

THERMAL-MECHANICAL BEHAVIOR OF SILICA-BASED GEOPOLYMER – CARBON COMPOSITE

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Abstract

Thermal silica-based geopolymer composites reinforced by approximately 35 weight or 53 volume percentage of unidirectional carbon fiber HTS 5631 1600tex 24K were synthesized and fabricated at optimal range of curing conditions, and the effects of calcination in a furnace at high temperatures up to 1000 °C for 1 hour on the thermal-mechanical properties were studied. The flexural properties of the resulting composites were determined on a universal testing machine under three-point bending mode in accordance with ASTM C 1341 – 06 and the results show that the flexural strength of geocomposites after calcination at 1000 °C still remained nearly 50 % compared with that of at 20 °C. The microstructure of composites were analyzed by means of Scanning Electron Microscope (SEM), after calcination at temperature higher than 800 °C the microstructure of geocomposite looks like foamed composites and the adhesion between the fiber and matrix still show very well. Energy Dispersive X-ray Analysis (EDX) was used to determine the initial reaction layer on the fiber will be presented as well.

Key words: thermal-mechanical, silica-based geopolymer, unidirectional fiber, geocomposite

1. Introduction

The remarkable achievements in inorganic chemistry made through geopolymerization include mineral polymers which termed as polysialate or geopolymers make us possible to fabricate composite materials not only with excellent mechanical properties such as lightweight and high strength but also with ideal fire resistant (they can sustain temperatures up to over 1000 °C with long term exposure), non toxic fumes and smokes, and resisting all organic solvents (only affected by strong hydrochloric acid) [1-6]. 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, 2, 5, 7,]. Conservative geopolymer materials 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) [1, 8, 9]. 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. Last but never least, most of types of fibers can be used with the geopolymer matrices and special ones can protect carbon from oxidation [5, 7]. 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, 5, 7, 8].

In Czech Republic, we have a project named *Advanced reinforcement geopolymer composites for technological use* (projekt ev. č. FT-TA4/068) which are conducted by Research Institute of Inorganic Chemistry, Inc., Ústí nad Labem; Department of Material Science, Faculty of Mechanical Engineering, Technical University of Liberec; Czech Mineral Company (České Lupkové Závody a.s. – ČLUZ) and Institute of Physical Chemistry, Prague (ÚFCH JH AV

ČR). Through the project, various new kinds of geopolymers were generated from different sources of raw materials. Chemical, physical structures, mechanical properties and thermal properties (fire resistant and heat insulation) were determined and compared. Additives and curing condition for the best properties of geocomposites reinforced by commercial fibers were recommended in order to apply into industries.

In this paper, thermal silica-based geopolymer with nanosized amorphous as a main component is better than conventional geopolymer resins 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 [10, 11] were reinforced by approximately 35 wt.% of carbon (HTS 5631 1600tex 24K, TohoTenax) roving fiber. The composites were synthesized and cured at optimal curing conditions and used for this investigation.

2. Materials and Methods

2.1 Materials

Geopolymer resin was prepared according to the simplified procedure described in the patent [12]. The geopolymer formulation included thermal silica, metakaolinitic components, potassium water glass solution, and other minor admixtures for improving application properties was abbreviated as M1.

The reinforcement used in the composites discussed in this paper is continuous fiber (roving) that came from carbon HTS 5631 1600 tex, TohoTenax. 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 [14].

Table 1. Tensile properties of used fibre

Kind of fiber	Average diameter [μm]	20°C			200°C			400°C			700°C		
		A [%]	R _m [MPa]	E [GPa]	A [%]	R _m [MPa]	E [GPa]	A [%]	R _m [MPa]	E [GPa]	A [%]	R _m [MPa]	E [GPa]
Carbon HTS 5631 1600tex 24K	7	1.84	3120	170	1.33	2340	176	1.66	2861	172	Fibers were destroyed totally (nearly disappeared)		

2.2 Preparation of composite specimens

Continuous fibers were impregnated (“wet-out”) with geopolymeric resin by means of home-made “impregnation machine” (**Chyba! Nenalezen zdroj odkazů.**), 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.

Impregnated cut-up rovings (pre-preg) were put manually into rubber silicon moulds 3×10×150 mm layer by layer. 16 bunches of pre-preg carbon 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 continuously to be cured in oven at 75 °C for 1 hour. The samples were then

post-cured by drying at 75 °C for 5 hours more. One cured specimen was cut into 2 samples with dimension approximately 3x10x75 mm.



