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Evaluation of Improving Mechanical Characteristics of Epoxy Binder after Dispersing Carbon Nanofibers Using Wave Processes and Ultrasound

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Abstract

The paper deals with adhesive compositions based on epoxy matrix modified with carbon nanofibers using ultrasound and wave processes. The mechanical characteristics of adhesive compositions have been determined; their effectiveness has been evaluated to increase the static strength and life of the compounds in metal-composite constructions.

Keywords

Nanoclue composition; carbon nanomaterials; ultrasonic dispersion; wave dispersion.

Introduction

Nowadays carbon nanofillers are widely used as modifiers to improve mechanical characteristics of source materials. In particular, the paper [1] has shown that when dispersing multi-layer carbon nanotubes in 1 wt. % polystyrene the elastic modulus and strength under breaking loads increased by more than 35 %. An increase in stiffness of the epoxy matrix up to 3.5 times has been observed when dispersing 2 wt. % of single-layer carbon nanotubes [2]. The results obtained in the works of other researchers [3, 4] have also demonstrated a significant decrease in the friction coefficient and an increase in wear resistance in hydroxyapatite composites with carbon nanotubes [5]. We have investigated the use of the nano-modified adhesive composition to increase the strength characteristics of bolted joints in metal-composite structures [6].

A good alternative to carbon nanotubes can be graphene, which also has a high compression ratio, a high elastic modulus, a unique structure, high heat conductivity and good interaction of the interfacial surface with the polymer matrix.

The use of functionalized graphene allows to obtain stable dispersions due to the occurrence of molecular interactions which contributes to the improvement and enhancement of pure interfacial interactions. Molecular interaction, along with the increase in stiffness and strength, raises the toughness and elasticity of a new composite material.

When creating highly efficient nano-modified adhesive compositions based on epoxy polymers with a significant increase in mechanical characteristics (intrinsic strength, viscosity and hardness), the uniform distribution of the nano-modifying material in the polymer matrix is of key importance.

Currently, several methods for dispersing carbon nanotubes in a polymer have been developed: solution mixing, melting method and “insitu” polymerization.

Now the effectiveness of most of these methods has reached its limit, and the dispersion of nanofillers in highly viscous polymers is practically impossible in some cases. Increasing the possibilities of modification can be provided by the ultrasonic dispersion of nanofillers. However the effect of ultrasound on a compound with a nanofiller can cause the compound to heat up which negatively affects its mechanical characteristics.

Another way to disperse a nanofiller in the epoxy binder can be the use of targeted wave action, developed under the guidance of Academician of the Russian Academy of Sciences R.F. Ganiev, based on nonlinear wave mechanics methods [7, 8]. The studies conducted in the laboratory of the Scientific Center for Nonlinear Wave Mechanics and Technology, Institute of Engineering of the Russian Academy of Sciences have shown that the capabilities of wave technologies allow a high degree of dispersion of various nanofillers in highly viscous media, including the production of nanomodified polymeric composite materials.

This article discusses the results of dispersing carbon nanofibers in the epoxy binder in two ways – by ultrasound exposure and using a targeted wave process. Characteristics of the formed nano-modified adhesive compositions, as well as the effectiveness of their use with increasing strength and life of compounds in metal-composite structures are experimentally determined.

Defects on the edges of details from polymeric composite materials as a result of their mechanical treatment after forming

Polymer composite materials are increasingly used in aviation equipment products. Metal fasteners, i.e. bolts or rivets, are used to connect them. It is the compounds in the construction of polymer composite materials (**PCM**) that are the most responsible, to the greatest extent determining the resource characteristics, and in this connection subject to constructive strengthening as a result of which the mass of the structure increases. Since the number of compounds in aircraft structures is very high, increasing the strength and life characteristics of compounds becomes important both in reducing weight and improving performance.

In the mechanical manufacture of holes for fasteners, defects such as microcracks, hairiness [9], splicing of the binder, delaminations are formed on the edges and the treated surface (Fig. 1). These defects in combination with stress concentrators in the form of holes and cuts can lead to a significant decrease in the strength and fatigue life of parts made of polymer composite materials [10, 11].

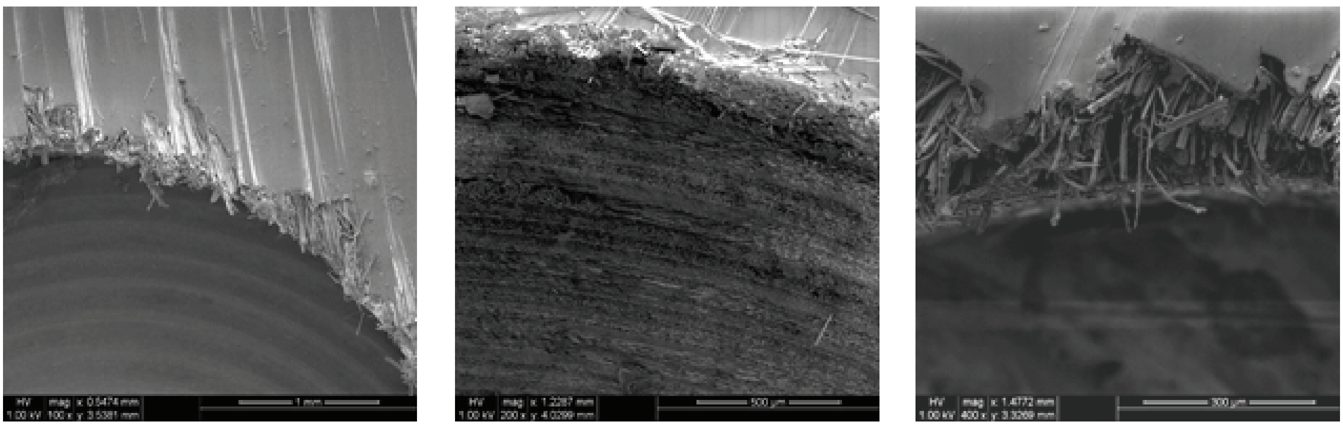
The damage of edges as a result of machining in parts made of polymer composite materials can be reduced by the following main methods [6]:

