

Mechanical Properties of Silica-Based Geopolymer Composites Cured at Ambient Conditions in Accordance with Size-Independent Method

D.H. Tran^{1*}, P. Louda¹, D. Kroisová¹, O. Bortnovsky² and P. Bezucha².

1) Department of Material Science, Faculty of Mechanical Engineering, Technical University of Liberec, Studentská 2, 461 17 Liberec 1, Czech Republic

2) Research Institute of Inorganic Chemistry, Inc., Revoluční 84, 400 01 Ústí nad Labem, Czech Republic

*Corresponding Author: hung.tulcz@yahoo.com

Abstract

In this paper, silica-based geopolymer matrix reinforced composites containing approximately 35, 50 or 55 wt.% of carbon (HTS 5631 1600tex 24K, TohoTenax), advanced basalt (BCF13-2520tex KV12 Int, Basaltex) or electrical grade glass (E-glass: E2400P192, Saint-Gobain, Vetrotex) roving fibers respectively were synthesized and fabricated at ambient conditions. The flexural properties of the resulting composites which are high toughness: the shear stress plays here a greater role in compared with other ceramic matrix composites were determined on a universal testing machine under three-point bending mode in accordance with novel size-independent method which based on testing specimens at different scale of sample height (H) to span length (L) ratios; The basic principles of the new size-independent approach are presented as well. Microstructures of composites were analyzed by means of scanning electron microscope (SEM) on perpendicular sections, the images show the adhesion between the fibers and geopolymer matrix are very good, and micro-cracks on both cross-sections and surfaces of geocomposites are determined as inborn defects of inorganic matrix composites.

Keywords: ambient conditions, mechanical properties, silica-based geopolymer, unidirectional fiber, geocomposite.

1. Introduction

Geopolymers are considered as a new material for coatings and adhesives, a new binder for fiber composites, and a new cement for concrete [1]. The term geopolymer has been first coined since 1979 by a French professor Joseph Davidovits, they are inorganic polymeric materials with a chemical composition similar to zeolites but containing an amorphous structure and possessing ceramic-like in their structures and properties. The amorphous to semi-crystalline three dimensional of silicate network consists of SiO_4 and AlO_4 tetrahedra which are linked alternately by sharing all the oxygens to create polymeric Si-O-Al bonds [2, 3].

Fiber-reinforced composites based on geopolymer matrix have been well-known for over 20 years, since the first Davidovits' patent was filed [4]. These materials can be fabricated and cured at room temperature or thermoset in a simple autoclave, after approximately several hours of curing, these new materials exhibit excellent features such as lightweight and high strength but also with ideal fire resistant (can sustain temperatures up to 1200°C with long term exposure), non toxic fumes and smokes, and resisting all organic solvents (only affected by strong hydrochloric acid) [1, 5-8]. These special properties permit us to use more efficiently geopolymer matrix composites in high-tech technologies such as aerospace, naval architecture, ground transportation or automotive industry, especially for various applications that require high temperature resistance [1, 5, 7, 9]. Conservative geopolymers can replace efficiently lightweight, high strength composites which are made from carbon or glass fibers and organic matrices or ceramic matrices (high costs associated with special

processing requirements and most organic matrix composites cannot be used in applications that require more than 200°C temperature exposure) [10, 11]. Moreover composites based on geopolymeric matrices are handled easily and do not require high heating, they are fabricated almost at room temperature or thermoset in a simple autoclave (usually under 150°C) for several hours. In addition, most of types of fibers can be used with the geopolymer matrices and special ones can protect carbon from oxidation [7, 9]. Due to the outstanding advantages of geopolymers more and more public and private research institutes and companies are investigating and finding applications in all fields of industry, such as civil engineering, plastics industries, waste management, automotive and aerospace industries, non ferrous foundries and metallurgy, etc [1, 7, 9, 10].

