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Modification of Construction Carbon-Reinforced Plastics with Carbon Nanoparticles

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Abstract—The influence of fullerenes and their derivatives on the formation of carbon-reinforced epoxy composites and service characteristics of the construction carbon-reinforced plastics thus formed have been studied. The technology of homogeneous distribution of two- or four-walled carbon nanotubes in the bulk of epoxy oligomers has been developed. A lightning-protective coating on the basis of a carbon-reinforced plastic (CRP) with a carbon-nanotube modifier has been designed. Owing to increased electrical and heat conduction, high thermal destruction temperature, and improved performance characteristics, the designed CRP coating exhibits improved safe damageability under direct stroke and lower weight compared to conventional brass grid lightning-protective coatings.

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Construction carbon-reinforced plastics (CRPs) have occupied a firm place among materials for aviation and space technics. Their share in the constructions of planers, light planes, and the most modern jet liners (such as Boeing 787 and Airbus A350) is more than 50%, and the total surface area of parts located at the outer contour of planers is 80%. Carbon-reinforced plastics are finding increasing use in gas turbine and solid-propellant rocket engines (GTRE and SPRE, respectively), hulls of rocket-space and interplanetary stations and artificial Earth satellites. Such a shift of the material balance was favored by exceptionally high properties of polymer composite materials (PCMs), especially if the load on a part acts along carbon fibers. In this case, the composites take advantage of such their characteristics as high specific strength, elastic modulus, and thermal stress. However, the high values of these parameters are largely due to the improvement of properties of the reinforcing filler. Carbon fibers are generally considered as a nanocomposite formed by definitely arranged nanocrystallites joint together with an amorphous (turbostratic) carbon [1–4]. Such fibers exhibit exceptionally high strength (above 700 MPa) and elastic modulus (above 60 GPa).

Quite a different situation takes place with the other component of composites, viz. the polymer matrix: Its elastic and strength characteristics are an order of magnitude lower than the respective characteristics of construction fibers. At the same time, the matrix functions not only to maintain reliably in the composite monolayer the highest degree of anisotropy of properties, but also to maintain a sufficient level the compression, interlaminar share, and transversal strengths, fatigue resistance, durability, heat distortion point, water, fuel, and cracking resistance, and other performance characteristics. Items made of laminar carbon-reinforced composites prove the most vulnerable in cases where mechanical load is applied in a direction not coinciding with the direction of carbon fibers in the reinforcing layers.

Encouraging perspective arose with the development of techniques for the improvement of characteristics of the polymer matrices of construction carbon-reinforced composites by their modification with fullerenes C_{60}, C_{70}, their mixtures and derivatives, as well as fulleroid carbon nanoparticles: astralenes and nanotubes [5–8]. The nature of nanoparticles, their purity, geometric dimensions which define the surface

