

Modification of Epoxy Resins: Modern Condition and Prospects.

Part II. Graphene and Graphene Oxide Modification

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Abstract

The paper describes the functionalization methods of graphene and graphene oxide. It is shown that the modification of epoxy resins with functionalized graphene structures can significantly increase the strength characteristics, which expands the scope of epoxy resins in industry. The options for modeling the structures of functionalized graphene nanostructures and the possibility of predicting the performance characteristics of modified epoxy resins are also considered.

Keywords

Epoxy resin; graphene; graphene oxide; elastic modulus; impact strength.

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Graphene oxide

In [91], attention was focused on the fact that the key point of polymer modification is the uniform distribution of the modifier in the matrix, which, in turn, depends largely on the affinity of the modifier for the polymer matrix. Graphite carbon has a very weak affinity for most of the known solvents and is difficult to disperse in the most used polymers. This is true for all macro- and nanoforms of graphite carbon, such as carbon fibers, carbon nanotubes, graphene, etc. In polymer composites, these materials tend to form aggregates, especially at higher concentrations, thus degrading the mechanical properties of composite materials [92]. The most common strategy for solving this problem is to functionalize carbon nanofillers to improve their adhesion to the polymer matrix [92, 93]. In [94, 95], this method was used in introducing partially reduced graphene oxidize (GO) into an epoxy. Thanks to its highly oxidized nature, GO forms stable colloidal solutions in water as well as in several organic solvents by peeling monatomic layers. However, according to the authors of [91], this does not mean that the GO will spontaneously disperse in the polymer matrix. Solid GO does not dissolve in any solvent except water, but can be transferred from the aqueous

solution to the alcoholic phase by gradually changing water to alcohols [96, 97]. During this transfer, GO does not agglomerate and remains in stratified condition. This is a key point for the production of polymeric composite materials with uniform distribution of GO. In an ideal situation, GO must remain in the form of sheets with one atomic layer. This will ensure the most efficient distribution of GO in the matrix, since GO has functional groups of the same character as the functional groups of the epoxy. The solid GO is not evenly distributed in anything but water, so the main task is to introduce GO into the polymer matrix without merging layers. Epoxy does not mix with water, so a direct transition from the aqueous solution to the epoxy phase is not possible. It is necessary to develop a chain of solvents that would provide such a transmission. In [91], isopropyl alcohol (IPA) was used as an intermediate solvent between water and epoxy. It is well mixed with both water and epoxy. In the literature, there are several studies that report a successful modification of the epoxy GO [98 – 107]. In most cases, GO is introduced into the epoxy through a dispersion in acetone [100 – 105]. After mixing the dispersion of GO-acetone with the resin, one evaporates the solvent. According to another approach, GO can be introduced into the epoxy in the

form of aqueous suspension, after which the water should be evaporated [106, 107]. The authors of [91] believe that both methods do not create single-layer dispersions of GO in the epoxy matrix. In the transfer through acetone method, GO is introduced into the polymer matrix in the aggregated state, which means that from the very beginning, there is no guarantee that the single-layer graphene exists in the resin. When transferred through an aqueous suspension, GO coagulates after mixing two immiscible liquids: aqueous GO and epoxy. Many researchers have reported good results on epoxy modification with graphene using the two methods mentioned above (the method of acetone transfer gives an increase in the elastic modulus by 9 % and in strength by 18 % [108], while transferring through water gives an increase in compressive strength by 48.3 % and in impact toughness by 1185.2 % [102]). So in [91], the authors reproduced these two techniques for comparison, in parallel with the development of their own approach. In the modification, flocculates the size of 0.5 to 30 μm were used, with the most typical size being 5 – 20 μm . SEM images confirm that all the GO flocculates were monatomic. The fact that no ultrasonic treatment was performed is of particular interest. According to the authors, a GO sample was dissolved in the water within 30 minutes, under magnetic stirring. Thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) spectra showed that GO has an oxidation level typical of GO samples obtained by the modified Hummers method [109, 110]. The C/O ratio obtained from the XPS data is equal to 2/1 which confirms sufficient oxidation of GO. Thus, the GO sample used in this work had a typical oxidation level sufficient for spontaneous exfoliation on the monatomic layer sheets upon dissolution in water. At the first stage, a suspension of graphene in isopropyl alcohol was prepared. This suspension was obtained from an aqueous suspension of GO by gradually changing the water to IPA in accordance with the procedure described in [96, 97]. The remaining amount of water in the final suspension of GO–IPA, according to the dilution factor was 0.048 %. The final mixture was prepared by adding a suspension of GO–IPA to the epoxy and mixing up to uniform distribution GO in the epoxy. The IPA was removed by evaporation. Adding homogeneous and transparent GO–IPA gel to colorless and transparent epoxy resulted in a completely homogeneous and transparent mixture. The appearance did not change after removal of the IPA and curing, so we can assume that during the curing process there is no coagulation. The results of studying the transparency of samples with a microscope, which

