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CARBON FIBER EFFECT ON STRUCTURE AND MECHANICAL PROPERTIES OF POLYMER COMPOSITES PRODUCED BY ADDITIVE MANUFACTURING

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The paper explores the products made of acrylonitrile butadiene styrene (ABS), a common thermoplastic polymer comprising up to 10 wt.% carbon fibers. These products are obtained by extrusion-based 3D printing. The mechanical properties of the obtained specimens are studied by tensile and flexural strength testing with regard to the carbon fiber content. The scanning electron microscopy is used to study the structure of the fracture surface of the tested specimens. The physical-and-mechanical properties of polymer specimens and products produced therefrom are investigated with respect to the different content of carbon fibers. Secondary ABS polymer subjected to natural ageing for 17000 hours is used to prepare the composite material. Described are the production techniques for the composite filament and the filament fabrication process, which is optimum from the viewpoint of achieving the improved properties of physical-and-mechanical properties of the specimens obtained.

Keywords: composite materials, additive manufacturing, filled polymers.

INTRODUCTION

The use of plastics and polymer composites is becoming more widespread in additive manufacturing. Their active development has begun in the 21st century, but the theoretical and technological prerequisites for their appearance were observed already in the last century. Thanks to additive manufacturing, parts of various shapes can be produced in a shorter period, including products that cannot be obtained by classical methods of the material processing. With the development of engineering technologies, the demands on the product operation in more severe conditions as well as on the structural materials are increasing.

Today, one of best ways to increase the physical-and-technical properties of materials is the creation of composites *via* the introduction of strengthening particles or fibers. This strengthening technique is applicable to both metal and polymer materials. The main production technique of polymer composites is the fiber introduction in the matrix followed by the polymer curing. The fiber content does not usually exceed 40% and varies depending on the required physical-and-mechanical properties and processing techniques. According to Li and Cai [1], the content of carbon fibers ranging 5 to 30 wt.% in the acrylonitrile butadiene styrene (ABS)-containing composite enhances its strength properties. It is known that in ABS-containing composites with strengthening fiber content over 2 wt.%, not only physical-and-mechanical properties, but also electrical conductivity are improved. The increase in the length of carbon fibers reduces the specific resistivity of composites [2].

One of the important characteristics of the composite materials is the fiber orientation. Nak-Ho and Suh [3] show that polymer composites with oriented fibers possess the higher physical-and-mechanical properties than composites with misoriented fibers of the same composition. This is manifested in flexural and tensile testing of

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composites with fiber orientation towards the load application. Fabrication of products from such composites implies the appearance of their anisotropic properties. In additive manufacturing with a proper selection of operating modes, it is possible to achieve the fiber orientation in the product [4], which also leads to the improved material properties in the given direction. This tendency is observed in composites with different matrices, namely ultrahigh-molecule polyethylene [5], ABS [6], polylactides [7], polycarbonate and polyamide [8, 9], polyphenylene sulfide [10], and biocompatible materials, *e.g*., dental plaster [11]. In all cases, the mechanical properties of the products are improved.

One of the important parameters affecting the composite properties is the fiber length. Quan *et al.* [12] used 640 μm long fibers, but in the authors' opinion, it was advisable to use longer fibers for the improvement of the strength properties, as the fiber-matrix adhesion increased.

The engineering industry currently requires not only new materials, but also technologies that are either advanced or improved. Selective laser melting and electron beam melting are commonly used in additive manufacturing, but they are very rarely applied to polymers. Fused deposition modeling (FDM) is one of the most widely used additive manufacturing techniques. It utilizes polymer materials, while having low cost as against other additive manufacturing techniques. FDM requires the creation of a filament, which will be used as a feedstock material for the development of new kinds of polymer materials [13, 14]. To ensure the high material properties, it is necessary to achieve the fiber orientation along the applied tensile load and a certain fiber size.

Today, there are still some interesting and relevant problems to be addressed. First, what structure has the composite made of secondary fiber-reinforced ABS polymer and, second, how the polymer degradation, the fiber addition and fiber orientation affect the mechanical properties of the material.

The aim of this work is to study the influence the fiber quantity and orientation on the mechanical properties of the obtained composite. The structural investigations are described for the discussion of the results obtained. Additive manufacturing of products based on initial and recovered ABS polymer including the filament synthesis, FDM process, and product testing are discussed herein.

