LATVIJAS UNIVERSITĀTE ANNO 1919 | NACIONĀLAIS ATTĪSTĪBAS PLĀNS 2020 | EIROPAS SAVIENĪBA Eiropas Reģionālās attīstības fonds

IEGULDĪJUMS TAVĀ NĀKOTNĒ

12M 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: 01.01.2018-31.12.2018.

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 first year of the project the main purpose was to choose, purchase and develop investigated materials: epoxy resin and at least two carbon nanofillers (nanotubes, nanofibres and/or graphene). The most promising material solution and the most optimal processing route were chosen and reported. Then two sets of epoxy and NC specimens were developed during Mobilities#2-3 to partner organization, Institute for Polymers, Composites and Biomaterials (Portici, Italy). The test specimens of epoxy and NC were subjected to environmental ageing: water absorption at 70 °C until equilibrium water content and heating at 70 °C, then freezing at ap. -20 °C to evaluate the most environmentally stable NC configuration. Based on preliminary results (without results after freezing), the most environmentally stable NC was epoxy filled with 0.1 wt. % of CNT/CNF, which had the lowest effect of temperature and moisture on thermal and electrical conductivities, along with the lowest equilibrium water content and diffusivity.

Contents

1. Objectives for the 1st year of the project

1) Design and development of the nanocomposites (NC) at optimal filler content filled with single and hybrid carbon nanofillers, having similar electrical conductivity and corresponding to electrical percolation threshold;
2) Characterization of the main mechanical, electrical and thermal properties of the NC before, during and after hydrothermal ageing by standard tests and analytical modelling;
3) Preparation of conference reports.

2. Explanation of the work carried per WP

WP1. Coordination and management

T1.1. Operational issues

During the first year several laboratory and three institute seminars (on January, October and December, 2018) were carried out in the Institute for Mechanics of Materials, University of Latvia (LU MMI) to evaluate progress and decide on next steps. One seminar was carried out in the Institute for Polymers, Composites and Biomaterials (IPCB) in Portici, Italy in March, 2018 to introduce Italian colleagues to the project aim and tasks during Mobility#1. Four quarter reports were prepared in Latvian for the University of Latvia (LU). 12M 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 LU 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 LU 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 strategy (D1.3, M4) was developed for identifying publishable subject matter, by registering and continuous updating of expected outcomes and foreground generated. Agreement between post-doctorate, scientific consultant and contact person from IPCB via keeping the rules of decision-making, IPR issues, and publications was set in the IPR strategy.

WP2. Design and development of the NCs and FRP plate

T2.1. Selection of the most optimal material solution

Several alternatives for purchasing test materials were analyzed, taking into account material costs, delivery time, processing conditions, and materials' characteristics. Short report specifying the most promising material solution un terms of environmental stability was prepared (D2.1, M3).

Figure 1. High-shear mixer Turrax.

T2.2. Optimization of the NC processing conditions

The most effective processing route for the dispersion of carbonaceous nanoparticles in the epoxy resin based on SWOT analysis was chosen during Mobility#2 and according report (D2.2, M6) was prepared. Thus, carbon nanotubes and nanofibres were dispersed in the epoxy resin by using high-shear disperser Ultra Turrax T25 by *IKA*. The manufacturing procedure was already designed and proved to be effective by researchers of IPCB as follows: 30 min at 90 ºC and 20 000 rpm in oil bath, degassing app. 30 min at 90 ºC, and curing 90 min at 160 ºC, 2h at 180 ºC.

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

1 set of NC specimens at different filler content was prepared in IPCB during Mobility#2 for the evaluation of electrical conductivity, by using the most optimal processing route (see D2.2). Prepared materials: RTM6 epoxy resin, RTM6 filled with 0.01, 0.02, 0.03, 0.04, 0.05 wt. % of carbon nanotubes (CNT), RTM6 filled with 0.1, 0.2, 0.3, 0.4, 0.5 wt. % of carbon nanofibers (CNF), and RTM6 filled with 0.02, 0.04, 0.06, 0.1, 0.2 wt% of CNT/CNF in ratio 1:1 by mass. For each material type 1 disc with diameter 8 cm and thickness 3 mm was prepared and cut into samples (see Figure 2).

