



ANTEC[®] 2021

2021 PROCEEDINGS

EXPERIMENTAL AND NUMERICAL ANALYSIS OF INDUCING CRYSTALLIZATION ON POLYMER MELT BY ALTERING FLOW AREA IN ADDITIVE MANUFACTURING

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Abstract

A novel additive manufacturing technique has been developed in the Manufacturing Science Laboratory at Lehigh University. The technique utilizes an extrusion based 3D printer, which has the ability to regulate the area of the polymer flow inside the extrusion head, thus, allowing precise control over shear rate applied to polymer melt. The controlled shear alters the melt rheology, which in turn controls the evolution of crystallinity in the printed parts. The temporal control of shear translates to spatial control of melt rheology. Thus, the localized evolution of molecular orientation and nucleation/crystallization kinetics as well as the mechanical and optical properties can be precisely controlled during the additive manufacturing process. In this research, a semi crystalline poly-lactic acid (PLA) was utilized to validate the developed technique of controlling the shear rate while printing. The confinement will induce shear on the polymer the degree of which can be controlled by the gap between the conical cavity and the conical extruder tip. The analytical modeling results indicate that this strategy can increase the induced shear rate. Preliminary experimental analysis validated an increase in crystallinity percentage up to 16%.

1. Introduction

The demand and usage of polymers have been growing since the late 1800s. Polymers can be petroleum based or can be derived from natural resources such as plants. A wide range of manufacturing processes have been used to produce polymer-based products.

Polymers can be generally divided into two types, thermoplastics and thermosets. Thermosets experience an irreversible cross linking between molecular chains when heated. On the other hand,

thermoplastics can be thermally recycled without any major effect on the material's properties. [1]

For thermoplastics, crystallinity plays a major role in improving the final product's properties. Namely, optimizing the crystallinity leads to enhancing the stiffness, strength, ultimate deformation, and temperature limitation of the final product. [2]

Crystallization occurs in two phases. The first phase is when the nucleation sites form, which triggers the subsequent formation of crystalline structure. Nucleation site formation increases at temperatures lower than the melting temperature especially when external forces are introduced. [3] The second phase is the crystalline structure growth, which is optimum between the melting temperature and the glass transition temperature. [4]

In order to control the crystallization kinetics of a thermoplastic, physical alteration of the polymer melt is required such as the application of shear rate or manipulating the thermal history during the manufacturing process. In addition, using additives is another method of controlling the crystallization kinetics of a thermoplastic. [3]

Although additive manufacturing has been around for decades, it has not lived up to its potential. Thus, a new manufacturing concept that enables additive manufacturing to optimize and/or control properties spatially throughout a product is proposed. [5]

Additive manufacturing (AM), also known as 3D printing, launched a breakthrough in the production of polymer products. This manufacturing process allowed for producing previously impossible to manufacture products. It also allowed for production customization. Nowadays AM processes allow for controlling the properties on defined locations on the

same product. One example is by using multi-material systems that allow for changing the material during the printing process. This means that for a single product the properties can be enhanced at certain locations of the same part by printing a second or even third material in these defined areas. Bandyopadhyay and Heer have investigated additive manufacturing of multi-material structures and have discussed the advantages and challenges associated with multi-material additive manufacturing. [6]

Extrusion based AM machines are the most common for polymer production. Fused Deposition Modeling (FDM), which uses polymer filaments, is commercially popular. However, extrusion screw based AM machines are also available and are more commonly used in selected industries and research facilities. The latter uses starting material in the form of pellets or powder. [7]

The current research investigation focused on extrusion screw based AM processing. A novel technique has been developed and numerically validated at Lehigh University. A previously published study focused primarily on numerical simulation of the new concept. [8] The technique allows for overall product quality optimization as well as spatial property tunability. The numerically validated hypothesis suggests that by controlling the flow area of the polymer melt, shear rate and in turn crystallization kinetics is also controlled. During the current investigation, an associated experimental study was completed to validate the effect of altering the polymer melt flow area on the final product's properties. The selected polymer for this investigation was semi crystalline poly-lactic acid (PLA), a plant based biodegradable polymer. The effect of application of shear on PLA was investigated analytically and validated experimentally. The primary focus was on the role of confinement of polymer melt near the extrusion head.

➤ Method

The proposed novel technique controls the flow area of the polymer melt in order to control the shear rate during the printing process. An extrusion screw based AM machine was modified in this study in order to allow for altering the flow area. The new modification introduced a conical cavity on the mount that connects the nozzle and the extrusion barrel. Also, a conical shaped tip that mimics that cavity is introduced to be attached to the extrusion screw. These modifications provided controllability of the polymer melt flow area. Figure 1 illustrates the modifications mentioned earlier.

