a molar ratio of 6 had much higher porosity. Although the CCS of each sample except for molar ratio of 5.5 was not carried out, the CCS would certainly be the maximum for this sample.

There is almost a linear correlation in the mechanical properties with porosity irrespective of the precursor type. Figure 1 shows such a result for the CCS and Young's modulus versus open porosity for each geopolymer composition. The properties are highly dependent on the porosity (i.e. range 20–32% porosity), and this dominates over the precursor chemistry. The lower the porosity the higher the CCS, Young's modulus, fracture toughness and MOR, although there is a slight discrepancy with MOR and toughness of SGP and LGP which both exhibited the same level of porosity. Furthermore, there is good linear correlation between all the measured mechanical properties.

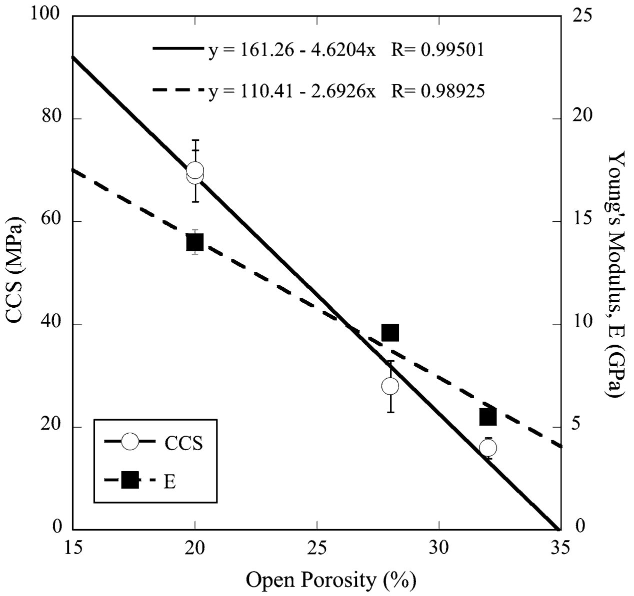

Fig. 1 Cold crushing strength (CCS) and Young's modulus (E) versus porosity of the four GP compositions. Solid and dashed lines are least squares fits to the CCS and E data, respectively

The effect of sand additions on mechanical properties of FSGP and SGP materials was investigated with 0, 40 and 60 wt% sand (only for SGP) and the results are shown in Table 5, along with comparative data for OPC. For SGP the addition of sand resulted in a small decrease in porosity over the material with no sand. The opposite is the case for FSGP. For SGP the MOR decreased with the addition of sand. However, the addition of sand led to improved MOR and Young's modulus (rule of mixtures) for FSGP even though the porosity increased. There is almost no change in the CCS values for both the precursor types with and without sand.

Figure 2 shows fracture toughness for materials FSGP, SGP and OPC with the differing level of sand addition. The addition of the coarse sand increases the fracture toughness as expected because the large-grained sand particles act as crack arrestors or bridging sites (see later Fig 3b) similar to coarse-grained polycrystalline ceramics [14]. For 60 wt% sand addition to SGP the strength and fracture toughness are only slightly different to that at 40 wt%. The increase in fracture toughness is more marked for FSGP than for SGP with the 40 wt% addition of sand. The fracture toughness of OPC does not change markedly with the addition of sand, but in comparison with the GP materials the toughness is higher. These values appear reasonable given that the toughness of OPC is generally within the range 0.2–1.0 MPam$^{1/2}$. The magnitude of the toughness of the GPs is low indicative of extremely brittle materials due to the large pores and other defects in the microstructure but is rather poor compared to silica glass ($\approx$0.7 MPam$^{1/2}$) and fine-grained alumina ceramics ($\approx$3 MPam$^{1/2}$).

The CCS values are dependent on the porosity in general, but they are also dependent on the chemical composition [4]. In this work even with the molar ratios of Si/Al $\sim$ 2 and Na/Al $\sim$ 1 the mechanical properties are dictated by the porosity levels attained as a result of the precursors used. Clearly, the microstructure (i.e. porosity level, pore size, other macrodefects) controls Young's modulus and strength properties of the GPs. This is in accord with Duxson's [15] findings that Young's modulus is more sensitive to the microstructure than the chemical composition when applied to GPs.