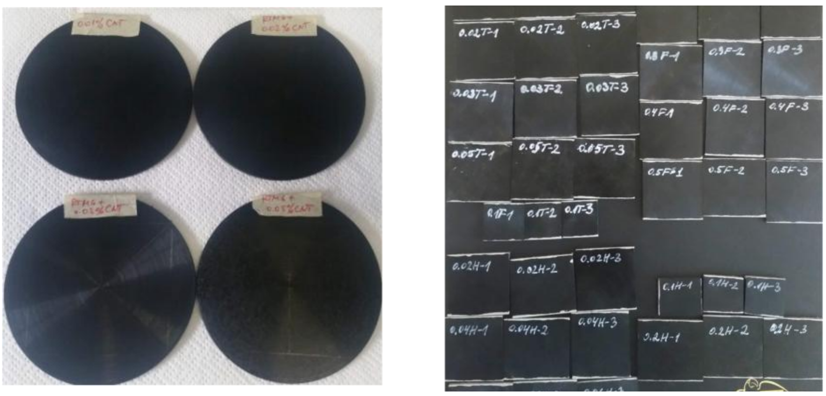

Figure 2. NC samples before and after cutting.

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

One set of epoxy and NC specimens was produced by the most optimal processing route for the characterization under WP3: electrical (electrical conductivity), thermal (thermal conductivity) and mechanical (flexural modulus, strength) properties before, during, and after environmental ageing (water absorption at +70 ˚C and freezing at -

20 ˚C). Five discs (the same as in Figure 2) for each material were developed: RTM6 epoxy resin, RTM6 filled with 0.05 wt. % of CNT, 0.3 wt. %of CNF and 0.1 wt. % of CNT/CNF (in the ratio 1:1 by weight). Totally, 128 specimens were prepared for mechanical and electrical characterization, and 16 specimens for thermal characterization.

WP3. Characterization of the NCs and FRP

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

Characterization of the NCs was performed by optical microscopy for the identification of the dispersion of carbonaceous nanoparticles' within the epoxy resin during Mobility#2. According report on micro/nano- structural characterization was prepared (D3.1, M8).

For each type of the material (RTM6 epoxy resin with carbon nanotubes (CNT, Nanocyl 7000 by Nanocyl), carbon nanofibers (CNF, SA 719781 by Sigma Aldrich) or hybrid nanofiller in ratio1:1) the filler content 0.1% was chosen as characteristic and representative content for optical analysis.

For the quantitative estimation of the filler dispersion the area of individual filler particles of the given systems was determined from the original images obtained from optical microscope using freely available *ImageJ* program. The area of individual filler particles was defined through the number of pixels in each specific case and was used for the subsequent analysis. The method of estimation filler dispersion degree was developed for model system[1] and further applied for epoxy filled with carbon nanotubes[2] by T. Glaskova-Kuzmina and the co-authors.

According to Figure 3 all nanofillers' particles mostly had bimodal distribution with a peak located at app. 0.2 μm^2 and 2.0 μm^2 which corresponds to radius of app. 0.2 μm and 0.8 μm in the case of spherical particles. The bimodality of distribution by particle area means that there was a tendency to form less and more single nanoparticles and their agglomerates. Considering the average sizes of the nanoparticles: 9.5 nm × 1.5 μm (CNT) and 100 nm×20-200 μm (CNF), it can be concluded that the filler dispersion was both satisfactory for single and hybrid nanofiller. Noticeably, at the lowest area of 0.12 μm^2 the impact of hybrid nanofiller was the highest of all. It means that the mixing conditions were efficient both for single and hybrid carbon nanofillers. Of course, the efforts can be made to improve it even more, but it should be emphasized that it was not the purpose of current study to get the most efficient dispersion of the nanoparticles within the epoxy resin.

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1 Glaskova T., Zarrelli M., Borisova A., Timchenko K., Aniskevich A., and Giordano M. "Method of quantitative analysis of filler dispersion degree in composite systems with spherical inclusions". Composites Science and Technology, 2011, Vol. 71, No. 13, p. 1543-1549.

[2] Glaskova T., Zarrelli M., Aniskevich A., Giordano M., Trinkler L., and Berzina B. „Quantitative optical analysis of filler dispersion degree in MWCNT-epoxy nanocomposite". Composites Science and Technology, 2012, Vol. 72, No. 4, p. 477-481.

