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Characterization of the Epoxy Resin and Carbon Fiber Reinforced Plastic Stress-Strain State by Modified Carbon Nanotubes

A.M. Yermakhanova[1,2*] and M.B. Ismailov[1,2]

[1]"National Centre for space research and technology" JSC, Almaty, Kazakhstan
[2]"Kazakh National Research Technical University named after K.I. Satpayev" Almaty, Kazakhstan

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Abstract

The epoxy resin in the form of Etal Inject-T compound, Sigratex KDK carbon fabric, Taunit-M carbon nanotubes conditionally named as CNT-1, as well as functionalized (modified) variety of them by grafting to the surface of new chemical groups: carboxylated – CNT-2, carboxyl-hydroxylated – CNT-3, amidated – CNT-4 were used in the work. The experiments were performed on the compression strength and bending strength of the samples. The injection of CNT-1 into epoxy resin or carbon fiber reinforced plastic did not produce the hardening. The injection of 0.05% of CNT-2 into the epoxy resin had the following effect: there is no influence in the area of quasielastic strains, the hardening was up to 25% in the areas of plastic and elastic-plastic strain. The injection of 0.15% of functionalized carbon nanotubes into the carbon fiber reinforced plastic produced the hardening for compression with CNT-2 – 6%, CNT-3 – 12%, CNT-4 – 17%, for bending – CNT-2 – 44%, CNT-3 – 59%, CNT-4 – 132%. It is established that with an increase in the strain rate of epoxy resin from 1 to 5 mm/min the areas of plastic and elastic-plastic strain gradually are reduced, there is only quasielastic strain with brittle fracture at 20 mm/min, this value can be accepted as its strength characteristic. With an increase in the strain rate of carbon fiber reinforced plastic from 1 to 20 mm/min the compression strength gradually increases from 398 MPa to 425 MPa, and then stabilizes.

1. Introduction

Epoxy resin and its carbon fiber reinforced plastic derivative are widely used as the structural materials, where their target quality is strength. In practice, the strength of epoxy resin and carbon fiber reinforced plastic is characterized by the tensile strength σ_s, modulus of elasticity E, total fracture strain ε_t [1, 2]. Figure 1 shows the stress-strain diagrams specific to epoxy resin and carbon fiber reinforced plastic. As can be seen from this figure, the curve for the epoxy resin has a complex character on which it is customary to allocate an area of quasielastic (almost elastic, where there is a small plastic component) strain (I) completed by the tensile yield σ_y. This is followed by a flowing and horizontal section (II) of plastic strain area which smoothly passes to the ascending section of the hardening area (III) up to the tensile strength σ_s with destruction of the sample [3, 4].

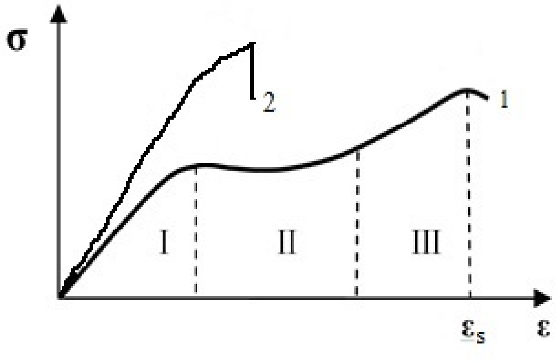

Fig. 1. Common dependencies of stress-strain state of epoxy resin (1) and carbon fiber reinforced plastic (2) under uniaxial compression.

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*Corresponding author. E-mail: a.yermakhanova@mail.ru

The nature of the curve for carbon fiber reinforced plastic indicates the strain close to elastic up to its destruction by the loss mechanism of adhesion bond of epoxy resin to carbon fibers and formation of cracks [5].

