ABSTACT
to the thesis **of YERMAKHANOVA AZIRA**

on the theme **« RESEARCH OF EFFICIENT WAYS OF STRENGTHENING CARBON FIBER REINFORCED PLASTIC BY MODIFICATION BY CARBON NANOPARTICLES »**

presented for the degree of Doctor of Philosophy (PhD) by specialty 6D071000 – Material science and technology of new materials

One of the urgent tasks of modern materials science is the production of polymer composite materials (PCM) with enhanced mechanical properties. Among PCM, carbon fiber surpasses almost all widely used structural polymeric and metallic materials due to a combination of such properties as wear resistance, high specific strength, rigidity, fatigue strength under static and dynamic loads. Improving the physicomechanical characteristics of carbon fiber can be achieved by modifying the epoxy resin (ER) or carbon reinforcement. One of the methods for modifying an ER is the introduction of various chemical compounds into its composition. One of such methods for modifying the ER is the introduction of carbon nanoparticles (CN) into its composition: carbon nanotubes (CNT), fullerenes, astralenes, graphenes. According to literary datas, with the introduction of the same amount of 0.3% CN in different ERs, an increase in compressive strength of 3-58% increases, in the case of carbon fiber reinforced plastic (CFRP) when entering 1% CN - by 33% -84%. Such a spread is not entirely clear due to unrecorded uncertainties in the process of technology modification of ER and CFRP:

- the origin of the CN;
- method of modifying CN and its dispersion in ER;
- strain rate at failure.

Meanwhile, at present, in the field of PCM hardening, the direction of work on the chemical activation of the properties of CN surfaces by means of additional processing by various chemical reagents, called functionalization, begins to develop. In the literatury sources there is evidence that the modification of CN allows to further increase the compressive strength of ER up to 34%. However, the role of CN modification on the hardening process of both ER and CFRP are investigated fragmentarily, the data of different authors differ.

In addition, the properties of the binder, first of all, viscosity and viability time (gelation time), which limit the technological process of obtaining products from carbon fiber, depend on the features of the process of polymerization of ER with the introduction of CN. The positive role of CN in CFRP technology can be negated if CN makes a liquid ER with a hardener viscous and shortens the viability time (gelation time). In view of this circumstance, the clarification of the effect of CN of various modifications on the process of gelation of ER is extremely important.

The strength characteristics of ER and CFRP are usually given without mentioning the strain rate. This circumstance is one of the reasons for the inconsistencies in the experimental data of various works among themselves. There

is a general pattern that the strength of polymeric materials depends on the rate of deformation; this effect should also manifest itself in the case of ER and CFRP. However, in the open literature, the dependence of the strength characteristics of ER and carbon fiber on the type of loading is poorly consecrated. Obviously, this effect requires systemic research.

The task of increasing the strength of CFRP and competent use of its strengths requires both knowledge of the dependence of strength on the strain rate and the possibility of hardening the ER modification by introducing CN various modifications (functionalization). The study of these issues is devoted to this work.

The basis and initial data for the research into the topic. In connection with the needs of the country in high-strength carbon fiber reinforced plastics, the main provisions were developed within the framework of state scientific programs funded from the state budget: “Develop domestic technology for the production of high-strength carbon plastics and products from them with boundary characteristics” under the program “Grant financing of scientific research” (GF0093 / GF4) for 2015-2017, “Develop domestic technology for producing high-modulus and high-strength products from carbon fiber aerospace” – Republic budget program 076 "Applied research in the field of space activities, transport and communications."

The Etal Injekt-T ER was selected as the initial data, the Taunit-M carbon nanotubes, the Sigratex KDK 2043 equal-strength carbon cloth, CFRP manufacturing method – vacuum infusion were chosen as the CNs.

Information about the planned scientific and technical level of development. High-strength carbon fiber composites are used in the production of of aerospace and defense equipment, therefore, their production technology is strictly classified by the International Agreements on Export Control of Dual, Rocket and Nuclear Technologies. According to the literary and patent analysis of open works, the topic of this dissertation is novel. At the same time, this is the first experimental work on carbon fiber in Kazakhstan.

