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Strength properties of epoxy resin modified with few-layer graphene

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The article presents the results of a study of the efficiency of few-layer graphene obtained under conditions of self-propagating high-temperature synthesis as a modifying additive in the creation of polymer composites based on epoxy resin. It was found that the introduction of few-layer graphene increased the bending strength and wear resistance of epoxy resin by 70% and 50%, respectively. This method of synthesizing few-layer graphene enables the acquisition of large volumes of high-quality material at an acceptable cost, making its use in polymer composites cost-effective.

Keywords: graphene, nanocomposites, epoxy resins, self-propagating high-temperature synthesis, few-layer graphene.

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Introduction

To date, polymer modification with carbon materials is one of the most widespread methods for producing durable and wear-resistant carbon- matrix-based materials. A classical example is introduction of carbon black into rubbers to achieve durable and UV-resistant rubber. Over the past two decades, the most popular technique in this field is polymer modification with carbon nanomaterials such as graphene, carbon nanotubes, carbon nanofibers and fullerenes. Interest in these materials is caused by high stress-strain and thermophysical properties. For example, thermal conductivity of graphene is about 5000 W/(m·K), Young's modulus is about 1 TPa, while its specific surface area is estimated at 2630 m^2/g [1]. With uniform distribution in and good adhesion to the matrix, such filler will facilitate increased bending and tensile strength, wear resistance, thermal conductivity and heat capacity.

Epoxy resin is used as a polymer base in such composite materials due to its chemical resistance to alkali and acids, and high adhesion to metals, which makes it possible to use it as anticorrosion coatings [2]. Epoxy resins are also used in carbon fiber-reinforced plastic production, and it has been already demonstrated that modification of epoxy resin/carbon fiber composite materials with graphene particles leads to the increase of bending strength of these composite materials [3].

The objective of this study was to investigate stress-strain and thermophysical properties of composite materials on the basis of epoxy resin modified with few-layer graphene. A self-propagating high-temperature synthesis technique was chosen to produce few-layer graphene. This technique is used to produce large amounts of few-layer graphene at minimum cost.

1. Experimental

Few-layer graphene was synthesized by the self-propagating high-temperature synthesis technique from dextrose (99.9%, Sigma-Aldrich, № 9004-34-6) using a procedure described in [4]. Images of the sample were made by the scanning electron spectroscopy (SEM) using the Mira-3M (TESCAN) scanning electron microscope. For SEM imaging, the powdered few-layer graphene sample was applied to double-sided carbon conductive carbon tape 8 mm in width (TED PELLA, INC.). X-ray diffraction analysis was performed on the Rigaku SmartLab 3 X-ray diffractometer (CuK_α, wavelength $\lambda = 0.154051$ nm). IR spectra of few-layer graphene were recorded using the Infralum FT-08 (Lumex-Marketing) spectrometer. The Raman spectrum of few-layer graphene was examined using the Confotec NR500 (Belarus) spectrometer with 532 nm laser wavelength. Few-layer graphene particle sizes were measured by the laser diffraction on the Mastersizer 2000 (UK), for this, 50 mg of few-layer graphene was dispersed in 50 ml of deionized water by shaking or ultrasonic treatment using a 60 W or 100 W transmitter during 15 min.

To examine the interaction between few-layer graphene and epoxy resin, few-layer graphene was subjected to vacuum annealing to remove all functional groups from the surface. 1 g of few-layer graphene was placed into the furnace (VTSh-K52-250, Oktan), then the atmosphere was evacuated to $6.6 \cdot 10^{-3}$ Pa. Then, the furnace was heated to 1100°C at a heating rate of 15°C/min, the sample was annealed at 1100°C during 2 h.