– firstly, to reduce the destruction of edges due to the selection of tools and processing modes [12];

– secondly, to use an effective adhesive composition (in particular, nano-modified) with increased tensile, compression and shear strength when installing fasteners.

Filling the material defects obtained during processing with the adhesive composition also eliminates the gaps between the hole and the fastener, which ensures its tight fit. As a result, the concentration of contact and tensile stresses on the contour of the hole decreases. In multipoint compounds this ensures simultaneous operation of all fasteners when a load is applied, which ultimately increases their strength characteristics.

Improving the efficiency of adhesive compositions is possible by using small nanomaterial additives of various nature, including carbon [5, 6], in aviation adhesives for construction purposes.



a) *b*) *c*)

Fig. 1. Defects on the edges of parts made of polymer composite materials arising during machining – milling (*a*, *b*) and drilling (*c*)

Selection of nanomaterials for an effective nano-modified adhesive composition

To improve the efficiency of mechanical characteristics (elastic modulus, strength, viscosity) of the adhesive composition, it was modified by carbon nanomaterials. The modification consisted in adding small concentrations of nanomaterials to the standard adhesive composition, which theoretically [13 – 16] due to the interaction between the nanofiller and the polymer matrix can increase its strength and, in the long run, the fatigue durability of parts and structures made of polymer composite materials. The choice of the type of nanomaterials for using in the adhesive composition was carried out by computer simulation of the interaction of epoxy resin ED-20 with a number of carbon nanomaterials, which is widely used in adhesive compositions.

The mechanisms of interaction of the epoxy matrix with the surface of particles of various fillers (amorphous carbon (CH) 170, fullerene C240 and carbon nanotubes (**CNTs**) of various structures) have been investigated. The energy and strength characteristics of the interfacial layers of filled epoxy adhesives have been studied in a computational experiment in the framework of the cluster method implemented in the original NDDO/sp-spd quantum mechanical software package.

Based on the structure of the ED-20 oligomer molecule, which simulates a fragment of an epoxy chain, and clusters that simulate filler particles, the geometry of the corresponding adsorption complexes has been constructed and optimized. Their structures are shown in Fig. 2

For each considered adsorption complex, the binding energy E_{bind} per one monomer unit of epoxy adhesive and the maximum shear friction force F_{shear_MAX} has been calculated as the gradient of the total energy of the system along the selected friction coordinate. The results of the calculations are presented in Table 1.

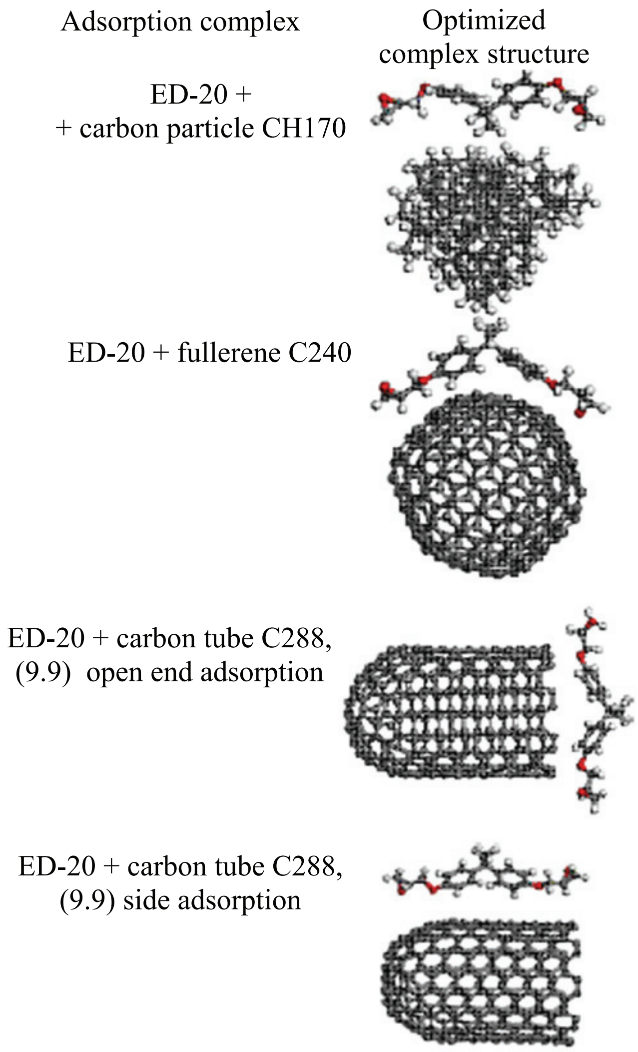


Fig. 2. Optimized structures of the oligomer ED-20 molecule adsorption complexes modeling a fragment of the epoxy chain and clusters modeling filler particles

Table 1

Geometric, energy and mechanical characteristics (data of KM modeling) obtained for adsorbed epoxy oligomer ED-20 and clusters modeling filler particles