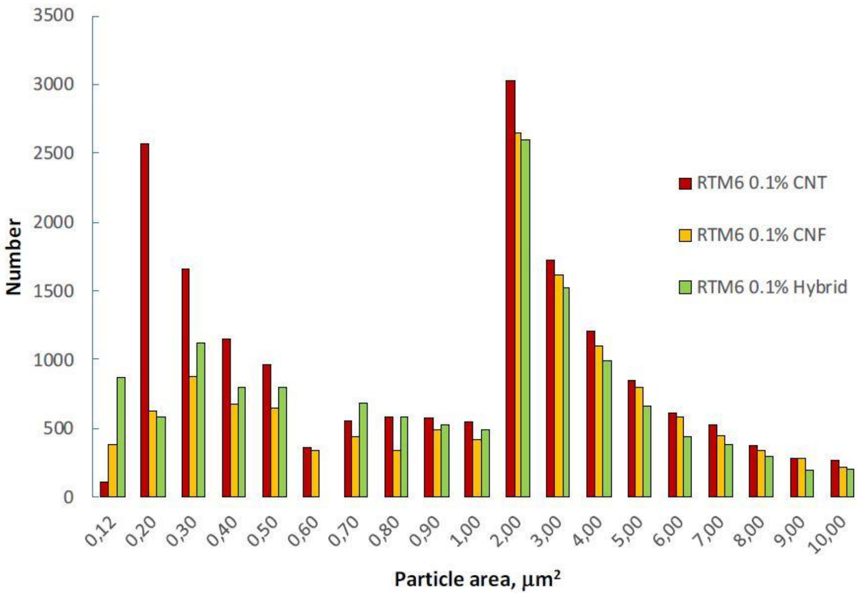

Figure 3. Distribution by particle area for different materials indicated in the figure legend.

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

Characterization of the NC specimens before, during and after hydrothermal ageing 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. In the initial state, before environmental ageing, the flexural properties were almost the same for all materials studied: flexural modulus was 2.9±0.1 GPa, strength was 140±5 MPa, maximal deformation was 6.5±0.5%. After environmental ageing, lasted 4 weeks, consisting of two parallel stages, water absorption at 70 °C and heating at 70 °C, increasing in flexural modulus was observed, respectively, of app. 7% and 13% for epoxy and all NC. No significant effect was revealed for the strength, while maximal deformation was reduced by app. 20% both due to water absorption and heating for all materials studied.

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. In initial state, the electrical conductivity of epoxy filled with 0.05 wt. % of CNT was 0.07 S/m, for epoxy filled with 0.3 wt. % of CNF – 0.007 S/m, and for epoxy filled with 0.1 wt. % of HN – 0.06 S/m. Both temperature and moisture affected the electrical conductivity for all NC samples. After 4 weeks of heating and water absorption it decreased by 16% and 19% for CNT-filled, by 9% and 19% for CNF-filled, and by 8% and 18% for HN-filled RTM6, accordingly.

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. In initial state, the thermal conductivity of epoxy and all NC was almost the same (0.23±0.01 J/mK). Heating and water absorption caused an increase (by 0.5-15%) of thermal conductivity for all materials tested. The lowest effect +0.5% and +2% was observed for epoxy filled with 0.1% of HN.

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 epoxy and epoxy filled with all carbon nanofillers obtained from DMTA was almost the same in initial state and after heating and water absorption: 235± 2 °C proving that the crosslinking degree was similar in all materials.

T3.3. Nonstandard environmental ageing

The environmental ageing, consisted of 1) water absorption at 70 °C until equilibrium moisture content was reached by all NC samples that lasted 4 weeks and 2) heating at 70 °C for the same time period, 3) freezing at -20 °C for 4 weeks. All samples were stored in the same shelf of the oven and freezer to get the same thermal conditions.

The peculiarities of moisture absorption in epoxy resin and NC samples were studied. The overall behaviour was similar for all materials following classical Fick's law for moisture diffusion. The addition of stiff moisture impenetrable carbon nanofillers caused slight reduction of equilibrium moisture content: 2.05% for epoxy resin, and 1.99%, 2.04%, and 1.81% for epoxy filled with 0.05 wt. % of CNT, 0.3 wt. % of CNF, and 0.1 wt.% of HN, accordingly. The diffusivity of the NC was also reduced slightly in comparison with neat epoxy resin. Final data was as follows: 1.70×10^{-4} cm^2/h for epoxy resin $1.62\text{-}1.67\times10^{-4}$ cm^2/h for epoxy filled with different carbon nanofillers.

