Method for production carbon plastics with multifunctional properties

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Abstract. The technology of metal coating of carbon tapes and fabrics, consisting of two technological operations: activation and deposition, is considered. To perform the process of activating the surface of carbon tapes and fabrics, UPM-500 plasma activation device at a low-temperature and plasma air were used. A laboratory magnetron sputter MIR-2 was used for applying metal coatings by magnetron sputtering. The diagram of the formation of metal coatings on plain carbon fiber, taking into account its structure, is given. The study provides the results of determining the carbon plastics interlayer shear strength manufactured using vacuum infusion method, which vary in the structure of the reinforcing filler, the metal coating type and the composition of the epoxy binder. It is shown that the composition of the binder, the reinforcing material and the type of coating equally play a significant role in the shear strength of carbon plastics.

1. Introduction
Composites based on carbon fibers and epoxy binders are used in the manufacture of load-bearing elements which require a combination of high strength, rigidity, durability and minimal weight [1, 2]. For such indicators as short-term tensile and compressive strength, as well as creep and corrosion resistance properties, carbon plastic in the temperature range up to 250°C is superior to aluminum and titanium alloys [3]. Carbon fibers (tapes, fabrics) have high biological and chemical resistance, good electrical and thermophysical properties. Carbon composites applications are constantly expanding due to improved molding methods, which have allowed to significantly reduce their cost [4-7].

Heavy operating conditions of carbon fiber composite products and constantly increasing demands to enhance their reliability make it necessary to improve the performance properties of existing materials [1, 3, 6-8]. For example, the insufficiently high thermal conductivity of carbon fiber leads to the need for additional cooling of compartments with electronic equipment and batteries, since the required heat removal is not provided. This leads to additional energy consumption on board, to an increase in the weight of the aircraft systems, which reduces the benefits of using carbon plastics.

The disadvantages of carbon plastics (in comparison with metals) also include insufficient electrical conductivity. For example, elements of Arctic infrastructure and equipment, including switchboard enclosures and elements of the buildings, require heating. Heating system in the Arctic region would solve a lot of problems related to rapid access to infrastructure in any weather, lack of
snow, ice, etc. Currently, the heating of such constructions is solved by installing metal heating elements that have a high energy consumption and heat loss.

Another major problem associated with the low thermal and electrical conductivity of carbon composite structures is their additional lightning strike protection. Currently, for this purpose are used a copper mesh, metal wires and etc. Requirements for lightning strike protection for composite structures are applied to the compounds of aircraft, unmanned aerial vehicles, wind power plants, protective shelters for radar antennas, etc.

The authors of [9-12] propose to improve the thermal conductivity of carbon plastic by using carbon nanotubes (CNTs) and other nanodisperse fillers, etc. Problems related to the use of nanodisperse fillers have been discussed in a large number of publications, but they often contain directly opposite results. Such a wide range of opinions in assessing the effectiveness of using CNTs as modifiers is probably due to the lack of technological modes for their introduction, taking into account the mass of the binder and the kinetics of changes in its rheological properties.

The authors of [8, 13-15] proposed to apply the method of magnetron sputtering of thin layers of metal coatings on carbon fabric. The main purpose of metal coating is to change the physicochemical properties of the carbon filler surface, which allows to give them a complex of new functional properties, such as radio absorption, electrical conductivity, antiseptic property, etc. Thus, the authors of [15] found that carbon tapes coated with stainless steel have been effectively used at negative temperatures as reinforcing materials in the manufacture of pipe repair bandages. However, for the design of composite structures that are operated in a wide range of temperatures, it is necessary to know their thermal properties.

The purpose of this paper is to study the structure and determine the mechanical properties of carbon composites made of metallized carbon tapes and an epoxy binder.

### 2. The Methodology

FibArmTape-230/300 and domestic (LUP) carbon tapes along with Twill Carbon Fabrics GG1200T and GG200T were used as objects of research (Table 1).

**Table 1. Reinforcing Materials Properties**

| Properties         | Carbon Tapes grade | Carbon Fabrics |
|--------------------|-------------------|---------------|
|                    | FibArm Tape-240/1200 | ЛУП | GG 1200T | GG 200T |
| Surface density (g/sq.m) | 240                | 170         | 1185     | 192  |
| Thickness (mm)     | 0,24               | 0,12        | 1,25     | 0,2  |
| Elastic modulus (GPa) | 250               | 260         | 240      | 240  |
| Poisson’s ratio    |                   | 0,3         |          |      |

The structure of metal coatings was assessed on plain carbon fibers of the domestic (LUP) carbon tape by the method of atomic force microscopy, using a “SOLVERHV” device.

