BASALT FIBER REINFORCED PLASTICS (BFRP) WITH ADVANCED MECHANICAL PROPERTIES

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Keywords: basalt fibers, BRFP, silane coating, wind turbine blades

Abstract
In the present research, the effect of contents network formers and modifiers oxides on mechanical properties of basalt continuous fibers (BCF) was investigated. The influence of surface modification basalt fibers on mechanical behavior of a basalt fiber reinforced plastics (BFRP) was explored experimentally. The basalt/epoxy laminates were fabricated by impregnating woven basalt fibers into epoxy resin via vacuum assisted resin transfer molding (VARTM). The results showed significant improvement in tensile strength after surface modification. The tensile strength and Young's modulus of BCF under study were amounted to 3700±250 MPa and 79±3 GPa respectively. Also BRFP with tensile strength 500±20 MPa, interlaminar shear strength 55±1 MPa and E-modulus not less than 25±1 GPa were obtained.

1. Introduction
High modulus and high strength fibers for fiber-reinforced polymeric composites (FRCs) are particular interest to production of longer wind turbine blades in the renewable energy market. For epoxy-based laminates fibers such as carbon fiber, glass fiber, and basalt fiber have been used as filler materials to improve the overall properties of the composite laminate [1].

The chemical composition of basalts differs to some degree, as shown in Table 1. Besides the chemical compositions, the mechanical properties of basalt fibers from different sources are also different [2-4], probably due to different chemical components and processing conditions like drawing temperature.

Chemical composition [wt.%]	Basalt [3]	E-Glass	S-Glass
SiO_2	48.8~51	52-56	64-66
Al_2O_3	14~15.6	12-16	24-26
$FeO+Fe_2O_3$	7.3~13.3	0.05-0.4	0-0.3
CaO	10	16-25	0-0.3
MgO	6.2~16	0-5	9-11
$Na_2O + K_2O$	1.9~2.2	0-2	0-0.3
TiO_2	0.9~1.6	0-0.8	
MnO	0.1~0.16		
B_2O_3		5-11	

Table 1. Comparison of chemical components between different fibers

The important characteristic is represented by the high mechanical performance comparable to that of glass fibre that together with the lower cost could make basalt fibers appropriate to potentially replace glass fibres in various industrial fields like aerospace, automotive, transportation and shipbuilding. Tensile strength of basalt fiber tends to increase with increasing drawing temperatures, between 1400 and 2100 MPa, between 1200~1550 °C. Young's modulus of basalt fiber varies between 65 and 75 GPa. Compared to glass, most references claimed that basalt fiber has higher or comparable modulus and strength, while a few reported much lower basalt fiber strength than claimed.

In this regard, the aim of this paper was to obtain BCF and BRFP with improved mechanical properties. Interest in studying of the basalt-based GFRP is due to their unique thermal (high temperature applications) and mechanical (high Young's modulus and strength, hardness, durability) characteristics. Furthermore, basalt fibers possess a high ability to crystallize, which greatly simplifies recycling BFRP [5]. In contrast to glass fiber plastic, in which glass fiber is sintered under combustion, basalt fiber polymeric composite materials crystallize and disintegrate into small particles which can be easily recycled.

2. Experimental

2.1. Materials

A commercial basalt fabric (Kamenny Vek, Russia) with 190 ± 20 g/m2 and basalt roving (Kamenny Vek, Russia) with 1200 tex were used. 3-Aminopropyltriethoxysilane (APS) and 3-Glycidyloxypropyltrimethoxysilane (GPS) with a purity of 99% (Penta-91, Russia) were used as a silane functionalization agents. Reagent grade materials SiO_2, MgO, ZnO, Al_2O_3, and Na_2CO_3 were used. The reagents used for the acid treatment were sulfuric acid (95%, Aldrich, USA), hydrochloric acid (36%, Aldrich, USA), acetic acid (100%, Aldrich, USA), isopropyl alcohol (99%, Aldrich, USA), distilled water (99%, Aldrich, USA). The epoxy used was Epikote 285 and the curing agent was Epikure 287.

