EAN 2020
58th conference on experimental stress analysis

Study of Degradation of Carbon and Basalt Fibres in Alkaline Environment

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Keywords: basalt and carbon fibres, tensile strength, alkali resistance, degradation, image analysis

Abstract. Basalt and carbon grids are used for building application as reinforcement for cementitious mortars and geopolymers composites. The environment in which these materials are incorporated alkaline and aggressive with pH ≥ 12. Influence and differences of long-term exposure of fibres in two liquids was observed; demineralized water and potassium water glass. Defects or cracks due to the effect of potassium water glass were expected to appear on the surface of the basalt fibres. It was stated that basalt fibres (BFs) treated with demi water and carbon fibres (CFs) treated with both liquids remained without significant damage within three months. The change in mechanical properties and the occurrence of degradation processes in composites were confirmed by using tensile strength test and using image analysis based on scanning electron microscopy (SEM).

Introduction

Grid (warp knitted fabric) based on the network structure made of basalt, carbon or glass fibres is a new option for reinforcing concrete, cement mortar or geopolymer composite. A typical property of building materials is a strongly alkaline environment (concrete pH 12, geopolymer composite pH 12-14), which causes degradation of mainly mineral reinforcements (basalt and glass fibres). Carbon fiber is corrosion resistant and chemically stable; it is fire resistant and non-flammable, with good thermal and electrically conductivity. Composite materials with carbon reinforcements are commonly available in automotive, aerospace and shipbuilding industry, machinery construction, energy production and intervene to medicine, sport and lifestyle [1]. Carbon fibres have a great chemical resistance [7, 9]. More interesting is investigation of thermal stability, thermal stability in aggressive environment and flammability of CFs and geopolymer composite with carbon fillers [13, 14, 15].

Basalt fibre (BF) is classified as technical, inorganic, mineral fibre. The fibre is made of basalt rock. The technology of basalt fibre production is similar to that of glass fibres. Production is based on melt spinning at a temperature of 1500-1700 °C. Basalt fabric usually reinforces plastics constructions (BFRP – basalt fibres reinforced plastics). Production of basalt fibres is cheaper than production of carbon fibres. Basalt fibre is a natural product. Recycling BFRP and other products reinforced basalt fibres has more environmentally friendly impact than disposal CFRP (carbon fibres reinforced plastics). They have outstanding temperature stability, large thermal range of applicability -200 to +700 °C, they are incombustible, and they have a good UV-stability, high corrosion resistance, low humidity absorption. Carbon fibers are resistant in aggressive chemical environments [2].

Literature sources [3-7] more often describe the degradation of glass fibres due to an acidic or alkaline environment. The degradation of glass fibres in an alkaline environment is characterized by the occurrence of mineral incrustations and their peeling out from the fibre surface. The process is quantified by the changing of the fibre diameter and by the tensile strength value or Young's modulus [3]. Basalt fibers degrade in a similar way as glass fibers, both types are mineral origin. Studies [4, 5, 6] describe the evaluation of changes in the mechanical strength of fibre grids influenced by an alkaline environment for different temperature and concentration. Accelerating aging test was carried out for warp bundles from carbon, basalt and anti-corrosion glass fibres. Tests of durability provided following experimental results: carbon fibres have very good resistance to alkali even at higher temperature. Degradation of the mineral fibres was demonstrated by a tensile strength test, which showed a decrease in strength after immersion in an alkaline solution. Higher temperature and concentration accelerate their degradation process. Authors [7] use analysis of chemical composition (EDX), weight loss and SEM analysis for description and quantification the degradation process of carbon, basalt and glass fibres in deionized water, acid, alkaline, and saline solutions. Carbon fibres proved very good chemical resistance against different types of liquids. Weight loss and decrease of fibers diameter (degradation) was typical phenomena of mineral fibers in alkaline environment. Authors [8] observed chemical resistance of basalt fibres in water, salt, acid, and alkaline environments. The degradation of basalt fibres in alkaline media and in water was described, where the fiber diameter and fibre strength decreased significantly. The cause of these phenomena is a chemical reaction between the fibre and the solution. The diffusion rate is related to OH- concentration and is influenced by the environment temperature. SEM microscopy is very suitable to show and detect corrosion shell morphology and texture changes. However, no calculation based on image analysis is available until today. Only verbal description of fiber surface or diameter changes is used in a wide range of papers [9, 11]. Image analysis proceedings are able to show and detailly calculate the shape, size, amount, texture of objects on the surface of the fibres; unfortunately, a few researchers use this method in their research [12].

