

ROLE OF CARBON MICROFIBERS ON ELEVATED TEMPERATURE PROPERTIES OF GEOPOLYMERS

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Abstract: The present work deals with the effect of carbon microfiber addition on the development of microstructure and mechanical properties of geopolymers at elevated temperature. The carbon microfibers were prepared from recycled inexpensive carbon fibrous wastes by ball milling and then subsequently incorporated under 5, 10 and 15 wt.% loading into metakaoline based geopolymers. The addition of carbon microfibers was found to produce compact structure of geopolymers due to their pore filling characteristics and formation of additional calcium silicate or calcium alumino-silicate and sodium alumino-silicate hydrates. The geopolymer composite of 15 wt.% carbon microfiber was found to maintain the residual compressive strengths of 33.55 and 23.96 MPa at 400 and 800°C, respectively and thus recording a minimum strength loss of 19 and 42%, respectively. This behavior was attributed to decreased thermal stresses and restricted swelling of unreacted geopolymer phases after addition of carbon microfibers.

Keywords: Carbon microfibers; geopolymer; thermal stability; mechanical strength; microstructure analysis.

1 INTRODUCTION

In recent years, geopolymers have received considerable attention for their cost efficiency, chemical stability, corrosion resistance, rapid strength gain rate, low density, low permeability, low shrinkage and freeze-thaw resistance [1, 2]. In addition, geopolymers are considered as an attractive replacement to ordinary Portland cement due to reduced energy consumption and less CO₂ emission during their manufacture [3-5]. The geopolymers are amorphous cementitious binders having cross-link chain of silica, oxygen and alumina (Si-O-Al) [6, 7]. They are synthesized by reacting aluminosilicate source materials (i.e. fly ash, slag, metakaoline, etc.) with highly alkaline activators. Despite many benefits, geopolymers still have certain limitations over ordinary Portland cement. Due to their cross-linked structure, geopolymers tend to be more brittle, susceptible to crack formation and undergo catastrophic failure as compared to ordinary Portland cement [8, 9]. Previous studies have reported their fracture energy about 40% of that of ordinary Portland cement [10]. Therefore, for further improvements of performance and durability, the improvement in fracture properties of geopolymers is extremely necessary. Although incorporation of different fibers (steel, polypropylene, polyvinyl chloride, and basalt fibers) have been found to be effective in controlling crack propagation and enhancing the fracture energy of geopolymers, the mechanical properties of geopolymers were

found non-consistent and inadequate when exposed to elevated temperatures [11-13]. During fire accidents, many of these fibers fail in providing effective reinforcements due to lack of structural strength and durability at higher temperature[14]. Therefore, further research is required to identify alternative fibers which possess good thermal resistance and maintain higher residual mechanical properties when exposed to elevated temperature. The present work deals with the effect of carbon microfiber addition on the development of microstructure and mechanical properties of geopolymers at elevated temperature. The carbon microfibers were prepared from recycled inexpensive carbon fibrous wastes by ball milling, and then subsequently incorporated under 5, 10 and 15 wt.% loading into metakaoline based geopolymers. Further, the composites were examined for change in microstructure, mechanical properties and toughening mechanisms after exposure to the elevated temperatures of 200, 400, and 800°C. To the best of the authors' knowledge, this is the first study on elevated temperature properties of geopolymers filled with carbon microfibers obtained from carbon fibrous wastes.

2 EXPERIMENTAL METHODS

2.1 Materials

The recycled carbon materials under trade name carbiso mil 100 μ were purchased from Easy composites, UK. The Baucis L110 alumino-silicate

geopolymer binder based on metakaoline was obtained from Ceske Lupkove Zavody, Czech Republic along with sodium alkali activator. The chemical composition of the kaolin was as follows [wt.%]: SiO₂ 47, Al₂O₃ 24, LOI 0.5, Fe₂O₃ 0.50, TiO₂ 0.8, MgO 3.5, K₂O 0.40, CaO 17.5. The mean particle size (d₅₀) was 5 μm. The alkali activator was mixture of Na₂SiO₃/NaOH in mass ratio of 2.0.

2.2 Preparation of carbon microfibers (CMF)

The size of carbiso mil 100 μ particles was further refined to the micro-scale using ball milling based on previous research experience [15, 16]. The 30 min grinding was carried out by high-energy planetary ball mill (Fritsch Pulverisette 7, Germany) in a sintered corundum container of 80 ml capacity using zirconium balls of 10 mm diameter. The ball to material ratio was kept at 10:1 and the speed was kept at 850 rpm. Later, Malvern zetasizer nano series based on dynamic light scattering principle of Brownian motion of particles was employed to characterize the particle size distribution of dry milled carbon particles. Deionized water was used as dispersion medium and it was ultrasonicated for 5 min with bandelin ultrasonic probe before characterization. In addition, microstructure of carbon particles was observed on scanning electron microscope (SEM) of Hitachi-model TM-3000 at accelerated voltage of 15 kV.

