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Polymer Composites Used in Rapid Prototyping Technology

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Abstract

New materials and filaments dedicated to 3D printing were obtained using the fused deposition modeling method, and the properties of the produced materials were investigated. Polylactide was used as a polymer base for the assays because of the desired properties of the polymer, mainly biodegradability, and the matrix was refilled by the addition of metallic nanofillers, such as bronze, copper, brass, and steel. For the composites obtained, mechanical properties were investigated to determine the dependence of the obtained results on the content and type of filler used and on the method of fabrication of the fittings. It was found that the additives present in the polymer matrix increased the fluidity of the material. The best results were obtained for the compositions with bronze and steel in which the mass flow rate was 72.97 and 79.99 g/10 min, respectively. The filled material that had lower hardness was measured by Rockwell and the impact strength was measured by Charpy. In addition, it was found that injection-molded parts obtained much better mechanical properties than those obtained by 3D printing.

Keywords

3D printing • FDM • composites • metal nanofiller • polymer processing

1. Introduction

Fused deposition modeling (FDM) is one of the first three-dimensional printing techniques. The FDM technique is based on heating the thermoplastic material above the melting point, and then extruding the material in layers applying it to the previously produced surfaces, the process continues until the full product geometry is reached. 3D printing, available in a wide range of colors, is developing at a surprising pace because the process has many advantages, such as prices of 3D printers are decreasing and filaments-materials for FDM are nontoxic. An additional advantage is the simple construction of printers, which guarantees low failure of the machine. The constantly growing market demand for this type of equipment and services necessitates the production of new materials, product procedures, or innovative equipment [1].
Akhoundi and Behravesh, in their work [2], stated that in the FDM technology, an important aspect is the selection of the right material and additives adequate to the planned product characteristics. Printing requires at least one material that can be filled with various types of additives (composites) or other materials (blends). In addition, they proved that the introduced auxiliary agents can not only affect the mechanical and functional properties of the detail but also the weight of the element, visual, or aesthetic aspects.

Recently, a lot has been heard about the recycling of polymer materials or the possibility of reusing the material; therefore, it is so important to use biodegradable raw materials [3]. Polylactide (PLA) is the most commonly used material in the FDM technology to meet this requirement. PLA is made from renewable raw materials, such as sugar beets, maize, and fully composted thermoplastic polyester. The polymer is characterized by a low melting point and therefore requires less energy during the 3D printing process as compared with other materials used for FDM, such as polyamide (PA) and butadiene-styrene-acrylonitrile terpolymer (ABS), although it has similar mechanical properties such as hardness, processability, or tensile strength [1, 3]. The material is a pro-ecological alternative in relation to other materials used in the FDM technology. PLA also has undesirable features such as low toughness, elongation at break of less than 10%, and slow degradation; therefore, unfilled PLA should be supplemented by the introduction of additives, that is, the synthesis of nanocomposites [4].

2. Nanofillers – modification of polymer properties

Traditional unfilled biodegradable materials exhibit poor thermal or electrical properties and a narrow range of processing

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possibilities. By creating polymer composites based on a biodegradable polymer, we obtain a composition that is degradable and meets practical requirements [5].

Sun et al., in their work [5], presented the three most important issues related to biopolymers, such as cost, processing, and efficiency. Scientists found that to improve efficiency and processing processes, nanoadditives (with particle sizes up to several hundred nanometers) are introduced into biomaterials. They also proved that the addition of a filler on the nanometric scale provides reinforcement and functionalization improvement due to the large specific surface area of the nanoparticles as well as the efficiency of biopolymers.

Łoś et al., in their work [6], stated that the possibility of choosing the composition of the polymer matrix and the content, type, and structure of the filler allows controlling the appropriate properties of the composition. The scientists noticed that polymer–metal composites with fillers in the form of flakes or powder are of increasing interest. The authors stated that the materials obtained in this way are characterized by corrosion resistance, ease of processing, and flexibility. Fillers with a large specific surface are, for example, metal particles to be introduced in a certain amount and the content that causes the particles to be packed close together, which guarantees an uninterrupted conducting path (guarantee of high-electrical conductivity).

3. Materials and methods

This research aimed to determine the mechanical properties of the obtained new materials (polymer–metal filament) dedicated to incremental printing. PLA was used as the polymer matrix, and the filled additives were bronze, copper, brass, and steel. The materials needed for the determinations were obtained after mixing together the appropriate amounts of ingredients (19.5% PLA, 70% nanofiller, and 0.5% compatibilizer), pre-homogenization using a twin screw extruder, and subsequently extruding the material needed for research on a specially designed for this purpose line for obtaining filament.

