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## Effect of silane/nano-silica on the mechanical properties of basalt fiber reinforced epoxy composites

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#### ABSTRACT

The present study explains the role of surface modification of constituent materials on composite material performance. The influence of silane and nano-hybrid coatings on mechanical properties of basalt fibers and composite materials on their base was investigated. Infrared spectroscopy indicated that modification of basalt fiber surface and nano-SiO<sub>2</sub> was successfully applied. The surface modification leads to the significant increase in the tensile strength of basalt fibers, indicating that silane plays a critical role in the strength retention of basalt fibers. Also it was pointed out that silane coupling agents can be used for the preparation of the nano-hybrid coating. Addition of SiO<sub>2</sub> nanoparticles into the fiber surface was incorporated to enhance the interfacial bonding of basalt fiber reinforced epoxy composite.

#### **ARTICLE HISTORY**

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#### KEYWORDS

Polymer-matrix composites; basalt fibers; nano structures; interface/interphase; mechanical properties

#### 1. Introduction

In recent years, the increase in the application of basalt continuous fiber (BCF) as reinforcement for the fabrication is observed globally. BCF is cost-effective and offers exceptional properties compared to glass fibers.[1] The interest in studying basalt fiber-reinforced plastics (BFRP) proceeds from 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.[2] In contrast to glass fiber plastics, in which glass fiber is sintered under combustion, basalt fiber crystallize and disintegrate into the small particles which can be easily recycled.

BCF is produced by fiber spinning of molten basalt (1300–1500 °C), consisting of plagioclase, pyroxene, and olivine. Its chemical structure is nearly related to glass. The most important components of basalt are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub> and FeO, Na<sub>2</sub>O, and K<sub>2</sub>O. TiO<sub>2</sub> is often presents.[3] BCF is attracted due to their high modulus, high strength, corrosion resistance, high-temperature resistance, extended operating temperature range, and easy to handle.[4,5]

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Mechanical properties of fiber-reinforced plastics depend on mechanical properties of constituent materials, the nature of interfacial bonds, mechanisms of a load transfer in an interface, and an adhesion strength between the fiber and the matrix.

The surface heterogeneities such as surface flaws, structure defects, and impurities [6] make the measured mechanical properties remarkably lower than their maximum theoretical values. In order to improve the mechanical properties of the BCF, a compressive residual stress on the basalt glass surface can be made. There are two popular techniques to produce the compressive surface stress on the glass surface, namely a thermal tempering [7] and an ion exchange (or a chemical tempering).[8]

The adhesion strength between the fiber and the matrix can be attributed to some combination of the following phenomena: mechanical adhesion, adsorption and wetting, electrostatic attraction, and chemical bonding.

Surface treatment of reinforcement is a common method to improve mechanical and adhesion properties by removing the surface flaws and increasing the electrostatic interactions or facilitating chemical bonding between the reinforcement material and the matrix, respectively.[9,10]

Organofunctional silanes can be served as a coupling agent to promote fiber-matrix interaction levels by various adhesion mechanisms such as the chemical bonding and molecule interdiffusion. Moreover, these multifunctional species can make a huge impact on the fiber strength. It has been reported that silanes seem to have ability to 'heal' surface flaws and improve the average fiber strength. It has been advocated by some authors that the silane deposits can patch up the flaws to some extent and in turn reduce the stress concentration at the flaws.[11,12]

Generally, the addition of nanofillers such as nanotubes and nanoparticles is the most efficient approach to enhance the mechanical properties and the interfacial adhesion, since the combination of conventional fiber and nanofillers in the polymer matrices led to a new generation of multiscale, multifunctional materials with a high performance.[13,14] Also, it is demonstrated that the addition of the nano-scale particles in the matrix can increase the toughness of the matrix and improve the interface properties of composites. Furthermore, the multiscale reinforcement, containing fibers together with nano-scale particles in the matrix or on the fibers surface can increase the delamination resistance of the fiber-reinforced composites.[15–17] However, the nano-scale particles have a high surface area. This hydrophilic surface does not process good compatibility with the polymer resin, and therefore the particles cannot be wetted very well by the resin. On the contrary, the nano-scale particles with the hydrophilic surface easily adhere to each other through hydrogen bonding and form irregular agglomerations. The agglomerations of the nanoparticles can form a network through the whole polymer matrix and occlude the liquid polymer in their interparticle voids, thereby affecting the rheology of the composite underfill and giving a significant rise to the viscosity as filler loading increases.[18] Silane coupling agents can be used for the treatment of the nano-scale particles due to their unique bifunctional structure (one end can react with the silanol groups on silica surface and the other end can react with the polymer). It is shown that the nanosilica treatment by silane with a longer reaction time assisted with the pre-treatment by sonication can achieve mono-dispersed silica.[19] Further, the use of preformed nano-scale silica particles suspended in fiber coating formulation offers a direct route to nano-scale fiber surface roughness.[20]

In the work reported here, attempt is made to meet the challenges of modifying the basalt fiber/epoxy interface by incorporating nano-SiO<sub>2</sub> on the fiber surface. For this purpose, composite structures reinforced by basalt fabric with modify surface are produced using a vacuum infusion process. The effect of modification by silane and nano-hybrid coatings with nano-silica on the mechanical properties of basalt fibers and the interface performance of the corresponding composite materials are investigated.

#### 2. Experimental

#### 2.1. Materials

The commercially available plain basalt fabric with surface density  $210 \pm 25 \text{ g/m}^2$  and with an average fiber diameter of  $13 \pm 2 \mu m$  (Kamenny Vek, Russia) was employed in this study.

The reagents with a purity of 99% used for the BCF modification were following: 3-aminopropyltriethoxysilane (APS) and 3-glycidyloxypropyltrimethoxysilane (GPS), acetic acid, ethanol, spectroscopic grade acetone, distilled water, supplied by Aldrich. Silica nanoparticles (SiO<sub>2</sub> powder) with diameter ranging between 15 and 25 nm and purity of 99.8% were used. Their specific surface area measured by the BET method was 140–180 m<sup>2</sup>/g.