Optical images of SGP containing 40 wt% sand are shown in Fig. 3. Figure 3a shows a large sand grain in the GP matrix, which is typical of all the compositions. The large round black spots ranging from about 40 μm to 70 μm in diameter are macropores and these were quite common in all four GP materials produced. Figure 3b reveals a crack blunted and deflected by a large sand particle, indicating an improvement in fracture toughness of GPs with large aggregates (see also Fig. 2). Observations

Table 5 Physical and mechanical properties of FSGP, SGP and OPC with and without sand

Material: % sand addition	Bulk density (g/cm^3)	Open porosity (%)	CCS (MPa)	MOR (MPa)	K_{1c} (MPa · m$^{1/2}$)	E (GPa)
FSGP 0%	1.42	20	35 (5)	3.1 (1.5)	0.26 (0.08)	5.3 (0.6)
FSGP 40%	1.48	28	28 (5)		0.43 (0.04)	9.6 (0.4)
SGP 0%	1.46	25	72 (5)	10.8 (0.7)	0.46 (0.06)	9.6 (0.3)
SGP 40%	1.60	20	70 (6)	7.2 (0.4)	0.56 (0.02)	14.0 (0.6)
SGP 60%	1.61	21	69 (5)	8.1 (0.7)	0.59 (0.02)	12.2 (1.1)
OPC 0%	1.86	14	57 (1)	13 (1)	0.67 (0.04)	19.1 (0.6)
OPC 40%	2.00	15	53 (2)	11 (0.6)	0.65 (0.04)	23.3 (1.5)

Standard deviations are given in parentheses

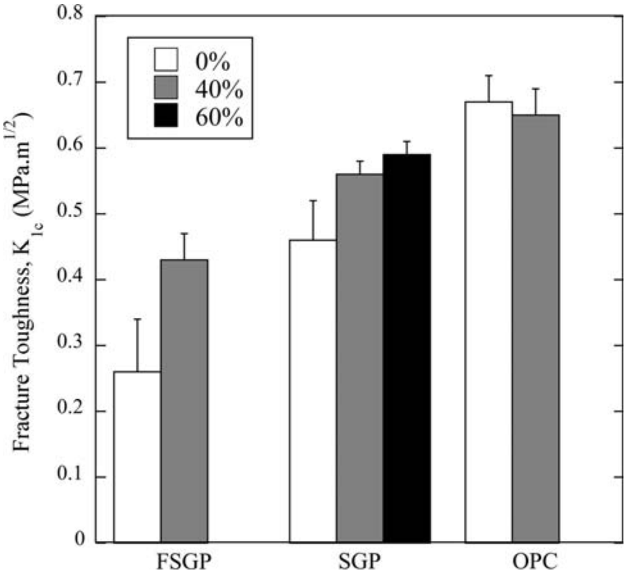

Fig. 2 Histogram showing fracture toughness values of FSGP, SGP and OPC with no sand and different levels of sand additions. Errors bars are standard deviations (five samples per set)

of fracture surfaces of MOR samples also indicated that large pores were the fracture origin sites.

The EDS analyses of the matrices were carried out on all the materials and the values are listed in Table 6. The lower the Na/Al ratio, the less Na is available for binding to form a coherent solid. Hence, this is reflected in the strength value of SAGP. The EDS analysis will give a lower Na value because of the migration of Na under the electron beam. Higher Si/Al ratio for LGP is not clear, but possibly all the SiO_2 (Ludox) added reacted more than in other precursors.

Table 6 EDS analyses of matrices of GPs (molar ratio)

	SAGP	FSGP	LGP	SGP
Si/Al	2.0	2.2	3.3	2.2
Na/Al	0.4	0.5	0.6	0.6

Although not shown the XRD traces of all GPs indicated the presence of an amorphous phase by the broad diffuse peak centred at a d-spacing of about 0.32 nm, together with weak peaks due to crystalline anatase and quartz impurities in the MK, as observed by other workers on MK-based GPs [4]. These impurities in the original clay were estimated at ≈1 mass% [16].

Typical SEM images of polished surfaces in the densified regions of the four GPs are shown in Fig. 4. The image of SAGP in Fig. 4a shows the presence of MK that has not reacted as well as porosity within the matrix. The SEM image of FSGP in Fig. 4b shows the presence of unreacted silica particles. Fig. 4c shows LGP surface, which is similar to FSGP. Figure 4d shows SGP and is denser compared with SAGP and FSGP; however, it also has some unreacted MK grains scattered throughout the matrix.

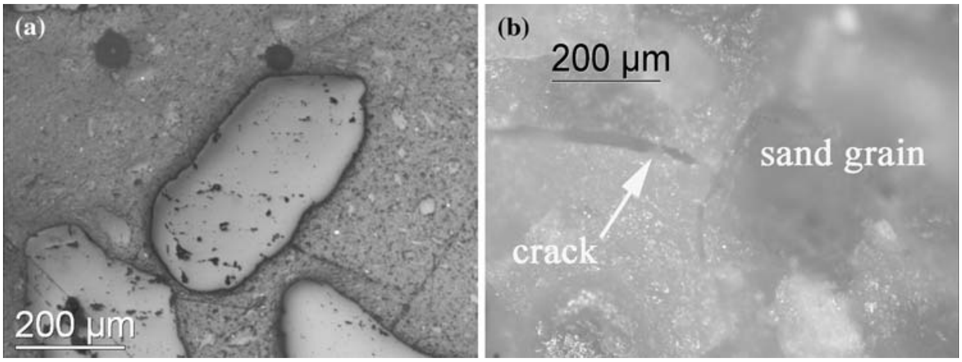

Fig. 3 Optical images of SGP with 40 wt% sand show: (**a**) typical sand particle in GP matrix and (**b**) crack blunted by sand particle. Black regions are pores