Figure 1. Home-made impregnation machine

Series of five samples were prepared in a batch and exposed to 200 °C, 400 °C, 600 °C, 800 °C and 1000 °C in oxidizing environment for 1 hour (Fig. 2).



Figure 2. Furnace for sample calcination

2.3 Mechanical testing setup

Series of five samples were prepared and tested for flexural properties before and after the calcination 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 span 64 mm (outer support span-to-depth Ratio is about 20).

2.4 Microstructure of the geocomposites

The sections perpendicular to fibers of the composites were inspected on scanning electron microscope (SEM) to estimate not only the adhesion between geopolymer matrices and fiber reinforcement 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

The σ_{fm} was computed using equation:

$$\sigma_{fm} = \frac{3FL}{2bh^2} \quad (1)$$

Where:

- σ_{fm} is the flexural strength, in megapascals (MPa)
- F is the maximal load, in newtons (N);
- L is the span, in millimetres (mm);
- h is the thickness of the specimen, in millimetres (mm);
- b is the width of the specimen, in millimetres (mm);

The flexural modulus E_f is calculated from equation:

$$E_f = \frac{L^3}{4bh^3} \left(\frac{\Delta F}{\Delta s} \right) \quad (2)$$

Where:

- E_f is the flexural modulus of elasticity, expressed in megapascals (MPa);
- Δs is the difference in the beam mid-point deflection (mm) between s'' and s' , which correspond to the given values of flexural strain $\varepsilon_f'' = 0,0025$ and $\varepsilon_f' = 0,0005$, by following equation:

$$s'' = \frac{\varepsilon_f'' L^2}{6h} \quad \text{and} \quad s' = \frac{\varepsilon_f' L^2}{6h} \quad (3)$$

ΔF is the difference in load F'' and load F' at s'' and s' respectively.

Calculating the relative deformation (ε) or the strain in the outer surface of the specimen at maximal beam mid-point deflection as following equation:

$$\varepsilon = \frac{6sh}{L^2} \quad (4)$$

The results of the effects of calcination temperature on flexural properties of silica-based geopolymer composite M1-carbon 5631 1600tex 24K is summarized in Table 2 and Fig. 3. The properties of the composites seemed to be constant when the samples were exposed up to 200 °C. It was easy to notice that the properties went down drastically after exposing up to higher than 200 °C of calcination, the flexural strength remained only 37% and elasticity modulus approximately 20% compared with the original ones when these composites were exposed up to 600 °C. At this temperature the difference of relative thermal expansion of geopolymer matrix and fiber could be maximum, which caused bad adhesion between matrix and fiber reinforcement (Fig. 4b). When the temperature of calcination increased the mechanical properties of the composites were better, because the adhesion was improved and

initial reaction layer might be created, so the flexural strength gained 54% and remained around 50% after calcination up to 800 °C and 1000 °C respectively, meanwhile the flexural modulus could be 65 % when compared with that of composites after curing.

Table 2. Residual properties of geocomposite reinforced by carbon fiber after exposed to high temperature for 1 hour at oxidizing environment

Temperature (°C)	Elasticity modulus		Flexural strength		Relative deformation	Weight lost
	E_f (GPa)		σ_{fm} (MPa)		ϵ (%)	(%)
Room	92.3	±6.9	470.9	±6.5	0.74	0
200	88.7	±5.3	437.3	±19.1	0.72	4.1
400	49.4	±2.4	275.8	±21.6	1.06	8.8
600	19.1	±3.8	173.5	±33.5	1.69	15.5
800	37.5	±2.6	255.2	±26.0	1.04	17.4
1000	59.4	±8.5	222.2	±57.5	0.66	18.1