MATERIALS AND METHODS

Recovered ABS polymer based on carbon fibers was used to synthesize the composite material, the ABS polymer used as the initial material was obtained after the ABS product grinding, and GZh-23/550k graphite braid (OOO "Argon", Balakovo, Russia) with a linear density of 562 tex – as carbon fibers. The ABS products were obtained by the fused deposition modeling (FDM) from commercial ABS polymers and then exposed to natural ageing for 17000 hours. A rotating cutting mill RM-120 (Vibrotekhnik, Saint-Petersburg) with a 2.5 mm diameter of mesh of sieves was used to grind the ABS products and graphite braid at a 1500 rpm rotational velocity.

The obtained components were stirred down to a homogeneous mixture in a Hei-TORQUE Value 100 overhead stirrer (Heidolph Instruments, Schwabach, Germany) for 30 min. A filament for FDM 3D printers must have a constant diameter over the total length.

When the filament is fabricated from a dry mixture of the ABS pellets and carbon fibers, the filament diameter cannot be fully controlled. Moreover, it is impossible to gain a uniform distribution of the carbon fibers and provide low porosity.

Therefore, after stirring we fabricated pre-filament with a 2 mm diameter using an EX2 Filament Extruder (Filabot, Vermont, USA) consisting of a Filabot Airpath air-cooling and Spooler systems. The obtained pre-filament was cut into pellets in a 10 mm Dia Twin Screw Extruder (Rondol Microlab, France). The filament with a diameter of 1.75 mm was then fabricated from the pellets on the EX2 extruder. The carbon fiber content in the filament was varied from 0 to 10 wt.%, the composition was specified during the preparation of dry mixes with the different ratio of the fibers and plastic. The filament was fabricated with 0, 3, 5 and 10 wt.% carbon fiber contents.

The highest homogeneity and stability of physical-and-mechanical properties was observed in specimens produced by the following procedure: grinding of fibers and secondary ABS polymer → stirring of the granulate obtained → extrusion of the mixture → granulation of the filament obtained → repeated extrusion. The procedure with only one extrusion process provided an insufficient fiber stirring in the polymer matrix. The increase in the number of extrusions led to an insignificant increase in the homogeneity.

The fabricated filament was used to produce test specimens with a rectangular section on a FDM 3D printer PrintBox3D One (RGT, Russia). The operating parameters included 0.40 mm nozzle diameter, 230°C nozzle temperature, 4 mm/s printing velocity, and 200 μm layer thickness.

The evolution of the mechanical properties of the FDM specimens manufactured from ABS-containing composite filaments was investigated by their tensile strength and three-point bending tests and measurements of the melt flow index of all the filaments. The specimens with a rectangular section were prepared for three-point bending tests, while the dogbone-shaped steel specimens were produced for tensile and flexural strength testing on a Gotech Testing Machine Al-7000-M (China). The melt flow index was measured on an IIRT-5M system (AO "LOiP", Russia) at 220°C temperature and 10 kgf load. Measurements were performed through a capillary of 2.1 mm diameter for 600 s. In tensile strength tests, we used anchor and mobile clamps to hole specimens, while in flexural strength tests we used a three-point bending installation with one loading head at the center and two supports on each side. The dependences between the load (N) and shear (mm) were processed on the UGNLab testing equipment. The mechanical properties were measured five times by testing five specimens with the different carbon fiber content.

After tensile strength testing, the specimen fracture surfaces were examined by LEO EVO 50 (Carl Zeiss AG, Germany) scanning electron microscopy (SEM). The SEM technique provided studies of only conductive materials. Therefore, the polymer specimens were coated with a pure (99.999%) copper layer of a nanoscale thickness. The coating was deposited by a JEE-420 vacuum evaporator (JEOL Ltd, Japan) in high vacuum during 30 min. The LEO EVO 50 and JEE-420 were situated in the Tomsk Regional Core Facility Centre "Nanotekh" of The Institute of Strength Physics and Materials Science SB RAS, Tomsk, Russia.

RESULTS AND DISCUSSION

Mechanical properties

All specimens were compared with the FDM-manufactured initial ABS specimens. The results are plotted in Fig. 1. Secondary ABS (zero point), without the addition of carbon fibers and initial ABS (horizontal line) demonstrated different strength properties. The difference in the tensile strength (Fig. 1*a*) and Young's modulus (Fig. 1*b*) between these two ABS was minimum with regard to measurement errors.

According to Fig. 1*c*, the tensile strength of the secondary ABS is 1.2 times higher than that of the initial, whereas its yield point is 2.5 times lower (Fig. 1*d*). This indicates that secondary ABS does not lose hardness after ageing and recovery, but acquires higher viscidity than initial ABS. As shown Fig. 1*c*, secondary ABS rapidly transfers to the plastic deformation stage, but plastic deformation required for its fracture must be higher (see Fig. 1*d*). This is because during the multiple ABS recycling and ageing, its molar weight lowers, molecules become more movable and require lower deformation load to transfer to inelastic deformation.