In this study two compositions of epoxy-dian resinED-20, differing in the type of hardener, were used as epoxy binders: triethylentetraamine (TETA) and dianidiphenylsulfone (DDS) (Table 2). All the characteristics shown in table 2 were obtained using epoxy-dian resin ED-20 as an oligomer [16].
Table 2. Properties of polymer materials

| Properties of binders and polymer matrices based on hardeners | Triethylentetraamine | Diaminodiphenylsulfone |
|-------------------------------------------------------------|----------------------|------------------------|
| Component Ratio resin: hardener, wt%                       | 100:11               | 70:30                  |
| Vitality at room temperature                               | 1 hour               | unlimited              |
| Hardening regime:                                          |                      |                        |
| - temperature °C;                                          | 20                   | 150                    |
| - time, hour                                               | 24                   | 3                      |
| Glass transition temperature, °C                           | 63                   | 180                    |
| Impact Strength, kJ/m²                                     | 4,7                  | 5,4                    |
| Breaking stress, MPa                                       | 72                   | 125                    |
| Breaking bending stress, MPa                               | 111                  | 140                    |
| Breaking compression stress, MPa                           | 82                   | 110                    |

TETA hardener, allows to produce the binder, the curing of which takes place at room temperature, while bonding with DDS solidified at elevated temperatures. The viscosity of these binder compositions is very high and to reduce it, diethylene glycol (DEG) was introduced into their composition in quantities of 10-15 wt%, which allowed reducing the viscosity is 0.8-1.3 PA·s.

Carbon fiber molding was performed by the vacuum infusion method [17].

The mechanical properties of fibers were assessed on a Zwick/RoellZ010 tensile testing machine. The average value of the strength of carbon fiber during interlayer shear was determined based on the results of five tests. The average value of the coefficient of linear thermal expansion was determined based on the results of 3 tests.

3. Results and discussion

A laboratory magnetron sputter MIR-2 was used for applying metal coatings on carbon tape and carbon fabrics [18, 19], which allowed for low temperatures (<150 °C) to obtain a nanocoating of adjustable thickness.

The essence of the technology of magnetron sputtering method is that from the surface of the cathode, which functions as a target, the substance is sprayed on a substrate, which serves as an anode. A carbon fabric is placed on the substrate, on which a thin coating film is formed. A laboratory magnetron sputtering unit was used to apply metal coatings (Figure 1). Copper, titanium, and stainless steel were used as targets in this study.

In this study, all metal coatings were applied to carbon tapes and fabrics on both sides, which doubled the duration of the process. The thickness of the metal coating was ≈100 nm. The modes of application of metal coatings: discharge current 2–4 A, the pressure of the plasma gas (1,4 – 1,8)-10^-3 Torr.

Before applying metal coatings, the surface of carbon tapes and fabrics was treated on UPM-500 plasma activation device (Figure 2). The purpose of plasma activation was to remove adsorbed moisture and other gaseous products from the surface of carbon tapes, which allowed to increase the strength of the metal coating adhesion to the tape.

The modes of plasma treatment: plasma gas pressure, discharge current, and deposition time. As a result of the study, the following values were obtained: the plasma-forming gas pressure was 75PA, the current strength was 0.45 A. A distinctive feature of processing at the plasma activation device was a very short time, which, together with the process of installing a fabric sample and vacuum infusion, did not exceed 15 minutes.

Figure 3 shows a diagram of the formation of a metal coating on the example of a plain carbon fiber, the surface of which has a micro composite structure, since it consists of a crystalline phases (1, Figure 3) and an amorphous (2, Figure 3) phases. To illustrate the composite structure of carbon fiber,
it was subjected to ion-plasma etching in an oxygen environment followed by the application a layer of gold, not more than 20 nm thick. As a result of such processing, the depth of etching on the amorphous sections of plain carbon fiber was larger than on the crystalline, which allowed their visualization: amorphous – shown in dark color, crystalline in light, (see Figure 3, a, b). After processing the carbon fiber with a low-temperature plasma, the formation of functional groups (see Figure 3, c, d) takes place on its surface, which first appear on amorphous sections of the carbon fiber surface. At these sites, initially, there is the formation of embryos (see Figure 3, f) around which a coating is gradually formed (Figure 3, g, h), the thickness of which is greater on amorphous sites than on crystalline ones.

Figure 4 demonstrates photos of stainless-steel and titanium coted carbon tapes, which show that the coating does not form a perfectly smooth layer on the elementary fiber.

