Production of few-layer and multilayer graphene by shearing exfoliation of graphite in liquids

V F Pershin1,*, M N Krasnyanskiy1, Z A A Alhilo1, A M R Al-Mashhadani1, A A Baranov1 and A A Osipov2

1Department of Technology and Methods of Nanoproducts Manufacturing, Tambov State Technical University, 106 Sovetskaya Street, 392000, Tambov, Russian Federation
2LLC “NanoTechCenter”, 51 Sovetskaya Street, 392000, Tambov, Russian Federation

*E-mail: pershin_home@mail.ru

Abstract. The article describes the process of liquid-phase shear exfoliation of graphite in a rotary apparatus with moving blades, in water and I-20A oil (Rosneft, Russia) used as a liquid. The linear dependence of the process intensity on the shear rate and graphite concentration in the initial suspension are established in the paper. To increase the share of graphene converted into graphene plates, it has been proposed to reduce periodically the concentration of graphene plates in suspension by adding pure liquid. It was found that the exfoliation rate of graphite is directly proportional to the concentration of graphite in the initial suspension and the rotor speed. The resulting graphene-containing oil-based suspension was used to modify greases.

1. Introduction

Nanomaterials have become a critical sector that can significantly push the boundaries of technology. The remarkable properties of carbon nanomaterials, such as high electrical (good electrical conductivity, as well as current density 108 A/cm² [1]) and thermal conductivities (thermal conductivity (5000 W/m·K) [2]), strength (Young's modulus (1 TPa) [3]), a large specific surface area (2630 m²/g) [4,5], optical transmission (97.7%) [6,7].

One graphite layer is well known as monoatomic or monolayer graphene, and two and three graphite layers are known as bilayer and trilayer graphene. Graphene having more than 5 layers up to 10 layers is usually called few-layers graphene, and 20–30 layer graphene is usually called multilayer graphene or nanocrystalline thin graphite [8].

Any process for the manufacture or extraction of graphene can be attributed to the synthesis of graphene, depending on the desired size and purity of a particular product. In recent years, various methods have been developed for the synthesis of graphene, but mechanical splitting (peeling) [9], chemical peeling [10,11], chemical synthesis [12], and thermochemical vapor deposition (CVD) [13] are the most common.

Since this paper addresses the issue of modifying various materials (frost-resistant plastic lubricants, concrete, epoxy resin), i.e. materials used in industry in large volumes, the interest is represented by scalable methods for the production of graphene plates, providing improved performance characteristics of the modified material with a low production cost.

There are examples of the successful use of multilayer graphene plates in the modification of grease [14], concrete [15] and epoxy resin [16].
The aim of this work is to study the process of liquid-phase shear exfoliation of graphite and the preparation of graphene-containing suspensions that are used in the modification of materials, in particular, frost-resistant greases.

2. Critical analysis of liquid phase shear exfoliation methods

In liquid phase shear exfoliation, two main points were distinguished: particles of graphite were in a liquid, which weakens the bonds between the graphene layers and prevents agglomeration; forces were applied to the particles, which stratify the graphite. As a liquid, various solvents or water with the addition of surface-active substances was used.

High quality graphene was obtained in high yield through a solvothermic process [17]. Graphite flakes were dispersed in an organic solvent that can efficiently penetrate between the layers and was heated to 1000-2000°C. After heating to 1000°C in the atmosphere (95% Ar, and 5% H₂), graphite was mixed with a highly polar organic solvent (acetonitrile), in a teflon-coated autoclave. The mixture was then kept for 12 h at 180°C and treated with ultrasound. As a result, single-layer and two-layer graphene sheets were obtained. The disadvantage of this method was the difficulty of scaling and transition to industrial scale.

In [18], graphite was dispersed in an ionic liquid and irradiated with microwaves for 30 min. The installation is somewhat similar to ultrasonic treatment, but the processing time was significantly reduced, and an improved route for graphene exfoliation has been demonstrated. The authors reported high peeling efficiency, a yield of 93 wt.% And a selectivity of 95% with respect to single-layer graphene.

