Polylactic Acid Biopolymer in Multi-Material Additive Manufacturing

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3D printing is a revolutionary additive manufacturing method that enables rapid prototyping and design flexibility. A variety of thermoplastic polymers can be used in printing. As it is necessary to reduce the consumption of petrochemical resources, alternative solutions are being researched, and the interest in using bioplastics and biocomposites is constantly growing. Multi-material printing using polymers is the subject of research led by many scientists worldwide. The number of materials for printing is practically unlimited, especially considering the independent production of filaments or their modification, which is becoming easier and is more available for research institutions. One popular and economic printing technique using polymers is the fused deposition modeling (FDM)/Fused Filament Fabrication (FFF) technology.

Keywords: multi-material printing ; PLA ; 3D printing ; biopolymers ; Additive Manufacturing

1. Introduction

Polymers are a group of materials used in the automotive ^[1], medical ^[2], construction ^[3], and textile industries ^{[4][5]}. The environmental approach to infrastructure requires more and more care for preserving the environment. A significant part of polymers is made from petrochemical products and is not biodegradable ^[6]. Among the polymers in production, there are biodegradable and non-biodegradable polymers of biological and synthetic origin ^{[Z][8][9]}. Biodegradable polymers have long been recognized as a possible replacement for materials produced from limited petrochemical resources. Fossil fuels and gases could be minimized and replaced by using polymers from green agricultural resources, reducing global CO₂ emissions ^[6].

Polymers have been used in the last five decades: polymer components are manufactured using many technologies such as hot stamping, injection molding, piston injection molding, thermoforming, and many more ^[10].

3D printing is a revolutionary additive manufacturing technique $\frac{[11][12][13]}{11}$ that enables rapid prototyping of complex geometric structures $\frac{[14]}{14}$ and flexibility during designing, even the most demanding structures $\frac{[15][16][17][18]}{110}$. Many thermoplastic polymers can be used for 3D printing, including modern biopolymers (i.e., protein- and carbohydrate-based materials) $\frac{[19]}{10}$.

Applications of additive manufacturing technologies include biomedicine ^{[20][21][22][23][24][25][26][27]}, dentistry ^[2], the automotive industry ^{[1][28]}, aviation ^[3], and optics ^{[29][30]}, but also textiles and everyday products ^{[31][32]}. The development of printing leads to more and more applications, including conductive, electrically functional, insulating, or semiconductor materials ^[33]. A wide range of polymers available for 3D printing enables the creation of geometries with shape memory, where structures change their shape under specific external stimuli such as temperature, light, or water ^{[33][34]}. When considering additive manufacturing technologies, it is necessary to analyze the types of 3D printing technologies and which of them enable additive manufacturing using polymers. 3D production can be divided into three main categories ^[35]. ^[36]: forming, subtractive, and additive manufacturing.

There are many additive manufacturing technologies using polymers [35]; most of them require the use of pre-prepared polymer material in the form of fiber [37][38], powder [39][40][41][42], or sheets [43]. Other technologies use hardening photosensitive resins [44][45][46][47], where a focused UV laser beam used on the surface of a photopolymer resin hardens molecular chains and solidifies the resin [48][49][50][51].

The constant development of printing technology and rapidly emerging technological innovations make it difficult for young users and industry workers to navigate the polymer printing processes [52] efficiently. The printing process requires a thorough analysis and selection of parameters to predict the properties of objects and obtain the expected results [53][54]. It

is necessary to obtain knowledge about the processed materials' characteristics and analyze the existing information on the chosen applications ^[55].

2. Layered Printing with PLA

Polylactic acid (PLA) is a biodegradable material ^[56] obtained from natural crops by biological fermentation ^[57]. It is characterized by good stability during printing ^[58] and a relatively low melting point (180–220 °C), with a glass transition temperature of 60–65 °C ^[59]. Printing parameters affect the quality of samples and their strength; print orientation, layer thickness, and process temperatures influence the creep strength of polylactide ^[60].