One of the methods of epoxy resin and carbon fiber reinforced plastic hardening is their modification by injecting the carbon nanotubes [6]. The carbon nanotubes can be introduced both as initial and functionalized one by additional processing in order to activate them. There are three main methods of carbon nanotubes functionalization, implying the chemical inoculation to nanotubes of functional groups [7]. The first method is carried out by processing the carbon nanotubes with nitric acid, as a result of which their surfaces are activated by -COOH graft carboxylic group. Such carbon tubes are called “carboxylated”. The second type of activation is the treatment of carbon nanotubes with a mixture of H_2SO_4 + HNO_3 acids, as a result, the surfaces of carbon nanotubes are covered by grafted carboxyl -COOH, carbonyl -CO and hydroxyl groups -OH [8, 9]. Such carbon nanotubes can be conditionally called carboxyl-hydroxylated. The amidated carbon nanotubes are the third type of functionalized ones. The functionalization process consists in the secondary treatment of carboxylated carbon nanotubes with ammonia, during which the surfaces are coated with NH_2 groups. [10]. For convenience, the listed types of carbon nanotubes are identified as: primary – CNT-1, carboxylated – CNT-2, carboxyl-hydroxylated – CNT-3, amidated – CNT-4.

The literature data of the carbon nanotubes influence on the tensile strength σ_s of epoxy resin and carbon fiber reinforced plastic is shown in Table 1.

Table 1

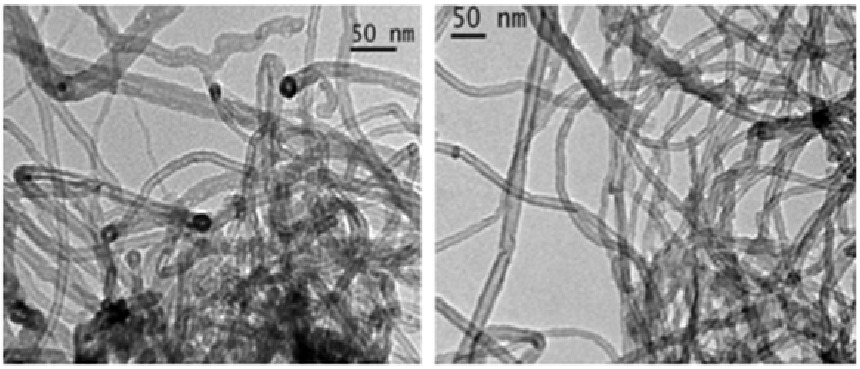
The influence of carbon nanotubes (CNTs) on tensile strength of epoxy resin (ER) and carbon fiber reinforced plastic (CFRP) on compression

#	Chemical composition of composite			σ_s, MPa	Ref.
	ER	CFRP	CNT		
1	100	-	-	126.5	[8]
2	99.95		0.05 (CNT-1)	111.9	
3	99.95	-	0.05 (CNT-3)	148.4	[11]
4	-	100	-	370	
	-	99.95	0.05 (CNT-2)	487	
	-	99.8	0.2 (CNT-2)	514	
	-	99.0	1 (CNT-2)	681	

As shown in Table 1, it follows that the injection of 0.05% of the primary CNT-1 in the epoxy resin resulted in a reduction of the compressive strength by 13%, in the case of 0.05% of the functionalized CNT-3, an increase of strength by 17% occurred. The positive effect of hardening of epoxy resin and carbon fiber reinforced plastic was obtained by modification with the injection of CNT-2, CNT-3. From the literature data [8, 11–13] it follows that the effect of hardening of epoxy resin and carbon fiber reinforced plastic can be achieved by their modification by functionalized carbon nanotubes. Comparative data on the reinforcing efficiency of carbon nanotubes of various types of functionalization could not be found.

The images of primary CNT-1 and modified CNT-2 are shown in Fig. 2, which shows that the modification does not change the geometrical characteristics of the material at all [12].

