

## Faculty of Chemical Technology and Metallurgy

### Projects under the Shota Rustaveli National Science Foundation grant

№	Grant Name	Supervisor	Project period	Total project sum	Status Completed/Ongoing	Grant code
1	"Production testing and optimization of an innovative automotive catalyst free of precious metals"	T. Natriashvili	2016-2019	240 000	Completed	217020
2	"Development of waste utilization technology of manganese mining and processing production"	T. Lezhava	2018-2022	240 000	Completed	AR-18-281
3	Calculation of thermodynamic parameters of the process of high-temperature thermochemical processing of plastic waste and obtaining high-tech nanostructured carbon	Akaki Peikirishvili	06.02.2023-31.12.2025	-	Ongoing	FR – 22 - 4275
4	Development of boron-containing complex ligature for multifunctional alloys on the basis of steelmaking waste by high-temperature synthesis and metallurgical methods	Levan Chkhartishvili	23.12.2022-31.12.24		Ongoing	STEM – 22 - 761
5	Influence of structural factors on tribocorrosion by sliding under dry friction of boron microalloyed bainite cast iron	Salome Gvazava	18.02.2022-27.12.2022	6000	Completed	MR-21-232
6	New high-tech diamond composite material and its production technology	Nikoloz Ioladze	2018 – 2022	548000	Completed	AR 18 - 1911
7	Codicological analysis of fragmentary manuscripts made on Parchment and structural study of the material	Tamar Abuladze	2019-2023	180 000 GEL	Ongoing	FR-19-7472

8	Obtaining multifunctional ceramic composite materials on $\beta$ -sialon matrix, with cheap raw materials and simplified technology	Young scientist N. Darakhvelidze	2018/10/12 2022/04/28	55900 (fifty-five thousand GEL)	Completed	N° YS-18-077
9	Production of periclastic high-refractory materials using local raw materials and production waste	Young scientist M. Balakhashvili	21.12.2021 21.12.2023	55900 (fifty-five thousand GEL)	Ongoing	N°YS-21-1473
10	Multifunctional nanocomposites B4C-TiC-SiC-BN-Al2O3-SiAlON-carbon fiber in the system for high-temperature and wear-resistant joints of armor plates, turbine discs and wings.	N. Nizharadze	21.03.2022- 21.03.2025	240,000 (two hundred and forty thousand GEL)	Ongoing	NFR-21-1413
11	" physics and kinetics of sintering "	Z. Kovziridze	2021	5000 (five thousand GEL)	Completed	SP-2-21-565
12	Modification of Georgian clay rocks into porous products for filling energy-efficient and weather-resistant concretes	Supervisor from GTU Prof. T. Cheishvili.*	19.12.2018- 19.12. 2022 - under completion, submitting the report in 2023.	560 000	Ongoing	AR-18-343
13	Method of cement production for purification of flue gases from (CO <sub>2</sub> , SO <sub>x</sub> , NO <sub>x</sub> ) before emission to the atmosphere by passing through a clinophthylolite sorber in a laboratory environment and determining usability through experimentation, proof of concept	Prof. G. Loladze	23.12.2022 - 23.12.2024	180 000	Ongoing	N° AR-22-1730
14	CO <sub>2</sub> sorbents based on natural zeolites, synthesis/ use/ utilization technological idea concept formulation, applicability determination and approval in laboratory environment.	Prof. V. Gordeladze	23.12.2022 23.12.2024	180 000	Ongoing	N° AR-22-2017

15	Synthesis and study of high mechanical strength, polyesterurea class pseudoproteins	Ramaz Katsarava, Nikoloz Chikhradze	2021-2023	31500	Ongoing	PHDF-21-184
16	Synthesis and study of graphene/polymer nanocomposites for 3D printing	Supervisor - Mamuka Maisuradze PHD student Sophio Mikaberidze 2022 Grant Funding Competition for Doctoral Education Programs	2022-2024	31500	Ongoing	PHDF-22-575

\*Georgian Technical University, Iv. Javakishvili Tbilisi State University, Levan Samkharauli National Bureau of Forensic Expertise, K. Zavriev Institute of Construction Mechanics and Seismic Resistance are members of the consortium that is implementing the grant awarded by the Shota Rustaveli National Foundation of Georgia. General supervisor M. Bazadze.

