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Production technology for polymeric composite materials by additive manufacturing methods

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Abstract. Additive manufacturing methods make it possible to create complex geometry parts, that cannot be produced by conventional methods. For manufacture of the products, composite polymeric materials can be used, both disperse-filled and filled with short or continuous fibers. Recently, more and more attention has been paid to reinforcing plastics with natural fibers. The study of the manufacturing process of a polymeric composite material filled with continuous natural fibers by the fused filament fabrication is presented

1. Introduction

1.1. Overview
Additive manufacturing (AM) or layer-by-layer technologies of production – one of the most rapidly developed direction of digital manufacturing. AM includes various technologies such as 3D printing, rapid prototyping, direct digital production, layered production [1].

Methods of additive technologies make it possible to create products of complex shapes that cannot be manufactured by conventional methods. These methods help to reduce the time between project design and product manufacturing compared to conventional methods [2].

A wide range of materials available for additive production (from metallic powders to polymer filaments) makes it possible to produce analogues of products obtained by conventional methods, often not inferior to them by mechanical characteristics [3, 4].

At present, all technologies of additive production are fully reflected in the literature [5, 6]. The main attention is paid to the manufacture of products from metal powders [7] using selective laser melting technology, in view of the increased interest in obtaining functional parts of various machines and mechanisms [8].

However, polymeric composite materials (PCM), filled with fibers of various types and composition [9, 10], already constitute a serious competition to metals. In this connection, on the wave of general interest in additive technologies, attempts are made to directly produce composite materials using 3D printing.

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1.2. Materials review

For manufacture of the products, PCM can be used, both disperse-filled [11] and filled with short or continuous fibers [12, 13].

PCM not only reflect the properties of the matrix and filler, but also have completely new characteristics, which are often not inherent in individual components.

Matrix of PCM, as the name implies, are polymers. The invention of polymers with new sets of properties led to the expansion of the possibilities for their use, which led to a rapid increase in production volumes from polymeric materials. However, the main problem associated with the use of polymeric materials is still their disposal, which involves a sets of complex and expensive processes. The wider use of biodegradable plastics can solve this problem.

According to the American Society for Testing and Materials (ASTM) standard, biodegradable plastics are plastics that decompose as a result of the action of natural microorganisms such as bacteria, fungi. The main advantage of biodegradable polymers is their ability to decompose quickly compared to polymers derived from petrochemical raw.

Despite the wide variety of biopolymers produced, a special place in this sector belongs to polylactide (PLA), a material based on lactic acid. Polycaprolactone (PCL) is also quite widespread. Due to its low melting point (about 60 °C), PCL is used only in medicine (the creation of self-dissolving implants) and in prototyping. Polylactide is widely used in industry.

Products made from polylactide compete in physical and mechanical properties with similar products from ABS plastic, one of the most popular materials both in the field of 3D-printing and in the polymer industry as a whole.

Currently, PCM have found application in almost all industries. PCM are widely used in the manufacture of machine parts and mechanisms, elements of various designs, electrical insulation [14, 15].

In terms of mechanical characteristics (per unit mass), fiber-reinforced polymer composites (FRPC) can significantly exceed traditional structural materials, which can reduce the volume and mass parameters of a product many times over.

The shapes and types of reinforcing fibers are also diverse. At present, fillers made of organic, aramid, basalt fibers, as well as carbon fibers, glass fibers, etc. are widely used for reinforcing composite materials. They are part of the composite in the form of short fibers, ribbons, threads, bundles, fabrics, nonwoven materials and other fibrous structures

The properties of FRPC significantly depend on the reinforcement scheme, as well as on the characteristics of the interaction of components at the interface. To achieve the required characteristics between the fibers and the matrix, a certain ratio of properties must be maintained, high adhesion between them and the wettability of the filler by matrix [16, 17].