Adsorption complex	*R*, A	E_{bind}, Kcal/mol	F_{shear_MAX}, Kcal/mol ·A
ED-20 + carbon particle CH170	2.7	–14.2	19.2
ED-20 + fullerene C240	2.8	–13.8	18.8
ED-20 + carbon tube C288 (9.9) open end adsorption	2.5	–23.5	26.8
ED-20 + carbon tube C288 (9.9) side adsorption	2.7	–15.4	22.7
ED-20 + graphene particle	2.8	–14.6	20.1
ED-20 + graphene oxide particle	2.2	–33.2	37.5

During the computational experiment, potential epoxy fillers have been considered. In the process of its implementation, the structural, energy and shear characteristics of the interfacial layer with a filler have been analyzed. The results have shown that the interaction of epoxy chain fragments with the side walls of carbon nanotubes is weaker than with open ends. Therefore, if it is possible, we should try to increase the number of open ends of the tubes before filling epoxy adhesives and also use short tubes to increase the proportion of open ends on the specific content of the filler in the adhesive composition. One of the ways to achieve this goal may be dispersion followed by fracture of nanotubes. In terms of the interaction energy and shear friction force, the side surfaces of carbon nanotubes have almost the same interfacial layer characteristics as the other adsorption complexes considered, for example, fullerenes or carbon particles.

It is obvious that the most effective filler is graphene oxide. Open carbon nanotubes are somewhat inferior to it. For them, the filler particles are held by fragments of epoxy chains by both hydrogen and van der Waals dispersion forces. Thus, based on the calculations, it has been found that graphene oxide and open carbon nanotubes are most promising to use as fillers for epoxy adhesives.

Materials and methods

In accordance with the conducted analysis, the following carbon nano-components were used: carbon nanotubes of the Taunit-M brand, graphene and graphene oxide (synthesized in the Institute of Applied Mechanics of the Russian Academy of Sciences), and ED-20 epoxy resin as the base adhesive composition.

The following task has been posed: to experimentally investigate the effect of graphene and graphene oxide, synthesized in the Institute of Applied Mechanics of the Russian Academy of Sciences, on the complex of properties of the adhesive composition and adhesive compounds based on ED-20 resin. This task is due to the fact that, according to the results of theoretical calculations presented in the previous section, the interaction with resin molecules ED-20 proves that graphene and graphene oxide appear to be the most promising additives for improving mechanical properties of the adhesive composition, even compared to carbon nanotubes.

Graphene was synthesized by the method of Hammers, in two stages:

1. Oxidation of graphite to graphene oxide – separation of graphite by adding oxygen bridges and hydroxyl groups to the graphite structure.
2. Restoration of graphene oxide to graphene.

The method of synthesis has been developed by a scientific group at the Institute of Applied Mechanics of the Russian Academy of Sciences and is based on the hard oxidation of graphite. The original graphite was oxidized with an excess of a mixture consisting of potassium permanganate, potassium dichromate, potassium nitrate with the addition of sulfuric acid. After filtration and washing, the resulting compound was subjected to hydrazine reduction in a strongly alkaline medium (pH > 12).

Graphene oxide was prepared according to the following method: an oxidizing agent – potassium permanganate – was added to stationery graphite, in a 1 : 1 ratio in a strongly acidic medium – with sulfuric acid, with a concentration of 35–45 %. The oxidation was carried out until the mixture thickened and reached a brown color. Then the mixture was filtered through the paper filter and washed with distilled water. The resulting graphite oxide was subjected to ultrasonic treatment to obtain a stable suspension of graphene oxide.

As a result of the graphene synthesis, according to the method described above, a black powder was obtained. The sizes of the powder agglomerates were estimated using a Zygo New View 5022 three-dimensional interference microscope (manufactured by Zygo Inc., USA). The method of interference contrast allows to evaluate the surface of various structurally complex objects with magnification up to 4000x from almost transparent samples to materials including low-contrast inclusions (phases) having different reflectivity with a high degree of resolution and precision accuracy. The obtained images (Fig. 3) show that the agglomerates of the synthesized graphene have micro-dimensions. According to the data obtained, the sizes of particles and agglomerates vary from submicron size to several micrometers.

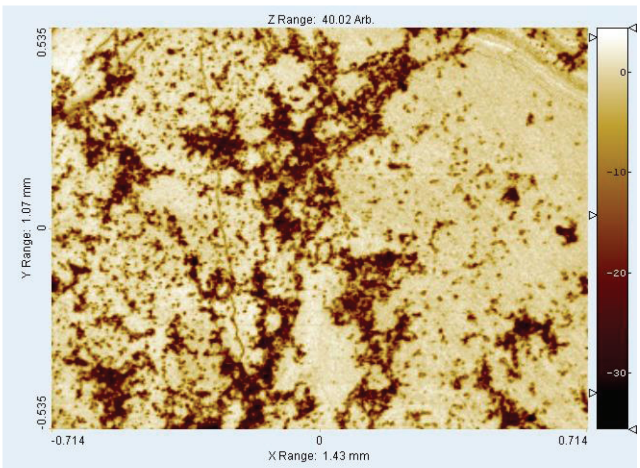


Fig. 3. The photograph of graphene agglomerates at a magnification of 200x

Graphene oxide was obtained in the form of brown powder. The sizes of the agglomerates were evaluated on a Nanosurf Easyscan DFM atomic force microscope. The longitudinal size of the smallest graphene oxide plates was about 100–200 nm with a thickness of about 2 nm (the limiting resolution of the device at height). The mass concentration of graphene oxide powder in the epoxy matrix (ED-20 resin) was 1 wt. %.