### Abstracts

-concrete result-

#### 1. "Production testing and optimization of an innovative automotive catalyst free of precious metals"

The goal of the project was to create a cheap and effective innovative nano hybrid catalyst free of platinum group metals and to develop a commercialization plan. During the grant period, the nanohybrid catalyst made on the basis of nanosilver obtained on the basis of different concentrations of oleic acid was tested on the laboratory equipment and stand with different ratios of the main components AgMnOx. The nanohybrid catalyst obtained with the addition of the third component (chromium oxides, cobalt, copper) was also tested. In total, more than 20 catalysts were tested on the stand. The best of them (AgMnOx) was selected for testing on the machine, which showed high activity towards carbon monoxide (100% conversion) and hydrocarbons (70-80% conversion). Their activity towards the conversion of nitrogen oxides did not exceed 20-30%.

- Recommendations

1. It is necessary that the fuel used in cars is guaranteed not to contain lead and sulfur (sulfur content is 15 times higher than the European standard), so that the surface of the catalyst is not poisoned by harmful elements of the fuel (lead and especially sulfur passivates silver).
2. In order to improve the catalyst, it is necessary to continue the research, which provides for the addition of various metals (Mn, Fe, Cr, V, Mo, Co, Ce, Ni, W, Cu, Sn) to the catalyst, the electrosynthesis of each component separately and with co-precipitation, which may lead to precious metals Without addition, it is sufficient to increase the degree of conversion of nitrogen oxides.

#### 2. "Development of waste utilization technology of manganese mining and beneficiation";

-concrete result-

Within the framework of the project electro-regenerative leaching of residual tailings (18.1%Mn) generated during the enrichment process of Chiatura manganese-free oxide raw ore has been carried out in a diaphragmless electrolyzer using the redox system  $\text{Fe}^{3+}/\text{Fe}^{2+}$  as a mediator under the conditions of a limited concentration of  $\text{Fe}^{3+}$  (up to 3.5 g/l $\text{Fe}^{3+}$ ). Using the redox system  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , the following technical solutions were implemented to efficiently conduct the electro-extraction process: use of a peristaltic pump and compressor for the circulation of the suspended electrolyte in the electrochemical reactor and for powerful turbulation; equipping the electrochemical reactor with graphite cathode or stainless steel grid cathodes with a developed surface; Extracting the suspension stream from the electrochemical reactor through the porous graphite felt or stainless steel mesh - cathodes and feeding it to the intermediate tank.

- Recommendations

The results of the project allow the solution obtained from the mass leaching of residual tailings generated in the process of beneficiation of Chiatura manganese-free oxide raw ore to be transferred unfiltered to the anode area to obtain electrolytic manganese dioxide, which is economically and ecologically justified.

### **3. Calculation of thermodynamic parameters of the process of high-temperature thermochemical processing of plastic waste and obtaining high-tech nanostructured carbon**

One of the most tangible results of anthropogenic activity is the generation of waste, among which plastic waste has a special place. Most plastic waste is not biodegradable, is not subject to decay and corrosion, practically does not decompose over time. It is established that the major fraction of pyrolysis of polyethylene terephthalate is gas flow, solid waste (along with benzoin, acetophenones and other organic compounds) and oil fraction. Thus, by pyrolysis treatment of polymer waste, a solid residue (coal) containing negative impurities is obtained. It is therefore necessary to develop additional technology for their mechanical and chemical enrichment. This is associated with additional costs, which will significantly increase the cost of the product. In fact, the existing methods of pyrolysis do not provide high-quality, nanostructured, activated carbon - "carbon black". Therefore, it is very important to study alternative methods of producing "carbon black", which will eliminate environmental problems and reduce its cost.