In this paper, the aim is to find the relationship between the change in mechanical properties and the results of the evaluation of image analysis. By conducting a series of experiments, we monitored the evolving degradation processes in basalt fibers in comparison with durable carbon fibers. Further study will be directed to the development of a proper methodology for the evaluation of degradation processes taking place on the surface of fibers in the volume of composite materials.

Materials and Methods

For experiment was used fibre rovings of witch grids are made. Carbon roving STS40 F13 24K from producer TohoTenax Europe GmbH has density 1.67 g/cm^3, linear density 1700 tex, tensile modulus 240 GPa, elongation 1.7 %, and filament diameter 7 µm. Basalt roving from producer Deutsche Basalt Faser GmbH has density 2.7 g/cm^3, linear density 2400 tex, tensile modulus 84 GPa, elongation 3 %, filament diameter 13 µm. Mineral composition of basalt roving present Table 1 [2].

Table 1: Mineral composition (weight ratio %)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	others
Min	45	12	5	6	3	0.9	2.5	2.0
Max	50	19	15	12	7	2.0	6.0	3.5

Experiment was based on comparison progress of degradation; chemical resistant carbon fibre roving (CR) and inorganic basalt fibre roving (BR) in alkaline environment was compared.

The test was realized according to Standard ČSN ISO 695 - Resistance to alkali [16]. Carbon (CRs) and basalt rovings (BRs) were treated with potassium water glass (KWG, concentrated solution of $K_2(SiO)_4$) and demineralized water (DW) at specified time intervals: two and six weeks (W2; W6), three, six and twelve months (M3, M6, M12). Experiment was carried at ambient temperature.

Samples for tensile strength test were prepared according to Standard ISO 11566 [17] with small differences, which respected rovings properties and dimensions. Rovings were sticked to paper frames. Samples prepared in this way minimize the possibility of roving break or other damage. The degree of mechanical properties degradation was observed with the help of tensile strength test according to EN ISO 13934 [18] (device Testometric). Clamping length was 100 mm and speed of test was 10 mms^{-1}. Each samples group contained ten samples. Scanning Electron Microscopy (UHR FE-SEM Carl Zeiss ULTRA Plus) was used for fibre surface changing investigation and results was processed using image analysis methods.

Image analysis of SEM pictures was performed within Matlab software (The MathWorks, Inc.); image was first corrected through the '*adapthisteq*' function (adaptive histogram equalization enhances the image contrast) and '*imadjust'* function (corrects image intensity values), then the image was converted to a grayscale form (8 bit image). The fibre diameter was obtain through the distance transform. Euclidean distance (straight-line distance) was calculated using the function 'bwdist, euclidean'. This computes the sum of pixels between each pixel and the nearest non-zero pixel; the maximum value of distance transform corresponds to fibre diameter determined at each point along the length of a fibre. The fibre surface roughness was determined along the fibre boundary, based to relative contrast of fibre to background, see green straight line in Figure 1. Low fibre roughness corresponds to a straight fibre with one-level gradient step to background along the whole border (see course of surface roughness on graph in Figure 1). The roughness is calculated as an average deviation of shadow level gradient to background.

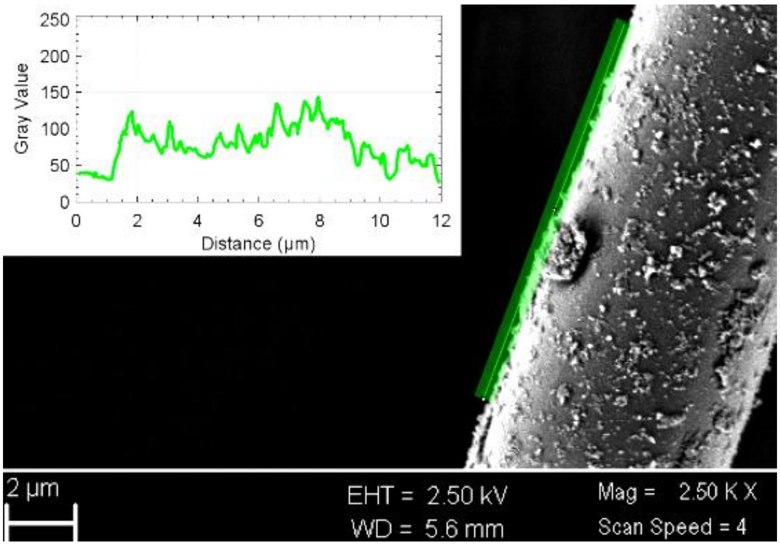

Fig. 1: Image analysis, representation of the roughness calculation along the fibre.