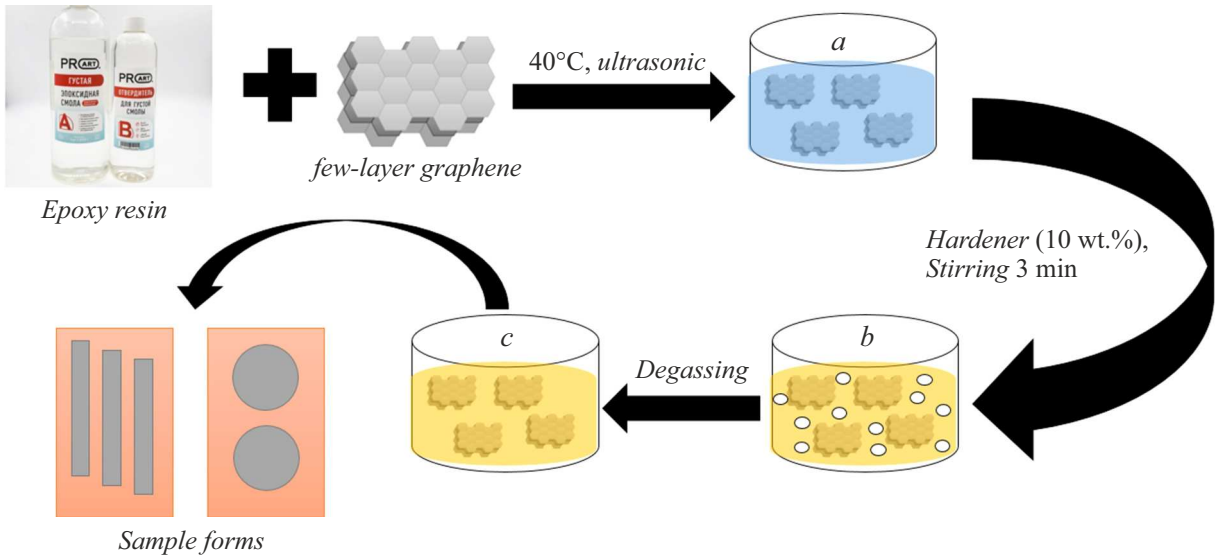

Figure 1. Flow diagram of composite material production from epoxy resin modified with few-layer graphene.

Epoxy resin composite materials were made as shown in the flow diagram in Figure 1. Initial KER 828 epoxy resin (South Korea) (mass fraction of epoxy groups 0.53 mol/g) was mixed with few-layer graphene in a ultrasound bath at 40°C (Figure 1, *a*), then hardener, tetraethylene tetramine (TETA), was added (Figure 1, *b*). The mixture was stirred in a overhead stirrer, then degassed with air evacuated until full removal of bubbles (15 min) (Figure 1, *c*). Then, the mixture was poured into moulds to make bend test samples ($80 \times 12 \times 2$ mm), friction test samples ($d = 40$ mm, $h = 4$ mm), thermal conductivity ($50 \times 50 \times 10$ mm) and hardness ($d = 30$ mm, $h = 6$ mm). Bending strength was measured in accordance with GOST 4648-2014 (ISO 178:2010), by the three-point method using the PM-MG4 test machine, loading rate 15 mm/min. Brinell hardness was determined by spherical indentation measurement ($d = 5$ mm) with loading of 62.5 kgf during 60 s using ITB-3000-AM (Russia) hardness tester. Shore hardness was determined by conical indentation using the Shore C Durometr LX-C-Y (China) hardness tester.

Thermal conductivity was measured by the hot disc method per GOST 34374.2-2017 (ISO 22007-2:2015) using the HS-DR001 (China) thermal conductivity tester. The method uses a temperature sensor in the form of a thin disk combined with a heat source and placed into the center of the test sample. Electric current flowing through the sensor induces a heat pulse in the form of a step function that generates a dynamic temperature field in the sample. Sensor temperature increase over time is measured [5]. Wear resistance and friction coefficient (steel/polymer) were measured on the UMT-200 (Russia) multipurpose friction machine, disk–cylinder friction scheme. An upper body of revolution is pressed against a lower body (which is the test sample) rigidly mounted on the support. When the upper body rotates, the lower body and support start rotating, and the support applies pressure to a strain gauge whose readings are used to calculate the moment of force M. Then, the friction coefficient was calculated using the following equation

$$\mu = (M/F \times R_1/R_2),$$

where M is the moment of force, F is the pressure force between the upper body and lower body, R_1 is the sample radius, R_2 is the radius of friction mark made by the upper body of rotation. Wear resistance was measured by the decrease in the pressure force over time.

2. Discussion of findings

The structure of few-layer graphene made by the self-propagating high-temperature synthesis was demonstrated many times in our previous works [6–8]. For the purpose of this study, few-layer graphene was made from dextrose. Figure 2, *a* shows that few-layer graphene particles are slices with even edges. Note also that the sample contains particles that differ very much from the slices in their shape. The EDX analysis detected oxygen atoms (12 at.%) and nitrogen atoms (15 at.%) on the few-layer graphene surface. These atoms are generated by the few-layer graphene production procedure because a large amount of nitrogen and oxygen is released in the synthesis process when ammonia nitrate is decomposed. Y-ray photograph of few-layer graphene (Figure 2, *b*) contains an X-ray amorphous halo with a maximum at $2\theta = 23°$ that is typical for graphene [9]. The Raman scattering spectrum (Figure 2, *d*) contains three principal bands: D — at 1362 cm^{-1}, G — at 1600 cm^{-1} and $2D$ — at 2800 cm^{-1} that are typical of graphene oxide or reduced graphene oxide [10]. Such spectrum form indicates that there are various defects in the few-layer graphene structure, including sp^3-hybridized carbon atoms,

