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FIBRE COMPOSITE MATERIALS

INFLUENCE OF CONDITIONS OF CATALYTIC GROWTH OF CARBON NANOSTRUCTURES ON MECHANICAL PROPERTIES OF MODIFIED CARBON FIBRES

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An investigation has been made of the process of catalytic growth of carbon nanostructures on the surface of carbon fibres (CF) by chemical vapor deposition (CVD) using a protective carbon coat based on α_2-fraction of coal-tar pitch. It is shown that the diminution of ultimate tensile strength of CF during the growth of the carbon nanostructures is associated with appearance defects on the fibre surface. It is found that the CF surface is filled uniformly by carbon nanostructures with preservation of the initial mechanical properties if the process is implemented for duration up to 30 min in the 700-800°C range using a mixture of benzene and cyclohexane.

Thanks to a combination of high stiffness and strength and low density, carbon fiber (CF) reinforced composites are widely used in high-technology industry and engineering, including in aviation, rocket engineering, and ship building. But use of carbon fibre reinforced plastics based on thermoreactive matrices in highly loaded structures is constrained in many cases by inadequate resistance to crack propagation, low shear strength, and possible foliation of the composite upon shock impact. The reason for this is often inadequate adhesion of the binders to the CF surface. Since precisely the strength of the fibre–polymer matrix interface determines the efficiency of stress transmission through the interface, the CF is often submitted to surface treatment.

Much attention is being focused lately on surface modification of fibres by carbon nanostructures (CNS), carbon nanotubes (CNT) [1-5], and carbon nanofibres (CNF) [6-7] alongside conventional surface treatment methods [8], such as oxidation by gaseous agents, liquid-phase oxidation, plasmochemical treatment, electrochemical etching, etc. Unlike the conventional surface treatment methods that lead to formation of functional groups on the CF surface, modification by CNS, CNT, and CNF leads to formation of highly developed fibre filler surface, i.e., the improvement in the mechanical properties of polymer composites (PC) occurs due to a marked increase in the interface area [9].

Furthermore, it is known that CNS, thanks to the peculiarities of the way the graphite plane lies, possess unique conductive properties. Because of this, a small quantity of filamentous carbon particles on the CF surface is enough to create a three-dimensional conducting grid. For instance, in the case of a hybrid composite based on epoxy matrix and carbon-reinforced cloth, the surface of which is coated 0.25 wt. % with CNT, the electrical conductivity was raised in the direction perpendicular to the reinforcement axis by 30% [10].

In spite of the positive aspects of surface modification of fiber filler by CNS, it is necessary to turn attention to an important problem that is common for most surface treatment methods. Almost all surface treatment methods, alongside

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augmentation of adhesion interaction, lead to formation on the CF surface of defects, which greatly affect the strength characteristics of the fiber and eventually the longitudinal strength characteristics of CF-based composites. In the case of surface modification by CNS using chemical vapor deposition (CVD) method, the catalytic growth of nanostructures may compete with the process of formation of carbides of transition metals with the involvement of the catalyst and the carbon from the CF surface, which gives rise to defects on this surface [11].

Methods are available for protecting CFs by producing on their surface a coat of amorphous silicon [12] or a coat based on carbon obtained by pyrolysis of phenol-formaldehyde resin [13]. The authors of the respective works, however, do not report data on the strength of carbon fibres after such treatment and of composites based on them.

We made an attempt to produce on the fibre surface a protective coat based on carbon from highly condensed fraction of coal-tar pitch. Particles of a transition metal catalyst were deposited on the CF surface so treated by reducing the salt in hydrogen atmosphere. Thereafter, carbon nanostructures were synthesized by the method of chemical vapor deposition of a benzene–cyclohexane mixture at temperatures ranging from 600 to 900 °C.

The goal of this work was to ascertain the influence of the parameters of the catalytic process of CNS growth (process time and temperature) on the strength characteristics of the CF with the deposited protective coat and to determine the optimum modification conditions.

