Improving the Impact Strength and Heat Resistance of 3D Printed Models: Structure, Property, and Processing Correlations during Fused Deposition Modeling (FDM) of Poly(Lactic Acid)

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ABSTRACT: A fused deposition modeling method was used in this research to investigate the possibility of improving the mechanical properties of poly(lactic acid) by changing the thermal conditions of the printing process. Sample models were prepared while varying a wide range of printing parameters, including bed temperature, melt temperature, and raster angle. Certain samples were also thermally treated by annealing. The prepared materials were subjected to a detailed thermomechanical analysis (differential scanning calorimetry, dynamic mechanical analysis, heat deflection temperature (HDT)), which allowed the formulation of several conclusions. For all prepared samples, the key changes in mechanical properties are related to the content of the poly(lactic acid) crystalline phase, which led to superior properties in annealed samples. The results also indicate the highly beneficial effect of increased bed temperature, where the best results were obtained for the samples printed at 105 °C. Compared to the reference samples printed at a bed temperature of 60 °C, these samples showed the impact strength increased by 80% (from 35 to 63 J/m), HDT increased by 20 °C (from 55 to 75 °C), and also a significant increase in strength and modulus. Scanning electron microscopy observations confirmed the increased level of diffusion between the individual layers of the printed filament.

INTRODUCTION

Fused deposition modeling (FDM) is a type of three-dimensional (3D) printing where a thermoplastic filament is heated above the melting temperature and then extruded onto a print surface in layers. It is applicable to many industries including healthcare, transportation, housing, and farming, as well as a variety of industrial applications where there is a benefit from the customization of individual items.1,2 The many benefits of FDM include promoting sustainable, inexpensive development with decreased material waste, eliminating tooling requirements, and a significantly shorter supply chain.1,2 The costs of 3D printers are decreasing, resulting in increased home usage and the need to better understand the properties of the material being printed, specifically for load-bearing purposes.3 FDM is currently undergoing a transition from rapid prototyping to rapid manufacturing. For that reason, new materials, equipment, and manufacturing procedures need to be developed further.3

Poly(lactic acid) (PLA) is a bio-based, compostable, thermoplastic polyester obtained from annually renewable resources such as corn or sugar beets.4 PLA has the potential to replace petroleum-based thermoplastics, and its low melting point is a major benefit as it requires less energy to 3D print compared to that for acrylonitrile butadiene styrene (ABS) and polyamides.5,6 PLA has a number of diverse uses, including biomedical and industrial applications. Its biocompatible and biodegradable properties provide many biomedical opportunities, and its good mechanical properties and compostability are well-suited for industrial applications.5,7 Different crystalline structures and degrees of crystallinity can be developed by varying the thermal history of the material, which allows for different properties to be tailored depending on the application.5–8

The significant effect of process parameters on the mechanical properties of the samples created using FDM has been extensively studied using acrylonitrile butadiene styrene (ABS) filaments. Because of the relatively long process time, selected process parameters can be monitored in real time. An
example of this type of in-line measurements is the utilization of fiber Bragg grating sensors. Simultaneous observation of the stress field and temperature allows the evaluation of the inter-/intralayer adhesion and distortion in the parts, structural inhomogeneity, and thermal history. These factors have a significant impact on the mechanical properties of the finished parts. Highly anisotropic properties were proven to be a function of how FDM extrudes the filament onto the print surface in layers. Process parameters including orientation, layer thickness, raster angle, raster width, air gap, processing temperature, and layout of samples on the print surface were studied to determine their effect on the mechanical properties of the ABS samples, and the results were used to optimize the parameters and greatly improve the mechanical properties of the 3D printed parts.

Studies concerning PLA and the relationship between its crystallinity and mechanical properties have also been conducted. Harris and Lee investigated how manipulating the process parameters, specifically increasing the annealing time of injection-molded PLA, would impact the crystallinity and in turn the mechanical properties of their samples. They found that optimizing the molding cycle as well as adding nucleating agents enhanced the crystallinity by 37%, resulting in an increase in flexural strength and modulus by 25% and heat deflection temperature (HDT) by 30 °C. In addition, constant crystallinity was observed throughout the parts after annealing. Wang et al. also observed in their study of FDM that an increase in crystallinity of 3D printed PLA corresponded to a high impact strength. Drummer et al. investigated FDM of PLA filled with tricalcium phosphate. They found that a greater extruder temperature resulted in increased crystallinity partially because previous layers deposited and bonded together were reheated by new filaments being extruded nearby. This was also observed to affect the tensile strength of the samples.