The use of supercritical fluids was also used for exfoliating graphite. Critical factors of this method were: high diffusion coefficient; extensibility and solvating ability of a supercritical fluid. Supercritical fluid can penetrate into the gap between the layers of graphite due to the high diffusion capacity and very low viscosity. When a rapid depressurization of the apparatus occurs, the supercritical fluid expands sharply, and forces arise that contribute to the process of graphite delamination [19, 20].

An attempt to increase the production of graphene using shear effects on particles of graphite created by a rapidly rotating blade, was made in [21]. In [22], hydrodynamics in supercritical CO₂ was investigated. This resulted in a yield of 63% monolayer graphene. The main problem of the supercritical fluid method is the need to provide a high-pressure reactor. For example, in [23], the pressure in the reactor was 12 MPa. In combination with temperature and the need to organize mechanical effects on graphite, even according to the authors, it is quite difficult to implement on an industrial scale.

Another shear-controlled process of exfoliation of graphite in an organic solvent is presented in [24]. In this approach, a rapidly rotating tube (diameter 16 mm, rotation speed 7000 rpm) was used to create an intense shear in a fluid containing graphite. In [25], a similar technology was used and multilayer with a thickness of not more than 20 nm and a small amount of flakes ~ 1 nm thick were obtained. This approach is less energy intensive than ultrasonic treatment, but industrial implementation is problematic.

Using a rotating disk (diameter 200 mm, rotation speed 2500 rpm) [26] generated the effects of transverse forces on graphite particles in dynamic thin films on the surface of the disk and this led to the exfoliation of graphite flakes and the production of graphene. In our opinion, the results of the studies confirm the possibility of obtaining graphene from graphite only due to shear effects, but has no prospects for industrial realization.

In [27], a mixer with a high rotor speed was used. A mixer with a diameter of 32 mm was used in the work, the rotation speed was 4500 rpm. The concentration of graphite in the initial suspension was 50 mg/ml, the volume of the suspension was 4.5 liters, and the processing time was 20 minutes. The treated suspension was centrifuged and the quality of the finished product was determined. As a result of the analysis, it was established that the thickness of the graphene particles obtained could be controlled by the gap between the stator and the rotor and the smaller this gap, the less layers in the graphene plates; the yield and quality of the product depend on the concentration of the initial suspension, the speed of rotation of the rotor, the processing time; rotor diameter. It is established that with a smaller stator diameter, the lateral dimensions of the graphene plates are smaller and vary from 0.35 to 0.9 µm, and
the thickness of the plates from 0.9 to 1.3 nm. The analysis made by atomic force microscopy has shown that graphene sheets consist of 10 layers and less.

Raman spectroscopy confirmed the presence of single-layer graphene in the final suspension. The transition to a pilot plant with a rotor diameter of 110 mm was implemented. Analysis of the results showed that this setup can produce a suspension with a concentration of low-layer graphene 0.07 mg/ml. Plant capacity is 5.3 g/h. The authors carried out calculations and found that several such plants with a total volume of the treated suspension of 10 m³ will be able to produce 100 g/hour. Judging by the fact that the pilot plant worked with a capacity of 0.3 m³, 33 installations would be required. In our opinion, the latter method of obtaining suspensions is the most successful and can be used on an industrial scale.

3. Experimental setup
The liquid-phase exfoliation process was carried out in a laboratory setup, as in [28]. The main difference from the rotor apparatus, which was used in [27], is that we used moving blades. Under the action of centrifugal forces, these blades were pressed against the inner surface of the stator and slide along this surface without a gap. Thus, shear forces are transmitted to the particles directly by e-blades. As shown by the results of experiments, this method of transferring shear forces to particles increases the intensity of the exfoliation process.

Experiments were performed as follows. Preparing 5 L of a suspension of crystalline graphite fuels and lubricants-1 with a concentration with a concentration of 3% to 10%, poured it into a cylindrical container, installed the apparatus and started processing the suspension. Every 10 minutes, the process was stopped and 100 ml samples were taken. The suspension was centrifuged, the precipitate was removed and the concentration of graphene nanostructures in the remaining suspension was determined. After analysis, the sample was mixed with the residue, poured into a container and the exfoliation process continued. After the concentration of the next sample increased by less than 5% of the concentration of the previous sample, the exfoliation process was stopped. During the experiments, the rotor speed was changed: 5000; 10,000; 12,000; 15,000 rpm.