Our experience shows that the strength characteristics of carbon fiber reinforced plastic are strongly dependent on many difficult-to-measure parameters during the manufacture procedures of the material. These include the use of epoxy resin and carbon matrix of the same brand of different



primary functionalized

Fig. 2. TEM images of CNT of Taunit-M brand [12].

delivery lots, the slightest deviations from the adopted regime of input and dispergating of carbon nanotubes in the modification of epoxy resin, as well as other factors. Since there is no uniform technological standard in the manufacture of carbon fiber reinforced plastic, the material from different authors is obtained with some different strength characteristics due to the raw material and technological differences. This circumstance makes it difficult to generalize. Another factor contributing to the dispersion of strength characteristics is the strain rate. It turned out that there is a strong dependence of strength on strain rate for epoxy resin, as for many polymers [14], which inevitably have a direct impact on the strength characteristics of carbon fiber reinforced plastic. Meanwhile, the strain rates are usually not given in the works on measuring the strength of epoxy resin and carbon fiber reinforced plastic [14].

The aim of work is to experimental study the influence of CNT-1 and CNT-2, as well as the strain rate on the stress-strain state and strength of epoxy resin, study of the comparative effect of CNT-1, CNT-2, CNT-3, CNT-4 and strain rate on the stress-strain state and strength of carbon fiber reinforced plastic.

2. Production of samples and their test methods

2.1. Production of epoxy resin samples

For the production of epoxy resin and carbon fiber reinforced plastic samples Etal Inject-T epoxy compound was used consisting of components: A – epoxy resin, B – hardener in a mass ratio of 100:49.9. The mixture of components was subjected to vacuuming before using. CNT-1 and CNT-2 were used (“NanoTechCenter” LLC, Tambov) as modifying additives, where CNT-1 is synthetically produced by CVD method in a reactor with heated substrate of propane-butane mixture on the catalyst Co/Mo/Mg/Al. The nanotubes are composed of 6–10 cylindrical graphene layers. The mass content of mineral impurities is not more than 4%. The geometric characteristics of CNT-1 are given in Table 2 [12].

The samples with CNT-1 and CNT-2 were injected into the component A of the compound at a temperature of 40 °C and dispersed using an ultrasonic mixer ST-400A at a working frequency of 65 kHz for 1 h, then the component B of the compound (hardener) was added and mechanically stirred to a homogeneous state.

Table 2
General characteristics of CNT-1 [12]

Characteristics	
Outer diameter, nm	8–15
Inside diameter, nm	4–8
Length, mkm	2 and more
Specific surface, m^2/g	120–130 and more
Pour density, g/sm^3	0.03–0.05

To obtain the samples of the cured epoxy resin, the liquid compound with carbon nanotubes or without them was used, poured and hardened in a cylindrical shape with diameter of 30 mm and height of 38 mm. The hardening process was carried out in the mode of thermal treatment within 5 h and temperature range: 1 h – 100 °C, 3 h – 150 °C, and 1 h – 180 °C.

Table 3 shows the characteristics of 4 experimental samples of epoxy resin.

Table 3
The characteristics of the manufactured experimental samples of ER

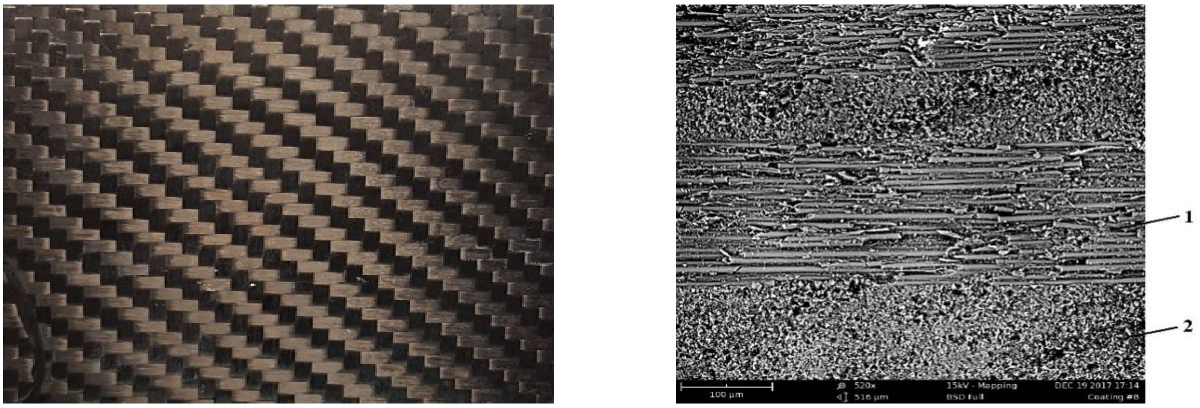
Sample №	Chemical composition (mass.), %		
	Epoxy compound	CNT-1	CNT-2
1	100	-	-
2	99.95	0.5	-
3	99.95	-	0.05
4	99.80	-	0.20