#### 2.2. Surface modification of BCFs

In order to remove any organic matter from the glass surface, as-received basalt fabric was subjected to two different cleaning processes: heat treatment at 300 °C for 3 h and extraction in acetone for 24 h. The type of surface modification and samples codes is summarized in Table 1.

Silanization process was performed using 3-aminopropyltriethoxysilane (APS) and 3-glycidyloxypropyltrimethoxysilane (GPS). Silane coupling agents were prepared under identical conditions in order to treat glass surfaces. In these solutions, the co-solvent of ethanol (95 wt.% in total solvent) and distilled water (5 wt.% in total solvent) was used, and the silane concentration was fixed at 1 wt.%. After the silane coupling agents were hydrolyzed at pH 4 for 1 h with acetic acid solution, the basalt fabric was dipped in the hydrolyzed silane solution for 30 min and then dried at 110 °C for 30 min. The scheme of silane interaction with BCF by hydrolysis process is presented in Figure 1.

To prepare nano-hybrid coating, previously, nano-SiO<sub>2</sub> was dried at 80 °C under vacuum for 24 h to eliminate the possible absorbed water on the particles surface. Solution with

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	ABF-GPS-SiO <sub>2</sub> -1.0	1 wt.% 3-glycidyloxypropyltrimethoxysilane: 1 wt.% nano-SiO <sub>2</sub>	

Table 1. Sample codes and type of surface treatment.



Figure 1. Interaction of silane with basalt fibers by hydrolysis process.

different contents of nano-SiO<sub>2</sub> (0.1–1 wt.%), 95 wt.% in total solvent of ethanol, and 5 wt.% in total solvent of distilled water was dispersed by sonication at 200 W output power for 1 h. Then, a 1 wt.% solution of silane coupling agent was slowly added into the mixture. The pH value was adjusted to around 4–5 by acetic acid. The mixture was dispersed by sonication for 1 h and then stirred for 8 h at refluxed temperature. After that, the cleaned basalt fabric was dipped into the designed coating solutions for 15 min. The fibers were then air-dried overnight at room temperature, followed by oven drying at 110 °C for 1 h. The coated fabric was cooled and stored in a desiccator prior to use. The procedure used for treatment nano-SiO<sub>2</sub> is described in Figure 2.

#### 2.3. Single fiber fragmentation test coupons

The single BCF was placed at the center of a dog bone-shaped cavity in a silicone mold. The fibers were kept straight by applying rubber cement to each end. Then, the epoxy mix was poured into the mold, covering the fiber completely. The cured specimens were sanded with paper of increasing grit size and then polished until they were transparent and perfectly flat.

#### 2.4. Preparation of BFRP

In order to produce plates with the desired thickness, the sufficient number of plies was impregnated by an epoxy matrix that was mixed with hardener. The impregnation of 16 sheets fibrous reinforcements was carried out using the vacuum infusion process. Bisphenol-A type epoxy resin (EPIKOTE LR 285) and curing agent 3,3'-dimethyl-4,4'-diamino-dicyclohexy-lmethan (EPIKURE LH 287) produced by the Hexion Specialty Chemicals company were used as the matrix system. The resin was mixed with the curing agent at 100:40 by weight



Figure 2. Mechanism of silane grafting on the surface of nano-SiO<sub>2</sub> particles.

and degassed under vacuum at room temperature. After being initially cured at 23  $^{\circ}$ C for 24 h, all samples were post-cured at 80  $^{\circ}$ C for 15 h.

#### 3. Methods

#### 3.1. Infrared spectroscopy

Samples for IR spectroscopy were prepared by compression of the mixture of powdered fiber or nanosilica and KBr in a weight ratio of 1:20, respectively. FTIR spectra were measured using FTIR spectrometer Bruker Tensor 27. The absorption spectrum was recorded in the range of 400–4000 cm<sup>-1</sup>.

#### 3.2. The thermal gravimetric analyzer

The thermal gravimetric analyzer (TGA) was used to measure the surface absorption of nanosilica and BCF before and after treatment. The weight loss of samples as a function of temperature was studied using Netzsch STA Jupiter 449C equipped with a high-temperature furnace (t = 20-1000 °C; heating rate: 10 °C/min). A high-sensitivity sample holder with Pt/Pt–Rh thermocouples was used. The TGA analyses were performed in air atmosphere.

#### 3.3. Scanning electron microscopy

The JEOL JSM-6390LA microscope was used for the scanning electron microscope (SEM) analysis. The accelerating voltage was set to 20 kV. The morphology of the fibers was determined in the secondary electron imaging mode. Before the examinations, all fibers were coated with a conducting gold layer.

#### 3.4. Optical analysis

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

#### 3.5. Characterization

The mechanical properties of the fibers were determined on the Hounsfield H100 K-S universal tensile testing machine. The specimens were mounted in paper support frames using epoxy. The gage length was 10 mm, and the crosshead speed was 5 mm/min (ISO 5079). Single-fibers were meticulously separated from the basalt fiber strands. To obtain the most accurate results, test was performed for at least 50 fibers. The errors of tensile strength measurements were less than  $\pm 5\%$  and Young's modulus measurements were less than  $\pm 4\%$ .