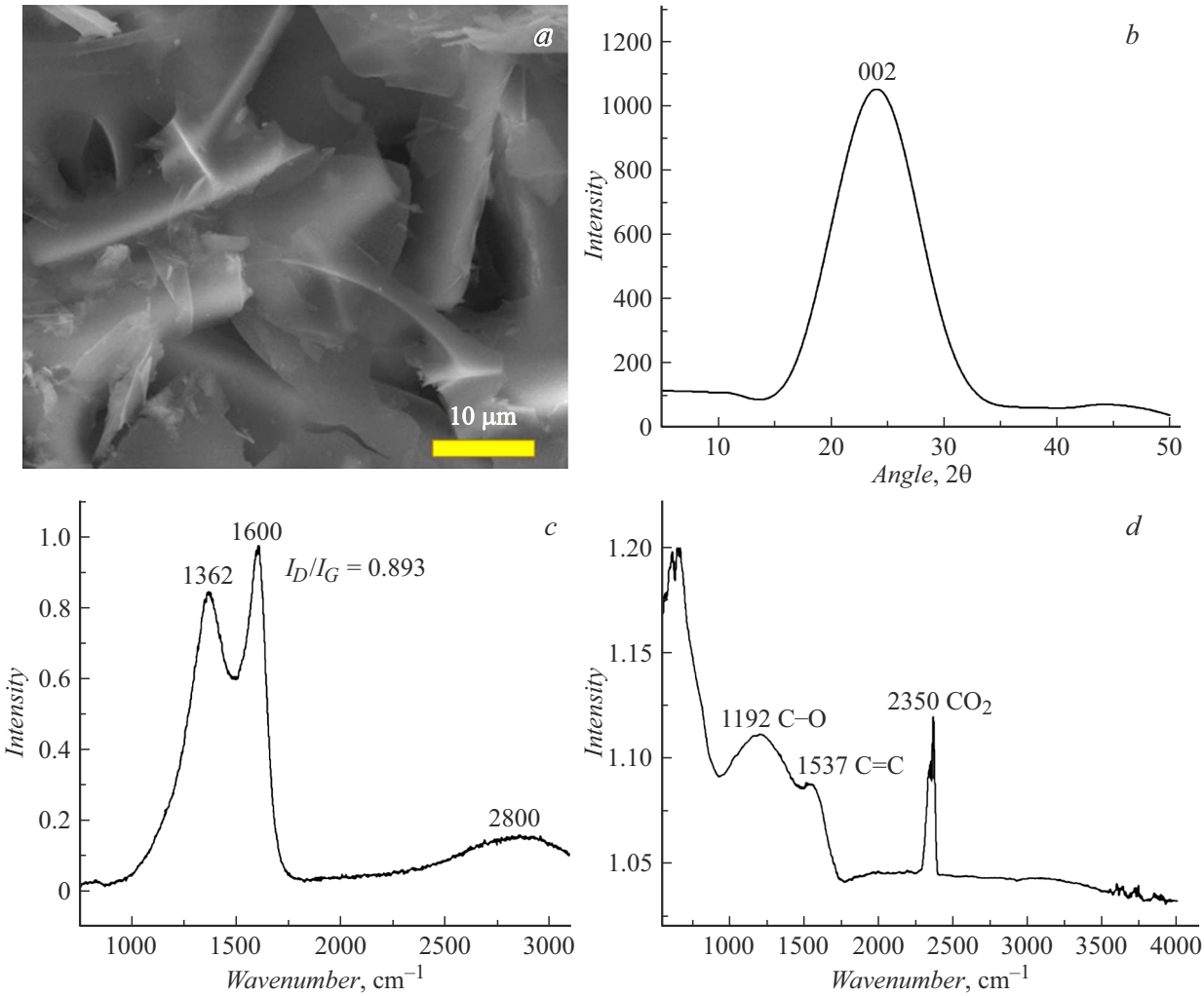

Figure 2. *a* — SEM image, *b* — X-ray pattern, *c* — RS spectrum and *D* — IR spectrum of few-layer graphene.

heteroatoms and dislocations. The IR spectrum of few-layer graphene (Figure 2, *d*) shows the bands that are responsible for vibrations ofC−O (1192 cm^{-1}) and C=C (1537 cm^{-1}) bonds, there is also a band at 2350 cm^{-1} that is responsible for molecular vibrations of CO2 that is present in air.