The structure of graphene particles was also evaluated using images obtained by a Lyra 3 Tescan scanning electron microscope (Fig. 4).

In the SEM-image, the synthesized graphene particles have submicro and micrometer sizes, with the length of graphene sheets reaching several hundred micrometers.

The evaluation of the graphene effect on the structure of nanoadhesive compositions was carried out using the surface topography of the obtained samples on the Easy Scan atomic force microscope operating in the contact mode in air at room temperature. At the same time, the power modulation mode was used to obtain the material contrasts of the studied samples.

Taunit-M carbon nanotubes were also used in the experiment (Fig. 5).

The properties of Taunit-M carbon nanotubes are presented in Table 2.

To improve the epoxy resin compatibility, carbon nanotubes were oxidized in concentrated nitric acid when boiled. The presence of carboxyl groups was confirmed by IR-spectroscopy and titration of the

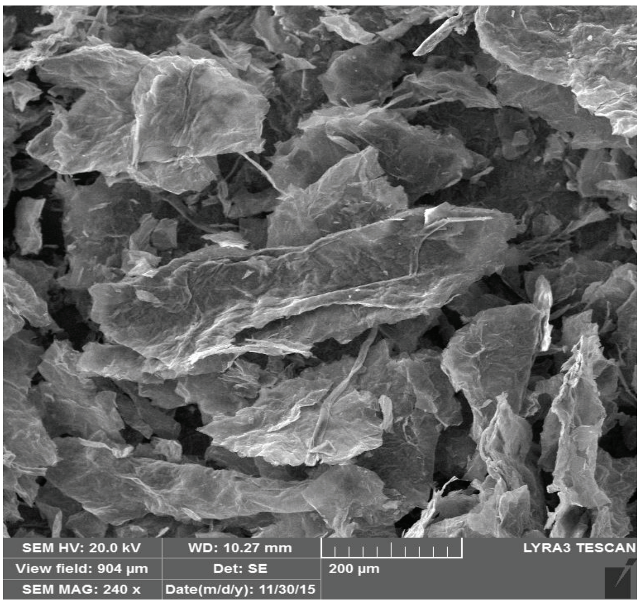


Fig. 4. The SEM-image of graphene agglomerates

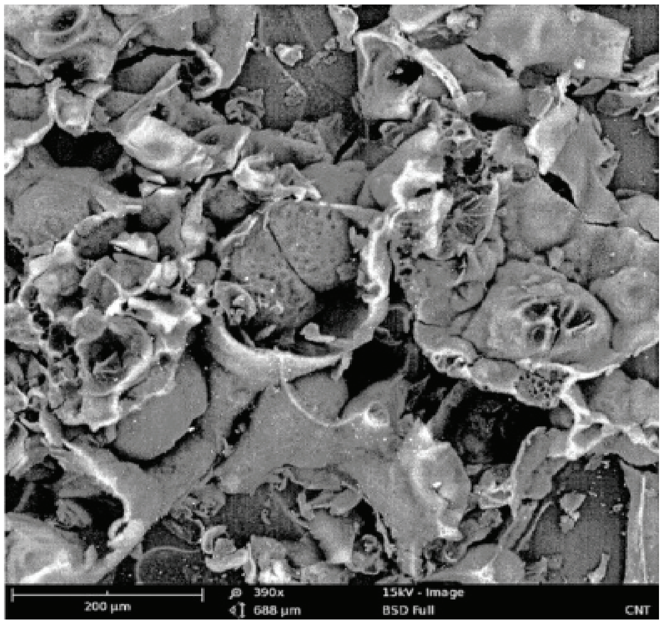


Fig. 5. The SEM-image of Taunit-M carbon nanotubes agglomerates

Table 2

Characteristics of Taunit-M carbon nanotubes

Parameters	Values
Outer diameter, nm	8 – 15
Internal diameter, nm	4 – 8
Length, µm	2 and more
Total impurities:	
before cleaning, %	up to 5
after cleaning, %	up to 1
Bulk density, g / cm^3	0.03 – 0.05
Specific geometric surface, m^2/g	300 – 320 and more
Thermal stability, °C	up to 600

aqueous dispersion with alkali. To prepare dispersions, carbon nanotubes with concentrations of 0.25 and 2.0 wt. % of the epoxy resin concentration were used.

Carbon nanotubes were added to ED-20 epoxy resin in two stages using high shear mixing on the Exakt three-roll mill (Bayer) and ultrasonic treatment on the IL-100 unit (frequency 24 kHz, power 2 kW).

Technological modes of dispersion were carried out as follows:

1) the epoxy resin and carbon nanotubes were mixed with a mechanical agitator at a speed of 250 rpm for 15 minutes at room temperature;

2) the obtained mixture was dispersed using a three-roll mill at room temperature in three passes: with a gap between the rolls of 60 : 30 μm, 30 : 15 μm and 15 : 5 μm;

3) the mixture was treated with ultrasound at 20 °C for 4 min with a concentration of carbon nanotubes 0.25 wt. % and 5 min with a concentration of oxidized carbon nanotubes 0.25 wt. %, and at a temperature not higher than 70 °C for the sample with a concentration of carbon nanotubes 1.50 wt . % for 20 min;

4) re-dispersion in a three-roll mill at room temperature with a gap between the rollers 15:5 μm in three passes;

5) the sample of carbon nanotubes dispersion with a concentration of 1.50 wt. % was calcined in the oven at a temperature of 120 °C for 2 hours.

