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New Generation of Geopolymer Composite for Fire-Resistance

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1. Introduction

The most popular matrix used for fiber-reinforced industrial composites is organic polymer. The nature flammability of the organic polymer matrix (Marsh, 2002), however, limits the use of these materials in ground transportation (Hathaway, 1991), submarine and ships (Demarco, 1991), and commercial aircraft (Davidovits, 1991), where restricted egress of fire hazard is an important design consideration, although traditional fibers, such as carbon and glass fibers or new developed, high temperature, thermal-oxidative stable fibers from boron, silicon carbide and ceramic are inherently fire resistant (Papakonstantinou et al., 2001). In other word, most of organic matrix composites cannot be used in applications that require more than 200 °C of temperature exposure. In these cases of applications, composites based on carbon matrix or ceramic matrices are being exploited. However, use of these materials is even strongly limited, due to high cost accompany with special and high-thermal processing requirements (Papakonstantinou et al., 2001; Papakonstantinou & Balaguru 2005).

In 1978, Joseph Davidovits proposed that binders could be produced by a polymeric reaction of alkaline liquids with the silicon and the aluminum in source materials of geological origin or by-product materials such as fly ash and rice husk ash (Davidovits, 1999). These binders have been coined as term geopolymers since 1979; they are inorganic polymeric materials with a chemical composition similar to zeolites but without defined crystalline structure and possessing ceramic-like features in their structures and properties. The amorphous to semi-crystalline three dimensional of silicate network consists of tetrahedral SiO₄ and AlO₄ which are linked alternately by sharing all the oxygens to create polymeric Si-O-Al bonds (Davidovits & Sawyer 1985; Davidovits, 1991). Geopolymers are still considered as a new material for coatings and adhesives, a new binder for fiber composites, and a new cement for concrete (Davidovits, 2008). They are mineral polymers and the essence of all mineral polymers is never burn (Davidovits, 2008). Therefore, we can state that geopolymer materials are ideal for high temperature and fire applications.

Fiber-reinforced composites based on geopolymer matrix (geocomposite) have been well-known for over 20 years, since the first Davidovits' patent was filed (Davidovits et al., 1989).

These new materials can be fabricated and cured at room temperature or thermoset in a simple autoclave. After approximately several hours of curing, these materials exhibit excellent features such as lightweight and high strength but are also ideally fire resistant, with non toxic fumes and smokes, and resist all organic solvents (Lyon et al., 1997; Davidovits, 2002, 2005, 2008; Duxson et al., 2007). These special properties permit us to use geopolymer matrix composites more efficiently in high-tech technologies such as aerospace, naval architecture, ground transportation or automotive industry, especially for those applications that require high temperature resistance (Lyon et al., 1997; Papakonstantinou et al., 2001; Davidovits, 2002, 2008). Geopolymer composites can efficiently replace lightweight, high strength composites which are made from carbon or glass fibers and ceramic matrices or organic matrices due to high costs associated with special ceramic processing requirements and impossibility of the application of most organic matrix composites at temperatures above 200 °C (Papakonstantinou et al. 2001; Papakonstantinou & Balaguru, 2005). In addition, wide scale of reinforcement fibers can be used, and special matrices can protect carbon from oxidation (Papakonstantinou et al., 2001; Sheppard, 2007).

In order to study the fire-resistant properties of materials in general and geopolymer composites, three following groups of specifications of materials should be investigated, including: Ignitability, heat release and smoke for the first group; the second group includes flame spread index and the last one is residual flexural strength (Lyon et al., 1996, 1997). Among these parameters, Richard E. Lyon and his colleagues determined that perhaps the most important fire behaviour parameter for structure applications is the strength retention of the composite after fire exposure (Lyon et al., 1996).

In this chapter, two formulations of geopolymer matrices, abbreviated as 'M1' and 'M2', based on thermal silica with fine size-particle and main molar ratio Si/Al \approx 10, potassium hydroxide solution and further minor admixtures for improving application features, were created and synthesized. Thermal silica-based geopolymer resin is better than conventional geopolymer resins based on metakaolin, fly-ash and similar materials which contain rather large size-particles and marked with high viscosity and therefore hardly used effectively for fiber impregnation or very high pressure must be applied to penetrate the resin into the spaces between single filament fibers (Bell et al., 2005). The properties of six geopolymer composites based on M1, M2 and approximately 45, 53 or 60 vol.% of unidirectional carbon fiber HTS 5631 1600tex 24K, basalt roving BCF13 - 2520tex - KV12 Int. or Saint-Gobain - Vetrotex E-glass E2400P192, which were fabricated under simplified pultruded home-made impregnation machine and cured at optimal range of curing conditions, were studied. The effects of severe thermal exposure in a furnace at high temperatures up to 1000°C for 1 hour on the thermal-mechanical properties of the geocomposites were evaluated. 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 DIN V ENV 658-3:1993-02. The microstructure of concerned composites M1/Carbon and M2/Carbon were analyzed by means of Scanning Electron Microscope (SEM). Moreover, Energy Dispersive X-ray Analysis (EDX) was used to determine whether initial reaction layer on the fibers and was presented as well.

2. Experimental design

2.1 Initial materials

The formulations of two geopolymer matrices (M1 and M2), consisted of thermal silica, potassium hydroxide solution or potassium water glass, and further minor admixtures for

improving application features. The difference between these two was in the nature of additives: alkali borate addition to M1 and alkali phosphate addition to M2. Details of chemical composition of two used geopolymer matrices expressed as main elements molar ratios are showed in Table 1.

Matrix	Si/Al	K/Al	K/Si	K/P	Si/P	K/B	Si/B	H ₂ O/K
M1	11.3	3.1	0.27	-	-	4.9	18.7	4.7
M2	9.7	2.4	0.24	4.2	17.5	-	-	5.2

Table 1. Chemical composition of geopolymer matrices M1 and M2 expressed as main elements atomic ratios

The reinforcement used in the composites discussed in this paper were continuous fibers (rovings) that came from carbon HTS 5631 1600 tex, TohoTenax; basalt roving BCF13 - 2520tex - KV12 Int. or Saint-Gobain - Vetrotex E-glass E2400P192. 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) before and after heat treatment at different temperatures in a furnace for 3 hours, Table 2 contains information of the properties (Tran et al., 2008; Nguyen et al., 2009).

Kind of fiber	d ₀	20 °C			200 °C			400 °C			700 °C		
		ε	σ	E	ε	σ	E	ε	σ	E	ε	σ	E
Carbon HTS 5631 1600tex 24K	7	1.84	3120	170	1.33	2340	176	1.66	2861	172	Fibers were destroyed totally (nearly disappeared)		
Basalt BCF13 - 2520tex - KV12 Int	13	3.98	2563	64	3.44	2111	61	1.7	1281	75	The fibers still remained in the furnace, but too brittle		
E-glass E2400P192	24	4.72	1504	32	3.26	1106	34	2.08	995	48	1.03	575	56

d₀ - Average diameter of fiber filament [μm]; σ - Tensile strength [MPa]; E - Tensile module [GPa]; ε - Failure strain [%]

Table 2. Estimated properties of applied fibers after treatment at different temperature

2.2 Method for geocomposite fabrication

Continuous fibres (rovings) were impregnated ("wetted-out") with geopolymeric resin on an impregnation machine - Fig. 1. The equipment has been designed based on simulating the real pultrusion or filament winding technique of a current composite manufacture. Pulling velocity 34 m/h of the fiber during impregnation process was chosen to achieve the best penetration of geopolymer resin into the fiber.

Impregnated cut-up rovings were laid manually into a silicon rubber mould 3×9×150 mm, layer by layer. Series of five samples were prepared from a batch, 16 bunches of pre-preg carbon fiber, 18 bunches of impregnated basalt fiber, or 20 bunches of geopolymer saturated E-glass fiber were needed for each specimen. The mold with pre-pregs was then covered by a peel ply fabric and suction tissue and placed into a sealed plastic bag.



Fig. 1. Details of pultrusion technique used for the preparation of geocomposites

The specimens were cured under optimal procedure of 3 stages by help of currently used technique of vacuum bagging (abbreviated by 1:1:5), in the first stage at room temperature for 1 hour under vacuum bagging, and then 1 hour in oven at optimal temperature, 80 °C for M1 system and 85 °C for M2 system with hot vacuum bagging. Finally, the specimens were released from bags, dried open in the oven at the same temperature for another 5 hours, and one long specimen (3x9x150 mm) was cut into two samples in dimension 3x9x85 mm and 3x9x65 mm for suit the planned spans. Only rough surface treatment with emery paper was applied.

2.3 Testing setup

Specimens were tested for flexural properties before and after the fire exposure up to high temperature to determine the residual properties of the composites. Generally, for testing the residual properties, the specimens are exposed to a 25 kW/m² radiant heat source for a duration of 20 minutes according to ASTM E-662 protocol for smoke generation in a flaming mode, after that they are tested in flexure for mechanical properties. Since the geopolymer composites would not burn, they are not subjected to the ASTM E-662 protocol (Lyon, Balaguru et al., 1997). As a replacement, the samples were tested at room temperature (20 °C) or subjected to temperatures of 200 °C, 400 °C, 600 °C, 800 °C and 1000 °C (1000 °C for carbon fiber reinforced geocomposites only) for 60 minutes of soaking time and at the oxidizing environment in a forced air furnace. The ramp of temperature was 10 K.min⁻¹ and samples then were cooled in the furnace with opening gate for 24 hours. At 400 °C of the furnace exposure is comparable to the equilibrium surface temperature of a vertically oriented, unit-emissivity surface exposed to 25 kW/m² of radiant energy in quiescent air for the same time period as the ASTM E-662 protocol (Foden et al., 1996).

