PART 2: PROGRAMME PROJECT INFORMATION

2.1. Project No. 5

Title	***Material mechanical micro- nano- scaled features and their impact on human safety***		
Project leader's name, surname	Jurijs Dehtjars		
Degree	Dr. hab. phys		
Institution	Riga Technical University, Institute of Biomedical Engineering and Nanotechnologies		
Position	Head of the Institute, Professor		
Contacts	*Phone number*		+371 29469104
	E-mail		jurijs.dehtjars@rtu.lv

2.2. Tasks and deliverables

(Describe the project goals and objectives so that the achievements reported below could be placed in context and evaluated)

Project goal: To research early destruction of surface of polymer composite materials, to develop methods of early diagnostics and analyze application of the methods in enterprises.

Task 1 of the 2nd Period: *Development of research methods for diagnostics of early destruction of surface of polymer composite materials: the method to research influence of aquatic microorganisms on early destruction of materials.*

The following was planned in order to accomplish the Task: (1) to perform TOC (*total organic carbon*) leaching and microorganisms counting experiments using aging acceleration of polymeric pipes (at 60 °C temperature); (2) to develop the research method for development of diagnostics of early destruction of surface of polymer composite materials using *in situ* electron emission spectroscopy (the Deliverable).

Task 2 of the 2nd Period: *Development of research methods for diagnostics of early destruction of surface of polymer composite materials: the method to research visual recognition of early destruction using destruction-induced staining.*

The following was planned in order to accomplish the Task: (1) to perform experimental measurements and simulations in order to determine mechanical properties of microcapsules embedded in an elastic matrix; (2) to develop the research method for development of diagnostics of early destruction of surface of polymer composite materials using destruction-induced staining (the Deliverable).

Time frame for the tasks is given in Annex 5-A.

The goal and tasks of the 2nd Period of the Project were fully achieved:

- Ability of the inner walls of polyethylene pipes to leach organic compounds into drinking water was tested at 60 °C temperature (under leaching promoting conditions). Using microbial consortium of Evian water and indicator of faecal contamination *E.coli* bacteria as an example, it was shown that the organic

compounds leached into the water serve as nutrients for bacteria and promote bacterial growth.

- Using the method of photoelectron emission spectroscopy, it was determined that structural changes in surface of polymer composite materials occur already in the region of elastic deformation.
- Two types of polymer composite materials containing dye and developer-filled microcapsules were prepared and tested for the main mechanical properties. Using Voigt and Reuss models of the general rule of mixtures, effective modulus of elasticity of the microcapsules was indirectly estimated.
- Electropassive unidirectionally reinforced composite based on nanomodified epoxy resin was prepared. Conductivity anisotropy of the composite was determined experimentally: longitudinal and lateral conductivity differed about 10 times.
- It was found that increase in the concentration of nanotubes in epoxy binder to 1.5% changes electric conductivity of the composite from insulator to electrical conductor and the resistivity drops about 100 times.
- Literature review about mechanical testing methods of microcapsules has been launched.

The following Deliverables were delivered upon the completion of the 2nd Period:

Nr.	Task	Deliverable	Responsible partner	Status
1.	Development of research methods for diagnostics of early destruction of surface of polymer composite materials: the method to research influence of aquatic microorganisms on early destruction of materials	Research method for development of diagnostics of early destruction of surface of polymer composite materials using *in situ* electron emission spectroscopy	J. Dehtjars, Institute of Biomedical Engineering and Nanotechnologies, RTU	Delivered Annex- NN
2.	Development of research methods for diagnostics of early destruction of surface of polymer composite materials: the method to research visual recognition of early destruction using destruction-induced staining	Research method for development of diagnostics of early destruction of surface of polymer composite materials using destruction-induced staining	A. Aņiskevičs, Institute of Material Mechanics of the University of Latvia	Delivered Annex- NN

2.3. Description of gained scientific results

(Describe scientific results achieved during reporting period, give their scientific importance)

Tasks of the Project	The main results
1. Development of research methods for diagnostics of early destruction of surface of polymer composite materials: the method to research influence of aquatic microorganisms on early destruction of materials.	***The method developed***
The following results were achieved during the report period: Ability of polyethylene pipes to leach organic hydrocarbons into drinking water was tested.	

Evian water filtered through 0.1 μm filter was used. Water was replaced daily in the pipes. After 72 hours increase in the number of bacteria found in the water with the leached organic compounds was measured. The results showed that the polymeric pipes leached organic substances into water and this promoted multiplication of bacteria. Moreover, not only number of Evian water consortium bacteria increased (which is a normal phenomenon because this is a common environment for the bacteria) but number of *E.coli* bacteria increased as well. Multiplication of *E.coli* indicates that polymeric pipes can promote growth of faecal bacteria in case of unintentional or intentional contamination.