2.2. Production of carbon fiber reinforced plastic samples

Etal Inject-T compound has been used during experimental works, carbon fabric of twill weaving of Sigratex KDK 8043/120 brand, carbon nanotubes CNT-1, CNT-2, CNT-3, CNT-4. The samples of carbon fiber reinforced plastic were produced in the form of plates by laying out 17 layers of carbon fabric by method [15]. The molded sample was placed in a vacuum bag for further vacuum blowing and placed into a drying oven where the hardening occurred at temperature regimes similar for epoxy resin.

Thirteen samples of carbon fiber reinforced plastic were manufactured, the chemical composition of which is shown in Table 4.

General view of the obtained plates is given in Fig. 3a, the image of their microstructure of the lateral section obtained with the Phenom ProX scanning electron microscope is shown in Fig. 3b. Figure 3a shows the longitudinal and transverse layers of filaments of fabric, as well as thin layers of epoxy resin gluing filaments.



(a) – CFRP sample (b) – lateral surface image (x520)

Fig. 3. CFRP sample and their microstructure: 1 –longitudinal carbon fibers; 2 -transverse carbon fibers.

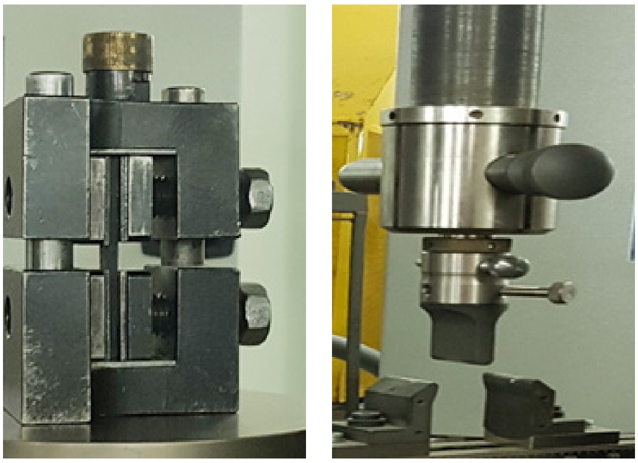
Table 4
The characteristics of the manufactured experimental samples of CFRP

№	Chemical composition, %				
	Compound	CNT-1	CNT-2	CNT-3	CNT-4
1	100	-	-		
2	99.95	0.05			
3	99.90	0.1			
4	99.85	0.15			
5	99.95		0.05		
6	99.90		0.1		
7	99.85		0.15		
8	99.95			0.05	
9	99.90			0.1	
10	99.85			0.15	
11	99.95				0.05
12	99.90				0.1
13	99.85				0.15

2.3. Methods of strength tests

Samples of cured epoxy resin have been tested for compression using Shimadzu AG-100 kNX electromechanical testing machine until the final force 100 kN was reached at strain rates: 1 mm/min, 2 mm/min, 5 mm/min, 20 mm/min.

The measurement of the mechanical strength of carbon fiber reinforced plastic plates with carbon nanotubes was carried out for compression using the tool in Fig. 4a, for three-point bending – the tool in Fig. 4b according to ASTM 6641/D6641 and GOST 25.604-82, respectively, at a strain rate of 10 mm/min on a mechanical testing machine Zwick/Roell Z050, as well as at different strain rates: 1 mm/min, 5 mm/min, 10 mm/min, 20 mm/min, 30 mm/min.



a – for compression b – for bending

Fig. 4. Tooling for CFRP plates strength test according to ASTM 6641/D6641 (compression) and GOST 25.604-82 (on a three-point bending).

