

EVALUATION OF THE EFFECTIVENESS OF METHODS FOR IMPROVING THE MECHANICAL PROPERTIES OF PLASTIC PRODUCTS MANUFACTURED IN THE FDM TECHNOLOGY - A MINI REVIEW

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Abstract: One of the rapidly developing technologies for the production of components and parts are rapid prototyping technologies. A large number of techniques exists, which use a large variety of materials depending on manufacturing characteristics. The post-process modification methods (modification of element after 3D printing) enable improving of the mechanical and surface properties. In the paper, the Fused Deposition Modeling technology is described, which is based on the production of models and components from thermoplastic polymers by depositing single fibers of half-melted plastic layer by layer. The paper describes experimental methods used for strengthening the internal and external structure of plastic, using both amorphous and semi-crystalline structures. The materials used for coating samples of polymeric materials that change the external structure (layer properties) are presented. The aim of the work is to show how the additional processing of samples and application of external coating affect the strength properties of materials. In this work, the obtained results are discussed and compared with samples that were not subjected to modification.

Keywords: Coatings, Outer layer modification, 3D printing, ABS, PLA.

1. Introduction

The article describes one of the additive manufacturing technologies - Fused Deposition Modeling (FDM), also called Fused Filament Fabrication (FFF). The method consists in extruding a material, where thermoplastic polymer fiber is fed through a heated nozzle in the aim deposit of the material in layers. Technology of 3D printing has many advantages; it enables the fast manufacturing of products tailored to the demands of customers at low costs and with the required geometric shape. The 3D printing process consists of simple steps and involves using a wide spectrum of materials used to produce of models with different properties. 3D printed parts have weaker mechanical properties in comparison to those obtained by traditional manufacturing processes such as injection molding or extruding. Its due to poor bonding between the deposited layers.

Often used materials are: ABS, PLA, ASA, PA, as well as materials modified, i.e., by adding glass fibers, copper, metals or carbon fibers additives. For such materials, the properties before and after influencing the external structure of manufactured elements are described. Mentioned materials have both some advantages and disadvantages. Requirements for their processing are different depending on the required material properties, such as tensile, bending or compressive strength. The choice of the material with optimal properties depends on the designed model and the type of the used device, because not all 3D printers are able to process all filament materials. Only a small amount of described research on the surface coating of 3D printed plastic parts exist. The use of coating materials for plastics or the modification of the surface layer is considered to be one of the most promising technologies. This leads to the possibility of wider use of parts printed in the FFF 3D technology. Our article focuses on an overview of the methods used for this purpose, and the assessment of the mechanical properties of the materials before and after coating.

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2. Annealing of samples

Annealing is a popular process to increase the mechanical strength and the percentage of crystallinity of the polymer in the FFF parts. Butt et al. (2020) in their paper described the subject related to the analysis of the annealing effect on two categories of polymers, i.e., semi-crystalline and amorphous. Niranjan et al. (2022) in their article focused on the dynamic mechanical properties of polylactide (PLA). Both articles are related to the interactions taking place among thermoplastics and show the results obtained during the tests.

Butt and coauthors presented comparative characterization of thermoplastics, i.e. (PLA) polylactide, (ABS) Acryl - butadiene - styrene and materials with an admixture of metals (Cu-PLA), polylactide with copper and (Al-ASA) acryl - styrene - acrylate with an admixture of aluminum. They focused on the application of annealing to evaluate its effects on the physical and mechanical properties of FFF-printed samples. The samples were made in a dog bone shape with 100% filling. Five samples were printed for each of the different materials for evaluation both before and after annealing. The process consisted in placing samples of variable temperature 70, 80, 90, 105, 115 and 125 °C for one hour in a convection oven providing a heat source with an angle of 360°, and then subjected to cooling inside for two hours. A dimensional analysis was then undertaken, which showed a change in dimensions with temperature. The shrinking for PLA was 5.6%, for Cu-PLA was 1.3% in temperature 90 ° C. For ABS was measured a minimum shrinkage of 2% and extension of 4.25%. Al-ASA about value 2.5% at 90 ° C. The use of higher temperatures resulted in significant deformation and, as a result, the samples were unusable for further investigation due to loss of shape. Ultrasonic examination allowed to assess changes in degree of crystallinity of polymers. Annealed PLA and Cu-PLA samples had a weaker correlation with the control samples, while for the annealed Al-ASA and ABS the values of correlation were somewhat lower or comparable in relation to the control samples. Results of tensile test showed a trend of an increase in strength with increasing annealing temperature for Cu-PLA samples up to temperature 90 ° C. The value of the breaking load also increased by 21%. Despite this, the pure PLA showed higher strength values. For ABS and Al-ASA, the increase in strength reached several percent, which fact shows that these materials are not very susceptible to strength increases after annealing. In summary, annealing can negatively affect the dimensional tolerances of FFF printed parts. Ultrasonic testing showed lower transmission times (higher speed) of sound waves for all materials at higher temperatures compared to non-annealed samples. Hardness evaluation using the Rockwell test showed that Al-ASA had the highest hardness and ABS the lowest.

