IEGULDĪJUMS TAVĀ NĀKOTNĒ

24M Progress Report

Project title: "Environmental effects on physical properties of smart composites and FRP modified by carbonaceous nanofillers for structural applications".

Project No. 1.1.1.2/VIAA/1/16/066.

Period concerning this report: 01.01.2019-31.12.2019.

Activity 1.1.1.2 "Post-doctoral Research Aid" of the Specific Aid Objective 1.1.1 "To increase the research and innovative capacity of scientific institutions of Latvia and the ability to attract external financing, investing in human resources and infrastructure" of the Operational Programme "Growth and Employment".

Summary

During the second year of the project the main purpose was to design and develop smart fibre-reinforced plastic (FRP) plate by using the most environmentally stable nanocomposite (NC) configuration. As a result, within the support of collaboration partner Institute for Polymers, Composites and Biomaterials (IPCB, Portici, Italy) during Mobility#4 four basalt FRP plates were produced: two $[0]_8$ plates impregnated with the epoxy or the NC, and two $[0/45/90/-45]_2$ also impregnated with the epoxy or the NC, and two $[0/45/90/-45]_{2.}$ Additionally, a set of the specimens for the epoxy and epoxy filled with 0.1 wt.% of hybrid nanofiller (carbon nanotubes and nanofibers in the ratio 1:1) was developed for full year environmental ageing. The characterization of flexural, thermophysical and electrical properties was performed for all materials in uncondensed state (before the environmental ageing). After that the first season of environmental ageing (summer, water absorption at room temperature) has been started for all materials. Moreover, water absorption at 20 and 50 ºC until equilibrium has been performed for all materials.

Contents

1. Objectives for the 2nd year of the project

1) Development, start of full-year environmental ageing and testing of a small-scale structural element prototype, smart FRP plate, impregnated with the most environmentally stable NC;
2) Characterization of the main mechanical, electrical and thermal properties of the epoxy, NC and FRP before hydrothermal ageing by standard tests and analytical modelling;
3) Preparation of conference reports, conference and scientific papers.

2. Explanation of the work carried per WP

WP1. Coordination and management

T1.1. Operational issues

During the second year several laboratory seminars were carried out in the Institute for Mechanics of Materials, University of Latvia (IMM) to evaluate progress and decide on next steps. One progress seminar was carried out in the Institute for Polymers, Composites and Biomaterials (IPCB) in Portici, Italy in September 2019 to discuss current results of the project during Mobility#5. Four quarter reports were prepared (in Latvian) and published at the website of the University of Latvia (UL, www.lu.lv). 24M public progress report was prepared in English for publishing in *Zenodo* repository (current document). Different communication activities such as e-mails, discussions by *Skype*, sharing of documents and files were performed with scientific consultant from IMM Dr. Sc. Ing. Andrey Aniskevich and representative person from IPCB Dr. Sc. Ing. Mauro Zarrelli.

T1.2. Scientific management

Post-doctorate monitored the project's progress to scientific consultant from IMM and representative person from IPCB and followed up the implementation, completing all deliverables assigned in project proposal. Continuous analysis of risks was carried out by post-doctorate to avoid delays, complete material resource preparation before the given tasks.

T1.3. IPR management

The IPR management was performed according to IPR strategy (D1.3, M4) developed for identifying publishable subject matter, by registering and continuous updating of expected outcomes and foreground generated.

WP2. Design and development of the NC and FRP plate

T2.1. Selection of the most optimal material solution

Completed during the 1st year of the project.

T2.2. Optimization of the NC processing conditions

Completed during the 1st year of the project.

T2.3. Development of NC specimens with single and hybrid fillers

Completed during the 1st year of the project.

T2.4. Design and development of the NC specimens at electrical percolation

One set of NC specimens at certain filler content was prepared in IPCB during Mobility#4 by using the most optimal processing route (see D2.2). Prepared materials: RTM6 epoxy resin, RTM6 filled with 0.05 wt. % of carbon nanotubes (CNT), RTM6 filled with 0.3 wt. % of carbon nanofibers (CNF), and RTM6 filled with 0.1 wt. % of CNT/CNF in the ratio 1:1 by mass. For each material type 5 discs with diameter 8 cm and thickness 3 mm were prepared and cut into samples (Figure 1). The characterization of flexural, thermophysical and electrical properties was performed for all materials in uncondensed state (before the environmental ageing). The test samples were subjected to the 1st season of full year environmental ageing (summer, water absorption at 20ºC).