2.4 Mechanical measurement

The residual mechanical properties of composites after exposing up to high temperature were measured on Universal Tensile Testing machine Instron Model 4202 with a mid-span deflection rate of 2 mm/min at two different outer support span-to-depth ratios

L/H = 20 to 1 in DIN V ENV 658-3:1993-02 and L/H = 16 to 1 as in accordance with ASTM C 1314 - 06. Virtual flexural values were evaluated in agreement with the size-independent method and presented as a visual presentation as well (Tran et al., 2010).

3. Preliminary results and discussion

Fig. 2. presents photographs illustrating of the typical condition of the specimens before and after thermal exposure.

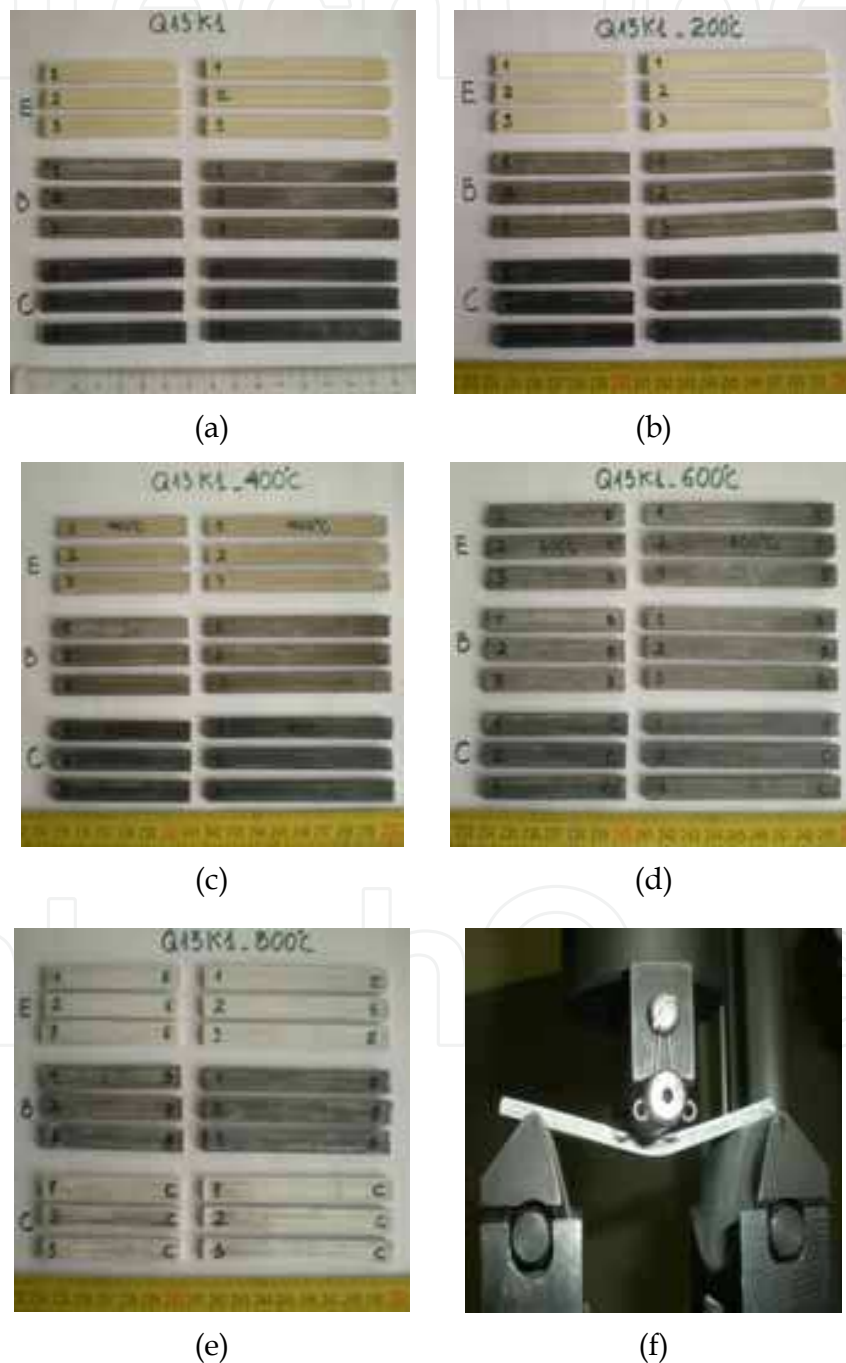


Fig. 2. Geocomposite specimens (M2 system) before (a) and after thermal exposure (b, c, d, e) and typical failure pattern of M2-Carbon after calcination at 800 °C (f)

Mechanical properties of the geocomposites after thermal exposure up to high temperature were evaluated by equations in agreement with DIN EN 658-3:2002 (L/H = 20 to 1) and ASTM C 1314 - 06 (L/H = 16 to 1). The degradation of specimen weight was also concerned. Residual flexural strength (σ_m), modulus (E), strain in the outer surface (ε_m) and weight lost (Δm) are presented in Table 3 to 8. Visual demonstrations are exhibited on Fig. 3 to Fig. 8 respectively. In order to make the figures clearly, no error of measurements are shown on the figures.

M1/Carbon	L/H = 16 to 1			L/H = 20 to 1			Δm [%]
	σ_m [MPa]	E [GPa]	ε_m [%]	σ_m [MPa]	E [GPa]	ε_m [%]	
20 °C	401.1 ±18.5	65.2 ±3.8	0.90	470.9 ±6.5	92.3 ±6.9	0.74	0.0
200 °C	316.3 ±14.0	62.5 ±1.6	0.77	437.3 ±19.1	88.7 ±5.3	0.72	4.1
400 °C	198.6 ±26.3	39.9 ±6.6	1.00	275.8 ±21.6	49.4 ±2.4	1.06	8.8
600 °C	111.8 ±2.1	11.3 ±1.1	1.43	173.5 ±33.5	19.1 ±3.9	1.69	15.5
800 °C	266.6 ±29.5	38.3 ±4.8	1.35	255.2 ±26.0	37.5 ±2.6	1.04	17.4
1000 °C	154.9 ±21.6	43.4 ±9.2	1.06	222.2 ±57.5	59.4 ±8.5	0.66	18.1

Δm - percentage of weight lost

Table 3. Flexural properties of geocomposites M1 reinforced by Carbon fibers cured at 80 °C after thermal exposure for 60 minutes at different L/H ratios

M1/Basalt	L/H = 16 to 1			L/H = 20 to 1			Δm [%]
	σ_m [MPa]	E [GPa]	ε_m [%]	σ_m [MPa]	E [GPa]	ε_m [%]	
20 °C	371.0 ±14.4	42.7 ±3.0	1.10	451.7 ±12.2	68.2 ±1.3	0.86	0.0
200 °C	291.4 ±20.0	45.9 ±1.8	0.84	307.9 ±7.1	55.5 ±1.4	0.72	5.3
400 °C	222.9 ±4.6	39.0 ±1.0	0.76	257.5 ±27.5	51.2 ±1.5	0.64	4.9
600 °C	94.4 ±8.2	39.9 ±2.3	0.27	84.4 ±1.5	48.1 ±0.7	0.21	5.1
800 °C	52.5 ±6.2	26.2 ±2.9	0.30	45.1 ±5.7	26.8 ±5.6	0.25	4.7

Table 4. Flexural properties of geocomposites M1 reinforced by Basalt fibers cured at 80 °C after thermal exposure for 60 minutes at different L/H ratios

M1/E-glass	L/H = 16 to 1			L/H = 20 to 1			Δm [%]
	σ_m [MPa]	E [GPa]	ε_m [%]	σ_m [MPa]	E [GPa]	ε_m [%]	
20 °C	109.2 ±13.3	32.6 ±4.0	0.59	144.5 ±11.2	44.0 ±2.3	0.53	0.0
200 °C	69.8 ±5.0	21.3 ±2.5	0.64	82.0 ±10.0	30.8 ±1.7	0.50	1.9
400 °C	42.7 ±0.6	9.7 ±2.0	0.71	54.9 ±6.0	18.2 ±4.0	0.52	4.0
600 °C	40.0 ±3.3	10.8 ±1.4	0.58	42.9 ±2.6	20.2 ±1.3	0.29	4.3
800 °C	41.0 ±4.8	11.8 ±1.3	0.75	24.9 ±0.4	6.9 ±1.2	0.48	4.5

Table 5. Flexural properties of geocomposites M1 reinforced by E-glass fibers cured at 80 °C after thermal exposure for 60 minutes at different L/H ratios

