MECHANICAL PROPERTIES OF FABRIC-REINFORCED GEOCOMPOSITES IN ACCORDANCE WITH NOVEL SIZE-INDEPENDENT FLEXURE-TEST TECHNIQUE

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ABSTRACT

In this paper, two silica-based geopolymer matrix systems reinforced composites were synthesized and fabricated at optimal conditions. The composites contained approximately 40 wt.% of Carbon HTA twill (TohoTenax) and 48 wt.% of advanced S-glass twill (Saint-Gobain, Vetrotex), respectively. The resulting composites exhibited quite high toughness, with the shear stress playing a greater role compared to other ceramic matrix composites. To determine the flexural properties of the composites, a universal testing machine was used under the three-point bending mode. This evaluation was conducted using a novel size-independent technique based on testing specimens at different scales of the sample height (H) to span length (L) ratio. Microstructure analysis of the composites was performed using a scanning electron microscope (SEM). The analysis aimed to assess the effective impregnation and adhesion between the fiber and geopolymer matrix, as well as to identify micro-cracks, which are inborn defects in inorganic matrix composites. The findings presented in this study highlight the potential of the synthesized silica-based geopolymer matrix composites and their applicability in various engineering fields.

***Keywords**: Geopolymer composite, fabric fiber, Size-independent flexure-test technique, flexural properties and microstructure.*

INTRODUCTION

In 1978, Joseph Davidovits introduced the concept of producing binders through a polymeric reaction involving alkaline liquids and source materials of geological origin or by-products like fly ash and rice husk ash [1]. These binders were subsequently termed geopolymers in 1979. Geopolymers are inorganic polymeric materials that possess a chemical composition akin to zeolites, lacking a well-defined crystalline structure, and exhibiting ceramic-like characteristics in terms of their structures and properties. The amorphous to semi-crystalline three-dimensional sialate network of geopolymers consists of SiO_4 and AlO_4 tetrahedra, which are interconnected by sharing oxygen atoms to form polymeric Si-O-Al bonds [2][3]. Geopolymers are still regarded as innovative materials with potential applications in coatings, adhesives, fiber-reinforced composites, and as promising alternatives to conventional cements in concrete formulations [4].

For over three decades, fiber-reinforced composites utilizing a geopolymer matrix, often referred to as geocomposites, have been recognized since the filing of the initial patent by Davidovits [5]. These innovative materials can be manufactured and cured at room temperature or through thermosetting in a straightforward autoclave process. Within a few hours of curing, these composites demonstrate exceptional properties such as lightweight and high strength, alongside desirable fire resistance characteristics, emitting non-toxic fumes and smoke, and exhibiting resistance to organic solvents [4][6][7][8][9]. These unique properties make geopolymer matrix composites highly advantageous for various high-tech industries, including aerospace, naval architecture, ground transportation, and the automotive sector, particularly for applications

necessitating high-temperature resistance [4][6][8][10]. Geopolymer composites offer a cost-effective alternative to lightweight, high-strength composites composed of carbon or glass fibers with ceramic or organic matrices. The high costs associated with specialized ceramic processing requirements and the limited applicability of most organic matrix composites at temperatures exceeding 200°C make geopolymer composites a viable option [10][11]. Furthermore, geopolymer matrices can accommodate a wide range of reinforcement fibers, and specific matrices can protect carbon fibers from oxidation [10][12].

In general, any mineral clay containing a high concentration of silicon oxide (silica) and aluminum oxide (alumina) can undergo alkaline dilution to initiate an exothermal polycondensation process, leading to the formation of geopolymer material. Commonly used raw materials for geopolymers include kaolin, metakaolin, fly ash, and furnace blast, among others. However, the use of geopolymer resin as a matrix for fiber-reinforced composites presents certain challenges. To ensure effective impregnation of fabrics or fiber rovings consisting of single filaments with diameters ranging from 7 to 25 µm, a resin with low viscosity and maximum particle size smaller than the filament diameter is preferred, typically around 5 µm [5][13]. Consequently, conventional geopolymer resin based on classical metakaolin and similar raw materials, characterized by relatively large particles and high viscosity, is not well-suited for efficient fiber impregnation, unless applied under very high pressure to penetrate the resin into the spaces between individual filament fibers [14]. However, utilizing a thermal silica-based geopolymer with nanosized amorphous silica as the primary component can overcome these challenges and enable effective impregnation of fibers [13].