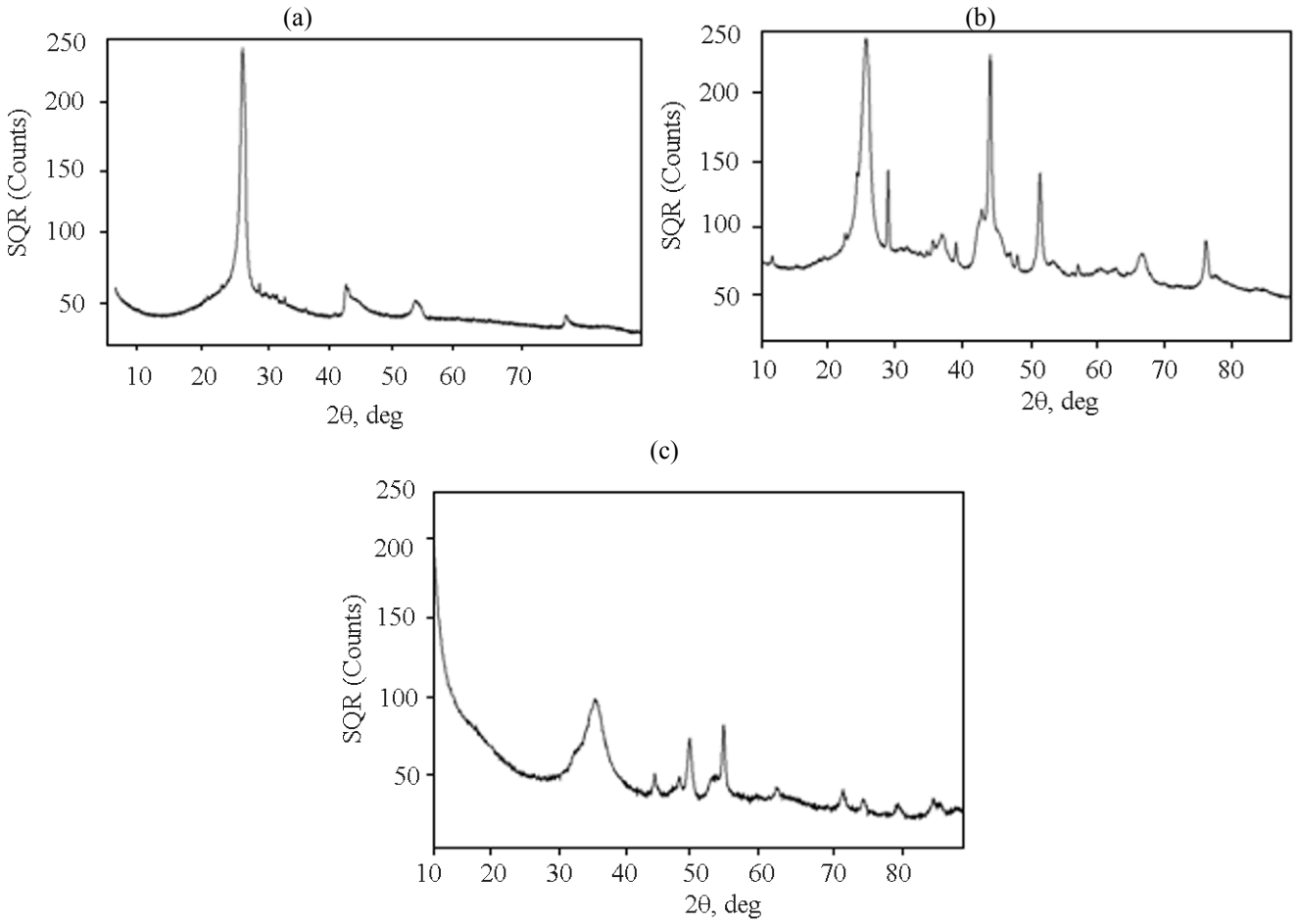

Fig. 1. Individual X-ray diffraction spectra of carbon nanotubes: (a) purified; (b) soot-containing; and (c) carboxyl-functionalized.

energy, presence or absence of surface chemically active functional groups capable of reacting with binder components strongly affect the formation, structure, and properties of the composite matrix and matrix–reinforcing filler interfacial layer.

The use of an up-to-date research laboratory equipment in their work, RIAM together with RAS institutes could initiate development of methods and reliable criteria for quality assessment of nanomaterials and their derived modifiers. Fullerenes, carbon nanotubes, and their derivatives were studies by X-ray structural analysis (XRD) on a RIGAKU D/MAX–2500 diffractometer with monochromatized CuK_α radiation. Microstructure was studied by high-resolution transmission electron microscopy (TEM), and interactions of components on the formation of carbon nanocomposites were studied on Mettler Toledo thermoanalyzers.

During structural studies on fulleroid carbon nanoparticles we could develop procedures for their identification by individual XRD spectra (examples of such spectra are shown in Fig. 1).