The project will develop an economically viable, environmentally safe combined method of thermal treatment of polymer waste - which involves low-temperature pyrolysis of the waste at the initial stage, and then - high-temperature thermo-chemical treatment in water steam environment. The mechanism of high-temperature thermo-chemical treatment of polymer waste in water steam environment will be studied. Mandatory operating parameters for waste thermal treatment will be defined and calculated for the design of the reactor, which will determine the course of the process, the composition of the product and the yield. Thermal treatment of plastic waste in the reactor is carried out at a temperature of 200-900°C. Water steam at low temperatures increases the initial decomposition reactions. As the temperature increases, the rates of adverse reactions (polymerization and cyclization) increase and the formation of a dry residue - carbon deposits containing various undesirable impurities - begins. At a temperature of 850-900°C, water steam activates the process and completely destroying the residual polymer compounds. As a result, the formation of carbon-free atoms in the gas, which, upon cooling and hardening, forms highly dispersed carbon particles takes place. The obtained high-quality, nanostructured, activated carbon - "carbon black" is obtained by milling / processing the obtained carbon mil.

Thus, the method allows to obtain from pyrolysis both oil and "carbon black", which will fully meet the technical requirements. The physical characteristics of the obtained "carbon black": density, porosity, free surface area, cleanliness and yield are determined in accordance with international standards.

#### **4. Development of boron-containing complex ligature for multifunctional alloys on the basis of steelmaking waste by high-temperature synthesis and metallurgical methods**

The goal of the project is to develop boron-containing complex ligatures for multifunctional alloys. As a raw material will be used the waste of steelmaking production mainly in the form of finely dispersed iron oxide. Such ligatures will be obtained by SHS (self-propagating high-temperature synthesis) metallurgy, the waste-free technology, whose additional advantages are: low energy consumption, relatively simple and small-sized equipment, high productivity and high purity and wide range of products. Using specifically designed complex ligatures, corrosion- and wear-resistant cast iron and steel specimens will be obtained. Chemical analysis and metallographic methods will be used to study the influence of boron and other component elements of ligatures on the operational characteristics of target alloys. The project is a joint research in "Materials Technology" and "Condensed Matter Physics" fields. The first of them aims at the further development of SHS and foundry production technologies, respectively, to obtain boron-containing complex ligatures and multifunctional alloys using them, and the second – the characterization of the physical mechanisms of these technologies and the investigation of the structure and physical-mechanical properties of the obtained ligatures and alloys. In the future, the implementation of the technology developed within the framework of the project will have positive ecological and economic impacts because in this way the existing waste resources will be directly used in the production of new expensive products.

#### **5. Influence of structural factors on tribocorrosion by sliding under dry friction of boron microalloyed bainite cast iron**

The materials which are used in modern technology, have number of requirements, such as: multi-functionality, technological cheapness and long exploitation life-time. Today, one of the most promising construction materials is high-strength sphericalgraphite cast iron. High-strength bainite cast iron is distinguished by technological diversity and the parts made from it allows to reduce the economical characteristics. It is known that in the world manufacturing industry the loss on the wear products of friction of machine parts is 6-8%, and according to the US data if 2016, corrosion damage is -1.1 trillion Dollars [1], and the economic losses caused by tribocorrosion exceed 300 billion dollars a year[2]. Therefore, the current problem is to reduce the wear loss during exploitation of benign cast iron under extreme conditions. High-strength bainite cast iron, developed in recent decades, is a new class of construction material with high tribo-technical characteristics. For the effective operation of modern brake systems in extreme conditions, it should be taken into account that the materials used for their production should be characterized with high mechanical strength, thermal resistance, corrosion and wear resistance, and an optimal friction coefficient. These requirements can be achieved by managing the alloy structure formation processes, optimizing the ratio of structural components and regulating the distribution of phase components.

Should be noted the high mechanical properties of bainite cast iron, high strength and the ability to manage the structure in a wide range. Based on the above described, bainite cast iron belongs to one of the most promising wear-resistant materials. As it is known, the degradation and erosion of the surface layers of the material is caused by different factors such as fatigue, adhesion and tribocorrosion. Based on the literature analysis, it is known, the main tribotechnical and tribocorrosion characteristics of bainite cast irons (friction coefficient, wear intensity,

thermophysical properties, etc.) depend on their structural characteristics and external influences (rotational speed and contact load).

It is known that the cast irons mainly used in practice today are alloyed with such expensive elements as Cu, Mo and Ni, which ensure a stable reception of the bainite structure. The high cost and necessary quantity of these elements (up to 2%) determines the high cost of the manufactured products. Therefore, it is important to replace the above-mentioned elements with multi-factor influencing and relatively cheap ones.