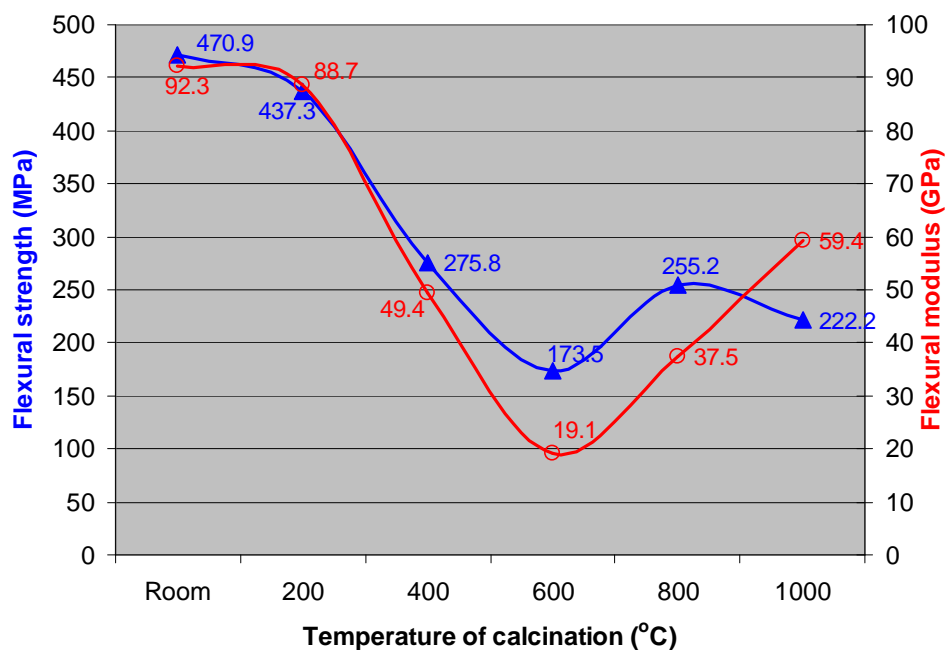


Figure 3. Flexural strength and modulus of geocomposit after exposing up to different high temperature

To study the microstructure of the geocomposites and adhesion between the carbon fiber and geopolymer matrix, the SEM images were investigated (Fig. 4). From the pictures, at large magnification we saw that after curing the adhesion between fiber and matrix was very good, some micro-cracks were detected, however (Fig. 4a). It could be seen from Fig. 4b that the interaction of reinforcement and geopolymer matrix was so loose, it seemed no connection between them. The reason is assumed that the difference of relative thermal expansion of these two component parts could be maximum around 600 °C of calcination, this problem should be next investigations. After calcinating up to higher 800 °C, at low magnification 500 x (Fig. 4c), the microstructure of geocomposite looked like foam. At higher magnification 2 kx, however, we also have the good adhesion between the fiber and matrix (see Fig. 4d).

From table 2, it is seen that when the temperature of calcination increased the weight of composites was reduced and it was noticeable up to 600 °C, weight loss 15.5 % up to this

temperature. Meanwhile this value was just 17.4 to 18.1 % of weight lost when the composites were exposed up to 800 °C to 1000 °C. The major weight loss during the calcination was supposed that evaporation of free water, condensed hydroxyl groups and a partial loss of fiber oxidation.

In the other hand, we could see from the table 1 that at temperature higher than 400 °C, the carbon fiber was destroyed totally by oxidization. However, the mechanical properties of geopolymer composite thereof still remained 50 % for flexural strength (222 MPa compared 470 MPa) and 65 % for elasticity modulus (59 GPa compared 92 GPa) even they were exposed up to 1000 °C in oxidizing environment, these values are over 10 times stronger than pure geopolymer matrix. The results confirm that carbon reinforcement is protected from oxidation by geopolymer matrix.

