Modification of Epoxy Resins: Modern Condition and Prospects.

Part I. Modification of Nanoparticles

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Abstract

Epoxy resins are oligomers containing epoxy groups and capable of forming cross-linked polymers under the action of hardeners. Epoxy resins are used in the production of adhesives, plastics, glass and carbon plastics, pouring compounds and plastoconcrete. These materials are widely used in construction, mechanical engineering, aircraft and rocket construction, shipbuilding. To improve the performance of epoxy resins, their chemical or physical modification is used. The paper focuses on physical modification of carbon nanomaterials in order to improve the strength characteristics. Methods for modifying epoxy resins with graphite, carbon nanotubes and graphene are analyzed. It is shown that graphene is the most promising material improving the strength characteristics of epoxy resins.

Keywords

Epoxy resin; silica; rubber; organosilicon compounds; epoxy-sulphide oligomers; carbon nanotubes; graphene.

Introduction

The physicochemical parameters of polymer nanocomposite materials are determined by the aggregation production technology, by the distribution of the filler particles, by the porosity of the material [1, 2,], and by physical properties of polymer materials and nanoparticles [3, 4], particle shape [5] and the chemical interaction between components of the composite [6–8]. Varying the interaction of atoms of nanoparticles and polymer macromolecules, all other things being equal, one can influence the performance characteristics of the materials. In the review [9], the regularities of changes in the mechanical properties of solids and nanostructured materials were discussed in detail with a decrease in the characteristic dimensions of the object of its morphological or structural units to individual molecules. Methods of experimental determination of physical and mechanical characteristics of nanoscale materials were presented. In [10], experimental data on the mechanical properties of low-dimensional objects and materials, film coatings, thin-surface layers, nanopolar fibers, nanotubes, and macromolecules were analyzed. The dependences of hardness, yield strength and strength on the grain size for nanocrystalline materials were considered. A simple classification of objects and tasks by their dimensions was used: three-dimensional (3D), thin-film or two-dimensional (2D), rod-like or one-dimensional (1D) and point or zero-dimensional (0D) nanomaterials. These materials, as a rule, have a much higher strength, which allows creating products with unique characteristics that are unattainable with conventional materials.

Thus, there is a real prospect of increasing the strength characteristics of epoxy resins, by their modification with nanomaterials.

Silicon dioxide

Fillers, the surface of which has a high reactivity and the possibility of modification by molecules with different functional groups, are silica particles widely used in polymer composites [10, 11]. The increase in the strength limit is explained by the binding of

polymer chains to the nitrogen atoms of the γ-aptes molecule [12]. The objects of research were compositions of epoxy resin of brand ED-20 and A-300 modified with nanosilica. Polyethylene polyamine was used as the hardener (components of the compositions are made in Ukraine). The average particle size of SiO^2 was 10 nm; the specific surface area was 300 m^2/g. The silica content of the composites was 2% by weight. Polymerization of resin was carried out at 130 ^oC for 10 hours; a relative degree of polymerization was 0.8. The surface modification of SiO^2 particles was made from the gas phase [13–16]. The concentration of grafted molecules was 0.6–0.8 mmol/g, which corresponded to a complete coating of the nanoparticle surface. It was shown that the grafted molecules of epoxy resin chemically bind to the molecules of the matrix. However, such interaction does not change the structure of polymer chains in the composite, so there is no reason to expect an increase in strength characteristics. When rigid fillers with concentrations greater than 20 % were added to viscous thermoplastics, the transition from plastic flow to brittle fracture was observed [17] and the toughness decreased [18]. The modulus of elasticity increased with increasing concentration, and so did the size and number of cracks occurring during the loading process. This possibly happens when the matrix is exfoliated from dispersed particles, at the moment of reaching the stresses corresponding to the adhesion strength of the system. Theoretical and experimental studies showed that by decreasing the size of the filler particles and the spread of their diameters, the probability of large defects could be significantly reduced [19]. To study this effect in [20] Tarkosil hydrophilic nanosized silica powders were used (series T) with a surface area 54, 74, 96 and 150 m^2/g, which corresponded to an average particle size of 50, 37, 30 and 18 nm, A-90 (30 nm), A-200 (14 nm), A-300 (9 nm), A-380 (7 nm). In all experiments, the epoxy resin ED-20 was used as the matrix. For curing, the polyethylenepolyamine hardener was added to the resin in a ratio of 1 part hardener to 6 parts resin. Ultrasound was used to disperse the nanopowder in the matrix. The value of Young's modulus for samples from pure resin was $E_0 = 1.2$ GPa. Further, the Young's modulus value assigned to this value was used. It was found that the maximum values of 7–15 % corresponded to a concentration of 0.3–0.5 wt%. With a further increase in the concentration of the filler, the Young's modulus decreased smoothly. To evaluate the effect of particle size the Tarkosil silica powders were taken T-05 (50 nm), T-15 (30 nm), T-20 (18 nm) and A-90, A-200,

