Carbon nanofillers used in epoxy polymeric composites: a brief review

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Abstract. The paper discusses scientific publications regarding polymer composites based on epoxy resins, which are the main competitor of many traditional structural materials. The review on carbon nanofillers for composite materials, such as graphene, graphene oxide, carbon nanotubes, etc., is given. Methods for introducing these nanomaterials into different binders are considered, and comparative results of improving the strength characteristics of nanocomposites are presented.

1. Introduction

Polymer composite materials such as fiberglass, carbon fiber, organoplastics, powder-filled polymers, textolites possessing unique characteristics [1,2] are the main component in manufacturing products used for solving diverse problems, ranging from the production of sports equipment and jewelry up to their use in the aviation aerospace industries [3-5].

Due to the widespread use of polymers, the requirements for their strength characteristics (tensile strength, Young's modulus, crack resistance, resistance to impact loads) [6] are becoming increasingly high. Carbon nanomaterials (CNMs) used as a modifier of polymer matrices can help in meeting the increased requirements for the strength characteristics.

Most often, when developing polymer composite materials (PCMs), an epoxy resin is used; it is one of the most common binders in the industry due to the variety of available grades [7] and curing agents [8], thereby making it possible to obtain materials with different property combinations [9]. With the advent of the CNM industrial production [10], there is a tendency for employing them as a PCM nanofillers which can increase tensile strength from +2.5 up to +47% [11,12].

Carbon fillers are of great interest in scientific publications. According to the database of peer-reviewed scientific literature, there are more than 10,000 papers, of which more than 1,000 publications are devoted to carbon nanofillers which possess high strength, an ordered structure, and unique geometry. Therefore, over the years, a large number of experiments and studies have accumulated in the scientific and technical literature that describe the modification of epoxy matrices with various nanomaterials. This makes it possible to identify an important trend, namely, that in recent years a large number of publications have been devoted to solving specific technological problems, and due attention has not been paid to the review work, which would enable the comparison of all the process parameters and properties of the nanocomposites obtained.

Using carbon nanofillers, different in structure, properties, percent of their application and methods of their introduction, allows obtaining materials with the desired combination of properties. In scientific
research, much attention is paid to carbon nanotubes (CNTs), both single- [13-16] and multi-walled [16-20], which can be used as a filler to improve the strength and conductive properties. The papers [21-25] discuss the introduction of graphene into the polymer matrix, whereas articles [26-28] deal with nanoparticles such as graphene oxide and reduced graphene.

Considering the aforementioned, the aim of the work was to study the current state of the issue of choosing CNMs and methods for their introduction to develop a nanocomposite with improved strength properties compared to the analogs.

2. Methods for introducing nanofillers into the epoxy matrix

Since carbon nanomaterials are subject to agglomeration, dispersion and uniform distribution of nanofillers in polymer binders appear to be one of the main problems that many researchers are facing. This is reflected in many scientific papers [18-20,27-44].

Based on the simplicity of the hardware design, introducing CNMs into the epoxy binder using mechanical action (dispersants, mixers) is the most common technique [12,19,25-31]. However, it is not always possible to destroy small agglomerates and distribute the CNMs using only the mechanical method. In the papers [11,20,22,29,32-34], the distribution of the nanofiller in the epoxy binder was carried out using an ultrasonic device, but without preliminary mechanical treatment, complete deagglomeration of the nanomaterial occurs over a long period of time. In the studies [22,35-40], a combination of several methods is described. At the first stage, the CNM is introduced into the binder using a mixing device, and then, the material is dispersed in an ultrasonic unit. In the works [20,27,28,41,42], CNMs were dispersed in solvents using ultrasound. After that, the resulting mixture was added to the epoxy binder, and the solvent was removed. However, the use of the solvent in this method adversely affects the strength properties of the final product. In [43,44], preliminary grinding of the CNMs in a ball mill and an ultrasonic device was used, then, the CNMs were introduced into the epoxy binder. The disadvantage of this method is grinding itself, meaning the ingress of grinding material particles.