Single fiber fragmentation test (SFFT) was used to measure the interfacial shear strength (IFSS) of each BCF-epoxy matrix system. The test samples were subjected to a gradual tensile load, which led to the breakage of the fiber into fragments. The tension load was increased until the number of fragments reached a maximal value (saturation state). The Olympus optical microscope with polarized light was used to determine the number of fragments and the length of each fragment. The IFSS was calculated with the Kelly–Tyson model [21]:

$$IFSS = \frac{\sigma_f d}{2 l_c}$$
(1)

where  $\sigma_{\rm f}$  is the fiber tensile strength corresponding to the fiber length equal to the critical fragmentation length  $l_c$ , d is the fiber diameter (µm), and  $l_c$  is the critical fragmentation length (µm), which can be calculated from following equation:

$$l_{\rm c} = \frac{4}{3}\bar{l} \tag{2}$$

where *l* is the mean fiber fragmentation length ( $\mu$ m) when the saturation sate is reached.

The Olympus optical microscope with polarized light was used to observe the photoelastic birefringence patterns generated around the fiber break when the number of fiber fragments reached saturation.

The different mechanical tests were carried out, according to the ASTM specifications, on the composites: tensile and short beam shear (SBS) tests. The tensile properties of the BFRP were measured according to ASTM D 3039 using Instron 5580 (USA) tensile test machine. Samples were cut into dimensions of  $250 \times 15 \times 3$  mm (Length × Width × Thickness). The test was conducted at a crosshead speed of 2 mm/min. The SBS test is designed to generate interlaminar shear indirectly through bending. It is the most popular method to characterize the apparent interlaminar shear strength (ILSS) of unidirectional, fiber-reinforced composites (ASTM D 2344). The specimen is placed on two cylindrical supports and the cylindrical head is moved down to apply the 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 ILSS of the composite. At least of 10 samples were tested in each case.

#### 4. Results

#### 4.1. Basalt fiber surface morphology

The fiber morphology and surface texture are investigated by SEM. The representative micrographs of the as-received, heat treated, and basalt fiber after extraction in acetone are



Figure 3. SEM micrographs of basalt fibers: (a) as-received; (b) heat treated at 300 °C for 3 h; and (c) after extraction in acetone 24 h.

presented in Figure 3(a)-(c). As-received basalt fiber is coated with a commercial sizing. The surface irregularities of as-received basalt fiber and fiber after thermal treatment are shown. However, long cylinders with smooth surfaces are the common morphological characteristics of fibers after extraction in acetone. It is a struggle to find anything besides vast regions of smooth fiber surface. The amount of sizing present on the BF, HTF, and CBF, as evaluated through the measurement of the TGA weight loss, is about 0.88, 0.24, and 0.11% of the fiber weight, respectively.

Comparing the SEM micrographs of the silane-treated basalt fiber (Figure 4(a), (e)) with fiber after extraction in acetone (Figure 3(c)), the coating layer is observed on the surface of fiber. Some differences can be observed for the silanizated fiber as a consequence of the silanization treatment. It is shown that the silane interaction is not uniform along the fiber surface. This is possibly owing to the nonuniform interaction between the silane coupling agent and the fiber surface. It seems, probably, that the fibers become bonded one to another when they are silanizated. The TGA weight of APS and GPS silane-treated basalt fibers is 0.43 and 0.39% of the fiber weight, respectively.

There are a lot of attachments when the basalt fiber is treated with the mixture of coupling agents and nano-SiO<sub>2</sub>. The representative SEM images of the fibers with the nano-hybrid coating are shown in Figure 4(b)–(d) and (f)–(h), which indicated the appearance of nano-SiO<sub>2</sub> on the fiber surface. It is clearly observed that nano-hybrid coating increases the fiber surface roughness as compared to the ABF and silanized fibers. Also, it is shown that in the case of ABF–APS–SiO<sub>2</sub>–0.5 and ABF–GPS–SiO<sub>2</sub>–0.5 systems, the mass fraction of nano-SiO<sub>2</sub> in the coating may be too high to cause the issues of nano-SiO<sub>2</sub> agglomeration.

#### 4.2. IR spectra

The IR spectra of analyzed fibers are shown in Figure 5. The spectra of thermal treated and extracted fibers exhibit none of the characteristic bands of commercial sizing. Therefore, it is indicated that the concentration of the extracted silanes could be below the detection limit. The broad band between 3200 and 3650 cm<sup>-1</sup> in the spectrum of as-received fibers is assigned to stretching in N–H/O–H bonded to C and Si alike. The collection of bands around 2800–3000 cm<sup>-1</sup> is attributed to stretching in C–H of CH, CH<sub>2</sub> and CH<sub>3</sub>, both in aromatic and aliphatic compounds. The small shoulder at about 1300 and 1730 cm<sup>-1</sup> can be



**Figure 4.** SEM micrographs of basalt fibers: (a) APS treated basalt fibers; (b)  $ABF-APS-SiO_2-0.1$ ; (c)  $ABF-APS-SiO_2-0.5$ ; (d)  $ABF-APS-SiO_2-1.0$ ; (e) GPS treated basalt fibers; (f)  $ABF-GPS-SiO_2-0.1$ ; (g)  $ABF-GPS-SiO_2-0.5$ ; (h)  $ABF-GPS-SiO_2-0.5$ ; (h)  $ABF-GPS-SiO_2-1.0$ .

Notes: ABF – basalt fibers after extraction in acetone for 24 h, APS – 1 wt.% 3-aminopropyltriethoxysilane, APS–SiO<sub>2</sub>-x – 1 wt.% 3-aminopropyltriethoxysilane: x wt.% nano-SiO<sub>2</sub>, GPS–SiO<sub>2</sub>-x – 1 wt.% 3-glycidyloxypropyltrimethoxysilane: x wt.% nano-SiO<sub>2</sub>, x = 0.1, 0.5, 1.