Many different process parameters in regard to FDM of PLA have been studied. These include the build orientation, layer thickness, feed rate, plate temperature, uniaxial direction of rasters, distance between filaments, extruder temperature, and color. All were found to have varying degrees of impact on the mechanical properties of 3D printed PLA. Tymrak et al. quantified the tensile strength and elastic modulus of PLA 3D printed under realistic environmental conditions on RepRap printers. Process parameters were not defined, and it was observed that the variety of different settings utilized had a large effect on the structure and properties of the samples. A high extruder temperature was found to result in increased thermal bonding and inter-/intralayer lamination and resulted in a higher tensile strength. Variation in the unidirectional raster orientation has also been studied with regard to FDM of PLA and was found to alter the mechanical properties of the parts. In one case, the ultimate tensile strength increased 55% with the change in raster angle. The effect of annealing on the crystallinity of the 3D printed PLA parts was briefly reviewed, with results indicating no change when the printed samples were annealed below the Tg; however, a reduction in strength between 10 and 30% was observed.

The majority of research concerning the impact of printing parameters on the mechanical properties of 3D printed components usually focuses on ABS-based materials, analyzing the impact of a wide spectrum of variables and predicting properties based on numerical simulations. In addition to the most frequently analyzed machine parameters, such as nozzle diameter, layer orientation, or printing speed, PLA-related research also often includes temperature parameters and additional thermal treatment. The main goal of the presented research was a comprehensive assessment of the most important factors from each of the parameter categories to provide a reliable evaluation of the benefits. On the basis of literature sources, the selection of variable parameters included the temperature of the printer nozzle and bed. The raster angle orientation was chosen as the main machine factor. Annealing treatment was chosen as the additional process-independent factor. For verification and comparative purposes, injection-molded samples were also prepared.

### RESULTS AND DISCUSSION

**Correlation of Thermal Parameters with the Density of FDM-Printed Samples.** The viscosity graphs shown in Figure 1 present the results of the frequency sweep measurements at various temperatures. Rheological tests can confirm only the viscosity changes occurring within the printing nozzle, which do not translate into real material viscosity after leaving the nozzle. In addition, it can be noted that any increase in print temperature can lead to the intensification of degradation phenomena, which is evident from the reducing viscosity in the low deformation frequency range. In the case of FDM techniques, these changes have a negligible effect on material degradation because the residence time of the material in the nozzle is very short. Even at temperatures significantly greater than the recommended printing conditions, it does not usually lead to visible changes in the quality of the model, which has also been confirmed by other researchers. This is primarily due to the very nature of the FDM printing method, as the material flowing from the nozzle, even with a significant reduction in viscosity, is rapidly cooled down when it comes in contact with the ground surface.

Dimensional accuracy of the FDM models also largely depends on the viscosity of the material used; in this case, the viscosity decrease usually has a negative impact on the model mapping, which is related to the inability to accurately controlling the height of the extruded material path. However, the high viscosity that allows for a proper control of the layer...
height of the model also increases the content of free spaces between the paths. The 3D model structure shown in Figure 2 presents the sample prepared at the parameters optimized to obtain the high dimensional accuracy of the model (bed temp = 60 °C; melt temp = 210 °C). The proper selection of the printing parameters is indicated by the constant distance of 200 μm between the successive voids. These voids occur at the intersection of consecutive layers, and the distance between them corresponds to the height of a single layer of the deposited filament given by the printer program.

Unlike conventional polymer processing techniques such as extrusion and injection molding, FDM printing does not allow for a wide variation of the flow characteristics through appropriate parameter selection. The viscosity of the polymer melt depends mainly on the temperature gradient between the print nozzle and the surface of the rising model. Most commonly used 3D printers offer the ability to controlling only the bed and nozzle temperatures, which simply leads to the need for multiple comparative tests to optimize the range of both temperature variations.10 Because the temperature range of both the melt and bed was relatively wide in the presented studies, changes in these parameters also caused changes in the degree of filling of the resulting sample models. The density values presented in Figure 3 show a comparison of the specific density measurements for samples printed at variable bed and nozzle temperatures. These results are also confirmed by the scanning electron microscope (SEM) picture presented in the same figure; the discussed images represent printed samples prepared at extremely different bed temperatures, 45 and 105 °C, respectively. The results confirmed the more significant consequences of bed temperature changes on the model’s filling level. Similar conclusions were formulated by Wang et al.,8 however, in their research, the bed temperature was the main variable and the temperature range was very high (from 30 to 160 °C).

Figure 2. Appearance of the sample structure after injection molding processing and under optimal conditions of the FDM printing process.

