Investigating the effect of cooling rate on strength of Fused Filament Fabrication parts using differential scanning calorimetry technique

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ABSTRACT

Desired mechanical properties are major area of interest within the field of Additive Manufacturing (AM) technologies. Fused Filament Fabrication (FFF) is an extrusion-based AM technique. In FFF process, the primary concern of strength is bonding between strands, and it is greatly influenced by the heat transfer during the manufacturing process. The extent of bonding not only influences the strength, but also the structural integrity of the part. To study the bonding between the extruded polymer strands of FFF process, investigation must be done to understand the influence of rate of cooling during FFF process. The present study focuses on investigation of cooling rate effects on FFF-ABS (Acrylonitrile Butadiene Styrene) parts over their tensile strength. Since glass transition temperature plays a key role in understanding the history of the thermal behavior, it is hence important to estimate its value for various extrusion temperatures. To understand this, glass transition temperature is estimated through Differential Scanning Calorimetry (DSC) experimentation technique as it records the thermal history of the polymer and hence this test is applied at different cooling rate. Additionally, to support the DSC graphs, tensile testing of FFF made parts is done on the parts manufactured at two extreme extruder temperatures namely 230° C and 250° C. Better bond formation between the strands contributes to higher strength and hence neck growth is estimated by capturing the scanning electron microscope graphs. The higher strength (as obtained for higher neck growth) is due to higher or proper cooling process. The results also show that the parts cooled at higher cooling rate have better bonding in terms of neck growth which proves a good agreement among the cooling rate, strength, and neck growth. The novelty of this work lies in polymer characterization to provide more insights in FFF layer deposition process (effect of different cooling rate on FFF process) using DSC and mechanical testing/analysis.

Key words: Additive Manufacturing; bond formation; cooling rate; Fused Filament Fabrication; neck growth

INTRODUCTION

Fused Filament Fabrication (FFF) is a solid based AM technique, earlier known as Fused Deposition Modeling (FDM), Stratasys™. General steps in any AM process is illustrated in **Figure 1**. In FFF process, a solid thermoplastic polymer filament is made to pass through the heated extruder where the polymer filament gets melted and gets deposited on a heated bed through the nozzle. Most of the thermoplastics can be used as a raw material in this process. Acrylonitrile Butadiene Styrene (ABS) is one among those popular materials. In these AM manufacturing processes, process parameters play a key role in deciding various properties, out of which the mechanical properties such as strength, surface roughness, volumetric shrinkage etc are of the most investigated properties. Researchers have conducted thorough investigations on the above said process parameters and studied their influence on mechanical properties to study the performance (Al-ahmari et al., 2021). Several attempts have been made to understand and enhance the mechanical properties (Fernandez-Vicente et al., 2016; Wang et al., 2016). The studies show that among several (many) parameters, extrusion temperature highly influence the mechanical properties. As the part orientation decides the length of layer, this parameter also plays the key role in strength because of the bonding among the strands present in a layer and among the layers. During solidification, polymer parts shrink because of uneven cooling process which is non-linear in nature. Various studies have been done to understand the thermal behavior of FFF process (Alafaghani et al., 2017; Bhalodi et al., 2019; Compton et al., 2017; Costa et al., 2015, 2017; Nidagundi et al., 2015). In FFF process, each layer is deposited with heated polymer material with the form of strands. A solid polymer filament is heated up to the semi-molten state and is pressurized to extrude out of the nozzle. As the pressure remains constant, material flows at constant rate with constant cross-sectional diameter. The process of bonding takes place between the two successively deposited strands after the deposited strands gets fully solidified. The same phenomenon repeats in inter-layer bonding as well (Gurrala & Regalla, 2014). Based on the structural integrity, it was proved that the mechanical properties of the fabricated parts prominently depend on the bonding between these successive strands and successive layers. During this process, as the number of layers in a part increase, the amount of heating and cooling cycles increases. This results in residual stresses due to increased amount of heating and cooling cycles. The changes experienced by these heating and cooling process over the past studies remain unprecedented (Jose et al., 2021; Ramos et al., 2021). Also, the ongoing literature states that the thermal study of this process is done by considering heating phenomenon only. Literature work states that the heat transfer analysis consider only heating phenomenon with a little or not much focus on the cooling phenomenon. In FFF process filament extrudes from the nozzle, cools down from its glass transition temperature to chamber temperature resulting in residual stress thereby resulting in deformation in bottom layers which is undesirable. This indicates a need to understand the various perceptions of cooling process that exist during layer deposition process. Also, researchers have not treated influence of cooling rate in much detail. To establish a better insight, it is highly essential to study, analyze and understand the cooling behavior as these factors influence the mechanical properties. The present work aims to fill gap of dependency of thermal history over mechanical strength of the part. In the current research work, the authors have attempted in studying the effect of different cooling rates on FFF-ABS made parts. Polymer characterization is used to study the complete fingerprint of material along with the thermal history. Also, through this work, the authors aim at studying the thermal behavior of FFF process and their relationship with the bonding phenomenon.