Recently, more and more attention has been paid to reinforcing plastics with natural fibers. [18]. Interest in natural fibers is associated with economic factors, since they are a renewable resource, and their cost is low compared to all other fibers. For this reason, natural fibers are promising for use in the manufacture of PCM as reinforcing fillers intended for the manufacture of a wide variety of products not exposed to a humid environment. PCM with this type of fibers has another important advantage - the possibility of processing and reuse. Due to its porous structure, plant fibers are well impregnated with a polymer matrix, which provides high strength at the polymer-fiber interface.

The properties of the most common fibers in the industry are presented in table 1 [19]. There is a superiority of the properties of glass fiber, and especially carbon fiber over natural fibers, however, if we compare the density of materials, and, accordingly, the mass of the product or specific strength, the difference does not look so significant.

Table 1. Properties of different fibers

Fiber	Density, g/cm^3	Fiber diameter, μm	Break elongation, %	Specific strength, g/tex
Cotton	1,2	11-12	7	0,8
Flax	1,3	5-40	3	1,3
Jute	1,5	8-30	2	0,5
Glass fiber	2,55	5-24	2-5	1
Carbon fiber	1,9	5-7	2	10

1.3. Production methods review

FFF (Fused Filament Fabrication) technology is one of the most widely used 3D printing technologies. Currently, consumer versions of FFF printers with open-source manufacturing modes occupy the widest part of the 3D printer market due to the simplicity of the manufacturing process, flexibility, and the low price of the installations and materials [20]. The most commonly used materials are thermoplastics such as ABS, PA, PLA [21].

The basis of fibrous fillers are elementary fibers (continuous or short). Elementary fibers can be used independently or for the production of other forms of fibrous materials - threads, ribbons, fabrics, canvases, etc.

When using additive technologies for the production of FRPC, equipment needs to ensure the integration of the reinforcing component into the matrix during printing

By type, the reinforcing components are divided into continuous and short fibers. With regard to the production of composite material on a 3D printer, it should be borne in mind that continuous fibers have a strong reinforcing effect, however, require laying. Short fibers can be pre-mixed with polymer powder or filament, but after printing they will be oriented randomly (unless orientation operations are provided).

The method of fiber integration is determined by the selected additive technology (FFF). One of the ideas for reinforcing in this process is as follows: in addition to the polymer, fiber is continuously fed through the extruder, which, under the influence of high temperature and pressure in the chamber, is impregnated with the base material and leave the nozzle in a single stream (Figure.1).

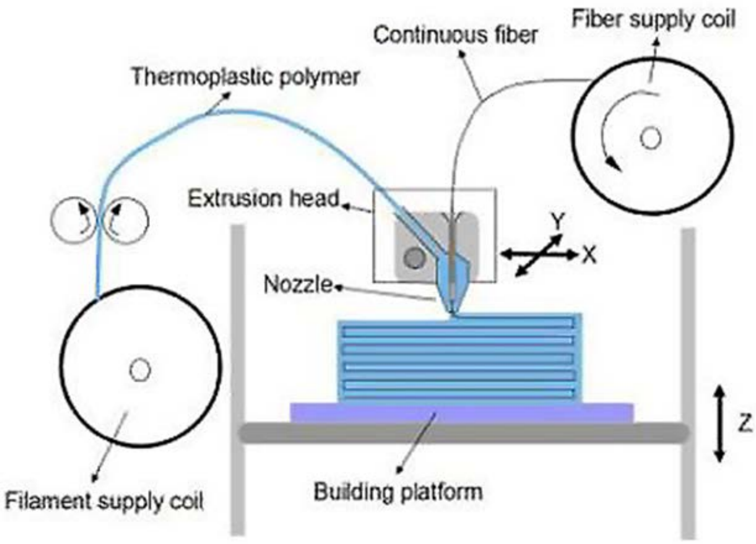


Figure 1. Manufacturing scheme of FRPC by FFF [22]

Authors [23] proposed a novel free-hanging 3D printing method for the first time to fabricate the core structure of a continuous carbon fiber reinforced composite sandwich structure. It uses continuous carbon fiber and PLA to print in the print head. The mixed ribbon is cooled and solidified after extrusion of the print head, and the angle of the print head speed is adjusted. Finally, a hanging print strip is formed (Figure.2).