Figure 5. The infrared spectra of basalt fibers: (a) as-received; (b) heat treated at 300 °C for 3 h; and (c) after extraction in acetone 24 h.

corresponded to stretching of C=O in esters or carbonyl. The bands around  $1100 \text{ cm}^{-1}$  are assigned the stretching of C–O and Si–O that could indicate the presence of polyethylene and or some kind of silicon oxide compounds.[22]

Figures 6 and 7 show a spectral subtraction between the spectra of the coupling agent on the basalt fibers treated with 1 wt.% APS and 1 wt.% GPS aqueous solution and then dried, and the basalt fiber after the acetone extraction. It is shown in Figure 6, that the difference spectrum is very similar to the highly crosslinked polyaminosiloxane homopolymer in



**Figure 6.** The infrared spectra of basalt fiber/coupling agent system: (a) fiber treated with 1 wt. % APS coupling agent and dried; (b) basalt fibers cleaned by acetone extraction; and (c) APS on the basalt fiber with the contribution of the fiber excluded.



**Figure 7.** The infrared spectra of basalt fiber/coupling agent system: (a) fiber treated with 1 wt.% GPS coupling agent and dried; (b) basalt fibers cleaned by acetone extraction; and (c) GPS on the basalt fiber with the contribution of the fiber excluded.

terms of band positions and relative intensities. The asymmetric Si–O–Si stretching mode is observed as a pair of peaks with maxima at about 1030 and 1130 cm<sup>-1</sup>. These two bands indicate that APS on the surface of basalt fibers is a linear or cyclic polyaminosiloxane and most of the polyaminosiloxanes consist of more than two APS units.[23] These results confirm that APS crosslinked on the basalt fiber surface. The infrared band that appears at 1570 cm<sup>-1</sup> is the deformation mode of the NH<sub>2</sub> group forming hydrogen bonds with silanols. The bands at 1350 and 1450 cm<sup>-1</sup> can be assigned to CH<sub>2</sub> groups. The characteristic stretching bands from methyl and methylene groups can be observed between 2860 and 2890 cm<sup>-1</sup> for all of the silanized samples. 10 🛞 K. L. KUZMIN ET AL.

The difference of IR spectrum of the film deposited from a 1 wt.% GPS solution on basalt glass fibers is shown in Figure 7. The strong band near 3380 cm<sup>-1</sup> was related to water and to silanol groups. The appearance of this band and the bands at about 910 and 800 cm<sup>-1</sup> (also due to silanol groups) indicated that the silane is hydrolyzed in solution to form silanol species. The epoxide groups absorb near 1300, 910, and 800 cm<sup>-1</sup> due to asymmetric and symmetric C–O–C stretching (ring breathing). The strong sharp band near 1320 cm<sup>-1</sup> is due to the ether (CH<sub>2</sub>OCH<sub>2</sub>) groups. The other distinct band which is characteristic of silanes was the band at 1130 cm<sup>-1</sup> due to the asymmetric Si–O–Si stretching. The bands near 1670 and 1730 cm<sup>-1</sup>, which is due to C=C and C=O stretching, are also seen in Figure 7.[24]

The chemical structures of untreated and treated nano-SiO<sub>2</sub> particles are analyzed using IR spectroscopy (Figure 8). For the untreated particles, the characteristic peaks of Si–O–Si at 1030–1130 cm<sup>-1</sup> and 470 cm<sup>-1</sup>, and Si–OH at 960 cm<sup>-1</sup> indicate the presence of SiO<sub>2</sub> compound. For the treated particles, the characteristic peaks of SiO<sub>2</sub>, multiple absorption peaks of CH<sub>3</sub>, CH<sub>2</sub>, appear in the range of 2850–3060 cm<sup>-1</sup>.[25] These peaks are the characteristic peaks of the organic coupling agent. In addition, the peaks at 1100 cm<sup>-1</sup> and 960 cm<sup>-1</sup> are wider than those for the untreated particles. For aminopropyl-SiO<sub>2</sub> particles, the symmetric and asymmetric stretching vibrations of NH<sub>2</sub> bond, located at 3290 and 3360 cm<sup>-1</sup>, are seen on the spectrum of aminopropyl-SiO<sub>2</sub> particles. For glycidoxypropyl-SiO<sub>2</sub> particles characteristic peaks of oxirane ring can be observed at 910 and 1310 cm<sup>-1</sup>. The characteristic peaks for the treated particles indicate that the coupling agents are successfully grafted on the SiO<sub>2</sub> particle surfaces during the silanization process.

#### 4.3. Single-fiber tensile testing and Weibull analysis

Due to the nature of brittle solid, basalt fibers normally exhibit the strength distribution, which needs to be analyzed using probabilistic approaches. A statistical analysis of the fiber tensile strength is commonly made using the two-parameter Weibull distribution. The



**Figure 8.** The infrared spectra of: (a) untreated nano-SiO<sub>2</sub>; (b) nano-SiO<sub>2</sub> treated by APS; and (c) nano-SiO<sub>2</sub> treated by GPS.

procedure is described in details in Refs.[7,8,26]. The tensile strength data are plotted in a Weibull plot, that is,  $\ln(\ln(1/1-P))$  vs.  $\ln(\text{tensile strength})$  from which the Weibull parameters  $\sigma_0$  and m are found by linear regression of the data.  $\sigma_0$  is the characteristic strength taken at the failure probability of 63.2%; and m is Weibull's modulus representing the slope of the strength distribution. Each test series contains 60–65 fibers. The Young's modulus is calculated as the average of the all tests results.

Figure 9 displays these Weibull plots for as-received (BF), heat treatment (HTBF), and basalt fiber after extraction in acetone (ABF). It is pointed out that the tensile strength of basalt fibers decreases after sizing removal. Weibull's modulus m slightly decreases after heat treatment from 7.5 to 6.8 as compared with as-received basalt fibers. Also, after heat treatment at 300 °C for 3 h noticeable knee in the Weibull data is shown. The removal of sizing does not cause any remarkable change in the Young's modulus.