The choice of the technique for introducing the nanofillers depends on the quality and structure of the nanomaterial or the viscosity of the polymer matrix. For instance, in [45-49], the CNMs are introduced gradually, using a three-roll mill, which functions on the principle of applying a high shear force to the material between two rolls rotating in opposite directions and at different speeds. Further, the material is dispersed in an ultrasonic setup.

As a whole, the CNM effect on the PCM depends on the uniform distribution of the nanofiller in the binder; therefore, the technique for introducing the CNMs into the polymer material through preliminary mechanical action with subsequent or simultaneous ultrasonic treatment is recommended.

3. Studying the carbon nanomaterial effect on the physical-mechanical properties of the PCMs

The results of using various nanofillers to increase the strength characteristics of epoxy matrices are shown in Table 1. From the data presented, it can be concluded that the use of the carbon nanofillers may significantly improve the strength characteristics of the composite material. Among the whole variety of nanoadditives, CNTs are considered as fillers with great potential for increasing the physical-mechanical properties. Moreover, they showed a better effect on the strength than the other fillers presented in the review. Besides, a great potential of modification and functionalization of the carbon nanofillers [50-52] was revealed after reviewing the scientific literature on their full potential as composite fillers.
Table 1. The effect of the carbon nanofillers on the physical-mechanical properties of the PCMs.

| Nanomaterial                          | Tensile strength increase/decrease, +/-% | Ref. |
|---------------------------------------|------------------------------------------|------|
| CNTs (1.5%)                           | +7                                       | [45] |
| CNTs (0.3%)                           | +5                                       | [46] |
| CNTs (0.3%)                           | +37                                      | [47] |
| Multi-walled CNTs (0.51%)             | +9                                       | [11] |
| Multi-walled CNTs (0.3%)              | +35                                      | [16] |
| Multi-walled CNTs (0.17%)             | +47                                      | [11] |
| Single-walled CNTs (0.3%)             | +44                                      | [16] |
| Double-walled CNTs (0.3%)             | +37                                      | [16] |
| ABS/CNTs (6%)                         | +12                                      | [17] |
| Graphene nanoplatelets (0.25%)        | +20                                      | [22] |
| Graphene nanoplatelets (6%)           | +1                                       | [17] |
| Graphene oxide (1%)                   | -18                                      | [12] |
| Graphene oxide (0.75%)                | -9                                       | [12] |
| Graphene oxide (0.5%)                 | +71                                      | [48] |
| Graphene oxide (0.5%)                 | +2.9                                     | [12] |
| Graphene oxide (0.25%)                | +2.5                                     | [12] |
| Graphene oxide (0.1%)                 | +38                                      | [48] |
| Carbon nanofiber (1.5%)               | +11                                      | [49] |
| Carbon nanofiber (0.5%)               | +18                                      | [50] |
| Carbon fiber+CNTs                     | +19                                      | [51] |
| Glass fiber+carbon nanofiber           | +26                                      | [52] |

4. Conclusion
Through the use of nanofillers, the PCMs can compete in the physical and mechanical properties with the other materials such as ceramics, glass, or even metal. It is worth noting that the conducted literature review on scientific publications does not cover the whole variety of nanoparticles used as PCM fillers. This is due to a large number of nanomaterials and ongoing studies to improve the physical-mechanical properties of different polymer matrices for various purposes. The recommended technique herein represents a complex that includes the combination of several the methods considered with the aim of maximizing the uniformity of localization of the nanofiller in the binder, and this, in turn, has a positive effect on the nanoPCM operational characteristics such as elastic modulus and tensile strength. This method is easily scalable for the commercial production of nanocomposites.

5. Acknowledgment
The present research was funded by RFBR (Russian Foundation for Basic Research) in the framework of Project No.18-29-19121\18.

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