The effect of organic and inorganic fibres on the mechanical and thermal properties of aluminate activated geopolymers

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ABSTRACT

The addition of fibres to a brittle matrix is a well-known method to improve the flexural strength. However, the success of the reinforcements is dependent on the interaction between the fibre and the matrix. This paper presents the mechanical and microstructural properties of PVA and basalt fibre reinforced geopolymers. Moreover low density and thermal resistant materials used as insulating panels are known be susceptible to damage due to their poor flexural strength. As such the thermal and fire resistance properties of foamed geopolymers containing fibre reinforcement were also investigated.

The results highlight that the presence of PVA fibres greatly increased the flexural strength and the toughness of the geopolymer composite, while the presence of basalt fibres improved the flexural behaviour of the composite after high temperature exposure.

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1. Introduction

Geopolymer is a class of three-dimensional alumino-silicate material based on units such as sialate [−Si−O−Al−O], sialate siloxo [−Si−O−Al−O−Si−O] or sialate disiloxo [−Si−O−Al−O−Si−O−Si−O] [1]. The polymerised materials contain tetrahedrally coordinated Al and Si, with charge balance of the Al tetrahedra being achieved by the presence of Na^+ or K^+ ions [2]. Geopolymers and alkali activated materials (AAM's) generally have attracted a lot of attention [3–5] as suitable alternative materials for constructions, due to their significantly lower CO_2 emissions during production [6]. A benefit of the use of geopolymer compared with ordinary Portland cement (OPC), the most commonly used building material, is the possibility of using high-volume industrial waste to manufacture geopolymer concretes, with a concomitant reduction in CO_2 emissions [7].

Fibre reinforcement has been used in various hardened binders to improve mechanical properties [8,9]. Short fibres are one of the most commonly used reinforcement and are effective in improving flexural strength, toughness and in converting failure mode from brittle to ductile. Compared to continuous fibres, short fibres permit easier handling and manufacturing processes. Fibre aspect ratio and fibre dispersion are the critical factors to consider when optimizing any improvement in strength.

Several studies assessing the mechanical performance of alkali-activated composites reinforced with different fibres have been reported in the literature [10–15] and some studies also investigated the thermal behaviour after high temperature exposure [4,16–18]. Due to their durability, PVA fibres are one of the most commonly used reinforcement materials in ceramic composites for structural applications [19]. However, the exposure to high temperatures degrades PVA fibres, due to their organic composition. In the temperature range between 30 °C and 1000 °C, PVA samples exhibit three different weight loss stages that correspond to different phase changes: between 30 °C and 210 °C the loss of physisorbed water, between 210 °C and 400 °C the decomposition of the polymeric side chains and between 400 °C and 540 °C the decomposition of the main polymeric chain [20]. Basalt fibres are inorganic and as such have a much higher melting point (~1000 °C) than organic fibres making them a suitable candidate for high temperature resistant geopolymer composites.

Light-weight materials are often required for materials used in building applications, particularly in high rise construction. The use of geopolymers of lower density is beneficial in terms of reduced structural load-bearing with further benefits of improved acoustic and thermal insulation [21,22]. However, the trade-off is that low density geopolymers generally exhibit low strength [1].

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Different foaming agents can be used to synthesise low density geopolymers. For instance, chemical products which react with the alkali to generate gas [23], metals, such as zinc or aluminium, which generate hydrogen gas [23,24] and metallic silicon present as an impurity in silicon carbides or silica fume also generates hydrogen gas when exposed to alkali [25,26]. Another class of chemical foaming agents is peroxides such as hydrogen peroxide and organic peroxides which react to evolve oxygen gas [24]. Bubbles of O_2 are trapped within the paste, resulting in lower density.

It is known that low density materials have low thermal conductivity and are more suitable for thermal insulation exposure [4]. Materials designed for refractory and fire resistance applications must be able to be exposed to high temperature for extended periods while retaining physical properties such as strength.

This paper presents a study where foamed geopolymers have been reinforced with two different types of fibres: organic (PVA) and inorganic (basalt) short fibres. Fibres have been introduced with the aim of modifying the brittle fracture behaviour of geopolymers. Low density formulations were synthesised using hydrogen peroxide and a chemical surfactant, exploiting the best results of a previous study [27].

First, mechanical, physical and microstructural properties are reported as well as the thermal behaviour of fibre reinforced geopolymers (FRGP) in order to assess the suitability of the different fibres in geopolymer composites. Then, thermal conductivity measurements and fire testing was performed on foamed and fibre reinforced geopolymers (FFRGP) in order to understand the behaviour of the different fibres in composites with low density matrices for possible thermal insulation applications.

Composite materials based on geopolymer matrices can be produced for various applications requiring good performances at elevated temperatures [16,17,28,29], but also for applications where thermal insulation [30] at room temperature is necessary (e.g. blocks and plaster for the building sector). The addition of short fibres in low density geopolymers also stabilizes the foam during synthesis by increasing the viscosity of the paste and consequently reducing pore collapse [4].