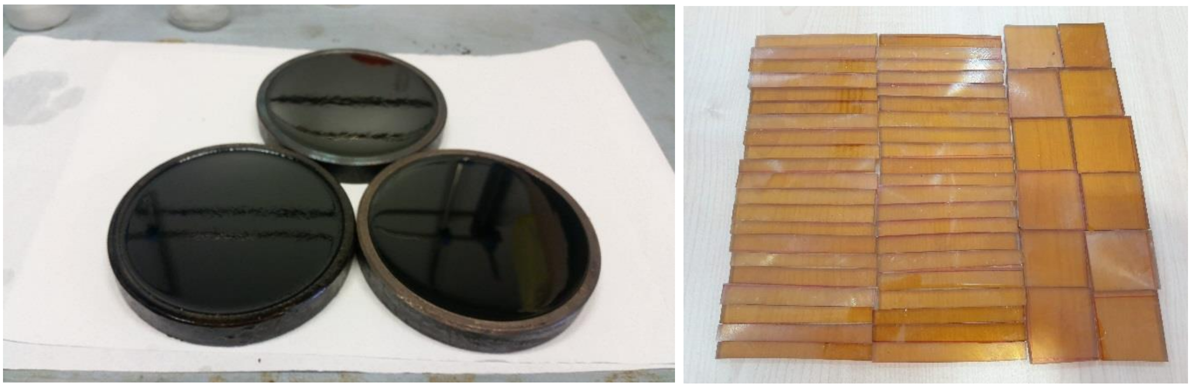

Figure 1. Steel moulds with the epoxy filled with 0.05 wt. % of CNT (to the left) and epoxy samples cut for flexural and thermophysical tests (to the right).

T2.5. Design and development of smart FRP plate

Within the support of collaboration partner Institute for Polymers, Composites and Biomaterials (IPCB, Portici, Italy) during Mobility#4 four basalt FRP plates were produced: two $[0]_8$ plates impregnated with the epoxy or the NC, and two $[0/45/90/-45]_2$ also impregnated with the epoxy or the NC, and two $[0/45/90/-45]_2$ by using vacuum assisted resin transfer moulding (VARTM). The development procedure and unidirectional basalt FRP are shown on Figure 2.

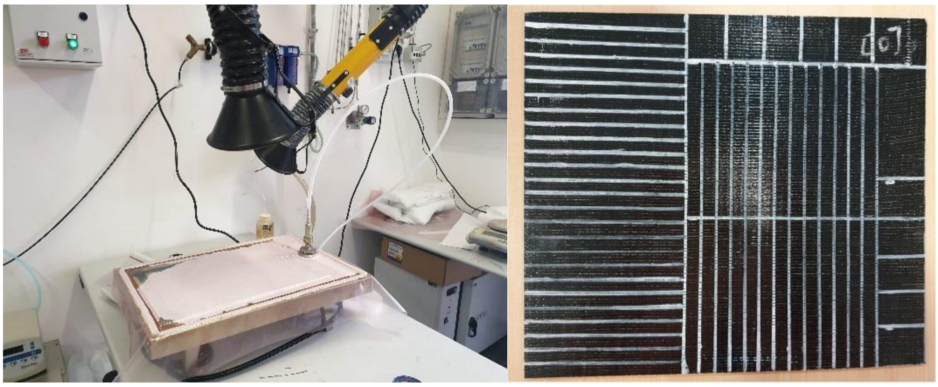

Figure 2. Development of FRP plate by using VARTM (to the left) and unidirectional basalt FRP plate (to the left).

WP3. Characterization of the NC and FRP

T3.1. Micro- and nanostructural characterization of the NC

Completed during the 1st year of the project.

T3.2. Standard mechanical, electrical, and thermal characterization

Characterization of the epoxy, NC and basalt FRP specimens before full year of environmental testing was carried out. The mechanical properties for epoxy and NC samples were tested under three-point bending mode according to ASTM D790. The samples of sizes 3×10×80 mm were tested with a support span of 56 mm and with a strain rate of 1.5 mm/min. The flexural modulus, strength and maximal deformation were evaluated from the stress-strain curves. Before full-year environmental ageing the flexural properties of neat and nano-modified epoxy and basalt FRP were almost the same. E.g., flexural moduli of the epoxy and the epoxy filled with 0.1 wt. % of hybrid nanofiller (CNT/CNF in the ratio 1:1 by weight) were 3.0 ± 0.2 GPa and 3.2 ± 0.1 GPa, accordingly. Similar results were obtained also for epoxy-based and nano-modified basalt FRP in the direction along (25.3 ± 2.3 GPa and 23.6 ± 0.5 GPa, accordingly) and perpendicular (10.0 ± 0.8 GPa and 10.1 ± 0.8 GPa, accordingly) to the fibres. Provisionally it can be concluded that the effect of the addition of hybrid carbon nanofiller to the epoxy resin and basalt FRP was insignificant mainly due to relatively low filler content and possible aggregation of the nanofillers causing weak nanofiller-matrix interfacial interactions.