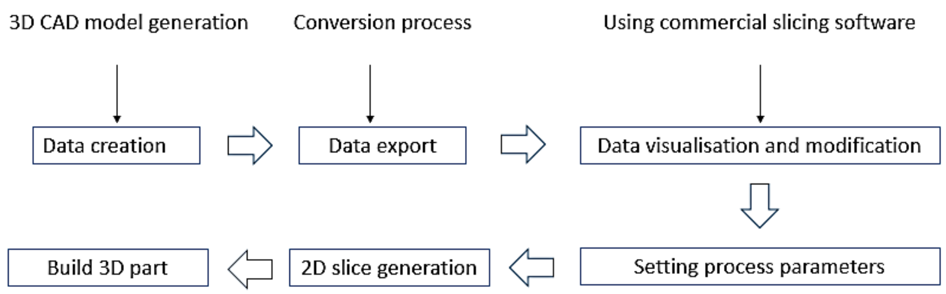


Figure 1 General steps in Additive Manufacturing process

METHODOLOGY

In the current study, the extreme temperatures are chosen based on the criteria that the parts cannot be manufactured beyond these temperature limits (upper and lower limits respectively). To understand the complete temperature profile, other machine parameters/settings have been set as constant for both samples namely A and B. From literature it is evident that for maximizing the tensile strength, one needs to consider lower build orientation (0°), lower raster orientation (0°), negative air gap and higher density (100 %). Hence, both the samples are fabricated using a single extruder Stratasys® single extruded FFF printer using the settings as mentioned in **Table 1**.

Table 1 Fused Filament Fabrication process parameters settings

FFE process parameters	Part-I	Part-II
Layer thickness (mm)	0.3	0.3
Extrusion temperature (°C)	230	250
Part orientation (°)	0	0
Part density (%)	100	100

Thermal characterization is widely used for polymer characterization (Dan-asabe, 2018). Details about DSC can be finds in literatures (Müller & Michell, 2016) In this work, DSC testing is considered to study the thermal behavior of ABS parts which is extruded at two different temperatures i.e. 230° C and 250° C as parts cannot be extruded below 230° C and above 250° C respectively. Heating-cooling-heating runs are performed to study the impact of different cooling rates on glass transition temperature. A total of four samples of 5 mg (two samples each, have been taken from a part manufactured at two different extrusion temperature of 230° C and 250° C respectively) are considered. Initially by taking heating rate as 10° C/min, sample is heated up to 250° C from the room temperature. Now cooling run is performed at four different cooling rates namely 1°C/min, 5°C/min, 10°C/min and 20°C/min independently in each of the specimen respectively. Afterwards the second heating run is performed again at 10° C/min heating rate by heating the same specimen from room temperature to 250° C. Now the cooling curves are recorded while the cooling the specimen is performed at different cooling rates (1° C/min, 5° C/min, 10° C/min and 20° C/min respectively). Once the cooling profiles are being recorded, glass transition temperatures have been extracted from the curves. The above procedure is demonstrated in **Figure 2**. To ensure same thermal history for each sample, DSC scan is performed on new sample. Also, to validate the literature stated results DSC curve is considered for 2nd heating cycle only.