2.3 Preparation of carbon microfiber/geopolymer composites (CMF+G)

The geopolymer (G) was synthesized from calcined kaolin and shale clay residues with Si/Al ratio of 2.0. The four parts of sodium alkali activator and five parts of metakaoline based geopolymer were manually mixed for 10 min to ensure homogeneous preparation of geopolymer binders. For preparation of geopolymer composites, the carbon microfibers were initially pre-dried for 60 min at 70°C in an oven. Next, the carbon microfibers were added into the prepared geopolymer binder at 5 wt.% (5% CMF+G), 10 wt.% (10% CMF+G) and 15 wt.% (15% CMF+G) loading. The mixing was homogeneously done in Hobart mixer for 5 min. Subsequently, the fresh prepared composite mortar was poured into 40 mm cubic-shaped moulds, vibrated for 2 minutes on the vibration table to remove air voids and wrapped using a thin plastic sheet to prevent water evaporation. The wrapped samples were demolded after 24 h of casting and then cured at room temperature (20±2°C) and a relative humidity of (70±10%) for 28 days.

2.4 Exposure to elevated temperature

The prepared geopolymer composites were exposed to elevated temperatures of 200, 400 and 800°C at age of 28 days. The specimens were placed into a furnace (Elektrické Pece Svoboda, Czech Republic) and heated at fixed heating rate

of 5°C/min. As soon as the target temperature was attained, it was maintained for an additional 60 min. The furnace was then shut down to allow the specimens in the furnace to cool down to room temperature. Meanwhile, the unexposed specimens were left undisturbed at ambient condition.

2.5 Characterization of carbon microfiber/geopolymer composites

Physical properties: The hardness of geopolymer composites was measured on the Rockwell H scale using an Avery Rockwell hardness tester. The samples were polished with emery paper to achieve flat and smooth surfaces before the measurement. Furthermore, the values of bulk density was determined in accordance with the ASTM Standard (C-20) and calculated using the Eq. (1). The test was repeated for 5 samples and an average of measurements was taken.

$$\text{Bulk density} = \frac{W_d}{W_a - W_w} \quad (1)$$

where W_d is weight of the dried sample, W_w is weight of the sample suspended in water and W_a is weight of sample saturated in air.

Microstructure analysis: The low vacuum scanning electron microscopy (SEM) of Hitachi-model TM-3000, coupled with X-rays microanalysis system of energy dispersive spectroscopy was employed to investigate the microstructure of geopolymer composites. It was carried out at 15 kV accelerated voltage. The samples were directly observed under the SEM without metallic coating due to low vacuum operations. The images were formed by acquisition of backscattered electrons at different magnifications.

Compression strength: The geopolymer composites were tested for compression testing using LaborTech universal testing machine, Czech Republic, with load cell capacity of 2000 kN. The 40 mm cubes were tested for the determination of compression strength according to ASTM C109 standard. The test was repeated for 5 specimens and an average of measurements was taken.

3 RESULTS AND DISCUSSION

3.1 Microstructure analysis

The CMF particles of around 10 μm diameter were obtained after the ball milling of carbiso particles. The SEM micrographs of neat geopolymer and geopolymer composites at different temperature exposure are shown in Figure 1. The microstructure of dense and homogeneous matrix consisting mainly of alumino-silicate gel can be observed for all samples before exposure to the elevated temperatures. The smooth surfaces of carbon fibers in the geopolymer matrix indicated no degradation of carbon fibers under action of alkali in the activating solution. The strong adhesion between the geopolymer gel and the surface of the fiber

can be confirmed based on presence of geopolymer layer on fiber ends pulled out from the matrix and more striations on fiber surfaces. When the samples exposed to elevated temperatures, the geopolymer composites showed lower micro structural deterioration than neat geopolymers due to mechanical percolation along with pore filling effects of carbon microfibers [17]. The carbon microfibers did not exhibit any observable degradation after elevated temperature exposure. This indicated the thermal resistance characteristics of carbon microfibers that can continue to provide the reinforcement to geopolymers when exposed to higher temperatures and therefore less strength loss.