The full specification of the filaments received is given in Table 1.

The obtained material was used to make necessary fittings (i.e., bars and paddles) using the injection molding method and the FDM technology, which, in subsequent stages of work, were used to carry out planned determinations of selected properties.

The material was used to obtain the necessary fittings by the injection molding method on the HAAKE MiniJet II mini injection molder, and the parameters of the injection molding process are summarized in Tables 2 and 3.

Figure 1. Designed as part of the work author's line to receive filament.

Table 1. Specification of received filaments.

Material Parameter	PLA	PLA + copper	PLA + bronze	PLA + brass	PLA + steel
Diameter [mm]	2.85	2.85	2.85	2.85	2.85
Tolerance [mm]	±0.05	±0.05	±0.05	±0.05	±0.05
Roundness [%]	$^{3}95$	$^{3}95$	$^{3}95$	$^{3}95$	$^{3}95$
Temperature application [°C]	180–210	190–210	210–230	190–220	190–210

The obtained filaments were used in the rapid prototyping technology with the Ultimaker 3 Extended printer with the parameters presented in Table 4.
The tests were carried out using the available equipment at the Rzeszów University of Technology.

- Mass melt flow index (MFR) – to a preheated temperature of the apparatus Plastometer DYNISCO 4781 was poured about 4 g of material, and then a preload of 240 s (plasticizing time) was applied. During the correct determination, the load was changed to the correct one and then measured. The sample extruded from the nozzle was cut off in 10 s and then weighed.
- Rockwell hardness – measured at ambient temperature on a Rockwell hardness meter, Zwick/Roell. The sample was placed on the work table and reached the position of the indenter. After appropriate machine signaling, a specific load was applied (load at which the indenter will sink to a thickness of 0.15–0.35 mm) and measurement lasted for 30 s. After the determination, the result obtained in N/mm^2 was visible on the monitor.
- Charpy impact strength – fittings to be marked and placed horizontally on the support of the apparatus in such a way that the impact force of PSW GERHARD ZORN hammer with a force of 1 J hits the center of the edge of the fixed fitting. The result was displayed on the monitor.
- Determination of strength characteristics during a static tensile test – a program for operating the apparatus was started, appropriate process parameters were given (stretching rate and dimensions of paddles), and then samples were placed in INSTRON 5967 testing machine holders. The progress of the process was observed on the monitor, and the measurement lasted until the assumed value was reached, for example, stress, strain, or until the fitting breaks. The results were recorded in the table format.

4. Results and discussion

1) The determination of the mass melt flow index made it possible to determine the fluidity of the composition and

Table 2. Parameters of the injection molding process-obtaining paddles.

Parameter \ Material	PLA	PLA + copper	PLA + bronze	PLA + brass	PLA + steel
Plasticizing time [s]	140	60	60	120	120
Injection temperature [°C]	210	210	210	210	220
Injection pressure [bar]	900	750	800	900	850
Injection time [s]	5	5	5	5	5
Mold temperature [°C]	50	50	50	50	60
Post pressure [bar]	850	700	700	850	800

Table 3. Parameters of the injection molding process-obtaining bars.

Parameter \ Material	PLA	PLA + copper	PLA + bronze	PLA + brass	PLA + steel
Plasticizing time [s]	120	60	60	120	120
Injection temperature [°C]	220	210	210	220	220
Injection pressure [bar]	900	750	800	850	850
Injection time [s]	5	5	5	5	5
Mold temperature [°C]	60	50	50	60	60
Post pressure [bar]	850	700	700	800	800

Table 4. Parameters of the FDM process.

Parameter \ Material	PLA	PLA + copper	PLA + bronze	PLA + brass	PLA + steel
Type of filling			Rectilinear		
Fill angle			45°		
Density of filling			100%		
Layer height			0.2 mm		
Extruder speed			70 mm/s		
Extrusion temperature			210°C		
Heated bed			60° C		
Duration of the process			45 min		

the effect of particular nanofillers on the process under investigation.