The purity of carbon nanotubes was determined by thermogravimetric analysis (TGA) on a Mettler Toledo TGA/SDTA 851 instrument. The object for study was single-wall carbon nanotubes (SWNTs) of two types: ED SWNTs were prepared by electric arc evaporation of graphite with a Ni/Y catalyst and VDT_{CO} SWNTs were prepared by CO decomposition on an iron catalyst under high temperatures and CO pressures.

The material obtained after synthesis contains, along with single-wall carbon nanotubes, catalyst metal particles and amorphous carbon. The aim of purification was to remove these admixtures. Amorphous carbon was removes of oxidizing the synthesis

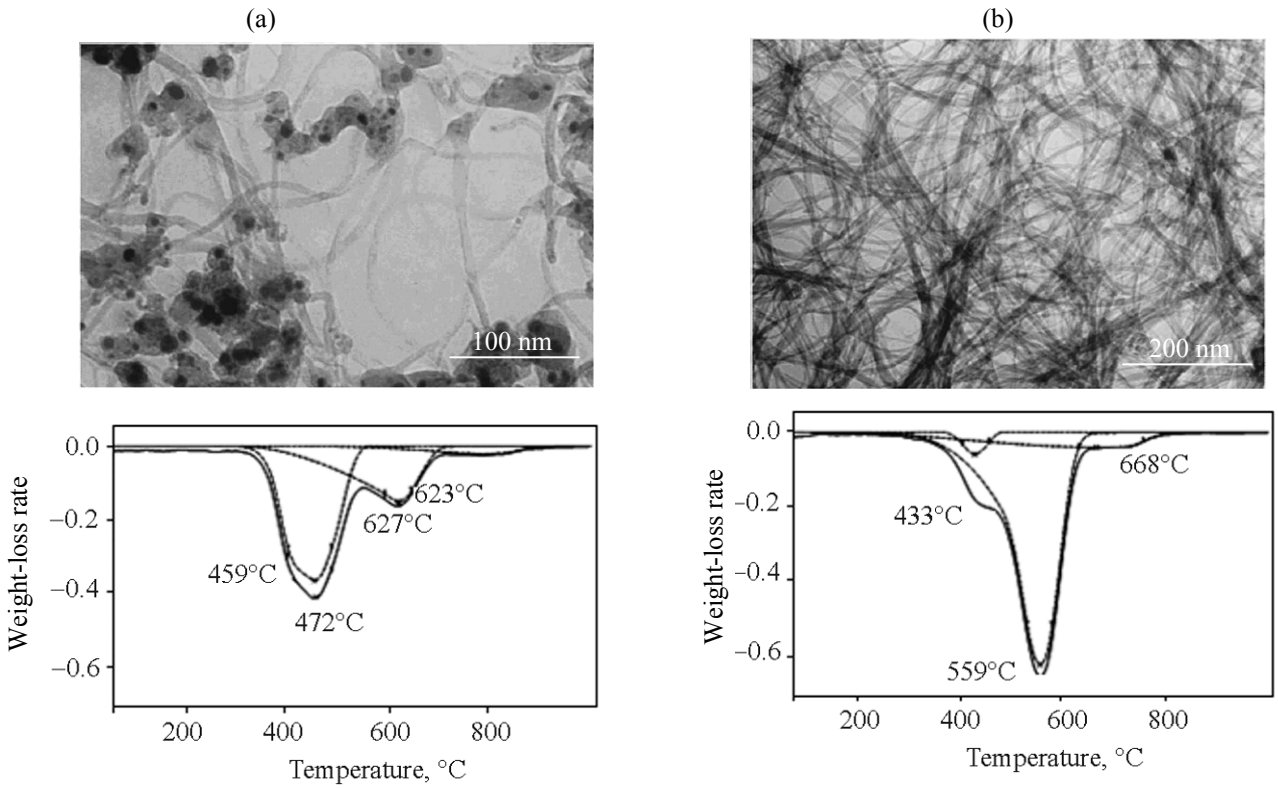

Fig. 2. Microphotographs and thermograms of the (a) starting and (b) purified single-walled carbon nanotubes.

product either by atmospheric oxygen under heating or by treatment with nitric acid under reflux, and the metal was removed by treating the materials with hydrochloric acid. Carbon nanotubes of varied purity were obtained by earlier developed procedures [9], and their purity was controlled by TGA and TSE (Fig. 2).

