The effect of temperature on micro-mechanical properties of fly ash based geopolymers activated with nano-SiO$_2$ solution by sol-gel technique

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This work presents a comparative study of the effect of temperature on fly ash based geopolymer properties. The geopolymers pastes were prepared using alkali silicate with nano-SiO$_2$ solution synthesized by sol-gel process and characterization of fly ash based geopolymer was carried out by X-rays diffraction, scanning electron microscopy (SEM) analysis and nanoindentation tests. Nanoindentation results show that there is no significant difference between micro-mechanical properties of fly ash based geopolymer and thermally treated geopolymers at high temperature. Therefore, this kind of geopolymers could be considered as a fire resistant material.

1. Introduction

Ordinary Portland Cement (OPC) is the main ingredient used in the production of concrete, which is the most widely used construction material in the world. In the past, concrete was simply a composite of OPC paste with aggregates. However, modern day concrete incorporates other cementitious materials which act as partial replacements of OPC. The manufacturing of OPC requires the burning of large quantities of fuel on decomposition of limestone. Both, burning of fuel and decomposition of limestone, result in significant emissions of carbon dioxide. Each ton of OPC manufactured implies production and emission to the atmosphere of nearly one ton of CO$_2$, depending on the production process adopted [4]. Industrial cement production plants are reported to emit up to 1.5 billion tons of CO$_2$ in the atmosphere annually. Hence, environmental preservation has become a driving force behind the search for new sustainable and environmentally friendly composites to replace conventional concrete produced from OPC [11]. OPC concretes generally provide adequate fire resistance for most normal applications. However, the strength of OPC concrete decreases at elevated temperatures due chemical and physical changes [6]. Further, spalling of conventional concrete occurs in fire, which causes a rapid layer by layer loss of concrete cover, potentially leading to the exposure of the main reinforcements within the concrete to fire. Therefore, efforts have been made to identify an alternative binder, which possesses good fire resistance in terms of strength loss in elevated temperature and spalling resistance [13].

Alkali-activation of aluminosilicates is a technology, often called geopolymerization, first developed by Joseph Davidovits. It involves a chemical reaction between aluminosilicate oxides and alkali metal silicates solutions under strongly alkaline conditions. This yields amorphous or semi-crystalline polymeric structures of Si-O-Al bonds. Geopolymers exhibit good physical, micro- and nano-porosity, low shrinkage, high mechanical strength, good thermal stability, durability, surface hardness, fire and chemical resistance. Given these desirable properties, they are seen as potential alternative materials for industrial applications, such as: construction, transport, aerospace, mining, and metallurgy. However, the major focus is that they can replace the use of OPC as a binder in concrete applications [2]. Most of these researchers uses metakaolin and fly ashes such as aluminosilicates source materials. Fly ash has an advantage over metakaolin in terms of lower cost [8]. Coal fly ash is generated during the combustion of pulverized coal in coal-fired power stations as such as industrial byproduct that, if not put to beneficial use, becomes a recognized environmental pollutant. It is estimated that 750 million tons of fly ash are generated on a global basis each year. Current fly ash utilization is estimated to be close to 25%. Thus, it is clear that a significant proportion of the annual production of fly ash must be disposed and the disposal of fly ash will soon be too costly [14]. The main reserve of mineral coal in Mexico is located in the state of Coahuila. Currently, 11.2 million tons of mineral coal are extracted per year for use in the iron and Steel industry, but it is mainly used to produce electricity in the two coal-fired power plants; Jose Lopez Portillo and Carbon II. The Jose Lopez Portillo coal-fired power plant burns 15000 tons of a mixture of coals daily to produce 1,200 MW/h of electricity and around 2,700 ton/day of solid residues. The main destination of this residual material is an open landfill [1]. Therefore, there is a significant amount of this residual material which could be used in manufacture of useful building materials.