Results

Table 2 demonstrates changes of average strength values of basalt and carbon fibre rovings. Comparison between reference sample (REF), samples treated with demi water (DW) and samples treated with potassium water glass (WGK) shows long-term influence on strength of rovings.

Table 2: Result of tensile strength test – F_{max} [N]

	REF	W2	W6	M3	M6	M12
BR/WGK	758 ± 51	239 ± 32	151 ± 31	97 ± 2	-*	-*
BR/DW	758 ± 51	478 ± 53	404 ± 40	413 ±5 4	408 ± 54	440 ± 82
CR/WGK	700 ± 44	821 ± 78	774 ± 64	791 ± 51	794 ± 89	726 ± 109
CR/DW	700 ± 45	736 ± 92	681 ± 103	672 ± 30	648 ± 108	730 ± 179

**Basalt roving fibers were unusable for mechanical testing after about 4 months.*

Table 2 presents significant changes of BRs strength treated with water glass; strength of rovings decrease significantly depending on time, fibres dissolved in liquid after 3 months. Dissolved sizing on surface of fibres – the result is a reduction of strength values between sample REF and strength values of other basalt rovings. The demi water decreased mechanical properties of basalt rovings by 42 % after long-term effects. The tensile strength of carbon roving treated with H_2O oscillates around references value; water dissolved sizing and it violated cohesion of carbon fibres bundle and simultaneously strength of carbon roving. Water glass influenced strength of carbon roving; chemical reaction between components of WGK and components of sizing can be probably the reason of this change.

Figure 3 presents tensile strength loss of basalt fibres and of carbon fibres. Tensile strength loss between reference value of BR and condition after 2W is 42%. Generally, strength loss after long-term influence DW moves from 42 % to 34 %.

Demi water first acts on the sizing, which is dissolved over time. Subsequently, the surface of the fibers changes, with small amounts of oxides beginning to be precipitated from the surface.. The reason for the strength decrease was slow creation of high-silica layer, which protect fibre surface simultaneously. The trend of strength loss after influence of potassium water glass is clearly declining. Decrease after W2 is 64 %, after three months was decrease almost 90 %, after six months are basalt roving completely dissolved. Tensile strength loss between reference strength of CRs and condition after 2W is -5%. For CF was observed the opposite trend. Following strength increase is from 3% to 7.5%. The reason is probably the disruption and slow dissolution of sizing of fibres. SEM analysis supports the assumption – surface of carbon fibres was smooth and without sizing residues gradually. In case of interaction between KWG and carbon rovings strength grew up on average about 13 %. For determination of source, it is necessary use chemical analysis

For comparison in study [8] changes in chemical composition was described together with degradation process. Ions type of Na, K, and Al are missing in the chemical composition of the treated fibre compared to the reference sample. When evaluating the surface of fiber treatments, it must be considered that the fibre consists of a core and an outer layer. The content of insoluble oxides of Mg, Fe, Ca, and Ti increases in this outer layer. BF retains 99 % of its original weight in water at 25 °C, the change of strength is small. The fibre treated with boiling water forms a high-silica layer on the surface, which causes a 20 % increase in strength; it has a protective function (covers cracks on fiber surface) and prolongs the degradation process. Images of EDS and SEM analysis in experiments confirmed the achieved results of mechanical tests. Authors [9] examined different corrosion mechanism of basalt fibres in NaOH solution and cement solutions. Solutions represented alkaline environment, pH value 12. Corrosion process is dependent on calcium ions concentration. NaOH solution causes creation and development of corrosion shell; it causes dissolution of fiber surfaces layer.

Aging of basalt fibres in study [10, 11] was realized according to Standards (ASTM C 1203-91, ISO 695:1991). EDX-analysis proved changes in weight ratio of elements between reference samples of BFs and fibres treated alkaline solution. Article describes creation of corrosion shell on surface of BFs in detail in NaOH solution. Cement mixture allows only local attack on surface – holes and cracks, creates small holes on surface of fibres, which are connected together over time. Process ends with fibre damage. Authors in [12] used these methods, they confirmed the fundamental effect of temperature and concentration on the rate of degradation. A detailed description of the degradation processes presented as the corrosion shell formation phases was related to the changes in the tensile strength of the fibre. The strength of the fibres does not trend to decrease only; it usually varies according to the current phase of degradation. The strength of the fibre decreases depending on the gradual formation and increase of mineral incrustations amount. When the corrosion shell is formed, it is peeled from the fibre and the fibre strength increases again (not to its original value). The process is repeated over time until the fibre is completely dissolved.

