Modern treatment technologies of carbon fibre for ensuring the high strength carbon fibre reinforced plastic production

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Abstract. The investigation results of physical and mechanical properties of carbon fibre and carbon fibre-reinforced plastics are presented. It is shown that the number of paramagnetic centres, which were determined by electron paramagnetic resonance method, were used as an index to define the chemical activity of the carbon fibre relative to the matrix. The number of paramagnetic centres in the carbon fibres and CFRP were analysed. The interlayers shear strength of CFRP based on epoxy resin was investigated.

Applications of carbon fibre-reinforced plastics structural products for various purposes are expanding every year due to their unique complex of strength and thermal properties [1, 2] and as well as the development of new moulding technologies [3-5].

It was shown in the paper [3] that oxygen-containing functional groups with the different chemical composition and stability are present on the surface of carbon fibres, which largely determine the magnitude of the adhesive interaction of the fibre-matrix pair.

Some of the functional groups are in ionized form, forming carboxylate ions. Depending on storage conditions, they are capable of hydrolysing according to various schemes, which leads to an increase (or decrease) in the reactivity of carbon fibres. It is quite difficult to quantitatively determine the concentration of oxygen-containing functional groups on the surface of carbon fibres, but it is possible to estimate experimentally the number of paramagnetic centres on the fibre and in CFRP, which also characterize their chemical activity.

The aim of this paper is to determine the number of paramagnetic centres on the fibre and in CFRP, depending on the carbon fibre processing technology.

1 Objects and methods

The objects of the research were domestic carbon fibres in the form of bundles and tape (VMN-4, LU-3, ELUR) and fibres with oxidized surface (LU-P и ELUR-P). Also, imported carbon fibres brands T-300, T-700, AS-4 and HTS-45 were used as research objects.

In the production of carbon fibre-reinforced plastics, an epoxy binder ENPB brand and vacuum infusion technology were used [6].

Interlayer shear strength (σ_{ab}) of six samples with cross section $6 \times 6 \text{ mm}^2$ and length of 41 mm on the working base 30 mm was determined by short beam method according to ASTM D 2344.

The maxing rate of the active gripper of the testing machine was 0.5 mm/min. Investigations of electron paramagnetic resonance (EPR) were carried out by the radio spectrometer RE-1301. To determine the intensity of the EPR signal, the area under the absorption curve, which is proportional to the amount of PMC in the sample, was measured. Their absolute number (N_I) was estimated by comparing the spectrum intensity of the investigated sample and standard, which used diphenylpicrylhydrazyl.

The treatment of carbon fibres was carried out by two methods: thermal oxidation and plasma treatment. A modified Bulat-6 machine unit (at the E8 department of Bauman MSTU) was used for plasma processing. The ion source "AI-200" with an ion beam diameter of 200 mm was designed in Bulat machine, which allows to treat an entire spraying surface area. The surface of LU-P carbon tape was only treated by modified Bulat-6 machine.

2 Results and discussion

In this paper assume that the functions of paramagnetic centres have defects in isotropic matrix of carbon and graphite bundles and tapes in the fibrils, and localization of the electron density which occurred due to the formation of oxygen-containing functional groups. Thus, the activity of the carbon fibre relative to the polymer matrix can be characterized both by the number of paramagnetic centres and by the number of oxygen-containing functional groups. In this study, only the number of paramagnetic centres was measured experimentally. The results of the experimental

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determination of the concentration of paramagnetic centres on the carbon fibre surface and in CFRP are given in Table. 1. The main disadvantage of this method is the large scatter of data, which is about 25%, which requires a large number of repeated measurements.

As follows from the obtained data, the number of paramagnetic centres in CFRP produced from the carbon fibre brands VMN-4 and LU-3, is almost twice higher than the same fibres in the initial state. At the same time, the number of paramagnetic centres in CFRP produced from the fibres brands ELUR, ELUR-P and LU-P is, on the contrary, significantly lower than the same fibres in the initial state.