3. Results and discussion

The results of mechanical tests of epoxy resin are shown in Figs. 5 and 6 at a strain rate of 1 mm/min, the chemical composition of which is shown in Table 3. Figure 6 data show that CNT-1 practically does not affect the strength of epoxy resin. This result is qualitatively confirmed by the data in Table 1.

The course of the curves σ-ε in Fig. 5 shows that the influence of CNT-1 on the strength properties of the samples is weakly expressed in all areas of strains, as evidenced by the data in Table 1.

The influence of modified carbon nanotubes on the example of CNT-2 with different content is shown in Fig. 6 and Table 5.

Figure 6 shows that their real influence is in the areas of plastic and elastic-plastic strain. It is seen

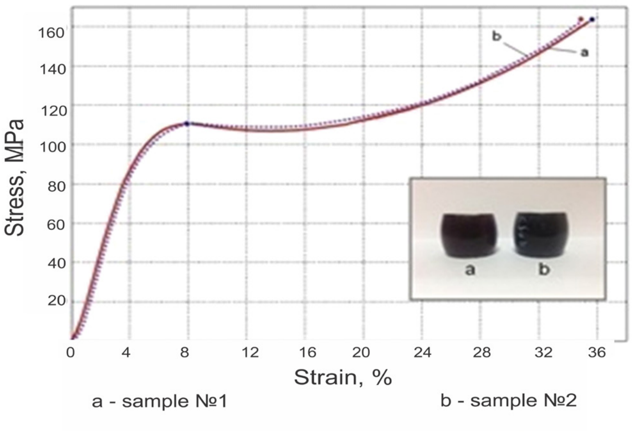


Fig. 5. The influence of CNT-1 on the stress-strain state of ER.

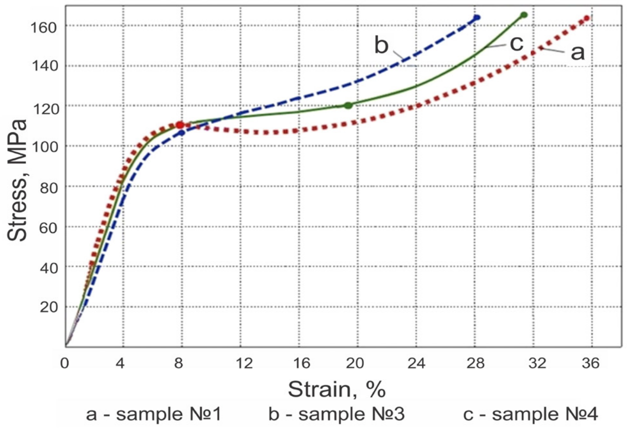


Fig. 6. The influence of CNT-2 on the stress-strain state of ER.

Table 5
The rate of strength growth of experimental samples of ER from the content of CNT-2

Sample strain degree, %	Strength growth of ER relative to sample № 1, %	
	Sample # 3 (0.05% of CNT)	Sample # 4 (0.2% of CNT)
12	9	4
16	13	8
20	17	9
24	21	8
28	25	12

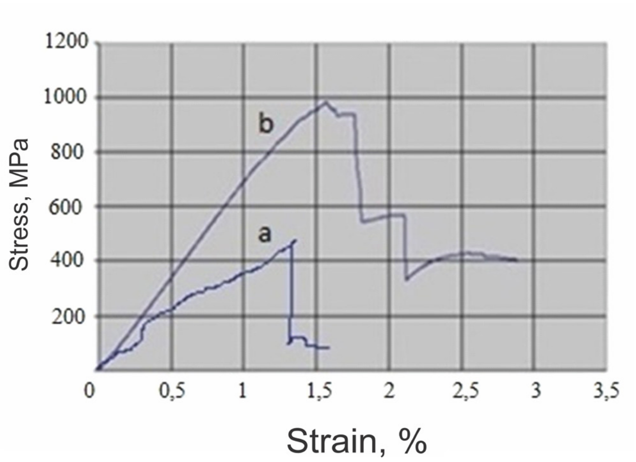


Fig. 7. Common dependencies of CFRP stress-strain state under compression (a) and bending (b) with uniaxial compression.