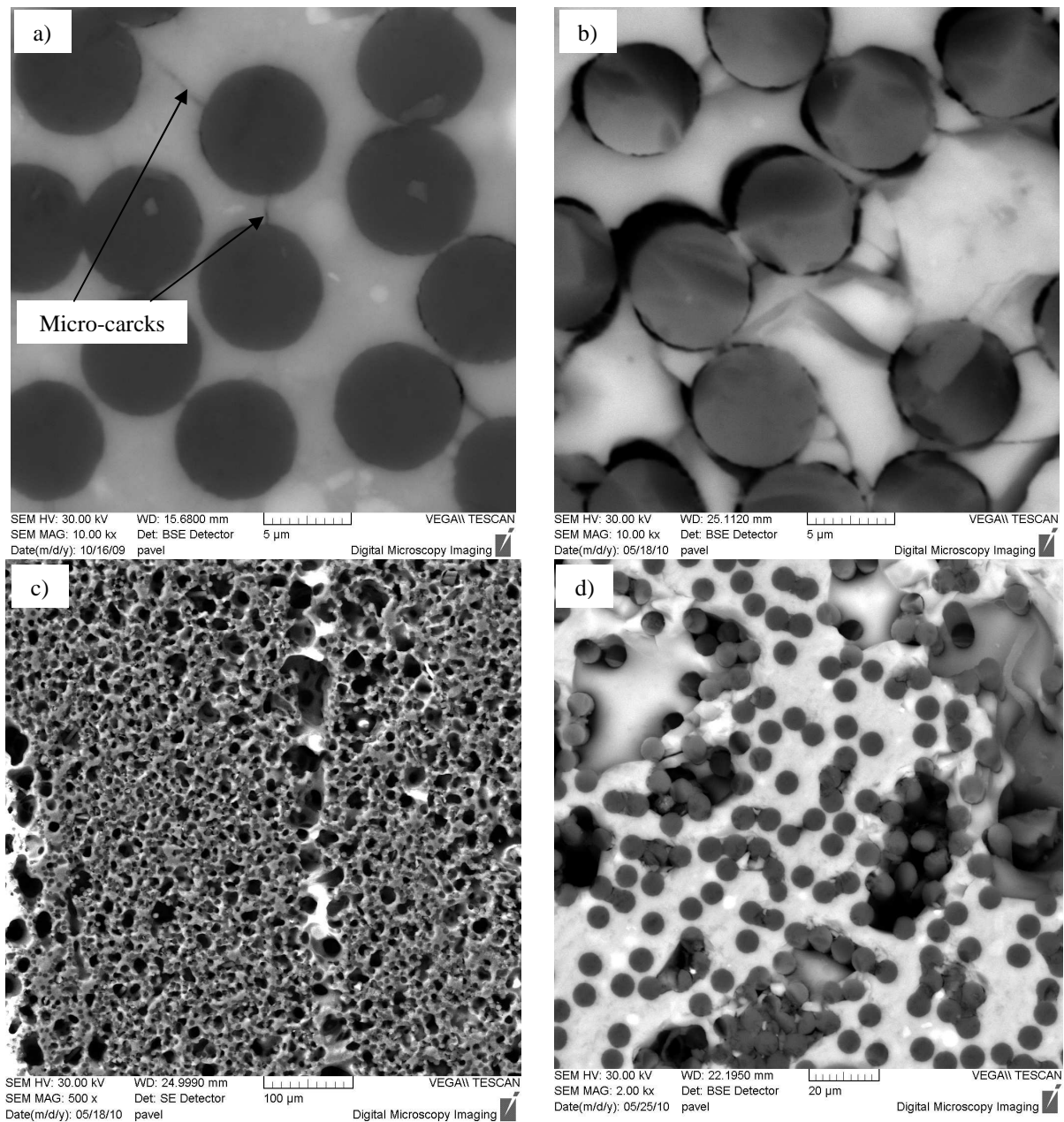


Figure 4. SEM images of cross-sections of geopolymer composite matrix M1-carbon after calcination at different temperature a) cured composite (10 kx), b) 600 °C (10 kx), c) 800 °C (500 x) and d) 1000 °C (2 kx)

With the hypothesis that at high temperature a chemical reaction between interface of carbon fiber and derivative silicon of geopolymer matrix might be taken place to generate SiC which could prevent fiber from oxidation in turn, the Energy Dispersive X-ray Analysis (EDX) was used. Fig. 4b and 4c show minor change of silicon and carbon atoms on the interface of fiber and matrix when compared with original one shows on Fig. 4a. This hypothesis may be confirmed by the initial reaction layer on the fiber on Fig. 4d.