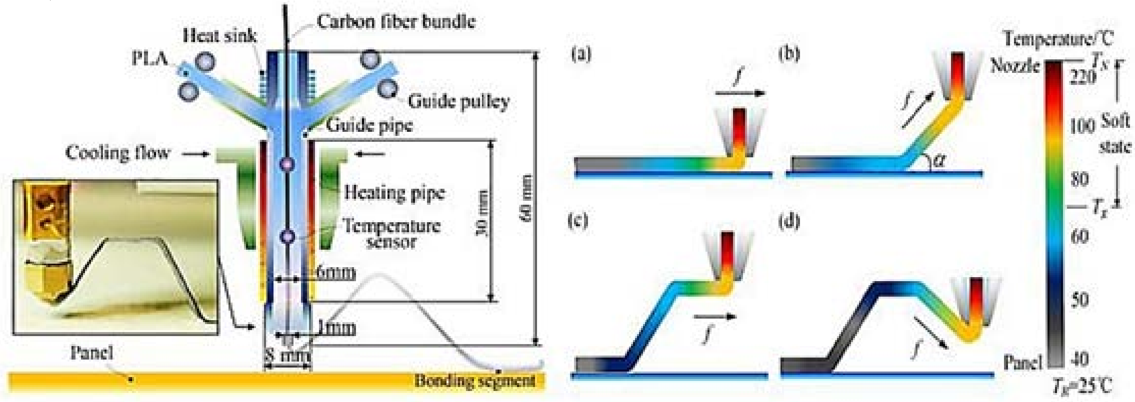


Figure 2. Free-hanging 3D printing schematic [23]

The above methods for producing a composite material based on the FFF method have a drawback. The high temperature sources used in both processes can limit the use of natural fibers as a reinforcing component due to the risk of damage to the fibers until complete combustion. However, this problem can be solved using rational design and temperature of the extruder.

Authors [24] for the manufacture of FRPC proposed the addition of a fiber feed tube synchronized with the nozzle in speed and direction of movement (Figure.3).

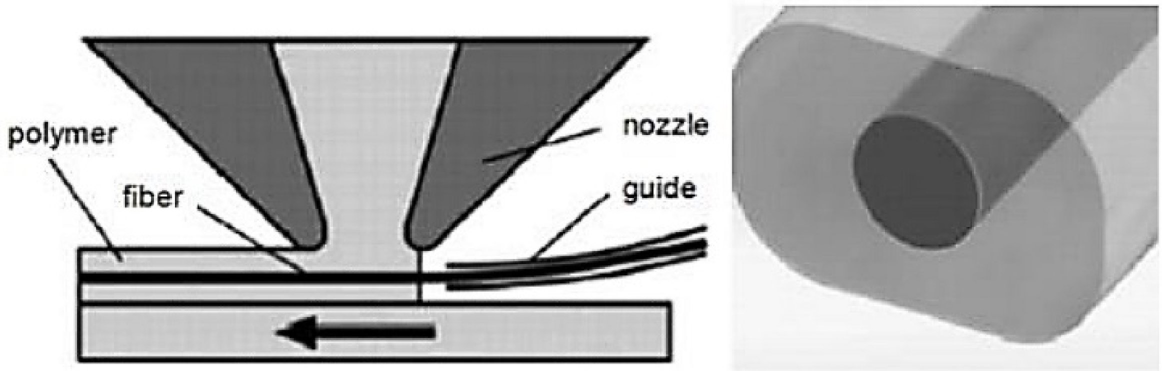


Figure 3. 3D printing schematic [24]

The fiber is laid directly in front of the nozzle, which allows the plastic to immediately cover it, forming a composite material. This process is good because it does not require the manufacture of a special prepreg, but for its implementation it is necessary to set the optimal trajectory of the nozzle and automate the fiber supply.

It should be noted that attempts to combine additive methods and principles for producing composite materials based on a polymer matrix into a single technology are rare. Additive manufacturing technologies for FRPC with the addition of organic, biodegradable natural fibers with a number of advantages, including environmental friendliness, are under development. At the same time, there are no works in this direction that take into account the environmental aspect in the literature.