A-300, A-380 at a weight concentration of 0.4 %. Thus, for tarkosil powders with dimensions from 50 to 18 nm, the Young's modulus increased by 30 %. It should be noted that in this case the greatest effect had a powder with a particle size of 14 nm. Reduction in the size of the filler up to 9 and 7 nm had a negative effect on strength (3–5 %). The authors made the assumption that the polymer molecules can have a certain characteristic size of the structure, in which the filler particles are located between the polymer mesh, filling it, thereby strengthening the structure of the substance.

Rubbers

The impact strength of brittle epoxies can be improved by introducing modifiers [21, 22], such as silicone, butadiene-acrylonitrile or polyurethane rubbers [23]. When developing multicomponent epoxy binders, the compatibility of components is of particular importance. It is believed [24] that the polymer phase precipitated during the curing process forms a homogeneous dispersion with a particle size of less than 1 μm, providing a reduction in internal stresses and an increase in toughness, elasticity and fracture toughness. Epoxy and epoxy-rubber polymers based on four grades of epoxy resins (EA, ED-20, DEN 431, NPPN 631), two hardeners (diaminodiphenyl-methane, iso-methyltetrahydrophthalic anhydride) and polyurethane rubber SKU-PFL-100 were obtained in [25].

Fig. 1 shows the data on the variation in modulus of elasticity when bending samples of epoxy polymers, obtained by curing four different resins with the
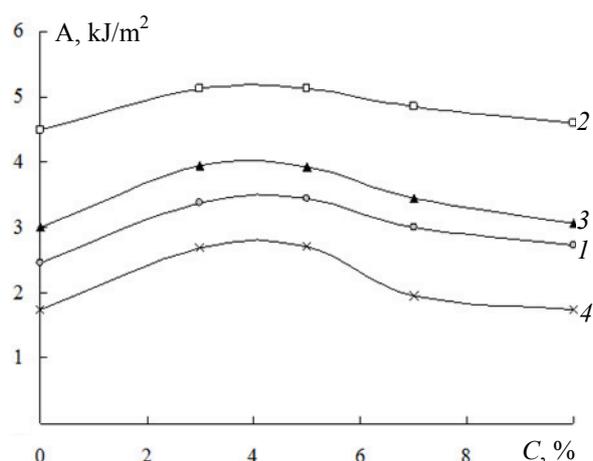

Fig. 1. Dependence of impact strength on the content of SKU-PFL-100, *C* in solidified epoxy rubber compositions.
Standard sample: EA (*1, 3*), NPPN 631 (*2, 4*). Solidifiers: diaminodiphenylmethane (*1, 2*), *iso*-methyltetrahydrophthalic anhydride (*3, 4*) [25]

diaminodiphenylmethane aromatic hardener, with different content of added polyurethane rubber SKU-PFL-100. Brand and type of epoxy resin: EA – nitrogen-containing; NPPN – two-stage resin.

With a rubber content of up to 5 % by weight in the obtained epoxy compositions, the modulus of elasticity at bending and the glass transition temperature practically do not change. In this case, the impact strength increases to 15–50 %.

As can be seen from the graphs, the best result for a combination of mechanical, thermophysical properties and impact resistance was achieved for the composition based on the novolac oligomer NPPN 631, solidified with diaminodiphenylmethane and modified with SKU-PFL-100 3–5% by weight.

