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Evaluation of selected properties and surface quality of cured pre-impregnated carbon-fiber fabrics after exposure to sulphuric acid

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Abstract
This paper deals with changes in selected properties of composite material and surface degradation after exposure to an acidic environment. A carbon fiber-reinforced composite (CFRP) produced from prepregs was tested. The weight change, micro-hardness, and surface degradation of the CFRP composite made of cured pre-impregnated laminates were evaluated in this study. Material consisting of a DT121R epoxy resin matrix with high reactivity and high viscosity, with two reinforcing carbon fabrics layers, is characterized by a low value of tensile strength. Evaluation of changes in the material properties was performed before and after exposure to specific environmental conditions, which are achieved by using a chemical solution of 15% H_2SO_4 at various temperatures. Subsequently, the effect of 15% H_2SO_4 at various temperatures on the material properties was monitored. The specimens were immersed in the solution for up to 3 and 6 weeks at the temperatures of 23°C, 40°C, and 60°C. It was found out, that the degradation of the composite material is conditioned by the aging of the epoxy resin (matrix). Carbon fibers (reinforcement) are relatively stable. The weight change, micro-hardness, and surface quality depend on the time of exposure to acidic solution and temperature. The micro-hardness tests show a significant influence on exposure time. The biggest changes in weight change and surface quality of the CFRP composite were observed after exposure at the temperature of 60°C.

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1. Introduction

Carbon fiber-reinforced polymer (CFRP) composites are most widely used in automotive, aerospace, and civil infrastructure applications because of their good properties. They exceed many advantages of steel, such as its low weight, high strength-to-weight, and stiffness-to-weight ratios. In addition, the CFRPs exhibit higher fatigue strength and higher corrosion resistance than metals (Zhu et al., 2019; Markovičová et al., 2017; de Paiva et al., 2006). The CFRP composites in many applications can be exposed to aggressive conditions, such as connection with aggressive solutions, elevated temperature, oxidation, and so on. The influence of environmental factors, such as humidity, elevated temperature, and corrosive solutions must be taken into consideration since they affect mechanical and physical properties of composite materials resulting in a change in the mechanical performance. The effect of the elevated temperature can be seen in the properties decrease of the CFRPs because of thermal softening. Especially in polymer-based composites, the matrix-dominated properties are more affected than the fiber-dominated properties. When those materials are exposed to humid air or water/chemical environment, many polymer matrix composites absorb moisture by instantaneous surface absorption followed by diffusion through the matrix. Analysis of moisture absorption shows that for epoxy matrix composites, the moisture concentration increases initially with time and approaches an equilibrium (saturation) level after several days of exposure to humid environments (Parnas et al., 2002).

The relation of micro-hardness to other properties of composite such as tensile strength in longitudinal and transverse directions has not been studied widely by researchers in the area of environmental degradation. It makes the research in

this area promising and has served as partial motivation for this study.

The aims of this work are focused on the evaluation of the effect of exposure to sulphuric acid on the micro-hardness of the composite material, weight (mass) change, and surface degradation. Material exposure to more aggressive conditions can cause degradation, this fact should be investigated more precisely. Evaluation of changes in examined properties is important from the point of view of quality and service life of composite material (Ji et al., 2017).

2. Experimental

2.1. Experimental material

Experimental material was prepared from commercially available pre-impregnated carbon-fiber fabrics. An autoclave system was used to cure the composite material, where the prepared cut pieces of pre-impregnated laminates are laid up in layers on steel metal plates to obtain the CFRP plates (Bere et al., 2019). The characteristic of the experimental material is described in Table 1. The CFRP plate consists of 2 layers of carbon fabrics (weave style twill 2×2) with the orientation of the first layer 0/90° and the orientation of the second layer ±45°. The designation of carbon fibers for the first layer is GG200T with a resin content of 42% and for the second layer is GG630T with a resin content of 37%.