2. Materials and methods

As the basis for the setup, it was decided to use the TEVO Black Widow 3D printer (Figure. 4), and modify it to be able to print with composite material reinforced with continuous natural fibers.

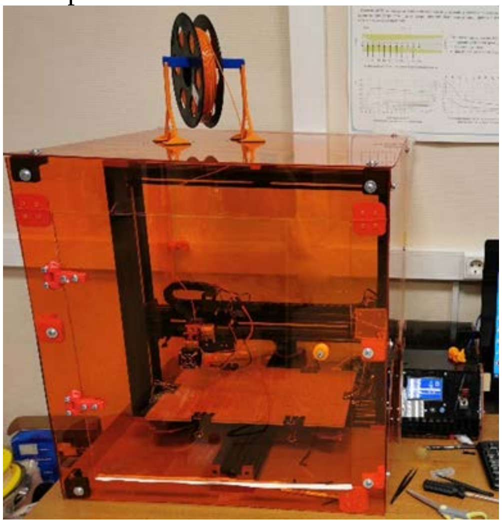


Figure 4. Basic 3D printer TEVO Black Widow

A commercially available thermoplastic was chosen as the matrix material, and a continuous natural fiber with a diameter of 0.2 mm was the reinforcing component.

The mechanical properties of the polymer were tested in the Zwick machine with a 500N force sensor in accordance with the GOST 4648-2014 (ISO 178: 2010).

Tests were conducted for samples made in two directions of printing (XZ and XY), as shown in Figure. 5

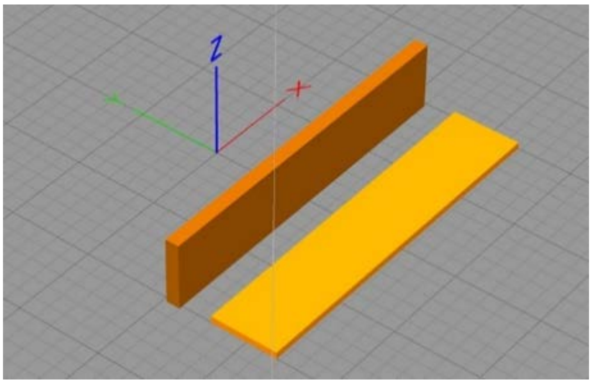


Figure 5. Printed samples in XZ and XY direction

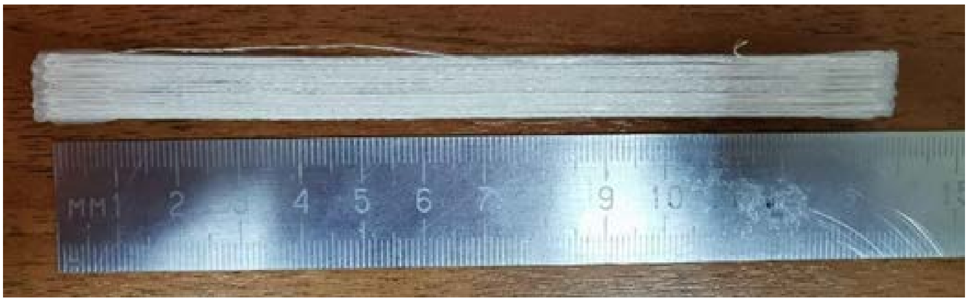
3. Results and discussions

Initially, the mechanical properties of the polymer matrix were investigated. The results are presented in table 2.