that CNTs-2 reduce the plastic strains. It is considered that the introduction of functionalized carbon nanotubes into epoxy resin leads to additional cross-linking of molecular chains [16, 17], then the obtained regularities become understandable. The theory says that there is no sliding of molecular chains relative to each other in the area of elastic strains and their cross-linking with the introduction of carbon nanotubes should not lead to hardening of the material. In the areas of plastic and elastic-plastic strains, the additional chain cross-linking will slow down the mutual sliding of molecular chains which leads to hardening of the material.

Another interesting effect is the existence of a critical content of CNT-2 giving the maximum hardening of the epoxy resin. The data of table 5 show that when exceeding the optimal injection of modifier CNT-2 in epoxy resin, its hardening influence drops sharply. The literature data given in the works illustrate that this effect is stable [18, 19]. In explanation of this effect there is a version that the injection of carbon nanotubes into epoxy resin hardens the material as long as the carbon nanotubes will not block the active sites ready for cross-linking on the molecular chains, and the excess of carbon nanotubes above the critical content will be simple ballast. However, this version does not explain why a small amount of ballast, in our case 0.2%, leads to a significant drop in the effectiveness of the modification. In our view, this effect requires further study.

The strength characteristics of carbon fiber reinforced plastic samples shown in table 4 were carried out by compression and three-point bending tests. Figure 7 shows common curves of dependence of stress-strain state of carbon fiber reinforced plastic.

The Fig. 7 shows, the course of the curves of the carbon fiber reinforced plastic stress-strain state under compression and bending are qualitatively similar, while the elastic strain goes up to the destruction of the samples. Figures 8 and 9 show the dependency of the carbon fiber reinforced plastic strength on the content of carbon nanotubes. It is seen from Fig. 8 that CNTs-1 do not affect the compressive strength, whereas with increasing in number of injection of functionalized CNT-2, CNT-3 and CNT-4 the gradual increase in strength is achieved. In the case of CNT-2 and CNT-3 the maximum hardening for compression was 6% and 12% respectively, the highest value of tensile strength of 17% was obtained with the introduction of CNT-4.

The results on the influence of carbon nanotubes on the carbon fiber reinforced plastic bending strength were higher compared to the data on compression according to Fig. 9. The degree of influence increases with the content of CNT-2, CNT-3, CNT-4. Hardening for CNT-2 and CNT-3 was 44% and 59%, but a maximum strength of 132% was obtained in the case of CNT-4 at 0.15%.

It can be assumed that the carbon fiber reinforced plastic hardening mechanism with functionalized carbon nanotubes consists in hardening of the adhesion of carbon fiber matrix to carbon fiber by the influence of functional groups grafted to carbon nanotubes. Functional groups provide the cross-linking of CNTs with carbon fiber.

The second part of the work is devoted to the influence of the strain rate on the stress-strain state of epoxy resin and carbon fiber reinforced plastic. The results of the epoxy resin experiments are shown in Fig. 10. It follows from Fig. 10 that the curve of epoxy resin stress-strain state qualitatively repeats the data in figure 1 at a low strain rate of 1 mm/min, the sample takes a barrel shape after strain. With the increase in the strain rate the area of the plastic strain of the curve σ-ε becomes less pronounced, the average modulus of elasticity increases. The slopes of the curves in the areas III varies depending on the strain rate, which indicates the mechanism of elastic-plastic strains. Processes in the area I are quasielastic, the strains in the areas II and III are irreversible. At a strain rate of 20 mm/min the strain character changes radically – the sample begins to "shoot" with fragments from the lateral surfaces forming the voids (in some cases destroyed by cracking). Thus, we get the following picture: at low strain rates (1–5 mm/min) the sample behaves in the area II as a viscous liquid, in the area III – as viscoelastic; at the strain rate above the critical value of 20 mm/min – the areas II and III disappear, the sample behaves as quasielastic, fragile body.