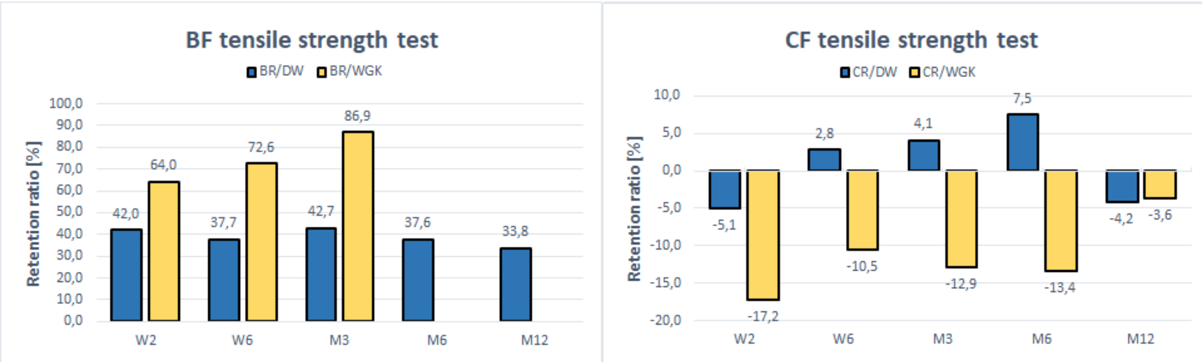

Fig. 3: Tensile strength loss in basalt and carbon rovings treated DW and KWG.

Figure 4 shows differences between basalt fibres (BFs) surface. Picture in the left side presents sizing on surface of reference sample (without other influence). Picture in the middle presents remaining of sizing on surface after treatment with demi water and picture in the ride presents corrosion coating - result of alkaline liquid influence after 3 months. Figure 5 shows carbon fibres surface; in the left - sizing on reference sample surface and clear carbon fibres surface after treated of demi water (12M) and potassium water glass (12M). Carbon fibres (CFs) surface is clean and smooth in both cases, without residues of sizing and without damage.

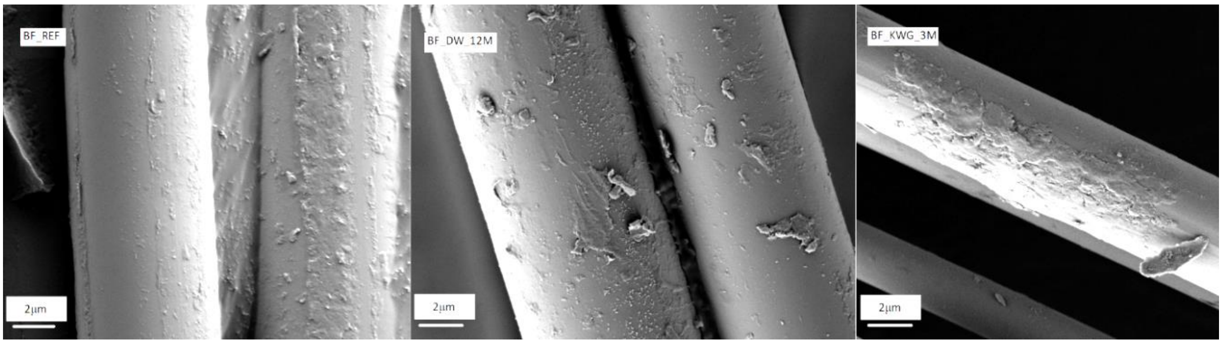

Fig. 4: Surface of BFs – reference sample, 12M in demi water, 3M in potassium water glass.

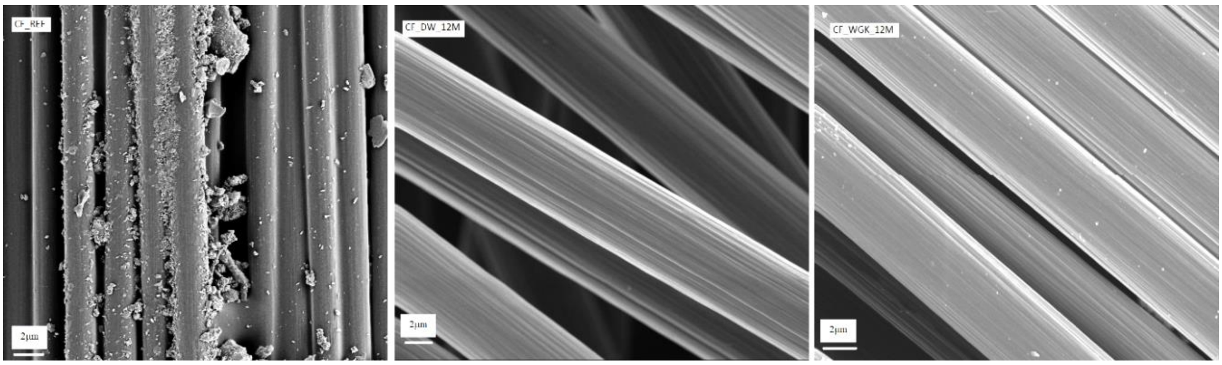

Fig. 5: Surface of CFs – reference sample, 12M in demi water, 12M in potassium water glass.