Relevance of the topic. Currently, the domestic space industry is actively developing in Kazakhstan. For the production of hulls, power elements of spacecraft, gliders, unmanned aerial vehicles, buildings of ultralight launch vehicles for space and geophysical purposes, high-strength carbon plastics are needed.

The relevance of this work is confirmed by the relevance of this subject to government programs at various levels, funded from the state budget.

The novelty of the theme lies in identifying the effectiveness of the method of modifying the ER and carbon fiber with carbon nanoparticles. In the thesis, for the first time at the system level, the effect of carbon nanoparticles of various modifications on the process of ER curing, the nature of deformation under the load of ES and carbon plastic is studied. The study of these parameters allows you to create a new efficient technology for high-strength CFRP with high performance and technological properties.

Scientific novelty of the results:

- the influence of primary CNT-1 and modified (carboxylated CNT-2, carboxyl-hydroxylated CNT-3, amidated CNT-4) CNT on the gelation time of Etal Inzhekt-T was investigated. The effect of increasing the gelation time with the introduction of CNT in the ES. At 150 ° C, the gel time of epoxy resin is 6.3 minutes. Adding 0.15% CNT-1 in the ER increases the gelation time by 79%, CUNT-2 by 106%, CNT-3 by 84%, CNT-4 by 98%.

Investigated the process of gelation in the first three minutes. The dynamic modulus of elasticity of the ER gel in all cases increases exponentially with time. The module of energy loss of the ER gel monotonously increases in time from 0 to 0.05 MPa, depending on the modification of the ER CNT, the loss modulus increases during the first 1-2 minutes from the beginning of the gelation time to 0.14-0.38 MPa, then sharply is falling. This means that the CNT after the gelation time significantly accelerates the process of ES curing.

- it was found that the introduction of primary CNT-1 into the ER did not give hardening, the modified ones increase the strength by 5-22% from 172 MPa to 210 MPa. The greatest strengthening effect is obtained for amidated CNT-4. According to the complex of positive properties, an increase in the gelation time and strength of the solidified ER, amidated CNTs showed the best results.

- at low strain rates for compression up to 20 mm / min, there are three zones of stress-strain state in the ER: elastic, plastic, elastic-plastic. Modification of the ER by functionalized CNT has practically no effect on the elastic zone, but strengthens the plastic and elastic-plastic zones. At strain rates ≥ 20 mm / min, only one zone of quasi-elastic strain is observed with brittle fracture of the sample at the end of the elastic zone. In all cases, the elastic zone of epoxy resin remains steadily constant, its end is characterized by the parameters: σ_f = 111 MPa, ε_f = 5%, E = 2.2 GPa.

- for the first time, comparative results were obtained on the effect of modified CNTs on the mechanical properties of carbon fiber. It was found that the primary CNT-1 does not affect the strength of carbon fiber. When 0.15% of functionalized carbon nanotubes were introduced into carbon fiber, the increase in strength was: a) for compression - CNT-2 - 6%, CNT-3 - 12%, CNT-4 - 17%, b) for bending - CNT-2 - 44%, CNT-3 - 59%, CNT-4 - 132%. The effect of hardening CFRP on bending was 3-7.6 times more than compression.

- at the rates of carbon plastic deformations up to 20 mm / min, zones of elastic, elastic-plastic and pseudoelastic deformation are observed. At strain rates ≥ 20 mm / min, the three-zone structure transforms into a single-zone pseudoelastic deformation with parameters: σ = 425 MPa, ε_f = 2.3%, E = 19.3 GPa. The strongest effect of carbon fiber reinforcement was given by amidated CNT-4, with their content 0.15%, the strength increased by 17%, in the range of strain rate from 20-30 mm / min, the strength is almost constant. It is established that the critical strain rate of carbon fiber 20 mm / min coincided with the critical strain rate of ER. When using ER and CFRP as structural materials, it is desirable to load them within the elastic zones, if the loads go beyond the elastic zone, then irreversible plastic deformations appear.

