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Using a Rod Drum Mill for Graphene Masterbatch Production

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Abstract. To improve the tribological characteristics of plastic lubricants, we have previously developed a technique for modification of such substances using a graphene masterbatch. This masterbatch represents a mixture of low-viscosity oil and few-layered or multi-layered graphene obtained via graphite exfoliation. In the present work, results of masterbatch preparation in a rod drum mill due to high-gradient shear actions on a mixture of an oil base and crystalline graphite are discussed. A 2-fold decrease in the friction coefficient was achieved when using the 1-wt% standard masterbatch or the 10-15-wt% masterbatch obtained from the graphite.

INTRODUCTION

Graphite is conventionally used as an antifriction material [1], but nanosized graphite derivatives have opened up fundamentally new horizons in tribology due to their unique properties, including surprisingly low friction coefficients.

It has been experimentally established that, when tested in hydrogen, a single graphene layer grown on steel can withstand 6,400 sliding cycles, whereas few-layered graphene (composed of 3-4 layers) withstands 47,000 cycles. Besides, it has been shown that these graphene layers completely stop wear, despite severe sliding conditions, including high contact pressures (≈0.5 GPa), which are usually observed in small-scale tests [2]. Experimental results demonstrate that the addition of 0.4 wt% graphene nanofiller to lithium lubricants yields good antifriction and wear resistance performance [3]. The theories of friction and wear of graphite are analyzed in [4]. The combined action of graphite and graphene in a plastic lubricant makes it possible to decrease the friction coefficient by 2.2-2.5 times [5]. Adding a graphene masterbatch to a standard lubricant is one of the promising ways of lubricant modification [6].

There exist many technologies for obtaining low-layer and multilayer graphene [7, 8]. For instance, mechanochemical exfoliation of graphite involves graphite intercalation with ammonium persulfate in sulfuric acid, cold expansion, treatment of the expanded graphite compound with carbamide and glycerol, and mechanical treatment under shear deformation conditions. This technique allows fabrication of few-layered graphene nanoplatelets without any surfactant [9]. By using certain solvents, graphene can be dispersed at concentrations of up to 0.01 mg mL^{-1} [10].

The paper [11] describes a low cost and simple method of ball milling of pristine graphene in the presence of dry ice to achieve a high yield of edge-selectively carboxylated graphite, which is very dispersable in various solvents to self-exfoliate into single- and few-layered graphene nanoplatelets.

To modify a graphite lubricant with graphene [5], we also employed a planetary mill with two independent drives, but during the experiments we came to the conclusion that it is difficult to use this mill in continuous mode for industrial graphene production. Planetary mill usually exert large pressures on materials to be crushed. However, for shear exfoliation of graphite, such pressures are not required [6].

Considering the aforementioned, the objective of the present work to study the process of graphite exfoliation in a rod drum mill, which has been used for a long time in various industries to grind materials.

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EXPERIMENTAL, RESULTS, AND DISCUSSION

At the first stage, we studied the motion of grinding bodies in a laboratory drum (diameter of 400 mm). The rotational speed of the drum varied from 0.5 to 90 rpm, which made it possible to investigate the motion in different modes. The transparent front wall of the drum served for taking pictures (photos) and videos of the process. Balls and rods (diameters of 10-40 mm) were used as grinding bodies. Since we were interested in shear effects on graphene particles, the main attention was paid to the mode, in which the balls or rods slide over the inner surface of the rotating drum.

Figure 1 demonstrates two typical positions of the rods in the rotating drum. The rods periodically move together with the drum shell from the position shown in Fig. 1(a) to the position shown in Fig. 1(b), and vice versa. When moving down, the rods slide relative to the inner surface of the drum. Video recording made it possible to establish that during this motion the rods rotate and slip with respect to each other. If graphite particles are placed into the drum together with the rods, then shear forces will act on the particles in the zones of rod sliding relative to the drum shell and each other. Under the action of the shear forces within the particles, shear stresses arise, and the graphite is exfoliated.

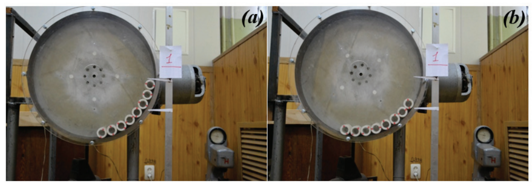

FIGURE 1. Motion of rods in the cross section of the rotating drum.

The studies on the joint motion of the rods and the material showed that the number of grinding zones does not decrease due to the shear effects. In the experiments, intensive movement of the material particles was observed; *i.e.*, new material portions were continuously supplied to the grinding zones.

We have developed a design of the rod drum mill, in which the rods do not rotate relative to their own axes, but slide over the inner surface of the drum (Fig. 2). The provision of this mode is possible at angular rotational speeds of the drum greater than the critical level. Thus, in the rod rum mill, we succeeded in arranging the same number of shear actions on the graphite particles per time unit as in the planetary mill.

FIGURE 2. An experimental rod drum mill.