**Table 3. Contact-angle values**

| Time after processing on the UPM-500 plasma activation device - min | Value of the contact angle, ° when using binders with hardener |
|-------------------------------------------------------------------|---------------------------------------------------------------|
|                                                                  | TETA                                         | IMTFE                                        |
| Immediately after processing                                     | 29 ± 0,5                                    | 17 ± 0,5                                     |
| 15                                                                | 34 ± 0,5                                    | 21 ± 0,5                                     |
| 30                                                                | 36 ± 0,5                                    | 23 ± 0,5                                     |
| 60                                                                | –                                            | 24 ± 0,5                                     |
| 120                                                               | –                                            | 25 ± 0,5                                     |
| 180                                                               | –                                            | 26 ± 0,5                                     |
Figure 3. Diagram of the formation of a metal coating on carbon fiber: a, b - image of carbon fiber showing crystalline (1) and amorphous (2) sections; c - image of the surface after activation by low-temperature plasma, which led to a change in roughness (3); d, f - formation of functional groups (4) and embryos (5); g, h - coating (6) and crystalline areas where there is no coating (7)
Figure 4. Photo of the surface of plain carbon fibers after coating them with stainless steel (a) and titanium (b)

The binder with the TETA hardener had a low viability, which led to the fact that the values of it contact angles were determined up to 30 minutes. The binder with the IMTFE hardener at room temperature maintained the initial viscosity, which allowed to determine the values of the contact angles for 3 hours after its activation.

The data obtained showed that the more time passes after activation, the higher the values of the contact angles, i.e., an increase in the time interval between activation and application of the metal coating leads to an increase in the values of the contact angles, which will negatively affect the value of the adhesive strength between the carbon fabric and the metal coating.

Using the selected types of carbon tapes and fabrics and two types of binders, we manufactured the samples using vacuum infusion method and conducted mechanical tests. Table 4 shows the average values of the five samples. All tests were performed at room temperature.

| Composition of carbon plastic | Interlay strength for carbon plastic with metal coatings fillers, MPa |
|------------------------------|---------------------------------------------------------------|
| The reinforcing material      | Without metal coating | Copper | Stainless Steel | Titanium |
| LUP                          | 46                  | 52     | 64              | 61       |
| FibArmTape                   | 44                  | 58     | 46              | 47       |
| GG1200T                      | 49                  | 66     | 60              | 62       |
| GG200T                       | 40                  | 42     | 42              | 42       |
| LUP                          | 50                  | 69     | 66              | 64       |
| FibArmTape                   | 49                  | 67     | 58              | 66       |
| GG1200T                      | 56                  | 88     | 72              | 84       |
| GG200T                       | 42                  | 55     | 49              | 48       |

Analysis of the obtained results shows that the maximum values of interlayer shear strength have carbon composites made of carbon fabric of the GG1200T. If we compare the mechanical properties of carbon plastics manufactured using this reinforcing filler, the best results are obtained when we used an epoxy binder DDS as a hardener. The lowest strength values were indicated when the FibArmTape carbon tape and epoxy binder with TETA hardener as the reinforcing material were used.

The study showed that applying metal coatings to carbon fabrics and tapes, in comparison with similar carbon plastics made of non-coated reinforcing materials, increases interlayer shear strength. However, there is no single pattern. For example, carbon plastics made of GG1200T carbon fabric
have the highest interlayer shear strength when using a copper coating, and the lowest when using a steel coating. The similar patterns were obtained for carbon fiber plastics made of FibArm Tape carbon tape. However, carbon plastics made of GG200T carbon tape and epoxy binder with TETA hardener have the same strength properties for all three types of metal coatings. Replacing the binder when using the same reinforcing material leads to some increase in the strength characteristics, most when using the copper coating and least for the titanium and steel coatings.

4. Conclusions
The technology of the surface activation of carbon tapes and fabrics and the technology of applying thin layers of metal coatings on them by magnetron sputtering has been established. The tests have shown that the activation efficiency is maintained for 30 minutes after treatment on UPM-500 plasma activation device at a low-temperature. An increase in the time interval between activation and application of the metal coating leads to an advance in the values of the contact angles. The obtained results have defined the values of carbon composites interlayer shear strength depending on the type of reinforcing filler, metal coating and binder.

The tests have shown that the binder plays a significant role in the carbon composite shear strength and the use of diaminodiphenylsulfone (DDS) as a hardener allows to obtain carbon composites with higher interlayer shear strength properties than the TETA hardener. The properties of the reinforcing filler and the chemical nature of the metal coating applied have a significant influence on the shear strength properties. The study defined that applying metal coatings to carbon fabrics and tapes, in comparison with similar carbon plastics made of non-coated reinforcing materials, increases interlayer shear strength. However, there is no single pattern. For example, carbon plastics made of GG1200T carbon fabric have the highest interlayer shear strength when using a copper coating, and the lowest when using a steel coating, while carbon composites made of GG200T carbon tape and epoxy binder with TETA hardener have the same strength characteristics for all three types of metal coatings.

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