2.2. Production of basalt fibers

Basalt continuous fibers were prepared using andesitic basalt from the Sil'tsevskoe deposit (Carpathians, Ukraine). A rock placed in a platinum crucible was heated in a high-temperature furnace at a rate of 250°/h to 1200 °C and at 50°/h in a range 1200–1600 °C and then held at 1600 °C for 20 h. The bulk glass was quenched from 1550 to 1590 °C by rapidly pouring the melt into water. Continuous fibers were produced from prepared bulk glass using a laboratory scale system (Fig. 1) [2]. BCF were drawn from melts and wound onto a take up reel. A fiber diameter was controlled by varying the rotation rate of the reel. In subsequent investigation, we used fibers that are 10 - 12 μm in diameter. Sizing was not applied in the fiber production .

2.3. Surface modification basalt continuous fibers

2.3.1. Treatment of basalt continuous fibers in weak acid solutions

In this research, samples were kept in sulfuric acid and hydrochloric acid solutions with varying concentrations for different immersion times at the room temperature. Thereafter, they were removed from the solution and rinsed with distilled water and finally were dried in the air.

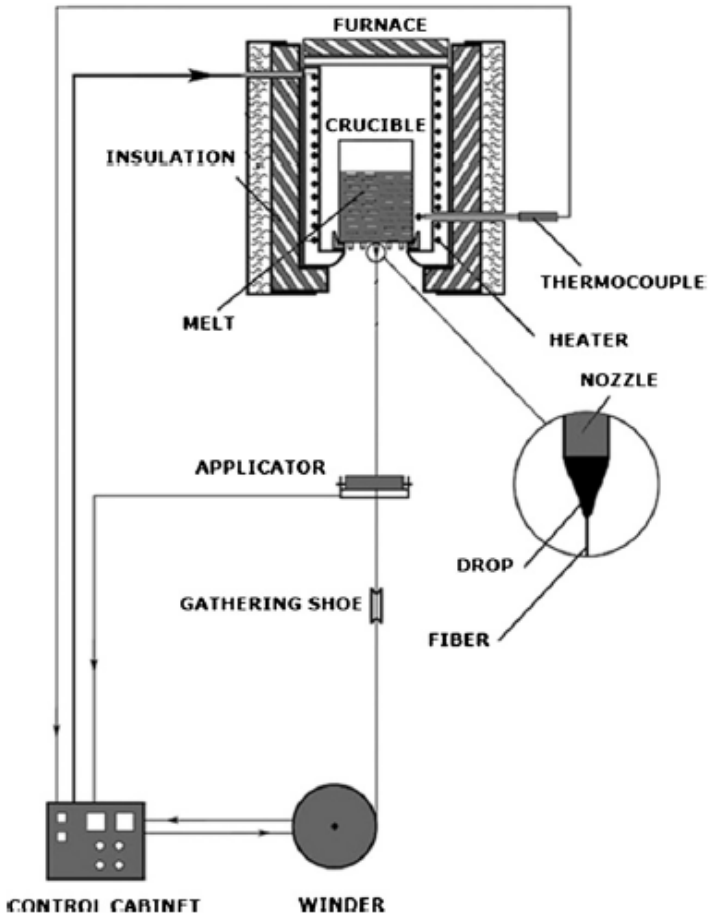

Figure 1. Laboratory scale system for continuous fiberglass production

2.3.2. Heat treatment process

The as-received samples were heat treated using high temperature oven. Prior to the heat treatment process, the fibres were first suspended using customised holding grips in order to isolate the sample from any physical contact which may result in fibre damage.