confirmed the uniform distribution of GO in epoxy, are of particular interest. The authors of [91] believe that transparency is an additional confirmation of the fact that the GO plates are single-layered. In the industrial use of epoxides, modifiers are often added thereto to increase impact strength and flexibility, to reduce viscosity and shrinkage, etc. [111, 112]. In particular, diglycidyl ether 1,4-butanediol (DEB) is used to improve the fracture toughness of epoxides [113, 114], therefore in [91], samples from the three-component GO-DEB-epoxy composite were investigated. The three-component mixture GO-DEB-epoxy was completely homogeneous and transparent at all tested concentrations of GO. It is very important that the adding DEB allowed to increase the concentration of GO by more than 0.2 %, which is almost impossible when pure epoxy is used. The strength characteristics of the composites were also studied; in particular, the flexural modulus was measured in two ways: with the dynamic analyzer DMA 242 E Artemis, Netzsch, Germany and with the universal testing machine Instron 5882 in accordance with ASTM D790. It was found that adding GO to epoxy leads to a significant increase in the Young's modulus, but this increase is not directly proportional to the GO concentration. The DMA measurements demonstrated an increase in Young's modulus by 14 and 48 % at GO concentrations of 0.05 and 0.10 %, respectively. With the further increase of the GO concentration, the flexural modulus practically did not change. The Instron measurements showed slightly different flexural properties, but the maximum increase in the modulus of elasticity (48.7 %) was recorded at the GO concentration of 0.1 %.

Firstly, preparatory to testing the GO-DEB-Epoxy samples, the mechanical properties of an epoxy resin containing 10 % DEB, with pure epoxy resin, were compared. The flexural modulus of the samples were almost identical, i.e. a small amount of the modifier reduces viscosity of uncured resin without deterioration of mechanical properties.

Further, the mechanical properties of four GO-DEB-Epoxy samples with different GO concentrations were checked. All samples showed higher values of elastic modulus compared to pure epoxy resin. The increase of the elastic modulus of 9.1 and 12.1 % was registered for concentrations of GO 0.10 and 0.15 %, respectively.

Graphene obtained by microwave

As known, graphene can be obtained by using various methods [115]; the most frequently studied technology is graphite oxide graphite-graphene [116].

This technology is easily scaled, and the resulting product is used to modify polymer materials. Various methods for the synthesis of graphite oxide from graphite have been developed [117, 118]. But the properties of graphene in its oxidized form differ significantly from those of graphene. Oxygen-containing groups can be removed by reduction, but the structure and electrical ones are not completely restored [119]. One of the promising ways to achieve simultaneous exfoliation and reduction of graphene oxide is microwave exposure. Graphene obtained by microwave exposure contains a certain amount of surface functional groups, which positively affects the distribution of graphene in the polymer matrix [120]. Graphene obtained by microwave exfoliation and reduction of graphene oxide (**MERGO**) [121], due to functional groups, not only disperses well in the polymer matrix, but also ensures the formation of active chemical bonds between graphene nanoplates and the polymer matrix [122].

Numerous publications consider options for modifying epoxy resins with layered silicates [123, 124], single-layer and multilayer carbon nanotubes (**CNTs**) [125, 126], natural graphite [127], etc. [128]. The main problem with the use of **CNTs** is the formation of agglomerates in resin and high cost. Functionalized graphene is considered as a new effective modifier [129]. In [130], the efficiency of modifying epoxy resins with graphene, in comparison with **CNTs**, was proved to be more effective. To obtain **MERGO** [121], graphite powder was used; sulfuric acid (98 % by weight); phosphoric acid (85 % by weight); potassium permanganate; hydrogen peroxide; hydrochloric acid (35 %); ethanol. All chemicals were used as industrial grade, without further purification. Araldite GY 250 epoxy resin based on diglycidyl ether of bisphenol A (**DGEBA**) and triethylenetetramine (**TETA**) curing agent under the trade designation HY 951 were used as the matrix. The following technology was used in the preparation of **MERGO**. 3.0 g of graphite and 18 g of KMnO_4 were added to the mixture $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (360 : 40 ml). The reagents were heated to 50 °C and stirred for 12 hours. The mixture was cooled to room temperature and poured onto ice (~400 ml). The 30 % hydrogen peroxide was slowly added to the mixture until the solution turned bright yellow. The resulting yellowish brown mixture was centrifuged and the solid was washed successively with 200 ml of water, 200 ml of 30 % HCl and 200 ml of ethanol. Then 200 ml of ether was added. The solid GO obtained after evaporation of ether was vacuum dried overnight at room temperature. The dried GO powder was exfoliated in a microwave oven (T.D.S, model MW73BD) under ambient