Figure 3. Density variations for different thermal conditions in the printing process. The picture comparison reflects the raster area cross section from high-porosity samples (bed temperature of 45 °C) and low-porosity samples (bed temperature of 105 °C).

In the case of density analysis, it is worth mentioning that for most of the parts printed with FDM techniques the filling density is often reduced in a targeted manner to reduce the material consumption and also the dimension accuracy.28 This modification occurs by reducing the density of the model’s filing mesh, while maintaining the solid structure of the shell layer. With such a constructed model, it is of course not possible to obtain the maximum possible strength of the samples, but taking into account the significant mass reduction, this operation has many advantages.

Taking into account the main objective of the research, which is to increase the mechanical performance of PLA-based 3D models, the porosity (void content) measured during the density measurements was only 5.5% in the worst case of samples printed at the bed temperature of 45 °C. Surprisingly, the density of the samples printed at the highest bed temperature (90 and 105 °C) does not differ from the values obtained for injection-molded samples, which proves not only very small porosity content but also confirms the density changes of PLA itself caused by increased crystallinity, which was observed for PLA previously.29 According to numerous studies,50,31 the density of fully amorphous PLA is 1.248 g/cm³ whereas that of 100% crystalline PLA is 1.290 g/cm³, which may confirm the unexpected increase in specific density for selected samples.

Differential Scanning Calorimetry (DSC) Measurements: Crystallinity Evaluation. Differential scanning calorimetry (DSC) was employed to determine the degree of crystallinity of the FDM samples as well as to gain an insight into the influence of sample thermal history on basic thermomechanical properties. The changes in the crystallinity level for printed samples can be seen in Figure 4; the basic thermal properties are listed in Table 1.

It can be seen from Figure 5 that the variation of the print temperature of the samples did not have a significant effect on the crystallinity or the melting peak. Some visible changes can be considered as negligible because they do not show any trend and generally are within the range of measurement error. Although crystallization half time (t1/2) decreases as the crystallization temperature (Tc) increases, with the crystal growth rate considered proportional, this has been reported to
be true only up to around 110 °C for pure PLA. At this point, the crystallization process becomes slower as the $T_c$ increases, which was observed by Sánchez et al.\textsuperscript{32} in a series of measurements of PLA crystallization kinetics. Although the print temperatures are much higher than the boundary temperature of 110 °C, the temperature fluctuation from the extruded filament and the rapid cooling after deposition do not keep the filament at the elevated temperature long enough for a significant difference in crystallinity to occur. This has in turn been reported in other studies, when bed temperatures reached 160 °C (close to the PLA melting point).\textsuperscript{6} The presence of a small double melting peak in the DSC signal can be observed for most of the samples. This is a result of the $\alpha'$ crystal structure melting and then recrystallizing into its $\alpha$ form with tighter and more ordered chain packing; this phenomenon is quite widely described by di Lorenzo et al.\textsuperscript{33} for PLA-based materials.\textsuperscript{34,35} Because there are so few $\alpha$ crystal structures as assumed from the very slight melting peak, the elongation at break and the modulus of the samples were not seen to be affected. All of the samples printed at varying print temperatures had no significant changes in their mechanical properties, apart from the samples printed at a temperature of 190 °C. This indicates that although having the same degree of crystallinity as that of the other samples there are other factors involved in determining the mechanical properties of the samples. The bonding between the filaments is also affected by the thermal history of the samples, and unsatisfactory bond strength between the filaments will lead to poor mechanical properties, regardless of the degree of crystallinity the sample has obtained. Because the filament diameter was so small, the printing temperature was seen to have a negligible effect on the crystallinity, as well as the mechanical properties of the samples (apart from the lowest print temperature).\textsuperscript{12}

As seen in Figure 6, varying the bed temperature of the FDM samples had a significant effect on their degree of crystallinity achieved, cold crystallization, and melting peak. The cold crystallization peak enthalpy was reduced greatly as the bed temperature increased, which suggests that the crystallization process is more pronounced at lower temperatures. This is consistent with the observations made by di Lorenzo et al.\textsuperscript{33} for PLA-based materials, where they noted that the crystallization rate increases with decreasing temperature.

