The use of concrete and epoxy resin, modified with few-layer graphene for the production, repairs, and strengthening of concrete beams

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Abstract. The paper deals with the modification of concrete and epoxy resin with a 2D carbon material (2DCM) obtained by liquid-phase shear exfoliation of graphite. It was experimentally established that the three-point bending strength of graphene-modified samples (0.05 wt.% of graphene in cement) is 1.5 times greater than that of pristine (unmodified) concrete. The water absorption of concrete modified with the 2DCM was found to decrease by 3 times. A method, differing from the known ones where few-layered graphene is obtained directly in the hardener through shear exfoliation of graphite, was developed for modifying the ED-20 epoxy resin using the 2DCM. It allowed us to increase the Charpy impact strength by 25-30%. The tensile and bending strength were increased by 10%. The test results of the restored beams after breaking at three-point bending, as well as on the adhesion of the reinforcing fabric to concrete, revealed a synergistic effect while using the concrete and epoxy resin modified with the 2DCM.

1. Introduction
Polymer composite fittings, in particular, fiberglass, are increasingly used in modern construction for internal and external reinforcement of beams. The results of experimental studies on a PBO-PRKM masonry reinforced composite are presented in [1,2]. Studies on the use of nanomaterials for modifying non-metallic reinforcement are of particular interest. In [3], the issues of modifying building composites with carbon Taunit nanotubes were considered. The article [4] describes the possibility of using complex polyfunctional additives for construction purposes based on carbon nanotubes and zeolites (synthetic and natural). The strength characteristics of composite reinforcement and, as a result, reinforced concrete products depend on the adhesion of reinforcement to concrete [5-7]. In fact, a binder is in contact with the concrete, which is used to form a fiber (fiberglass, basalt or carbon) rod. Thus, increasing the strength of the binder and adhesion of this binder with concrete is a reserve for improving the performance characteristics of composite reinforcement, when used in concrete products.

Improving the performance characteristics of concrete, such as compressive and tensile strength, crack resistance, water absorption, resistance in corrosive environments, etc. is a very urgent task. Many solutions have been developed to solve individual problems, but there is still no comprehensive solution. The recently introduced new material on the market, the so-called “nano-concrete”, is not much different...
from ordinary concrete mixes. It also contains a mineral binder, aggregate, and water, only nanomaterials are used as modifiers: titanium dioxide nanoparticles [8], carbon nanoparticles [9], Melflux 1641 nanoparticles and plasticizer, carbon nanomaterials obtained as a by-product during plasma gasification of coal [10]. When these nano initiators interacting with cement crystallize and change its structure at the molecular level. In [11], issues of the influence of fillers containing nanosized particles on the formation of macro- and microstructures of concrete, the effect on the properties of concrete composites of early freezing of concrete mixtures with nano-modifiers were considered. It is revealed that frost resistance decreases, water resistance increases from 3 to 10 times.

In our opinion, the most promising direction in the use of nanomaterials for modifying concrete is the use of suspensions with 2D carbon materials (2DCM) in particular few-layers graphene [12], obtained by liquid-phase exfoliation of graphite into stator-rotor apparatuses [8].

In 2017, the International Organization for Standardization (ISO) published the first standard associated with the nomenclature of 2D materials [13]. The following classification has been proposed for graphene: graphene - single layer of carbon atoms; Bilayer graphene: two well-defined stacked graphene layers; few-layer graphene: consisting of three to ten well-defined stacked graphene layers; graphene nanoplatelet: thickness between 1 and 3 nm and lateral dimensions ranging from \(\approx 100\) nm to 100 \(\mu\)m. In the work [14], the authors note that these definitions are rather arbitrary from the physical point of view. Moreover, the term “graphene nanoparticles” is incorrect, since physically graphene represents essentially fine graphite. Given this circumstance, we use the term “2DCMs”. The fact is that as a result of the liquid-phase shear exfoliation of graphite, a suspension is obtained, which simultaneously contains: graphene; double layer graphene; a small layer of graphene; and graphene nanoplatelets. Depending on the process conditions, only the percentage of the indicated suspension components changes.

Considering the aforementioned, the present paper discusses options for modifying concrete epoxy resin with a 2DCM for the production, repair, and reinforcement of beams.

2. Concrete modification with few-layered graphene

To modify concrete, we used a 2DCM prepared in a rotor device with moving blades according to the technology described elsewhere [15]. After processing the suspension (5 L) for 45 min, it was centrifuged at accelerations in the sedimentation zone of 700 m/s\(^2\). After removal of the precipitate, the concentration of few-layered graphene in the suspension ranged from 1.7 to 2.0 mg/mL. The aqueous suspension of this graphene was used as mixing water in the preparation of concrete slurries for the manufacture of samples. The suspension was diluted with pure water so that the few-layered graphene concentration ranged from 0.02 to 0.07 wt.% relative to cement. In the manufacture of control samples, the same ratio of cement, sand and pure water was used. During the experiments, the cement/sand ratios were changed in such a way as to obtain compressive strength of control samples from 5 to 30 MPa. To determine the strength characteristics of the cement, sample beams of 40\(\times 40\times 160\) mm were made. The cement solutions and samples were prepared as described in [16]. The samples obtained were tested for compression, three-point bending, and water absorption. Figure 1 shows the characteristic dependences of the ultimate normal stresses under three-point bending at the moment of beam destruction, on the percentage of the few-layered graphene in concrete. The weight concentration was calculated for dry 2DCM with respect to cement.