Organic silicon compounds

The modification of epoxy oligomers with organic silicon compounds is widely reported in the literature, for example, in [26] a modification process based on the reaction of alkoxysiloxanes with epoxy compounds is studied. As a result, epoxy-silicone resins are formed, i.e. functional groups of organosilicon modifiers form a joint structure with epoxy resins. In [27], the influence and efficiency of modification of epoxy resins with titanosiloxanes were considered. It is shown that when titanosiloxane is added to the composition of the composite material, the degree of conversion of epoxy groups is increased and the physical-mechanical properties of the composite material are changed. The influence of ethylsilicate-40 (ETS-40) and tetra-ethoxysilane (TEOS) on the curing process and the physical and mechanical properties of epoxy compositions based on the diane oligomer (ED-20) and ETAL-45 solidifier was studied in [28]. In addition, an evaluation of the effectiveness of the modification of ED-20 by the introduction of alkoxysilane and the introduction of alkoxysilane and maleinized oligobutadiene (PBN-M) containing 15 % of maleic groups is given. It has been found that the introduction of modifiers into the epoxy oligomer in an amount of 3 % by weight leads to a significant increase in both the impact strength and the adhesive strength, for example, for ETS-40, the bending strength increases by 38 % and the toughness by 13 %. It should be noted that the compressive strength has decreased by 10 %.

Epoxy-sulphide oligomers

In [29], the process of modification of epoxy resins with epoxy-polysulfide oligomers, a class of compounds with a basic polysulfide chain and terminal

epoxy groups, is considered. It is shown that their introduction of compositions based on epoxy resins significantly improves the elasticity of the material without impairing its technological properties. Modification of thermosetting binders with different heat-resistant thermoplastics such as polysulfones, polyetherimides, and a variety of rubbers, is widespread in the development of polymer composite materials. Polysulfones are of particular interest, as they have high mechanical characteristics combined with oxidative and thermal stability [30–35]. It was shown in [36–39] that furfuracetone resins significantly reduce the viscosity of epoxy resins without exerting a negative effect on the glass transition temperature of the cured polymer, as are the traditional active diluents of α-aliphatic glycidyl ethers. The use of such systems provides the possibility of obtaining low-viscous binders suitable for manufacturing heat-resistant polymer composite materials by non-autoclave molding methods. It was shown in [40] that as a result of the modification of furfuralolacetone resin (FA) with polysulfone (PS) and a mixture of furfuralacetone resin-polysulfone, the crack resistance of the matrix increases 3–4 times. Typical load-strain diagrams observed in the determination of fracture toughness are shown in Fig. 2.

As can be seen from the diagrams, the character of the destruction of samples in the process of splitting is the same and does not depend on the type of modifier and its quantity. The crack begins to germinate only at the moment when the load in the material reaches a critical value, while cracking causes a momentary load drop.
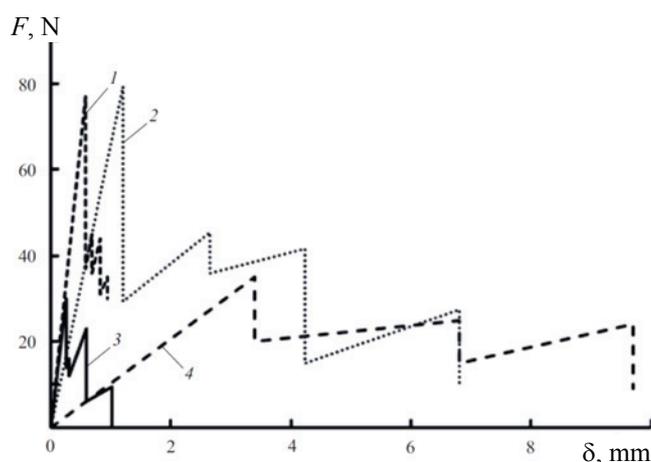