When few-layer graphene powder is added to epoxy resin, the bending strength decreases (Figure 3, *a*), and the higher the concentration of few-layer graphene, the lower final composite material strength is compared with pure epoxy resin. Epoxy resin hardening at the phase interface may cause stresses that in turn lead to cracking.

To remove the stresses induced after epoxy resin hardening, the samples were placed into a muffle furnace and annealed for 1 h at 100°C. A small growth of bending strength was eventually achieved at a few-layer graphene concentration of 0.1 wt.%. Further increase in the few-layer graphene concentration in annealing doesn't lead to any significant decrease in strength as opposed to unannealed samples. Note also general increase in the bending strength after furnace annealing, which is caused by additional cross-linking of epoxy resin by a hardener [11]. Figure 3, *b* shows that introduction of few-layer graphene doesn't affect the epoxy resin hardness, and furnace annealing increases the hardness of all samples for the above-mentioned reason.

Due to high surface energy, the few-layer graphene particles may agglomerate [12], and when the few-layer graphene powder is introduced into the epoxy resin, few-layer graphene particle aggregates are actually introduced, therefore, the desired strength growth cannot be achieved for composite materials compared with pure epoxy resin.

To solve this problem, few-layer graphene was dispersed in isopropyl alcohol (AR) using ultrasonic treatment at different powers (60 W or 100 W). Then the prepared suspension was added to the epoxy resin and followed by alcohol evaporation in vacuum. After alcohol evaporation, the resin polymerization process was performed as described in the experimental section and followed by furnace annealing of the samples. Flow diagram of this process is shown in Figure 4: powdered few-layer graphene was added to epoxy resin (Figure 4, *a*), few-layer graphene was dispersed in alcohol using an ultrasonic bath (60 W) (Figure 4, *b*), few-

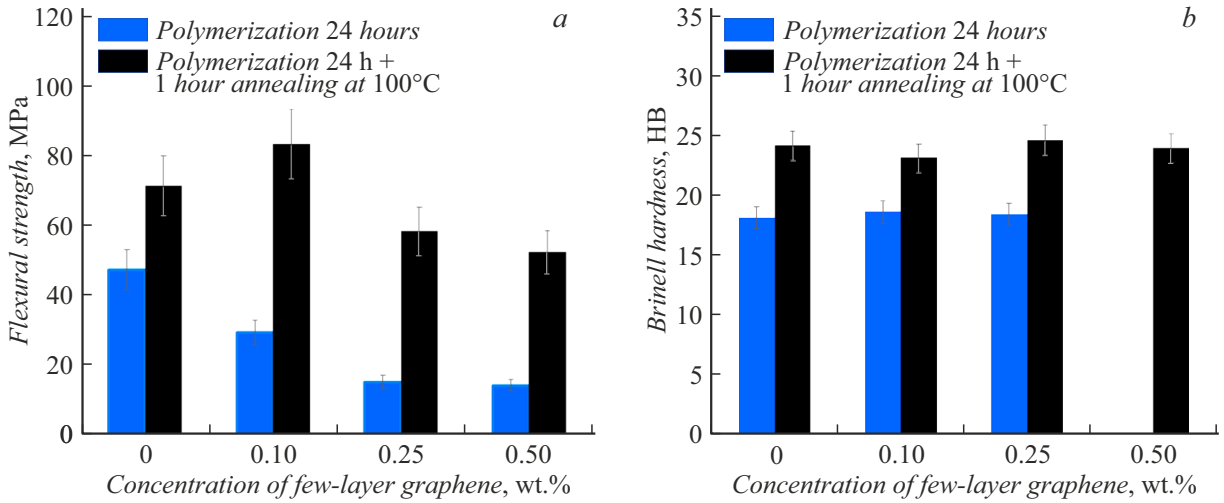

Figure 3. Dependence of the bending strength (*a*) and Brinell hardness (*b*) on the few-layer graphene concentration in epoxy resin.