Thermogravimetry is widely used for purity control of SWNTs, since it is known that the burning point of pure tubes is higher than that of amorphous carbon, and the metal remains in the unburned residue as oxides. Figure 2 shows the differential weight loss curves (DTGA). Peak deconvolution in the DTGA curves was performed using the Mettler Toledo software. The content of admixtures in carbon nanotubes was determined by integration of DTGA peaks after their deconvolution.

Carbon nanoparticles, having high specific surface area and surface energy, are extremely prone to aggregation. Therewith, they lose most of their activity. In this situation, disintegration of nanomaterial, uniform distribution of nanoparticles in the bulk, and mobilization of their active interaction with an object to be nanomodified (matrix and matrix–fiber interface) are the most problematic stages of nanotechnology.

Nanoparticle associates can be disintegrated by means of surfactants, but such substances can block the structural energetic potential of a separate nanoparticle. Fullerene C_{60} can be dissolved in a liquid medium. However, here, too, a disadvantage takes place, specifically, formation of stable solvates. A continuous inert medium is required, which separates nanoparticles and does not block their activity in the reaction medium. Such medium has been found. It can fulfill four concurrent functions: disintergator, transportation means (transport and distribution of nanomodifier over the bulk of oligomer binder), and softener for solid oligomer and plasticizer, which decreases the brittleness of the cured polymer matrix. The difficulty with uniform distribution arises not only with energy characteristics of carbon nanoparticles, but also with their tendency for sedimentation in a liquid oligomeric medium. To prevent this process, a high-density inert liquid medium was tested. An efficient and accessible tool for overcoming sedimentation of carbon nanoparticles in viscous oligomers is ultrasonication. This also favors disintegration of

nanomaterial particles. The treatment regime should be controlled to prevent mechanical destruction of starting components.

The technology of fabrication of nanomodified carbon plastics includes the following operations.

(1) Finishing carbon fillers with a solution of fullerene C_{60} and its functional derivatives in an inert medium.

(2) Disintegration of nanotubes and astralenes in a solvent medium by means of an immersion ultrasonic activator.

(3) Preparation of an ultradisperse suspension of nanotubes and astralenes in epoxy monomer and oligomer media in an unltrasonic bath.

(4) Preparation of binders on the basis of modified epoxy oligomers and hardeners.

(5) Impregnation of finished carbon fillers.

(6) Drying prepregs at room temperature to remove the solvent.

(7) Cutting prepregs and forming their batches according to the required reinforcement scheme.

(8) Curing prepreg batches by step temperature–time regimes, based on refined kinetic and rheological data for binders and prepregs.

It has become clear already at the first stage of research that the best results could be reached by fixing nanoparticles in a composite matrix via their chemical bonding. Therefore, the Institute of Problems of Chemical Physics, Russian Academy of Sciences (IPCP RAS, Chernogolovka) and the Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences (IIC RAS, Novosibirsk) were set the task to activate the surface of fullerenes and nanotubes by grafting functional groups capable of forming network structures including nanoparticles due to interaction with the functional groups of polymer binders. In particular, the procedures developed at the IPCP RAS [9, 10] were used to synthesize fullerene derivatives with grafted amino groups. Benzylamine (an aromatic amine) and heptylamine (an aliphatic amine) were tried as starting amines.

The activity of grafted amines with respect to the epoxy resin was assessed in reactions of fullerene derivatives C_{60}-BA-4 and C_{60}-GA with DER-330 epoxy diane resin. The component ratios in the compositions to be tested were chosen to be close to stoichiometric. This choice was motivated by the aim of this experiment, specifically, to establish that the components react with each other and to assess roughly the temperature and time of chemical fixation of the carbon nanomodifier in the structure of the epoxy matrix. The reference composition in the research on this process was a mixture of DER-330 resin and a well-known aromatic amine diaminodiphenyl sulfone (DADPS) which is commonly used for curing epoxy resins.