Weibull plots for silanized basalt fibers are shown in Figure 10. The comparison of Weibull plots in between basalt fiber after extraction in acetone- and silane-treated basalt fibers clearly shows that the silanes have the significant effect on the fibers strength. In the same Weibull coordinate, the Weibull plots of ABF are located on the left of those from APS-ABF and GPS-ABF. The tensile strength of silanized basalt fibers increases to 3361 MPa for APS treated and 3518 MPa for GPS treated compared with basalt fibers after acetone extraction. In general, Weibull's module of the silanized fibers is higher, as shown in Table 2. However, the silane-treated basalt fibers apparently show nonlinear Weibull plots in Figure 10.

After the surface modification of the basalt fibers with nano-hybrid coating, the tensile strength increases compared to unmodified ones, as shown in Figures 11 and 12. The tensile strength of the basalt fibers modified by coating with 0.1 wt.%  $SiO_2$  reaches its maximum value compared to other surface modifications. It can be seen that the regression coefficients  $R^2$  are close to unity for studied conditions. The tensile strength evaluation by the



**Figure 9.** Tensile strength distribution in Weibull diagrams.

Notes: That is the plot of  $\ln(\ln(1/1-P))$  vs. In(tensile strength). Where P is the probability of failure for as-received, heat treated at 300 °C for 3 h and basalt fibers after extraction in acetone for 24 h.



**Figure 10.** Tensile strength distribution in Weibull diagrams. Notes: That is the plot of  $\ln(\ln(1/1-P))$  vs. In(tensile strength). Where *P* is the probability of failure for APS and GPS treated basalt fibers.

**Table 2.** Values of the shape (*m*) and scale ( $\sigma_0$ ) unimodal Weibull two-parameter cumulative distribution function and Young's modulus of differently treated basalt fibers.

Sample	$\sigma_{_0}$ (MPa)	т	R <sup>2</sup> (%)	E (GPa)
BF	3093	7.5	0.98	58.6 ± 2.4
HTBF	2510	6.8	0.92	$61.2 \pm 3.2$
ABF	2860	7.1	0.96	59.1 ± 2.3
ABF–APS	3361	9.3	0.97	61.1 ± 1.9
ABF-APS-SiO <sub>2</sub> -0.1	3466	11.1	0.99	$61.0 \pm 2.0$
ABF-APS-SiO <sub>2</sub> -0.5	3282	9.2	0.96	60.9 ± 2.1
ABF-APS-SiO <sub>2</sub> -1.0	3179	8.2	0.93	61.1 ± 2.3
ABF–GPS	3518	9.9	0.96	$60.8 \pm 1.8$
ABF-GPS-SiO <sub>2</sub> -0.1	3673	12.4	0.99	$61.0 \pm 1.8$
ABF-GPS-SiO <sub>2</sub> -0.5	3310	10.5	0.96	61.1 ± 1.9
ABF-GPS-SiO <sub>2</sub> -1.0	3222	8.7	0.94	61.0 ± 2.0

Weibull distribution indicates that parameters m and  $\sigma_0$  slightly increase for samples with concentrations of 0.1 wt.% SiO<sub>2</sub> particles and then decrease when the concentration of SiO<sub>2</sub> particles continues to increase, as shown in Table 2.

#### 4.4. Interfacial shear strength

For better understanding, the relationship between properties of coatings and mechanical properties in the interface region, a SFFT is employed to measure the IFSS of the basalt fibers and the epoxy matrix interface. The IFSS corresponding to each system is tabulated in Table 3.

The removal of the sizing leads to decrease in the IFSS, probably, because the adhesion promoters present in the sizing is removed. Samples HTBF and ABF have approximately the same critical aspect ratio  $(l_c/d)$ , but the values of IFSS vary by as much as 6%. This variation is solely due to the variations in the strengths of the individual fibers.



**Figure 11.** Tensile strength distribution in Weibull diagrams. Notes: That is the plot of  $\ln(\ln(1/1-P))$  vs.  $\ln(\text{tensile strength})$ . Where *P* is the probability of failure for basalt fibers; for APS treated and basalt fibers with nano-hybrid coating (ABF – basalt fibers after extraction in acetone for 24 h, APS–SiO<sub>2</sub>–x – 1 wt.% 3-aminopropyltriethoxysilane: *x* wt.% nano-SiO<sub>2</sub>, *x* = 0.1, 0.5, 1).



**Figure 12.** Tensile strength distribution in Weibull diagrams. Notes: That is the plot of  $\ln(\ln(1/1-P))$  vs.  $\ln(\text{tensile strength})$ . Where *P* is the probability of failure for basalt fibers; for GPS treated and basalt fibers with nano-hybrid coating (ABF – basalt fibers after extraction in acetone for 24 h, GPS–SiO<sub>2</sub>–x – 1 wt.% 3-glycidyloxypropyltrimethoxysilane: *x* wt.% nano-SiO<sub>2</sub>, *x* = 0.1, 0.5, 1).

With constant fiber strength, shorter fragment length normally indicates better fiber/ matrix adhesion. However, modification process resulted in a change of the fiber strength, as demonstrated in the single fiber tensile tests. Therefore, a quantitative study of the IFSS is carried out using the Kelly–Tyson model.

Sample	l <sub>c</sub> /d	IFSS (MPa)	Relative increase (%)
BF	47 ± 3	35 ± 3	_
HTBF	$52 \pm 3$	25 ± 2	_
ABF	49 ± 3	30 ± 2	_
ABF–APS	42 ± 3	42 ± 3	42
ABF-APS-SiO <sub>2</sub> -0.1	38 ± 2	49 ± 2	47
ABF-APS-SiO <sub>2</sub> -0.5	40 ± 3	44 ± 3	43
ABF-APS-SiO <sub>2</sub> -1.0	43 ± 3	39 ± 3	38
ABF–GPS	42 ± 2	43 ± 3	43
ABF-GPS-SiO <sub>2</sub> -0.1	36 ± 1	54 ± 2	53
ABF-GPS-SiO <sub>2</sub> -0.5	38 ± 2	46 ± 3	46
ABF-GPS-SiO <sub>2</sub> -1.0	$44 \pm 3$	38 ± 3	38

**Table 3.** Interfacial shear strength (IFSS) of basalt fiber/epoxy systems measured by the fragmentation test, where  $l_c$  – critical fragment length and d – diameter of fiber.