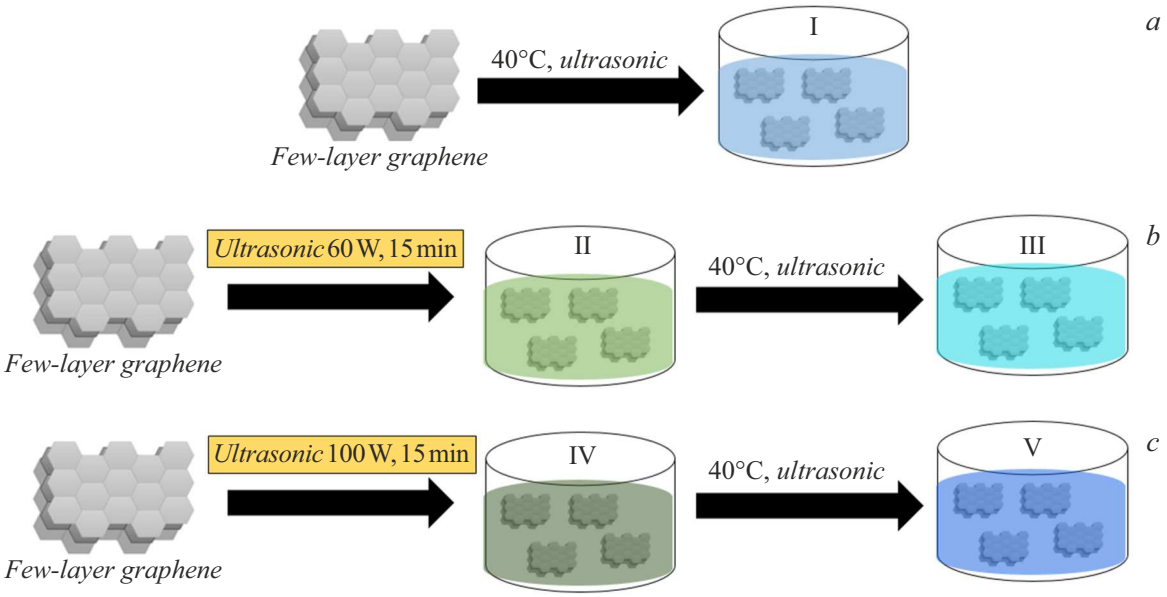

Figure 4. Flow diagram of few-layer graphene introduction into epoxy resin: *a* — without disaggregation, *b* — 60 W ultrasonic disaggregation, *c* — 100 W ultrasonic disaggregation.

layer graphene was dispersed in alcohol using an ultrasonic probe transmitter (100 W) (Figure 4, *c*).

Thus, the maximum growth of bending strength was achieved when using a more powerful ultrasonic treatment for few-layer graphene dispersion. Figure 5, *a* shows that, when a few-layer graphene concentration was equal to 0.1 wt.% and 100 W probe ultrasound was used, the bending strength of epoxy resin from 70 MPa to 120 MPa was achieved. A strength growth is observed at higher concentrations compared with pure epoxy resin: Introduction of disaggregated few-layer graphene has no any significant effect.

Few-layer graphene aggregate sizes were measured before and after US treatment at various powers. Increase in the US treatment power causes the decrease in mean particle sizes of few-layer graphene (Figure 6). The maximum of few-layer graphene aggregate size distribution without US treatment is in the range from 0.75 to 0.8 μm. The few-layer graphene particle size distribution curve also has a wide shoulder from 1 to 5 μm, which indicates that particles with this size are present in the powder. As a result of ultrasonic treatment of few-layer graphene powder at a transmitter power of 60 W, the mean particle size distribution maximum shifted to 0.39–0.41 μm, the number of particles larger than 1 μm also became much less. Increase in the transmitter power to 100 W shifted the mean particle size distribution maximum even greater — to 0.25–0.26 μm. Thus, the increase in the strength of the composite material with