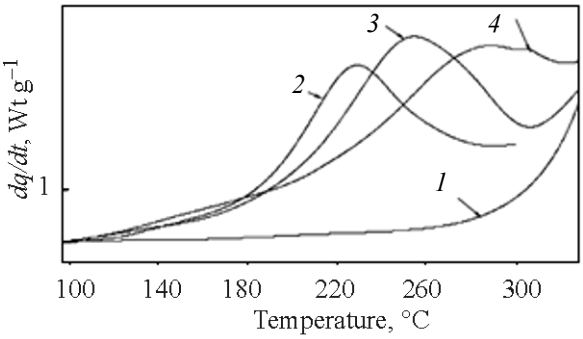

Fig. 3. DSC curves of the hardening reactions of (*1*) DER-330 epoxy–diane resin and its compositions with (*2*) DADFS hardener and (*3*) C_{60}-BA-4 and (*4*) C_{60}–GA-4 fullerenes.

The study was performed by means of differential scanning calorimetry (DSC) on a Mettler Toledo DSC 822 calorimeter at a heating rate of 10 deg min^{-1}.

It was found (Fig. 3) that the epoxy resin reacts with amino derivatives of fullerene at higher temperatures than with DADPS: The exothermic effect of the reaction of amino with epoxy groups shifts by no less than 30°C to higher temperatures. The reactions occur with a well-defined exothermic effect which compares for this model composition with those characteristic of traditional epoxyamine systems. Fullerene C_{60} does not react with the epoxy resin in this temperature range.

Hyperbranched polymers in the basis of methacrylic monomers make it possible to obtain thrmodynamically stable dispersions of carbon nanotubes in methyl methacrylate. Together with the Mendeleev Russian Chemical Technological Institute (RCTI) we developed a technology for preparing uniform bulk dispersions double- and tetrawalled carbon nanotubes in epoxy monomers. The quality of distribution of nanotubes dispersed in binder bulk was evaluated from TSM microphotographs.

