



# FIFTH AMAZON GREEN MATERIALS

MANAUS - AMAZONAS - BRASIL

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## DEVELOPMENT OF A GREEN DUCTILE GEOPOLYMER COMPOSITE

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**Abstract.** *Green alternatives to conventional cement materials have been intensively explored in the past few decades. Fly ash-based geopolymer is a promising candidate that does not use energy/carbon intensive cement but utilizes fly ash, an industrial byproduct from coal-fired power plants. While geopolymer concrete has good strength and chemical stability besides the excellent material greenness, those performances can be severely deteriorated by large cracks that often occur in large-scale field applications. As in conventional cement concrete, the durability, another important factor for sustainability, is restricted by low tensile ductility due to the inherent brittleness of geopolymer. In this study, ductile fiber reinforced geopolymer composites were developed by using randomly oriented short Poly-Vinyl Alcohol (PVA) fibers. The material greenness was first evaluated based on Material Sustainability Index (MSI) in comparison with normal cement concrete. The mechanical properties were then investigated by cube compressive and dogbone tensile testing. It was demonstrated that the developed composites had very high tensile ductility of over 4 %, which is several hundred times that of normal concrete. Crack width distributions were also investigated by using the Digital Image Correlation technique. Tightly controlled multiple cracks were observed even under high imposed strain conditions.*

**Keywords:** *Geopolymer, Fly ash, Fiber reinforced composite, Material greenness, Durability*



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## 1. INTRODUCTION

Geopolymer is a green alternative to conventional cement materials and has been intensively studied in the past few decades. Geopolymer paste is basically formed from solid aluminosilicate sources activated by alkaline solution and has a similar hardening property to cement binders. Among various types of geopolymer materials, fly ash-based geopolymer is a promising candidate that does not use energy/carbon intensive cement but utilizes fly ash, an industrial byproduct from coal-fired power plants. In addition to the great environmental benefit of geopolymer, good strength and chemical stability have been experimentally demonstrated (Provis and van Deventer, 2007). It is, however, anticipated that those performances can be severely deteriorated by large cracks that often occur in large-scale structural applications. As in conventional cement concrete, the durability, another important factor for sustainability, is restricted by low tensile ductility due to the inherent brittleness of geopolymer. Therefore, its brittleness should be suppressed to achieve not only green but also durable geopolymer materials.

In parallel with the intensive studies on geopolymer, significant efforts have been made over the last decades for the development of strain hardening cementitious composites (SHCC). Engineered Cementitious Composite (ECC) is an ultra-ductile SHCC reinforced by randomly oriented short fibers with moderate fiber volume fraction (less than 2%). ECC, also known as bendable concrete, has very high tensile strain capacity of 3-6% which is several hundred times that of plain concrete. Further, multiple cracks occurring in the strain-hardening stage are tightly controlled (typically below 60  $\mu\text{m}$  in average), leading to improved durability due to lower permeability of water and chloride ions and better self-healing property. The design of ECC is largely based on the micromechanical modeling methodology developed by Li and fellow researchers (Li et al., 1991). It is highly possible that fiber reinforcing based on the micromechanical modeling is also effective to suppress the brittleness of geopolymer.

The present paper reports the development of a ductile fiber reinforced geopolymer composite. The material greenness is first evaluated based on Material Sustainability Index (MSI) in comparison with normal cement concrete and ECC. Subsequently, experimental studies are conducted to demonstrate the very high tensile ductility and tightly controlled crack width. The mechanical properties are investigated by cube compressive and dogbone tensile testing. Crack width distributions are analyzed by using the Digital Image Correlation technique.