The electrical resistance of the NC samples was measured by using a multimeter DMM 4020 (*Tektronix*) following a two-point methodology. Opposite facets of the samples were covered with conductive silver paint to reduce contact resistance effect. Before full-year environmental ageing the electrical conductivity of the epoxy filled with 0.1 wt. % of CNT/CNF in the ratio 1:1 by weight: 0.008 ± 0.002 S/m, nano-modified basalt FRP in the direction along the fibres: 0.020 ± 0.002 S/m, perpendicular to the fibres: 0.016 ± 0.002 S/m, and in symmetrical basalt FRP: 0.006 ± 0.001 S/m. The increase of electrical conductivity of nano-modified basalt FRP could testify about the improvement in the electrical percolation along the fibres.

The thermal conductivity was measured by using thermal constants analyzer TPS 500 (*Hot Disc*) at a heating power 50 mW and heating time 40 s by using Kapton sensor with radius 3.2 mm. Before full-year environmental ageing the thermal conductivity of epoxy and the NC was almost the same (0.24 ± 0.02 J/mK). Similarly, for epoxy-based and nano-modified basalt FRP in different directions it can be roughly estimated as 0.30 ± 0.02 J/mK proving that the content of hybrid nanofiller (0.1 wt. % for the NC and only 0.03 wt. % in the basalt FRP) is too small to improve the thermal properties. Nevertheless, it allowed to ensure electrical conductivity that was twice higher than it was for the NC.

The dynamic mechanical thermal analysis (DMTA) was carried out by using a Mettler Toledo DMA/SDTA861 in tensile mode at a given force 4 N, frequency 10 Hz and T = 30-280 °C at 3 K/min heating rate to evaluate hygrothermal ageing effects in both initial and environmentally "aged" NC samples. Glass transition temperature for the epoxy and the epoxy filled 0.1 wt. % of CNT/CNF in the ratio 1:1 by weight obtained from DMTA was almost the same before full-year environmental ageing: 236± 2 °C proving that the crosslinking degree was similar in all materials. Similarly, for the epoxy-based and nano-modified basalt FRP in the direction along

(255 ± 2 °C and 241 ± 2 °C, accordingly) and perpendicular (238 ± 1 °C and 237 ± 1 °C, accordingly) to the fibres.

T3.3. Nonstandard environmental ageing

The first season of environmental ageing (summer, water absorption at room temperature) has been started for all materials. Moreover, water absorption at 20 and 50 ºC until equilibrium has been performed for all materials. All samples are being stored in the same shelf of the oven to get the same thermal conditions.

The peculiarities of moisture absorption in epoxy resin and NC samples are being studied. Preliminary it can be concluded that the overall behaviour is similar for all materials following classical Fick's law for moisture diffusion. Since water absorption is still in process the sorption characteristics of all materials investigated can't be analysed until it is finished.

WP4. Dissemination, communication and data management

T4.1. Dissemination of results

During the second year of project implementation 4 quarter press releases (#5-8) were prepared and published in the website of UL (https://www.lu.lv/index.php?id=53864).

Current project results were discussed in two international scientific conferences *ICSAAM 2019*, September 12-15, 2019 (Ischia, Italy) and *DFMN 2019*, November 19-22, 2019 (Moscow, Russia). According conference full papers were prepared and accepted for the publication by *American Institute of Physics-Conference Proceedings (AIP)* and *IOP Conference Series: Materials Science and Engineering*.

In the synergy with project activities two conference reports were done in collaboration with colleagues from Riga Stradins University (RSU) at *RSU Scientific Conference*, April 1-3, 2019 (Riga, Latvia) and *Medical Physics in the Baltic States 14*, November 7-9, 2019 (Kaunas, Lithuania).

Based on the project results one scientific paper was published in Q1 scientific journal having open access (*Polymers*).

For the dissemination of project results among general public one popular scientific publication (in Latvian with a summary in English) was published in the journal "Alma Mater" by the University of Latvia based on the project idea and activities.