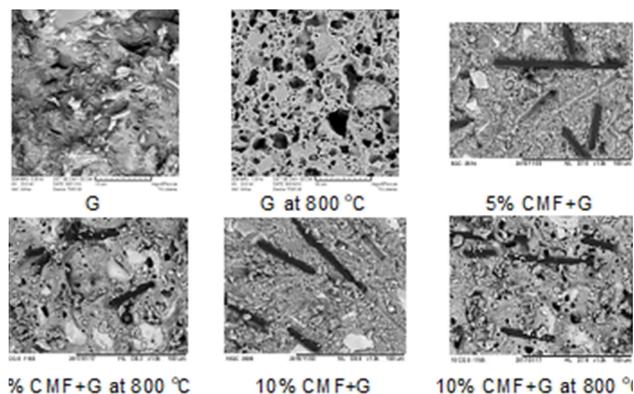


Figure 1 Microstructure of geopolymer composites

3.2 Physical properties

Table 1 illustrates the physical properties (i.e. hardness Vickers Pyramid Number HV and bulk density [g/cm³]) of the neat geopolymer and its composites before and after exposure to elevated temperature. The density was found to reduce with increase in carbon microfiber loading. The carbon microfiber filled geopolymers exhibited significant increase in viscosity due to high aspect ratio and smooth light surfaces of microfibers. This subsequently resulted into the entrapment of more air and thus possible reduction in density of geopolymer composites than neat geopolymers [18]. The higher hardness of geopolymer composites over neat geopolymers can be ascribed to the extra precipitation of Calcium Alumina Silicate hydrates formation due to nucleating sites present on carbon microfibers [19]. When exposed to elevated temperature of 200, 400 and 800°C, all the samples showed reduction in bulk density and hardness values. The neat geopolymers became more porous than geopolymer composites when exposed to elevated temperatures. This behavior can be attributed to evaporation of water and increase in Si/Al ratio as temperature increased [20, 21]. A similar phenomenon was observed previously which resulted in foam like structures by formation and growth of bubbles with increasing the Si/Al ratio [22]. The intact structure of geopolymer composites

at elevated temperatures can be attributed to the pore-filling effect of carbon microfibers.

Table 1 Physical properties of geopolymer composites

Temperature [°C]	G		5% CMF+G		10% CMF+G		15% CMF+G	
	HV	ρ [g/cm ³]	HV	ρ [g/cm ³]	HV	ρ [g/cm ³]	HV	ρ [g/cm ³]
30	536	1.51	558	1.48	569	1.49	562	1.48
200	395	1.49	489	1.44	494	1.51	482	1.48
400	290	1.42	435	1.40	482	1.36	577	1.35
800	330	1.31	367	1.27	371	1.26	379	1.22

3.3 Compression strength

Table 2 shows the compression strength [MPa] results of geopolymer and geopolymer composites before and after exposure to elevated temperatures. The geopolymer composites showed higher compression strength than neat geopolymers over all range of temperature exposures. The neat geopolymer indicated a typical brittle failure mode, whereas geopolymer composites exhibited an extended period of plastic deformation (i.e. pseudoplastic behavior) unlike short drop at the point of maximum load. This non-linear behavior of geopolymer composites can be explained from the fiber-bridging and sliding after debonding and pulling-out of carbon fibers from the geopolymer matrix. This further indicated more favorable interaction between carbon microfibers and the matrix possibly due to a combination of physical and chemical bonding. With increase in temperature till 200°C, all samples showed increase in compression strength. This behavior was attributed to the formation of discontinuous nano-pores and dehydration shrinkage of geopolymers due to expel of free water at 200°C. However, the compression strength deteriorated for all samples at 400 and 800°C. This behavior can be attributed to thermal incompatibility (i.e. differential thermal expansion between geopolymer and carbon microfibers), pore pressure effects (i.e. movement of free water and hydroxyls) and possible phase transition in geopolymers at elevated temperature. The less deterioration for geopolymer composites indicated the thermal resistance characteristics of geopolymers after the addition of carbon microfibers, which further decreased the thermal stresses and restricted the swelling of unreacted geopolymer phases.