Niranjan et al. describes the effect of Dynamic Mechanical Analysis (DMA) on samples made of PLA. The samples were divided into groups, each sample having dimensions of 50 x 11 x 3 mm. The samples were annealed in a convection oven. The first group was tested for different annealing times (15, 30 and 60 minutes) at 90 $^{\circ}$ C. The second group was annealed at different temperatures (80, 90, 100 and 110 $^{\circ}$ C) for 30 minutes. The temperature has been limited to 110 $^{\circ}$ C as above 120 $^{\circ}$ C PLA begins to degrade. This causes a loss of mechanical properties and geometric features. The samples were cooled down to the ambient temperature inside the oven. After removal, they were stored at room conditions for two days in order to simulate realistic operating conditions prior to DMA analysis.

After the tests, it was observed that the glass transition temperature (Tg) changed due to annealing. It was found that the Tg increased to 81 ° C (53.10 % increase) after annealing at 100 ° C, compared to the untreated samples. After increasing the annealing temperature to 110 ° C, the Tg drops to 74.6 ° C, which corresponds to a decrease of 8.1% compared to the Tg value of the samples annealed at 100 ° C. The conservative modulus (E') is a property of a viscoelastic material that determines the ability of the material to store energy during load cycles. The higher of value E' at a given temperature indicates the higher energy stored in sample. PLA samples subjected to annealing at 100 ° C showed an increase in the modulus E' about 35 times compared to the PLA samples in temperature 57 $^{\circ}$ C. In the range of temperature 80 \div 90 $^{\circ}$ C, all tested samples showed an almost identical decrease in the value of the E' modulus. The highest value of the conservative modulus was shown by PLA samples annealed at the temperature of 110 ° C, it was 2647 MPa, then at 100 ° C was the value of 2555 MPa. When assessing the effect of the holding time at 90 ° C on the Tg temperature, the highest increase as compared to the control samples was obtained after 15 minutes (Tg increased from 53 ° C to 73 ° C). With an annealing time of 30 minutes, the Tg rose slightly to 76 ° C. With a further increase in the soaking time, a decrease in Tg was observed to 72.19 ° C. In the case of annealing at the temperature of 90 $^{\circ}$ C up to 30 minutes, all tested samples show an increase in the E' modulus, after annealing longer than 60 minutes this modulus decreased. PLA has a tendency towards a higher strength with increasing annealing time and temperature. By increasing the degree of crystallinity of the polymer, increase in its stiffness can be obtained. But it has a negative effect on the shape and dimensions of the samples. The results of the tests carried out confirmed the influence of annealing on the increase of mechanical properties. Therefore, heat treatment can be considered as a low-cost process leading to an increase in the strength of samples made of PLA and manufactured in FDM processes.

3. Acetone vapors

After printing elements from the ABS material, a common procedure is to modify the properties of the printed elements with acetone. As a result, a better appearance and less surface roughness can be obtained. Beniak et. al. (2017) focused on the assessment of changes in roughness and compressive strength of ABS samples printed in FDM technology under the influence of acetone vapors. The samples were placed in a closed container with a small amount of acetone (100 ml) at the bottom. The samples were suspended above the surface of the fluid without being in contact with it. The container was then placed in a 100 $^{\circ}$ C hot water tank. As a result, acetone in the closed container began to evaporate, which led to the etching of the surface of the test sample.