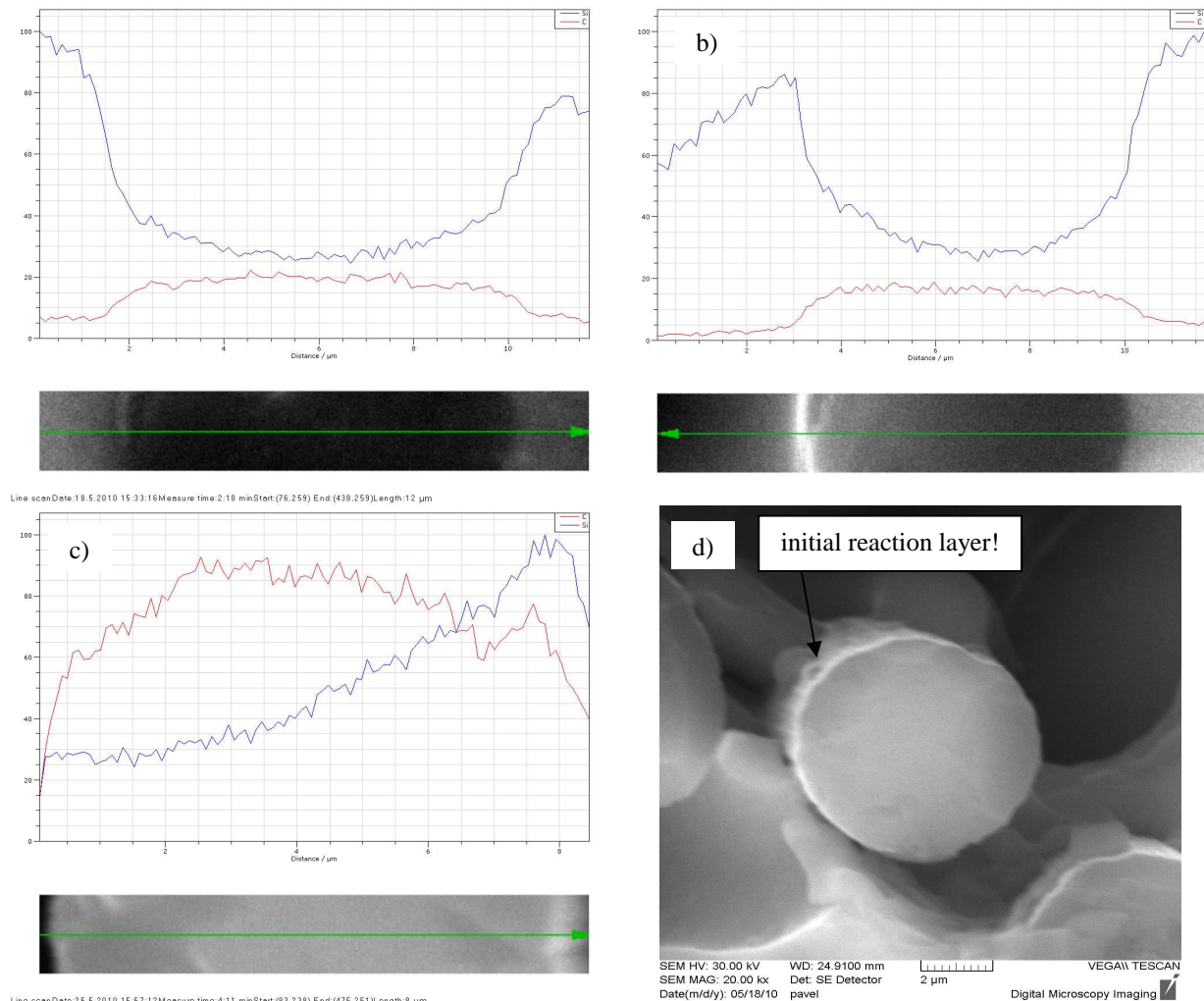


Figure 4. EDX of line profiles through cross-section of filament fiber in the composite after calcination at a) room temperature, b) 800 °C, c) 1000 °C and d) SEM after exposing up to 800 °C (20 kx)

4. Conclusions

Thermal silica-based geopolymer reinforced composite possessing ceramic-like properties can be fabricated with simple process (using pultrusion, 1 hour at room temperature and 1 hour in oven at only 75 °C under vacuum-bagging technique and post-cured by drying at the same temperature for 5 hours more).

The geocomposite reinforced by 53 vol.% unidirectional carbon 5631 1600tex 24K shows very good thermal-mechanical properties, remains nearly 50 % of flexural strength and 65 % of elasticity modulus even after fire exposure up to 1000 °C for 1 hour in oxidation medium.

The adhesion between geopolymer and carbon fiber shows very good after curing and even exposing up to over 800 °C, after calcination at higher temperature the morphology of composite look like foam and initial reaction layer of SiC may be created as well. Around 600

°C, however, the loose interaction of fiber and matrix is detected, that causes low mechanical properties. In addition, non toxic fumes and smokes are generated during calcination.

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