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**Table 1. Thermal Properties of PLA-Based Samples**

| Sample           | 1st Heating | 2nd Heating |
|------------------|-------------|-------------|
|                  | $\Delta H_{cc}$ | $\Delta H_{m}$ | Crystallinity (%) | Crystallinity (%) |
| Injection molded | 24.9        | 26.3        | 1.44               | 22.11              |
| 45 °C            | 22.7        | 26.1        | 1.48               | 21.19              |
| 60 °C            | 22.0        | 28.4        | 6.41               | 22.51              |
| 75 °C            | 18.5        | 27.5        | 9.62               | 23.40              |
| 90 °C            | 13.4        | 24.5        | 11.92              | 23.80              |
| 105 °C           | 7.7         | 24.9        | 18.30              | 21.08              |
| Melt Temperature | 20.3        | 26.3        | 6.32               | 23.87              |
| 190 °C           | 22.3        | 28.5        | 6.65               | 24.72              |
| 200 °C           | 22.1        | 28.1        | 6.41               | 25.61              |
| 210 °C           | 22.1        | 27.7        | 6.00               | 25.88              |
| 220 °C           | 22.1        | 28.9        | 7.21               | 25.37              |
| 230 °C           | 22.1        | 28.9        | 7.21               | 25.37              |
| Annealing 80 °C  | 25.2        | 26.89       | 29.19              |                    |
| 100 °C           | 27.4        | 29.24       | 29.40              |                    |

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**Figure 4.** Comparison of crystallinity degrees for samples printed with different thermal conditions and injection-molded samples (DSM).

**Figure 5.** Comparison of the DSC curves obtained from the 1st heating stage for PLA samples printed at different melt temperatures and injection-molded PLA.

**Figure 6.** Comparison of the DSC curves obtained from the 1st heating stage for PLA samples printed at different bed temperatures and injection-molded PLA.
temperature increased gradually from 45 to 105 °C, indicating the increase in sample crystallinity. Also, the transition from α′ to α crystals could be observed as the bed temperature increased. Up to the bed temperature of 75 °C, the shape of the DSC curves remain similar with a sharp melting peak at around 150 °C. Visible changes are observed for the sample printed at 90 °C, where top of the melting peak is clearly flattened, which is potentially the result of the convolution of two melting peaks. Two clearly defined melting peaks appear for samples printed at 105 °C; this phenomenon, already described in the literature, indicates the existence of two separate crystalline structures, formed as a result of different crystallization kinetics. A large increase in overall crystallinity was observed for the whole observed range of bed temperature from 45 to 105 °C. The crystallinity level of 1.5% reported for the samples printed at the lowest bed temperature of 45 °C is most similar to the value obtained for injection-molded samples. The greater impact of bed temperature changes could be a result of shifting the crystallization regimes. This gradual change in crystallization kinetics, described in detail by Sayedlou et al., is associated with a favorable transition of thermodynamic conditions from regime III (where the low chain motion limits the lamella growth) to regime II (where the crystal growth occurs from prolific multiple nucleation at a lower temperature, resulting in a faster crystallization process). For PLA samples, this transition phenomenon has been reported to occur at around 120 °C but again, with the fluctuating temperature cycles and the print temperature decreasing rapidly, it is difficult to say the exact average temperature each print achieved. The change of regimes promotes increased and faster crystallization, as evidenced by the increase in crystallinity. The regime change and growth of two crystal structures were found to occur at the same temperature and are both associated with the double melting peak.

Although the increased bed temperature caused a significant increase in crystallinity and mechanical properties, this effect may be lost in the case of printing real models. Because of their geometry and size, it would be difficult to maintain identical thermal conditions of printing, as is the case with research samples. This problem is indicated by numerous studies, especially because this problem concerns not only the level of crystallinity but also an equally important issue regarding the weld formation of individual model layers. The role of these factors becomes even more important if we take into account the growing importance of large-scale additive manufacturing technology, where the maximum size of printed elements reaches several meters, which causes numerous problems related to the need to ensure thermal stability on such a large scale. The classical solution to most of the problems related to the heterogeneity of the 3D model structure is post-processing. For PLA especially, annealing allows us to obtain measurable benefits, especially in the context of improving mechanical properties. Post-print annealing was done to observe the effects on the samples and to evaluate whether it would be a viable method of obtaining the same outcomes on parts with different dimensions. Different variations of 3D printers for FDM exist and include models with the print area in an enclosed space with the option to adjust the ambient temperature.

Two sets of samples 3D printed at a bed temp of 60 °C and print temperature of 200 °C were annealed at 80 and 100 °C for 1 h each. Harris and Lee found that annealing longer did not increase the crystallinity after 1 h (annealed at 80 °C). The maximum crystallinity of PLA is reported to be just below 45%; however, the maximum crystallinity achieved with the studied samples was around 30%. There was not a significant increase in crystallinity between the two different annealing temperatures (see Figure 7); however, the appearance of the melting peaks was quite different. The 80 °C annealed sample displayed a double melting peak, indicating the formation of two different crystalline structures, α and α′. The 100 °C annealed sample had a single wide peak; perhaps, the two melting peaks were superimposed, indicating that there were more α crystals formed. Further supporting that theory, when observing the mechanical properties, the mechanical properties are quite different despite only a small difference in crystallinity.

