The impact of the "4d-Rheoprinting" additive manufacturing technique on molecular orientation and thermal properties of polymeric parts

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Abstract

This paper discusses a novel additive manufacturing technique that was developed in order to 3D print polymeric parts with tunable properties. This technique, known as 4D-Rheoprinting, can be applied to a number of common additive manufacturing processes including any extrusion or fused deposition based system. The applied processing shear rate can be tuned precisely within each printing road or strand to proactively control the resulting localized molecular orientation and/or crystallinity level in the final product. Molecular orientation and crystallinity in turn have enormous impacts on mechanical, thermal and biodegradation properties of polymeric parts. Since additive manufacturing parts are built using layers from the ground up, we can build one product with different core and surface properties by controlling molecular orientation of each strand which significantly broadens the range of potential 3D printing applications. The current alternative approaches to customize 3D printed parts are to optimize infill, add different material and perform post processing steps such as annealing or treating with chemicals, our technique of tuning shear rate to affect molecular orientation and crystallinity could be combined with any of the previous approaches for maximum performance in wide range of applications. In this investigation a polymer part is 3D printed using the RheoPrinting technique under different shear rate conditions. DSC and WAXD are preformed and the results of the samples printed using this technique are compared to the samples that were printed using conventional extrusion based 3D printers. The experimental results show that higher shear rate can induce crystallization kinetics which results in higher crystallinity and therefore improve overall performance.

Keywords: Additive manufacturing, 3D printing, Crystallinity, Shear rate, PLA.

1. Introduction:

Additive manufacturing (AM) is revolutionizing the way in which products for a variety of applications are designed and manufactured. For polymer extrusion based additive manufacturing, we have expanded on this concept by developing a novel additive manufacturing technique that is called "4-D RheoPrinting" which enables precise material and physical property control within each deposited polymer strand of the built up structure. This technique adds tunable control of melt rheology which plays a significant role in final polymeric products mechanical, thermal and biodegradation properties. Shear rate, melt temperature and stage temperature are precisely control in the printing device to optimize the molecular orientation and crystallinity that evolve during the printing process.

It is known that the crystallization of semi crystalline polymers depends strongly on the thermal processing conditions. In 3D printing, melt temperature and stage temperature can strongly effect the overall crystallinity of final products. Printing on a heated bed will not just help parts to stick to the stage but it will increase the overall crystallinity. The longer it takes to print a part on a heated bed the more crystallinity that part will have. Theoretically, the heated bed should be set at the crystallization temperature Tc in order to allow the maximum formation of nuclei and accelerate growth of spherulites [1]. The rate of crystallization drops dramatically below the glass transition temperature as the molecular motion becomes so sluggish.

Previous studies performed on different thermoplastic materials have shown that imposing shear rate can orient the macromolecules chains which enhances the crystallization kinetics and crystal structure of semi crystalline polymers [2–5] thus, polymeric products properties such as mechanical, physical, and biodegradation properties will be influenced [6]. High shear rate has shown to influence crystallizations by enhancing the nucleation and the growth rate while very low shear rate has shown no effect on kinetics [4]. High shear rate in short time can affect the degree of crystal orientation more than lower shear rate at a longer time [7].

Method

The RheoPrinting concept is aimed at optimizing plastic material properties by controlling the temperature and shear rate history that the polymer melt experiences during the printing process. The nozzle of the RheoPrinter can rotate at different angular velocities (RPM) to induce varying shear rates as shown in Figure 1. As a result, the formation and relaxation of the dynamically oriented chains can be tuned via precise shear and temperature control of material passing through the device.

Axial and circumferential molecular orientation will initially be induced by the screw which mixes the material and pushes it down for extrusion. Additionally, the rotating nozzle induces stretching such as the one founded by Cao[8] to affect molecular orientation in the circumferential direction.

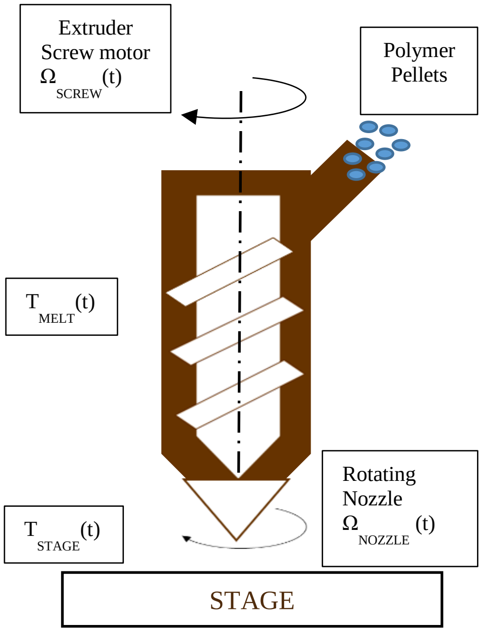

Figure 1: Diagram of RheoPrinter Concept

The aim of this research was to investigate the influence of various shear and thermal conditions of 3D printing on the crystallinity and crystal structure of poly (lactic acid). The crystallinity of PLA was calculated by the Differential Scanning Calorimetry (DSC) and Wide Angle X-ray Diffraction (WAXD).