The cylindrical samples with a diameter of 12.7 and height of 25.4 mm in size were exposed to acetone for 5, 7.5 and 10 minutes. The results of measurement of compressive force of samples indicate that the best results were obtained when they were exposed to acetone vapors for 5 minutes. An increase in mechanical properties by 21% was observed compared to the control samples. The longer exposure times to acetone vapors result in the lower strength gains. The roughness of the samples treated with acetone for 5 minutes decreased by a value of 2.36 μ m, which corresponds to a decrease of 13.95% compared to the control samples for which it was 16.92 μ m.

The obtained results indicate the high importance of the acetone smoothing process on the surfaces of ABS parts produced on the FDM device. The strength increased the most when the samples were exposed to acetone for 5 minutes. Longer duration of action did not increase the strength.

4. Effect of acrylic coating

Barone et al. (2020) described an experiment that was based on the evaluation of the influence of two different coatings, i.e., UV-cured acrylic resin and acrylic varnish for moisture absorption by printed samples made of carbon fiber-reinforced polyamide (carbon PA). Moisture absorption is a factor that significantly affects the processability of the material, as well as its mechanical properties, dimensional stability and strength.

45 dog bone-shaped samples were printed with a fill density of 100%, 15 of them were coated with an acrylic spray and 15 with UV resin. Prior to applying the protective coatings, the samples were heated in an oven at 100 $^{\circ}$ C for 1 hour to ensure that all samples had the same minimum water content. The acrylic coating was applied by hand spraying in two steps to obtain a uniform layer on each sample. After the first coat was applied, the samples were air dried for 2 hours, then a second coat was applied and dried again for 2 hours. The resin coating was based on immersing each sample in the resin for 30 minutes at room temperature, followed by UV curing for 2.5 hours at 80 $^{\circ}$ C.

The water absorption test was performed as follows: first the samples were weighed, then they were immersed in a tank of distilled water at 23 ° C for 2, 24 and 168 hours. Next, the samples were dried in an oven for 24 h at 50 ° C. Water absorption tests were performed on 10 samples of each type. The results of water absorption after 168 h showed 4.04 ± 0.3 % weight gain for the uncoated samples, 2.06 ± 0.6 % for the acrylic coated samples and 1.66 % for the UV-coated samples. Tensile tests were performed on 15 samples of each type. The results showed an approximately twofold increase in Young's modulus for the acrylic coated samples (up to 5570 MPa) compared to the uncoated samples (2650 MPa). Results of tensile test showed a significant improvement in the mechanical properties by using one of the two proposed coating processes.

5. Polyester resin and aluminum oxide coating

Another method to increase the strength properties of PLA material is to apply coatings of marble-powder and aluminum oxide mixed with resin. In his experiment, Kocak et al. (2021) used samples with a filling of 50%, which were placed in a metal mold to be able to apply a layer of equal thickness of 0.5 mm on all their surfaces. Next, the samples were left for 48 hours for the polymer resin to solidify.

The tensile strength of the samples covered with the composite coating was 34.4 MPa. The compression test showed a lower strength than the uncoated sample due to the greater brittleness and lower tensile strength of the coating compared to PLA. The bending strength, measured for the uncoated sample, was 79.8 MPa.

It is higher than in case of coated samples, where the strength fluctuates in the range of 54.15 - 64.4 MPa. The results of the coating adhesion test were 8.2 MPa for the coating with marble powder and 5.5 MPa for the coating with aluminum oxide.

The powder marble coated samples showed the highest tensile and bending strength. On the other hand, the surface hardness of the aluminum oxide reinforced composite coating was higher than pure PLA. The author concluded that the best results in terms of strength, adhesion and abrasion can be obtained by modifying the surface by a covering layer containing marble powder, and subsequent covering with an aluminum oxide layer.

6. Conclusions

The discussed papers showed methods of surface modification of plastics in order to obtain higher strength and hardness of surface. Such changes permit on the wider usage of plastics. In most cases, there is a relationship between the duration of the post-treatment and the maximal increase in the strength value of printed elements.

For coated materials, an important factor is the adhesion force which occurs between the material of coating and the basic material, because it defines the strength of the outer layer. The value of the adhesion force is influenced by the way the surface layer is applied and the degree of smoothing of the basic material surface. It significantly affects the strength values of the coated elements.

However, for some of materials, not all methods of modification the outer layer may bring the expected results. For example, the annealing of plastics with added metals did not bring the expected results in terms of improving mechanical properties.

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