Development of gradient polymer composite and technology for its production for revolved parts with increased surface wear resistance

V N Sharshin, D V Sukhorukov and E V Sukhorukova

Vladimir State University named after Alexander and Nikolay Stoletovs, 87 Gorky Street, Vladimir, 600000, Russian Federation

E-mail: info@inlittech.ru

Abstract. The work is aimed at creating polymer composite materials with desired properties. One of the ways to create such materials is to create gradient layers characterized by a smooth spatial change (gradient) of properties in the direction of one or two coordinate axes. The results of studies on the rotation of the polymer composition at the time of polymerization are shown. A device for producing polymer composite materials with a gradient layer has been created. The values of the distribution of additives and hardness along the height of the samples are given. Mathematical processing of the experimental results was carried out.

1. Introduction

The problem of obtaining new materials with a desired set of properties is being solved today both through the development of bulk-reinforced composites [1-3], and through the creation and application of functional-gradient materials characterized by a smooth spatial change (gradient) of properties in the direction of one or two coordinate axes [4-7].

Gradient polymer composite materials are solid suspensions containing a dispersed phase, distributed in a predetermined manner in a polymer matrix, the physical and functional properties of which smoothly change in the direction of the reinforcement concentration gradient [8]. The gradient of properties in a composite material, due to a change in the composition and concentration of the dispersed phase, makes such materials different in their behavior from homogeneous and traditional composite materials. Such systems make it possible to optimize the structure to obtain the required properties [9].

Gradient composites based on cast polymer materials reinforced with ceramic or metal particles are promising for the manufacture of various parts for machines and mechanisms due to a combination of unique properties: lightness, high specific strength and stiffness, dimensional stability, wear resistance, and corrosion resistance [10], but have some problems for recycling [11].

The aim of this work is to develop a cast gradient polymer composite material (GPCM) and a technology for its production by centrifuging a liquid suspension for the manufacture of machine parts in the form of bodies of revolution with increased surface wear resistance.

To achieve this goal, the following research tasks were set:

- theoretical substantiation of the technology of obtaining gradient composite materials with increased surface wear resistance by the method of centrifuging suspensions based on a cast
polymer compound with additives of particles of metallic and non-metallic materials in a rotating casting mold;

- development of methods and experimental studies of the influence of technological factors of centrifugation on the nature of the distribution of the particles in samples of GPCM;
- analysis of research results and determination of optimal modes of centrifugation in the production of GPCM based on two-component polyurethane compounds.

2. Methods

The wear resistance of polymeric materials can be increased in two ways: either by increasing the lubricity of the surface of the part, or by increasing its mechanical properties.

The lubricity of PCM can be increased by saturating the surface of the part with particles of graphite or talc, while the wear resistance of the surface on the skin increases by 2 - 2.5 times. When graphene particles were used, the coefficient of friction against steel decreased by 13%, and the wear resistance increased by 42%.

In the second case, the wear resistance of the material surface can be increased by increasing its strength and hardness due to saturation of the surface with dispersed metal particles. In particular, it has been shown that the relative wear resistance $\Delta I$ depending on the hardness HB can be represented in a linear form

$$\Delta I = b \cdot HB$$

where $b$ is the coefficient of proportionality, for polymers it is 3.2 times higher than for metals. One of the founders of the theory of wear resistance of plastics, S.B. Ratner defines wear as the destruction of material on the friction surface in accordance with the formula

$$V = \mu / H \sigma \varepsilon$$

where $V$ - wear on sandpaper; $\mu$ - coefficient of friction; $H$ - hardness; $\sigma$ - tensile strength; $\varepsilon$ - relative elongation. The higher the hardness and strength, the higher the wear resistance of the material.

Thus, the wear resistance of the surface of parts made of polymeric materials can be increased by saturating the working surfaces with particles that can either increase the lubricity or increase its hardness and strength. In this regard, for experimental studies, we selected powders of graphite, which increase the lubricity, and powders of metals - aluminum and iron, which increase the hardness.

In this work, it is proposed to saturate the surface layer of the part with dispersed particles by centrifuging a previously prepared suspension in a rotating casting mold. Suspensions were prepared on the basis of cast polyurethane compounds with increased strength properties. For this, before pouring into the compound, additionally introduced a reinforcing powder consisting of particles of metallic or non-metallic materials. The number of particles was determined individually based on the specified thickness of the wear-resistant layer on the sample surface. High adhesion and increased fluidity of most injection molding compounds contribute to the rapid and favorable assimilation of powder particles of almost any metal or ceramic reinforcement. However, to ensure the maximum adhesion of the phases, the mixing process was carried out for at least 1 - 1.5 min. The resulting liquid suspension was poured into a mold rotating at a given frequency and centrifuged. The centrifugation mode, including the time and frequency of rotation of the mold, was assigned depending on the properties of the compound and reinforcing particles. Under the action of the centrifugal force and the force of inertia of rotation in the liquid suspension, the process of sedimentation of particles of the dispersed phase arose. Centrifugation was carried out until the material was completely solidified. In all experiments, the “time of loss of vitality” of the compound was 4 minutes. As a result, we obtain the form of a body of revolution made of a gradient composite material with a given distribution of reinforcing particles.
3. Results and discussion

The process of sedimentation of particles of various suspensions in a centrifuge is well studied. To describe it, the Stokes equation in differential form can be used:

\[ 6\pi \eta (dx / d\tau) = 4/3r^3 \Delta \rho \pi \omega^2 x \quad \text{or} \quad dx / d\tau = \left( \frac{2}{9} \right) \left( \frac{1}{\eta} \right) \omega^2 r^2 \Delta \rho \]