Table 1. Characteristic of experimental material

Layer	Orientation	Carbon fabric	Epoxy resin
1	0/90°	GG200T	DT121R-42
2	±45°	GG630T	DT121R-37

Fabric technical data for carbon fabric GG200T are:

- weave style twill 2×2;
- FAW 200 g.m^{-2};
- yarn type HS – 3K;
- warp count 4.9 th.cm^{-1};
- weft count 5.0 th.cm^{-1};
- laminate thickness 0.33 mm.

Fabric technical data for carbon fabric GG630T are:

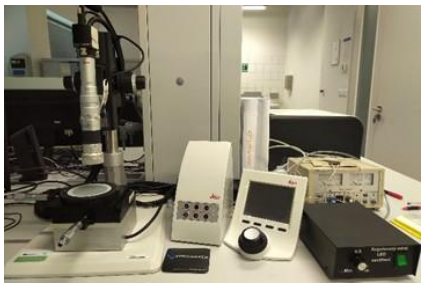
- weave style twill 2×2;
- FAW 630 g.m^{-2};
- yarn type HS – 12K;
- warp count 3.9 th.cm^{-1};
- weft count 3.9 th.cm^{-1};
- laminate thickness 0.66 mm.

After the preparation of the experimental CFRP plates, specimens were taken for change evaluation of micro-hardness, weight, and surface quality. After that prepared experimental specimens were exposed to an acidic environment. Sulphuric acid was diluted with distilled water to attain a 15% concentration solution. After an exothermic reaction during the dilution process, the acidic solution was stored in chemically sealable glass containers (Ji et al., 2017). The CFRP composite specimens were immersed and conditioned for up to 3 and 6 weeks. A comparison of chosen evaluated parameters of composite material was performed between reference material and exposed material.

2.2. Micro-hardness

The micro-hardness tests were carried out at room temperature using Bruker UMT TriboLab (Fig.1a) with a diamond square pyramid having an included angle at the tip of 136°. The testing load was applied for 10 s each from the time of contact with the diamond until the load 5 N was removed. The two diagonals of the indentation left in the surface of the experimental material after the removal of the load were measured using a microscope and their average was calculated. The area of the sloping surface of the indentation was calculated (Grabco et al., 2008; Mohamed et al., 2018). The Vickers hardness is the quotient obtained by dividing the load in Newtons per the square mm area of indentation. The measurements were performed by the ASTM E-384 standard on square specimens with dimensions of 20×20 mm. The micro-hardness was computed at ten different locations for each specimen of exposed condition (for various temperatures and times) where the average value was recorded. Using optical microscope Leica (Fig. 1b) and program LAS – V4.8 the indentations were evaluated based on the area of indentation.

a) Bruker UMT TriboLab



b) optical microscope Leica

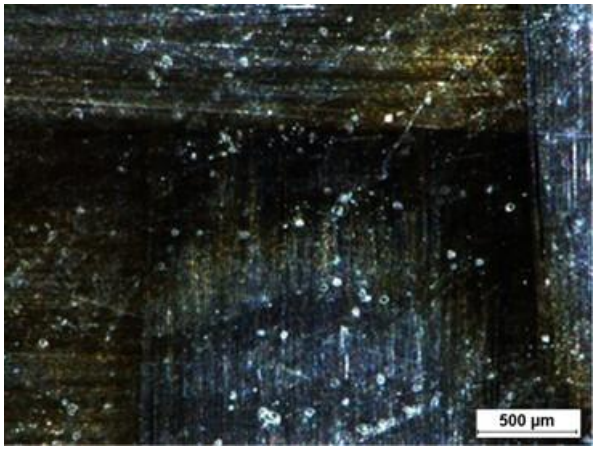
Fig. 1. Micro-hardness test

At every specimen, ten indentations were made and the average Vickers micro-hardness value was calculated according to formula 1 and converted to MPa:

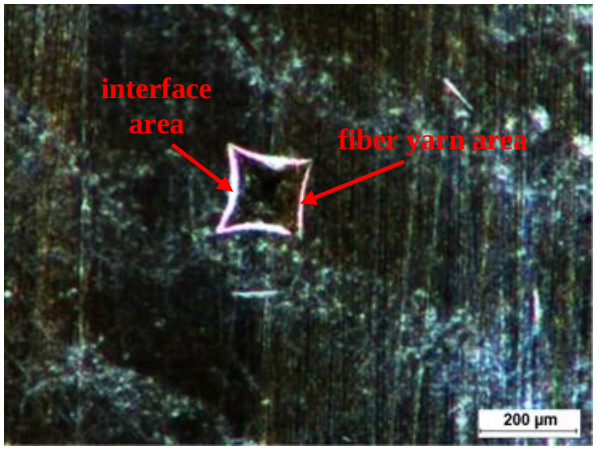
$$HV = 1.854\frac{F}{d^2} \quad (1)$$

where HV is Vickers hardness in MPa, F = load in kgf and d is the arithmetic mean of the two diagonals, d_1 and d_2 in mm.

The surface of the tested CFRP composite after sulphuric acid exposure before the micro-hardness measurement is documented in Fig. 2a. In this case, the biggest degradation effect of sulphuric acid on epoxy resin can be observed in the interface area between two fiber yarns. In Fig. 2b an example of Vickers indentation, prepared for measurement of two diagonals of the indentation and subsequent micro-hardness calculation is documented. Part of the indentation is located in the interface area and the rest of the indentation area extends into the fiber yarn area.



a) after sulphuric acid exposure before micro-hardness measurement



b) after indentation

Fig. 2. The surface appearance of the CFRP composite

2.3. Gravimetric measurement

Monitoring of weight changes of the experimental CFRP composite was performed by gravimetric measurement of specimens in acidic solution. The method consists in determining the weight gain of tested specimens immersed in the chosen environment over a defined time. All specimens should have the same shape and dimensions. At least 3 specimens shall be tested and immersed in chemically sealable glass containers. At the end of the defined time, the specimens are taken out of the acidic solution, rinsed with tap water and distilled water, dried, and weighed with an accuracy of 1 mg on a lab-scale (Kojnoková et al., 2020). To calculate the weight change, we need to know the weight of the specimen before immersion in the solution (m_1) and the weight of the specimen after the removal from the solution (m_2). Specimens in the shape of a square (20×20 mm) and thickness of 1 mm, were periodically weighed to monitor the weight change with time and temperature (Singer et al., 2018), which was calculated as follows:

$$X = m_2 - m_1 \quad (2)$$

$$X = \frac{m_2 - m_1}{m_1} 100 \quad (3)$$

where X is the weight change in g for formula 2 and in % for formula 3, m_2 is the initial weight of the specimen in g and m_1 is the weight of the specimen after exposure in g.

2.4. Surface quality

The macrostructure of the surface of the material before and after the effect of acidic solution at various temperatures after a defined time of exposure was monitored by light microscopy using a Leica stereo microscope on square specimens with dimensions of 20×20 mm.

3. Results and discussion

3.1. Micro-hardness

The micro-hardness tests were conducted at one specimen of reference material and six specimens of material after exposure. The obtained values were determined based on the indentation place of the diamond square pyramid. For each specimen, 10 points were taken and evaluated indentation place: fiber yarn or interface, then the values were averaged. Conversion between Vickers Hardness into SI unit MPa could be made to represent the hardness in the form of stress value. Vickers hardness (HV) to hardness stress in MPa unit is multiplied by 9.807 (Ab Ghani et al., 2019). Obtained results are documented in Table 2.