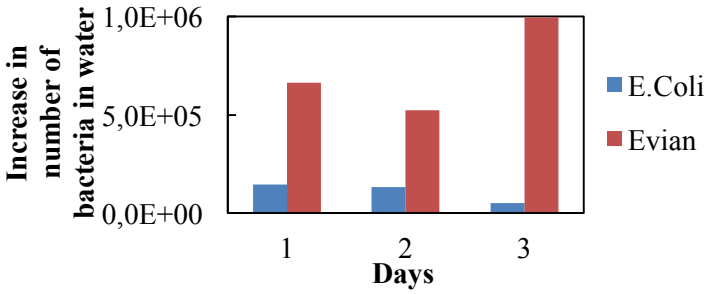

Fig.1. Increase in the number of bacteria in water that was held 24 hours in polyethylene pipes

The research method for development of diagnostics of early destruction of surface of polymer composite materials using *in situ* electron emission spectroscopy was developed (the Deliverable): in order to detect early mechanical changes in the surface of materials, it is necessary to measure photoelectron emission during mechanical deformation of the samples and monitor photoelectron emission current changes that occur in the elastic deformation region. Fig. 2 (a) shows behaviour of PE-80 polymeric pipe during deformation. Stress is linearly dependent on strain until the strain reaches 1.6 %. One may conclude that PE-80 pipe behaves like an elastic material in the strain region from 0 to 1.6%, however, there is a sharp decrease in the electron emission current at a strain of 0.8% (shown with the black dashed vertical line in Fig. 2 (a)). This decrease can happen due to structural changes in the polymeric pipe. Changes in electron emission during elastic mechanical loading of fiberglass and epoxy resin composite are shown in Fig. 2 (b). There is an increase in photoelectron emission intensity at a stain of 1.8% which means that structural changes occurred in the material.

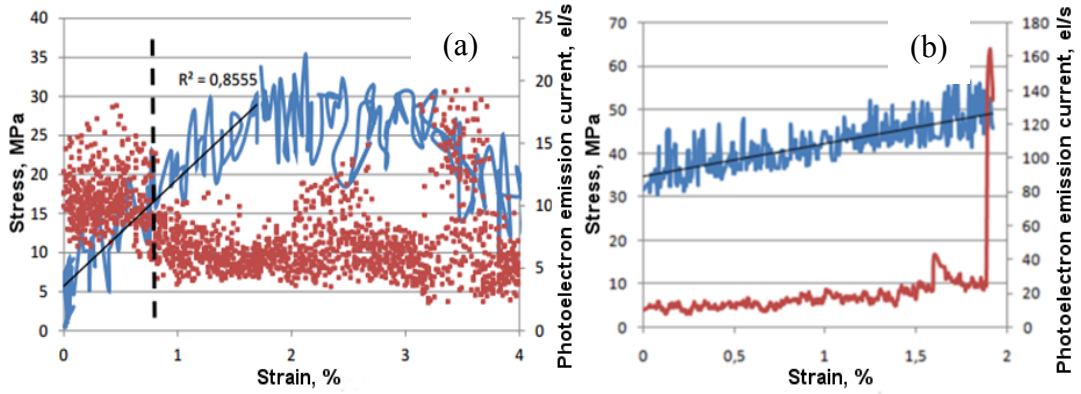

Fig.2. Stress-strain relationship (in blue) and dependence of photoelectron emission intensity on stain (in red): (a) PE-80 polymeric pipe; (b) fiberglass and epoxy resin composite

2. Development of research methods for diagnostics of early destruction of surface of polymer composite materials: the method to research visual recognition of early destruction using destruction-induced staining.	***The method developed***

The following results were achieved during the report period:

Two types of polymer composite materials containing different concentrations of dye and developer-filled microcapsules were prepared: 1) microcapsules in PVA (polyvinyl acetate) glue

matrix, 2) microcapsules in epoxy resin matrix. All samples were tested in tension. In addition, effective modulus of elasticity of the microcapsules was indirectly estimated using Voigt and Reuss models of the general rule of mixtures.

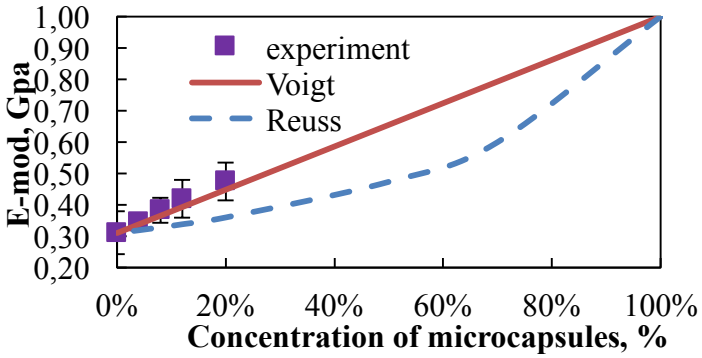

Fig.3. Effective modulus of elasticity of the microcapsules that was measured experimentally and estimated indirectly using Voigt and Reuss models