All measured strength properties of the ABS polymer changed after the addition of carbon fibers. The examined specimens were manufactured under the same 3D printing conditions despite the different melt flow index and other composite filament parameters, depending on the carbon fiber content. Technologically, this was not an optimum solution, but it allowed us to experimentally compare the obtained specimens. Measurements of microporosity showed that it did not change with increasing content of carbon fibers (pores between the layers and filament tracks and inside the filament were considered also). Thus, the change in the strength properties depended on the carbon fiber content, rather than on the porosity.

The addition of 3 wt.% carbon fibers leads to a considerable change in the tensile strength of the obtained materials. Moreover, this parameter is lower than in the ABS polymer without carbon fibers. These results are discussed below in the *Fracture Surface Section*.

The addition of 5 wt.% carbon fibers leads to the approaching of the tensile strength and Young's modulus values to that of initial ABS, but the plastic properties decrease. In addition, the difference in the strength properties of the ABS polymer with and without the carbon fibers is not great. Significant changes are observed in the strength properties of composites containing 10 wt.% carbon fibers. The values of the tensile strength and Young's modulus of such composites exceed that of initial ABS (see Figs 1*a*, 2*b*), while the plastic properties are close to it (see Figs 1*c*, 2*a*).

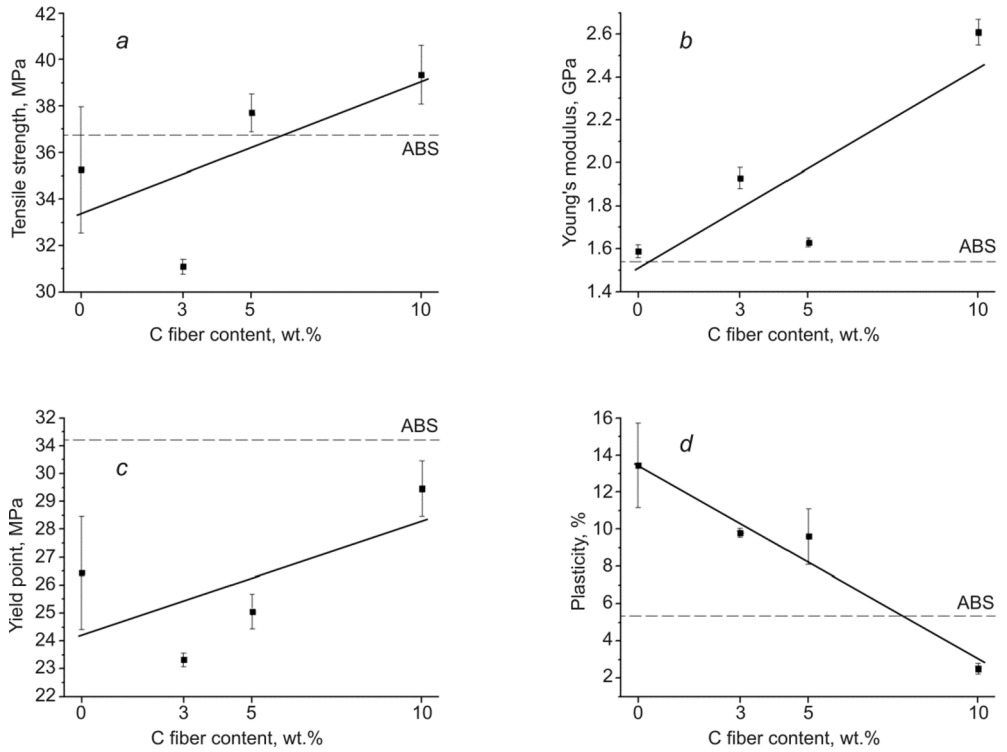

Fig. 1. Dependences between the carbon fiber content and tensile strength (*a*), Young's modulus (*b*), yield point (*c*), plasticity (*d*).