The course of experimental studies allowed observing that heating changed the external consistency of the dispersion. The dispersion became more viscous, but mobile and convenient for work.

The mechanical properties of the nanoadhesive composition were determined by the method of nanoindentation on the Nano Test 600 measuring complex (Micro Materials Ltd., the United Kingdom). The Nano Test 600 measuring complex has a theoretical extension of the introduction 0.001 nm and allows determining the hardness and the reduced elastic modulus depending on the depth of indentation on the samples and coatings from 20 nm thick.

The method consists in introducing a geometrically and physically certified pyramid (Berkovich pyramid with a vertex angle of 65.3° and a curvature radius of 200 nm) into the material and determining the load-depth indentation with high accuracy. When calculating the reduced elastic modulus, the Oliver-Farr method [17] was used, according to which a part of the load-depth indentation dependence on the unloading cycle was described.

The experiment on the Nano Test 600 device was performed according to the following procedure. Samples of the adhesive composition were deposited on the glass and fixed on the substrate with the adhesive, then the sample was brought to the indenter. The indentation of the sample was carried out at 10 points with an interval of 30 μm. The load increased at a constant speed until the specified maximum load was reached (5 mN). The indentation rate varied in accordance with the magnitude of the maximum load on the basis that the load cycle should take 20 seconds. Then the maximum load was fixed for 10 seconds and the “creep” effect was controlled, i.e. the determination of a possible further increase in the indentation depth occurred at a fixed load. Unloading was carried out at the same speed as the loading. At the unloading stage, the temperature drift was controlled by fixing the indenter during the unloading process (at 80 % unloading) for 60 seconds and determining the possible displacement. The presented experimental data are given with considering the possible temperature "drift".

The experiment used a conical diamond indenter with an apex angle of 60° and a radius of 10 μm. This indenter was chosen to level the possible surface roughness due to the porosity of the samples surface. The indentation was carried out in a controlled load mode, with a preload of 0.01 mN. The dependencies of load-depth indentation were removed at the stages of load and unloading.

Results and discussions

To evaluate the effect of graphene on the structure of adhesive compositions, the surface topography of the obtained samples has been investigated. Fig. 6 shows micrographs of the adhesive compositions surface structures.

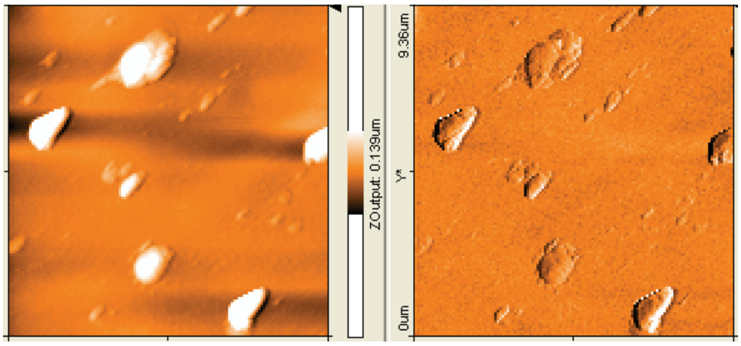
Fig. 6 shows that the best dispersion of graphene particles is observed in the sample where graphene has been added to the adhesive composition through the benzene solvent.

However, micrographs (Fig. 3) obtained by the method of interference contrast show graphene agglomerates. Perhaps this is due to the fact that the solvent is not completely removed from the epoxy binder. The presence of graphene aggregates can lead to the decrease in intermolecular interaction. For this reason, Taunit-M carbon nanotubes were used as a filler in the epoxy binder in the further practical work.

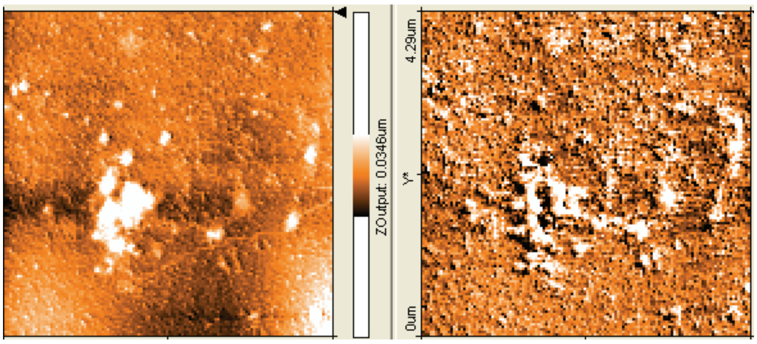
The research results of the material properties by the method of nanoindentation are presented in Table 3.

The obtained experimental data suggest that the addition of carbon nanotubes to adhesive compositions, even in low concentrations (up to 2 wt. %), has led to the increase in their elastic properties. This was especially evident at low loads (0.2 mN): the resulting reduced elastic modulus was 3.6 GPa for the initial composition and 4.6 GPa for the composition with carbon nanotubes.