Geopolymers are generally considered to perform better than conventional concretes in fire, due to their ceramic-like properties [5]. Though, research on geopolymer as a binder has been plentiful, studies of its behavior under elevated temperature condition is not so much investigated. To our knowledge, there is almost no report about micro-mechanical properties of fly ash based geopolymers at elevated temperatures using a nano-SiO$_2$ solution by sol-gel technique. In this work, fly ash based geopolymers were prepared using a nano-SiO$_2$ solution by sol-gel technique and exposed at...
temperature about 1,000 °C. The morphologies, crystalline structures and micro-mechanical properties of geopolymers were determined.

2. Experimental

2.1 Materials and preparation
The fly ash (class F) was obtained from Jose Lopez Portillo power station in Coahuila state, Mexico. Nano-SiO₂ particles in aqueous solution were supplied by OPTA® (30%, 20-30 nm average size), sodium silicate was acquired from Insumos Químicos del Centro® and sodium hydroxide was purchased in KisKam® Company. All materials and substances were used without any pre-treatment of purification. Nano-SiO₂ sol-gel solution without extra water (activating solution) was prepared by mixing nano-SiO₂ and sodium silicate previously to the sodium hydroxide incorporation, according to a previous work [7]. Geopolymeric material was synthesized mixing the sol-gel solution with fly ash by hand for 5-10 min. The reactive mixture was then placed and cured in a polystyrene mold at 25 °C ± 5 °C to develop mechanical properties.

2.2 Thermal treatment
After 60 days, geopolymeric material was subjected to temperatures of 1,000 °C at an incremental rate of 2.5 °C/min. Once the desired temperature (1,000 °C) was reached, it was maintained for 2 h before the material was allowed to cool naturally to room temperature inside the furnace.

2.3 XRD and Nanoindentation tests
X-ray diffraction was conducted using a Bruker AXS diffractometer, model D8Advance with K_Cuα₁ (1.5406 Å) with an 1.0 mm slit, 40 mA, 40 kV, scanspeed 3 s/step, increment 0.04 step/°, and a range from 1.5 to 70° (2θ).

In this study, nanoindentation tests were performed using an IBIS nanoindentation system (Fisher-Cripps Laboratories), and indents were made by a three-sided pyramidal diamond Berkovich tip with nominal radius of curvature between 100 and 200 nm. A series of 36 indents were performed on specimens with loads decreasing from 100 to 20 mN in steps of 20mN, and the distance between the indentations was 50 microns to avoid plastic deformation interaction. The Berkovich tip of the nanoindenter was calibrated against a fused silica (E = 72.5 GPa and H = 9.5 GPa) and polycarbonate (E = 3 GPa and H=0.19 GPa) standards prior to nanoindentations on polished sample specimens.

2.4 AFM and Optical Profilometry
The set point deflection to measure AFM was 2V with a sensibility of 184.4 nm/V, scan rate was 1 Hz, 256x256 image size and scan size was 20x20 micron. The measures of AFM were carried out at 22.4 °C and a relative humidity of 0.6. The images of optical profilometry were obtained by CountourGT-K systems of optical surface-profiling system.

3. Results

3.1 XRD diffractograms
Figure1 show XRD patterns of fly ash and geopolymers samples processed at ambient conditions and at high temperature. The main crystalline phases of fly ash identified were quartz, mullite and cristobalite. According to the XRD results for fly ash based geopolymer without thermal treatment (Curve b), this geopolymer was more amorphous than fly ash, which could be attributed to that the alkali-activation process can change vitreous structure and dissolve a certain amount of silica and alumina of raw material particle to form a well-compacted and cementitious composite [2]. Thus, this finding shows that this process disorganized the structure of the crystalline phases of the fly ash particles. The spectra of fly ash based geopolymer at high temperature shows that almost there were not variations between diffractograms except by a peak around 20 = 21.8°, which would be attributed to cristobalite, but it is still being investigated.
3.2 Nanoindentation

Geopolymers are generally considered to provide good fire resistance due to their ceramic-like properties according to previous studies. It was found that concrete specimens underwent 70% strength loss after elevated temperatures exposure. Mortar on the other hand did not retain any residual strength after similar temperature exposure. Conversely, the geopolymer displayed a 58.4% strength reduction after similar exposure. The strength of geopolymer paste specimens can be increased as temperature increases, attaining peak strength at 300 °C. Subsequently, this strength was observed to deteriorate gradually along the rest of the heating regime [10].