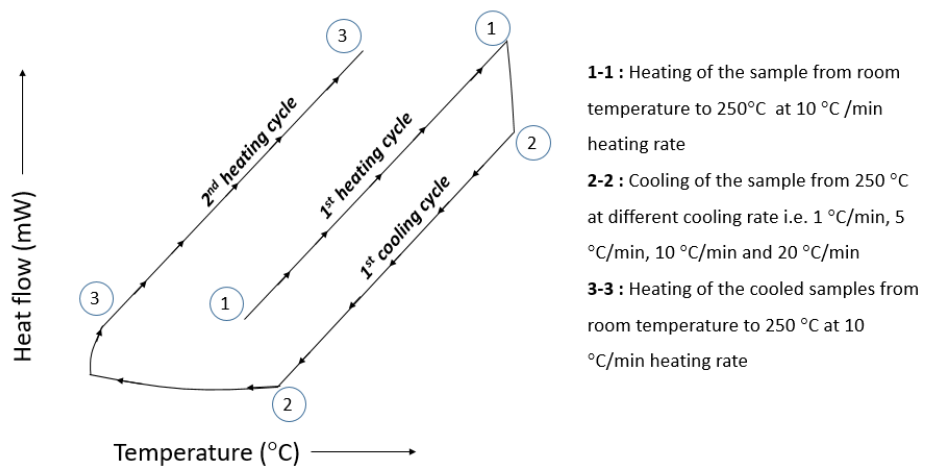


Figure 2 DSC procedure for 250° C specimen

To investigate the effect of different cooling rates on bonding, the tensile tests are performed. As already highlighted in the previous section, for the purpose of tensile testing, two samples each are fabricated at two different extrusion temperatures i.e., 230° C and 250° C and are tested as per ASTM D638-Type-I using INSTRON™ tester.

RESULTS AND DISCUSSIONS

DSC TESTING

The DSC curves of the part (at 250°C extrusion temperature) are shown in **Figure 3**. The curves A, B, C and D are the curves obtained at 1°C/min, 5°C/min, 10°C/min and 20°C/min respectively. In **Figure 3** there is a clear trend of decreasing glass transition temperature (T_g) as the cooling rate is decreased. Using the tangent method, the glass transition temperatures are estimated. **Table 2** lists down the glass transition temperature as estimated for the same parts at different cooling rates. From the **Table 2**, it can be observed that as the cooling rate is increasing there is a considerable raise in glass transition temperature (T_g) due to quenching process of amorphous polymer. Results show that amorphous quenching process occurs at higher cooling rates. Due to that quenching process, more certain arrangements of molecules are formed. The study proves that when a part is cooled at different cooling rates, the crystallization process gets noticeably affected. As shown in DSC graphs, peak is at 20°C/min cooling rate, some crystallization peaks are visible. This may be because of multiple reasons namely the polymer is able to crystalline at higher cooling rate or there are necessary nuclei for crystallization present. Also, this phenomenon (cold crystallization) occurs for finite amount of time and the same can be observed for the sample cooled at 20°C/min, that shows a broader peak (refer **Figure 3**). The results show that at different cooling rates, the position and magnitude of exotherms get changed. Sufficient cooling allows greater molecular interaction which increases the glass transition temperature (T_g).