Therefore, it is important to replace the above elements with relatively inexpensive and multifactorial ones. For example, microalloying with boron not only reduces the cost of the technological process, but also leads to the formation of new, dispersed phases in the structure (borides, carbides, boron nitrides and carbonitrides), which should probably have a positive effect on the set of operational properties of the material.

At the same time, it should be noted that the influence of the structural factors of boron microalloyed bainitic cast irons on their tribotechnical and tribocorrosion characteristics has not been practically studied, which prevents the wide use of this material in extreme operating conditions.

Proceeding from the above described, the aim of the work is:

- Study of the influence of the structural factors of a new construction class material - boron microalloyed high-strength bainitic cast irons on their corrosion resistance and tribotechnical characteristics.
- Determination of optimal structural ratio (residual austenite and bainite) of the base metal of boron microalloyed bainitic cast irons.

The influence of the contact load and the amount of residual austenite on the friction coefficient, the wear resistance of the material and the temperature change in the friction contact zone were determined. The influence of boron micro-additive (B-0.03%) on the structure of bainitic cast iron was investigated by metallographic analysis.

In order to determine the tribo-corrosion characteristics of high-strength bainitic cast iron microalloyed with boron, samples with different bainitic matrices were selected for tribological studies in periodic wetting mode, during which the coefficients of friction, wear mechanisms and the kinetics of temperature changes in the frictional contact zone were determined. The corrosion behavior of the mentioned samples was determined through Tafel potential-dynamic curves.

The influence of the amount of residual austenite on the kinetics of the change of the friction coefficient of the experimental samples was studied.

Based on the obtained results, the influence of structural factors on the tribocorrosion characteristics of boron microalloyed bainitic cast iron was determined, which will allow us to optimize the structure and ensure the effective use of this material for the production of various elements of brake systems and mill balls.

## **6. New high-tech diamond composite material and its production technology**

The goal of the scientific Project was to develop a low-cost diamond composite material for diamond tools with improved performance compared to best existing analogues for use in various fields of industry. In the process of fabricating diamond composite, pre-determined chemical and phase composition multi-component metal alloy compositions were used. As a result of theoretical and extensive experimental studies, a multi-component copper-based alloy with a high content (7-13%) of carbon-active elements (Ti, Si) was selected as such composition.

Fabricating the metallic component of the planned properties was carried out using modern melting technologies and subsequent dispersion of the created alloy ingots to obtain powders of the desired granulometry. By adjusting the melting and crystallization modes, the phase composition and structure of the alloys were varied. The main idea of the innovation is that for the formation of the metal matrix of the diamond composite, dispersed powders of the produced alloys were used in the sintering process, and not a mixture of powders of individual components (which is used by brand companies), which determines the special effect of the final result. The use of pre-alloyed powders as initial raw materials for the formation of the metal matrix of diamond composites no longer requires the use of expensive pure metal dispersion powders (which nowadays are widely used). All of the above-mentioned simplifies the technological process and that is why it is more cost-efficient. The use of new diamond composite material developed within the framework of the Project in diamond tools, in particular, the large-scale production tests on concrete cutting operation, demonstrated that the diamond tools developed within the framework of the project are actually on the same level as the best foreign analogues in terms of cutting ability and durability. The obtained result is a precondition that the material created within the framework of the Project can be widely used in the construction field of our country.

#### **7. Codicological analysis of fragmentary manuscripts made on Parchment and structural study of the material**

**Concrete result** - the project is interdisciplinary and involves the codicological research of fragments and the diagnosis of written material, as well as the development of relevant recommendations. From the codicological point of view, the fragments preserved in the funds of the Korneli Kekelidze National Center of Manuscripts, as well as the Mestia Museum of Local Lore and the University of Graz (Austria) were described; The degree of their damage was analyzed - Parchment, surface, ink, painting; A study of the structure of the remaining letters of the 11th-15th century parchment and the texts written on it in red and black ink was carried out using Fourier. IR spectroscopic method.

A database was created according to specially selected parameters; The results were presented at the international conference "Archival science, source science - trends and challenges;

A Georgian-English monograph was prepared for publication - research, texts of fragments, photos.