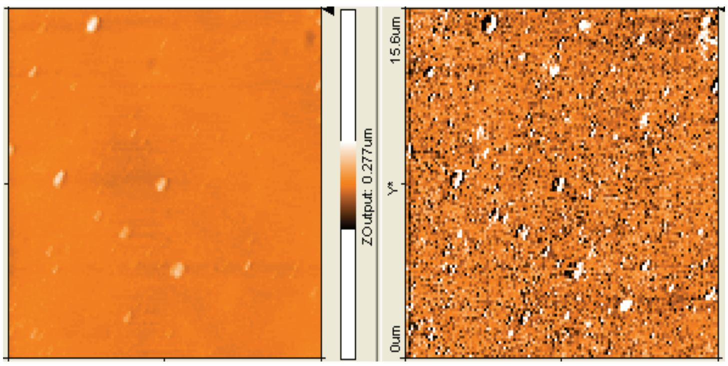
The hardness for samples with nanotubes (initial – 208 MPa, with nanotubes – 273 MPa at 0.2 mN) has also increased. It should be noted that the experiment presents a significant variation in the obtained parameters on nanoindentation, which, apparently, is connected with the peculiarities of the preparation of adhesive composition samples. When analyzing images taken with an optical microscope of a thin section of a nano-modified adhesive layer cut from a biaxial sample, the adhesive layer porosity was detected.



a)



b)



c)

Fig. 6. AFM images of the adhesive compositions surface structures with the addition of 1 wt. % graphene:
a – graphene is added without solvent; *b* – graphene is added through the diethyl ether solvent in the presence of a surfactant;
c – graphene is added through the benzene solvent

Table 3

Mechanical characteristics of adhesive compositions obtained on the Nano Test 600 measuring complex using the nanoindentation method for the initial sample and the sample with carbon nanotubes (2 wt. %)

Parameter	Sample 1 (initial)		Sample 2 (CNT)	
	Value	Scatter, %	Value	Scatter, %
1	2	3	4	5
Load 0.2 mN				
Maximum indentation depth (introduction), nm	223.4	10.7	193.0	6.3
Plastic introduction, nm	187.2	12.4	160.0	7.3
Hardness, MPa	208.9	19.5	273.7	13.0

Continuation of Table 3

1	2	3	4	5
Reduced elastic modulus, GPa	3.6	14.9	4.6	16.0
Elastic recovery	0.20	12.5	0.21	15.9
Contact compliance, nm / mN	240.3	7.5	220.3	13.0
Plastic work (energy dissipated in the sample), nJ	0.017	28.8	0.016	9.8
Elastic work (work when unloading), NJ	0.007	6.3	0.006	10.6
Load 5.0 mN				
Maximum indentation depth (introduction), nm	1283.5	17.9	1054.6	2.2
Plastic introduction, nm	1119.2	20.6	911.6	2.5
Hardness, MPa	77.6	15.8	91.5	2.3
Reduced elastic modulus, GPa	2.5	9.5	3.2	8.5
Elastic recovery	0.2	20.7	0.2	9.4
Contact compliance, nm / mN	43.8	7.2	38.1	8.8
Plastic work (energy dissipated in the sample), nJ	4.1	5.2	3.4	2.6
Elastic work (work when unloading), NJ	0.7	4.4	0.6	5.0

The mechanical properties of epoxy binder under ultrasound dispersion and exposure to the directed wave process

The Taunit-M nanofiller into the base adhesive composition on the increase of its strength properties with respect to the use of metal-composite structures in compounds was investigated. The properties included hardness, the elastic modulus and shear strength.

For ultrasonic dispersion, a mass concentration of the nanofiller equal to 2.0 % was experimentally determined, providing maximum shear stresses when testing adhesive compounds. At the same time, it was not technically possible to reduce the concentration of the nanofiller below 0.1 %. The use of the directed wave process allowed the dispersion of the nanofiller with a concentration of 0.01 %. At the same time, the effect of the wave processes reduced the formation of agglomerated nanofiller structures and increased the uniform distribution of its particles in a viscous adhesive matrix, significantly increasing the contact area of the nanomodifier with the epoxy binder. The size of the agglomerates with the ultrasonic dispersion was 100 μm, and it did not exceed 2 μm with the wave processes (Fig. 7).

Along with this, the ultrasonic dispersion led to breaking the nanofiller particles, but their integrity was preserved under wave process. In accordance with previously obtained results [9], open carbon nanotubes formed during fractures are the most effective in improving the mechanical shear strength of the additive

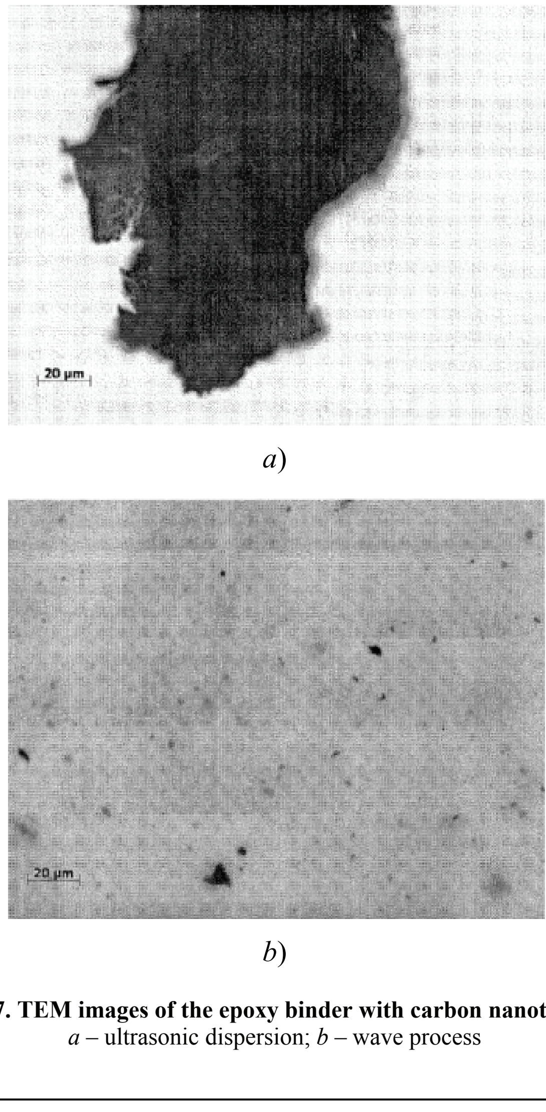


Fig. 7. TEM images of the epoxy binder with carbon nanotubes: *a* – ultrasonic dispersion; *b* – wave process