However, its strength properties may be insufficient for many industrial applications—it needs to be strengthened or modified ^[61].

To use the ecological potential of biodegradable polymers, material modifications are necessary (e.g., the creation of composites based on PLA). Multi-material 3D printing makes it possible to modify the properties of objects using various polymers ^[62] and additives in one printing process ^[63]. Annealing can be used to stereo-complexity 3D samples made of PLA—placing the samples in a vacuum oven at 50 °C for 24 h and then subjecting them to a temperature of 160–210 °C for an hour. Results show ^[64] that steam treating the printed parts with acetone significantly improves the surface finish of the products, with minimal variations in the geometric accuracy of products after treatment. Manipulation of the printing and heat treatment process parameters may lead to specific properties and structures of objects ^[57]. Multi-material printing is often performed using two nozzles, where the printer feeds material from separate feeders. One nozzle can also be used, but then the participation of the printer operator who changes the filament during the process is necessary.

In an research written by Ribeiro M. et al. ^[65], the effect of the bonding surfaces of materials in printing with multiple materials (face-to-face interface) was investigated, and a solution was proposed in the form of mechanical interlocking systems on bonded layers—three different geometries were tested (T-shape, U-shape, and dovetail shape). The positive influence of the mechanical bonding of TPU and PLA on the elasticity of the samples was demonstrated. The overlapping of material boundaries contributed to the achievement of higher Young's modulus values.

The research ^[58] analyzed the influence of surface development and roughness on the interlayer adhesion of PLA and TPU (thermoplastic polyurethane). The best combinations of surface pattern bonds common for both printing orders with polymers in cylindrical samples were indicated: pattern concentric for the combination of PLA/TPU (shear strength 0.43 MPa) and TPU/PLA (shear strength 0.38 MPa). At the same time, the best surface development for the TPU/PLA sequence is the TPU-linear pattern at 0° and the PLA-linear pattern at 45° (shear strength 0.63 MPa).

To explore the topic of layered bonds of materials during printing, it is worth analyzing the work of Tamburrino et al. ^[66], where the following aspects were investigated: the order of printed materials, the pattern development of the upper and lower printed layers and their influence on the interlayer adhesion strength. Three pairs of PLA-TPU, CPE-TPU, and CPE-PLA materials were tested. The use of a lower filling density (80%), compared to 100% density, harmed the adhesive strength; at the same time, a solution was proposed in the form of a Mechanical Interlocking mechanism (two materials were combined on several central print layers, a frame made of one material and an internal space was filled with the second material so that the materials overlapped on several print layers), which increased the adhesive strength of the samples (for the PLA-TPU connection, thanks to the mechanism, an increase in Peak stress from 0.28 MPa to 1.32 MPa was observed).

Research led by Kumar S. et al. ^[67] concerns multi-material printing based on Polylactic Acid (PLA). Several mixtures were combined: pure PLA, PLA with PVC admixture, PLA with wood powder, and PLA with magnetite (Fe_3O_4). During the experiments, the parameters of the filling—at which the highest breaking strength of 41.65 MPa was achieved—were determined. The best filling parameters were: infill density of 100%, infill angle of 45°, and infill speed of 90 mm/s. At the same time, the research showed a negative impact of lower print densities and their roughness on the quality, strength, and mechanical properties of objects compared to samples printed with a high density of up to 100%.

Multi-material prints made of ABS and PLA reinforced with carbon fiber were tested to determine the influence of printing parameters on the strength of interfacial bonding ^[68]. The optimum printing parameters were determined (a printing speed of 50.54 mm/s, infill density of 79.82%, layer height of 0.15, and a layer thickness ratio of 0.49). It should be noted that PLA is less toxic than ABS. Attempts to use PLA reduce environmental pollution with volatile organic compounds such as, for example, styrene, butanol, cyclohexanone, and ethylbenzene ^[69]. From the point of view of the respiratory health of printer users, the preferred combinations of polymers in printing are PLA, PET, and TPU, as those materials used at lower

temperatures have lower FP (fine particle emissions) than ABS. Moreover, when printing with ABS, an increase in inhaled nitric oxide (FeNO-nitric oxide) and the presence of an unpleasant odor are observed compared to printing with PLA ^[70].