- **Recommendations** - specific recommendations for the protection, storage and conservation measures of Parchment fragments were developed by the restorers and chemists involved in the project.

**8.** As a result of experiments, composites with high physical and technical properties were obtained by hot pressing at a temperature of 1600°C with a pressure of 30 MPa: strength limit in compression - 14 GPa; Strength limit in compression - 1940-1960 MPa; Bending strength limit - 460-490 MPa, most importantly, these composites maintain these properties even at high temperatures. In addition, they are characterized by high thermal, corrosion and wear resistance, etc.

The resulting composites can be used in rocket and space technology, as composite coverings for high-temperature products, for making high-temperature furnace linings, thermocouple protective casings, as metal cutting tools, for metal and stone processing, dental drills, bearings, and others.

During the reporting period, the research results were presented at international conferences, both in Georgia and abroad.

One scientific paper was published in an internationally refereed, highly cited journal with the final results of the research

**9.** In the reporting period of 2022, literary materials were searched for the raw materials of high-refractory base composition, refractories used in metallurgy (electrical and induction furnaces) and high-temperature furnaces for burning cement. For the area of the first zone. An analysis was made based on the literature. As a result of

comparative studies of dolomite of local deposits, dolomite from the Skur deposit was selected as the main raw material, and the selected raw material was inspected and imported.

Khrol sand and brick mortar were imported and studied. Initial materials for further studies have been prepared. Composite compositions have been developed.

**10.** One of the most important directions in modern technology is obtaining and using highly fire-resistant materials. Mostly it is related to the increase of working temperature in energy, transport and other installations. Despite the great advantage of materials derived from high-refractory oxides, it is mainly characterized by a high coefficient of thermal expansion and, as a result, low thermal resistance. Ceramics of oxygen-free refractories are easily oxidized at high temperatures. In the reporting period, a literary analysis of the modern state of this problem was conducted and relevant conclusions were drawn, which will be a precursor to obtaining composites with high technical properties based on oxide and non-oxide compounds.

The tools and equipment necessary for the research were prepared, the mixtures were prepared for obtaining sialons by the aluminothermic method, the technological parameters and the optimal composition were determined. Materials were prepared for publication in a scientific conference and a high-rated journal.

**11.** In the mentioned book, the matrix and operational properties of the ceramic material are related to one of the main constituents of its phases – the porous phase, which has a significant impact on the operational properties, pore sizes, their content, and the redistribution factor in the matrix, how it affects the operational properties of the product, how it develops, redistributes-moves, annihilates, heals-disappears, or is deformed on the material under conditions of thermal aggression, consolidation and baking.

**12.** Based on previous studies, the clay, argillite and clay shale of three locations were treated with the prescribed thermal regimes with the participation of the employees represented by GTU consortium members. The product obtained from them by low-temperature treatment (600-800°C) was purposefully used as pozzolanic cement additive. The amount of acceptable additions to the cement taken for the production of test samples is determined by the chemical and mineralogical composition of the initial raw material and the mode of its thermal treatment, which was also carried out based on the data established in the previous period. Also, a number of clay rocks of Georgia (Kvareli clay slate, Teleti argillite and Gardabani clay) are subjected to high-temperature (1150- 1250°C) with modifications, it was established on their basis to obtain a lightweight concrete filler - ceramsite. In order to obtain light concrete from them, presentation samples were prepared based on the developed recipes. Presentation samples of pozzolanic additive and cement clinker obtained by grinding them together with cement clinker were prepared.

The material was collected for advertising documentation, which includes the description of the technological processes of the products obtained by temperature transformation of Georgian clay rocks and the methods of obtaining products from them. This material will be used for transfer and commercialization purposes on the creation website.