2.3.2. Silane treated process

APS was mixed with distilled water. Thereafter, the samples were immersed into a 1 wt % solution of APS at pH = 4 at room temperature. Then washed several times with distilled water (at room temperature) again and they were then placed in a oven at 105°C for 1 h. GPS was mixed with isopropyl alcohol. Then samples were immersed into a 10 wt % solution of GPS at room temperature. Then samples were dried in the air for 24 h.

2.4. Fabrication of composites

In order to produce plates with the desired thickness, a sufficient number of fabric plies were impregnated by an epoxy matrix (Epikote 285 + hardener Epikure 287) via VARTM process. The weight ratio of epoxy resin and hardener was 100:40. Six layers of basalt fabric with a size of 250 mm x 250 mm were stacked in the VARTM glass plate mold (size: 300 mm x 500 mm), and were wrapped with vacuum bagging film using a sealant tape. Epoxy solution was then injected into the mold through a vacuum pump for 3–4 min. All the laminates have been cured at room temperature for 24 h and then post-cured at 60°C for 7 h.

2.4. Characterization

The tensile strength of the fibers was determined on a Hounsfield H100K-S universal tensile testing machine. Specimens were mounted in paper support frames using epoxy. The gauge length was 10 mm, and the crosshead speed was 5 mm/min (ISO 5079) [6].

Tensile test of basalt fabric was performed according to ISO 4606 [7] using a universal testing machine (Hounsfield). The test samples in a rectangular shape were cut with dimensions 200 x 25 mm, and the crosshead speed was 100 mm/min.

Tensile test of BFRP was performed according to ASTM D 3039M [8] using a universal testing machine (Hounsfield). The composite plates were cut into dog-bone shape test specimens (L = 250 mm) by water jet cutting. At least five specimens were tested for each sample and the average of which is reported here. The test was conducted at a crosshead speed of 600 N/min at room temperature.

The short beam shear (SBS) test is designed to generate interlaminar shear indirectly through bending and is the most popular method to characterize the apparent interlaminar shear strength of unidirectional, fiber-reinforced composites (ASTM D 2344) [9]. The specimen is placed on two cylindrical supports and a cylindrical head is moved down to apply a force at the center and generate an increasing transverse load until the first failure is recorded. The load at failure is then used to determine the apparent interlaminar shear strength of the composite.

X-ray fluorescence analysis of the specimens was performed on a PANanalytical Axios Advanced spectrometer. Characteristic X-rays were excited using a 4 kW Rh-anode X-ray tube. The excited radiation was recorded by a scanning channel with five exchangeable wave crystals and a detector. Measurements were made in transmission geometry in vacuum. Specimens were prepared in the form of pellets with a binder.

Optical analysis of the fibers and fiber diameter measurements were performed at magnifications of 200× to 1000× on an Olympus BX51TRF modular optical microscope (12V100WHAL lamp (Philips 7724) in transmission, U-LH75XEAPO xenon lamp in reflection) equipped with an Olympus C-5060 camera. The linear dimensions of the fibers were determined by analyzing their images using ImageScope Color software.

Surface analysis was carried out on a Leo Supra 50VP scanning electron microscope (SEM) (Carl Zeiss, Germany). The accelerating voltage of the electron gun was 15 kV, and the magnification was 1000× or higher. Before examination, a carbon layer was deposited onto the surface of the specimen in a Scancoat deposition system (Edwards, UK).

3. Results and discussion

3.1. Composition modification

The content as network formers (SiO_2, Al_2O_3) and network modifiers (MgO, ZnO, Na_2O) was changed. The chemical composition of basalt glasses was determined by X-ray fluorescence analysis as shown in Tab. 2.The influence of different oxides content on the mechanical properties of monofilaments was determined (Tab. 3). Low tensile strength values of untreated BCF are associated with any sizing agent disuse. However, we assume that all regularities at the transition from the laboratory scale to the commercial scale are saved.