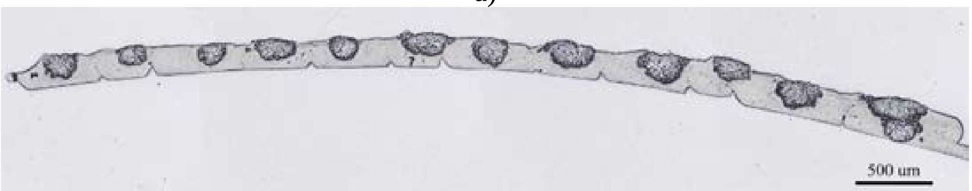
Table 2. Mechanical properties of FRPC matrix

	E_{flex}, MPa	σ_y, MPa	σ_{ult}, MPa	ε_f, %
XY orientation	393.91±20.74	10.5±0.54	14.5±0.75	6.2±0.11
XZ orientation	499.83±18.4	13.2±0.45	17.9±0.62	6.24±0.13

Samples of composite material for testing in accordance with ISO 527-4 were manufactured on the above equipment. The image of the sample and the cross section of the monolayer are shown in Figure. 6 a, b



a)



b)

Figure 6. Specimen (a) and the cross section of the monolayer (b)

The porosity of the samples is quite low (~ 4%), compared with printed samples filled with synthetic (glass and carbon) fibers, the porosity of which reaches ~ 15% [25, 26].

Rational regimes of material fabrication were found and showed in Table 3.

Table 3. Rational regimes of material fabrication

Parameter	Value
Chamber type	closed
Extruder temperature, ^{0}C	220
Bed temperature, ^{0}C	100
Layer height, mm	0,3

Filling degree of obtained composite is 30%. It is close enough to commercially available high-strength carbon fiber filaments with a polymeric matrix [27]. The distance between the filaments within one layer was ~ 480 μm, the layer height ~ 290 μm.

4. Conclusion

The possibilities and prospects of manufacturing polymeric composite materials by the methods of additive technologies are considered.

A study of the manufacturing process of the polymeric composite material filled with continuous natural fibers by the FFF is presented.

A technological process developed for producing a new easily processed polymeric composite material by the FFF with a ratio of components: 70% (by volume) of the polymer and 30% (by volume) of continuous natural fiber.

Future work will be aimed at studying the physic-mechanical properties of the obtained composite material. As well as various options for placing fibers and the development of technology for controlling the degree of filling in various sections of the specimen.

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References
[1] ISO / ASTM52900 – 15. Standard Terminology for Additive Manufacturing – General Principles – Terminology.
[2] Grigoryev S.N., Tarasova T.V. Possibilities of additive production technology for the manufacture of complex parts and the production of functional coatings from metal powders // *Metallurgy and heat treatment of metals.* - 2015. - No. 10.
[3] Terekhina, S., Skornyakov, I., Tarasova, T., Egorov, S Effects of the infill density on the mechanical properties of nylon specimens made by filament fused fabrication //*Technologies.* – 2019. – T. 7. – №. 3. – C. 57.
[4] Grigoriev, S., Tarasova, T., Gusarov, A., Khmyrov, R., & Egorov, S. (2019). Possibilities of Manufacturing Products from Cermet Compositions Using Nanoscale Powders by Additive Manufacturing Methods. *Materials*, 12(20), 3425.
[5] Gibson I., Rosen D., Stucker B. Additive manufacturing technologies: 3D printing, rapid prototyping, and direct digital manufacturing. Second Edition. New York, *Springer-Verlag Publ*., 2015, 498 p. DOI: 10.1007/978-1-4939-2113-3.
[6] Tarasova T.V. Additive Manufacturing: Teaching Guide; Higher Education; INFRA-M: Moscow, Russia, 2019; 196p. doi:10.12737textbook_5c25c2b3a03f99.16774025. Available online: http://znanium.com/catalog/product/1046704 (accessed on 2019).
[7] Zlenko M. A., Nagaytsev M. V., Dovbysh V.M. Additivnye tekhnologii v mashinostroyenii: posobie dlya inzhenerov [Additive technologies in mechanical engineering: a manual for engineers]. Moscow, NAMI Publ., 2015, 220 p.
[8] Grigor’ev S. N., Tarasova T. V., Gvozdeva G. O. et al. Solidification behavior during laser microcladding of Al–Si alloys [Text] / S.N. Grigoriev T.V. Tarasova, G.O. Gvozdeva, Nowotny St. // *Surface and Coatings Technology*. – 2014. – № 2. – DOI:10.101.
[9] Perepelkin K. E. Armiruyuschie volokna i voloknistye polimernye kompozity. Monografiya [Reinforcing fibers and fibrous polymeric composites. Monograph]. St. Petersburg, Scientific basics and technologies Publ., 2009. 380 p..
[10] Skornyakov I. A., Tarasova T. V., Terekhina S. M. Investigation of the strength characteristics of samples made of nylon by FFF technology. *ARPN Journal of Engineering and Applied Sciences*. 2019. Vol.14. №13. P. 2427-2432.
[11] Khatri, B., Lappe, K., Habedank, M., Mueller, T., Megnin, C., & Hanemann, T. (2018). Fused deposition modeling of abs-barium titanate composites: A simple route towards tailored dielectric devices. *Polymers*, 10(6), 666.
[12] Sodeifian G., Ghaseminejad S., Yousefi A. A. Preparation of polypropylene/short glass fiber composite as Fused Deposition Modeling (FDM) filament //*Results in Physics*. – 2019. – T. 12. – C. 205-222.
[13] Heidari-Rarani M., Rafiee-Afarani M., Zahedi A. M. Mechanical characterization of FDM 3D printing of continuous carbon fiber reinforced PLA composites //*Composites Part B: Engineering*. – 2019. – T. 175. – C. 107147.
[14] Jansson A., Pejryd L. Characterisation of carbon fibre-reinforced polyamide manufactured by selective laser sintering //*Additive Manufacturing*. - 2016. - T. 9. - C. 7-13.
[15] Krasny V.A., Maksarov V.V., Olt Yu. Application of polymer composite materials in friction units of downhole oil pumps // Zapiski Mining Institute. - 2015 .-- T. 211.
[16] Berlin A. A. Modern polymer composite materials (PCM) // Steel. - 1995.- T. 35.- S. 2.
[17] Shevchenko V.G. Fundamentals of Physics of Polymer Composite Materials // M .: Moscow State University. - 2010.
[18] http://newchemistry.ru/letter.php?n_id=1588.