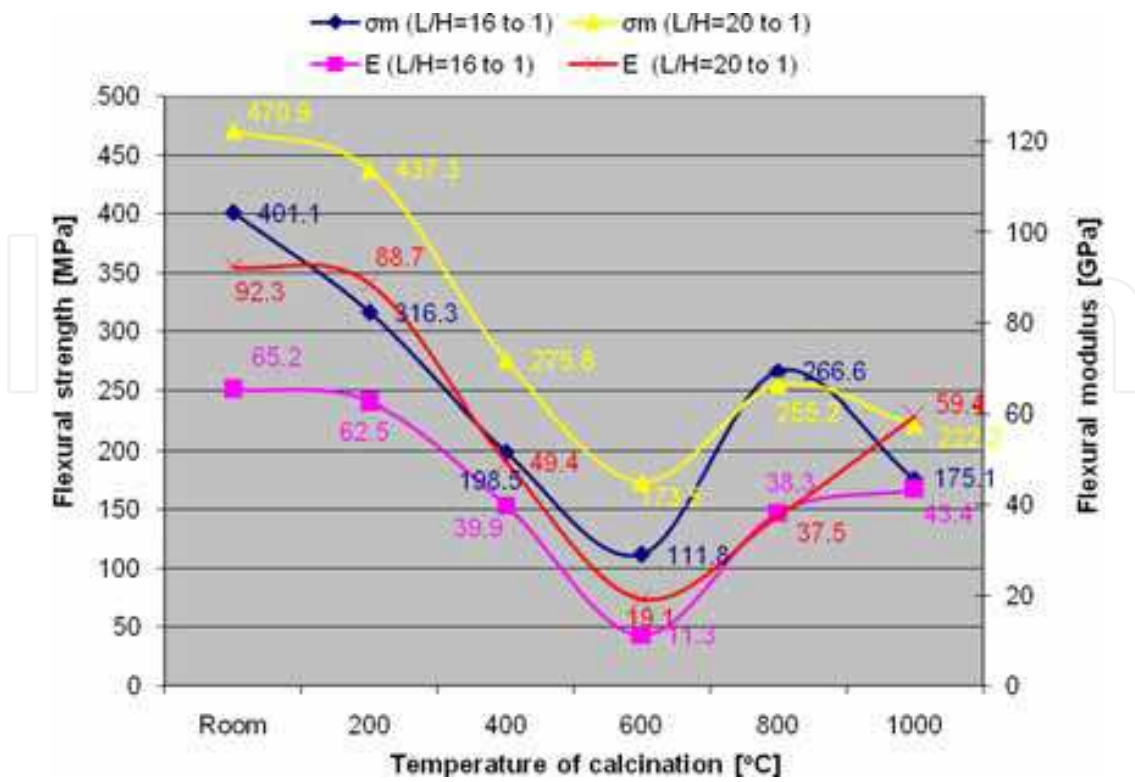


Fig. 3. Residual mechanical properties of geocomposites M1/Carbon fibers

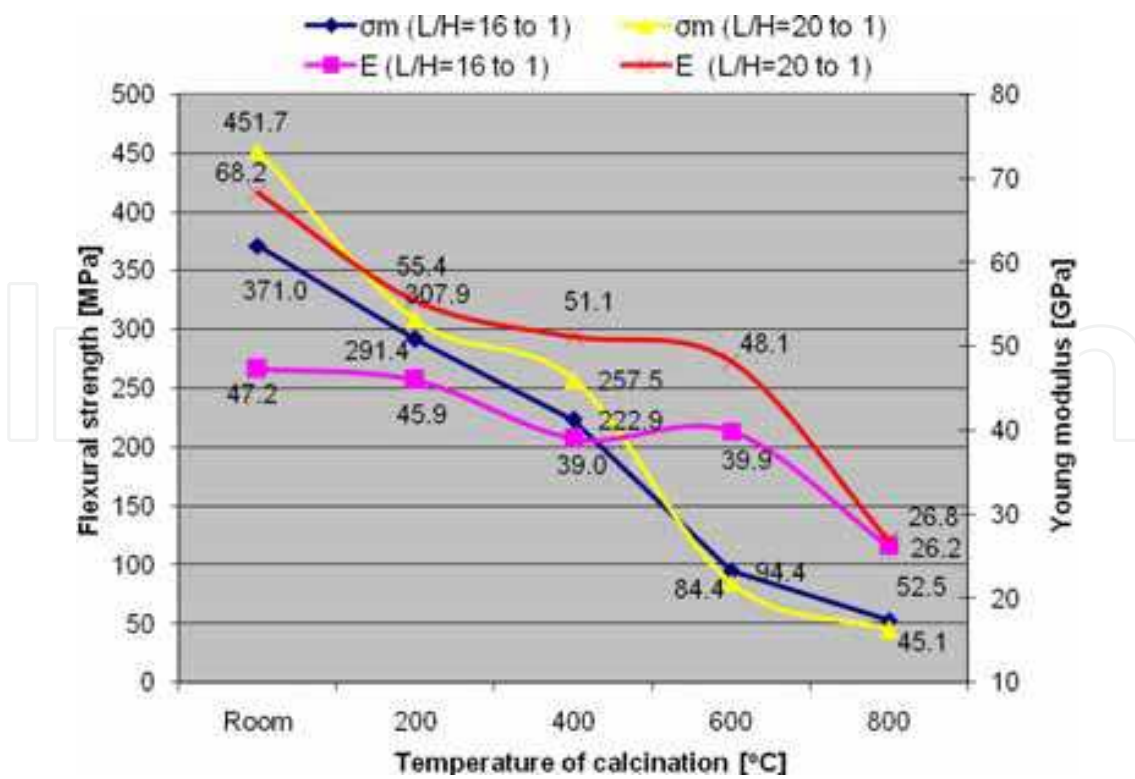


Fig. 4. Residual mechanical properties of geocomposites M1/Basalt fibers

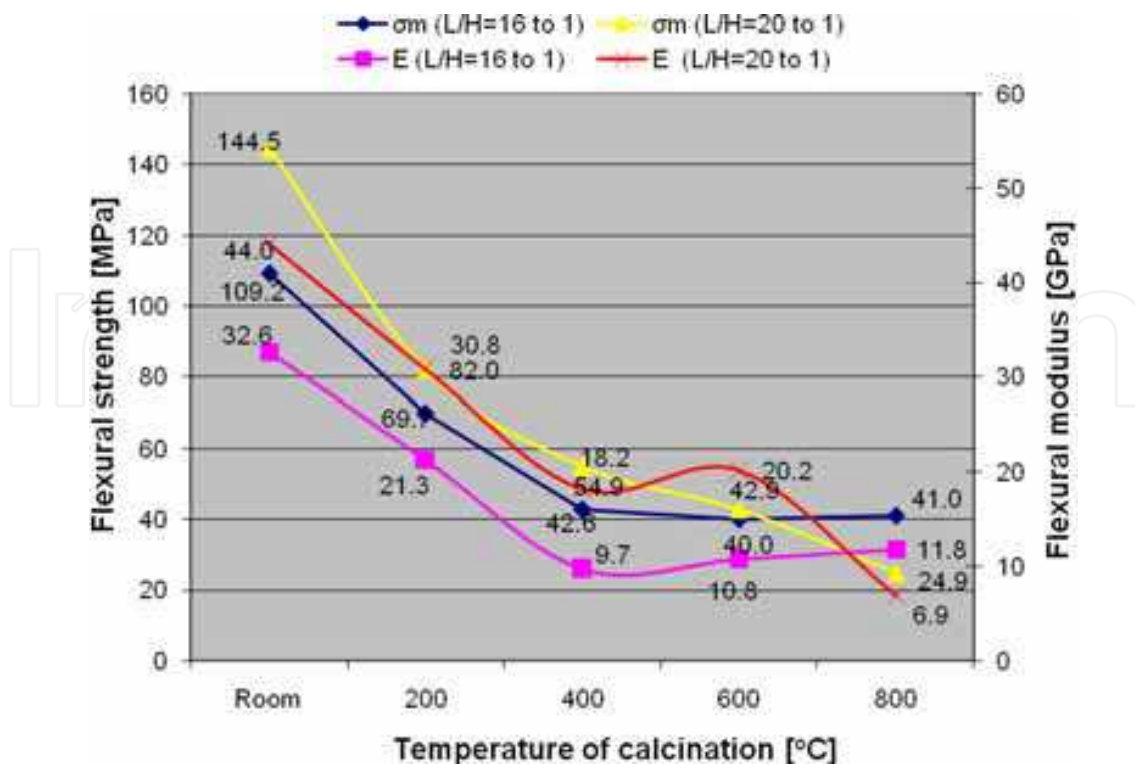


Fig. 5. Residual mechanical properties of geocomposites M1/E-glass fiber

M2/Carbon	L/H = 16 to 1			L/H = 20 to 1			Δm [%]
	σ_m [MPa]	E [GPa]	ϵ_m [%]	σ_m [MPa]	E [GPa]	ϵ_m [%]	
20 °C	290.9 ±15.7	85.3 ±1.4	0.49	355.7 ±10.8	106.6 ±5.7	0.40	0.0
200 °C	283.4 ±2.5	69.3 ±7.1	0.84	322.4 ±19.7	99.7 ±13.8	0.56	4.0
400 °C	259.1 ±17.9	64.0 ±1.2	0.86	269.4 ±6.8	77.4 ±4.1	0.87	5.8
600 °C	184.0 ±7.5	36.0 ±1.5	1.11	204.9 ±7.5	47.2 ±1.5	0.80	11.6
800 °C	173.6 ±10.0	28.9 ±1.1	1.25	211.7 ±11.8	35.3 ±3.8	1.24	18.6
1000 °C	190.1 ±13.3	28.9 ±1.1	1.11	206.1 ±8.9	36.6 ±1.5	0.98	18.5

Table 6. Flexural properties of geocomposites M2 reinforced by Carbon fibers cured at 85 °C after thermal exposure for 60 minutes at different L/H ratios

M2/Basalt	L/H = 16 to 1			L/H = 20 to 1			Δm [%]
	σ_m [MPa]	E [GPa]	ϵ_m [%]	σ_m [MPa]	E [GPa]	ϵ_m [%]	
20 °C	220.5 ±11.4	53.5 ±3.5	0.58	273.1 ±2.0	65.9 ±1.4	0.49	0.0
200 °C	221.3 ±12.4	48.9 ±4.4	0.78	250.3 ±13.5	58.7 ±2.1	0.61	2.3
400 °C	211.8 ±7.0	52.4 ±5.0	0.55	221.0 ±10.5	55.8 ±2.0	0.57	3.0
600 °C	152.6 ±15.1	56.2 ±1.5	0.35	153.6 ±19.7	68.3 ±2.7	0.28	4.4
800 °C	44.9 ±26.3	46.3 ±4.1	0.12	47.0 ±8.6	56.4 ±5.0	0.07	5.0

Table 7. Flexural properties of geocomposites M2 reinforced by Basalt fibers cured at 85 °C after thermal exposure for 60 minutes at different L/H ratios

M2/E-glass	L/H = 16 to 1			L/H = 20 to 1			Δm [%]
	σ_m [MPa]	E [GPa]	ϵ_m [%]	σ_m [MPa]	E [GPa]	ϵ_m [%]	
20 °C	158.1 ±8.8	51.9 ±5.0	0.46	202.0 ±6.9	56.6 ±4.6	0.40	0.0
200 °C	128.2 ±11.8	42.5 ±4.6	0.42	165.6 ±2.8	57.2 ±0.6	0.40	2.7
400 °C	140.8 ±15.5	51.1 ±8.8	0.35	133.8 ±5.4	64.0 ±2.6	0.23	3.3
600 °C	95.9 ±7.6	46.8 ±8.2	0.37	126.0 ±25.1	66.0 ±3.7	0.28	4.0
800 °C	56.1 ±5.0	51.1 ±5.3	0.14	61.8 ±1.9	63.7 ±3.8	0.07	4.0

Table 8. Flexural properties of geocomposites M2 reinforced by E-glass fibers cured at 85 °C after thermal exposure for 60 minutes at different L/H ratios

In general, the mechanical properties of geocomposites reinforced by carbon, basalt or E-glass fibers remained approximately around 90% after sustaining up to 400 °C for 1 hour. Almost all composites remained over 50% of strength after calcination at 600 °C, for carbon fiber reinforced geocomposites the temperature can be over 1000 °C; exceptionally, geocomposite M1/E-glass, due to degradation in alkaline medium and by themselves at high temperature.

