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MECHANICAL PROPERTIES OF EPOXY RESIN WITH ADDITIVES SOOT AND NANOTUBES

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Abstract. The article presents the results of a study of a composite material based on epoxy-diano resins containing a nanocarbon dispersed filler. The effect of small soot and carbon nanotube inclusions on the change in the mechanical characteristics of the cured epoxy resin ED-20 depending on the degree of filling was investigated. Measurements of the ultimate strength, effective modulus $E^* = d\sigma/d\varepsilon$ and maximum deformation before specimen fracture were performed during tensile tests, compression, and bending. The study of the mechanical properties of the specimens was carried out on an AG-X Autograph Series Shimadzu universal testing machine under typical conditions, i.e. room temperature. Found a significant increase in the ultimate strength and plastic deformation of the cured resin with the introduction of the addition of carbon black and nanotubes. The change in the effective modulus during the deformation up to the destruction of the material was determined. Two stages of deformation with a different character of modulus change are revealed: its monotonous decrease and its almost constant value. On this basis, it was concluded that the process of deforming epoxy composites with a consistent change in the deformation mechanisms is complex.

Keywords: epoxy composites, soot, nanotubes, strength, plasticity

1. Introduction. The development of composite materials (CM) is one of the most promising areas of physical, chemical, and technical materials science. The uniqueness of the properties of these materials is due to the presence and interaction of two or more phases in them, which differ significantly in their properties. The most common practice is to create composites in order to improve the stress-strain characteristics of known materials, in particular, polymers. Composite materials based on polymers are widely used in various industries, due to the extremely wide range of their physical, chemical, and other properties [1-14]

In the construction industry, thermosetting polymers based on low molecular weight epoxy and diano resins are the most common [15-23]

Of particular interest are polymeric materials with carbon fillers [24-25]. The first of them – carbon fibers – in the second half of the last century began to be used for the production of carbon plastics, which have found wide application in aerospace and other industries.

As dispersed (powdered) plastic fillers, furnace soot (carbon black) is the most common [1-3,13] In [14], high-density polyethylene was used as the polymer matrix, and the technical carbon (CB) was used as the filler. It was shown, in particular, that the effective modulus of

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filled compositions with an increase in the content of technical conditions increases up to 30 mass. % CB about two times.

One of the most interesting and promising areas in materials science is the preparation and study of polymer nanocomposites, that is, polymers comprising nanoparticles [27-41] Of the entire set of nano-objects, carbon nanotubes discovered in 1991 are the most famous. They have interesting optical, chemical, and mechanical properties, in particular, exhibit the properties of excellent semiconductors.

For example, in [38], the effect of small additions of carbon nanotubes (CNT) and carbon black on the physicomechanical properties of high-density polyethylene was studied. It is shown, in particular, that the introduction of 0.1% CNT leads to an increase in ultimate tensile strength by approximately 20%, and the addition of 2% carbon black increases the strength by 10%.

In [26-48] the influence of the content and length of nanotubes on the cure kinetics, viscoelastic and mechanical properties and glass transition temperature of epoxy composites is shown. The nonmonotonic (anomalous) behaviour of the dielectric constant as a function of the filler concentration was shown in [49] when studying the dielectric properties of an epoxy-amine composite modified with carbon nanostructures up to 2 wt.% At a frequency of 2.73 GHz. The authors suggested that this behaviour of the dielectric constant may be due to the restructuring of the nanotube bundles in the composite. At low filler concentrations (less than 0.4-0.5 wt.%), the mesh structure of nanotubes is formed in the composite. However, with increasing concentration and due to the large difference in the surface energy of epoxy resin and nanotubes, the composite structure becomes unstable and nanotubes form agglomerates, the surface of which is smaller than the total surface of their nanotubes.

Naturally, the widespread use of composites is accompanied by their active and comprehensive research. So, on the website dedicated to polymer composite materials [25], the main reasons for the hardening of polymers by particles of highly dispersed filler are named:

- the cost of external energy for the formation of a large number of microcracks near the filler particles;
- limiting the growth of micro-cracks and their branching when meeting with filler particles;
- an increase in the elastic modulus of the matrix due to the limited mobility of a part of macromolecules adsorbed on the filler.