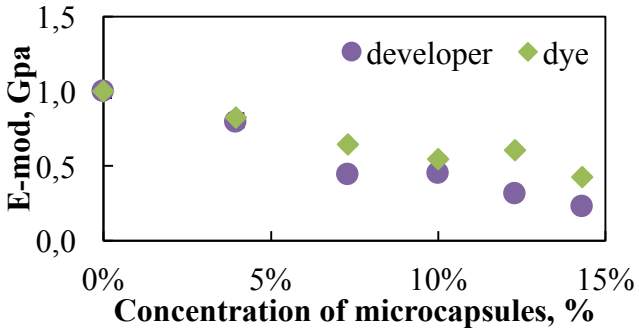

Fig.4. Effective modulus of elasticity of epoxy resin containing microcapsules

Electropassive unidirectionally reinforced composite based on nanomodified epoxy resin was prepared. Conductivity anisotropy of the composite was determined experimentally: longitudinal and lateral conductivity differed about 10 times.

Increase in concentration of nanotubes in Araldite LY 1564 + Aradur 3486 epoxy binder up to 1.5% changes electric conductivity of the composite from insulator to electrical conductor and the resistivity drops about 100 times (to 20 Ω·m).

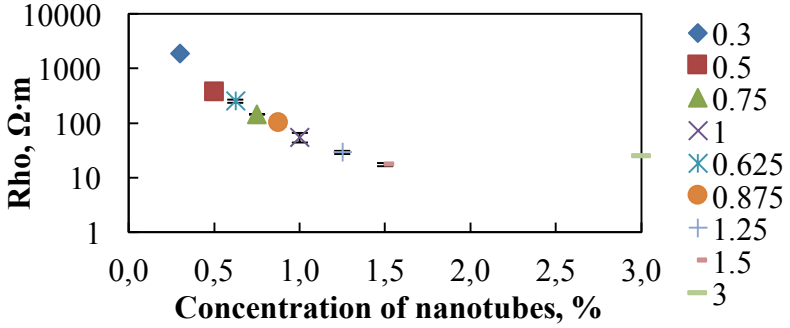

Fig. 5. Conductivity of Araldite LY 1564 + Aradur 3486 epoxy binder depending on concentration of nanotubes

Literature review about mechanical testing methods of microcapsules has been launched. Analysis of scientific publications about micro-manipulation techniques and AFM (atomic force microscopy) for testing of microcapsules was performed.

The research method for development of diagnostics of early destruction of surface of polymer composite materials using destruction-induced staining was developed (the Deliverable).

The achieved results have the following scientific and practical importance:

- It has been proved that in order to predict destruction of polymer composite materials, it is important to take into account structural changes in the material that occur at micro and nano scale already in elastic deformation region.
- Nowadays polymeric pipes are widely used in water supply systems, however not much information is available on the influence of organic compounds leached into water from the walls of the pipes on human health. The results obtained in the project draw this problem to attention.

2.4. Further research and practical exploitation of the results

(Describe further research activities that are planned, describe possibilities to practically exploit results)

Technological readiness has been achieved for the implementation of the 3rd Period of the Project. The achieved results demonstrate ability to continue implementation of the Project in accordance with the original application and develop methods for diagnostics of early destruction of polymer composite materials. **Therefore, two following tasks are planned for the 3rd Period:**

1. Development of methods for diagnostics of early destruction of surface of polymer composite materials: the method for diagnostics of early destruction using *in situ* electron emission spectroscopy; the method for diagnostics of early destruction, based on influence of aquatic microorganisms.
    - The method for diagnostics of early destruction of surface of polymer composite materials using *in situ* electron emission spectroscopy will be developed (the Deliverable).

2. Development of methods for diagnostics of early destruction of surface of polymer composite materials: the method of visual recognition of early destruction using destruction-induced staining.
    - The method for development of diagnostics of early destruction of surface of polymer composite materials using destruction-induced staining will be developed (the Deliverable).

The following research will be done:

- Influence of aquatic microorganisms on mechanical strength of polymeric pipes will be studied. First, polymeric pipes will be treated with water to which typical aquatic bacteria and *E.coli* bacteria will be added. After that, photoelectron emission of the pipes will be measured during mechanical loading and the results will be compared with those obtained for the new pipes.
- Influence of micro and nanoparticles on mechanical properties of polymer composite materials will be studied by measurements of photoelectron emission during mechanical loading. SiO_2 micro and nanoparticles will be used.
- Data on mechanical properties of microcapsules obtained during the 2nd Period of the Project will be used to create theoretical model and simulate mechanical behaviour of polymeric matrix with embedded microcapsules.