This paper investigates the mechanical properties of composites based on two high silica-based geopolymer resin systems, namely M1 (containing metakaolin and boric acid, H_3BO_3) and M2 (containing kaolin and phosphoric acid, H_3PO_4). The composites were reinforced with carbon fabric (Carbon HTA twill - type 200, Toho Tenax) and advanced S-glass (Space glass twill - type 280, Toho Tenax). The specimens were tested at different ratios of height (H) to span length (L) in accordance with the recommended test spans outlined in DIN V ENV 658:1993-02 and ASTM C1341-06. Fabrication and curing of the composites were carried out under optimal conditions. Subsequently, the microstructure of the resulting composites was analyzed using a scanning electron microscope (SEM). This analysis aimed to evaluate the impregnation and adhesion between the fiber and geopolymer matrix, as well as identify micro-cracks, which are inherent defects in inorganic matrix composites. By examining the mechanical properties and microstructural characteristics, this study provides insights into the performance and structural integrity of the synthesized geopolymer matrix composites reinforced with carbon and advanced S-glass fabrics.

II. EXPERIMENTAL INVESTIGATION

1. Matrices and reinforcements

In this study, two geopolymer matrix systems, referred to as M1 and M2, were prepared following the simplified procedure outlined in the patent titled "Inorganic matrix compositions, composites, and process of making the same" [15]. The geopolymer matrices were formulated using thermal silica obtained from Saint-Gobain in France, which has a fine particle size (D_{50} 0.62 µm, D_{90} 3.24 µm) and consists of 93.8 wt.% SiO_2 and 2.9 wt.% Al_2O_3. The thermal silica was mixed with 48.5 wt.% KOH for 30 minutes, followed by the addition of network formers such as boric acid (H_3BO_3) for M1 or phosphoric acid (H_3PO_4) for M2. The network formers were diluted with water in a 1:1 weight ratio. To complete the formulation, an alumina source was included, either metakaolin (calcined shale, Czech Kaolin Company, Inc.) for M1 or kaolin (KKAF, LB MINERALS, Ltd.) for M2. The mixtures were thoroughly mixed until homogeneity was achieved. Table 1 provides approximate chemical composition details and molar ratios for the three geopolymer matrices used in this study.

Table 1. The chemical composition of geopolymer matrices M1 and M2 can be described by the atomic ratios of their main principal elements

Matrix	Si/Al	K/Al	K/Si	K/P	Si/P	K/B	Si/B	H_2O/K
M1	11.3	3.1	0.27	-	-	4.9	18.7	5.2
M2	9.7	2.5	0.24	4.2	17.5	-	-	5.2

The composites discussed in this paper were reinforced with fabric fibers (twill) from two groups: F1, consisting of carbon fabric (Carbon HTA twill - type 200, Toho Tenax), and F2, comprising advanced S-glass (Space glass twill - type 280, Toho Tenax). Table 2 presents relevant information regarding the reinforcement properties employed in the geocomposites.

Table 2. Kinds of used fabric fibers

Fiber type	Weaving	Density [g/m^2]
Carbon HTA twill - type 200 (F1)	twill	200
Space glass twill – type 280 (F2)	twill	280

2. Preparation of the composite specimens

The geocomposites were fabricated using the wet hand lay-up technique. For sample preparation, a woven fabric was placed on a flat mold, and the geopolymer was gently rolled or squeegeed into the fabric layer by layer until the desired thickness was achieved. The saturated fabrics were then covered with a peel ply fabric and suction tissue, followed by sealing them in a plastic bag. The fabric laminate was cured under optimal conditions in three stages. Initially, it was kept at room temperature for one hour, followed by an hour of elevated temperature in an oven under vacuum bagging. Finally, the laminate was dried for an additional five hours at the same temperature as the previous stage. For the M1 system, the temperature used in the second and third curing steps was 80°C, while for the M2 system, it was 85°C [16][2002].

The resulting laminate, with dimensions of approximately 120x120x2 mm³, was then cut into samples measuring 120x12x2 mm³, with a suitable length for flexural testing. This fabrication process ensures the integrity and proper curing of the geocomposite samples, allowing for accurate evaluation of their flexural properties.

