Formation of the structure of polymeric products on the based of polyamide 6 produced by fdm-printing

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Abstract: *An analysis of the prospects for the development of FDM printing technology has been carried out. The paper studies the possibility of obtaining polymer products based on polyamide 6 and its compositions by layer-by-layer deposition. Tests of the strength indicators of the printed experimental products were carried out. The mechanism of the influence of the composition and modes of formation of printed products on their strength characteristics is proposed. The influence of the composition of the composite polymer material based on PA6 on the quality of printing products has been studied. Methods for controlling the shrinkage parameters of products obtained by layer-by-layer deposition are proposed. The obtained results of the study can be used in the development of composites for the production of polymer filament to ensure the process of FDM printing of polymer products, including for the needs of mechanical engineering.*
KEYWORDS: *FDM PRINTING, POLYAMIDE 6, TECHNOLOGICAL PARAMETERS, TENSILE STRENGTH, RELATIVE ELONGATION, POLYMER PRODUCTS*

1. Introduction

The production of polymer products using additive technologies has become available due to the intensive development of the production of FDM printers, as well as consumable polymer materials (filaments), which allows solving various production problems. At the same time, during the printing process, control over the main operational characteristics of products is ensured by choosing the composition of the polymer filament, as well as the technological settings of the FDM printer. In the Republic of Belarus, aliphatic polyamides and composites based on them are actively and effectively used for the production of structural products with high values of consumer characteristics of the widest range. At the same time, the effective processing of polyamides into products and the realization of the advantages and advantages of the indicated thermoplastic polymer when using various technologies are hampered by high values of hygroscopicity (up to 12 wt.% with an acceptable value during processing of 0.05-0.1 wt.%) and thermal shrinkage (up to 2.5% for unfilled materials) polyamide 6. For the active use of polyamide 6 in additive technologies, this is a significant drawback that affects the quality of the resulting products. And if polyamide processors effectively cope with a high tendency to moisture absorption by pre-drying the raw material and using heating of the material in the loading zone of the process equipment, then the thermal shrinkage of the binder requires more complex solutions. Most often, it is possible to reduce the thermal shrinkage of the polyamide matrix by modifying it with polymer components [1], as well as by introducing dispersed and (or) fibrous fillers [2]. At the same time, glass fibers in the composition of polyamide 6 can significantly increase the level of deformation and strength parameters of products, and carbon fibers increase impact strength and wear resistance. Polyamide 6 and composites based on it are mainly processed into products by injection molding due to the high values of the melt flow parameter. The use of PA6 for FDM printing in products seems difficult due to the high melt fluidity (MFR PA6 210/310 is more than 20 g/10 min), and therefore the use of composite compositions based on it for 3D printing is promising.

In modern conditions of limited availability of the raw material base, as well as increasing logistics costs for the supply of material resources and components of machine-building equipment, it is promising to study the possibility of using domestic polymer composite materials to obtain piece products in the conditions of enterprises operating and maintaining equipment that includes products based on polymer materials.

Thus, the purpose of the work is to substantiate the feasibility and effectiveness of using a polymer filament based on polyamide 6 and its composites for printing polymer products by the layer-by-layer deposition method.

2. Materials and Methods

To study the features of the formation of the structure of the material in products obtained by 3D printing, in this article, the authors used polyamide PA6-210/310 (Grodnamid) TU RB 500048054.009-2001 in granules produced by GrodnoAzot OJSC, carbon fiber UPA6-10 TU RB 00204056-086-94 in granules produced by OJSC SvetlogorskKhimvolokno, composite material PA6 + 10 wt.% HDPE, obtained by thermomechanical combination of components during extrusion. To study the parameters of polymer products, a filament with a diameter of 1.75 mm was obtained for these materials by extrusion on a Z-7M laboratory extruder (Russia) in modes that take into account the rheological characteristics of the starting materials. The parameters of the extrusion process when obtaining a filament are shown in Table 1.

Table 1: *MFR values for PA6-210/310 (Grodnamid)*

Options	Material		
	PA6-210/310	UPA6-10	ΠA6+10 mas.% HDPE
Cylinder temperature by zones, °C (±10°C)	230	230	230
Head temperature, °C (±10°C)	240	240	240
Feed-screw speed, rpm	20	10	20
Retraction speed, m/min	0,9	0,5	0,8