Fig. 2. Loading diagrams for measuring the fracture toughness of samples modified with polyepoxides:
1 – 0 % FA, 20 % PS; *2* – 20 % FA, 20 % PS; *3* – 0 % FA, 0 % PS; *4* – 20 % FA, 0 % PS [40]
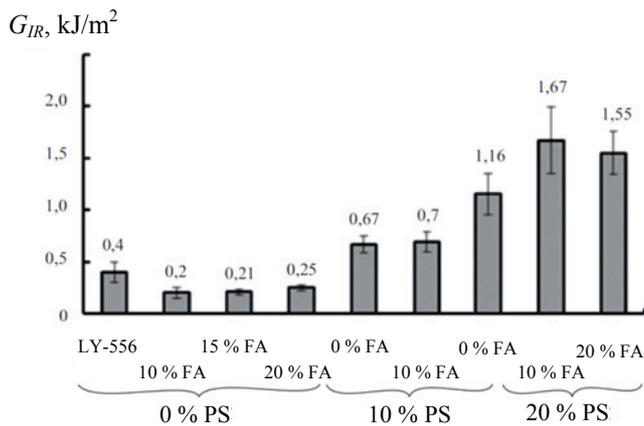
G_{IR}, kJ/m^2

Fig. 3. Specific fracture energy (crack resistance) of modified epoxy compositions [40]

The specific energy of destruction G_{IR} calculated from the F–δ diagrams is shown in Fig. 3. As can be seen from the diagram, when polysulfone is added to the epoxy resin, the crack resistance increases significantly. The values of G_{IR} compositions containing 20 % polysulfone reach 1.16 kJ/m^2, which is 3 times the G_{IR} values for the unmodified cured resin. The authors explain the significant increase in the crack resistance after the introduction of a thermoplastic by the effect of a more elastic additive, which retards the propagation of the crack and changes in the phase structure. Adding of active diluent FA without PS leads to a 1.5-2.0-fold decrease in G_{IR} values, which in combination with the type of F–δ diagrams (see Fig. 2) indicates an increase in the brittleness of the epoxy composition.

A deep analysis of the applications of epoxy resins and ways to improve their performance characteristics was given in [41]. Methods for modifying halloysite and further applications of the modified mineral as a filler for epoxy resins were presented in [42]. It was experimentally confirmed that ultrasonic treatment prior to chemical modification with an organic compound has an advantage for production of a hybrid filler. It was found that by adding 3 % by weight of the modified halloysite to the epoxy resin, the impact strength is increased by a factor of 6 from 2 kJ/m^2 to 12 kJ/m^2. The bending strength increased from 64 MPa to 96 MPa.

Carbon nanotubes

Carbon nanotubes (CNTs) are considered as one of the promising types of modifiers, since they possess good mechanical characteristics, as well as the possibilities of surface functionalization [43], which provides a covalent interaction with the polymer matrix. CNTs improve the physical-mechanical properties of epoxy-nanocomposites due to the effective redistribution of the load in the volume of the binder. The conditions for effective modification are [44]:

– uniform distribution of CNTs in the volume of the matrix;

– high adhesion of the CNT surface to the polymer matrix;

– orientation of CNTs in the direction of the load.

In addition to reinforcing the polymer matrix, CNTs affect the kinetics of curing epoxy oligomers and the structure of the resulting composites. It is established [45] that under isothermal conditions of heating, the composition based on tetraglycidyl-4,4-diaminodiphenylmethane is not completely cured in the presence of 4,4-diaminodiphenylsulfone as a hardener. At a curing temperature of 190 °C, the degree of conversion of the composition modified with 5 % CNT is 10 % higher than that of the original system, but at a curing temperature of 220 °C the situation becomes opposite, i.e. the degree of conversion of the initial system is 4 % higher than the conversion rate of the modified composition. In [46], the results of a study of the curing process of the composition (diglycidyl ether of bisphenol F/diethylenetoluylenediamine) modified with multiwalled carbon nanotubes (MWCNT) at a concentration from 0.5 to 1.5 % in the isothermal regime in the temperature range from 130 to 170 °C are given. It was found that MWCNTs accelerate the curing reaction and increase the final conversion in the entire range of cure temperatures studied. It was shown that in the conditions of the lack of solidifier (in comparison with the stoichiometric amount) when the UP-643 epoxy resin was cured with the Diamet X solidifier in the presence of carboxylated CNTs, more regular and frequent grids were formed [47]. The effect of a simultaneous increase in the physical-mechanical properties and the glass transition temperature under conditions of two-stage curing was observed in a number of studies [48–53]. In this case, two-step curing with a first-stage temperature substantially less than the glass transition temperature of the epoxy composition is important. It was found that in the case of isothermal curing at the temperature of the second stage [54], such a conversion depth is not achieved. It was shown in [55–58] that the curing of epoxy oligomers modified with CNTs under conditions of high temperatures or excess solidifier leads to a decrease in the glass transition temperature of epoxynanocomposite compared to the original sample. The efficiency of the modification is determined by the condition for

achieving the optimal ratio of the number of physical and chemical assemblies for a specific polymer matrix [58]. The introduction of CNTs into the polymer matrix contributes to an increase in the number of physical nodes of the meshing network and makes the matrix more prone to the flow of relaxation processes.