Testing of flexural properties

The mechanical properties of the geocomposites were evaluated using three-point bending tests at various outer support span-to-depth ratios (*L/H*) of 20 to 1, 32 to 1, and 40 to 1, following the test spans recommended by DIN V ENV 658:1993-02 and ASTM C1341-06. The tests were conducted using a Universal Testing Machine, specifically the H50K-S model, with a maximum load capacity of 50,000 N. A centre-point load was applied, and the deflection of the samples was controlled using a mid-span deflection rate of 2.0 mm/min under laboratory conditions. The transversal dimensions, including the height (H) and width, of each tested beam were carefully measured at the midpoint to ensure accurate data analysis.

To estimate the Young's modulus (*E*), shear modulus (*G*), and flexural strength (σ_m), linear regression analysis was performed using a fictitious Young's modulus (*E**) and fictitious flexural strength (σ_m*) plotted against the reciprocal of the span-to-height ratio, $(H/L)^2$. The values of *E** were calculated for each height-to-span ratio using Eq. (1), which is applicable for isotropic materials.

Through these analyses, the actual mechanical properties of the geocomposites, including Young's modulus, shear modulus, and flexural strength, were determined based on the regression results obtained from the bending tests.

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

Where:

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);

E^* is the flexural modulus of elasticity, expressed in megapascals (MPa);

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

To obtain the effective values of the modulus (E*), the data points are plotted as $1/E^*$ versus $(H/L)^2$, as described in Eq. (1). By performing linear regression analysis, the values of the virtual modulus (E) can be accurately determined as Eq. (2).

$$E \cong 1 \Big/ \left(1/E^*\right)_{(H/L)^2 \to 0} \qquad (2)$$

The shear modulus (G) of the material was determined using Eq. (3), which incorporates a correction factor α, typically equal to 1.178. The variable in the denominator of the equation represents the slope obtained from the regression analysis.

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

Similarly, the fictitious flexural strength (σ_m^*) was calculated using Eq. (4), which is applicable to isotropic materials.

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

In Eq. (4), F_m represents the maximum bending load and is a quantity dependent on the dimensions of the sample. It is observed that the linearity of $(1/\sigma_m^*)$ remains reasonable with the same independent variable $(H/L)^2$ as mentioned previously. Therefore, the actual material property σ_m (referred to as flexural strength for simplicity) can be determined as the reciprocal intercept of the regression analysis.

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

4. Microstructure of the geopolymer composites

The cross-sectional views of the composites, perpendicular to the fibers and surfaces, are examined using a scanning electron microscope (SEM). This analysis allows us to assess the effective impregnation and adhesion between the geopolymer matrices and fiber reinforcements, as well as evaluate the microstructure of the composites. Additionally, the failure patterns observed in the samples and the stress-strain curves are investigated to gain insights into the behavior of the composites under bending conditions.

III. RESULTS AND DISCUSSION

The fiber contents of geocomposites with fabric reinforcement F1 (both M1/F1 or M2/F1) and F2 (M1/F2 or M2/F2) are approximately 40 and 48 % by weight respectively.

The flexural properties (effective flexural strength: σ_m^*, elasticity modulus: E* and the maximum strain in the outer fibers: ε_m) of geocomposites reinforced by the woven fabrics at various outer support span-to-depth ratios in accordance with test spans of DIN V ENV 658:1993-02 and ASTM C1341-06 are shown in the Table 3.

Table 3. The bending properties of the geocomposites at different outer support span-to-depth ratios

| Matrix/ fiber | Outer support span-to-depth ratio | | | | | | | | |
| | L/H = 20 to 1 | | | L/H = 32 to 1 | | | L/H = 40 to 1 | | |
	σ_m^* [MPa]	E* [GPa]	ε_m [%]	σ_m^* [MPa]	E* [GPa]	ε_m [%]	σ_m^* [MPa]	E* [GPa]	ε_m [%]
M1/F1	229.0±27.7	43.6±0.0	0.65	159.2±29.5	44.6±0.6	0.40	153.8±29.6	45.5±0.7	0.37
M1/F2	142.1±9.9	18.7±1.8	1.01	129.7±4.8	19.7±1.7	0.75	117.0±16.6	22.6±0.4	0.65
M2/F1	213.7±16.6	41.2±1.3	0.64	226.8±12.4	45.1±0.5	0.58	189.0±11.3	48.8±0.4	0.40
M2/F2	113.8±4.1	20.9±1.0	0.65	103.9±6.4	25.4±1.5	0.49	113.0±4.2	26.6±0.0	0.48