The shear strength could even take an important role in the failure pattern of fiber reinforced geocomposites after exposing up to high temperature. For both geocomposites reinforced by basalt fibers, however, after calcinating to over 400 °C their flexural strengths of testing at different L/H ratios were nearly similar (see Fig. 4 and 7). Some unusual behavior of elastic moduli of geocomposites M2/basalt and M2/E-glass were determined (Fig. 7 and 8). It may need more experiments for explaining the mechanism of these behaviors.

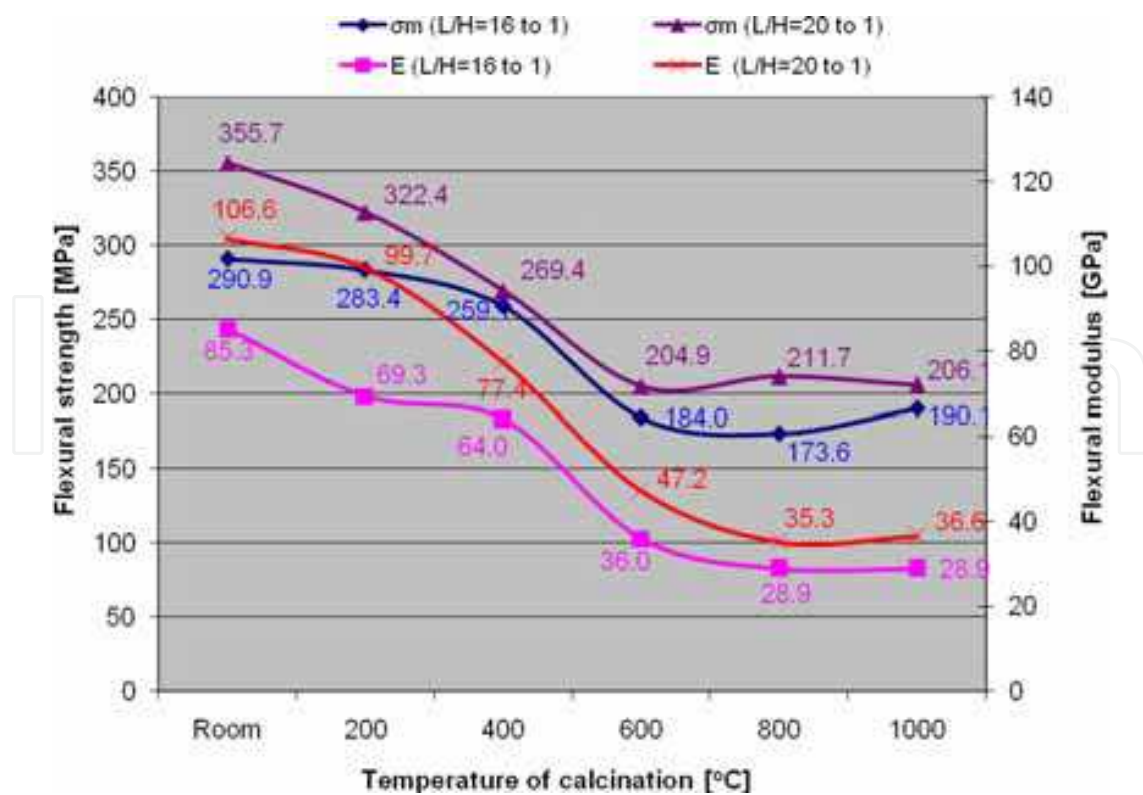


Fig. 6. Residual mechanical properties of geocomposites M2/Carbon fiber

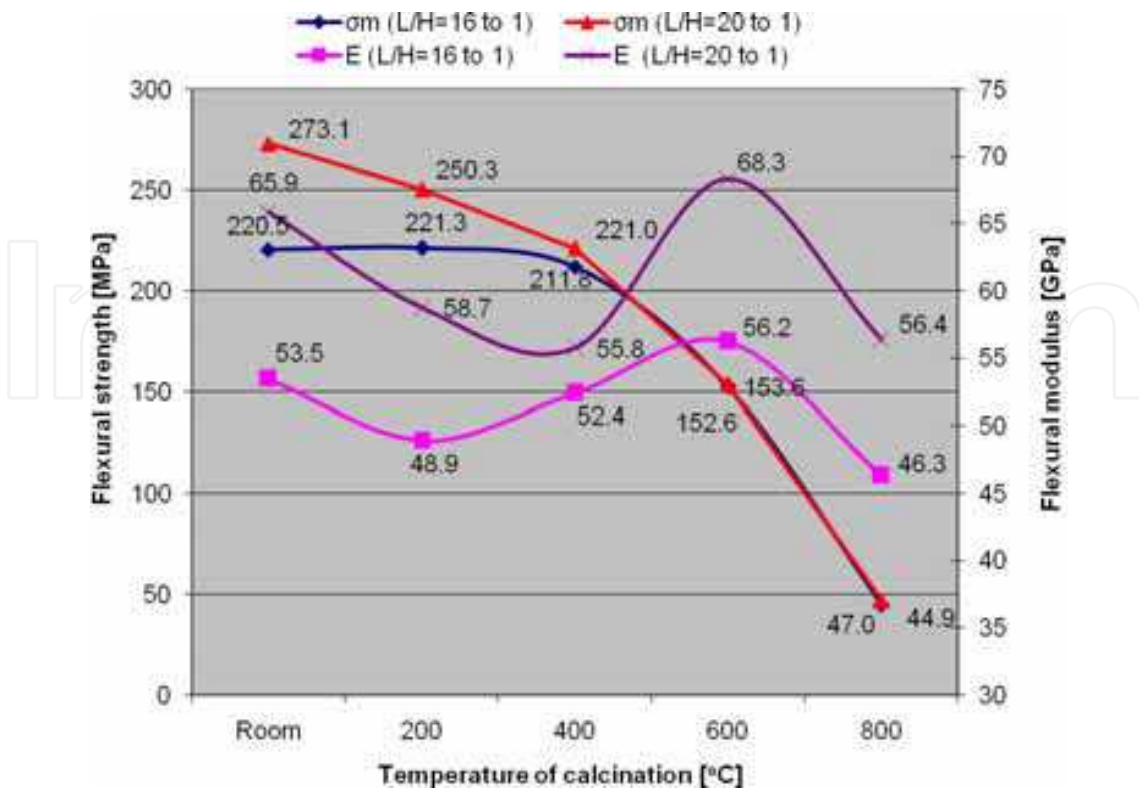


Fig. 7. Residual mechanical properties of geocomposites M2/Basalt fiber

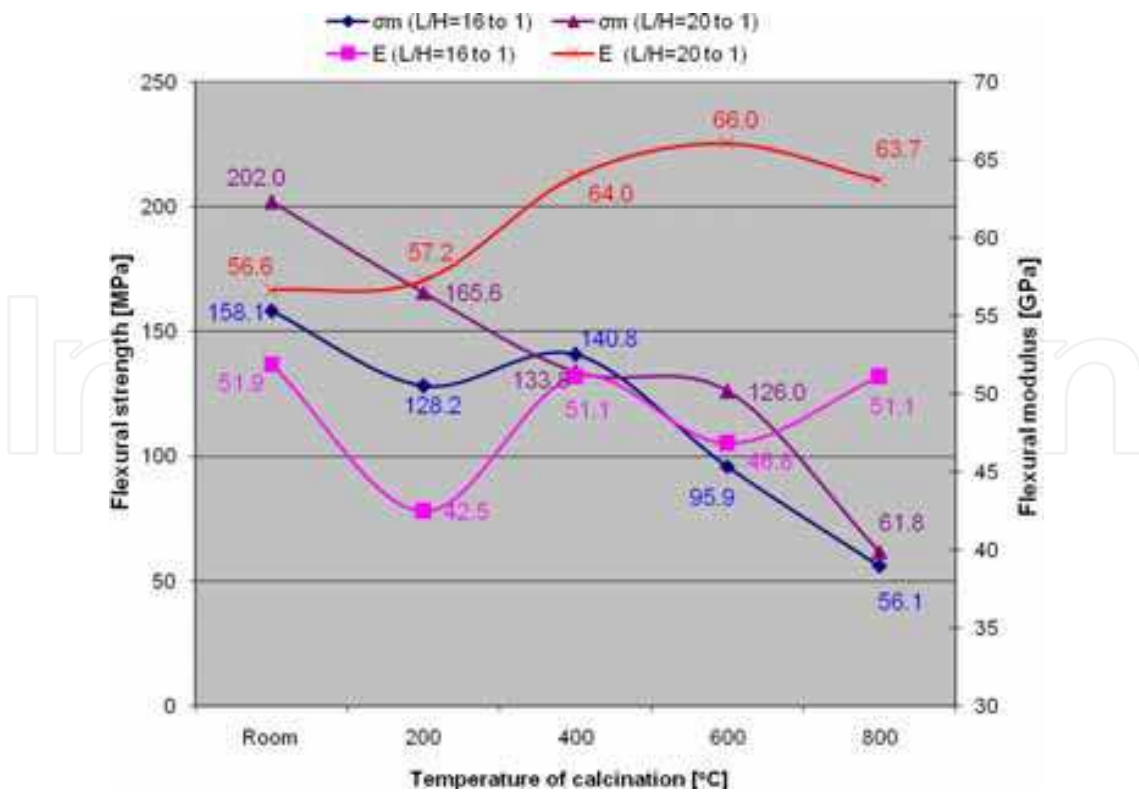


Fig. 8. Residual mechanical properties of geocomposites M2/E-glass fiber

Meanwhile the major weight lost of geocomposites reinforced by basalt or E-glass during the calcination is assumed that from evaporation of free water of 4.5 to 5.0 wt.%, the value can be reached after the composites are exposed up to over 400 °C. The value of carbon fiber reinforced geocomposites must be caused by not only free water evaporation but also partial carbon fiber oxidizing of the outer layers at temperature higher 400 °C, it was estimated that approximately 14 wt.% of carbon fibers is disappeared (see the last columns of Table 3 to Table 8).