As can be seen from the graph, the dependence has rather pronounced extremes of the maximum. The strength of the graphene-modified (graphene concentration of approximately 0.05 wt.% in relation to cement) was found to be about 1.5 - 1.8 times more than that of pristine (unmodified) concrete, whereas the water absorption of the 2DCM-modified concrete decreases by 3 times.
3. Epoxy resin modification with few-layer graphene

In [17], the limiting stresses were experimentally determined for the transverse shear of glass composite reinforcement and the adhesion of reinforcement to concrete. It was established that the climatic conditions of operation of reinforced concrete products, in particular, cyclic freeze-thawing and soaking-drying, reduce the strength characteristics, especially the strength of adhesion of the reinforcement to the concrete, and these reductions for the ASC reinforcement are lower than for the metal reinforcement. It was especially noted that when testing the pulling of the reinforcement from concrete, quite often (approximately in 50% of cases), there was a violation of the integrity in the binder material (epoxy resin), as well as the connection of the reinforcing fibers with the binder. Thus, one of the promising ways to improve the performance characteristics of the ASC is to increase the strength of the binder and its adhesion both with reinforcing fibers and with concrete.

A detailed analysis of methods for modifying epoxy resins with nanomaterials is given in [18, 19]. When modifying epoxy resins with graphene, a number of problems arise, in particular, in [20] attention is paid to the fact that the key point of polymer modification is the uniform distribution of the modifier in the matrix, which, in turn, largely depends on the affinity of the modifier polymer matrix. Usually, an interstitial fluid, usually acetone or isopropyl alcohol, is used to introduce graphene structures into the epoxy resin [20].

The results of our research have shown that both of these methods give unstable results and require a lot of labor and time.

We have developed a method for producing the 2DCM directly in an epoxy hardener. The exfoliation of graphite in polyethylene polyamines (PEPA) was carried out as follows. An initial suspension (approximately 1000 cm³) was prepared with a graphite (GSM-2) concentration of about 45–55 mg/mL using a standard laboratory paddle mixer. After that, the suspension was weighed and poured into a cylindrical container with a diameter of 100 mm and a height of 150 mm. The rotary device was installed in the tank, and the graphite exfoliation was performed according to the procedure described above in Section 2. After 90 min processing the suspension, it was centrifuged at 5000 rpm (centrifugal accelerations in the sedimentation zone was 70 m/s²) for 30 min, and then, the sediment was removed. The precipitate and graphene-containing hardener were weighed, and the graphene concentration in the hardener was calculated. Usually, about 2-4 g of graphite were converted to graphene, and the graphene concentration in the hardener was found to be about 0.2-0.4 wt.% Since the epoxy resin:hardener ratio is 10:1, this concentration in the hardener is not sufficient to obtain a concentration of 0.07% in the cured resin as originally planned. Considering this circumstance, repeated centrifugation was carried out.
at a speed of 5000 rpm until ¾ of the volume in the container, which was installed on the centrifuge, turned the color of a pure hardener. This part of the hardener was discharged, and its weighing and weighing of the residue were carried out. According to the weighing results, the concentration in the sediment was calculated. After that, the precipitate was mixed and used to prepare samples. The desired concentration of graphene in the epoxy resin was achieved by diluting the precipitate with the pure hardener in the required quantities. After the hardener was prepared with the required graphene concentration, it was mixed with ED-20 epoxy resin and samples were prepared for tensile, bending, and impact tests.

The forms and methods of making samples were described in [21]. A working hypothesis was formulated and experimentally confirmed that if the process of shear exfoliation is carried out in one of the epoxy resin components, then not only a good distribution will be ensured, but also good compatibility with the other components. A method of modifying the ED-20 epoxy resin with the 2DCM was developed, which, when the graphene concentration is 0.05 wt.%, increases the Charpy impact strength by 25-30 %. The method differs from the known ones, where few-layered graphene is obtained directly in the hardener by shear exfoliation of graphite. The tensile and flexural strength were increased less significantly, by only 10 %.

4. Use of modified epoxy to restore concrete beams

As shown by the results of the studies on three-point bend concrete beams with a size of $40\times40\times160$ mm, when the beams break, practically no small fragments of concrete are formed. In other words, after the destruction, the two halves of the beam can be quite tightly interconnected, since the destruction surfaces are mirror reflections of each other (figure 2).