Table 2. Values of micro-hardness before and after exposure

Material	Reference material		
Temperature [°C]	-		
Fiber yarn [MPa]	414.59		
Interface [MPa]	192.76		
Time of exposure	After 3 weeks		
Temperature [°C]	23	40	60
Fiber yarn [MPa]	534.13	565.46	528.88
Interface [MPa]	280.72	189.90	243.72
Time of exposure	After 6 weeks		
Temperature [°C]	23	40	60
Fiber yarn [MPa]	519.88	465.79	346.45
Interface [MPa]	307.11	221.50	149.80

After 3 weeks of exposure, based on exposure temperature, depending on the acidic solution we can see higher values of micro-hardness caused by the effect of 15% H_2SO_4 at the point of the fiber yarn and also in the case at the point of the interface at 23°C and 60°C in comparison with reference material. At the temperature of 40°C is recorded the highest value of

micro-hardness at the point of the fiber yarn and the lowest value of micro-hardness at the point of the interface in comparison with reference material.

After 6 weeks of exposure, the measured values are more relevant. The highest value of micro-hardness was obtained after exposure at 23°C in the case at the point of the fiber yarn and interface also. On the other hand, there was observed a decreasing trend of micro-hardness with increasing temperature (Fig. 3).

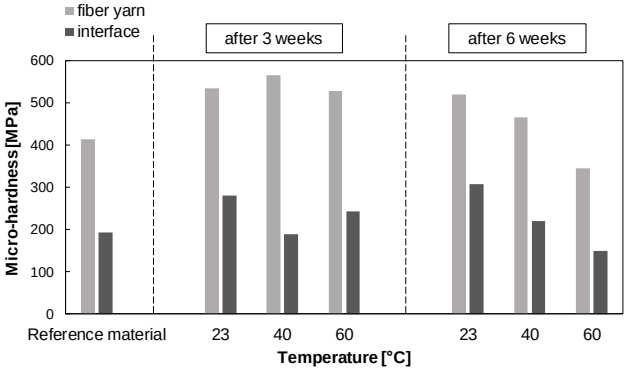


Fig. 3. The micro-hardness values of the CFRPs

3.2. Gravimetric measurement

The gravimetric measurement of the experimental material was used to monitor the change in weight before and after exposure to sulphuric acid at various temperatures over different times.

Firstly, the weight change of the CFRP composite after 15 minutes after the removal of specimens from the end of the exposure was measured. The average values of weight change after the effect of sulphuric acid are given in Table 3. The test showed an increasing trend in the weight of the CFRP specimens with increasing temperature after exposure to sulphuric acid. The CFRP composite absorbed moisture through the matrix. The fibers do not absorb moisture. Epoxy resin absorbs moisture and this was reflected in weight gain. The weight of specimens is higher because of diffusion through the matrix (up to 7.7% at 60°C). There have been changes in the molecular conformation due to thermal degradation.

Table 3. Values of weight change after exposure (15 minutes after the removal of specimens)

Time of exposure	After 3 weeks		
Temperature [°C]	23	40	60
m_1 [g]	0.508	0.377	0.481
m_2 [g]	0.517	0.390	0.518
Increase of weight [g]	0.009	0.013	0.037
Increase of weight [%]	1.772	3.448	7.692
Time of exposure	After 6 weeks		
Temperature [°C]	23	40	60
m_1 [g]	0.507	0.320	0.468
m_2 [g]	0.518	0.335	0.504
Increase of weight [g]	0.011	0.015	0.036
Increase of weight [%]	2.170	4.688	7.692

Subsequently, the specimens were allowed to dry completely and they were weighed 1 month after the removal of specimens from the end of the exposure. The weight of specimens was lower due to the evaporation of the sulphuric acid. The average values of weight change after the evaporation of the sulphuric acid are given in Table 4.

Table 4. Values of weight change after exposure (1 month after the removal of specimens).