**13.** Climate change towards global warming is the biggest problem of humanity of the 21st century, its prevention is also the biggest challenge and a priority task. The research suggests an innovative way to prevent the irreversible emission of cement production flue gases (CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>) into the atmosphere and their use in cement (concrete): in order to purify the flue gases from "harmful" compounds, the zeolitic tuff should be contacted in two stages: in the first stage (CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>) flue gases at a temperature of 150-350°C are supplied to the dryer to dry the zeolitic tuff containing the mineral clinophthylolite, at which time the zeolitic tuff is dehydrated and activated, and with the water-free voids, it absorbs a large part of (CO<sub>2</sub>;SO<sub>x</sub>;NO<sub>x</sub>) from the flue gases and at the same time, it is partially modified; In the 2nd stage, the flue gases "cooled" to 70-150°C and partially purified are supplied to the sorber installed before the smoke pipe, where the sorbent is the zeolitic tuff modified in the first stage. In the sorbent, flue gases are "cooled" to 20-60°C, and (CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>) is captured by



zeolitic tuff, after which completely purified flue gases are emitted into the atmosphere, while (CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>) saturated and fully Modified zeolitic tuff is fed to a cement grinding mill.

The purpose of the research is to prove the concept and applicability of cement production by experimenting in a laboratory environment. The result: from the TRL-1 level of the preliminary patent search of the "method of cement production", the production of the required mass of cement by experimentation in the laboratory environment (TRL-2 level), the determination of the applicability in concrete and the approval of the concept (TRL-3 level), finally the transfer of technology Achieving TRL-4 level.

**14.** Due to the aggravation of the global warming problem, the prevention of CO<sub>2</sub> emissions in the atmosphere with flue gases has become a priority task that requires appropriate technologies and specifically, solid sorbents. There is a shortage and high cost of solid CO<sub>2</sub> sorbents on the market, which prevents the creation and development of CO<sub>2</sub> sorption capture and utilization technologies from flue gases.

The aim of the research is to prevent CO<sub>2</sub> emission in the atmosphere from flue gases using cheap, non-deficient natural sorbents.

The idea of the research is: To synthesize CO<sub>2</sub>-increased dynamic capacity, i.e. super-sorptive ability, high mechanical strength, wear-resistant solid sorbents SSZDL, clinophtilolitic zeolitic tuff, diatomite, lime with Synergy of sorption abilities, with the required ratio of components, wt.%. Also, the best geometrical form for CO<sub>2</sub> sorption by SSZDL will be selected, technologies for the production of value-added products will be developed in the utilization of SSZDL modified by carbonation, amortized and unusable by saturation with CO<sub>2</sub> during sorption.

The scientific novelty of the research is: by formation-synthesis under conditions of appropriate moisture, temperature, and pressure, obtaining SSZDL containing the expected  $m\text{CaO} \cdot n\text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$  type compound with Synergy of sorption abilities of components, which will have: sorption ability of CO<sub>2</sub> higher than 10.0 mass%; High mechanical strength and wear resistance of granules above 4.0 Mpa.

The essence of the project is to synthesize CO<sub>2</sub> "capturing" solid sorbents from flue gases by Synergy of sorption abilities of natural and artificial sorbents. To formulate the concept of the technological idea of synthesis, use, utilization, to determine the applicability and to prove it by experimenting in the laboratory environment.

According to the project, preventing the emission of CO<sub>2</sub> into the atmosphere will prevent "a global increase in climate temperature by 1.5°C." It is possible to create, for example, 0.98 t of CO<sub>2</sub> emitted into the atmosphere during the production of 1 ton of cement, will be captured and utilized in the composition of cement, which will create another 0.98 t of cement. If the cost of 1t of cement is \$70, then the additional value created will be:  $0.98\text{t} \times \$70 = \$68.6/\text{t. cement}$ .

**15.** Polymeric materials have penetrated practically in all spheres of human life and activity. Today, the resistance of these "good" materials to chemical or biological degradation is considered a serious threat to the environment. Sustainable polymer waste becomes unacceptable from an environmental point of view. Therefore, at the modern stage of development, it has become an important challenge for the chemistry and technology of polymers to create such materials that degrade and "disappear" after performing the assigned function, be it medicine, engineering or any other field of human activity. Nowadays, a number of biodegradable polymers (BP) have been created and are already commercially successful, most of which belong to the polyester class. Relatively new representatives of BP are polymers based on natural  $\alpha$ -amino acids, the so-called Biomimetic polymers - synthetic analogues of proteins. One promising family of biomimetics is pseudoproteins (PP).

