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INFLUENCE OF BASALT FIBRES ON THE PROPERTIES OF FLY ASH BASED GEOPOLYMER BINDER

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Abstract

The influence of basalt fibres on the compressive strength of the geopolymer type binders has been studied. For the experiments 2 types of the basalt fibres were used, namely chopped and spooled fibres. Both types of basalt fibres were 7-10 micron thick in diameter and cut into pieces of 6 mm length. The fibres were mixed with 1% weight to the fly ash powder, followed by the addition of the activator solution (8M NaOH). The pastes obtained were cured at 70°C for 20 h revealing compact bodies. Compressive strength was measured after 7 days and microstructure observation performed with SEM. The cube bodies (2x2x2 cm) reveal compressive strength of 47.25(4.03) MPa, while it decreased to 34.0(9.05) MPa in spooled basalt fibres and to 17.33(5.86) MPa in the chopped basalt fibres containing binder, i.e 76% and 36% of the strength without fibres, respectively. The much weaker compressive strength of the chopped fibres containing binder is related to the absence of significant adhesion between the geopolymer binder and the basalt fibres, forming voids instead. Alkali leaching effect of basalt fibres could probably explain the drop in the compressive strength with spooled and chopped fibres, respectively.

Keywords : fly ash; geopolymers; basalt fibre; mechanical property

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1. Introduction

Geopolymers are a class of alkali activated materials which have applications within a wide range from the building and construction materials (Pacheco-Torgal, 2014) to an advanced materials field such as chemical and thermal resistant materials (Temuujin et al., 2013). New applications hosting hydrogen storage materials have been reported (Ruescher et al. 2013, Schomborg et al. 2014). For a comprehensive review on new application compare MacKenzie (2014).

At presently geopolymer type materials prepared from the industrial wastes such as fly ash, are having some industrial applications such as substitute or addition to ordinary Portland cement (OPC) based mortars and concretes. However, due to their brittle and ceramic-like nature the tensile and flexural strengths exhibited by geopolymers could be too low for certain applications. This could lead to catastrophic failure and represent the main drawback, limiting the use of those materials, Natali et al (2011). One method to improve tensile and flexural strengths of brittle materials is the incorporation of fibres. Fibre reinforcement increases ductility, toughness, and resistance to cracking induced by thermal effects, shrinkage or other causes. Furthermore, fibres act to prevent crack growth and transfer stresses across cracks, Bernd and Philippacopoulos (2002). In general, the properties of fibre-reinforced materials are dependent on the physical and mechanical properties of the fibres, fibre length and volume fraction, interfacial bond strength, orientation of fibres and aspect ratio. Fibre reinforcement of geopolymer composites (FRGC) has been reviewed recently, Shaikh (2013). It could be summarized that significant improvements in flexural and tensile strength of FRGC are observed at early ages up to 28 days regardless of fibre types and contents, without any significant change in compressive strength at early and late ages of slag based FRGC, e.g. using fibres out of steel or polypropylene.

It has been observed that different types of fibres, e.g. High Tenacity (HT) carbon, E-glass, polyvinyl alcohol (PVA) and polyvinyl chloride (PVC) fibres, improved the flexural strength ranging from 30% up to 70%, compared to the unreinforced material, Natali et al. (2011). Some authors observed reduction of compressive strength with basalt fibre containing OPC concrete while no significant change could be detected in basalt fibre containing geopolymer concrete, Dias and Thaumaturgo (2005). These authors observed a fast failure of the specimens without fibres without any "warning". In contrast, in the case of the specimens with fibres, the specimens still deformed and the rupture was more ductile after the ultimate load was reached. Positive effect of basalt fibres as strengthening material for concrete structures have been observed and reported better structural integrity of the fibres with the concrete structure, Sim et al. (2005). The addition of basalt fibre can significantly improve deformation and energy absorption capacities of geopolymeric concrete (GC), while there is no notable improvement in dynamic compressive strength, Li and Xu (2009). Rill et al. (2010) reported 10 fold increase in 3 point flexural strength of the KOH activated metakaolin based geopolymers by addition of 10wt.% chopped basalt fibres.