Time of exposure	After 3 weeks		
Temperature [°C]	23	40	60
m_1 [g]	0.509	0.491	0.506
m_2 [g]	0.512	0.499	0.523
Increase of weight [g]	0.003	0.008	0.017
Increase of weight [%]	0.589	1.628	3.428
Time of exposure	After 6 weeks		
Temperature [°C]	23	40	60
m_1 [g]	0.520	0.324	0.518
m_2 [g]	0.524	0.332	0.535
Increase of weight [g]	0.004	0.008	0.017
Increase of weight [%]	0.705	2.467	3.215

The increasing trend in the weight of the CFRP specimens with increasing temperature after 1 month after the removal of specimens has also been observed (Fig. 4). These results also suggest that there were changes in molecular conformation and an increase in weight of up to 3.5% at 60°C.

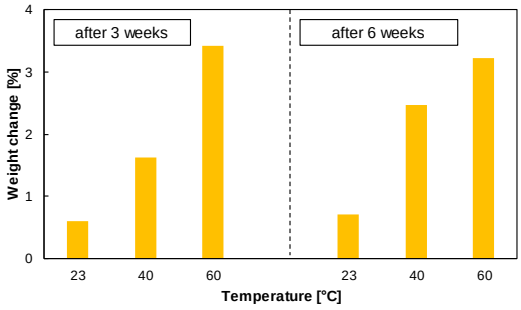


Fig. 4. Weight change of the CFRPs exposed in 15% H_2SO_4

3.3. Surface quality

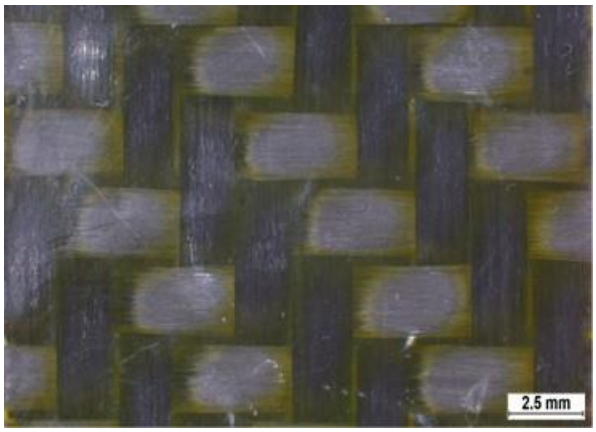
Fig. 5 shows the macroscopic image of the reference CFRP composite. The surface quality of reference material is relatively good due to the proper technological parameters after which the material contains a small number of imperfections (shallow scratches). Those surface imperfections do not affect the mechanical properties of the CFRP composite.

Fig. 5. Reference material before the test

The CFRP composite exposed to sulphuric acid for 3 weeks is shown in Fig. 6a, 6b, and 6c. As the exposure temperature of the chemical solution increases, larger surface differences can be observed. The biggest differences are observable at the temperature of 60°C.

a) after 3 weeks of 15% H_2SO_4 exposure at 23°C

b) after 3 weeks of 15% H_2SO_4 exposure at 40°C



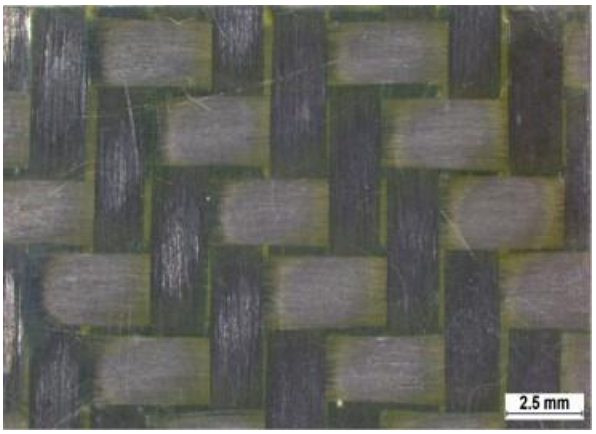
c) after 3 weeks of 15% H_2SO_4 exposure at 60°C