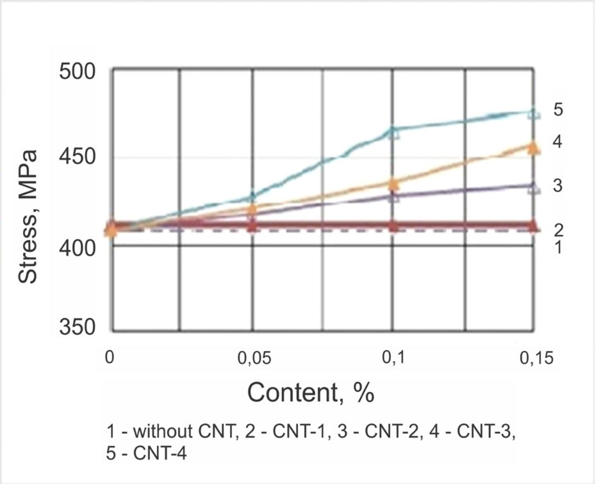


Fig. 8. The dependency of the CFRP compressive strength on the content of CNTs.

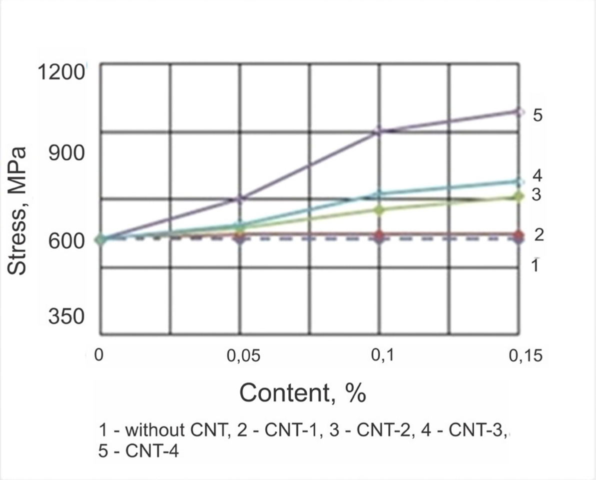


Fig. 9. Dependence of the CFRP bending strength on the content of CNTs.

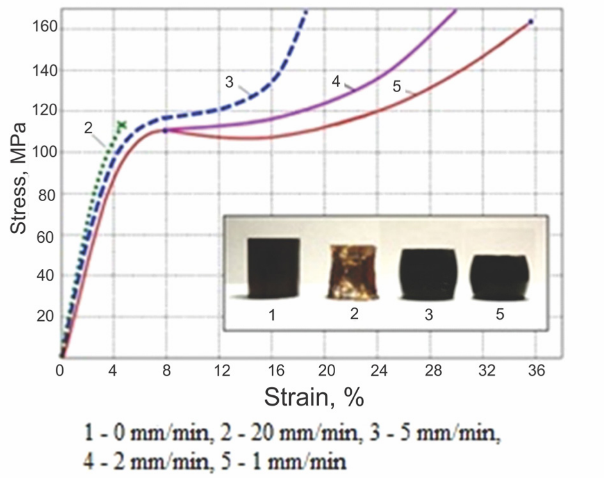


Fig. 10. The stress-strain state of the initial ES at different strain rates.