However, despite significant progress in the creation of high-quality composites with a unique combination of key indicators necessary for practical application, the molecular mechanisms for the formation of their structure and properties are still not well understood.

The purpose of this paper is to study the mechanical properties of the cured epoxy resin with the addition of a small number of carbon materials: furnace soot and carbon nanotubes "Taunit-M".

2. Details on manufacturing and testing

The composite was manufactured using epoxy resin ED-20, hardener PEPA, additives of carbon black (soot) brand P 234, and carbon nanotubes "Taunit-M" produced by LLC Nanotehtsentr [26]

Carbon nanotubes "Taunit-M" are micrometer-sized agglomerates, therefore, their introduction into epoxy monomer with the purpose of dispersion was carried out in two stages:

- the effect of tensile and shear forces in the space between the rolls of a three-roll mill (gaps between the rollers 10 and 5 microns, the material was subjected to double processing);

- ultrasonic effect at a frequency of 22 kHz on an ultrasonic device with an energy intensity of about 350 kN / (m · s) (exposure time 30 min., volume 200 g.) [27]

Particle size measurements were carried out by the method of dynamic light scattering on the Nicomp 380 ZLS analyzer. The average dispersion was about 330 nm. The outer diameter of the tubes was between 8-15 nm, the inner diameter reached 4-8 nm, and the length was expressed by ≥ 2 μm.

The introduction of soot into the resin was carried out similarly to the introduction of CNTs.

The study of the mechanical properties of the composite was carried out using a universal testing machine i.e. the AG-X Series Autograph Shimadzu. The management of the test process and the preliminary processing of the data obtained on this machine were performed by means of the software TRAPEZIUM X×1. Values of effective modulus, ultimate strength, and total strain were determined in tensile, compression, and bending tests. For mechanical tests, samples with dimensions 10×10×30 mm were used. All measurements were carried at room temperature.

Fracture zones of the specimens were analysed using a scanning electron microscope technique (SEM). The following device Phenom ProX was used.

3. Results and Discussion

When analyzing the results obtained, attention is drawn to the relatively large variety of indicators for different samples of the same material. Thus, the standard deviation (range of values) for tensile strength in tensile testing varies within 15 ÷ 35%, for maximum deformation before failure within 30 ÷ 75%. This implies, in particular, that the mechanical properties of the composites strongly depend on practically uncontrollable parts of the technology for obtaining samples in the laboratory. This conclusion is confirmed by a detailed analysis of the strain-stress curves.