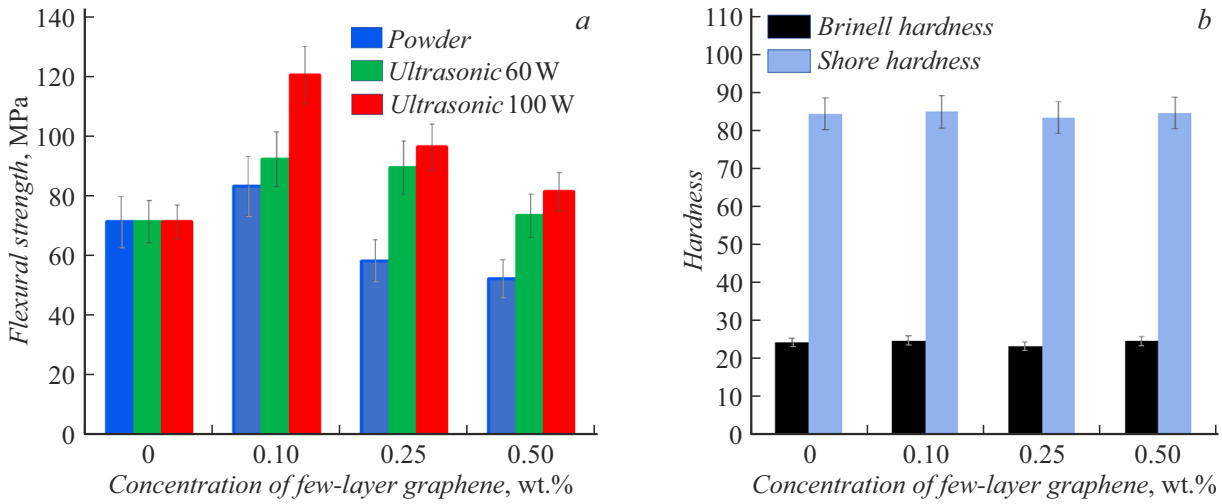

Figure 5. Dependence of the bending strength (*a*) and hardness (*b*) on the few-layer graphene concentration in epoxy resin.

US-treated (100 W) few-layer graphene may be associated with breakdown of large particle aggregates, which in turn increases the fraction of few-layer graphene surface available for interaction with the epoxy matrix.

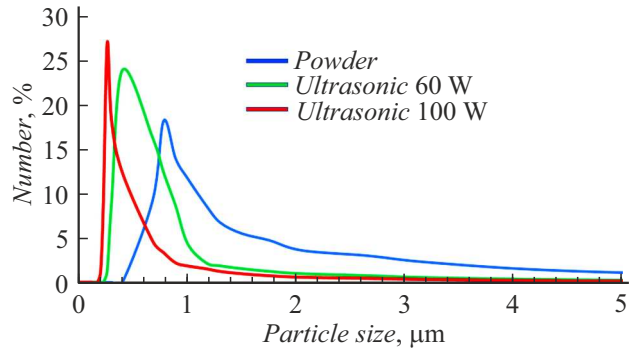

Figure 6. Few-layer graphene particle size distribution before and after ultrasonic treatment with the transmitter power of 60 W and 100 W.

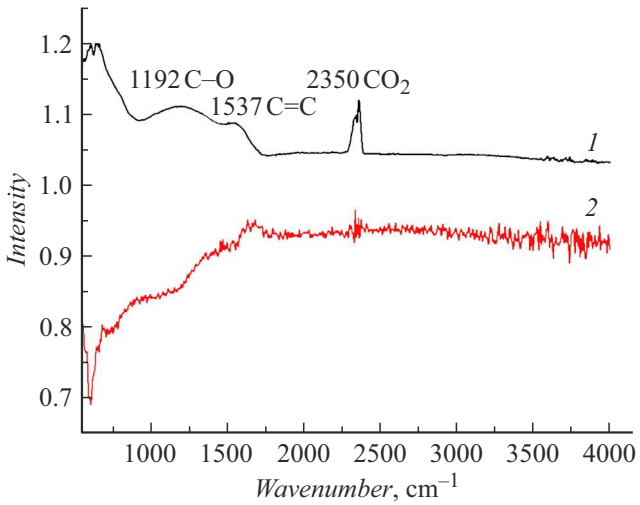

Figure 7. IR spectrum of few-layer graphene (*1*) and few-layer graphene after vacuum annealing at 1100°C (*2*).

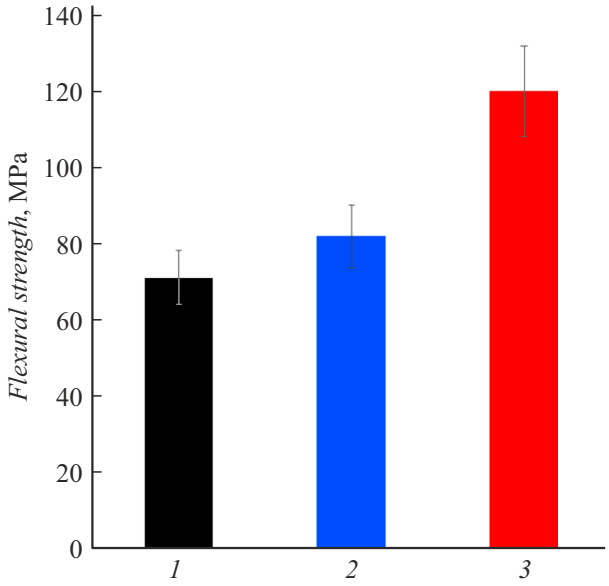

Figure 8. Bending strength of epoxy resin (*1*), epoxy resin modified with few-layer graphene annealed in vacuum at 1100°C (0.1 wt.%) (*2*), epoxy resin modified with few-layer graphene (0.1 wt.%) (*3*).