During the impact tests of mesh samples printed with the FDM technology, it was found that the use of external walls in such structures strengthens the impact strength of the samples by 60%. The combination of ABS and C-PLA (carbon fiber + polylactic acid) material shows a much higher impact strength (280 to 365%) compared to samples from C-PLA. The impact strength of the samples was from 7672.9 to 23,465.6 kJ/m² ^[71].

Laminar composites are widely used in the industry. To manufacture them in 3D printing processes, manufacturing parameters should be selected to strengthen the objects. Such parameters include low printing speed, layer height, and the clad ratio ^[72]. Strength tests were carried out on samples made of two materials—ABS and PLA reinforced with carbon fiber. It has been shown that multi-material samples are characterized by higher strength than individual materials. The following parameters were considered the best: speed 1/4 20 mm/s, infill density 1/4 67.838%, layer height 1/4 0.23 mm, and clad ratio 1/4 0.25. The highest values on strength tests were elastic modulus = 2204.45 MPa, ultimate strength = 51.34 MPa and elongation = 9%.

3D printing from multiple recycled polymers such as ABS, PLA, and HIPS is feasible because these thermoplastics have a similar heat input during heating (13.63 mJ for ABS, 14.71 mJ for PLA, and 11.71 mJ for HIPS). Compared to single-material 3D printing, multi-material 3D printing offers more flexibility to functional prototypes (with completely different/improved multi-dimensional properties) ^[73]. Considering sandwich structures made of several materials, samples with HIPS outer layers and a rectilinear ABS core showed the worst performance, with average tensile stress of 22.21 MPa and Young's modulus of 992.02 MPa—which is less than 50% and 28%, respectively. Of the best layer structure tested, it was PLA-ABS-PLA. The average values were 44.40 MPa for tensile strength and 1364.25 MPa for Young's modulus for the best configuration. Moreover, the elongation at break (6.14 mm) for this configuration was higher than the homogeneous material ^[74]. The PLA/ABS/PLA layered structure showed higher tensile strength than the pure ABS sample, which leads to the conclusion that the strengthening of ABS with PLA biopolymer is effective for selected applications.

The quality of the interlayer bond is influenced by the surface development and the surface finish pattern. At the same time, the printing parameters have a very significant impact on wettability, and attention should be paid to the optimization of process parameters combination selection: layer thickness, filling method, and printing speed ^[75]. In an experiment, a combination of process parameters such as the mesh fill method and a layer thickness of 0.25 mm can be used to produce parts with the maximum bond angle. To modify the surface morphology of multi-material prints, ICP-CFx (inductively coupled plasma and coated by fluorocarbon-based material) treatment is used. The treated PLA/PE-HD (high-density polyethylene) surface in the proportion 90/10 showed a bond angle of 121.6°, 36° higher than the bond angle measured on the untreated surface ^[76].

The quality of material bonds is directly related to sample type. During their research, Lopes et al. proved the negative influence of geometric boundaries between the same printed material from two embossing heads; the lack of chemical affinity between the materials worsens the effect—a decrease in Young's modulus tensile strength is observed ^[77].

Kumar S. et al. ^[78], on multi-material printing in FDM technology, studied the combination of PLA with a polyamidetitanium dioxide (PA6-TiO₂) composite. The best printing parameters, such as a printing speed of 90 mm/s and a rectilinear filling pattern, were determined. The influence of the number of layers of each material on sample peak strength was also investigated—it was found that 5 PLA layers and five composite layers were the best combinations. The selected combination showed higher strength (61 MPa) than that of pure PLA (42–45 MPa)—the same was discovered for thermal stability. Pin on disc wear tests showed that PA6/TiO₂ material consumes less material compared to PLA; hence, samples based on PA6/TiO₂ can be used for applications with high wear rates ^[79].