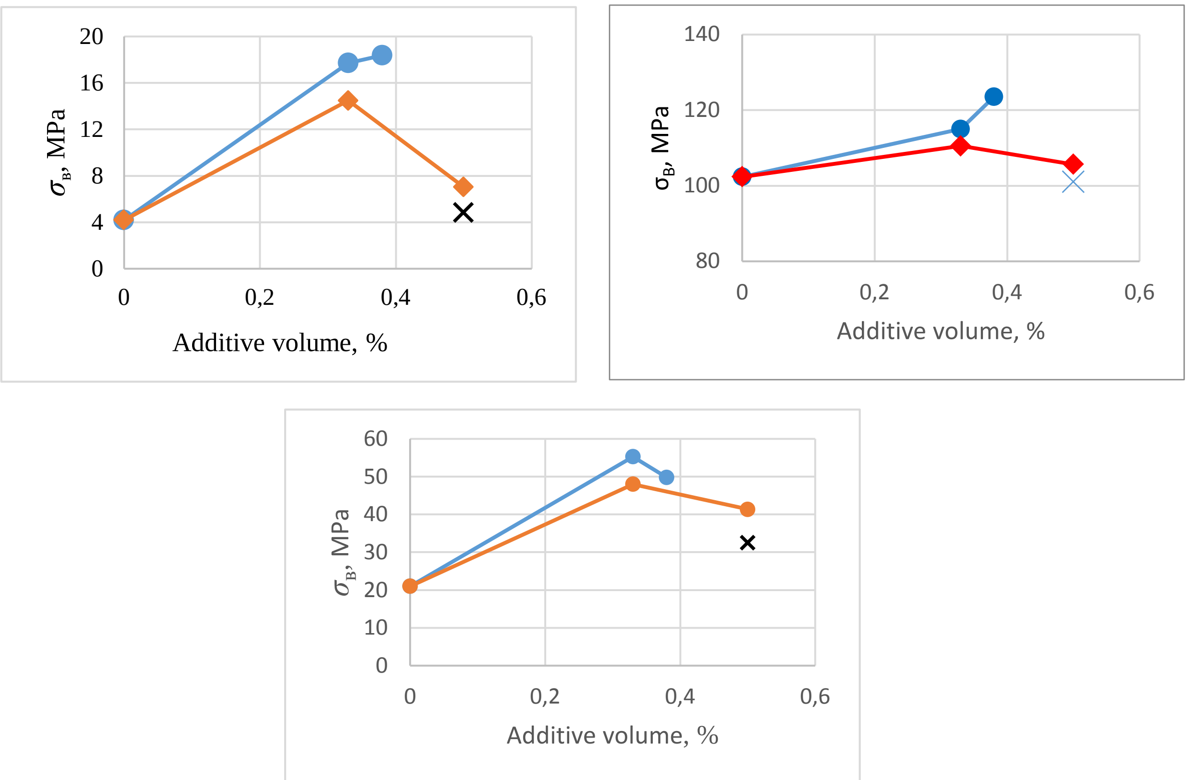

Fig. 1. Ultimate strength versus the additive volume, determined in tensile testing (left), compression (right) and bending (below): • – soot, ♦ – CNT, ×– soot + CNT

Figure 1 shows the ultimate strength of the tested materials captured in tensile, compression, and bending tests as a function of the amount of soot and CNT additives. The dependences of the modulus of elasticity, determined on a stress range of 0.5-1 MPa, on the composition of the material are presented in Fig. 2. As can be seen, they are qualitatively similar to the variations of the ultimate strength. If there are only three points, the obtained dependencies can be unambiguously interpolated by polynomials of the second degree, however, the reliability of such interpolation is insufficient for detailed analysis, additional studies with a large number of compositions are needed.