A well-organized molecular structure increases the glass transition temperature and that is the reason that higher glass transition temperature is observed during the DSC study. In other words, samples cooled at higher cooling rates have better molecular interaction and better molecular arrangements as compared to samples cooled at lower cooling rates. So, at higher cooling rate i.e., 20°C/min, molecular chain re-organization process eventuates as the initial amorphous structure is crystallizing. During FFF deposition process, chain kinetics of ABS polymer behaves as per the cooling process. Since molecular mobility is severally restricted below the glass transition temperature the part which is extruded at higher temperature has better chain organization. Strands extruded at higher temperature has higher glass transition temperature and hence better chain reaction during layer deposition process. Also, the part made at lower extrusion temperature (230° C) has lower glass transition temperature than that of at higher extrusion temperature (250° C). When cooling from the melt, these materials can partially or does not crystallize. The most notable aspect found in the DSC curves through changes in heat flow is “cold crystallization” (*it is a process in which some small amount of material undergoes crystallization phase during heating process*). For polymers, cold crystallization appears as a non-equilibrium effect strong evidence of cooling rate influence is found where this phenomenon can be observed in the SEM graphs represented in **Figures 4a** and **4b** (*a detailed discussion on the SEM micrographs is explained in the coming sections*). Since the part in **Figure 4b** has been manufactured at 250° C, here has been a better bonding with the adjacent strands on comparison with that of the parts manufactured at 230° C.

This phenomenon of bonding between the adjacent strands is better at elevated temperatures since the glass transition temperature is higher and small crystallizes are formed.

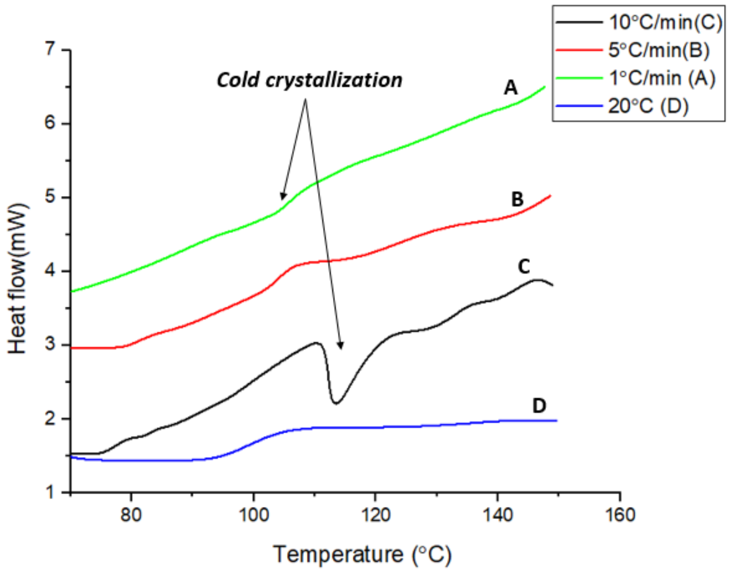


Figure 3 DSC testing curve 2nd heating cycle (for the part manufactured at 250° C extruder temperature)

Table 2 Glass transition temperature at different cooling rates (for parts A and B)

Points (on the graph)	**DSC cooling rate (in °C/min)**	**Glass transition temperature (in °C)**	
		Part-A (230° C)	**Part-B (250° C)**
A	1	94	98
B	5	96	100
C	10	99	103
D	20	102	108

TENSILE TESTING

From the previous sections it has been established higher glass transition temperature results in better chain organization and therefore better layer bonding during extrusion process, tensile tests have been performed. Performing the tensile tests and estimating the tensile strength is the best possible way to understand the bond formation within the strands as obtained during the extrusion process. To accomplish this, tensile test specimens are manufactured and tested as per ASTM-D638 standard (specifications highlighted in **Table 1**). Tensile tests are performed on INSTRON™ tensile testing machine and the results are shown **Table 3.** Also results show that higher glass transition temperature leads better strength. These results are well justified with the outcomes of DSC results that show that the parts made at higher extruder temperature shows the better bonding. The tensile test shows that the part having higher glass transition temperature has more tensile strength i.e., 45 MPa. The strength is improved by 25% at higher temperature which is quite significant.

