Research of new materials and approaches in additive technologies in the manufacture of prototypes in industrial design

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Abstract. In industrial design, in the manufacture of the prototype, the task of choosing the technology and material for its manufacture is taken. At the minimum cost of material, it is necessary to obtain a prototype with high strength indicators, which will guarantee the implementation of the tasks for which the prototype was conceived. The use of additive technologies allows you to get prototypes with a cellular internal structure, which can significantly save the expendable material when prototyping the future product. In this paper, we analyze the approaches that contribute to improving the strength characteristics of a prototype made using additive technology, and also show the promise of research in the direction of finding the shape of cells with the greatest strength. As a hypothesis, it has been suggested that an increase in the strength characteristics of the prototype can be achieved by introducing nanostructured materials into the polymer. Studies were conducted on the synthesis of nanostructured materials in low-temperature plasma and their modification of polylactide. Samples were made from modified polylactide and their strength characteristics were investigated. An analysis of the results showed an increase in the strength characteristics of samples of modified polylactide compared with samples made of primary polylactide without nanostructured components.

1. Introduction

Composite building materials based on inorganic and organic binders are widely used in the construction industry. In their manufacture, various technologies are used, including nano- and biotechnologies. Currently, intensive technologies for the production of concrete, polymer concrete and other composites are widely known, which contribute to improving the properties of materials and self-healing in the event of defects. First of all, it is polymer concrete formed by vacuum, pressing and vibrocompression methods, according to frame technology, powder-activated concrete activated by alkaline waste, modified by microbiological environment, etc. [1–13, 16–19, 22–29].

Recently, in industrial design, widespread use of additive technologies. Additive technologies have advantages such as rapid prototype manufacturing, dimensional accuracy, and mobility. However,
these technologies have several disadvantages and limitations. For example, a prototype should have strength characteristics close to the designed product, and at the same time, a minimal amount of material should not be used. Additive technology allows you to get a prototype with a cellular internal structure, this significantly saves raw materials when prototyping a future product. Moreover, the smaller the degree of filling of the cells when creating a prototype, the lower strength characteristics it will have. Accordingly, such a prototype will not fulfill the strength requirements for the product being designed. It is necessary to find a balance between the minimum required amount of material used for prototyping and the required strength of the prototype. This problem can be solved in several directions. The most obvious solution is to obtain the dependence of the strength of the prototype on the degree of filling of the cellular structure, expressed as a percentage (%). This dependence will allow for the required strength of the prototype to choose the percentage of filling of the cellular structure.

Another way to solve the problem is to search for the shape of the cells with the greatest strength. As a natural analogue, we consider bionic structures (Fig. 1) [36].

![Figure 1. Natural analogues of bionic structures:](image)

- a - surface coverings of beetles and butterflies; b - lipid binary layers; c - block copolymers [36].

Such structures are found in the chloroplast membranes of plants and in cuticular formations on the wings of butterflies. They combine high strength characteristics and low weight [36].

An artificial analogue of such structures is a cellular structure called a “gyroid” with the topology of a triple periodic surface of minimum energy, consisting of repeating elements with the smallest possible area (Fig. 2) [43].

![Figure 2. Cellular structure with the topology "gyroid" [43].](image)

Such a structure was made using additive technology from polylactide by the FDM method (Fused Deposition Modeling) - layer-by-layer casting by extruded molten plastic. The physicomechanical properties of the samples were studied. A qualitative improvement of the strength characteristics of the structure using the topology of cells of the “gyroid” type is shown. The authors of the study found that
fracture during loading of the sample in different directions relative to the axis of construction occurs, depending on the direction, brittle or plastic [36]. Obviously, further study of this issue is required to describe recommendations on the use of the cell topology of the “gyroid” type in additive technology. This area of research is promising and will allow to qualitatively increase the strength characteristics of the prototype.

No less promising is the direction of using composite materials in additive technology. A large number of studies have been carried out on the introduction of nanostructured additives into polymers, the use of which makes it possible to obtain composites with useful properties [30–33, 35, 37, 42, 44, 45].