Using PLA and poly (3-hydroxybutyrate) PHB, thermal stability and interfacial adhesion of prints can be improved using cellulose nanocrystals and DCP dicumyl peroxide as a crosslinking agent ^[80]. A nanomaterial that meets the high standards of engineering applications was produced by obtaining cellulose from plum pits. PLA/PBAT/PBS composite (polylactic acid/poly (butylene adipate-co-terephthalate)/poly (butylene succinate) with nano talc was discovered to be the best combination and the best roughness and dimensional accuracy parameters were obtained for the proportion of 70/10/20/10 ^[81].

3. Modifications of the PLA Filament

A constantly developing trend in 3D printing is the modification of ready-made polymer filaments, enriching them with biodegradable components and testing their properties. An example of this approach is the research of Singh M. et al. ^[82], where shear resistance using cancellous screws of objects printed in FDM technology with PLA filament with the addition of almond skin powder was examined. The study suggested that the maximum peak shear strength (23.02 MPa) and the maximum shear strength at break (22.90 MPa) were observed for the honeycomb fill pattern at 100% screw insertion and a 30° rake angle.

An innovative approach consisting of overwhelmed physical interlocking and minimum chemical grafting in the production of PLA filament with polypropylene for 3D printing ensured high structural stability (mechanical and intermolecular) concerning thermal degradation (compared with pure PLA) ^[83].

Attempts to strengthen PLA with silicon nanocomposites (clay nanocomposite) ^[84] proved that the addition of nanoclay increased thermal stability and the modulus of elasticity. The samples were made of pure PLA and PLA with nanoclay. The color of samples with nano clay changed. As the printing temperature increased, the samples turned brown, but it is worth noting that at the same time, despite the color change, they became more transparent. This indicates another essential aspect when printing from composites, where the filament composition and the printing parameters are crucial for the design and further applications of objects.

Enrichment of PLA with silica (silica-silicon dioxide SiO₂) strengthens PLA: adding 10% silica by weight increased tensile strength from 62.8 MPa for pure PLA to 121 MPa for enriched PLA ^[85]. As a natural material, silica can strengthen polymers and create biodegradable composites for 3D printing. The silica additives can enhance the handling and quality performance of composites and thermoplastic polymers because of their diverse potential.

Attempts to strengthen PLA with flax fibers indicated the need to plan the additive manufacturing process carefully. The researchers indicated ^[86] that flax fibers could strengthen the samples, but their disadvantages, such as intra-filament porosity and the surface condition, should be eliminated. These disadvantages contributed to internal material gaps and the weakening of bonds. The fatigue behavior of specimens made of PLA and PLA reinforced with filler based on pinewood, bamboo, and cork using FDM was tested ^[87]. Testing did not significantly affect the change in tensile strength and associated durability during this loading interval for PLA-based materials reinforced with natural filler.

SEM analysis showed the presence of porosity, interlayer disturbances, and at the same time, good interfacial compatibility of PLA with the natural filler. Under cyclic loading, the visco-elastic behavior of the tested materials was found to increase with increasing values of cyclic loading of 30%, 50%, and 70%, and the permanent deformation of the tested materials, i.e., viscoelastic behavior (creep), also increased.

In Guessasma S. et al. ^[88], wood-based fibers' microstructure and mechanical properties were investigated in FDM technology (with experimental and numerical methods) about the PLA/PHA wood printing temperature. The optimum printing temperature was determined—220 °C for printing with wood-based filaments while maintaining adequate tensile strength, compared to objects printed at temperatures in a range of 210–250 °C. Water adsorption and desorption properties of wood change the dimensions of wooden objects, which is often considered a disadvantage. Using those properties in filament modification can lead to producing objects that change shape with humidity. PLA was modified by adding different wood contents to produce shape-changing double-layer actuators. The higher the wood content, the greater the observed shape change. PLA with wood can be used in 3D printing elements induced by humidity control—changing shape under changing climatic conditions ^[89].