In this paper, thermal silica-based geopolymer with nanosized amorphous as a main component is better than conventional geopolymer resin based on metakolin and similar materials which contains rather large particles and marked with high viscosity, hardly used effectively for fiber impregnation or very high pressure must be applied to penetrate the resin into the spaces between single filament fibers [12] were reinforced by approximately 35, 50 and 55 wt.% of carbon (HTS 5631 1600tex 24K, TohoTenax), advanced basalt (BCF13-2520tex KV12 Int, Basaltex) and electrical grade glass (E-glass: E2400P192, Saint-Gobain, Vetrotex) roving fibers respectively. The composites were synthesized and curing at ambient condition up to 30 days to get totally cured geopolymerization process [13].

The resulted composites possess different and better properties than traditional composites, use of standards organic-matrix or ceramic matrix fiber composites

are inefficient, therefore geopolymer composite materials require a more exact description of their mechanical properties [14]. By means of testing specimens with three scale of height H to span length L ratios, the mechanical properties of composites of high silica-based geopolymer resin reinforced by carbon, advanced basalt and electrical grade glass (E-glass) roving fiber were studied. Microstructure of resulted composites were analyzed by means of scanning electron microscope (SEM) to determine the adhesion between the fiber and geopolymer matrix and micro-cracks as inborn defects of inorganic matrix composites as well.

2. Materials and Methods

2.1 Materials

Geopolymer resins were prepared according to the simplified procedure described in the patent [15]. The geopolymer formulation included thermal silica, metakaolinitic components, potassium hydroxide solution, and other minor admixtures for improving application properties was abbreviated as Q17.

Table 1. Tensile properties of used fibres

Filament (roving)	carbon C24	basalt ARG	E- glass
Filament average diameter [μm]	6,92	13,3	24,7
Tensile failure strain [%]	0,80	2,70	1,70
Tensile strength [MPa]	5584	1520	1395
Young's module [GPa]	546	75	56

The reinforcements used in the composites discussed in this paper are continuous fibres (rovings) that came from the three groups: carbon (HTS 5631 1600 tex, TohoTenax), basalt (BCF13-2520tex KV12 Int, Basaltex)

and E-glass (E2400P192, Saint-Gobain, Vetrotex). The mechanical properties of single filament was tested on Universal Tensile Testing machine LaborTech 2.050 (maximum load of sensor: 5 N) at ambient conditions in accordance with Japanese Industrial Standard (JIS R 7601), Table 1 contains information of the properties [16].

2.2 Preparation of composite specimens

Continuous fibres (rovings) were impregnated ("wet-out") with geopolymeric resin by means of home-made "impregnation machine" (Error! Reference source not found.), this equipment was designed based on simulating the real pultrusion or filament winding technique. The velocity of the fiber during impregnation process was chosen based on the best penetration of geopolymer resin into the fibers, this value was around 34 m/h.



Fig. 1 Home-made impregnation machine

Impregnated cut-up rovings (pre-preg) were put manually into rubber silicon moulds $3 \times 10 \times 150$ mm layer by layer. Series of eight samples were prepared in a batch. 16 bunches of pre-preg carbon fiber or 18 bunches of impregnated basalt fiber or 20 bunches of geopolymeric saturated E-glass fiber were used for each specimen.

The samples were cured by means of 'vacuum bagging' in first stage at room

temperature for 1 hour, and then continued curing at the ambient conditions (temperature about $22\pm 2^\circ\text{C}$ and relative humidity 65%) for over 30 days and cut up to suit the planned spans.

During the preparing and curing processes the samples were weighted to calculate the percentage of fibers in impregnated, uncured and cured composites (by weight).

2.3 Mechanical testing set up

Series of eight samples were prepared and tested for each kind of composites under laboratory conditions by three-point bending mode on Universal Testing Machine, Instron Model 4202 (maximum load: 10 000 N) with a mid-span deflection rate of 2mm/min. at 3 different span to height ratios with supporting spans $L = 50$ mm (3 samples), 64 mm (3 samples) and 120 mm (2 samples), which are equivalent to the ratios (L/H) of around 17, 21 and 40 respectively.