In general, for both geocomposite systems, the σ_m^* and E^* are varied in the similar trend and size-dependent of testing parameters. For M1 system, we can see that the ultimate strength (σ_m^*) of the composites decrease slightly for both carbon and s-glass fabrics when the outer support span-to-depth ratios (L/H) are varied, especially when L/H = 20 to 1 to L/H = 31 to 1, the σ_m^* of M1/F1 was dropped nearly 30.5% (σ_m^* = 229.0 MPa is comparation to 159.2 MPa). This trend is almost the same for those of M1/F2, the Rmo was down 8.7% (142.1 MPa is compared to 129.7 MPa). For M2 system, the ultimate strengths varied insignificantly, around 5%, when changing the L/H ratios for both M2 reinforced with F1 or F2. The ultimate strengths of the geocomposites with both matrix systems are comparable to the result of published parameters from Nicolas Davidovits and his colleagues's investigation

[5]. The properties of the geocomposites are much higher than the demands of technical parameters for materials of ship construction by fibreglass reinforced plastics [17].

Using linear regression of a fictitious Young's modulus E and a fictitious flexural strength σ_m against (H/L)^2 value for M1 and M2 reinforced by fabric F1 and F2 (see Fig. 1), the bending properties are summed up in Table 4.

It can be seen from Fig. 1 and Table 4 that the mechanical properties of the woven fabric reinforced geocomposites are not so much dependent on the outer support span-to-depth ratio. These results are quite different from those of geocompossites reinforced by unidirectional fibers [18]. For geocomposites based on M1 and M2 systems, however, the negative trend between flexural strength and modulus and H/L ratios are determined.
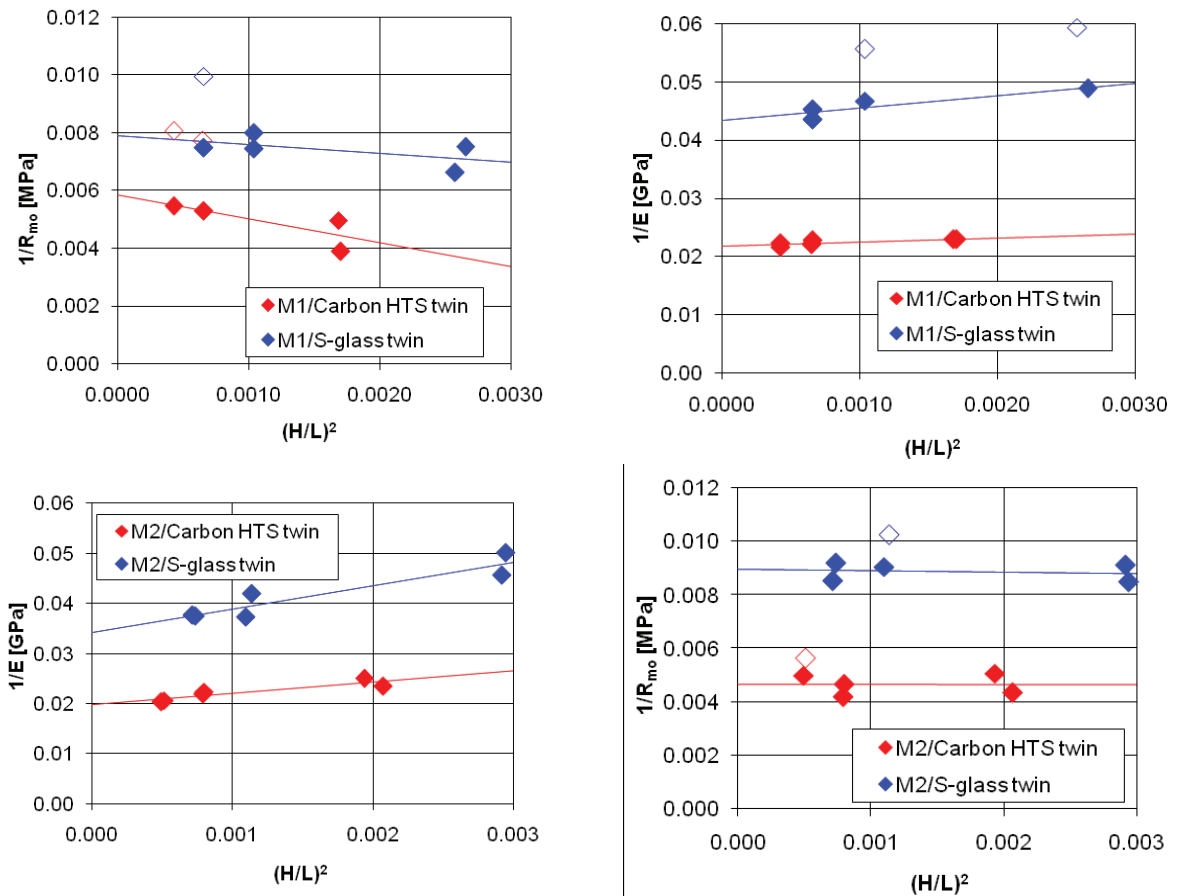

Fig. 1 Reciprocal effective flexural properties of M1 or M2 reinforced by F1 or F2 vs.(H/L)² ratio.

