Investigating the adhesive properties of polymers for 3D printing

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Abstract. The article presents the research of adhesive properties of various polymers used in additive manufacturing by fused deposition modeling. Tensile tests of additively manufactured samples of various polymers are carried out, electro-microscopic photographs of the working area are taken before and after tests, and studies on the manufacturability of printing are performed to exclude further typical errors identified during these tests. Samples of the following polymers are studied: thermoplastic resin acrylonitrile butadiene styrene (ABS +), thermoplastic resin acrylonitrile butadiene styrene with the addition of titanium nitride as a dye (ABS + TiN), thermoplastic resin acrylonitrile butadiene styrene with the addition of polyester inserts (ABS polylactide (PLA), polylactide based compound (PLA HP), thermoplastic polyethylene terephthalate glycol (PETG), and nylon with carbon inserts (NSC). The work reveals the advantages and disadvantages of the investigated plastics. For example, deformations occur when the part is cooled down during printing process of ABS +, and a crack could form in stress concentrators as a result of the influence of cold air flows.

1. Introduction

Currently, additive technologies are rapidly developing. One of the promising areas is the method of fused deposition modeling (FDM) [1–2]. The materials for these technologies are various polymers and compounds. Such materials are poorly studied in relation to engineering problems, so, problems may arise in the manufacture of parts. In this regard, it is necessary to carry out not only strength, but also microscopic analysis to get an idea about a general structure of the material and about certain defects in this material after printing.

This paper summarizes and supplements the research material [3] on the most common plastics for 3D printing today, examines the manufacturability of printing, describes common errors in printing with various polymers and ways to solve them, and studies the adhesion of materials by microscopy.

Some difficulties may appear in the production of finished parts during the printing with various plastics. This fact is a result of a high percentage of rejects. To avoid this, it is necessary to investigate the manufacturability of printing, including by microscopic analysis.

2. Manufacturability of printing

The manufacturability of printing is a set of characteristics that shows the labor intensity of its production, maintainability and a set of performance characteristics that allow you to match the dimensions, deviations, roughness and shape tolerances in a part drawing and the part obtained as a...
result of printing. Each of the researched polymers has its own advantages and disadvantages. A review of information on ABS plastic [4] allows analyzing the manufacturability of printing:

ABS+ is the modified ABS plastic (petroleum-based thermoplastic resin) for printing with minimal deformation shrinkage and high interlayer adhesion. The composition of this compound ABS+ remains unknown. Considering advantages, ABS+ plastic has a long service life, chemical inertness, lack of hygroscopicity, among its disadvantages there are weak resistance to ultraviolet radiation, toxicity, and strong expansion at heating. ABS+ has higher physical and mechanical characteristics in comparison with standard ABS plastic. The tensile strength is 34–52 MPa.

ABS plastic is mostly used in the manufacture of cases for various household appliances and in the automotive industry. This plastic has a variety of compounds. In this work we study ABS+ (no impurities), ABS+TiN (impurities of titanium nitrite for color) and ABS Carbon (carbon fiber inserts).

According to the experiments, the following information was obtained: difficulties arise due to material shrinkage (2.5–3%) during printing parts with ABS+ plastic; this property distorts all dimensions of the finished part and leads to deformations and high stresses; while during the printing process the part loses its stability detached from the desktop of the 3D printer, and then exfoliates in places with increased internal stress (Fig. 1a). During printing, the material may be exposed to uneven heating, leading to additional deformations, as a result of which the integrity of the parts is violated and an interlayer crack is formed (Fig. 1b). All the phenomena associated with ABS+ printing can be prevented by placing the 3D printer in a thermostatic room, and using a protective box for the 3D printer, which allows maintaining a stable temperature inside the chamber.

![Figure 1. a) Edge deformation of ABS+ part, b) Interlayer crack of ABS+ part.](image)

In addition to the above, since during the part manufacturing the ABS+ plastic releases toxic substances when heated, it is necessary to extract it from the printing area to avoid damaging the 3D printer operator's health. This affects the manufacturability of printing, and drawing leads to uneven heating (cooling) of the material. Manufacturability of printing with ABS+TiN plastic is identical to ABS+ plastic, and the plastic retains high shrinkage (2.5–3%), increased internal stresses and deformations.

The performed analysis of the ABS Carbon compound has shown that the smallest carbon particles in ABS Carbon plastic serve to almost completely get rid of volumetric shrinkage during cooling (1%). Deformation of the part is not observed during printing. Carbon inclusions make ABS Carbon viscous when it is heated to extrusion temperature. Carbon allows getting overhanging elements of the part of up to 65° without loss of quality, in comparison with ABS+, which can make a maximum overhanging element of 40°.

A review of information on nylon used in additive manufacturing of various suppliers allows analyzing the manufacturability of printing:

Nylon is used industrially for insulating bushings, thin coatings, films or clamps. Pure nylon is not used in 3D printers as it has not been modified for this type of use. The paper investigates a
modification of nylon with the addition of carbon fibers - Nylon Super Carbon (NSC). This plastic has improved interlayer adhesion compared to conventional nylon. NSC has high ductility, high impact strength and resistance to deformation, but is hygroscopic and can absorb up to 10% water by weight. Its tensile strength is about 25 MPa.

The following information has been obtained from the experiments: NSC plastic is one of the most unstable materials. The difficulty of printing is associated with a large shrinkage during cooling, which ranges from 3% to 5%. Because of this, during the printing process, internal stresses accumulate inside the part and lead to deformation of the product even during the manufacturing process. These deformations can change the geometry of the grown part; under these circumstances, the print head may collide with the part or detach the part from the worktable, the consequences of such a situation are shown in Fig. 2.