conditions and 700 W for 1 minute. At microwave irradiation, a large volume of GO powder was formed, with strong smoke emission. Further, the required amount of **MERGO** was dispersed in acetone and added to the epoxy oligomer under mechanical agitation for 45 minutes, followed by sonication for 30 minutes. The resulting mixture was degassed at 40 °C in vacuo for 30 minutes to remove the solvent as well as air bubbles. The hardener was then added, followed by mixing and degassing. The mixture was then loaded into Teflon molds and held for 24 hours at room temperature. Final hardening was carried out at 80 °C for 4 hours. A complex study of GO and **MERGO** samples was carried out. The X-ray diffraction analysis (**XRD**) used graphite XRD, GO and **MERGO** templates. Samples were scanned in the range from 2 to 250 with a step of 0.020 at a wavelength of 1.541 Å, 40 kV, 35 mA. The Raman spectroscopy was used for non-destructive determinations of the characteristics of graphite structures. Raman spectra GO and **MERGO** were recorded with Horiba Jobin Yvon Lab Ram HR system with a resolution of 2 mm when using a 514.5 nm excitation laser. The X-ray photoelectron spectroscopy (**XPS**) was performed on the X-ray photoelectron spectrometer Kratos Axis Ultra (UK). The thermogravimetric analysis of the samples was carried out in a nitrogen atmosphere at a heating rate of 20 °C/min in TGA Q 50 (TA Instruments). In all cases, the weight of the sample was from 5 to 10 mg, at a temperature of up to 600 °C. Infrared Fourier transform (**FTIR**) spectra were recorded on Jasco FT/IR-4100. The UV-vis spectra were obtained on an ultra-sensitive spectrophotometer Evolution 201. The scanning electron microscopy (**SEM**) of graphite, GO, **MERGO** and epoxy and nanocomposites was carried out on the electronic microscope JEOL Model JSM.6390 LV. The surfaces of destruction of the composites were coated with gold to make them conductive. To carry out transfer electron microscopy (**TEM**), **MERGO** was dispersed in acetone by ultrasound and some pieces were collected on a 200 mesh copper mesh. For the E/**MERGO** nanocomposite, an ultrathin sample with a thickness of 70 nm was cut using Leica Ultracut UCT Ultramicrotome at room temperature. Thin sections were collected on a 200 mesh copper grid and examined using a JEM 2100 TEM at 200 kV in a bright field mode. In determining the mechanical properties for stretching, a Shimadzu universal testing machine was used at a speed of 5 mm/min at room temperature according to ASTM D 638. The flexural properties were determined using rectangular rods on the same machine at a speed of 10 mm/min according to ASTM D790. Impact strength was measured according to

ASTM D 4812-99 on the Impact Analyzer (Junior) at a speed of 3.96 m/s. Three-point bending tests were performed according to ASTM D5045 using rectangular patterns at a speed of 10 mm/min. The improvement in the mechanical properties of composites was observed with an increase in the concentration of MERGO to 0.25 %. At this concentration, an increase of 32, 103, and 85 % of the tensile stress, toughness, and flexural modulus was observed, respectively, compared to pure epoxy resin. With a further increase in the MERGO concentration, deformation before fracture decreases, most likely due to the rigidity of graphene, which limits elongation and hence deformation. Because MERGO behaves as a functionalized graphene, it can form chemical bonds

with DGEBA, which improves interphase connections. Epoxy functional groups MERGO can also react with an amine curing agent. In addition, the wrinkled MERGO topology will create an improved mechanical interlock and adhesion to the epoxy chains and, therefore, enhances the interaction and transfer of the load between MERGO and the epoxy matrix. When the distribution of the fillers is more uniform and there is no obvious agglomeration, stress transfer between the fillers and the epoxy matrix is more effective [131]. The MERGO dispersion is good at lower concentrations, and at higher values, due to the numerous MERGO/MERGO interfacial contacts, the mechanical properties of the nanocomposites deteriorate [132].