In Figure 1, it is clear that in the initial state the mount had a T-shaped cavity that contained the polymer melt before being extruded through the printing nozzle. The mount height was enlarged to increase the area of affect. A conical cavity was then introduced with a corresponding conical tip added to the extrusion screw. The combination of these two members provided a controllable narrow path for the polymer melt. By controlling the flow area, the shear rate applied to the polymer melt can thus be also controlled. [9] Shear rate plays a major role in the crystalline evolution process. Thus, the concept is able to provide spatial tunability of crystalline evolution along the same product. [10]

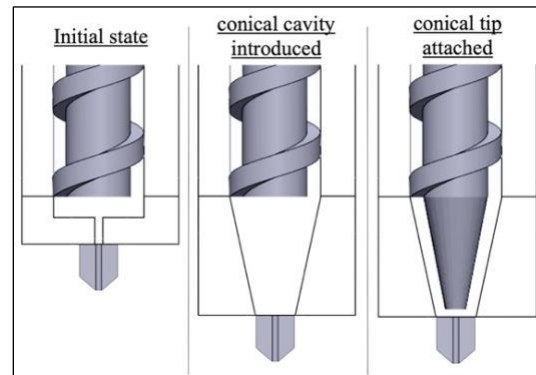


Figure 1: A schematic of the upgrades needed for the proposed concept. [8]

A broader view of the AM machine modified is shown in Figure 2. All of the modifications were done in the area between the nozzle and the extrusion nozzle. In order to control the flow area of the polymer melt, an elevation mechanism was established to allow the mount with the cavity to move upward and downward. The higher the mount is elevated the smaller the flow area, and vice versa.

In order to test the concept, two different settings were used. The first one, setting A, is when the mount is at its highest position leaving a gap to 2 mm in diameter between the wall of conical cavity and the conical tip. This setting applies maximum capable shear rate to the polymer melt. The second one, setting B, is when the mount is lowered halfway. In this position, the gap left between the conical cavity wall and the conical tip is 4 mm, and the shear rate applied to the polymer melt is lower.

Figure 3 illustrates a cross section of the AM machine showing the two different settings that were studied and analyzed numerically and experimentally. The regions that represent the polymer melt flow area are shown in black in the figure. It is clear that the flow area for setting B is much larger than the flow area for

setting A. Thus, a system is being made where the flow area of the polymer melt is controlled in order to control the shear rate applied to it leading to crystalline evolution control.

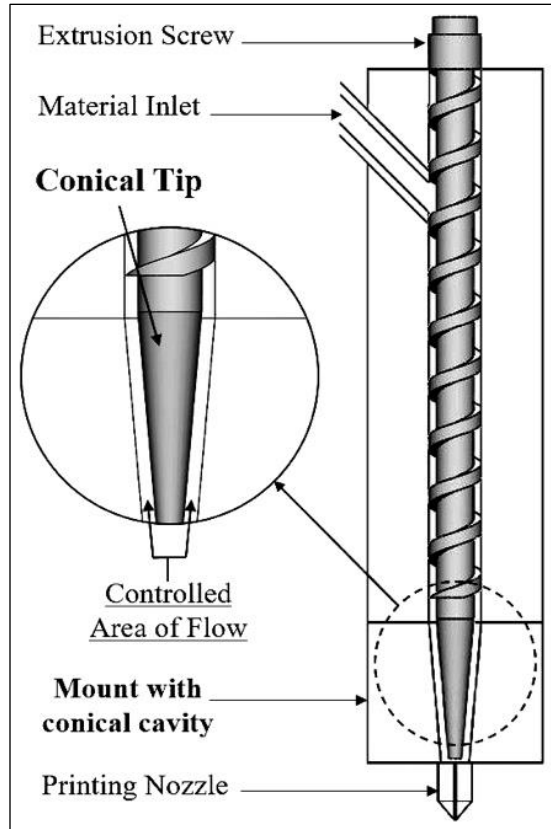


Figure 2: A schematic illustrating the AM machine used with the proposed mechanism assembled. [8]

A CAD model was made representing the path of the polymer melt flow area for both settings. The models were then imported into the simulation software. The simulation software used in this study was Ansys Fluent.