For the modification of polymers, the most promising is the modification method under the influence of low-temperature plasma [34, 39,46].

In this work, we studied the strength properties of samples of a modified polymer made by 3D printing. As a modified polymer, a composite of polylactide polymer and nanostructured materials is used.

2. Research methods

To modify the polymer, nanostructured materials were used, which were synthesized by the low-temperature plasma method. In the method used, low-temperature plasma is formed at the site of an electric discharge between two graphite electrodes. The process of polymer modification takes place in one technological volume simultaneously with the synthesis of nanostructured materials during thermal decomposition of graphite by passing polymer strands in the immediate vicinity of the synthesis zone of nanostructured materials. The method allows us to solve several problems in one technological cycle: the direct synthesis and activation of carbon nanostructured material, as well as the modification of polymers in the solid state, synthesized nanostructured materials.

The study of the obtained nanostructured materials was carried out using the methods of derivatography and electron microscopy [40, 41]. A Q1500 D derivatograph and an EMV-100A electron microscope were used for research.

The polymer used was polyamide, a polyester of lactic (2-hydroxypropanoic) acid CH₃-CH (OH) - COOH.

The tensile test specimens were manufactured using additive technology on a Maker Bot Replicator Z18 3D printer with 100% fill of the mesh structure according to the settings recommended by the equipment manufacturer. The geometric dimensions of the samples were: total length - 150 mm, the distance between the wide parts with parallel sides - 108 mm, the length of the narrow part with parallel sides - 60 mm, the radius of the head - 60 mm, the width of the wide part - 20 mm, the width of the narrow part with parallel sides - 10 mm, thickness - 4 mm (GOST 33693-2015).

The tensile strength study was carried out by stretching samples of primary and modified polylactide on a tensile testing machine MP-0.5-1 according to the manufacturer's instructions.

3. Research results

The carbon nanostructured material synthesized by thermal decomposition of graphite was subjected to derivatographic studies in order to identify the type of nanostructured formations and their percentage in the total mass of the material. Studies were carried out on the bulk of the synthesized nanostructured material weighing 230 mg. The decomposition of the samples was carried out with a constant increase in temperature in the open sample holder - crucible. The tests were carried out with a change in the heating rate in increments of 10 °C per minute until a temperature limit of 1000 °C was reached, followed by the completion of the research.

As can be seen from the graph of the dependence of the sample mass (m, mg) on the annealing temperature (T, °C), the decay of the carbon material began at a temperature of about 530 °C and ended at a temperature of about 900 °C (Fig. 3). The nonlinear dependence of the mass decrease with increasing temperature was monitored, since a sharp decrease in the mass of the samples was observed at a temperature of 630 °C and 846 °C. Most likely, this is due to the presence in the synthesized
nanostructured material of nanofibers with a decay temperature of 630 °C and nanotubes with a decay temperature of 846 °C. This assumption was further confirmed by the results of electron-optical studies. Between the indicated points on the temperature scale, the decrease in the mass of the samples occurred close to a linear dependence.

![Figure 3. Derivatogram of annealing of carbon nanostructured material](image)

Investigations of the obtained carbon nanostructured materials using an electron microscope made it possible to evaluate the size and morphology of nanoobjects. It was found that during the synthesis of carbon nanomaterials in a low-temperature plasma, carbon nanotubes and nanofibers are formed (Fig. 4, a), as well as needle nanotubes (Fig. 4, b). The method of synthesis of carbon nanostructured materials during thermal decomposition of graphite allows to obtain a sufficient amount of them necessary for polymer modification.

Subsequently, samples of the modified polylactide prepared by the method of exposure to low-temperature plasma were subjected to investigation. An analysis of the data showed that the composition of the modified polylactide contains up to 1% of nanotubes and up to 3% of nanofibers of the total mass of the composite.

It should be noted that carbon nanostructured material is located in the surface layer of polylactide and is evenly distributed over the entire area.
Figure 4. Photos of synthesized nano-objects: a – carbon nanotubes and nanofibres; b – needle nanotubes

Samples were made from modified and primary polylactide by 3D printing. Prior to further research, samples were stored in a package of vapor- and moisture-proof material.