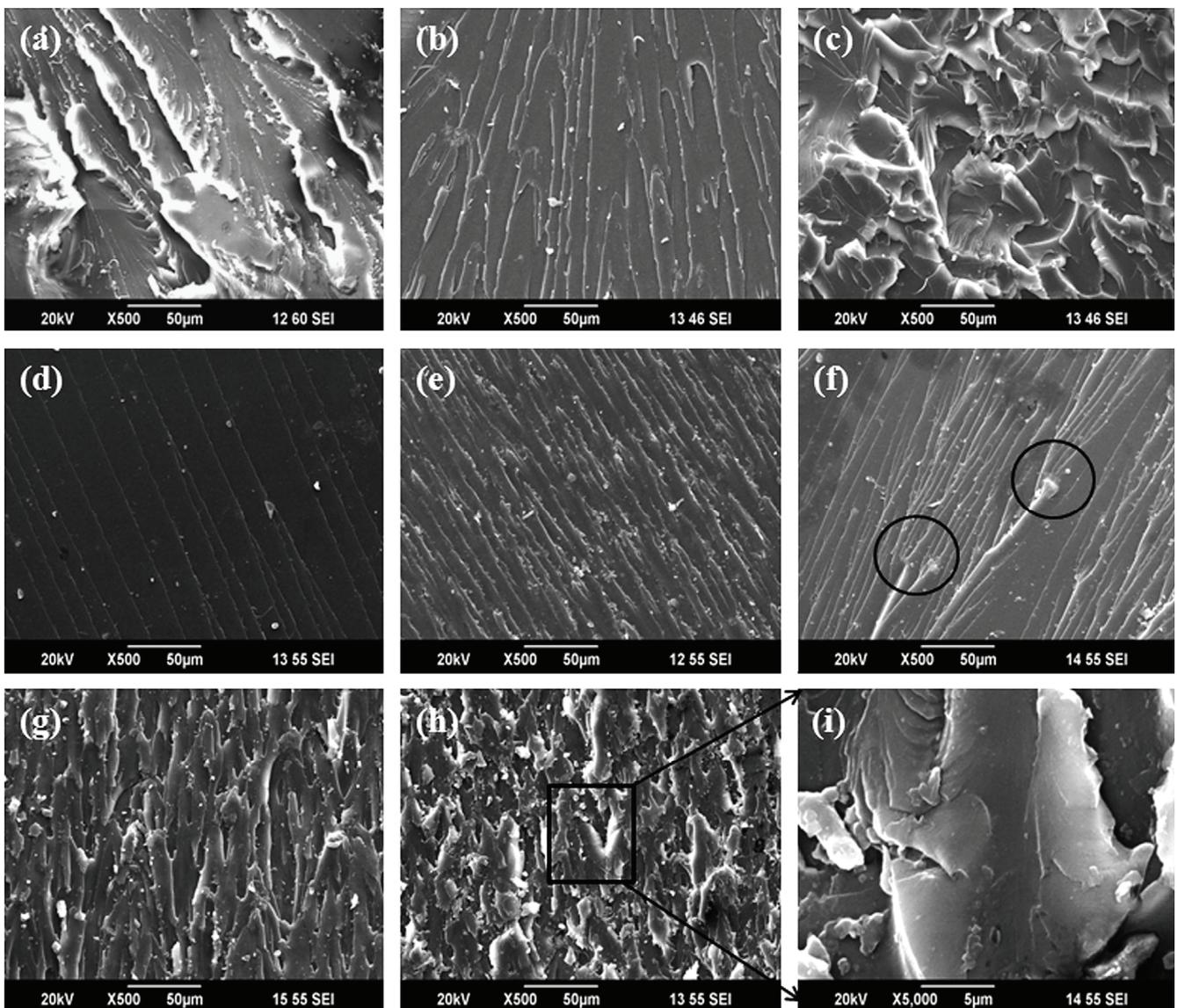


Fig. 7. SEM photographs. (a, e, c) Fractured surfaces of tensile test specimens of (a) pure epoxy, (b) E/MERGO at 0.25 phr, (c) E/MERGO at 0.5 phr. (d, e, i) Fractured surfaces of SEN-TPB test specimens of (d) pure epoxy, (e) E/MERGO at 0.1 phr, (f) E/MERGO at 0.25 phr, (g) E/MERGO at 0.5 phr (h, i) E/MERGO at 1 phr nanocomposites [132]

The SEM image shown in Fig. 7a is a crude epoxy resin with a relatively smooth surface and irregular river patterns. The resistance of the material during crack propagation is minimal and leads to brittle fracture, which explains the low fracture viscosity of unfilled epoxy resin. Fig. 7b and 7c show the surfaces of the nanocomposite containing 0.25 and 0.5 phr MERGO, respectively. A significant difference is observed between the destructive surface of pure epoxy resin and the E/MERGO system. By adding 0.25 phr MERGO (Fig. 7b), the surface becomes rough due to the dispersion of graphene nanolayers in the epoxy matrix. Good compatibility between graphene and the epoxy matrix makes it difficult to propagate the crack. From Fig. 7c, it is clear that there is an irregular entanglement of the nanoscale at higher MERGO contents. The morphological studies of the fracturing surfaces of pure epoxy resin samples and E/MERGO nanocomposites were also checked by SEM and the corresponding micrographs are shown in Fig. 7d, e, i. Pure epoxy resins have a smooth mirror surface (Fig. 7d). Specimens of resin modified by MERGO (Fig. 7e) have a rougher surface, indicating that the presence of MERGO caused the crack to spread along a very tortuous path. Fig. 7f shows how the crack deviated when it was faced with a hard inclusion. The effect of the bridge, which prevents the opening of a crack, increases strength in E/MERGO nanocomposites.