From the previous reports tensile and flexural strength of OPC based and geopolymer based concretes are improved with the incorporation fibres. However, as discussed above some contradicting results were shown for the compressive strength. It is the purpose of this study to consider the compressive strength of fibre reinforced geopolymers in some more detail using locally available fibres and fly ash raw materials. Geopolymer type alkali activated materials are prepared in various alkaline liquids. Some authors have shown that surface of the fibre deteriorates in alkaline condition, Wei et al. (2010). Therefore, the possible surface modification of the basalt fibres will be investigated, too.

2. Methodology

2.1 Materials and methods

Baganuur fly ash from the 4th Thermal power station of the Ulaanbaatar city (Mongolia) was used as raw material for the preparation of the geopolymer pastes. Its chemical composition is mainly SiO_2 (56%), Al_2O_3 (14%), CaO (14%), Fe_2O_3 (10%) and smaller amounts of Na_2O/K_2O (< 2%) (all by wt%) as determined previously by Temuujin et al. (2014). Basalt Wool LLC (Ulaanbaatar, Mongolia) donated 2 types of fibre materials, called chopped and spooled basalt fibres. The diameter of each fibre was 7-10 micron. The chopped fibers have a length of about 2 cm and in bundles of several individuals as seen in Fig. 1A. The spooled fibres seems to be more hair like, composing a much smaller number of individuals in one strand (Fig. 1B). All fibers were cut into 6 mm length as used for the experiment. Due to contact area of the fibre surface with the geopolymeric surface the size (length) of the fibre should show influence on the mechanical properties. Therefore one length only was chosen to study the influence of the fibres in general. The effect of different fibre lengths was not further studied here.

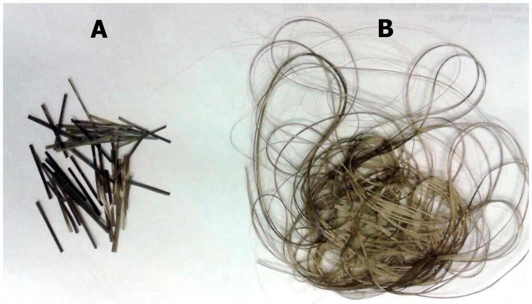

Figure 1. Basalt fibres, chopped (A, length about 2 cm) and spooled (B)

Chemical composition of the basalt and spooled fibres measured with the SEM-EDX analysis is shown in Table 1. The content of the main oxides present in both of the fibres closely agree, i.e. the SiO_2 content of spooled fibers appears about 5% wheras the CaO, MgO and Fe_2O_3 content are by about 2% less.

Table 1. Chemical composition (wt%) of the used basalt fibres measured with the SEM-EDX analysis.

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	TiO_2	K_2O
Chopped basalt fibre	50.83	15.51	9.57	6.11	13.03	3.34	1.31	0.31
Spooled fibre	55.74	14.82	7.91	4.54	11.18	2.90	0.77	2.14

Geopolymer type paste was prepared by mixing the Baganuur fly ash with the 8 M solution of sodium hydroxide (NaOH). An amount of fibres of 1 wt.% of the total fly ash weight was added. In a first step the fibres were mixed with the fly ash powder and then poured sodium hydroxide solution into mixture until the workable consistence and hand mixed for 5 minute and poured in 2x2x2 cm metal molds. Then molds were covered by a plastic bag and cured at 70°C for 22 h. The molarity of the sodium hydroxide solution was based on our previous research on the preparation of high calcium fly ashes for alkali-activated geopolymer-type concrete (Temuujin et al. 2013). A possible interaction of alkaline solution with both types of basalt fibres was evaluated by leaching in 1 M NaOH solution at 70°C for 30 minutes.