Experimental findings show that composites based on geopolymer matrix M2 were very good at thermal dimensional stability, the composites exhibited no thermal expansion even they were calcinated up to 800 °C for basalt and E-glass reinforcements and 1000 °C for carbon fiber reinforcement. On the contrary, the geocomposites based M1 and carbon, basalt and E-glass have different expansion under thermal conditions. Meanwhile dimensional stability was recorded up to 600 °C for M1/basalt, the temperature for M1/carbon and M1/E-glass remain dimensional stability is 400 °C and 200 °C respectively. After exposing up to 600 °C, the expansion of M1/C and M1/E-glass were 40.7 vol.% and 30.8 vol.% in comparison with values at room temperature. After exposing to 800 °C, expansion of M1/E-glass was 135.2 vol.% and M1/basalt was 53.1 vol.%. Moreover, over 800 °C of thermal exposure, white outer calcinated layer of the composite is formed (Fig. 2 and 9).

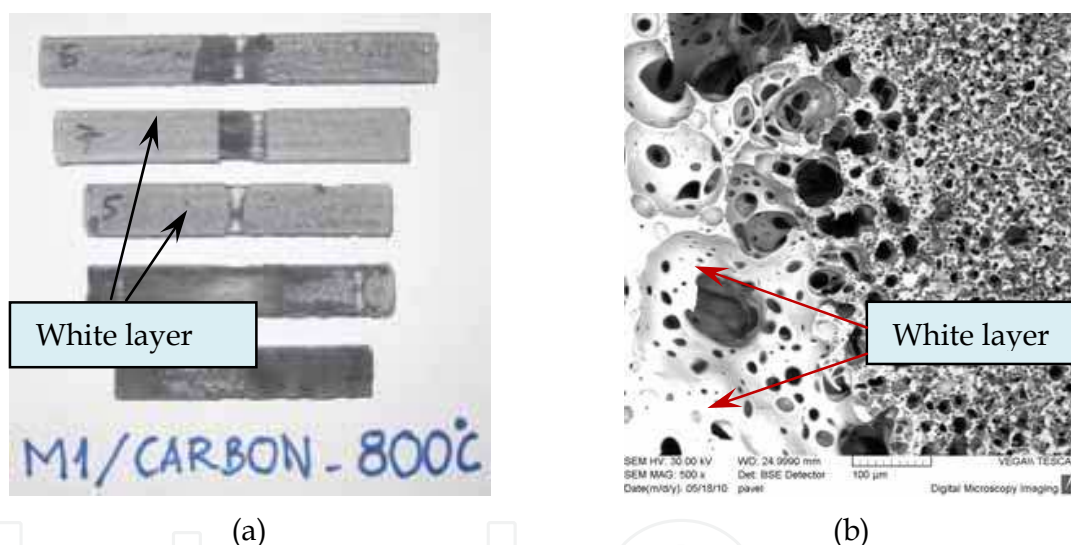
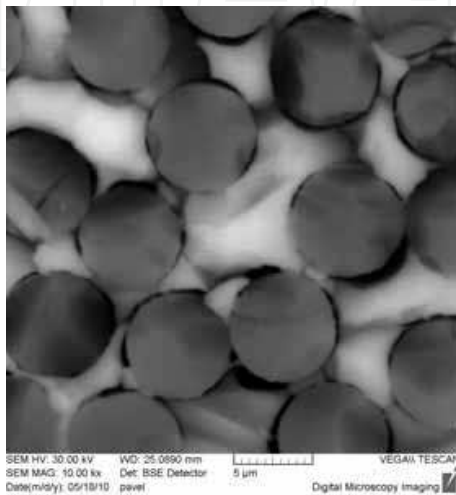


Fig. 9. Outer calcinated layer of composite M1 after exposing up to 800 °C at macro structure (a) and micro-structure (b at 500x)

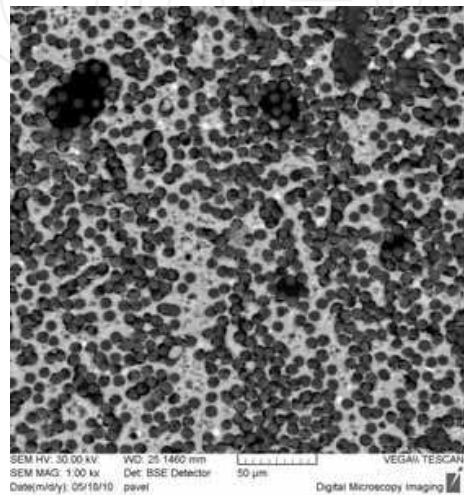
The most advantages of geopolymer materials are they possess ceramic-like properties, meanwhile they can be fabricated at room or very low temperature (in our research, 65-85 °C is recommended) and special ones can protect carbon fiber from oxidation. Among three kinds of commercial selected roving fibers, carbon (HTS 5631 1600tex 24K, TohoTenax), advanced basalt (BCF13-2520tex KV12 Int, Basaltex) or electrical grade glass (E-glass: E2400P192, Saint-Gobain, Vetrotex) which used to reinforce geopolymer composites, the combination between geopolymer and carbon fiber reinforcement attracted much more our attention. The materials have a great expectation for applying into high-tech applications.

Mechanism of mechanical behavior of geocomposite M1/Carbon was very special (Table 3 and Fig. 3). At support span-to-depth ratios $L/H = 20$ to 1, the properties of the composites

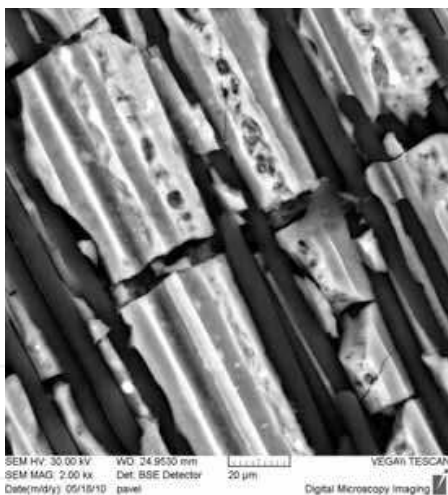
seem to be constant when the samples are exposed up to 200 °C. It was easy to notice that the properties went down drastically after exposing up to higher than 200 °C of calcination, when these composites were exposed up to 600 °C, the flexural strength remained only 37% and elasticity modulus approximately 20% compared to the original ones. It can be seen from Fig. 10 that the interaction of the fiber reinforcement and geopolymer matrix is so loose, it seems 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.



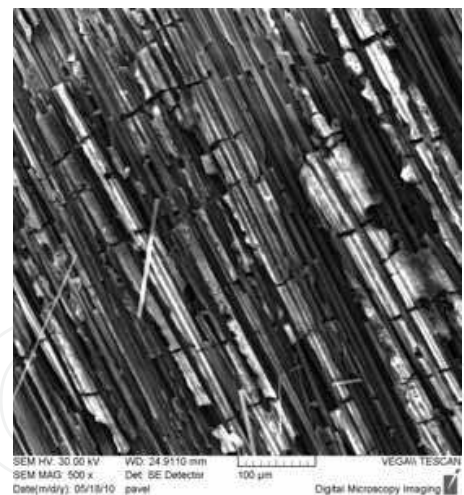
(a)



(b)



(c)



(d)

Fig. 10. SEM images of M1/carbon after exposing up to 600 °C on sections perpendicular to fibers (a) 10kx and (b) 1.0 kx and surfaces of composite (c) 2.0 kx and (d) 500x

When the temperature of calcination was higher than 600 °C, the mechanical properties of the composites were shown 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 % compared to those of composites at room temperature (Fig. 11a and c). In addition, after exposing up to higher 800 °C, at low magnification 500x (Fig. 11b and d), the

microstructure of geocomposite looked like foam structure. Fig. 12 shows many microcracks in the composites M1/Carbon after high temperature exposing.