2.4 Microstructure of the geocomposites

The sections perpendicular to fibers and surfaces of the composites were inspected in scanning electron microscope (SEM) to estimate not only the adhesion between geopolymer matrices and fiber reinforcements but also the microstructure of the composites. The failure patterns in samples and stress vs strain curves were investigated to study about behavior of the composites at bending conditions.

3. Results and discussion

From linear regression of a fictitious Youngs modulus E^* and a fictitious flexural strength σ_m^* against $(H/L)^2$ (reciprocal span: height ration) value, Youngs modulus (E), shear modulus (G), and flexural strength (σ_m) were estimated.

A fictitious Youngs modulus E^* , calculated for each height / span ratio according to the equation (1), which is valid for isotropic materials

$$E^* = \frac{L^3}{4.B.H^3} \times \frac{\Delta F}{\Delta s} \quad (1)$$

Where:

L is the span, in millimetres (mm);

H is the thickness of the specimen (mm);

B is the width of the specimen (mm);

E_f is the flexural modulus of elasticity, expressed in megapascals (MPa);

$\Delta F/\Delta s$ is evaluated as ratios $s/L = 1/200$ and $s/L = 1/500$.

The effective values E^* are evaluated on the base of Equation (1), but they are now plotted as $1/E^*$ vs. $(H/L)^2$. The values of the virtual modulus E are best obtained by linear regression, where

$$E \cong 1/(1/E^*)_{(H/L)^2 \rightarrow 0} \quad (2)$$

The material shear modulus G was calculated by the equation (3):

$$G = \alpha \frac{d(1/E^*)}{d(H/L)^2} \quad (3)$$

where α is a correction factor, theoretically equaling 1.178, the the variable in the denominator is the slope in this regression.

Quite similarly, a fictitious flexural strength σ_m^* , calculated by equation (4), which is valid for isotropic materials:

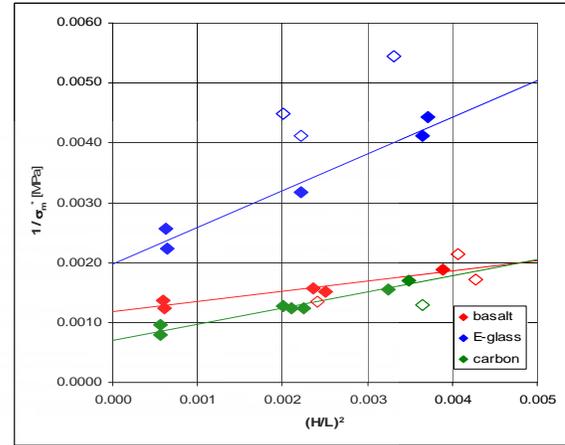
$$\sigma_m^* = \frac{3 F_m \times L}{2 B \times H^2} \quad (4)$$

where F_m is the maximum bending load, is a dimension dependent quantity. It appeared that the linearity of $(1/\sigma_m^*)$ is reasonable with quite the same independent variable $(H/L)^2$ as above. The true material property σ_m (here for simplification still called flexural strength) is thus even here obtainable as the reciprocal intercept of the regression.

$$\sigma_m \cong 1 / \left(1 / \sigma_m^* \right)_{(H/L)^2 \rightarrow 0} \quad (5)$$

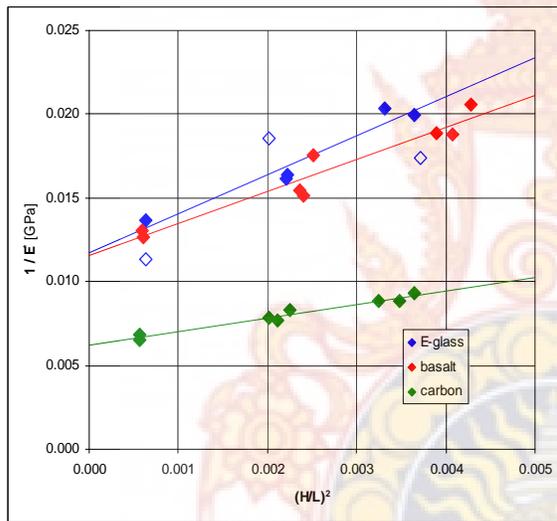
The results of mechanical properties are represented in Figs.2 Table II.