Previously to printing product samples, the polymer filament was subjected to thermostating in an oven at a temperature of 95 ± 5 °C for 4 hours to reduce the moisture content by no more than 0.1 wt%. To assess the deformation-strength characteristics of materials under uniaxial tension and to study the features of the formation of the structure of materials during layer-by-layer deposition, a product was printed in the form of standard blades (type 1) GOST 11262-80 on an Ultimaker 3 3D printer. The FDM printing parameters of the blades were set in the CraftWare 1.19 slicer program. A series of 6 standard samples was printed in the given technological parameters of the print settings per cycle (table 2). Evaluation of the deformation-strength characteristics of the studied samples was carried out on a tensile testing machine RM-500 in the mode of uniaxial tension at a speed of 10 mm/min with fixation of the deformation and tensile force. It was of interest to investigate the mechanism of the formation of autohesive bonds within the slab space and between the layers of a polymer product during the manufacture by the method of layer-by-layer deposition. The resulting samples of polymer products in the form of blades with different orientations in the intralayer volume (± 45º and 0º/90º) were subjected to 5% deformation in uniaxial tension for further study of brittle cleavage of product images obtained in the longitudinal direction of the tension axis. The structure of the materials was studied by scanning electron microscopy on blades that were brittle fractured after soaking in liquid nitrogen. At the same time, in order to manifest the effects of interlayer autohesion and study the effect of fillers on the structure of composites in the product, the blades were subjected to deformation within a 5% elongation under uniaxial tension. It was of interest to analyze the interaction of the polyamide-based filament melt in the interlayer and intralayer locations.

Table 2: *Parameters of print settings for test samples*

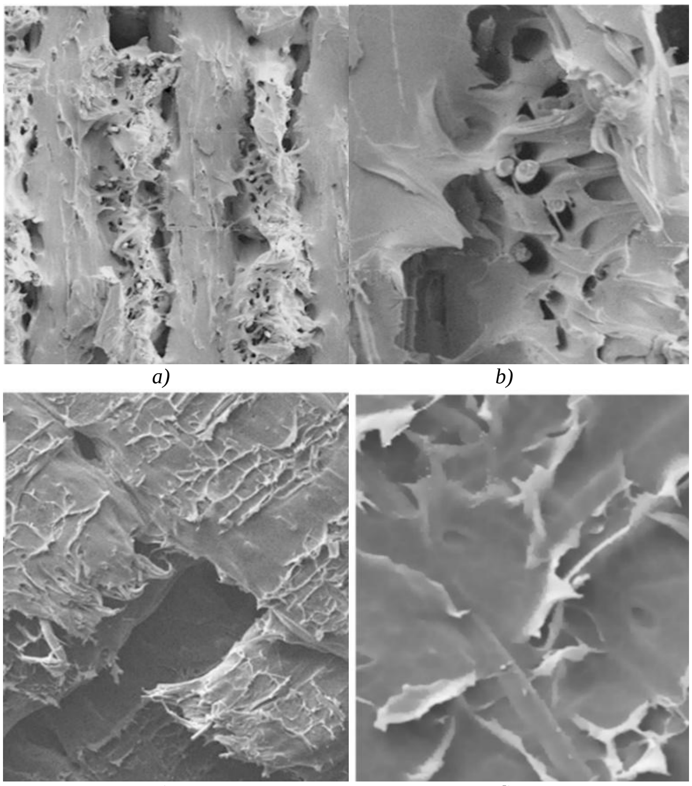
Basic print settings	PA 6	UPA 6-10	PA6+10 mas.% HDPE
The speed of movement of the nozzle of the extruder during printing, mm / sec	40	20	40
Print layer thickness, mm	0,2	0,2	0,2
Print width, mm	0,4	0,4	0,4
Number of layers of the perimeter of the product	2	2	2
Table temperature, ℃	100	70	100
Extrusion Temperature,℃	250	250	240
Unspecified print settings were the same for all samples			

3. Results and discussion

As a result of visualization of internal stresses arising in a polymer material obtained by layer-by-layer deposition of Nylon, a higher level of stresses arising in the peripheral part of the material, in comparison with the volume [3], was shown. In this case, the level of internal stresses decreases with a decrease in the degree of filling of the product volume with a polymer melt. It was shown in [4,5] that the degree of filling of the volume of the material affects the dimensional stability of products obtained by layer-by-layer deposition. At the same time, a number of research authors indicate [6,7,8] that the highest values of the deformation-strength characteristics of the material in the product are achieved at zero angles of orientation of the printing direction to the tension axis. However, to ensure the isotropy of strength indicators, layer-by-layer filling of the volume of the product was carried out in the “parallel lines” mode, changing the direction of printing in the next layer by 90 º, as recommended by many researchers [6,8].

The analysis of the morphology of the brittle fracture surface of blade samples based on UPA 6/10 carbon fiber, obtained by FDM printing with polymer orientation ±45º inside the layers when filling the volume of the product, was carried out on SEM images of the surface shown in Figure 1. A snapshot of the sample surface within the interlayer brittle The cleavage is shown in Figure 1a, which shows several adjacent layers of fibers with print orientation in the layer at angles of +45° and -45°. In Figure 1a, several important morphological features of the destruction of the polymer binder can be distinguished: interlayer voids resulting from the 3D printing process, layers with a rough fracture surface morphology, and layers with a smoother surface. For a detailed display of the nature of the contact of adjacent layers, an increase in the survey area is given (Figure 1b). The presented images indicate that between the threads between the layers, insufficient adhesion is characteristic along the tension axis, at which the formed crack grows. A rough fracture surface can also be noted in the interlayer region where fibrillation of the polymeric binder is noted with the formation of filamentous fragments.