To examine the mechanism of interaction between few-layer graphene and epoxy resin, few-layer graphene was annealed in vacuum at 1100°C. Figure 7 shows that the IR spectrum of the vacuum-annealed few-layer graphene absorbs almost in the whole recorded spectrum range, unlike the IR spectrum of few-layer graphene where bands responsible for vibrations of C–O and C=C bonds can be clearly seen. The EDX method also identified that the content of oxygen and nitrogen atoms in few-layer graphene decreased from 12 at.% to 4 at.% and from 15 at.% to 0 at.%,

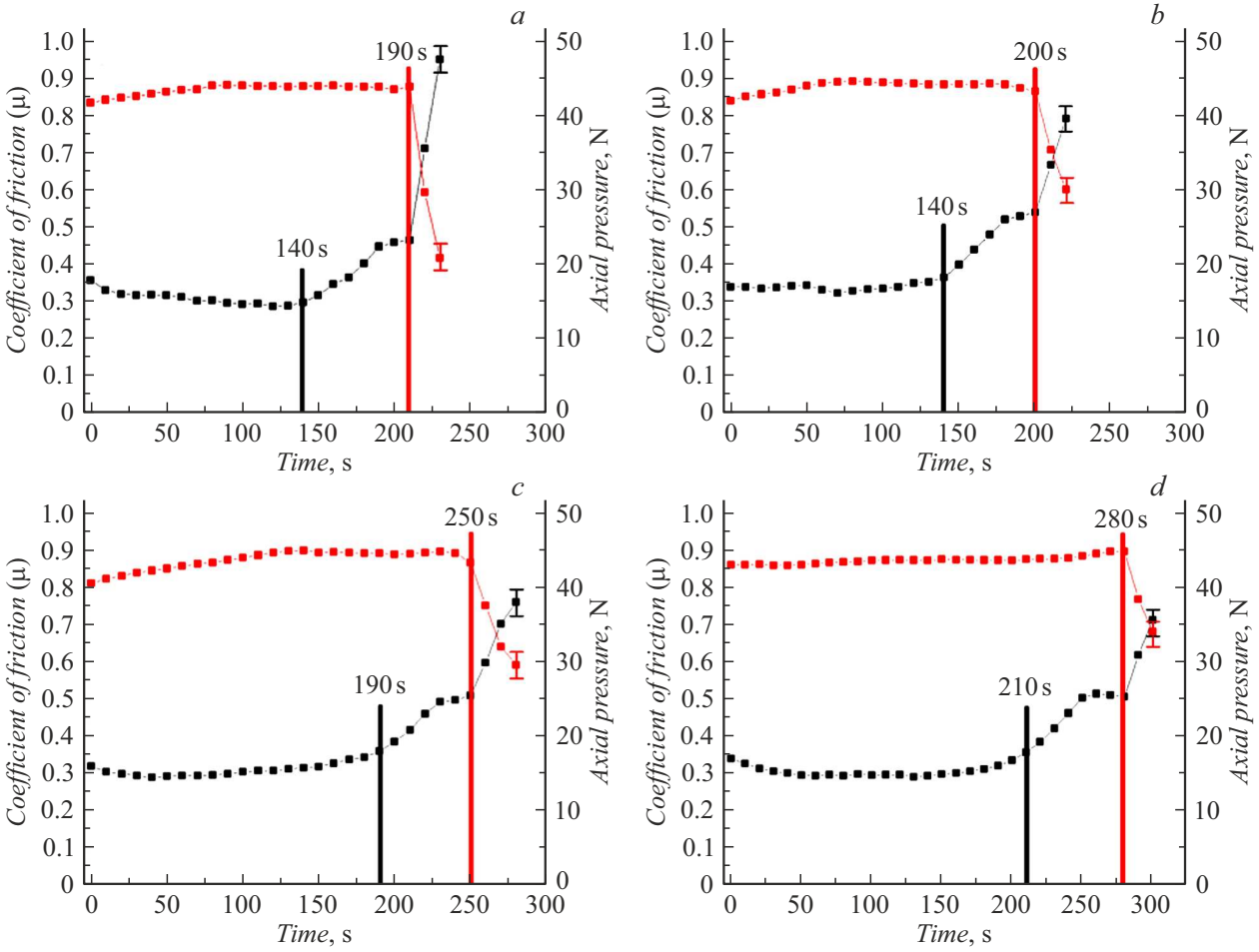

Figure 9. Dependences of the coefficient of friction (μ) and axial pressure applied to the sample on the friction time: *a* — initial epoxy resin, *b* — 0.1 wt.% few-layer graphene, *c* — 0.25 wt.% few-layer graphene, *d* — 0.5 wt.% few-layer graphene.

respectively, after vacuum annealing. Thus, almost all functional groups are removed from the few-layer graphene surface.