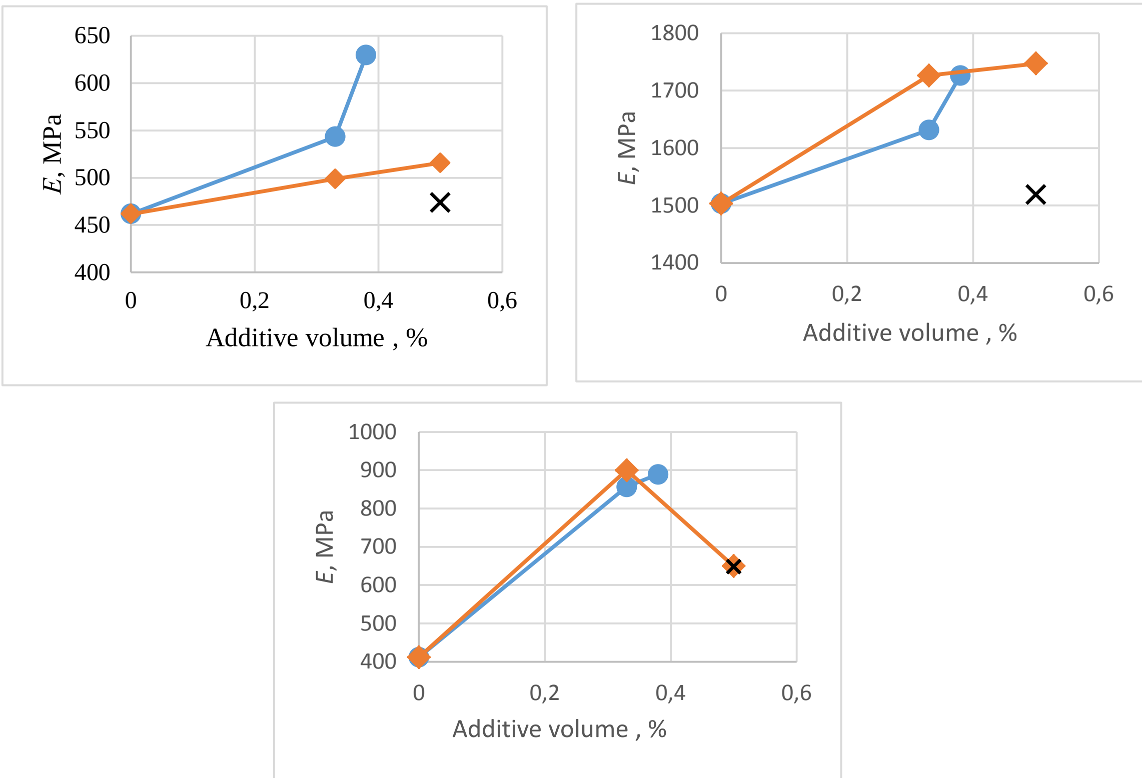

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Fig. 2. Effective modulus versus the additive volume captured in tensile testing (on the left), compression (on the right), and bending (bottom): • – soot, ♦ – CNT, × – soot + CNT

However, at this stage, a significant influence of small additives and soot and carbon nanotubes on the mechanical properties of the cured epoxy resin is found. So the ultimate tensile strength and elongation at the fracture during the tensile test increased almost five times when in the case of the bending experiment a value of this physical quantity becomes three times higher. The effect of nanotubes in most cases turned out to be somewhat less compared to soot.

A significant change in the mechanical properties of epoxy resin upon the addition of very small additions of carbon black and carbon nanotubes (not more than 0.5%) it makes it possible to classify the materials studied as composites.

Figure 3 shows values of the maximum total deformation ε_{max} from tensile testing of the composites characterizing the elastic-plastic feature of the material examined. As can be seen, Figs. 1, 2, and 3 indicate almost the same information on the composite tested. i.e. an increase in percent volume of additives leads to increasing of the selected mechanical parameters.

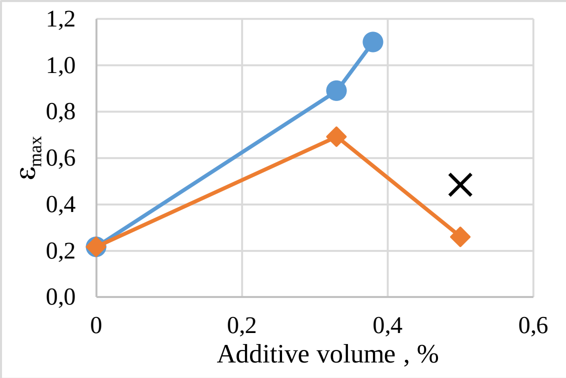

Fig. 3. Maximum total deformation versus the additive value, obtained in tensile tests: • – soot, ♦ – CNT, × – soot + CNT

Note that the shape of the curves in Figs. 1-3 for resin with carbon nanotubes leads to an assumption about the possibility of a maximum presence in the concentration range studied.

Figures 1-3 show the data averaged over several specimens. As mentioned above, there is a significant variation in performance between materials with the same composition. In this regard, to clarify the relationship between ultimate strength and ductility, all values representing these mechanical parameters are collected together as shown in Fig. 4. As it is visible, an obvious correlation of these properties is indeed observed – the data set is interpolated by a second-order trend line with a fairly high value of the coefficient of the accuracy of the approximation $R^2 = 0.907$:

$$\varepsilon = 0.0031\sigma^2 - 0.0097\sigma + 0.168.$$

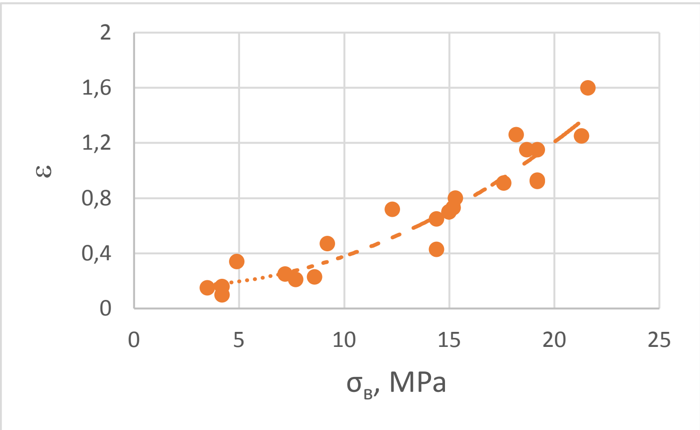

Fig. 4. The relationship between ultimate strength and total deformation at fracture from the tests conducted on the materials studied