Note: Relative increase (%) calculation: ABF is considered as the reference material.

The IFSS for the APS- and GPS-coated basalt fibers is significantly higher than that for the uncoated fibers. The value on IFSS of E-glass fiber epoxy composites is 30 MPa according to Zhou et al. [27]. The treatment of the ABF with APS and GPS increases the IFSS by 42 and 43%, respectively.

It is clearly demonstrated that the presence of nano-SiO<sub>2</sub> on the fiber surface improves the IFSS. The best results are achieved for the case where SiO<sub>2</sub> concentration is low. The concentration in SiO<sub>2</sub> particles of 0.1 wt.% resulted in the shortest fragments lengths. The surface modification of the basalt fibers modified by nano-hybrid coating with 0.1 wt.% SiO<sub>2</sub> increases the IFSS by 47 and 53%, respectively, over that of the ABF. The estimated average IFSS values are 49 (3) and 54 (2) MPa for these samples, respectively. However, the samples with high concentrations of nano-SiO<sub>2</sub> show weaker interfacial adhesion, and thus the stress transfer is not effective.

#### 4.5. Mechanical characterization of basalt fiber composites

The basalt fiber-reinforced plastic specimens are subjected to tensile standard tests. The reported data consist of the mean values of 10 or more tests together with the confidence interval represented by vertical bars.

The variations of tensile properties of composites based on heat-treated fibers and fibers after acetone extraction composites are shown in Figure 13. The tensile strength of epoxy composite containing ABF reinforcement is higher than that of HTBF composite. However, the removal of the sizing by acetone extraction slightly decreases the tensile strength of BFRP from 515 (15) to 490 (20) MPa. The Young's modulus does not change dramatically.

As shown in Figure 13, the use of silane coupling agent for surface treatment improves the tensile strength of basalt fiber epoxy composite in comparison with as-received one. If we observe Figure 13, we can see that APS and GPS treatment lead to an increase in the tensile strength value between 530 (15) MPa and 545 (15) MPa. Also, the surface modification of basalt fibers with nano-hybrid coating leads to an increase in the tensile strength. It is clearly seen that among the surface-treated fiber composites with nano-hybrid coating, 0.1 wt.% SiO<sub>2</sub>-treated fiber composite shows the improvement in terms of the tensile strength. Moreover, the tensile strength decreases with an increase in the SiO<sub>2</sub> particle concentration in the range of 0.5–1.0 wt.%. The tensile strength is increased from 490 (20)



**Figure 13.** Tensile strength of the composites with various surface treatments of basalt fibers. Notes: BF – As-received basalt fiber, HTBF – Heat treatment basalt fiber at 300 °C for 3 h, ABF – basalt fibers after extraction in acetone for 24 h, APS – 1 wt.% 3-aminopropyltriethoxysilane, APS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-aminopropyltriethoxysilane: 0.5 wt.% nano-SiO<sub>2</sub>, APS–SiO<sub>2</sub>–0.5 – 1 wt.% 3-aminopropyltriethoxysilane: 0.5 wt.% nano-SiO<sub>2</sub>, APS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-aminopropyltriethoxysilane: 0.5 wt.% nano-SiO<sub>2</sub>, APS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-glycidyloxypropyltrimethoxysilane; GPS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-glycidyloxypropyltrimethoxysilane: 0.5 wt.% nano-SiO<sub>2</sub>, GPS–SiO<sub>2</sub>–0.5 – 1 wt.% 3-glycidyloxypropyltrimethoxysilane: 1 wt.% nano-SiO<sub>2</sub>.

MPa for the composite based on basalt fiber cleaned by acetone to 560 (15) and 570 (15) MPa for the ABF-APS-SiO<sub>2</sub>-0.1 and ABF-GPS-SiO<sub>2</sub>-0.1 epoxy composite, respectively.

The ILSS of the basalt fiber-reinforced composite before and after surface modification is represented in Figure 14. The removal of the sizing decreases ILSS from 38 (1) to 35 (1) MPa after acetone extraction. It is observed in Refs. [13,28] that average value on ILSS of E-glass fiber epoxy composites is about 32 MPa. The presence of coupling agents does lead to an increase in the ILSS of the composites. It can be related to the effect of an increased degree of adhesion at the interfaces between the three elements in this system, that is the basalt fiber, the matrix, and the silane coupling agent. The nano-hybrid coating shows a more significant increase in ILSS than the silnized basalt fibers. The best results are, however, achieved for the samples with 0.1 wt.% concentrations of nano-SiO<sub>2</sub> particles. The interlaminar strength for the samples ABF–APS–SiO<sub>2</sub>–0.1 and ABF–GPS–SiO<sub>2</sub>–0.1 is enhanced by approximately 40 and 43%, respectively, in comparison with that of the ABF sample. However, a further increase in nano-SiO<sub>2</sub> content in the coating to 1.0 wt.% is not beneficial, due probably to agglomeration of nano-particles in the coating.

#### 5. Discussion

#### 5.1. Chemical reactions

It is well known that to improve the properties of glass fiber-reinforced polymer matrix composites, it is necessary to form high-strength, chemically stable interfaces between the



Figure 14. Interlaminar shear strength (ILSS) of the composites with various surface treatment of basalt fibers.