From the figure 2 we see that the effective values of flexural modulus (E^*) and flexural strength (σ_m^*) of geopolymer composites reinforced by unidirectional E-glass, basalt or carbon fiber are remarkably size dependent. This is caused by higher toughness of geocomposites and they all exhibit substantially the same positive trend in both reciprocal effective quantities E^* and σ_m^* vs. $(H/L)^2$.



b)

Fig. 2 Reciprocal effective flexural properties vs. $(H/L)^2$ ratio a) elasticity modulus, b) flexural strength



a)

It is obviously that the E/G ratios of geocomposites are much high than that of isotropic materials, E/G of geocomposites reinforced by E-glass fiber is about 169, basalt is 140 and carbon fiber is approximately 110, meanwhile E/G of isotropic material usually less than 3. Mechanical properties are as much effected by sample sizes when the ratio E/G is greater. So, the geocomposite that created by combining geopolymer matrix with carbon fiber is less anisotropic than the other ones.

Table 2. Averaged parameters of composites cured at ambient condition after 30 days

fibre	Density ρ	Young's module			shear module		flexural strength		
		average	E av.dev.	av.var.coef	G	E/G	average	σ_m av.dev.	av.var.coef
	g/cm^3		GPa		GPa		MPa		
E-glass	2.32	85.5	6.4	7.5%	0.5	169.0	507	45.2	8.9%
basalt	2.15	86.5	4.6	5.3%	0.6	140.9	850	49.2	5.8%
carbon	1.83	160.9	4.3	2.7%	1.5	110.7	1412	112.7	8.0%

av.dev. is average of standard mean deviation; *av.var.coef.* is average of variation coefficient

Although the strength of basalt fiber is nearly the same as the strength of E-glass fiber and 4 times smaller that that of

carbon fiber (table I), when combining with silica-based geopolymer matrix, its flexural strength (850 MPa) is double the flexural

strength of geocomposite – E-glass (507 MPa) and just twice smaller that geocomposite – carbon (1412 MPa).