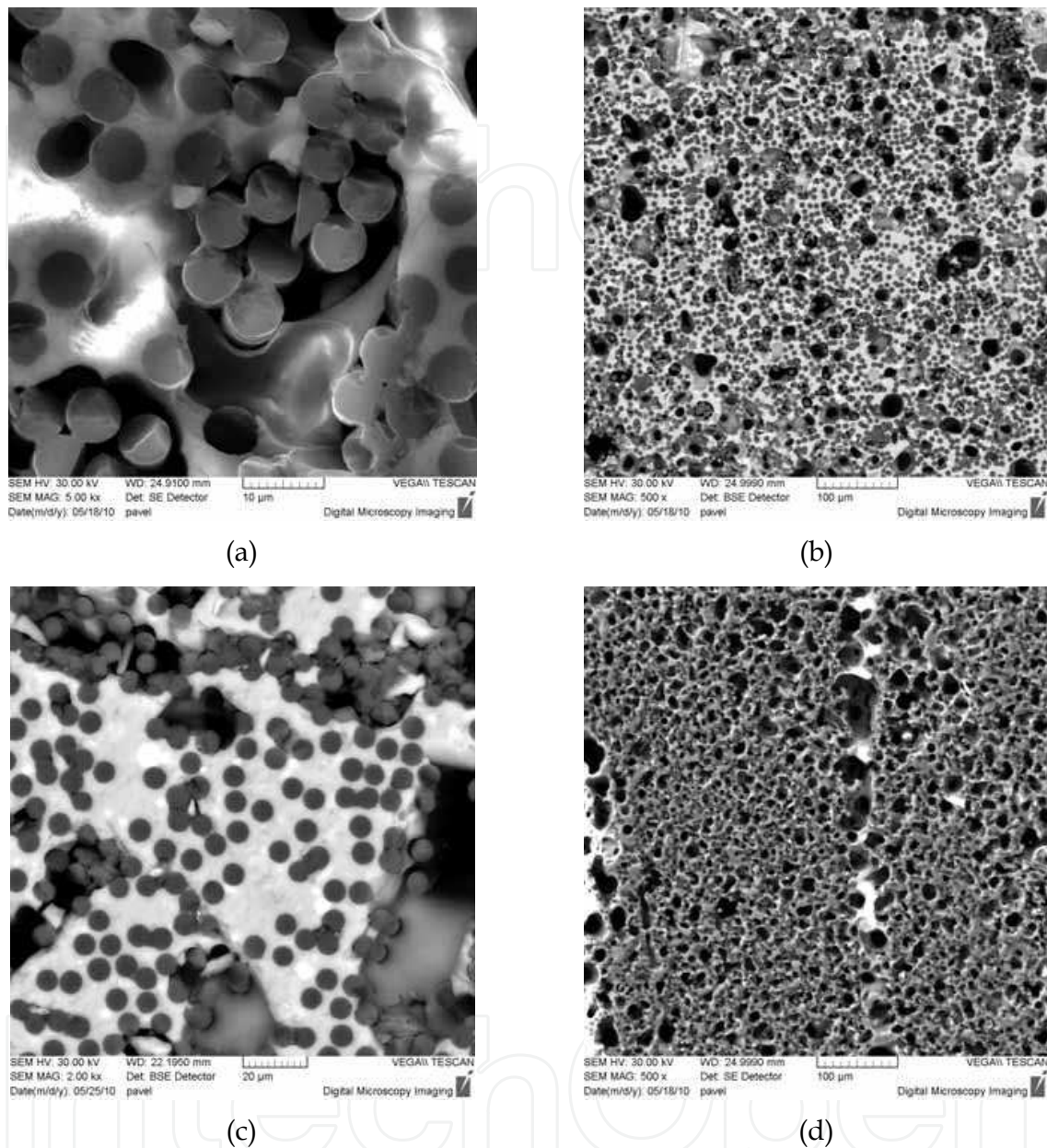


Fig. 11. SEM of M1/carbon after exposing up to 800 °C (a) 5.0kx and (b) 500x and 1000 °C (c) 2.0kx and (d) 500x on sections perpendicular to fibers

For M2/carbon fiber composites (Table 6 and Fig. 6), with the span of testing was 64 mm ($L/H = 20$ to 1), the flexural strength and modulus of elasticity seemed to go down quite dramatically when the temperature of calcination increased from 200 to 600 °C, retained around 57 % of flexural strength (204,9 MPa compared to 355,7 MPa) and 45% of elastic modulus (47,2 MPa in contrast with 106,6 MPa). However, the flexural properties seemed constant even when the composites were exposed up to 800 °C and 1000 °C. Microstructure of the composites is also presented on Fig. 13, as can be seen from this figure that after exposing the composite at 600 °C, the adhesion between carbon fiber and M2 matrix was

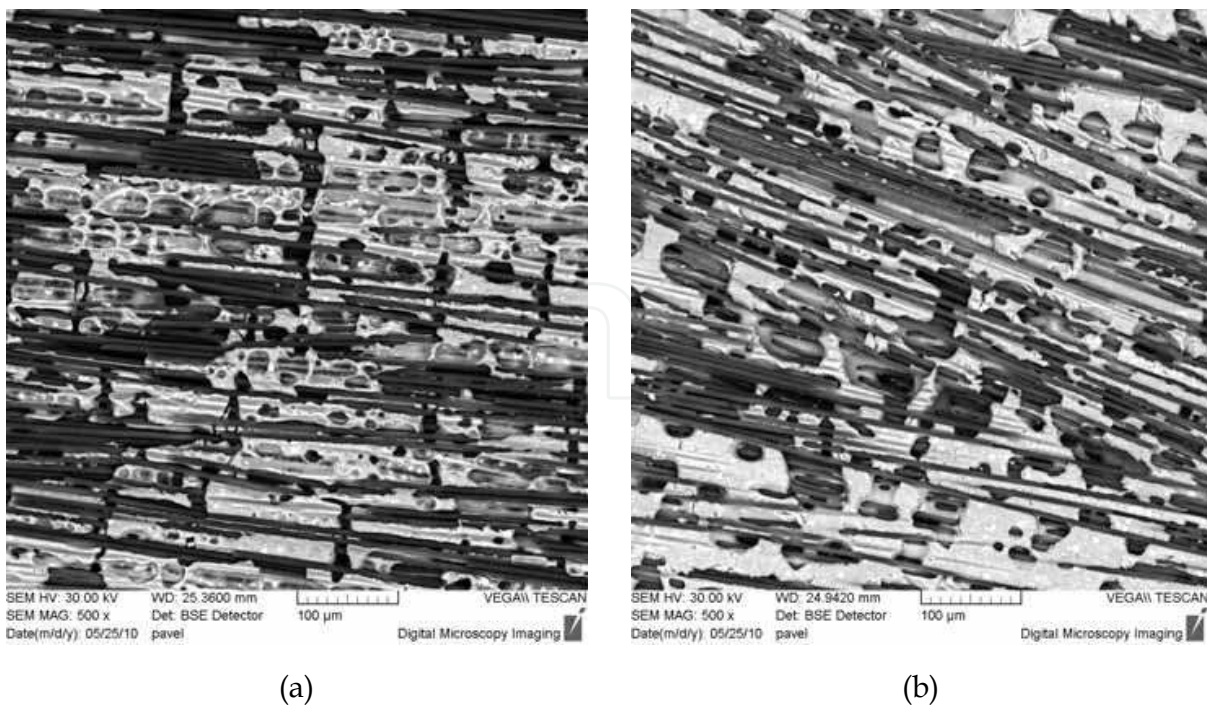


Fig. 12. SEM of M1/carbon after exposing up to 800 °C (a) and 1000 °C (b) on the surfaces of composite at magnification 500x

also not very good (Fig. 13a and b) and shown better after 1000 °C of exposure (Fig. 13c and d). The behaviors looked like the same as composites M1/carbon. However, for M2/carbon nearly non difference of flexural strength, modulus and dimensional stability were determined in range of 600 to 1000 °C of thermal exposure. Furthermore, the microstructure of geocomposite M2/carbon after exposing high temperature was exhibited on Fig. 14.

It seemed quite interesting when both M1/carbon and M2/carbon possess nearly the same flexural strength around 220 MPa after thermal exposing up to 800 °C and 1000 °C, although their microstructures were presented differently on Fig. 12 and Fig. 14. For composite M2/carbon (Fig. 14), it is visible to the naked eye that not so many cracks and porosities were determined in comparison with composites M1/carbon. This means that the composites based on geopolymer matrix M2 with phosphoric acid as functional additive, the chemical and physical properties of this matrix were stable at high temperature and the thermal dimensional stability was determined as unavoidable results.

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 carbon fiber from oxidation in turn, the Energy Dispersive X-ray Analysis (EDX) was used. Fig. 15b and 15c show minor change of silicon and carbon atoms on the interface of fiber and matrix when compared with original one shown on Fig. 15a. These results show that it is very difficult to confirm at temperature higher than 800 °C the carbon fiber could be protected from oxidization by the initial reaction layer on the fiber (Fig. 15d). Until now the mechanism of geopolymer for protection carbon fiber from oxidation is not identified clearly. The mechanism would be assumed that at high temperature the slowly continuous free water evaporation could create a vapor that can protect carbon fiber and with an special medium the SiC would be create at lower temperature instead of over 1400 °C as usual. Many investigations must be taken place to explain these assumptions.