Notes: BF – As-received basalt fiber, HTBF – Heat treatment basalt fiber at 300 °C for 3 h, ABF – basalt fibers after extraction in acetone for 24 h, APS – 1 wt.% 3-aminopropyltriethoxysilane, APS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-aminopropyltriethoxysilane: 0.1 wt.% nano-SiO<sub>2</sub>, APS–SiO<sub>2</sub>–0.5 – 1 wt.% 3-aminopropyltriethoxysilane: 0.5 wt.% nano-SiO<sub>2</sub>, APS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-aminopropyltriethoxysilane: 1 wt.% nano-SiO<sub>2</sub>, GPS–1 wt.% 3-glycidyloxypropyltrimethoxysilane, GPS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-glycidyloxypropyltrimethoxysilane: 0.1 wt.% nano-SiO<sub>2</sub>, GPS–SiO<sub>2</sub>–0.5 – 1 wt.% 3-glycidyloxypropyltrimethoxysilane: 0.5 wt.% nano-SiO<sub>2</sub>, GPS–SiO<sub>2</sub>–0.1 – 1 wt.% 3-glycidyloxypropyltrimethoxysilane: 0.5 wt.% nano-SiO<sub>2</sub>, GPS–SiO<sub>2</sub>–0.5 – 1 wt.% nano-SiO<sub>2</sub>.

reinforcement and the matrix. Surface treatments of fiber are usually carried out by reacting surface silanol groups with silane coupling agents. The contribution of silane coating is ascribed to the chemical bonding formed between basalt fiber and epoxy matrix. Figure 1 shows that with addition of the silane to the ethanol–water mixture, the alkoxyl groups are hydrolyzed and formed a silanol. This silanol then underwent condensation reactions with the hydroxyl groups of the fiber surface and other silanol in solution and on the fiber surface to form a partially crosslinked silane network.

Figures 6 and 7 provide the evidences for the mechanisms mentioned above. It is shown that APS and GPS coupling agents crosslink on the basalt fiber surface. However, there are the differences between the interaction of APS and GPS coupling agents with a glass surface, as shown by IR spectroscopy. The glass surface interacts with the amino groups forming linear or cyclic polyaminosiloxane. The most of the polyaminosiloxanes consist of more than two APS units.[23] The band that appears in IR spectra of APS at 1570 cm<sup>-1</sup> is the deformation mode of the amino group in SiO<sup>-</sup> ...H–NH<sub>2</sub><sup>+</sup> and probably contains contributions from the various layers on the surface (Figure 6).

Wherein, IR spectra of GPS treated basalt fibers indicate the formation of C–C and C=O groups. It is observed in [24] that C=O groups can be formed in the following sequence of hydrolysis, dehydration, and enol-keto rearrangement of epoxide groups (Figure 15(a)). The acid catalyzed dehydration of diols can be accounted for by a pinacol–pinacolone



**Figure 15.** Two simultaneous reaction schemes: (a) involves the hydrolysis of the epoxide group in GPS, followed by dehydration; (b) involves termination of the anionic epoxide groups polymerization.

rearrangement and involves the formation of a carbonium ion followed by group migration. With GPS, the migrating group would be a proton and the final product is an aldehyde.

A route to C=C groups involves the anionic polymerization of epoxides that can be initiated by methoxide ions in the following way as shown in Figure 15(b). The methoxide ions could arise from the hydrolysis of the  $Si(OCH_3)_3$  moiety. However, there is another mechanism. Termination of polymerization can lead to the observed vinyl groups.

So, the type and functionality of the silanes plays the important role in the experiment. The SEM pictures in Figure 4 show that the amino silane has slight effect in breaking the particle agglomerations, while epoxy silane effectively broke the agglomerations and achieved particle mono-dispersion. It is shown in Ref. [19], that epoxy silane is superior to amino silane in term of the nanosilica modification because of the hydrophilicity of their functional groups. Compared with epoxy group, the amino group is still hydrophilic. On the other hand, the amino group in the silane easily forms hydrogen bonding with silanol groups on the silica surface which also influence on the proceeding of reaction between silica surfaces cannot be fully eliminated by the amino silane treatment, so as the irregular agglomerations of nanosilica.

#### 5.2. Reinforcing mechanisms of basalt fiber composites

One of the important factors that determines mechanical properties of fiber-reinforced plastics is the strength of the constituent materials.[28] Decreasing mechanical properties of basalt fibers and as a consequence mechanical properties of BFRP on their base after the removal of the sizing by thermal treatment are observed (Table 2), whereas extraction in acetone does not significantly change mechanical properties. We suggest that strength

degradation is a result of larger surface flaws present after treatment at high temperature. It is known that the failure of the glass fibers commonly originates from small surface flaws. From the preexisting flaws representing weak sites along the glass fiber, pits can be developed. Pit formation generally occurs over long exposure times, but is accelerated by elevated temperature.[29]

It is shown that the strength of the silanized basalt fibers noticeably higher than noncoated fibers (Table 2). As reported by Schmitz and Metcalfe,[30,31] the failure of the glass fibers is governed by several types of flaws. Zinck et al. [32] indicate that silane coating could act as 'healing' agent to recover flaws on fiber surface. This can be also viewed as a disappearance of the severe surface flaws by the three-dimensional-graded network issued from the interaction between the silane and the basalt fiber surface. This healing can be understood as an increase in the crack tip radius; the flaw after surface treatment being either elliptical than sharp.

It is seen in Figure 10 that the Weibull plots of silane-treated basalt fibers can be fit by the bimodal Weibull distribution, suggesting that failure of the treated fibers may be controlled by two exclusive types of flaw population, which are referred to be as types A and B hereafter. Type A flaws might appeared at the bare surface while type B flaws might be related to the surface flaws existing on the glass surface coated with silane [12] or can be supposed to be internal ones.[32]

It is shown in [33] that healing can be efficient only for flaws whose dimensions enable sufficient interactions with the coupling agent aggregates in the aqueous solution. The concept of a critical dimension up to which defects are not healed, that is interactions between the flaw and the aggregates of hydrolyzed silanes are not sufficient is introduced. Measured dimensions are attributed to aggregates of small molecules rather than unseparable molecular species.