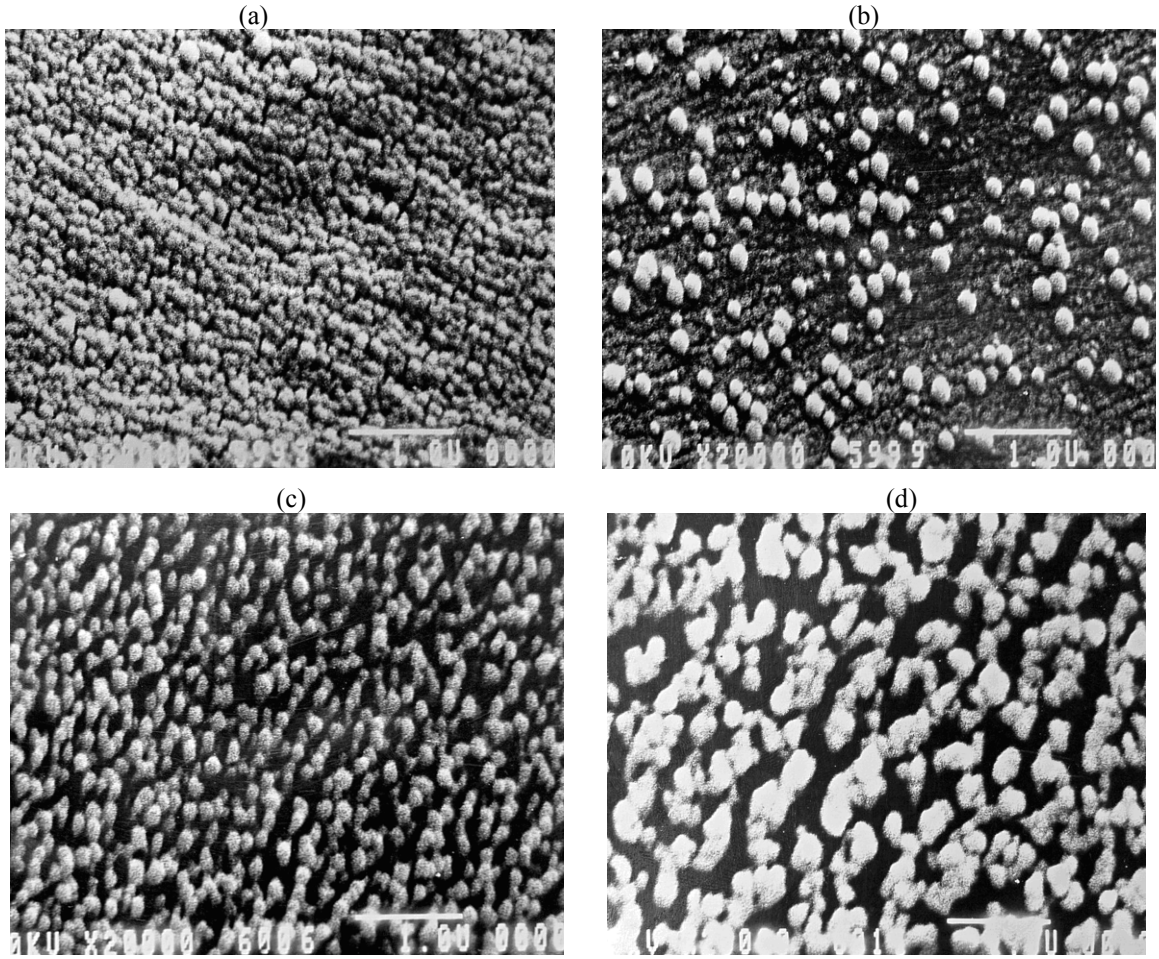

Fig. 4. Microphotographs of epoxy plastics with varied contents of functionalized carbon nanotubes. Nanotube content, wt %: (a) 0; (b) 0.01; (c) 0.1; and (d) 0.5.

The quality of nanoparticle distribution affects the morphology of the epoxy matrix of the carbon composite. This is well-illustrated in Fig. 4 which shows the TEM microphotographs of chips of resin samples with successively increasing concentrations of nanoparticles.

The microphotograph of the surface of an eched chip of the matrix containing 0.01 wt % of multiwall carbon nanotubes (tMWNTs) shows almost regular spherical formations of about 100 nm.

These formations are not destroyed by ionic beam and, probably, involve stronger intermolecular interact-tions than the surrounding matrix. Their mutual location suggests that they, like beads, are strung to nanotubes. As the tMWNT concentration increases, the number of formations increases, and they are uniformly distributed over the whole observation field. The maximum density of "beads" is attained at tMWNT concentrations of 0.05–0.1%, and the corresponding samples have the highest elastic moduli and glass-transition temperatures (T_g). Further increase of the concentration of nanotubes initiates formation of irregularly shaped agglomerates, and the elastic modulus therewith decreases. The essential structural changes in the doped samples are also evidenced by changed shaped of small-angle X-ray scattering curves.

The above data suggest that the change of characteristics of polymer matrices is associated with the changes in their supramolecular structure, produced by nanoparticles.

As known, the absolute value of the elastic modulus of polymer materials and their glass transition point depend on a combination of such parameters as macromolecular packing density, molecular mobility, degree of intermolecular interaction, and density of