In the case of achieving an optimal balance between the number of physical and chemical sites in the modified nanocomposite, compared with the initial material, the tensile strength increased by 25 %, the breaking strain increased by 40 %, and the toughness increased by 50 %. The glass transition temperature for the investigated series of nanocomposites remained constant or slightly decreased; the concentration of CNTs was 0.05 % (by weight). The studies of epoxy-nanocomposites using electron microscopy methods showed that the curing process begins on the surface of a CNT [53] and this confirmed the assumption of a change in the supramolecular structure of the polymer matrix in the presence of carbon nanotubes.

In [55, 59], the functionalization of CNTs was carried out in toluene diamine, which was used as a hardener. The curing of the composition took place at a temperature of 177 °C (the glass transition temperature of the original composition was 170 °C), which resulted in almost complete conversion. The modulus of elasticity increased by 25 %, tensile strength – by 22 %, relative retardation – by 39 % [55, 59]. The fact of increase in fracture deformation in epoxy resins modified with CNTs, as well as an increase in the efficiency of modification of epoxy resins in the series: initial CNTs, oxidized CNTs, aminated CNTs was confirmed in [51, 55, 59]. Apparently, the increased concentration of hydroxyl and carboxyl groups on the surface of oxidized CNTs contributes to covalent bonding to the matrix during heat treatment. Amino groups grafted onto the surface of CNTs easily open epoxide cycles during the curing process. The authors of [60] concluded that in order to increase the efficiency of epoxy binder modification, it is necessary to optimize the composition and the number of functional groups.

The results of studies of carbon nanomaterials "Taunit" and "Taunit-M" for the modification of epoxy resin are presented in [61, 62]. "Taunit" is nanofibers with a conical orientation of carbon layers, 30–60 nm in diameter, with a specific surface of 120 m^2/g and a bulk density of 0.4–0.6 g/cm^3. "Taunit-M" is a coaxial carbon nanotube with a diameter of 8–15 nm, with a specific surface of 300 m^2/g and a bulk density of 15–30 g/dm^3. It was experimentally established that at concentrations of carbon nanomaterials of 0.05–0.1 % (by weight), the modulus of elasticity of the polymer composite significantly increased.

Graphene

In [63], the modification of epoxy resin by graphene was carried out by the situ-synthesis method. The mass concentration of graphene was: 0; 0.1; 0.4; 0.7 %. The mechanical and thermal properties of coatings with epoxy resin were studied using nanoindentation techniques and thermogravimetric analysis. The characteristic values of the Young's modulus, hardness, and plasticity index from the concentration of the modifying additive (polyvinylpyrrolidone + partially reduced graphene oxide) in epoxy resin are presented in Table 1.

As can be seen from Table 1, the maximum increase in hardness (293 %) and Young's modulus (213 %) was at graphene concentrations of 0.7 %. In addition, by electrochemical methods, the erosion resistance of the coating was determined by the initial and modified epoxy resin. The results showed that the erosion of the initial epoxy resin is 3 mm/year, and the modified one – 0.3 mm/year. The effect of graphene on the thermal stability of the epoxy coating was characterized by TGA. The TGA curves showed that the heat resistance of the epoxy resin coating increases with graphene modification. For example, the temperature at 20 % weight loss of the initial epoxy resin 284.7 °C after adding 0.1 % graphene increased to 322.4 °C, and at 0.7 % it increased to 356.3 °C.

The thermal properties of structural materials are of great importance in the electrical engineering industry [65], automotive industry [66] and aerospace [67]. Lightweight, polymer nanocomposites are promising materials for heat transfer problems. For example, the excellent thermal conductivity of carbon nanotubes improves the transport of heat when they are added to polymers [68]. However, carbon nanomaterials, which have extremely high thermal conductivity and low specific gravity, do not always show the expected improvement in thermal conductivity, mainly due to the poor distribution of these nanomaterials over the polymer volume [69, 70].