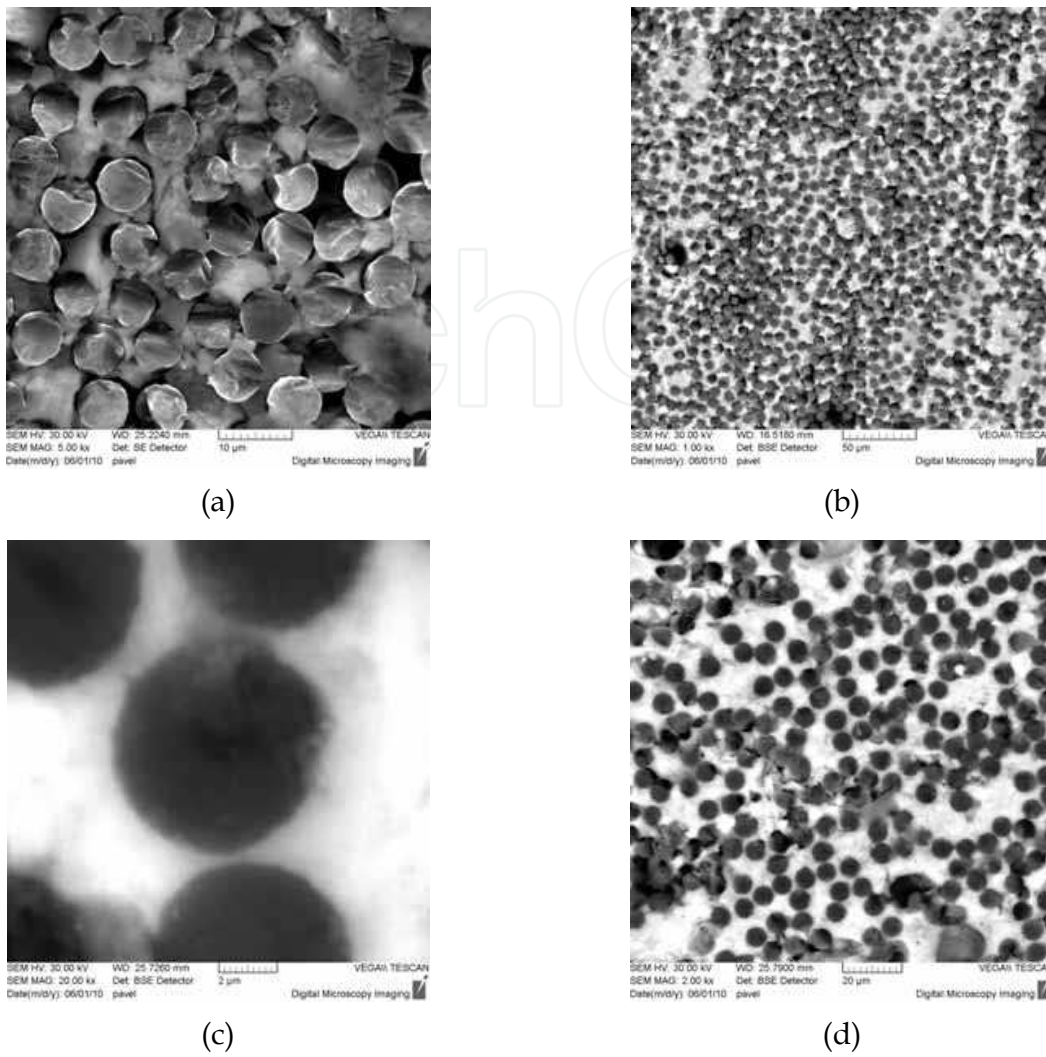


Fig. 13. SEM of M2/carbon after exposing up to 600 °C (a) 5.0kx and b) 1.0kx and 1000 °C (c) 20.0kx and (d) 200x on sections perpendicular to fibers and surfaces of composite

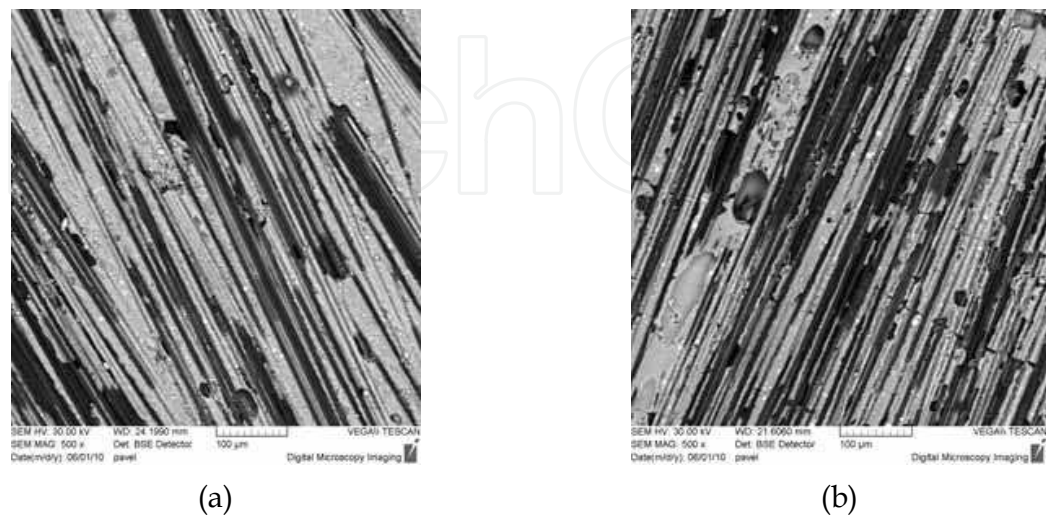


Fig. 14. SEM of M2/carbon after exposing up to 600 °C (a) and 1000 °C (b) on the surfaces of composite at 500x

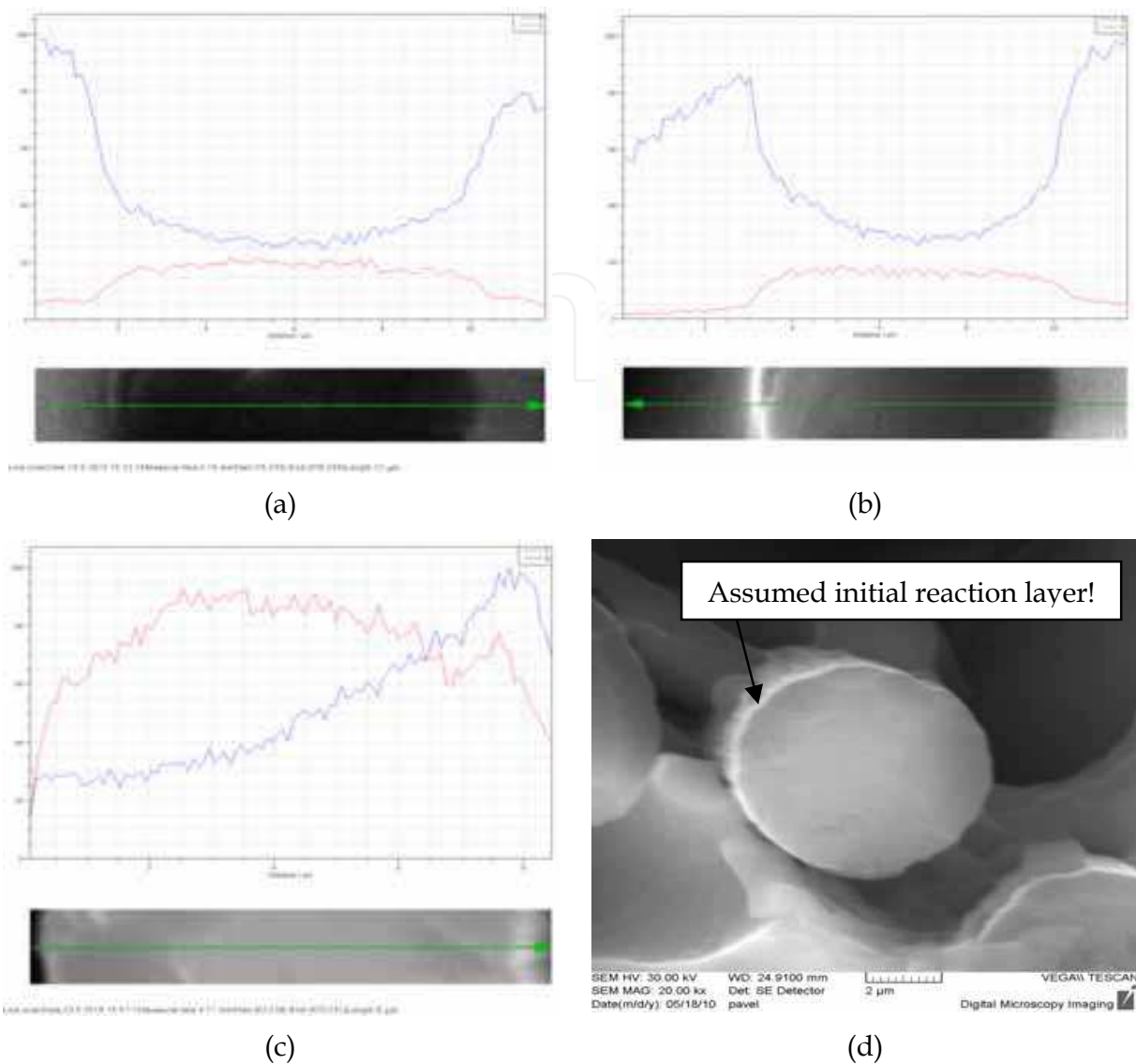


Fig. 15. EDX of line profiles through cross-section of filament fiber in the composite M1-carbon after calcination at (a) room temperature, (b) 800 °C, (c) 1000 °C and (d) SEM after exposing up to 800 °C (at 20kx)

Comparison of the composite resin categories on the basis of percent residual flexural strength retained after the fire exposure is shown in Fig. 16. They are exhibited a combined average for the thermoset (vinyleste, epoxy), advanced thermoset (BMI, PI), phenolic, and engineering thermoplastic (PPS, PEEK) (Lyon et al. 1996, 1997). A big notice should be taken into account is the values here just evaluated after the materials are exposed to a 25 kW/m² radiant heat source (equivalent to thermal exposure at 400 °C) for 20 minutes according to ASTM E-662 protocol. In our case of study all the geocomposites were subjected to a much more severe thermal condition (example 800 °C equivalent to 75 kW/m²) but geocomposites retained 50 to 60% of their original strength at room temperature after exposing up to 600 °C for one hour for M2/basalt and M2/E-glass. Especially the temperature for M1/carbon and M2/carbon can be higher than 1000 °C.