This nature of the destruction of UPA 6/10 carbon fiber suggests that the binder layers oriented perpendicular to the tension axis hinder the growth of cracks. In this case, the participation of the remaining layers of the material in the mechanism of resistance to destruction of the matrix can be considered insignificant due to insufficient adhesion between them, due to the limited mobility of the binder polymer filled with carbon fibers.



a) b)

c) d)

a) general view of the fracture surface morphology of the sample in the interlayer location (magnification ×100); b) close-up of surface features in adjacent layers (×500 magnification); c) general view of the fracture surface morphology of the sample in the intralayer location (magnification ×100); d) close-up of surface features within the layer (×500 magnification)

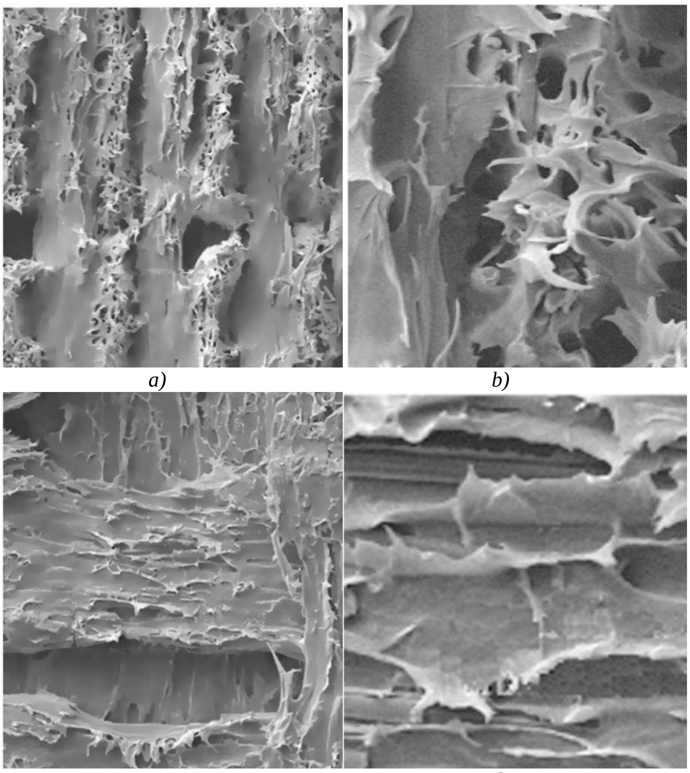
Figure 1 *SEM images of brittle fracture surfaces of samples with a print orientation of ± 45°*

The role of short elements of carbon fiber contained in the PA6 matrix in the process of deformation destruction of the layered structure of a carbon fiber product is also noticeable. Fibrillation of the polymer matrix during uniaxial tension of the carbon-filled PA6 sample suggests the implementation of a local mechanism of strengthening the polymer matrix in the product formed by the FDM-printing method.

At the same time, within the imprinted layer, a sufficiently strong autohesive adhesion is observed in the intralayer location of the matrix, which is observed in the image of the brittle fracture morphology of the sample (Figure 1c). This is due to the good rheological characteristics of PA6, which contribute to the realization of the phenomenon of autohesion between the polymer threads within the printed layer. Figure 1d shows that the traces of fracture surface roughness are concentrated along short fibers. This fact confirms the assumption that short carbon fibers enhance autohesion during FDM printing of polymer products based on carbon fiber.

Figure 2 shows SEM images of the brittle cleavage surfaces of specimens based on UPA6-10 carbon fiber obtained with the printing direction oriented in the 0º/90º layer. The surface of a brittle fractured sample, representing the interlayer space of the matrix, is shown in Figure 2 a. The image shows layers located at an angle of 0º and at an angle of 90º. At the same time, layers at an angle of 0º under conditions of preliminary 5% deformation have a rough surface, and layers at an angle of 90º retain a smooth appearance. An enlarged view of the cleavage surface of this sample is shown in Figure 2b. It should be noted traces of stretching of the fibers in the layers located at an angle of 0º, which indicate the course of the processes of fibrillation of the polyamide binder during deformation.

The surface morphology of a brittle cleavage of a sample of the studied carbon fiber with a polymer orientation angle of 0º/90º demonstrates a similar morphological pattern, as in the case of printing products with an orientation of ± 45º. The brittle fracture surface of CFRP contains traces of piles of polymer fibrils of destroyed threads. The presented images indicate some similarity of the fracture mechanism in the case of deformation of the sample obtained by printing with an orientation of ± 45º.