Table 2 Compression strength [MPa] at elevated temperature

Temperature [°C]	G	5% CMF+G	10% CMF+G	15% CMF+G
30	28±3	39±4	44±4	41±4
200	37±4	44±5	49±5	45±5
400	15±3	24±3	30±3	34±4
800	11±5	20±4	21±4	24±4

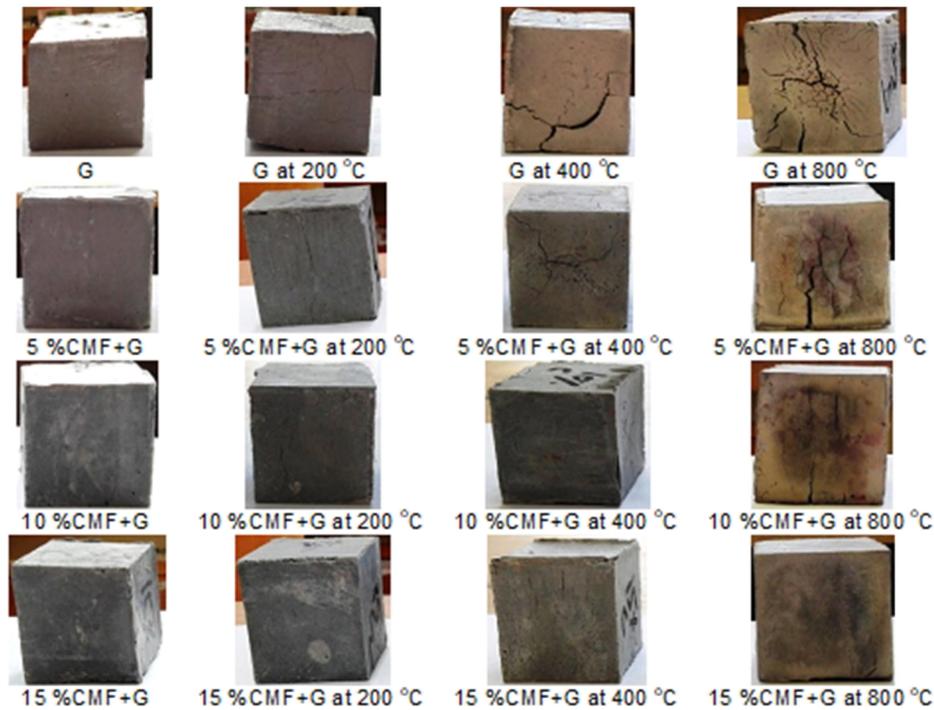


Figure 2 Physical observations of composites after exposure to elevated temperature

3.4 Physical observations

Figure 2 illustrates photographs of the physical observation of the neat geopolymers and geopolymer composites when exposed to the elevated temperatures of 200, 400, and 800°C, respectively. The neat geopolymers showed increased amount, width and length of thermal cracks than geopolymer composites. The cracks further increased with increasing the elevated temperatures. The development of cracks at higher temperature exposure can be explained from dehydration/dehydroxylation of the geopolymers and the volumetric expansion of unreacted silicon dioxide [23]. The intact original structural characteristics with minimum development of thermal cracks in case of geopolymer composites were found due to the presence of high thermal resistant thin carbon microfibers which possibly bridged the cracks when exposed to the elevated temperatures [24].

4 CONCLUSIONS

In present study, the role of carbon microfibers for improvement in elevated temperature properties of geopolymer composites was studied. The carbon microfibers were produced by 30 min dry pulverization of short carbon fibrous wastes in high energy planetary ball milling. The geopolymer composites were prepared by addition of 5, 10 and 15 wt.% of carbon microfibers and later exposed to the elevated temperatures of 200, 400, and 800°C. Further, the carbon microfiber/geopolymer composites were evaluated for physical properties, microstructural analysis and compression strength.

The addition of carbon microfibers was found to produce compact structure of geopolymers due to their pore filling characteristics and formation of additional calcium silicate or calcium aluminosilicate and sodium aluminosilicate hydrates. The presence of geopolymer layer on surface of fiber ends pulled out from matrix indicated strong adhesion between the geopolymer and the carbon microfibers. The carbon microfibers did not exhibit any observable degradation after elevated temperature exposure, which indicated their thermal resistance characteristics. Furthermore, more number of curvilinear small cracks was found in case of geopolymer composites due to crack deflections by carbon microfibers. Therefore, the addition of carbon microfibers ensured the effective toughening mechanism to prevent the catastrophic fracture of geopolymers. When samples exposed to elevated temperatures, the compression strength deteriorated for all samples at 400 and 800°C. This behavior was attributed to thermal incompatibility (i.e. differential thermal expansion between geopolymer and carbon microfibers), pore pressure effects (i.e. movement of free water and hydroxyls) and possible phase transition in geopolymers at elevated temperature. The less deterioration for geopolymer composites indicated the thermal resistance characteristics of geopolymers after the addition of carbon micro fibers, which further decreased the thermal stresses and restricted the swelling of unreacted geopolymer phases. In this way, the carbon microfibers filled geopolymers could be suitable for high temperature applications in thermal barrier coatings and panels.

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