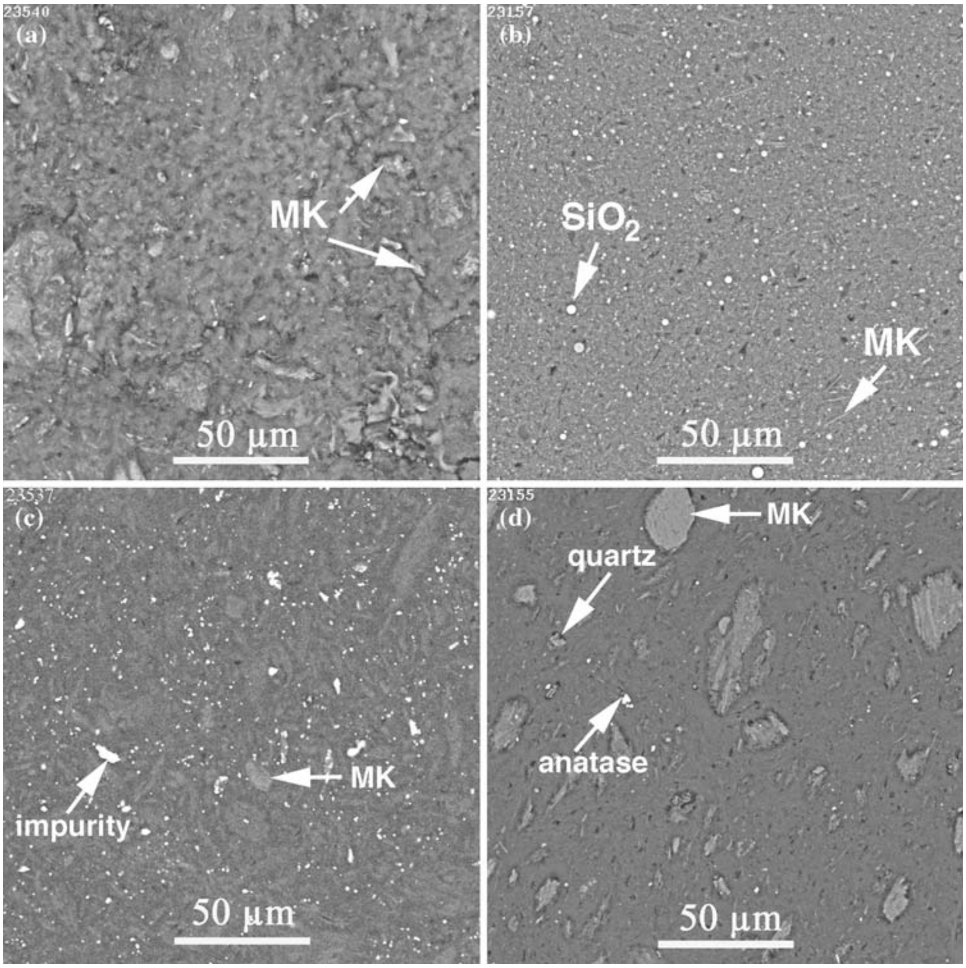

Fig. 4 Backscattered scanning electron micrographs of polished sections of (**a**) SAGP, (**b**) FSGP, (**c**) LGP and (**d**) SGP. MK relics are shown in each image and are marked by an arrow and other minor phases are identified where appropriate

Conclusion

The mechanical properties of four GP compositions with molar ratios of Si/Al ~ 2 and Na/Al ~ 1 produced using different precursors with and without sand additions have been examined. The main findings are summarised as follows:

(1) The highest CCS obtained was for SGP and the lowest value was for SAGP with 40% sand.
(2) The highest MOR obtained was for LGP and the lowest value was for SAGP with 40% sand.
(3) The pore size and porosity level dictate the mechanical properties and Young's modulus of the GPs irrespective of precursor type or composition.
(4) Young's modulus and fracture toughness exhibited the same trend as CCS and MOR for the 40% sand GPs.
(5) Addition of sand aggregate leads to an improvement in the fracture toughness of the GPs by up to 65% and Young's modulus of up to 80% compared to materials with no sand.
(6) Some GPs produced exhibit generally equivalent mechanical properties to OPC.

This work has demonstrated that porosity is a controlling factor on the mechanical properties of GPs. The removal of large macropores (defects) and minimisation of the overall porosity is a requisite for improved strength and toughness. Further work should examine the influence of pore size on strength and aggregate size effects on toughness and R-curve behaviour. Investigations are currently underway in our laboratory to produce defect free high-density GPs.

Acknowledgement The authors thank Lou Vance for helpful discussions and Ted Roach for polishing the samples.

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