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INFLUENCE OF ION-BEAM CARBON-FIBER SURFACE TREATMENT ON THE ANGLE OF WETTING BY EPOXY OLIGOMERS

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The influence of the regimes of modification of carbon fibers by an argon ion beam on the change in the angle of their wetting by an epoxydiane oligomer has been investigated. It has been shown that ion-beam treatment of carbon fibers leads to a considerable decrease in the wetting angles (the difference between the wetting angles for nonmodified and modified fibers is up to 32.2–38.7^{o}*). Accordingly, there is also an increase in the value of the equilibrium work of adhesion by 36.2–41.6% in the contact zone. It has been established that ion-beam treatment of carbon fibers by argon ions leads to an increase in the shear strength when microplastics based on them are formed.*

As was predicted as far back as the last century, carbon fibers (CF) remain the most promising filler of polymer composite material in the current century as well [1, 2]. The problem of maximal realization in the compositions of the unique properties of the carbon-fiber filler determined by the interphase interaction of heterogeneous components is as acute [3]. Surface and internal defects have a negative effect on the cohesive strength of fibers with the polymer binder as well as on the strength of the fibers. The numerous experimental data show that under extension of carbon fibers a break occurs almost exclusively at the place of a visually observable defect. Therefore, the problem of increasing the adhesive strength at the interface and its stability under operating conditions remains central and the most important. Modification of the fiber surface is one of the easiest and most promising ways of controlling the interphase interaction of fibers with the polymer matrix. Various modification techniques are known, e.g., oxidation, grafting of functional groups, and their electrochemical or plasmachemical treatment [4–6]. The modification efficiency depends on the surface purity of fibers.

The CF surface can also be polluted as a result of the technological features obtaining them. The surface defects that most strongly affect the observed strength of fibers, the quality of modification, and their adhesion to the binding material can be removed by chemical etching (in a liquid medium or by oxidation in a gaseous medium), as well as by ion-plasma or ion-beam treatment of CFs. However, the chemical cleaning methods do not always allow one to obtain a surface free of organic solvents, chemical reagents, and films of complex composition not interacting with solvents. Since the composition of pollutions is different and is often not known, sputtering by argon ions is the most effective method for removing the hyperfine surface layers [7].

A promising method for directional modification of the surface of polymers and fibrous materials, as noted in [8], is ion implantation, since, as the dose is accumulated, processes radically differing in their nature proceed, and they can be controlled by varying the energy and mass of the ions being implanted. In [9], it was suggested to use the ion-beam method to modify the surface of track diaphragms in order to regulate their hydrophilic–hydrophobic balance. It may be supposed that this method can also be used to clean the CF surface, which is impossible in the case of treatment by liquid methods. Despite the available works along these lines, the method of ion-beam treatment of carbon fibers for both cleaning and subsequent modification is still not clearly understood.

At the same time, the technological features and ecological cleanliness of the process, the good reproducibility and possibility of providing exact and flexible tests, the high homogeneity of treatment of large surface areas, and the

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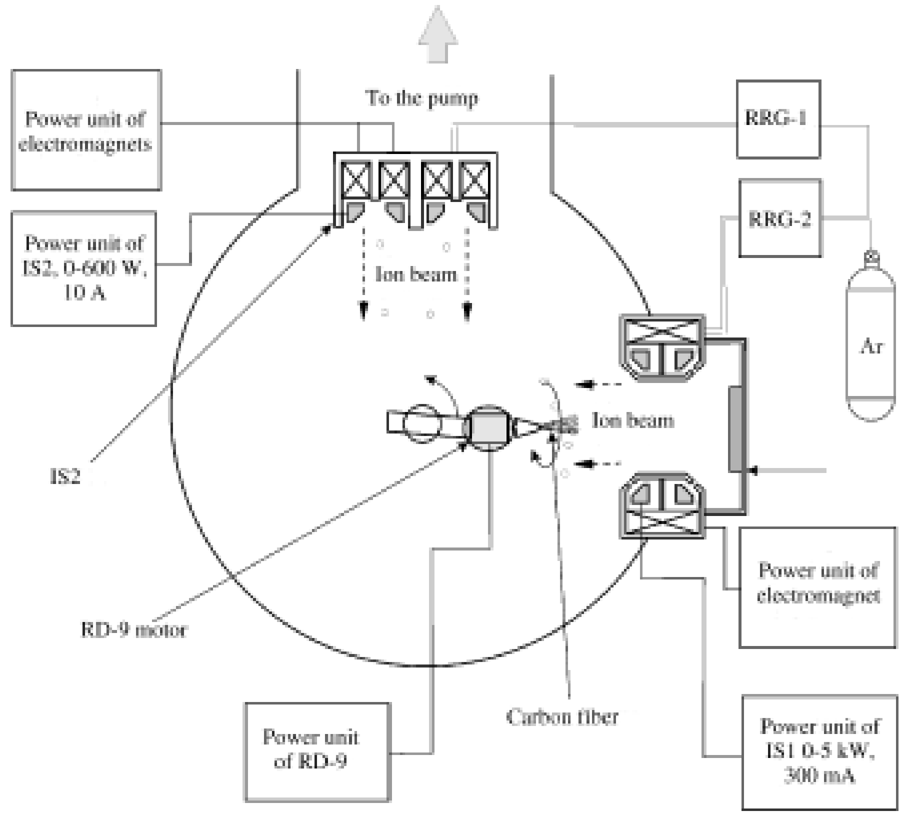