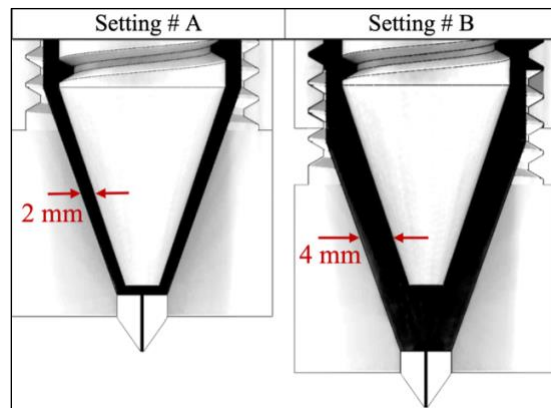


Figure 3: A schematic of the proposed mechanism showing 2 different settings. [8]

2. Materials

Poly (lactic acid) – PLA – was the polymer used in the numerical simulation and the experimental analysis; precisely, PLA grade Ingeo 2500HP. The polymer pellets were provided by NatureWorks LLC. Ingeo 2500HP is made to crystallize during the extrusion process and is affected by the conditions of the process. The melt temperature for this grade of PLA is 210 °C. [11]

➤ Shear rate

The shear rate in a flow depicts the localized degree to which material regions are sheared during its flow. [12] When a higher shear rate is applied to a polymer melt, the extruded product is more likely to contain a larger number of nucleation sites and overall crystallize faster. [10] In addition, shearing a polymer at a lower temperature influences the resultant crystal structure and molecular orientation that evolves into the final product. [13]

3. Numerical Simulations

After importing the CAD models into the simulation software, initial and boundary conditions were modified in order to match the actual values of the printing conditions. The extrusion screw rotation rate was set to 100 RPM. Since the conical tip is attached to the extrusion screw, it also rotates at this rate imposing higher shear rate. The nozzle temperature was set to 193°C, the recommended extrusion temperature for the selected material.

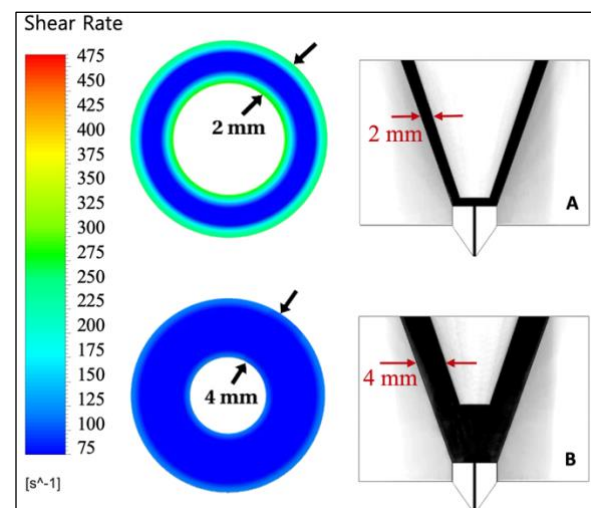


Figure 4: The simulation cross-sectional results of the proposed mechanism.

The first model represents the flow area for setting ‘A’ with a gap of 2 mm. The second model represents setting ‘B’ with a gap of 4 mm.

Figure 4 shows sample simulation results for both settings. The results are shown as horizontal cross-sectional views of the polymer melt flow area for each setting. The cross sections were taken from the same location relative to the conical tip. The views were scaled in the figure for fitting purposes.

As shown in figure 4, setting A had a maximum shear rate of 230 s^{-1} , and setting B had a maximum shear rate of 120 s^{-1} . Thus, by elevating the mount, as in setting A, the shear rate imposed to the polymer melt increases. And, by lowering the mount, as in setting B, the shear rate imposed to the polymer melt decreases. Although the two settings were tested in this experiment, the proposed technique can impose different values of shear rate by tuning the gap area. The wider the gap the lower the amount of shear rate and vice versa.

It is important to compare the amount of shear rate applied using the proposed mechanism with the amount of shear rate applied by a conventional mm printing nozzle. The passage within the printing nozzle represents the narrowest flow area in the AM machine used in this study.

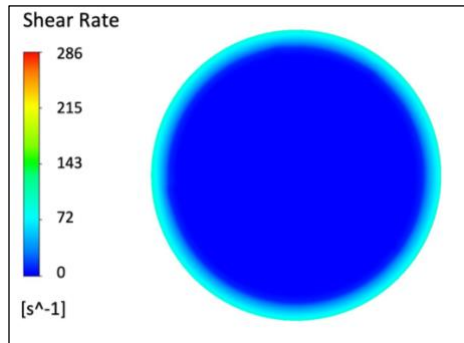


Figure 5: cross-sectional simulation results of the printing nozzle passage.