Table 4. Flexural strength of M1 and M2 reinforced by F1 and F2 in accordance with Size-independent technique

Matrix/fabric fiber	Young's module		Shear module		Flexural strength	
	E [GPa]		G [GPa]	E / G [1]	σ_m [MPa]	
M1/F1	45.8 ± 0.6	$\pm 1.3\%$	1.7	26.4	179.3 ± 1.8	$\pm 1.0\%$
M1/F2	23.0 ± 0.6	$\pm 2.6\%$	0.6	41.5	131.1 ± 8.6	$\pm 6.5\%$
M2/F1	50.3 ± 1.7	$\pm 3.5\%$	0.5	95.8	214.8 ± 19.7	$\pm 9.2\%$
M2/F2	29.2 ± 1.5	$\pm 5.1\%$	0.3	115.5	114.5 ± 5.7	$\pm 5.0\%$
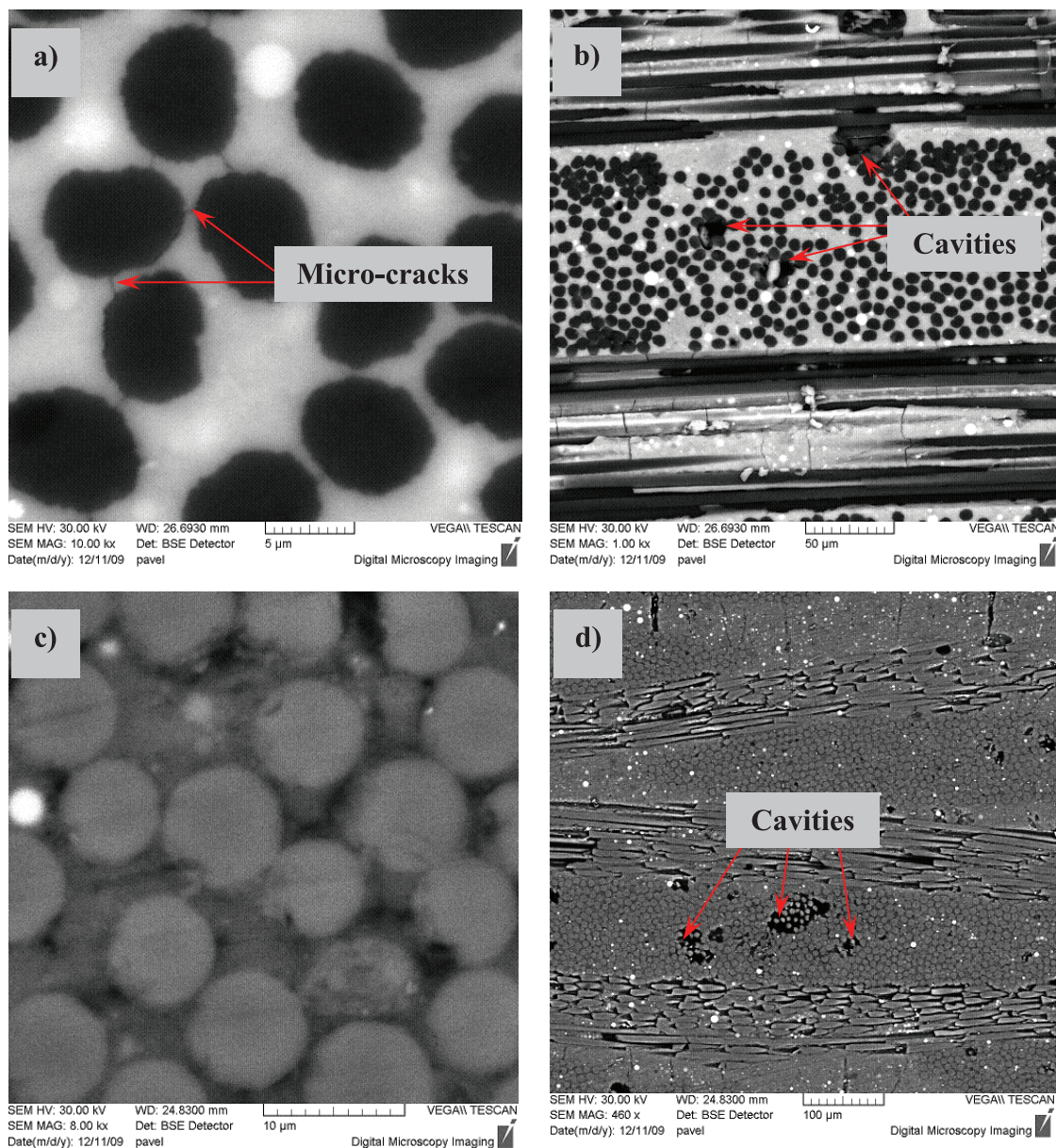
Fig. 2 SEM images on polished sections of geopolymer composite matrix M1 and carbon HTS twill. a) 10.0kx; b) 1.0kx and S-glass twill c) 8.0kx and d) 400x.