2.2 Characterization

The compressive strength of the pastes was measured with Universal testing machine WDW-50 (Jinan). The reported value is the average of 4 measurements. Geopolymer type pastes were characterized by XRD (Bruker, Advance D8) and SEM (JEOL, JSM-G390A) techniques. The fibres were investigated using micro Raman spectroscopy (Bruker, Senterra, 532 nm, 20 mW) to determine possible surface coatings.

After 30 minute alkaline leaching, the fibres were washed and dried at 80°C for 48 h and characterized by SEM-EDX, too. Density of the specimens was determined by the weight to volume ratio. The weight loss was determined by TG (Setaram Setsys ev. 1750) by heating the sample to 1000°C (10°C/min, O_2/N_2 20/80). Water absorption was evaluated by weight change of the dry and 30 minute boiling water immersed specimens.

3. Results and discussions

3.1. Influence of basalt fibres on the mechanical properties of paste

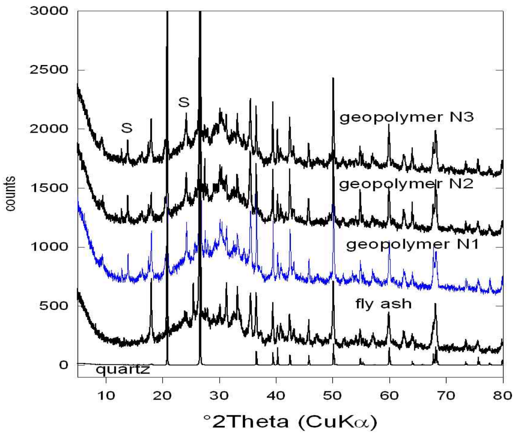

Figure 2. XRD patterns of the fly ash, geopolymer paste (N1), chopped fibre (N2) and spooled fibre (N3) reinforced geopolymer pastes. A quartz pattern is included for comparison. S denotes sodalite. (Note: peak at 18°2Theta is due to sample holder).

Fig.2 shows XRD patterns of the Baganuur fly ash and geopolymer cement without (N1) and with fibre reinforcement (N2, N3). XRD pattern indicated that Banganuur fly ash contains mainly X-ray amorphous glass type phase beside quartz and some smaller content of feldspars and hematite. Only the glass type phase becomes alkali activated and thus transformed to the geopolymer type binder possessing a binder specific broad geopolymer diffraction peak (BGDP) as also discussed recently. However, unlike for alkali activated metakolin based geopolymers (Tchakoute et al. 2015) there is no distinction between unreacted parts and the geopolymerized binder possible in the BGDP since it nearly exactly coincides with the amorphous part of the fly ash. In the alkali activated samples some small content of sodalite is observed, which is formed from the amorphous gel phase during the curing. There are no effects of the fiber detected in the XRD pattern.

The effect of binder formation can be suggested due the developed mechanical properties. For comparison the composition and the 7 days compressive strength the geoolymer binder (N1) and fibre reinforced binders (N2, N3) are given in Table 2. It is observed that the compressive strengths of the fibre reinforced pastes were reduced up to 28% in the spooled fibre and up to 63% in the chopped fibre reinforced specimens. Thus basalt fibre addition to the Banganuur fly ash based binders significantly decreases the compressive strength of the geopolymer type pastes. In so far the flexural strength could not be measured. Generally the flexural strength shows the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The compressive strength of a material depends on its ability to sustain a load without undue deformation or failure. Compression tests are used primarily to determine the relationship between the average normal stress and average normal strain in engineering materials. The compressive strength is very sensitive to density. Thus a lower density of binder N3

Table 2. Composition and mechanical property of the geopolymeric paste and fibre reinforced geopolymeric pastes

No.	NaOH (8M)	Compress strength (MPA)	Water absorption (wt%)	Density (g/cm^3)
N1	Geopolymer paste	47.25(4.03)	16.14	1.68(0.02)
N3	Paste +1% spooled fibre	34.0(9.05)	15.71	1.68(0.009)
N2	Paste + 1% chopped fibre	17.33(5.86)	16.19	1.63(0.02)

(Tab. 2) could be due to an increased contribution of voids, which could lead to weaker compressive strength of the chopped fibre reinforced material. The observed weight loss (11-12 wt %) measured by the DTA-TG instrument and their curves for heating to 1000°C rather closely coincides for N1, N2 and N3 sample, showing no difference in their contents of evaporations.