Polymers for 3D printing can be given bioactive properties directly from natural extracts (e.g., from Mango extracts), which will allow the use of 3D printing with polymers in medicine ^[90]. Polymers could be used as carriers for medicinal substances released only after implantation in the patient's body. The use of polylactic acid with methotrexate or an anticancer drug (PLA/MTX) made it possible to print a frame that releases the active ingredient at the implantation site for more than 30 days, reducing side effects caused by injection or oral administration. This makes it possible to 3D print frames and use them in drug delivery ^[91]. Filament made of biomaterials such as PLA, polycaprolactone PCL, and hydroxyapatite HA became the building blocks of interlocking nails used for bone fractures in dogs. The highest compressive strengths of 82.72 MPa and tensile strengths of 52.05 MPa were achieved with the highest tested hydroxyapatite content of 15% ^[92]. Assessment of the cytotoxicity of the PLA/PCL/HA combination showed that the cells could be viable and increase in the frames. The most favorable PLA/PCL weight ratio in biocompatibility, viability, and osseointegration was 70/30 ^[92]. A strong interaction between PLA and HA resulted in the high mechanical strength of the composite ^[93]. After mechanical testing, the optimum ratio for biological research and 3D printing was selected. Biological experiments showed that the synthesized PLA/HA composite had excellent in-vitro viability. HA/PLA (10:90) had the highest mechanical strength comparable to natural bone among the various tested HA to PLA ratios. At the same time, the HA/PLA sample (10:90) showed excellent printability in 3D bioprinting using the FDM approach ^[91]. Biopolymer-based materials have the potential for use in prosthetic components, e.g., acetabular components in total hip prosthesis ^{[94][95]}.

The potential application of the TPU and PLA polymer composition is the production of antibacterial wound dressings using 3D printing. The mechanical, structural, and microscopic analysis and degradation allowed the selection of the most promising combination for further antibacterial modification (filament COMP-7,5PLA: consists of 12 parts of TPU filament and 1 part of PLA). It has been proven that the antibiotic amikacin is stable during extrusion at elevated temperatures, which, in combination with biodegradable PLA, makes it possible to produce short-term implants ^[96].

3D printing is used for the production of personal protective equipment. TPU and PLA polymers allow re-sterilization; therefore, their use would reduce the amount of biomedical waste ^[97] due to the possibility of multiple sterilizations and reusing the same elements.

In deliberations ^[98] on the environmentally friendly, rapidly degradable plastic-enzyme composites, Polycaprolactone/Amano lipase (PCL/AL), PLA, was used as the basis for the application of composites on complex structures.

Blending thermoplastic polyurethane (TPU) with polylactic acid (PLA) is a proven method of obtaining a mechanically more robust material. The addition of graphene oxide (GO) is increasingly used in polymer nanocomposites to customize their properties further. The addition of GO significantly improved the mechanical properties of the polymer matrix; 167% in terms of the compression modulus and 75.5% for the tensile modulus ^[99]. Cell viability, bonding, proliferation, and differentiation assays using MG-63 osteosarcoma cells have shown that PLA/GO frames are biocompatible and promote cell proliferation and mineralization more effectively than pure PLA frames ^[100]. The 3D-printed nanocomposite is a promising frame with the appropriate mechanical properties and cytocompatibility that could enable osseointegration and bone formation. A model of the trachea for tissue engineering was developed ^[101], consisting of multilevel structural polylactic acid (PLA) membranes surrounding thermoplastic polyurethane (TPU) skeletons—polymers were modified with GO-IL (ionic liquid) graphene oxide. The in-vivo result confirmed that the subjects displayed favorable biocompatibility and promoted tissue regeneration.

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