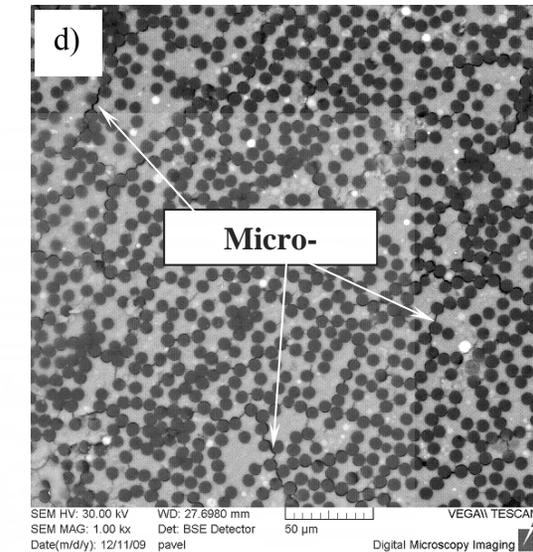
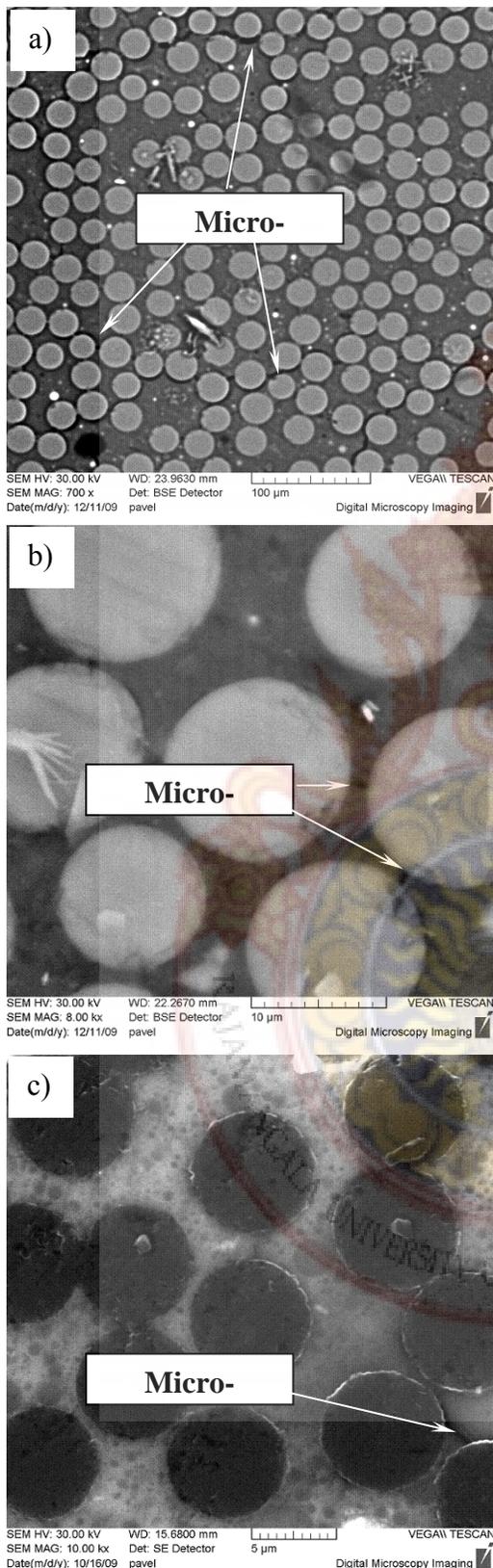


Fig. 3 SEM images of cross-sections of geopolymer composite matrix Q17 with a) E-glass (700x), b) basalt (8.000x), c) carbon (10.000x) and d) carbon (1000x)

To study the microstructure of geopolymer matrix composites, the SEM images were investigated (Fig. 3 and 4). From the pictures of perpendicular sections we can see that the adhesion between this geopolymer matrix and E glass, basalt or carbon fiber seems quite good (Fig. 3a, 3b and 3c). With higher magnification 1880x (Fig. 3d) and from the surface images (Fig. 4a, 4b and 4c), however, the micro-cracks are determined as the typical micro-defects of geocomposite systems. Geopolymer matrices are considered like a kind of inorganic matrices, so the existing of micro-cracks can be considered as inborn defects of inorganic matrix composites [1].

In other series of our investigations, to accelerate geopolymerization, elevated temperature was applied for curing and we found that the optimal range of curing temperature of this kind of geopolymer resin and the E glass, basalt or carbon fiber are quite large, from about 60 to 100 °C. Fig. 4d shows the microstructure on the surface of geocomposite M17/carbon cured 5 hours and dried 5 hours more at 80 °C.

With the same magnification (1880x), the micro-cracks in this composite is bigger than that of in the same kind of geocomposite reinforced by fiber carbon. This conclusion is demonstrated when the flexural strength and bending modulus of Q17/carbon cured at 80 °C are 666 MPa (47%) and 176.4 GPa (109%) respectively, when compared that of the values which cured at ambient temperature are 1412 MPa and 160.9 GPa.