In this work, we used carbon fibre of the trademark UKN-M based on polyacrylonitrile (PAN) precursor (monofibre diameter 7.5±0.5 μm). Chemically pure $Ni(NO_3)_2 \cdot 6H_2O$ was used as the catalyst precursor and medium-temperature coal-tar pitch produced by JSC Mittal Steel in Temirtau (Kazakhstan), the properties of which are cited below, was used as the base for formation of the protective coat:

Softening point, °C	90
Proportion of matters insoluble in toluene, wt. %	31
Proportion of matters insoluble in quinoline, wt. %	6
Ash content, %	0.1
Coke residue, %	57
Yield of volatiles, %	57

The CF surface modification process consisted of the following stages:

– removal of epoxy finish coat from the CF surface by washing the fibres in acetone;

– deposition of protective coat based on α_2-fraction of coal-tar pitch on CF surface;

– deposition of catalyst precursor by impregnating the fibres with 0.05 M nickel nitrate solution in acetone;

– decomposition of nickel nitrate to oxide at 400 °C, followed by reduction to the metal in a hydrogen stream for 15 min;

– synthesis of carbon structures by the method of vapor deposition in a stream of argon as carrier gas and azeotropic mixture of benzene and cyclohexane: flow rate 0.04 liter/min, treatment time 30 min, temperature 600-900 °C.

The solution of α_2-fraction was obtained by fractional separation of coal-tar pitch and its gradual dispersion by organic solvent in an ultrasonic bath (35 kHz) for 15 min. A 100 g aliquot of the pitch was first treated in 300 ml of hexane for removing volatile components (γ-fraction) and then the obtained residue was treated in 300 ml of toluene for separation of the β-fraction. The insoluble α_1-fraction was separated by subsequent treatment of the dry residue of the α-fraction of the pitch in 1-methyl-2-pyrrolidine.

The ultimate tensile strength of the original and modified CFs was determined on a Tinius Olsen H5KS universal tension testing machine in conformity with ISO 11566:1996. The test specimens consisted of individual monofibres taken from a tow. A set of 20 specimens was used for each type of CF.

The study of CF surface was carried out using a Quanta 3D FEG scanning electron microscope (SEM). The accelerating voltage varied between 10 and 20 kV. The length of the working segment of fibre was 10 mm.

The thermal analysis was performed on a Netzsch STA 449C Jupiter synchronous thermoanalyzer. The specimens were studied in the 40-900 °C range in a current of air (50 ml/min) at the heating rate of 5 °C/min. The derived data were processed by Netzsch Proteus software.

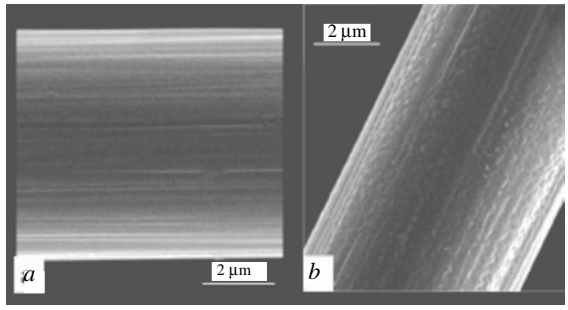

Fig. 1. SEM image of surface of original CF (*a*) and CF with a protective coat (*b*).

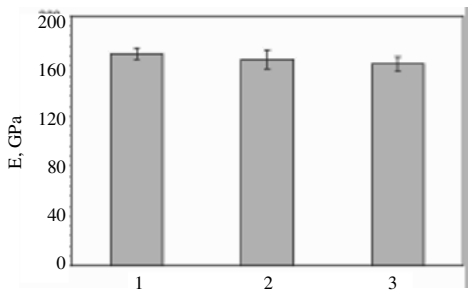

Fig. 2.

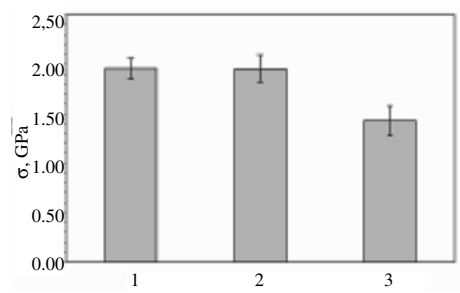

Fig. 3.

Fig. 2. Comparison of elasticity modulus of original CF (*1*), modified CF with a protective coat (*2*) and without a protective coat (*3*).

Fig. 3. Ultimate tensile strength of original CF (*1*) and modified CF with (*2*) and without (*3*) a protective coat.