PP is obtained by polycondensation of key monomers - diamino-diester (DADE) with various bis-electrophiles. Simplicity of synthesis, diversity of  $\alpha$ -amino acids and diols, availability and cheapness, high yields of DADE (90-95%), purification by recrystallization from water, absence of ecologically undesirable toxic residues, determine DADE's cheapness and high-tech production. This, in turn, leads to the low price and wide range of pseudoproteins, their prospects for both medical and engineering applications. Pseudoproteins of the

polyesterurea class - PP-PEU - are particularly promising for the latter field. Biomimetics of the mentioned class were first obtained by Prof. by R. Katsarava and co-workers and is protected by a US patent. Today, PP-PEUs are the strongest (high-modulus) BD polymers - Young's modulus  $E=6.0\pm 1.1$  GPa. High-modulus PP-PEU is also promising for obtaining eco-friendly engineering composites, which is the subject of our research. The project involves the synthesis of new, key monomers - diamino-diesters (DADE) based on rigid, cyclic diols by their direct thermal condensation with  $\alpha$ -amino acids in boiling organic solvent in the presence of p-toluenesulfonic acid. The content of ester bonds in the DADE molecule determines the biodegradability of the polymers obtained on their basis.

The scientific value of the project is the synthesis of new, not yet described DADE monomers with a rigid molecular skeleton and new PP-PEU based on them. It is highly probable that based on the new DADE monomers, not only PEU (which is the object of our research), but also other classes of PPs (such as PEA and PEUR) will have a high potential for use in medicine and veterinary medicine, agriculture and food industry, packaging, in the form of engineering and other eco-friendly materials. We note that the world market for such materials is growing steadily, by 20-25% per year.

At the current stage of the research, the main part of the work is completed, but the additional study of the mechanical characteristics of the obtained polymers continues in order to determine the specific field of application.

- specific result

At this stage of the project, a total of 12 new structural substances have been obtained, including 6 monomers, 6 polymers. One of them (PEU L-CHDM) showed a record strength rate among similar polymers, and additional studies are ongoing. 3 articles have been published within the grant.

- Recommendations

1. A modified eco-friendly polymer composite with a matrix content of 2% PEU 98% PE is obtained.
2. Biodegradable matrix manufacturing technology has been developed, which is fast, simple and convenient for manufacturing many types of products.
3. The impact of the biodegradable component - PEU on the non-degradable PE resin matrix is studied. An increase in the concentration of PEU in the polymer matrix leads to an increase in the biodegradation rate of the product, which indicates that the first degradation process in the hybrid polymer matrix is experienced by PEU. Biodegradation was studied for different percentages of polymer samples in aqueous solution, mushroom compost and soil model.
4. Much more accurate results of biodegradation of polymer samples were obtained through TOC analysis. At this time, we studied the amount of organic carbon released as a result of polymer degradation. The analyzes confirmed the results of the gravimetric analysis. As I mentioned above, PEU is the first to suffer degradation. Based on the intensity of the process (degradation of the product) and the porosity of the test polymer samples (a total of 5 types of samples with different concentrations of polymers were made), we considered the share of 2% PEU in the hybrid polymer matrix to be completely sufficient. The obtained eco-friendly polymer matrix was handed over to the Laboratory of Polymer Composites and High-tech Materials of the Grigol Tsulukidze Mining Institute of LSI for the production of composites and for large-scale research in the future.
5. Monomer and polymer synthesis methods were utilized, using which we synthesized 6 new monomers based on three rigid cyclic diols and two amino acids. For this purpose, high purity diols and amino acids (1,4-cyclohexanediol (CHD), 1,4-cyclohexanedimethanol (CHDM) and 1,4:3,6-dianhydro-D-sorbitol (DAS), leucine and phenylalanine were selected. All of them supplied from Sigma-Aldrich).