For the same purpose a professional *FACEBOOK* profile was updated with 11 press releases (https://www.facebook.com/tatjana.glaskovakuzmina) on the project activities. The profile will be also regularly updated with the actual project information/results. More information can be found in dissemination/communication report for 2018 (D4.1, M12).

T4.2. Communication

According to dissemination/communication plan (D4.1, M12) developed during the first year of project implementation certain dissemination/communication activities were carried out.

During the second year of project implementation seminars organized by State Education Development Agency of the Republic of Latvia (www.viaa.gov.lv) were attended for better project implementation and preparation of project reports.

Popular scientific seminar was carried out for the schoolchildren of the postdoctoral researcher's native school within the activity "Back to School" on May 2019.

The project activities were presented and discussed with wide audience at the *European Researchers' Night 2019*, demonstrating to all its visitors nonordinary adventures of ordinary materials, telling about the components and applications of smart composite materials, and showing the real test samples and products. The interview at Latvian Television was performed speaking about activities of the University of Latvia at *European Reserchers' night*.

Several presentations about the project and its current results were made for the progress seminars organized in Institute for Mechanics of Materials of UL (Riga, Latvia) and IPCB (Portici, Italy). 2nd year progress seminar for the discussion of current project results and future steps was organized in the Institute for Mechanics of Materials, UL.

During the second year of project two mobilities to IPCB (Portici, Italy) were carried out by the post-doctorate: 15.-22.06.2019 and 07.-17.09.2019. During these mobilities one set of epoxy and NC specimens and four basalt FRP plates were prepared, a presentation at a progress seminar was performed, next project steps were planned, discussed and implemented.

Wide communication with international researchers discussing project results was carried out during *ICSAAM 2019* and *DFMN 2019* conferences.

T4.3. Knowledge and data management and protection

All data generated (raw and ready data files, reports, presentations) were transferred to the folder of POSTDOC project in the central database *Dropbox* providing access to scientific supervisor from LU Dr. Sc. Ing. Andrey Aniskevich and representative person of IPCB Dr. Sc. Ing. Mauro Zarrelli. All data files will be preserved in *Dropbox* during the project implementation and at least five years after completion of the project.

3. Preliminary conclusions

Based on similar results of characterization of flexural, electrical and thermophysical properties of the epoxy, NC and basalt FRP specimens before full year of environmental testing it can be concluded that the effect of the addition of hybrid carbon nanofiller to the epoxy resin and basalt FRP was insignificant mainly due to relatively low filler content (0.1 wt. % for the NC and only 0.03 wt. % in the basalt FRP) and possible aggregation of the nanofillers causing weak nanofiller-matrix interfacial interactions. Nevertheless, it allowed to have electrical conductivity in preliminary nonconductive basalt FRP that was twice higher than it was for the NC. The increase of electrical conductivity of nano-modified basalt FRP could testify about the improvement in the electrical percolation along the fibres.

4. Main results

Scientific publications

1. Glaskova-Kuzmina T., Aniskevich A., Sevcenko J., Borriello A., Zarrelli M. "Cyclic moisture sorption and its effects on the thermomechanical properties of epoxy and epoxy/MWCNT nanocomposite". Polymers, 2019, Vol. 11 (9), 1383, p. 1-14. DOI: 10.3390/polym11091383.
2. Glaskova-Kuzmina T., Aniskevich A., Sevcenko J., Zotti A., Borriello A., and Zarrelli M. Environmental effects on mechanical, thermophysical and electrical properties of epoxy resin filled with carbon nanofillers. *Proceedings of ICSAAM 2019 published by American Institute of Physics-Conference Proceedings*, September 12-15, 2019, Ischia, Italy (in press).
3. Glaskova-Kuzmina T., Aniskevich A., Zotti A., Borriello A. and Zarrelli M. "Flexural properties of the epoxy resin filled with single and hybrid carbon nanofillers". *IOP Conference Series: Materials Science and Engineering*, 2019 (in press).
4. Priladiša K., Siliņš J., Glaskova-Kuzmina T., Proskurins J., Bērziņa S., and Jaunozola E. "Environmental ageing and its effect on compressive properties of dental composite". *Proceedings of International Conference Medical Physics 2019*, p. 105-108, November 7-9, 2019, Kaunas, Lithuania (in press).

Popular scientific publications

1. Tatjana Glaskova-Kuzmina. Perspektīvie materiāli un to stabilitāte pret ārējās vides faktoru iedarbību. Alma Mater, 2019, #3, Latvijas Universitāte (in Latvian with summary in English).