Table1. The determining results of the number of paramagnetic centres

Carbon Fibre Brands	The number of paramagnetic centres, 10^{-17} , spin/cm ³	
	Fibre, N_f	CFRP, N_{PTP}
VMN-4	1.4	2.7
LU-3	1.3	2.6
ELUR	3.4	1.7
ELUR-P	13.5	0.7
LU-P	7.9	1.1
T-300	3.5	3.7
T-700	7.1	1.2
AS-4	3.3	3.1
HTS-45	3.3	2.6

To explain this paradoxical phenomenon, the study assumes that paramagnetic centres are present on any carbon fibres, but they can be located on the surface (in this case, they are active and interact with the matrix), or they are located in the core of the fibre (in this case, they are not active and do not enter into interaction with the matrix). During the CFPR production, if there is interaction between the carbon fibre and epoxy matrix, then in this case must be inequality: $N_f > N_{KPK}$.

Thus, from the presented data in Table. 1, the fibres brands LU-3, VMN-4, T-300 are inert (they do not interact with the epoxy matrix), and the fibres Elur-P, LU-P, T-700, on the contrary, are active (there is a strong inter-component interaction between the fibre and the matrix).

Table 2 shows the values of the interlayers shear strength obtained from the carbon fibres, for which the number of paramagnetic centres was previously determined.

Table 2. Interlayer shear strength of CFRP

Carbon Fibre brands	Interlayer shear strength of CFRP, MPa
VMN-4	22
LU-3	31
ELUR	43
ELUR-P	78
LU-P	64
T-300	30
T-700	64
AS-4	46
HTS-45	34

All CFRP products were manufactured by using the same technology and same epoxy binder under the same conditions.

In this paper assumes that the more the number of paramagnetic centres on a carbon fibre and the less of them remain in CFRP, and the higher the adhesion interaction. The presented results confirmed this assumption, since the maximum value of the interlayer shear strength obtained by using carbon fibre brand Elur-P, which is characterized by the greatest difference between the number of paramagnetic centres in the fibre and carbon fibre reinforced plastics CFRP ($13.5 - 0.7 = 12.8 \times 10^{-17}$, spin / cm³)

In this study, a number of chemical activities of oxygen-containing functional groups located on the surface of a carbon fibre are compiled:

As presented in the paper [3], the most chemically active functional groups are formed mainly on the defects of the quasi-amorphous matrix of carbon in areas saturated with nano-and micro-pores. To change the content of oxygen-containing functional groups on the surface of carbon fibre is possible as a result of oxidative treatment of carbon fibre. Oxidation of selected fibres was conducted under isothermal conditions in the temperature range 550-850°C. In addition to the oxidation method, the plasma treatment was also used by modified Bulat-6 machine. The following processing modes were used: voltage 300 V, discharge current 113 mA, working gas - argon.

The choice of optimal carbon fibre surface processing mode as a result of plasma treatment was carried out by the criterion of the CFRP interlayer shear strength. However, as a result of the conducted studies, it was not possible to find a treatment mode, in which it would be possible to increase the strength of CFRP. On the contrary, with this treatment, there were large mass losses and a significant decrease in

the strengths of carbon fibre and CFRP. Probably, there was a drop in strength due to a significant damage of the structure of the carbon fibre. Thus, the conducted research did not allow to determine the optimal modes. However, work is underway in this direction, because this direction is very potential, since it is a simple and very effective way of changing the structure and chemical activity of carbon fibre.

Along with the use of plasma treatment, the study also carried out the oxidation on the surface of the carbon fibre by standard methods. The choice of the optimum mode of thermal oxidation was carried out according to the criteria of the highest strength and minimum mass loss. Mass loss was determined by thermo gravimetric analysis. The studies found that the mass loss at temperatures up to 650 °C does not exceed 1.5%. When the temperature is raised to 700 °C, it was a little over 4%, and the temperature increases to 750 °C, mass loss also increases to 7.5%.

Thus, as the studied results have established that the optimum oxidation temperature is 650 °C, the oxidation time at a given temperature must not exceed 10 min. Increasing in the duration of oxidation or temperature, there is an increase in the number of paramagnetic centres on the surface of the carbon fibre, but at the same time occur significant drop in the mass of the carbon fibre, which leads to a loss of its strength.