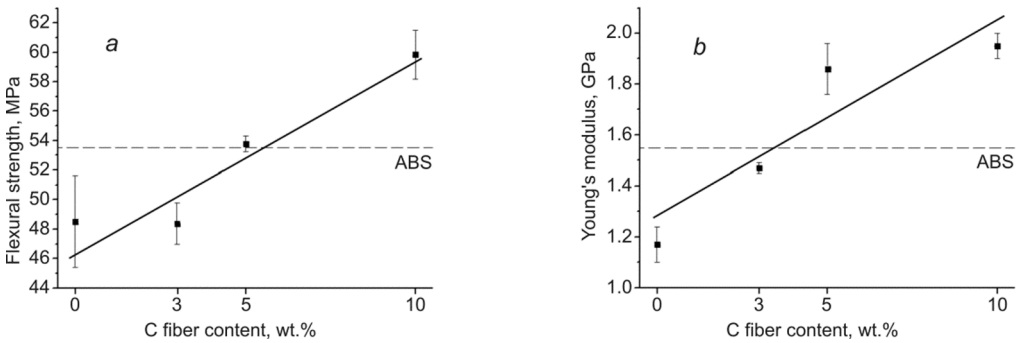

Fig. 2. Dependences between the carbon fiber content and flexural strength (*a*), Young's modulus (*b*).

These composites are therefore rather attractive for practical implementations. Further increase in the content of carbon fibers in filaments is not advisable because the higher fiber content results in a lower melt flow index and complicates both the filament fabrication and the FDM process.

Flexural strength testing is conducted up to the specimen fracture, i.e., its maximum deformation. This is plotted in Fig. 2. Young's modulus demonstrates considerably low values for secondary ABS against initial ABS. At the same time, the tensile and flexural strength tests show that this parameter is the same for initial ABS.

In general, flexural strength testing demonstrates monotonous increase in the strength properties of composites with increasing carbon fiber content. The tensile strength of specimens with a 5 wt.% fiber content approaches to that of

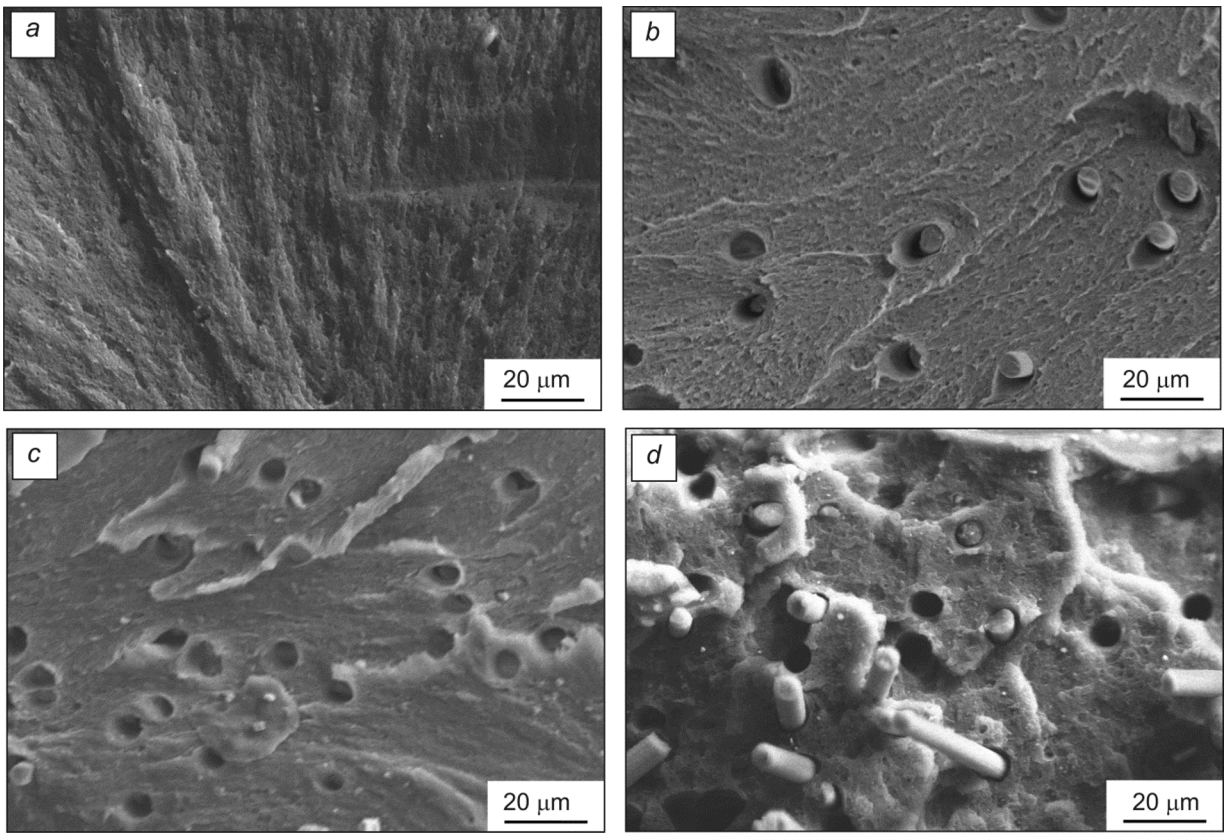

Fig. 3. SEM images of fracture surface after tensile strength testing of specimens with different carbon fiber content: *a* – 0 wt.%, *b* – 3 wt.%, *c* – 5, *d* – 10 wt.%.

the initial ABS, whereas Young's modulus is higher. The tensile strength and Young's modulus of specimens with a 10 wt.% fiber content are much higher than in the initial ABS polymer.