Presentations at international conferences

1. Priladiša K., Siliņš J., Glaskova-Kuzmina T., Proskurins J., Bērziņa S., and Jaunozola E. Environmental effects on mechanical properties of dental composite. RSU Scientific Conference, April 1-3, 2019, Riga, Latvia.
2. Glaskova-Kuzmina T., Aniskevich A., Sevcenko J., Zotti A., Borriello A., and Zarrelli M. Environmental effects on mechanical, thermophysical and electrical properties of epoxy resin filled with carbon nanofillers. *ICSAAM 2019*, September 12-15, 2019, Ischia, Italy. Book of abstracts, p. 11.
3. Glaskova-Kuzmina T., Aniskevich A., Zotti A., Borriello A., and Zarrelli M. Flexural properties of the epoxy resin filled with single and hybrid carbon nanofillers. *DFMN 2019*, November 19-22, 2019, Moscow, Russia. Book of abstracts, p. 350.
4. Priladiša K., Siliņš J., Glaskova-Kuzmina T., Proskurins J., Bērziņa S., and Jaunozola E. Environmental ageing and its effect on compressive properties of dental composite. *Medical Physics in the Baltic States 14*, November 7-9, 2019, Kaunas, Lithuania. Book of abstracts, p. 105-108.

5. Deviations from the working plan

Some positive deviations from the working plan of dissemination/communication were obtained by the post-doctorate. It is expected that the number of conference presentations and submitted/published scientific papers written in project proposal (2 presentations and 2 scientific papers) will be higher maximizing the impact of the project.

6. Corrective actions

In the case of appropriateness and need, inclusion of all additional and relevant scientific and dissemination/communication activities within the project implementation and adding them to project work was done improving the visibility of project results.

7. Plans for the next reporting period (2020)

Submission of at least one scientific paper to peer-reviewed Q1 scientific journals and popular scientific paper in Latvian press is planned for the next year.

The scientific results obtained during the second year will be published in 2020 in peer-reviewed Q1 scientific journal (ensuring open access) with SCI higher than app. 1.15 (Material science, multidisciplinary) and included in the SCOPUS (A or B) databases. The draft version of the article will be prepared early in 2020 and will be discussed with scientific supervisor from the UL Dr. Sc. Ing. Andrey Aniskevich and representative person of collaboration partner IPCB Dr. Sc. Ing. Mauro Zarrelli.

The scientific and public dissemination of the project will continue to be developed to achieve all planned objectives. The professional profile on *FACEBOOK* will be updated with the information on project results for general public. The open-access to project scientific results will be provided via self-archiving in *ZENODO* and *ResearchGate* repositories.

It is planned that project results will be presented in two international scientific conferences "*Advanced Problems in Mechanics*" in June 21-27, 2020 (Saint Petersburg, Russia) and *ICSAAM* in September 4-8, 2020 (Patras, Greece).

Full-year environmental ageing of epoxy, epoxy filled with 0.1 wt.% of hybrid nanofiller (CNT/CNF in the ratio 1:1 by weight), basalt FRP and nano-modified FRP will be performed which includes: 1) Summer: three months at T = +20 ºC (room temperature), 2) Autumn: three months at T = +10 ºC (in a fridge), 3) Winter: three months at T = -10 ºC (in a fridge), and 4) Spring: three months at T = +10 ºC (in a fridge). After the hydrothermal ageing (of each season and full year) all materials' specimens will pass standard characterization of the main mechanical, electrical and thermal properties. The results obtained will be compared with the predicted ones, by using experimental results for the NC.

8. Deliverables and Milestones for reporting period (M13-M24)

Table 1. List of deliverables

No.	**Deliverable name**	**WP**	**Type**	**Diss. level**	**Date**
D3.2	Conference report#1 on mechanical, electrical and thermal characterization of the NCs	3	PU	OTHER	M18
D3.3	Scientific paper#1 on mechanical, electrical and thermal characterization of the NCs submitted for publication	3	PU	OTHER	M19
D2.3	Development of smart FRP plate	2	CO	OTHER	M20
D1.1	Annual LU MMI progress seminars (M12, M24, M36)	1	PU	OTHER	M24
D1.2	Annual public reports published (M12, M24, M36)	1	PU	R	M24
D4.1	Dissemination/communication plan and annual dissemination/communication report (M12, M24, M36)	4	PU	R	M24

Type: R- report, OTHER.
Diss. level: CO -confidential, PU – public.

Table 2. List of milestones

No.	**Milestone name**	**WP**	**Est. date**	**Means of verification**
M3.2	The most stable NC configuration/influent environmental factor specified	WP3	M18	Conference report#1 and preparation of publication#1