4. Results and discussion
In the first series of experiments, water was used as a liquid. Figure 1 (curve 1) shows the results of changes in the concentration of graphene structures over time, with a rotor speed of 10,000 rpm and a concentration of graphite in the initial suspension of 50 mg/ml. It can be seen that at the beginning of the process (up to a concentration of graphene nanoplastic of 1.7 mg/ml) the dependence is linear and this fully agrees with the results of [29]. With further processing of the suspension, the concentration grows more slowly and at a concentration of about 1.9-2.0 mg/ml, the exfoliation process stops. We decided to reduce the concentration of graphene nanoplates by adding pure water. The results of the experiments presented in figure 1 (curve 2) show that after reducing the concentration, the exfoliation process continues with the same intensity. Thus, periodically reducing the concentration of graphene nanoplastic materials can significantly increase the proportion of graphite, which is converted to graphene. The resulting suspension can be used to modify concrete [30].

With an increase in the concentration of graphite in the initial suspension from 5% to 10%, the maximum concentration of graphene structures in the suspension (1.79 mg/ml, figure 1, curve 2) was reached not in 25 minutes, but in 14 minutes. With an increase in the rotor speed, a similar situation was observed. For example, with an increase in speed from 10,000 rpm to 15,000 rpm, the time for which the maximum concentration was reached decreased from 25 minutes to 18 minutes, but the nature of the curve did not change.

In the second series of experiments, I-20A industrial oil (Rosneft, Russia) was used as a liquid. The concentration of graphite in the initial suspension was 5%, and the rotor speed was 10,000 rpm. The original suspension was passed through a rotary apparatus and after every five processing cycles, samples were taken for analysis. The intensity of the process of the formation of graphene structures was estimated from the change in the optical density coefficient (K), the numerical value of which characterizes the average integral number of layers in graphite particles [31].
Figure 1. The dependence of the concentration of graphene nano-plates (C$_{\text{graphene}}$) on time: 1 – continuous mode; 2 – cyclic mode with a decrease the concentration of graphene structures.

Figure 2. The dependence of the optical density coefficient on number of cycles.

Figure 2 shows the dependence of the coefficient K on the number of suspension processing cycles. The duration of each cycle is 3 minutes. As you can see, up to 15 cycles this dependence is linear, and then the intensity of the peeling process begins to decrease, so we used the same technological method as in the preparation of the aqueous suspension, i.e. decrease in concentration. The resulting dependence is similar to that shown in figure 2.

We carried out similar experiments in which the concentration of graphite in the initial suspension varied from 5% to 20%. It was found that with a decrease in concentration of graphite by 2 times, the intensity of exfoliation decreases by about 2 times, and with an increase in the concentration by 2 times, it increases by about 2 times. Thus, there is reason to believe that the intensity of the exfoliation process is directly proportional to the concentration of graphite in the initial suspension. At the same time, it should be noted that with a further increase in the concentration of graphite, the intensity of the process grows more slowly, so it makes no sense to use the initial suspension with a graphite concentration of more than 20%.

Graphene-containing suspensions are used in the modification of greases [31], including frost-resistant [32]. The results of determining the tribological characteristics showed that at a concentration of graphene structures obtained in this work of 0.15%, the diameter of the wear spot 50% reduction, attrition rate showed almost increased 2.7 times, carrying capacity increased 3 times. These results are in good agreement with previous ones. In the work [32], the concentration was slightly lower (0.1%), but the price of graphene structures obtained using long-term treatment of the suspension with ultrasound was at least 10 times higher than using shear exfoliation. Thus, the proposed technology of shear exfoliation of graphite directly in oil has great prospects for industrial use.

5. Conclusion

As a result of experimental studies, it has been established that the concentration of graphene structures in the finished suspension is directly proportional to: the number of processing cycles; rotor speed; the concentration of graphite in the original suspension. In addition, it was found that to increase the efficiency of the exfoliation process, the fraction of graphite that could be converted into graphene structures can be achieved by periodically reducing the concentration of graphene structures in the suspension being processed, by adding pure liquid to this suspension. The technology for producing
graphene structures directly in oil by shear exfoliation of graphite has good prospects for industrial implementation.

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