Results of image analysis (diameter and roughness determination) are depicted in Figure 6. Carbon fibres test show very low change in fibre diameter within 6 weeks (only the deviation of the diameter measurement is different for some samples). Fibre surface roughness (expressed in percentage in relation to the reference sample in zero-time, which is equal to 100 %) decrease in demi water, and increase in water glass (KWG). Basalt fibres test show almost 50 % decreasing in fibre diameter in KWG; and of up to 16 % changing of fibre diameter in demi water. Fibre surface roughness increase in demi water; and has no significant changes in water glass.

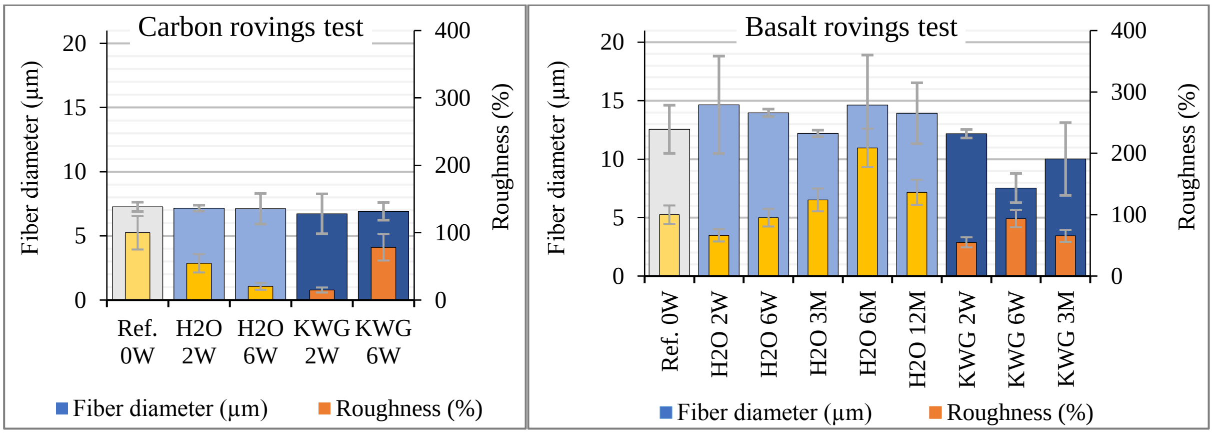

Fig. 6: Image analysis result showing fibres diameter (as blue) and fibres surface roughness (as orange).

A combination of the following methods was used to determine the degree of degradation of basalt and carbon fibers: tensile strength test, SEM and image analysis. SEM analysis and image analysis provided information about corrosion processes and development of corrosion aggregates on surface of basalt fibres. Chemical stability was assumed for carbon fibres, which was confirmed by laboratory experiments. Tensile strength test was supported by image analysis results. Both methods (SEM and image analysis) provide reliable information on fibre degradation due to the solutions used. Research shows that using image analysis, when using multiple SEM images changes in thickness and roughness of the examined fibres can be well monitored.

Conclusion

Experiment based on long-term influence of demineralized water and aggressive alkaline solution brought following results.

1. The presence of water affected the strength of BRs (decrease compared to the reference sample by approximately 40 %). Image analysis showed fibre swelling, the fibre diameter increased and gradually decreased. The contact of CRs with water showed only the dissolution of the sizing of fibres, which caused a slight decrease in strength.
2. Alkaline environment (in this case - potassium water glass) caused dissolution of BRs. Result confirmed tensile strength test and results of image analysis (decrease of diameter and increase of roughness).
3. Results for determination of CRs degradation is not possible conclusively express. Strength of carbon rovings has grown after treatment by alkaline environment. Image analysis did not reveal the cause. There is a need to use chemical analysis for exact determination of reason.

Acknowledgement

This work was supported by the Student Grant Competition of the Technical University of Liberec under the project No. SGS-2020-5019.

The work was supported by the Ministry of Industry and Trade in the framework of the targeted support of the Application, Call VII, the Operational Program Enterprise and Innovations for Competitiveness – “Research and development of textile products focusing on knitting technology and using aqueous chemicals”, reg. number CZ.01.1.02/0.0/0.0/19_262/0020121.

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