The injection-molded sample displayed low crystallinity. This was mainly due to the fact that the grades of PLA used in 3D printing are intended mainly for the production of film, which in the end improves the dimensional stability of the products by reducing the shrinkage but also reveals the majority of defects caused by the amorphous structure of the material. Cold crystallization and a single melting peak of prepared samples indicated that there were only α prime crystals formed during this process. Despite being one of the samples with the lowest degree of crystallinity, all of the mechanical properties displayed were among the highest with the exception of the notched Izod impact strength, which was similar to that of samples 3D printed at lower bed temperatures.

**Mechanical Tests.** The values of the basic mechanical parameters obtained from static tensile/flexural testing and impact resistance measurements are collected in Table 2. Most important changes in the strength and modulus followed similar trends, both in tensile and flexural tests (see Figure 8).

In the case of printed samples, changes in mechanical properties follow the increase in the crystallinity of PLA; this is evident for samples printed at constant nozzle and variable bed temperatures. In the case of variable nozzle temperature, changes in strength and modulus were not so evident because the content of crystalline phase for this group of samples does not change significantly. The comparative analysis of the 3D printed, molded, and annealed samples is presented in Figure 9.
Histories. Thermal bonding of samples with similar crystallinities but different factors, not just the degree of crystallinity. This is because of stress concentration on the surfaces.

The injection-molded samples with a crystallinity of 1.5% had tensile properties very similar to those of the sample 3D printed at a bed temperature of 105 °C and a corresponding crystallinity of 18%. These results indicate that the tensile strength and modulus are dependent mostly on other factors, not just the degree of crystallinity. This is corroborated by the large variety of properties displayed in samples with similar crystallinities but different processing histories. Thermal bonding of filaments and crystal size may have contributed to this, as annealing creates larger crystals and temperature fluctuation was found to create smaller ones. Some sets of samples display a much higher standard deviation than others. This has been attributed to an unstable morphology where some of the polymer chains are more mobile than others, leading to a greater fluctuation in results. Both the flexural strength and modulus increased with the increase in crystallinity. As was seen with the tensile properties, all of the samples with crystallinity of ~5% have different flexural properties. The properties vary depending on the processing history, regardless of the degree of crystallinity. Unlike the tensile properties, the flexural modulus and strength both increase slightly with annealing.

The injection-molded samples had properties similar to those of the most promising 3D printed samples (FDM at a bed temperature of 105 °C), despite the large difference in crystallinity. The poor bonding between the FDM samples, in which elongation is mostly reduced because of stress concentration on the surfaces. Green painter’s tape was applied to the print surface for samples printed at 90 and 105 °C to promote the adhesion of the samples to the print surface. Although there was significant