## 2. MATERIAL GREENNESS EVALUATION

### 2.1. Materials and mix proportions

The fly ash-based geopolymer composite developed in this study comprises fly ash, fine silica sand, sodium silicate, sodium hydroxide, water and Poly-Vinyl Alcohol (PVA) fiber. The mix proportion of the ingredients is listed in Table 1. Two types of fly ash, labeled Fly ash A and B, respectively, were blended in the mixture to control the hardening property and rheology. Both are classified as class F fly ash as designated in ASTM C618. Table 2 shows the chemical analysis result reported by each manufacture. Since slight variation was found in the reported data depending on the report date, the averaged values are shown in Table 2. The alkaline activator is the mixture of sodium silicate solution (8.9 wt%  $\text{Na}_2\text{O}$ , 28.7 wt%  $\text{SiO}_2$ ,

and 62.5 wt% H<sub>2</sub>O) and sodium hydroxide in pellet forms dissolved with tap water (labeled Pre-mix water in Table 1). Mix water listed in Table 1 is added to control the rheology of fresh geopolymer when the fly ashes, sand and alkaline solution are mixed. As in ECC, US Silica F110 sand and Kuraray REC15 PVA fibers with 1.2% oil-coating by weight and length of 12 mm are employed. The material greenness evaluation was conducted based on the ingredients and mix proportion.

Table 1. Mix proportion of fiber reinforced geopolymer (in terms of weight)

Fly ash A	Fly ash B	Sand	Na <sub>2</sub> SiO <sub>3</sub>	NaOH (pellet)	Pre-mix water	Mix water	Fiber (V <sub>f</sub> =2%)
0.8	0.2	0.3	0.256	0.056	0.039	0.12	0.0235

Table 2. Chemical analysis on major constituents of fly ash (wt%)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	SO <sub>3</sub>	LOI
Fly ash A	46.57	22.99	18.36	3.73	0.39	2.93
Fly ash B	43.74	23.73	8.19	13.63	1.39	0.91

## 2.2. Material sustainability index

Environmental performances of the geopolymer composite, normal cement concrete (with 35 MPa compressive strength) and ECC were evaluated in terms of the Material Sustainability Index (MSI) (Li et al., 2004). MSI of a product is derived from cradle-to-gate life cycle inventory data of ingredients. Although MSI is a partial life cycle assessment depending only on component materials, it is a good preliminary indicator for determining the overall sustainability of the composite design. In this study, the primary energy and the CO<sub>2</sub> emission associated with unit volume of a material were measured. It should be noted that energy and emissions associated with fly ash were assumed to be zero because fly ash is a byproduct most of which are disposed of in landfills. Energy and emissions associated with water were also assumed to be zero since they are negligible compared to other materials. MSI of the materials were calculated based on data from PasticsEurope and literatures (Frazão and Fernandes, 2004, Marceau et al., 2007, Kendall, 2007 and Ranade, 2014).

Figure 1 illustrates the primary energy and CO<sub>2</sub> emissions of normal concrete, ECC M45 (a typical version of ECC materials) and the fly ash-based geopolymer composite (labeled FAGP). Although the primary energy of FAGP is slightly lower than that of ECC M45, it is more than twice that of normal concrete mainly due to the use of polymer fiber. As in ECC M45, the PVA fiber accounts for more than 50% of the total primary energy of FAGP since its primary energy includes not only process energy (energy consumed for manufacturing) but also feedstock energy (embodied energy of petroleum-based synthetic fibers). It has been, however, indicated in a previous study (Keoleian, et al., 2005) that an ECC bridge deck system causes 40% less life cycle energy consumption due to the improved durability than a conventional concrete-based system. Therefore, it is possible that the geopolymer composite also has advantages in energy consumption when assessed for actual infrastructure applications over the life cycle. In terms of the CO<sub>2</sub> emission, FAGP performs better than ECC M45 and even normal concrete. This is mainly because FAGP does not use carbon intensive cement but utilizes fly ash. It can be, thus, concluded that the geopolymer composite

is highly promising as a green alternative to cement materials in terms of energy consumption and carbon emission.