Another interesting pattern was the weak dependency of quasielastic strain area on the strain rate. The magnitude of the characteristic σ_y was close to 110 MPa in all cases, close values showed the modulus of elasticity. For the fast variant of

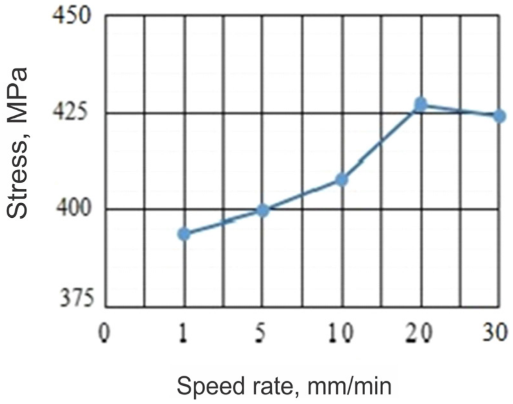


Fig. 11. Dependency of CFRP strength on its strainrate.

strain there is $\sigma_y = \sigma_s$, in other words, the characteristics of the epoxy resin σ_s and E should be measured at strain rates of the order of 20 mm/min and above – only then they can be objective characteristics of the material. The characteristics for areas II and III are meaningless without mentioning the strain rate. By the way, the authors of the works given in Table 1 do not report the strain rate of tested epoxy resins. Therefore, when measuring the strength of the epoxy resin, the strain rate must be indicated.

The results of measuring the carbon fiber reinforced plastic compression strength at different rates are shown in Fig. 11.

From Fig. 11 it follows that the carbon fiber reinforced plastic strength improvement to the strain rate of 20 mm/min increases by 7% from 394 MPa to 425 MPa, with a further increase the strength improvement discontinues. With increasing in load from 1 mm/min to 20 mm/min, the carbon fiber reinforced plastic is deformed by quasielastic mechanism, where the plastic component is gradually falling. It follows that the strain rate of 20 mm/min is critical as for carbon fiber reinforced plastic and epoxy resin, in both cases there is the hardening in the same points of stabilization.

4. Conclusions

1. The injection of primary CNTs-1 into the epoxy resin and carbon fiber reinforced plastic practically do not give the effect of hardening, the functionalized carbon nanotubes give the hardening. They have a selective influence on the stress-strain state of epoxy resin: there is no influence in the area of quasielastic strains, the hardening takes place in the areas of plastic and elastic-plastic strain. So, when injecting into the epoxy resin of 0.05% of carboxylated CNTs-2, the hardening observed in two areas amounted to 9–25%, when injecting of 0.2% of CNTs-2, the hardening effect was reduced to 4–12%. The decrease in the efficiency of functionalized carbon nanotubes at its content in epoxy resin above some critical value is not quite clear, the question requires additional research.

2. Primary CNTs-1 does not affect the strength of carbon fiber reinforced plastic. With the injecting 0.15% of functionalized carbon nanotubes into carbon fiber reinforced plastic the strength enhancement was: a) for compression – CNT-2 – 6%, CNT-3 – 12%, CNT-4 – 17%, b) for bending – CNT-2 – 44%, CNT-3 – 59%, CNT-4 – 132%. Thus, the hardenable efficiency of CNTs placed in ascending order – carboxylated, hydroxyl- carboxylated, amidated. The effect of carbon fiber reinforced plastic hardening on bending was 3–7.6 times more than on compression.

3. With uniaxial compression of epoxy resin at the rate of 1–5 mm/min the consecutive areas of quasielastic, plastic and elastic-plastic strain are observed. With the increase in the epoxy resin compression, the plastic strain area is reduced, gradually moving into the elastic-plastic strain area, the average modulus of elasticity increases. At a compression rate of 20 mm/min, there is only one quasielastic strain area with brittle destruction of the sample, this characteristic can be taken as the strength characteristic of the epoxy resin.

4. For the investigated range of carbon fiber reinforced plastic strain rate of 1–30 mm/min the process is according to the quasielastic mechanism up to destruction. At the rate of from 1 to 20 mm/min the CFRP is hardened from 395 MPa to 428 MPa, i.e. by 7%, the strength is almost constant in the range of 20–30 mm/min. The effect of carbon fiber reinforced plastic hardening with increasing in strain rate can be associated with a gradual decrease in the plastic component of strain. It was found that the carbon fiber reinforced plastic critical strain rate 20 mm/min coincided with the epoxy resin critical strain rate. Obviously, this coincidence is not accidental, this effect requires further explanation.

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