Fig. 1. Scheme of the technological facility.

improvement of their quality due to the directional action permit classifying such a process of carbon-fiber treatment as the most perfect one. Therefore, the aim of the present work is to investigate the influence of treatment of carbon fibers in an argon (Ar^+) beam in the 50–1000-eV range of energies on the angle of wetting of carbon fibers by an epoxydiane oligomer, which is one of the basic indices of the adhesive strength at the interface in carbon-fiber composites.

The advantages of the CF treatment by an ion beam are as follows:

(a) high vacuum;

(b) possibility of using beams of ions of both inert and chemically active gases in one technological process;

(c) control over a wide range of the ion energy and the ion current density;

(d) charge regulation on the surface being treated;

(e) absence of an electric field near the surface being treated.

The most effective way is to use cleaning by a beam of inert-gas ions just before the subsequent operation of CF modification by various reagents in a single vacuum cycle. The perfectly cleaned surface of fibers should lead to a higher quality of their subsequent modification due to the surface activation, since on the surface free bonds are formed, which, upon subsequent treatment by different substances (compositions), can become artificial nucleation centers. Thus, the ion-beam action of inert gases on the CFs can be considered as the first stage of cleaning and deep surface modification of fibers.

To investigate the process of surface modification of carbon fibers by the method of ion-beam treatment, at the Belarusian State University of Informatics and Radioelectronics an experimental complex based on a VU-1Bs vacuum station was developed and manufactured. The choice was due to the convenience of access to the intrachamber equipment when placing and removing samples and the relatively high power of the evacuators at a small volume of the working chamber, which made it possible to work in wide ranges of gas flow rates. The facility is equipped with two ion sources providing generation of ion flows of inert and active gases in a wide range of ion energies and their current densities. The experimental complex is schematically represented in Fig. 1. One ion source (IS) is a two-beam anode layer accelerator (ALA) of flange design and the other one — an end Hall source (EHS) set inside the chamber.

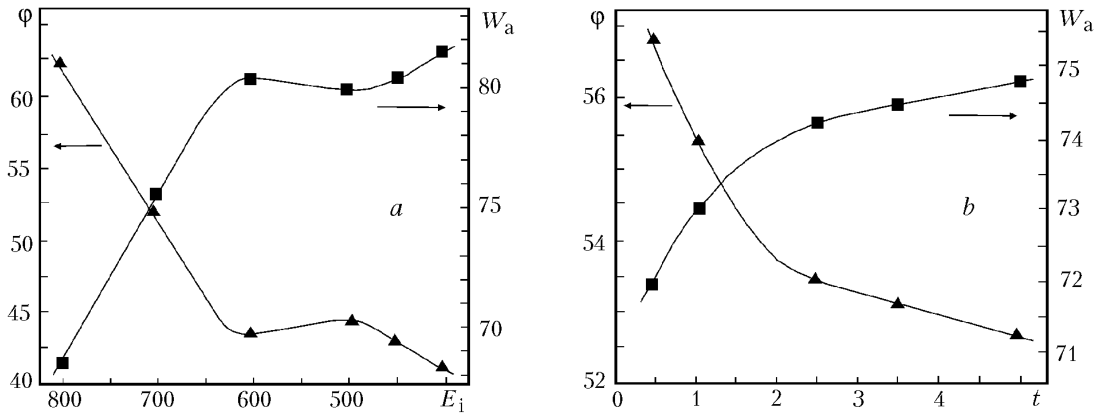

Fig. 2. Wetting angle and work of adhesion versus the treating-ion energy (a) and treatment time (b).

The facility for modifying the fiber surface by the method of ion-beam treatment provides the following technological parameters of the process:

(1) residual chamber pressure — $< 10^{-3}$ Pa;
(2) working pressure — $(2.0–6.0)\cdot10^{-2}$ Pa;
(3) working gas — argon;
(4) energy of bombarding ions — 50–1000 eV;
(5) bombarding-beam current density from 50 to 1000 μA/cm^2.