In comparison with the fiber reinforced ceramic matrix composites, the residual flexural strength of SiC/SiC composite retained about 80% of the room temperature at 800 °C and

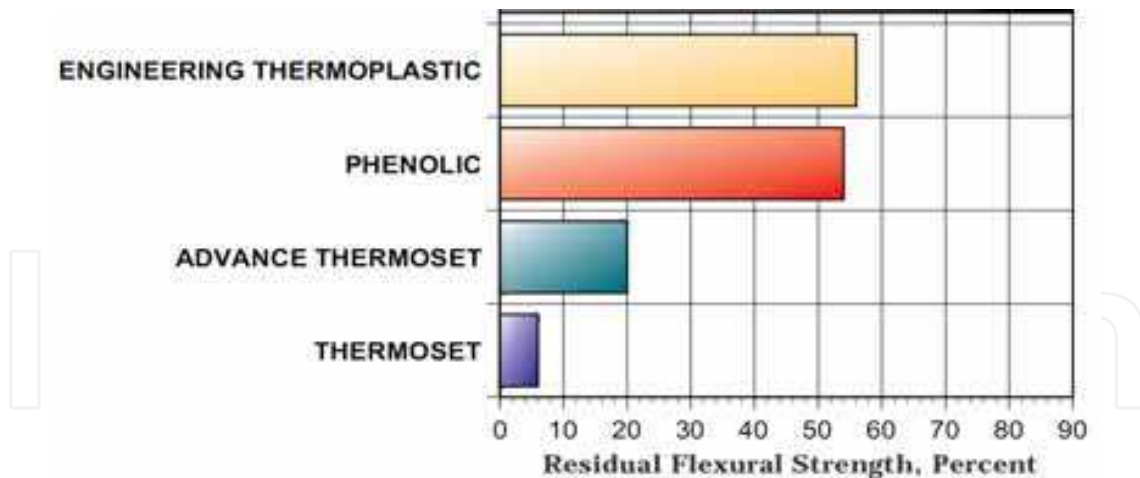


Fig. 16. Residual flexural strength of some commercial composites after fire exposure at a 25 kW/m² radiant heat source for 20 minutes (Lyon, Usman et al. 1996; Lyon, Balaguru et al. 1997)

dropped almost linearly to 55% at 1200 °C (Gomina et al. 1991). For alumina/glass and alumina/tin/glass composites behaved comparably well up to 400 °C, and retaining almost 75% of their strength, but at 600 °C the glass matrix softened (Papakonstantinou, Balaguru et al. 2001). Meanwhile in oxidizing environments, typical carbon/carbon composites oxidized at 400 °C (Luo, Yang et al. 2000); at 1000 °C the carbon/carbon composites retained only 20% of the room temperature strength and even optimal anti-oxidative fillers (MoSi₂) was added, the strength of the composites could increase up to only 41% of origins at room temperature (Park and Cho, 2000).

Material	Density	Tensile Modulus	Specific Modulus	Flexural Strength	Specific Flexural Strength	T _{MC}
	[kg/m ³]	[GPa]	[MPa.m ³ /kg]	[MPa]	[MPa.m ³ /kg]	[°C]
Fiber-Reinforced Concrete	2300	30	13.0	14	0.006	400
Structural Steel	7860	200	25.4	400	0.053	500
7000 Series Aluminium	2700	70	25.9	275	0.102	300
Phenolic-Carbon Fabric Laminate	1550	49	31.6	290	0.187	200
Phenolic-E-glass Fabric Laminate	1900	21	11.0	150	0.074	200
M1/Carbon	2000	x	x	471	0.236	≥1000
M1/Basalt	2400	x	x	452	0.188	≥400
M2/Carbon	2000	x	x	356	0.178	≥1000
M2/Basalt	2400	x	x	273	0.114	≥600
M2/E-glass	2400	x	x	202	0.084	≥600

T_{MC} - Maximum Temperature Capacity

Table 9. Typical properties of structural materials (Lyon, Balaguru et al. 1997)

Table 9 presents the thermomechanical properties of fiber reinforced concrete, structural steel, 7000-series aluminium used in aircraft structures, phenolic - carbon fabric laminate,

phenolic - E-glass fabric laminate (Lyon et al. 1997) and fiber reinforced geocomposites based on thermal silica geopolymer matrices M1 and M2. Maximum temperature capacity is defined as the temperature in air at which the nominal tensile or flexural strength falls to one-half of its room temperature value. The results show that the composites based on geopolymer matrices and fiber reinforcements are much better in both specific flexural strength and maximum temperature capacity.

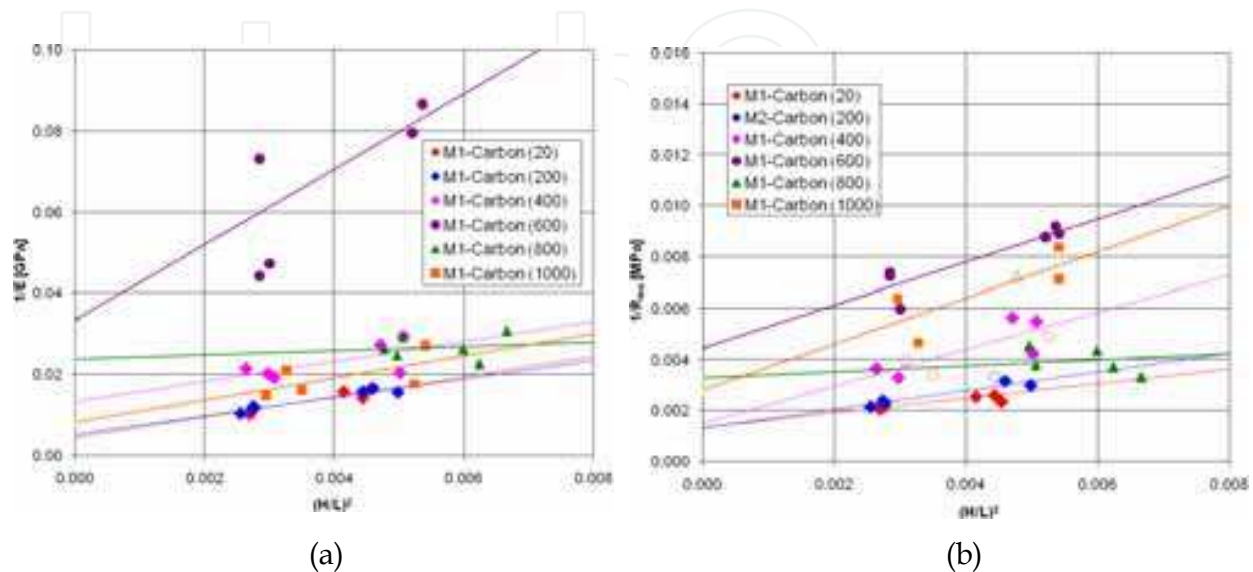


Fig. 17. Reciprocal effective flexural properties vs. $(H/L)^2$ ratio a) elasticity modulus, b) flexural strength of M1/Carbon after thermal exposure

In order to estimate the virtual flexural strength (σ_m^*) and virtual modulus (E^*) of the geocomposites when support span-to-depth ratios $L/H \rightarrow \infty$ to 1. The novel size-independent method was utilized and the typical of reciprocal effective flexural properties vs. $(H/L)^2$ ratio of geocomposites M1/Carbon after thermal exposure are presented on Fig. 17. However, the linear regressions are created on two series of H/L ratios so large error could be involved in extrapolation. In some cases, the error can reach nearly 100%, it is supposed that the results from these calculation are not enough accurate and no detailed presentation in our works.

4. Conclusions

Thermal silica-based geopolymer reinforced composites possessing ceramic-like properties can be fabricated with simple process (using pultrusion technique, 1 hour at room temperature and 1 hour in oven at only 80 °C for M1 and 85 °C for M2 under vacuum-bagging technique and post-cured by drying at the same temperature for 5 hours more).

Generally, all the geocomposites reinforced by 45, 53 or 60 vol.% of unidirectional carbon fiber HTS 5631 1600tex 24K, basalt roving BCF13 - 2520tex - KV12 Int. or Saint-Gobain - Vetrotex E-glass E2400P192 exhibit very good thermal-mechanical properties, retain nearly 50% of flexural strength even after severe thermal exposure up to 600 °C for basalt and E-glass fiber reinforced geocomposites and 1000 °C for geocomposites with carbon fiber reinforcement for 1 hour in oxidation environment. The geopolymer resins can protect carbon fibers from oxidation; however, approximately 14 wt.% of carbon fibers is oxidized after the composites are exposed higher 800 °C. In addition, experimental findings show that

composites based on geopolymers are very good at thermal dimensional stability, especially for matrix M2, the composites exhibit no thermal expansion even they are calcinated up to 800 °C for basalt and E-glass reinforcements and 1000 °C for carbon fiber reinforcement.

The adhesion between geopolymers and carbon fibers 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 thermal exposure.

Base on the preliminary results, fiber reinforced geopolymer composites open a nice view of a new generation of fire-resistant materials which possess ceramic like properties while fabricated under very simple procedures and at low temperature.

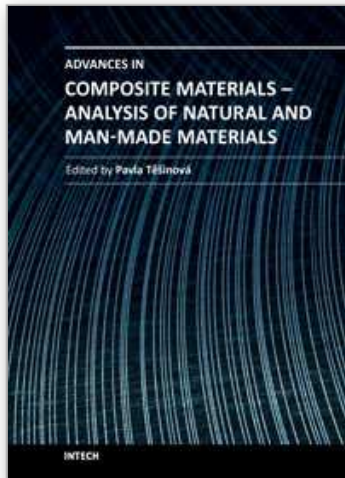
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Composites are made up of constituent materials with high engineering potential. This potential is wide as wide is the variation of materials and structure constructions when new updates are invented every day. Technological advances in composite field are included in the equipment surrounding us daily; our lives are becoming safer, hand in hand with economical and ecological advantages. This book collects original studies concerning composite materials, their properties and testing from various points of view. Chapters are divided into groups according to their main aim. Material properties are described in innovative way either for standard components as glass, epoxy, carbon, etc. or biomaterials and natural sources materials as ramie, bone, wood, etc. Manufacturing processes are represented by moulding methods; lamination process includes monitoring during process. Innovative testing procedures are described in electrochemistry, pulse velocity, fracture toughness in macro-micro mechanical behaviour and more.

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