The choice of the pitch binder for forming the protective coat on the CF surface was dictated by good adhesion in conjunction with high yield of coke residue [14]. The solution of α_2-fraction of the pitch, on the one hand, contains polycyclic aromatic structures with a higher degree of condensation than γ- and β-fractions of the pitch, i.e., the process of pyrolysis of α_2-fraction will be characterized by a lower yield of volatile compounds. On the other hand, use of soluble α_2-fraction precludes the influence of coke particles (carboids) contained in the original pitch. It can be suggested that in this approach a uniform coat will be formed on the CF surface, which will provide effective protection from the negative influence of the catalyst particles. The morphology of the surface of the original fibre and the CF having a protective coat based on the α_2-fraction of the pitch is compared in Fig. 1. As will be seen (Fig. 1*b*), after the treatment, a continuous uniform protective coat is formed on the CF surface.

As a result of mechanical tests of the original CF and the CF modified by CNS with and without a coat, it was established that the elasticity modulus of all specimens remained unchanged within the error limits (Fig. 2). From this it can be suggested that the process of catalytic growth of CNS on the CF surface does not materially affect the internal structure of the fibre.

At the same time, it was observed that the ultimate tensile strength of the modified fibre without a protective coat fell by 30% relative to the strength of the original CF. In this case, the ultimate tensile strength of the fibre with a protective coat remained virtually unchanged (Fig. 3). Thus, the strength loss of the modified CF can be attributed to formation of surface defects on account of interaction between the catalyst particles and the surface coat of the fibres. For CF with a protective coat, the following mechanism of functioning of the protective coat can be suggested: the fibre surface is covered by a continuous film of condensed polyaromatic hydrocarbons of the α_2-fraction of the pitch, on the surface of which lie fine catalyst particles, the film of polyaromatic hydrocarbons blocks interaction between the catalyst particles and the carbon of the surface layer of the CF, as a result of which occurs the process of interaction of the catalyst with the carbon from the gas phase with prevalence of growth of CNS by the apical mechanism.

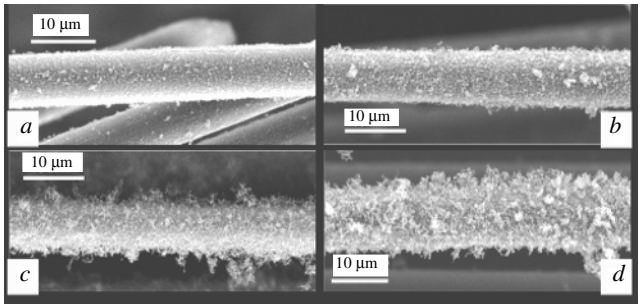

Fig. 4. SEM images of modified CF for synthesis temperature of 800 °C and various synthesis durations (in min): *a* – 5, *b* – 10, *c* – 20, and *d* – 30.

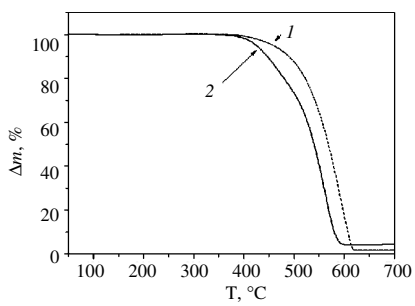

Fig. 5.

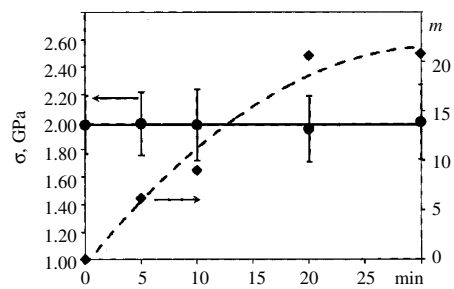

Fig. 6.

Fig. 5. TGA curves for original CF (*1*) and CF with modified surface (*2*) at 800 °C for 20 min.

Fig. 6. Ultimate tensile strength (left Y-axis) and relative weight change (right Y-axis) of modified fibres versus synthesis time.