| Table 2. Mechanical Properties of All Prepared PLA-Based Samples from Tensile, Flexural, and Izod Impact Measurements |
|---|---|---|---|---|
| | tensile test | flexural test | Izod test |
| | modulus (MPa) | strength (MPa) | elongation at yield (%) | elongation at break (%) | modulus (MPa) | strength (MPa) | impact strength (J/m) |
| injection molded | 3223 (±122) | 63.5 (±1.2) | 2.6 (±0.14) | 72.6 (±42.0) | 3864 (±118) | 103.3 (±1.9) | 23.5 (±9.1) |
| Bed Temperature (°C) | | | | | | | |
| 45 °C | 2877 (±76.3) | 54.2 (±1.3) | 2.6 (±0.04) | 5.49 (±0.85) | 2314 (±78.9) | 74.4 (±2.2) | 32.8 (±2.4) |
| 60 °C | 3014 (±58.9) | 62.0 (±1.0) | 2.7 (±0.04) | 7.45 (±3.0) | 3002 (±157.4) | 93.6 (±4.8) | 35.5 (±2.7) |
| 75 °C | 3258 (±72.2) | 60.7 (±1.4) | 2.5 (±0.05) | 4.58 (±0.95) | 2927 (±169.1) | 93.9 (±5.5) | 47.2 (±9.5) |
| 90 °C | 3298 (±101.1) | 64.1 (±0.9) | 2.5 (±0.20) | 5.34 (±0.85) | 3217 (±131.0) | 100.4 (±6.2) | 61.6 (±16.9) |
| 105 °C | 3317 (±92.7) | 65.9 (±2.0) | 2.2 (±0.12) | 4.98 (±1.2) | 3529 (±236.0) | 106.7 (±5.6) | 63.4 (±22.6) |
| Melt Temperature (°C) | | | | | | | |
| 190 °C | 2748 (±123.9) | 54.3 (±1.8) | 2.7 (±0.13) | 3.1 (±0.5) | 2247 (±40.4) | 71.7 (±2.1) | 34.5 (±3.9) |
| 200 °C | 3105 (±38.2) | 63.8 (±0.7) | 2.8 (±0.06) | 4.7 (±0.6) | 3147 (±87.3) | 98.7 (±4.0) | 34.7 (±3.3) |
| 210 °C | 3014 (±58.9) | 62.0 (±1.0) | 2.7 (±0.04) | 7.4 (±3.0) | 3002 (±157.4) | 93.6 (±4.8) | 35.5 (±3.7) |
| 220 °C | 3040 (±95.3) | 61.4 (±1.3) | 2.5 (±0.06) | 5.3 (±2.8) | 2899 (±150.4) | 94.3 (±4.6) | 32.4 (±2.9) |
| 230 °C | 3032 (±67.1) | 61.9 (±1.2) | 2.6 (±0.12) | 4.1 (±1.0) | 3097 (±165.5) | 97.1 (±3.7) | 35.7 (±5.0) |
| Annealing (°C) | | | | | | | |
| 80 °C | 3360 (±102.5) | 61.9 (±1.0) | 2.5 (±0.3) | 4.5 (±1.3) | 3516 (±115.6) | 103.9 (±3.0) | 136.7 (±10.9) |
| 100 °C | 3334 (±162.5) | 59.4 (±2.3) | 2.4 (±0.2) | 4.4 (±1.3) | 3739 (±236.4) | 109.4 (±6.4) | 127.6 (±17.1) |
| Raster Angle (°) | | | | | | | |
| 45/45° | 3014 (±58.9) | 62.0 (±1.0) | 2.7 (±0.05) | 7.4 (±3.0) | 3002 (±157.4) | 93.6 (±4.8) | 35.5 (±2.7) |
| 30/60° | 3270 (±35.6) | 61.5 (±1.8) | 2.7 (±0.1) | 3.6 (±0.9) | 3175 (±99.3) | 86.1 (±2.2) | 32.9 (±1.1) |
| 15/75° | 3286 (±66.7) | 62.5 (±1.1) | 2.6 (±0.1) | 3.7 (±0.3) | 3215 (±214.0) | 87.1 (±3.8) | 33.1 (±4.6) |
| 0/90° | 3211 (±102.4) | 61.5 (±2.2) | 2.5 (±0.1) | 3.7 (±1.0) | 2974 (±123.5) | 84.9 (±4.4) | 30.9 (±2.3) |

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improvement in the adhesion, there was still some warping observed on a number of samples. This had a negligible effect on the mechanical properties; they still increased with the increasing crystallinity and bed temperatures. Depending on the quality of the surface finish and accuracy of dimensions required, it is not feasible to increase the bed temperature further with the current filament and print surface.

In previous studies, the mechanical characteristics for a unidirectional raster angle were found to reduce when the raster angle was increased from 0 to 90°. The 90° angle was also observed to make the sample more brittle. For this study, the 45/45° raster angle was overall the most consistent and stable of the angles. There was not a significant difference between most of the properties when compared. This is a result of the multidirectional nature of the filament in the sample. All previous studies were completed on unidirectional raster angles and, as a result, saw a much larger difference in properties. The flexural modulus was the only property where the 15/75 and 30/60° angles were superior.

Most of the values of strength and modulus for samples printed at 75 °C and above are very similar; taking into account the standard deviation values, these differences are negligible. In

Figure 8. Tensile (A) and flexural (B) modulus/strength comparison for FDM-printed samples.

Figure 9. Comparison of tensile strength and modulus values for injection-molded samples and FDM-printed specimens at different bed temperatures and annealing treatments.

Figure 10. Comparison of flexural strength and modulus values for injection-molded samples and FDM-printed specimens at different bed temperatures and after annealing treatments.

Figure 11. Elongation at break and notched Izod impact strength for injection-molded samples and FDM-printed specimens at different bed temperatures and after annealing treatments.
our opinion, this is a beneficial behavior, especially taking into account that similar properties were obtained after injection molding of the same material. The mechanical characterization as presented in the article is aimed at highlighting the differences for samples printed with the use of heated printing bed and without it (such as for low-cost desktop printers). In contrast to impact strength, where the PLA crystallinity level is very important for results, most of the parameters obtained in static samples are very stable even for samples with different printing parameters.