to the adhesive epoxy matrix. For them, the filler particles were held by fragments of epoxy chains by both hydrogen and van der Waals dispersion forces. The measurement results of the properties of the nano-modified adhesive composition after its curing showed that with ultrasonic dispersion of the nanofiller the hardness increased by 31 %, and the reduced elastic modulus increased by 28 % compared with the base adhesive composition. When dispersing nanofillers in the directional wave process, the hardness and reduced elastic modulus increased to a lesser extent, by 13 and 12 %, respectively.

Thus, the resulting destructive effect on the filler – fracture of the filler fibers directly in the polymer matrix under ultrasonic dispersion – led to a more efficient interaction of carbon nanofibers and polymer binder for its structuring and, as a result, to increasing mechanical characteristics.

Determination of the mechanical properties of adhesive compounds

Along with the determination of the mechanical properties of the nano-modified adhesive composition, the mechanical properties of adhesive compounds were studied.

The samples of adhesive compounds of aluminum alloy elements and samples of adhesive compounds of fiberglass and titanium alloy elements were made for testing. The scheme and photograph of the sample are shown in Fig. 8, 9, respectively.

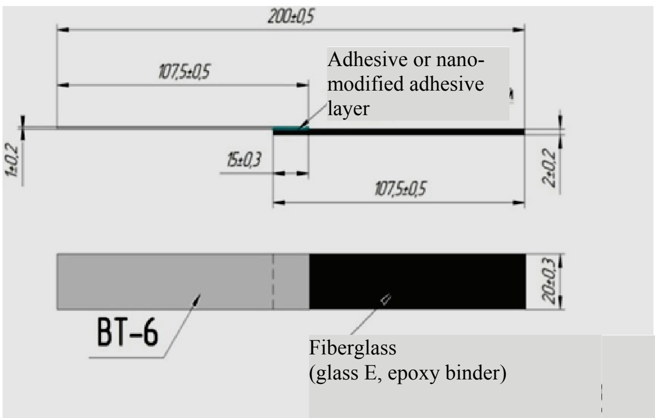


Fig. 8. The scheme of the sample for testing the adhesive compound of fiberglass and titanium alloy elements

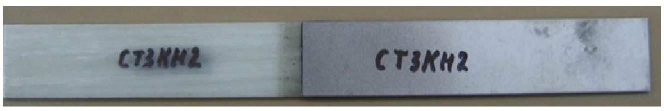


Fig. 9. The photograph of the sample for testing the adhesive compound of fiberglass and titanium alloy elements

The use of the nano-modified adhesive composition made it possible to increase the minimum value of the adhesive compound strength at shear by 25 %, and the average value – by 17 %.

The strength test results for constructive-like samples of compounds with a biled cut at strengthening the developed nano-modified adhesive composition

The use of the nano-modified adhesive composition was investigated during the hardening of metal-composite compounds. When making a hole in a sample of the polymer composite material, defects appear on the surface and edges of the hole (shown in Fig. 1). Along with the appearance of defects, gaps between the bolt and the hole also appear because of damage when pressing the metal connecting element into the PCM part. In multi-row bolted compounds, gaps between bolts and holes lead to the non-uniform bolt loading, which can result in inappropriate, premature failure. It is known [18] that the presence of a gap between the bolt and the hole also leads to the concentration of contact tensile stresses on the contour of the hole (Fig. 10). Therefore, the use of the nano-modified adhesive composition in bolted compounds by eliminating defects at the edges in the hole and filling the gaps between the bolt and the hole should lead to the increase in the strength and fatigue durability of the compounds.

In the present work, two series of experimental studies were carried out to determine the effectiveness of using the nanoadhesive composition:

– hardening of a single-point metal-composite compound (Fig. 11) to evaluate the effect of the nano-

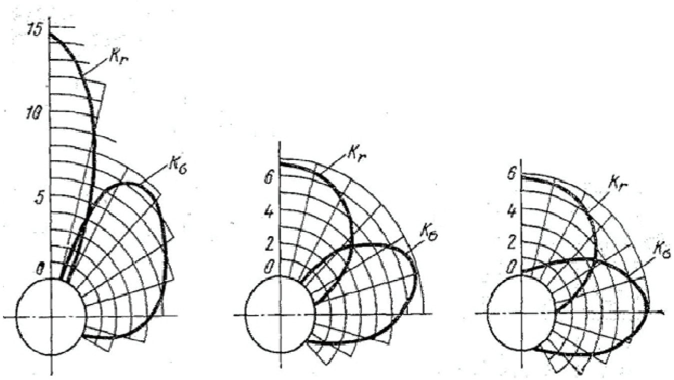


Fig. 10. The dependence of the contact and tensile stress concentration factors (K_r and K_σ) in the hole contour on the relative gap between the hole and the bolt in the bolted compound