6. We studied the structure and main characteristics of each synthesized monomer; (IR-spectra were recorded in potassium bromide, NMR-spectra in deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) solutions, melting temperatures were determined by capillary method);
7. Through the PASS program, we studied the probable biological activity of each obtained monomer. Most of them, with a high percentage of probability, can inhibit certain processes.
8. On the basis of obtained monomers, 6 polymers of new structure - PEU were synthesized;
9. The molecular-mass characteristics of the obtained polymers were studied by the gel-chromatographic method in dimethylformamide;
10. It is shown that all obtained polymers are characterized by absorptive ability; Mechanical characteristics (Young's modulus) are studied on the basis of abscissas;
11. PEU was obtained, whose Young's modulus (9.15 GPA) is significantly higher than the characteristic of the polymer obtained on the basis of 1,6-hexanediol;
12. The acute toxicity of polymer biodegradation products was studied in rats by the GUSAR program;
13. Among the newly synthesized polymers, PEU L-CHDM stands out in terms of characteristics, price and toxicity index, the possible area of application of which is engineering and medical field (bone surgery).

## **16. Synthesis and study of graphene/polymer nanocomposites for 3D printing**

### **PHD student Sophio Mikaberidze**

1. Value and importance of the project, actuality of the research/project topic, novelty of the research  
 The formal term 3D printing for additive manufacturing was first proposed in 1980 by Hally. Since then, scientists have developed the so-called production methods. They revolutionized the impact of polymers on our society. This technology has become the driving force for the production of well-defined complex 3D structures. Besides, with this technology, it is possible to produce products of a wide range - from micrometer to large scale. In recent years, the price of commercially available 3D printers has come down significantly (>\$500), making it possible to 3D print certain products at home, such as bicycle parts, jewelry, and electrical components. This technology has several advantages, such as operational simplicity, customizable design, reliability, costeffectiveness, and a variety of compatible materials, which are very promising for a wide range of technological applications, such as biotechnology, medicine, energy/environment, robotics, space et al. 3D printing begins with the creation of a virtual design on a computer using a special program (CAD software). This design is then converted into a computer-readable format that describes the details of the object. There are several types of 3D printing, but the most important and common methods are: Fused Deposition Modeling (FDM), Laser Stereolithography (SLA), selective laser melting (SLM), etc. Due to our work objectives, our interest is directed toward the production of polymer composites suitable for use in Laser Stereolithography and Fused Deposition Modeling. Laser Stereolithography (SLA) is a 3D printing technology, which is based on the solidification of a liquid material (photopolymer) in layers by the action of laser rays. The degree of hardening of the photopolymer, in turn, depends on the range of ultraviolet waves and the duration of the irradiation. This method has several advantages: production of any complexity, thin-walled details, high surface quality, large working chamber compared to other types of printers, low percentage of material wastage, and low level of production noise. SLA 3D printing technology is widely used in medicine, art, the food industry, etc.  
 Fused Deposition Modeling (FDM) is the most common technology in 3D printing worldwide. With its help, it is possible to produce products with both simple home printers and high-precision production systems. Its principle consists in growing the product in layers with pre-melted plastic thread. With this method, it is possible to cast large products with the best mechanical properties (firmness,

endurance, flexibility). It is characterized by the following advantages: durability, low cost, and the wide possibility of further processing.

The materials used in 3D printing are very important components that determine the performance of the final product. Due to their easy processing and low cost, polymeric materials are the most used class of materials for 3D printing. Various types of polymers are used in 3D printing, i.e. thermoplastics, thermosets, elastomers, hydrogels, functional polymers, polymer blends, etc., however, obtaining polymers that have improved mechanical, physical, and other integrated properties remains a challenge. To solve this challenge, we plan to dope graphene structures in polydimethylsiloxane with different molecular weights and further study it.

The purpose of the research:

the purpose of the research is the synthesis of polymer composites suitable for use in 3D printing, in which various structures of graphene will be doped, and the study of the physical-mechanical indicators and properties of the obtained materials in compliance with the standard. Research goals:

1. Synthesis and research of graphene structures Graphene structures will be synthesized from graphite by intercalation and improved Hammers methods, which consist of graphite oxidation using potassium permanganate and sulfuric acid. The obtained materials will be identified by ultraviolet and Raman spectroscopic methods.

2. Synthesis of graphene/polydimethylsiloxane composites The doping of graphene structures in the polymer with different concentrations will be carried out by the methods of mixing solutions and mixing solutions. Graphene/polydimethylsiloxane composites will be obtained by extrusion. 3.

Examination of obtained polymer nanocomposites The physical-mechanical characteristics of the polymer nanocomposites made within the project will be studied, as well as their structural-morphological research.