Properties of lightning-protective layers of gradient carbon nanocomposites

Properties	UT-900-3k fabric			Porcher Ind. 3692 fabric		
	without nanoparticles	with nanoparticles	superiority, %	without nanoparticles	with nanoparticles	superiority, %
Compressive stress, MPa	620	710	15	680	750	10
Interlaminar shear stress, MPa	40	48	20	48	56	17
Glass-transition point, °C	180	200	11	180	200	11
30-day water absorption	1.12	0.52	300	–	–	–
Lightning resistance, grade	3	9	200	4	9	125
Tensile stress, MPa	580	590	2	930	940	1
Tensile modulus, GPa	72	72	0	68	68	0

chemical network. Yu.S. Lipatov showed in his classical works that for moderate filling (much lower the percolation threshold) of importance are changes of the structure and properties of polymer boundary layers under the action of solid surface [11]. The formation of these layers depends on the nature of the polymer and the surface of the filler, their relative surface energies, and temperature and time conditions of composite formation. The structural changes induced in polymers on their contact with solid surface are large in value and develop over a long distance, and, therefore, filled polymers can be considered as a three-phase systems comprising the filler, polymer boundary layer at the filler surface, and "free" polymer with the structure unaffected by the interface. The change of properties under the action of filler surface can develop from the interface into the depth by up to 9 μm. With carbon nanotubes or fullerenes, which possess a high interaction energy and huge (up to 1000 $m^2 g^{-1}$) specific surface, it would be expected that already at extremely low concentrations (<0.1 wt %) concentrations of fillers the entire volume of the matrix will turn into the boundary layer, and the matrix will acquire quite different properties.

Further quite an interesting result is that a considerable rise of the glass-transition temperature and compressive elastic modulus of the epoxy matrix filled with functionalized nanoparticles is attended with decrease of the heat effect of polymerization. Consequently, the improvement of the above properties of the matrix is associated with increasing density of the anchoring network rather than with enhancing chemical cross-linking. This result raises the problem of developing a modifier on the basis of functionalized carbon nanoparticles for complex improvement of performance characteristics of epoxy binders.

Actually, presently polymer composite materials pose high requirements to binders, including high glass-transition temperature and compressive elastic modulus, as well as a high tensile strength. These properties are quite difficult to combine in one material. For high glass-transition temperatures and compressive elastic moduli it is necessary to ensure a highly dense chemical cross-linking. However, beginning with a certain limit, further increase of cross-linking density leads to a sharp decrease of tensile deformation and strength. With binders modified with carbon nanoparticles, increased glass-transition temperatures and compressive elastic modulus are due to interaction of macromolecules with the filler surface. Therewith, the deformation characteristics of the matrix remain virtually unchanged.

The results of the basic research were used in the RIAM to develop concrete materials.

Introduction of about 0.05% of carbon nanoparticles, such as fullerenes, nanotubes, or astralenes, endows CPRs with enhanced mechanical and performance: The compression and share strengths increase by 20%, shock resistance by 45%, residual strength by a factor of 1.5, water and fuel resistance by a factor of 1.5–2, working temperature by 30%, and durability by a factor of 1.8 (see table). Simultaneously the material acquires special properties, such as electro- and thermoconductivity, X-ray and sound transparency, and lightning resistance.

The RIAM developed a lightning-resistant CRP coating comprising astralenes and fullerenes for MS-