The relation of the work with funded research programs. This research work is related to the activities of the State Program "Development of space activities in the Republic of Kazakhstan for 2009-2020" and the Republican budget program 008 "Applied scientific research in the field of space activities" for 2015-2017.

The aim of the thesis is to increase the strength of carbon fiber based on studies of the effect of modified carbon nanoparticles on the properties of a composite material.

The object of the study are samples of ER of the Etal Inject-T brand and carbon plastics modified with CN.

The subject of the research is a method for producing high-strength carbon fiber modified with CN.

Tasks of the research. The main objectives of the research include:

1. Analysis of carbon nanoparticles used in the strengthening of carbon fiber and the choice of optimal materials and methods for its processing.
2. Conducting experimental work on the effect of carbon nanotubes of various modifications on the process of ER curing.
3. Study of the effect of strain rate on the compressive strength of ER. Determination of the dependence of the stress-strain state of an ES on a modified of CN.
4. Investigation of the effect of strain rate on compressive strength of CFRP modified CN.

Methodological basis of research. The main methods of research and analysis used in the performance of the thesis are:

- structural analysis of manufactured samples of ER and CFRP macro-, micro-level using optical (Leica 6000M, Al-Farabi Kazakh National University) and electron scanning microscope (Phenom Pro X, Moscow State Technical University named after N.E. Bauman)
- studies of the rheological properties of the made binders using a rotational viscometer (CAP 2000+ Brookfield, Bauman Moscow State Technical University named after N.E. Bauman);
- study of gelation time using a dynamic mechanical analyzer (DMA 242 E Artemis, Bauman Moscow State Technical University named after N.E. Bauman);
- mechanical tests of manufactured samples of ES and CFRP on a tensile machines (Shimadzu AG-100 kNx, IMOB JSC, Zwiek Roell Z050, NE Bauman Moscow State Technical University named after N.E. Bauman).

Provisions for the defense:

- the influence of the type of modification of carbon nanoparticles on the curing process of epoxy resin;
- patterns of formation of the stress-strain state of epoxy resin and carbon fiber, depending on the type of loading;
- the dependence of the strength characteristics of epoxy resin and carbon fiber on the content and type of modification of carbon nanoparticles.

The practical significance of the work lies in the fact that the obtained experimental data on the mechanical properties of carbon plastic based on the

modified Etal Injekt-T epoxy resin with carbon nanoparticles can be used to obtain structural materials for aerospace purposes in “Galam” Ltd. (Nur-Sultan). The possibility of effective hardening of carbon plastic is shown, taking into account optimal amount and the type of CN input, gelation time, strain rate.

Approbation of the work. The main provisions and results of the thesis were reported and discussed:

- on: international conference "Satpayev's readings" Competitiveness of technical science and education "dedicated to the 25th anniversary of the independence of the Republic of Kazakhstan (Almaty, April 12, 2016);
- at the international conference “International Conference on Energy Development and Environmental Protection” (18-20th August, 2017, Guilin, Guangxi, China, 2017);
- at the X International Symposium “Physics and Chemistry of Carbon and Nanoenergy Materials” (September 12-14, 2018, Almaty)
- at the international practical Internet conference "Actual problems of science" (Almaty, November 22, 2018);
- At scientific seminars of the Department of Engineering Physics at the Kazakh National Research and Technical University named after K.I. Satpayev and at the Composite Center of Russia, Moscow State Technical University named after N.E. Bauman.

Publications. According to the results of the dissertation, 8 published works were published, including 3 articles in publications recommended by the Committee for Control in Education and Science of the MES RK, including 1 publication in the publication, indexed in the Scopus database, the list of works is given at the end of the thesis. The novelty of technical solutions is confirmed by the Patent of the Republic of Kazakhstan “Method for producing carbon fiber plastic for space use” No. 2017 / 0632.2 dated 09.07.2018, bull. №25.

The structure and volume of the work. The thesis work consists of introduction, 4 chapters, conclusion and list of used sources from 120 titles. The total volume is 92 pages of computer text, illustrated with 52 figures, 7 formulas and 19 tables.