Table 5. The results of the MFR study

Filament	Temperature[°C]; load [kg]	MFR [g/10 min]
PLA	200°C; 2.16 kg	13.10 ± 0.17
PLA + Bronze	220°C; 2.16 kg	72.97 ± 0.69
PLA + Copper	190°C; 2.16 kg	36.92 ± 0.32
PLA + Brass	180°C; 2.16 kg	37.19 ± 0.75
PLA + Steel	180°C; 2.16 kg	79.99 ± 2.36

The introduction of nanoadditives into the polymer matrix was allowed to obtain a composite with increased mass melt flow index in relation to unfilled material. PLA is characterized by a fluidity of 13.10 g/10 min, and it is the lowest result among the tested materials. The presence of copper and brass in the material increases the flowability by 23.82 and 24.09 g/10 min, respectively. The highest MFR result was obtained with a PLA filled with steel (79.99 g/10 min), and slightly lower results were obtained with the composition containing brown (72.97 g/10 min). By analyzing the results obtained, it can be concluded that the introduction of reinforcing fillers of various shapes and sizes (nanometer scale) facilitates the flow of the material, which improves the usability of the composition in the processing processes and reduces the processing shrinkage.

2) Determination of hardness allows for the initial determination of the composite's resistance to permanent deformation, such as dents.
A significant effect on Rockwell's hardness results was obtained by the technique of producing fittings needed for research – the results for one composition differ significantly. Details obtained by the FDM method were characterized by lower hardness than elements obtained by injection molding. The largest discrepancy in the results between the two production techniques presented is the composition of PLA filled with bronze, and the difference is 104.47 N/mm^2.
The introduction of metallic nanofillers caused a decrease in the hardness of the unfilled material. The composition of PLA filled with steel obtained the lowest results among the tested materials (52.52 N/mm^2 for details obtained by 3D printing and 85.4 N/mm^2 for elements obtained by the second method).

3) Determination of materials' impact strength is a measure of their brittleness.
The collected results of the test allow to conclude that the higher resistance to impacts is characterized by fittings obtained by injection molding. The PLA composition filled with brass is characterized by the most visible difference between the techniques of obtaining details.
The presence of nanoadditives caused a significant decrease in the impact results obtained. The most brittle is characterized by the composition of PLA with bronze; in this case, the difference between the unfilled materials is 27.29 N/mm^2 (respectively for details made by 3D printing), and the difference between fittings made by injection method is 24.76 N/mm^2.

4) The strength tests of the materials were carried out by a static stretching test.
FDM fittings are characterized by poorer mechanical strength than details made by injection molding, and the differences can be caused by a lower density of filling in the case of elements obtained from FDM.
The results of Young's module allow to conclude that the compositions obtained by the injection method are characterized by a higher elasticity than the shapes obtained

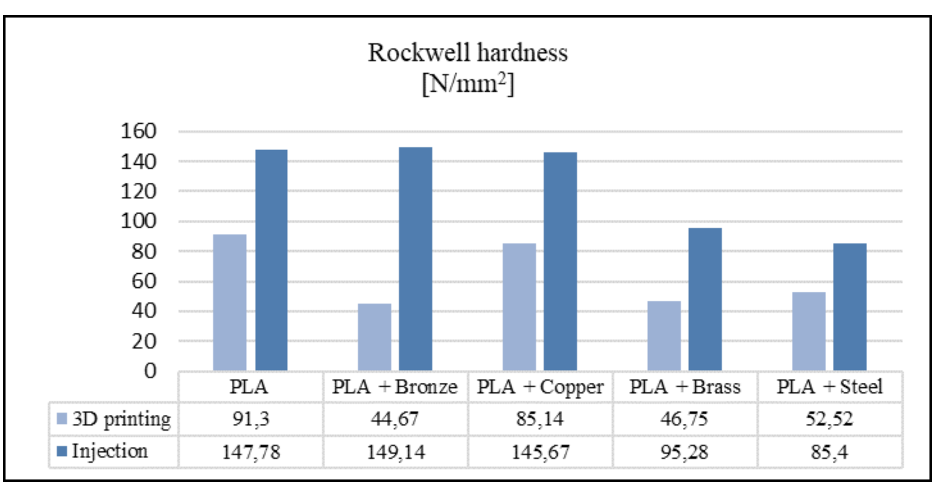

Figure 2. The hardness results of individual compositions.

by the second method. Only in the case of PLA compositions filled with copper, the results present an inverse connection. The obtained results do not allow to determine the influence of the metal filler additive because, in the case of a PLA filled with bronze or copper, the elasticity of the composition improved to the plastic without additives, while the remaining compositions have lower elasticity.