Bundles of fibers were fixed by a clamp on a stainless steel pedestal turned by an RD-9 motor. Pedestal positioning in the working zone of the ion beam was accomplished by a carousel-type device. The working gas (argon) was fed into the ion sources by GFR-1 and GFR-2 automatic gas flow regulators to maintain the working gas pressure in the course of the process.

In the ion-treatment processes, the determining effect on the structure and properties of the surface is produced by the irradiation time and the composition, the energy characteristic, and the density of the ion flow bombarding the substrate. Preliminarily, for each source the energy characteristics of the generated ion beam had been investigated by the method of differentiation of the delay curves taken at various values of the anode voltage. It has been established that the ALA generates an ion beam in the 350–1000-eV range of energies and the EHS — in the range from 50 to 500 eV [10]. The ion current density was set by regulating the inleakage of the working gas into the discharge region of the source. The range of working pressures in the vacuum chamber for the ALA was 10^{-2}–$6\cdot10^{-2}$ Pa and for the EHS — 10^{-2}–$4\cdot10^{-1}$ Pa. For quick determination of the ion current density in the process of CF treatment, in each experiment a Faraday cylinder was located adjacent to the samples.

The adhesive interaction between the oligomeric or polymeric matrix and the CF surface begins with wetting. We investigated the influence of the regimes of modification of carbon fibers (in energy, beam density, treatment time) on the change in the wetting angle. Good wetting providing a closer contact on a large interface also predetermines a higher adhesion of the fiber to the matrix. The equilibrium work of the epoxyoligomer adhesion to the fibers was estimated by the values of the wetting angles and the measured surface tension of the epoxyoligomer, using for the calculations the Dupree–Young equation [11].

The most reliable results in determining the angles of wetting by oligomers of fibers of diameter about 10–30 μm are obtained by the method proposed by A. K. Kurilenko and described in detail by us in [12]. According to this method, a slightly stressed monofiber was placed on a microscope slide and the fiber ends were glued to the microscope slide edges. A binder drop was applied to the monofiber, the latter was covered with glass, and the angle at the boundary between the monofiber and the liquid drop formed was measured. Measurements were taken in the air at room temperature with a magnification of 100 times. An MIN-8 microscope having a horizontal limb with a division value of 0.1° was used. For the value of the wetting angle, the mean value of 12–16 measurements was taken. The measurement error was no more than $\pm1.5^{\circ}$.

TABLE 1. Change in the Wetting Angle and the Work of Adhesion of CFs Depending on the Energy and Flow Density of Treating Ions

Ion energy E_i, eV	Ion flow density J_i, μA/cm^2	Wetting angle of CFs φ, deg	Work of adhesion W_a, J/(m^2·10^{-3})
80	200	63.4	67.38
150	150	59.9	69.88
200	200	50.7	76.02
250	250	50.3	76.27
300	500	42.4	81.02

As the experimental studies have shown, irradiation of carbon fibers by argon ions leads to a considerable decrease in the values of the angles of their surface wetting by the oligomer. The difference between the wetting angles for nonmodified fibers and ion-beam-treated fibers can reach 32.2–38.7^o. Accordingly, the values of the equilibrium work of adhesion increase by 36.2–41.6% in the contact zone. The dominant factor in the change in the surface properties of fibers is the energy of ions (Fig. 2a). These properties are influenced by the irradiation time to a lesser extent (Fig. 2b). A certain role in the surface modification of fibers is also played by the ion-beam density (see Table 1).

We also investigated the strength characteristics of microplastics obtained on the basis of a carbon cloth treated by an argon ion flow in different regimes. Samples were obtained by impregnating cloth cuts with an epoxide binder of cold and hot hardening. The tensile strength of hardened samples of microplastics was determined on an RMU-0.05-1 tension testing machine according to the State Standard GOST 15140-78. It has been revealed that under the same temporal conditions of treatment of carbon cloth by an argon ion beam the strength of the cloth with a binder hardened on its surface is somewhat higher than the value for the nonmodified cloth. It should be noted that the increase in the strength is greater for the carbon cloth treated by argon ions having a lower energy. The shear strength (GOST 28840-90) increases in the same way in testing lap-glued samples.

Thus, the investigations performed point to the possibility of effective use of ion-beam treatment of carbon fibrous materials for improving the physicochemical interaction between the modified carbon-fiber filler surface and the epoxide binder.

NOTATION

E_i, ion energy, eV; J_i, ion flow density, μA/cm^2; t, time of CF treatment by ions, min; W_a, work of adhesion, J/(m^2·10^{-3}); φ, wetting angle of CFs, deg.

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