![Figure 2. Deformation consequences of NSC part.](image)

A review of information on PET allowed us to analyze the manufacturability of printing: PET material is used in the creation of bottles, transparent vials or food containers. 3D printers use one of the compounds of this plastic (with the addition of glycol to the structure, which prevents crystallization and brittleness under strong heat) - PETG. This compound has good adhesion and low volumetric shrinkage (0.5 to 1%). The plastic is chemically resistant and has low thermal expansion. Its tensile strength is 37.6 MPa.

The following information was obtained from the experiments: the disadvantage of this plastic is the relatively low viscosity in the heated state, which causes plastic to heat up above the heating point (thermal barrier) of an extruder, and then the plastic gets stuck. This leads to various printing defects, for example, material skips on the surfaces of the part. This problem can be solved by intensively cooling the thermal barrier in the extruder. Low shrinkage of the material was confirmed in practice and did not exceed 1%.

A review of information on PLA [5] allowed analyzing the manufacturability of printing: biodegradable thermoplastic plastic, based on corn and sugarcane raw material, is used in the production of environmentally friendly biodegradable packaging, disposable tableware or in medicine, mainly in elements with a short (up to two years) service life. PLA is considered an environmentally friendly material, it is hygroscopic, which makes the material more fragile over time. Its tensile strength is 49.5 MPa.

In this work, two variants of this plastic are investigated: pure PLA, and a PLA-based compound, specially made for the use in 3D printing, called PLA HP. The composition of this compound remains unknown. PLA HP, unlike PLA, is less susceptible to degradation and remains the same environmentally friendly, while significantly reducing hygroscopicity. Its tensile strength is 54 MPa. PLA is one of the best materials in terms of printability. This plastic has excellent adhesion, which greatly simplifies the process of growing the part and makes it stable. Volumetric shrinkage is extremely small (less than 0.5%), so, it may be ignored on small parts. PLA HP has similar properties
to PLA in 3D printing. Consequently, the addition of additives to PLA plastic do not affect the manufacturability of printing, but improve the mechanical properties [6].

3. Investigating samples by microscopy
Sample tests (Fig. 3), prepared by fused deposition modeling according to ISO 527-2:2012, are studied using a POLAR 1 microscope of the “Micromed” company in order to study adhesion during 3D printing. For this, photos of the working part of the samples are taken before and after the tensile strength tests (Fig. 3). The structure of the material [7–8] is considered, and the adhesion between filament fibers in the printed layer is evaluated.

![Figure 3](image)

**Figure 3.** Model of a sample for tensile tests, where 1 is the working part of the sample, which is examined before and after strength tests.

Figures 4a and 4b show the adhesion between the printed filament lines in the top layer of ABS+ plastic at the break after tensile tests. Figure 4a shows a weak adhesion of ABS+, and during the tests there was a loss of adhesion. A distinctive feature of ABS+ and ABS+TiN plastics is strong elongation, during which concentrators are formed along the entire working area (Fig. 5). In one of the concentrators, material rupture subsequently occurs during testing.

![Figure 4](image)

**Figure 4.** Material structure, adhesion between printed filament lines in an upper plastic layer after tensile tests a) ABS+, b) ABS+TiN

![Figure 5](image)

**Figure 5.** Working area of ABS+ plastic after testing, where 1 are the stress raisers.
Figure 6a shows a structure of ABS Carbon, where the adhesion of this plastic after tensile tests is clearly visible. According to the developer of this plastic, carbon microfibers are included in ABS Carbon, but microscopy shows (Fig. 7a) that carbon is mostly present in the dust form, which greatly affects its strength characteristics [9]. Figure 6b shows that where the NSC plastic breaks, this plastic is highly stretched. In this case, separate lines of the filament are torn off, and this is clearly visible with microscopy. Unlike carbon dust (below 0.01 mm) ABS Carbon, NSC plastic actually contains inclusions of carbon microfibers (Fig. 7b), which exceed 0.05 mm, which also affects its characteristics [9].

![Figure 6. Material structure, adhesion between printed filament lines in an upper plastic layer after tensile tests. a) ABS Carbon, b) NSC](image1)

![Figure 7. a) Carbon dust in ABS Carbon, b) Interspersed with carbon microfibers in NSC.](image2)

The adhesion of PETG plastic is shown in Figure 8a. Breaks appear between the filament lines closer to the point of rupture, although this does not affect the characteristics of the plastic themselves [9]. Figure 8b shows the surface of a PLA sample after testing. Unfused non-adherent fibers are visible. The adhesion of PLA HP plastic is shown in Figure 8c, where areas of sintered plastic are visible. In comparison with PLA plastic, it has better adhesion properties. PLA plastic has neither ABS properties (no white, stretched areas along the working area) nor NSC and PETG properties when cracks appear between filament lines in tensile tests.
Conclusions
The article presents research on the manufacturability of printing of tested plastics. Advantages and disadvantages of these plastics have been revealed. So, for example, deformations occurred when the part cooled down during printing with ABS + plastic. A crack could form in stress raisers as a result of exposure to cold air currents during the printing process. This necessitates a completely thermostatic room during printing with this plastic. ABS Carbon partially improves this situation by eliminating thermal deformation due to less material shrinkage. NSC can also be affected by thermal expansion as the plastic cools, but unlike ABS +, it deforms strongly relative to the worktable.

The article has also studied the adhesion of plastics using a microscope. The difference between the adhesions of plastics after printing has been found. For example, the addition of coloring agents to ABS + plastic did not change the adhesion of the plastic, and in case of PLA HP, it significantly increased the adhesion between layers and filaments. It has been also found that carbon dust is included in ABS Carbon, instead of a declared carbon fiber, and this affects the characteristics of the plastic. In the NSC, the plastic developers have added the declared carbon microfibers.

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