WP4. Dissemination, communication and data management

T4.1. Dissemination of results

Four quarter press releases were published in the website of LU (https://www.lu.lv/index.php?id=53864). Two reports were made on international scientific conferences (*ECCM18* and *76th International Conference of the University of Latvia*). Self-activation within subject-based repository (*ResearchGate)* was made for *ECCM18* full-paper to assure open-access. Professional profile on *Facebook* () was developed and regularly updated. More information can be found in dissemination/communication report for 2018 (D4.1, M12).

T4.2. Communication

Dissemination/communication plan (D4.1, M12) was prepared and implemented. Local seminars, conferences, and other public events (e.g. *Researchers' night*) were attended. More information can be found in dissemination/communication plan and report for 2018 (D4.1, M12).

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

No significant nanofiller effect was found for sorption, mechanical and thermophysical characteristics of RTM6 epoxy resin.

Two concurrent factors, temperature and moisture, led to post-curing of all materials studied without significant plastization.

Based on experimental results the most environmentally stable NC was epoxy filled with 0.1 wt. % of CNT/CNF, which had the lowest effect of temperature and moisture on thermal and electrical conductivities, along with the lowest equilibrium water content and diffusivity.

Testing of all properties for moistened epoxy and NC samples after freezing is planned in January, 2019.

4. Main results

Scientific publications

1. Glaskova-Kuzmina T., Aniskevich A., Sevcenko J., Borriello A., and Zarrelli M. Moisture sorption by epoxy resin filled with MWCNT of different thickness. Proceedings of European Conference on Composite Materials, June 25-28, 2018, Athens, Greece.
2. “Creep and fatigue in polymer matrix composites” 2e edited by Rui Miranda Guedes, Elsevier, chapter “Effect of moisture on elastic and viscoelastic properties of fibre reinforced plastics: retrospective and current trends” by Aniskevich A. and Glaskova-Kuzmina T., 2018 (in press).

Presentations at international conferences

1. Glaskova-Kuzmina T., Aniskevich A., Sevcenko J., Zarrelli M., and Borriello A., „Moisture sorption by epoxy resin filled with MWCNTs of different thickness”, ECCM18, 25.-28.06.2018, Athens, Greece.
2. Glaskova-Kuzmina T., “Smart polymers and FRP modified by carbonaceous nanofillers for structural applications” LU 76. konferences plenārsēdē „Nano and quantum technologies and innovative materials for economy”, 01.02.2018., Rīga, Latvija (https://www.lu.lv/konference/programma/?session=587).

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 periods (2019, 2020)

Submission of two scientific papers to peer-reviewed scientific journals and two popular scientific papers in Latvian press is planned in the next two years.

Some of scientific results obtained during the first year will be published in 2019 in peer-reviewed Q1-Q2 scientific journals (ensuring green 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 2019 and will be discussed with scientific supervisor from the LU Dr. Sc. Ing. Andrey Aniskevich and representative person of collaboration partner Institute for Polymers, Composites and Biomaterials (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 (presentations/posters/papers) will be provided via self-archiving in *ZENODO* and *ResearchGate* repositories.

Project results will be presented in *ICCM22* in 2019, *ECCM19* in 2020, scientific popular events such as *Researchers' night* and *Scientific Café* in 2020. For these events exhibits, posters, booklets, and leaflets will be prepared.

Development of smart FRP plate (D2.3, M20) and implementation of full-year environmental ageing of epoxy, most stable NC, FRP and nano-modified FRP.

8. Deliverables and Milestones for reporting period (M1-M12)

Table 1. List of deliverables

No.	Deliverable name	WP	Type	Diss. level	Date
D2.1	Short report specifying the most promising material solution in terms of environmental stability	2	CO	R	M3
D1.3	IPR strategy prepared	1	CO	R	M4
D2.2	Short report assessing the most optimal processing route based on SWOT analysis	2	CO	R	M6
D3.1	Short report on micro/nano structural characterization	3	CO	R	M8
D1.1	Annual LU MMI progress seminars (M12, M24, M36)	1	PU	OTHER	M12
D1.2	Annual public reports published (M12, M24, M36)	1	PU	R	M12
D4.1	Dissemination/communication plan and annual dissemination/communication report (M12, M24, M36)	4	PU	R	M12

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

Table 2. List of milestones

No.	Milestone name	WP	Est. date	Means of verification
M2.1	The most effective processing route for all NCs assessed	WP2	M6	Short report with the details regarding the selection
M3.1	Electrical percolation of all NCs identified	WP3	M8	Public report in progress seminar