Table 1

Strength characteristics of epoxy compositions

Concentration of the modifier, %	Young's modulus, GPa	Hardness, GPa	Index of plasticity, %
0	2.44	0.17	43.4
0.1	2.60	0.19	43.1
0.4	3.64	0.41	34.4
0.7	5.62	0.51	31.7

The results of polymer modification with graphene and the effect of the uniform distribution of graphene on heat capacity and thermal conductivity were described in [71]. Analyzing the results of [72], in which a composite with a thermal conductivity of 5.8 W/mK was obtained as a result of the uniform distribution of 20 % graphene oxide functionalized with silane in epoxy resin, the authors of [71] believe that unoxidized graphene at such a high concentration can increase thermal conductivity. According to the authors, the main problemis the high energy of van der Waals (5.9 kJ/mol) in unoxidized graphene, which makes it difficult to achieve an even distribution of graphene in epoxy resin [73]. Usually this problem is solved by using specially selected solvents [74] or by exfoliation of intercalated graphite using a surfactant [75, 76]. The novelty of the paper [71] is mainly to create a method of non-covalent functionalization of organic polymers by graphene, which improves the thermal conductivity of the composition and its mechanical properties, due to a more even distribution of graphene in the epoxy resin.

In [77], complex studies were carried out to determine the thermal conductivity and mechanical characteristics of composites based on epoxy resin with graphene. The samples were made in the form of disks with a diameter of 50 mm with a mass content of graphene: 0.1; 0.3; 0.6 %. The Shore hardness was determined using a Durometer device in compliance with ASTM D 2240 standard, i.e. using an indenter with a calibrated spring, the depth of penetration of the indenter into the sample was measured at a fixed load.

The diametric compression force was determined by loading the specimens in the shape of a disc along their diameter, thus generating a tensile stress in the center of the disk in a direction perpendicular to the direction of the applied load, according to ASTM D 3967. Fig. 4 shows the characteristic dependence of the Shore hardness on graphene concentration.
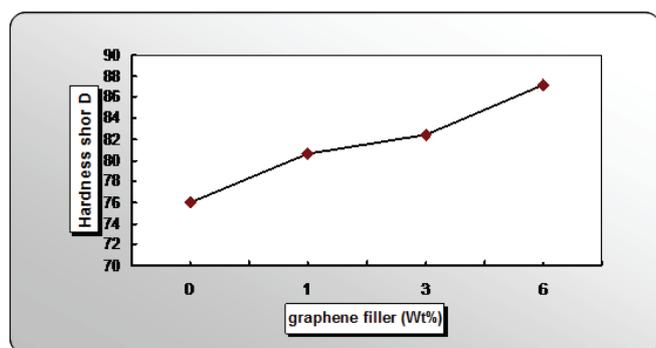

Fig. 4. Relation between the Shore hardness and the weight percentage of graphene (wt %) [77]

As can be seen from the graph, when the concentration of graphene is 6 %, the hardness increases by 14.5 %.

The thermal conductivity of the samples was measured by the method proposed in [78]. An increase in hardness by 14.5 % is explained by the authors of Ref. [77] by the high specific strength of graphene (~ 1.0 TPa) and the modulus of elasticity (125 GPa) [79]. In addition, it was assumed that the formation of non-hexagonal rings is of decisive importance in the transfer of nanosized interlayer interactions with their macroscopic mechanical properties. It is assumed that the limit diametrical compression increases because graphene dispersed in an epoxy matrix, can create the crumpled structure, which tend to unfold rather than stretch when a load is applied. This is confirmed by the effective suppression of the propagation of cracks in the epoxy matrix [80, 81].