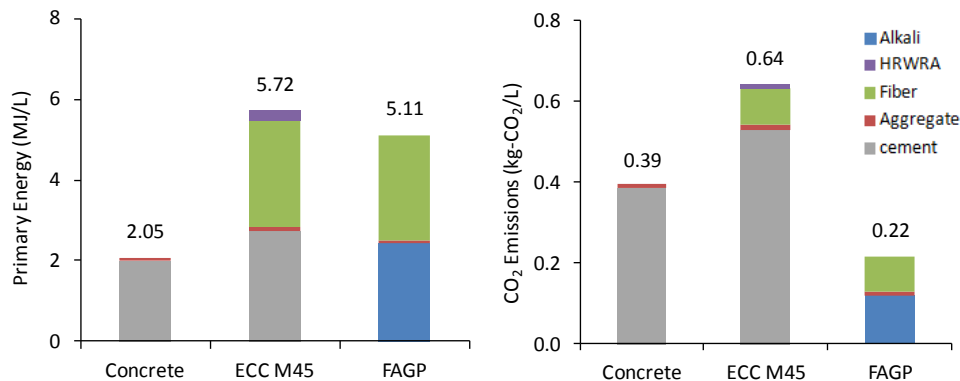


Figure 1- Geopolymer composite (FAGP) shows good material greenness.

### 3. EXPERIMENTAL INVESTIGATION

#### 3.1. Specimen preparation

Solid materials (Fly ash A and B and sand) were first mixed in a 3 L Hobart mixer. The alkaline solution and Mix water were then added and mixed until the desired fresh state was achieved. PVA fibers were then slowly added. After the fibers were properly distributed, the mixture was cast into molds on a vibration table. All specimens were demolded 24 hours after casting and then put in an oven at 60 °C for 8 hours, followed by room-temperature curing ( $23 \pm 3$  °C) in air until the age of 28 days prior to mechanical testing. 50-mm cube specimens and dogbone-shaped specimens with 33-cm long, 6-cm wide and 1.27-cm thick were prepared for compressive and tensile testing, respectively.

#### 3.2. Mechanical testing

Three cube specimens were subjected to uniaxial compression testing in accordance with ASTM C109 to measure the peak compressive load. Dogbone tensile testing was conducted on four dogbone specimens following the testing method recommended by Japan Society of Civil Engineers (JSCE, 2008). Specimens were subjected to uniaxial tension loading under displacement control at the rate of 0.5 mm/min. Two LVDTs were attached on each specimen to measure extensions within the gage length of about 100 mm. Tensile strain was computed from the average of extensions divided by the gage length. The actual specimen geometry used in this study can be found in the literature (Ranade et al., 2011).

#### 3.3 Crack pattern analysis

Crack width distributions were investigated by using Digital Image Correlation (DIC) technique. DIC is an optical non-contact measurement method to compute surface displacement/strain within an area of interest (AOI) of an object. In digital images, each pixel contains its grey scale data ranging from 0 to 255. A small region (called subset) consisting of a set of pixels then has its grey scale distribution. By matching the distributions, the movement of each subset is tracked between a reference image (undeformed state) and images

of deformed states. The displacement/strain field is computed from the movement of subsets using various correlation/interpolation functions for higher accuracy. The detailed theory is available in the literature (Sutton et al., 2009).

Additional dogbone specimens were prepared for the DIC analysis following the same preparation method above. Random speckle patterns were then created on the specimen surface by white and black spray painting so that each subset has a unique grey scale distribution. Digital images were taken at a five-second interval during tensile testing. 2-D image correlation analysis was conducted by using a commercial software (Vic2D) to measure in-plane deformation/strain fields. Crack widths were then computed from the obtained strain distribution. To avoid computational errors, very small cracks whose widths are less than 20  $\mu\text{m}$  were not taken into account for the number of cracks, average crack width and its standard deviation. The actual test set up and theory for crack width computation has been documented in Ohno and Li (2014).

## 4. RESULTS AND DISCUSSION

### 4.1. Compressive and tensile properties

The average compressive strength of three cube specimens and the average tensile strength and strain capacity of five dogbone specimens (including one analyzed by DIC) are summarized in Table 3. While the compressive and tensile strength are moderate, the tensile strain capacity is very high. Figure 2 shows stress–strain curves obtained from dogbone testing (the specimen analyzed by DIC is shown in red). It can be seen that all specimens exhibit the strain-hardening behavior. Compared with ECC materials, the developed geopolymer composites have lower strength, but comparable or better tensile ductility. Therefore, the intended strain-hardening characteristic and very high tensile ductility have been achieved.

Table 3. Mechanical properties of geopolymer composites at the age of 28 days.