Table 3 Tensile strength comparison for various extruder temperature

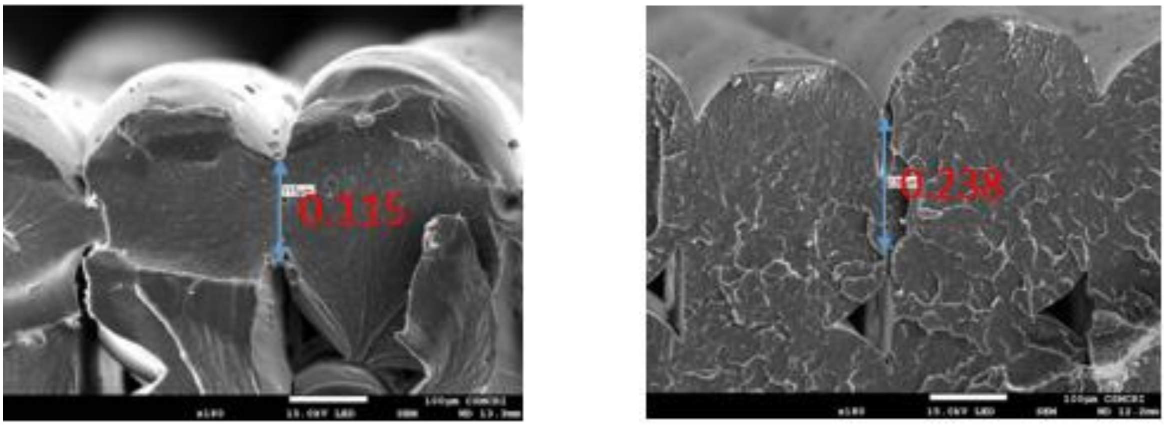
Extruder temperature (° C)	230	250	Increment of 25%
Tensile strength (MPa)	36	45	

SCANNING ELECTRON MICROSCOPE (SEM) TESTING

Bonding between the strands contributes to better structural integrity. To investigate this phenomenon, visualization between the strands needs to be clearly understood. For this a Scanning Electron Microscope (JFM 7100 F machine) graphs are used. The samples for the SEM graphs are obtained from the fractured specimens of the tensile tests (of both the specimens of A and B). **Figures 4a** and **Figure 4b** provide a detailed microscopic view of both the parts at fracture. Comparing **Figure 4a** and **Figure 4b,** it can be observed that more voids are being observed in a part extruded at 230° C (**Figure 4a**) as compared to part extruded at 250° C (**Figure 4b**). Voids are a result of the restricted movement of the polymer melt. This may be due to many reasons like improper cooling, un-availability of enough internal energy for the melt mobility etc. The results show a good agreement with the and the tensile strength values. From the previous section of the DSC study, it has been established that the part made at 250° C extrusion temperature has higher glass transition temperature. In other words the part made at 250° C extrusion temperature has well-arranged structure. It is due to the better bonding between adjacent strands and between the layers. Additionally, to quantify the extent of the bonding, neck growth has also been estimated. Neck growth quantifies the extent of bonding between the deposited strands within the layer. **Figures 4a** and 4b show the neck growth for both the parts as estimated through the inbuilt software. As a random observation, part made at 230° C has an approximate neck growth of 0.115 mm while the part made at 250° C has neck growth of 0.238 mm. **Table 4** shows that part made at 250° C have 52% higher neck growth than that of parts made at 230° C. The reason for that is the thermal behavior during the printing process. As DSC results suggest that part made at higher temperature has better layer bonding. Tensile testing also confirmed the same. A comparison of the two SEM graph results reveal that 250° C extruded part has higher neck growth and that leads to better bonding and higher strength. These results conclude that part extruded at 250° C part has higher T_g and better chain organization than that of extruded at 230° C.