In the experiments, we used: 6 destroyed beams of standard concrete; 6 destroyed beams of modified concrete (0.05% 2DCM); ordinary (pristine) and modified epoxy resins. Three reference concrete beams were glued together with the ordinary epoxy resin and three beams – with the modified one. Similarly, glued beams made of modified concrete. After gluing, the beams were kept for 48 h at 22 °C. The results of the three-point bending tests are given in table 1.

| Composition                        | Maximum load P, N |
|------------------------------------|-------------------|
|                                    | Sample 1 | Sample 2 | Sample 3 | Average |
| Concrete                           | 830      | 780      | 800      | 803     |
| Concrete + epoxy resin             | 790      | 770      | 800      | 787     |
| Concrete                           | 840      | 790      | 750      | 803     |
| Concrete + modified epoxy resin    | 890      | 840      | 800      | 843     |
| Modified concrete                  | 1090     | 1100     | 1020     | 1070    |
| Modified concrete + epoxy resin    | 820      | 800      | 840      | 820     |
| Modified concrete                  | 1060     | 1040     | 1030     | 1043    |
| Modified concrete + modified resin | 1288     | 1368     | 1256     | 1304    |

It should be especially noted that the destruction of the repaired beams, i.e. glued together with the pristine epoxy resin, took place almost exactly along the plane of the foregoing destruction, and the epoxy resin was placed on two halves in separate sections. When using the modified epoxy resin, the newly formed surface displaced from the surface of the previous fracture towards one of the fixed supports. It has been concluded that at the restoration of beams from usual concrete by epoxy, bending strength decreases to 5%. Then, when restoring beams from ordinary concrete with epoxy resin modified
with 2DCM, the flexural strength rises to 7%. Finally, when restoring beams from modified concrete with modified epoxy, bending strength increases by 20-30% (table 1).

The increase in the bending strength shows good compatibility of the modified concrete with the modified resin. It is possible that during the bonding process, the graphene structures in concrete are joined to the graphene structures located in the epoxy resin.

5. The study of adhesion of reinforcing fabric with concrete, using modified epoxy resin

As noted above, composite materials, in particular, fiberglass and epoxy resin are widely used to strengthen and repair concrete products, by external reinforcement. In this case, the main role in the effectiveness of the external reinforcement is played by the strength of the joint between the reinforcing fabric and concrete.

The experiments were carried out as follows: strips of fabric 40, 50, and 60 mm wide were glued to the beam in the form of a loop (figure 3, left). The sample was mounted on a tensile testing machine (figure 3, right). The tensile force was increased until the fabric was torn off from the concrete.

The following combinations were used in the experiments: concrete + fabric + epoxy resin (BFC); concrete + fabric + modified epoxy resin (BTME); modified concrete + fabric + epoxy resin (MBTE); modified concrete + fabric + modified epoxy resin (MBTME).

To clarity that, in figure 4, the test results are presented in relative terms (the ratio of the effort of separation of a particular sample $P$ to the force of separation of BFC – $P_o$). For all the samples, the cement:sand:water ratio, i.e. normal compressive stresses, were the same.

The deviations of the absolute values of the effort of separation from the average values did not exceed 5-7%. For all the samples, in which the connection of the reinforcing fabric with concrete was carried out with the pristine, epoxy resin, the gap was practically observed on the resin layer adjacent to the concrete. The histogram does not show the relative tearing forces for the MBTE samples, since the efforts were equal, the efforts for BFC samples and destruction in all samples occurred on epoxy resin without damaging the concrete. In the BTME samples, as well as in the MBTM samples, the destruction occurred along the concrete, but in the MBTM samples, the zone of destruction was located farther from the outer surface. It is likely that when using the modified concrete and modified resin, a connection is made between the graphene structures that exist in the resin and in the concrete.

The diagram shows that when using both the concrete and epoxy resin modified with the graphene, the adhesion strength of the reinforcing fabric with the concrete increases, on average, by 30% (figure 4).
Figure 4. Histogram of the relative effort of separation of reinforcing the fabric from concrete.

Since the external reinforcement is mainly used when repairing damaged beams, comparing these results with the results presented in table 1, it can be concluded that with simultaneous use of concrete and epoxy resin modified with the graphene, there is a synergistic effect of increasing the strength of the repaired concrete products.

6. Conclusion

It has been experimentally established that the three-point bending strength of the graphene-modified samples (graphene concentration of about 0.05 wt.% with respect to cement) is about 1.5 times greater than that of the pristine concrete, whereas the water absorption of the 2DCM-modified concrete decreases by 3 times. Using the method for modifying the epoxy resin with the 2DCM the Charpy impact strength is increased by 25%. The tensile and bending strength increase by 10%. The test results of the repaired beams after breaking at three-point bending, as well as on the adhesion of the reinforcing fabric to the concrete, revealed a synergistic effect while using the 2DCM-modified concrete and epoxy resin.

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