An increased contribution of voids in the binders containing chopped fibres (N2) compared to the spooled fibres ones (N3) could be supported by SEM investigations (Fig. 3.). It is observed that the formed gel could be better attached to spooled fibres. No such adhesion is observed for chopped fibers, forming only weak or no contacts. Instead voids are seen more often. Thus this seems to be very likely the reason of poor mechanical property of the chopped fibre reinforced geopolymeric binder.

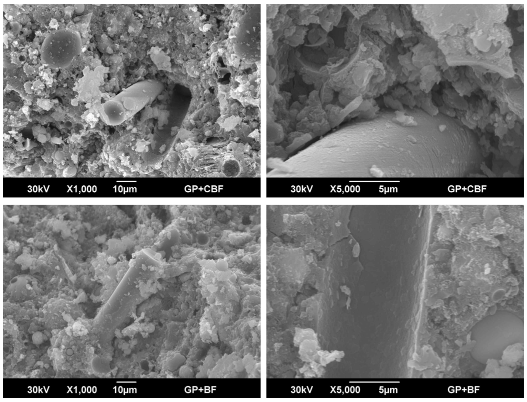

Figure 3. SEM micrograph of the geopolymer binders reinforced with chopped basalt fibre (N2), top, and spooled fibres (N3), bottom with lower (1000, left) and higher (5000, right) magnification, respectively.

The reason of poor bonding could possibly be related either to the glassy smooth surface of the fibres or their coatings or leaching effects of the alkaline solution. Basalt fibres are produced by melting the basalt rock at about 1400-1500°C and extruding. Therefore, basalt fibres show rather smooth glassy surface as shown for chopped and spooled basalt fibres in Fig. 4.

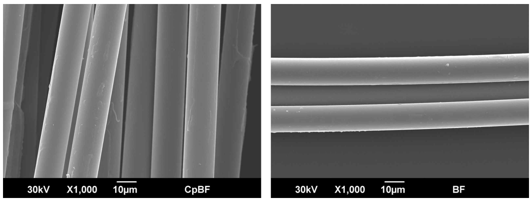

Figure 4. Surface morphology of chopped (left) and spooled (right) basalt fibre.

3.2. Surface studies of the basalt fibres.

Surface studies of the basalt fibres with the micro Raman spectroscopy revealed the presence of the amorphous carbon layers on the surface of the spooled fibres (Fig. 5). Both fibres showed peaks at 480, 566 and 1000 cm^{-1} due to the glassy aluminosilicate. These peaks are observed at all spots in the depth profile into the fiber, too.

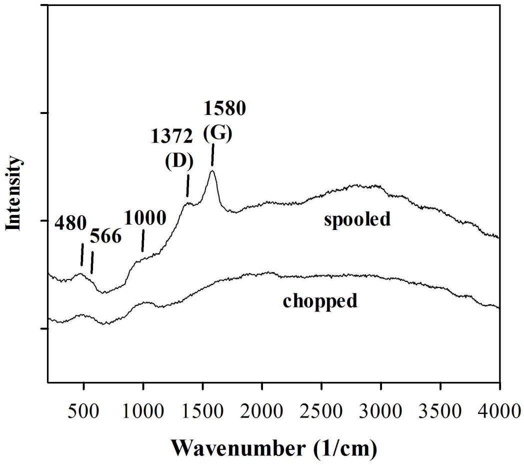

Figure 5. Micro Raman spectra of the chopped and basalt fibres

Following Ferrari and Robertson (2000), the peaks denoted as G and D could be classified as stage 2 between nano-crystalline graphite and amorphous carbon according to their position and relative intensity. G and D peaks were mostly absent for chopped fibres.