Fig. 6. Surface changes of experimental the CFRP composite; magnification 6× (after 3 weeks)

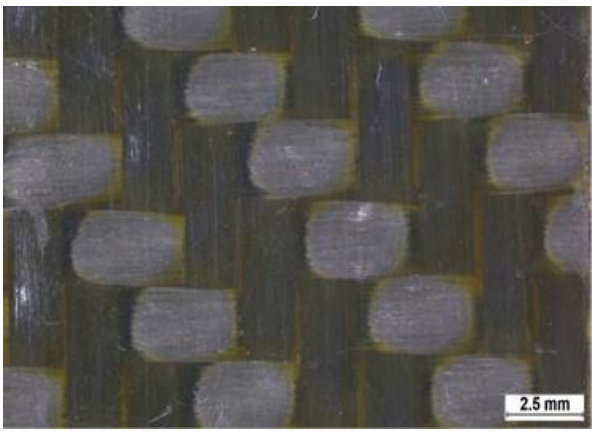
This exposure results in a change in the surface colour. The transparent resin gets yellow colouring.

Fig. 7a, 7b, and 7c show the macroscopic images of the CFRP composite exposed to sulphuric acid after 6 weeks. No major surface changes are observable after 6 weeks of exposure compared to 3 weeks of exposure.

a) after 6 weeks of 15% H_2SO_4 exposure at 23°C



b) after 6 weeks of 15% H_2SO_4 exposure at 40°C



c) after 6 weeks of 15% H_2SO_4 exposure at 60°C

Fig. 7. Surface changes of experimental the CFRP composite; magnification 6× (after 6 weeks)

4. Summary and conclusion

Material changes of the CFRP composite prepared from cured pre-impregnated laminates after exposure to 15% H_2SO_4 were studied and it was found out that the weight change, micro-hardness, and surface degradation depend on the exposure temperature and time.

The biggest surface changes of the CFRP composite were observed after an exposure time of 3 weeks at a temperature of 60°C. After 6 weeks of exposure, there are any observable major surface changes compared to 3 weeks of exposure. The surface changes and weight changes are strongly temperature-dependent. Contrary to that, as recorded by (Ji et al., 2017), the duration of the exposure period does not play any significant role. However, the micro-hardness tests show a significant influence on exposure time.

The flat surface of specimens after already 3 weeks became wrinkly. This can be caused by cross-linking of the polymer chain in the molecular structure of the CFRP composite. Compare to the exposure time of 3 weeks there were very small changes in the weight of the the CFRP composite after 6 weeks, which can be connected with slight surface changes.

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暴露于硫酸后固化的预浸渍碳纤维织物的选定性能和表面质量的评估

關鍵詞
碳纤维布
环氧树脂
显微硬度
体重变化
表面质量

摘要
本文讨论了暴露于酸性环境后复合材料选定性能的变化和表面降解。 测试了由预浸料制成的碳纤维增强复合材料 (CFRP)。 本研究评估了由固化的预浸渍层压板制成的 CFRP 复合材料的重量变化、显微硬度和表面降解。 材料由具有高反应性和高粘度的 DT121R 环氧树脂基体组成，具有两个增强碳纤维层，其特点是抗拉强度值低。 在暴露于特定环境条件之前和之后，对材料特性的变化进行了评估，这些条件是通过在不同温度下使用 15% H2SO4 的化学溶液实现的。 随后，监测了不同温度下 15% H2SO4 对材料性能的影响。 在 23°C、40°C 和 60°C 的温度下，将样品浸入溶液中长达 3 周和 6 周。 已发现，复合材料的降解受环氧树脂（基质）老化的制约。 碳纤维（增强）相对稳定。 重量变化、显微硬度和表面质量取决于暴露于酸性溶液的时间和温度。 显微硬度测试显示对暴露时间有显着影响。 在 60°C 的温度下暴露后，观察到 CFRP 复合材料的重量变化和表面质量的最大变化