MERGO sheets are embedded in matrices and tightly held by epoxy resin, as shown in Fig. 7g. The rougher surface of the crack is shown in Fig. 7h and with a larger magnification (Fig. 7i), one can see how a single graphene or a stack of graphene several nanometers thick protrude from the surface of the crack. Thus, using various methods (XRD, Raman, EDX, TGA, XPS, FTIR, C13 NMR, SEM, TEM and UV-vis), it was found that modifying MERGO improves both the mechanical and technological characteristics of polymer nanocomposites, which are widely used in various industries.

Inorganic nanomaterials

The effect of nanomaterials on the thermal and physical characteristics of various epoxy resins was studied in [133]. It was found that these characteristics are influenced not only by the modifying material, but also by its compatibility with a particular resin brand. Apparently, a similar situation develops when trying to improve the physical and mechanical properties of epoxy resins. In industrial use, the most common classical epoxy resins (ER), such as bisphenol A. The study of the structure showed that the molecular

chain of the resin contains more reactive functional groups, such as the ester bond, epoxy groups, and hydroxyl. This structure gives ER excellent chemical properties, such as high viscosity, good compressibility, high stability, and good alkaline resistance, etc. [134]. Thus, the ER is widely used in construction, electronics, aerospace, military and other industries. However, since the ER contains many benzene or heterocyclic rings, the flexibility of the molecular chain is poor, the cross-linked epoxy resin has a high density, and the cross-linked structure is difficult to deform along with the high internal temperature, which causes the solidified EP to be brittle and have poor impact resistance. All this, to some extent, limits the use of ER in many high-tech areas [135].

Rubber elastomers are most widely used in the ER modification, but this significantly reduces the strength of the EP and the glass transition temperature of the system. Organic silicone resins are usually organic-inorganic polymers based on the molecular chain of Si-O-Si bonds, with the silicon atom combined with organic groups. Since the Si-O-Si bond length is longer and the bond angle is large, the shielding effect of the methyl group on the silicon-oxygen chain reduces the interaction between the silicon-oxygen bond, so that the flexible segment of the spiral structure can improve the flexibility of the resin [136]. Meanwhile, silicone has high thermal stability, low surface energy, flexibility at low temperature, etc., but has low adhesion strength, weak bonding properties. Thus, it can be expected that the modified silicone ER will give an additional effect. Researchers believe that the introduction of functional groups, such as hydroxyl, carboxyl, amino, etc., which can react with the epoxy group and silicone, can improve compatibility [137].

Currently, groups introduced into silicone to improve compatibility include polar phenyl groups and polyether chain links. They increase the polarity of silicone molecules and its compatibility with epoxy resin [138]. The main methods of ER modification using silicone are as follows: the reaction between isocyanate and active hydrogen; radical polymerization; condensation reaction; reaction between reactive groups and epoxy groups; hydrosilylation of polysilanes containing Si-H and vinyl resin groups [139]. A hybrid material was obtained on the basis of silicone acrylate and epoxy resin by copolymerization. The result showed that the mass fractions of tetraethyl orthosilicate (TEOS) are 15 and 25 %, the average diameters of SiO₂ particles of the inorganic phase in the hybrid material are 36 and 45 nm, respectively, and the SiO₂ nanoparticles are homogeneously dispersed inside the polymer. Inorganic nanomaterials used in the EP modification include SiO₂, TiO₂, and graphene.

Compared with other inorganic materials, graphene has practically no impurities, but has a high modifying efficiency [140].

Graphene oxidize is used because it has oxygen-containing functional groups, such as hydroxyl, carboxyl, and epoxy. The GO combines with the ER to form a new bond, which improves dispersion and interfacial adhesion [141]. A graphene/epoxy resin composite was made using in-situ reduction, in which the GO was partially recovered. As a result, tensile strength and flexural strength were increased by 40.5 and 9.4 %, respectively [142].

In [143] it was concluded that a binary or even triple modification of epoxy resin is needed in the future for further functionalization and high performance in order to increase the compatibility of the modifying additives with the resin and improve its performance while ensuring low cost.