Composition [mol.%]	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	ZnO
0	60,1(6)	13,3(2)	12,4(3)	4,3(2)	3,8(2)	3,4(1)	1,6(1)	1,1(1)	-
Si+5	65,1(6)	11,6(2)	10,9(3)	3,8(2)	3,3(2)	3,0(1)	1,4(1)	0,9(1)	-
Mg+14	56,4(6)	7,4(2)	12,4(3)	1,5(2)	17,8(2)	2,6(1)	1,0(1)	0,7(1)	-
Al+4	53,8(6)	17,3(2)	13,5(3)	4,7(2)	4,1(2)	3,7(1)	1,8(1)	1,2(1)	-
Zn+4	57,1(6)	11,3(2)	11,9(3)	4,8(2)	5,2(2)	2,9(1)	1,5(1)	1,0(1)	4,0(3)
Na+3	61,1(6)	9,8(2)	11,2(3)	5,0(2)	4,5(2)	6,4(1)	1,2(1)	0,9(1)	-

Table 2. Glass chemical composition

Sample	Tensile strength [MPa]	Young's Modulus [GPa]
0	1700±100	56±2
Si+5	1445±120	54±1
Mg+14	1700±110	66±2
Al+4	1870±110	58±2
Zn+4	1800±100	64±2
Na+3	2000±100	57±2

Table 3. Mechanical properties of basalt fibers

3.2. Effect of monofilaments treatment

Specimens of monofilaments from roving were treated in 0.5 and 1mol/L sulfuric acid solutions for 0.5, 1, 2; 3 and 4 hours at room temperature (Tab. 4). Increasing of the mechanical properties is due to the removal of the defective surface layer by dissolving it (Fig.2). The process of removing surface defects accompanied by a process of "rise" internal defects on the surface [10].

Time [h]	Tensile strength [MPa]		Young's Modulus [GPa]	
	H_2SO_4, 0.5 [mol/L]	H_2SO_4, 1 [mol/L]	H_2SO_4, 0.5 [mol/L]	H_2SO_4, 1 [mol/L]
0.5	3100±200	2800±250	70±1	67±1
1	2900±150	3000±190	67±1	69±2
2	2800±220	3100±170	67±2	72±1
3	2800±280	3500±200	66±2	75±2
4	2800±180	3700±250	65±1	79+3

Table 4. Mechanical properties of basalt fibers after chemical treatment

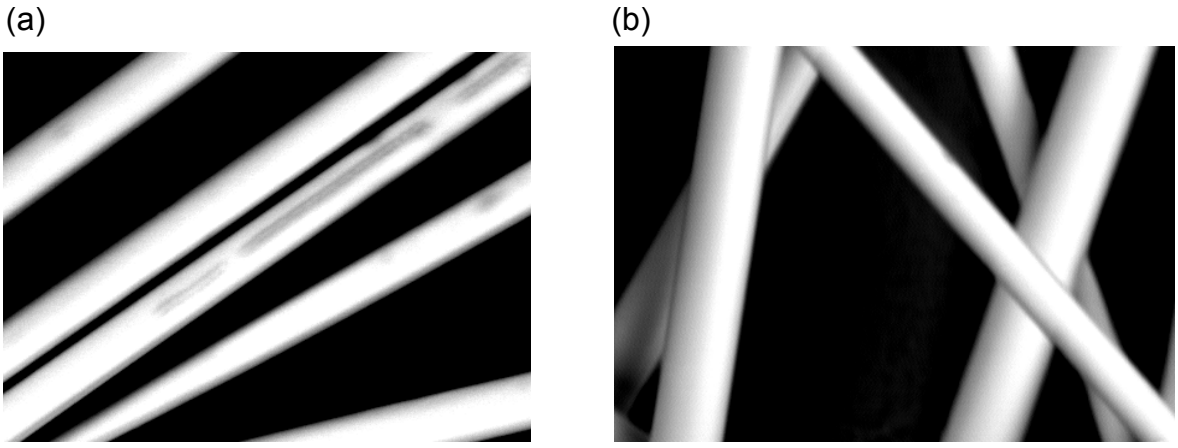

Figure 2. SEM image of as-received basalt fibers (a) treatment in 1mol/L sulfuric acid solutions for 1h (b)