2. Experimental

Material

The material that was used in this experiment is Ingeo 2500HP supplied by NatureWorks LLC. This material was designed for extrusions applications and it was also designed to crystallize during processing, and the amount of crystallinity depends on the processing conditions [9].

Sample preparation

The material in form of pellets was dried to prevent viscosity degradation. Then, samples were prepared under the following conditions shown on table 1.

Table 1: Processing conditions of the prepared samples

Sample #	Nozzle Diameter	Screw (RPM)	Nozzle (RPM)	$T_{Extruder}$ (°C)	T_{Nozzle} (°C)	T_{Bed} (°C)
1	0.4	50	0	210	190	70
2	0.4	50	100	210	190	70

The samples were printed in the shape of (0.8in ×0.5in and a thinness of 0.025in) to be able to fit it in the WAXD specimen holder as shown in Figure 2.

Figure 2: Printed Sample

WAXD test was performed first on the specimens. Then, DSC samples were taken from the core of the specimens to prevent any differences in the results due to the sample location, since core samples usually grow different crystal structures compared to the skin samples as a result of an uneven cooling from the skin to the core regardless of the process weather it was injection molding or 3D printing [10].

Wide Angle X-Ray Diffraction (WAXD)

WAXD experiments were performed using a Rigaku MiniFlexTM II machine. Samples were scanned at a scanning voltage of 30 kV and speed of 1°/min (2θ); using a tube current of 15 mA and sampling power of 0.02 W, over a Bragg angle range of $10° < 2\theta < 30°$.

- **Differential Scanning Calorimetry (DSC)**

DSC was performed using a TA Instruments Q2000 DSC. Only the first heating scan, at 10 °C /min, was collected to obtain the influence of the printing process on the material. The degree of crystallinity (X_C) was calculated using Equation (1) [11].

$$Xc = \frac{\Delta \mathrm{Hm} - \Delta \mathrm{Hc}}{\Delta Hm^{\circ}} \times 100 \text{ …….(1)}$$

Where ΔHm is the melting enthalpy, ΔHc is the enthalpy of crystallization, and ΔHm° is the melting enthalpy of 100% crystalline PLA which is (93 J/g).

3. Results and Discussion

In this study, we are investigating the effect of two factors bed temperature and shear rate on the overall crystallinity of 3D printed PLA samples. It is known that semi crystalline polymers crystallize at a temperature called the crystallization temperature Tc which is a temperature between the glass transition temperature Tg and the melting temperature Tm.

In the first experiment, the bed temperature was set at the crystallization temperature which is 100 °C for PLA in order to achieve the highest crystallinity. Dog bones were printed at this temperature and it is shown in Figure 3.

Figure 3: Dog bone printed at a bed temperature of 100 °C

As shown in Figure 3, the 3D printed dog bone got wrapped due to the higher bed temperature. The heated bed causes the bottom part of the print to be exposed to higher temperature more than the top since polymers are poor conductors, and therefore the bottom will end up with higher crystallinity. The crystalline structure have more ordered molecules than the amorphous structure [12] and because of these properties semi crystalline parts will shrink or expand depending on the process if it is annealing or cooling. In the case of additive manufacturing of PLA, when using heated bed at a temperature closer to the crystallization temperature, usually parts will not stick to the bed due to the shrinkage. We found that the best bed temperature to print for this particular grade of PLA is between 50°C and 70°C to help the parts to stick to the bed or the stage.

As mentioned in the sample preparation section, two samples were prepared at a bed temperature of 70 °C with varying shear rates. Sample 1 was printed at lower shear (without nozzle rotation) while higher shear rate was introduced in sample 2 by rotating the nozzle at 100 RPM. Then, WAXD and DSC were performed on the samples and the results are shown in figures 4 and 5.

Figure 4 shows the WAXD profiles for two samples that were 3D printed under different shear conditions. The most intense peaks are observed at 2θ = 16.5° which can be attributed to the (110) and/or (200) planes. It is clear that higher shear rate that was introduced in sample 2 caused the peak to be sharper compared to sample 1 which was 3D printed at lower shear rate. These results are consistent with another study which investigated non-isothermal crystallization of PLLA under steady shear and quiescent conditions, where higher shear rate causes an improvement of peak intensity [13]. The other strong reflections are of the (203) and/or (113) planes. Also, the reflection at (010) appear to be weaker with nozzle rotation.