Functionalized graphene oxide

As noted above, the use of epoxy resin is sharply limited by its brittleness and poor resistance to crack propagation. In general, the properties of epoxy are determined by its own structure [144]. To compensate for the shortcomings of epoxy resin use a variety of nanometer particles [145]. However, not always, the addition of nanometer-sized particles can effectively improve the mechanical properties of the matrix [146]. In recent years, graphene is widely used as a reinforcing nanofiller for a polymer with the formation of functional and structural composites [147] in the form of expanded graphite, graphite nanometer platelets and graphene nanometer tapes. Due to the π - π interaction of aromatic stacking and strong attraction

between graphene sheets, there is an aggregation of two or more graphene nanometer sheets, which limits the use of graphene [148]. To avoid the above problems, graphene is sonicated for several tens of minutes and with increasing frequency and processing time, the space between the graphene layers gradually increases. It should be noted that the product treated with ultrasound is sufficiently pure [149]. The structure of graphene plays an important role in increasing the mechanical effect of blocking and the redistribution of stresses in the composite material.

In work [150], graphene oxide and nano particles of copper were chosen as materials for the reinforcement of epoxy resin, since copper effectively increases heat resistance and is relatively inexpensive. The GO was prepared from natural graphite powder by the modified Hummers–Offeman method. To allow the GO to fully react during the reaction, the prepared GO was sonicated for 30 minutes at 308 K. At the same time, the dissolved copper sulfate in distilled water was sonicated for 30 minutes. The aforementioned solution of CuSO_4 and GO was placed in a three-neck flask and also sonicated at room temperature for about 40 minutes to ensure even distribution. After sonication, the mixture was heated and stirred in a water bath. When the temperature of the water bath rose to 343 K, sodium hydroxide solution was added to make the solution alkaline. The hydrazine hydrate solution was added as a reducing agent and stirred for 2 hours in a water bath. After the reaction, the product was cooled to room temperature, filtered and then washed with plenty of distilled water and anhydrous ethanol. The wet product was dried in a vacuum oven for 24 hours.

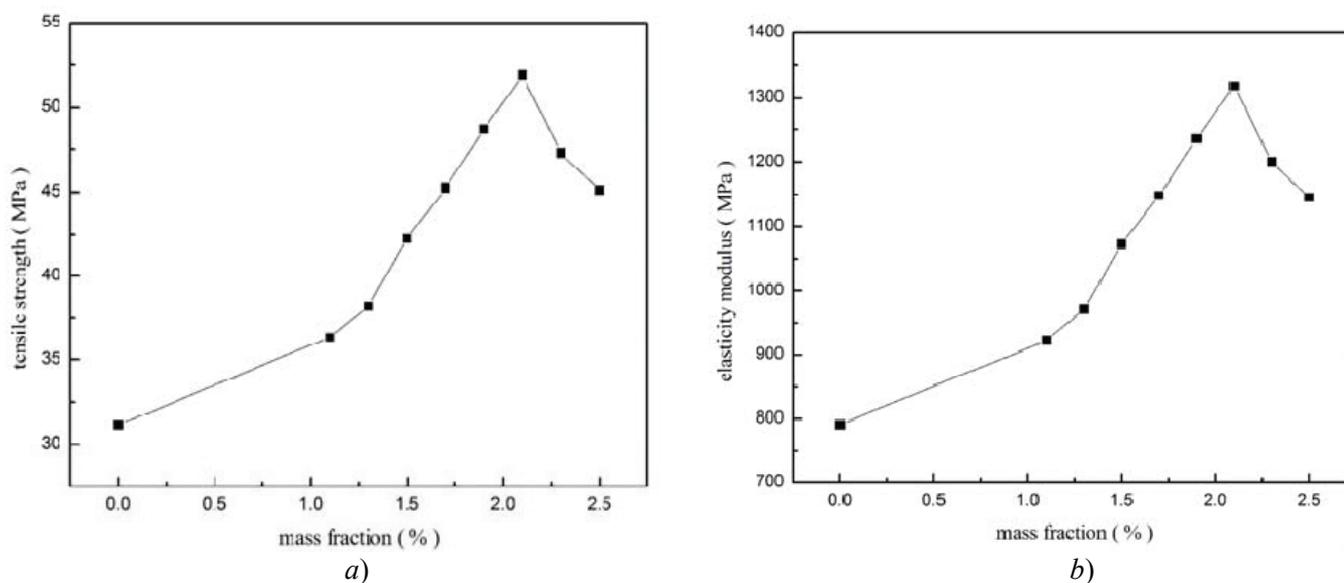


Fig. 8. Tensile strength (a) and elasticity modulus (b) curve of ER/graphene/nanocopper composites [150]

Then the hardener and the mold were preheated at 333 K for 2 hours. The epoxy resin and a fixed amount of graphene/Cu were mixed using a high shear machine for 6 minutes at 8,000 rpm. Then the composition was placed in a vacuum oven at 323 K for 6–7 days to remove bubbles and the remaining solvent. Next, the hardener was mixed with the compositions and stirred for 5 minutes until a uniform mixture was formed. The mixture was poured into a preheated form of PTFE, cured at 348 K for 2 hours, at 398 K/2.5 h, at 423 K/1 h. To improve the mechanical properties, graphene/Cu was added to the epoxy resin.