Practical exploitation of the achieved results:

Possibility to develop a method for diagnostics of early destruction of polymer composite materials has been confirmed. As a result:

a) The knowledge about destruction processes taking place in polymer composite materials and water-supply polymeric pipes at nano and micro scale will be developed.
b) Quality and safety of polymer composite materials and corresponding constructions, as well as sustainability and safety of water supply systems will be improved.

2.5. Dissemination and outreach activities

(Describe activities that were performed during reporting period to disseminate project results)

Participation at scientific conferences in 2015:

1. Aniskevich, A., Bulderberga, O., Dekhtyar, Yu., Denisova, V., Gruskevica, K., Juhna, T., Kozak, I., Romanova, M. Coloured Reactions and Emission of Electrons towards Early Diagnostics of Polymer Materials Overloading. *2nd International Conference Innovative Materials, Structures and Technologies (IMST 2015)*, September 30 – October 2, 2015, Riga, Latvia, Book of abstracts, p.19. (abstract and poster presentation)
2. Dombrovskis E., Kozaks I., Gruskevica K., Dekhtyar Yu. Diagnostic method for early collapse of polymer pipes under mechanical load. *Riga Technical University 56th International Scientific Conference*, October 14-16, 2015, Riga, Latvia (oral presentation)
3. Aniskevich, A., Kulakov, V. Express procedure for evaluation of durability of complex shape pultruded composite profiles. *Baltic Polymer Symposium 2015*, September 16-18, 2015, Sigulda, Latvia, Book of abstracts, p. 67. (abstract and poster presentation)
4. Zeleniakiene, D., Leisis, V., Griskevicius, P., Bulderberga, O., Aniskevich, A. A numerical study to analyse mechanical properties of polymer composites with smart microcapsules for high performing sensing applications. *Baltic Polymer Symposium 2015*, September 16-18, 2015, Sigulda, Latvia, Book of abstracts, p. 71. (abstract and poster presentation)

Conference abstract and journal paper were submitted and accepted:

1. Aniskevich A., Bulderberga O., Dekhtyar Yu., Korvena-Kosakovska A., Kozak I., Romanova M. Electron emission of the carbon nanotube-reinforced epoxy surface nano layer towards detection of its destruction induced by elastic deformation. *International Nanotechnology Conference & Expo (Nanotech-2016)*, April 4-6, 2016, Baltimore, USA
2. Ivanov, D. S., Le Cahain, Y. M., Surush Arafati, Dattin, A., Ivanov, S. G., Aniskevich, A. Novel method for functionalising and patterning textile composites: liquid resin print. *Composites Part A: Applied Science and Manufacturing* (SNIP 2.518)

Two master theses were defended:

1. Inguna Krista Anspoka. Influence of destruction of composite material on electron emission from composite material surface, supervisor Prof. A.Balodis
2. Irina Golovko. Influence of plastic water supply material on quality of drinking water, supervisor Asoc. Prof. K. Tihomirova

Three bachelor theses were defended:

1. Anna Korvena-Kosakovska. Early failure of composite material under mechanical load, supervisor Prof. A. Balodis
2. Ēriks Dombrovskis. Diagnostic method for early collapse of polymer pipes under mechanical load, supervisor Prof. J.Dehtjars
3. Toms Vāvere. Indirect determination of mechanical properties of polymer matrix spherical fillers, supervisors Dr. Sc. Ing. Andrejs Aņiskevičs, Msc. Olga Bulderberga

The doctoral thesis is being developed:

O. Bulderberga. Polymer composite with damage indication ability: development and determination of properties. Supervisor A. Aņiskevičs, the defence is planned in 2017.

Dissimination of the results:

Project participants held **four meetings** to discuss the results of the Project (13.04.2015, 13.05.2015, 10.09.2015, 21.12.2015). The stuff of the departments involved in the implementation of the Project as well as bachelor and master students who participated in the research were invited to participate in the meetings.

Results and performance indicators of the Project were presented on May 26, 2015, at the **seminar on the research progress of IMATEH Programme.**

On October 2, 2015, the results and performance indicators of the Project were presented during special session of IMST 2015 conference dedicated to IMATEH Programme: J.Dehtjars "Material mechanical micro- nano- scaled features and their impact on human safety".

On March 3, 2016, the **seminar was organized** at "Aviatest" Ltd. company, Rezeknes Str.1, Riga. The aim of the seminar was to present the results of the Project to entrepreneurs and discuss future cooperation possibilities.

Information about implementation of the Project is regularly updated on the website of IMATEH Programme: http://imateh.rtu.lv/.

Leader of the project No. 5 _____Jurijs Dehtjars_____

(signature and transcript)

(date)