Dynamic Mechanical Analysis (DMA) and Heat Deflection Temperature Changes. For most of the tested samples, the significant changes in mechanical characteristics are mainly caused by the changing content of the crystalline phase. This trend applies in particular to impact resistance. For PLA, the same dependence leads to an increase in thermal resistance parameters, such as heat deflection temperatures (HDTs) or Vicat temperatures. Previously, an inverse relationship between HDT and impact strength has been reported;\textsuperscript{48,52,53} however, this was not observed in the present study. The results showed that as the crystallinity increased, so did both the HDT\textsuperscript{54} and the impact strength, which has been previously reported for FDM-printed PLA composites.\textsuperscript{26}

Usually, a low softening point limits the range of application of PLA to 50–60 °C, which corresponds to the glass-transition region of its amorphous phase. The analysis of the DMA thermograms complements the DSC measurements in terms of changes in mechanical properties. As can be seen in Figure 13, in the glassy state, the highest value of storage modulus belongs to the injection-molded samples; similar values were reported for the printed samples after the annealing treatment. In the case of storage modulus, the initial room temperature values reflect the two dominant phenomena also observed in the previous analysis. The lowest values are observed for the samples prepared at the lowest range of printing parameters, respectively, the bed and melt temperatures. The apparent change occurs when both of the printing parameters are raised to higher values.

The importance of crystallinity becomes more evident at around 55 °C, when the majority of the tested samples reached the maximum deflection point in the HDT measurement (see Figure 14); this also applies to the injection-molded specimens. The difference in this aspect is in favor of the annealed samples.

Figure 12. Impact resistance from the notched Izod measurements for FDM-printed samples under different thermal conditions.

Figure 13. Thermograms of storage modulus (A) and tan δ (B) for samples obtained with different preparation methodologies.

Figure 14. Comparison of HDTs and crystallinity levels for injection-molded samples and FDM-printed specimens.
The highest HDT values were observed in both annealed samples. A significant increase was also observed for samples printed at the highest bed temperature (105 °C). Despite the difference in the initial value of storage modulus in both of these examples, the DMA thermograms have a very similar course, with apparently less reduction in stiffness at the relaxation stage, because of the lower content of the amorphous phase. This difference is particularly evident in the tan δ plots (Figure 13B), where for the samples printed at the highest bed temperature and the annealed samples, the additional cold crystallization peak does not occur, whereas for the rest of the samples it is clearly marked. This type of behavior has already been reported for PLA and its blends.35,55

**Structure Evaluation.** Some of the structural changes resulting from changes in crystallinity for selected samples can be easily assessed using thermal analysis. However, in the case
of tested samples, some trends of changes in mechanical properties cannot be correlated with the PLA phase morphology, particularly for samples printed with variable melt temperatures. In this case, the most important factor affecting the mechanical characteristics is the bonding strength between the individual layers of the printed material. For optimal selection of the parameters, the temperature of the polymer melt should allow partial melting of the previously applied layer. Under such conditions, diffusion is possible at the boundary of both printed layers, which in consequence not only provides better mechanical properties but also improves the surface quality of the printed model. Comparisons of samples printed at low and high nozzle temperatures reveal significant differences in the structure, which was reported previously for other FDM-printed polymers.37,51

For comparative purposes, cross sections of samples were presented both in the interior raster area of the specimen and on the edge of the sample where individual layers of filament form the so-called shell layer. In all printed samples, the outer layer of the sample is characterized by the large size of the trapezoidal holes. This indicates a rapid cooling of the material, which prevented the extruded filament from filling the free space of the model. However, the first significant differences can be observed by comparing the change in pore size within the interior of both samples. For low printing nozzle temperatures (Figure 15B), the size of the holes remained practically unchanged relative to that of the shell layer. In turn, for high printing nozzle temperatures, the pore size is significantly reduced in the raster area (Figure 15B'). Some similar trends were also reported in other studies.12,40 However, considering the changes in the density of the samples, the apparent difference in pore size is not significantly influencing the total volume of voids, which should not significantly affect the mechanical properties. The more significant structural differences are visible within the joining lines of the individual layers of materials. A visible enlargement of the pore area suggests a clear lack of diffusion between filament layers for samples printed at 190 °C (see Figure 15C,D). A clear bonding line is visible throughout the structure of the entire model; thus, the reduced mechanical properties in this case are clearly due to the poor diffusion and lack of consistency between the individual layers of the filament.

Similar trends in structural changes can also be observed in the case of variable bed temperature. In this case, the pore size difference for the shell layer and raster area is even more visible. For samples printed at 105 °C, the viscosity of the already applied filament layers remains low enough to fill the free space of the model, leading to a nearly completely solid structure in the raster area, which is not possible for the outer/shell layer because of intensive heat exchange with the environment (Figure 16). A closer view at the void area also reveals some structural changes. As was observed with low nozzle temperatures, the reduction of the bed temperature also limits the diffusion process, leading to reduced interfacial adhesion between the printed layers.