Additional information about the processes occurring in the material during its deformation can be obtained by analysing the behaviour of an effective module

$$E^* = \frac{d\sigma}{d\varepsilon},$$

where $d\sigma$ and $d\varepsilon$ represent stress and strain increment, respectively. Figure 5 shows the dependences of this value on the current values of stress (a) and strain (c) for pure resin.

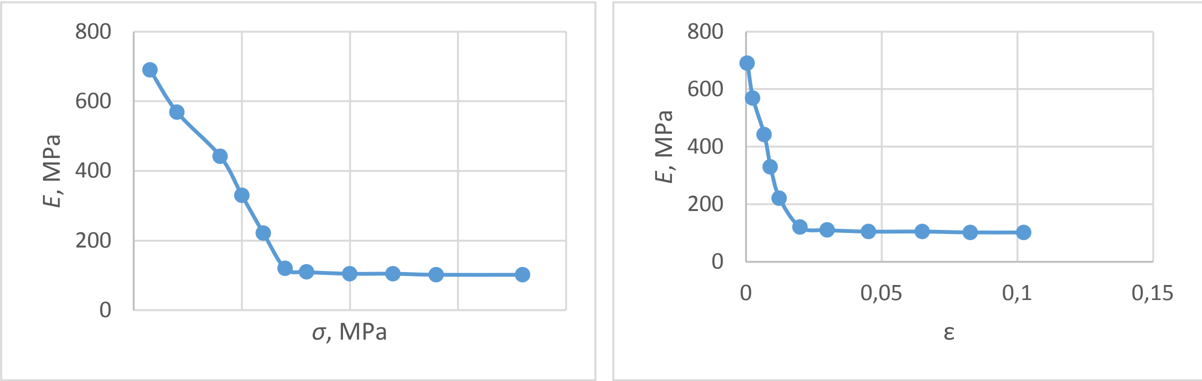

Fig. 5. Dependence of the effective modulus on the mechanical stress (left) and total stress (right) of pure resin, results from tensile tests

From these figures it can be concluded that the total deformation of the resin can be divided into two stages: 1 – a strong decrease (several times) in the effective modulus, 2 – an almost constant value of this value. Note that some specimens were destroyed before reaching the stress corresponding to the second stage.

Variations in values of $E^*(\sigma)$ and $E^*(\varepsilon)$ indicates a change in the molecular mechanism of deformation. At the first stage, a significant change in the molecular structure of the material occurs, leading to the simplification of the deformation process, and the formation of a dynamically relatively stable structure.

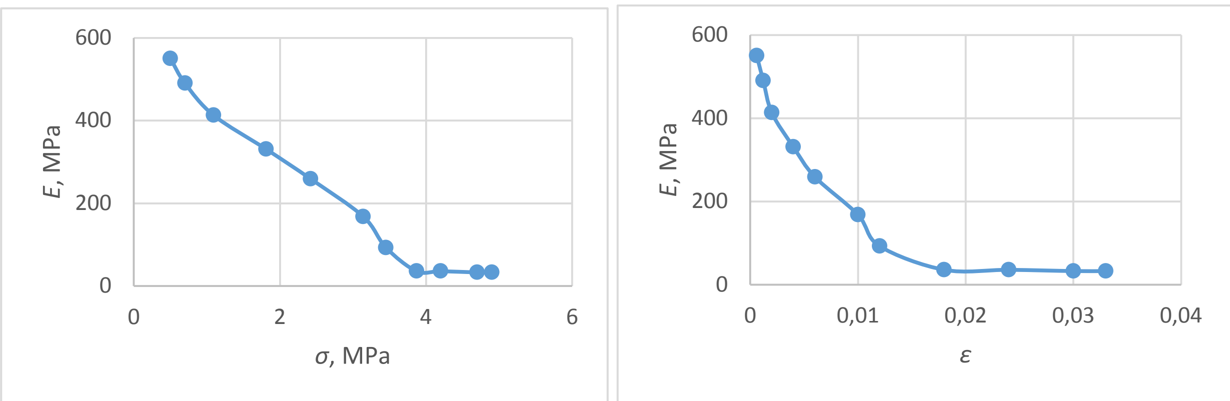

Fig. 6. Dependence of the effective modulus on the mechanical stress (left) and total deformation (right) of the resin with the addition of 0.33% CNT, results from tensile tests