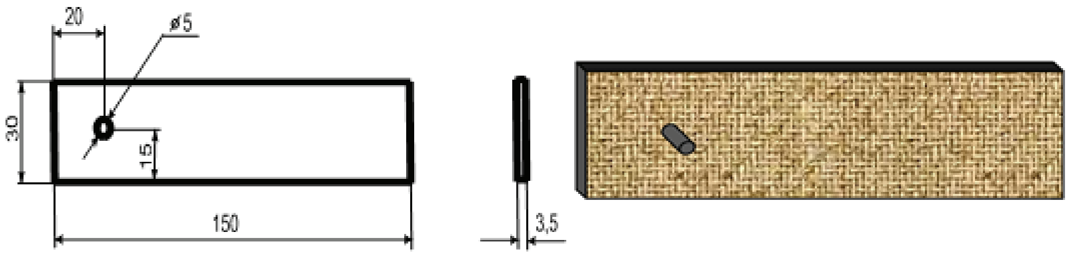


Fig. 11. The image of the carbon-fiber sample with a pin

modified adhesive composition on increasing the resource strength due to filling the gap between the bolt and the hole (ensuring tight fit and reducing stress concentration) and healing the damage after machining;

– hardening of structurally similar multi-row metal-composite compounds (Fig. 12), in which, along with the filling of the gaps between the hole and the bolt, all fasteners are simultaneously included in the work.

The test results showed that:

– when using the nano-modified adhesive composition in the gap between the pin and the hole, the fracture strength of the samples of single-point compounds made of carbon fiber increased. For samples with longitudinal fibers of 0° (100 %), the increase in strength was ~ 50.0 %. For the samples with combined fibers: longitudinal 0° (25 and 60.0 %), and at an angle of 45° (50 and 32.5 %) and at an angle of 90° (25 and 7.5 %), the strength increased from 18.0 to 20.5 %. The fatigue durability of compound samples with complex laying of fibers, when used in the gap between the pin and the hole of the nano-modified adhesive composition, increased more than 4 times;

– when using the nano-modified adhesive composition in the gap between the bolts and holes of structurally similar samples of multipoint metal-composite compounds, the tensile strength increased on average by 23 %. Initial compounds when carrying out life tests with alternating loading were destroyed after 100,000 cycles. Samples reinforced with the nano-modified adhesive composition, during the fatigue tests, withstood 1,000,000 loading cycles (i.e., 10 times more compared to non-reinforced samples). Since the destruction of the samples did not follow, it was decided to stop the life tests and bring the samples to failure when repeated static loading. Destructive loads under static tension coincided with the results of previous static tests. Under cyclic alternating loading, the temperature was measured. It was found that the samples of the hardened nano-modified adhesive composition, on average, had a temperature in the junction zone 5 °C lower compared to the initial ones. Thus, it has been established that due to the use of the nano-modified adhesive composition, the fatigue life of structurally similar samples of multi-row metal-composite compounds with complex fiber laying is increased not less than 6 times.

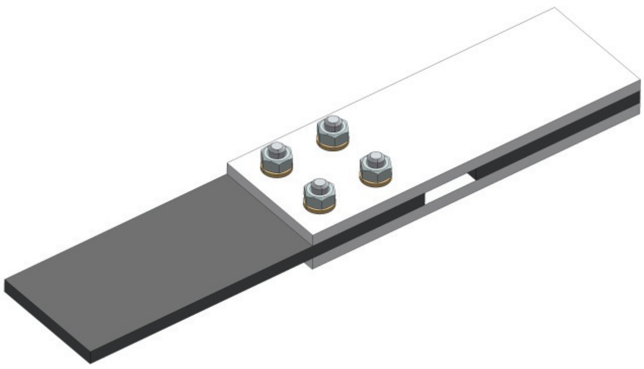


Fig. 12. The image of the structurally similar sample of the multipoint metal-composite compound

Conclusion

1. The results of numerical simulation showed that one of the most effective additives to increase the mechanical shear performance of the adhesive composition based on the epoxy matrix is open carbon nanotubes and graphene oxide. For them, the filler particles are held by fragments of epoxy chains by both hydrogen and van der Waals dispersion forces.

2. The research of the influence of the two dispersing methods of the Taunit-M nanofiller into the base adhesive composition to increase the strength characteristics with respect to compounds of aircraft structures has been conducted.

3. The properties of the nano-modified adhesive composition after its curing showed that after ultrasonic dispersion of the nanofiller the hardness increased by 31 %, and the reduced elastic modulus increased by 28 % compared with the base adhesive composition. The wave process of dispersing nanofillers in the binder increased the hardness and reduced elastic modulus to a lesser extent, by 13 % and 12 %, respectively. Higher strength values after ultrasonic dispersion are explained by the fracture of the filler

fibers directly in the polymer matrix, as a result of which the efficiency of the interaction between carbon nanofibers and the polymer binder for its structuring increases, and, consequently, the mechanical characteristics increase.

4. It is advisable to develop a dispersion technology using the directional wave process with the provision of nanofiber fractures. It seems also appropriate to continue the research on the choice of the nano-filler type (carbon nano-fibers, nano-graphene) with the definition of the most rational concentration.

5. It was established experimentally that the use of the nano-modified adhesive composition in single-point bolted compounds, in the gap between the pin and the hole, leads to the increase in strength by 18 %, and the fatigue life by more than 4 times. The use of the nano-modified adhesive composition in structurally similar samples of multi-row metal-composite compounds with complex laying leads to the increase in their strength by 23 % and the fatigue life more than 6 times.

6. The use of the nano-modified adhesive composition to increase strength and resource creates the basis for reducing the weight of the structure, as well as reducing the cost of operation.

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