The graphs in Fig. 8 show that with an increase in the graphene/Cu content, the ultimate tensile strength and elastic modulus tend to increase and reach a maximum at a concentration of 2.1 wt. %. With increasing graphene/Cu content, the tensile strength and modulus of elasticity of the composites decrease. Thus, at a graphene/Cu concentration of 2.1 wt. %. The shear strength of the composites reaches a maximum value of 34.78 MPa, which is about 69 % higher than the shear strength of pure epoxy resin. In addition, the addition of graphene/Cu improves the thermal stability of the cured epoxy resin.

Modeling the structure of modified graphene oxide

In [151], computer models of the most probable types of possible configurations of low-layer graphene (few-layer graphene) and polymer molecules are considered. Widely used polymers, polyethylene (PE) and polydimethylsiloxane (PDMS), were used as model polymer structures. First of all, the edges of graphene nanostructures were considered as probable zones for the attachment of polymer molecules to graphene nanofragments, assuming the existence of a large number of free bonds there. Studies of the energy characteristics of possible structures showed that, under certain conditions, it was possible to form covalent bonds between fragments of graphene and PE molecules. Calculations showed that at the first stage in the contact zone one or two hydrogen atoms transfer from the PE molecule to the edge carbon atoms in the graphene structure, as a result of which free bonds appear on the polymer molecule. After that, a C–C bond was formed between the PE molecule and the edge atoms of graphene. A clear change in the spatial arrangement of hydrogen atoms on the PE molecule and its deformation should be noted. When the molecule was located parallel to the surface of ideal graphene, the binding energy was mainly determined by the van der Waals interaction, and the formation of strong bonds was possible only at the ends of the

graphene fragment. Simulation and calculation of the configuration with a defect in the structure of graphene showed that in this case, the formation of covalent bonds between the molecule and carbon atoms in the zone of the defect was possible. To create composites, several types of polymer matrices were used – polyethylene, PVA, epoxy resin. An experimental sample of PE was formed in the form of a “sandwich” of two thin films $\sim 3 \mu\text{m}$ thick, between which graphene fragments were distributed. Polyvinyl alcohol (PVA) is an artificial, water-soluble, thermoplastic polymer, which is an excellent emulsifying, adhesive and film-forming polymer. It has high tensile strength and good flexibility. PVA is stable against oils, fats and organic solvents. In addition, during the work a new graphene-PVA composite was prepared. Graphene was prepared by chemical vapor deposition on a copper substrate and then transferred to a film. The resulting composite was PVA-graphene-PVA, which has good electrical conductivity, transparency and high mechanical properties. Based on the results of measurements of microhardness of specimens, the addition of graphene structures led to a significant increase in hardness. Also, the addition of graphene structures increased the strength characteristics, since when testing with high loads on the PVA film, cracks were formed, and when adding low-layer graphene at high concentrations, no cracking was observed. Adding more graphene oxide increases the concentration of graphene structures, and as a result, hardness values increase.

In [152], GO was prepared using a modified Hummer method from extended acid graphite flakes [153]. The reduced graphene oxide (rGO) was prepared using benzylamine as a reducing and functionalizing agent [154] and sodium borohydride as a reducing agent [155, 156]. To characterize chemical parameters (SEM, XPS and Raman spectroscopy), GO and rGO were precipitated from a suspension on Si/SiO₂ substrates by immersion and dried at 80 °C. To determine optical parameters and study morphology using atomic force microscopy (AFM), GO and rGO were precipitated on fused quartz windows using a homemade applicator and slowly dried at 40 °C. Graphene oxide flakes had a relatively large surface (micrometers) and its morphology resembled a thin curtain. These parameters indicated a very good exfoliation of graphite during the oxidation process. The rGO sheets deposited on the Si/SiO₂ substrate overlapped more and seemed to form a compact structure. The surface morphology resembled a heavily folded curtain, which indicated that the rGO flakes overlapped rather than aggregated. The relative

intensity of both peaks (D/G) is a measure of the degree of disorder and is inversely proportional to the average size of the sp^2 clusters [157, 158]. It was found that for rGO the intensity D/G was greater than for GO (1.70 and 1.21, respectively). It was assumed that new graphite domains were formed, and the number of sp^2 clusters increased after the process described above, demonstrating the good efficacy of reducing benzylamine and sodium borohydride.