The microstructure of these geopolymer matrix composites has been examined using Scanning Electron Microscopy (SEM). Observations from the SEM images (see Fig. 2) of polished sections reveal a favorable adhesion between the geopolymer matrices and the fabric fibers, indicating good penetration of geopolymer resins into the spaces between individual filament fibers, even without the use of compression techniques. However, the analysis also revealed the presence of micro-cracks and several defects, including voids and areas lacking resin. Further investigations are warranted to improve the fiber content, reduce voids, and ultimately enhance the mechanical properties of the composites.

IV. CONCLUSIONS

This study aims to assess the effective impregnation and adhesion between the fiber and geopolymer matrix, as well as to identify micro-cracks, which are inborn defects in inorganic matrix composites. In conclusion, the key results of this study can be summarized as follows:

Geocomposites based on thermal silica from Saint-Gobain - France (very fine size-particle) reinforced with the chosen fabric fibers have been produced and characterized. The flexural properties of four geocompossite systems were evaluated at three scale of sample height (H) to span length (*L*) ratio *H/L* = 20 to 1, *H/L* = 32 to 1 and *H/L* = 40 to 1 in accordance with test spans of DIN V ENV 658:1993-02 and ASTM C1341-06. For geocomposites reinforced by the carbon fabrics, the strengths varied from 229.0 MPa to 153.8 MPa for M1-F1 and 213.7 MPa to 189.0 MPa for M2-F1, the elastic modulus vary around 41 – 48 GPa for boths (M1 or M2/ F1). For geocomposites reinforced by the S-glass fabrics, the strengths varied from 142.1 MPa to 117.0 MPa for M1-F2 and about 110 MPa for M2-F2, the elastic modulus vary around 18 – 26 GPa for boths (M1 or M2/F2).

The flexural properties of the testing coupons exhibit high values that depend on the *H/L* ratios of the tests. By utilizing linear regression, the fictitious Young's modulus (*E*) and the fictitious flexural strength (σ_m) were estimated for the *M1* and *M2* geopolymer matrix systems reinforced by fabric F1 and F2. For the M1/F1 combination, the virtual bending strength is calculated to be 179.3 MPa, with a virtual bending plastic modulus of 45.8 GPa. Similarly, for the M2/F1 combination, the virtual bending strength is estimated to be 214.8 MPa, with a virtual bending plastic modulus of 50.3 GPa. In the case of the geocomposite reinforced by fabric F2, the virtual bending strengths are determined to be 131.1 MPa for M1/F2 and 114.5 MPa for M2/F2, with corresponding virtual bending plastic moduli of 23.0 GPa and 29.2 GPa, respectively.

The scanning electron microscopy analysis proved that the adhesion between geopolymer matrices and the fabric fibers seem quite good and geopolymer resins are well penetrated into the fibers although no compression technique is used, the filament diameter of the using fibers is quite fine (carbon around 5.0 - 7.0 µm and S-glass around 8.0 – 11.0 µm) even though. The micro-cracks as inborn defects of inorganic matrix composites as well.

The obtained results demonstrate that the bending properties of the composites meet the requirements of the composite shipbuilding industry. This suggests that the composites have potential for further exploration, particularly in areas of ship construction that require fire-resistant materials.

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