It is well known that the growth of CNS on the surface of a particle of a 3d metal catalyst is accompanied by decomposition or disproportionation of the gaseous carbon-containing compound on the active surface of the catalyst, its decomposition with formation of a chemisorbed carbon-containing complex with the metal, dissolution of the carbon in the metal, its diffusion through the metal, and formation of graphitic carbon [15]. It is also believed that the growth of CNS ceases if the surface of the catalyst particle is fully covered by a carbon layer. Further pyrolysis of the hydrocarbon causes deposition of a disordered carbon shell.

Study of the influence of the duration of CF surface modification at 800 °C showed that the growth of CNS occurs in the first 20 min (Fig. 4) and further prolongation of the process does not lead to appreciable increase in volume of CNS formed on the fibre surface.

For a quantitative determination of the proportion of CNS, thermogravimetric analysis (TGA) of the obtained specimens was performed. Modification of fibres causes a change in the behavior of the TGA curve of oxidation of the specimens. The weight loss curve of the original carbon fibre shows a single stage of weight loss, but the GTA curves for the treated specimens show two stages (Fig. 5).

The weight loss in the first stage can be used to determine the quantity of the carbon structure formed. In this particular case, the determination does not provide accurate values of the weight of the new phase because the weight loss effects are quite strongly overlapped, but shows a general trend toward increase or decrease of the quantity of the structure.

In Fig. 6, the weight loss in the first stage is plotted against the specimen treatment time. It can be seen that for specimens treated for less than 20 min, the proportion of CNS rises smoothly roughly to 20 wt. %, and further prolongation of treatment barely augments the proportion of CNS. In this regard, the ultimate tensile strength of the obtained fibres does not depend on the modification time.

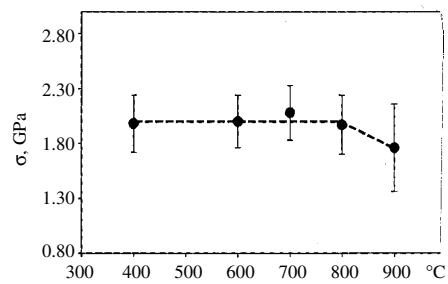

Fig. 7. Ultimate tensile strength of modified fibres versus synthesis temperature.

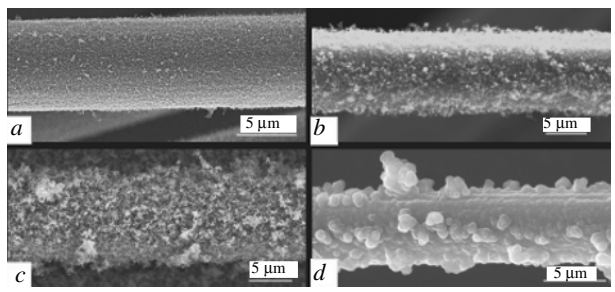

Fig. 8. SEM of CF modified for 30 min at various temperatures (°C): *a* – 600, *b* – 700, *c* – 800, *d* – 900.

It is interesting to note that the protective coat does not fulfill its function in the 800-900 °C range. The ultimate tensile strength diminished roughly by 16% when the process was executed at 900 °C (Fig. 7), and vapor-phase deposition in the 600-800 °C range had no effect on the strength characteristics of the modified CFs.

The morphological characteristics of the modified CFs (Fig. 8) indicate that filamentous CNS and mixture of CNT and CNF are formed at temperatures up to 800 °C when a mixture of benzene and cyclohexane is used as the source of carbon. At 900 °C the CF surface is covered by an uneven coat of spherical submicroscopic particles. As evident from Fig. 8*d*, the metallic catalyst particles are covered by carbon shell. Apparently, elevation of vapor-phase deposition temperature above 800 °C causes premature poisoning of the CNS growth catalyst due to condensation of gaseous benzene and cyclohexane and subsequent deposition of pyrolytic carbon on the passive surface. It can be suggested that the strength of the CF diminishes at 900 °C because the catalyst particles react essentially with the carbon of the protective coat and later with the fibre surface, forming defects.

Another characteristic of CF modification is observed at 600 °C (Fig. 8*a*), at which a smaller quantity of CNS is produced compared to the CVD temperature range 700-800 °C. The reason for this probably is inadequate activity of the catalyst taking part in CNS formation. On the contrary, at 700-800 °C filamentous CNS with an average size of 70 nm fairly densely cover the CF surface. Thus, it can be concluded that CNS grow vigorously in the 700-800 °C range.

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