The nanoindentation technique has proven to be useful for the evaluation of mechanical properties at the nano- and micro-scale materials. The Figures 3 and 4 show the evolution of the indentation force with the penetration depth, with the results of elastic modulus and hardness (Table 1), for fly ash geopolymers at ambient and high temperature, respectively. According to these figures, there is noticeable difference on the elastic regime in both geopolymers, but it is easier to identify in fly ash based geopolymer than geopolymer at high temperature.
The estimated elastic modulus values have no significance difference. Nonetheless, geopolymer at high temperature hardness resulted better than without annealing geopolymer. Values estimated for average elastic modulus (about 23-24 GPa) and for average the hardness (0.6-1 GPa) were similar to values for hydrated Portland cement and for silicate hydrates [12], and for C-S-H synthesized with a high Ca/Si molar ratio normally produced in the cement paste [3]. The micromechanical obtained results show that both geopolymers in this study exhibited elastic modulus and hardness such as that of the hydrated Portland cement and geopolymers, but with good fire resistance. This combination results promising for development of this kind of alternative materials.

**Table 1** Statistics of elastic modulus and hardness of fly ash based geopolymer.

<table>
<thead>
<tr>
<th>Fly ash based geopolymer</th>
<th>N total</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Minimum</th>
<th>Median</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(Gpa) 20</td>
<td>23.8</td>
<td>14.4</td>
<td>5.2</td>
<td>21.2</td>
<td>53.8</td>
<td></td>
</tr>
<tr>
<td>H(Gpa) 20</td>
<td>0.64</td>
<td>0.67</td>
<td>0.067</td>
<td>0.30</td>
<td>2.23</td>
<td></td>
</tr>
<tr>
<td>Fly ash based geopolymer at temp. elevated</td>
<td>24</td>
<td>24.8</td>
<td>11.9</td>
<td>3.8</td>
<td>25.1</td>
<td>48</td>
</tr>
<tr>
<td>E(GPa) 24</td>
<td>24.8</td>
<td>11.9</td>
<td>3.8</td>
<td>25.1</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>H(GPa) 24</td>
<td>1.06</td>
<td>0.83</td>
<td>0.06</td>
<td>0.88</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

3.3 AFM and optical profilometry

The topographies of both geopolymers were characterized by 3D AFM and 3D optical profilometry images. Figure 4 shows that according to 3D AFM images, the geopolymers have not noticeable differences between their topographies, while in the Figure 5 micropores were observed with a pore size between 8-50 µm.

![Fig. 4 3D AFM images of (a) fly ash based geopolymer, and (b) geopolymer at 1,000 °C.](image-url)
Exposure of geopolymers to high temperatures leads to changes in chemical structure and the dehydration of free and chemically-bound water. As the external temperature increases, moisture within the specimen rapidly migrates towards the surface of specimen and escape. This, in turn, causes surface cracking and internal damage in the overall structure of the geopolymer. These small pores facilitate the escape of moisture during thermal treatment, causing minimal damage to the geopolymer matrix [9]. This may account for the almost no strength loss after annealing at high temperatures in this kind of geopolymer.

4. Conclusions

A new fire resistant geopolymer has been prepared using fly ash and Nano-SiO$_2$ solution by sol-gel technique, both geopolymers shown good micromechanical properties according to nanoindentation tests. XRD show almost no differences in crystallinity during annealing up to 1,000 °C of specimens. Finally, microporosity of geopolymers reduces the strength loss during high temperature exposure. Thus, fly ash based geopolymers can be considerate as a fire resistant construction material alternative to OPC concrete.

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References


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