2. Experimental

2.1. Materials

Fly ash was sourced from Eraring power station in New South Wales, Australia. Sodium aluminate solution was used as the alkali activator. Solutions were prepared by dissolving sodium hydroxide pellets from Univar Pty Ltd and sodium aluminate powder supplied by Sigma–Aldrich in deionised water. The chemical composition of sodium aluminate used in this study was Al_2O_3 50 wt%, Na_2O 50 wt % and some impurities of Fe_2O_3 (<0.05 wt%). The pellets and powder were allowed to dissolve overnight at 70 °C and used for synthesising geopolymers after 24 h. Activator solutions were characterised by $Na_2O:Al_2O_3 = 0.5$ and $H_2O:Na_2O = 2,1$. PVA short fibres (Nycon-PVA RECS 15, Australia) 8 mm long and 38 μm in diameter and basalt chopped fibres (Technobasalt, Ukraine) 5 mm long and 16 μm in diameter were used as the fibre reinforcement. Hydrogen peroxide solution with 30 wt% supplied by Rowe Scientific was used as the chemical foaming agent. Sika® LIghtcrete 02 was used as the surfactant for foam stabilization.

2.2. Geopolymer synthesis

Geopolymers were synthesised with targeted compositional ratios of Si:Al = 2.0, Na:Al = 1.1 and a water content of 21 wt%. Samples were made by mixing the fly ash with the activating solution for 10 min. Fibre reinforced geopolymer (FRGP) were synthesised by adding different concentrations of fibres (0.5 vol% and 1.0 vol%) after 5 min of the initial mixing time and mixed for another 5 min. Foamed and fibre reinforced geopolymer (FFRGP) samples were produced by foaming the pastes with surfactant and hydrogen peroxide (1 wt% of surfactant added at 5 min together with the fibres, and 0.1 wt% of hydrogen peroxide added after 10 min and mixed for a further 20 s). Immediately after mixing samples were poured into moulds, sealed and cured at 70 °C for 24 h.

2.3. Physical testing and microstructure

Workability was measured using a mini-cone slump tester (57 mm high, with 19 mm and 38 mm top and bottom diameters, respectively). Geopolymer slurry was poured to fill the cone and after lifting the cone up, the slurry was allowed to flow for 1 min prior to measuring the diameter.

The density of the samples was measured by dividing the dry mass by the volume. Cylindrical samples (50 mm diameter, 100 mm high) were used for density measurements. All reported results are an average of measurements from 4 samples.

Pore size distribution measurements were carried out on all specimens by a mercury intrusion porosimeter (MIP, Carlo Erba 2000) equipped with a macropore unit (Model 120, Fison Instruments). Samples for porosimetry were cut by diamond saw to approximately 1 cm³, dried under vacuum and kept under a P_2O_5 atmosphere in a vacuum dry box until testing. The MIP measurements were carried out using a contact angle of 141.3° and Hg surface tension of 480 dyne/cm. The suitability of MIP for pore size and pore size distributions is frequently debated [31–33], however its use in cement based materials is accepted [34–36] and it is also becoming common in the field of inorganic polymers [37–39].

Scanning electron microscopy (SEM) was conducted on a NEON 40EsB (Zeiss, Germany) field emission SEM. Sample fragments of FRGP were mounted onto aluminium stubs and out-gassed in a desiccator over a 24 h period. The samples were then coated with a 5 nm layer of platinum prior to imaging.

2.4. Mechanical testing

All the mechanical tests were conducted by means of a Lloyd universal tester EZ50 on FRGP after 7 days of sealing at room temperature in plastic bags (i.e. 100% rH). This time was selected as it is the time after which most of the mechanical properties have been developed in geopolymers cured at elevated temperatures [18,40]. Cylinders of 25 mm diameter and 50 mm height were prepared for compressive strength testing. A load rate of 0.25 MPa/s was used to comply with ASTM C39 [41]. Flexural strength and fracture toughness tests were performed on 20 × 20 × 90 mm cuboids. Flexural strength testing was conducted in accordance with ASTM C78 [42] and fracture toughness was conducted in accordance with ASTM C1421-10 [33]. A span of 40 mm was set up for the three points bending tests and a preload force of 50 N was used to ensure no movement during the specimen testing and a load rate of 1 mm/min was used. Before the fracture toughness testing, samples were prepared by creating an initial crack with a depth of 4 mm and a thickness of 0.1 mm width. The values for fracture toughness of each samples was calculate using Eq. (1) [43]:

$$K_{Ipb} = g\left(\frac{P_{max}S_0 10^{-6}}{BW^{3/2}}\right)\left[\frac{3(a/W)^{1/2}}{2(1 - a/W)^{3/2}}\right] \qquad (1)$$

where K_{Ipb} = fracture toughness for each specimen (MPa$\sqrt{m}$); P_{max} = maximum force (N); S_0 = span (m); B = width of the test