Figure 6 shows the same dependencies of effective modulus versus mechanical stress and total deformation for the resin with the addition of 0.33% CNT. As mentioned above, the addition of nanotubes led to a significant change in the ultimate tensile strength and ductility of the resin. However, the value of the effective modulus, depending on the current values of stress and relative deformation, did not change qualitatively. The same two stages of a strong decrease in the modulus and its almost constant value are observed, only the boundary between the stages shifts slightly towards higher values of stress and strain. The same applies to materials with other additives. The same applies to materials with other additives. It follows that the introduction of impurities into the resin does not fundamentally affect the basic molecular mechanisms of the deformation process.

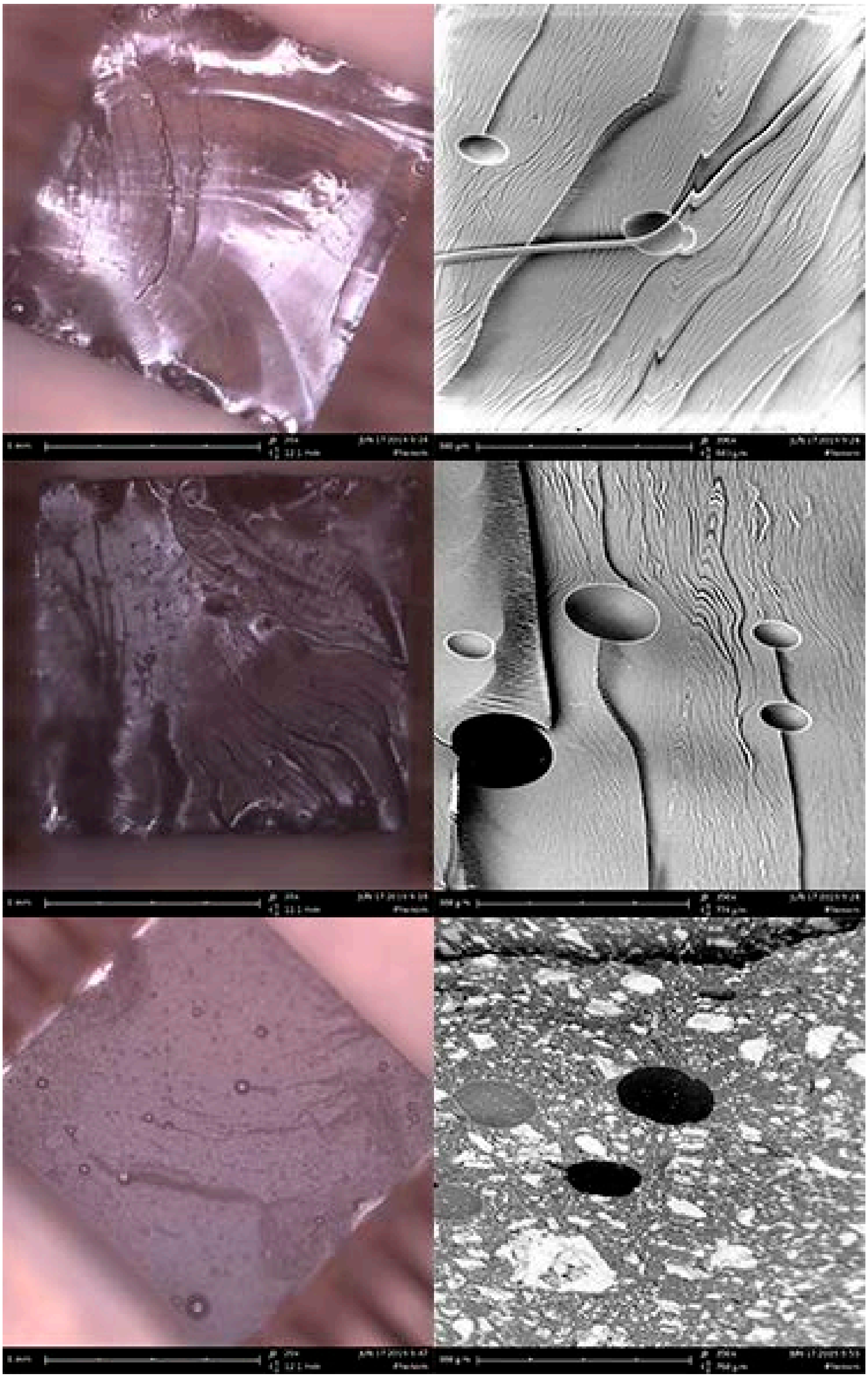

Fig. 7. The microstructure of destruction surface of the specimens: the left column is the mode of the optical microscope, the sample size is 10 × 10 mm; the right column – electron microscopic images, the size of the region 768 × 760 microns. The top row is a sample with 0.5% CNT; the middle row is a sample with 0.38% carbon black; the bottom row is a sample with 0.25% CNT and 0.25% carbon black

In the case of all specimens, fracture surfaces expressed the brittle fracture of amorphous materials (Fig. 7). It can be noticed on the regular edges of holes and dimples for reinforcement as well as sharp edges of degradation sub-regions of the fracture zone. Nevertheless, the differences due to the percent volume of additives are visible. It is clearly seen that the degradation of the composites is strongly related to cracks that reach the nanoparticles, but not soot globules.