Introduction of the annealed few-layer graphene as a filler doesn't give rise to any significant growth of the epoxy resin bending strength (Figure 8). Oxygen and nitrogen atoms present on the few-layer graphene surface are supposed to provide interphase interaction between the polymer molecules and filler particles. This interaction may be induced by formation of hydrogen bonds between the hydroxyl groups of epoxy resin and oxygen and nitrogen atoms on the few-layer graphene surface.

Wear resistance is another parameter that characterizes the polymer material. This study determined the wear of epoxy resin and epoxy-resin-based composite samples by rotating a steel cylinder on the polymer surface. Figure 9 demonstrates the variation of the coefficient of friction (μ) and axial pressure applied by the steel cylinder on the polymer surface over the friction time. Abrupt change on the curves of coefficient of friction and axial pressure indicates that the sample is fractured. Figure 9, *a* shows the dependences for pure epoxy resin. It can be seen that μstarts increasing upon the expiry of 140 s, which indicates that the sample fracture has started and takes place at 190 s. Increase in the concentration of few-layer graphene from 0 wt.% to 0.5 wt.% (Figure 9, *b*–*d*) leads to the shift of the fracture start time from 140 s to 190 s and actual sample fracture time from 190 s to 280 s.

Increase in the wear resistance of polymers modified with graphene materials is most often explained as a consequence of graphene film formation on the surface of the upper body of friction. Due to the occurrence of such film, the coefficient of friction and wear of samples decreases [13]. Figure 9 doesn't show any significant decrease in the coefficient of friction of the steel/polymer pair as the concentration of few-layer graphene increases. This is possible due to a low concentration of few-layer graphene in epoxy resin. Increase in the wear resistance with the increase in the concentration of few-layer graphene could have been explained by the increase in thermal conductivity of composite materials, which is also of frequent occurrence when graphene is introduced into polymer matrices [14]. Increase in the thermal conductivity may facilitate better heat removal from the friction body

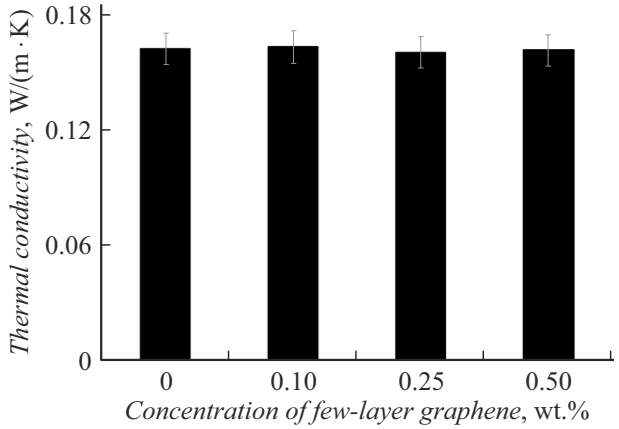

Figure 10. Dependence of the thermal conductivity of epoxy resin composite material on the concentration of few-layer graphene.

contact zone and, consequently, to the decrease in thermal fracture of the material. However, introduction of few-layer graphene into epoxy resin didn't give rise to the increase in thermal conductivity (Figure 10). Thus, the wear resistance variation mechanism for composite epoxy resin materials needs further investigation.

Conclusion

The study achieved the increase in bending strength of the KER-828 epoxy resin by 70% through the introduction of 0.1 wt.% few-layer graphene made by the self-propagating high-temperature synthesis method. It was shown that the bending strength depends highly on the few-layer graphene distribution within the polymer matrix and on the few-layer graphene particle sizes. To achieve the best distribution, few-layer graphene may be introduced into epoxy resin through suspension in isopropyl alcohol followed by evaporation of the isopropyl alcohol. Strength properties also depend on the content of functional groups on the few-layer graphene surface — decrease in the number of functional groups leads to the degradation of interphase interaction and, consequently, to the decrease in strength. Introduction of few-layer graphene to 0.5 wt.% into epoxy resin gives rise to the increase in wear resistance of composite material by 50%. This mechanism requires further investigation.

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Conflict of interest

The authors declare no conflict of interest.

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