Since the chemical composition difference between the chopped and spooled fibres was rather small (Tab. 1), a better adhesion of the geopolymer matrix with the fibre surfaces is indicated for the spooled fibres. Rill et al. (2010) described higher flexural strength of the specimens with silane coated fibres compared to un-coated fibres. Wei et al. (2011) reported that surface modification of the basalt fibres occurred by acid or alkali leaching. Therefore, curing of the fibre reinforced geopolymer paste at 70°C for 20 h is expected to show some influence on the fibre surface, consequently its binding behavior with the geopolymer matrix.

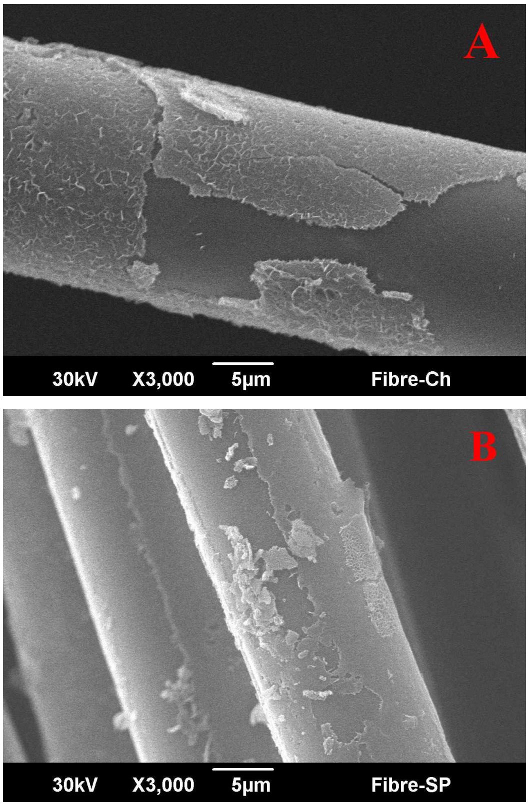

Figure 6. SEM micrographs of alkali treated chopped (A) and spooled (B) fibres.

The surface morphology of the fibres treated with 1 M NaOH is shown in Fig. 6. However, there is not distinction between carbon coated (spooled) and non-coated (chopped) fibres obvious. Alkali leaching destroyed the outer surface of both fibres. The surface erosion of both fibres is looking almost the same, possibly because of the high volume of the alkaline solutions used for the leaching.

Singha (2012) showed that the basalt fibre surface is more damaged by alkali leaching than that of carbon fibre surface. Therefore, we suggest that the spooled fibre could be much less affected by the alkaline solution within the geopolymer paste. In contrast the chopped fibre does not show any significant carbon coating and thus receives no protection against the alkaline solution within the geopolymer paste. It can be suggested that interaction of the basalt fibre surface with the alkaline solution causes surface distortion of the chopped fibre thus leading to appearance of the voids between the geopolymer matrix and fibre. It could be the possible reason of the compressive strength weakening of the basalt fibre added geopolymer paste. Further detailed investigations on elucidation of basalt fibre coating elements influence on adhesion to geopolymer matrix seem to be required.

4. Conclusions

Compressive strength of the geopolymer type fly ash based paste weakens with basalt fibre reinforcement. The main reason of this effect is related with non-ultimate bonding of the fibre surface and paste. Difference of the bonding behavior between chopped and spooled fibres is likely to be caused by the difference of coatings. Spooled fibre coated by the carbon layer is more resistant to alkaline solution and shows better adhesion between the geopolymer matrix and fibre surface. The chopped fibre does not have coating and more vulnerable to alkaline solution thus forms void between the geopolymer gel and fibre surface without ultimate adhesion. It is concluded that the basalt fibre coating is an important factor for bonding. Non-coated basalt fibres seems to be inappropriate for reinforcement of the geopolymer materials.

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