■ EXPERIMENTAL SECTION

Materials. The material used for all samples was a commercial PLA filament from polymer(True Red PolyLite PLA). Like most of the commercially available materials, this PLA was supplied in the form of a bobbin with a wound filament line, with a diameter of 2.85 mm. Because of proprietary reasons, it was not known what nucleating agents or plasticizers were added, if any.

Sample Preparation. Fused Deposition Modeling. The fused layer modeling was performed using a LulzbotTaz 6 3D printer. Except the raster angle, all of the other machine parameters were kept constant, including a print speed of 50 mm/s, a travel speed of 200 mm/s, and a 100% fill density. The print time was also kept constant at 6.5 h for each variable printing parameter. Seven impact samples and five each of tensile and flexural samples were printed at a time. Painter’s tape was laid out on the print surface for samples printed at bed temperatures of 90 and 105 °C to promote adhesion of the samples to the print surface.6

Injection Molding. Before injection molding, the filament was pelletized using a Reduction Engineering Bullet 64 pelletizer. After pelletizing, the pellets were dried for 16 h in the oven at 75 °C. Injection molding took place in a DSM 15cc micro compounder and injection molder following ASTM D3641 standards for PLA processing. The mold temperature was set at 30 °C, the barrel temperature at 180 °C, the injection pressure at 4 bar, and the hold pressure at 8 bar. Five flexural, five tensile, and seven impact samples were formed. Before testing, the samples were stored for 40 h at room temperature.

Annealing. To evaluate the effects of annealing on the mechanical properties of 3D printed models, it was decided to process only one type of prepared specimens. Before the annealing step, the samples were printed at a nozzle temperature of 210 °C and a bed temperature of 60 °C and a 45/45° raster angle and all other printing parameters were the...
same as those in the previous prints. They were then annealed in the oven for 1 h, the first set of samples at 80 °C and the second at 100 °C.

**Characterization.** Thermal Analysis (DSC, DMA, HDT). Using TA Instruments DSC Q200, the thermal properties of the samples were studied. Two tests per sample were performed to create a standard deviation. Approximately, 5 mg was cut from each sample and was encapsulated in aluminum. With a 50 mL/min flow rate, the samples were ramped at 5.00 °C/min using a heat/cool/heat method. The crystallinity of the samples was calculated using the following formula

\[
\% \text{ crystallinity} = X_c = 100 \times \frac{\Delta H_m - \Delta H_c}{\Delta H_0^0}
\]

(1)

where \( \Delta H_m \) is the measured melting enthalpy, \( \Delta H_c \) is the measured enthalpy of cold crystallization, and \( \Delta H_0^0 \) is the theoretical melting enthalpy of 100% crystalline PLA, taken from the literature to be 93.7 J/g. Dynamic thermal analysis (DMA) was performed with the use of a DMA Q800 (TA Instruments, New Castle, DE). All measurements were carried out at a constant frequency of 1 Hz and strain amplitude of 0.01%. The temperature range was 30–150 °C, whereas the heating rate was 3 °C/min. The viscoelastic properties were collected from rectangular samples (3.2 × 12.7 × 50 mm) using the dual cantilever measurement mode.

The heat deflection temperature (HDT) of the samples was acquired using TA Instruments DMA Q800 following ASTM D648. The desired stress of 0.455 MPa was applied to the samples, they were stored for 40 h after notching using a TMI 43-02 notched Izod impact tester with a 5 ft-lb hammer following ASTM D256. Before testing the samples, they were stored for 40 h after printing or injection molding. The impact testing was conducted using an MD300 densimeter (Alfa Mirage Co., Osaka, Japan) according to ASTM D792 standard method.

**Morphology, Density, and Viscosity of the Materials.** The morphology of the fractured surface of notched Izod samples was investigated by a Phenom ProX SEM microscope using a 10 kV acceleration voltage. The surface of the samples was coated with a thin layer of gold. Density measurements were conducted using an MD300 densimeter (Alfa Mirage Co., Osaka, Japan) according to ASTM D792 standard methodology. Rheological measurements were conducted using an MCR 302 rheometer (Anton Paar GmbH, Graz, Austria). The configuration used was plate–plate geometry with a gap distance of 1 mm. The strain amplitude was set at 5%, and the angular frequency range was varied from 0.01 to 500 s⁻¹. Measurements were conducted under a nitrogen atmosphere at different temperatures from 190 to 230 °C, reflecting the melt temperatures selected for the printing process.

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