Compressive strength (MPa)	Tensile strength (MPa)	Tensile strain capacity (%)
$27.6 \pm 1.7$	$3.4 \pm 0.6$	$4.4 \pm 0.4$

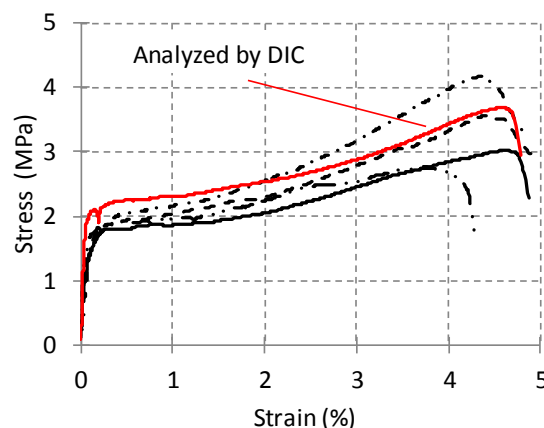


Figure 2- All samples show strain-hardening behavior with very high tensile ductility.

## 4.2. Crack pattern analysis by DIC

Table 4 lists the number of cracks, maximum crack width and average crack width at various strain levels. The number of cracks, average crack width and its standard deviation are those for cracks with larger than 20  $\mu\text{m}$  width. According to the analysis result, the maximum crack width is 117  $\mu\text{m}$  even at a high imposed strain of 4.5% (tensile ductility of this specimen was 4.6%). The average crack width is maintained at almost the same level of about 45  $\mu\text{m}$  from 1.0 to 4.5 % strain.

Figure 3 illustrates the strain maps for 1.0 and 4.0% strain obtained from the DIC analysis. It can be found that lots of fine cracks occur and are saturated over the intended area. It should be also noted that cracks are not localized even at a high imposed strain of 4.0%. Therefore, the ability to control crack width has been demonstrated.

Table 4. Crack width distributions computed from DIC analysis.

Strain level (%)	Number of cracks	Maximum crack width ( $\mu\text{m}$ )	Average crack width ( $\mu\text{m}$ )
1.0	12	79	$47 \pm 17$
2.0	27	83	$43 \pm 17$
3.0	36	92	$47 \pm 19$
4.0	43	100	$45 \pm 22$
4.5	45	117	$45 \pm 23$

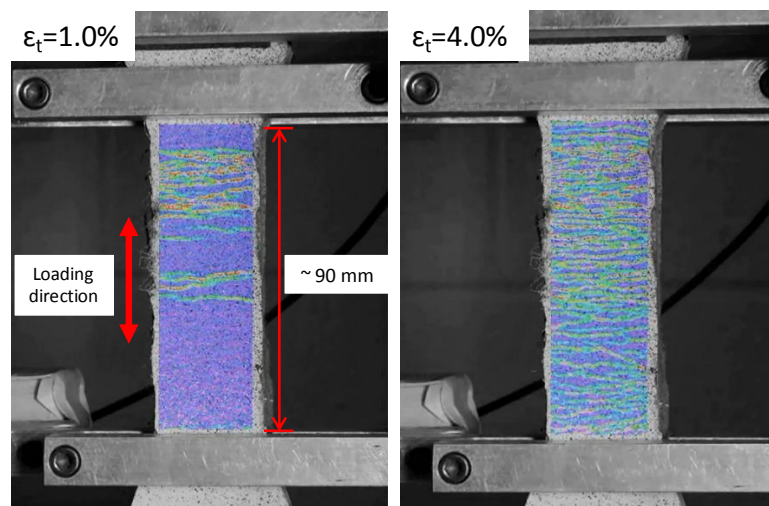


Figure 3- Fine multiple cracks are saturated without localization.

## 5. CONCLUSION

A ductile fiber reinforced fly ash-based geopolymer composite was developed in this study. The material greenness evaluation based on MSI indicated that the environmental performance of the geopolymer composite would be better than ECC and normal cement concrete. Experimental investigation showed that the developed composite exhibited strain-hardening behavior with very high tensile ductility over 4%. DIC analysis visualized the multiple cracking patterns and the computed maximum and average crack widths were 117





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and 45  $\mu\text{m}$ , respectively, at a high imposed strain of 4.5%. Although the developed composite has moderate strength, the intended very high ductility and self-controlled tight cracks have been established.

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