Studies of the ultimate tensile strength of the primary and modified polylactide were carried out on an MP-0.5-1 tensile testing machine.

The first group consisted of control samples from primary polylactid without nanostructure additives - 6 samples. The second group - samples from modified polylactide - 6 samples. Using optical microscopy, fractures of samples from primary and modified polylactide were studied. A typical view of the fractures is shown in Fig. 5.

Figure 5. Fracture of samples made of primary (a) and modified (b) polylactide

Visual studies showed that the fracture surface of the samples of each of the two groups was porous. Polymer filaments that formed the samples were clearly visible. By the degree of plastic deformation, the samples of both groups are fragile. The fracture of the samples under the action of the load is flat with bevels. Light reflection by fractures of samples is uneven, matte and shiny areas with yellow and blue tint are observed, occupying up to 30% of the fracture area. Optical studies showed a similarity in the appearance of fractures in all the samples under study. The results of testing two groups of material samples on a tensile testing machine and their statistical analysis are summarized in table 1.

It was found that the values of the mass index within each group of samples are not significantly different. The relationship between the change in the mass of polylactide and its modification is not monitored, since the difference in the average mass of the samples of the two studied groups is less than 1%. A characteristic is the elongation rate of the samples upon rupture of the modified polylactide. Its value decreased by almost 2 times (by 40.8 relative%) compared with the control samples from the primary polylactide. The decrease in the plasticity of the modified polylactide is obviously associated with the presence of nanostructured materials in its structure. The effect obtained requires a more detailed study.

In each group of the studied samples there is a spread in the value of the tensile strength of the material. The tensile strength of samples from modified polylactide, in comparison with control samples, increased by up to 10%.

An analysis of the experimental results showed that it is necessary to conduct additional studies of modified polylactide with varying degrees of filling of the cellular structure of the samples.

The obtained results show the prospect of further research in the direction of polylactide modification and the study of the physicomechanical properties of products made from it.
Table 1. Test results of samples of primary and modified polylactide rupture

| № sample | Primary polylactide | Modified polylactide |
|-----------|---------------------|----------------------|
|           | weigh, g | elongation, mm | breaking load, MPa | weigh, g | elongation, mm | breaking load, MPa |
| 1         | 9.65     | 15             | 20.74            | 9.72     | 7             | 22.06            |
| 2         | 9.68     | 14             | 21.37            | 9.84     | 7             | 22.75            |
| 3         | 9.65     | 11             | 21.33            | 10.22    | 8             | 21.57            |
| 4         | 10.04    | 15             | 20.7             | 9.78     | 6             | 23.53            |
| 5         | 9.78     | 9              | 18.39            | 9.71     | 10            | 22.26            |
| 6         | 9.66     | 12             | 21.13            | 9.73     | 7             | 22.75            |
| Average   | 9.74     | 12.7           | 20.61            | 9.83     | 7.5           | 22.49            |
| Range of variation | 0.39     | 6              | 2.98             | 0.51     | 4             | 1.96             |
| Dispersion | 0.0235   | 5.8667         | 1.2640           | 0.0382   | 1.9           | 0.4602           |
| Standard deviation | 0.1534   | 2.4221         | 1.1243           | 0.1785   | 1.3784        | 0.6784           |

4. Conclusions
A brief overview of possible approaches to improve the strength characteristics of prototypes made by additive technology of polymers is given.

A method of manufacturing samples from polylactide containing nanostructured materials is proposed. The method made it possible to increase the tensile strength of modified samples by up to 10%. This confirms the assumption about the possibility of increasing the strength characteristics of the prototype when using nanostructured materials. The authors believe that research in the following areas will be promising:

- obtaining the dependence of the strength of the prototype on the degree of filling of its cellular structure;
- conducting research on products made with a cellular structure of the “gyroid” type;
- conducting a study of the strength characteristics of modified polymers depending on the modes of their modification;
- identification of the best option for the dependence of the strength of the product on the above approaches.

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