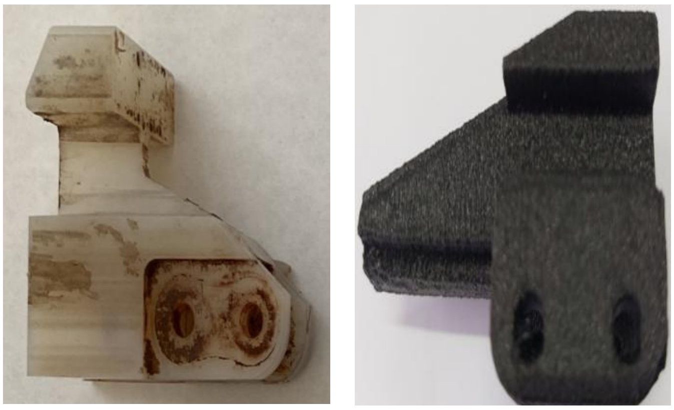
a) b)

c) d)

a) general view of the fracture surface morphology of the sample in the interlayer location (magnification ×100); b) close-up of surface features in adjacent layers (×500 magnification); c) general view of the fracture surface morphology of the sample in the intralayer location (magnification ×100); d) close-up of surface features within the layer (×500 magnification)

Figure 2 *SEM images of brittle fracture surfaces of specimens with print orientation 0º/90º*

An analysis of the features of the operation of the specified product indicates the predominant destruction in the place of the most weakened section, located between the body of the pusher and the surfacing. An example of a destroyed product is shown in Figure 3.



a) b)

Figure 3 *Appearance of the products "Pusher F08575326" (a) and "Pusher 406.42.0490" (b), obtained by injection molding (a) and FDM printing technology (b)*

3. Conclusion

Thus, the results of the study of the accuracy parameters of FDM printing of polymer products based on PA6-210/310 (Grodnamid), as well as the indicators of their deformation and strength characteristics, indicate the promise of using polyamide both in the initial state and in the state of the composite. The printing efficiency of PA6 in the product is achieved by ensuring a stable geometry of the polymer filament, as well as choosing the optimal printing temperature not exceeding 250℃. The obtained results of the work can be taken into account when determining the technological modes of production of filaments based on PA6, as well as when choosing the modes of FDM printing of thin-layer elements of polymer structures and elements of parts that are most loaded during operation. The data obtained indicate the prospects for conducting scientific research in the creation of materials based on aliphatic polyamides and their composites, as well as studying the influence of technological factors in the process of processing polyamide filaments into products by FDM printing.

4. References

1. Nanocomposite and nanostructured engineering materials and technologies for their production. Monograph / S.V. Avdeychik and [others], Ed. A.V. Kirichek. – M.: Spektr Publishing House, 2013. – 224 p.
2. Liopo, V. A. Physical bases of polymer modification with doping additives of layered minerals / V. A. Liopo, G. A. Kuznetsova, V. A. Struk, A. A. Skaskevich // Materials, technologies, tools. - 2002. - T. 7, No. 4. - S. 54-58.
3. Skaskevich, A. A. Influence of technological parameters of FDM-print on the strength characteristics of samples of polyamide / A. A. Skaskevich, A. Sudan, D. Dzhendov // Machines. Technologies. Materials. – 2020. – T. XIV. – № 5. – С. 210-212.
4. Skaskevich, A. A. Features of the formation of the structure of polymer products based on carbon fiber plastics obtained by the FFF-printing method / A. A. Skaskevich, A. S. Sudan // Petrochemistry-2021: materials of the IV Intern. sci.-tech. forum on chem. technologies and oil and gas processing, Minsk, November 22-23. 2021 - Minsk: BSTU, 2021. - S. 88-91.
5. Sudan, A. On the prospects for the production of filaments based on polyamide 6 for FDM printing / A. Sudan, A. N. Gaiduk, A. A. Skaskevich // Bulletin of Yanka Kupala Grodno State University. Ser. 6. Technique. - 2021. - T. 11. - No. 2. - S. 83-90.
6. Kondrashov, S.V. Influence of technological modes of FDM printing and the composition of the materials used on the physical and mechanical characteristics of FDM models (review) / S.V. Kondrashov [and others] // Proceedings of VIAM. - T.82, No. 10. - 2019. - S. 34-49.
7. Nefelov, I.S., Baurova, N.I. Ways to prevent technological defects in machine parts manufactured using additive technologies / I.S. Nefelov, N.I. Baurova // Bulletin of modern technologies. - No. 5. - 2017. - P.36-40.
8. Erofeev, V.T. Study of the physical and mechanical characteristics of polylactide samples in additive technology / V.T. Erofeev [et al.] // Building materials and products. - Number 3. - 2019. - P.92-101.