The mixture of the industrial oil and the graphite was processed in that mill; *i.e.*, the graphene masterbatch was obtained directly from the graphite. The effectiveness of this method was evaluated by comparing the sliding friction coefficients of the Solidol-G plastic lubricant modified with a standard graphene masterbatch and the masterbatch synthesized using the graphite according to the procedure described in [5]. It was found that a 2-fold decrease in the friction coefficient is observed at a content of 1 wt% of the standard concentrate or 10-15 wt% of the masterbatch obtained from the graphite in the rod drum mill.

Then, we studied the uniformity of graphene distribution in the industrial oil. It was found that at concentrations of up to 2 wt%, the graphene is distributed rather uniformly in the oil and forms a homogeneous structure. At higher concentrations, the viscosity of the masterbatch increases significantly, which requires an increase in the diameter of the rods. This adversely affects the intensity of shear stresses as a result of a decrease in the number of shear zones.

When using an aqueous solution of glycerin as the liquid phase, it was established that the average number of layers in the graphene nanostructures decreases after processing the masterbatch in the rod mill. Furthermore, it was found that as a result of processing the mixture for 50 h, a part of the graphite passes into the graphene, as evidenced by an increase in the stability of the aqueous suspension.

To develop a physical model of the graphite shear exfoliation process, we considered a particle (Fig. 3) located between the rod and the inner surface of the rotating drum when the rod slides from the position shown in Fig. 1(a) to the position shown in Fig. 1(b). The parameters affecting numerical values of the forces that act on the particle are as follows: radius of the drum (*R*, m), radius of the rod, (*r*, m), weight of the rod (*m*, g), coefficient of the graphite friction along the rod material (f_r), coefficient of the graphite friction along the drum material (f_R), coefficient of the graphite friction between graphene platelets which compose the graphite particle (f_G), and vertical angle determining the position of the rod in the drum (ϕ).

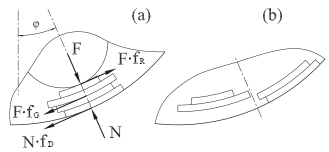

FIGURE 3. Shearing effects of forces acting on a graphite particle.

The force *F* of the rod pressure on the particle (Fig. 3(a)) is mainly defined by the weight of the rod and its position in the drum. The normal pressure force *N* is equal to the force *F*. Apparently, in addition to the friction, the coefficient f_G includes van der Waals forces; *i.e.*, this coefficient is complex and can be determined experimentally, like the coefficients f_r and f_R. Since, textitf$_G$ is much smaller than f_r and f_R, as shown by the results of our experiments, the graphene platelets are shifted, and two particles are obtained from one particle (Fig. 3(b)).

Each of the newly formed particles consists of a smaller number of graphene platelets. Multiple exposures make it possible to obtain multi-layered graphene particles, and then few-layered ones, from the graphite particle. The sequence of formation of graphene structures from graphite due to shearing effects represents a physical model of the process. Since the penetration of particles between the rod and the drum is probabilistic in nature, a mathematical apparatus of random Markov processes, discrete in space and time, was implemented to describe this process. The system represents a suspension of graphite particles of a certain granulometric composition in oil with a certain graphite concentration.

The state of the system can be characterized by the vector *S(k)*:

$$S(k) = [c(1,k), c(2,k), \cdots, c(i,k), \cdots, c(N,k)], \quad (1)$$

where *k* is the transition number, *i* is the cell number, *c* is the amount of particles with a certain number of graphene layers in the cell, and *N* is the total amount of cells.

Element values of the initial state vector *S(0)* of the system are determined by the characteristic of initial graphite and its concentration. The transition of the system from one state to another takes place abruptly during the time interval Δt. The system change over time can be expressed by the following relationships:

$$S(1) = S(0)P, \quad (2)$$

$$S(2) = S(1)P, \quad (3)$$

$$\ldots \quad (4)$$

$$S(i) = S(i-1)P, \quad (5)$$

$$\ldots \quad (6)$$

$$S(k) = S(k-1)P, \quad (7)$$

where *P* is the matrix of transition probabilities.

Since the numerical values of the probabilities depend on the parameters of the rods and the drum (f_R, f_r, f_m, f_R, f_r, and the rod number), as well as on the mode parameters of the process (drum rotation speed, graphite concentration in suspension, granulometric composition of graphite, and f_G), this mathematical model allows calculation of the shear exfoliation of graphite implemented in the rod drum mill.

CONCLUSION

It was experimentally established that in the rod drum mill, it is possible to arrange the sliding of the rods relative to the inner wall of the rotating drum and, as a result, graphite exfoliation takes place - *i.e.*, graphite is converted into graphene.

A 2-fold decrease in the friction coefficient was observed in the case of using the 1-wt% standard masterbatch or the 10-15-wt% masterbatch obtained from the graphite.

To estimate the mode and geometric parameters providing the synthesis of graphene masterbatches that could increase the tribological properties of plastic lubricants, a physical model was developed.

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