Similar connections to those discussed earlier present the results of strain. Compositions obtained by FDM are characterized by lower strain than samples obtained with the second technique. The introduction of metallic fillers produced different effects depending on the material. The compositions containing copper and bronze showed higher deformation from PLA, and the remaining compositions are characterized by similar results of the assay.

The highest stress value at the time of fracture of the sample showed a composition of unfilled PLA. Fittings made by the injection molding method in each case obtained a result higher than the details made by the FDM method. However, the obtained results do not differ significantly, and the highest discrepancy is 9.15 MPa for PLA with the addition of bronze. The introduction of metallic nanofillers caused a significant drop in the breaking stress by at least 30 MPa during the examination of all compositions.

5. Conclusions

- The developed author's line for obtaining composites based on polymeric materials in the form of a filament allows to increase the range of polymeric materials used in the FDM technology.
- The mechanical properties of the tested composites were significantly influenced by the technique of their production as well as the introduction of appropriate powdered metallic fillers, such as bronze, copper, brass, and steel.
- The fittings obtained by injection molding had much better

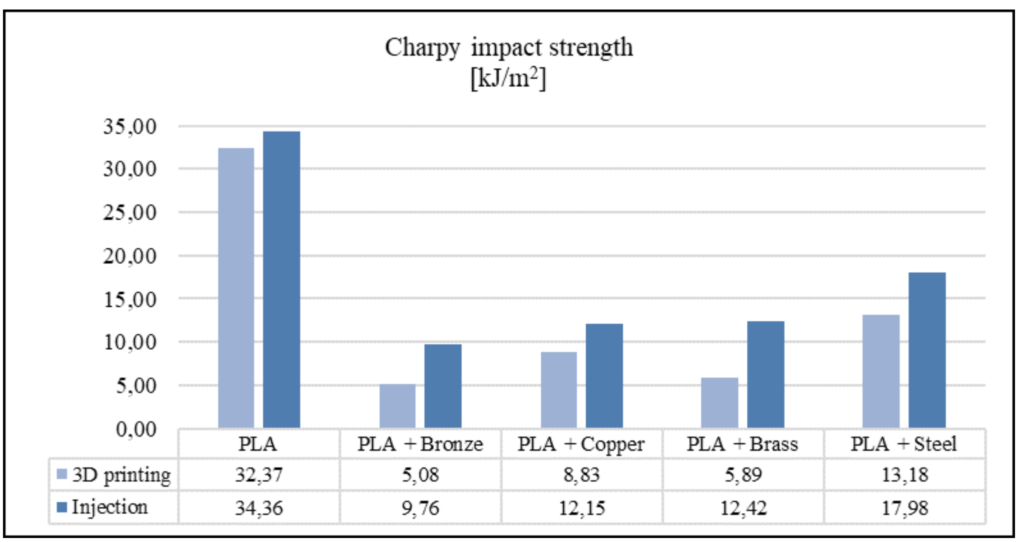

Figure 3. Impact strength of individual compositions.

Table 6. List of results of marking strength characteristics for individual materials.

Parameter \ Material	PLA	PLA + bronze	PLA + copper	PLA + brass	PLA + steel
			3D printing		
Young's modulus [GPa]	2.23 ± 0.03	2.91 ± 0.01	4.33 ± 0.1	2.11 ± 0.03	1.96 ± 0.05
Strain [%]	4.57 ± 0.56	6.91 ± 1.03	13.93 ± 1.7	3.54 ± 1.1	5.66 ± 0.88
Stress [MPa]	53.42 ± 2.64	14.97 ± 0.24	17.63 ± 1.03	16.40 ± 0.35	21.48 ± 1.19
			Injection		
Young's modulus [GPa]	2.5 ± 0.07	3.3 ± 0.1	2.81 ± 0.35	2.39 ± 0.48	2.27 ± 0.22
Strain [%]	6.55 ± 2.18	13.92 ± 3.89	11.35 ± 1.87	5.92 ± 0.71	5.96 ± 0.64
Stress [MPa]	54.71 ± 4.16	24.12 ± 0.91	23.58 ± 1.08	24.70 ± 0.29	24.29 ± 0.83

mechanical properties than those obtained with the FDM printer.

- The addition of the introduced metal filler to the polymer matrix resulted in improved fluidity of the material (MFR). Unfortunately, a reduction in Rockwell hardness and Charpy impact strength was observed.

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