3.2. Effect of basalt fabric treatment

Basalt fabric specimens were subjected to tensile standard tests. The reported data consist of the mean values of five or more tests together with the standard deviations. As it can be noted from Tab. 5, heat treatment at 200°C for 3 h does not lead to a loss of strength. Heat treatment at 400°C for 30 min leads to decrease mechanical strength of basalt fibers. We suggested that decrease mechanical properties are due to both the removal of the commercial coupling agent, and glass recrystallization. Treatment with coupling agents after heat treatment increases the mechanical strength of the samples. The observation is in a good agreement with the findings from Zinck et al. [11] which indicates that silane coating could act as "healing" agent to recover flaws on fibre surface.

Samples	**Ultimate tensile strength [N]**
As-received	1500±100
Heat treatment at 200°C	1400±80
Heat treatment at 400°C	350±20
Heat treatment at 200°C, APS	2300±150
Heat treatment at 200°C, GPS	1800±100
Heat treatment at 400°C, APS	450±30
Heat treatment at 400°C, GPS	400±20

Table 5. Mechanical properties both as received and treated fabrics

Further, specimens were treated in 16 wt.% hydrochloric acid solutions for 10, 20 and 40 min at room temperature. Fig.3 shows the mechanical properties of basalt fabric after treatment. The tensile strength gradually increases with increasing immersion time.

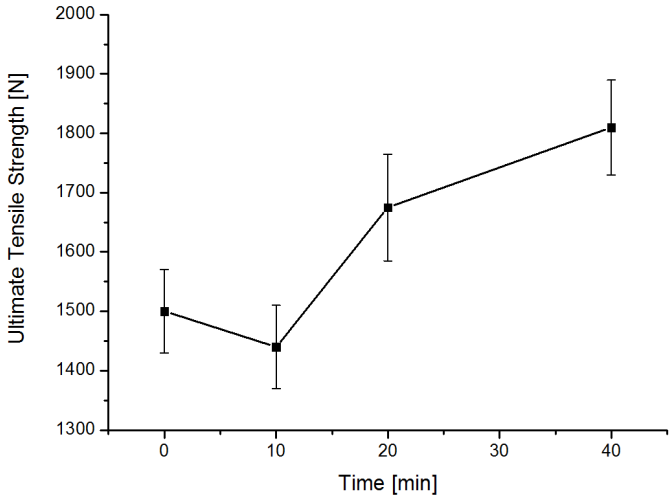

Figure 3. Tensile strength of basalt fabric vs. immersion times

3.3. Tensile test

BFRP showed the lowest tensile strength while the surface modification of fabric has increased the tensile strengths of the composites. Table 6 shows the average tensile strength and Young's modulus of the present samples. Removal of the commercial sizing reduces the mechanical strength of the composite, but has practically no effect its modulus of elasticity. When the basalt fibers are treated at 400°C, the tensile strengths of the composites seem to decrease significantly. It is known that the change in fiber strength has a direct influence on the mechanical properties of glass fiber composites because the fiber strength determines the ultimate load-bearing capacity of the composites. Treatment with APS after heat treatment despite the dramatic increase in the strength of the fabric does not increase the mechanical strength of the composite. Apparently, this is due to insufficient adhesive strength between epoxy and fabric. Treatment with GPS, conversely, increases the mechanical strength of the composite is about 15%. We assumed that in this case the enhanced performance of BFRP is attributed to a good adhesive strength between epoxy and filler providing increased surface area for strong interfacial interaction and good load transfer [12].