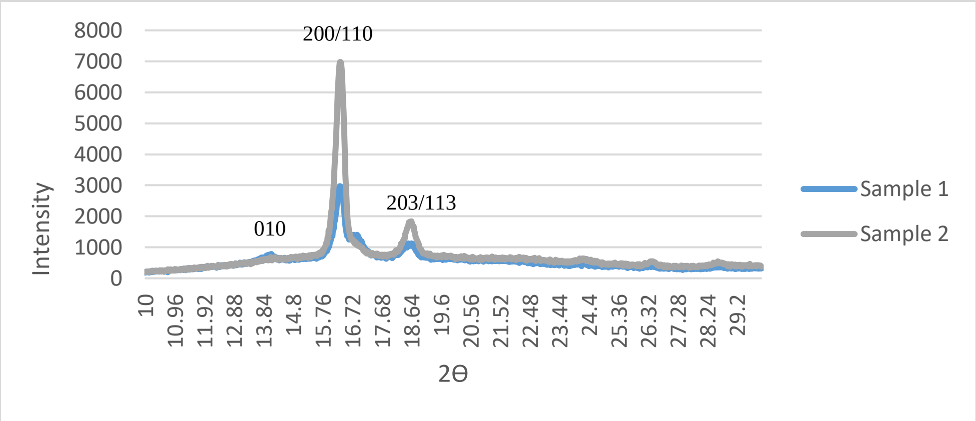

Figure 4: WAXD of samples 1 and 2. (Sample1) Nozzle not rotating, (Sample2) Nozzle rotating at 100 RPM

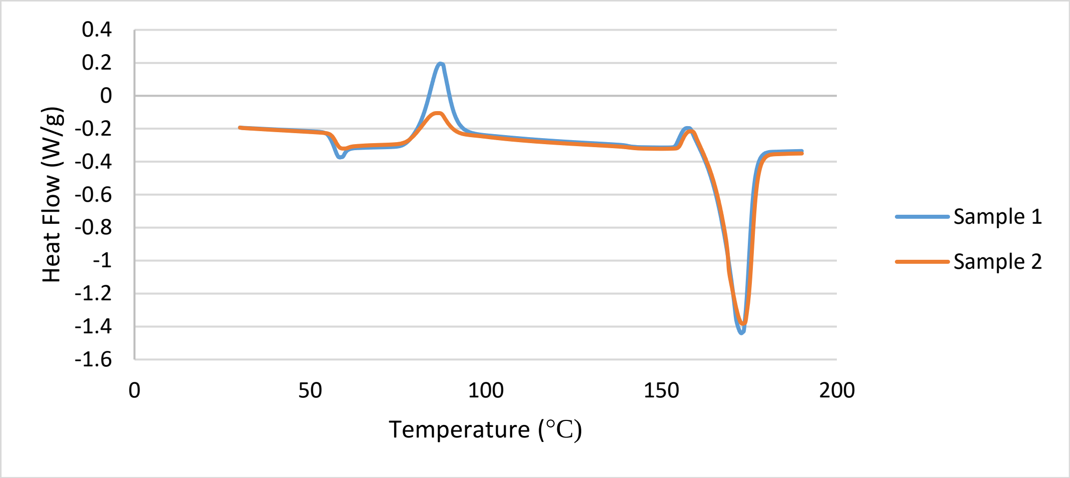

Figure 5: DSC heating curve of samples 1 and 2. (Sample1) Nozzle not rotating, (Sample2) Nozzle rotating at 100 RPM

The thermal properties of the samples were determined using differential scanning calorimetry (DSC) in Figure 5. DSC can show glass transition temperature (Tg), cold crystallization temperature (Tc), and melting temperature (Tm). By observing the two curves shown in Figure 5, the obvious difference is on the cold crystallization peak. The exothermic cold crystallization peak was lower when the nozzle rotation (NR) was applied as in sample 2. The overall crystallinity of sample 1 was 40% which was printed without NR, while sample 2 that was printed with NR achieved crystallinity of 52%. Another study which investigated the influence of shear rate on crystal structure and morphology has shown that shear can accelerate polymer crystallization kinetics by inducing the nucleation process and forming a large number of spherulites in a short time [3].

4. Conclusion

The novel technology introduced in the 4D RheoPrinting concept creates a unique enhancement that adds control of melt rheology, printed part molecular orientation and polymer crystallization kinetics throughout the printing process. Higher Crystallinity was achieved by introducing higher shear rate which induces the formation of new nuclei and accelerate the crystallization process. Therefore, this technology would enable tunable mechanical, thermal and biodegradation properties and can build customized parts to meet specific applications and provide new functionalities. This widens the use of 3D printed product for optimized performance in niche applications that require anisotropic and specific orientation of biodegradation, part strength, and barrier properties.

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