Figure 5 illustrates a horizontal cross-sectional view of the polymer melt flow area within the printing nozzle. The simulation result shows that the polymer melt experiences a maximum shear rate of 110 s^{-1} within the printing nozzle passage.

The previous results emphasize the impact of the proposed mechanism on the polymer melt. With the ability to control shear rate values, the proposed mechanism can apply higher shear rate values compared to the printing nozzle passage. This is a result of the combination of small flow area and

frictional forces caused by the rotation of the cone. The cone rotates because of its attachment to the extrusion screw.

4. Experimental Study

➤ Samples Preparation

To validate the concept experimentally, samples were printed undergoing the same conditions. The first set of samples was made using setting A, and the second sample set was made using setting B. Both sample sets were made using PLA grade Ingeo 2500HP.

➤ Differential Scanning Calorimetry (DSC)

After obtaining the samples, DSC characterization was performed using TA Instruments Q2000. One heating scan was performed for each sample at a temperature increase of $10 \text{ }^{\circ}\text{C} / \text{min}$. The degree of crystallinity was calculated using Equation (1). [14]

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^{\circ}} * 100 \quad (1)$$

where:

X_c = the degree of crystallinity (%)

ΔH_m = melting enthalpy (J)

ΔH_c = enthalpy of crystallization (J)

ΔH_m° = ΔH_m of 100% crystalline PLA = 93 (J/g)

5. Results and Discussion

The simulation results clearly show that altering the flow area of the polymer melt affects the shear rate applied to the material. Now, DSC characterization was used to analyze the samples obtained using the two previously discussed settings. The DSC results helped to identify the degree of crystallinity for each sample class.

Figure 6 combines the results obtained from a typical DSC characterization for both samples. The difference between the samples is noticeable. An increase in the melting temperature, the cold crystallization temperature, and the glass transition temperature is seen for setting A sample that was prepared under higher shear rate.

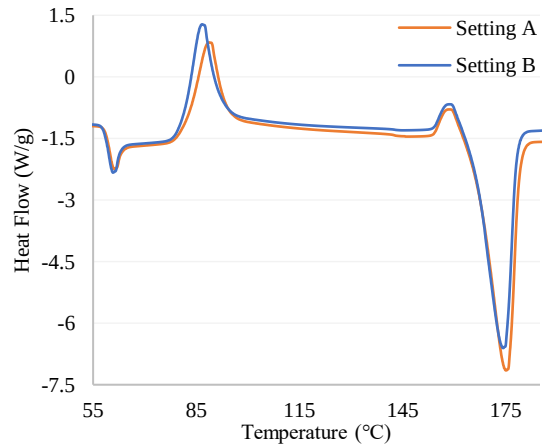


Figure 6: DSC results of samples made using different settings of the proposed mechanism.

To calculate the degree of crystallinity of the samples, equation (1) was used. The crystallinity of setting A samples was 42.89%, and the crystallinity of setting B samples was 36.93%. Thus, the setting that applied higher shear rate values to the polymer melt produced a sample with higher crystallinity.

Table 1 lists the thermal properties obtained from the DSC characterizations along with the degree of crystallinity for both samples.

Table 1: DSC results of samples that were prepared by the proposed mechanism.

Sample	T_c	T_g	T_m	X_c
Setting A	61.1 °C	88.8 °C	175.1 °C	42.89 %
Setting B	60.6 °C	86.7 °C	174.3 °C	36.93 %

As seen in table 1, all the thermal properties from setting A sample increased along with the crystallinity. The level of crystallinity increase observed between setting B samples – low shear rate – and setting A samples – high shear rate – was 16.13%.

Thus, the proposed mechanism was validated experimentally and numerically. The concept allows for changing the polymer melt flow area which results in applying different and controlled shear rate values. Shear rate plays a major role in the evolution of crystalline regions throughout printed polymer products. Developing a mechanism that allows for spatial controllability over this important parameter also enables control over crystalline evolution in the same polymeric product.

Conclusion

Customization and spatial property tuning are major advantages that additive manufacturing can

bring when compared to other manufacturing processes. Improving these two attributes can help AM technologies reach their full potential. In this paper, a novel mechanism that enhances the quality of printed parts was proposed and validated numerically and experimentally. The novel concept provides a unique technique to change the polymer melt flow area in order to control the shear rate application. As a result, crystallization is induced via shear rate modulation and as a result the spatial control of crystalline evolution is achieved.

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