After integration within the limits from \( x_o \) to \( x \) and, respectively, from 0 to \( \tau \), we obtain

\[ \ln \left( \frac{x}{x_o} \right) = \frac{2}{9} \left( \frac{\Delta \rho}{\eta} \right) \omega^2 r^2 \tau \]  

\[ \tau = \left( \frac{9}{2} \right) \left( \frac{\eta}{\Delta \rho} \right) \ln \left( \frac{x}{x_o} \right) \left( \frac{30}{\pi n r_{av}} \right)^2 \]  

where \( x \) and \( x_o \) are the final and initial distances from the initial position of the particle to the axis of rotation, m; \( r_{av} \) - average value of the radius of the filler particles, m; \( \tau \) is the centrifugation time; \( \Delta \rho = (\rho_r - \rho_c) \) - the difference between the densities of the reinforcement (\( \rho_r \)) and the liquid compound (\( \rho_c \)), kg/m\(^3\); \( \eta \) - suspension viscosity,Pa; \( \omega \) - angular speed of rotation of the form, rad/sec; \( n \) - mold rotation frequency, 1/min.

Formulas (1) and (2) make it possible to predict the desired result of the distribution of particles in the GPCM with a sufficient degree of reliability, as well as to approximately determine the centrifugation time. Deviations from the calculated parameters are mainly explained by the deviation of the particle configuration from the spherical one, since the indicated formulas were obtained precisely with this approximation taken into account.

The above dependences obtained from the Stokes equation are suitable not only for approximate practical calculations, but also for the analysis of the sedimentation process, namely: with an increase in the difference between the densities of the reinforcement and the compound \( \Delta \rho \), the rotation frequency of the form \( n \) and the particle size \( r_{av} \), the time for centrifuging the suspension decreases, and an increase in the viscosity of the compound \( \eta \) - increases.

In this work we used:

- liquid polyurethane compound ADV 13-2 according to TU 2226-046-227369360-99, density 1.26 g/cm\(^3\);
- aluminum powder PA-4 GOST 60-58-73;
- iron powder grade PZhV2 GOST 9849-86;
- crystalline graphite of GL grade in accordance with GOST 5279-74.

It is important to note that the direction of the process of sedimentation of reinforcing particles (to the axis of rotation or to the periphery of the mold) is determined by the sign of the difference between the densities of the filler and the liquid compound \( \Delta \rho = (\rho_r - \rho_c) \). With a positive value of the density difference, the dispersed phase enriches the compound at the periphery of the mold, with a negative value - near the axis of rotation. This circumstance largely determines the choice of filler material. The values of \( \Delta \rho \) for the materials participating in the experiment are presented in table 1. As follows from the data presented, \( \Delta \rho \) is positive in all studied systems.

| Particles       | Density of reinforcement, \( \rho_r \), g/sm\(^3\) | Density difference \( \Delta \rho = (\rho_r - \rho_c) \), g/sm\(^3\) |
|-----------------|--------------------------------------------------|--------------------------------------------------|
| Aluminum powder | 2.65                                             | 1.39                                             |
| Iron powder     | 7.2                                              | 5.94                                             |
| Crystalline graphite | 1.7                                                 | 0.44                                             |

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For an experimental study of the sedimentation process during centrifugation of polymer suspensions, samples were made from polymer composite materials that were obtained in hollow cylinders (1) with an inner diameter of 14 mm and a length of 170 mm, fixed in special clamps (2) on a flat base (3), closed with a protective casing (4). This equipment, rigidly fixed on the shaft, was placed in the clamps of a lathe (5).

In the studies, a DIP-500 lathe was used as a centrifugation device, which has a powerful drive and a significant mass of the bed. This made it possible to significantly reduce the vibration of the tooling, which inevitably occurs when the centering is misaligned when fixing the samples. The rig was brought into rotation. The rotation speed was varied in the range from 40 to 200 min⁻¹.

The finished samples were sawn in height into five parts at a distance of 30, 60, 90, 120, 150 mm from the bottom end surface and examined. Microsections were made from each cut, as well as from the upper and lower end parts of the samples. The structure of the obtained samples was examined using a Nikon EPIPHOT 200 microscope. The number of particles per 1 mm² was calculated on each microsection. The hardness of samples made of polymer composite material was determined according to the standard method according to the Brinell method.

The results of calculations and measurements processed in the STATISTICA 10 software are shown in figure 2.
Figure 2. Dependence of the hardness of GPCM with additives of PA-4 aluminum powder (a), iron powder PZhV 2 (b), and crystalline graphite GL grade (c).
As follows from the data presented, the maximum values of the hardness of the GPCM were obtained:

- for GPCM with additives of aluminum powder PA-4 - with a fraction size of 1.2-1.6 mm and an amount of 25-35% of the mass;
- for GPCM with additives of iron powder PZhV 2 - with a fraction size of 1.0-1.6 mm and an amount of 40-50% of the mass;
- for GPCM with additives of crystalline graphite GL - with a fraction size of 1.2-1.6 mm and an amount of 10-20% of the mass.

In addition, the analysis of the research results showed that in all experiments the filler particles were located along the height of the samples in an exponential relationship in full accordance with formula (1).

4. Conclusions
A technique was developed and experimental studies of the influence of technological factors of centrifugation on the nature of particle distribution and the hardness of GPCM samples were carried out. An exponential dependence of the distribution of particles over the height of the samples is obtained, which corresponds to the well-known Stokes law, which makes it possible to use the known mathematical apparatus for predicting the properties and developing technological modes for obtaining new GPCM.

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