However, we observe an increase in Weibull's modulus,  $\sigma_0$ , and very good agreement with a linear fit as established by the  $R^2$  curve fit value (Table 2) after the surface modification of basalt fibers with nano-hybrid coating. The Young's modulus does not change significantly because it is essentially a materials property. It reflects order in a given system and is therefore affected by crystallinity and morphology. Unlike the tensile strength, it does not change much with form, shape, and uniformity of a material. We suggest that the improvement in the fiber tensile strength could be attributed to the SiO<sub>2</sub> nanoparticles in coatings, which can heal the nanoscale defects and act the as the 'bridges' at the defect tips on the fiber surface, and in turn delay the crack opening.[34] However, agglomeration of nanoparticles on the basalt fibers surface causes the formation of stress concentration fields and as a result decreases the strength.

#### 5.3. Enhanced interface between basalt fiber and epoxy matrix

To address the question of bonding of coating with the epoxy resin and the dependence of bonding on amine or glycidil groups, SFFTs are performed. Also, the ILSS of BFRP is investigated.

The interfacial bond strength is expected to be dependent on the strengths of the interactions (van der Waals, H-bonding, covalent) between the species comprising the interfacial layer. In the case of the untreated fibers, interfacial bond strength is poorest. The use of APS- or GPS-coated basalt fibers increases interfacial bond strength, indicating that the silane molecules do act as the coupling agents, chemically reacting both with the silica (via the methoxy end) and the matrix (via the amino or glicidoxy end).

It is known that good bonding is achieved when the resin is able to completely wet the silanated glass surface. The data suggest that silanes which provide good wettability do increase the mechanical properties of composites. In our case, all coupling agents used are reactive with the matrix. Finally, it is suggested [35] that the coupling agent modifies the matrix polymer morphology, either weakening (deformable layer theory) or strengthening the matrix (restrained layer theory).

It is important to note that the glass fiber surfaces are treated with sizing during manufacturing. Sizing consists of several components, including the film former and the silane coupling agent that is important for adhesion between the glass fibers and the matrix. The sizing highly affects the composite interface and thus the strength of the composites.[36] We assume that the thermal treatment and acetone extraction lead to remove partially all organic materials and organic functional groups leaving the part of the sizing that is bonded to the fiber surface. Thus, IFSS and ILSS decrease after the sizing removal.[37]

Also, we observe that IFSS of APS-SiO<sub>2</sub>- and GPS-SiO<sub>2</sub>-coated basalt fibers have a higher IFSS compared to non-coated and only APS and GPS coated samples. The maximum value is obtained for a concentration in SiO<sub>2</sub> particles of 0.1 wt.% and represented an increase of 50% compared to ABF. Because of the incorporation of the silica-nanoparticles in the interface region, the shear modulus of the matrix in the interface region is higher in comparison to the bulk. However, when the concentration of  $SiO_2$  particles is too high, large agglomerates are produced as shown with a concentration in SiO<sub>2</sub> particles of 0.5 and 1 wt.% (Figure 4). The SiO<sub>2</sub> agglomerates act as stress concentrators, decreasing the strength of the interface region. These larger particles are not well adhered for the level of shear force applied between the fiber and particles. It is prevented the effective mechanical interlocking and interfered with the adhesion of the matrix to the fiber. When a crack propagating through the matrix reaches a fiber, the relatively weak bonding (debonding) between the matrix and the fiber at their interface allows their relative sliding, which prevents the fiber fracture. The fiber bridges the cracked matrix.[38] Thus, the presence of SiO, nanoparticles in the interface can provide the crack deflection mechanism and possibly cavitation at the interface due to the particle debonding.[39] It results in longer fragments lengths during the SFFT, lower values of the IFSS (Table 3) and decrease ILSS of composites (Figure 14). Further, the APS-SiO<sub>2</sub> and GPS-SiO<sub>2</sub> provide both more wettable surface area and fiber separation to avoid fiber-fiber touching. The combination of fiber spacing increased wettable surface area and particle-matrix complexing provided by the hybrid-coated fiber systems produced the greatest effective IFSS values. Overall, higher values of IFSS and ILSS of BFRP can be attained by incorporating silica nanoparticles into the interface region through a fiber coating process, but only if the dispersion of those particles is optimal in terms of concentration, homogeneity, and separation of individual particles.

#### 6. Conclusion

We experimentally studied the mechanical properties of fiber-reinforced plastics depending on the various surface modifications of the constituent materials, using two methods: silane treatment and treatment with nano-hybrid coating with different contents of nano-SiO<sub>2</sub> (0.1–1 wt.%). Further, the nano-hybrid coating was successfully formed on the surface of

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the basalt. The incorporation of nano-SiO<sub>2</sub> dramatically modified the fiber surface texture which increased the fiber surface roughness. It was shown that the nanoparticles distributed on the basalt fiber surface evenly for the case where SiO<sub>2</sub> concentration was low. The mechanical performance of the basalt fibers before and after surface treatments was characterized by means of the single-fiber tensile test. The mechanical properties of the silanized basalt fibers got significant improvement. The tensile strength of silane-treated fibers was found 23% higher than the ABF, indicating that silane plays an important role in the fiber strength. Also, nano-hybrid coating proved to be the most effective way to enhance interface between epoxy matrix and basalt fiber. IFSS and ILSS for samples with nano-hybrid coating showed higher values compared to non-coated and only APS- and GPS-coated samples. The maximum value was obtained for a concentration in SiO<sub>2</sub> particles of 0.1 wt.% and represented an increase IFSS and ILSS to 53 and 40%, respectively, compared to ABF. This approach could become another promising method to improve the interlaminar properties of fiber-reinforced plastics without harming the tensile strength of fibers.

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#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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