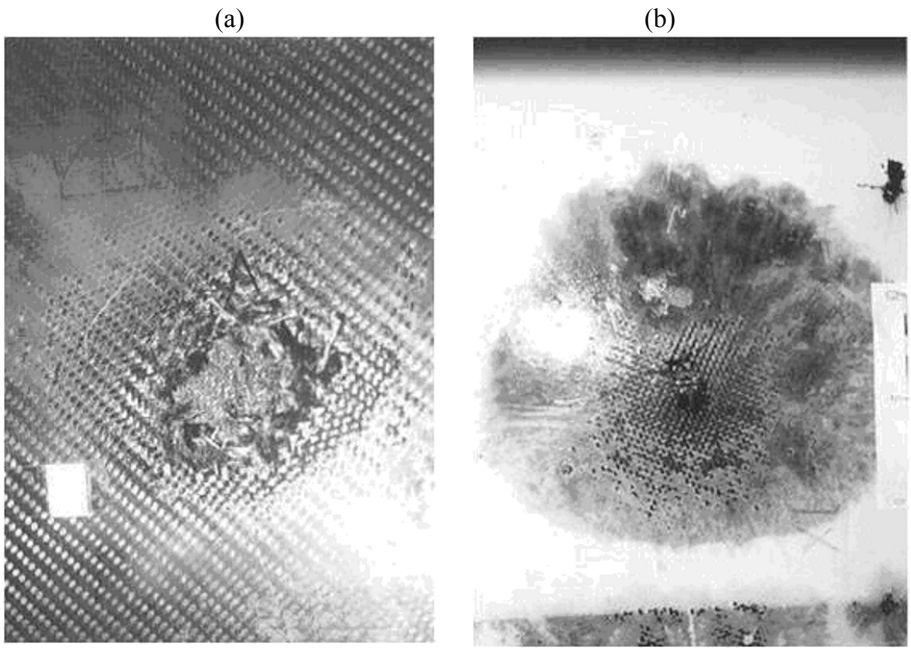

Fig. 5. Lightning resistance of carbon-reinforced plastics with protective coatings containing carbon nanoplastics: (a) with no coating and (b) with lightning-protective coating.

21, PAK-FA, and a series of helicopters, whose outer surface consists by more than 50% of CRP constructions [12]. Possessing increased high-tem-perature electro- and thermoconductivity, thermal degrada-tion temperature, and construction characteristics, this coating imparts safe damageability to CRP constructions on exposure to lightning strokes and decreases the weight of the these constructions by 300–500 g m^{-2} protected surface compared to traditional brass grid coatings.

The efficiency of the developed lightning protect-tion was tested on domestic and foreign fabrics (Fig. 5).

On exposure to lightning strokes aircraft airframe CRP parts without special protection undergo damages which pose threat to flight safety.

To bring the weight share of airframe CRP parts in an aircraft to 60%, thereby decreasing the aircraft weight by 15–20%, the following actions are required.

(1) To use lightning protection coatings to decrease damageability under lightning stroke (current parameters: I = 200 kA and Q = 20 C for zone B and I = 200 kA and Q = 200 C for zone A).

(2) To enhance high-temperature mechanical parameters by 15–40%.

(3) To enhance climate resistance and durability by a factor of 1.2–1.5.

(4) To enhance shock resistance by a factor of 1.2–1.5.

The described technology was used to produce a KMU-7eNM CRP on the basis of a UT-900-2.5 full-strength roving fabric and an epoxy binder modified with fullerenes and astralenes. Reference CRPs without modifiers were produces by a conventional technology. The compositions of CRPs were determined by X-ray analysis, and CRP samples were tested for the interlaminar shear t_{xz} (Methodical Recommendations 49-82) and longitudinal σ_s^0 and transversal σ_s^{90} compression strengths (State Standard 25602-80), therewith determining residual compression strength σ_c (Methodical Recommendations 65–82).

Compared with standard materials, nanostructured CRPs showed much better characteristics. The most essential gain was observed in the transversal compression strength (about 60%). Conductivity characteristics of carbon nanoparticles proved also to be of service. Therewith, the concentration percolation threshold of charge carriers (phonons and electrons) was found to be quite low (< 2%) due to a huge specific surface area of nanoparticles (for comparison, in the case of technical carbon particles such threshold

reaches 20%). The transversal thermoconductivity of CRPs is increased 1.5 times and their electroconductivity 3 times. The increased conductivity improves the ability of PCMs to dissipate the external force and thermal loading energy. Furthermore, the water absorption at modifier concentrations of about 0.003–0.02 wt % decreases two times.

The CRP samples were tested at the Semenov Institute of Chemical Physics, Russian Academy of Sciences, by double-cantilever beam delamination. The resulting data showed that the residual compression strength of the nanostructured CRP, which is indirectly related to fracture resistance and toughness, has increased. Direct evidence for the efficiency of carbon nanomaterials as microfracture stoppers was provided by the specific destruction energy G_{1c} which characterizes the fracture resistance of materials under normal stresses.

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