Table 4 Neck growth comparison for different extruder temperature

Extruder temperature (° C)	230	250	Increment of 52%
Neck growth (mm)	0.115	0.238	



(a) (b)

Figure 4 Evolution of neck growth using SEM at (a) 230° C (b) 250° C

CONCLUSION

The study offers important insights about the influence of cooling rate on FFF made part. The most interesting finding was that during cooling process cold crystallization also takes place. In the present work, the study of effect on different cooling rates has been done using DSC testing. Tests conducted using DSC showed that parts extruded at higher temperature has higher T_g that results in better chain organization. To validate this fact, two test specimens have been manufactured at two different extrusion temperatures using FFF technique. Tensile tests have been performed on these two specimens. Tensile test results showed that part extruded at higher temperature has 25% more strength than that of the part at lower temperature. The reason for this is because the part extruded at higher temperature has better cooling process and hence leads to higher glass transition temperature. The tensile test results were supported by the scanning electron microscope graphs that showed that the bonding between strands of the part extruded at higher temperature has 52% higher neck-growth than that of the part extruded at lower temperature. Therefore, through this study it has been established that the cooling process during FFF technique is a very important parameter as it influences the structural integrity of the part. This work can therefore help in not only understanding the nature of the material but also cooling rate which can be considered as a future work. This work provides the designers and manufacturers of FFF technique an insight about how the cooling should be planned while designing the printer for better mechanical properties. The present study can be extended to study the different FFF materials and effect of different cooling rates on respective glass transition temperatures.

REFERENCES

Al-ahmari, A., Mian, S. H., & Ameen, W. 2021. Performance assessment of fused deposition modeling process. 9 (1), 200–213.

Alafaghani, A., Qattawi, A., Alrawi, B., & Guzman, A. 2017. Experimental Optimization of Fused Deposition Modelling Processing Parameters: A Design-for-Manufacturing Approach. Procedia Manufacturing, 10, 791–803.

Bhalodi, D., Zalavadiya, K., & Gurrala,. 2019. Influence of temperature on polymer parts manufactured by fused deposition modeling process. Journal of the Brazilian Society of Mechanical Sciences and Engineering, 41(3), 1–11.

Compton, B. G., Post, B. K., Duty, C. E., Love, L., & Kunc, V. 2017. Thermal analysis of additive manufacturing of large-scale thermoplastic polymer composites. Additive Manufacturing, 17, 77–86.

Costa, S. F., Duarte, F. M., & Covas, J. A. 2015**.** Thermal conditions affecting heat transfer in FDM/FFE: a contribution towards the numerical modelling of the process. Virtual and Physical Prototyping, 10(1), 35–46.

Costa, S. F., Duarte, F. M., & Covas, J. A. 2017**.** Estimation of filament temperature and adhesion development in fused deposition techniques. Journal of Materials Processing Technology, 245, 167–179.

Dan-asabe, B.2018. Thermo-mechanical characterization of banana particulate reinforced PVC composite as piping material. Journal of King Saud University - Engineering Sciences, 30(4), 296–304.

Fernandez-Vicente, M., Calle, W., Ferrandiz, S. & Conejero, A. 2016. Effect of Infill Parameters on Tensile Mechanical Behavior in Desktop 3D Printing. 3D Printing and Additive Manufacturing, 3(3), 183–192.

Gurrala, P. K., & Regalla, S. P. 2014. Multi-objective optimisation of strength and volumetric shrinkage of FDM parts. Virtual and Physical Prototyping, 9(2), 127–138.

José LuisPérez-Castilloab, EnriqueCuan-Urquizoab, ArmandoRoman-Floresc, OscarOlvera-Silvaa, VíctorRomero-Muñoza, lfonsoGómez-Espinosa, RafiqAhmad. 2021. Curved layered fused filament fabrication: An overview. Additive Manufacturing, 47,109-116.

Kashan, J. S., Jha, A., Thamir, A. D., & Al-haidary, J. T. 2018. ORIGINAL ARTICLE A kinetic analysis of the melting HA / Y-PSZ / HDPE nano bio composite for hard tissue materials. Journal of King Saud University - Engineering Sciences, 30(4), 286–295.

Müller, A. J., & Michell, R. M. 2016. Differential scanning calorimetry of polymers. Polymer Morphology: Principles, Characterization, and Processing, 72–99.

Nidagundi, V. B., Keshavamurthy, R., & Prakash, C. P. S. 2015. Studies on Parametric Optimization for Fused Deposition Modelling Process. Materials Today: Proceedings, 2(4–5), 1691–1699.