[19] Donetsk K. I., Khrulkov A. V. The use of natural fibers in the manufacture of polymer composite materials // *Transactions of VIAM*. - 2015. - No. 2.
[20] Chen Z. et al. 3D printing of ceramics: A review //*Journal of the European Ceramic Society*. – 2019. – T. 39. – №. 4. – C. 661-687.
[21] B. Wittbrodt, J.M. Pearce, The effects of PLA color on material properties of 3-D printed components, Additive Manufacturing 8 (2015) 110–116.
[22] Yang, C., Tian, X., Liu. T., et al. (2017) 3D printing for continuous fiber reinforced thermoplastic composites: mechanism and performance. J. Rapid Prototyping Journal.,23: 209-215.
[23] Liu, S., Li,Y., Li, N. (2017) A novel free-hanging 3D printing method for continuous carbon fiber reinforced thermoplastic lattice truss core structures. J. Materials&Design. ,137: 235-244.
[24] Saari, M., Cox, B., Richer, E., Krueger, P. S., & Cohen, A. L. (2015). Fiber encapsulation additive manufacturing: An enabling technology for 3D printing of electromechanical devices and robotic components. 3D Printing and Additive Manufacturing, 2(1), 32.
[25] Goh G. D. et al. Characterization of mechanical properties and fracture mode of additively manufactured carbon fiber and glass fiber reinforced thermoplastics //Materials & Design. – 2018. – T. 137. – C. 79-89.
[26] Dickson, A. N., Barry, J. N., McDonnell, K. A., & Dowling, D. P. (2017). Fabrication of continuous carbon, glass and Kevlar fibre reinforced polymer composites using additive manufacturing. Additive Manufacturing, 16, 146-152.
[27] Chabaud, G., Castro, M., Denoual, C., & Le Duigou, A. (2019). Hygromechanical properties of 3D printed continuous carbon and glass fibre reinforced polyamide composite for outdoor structural applications. Additive Manufacturing, 26, 94-105.