A comparative analysis of the tensile and flexural strength tests demonstrates that secondary ABS-containing composites with the properties close to that of initial ABS, are composites with 5 wt.% carbon fiber content. This content is sufficient for a compensation of decrease in most of strength parameters, which occur after ABS ageing and recovery. The introduction of a large amount of carbon fibers results in the growth in the strength properties of the composite material and the decrease in its plastic properties.

Fracture surface

Figure 3 presents SEM images of the fracture surface after tensile strength testing, which shows that the carbon fiber orientation in FEM-manufactured specimens occurs along the filament printing direction, the maximum angle of misorientation being 5 degrees. This can be explained by the fact that the nozzle diameter of the FDM 3D printer is smaller (400 μm), than that of the filament extruder (1750 μm) and approaches to the length of a carbon fiber up to 300 μm. In these conditions, the fibers are forced to orient in the extrusion direction. Otherwise, the fibers inhibit the plastic extrusion, and emergency stop will be conducted for the FDM process. Thus, the high fiber orientation in the filament simplifies the 3D printing process and reduces risk of the nozzle blockage during the FDM process.

According to SEM observations, the fracture surface of specimens with carbon fibers has pores that formed after the picking up fibers during tensile strength testing. In some pores one can see the fiber residues pulled out of the matrix. The pores without fibers indicate that they locate in this very place of the specimen's counterpart. The pores left

by the pulled fibers help us to estimate the microporosity of the specimens obtained. The pore diameter almost coincides with the fiber diameter in these pores. This holds for specimens with 5 and 10 wt.% carbon fiber content; in specimens with 3 wt.% carbon fiber content, the pore diameter exceeds the fiber diameter. Thus, in the latter specimens, the microporosity is the highest and, consequently, the fiber-matrix adhesion is the lowest. This also explains the low values of tensile strength of these specimens as compared to others (see Fig. 1), because the lower interaction with the matrix reduces the carbon fiber contribution to the strength and increases the negative effect from pores.

The tensile strength of carbon fiber-reinforced composite materials depends on the fiber-matrix adhesion. The higher fiber-matrix adhesion allows fibers to stretch together with the matrix material, thereby providing high values of the strength properties. The lower fiber-matrix adhesion or a free fiber motion in the matrix provides tension only for the matrix material. The porosity produced by fibers reduces the matrix strength, and the strength of the composite material becomes lower than the strength of the pure matrix.

It is impossible to measure the fiber-matrix adhesion, and it is therefore expedient to employ judgmental methods. Tekinalp *et al*. [4] propose a judgmental method for this purpose, which implies studying carbon fibers on the fracture surface after tensile strength testing. If the protruded fibers do not have ABS, the fiber-matrix adhesion is low. In our case, the carbon fibers do not contain ABS even in composites with 10 wt.% carbon fiber content.

The literature shows a variety of approaches to the improvement of the fiber-matrix adhesion. The main approach is the coating deposition onto the carbon fibers. In our case, we do not coat the carbon fibers with anything, although many manufacturers of carbon fibers prepare their surface for coating. They utilize different techniques, for example, oxidation, plasma electrolytic carbonitriding and others. The process coating deposited onto the carbon fibers by a manufacturer, is most likely preserved on the fiber surface after its cutting. According to SEM images and mechanical tests, the contact points between the matrix and processed fibers possess the high adhesive strength.

CONCLUSIONS

1. According to tensile and flexural strength tests, the strength properties of pure secondary ABS were lower than that of initial ABS. The addition of 5 wt.% carbon fibers allowed to achieve the mechanical properties of initial ABS. The addition of carbon fibers in the content of 10 wt.%, led to much higher strength and lower plastic properties.

2. SEM observations showed that the fiber-matrix adhesion was low in all specimens. Macroporosity (pores between the layers and filament tracks) was identical for all specimens, while microporosity (pores inside the filament) was the highest for composites containing 3 wt.% carbon fibers. That led to lower values of the strength properties of such specimens.

3. The low fiber-matrix adhesion led to a reduction in the tensile strength due to an insufficient interaction between the fibers and the matrix. This problem can be solved by the coating deposition onto the carbon fibers.

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