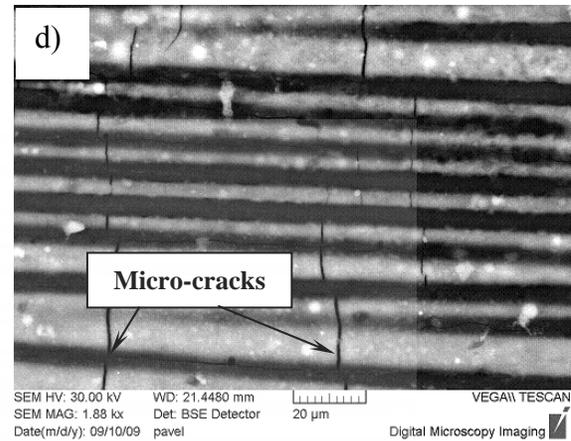
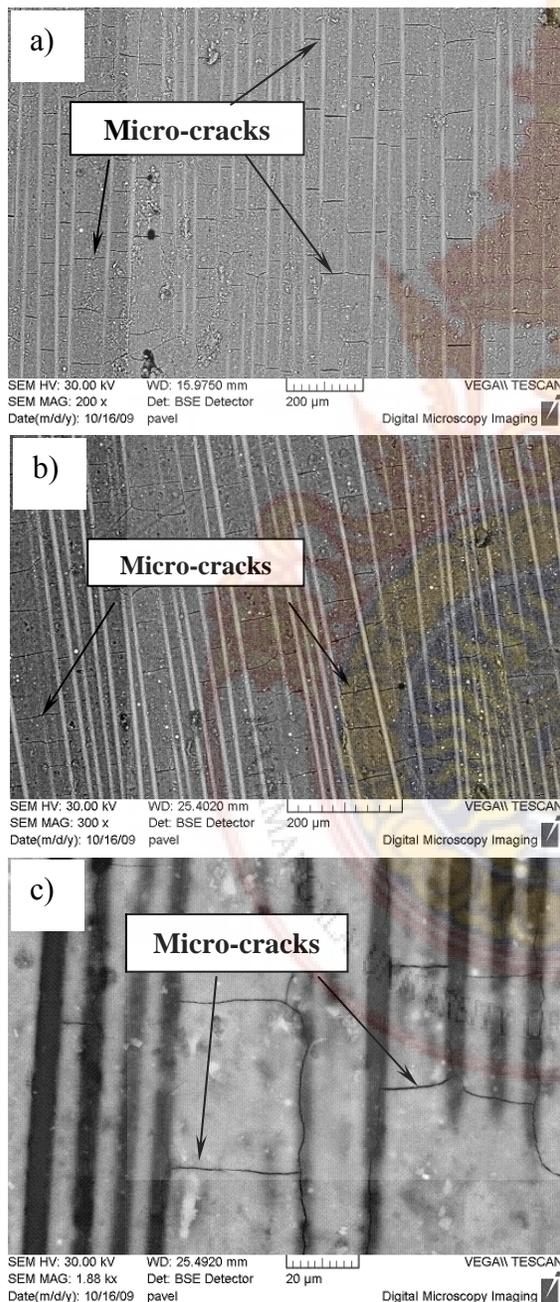


Fig. 4 SEM surface images of geocomposite matrix Q17 and a) E-glass, b) basalt, c) carbon (1880x) and d) typical microcrack of Q17/C composite cured at 80 °C for 5 hours (1880x)

4. Conclusions

After 30 days at ambient condition (temperature about 22±2 °C and relative humidity 65%), silica-based geopolymer matrix reinforced by the carbon 5631 1600tex 24K, basalt BCF13 - 2520tex - KV12 Int or E glass E2400P192, Saint-Gobain - Vetrotex fiber were completed the geopolymerization process. The effective flexural properties of the composites (E^* and σ_m^*) are dependent on size samples. By means of testing specimens within a wide scale of height H to length L ratio, it is possible, however, to obtain extrapolated flexural elastic modulus E and shear modulus G and flexural strength (Table 2) that can be considered as size independent material characteristics.

The adhesion between the fibers and geopolymer matrix seem excellent. Moreover, geocomposites based on silica cured at ambient conditions show better properties than the same kinds cured at elevated temperature 80 °C which are just about 50 % for flexural strength when compared the bending properties of Q17/carbon composites and the micro-cracks are also smaller. The micro-cracks in

geopolymer composites are considered as inborn defects of inorganic matrix composites.

Adding plasticizers to geopolymer matrix should be investigated for reducing the micro-cracks and improving the ductile of the composites and finally is to find out potential applications in industries.

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