In [82], the results of compression, stretching and bending tests of samples from pure epoxy resin modified with 2 % graphene were described. The authors substantiated the relevance of the studies, primarily by the fact that steel pipelines, which are widely used in the oil and gas industry, constantly require repair due to damage from natural mechanical influences and corrosion [83, 84]. In recent years, the most promising materials for repair have become polymeric composites and, first of all, epoxy resins [85]. Epoxy resins are widely used as matrix composites because of their unique characteristics, such as high stiffness, high adhesion strength and low shrinkage upon curing [86, 87]. Epoxy solutions play a key role in transferring loads from the pipeline to the reinforcing material. This means that if the epoxy resin does not transfer the load to the reinforcing fibers, they cannot strengthen the construction [86]. Table 2 gives the results of testing samples from neat and graphene-based resin upon stretching.

Figure 5 shows the characteristic dependences of relative deformations on compressive stresses, and Fig. 6 – on tensile stresses.

Table 2

Tensile test results

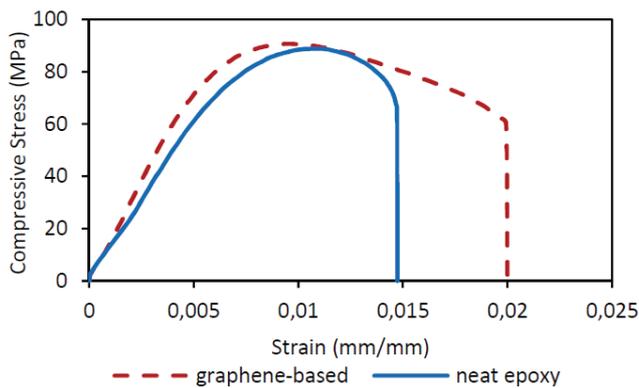| Material	Stretching stresses, MPa	Elastic modulus, GPa
Neat epoxy resin	15.18 ± 0.32	17.35 ± 1.67
Graphene-based resin	18.82 ± 4.62	18.82 ± 4.42

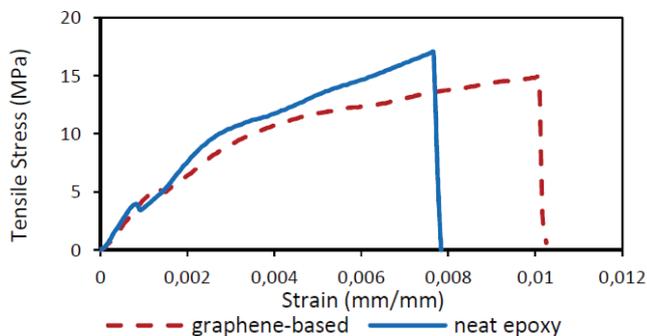**Fig. 5. Typical stress-strain curves for compressive stress [82]**

Fig. 6. Typical stress-strain behavior of tensile specimens [82]

As can be seen from the graphs, the relative deformations of the modified epoxy resin were 33 % higher when compressed and 50 % higher when stretched than the pure resin.

Numerous studies concerning the improvement of the mechanical properties of epoxy show that carbon nanotubes, nanofibers and graphene are effective modifiers [88–90]. Compression tests were carried out using a universal testing machine (Instron) in accordance with ASTM: D695, using five samples measuring 12.7 mm by 12.7 mm and 50.8 mm. The samples were tested at room temperature. For the tensile tests, five samples were prepared in accordance with the ASTM standard: D638. The tensile strength and modulus of elasticity were determined from the stretching curves. The bend was tested five samples with dimensions of 127 mm by 12.7 mm and by 3.2 mm in accordance with ASTM D790. Tests were carried out at a constant loading rate of 1.365 mm/min, at room temperature. Compression tests have shown that the destruction of a sample from a pure epoxy resin occurs suddenly along a plane inclined approximately at an angle of 45° to the normal section. Thus, in these samples, the destruction occurs due to the cutoff. In the samples from the modified epoxy resin, cracks

appeared first and only then there was a failure. Despite the fact that the samples from the modified epoxy resin showed a slight increase in strength, the relatively long plastic deformation during stretching and bending, as compared to the pure epoxy resin, makes it possible to expect to improve the performance characteristics of the modified composite.

Conclusion

Using the findings obtained in the study on the modification of epoxy resins, the following main conclusions can be drawn: modification of epoxy resins is a promising direction of improving their performance characteristics; the most effective modifier for improving mechanical characteristics is graphene; it is quite difficult to improve all the strength characteristics at the same time by modifying, but a significant increase in some properties is quite achievable.

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