For the investigated carbon fibres, the number of paramagnetic centres on the fibre and in the CFRP were determined before and after oxidation. As a result of experimental studies, there was increase in the number of paramagnetic centres during the oxidation. For example, for LU-P fibre the number of paramagnetic centres increased 2.6 times. In CFRP, on the contrary, after oxidation, it decreased 1.4 times. Similar results were obtained for other carbon fibres brands.

Raman method allows a quantifying ratio of amorphous (active) and crystallite (passive) phases of the surface of carbon fiber. We carried out measurements at a diameter of the laser beam of 1 µm, laser wavelength of 473 nm, spectral resolution of 2 cm⁻¹, delay time of 10 seconds. Area under spectrum curve (ID) with average frequency D characterized a scattering intensity of the radiation on ordering graphite-like fragments of surface of carbon fiber. Spectrum area (IG) at average frequency G characterized the intensity on unordered amorphous fragments. We calculated fraction of amorphous phase using equation:

$$f_s = \frac{I_G}{I_G + I_D}$$

Table 3 shows the values of the quantity of amorphous and crystallite phase of the surface of carbon fiber.

Table 3. Effect of oxidation on ratio of surface amorphous phase of carbon fiber

Brands of carbon fibers	Ratio of phase	
	Amorphous	Crystallite
LU before oxidation	0.38	0.62
LU after oxidation	0.53	0.47
ELUR before oxidation	0.43	0.57
ELUR after oxidation	0.65	0.35
AS-4 before oxidation	0.49	0.51
AS-4 after oxidation	0.6	0.4

Results of experimental determination of ratio of amorphous phase f_s .. for investigated carbon fibers brands before and after their oxidation and CFRP strength at interlaminar shear are shown in Table 1. From the experimental data it follows that increase in 1.2 – 1.5 times of relative content of amorphous phase occurs at the oxidation. Also, there is a strength enhancement in 1.5 – 2.1 times of CFRPs at interlaminar shear at oxidation.

We found that a correlation between the values of strength at interlaminar shear tab and a ratio of amorphous phase f_s is linear after analyzing data from Table 1. Thus the unique deterministic bond is presented and changing of amorphous carbon content on the surface of fiber increases CFRP strength at interlaminar shear.

Specific concentration of active centers per unit surface of carbon fiber is constant at oxidation. This allows us to assume that crystal-chemical structure of carbon fibers is of the same type, although they are made by different manufacturers from different raw materials using different technologies.

3 Conclusions

As a result of the conducted studies, the difference between the amount of paramagnetic centres on the surface of CFRP and in the initial fibre can be used as a quantitative characteristic of the inter-component interaction between the fibre and the epoxy matrix. It was shown that among all of the investigated carbon fibres brands, the most active fibre brands were Elur-P, LU-P, T-700.

The influence of the carbon fibres heat treatment modes on the magnitude of their mass loss and on the interlayer shear strength of CFRP was investigated. It was shown that the optimum value of the oxidation temperature was 650 °C for 10 min duration. By using the oxidation method, it was possible to increase the number of paramagnetic centres on the carbon fibre.

Effect of thermo-oxidation treatment of phase content of surface of carbon fibers was investigated using Raman spectroscopy. We showed that their adhesion to epoxy matrix is defined only by relative content of amorphous part of fiber surface.

References

1. G.V. Malysheva, Y.Y. Shimina, Fibre Chemistry, **46 (4)**, 237-240 (2014)
2. N.I. Baurova, Polymer Science - Series D, **2 (1)**, 54-57, (2009)
3. V.A. Nelyub, Fibre Chemistry, **47 (1)**, 40-42 (2015)
4. G.V. Malysheva, E.S. Akhmetova, Y.Y. Shimina, Polymer Science - Series D, **8 (1)**, 17-21 (2015)
5. V.A. Nelyub, A.S. Borodulin, L.P. Kobets, G.V. Malysheva, Polymer Science - Series D, **9 (3)**, 322-325 (2016)
6. N.I. Baurova, A.Y. Sergeev, Polymer Science - Series D, **7 (2)**, 140-144 (2014)