Based on the analysis of images for SEM (Scanning Electron Microscope) technique and the data of mechanical tests, it can be concluded that nanotubes are not a reinforcing additive, but rather a modifier (builder), contributing to the emergence of multiple centers of the solid phase during the curing of the liquid resin, and possibly providing more full polymerization [50]

In the boundary layer, ordering of the polymer structure is observed, which is characterized by a significantly smaller number of conformations, so that we can talk about the orientation of macromolecules within the layer (Fig. 8).

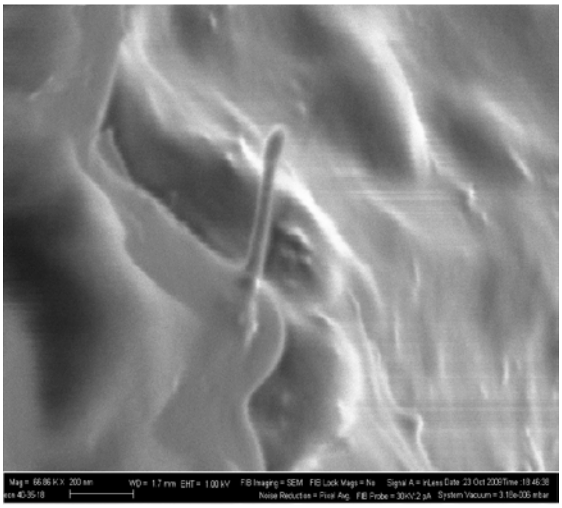

Fig. 8. Carbon nanotube coated with a layer of epoxy resin on the fracture surface after fracturing in tensile tests

The condensed structure of the boundary layer passes to the bulk state of the polymer through a loose defective layer, which arises as a result of the separating mass transfer of macromolecules to the centers of structure formation, on the one hand to the surface of the filler, and on the other, to the polymer mass, to globular formations. It is this layer that is the weakest and is destroyed first of all.

6. Conclusions

1. Introduction small additives (up to 0.5%) of soot and carbon nanotubes to epoxy resin led to 3-5 times increasing value of ultimate tensile strength.
2. The increase in the ultimate strength was accompanied by an increased value of deformation at fracture.
3. The introduction of additives into the resin does not make fundamental qualitative changes in the dependence of the effective modulus on the stress and degree of deformation.
4. It has been suggested that nanotubes are more likely not a reinforcing additive, but a modifier (structure-forming agent), contributing to the emergence of multiple centers of phase formation and additional polymerization.

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