Composite	**Tensile strength [MPa]**	**Young's Modulus [GPa]**
As-received	440±40	19±1
200°C	410±10	20±1
400°C	240±20	18±1
200°C, APS	450±20	22±1
200°C, GPS	500±20	25±1

Table 6. Summary of the tensile properties of BFRP

3.4. Interlaminar shear strength (ILSS) test

The results from the short beam shear tests of the composites show the relationship between surface treatments of the glass fibers and mechanical interlaminar properties of the composites (Tab.7). When the basalt fibers are treated with 16 wt.% HCl solution for 10 min and 40 min, it can be seen that the ILSS values of the BFRP increased as compared to that of composites containing as-received fibers. The interlaminar strengths of the composites are increased by approximately 18% for 10 min 16wt.% HCl treatment of the basalt fibers and 25% for 16wt.% HCl treatment of the basalt fibers in comparison with that of the as-received sample.

Composite	ILSS [MPa]
As-received	44±2
16 wt.% HCl, 10 m	52±1
16 wt.% HCl, 40 m	55±1

Table 7. Interlaminar shear strength (ILSS) of BFRP measured by short beam shear (SBS) test

4 Conclusions

Object of research was eight-component system Na_2O-K_2O-MgO-CaO-FeO-Fe_2O_3-SiO_2-Al_2O_3. Andesite basalt was used as a raw material. BCF with various contents of network formers (SiO_2, Al_2O_3) and modifiers (MgO, ZnO, Na_2O) oxides were obtained. Based on "composition - structure - mechanical properties" relationships the follows methods for BCF surface modification were developed: weak acid solution treatment, short-term heat treatment, application of sizing agent. The tensile strength and Young's modulus of BCF under study were amounted to 3700±250 MPa and 79±3 GPa respectively. Also BRFP with tensile strength 500±20 MPa, interlaminar shear strength 55±1 MPa and E-modulus not less than 25±1 GPa were obtained.

References

[1] P. S. Veers, T. D. Ashwill. Trends in the design, manufacture and evaluation of wind turbine blades. *Wind Energy*, 6:245-259, 2003.

[2] S. I. Gutnikov, M. S. Manylov, Ya. V. Lipatov, B. I. Lazoryak, K. V. Pokholok. Effect of the reduction treatment on the basalt continuous fiber crystallization properties. *Journal of Non-Crystalline Solids*, 368:45-50, 2013.

[3] S. E. Artemenko. Polymer composite materials made from carbon, basalt, and glass fibers. Structure and properties. *Fiber Chemistry*, 35(3):226-229, 2003.

[4] J. Sim, C. Park. Characteristics of basalt fiber as a strengthening material for concrete structures. *Composites Part B: Engineering*, 36(6-7):504-512, 2005.

[5] M. S. Manylov, S. I. Gutnikov, K. V. Pokholok, B. I. Lazoryak, Ya. V. Lipatov. Crystallization mechanism of basalt glass fibers in air. *Mendeleev Communications*, 23:361-363, 2013.

[6] ISO 5079. *Determination of breaking force and elongation at break of individual fibres*, 1995.

[7] ISO 4606. *Determination of tensile breaking force and elongation at break by the strip method*, 1995.

[8] ASTM D3039M. *Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials*, 2008.

[9] ASTM D2344. *Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates*, 2013.

[10] V. M. Sglavo, R. Dal Mashio, G. D. Soraru. Effect of etch depth on strength of soda-lime glass rods by a statistical approach. *Journal of the European Ceramic Society*, 11(4):341-346, 1993.

[11] P. Zinck, E. Maeder, J. F. Gerard. Role of silence coupling agent and polymeric film former for tailoring glass fiber sizings from tensile strength measurement. *Journal of Materials Science*, 36:5245-5252, 2001.

[12] K. Sever, M. Sarikanat, Y. Seki, V. Cecen, I. H. Tavman. Effects of fiber surface treatments on mechanical properties of epoxy composites reinforced with glass fabric. *Journal of Materials Science,* 43(13):4666-4672, 2008.