Graphene is a two-dimensional layer with carbon-carbon sp^2 -hybridized covalent bonds that lead to very good mechanical properties. However, the crystalline and smooth surface of graphene prevents the adhesion of graphene to the polymer matrix. There is reason to hope that the covalent bond of functional groups with graphene can solve this problem [159]. The presence of functional groups affects the mechanical properties of graphene due to changes in hybridization and the introduction of defects. In particular, a change in the carbon bonds from sp^2 to sp^3 leads to the elongation of bonds between the sp^3 carbon and its neighboring sp^2 hybridized atoms [160]. The influence of functional groups on the mechanical properties of graphene was considered by several authors using molecular dynamics (MD), in particular, the density of transplanted, orientation and/or location of hydroxyl, methyl and carboxyl groups [161 – 163]. On the other hand, the adhesion between the polymer and graphene is connected with the chemistry of both surfaces and due to the covalent bonding of the chemical groups of graphene and the polymer matrix, the efficiency of load transfer can be improved [164]. Thus, it is necessary to find a compromise between increasing the possibility of load transfer and reducing the mechanical properties of graphene due to functionalization.

The interphase bonds of graphene with vinyl ether were investigated using molecular dynamics (MD) [165], and a comparison was made for two different matrices: polyethylene; polymethyl methacrylate [166]. In [167] the MD used to calculate the interfacial shear strength (ISS) between epoxy resin and functionalized graphene layers. Each layer had one type of chemical group, carboxyl, carbonyl, and hydroxyl, and was dispersed on graphene with a 10 % concentration. Their mechanical and structural properties, the effect of concentration (3.0 and 5.0 %) and the placement of hydroxyl groups were also assessed. The value of Young's modulus for pure graphene turned out to be close to what is reported in the literature for modeling MD [168 – 170]. Young's modulus of pure graphene turned out to be equal to 1.35 TPa, which is due to its

hybrid sp^2 -structure. Both groups –COOH and –OH groups reduced the Young's modulus of graphene by 42 and 47 %, respectively. The largest drop was observed for carbonylated graphene, and equaled 53 %. The interaction energy was estimated by the difference between the total potential energy of the composite and the sum of the potential energies of the individual molecules. The results showed that the force required to draw pure graphene from the polymer is much less than for functionalized layers. Apparently, carbonylated graphene interacts very well with epoxy. In general, the results of studies showed that the improvement in interfacial strength can be realized using carboxyl functional groups.

Graphene quantum dots

The studies of the features of graphene quantum dots started almost simultaneously with the production of graphene [171]. When the lifted graphene film formed a dome, the area at its top acquired the properties of a quantum dot, i.e. a semiconductor in which electrons are held in a small region of space. According to the researchers, this effect is explained by the fact that the flow of electrons through graphene is determined by its hexagonal structure. When stretching hexagons, the energy near the top point of the graphene film decreases, forcing electrons to move in orbits that resemble the shape of a leaf of clover – almost as if they moved in a vertically changing magnetic field. Considering the electrochemical activity of quantum dots, it can be assumed that they will have a significant influence on the behavior of graphene when modifying polymers. Graphene quantum dots (GQDs) are a kind of 0D material with characteristics derived from both graphene and compact discs, which can be considered as incredibly small pieces of graphene [172 – 175]. Transforming two-dimensional graphene sheets into 0D GQD, GQDs exhibit new phenomena due to quantum confinement and edge effects [175].

Conclusion

Through the analysis of the results of studies on the modification of epoxy resins, we can draw the following main conclusions:

1. Modification of epoxy resins is a promising direction for improving their performance.
2. The most effective modifiers for increasing mechanical properties are graphene and graphene oxide.
3. Due to the functionalization of graphene, it is possible to purposefully improve certain characteristics

of epoxy resins, such as impact strength, elastic modulus, hardness, etc.

4. The main problems in the modification of epoxy resins with graphene are: weak bonds between the graphene and the polymer matrix; uniformity of graphene distribution in epoxy resin.

These conclusions bring us to the problems of further research, namely, studying the effect of functional groups on the relationship of graphene with the polymer matrix and to determine the type of functionalization of graphene depending on the properties of the matrix; selecting the type of intermediate solvent, as well as methods and regime parameters for the introduction of graphene into epoxy resin.

In addition, a serious factor hindering the industrial use of graphene for modifying epoxy resins is its high price. Fiberglass internal reinforcement for concrete products is widely used in many countries, and its performance depends largely on the strength properties of the binder, which is epoxy resin [176]. Thus, for a significant expansion of the industrial use of modified epoxy resin with enhanced performance characteristics, it is necessary to develop new technologies for the production of graphene and graphene oxide.

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