

THE INFLUENCE OF DIFFERENT CONCENTRATIONS OF OROTIC ACID ON THE POLY- LACTIC ACID CRYSTALLINITY DEVELOPMENT DURING VIBRATION-ASSISTED INJECTION MOLDING

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ABSTRACT

This research investigated the effect of the addition of different concentrations of orotic acid (OA) on the crystallization kinetics of Poly-lactic acid (PLA) in non-quiescent conditions. DSC technique was utilized to capture the crystallinity, melting point, and other thermal parameters of PLA-OA blends. The influence of adding OA into PLA under non-quiescent conditions was investigated by using conventional injection molding (CIM) and vibration-assisted injection molding (VAIM). Two concentrations of orotic acid, 0.3 wt% and 0.7wt% were mixed with neat PLA and then molded at two different mold temperatures as following 80°C and 90°C. It was observed that the VIAM reduced overall cycle time while maintaining the degree of crystallinity. At 90°C mold temperature, cooling time was reduced to 50% for both blends compared to samples molded at the 80°C mold temperature. Orotic acid showed to be an effective nucleating agent for the tested PLA grade. A small amount (0.3 wt%) of Orotic acid was sufficient to achieve 61% of crystallinity in conventional injection molding at 80°C mold temperature for 100 seconds of cooling time. Also, the blend of PLA-0.3OA at 90°C mold temperature, able to achieve 50% of crystallinity during VAIM within only 45 seconds of cooling time.

Keywords: Orotic acid (OA), Poly-lactic acid (PLA), injection molding, Vibration-assisted injection molding

1 INTRODUCTION

1.1 Injection Molding

Plastic manufacturing processes have advanced, including the most widely used, injection molding technology [1]. Injection molding is a manufacturing process that consists of four major stages: injection, packing, cooling, and ejection [2]. Polymer pellets are put into the heated barrel from the hopper or other feeding methods during the injection phase. After the polymer material has melted in the barrel, the injection screw pushes it into the mold cavity via the injection nozzle. In the

second phase, the polymer material is packed under high pressure for a set period to compensate for volumetric shrinkage and provide dimensional stability until the gate of the runner channel solidifies. At the same time, the temperature of the polymer composite in the mold cavity decreases. Before fabrication, a specific mold temperature and cooling time are set to ensure product solidification. In the final stage, the finished product is released from the mold cavity. The packing and cooling phases are thought to be the most influential for crystallinity formation during the four stages.

1.2 Vibration Assisted Injection Molding

Subjecting the polymer melt to dynamic shear stresses during molding is an effective way of improving crystallinity in injection molded products. Vibration-assisted injection molding (VAIM) is a dynamic melt technique in which the injection screw is subjected to a controlled oscillatory movement during the injection molding process. An external system may accurately control the frequency, amplitude, and duration of the vibration as the melt is injected and packed into the mold. Figure 1 depicts a schematic of this system.

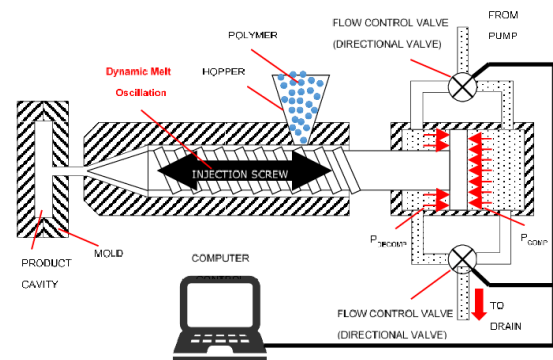


Figure 1. Schematic of the vibration-assisted injection molding setup

1.3 Crystallization Kinetics

The crystallinity of semi-crystalline polymers is a key factor in their performance and properties. The degree of crystallinity, crystalline structures, and crystal phases all influence mechanical properties, thermal/electrical conductivity, and degradation behaviors [3]. An increase in crystallinity can result in higher tensile strength and a slower rate of degradation [4]. The process of generating crystals is known as crystallization. Any system, from a thermodynamic standpoint, seeks to reduce its energy. Because polymer crystals are ordered during crystallization, entropy and enthalpy drop, which may be explained by Gibbs free energy, as indicated in equation (1)[5]. Crystallization becomes useful when the change in enthalpy (H) is larger than the change in entropy (S), resulting in a lower Gibbs free energy value (G).

$$\Delta G = \Delta H - T \cdot \Delta S \quad (1)$$

Polymer crystallization occurs in two stages: The first stage is the establishment of nucleation sites, which serves as the starting point for crystal formation. The development of individual crystalline domains is the second phase. The growth rate is the rate at which crystals develop from nucleation sites [6-8]. Controlling the two components that govern crystallization kinetics, nucleation site generation, and growth rate, allows one to influence the total crystallinity of polymers and manage their crystallization kinetics.

When transforming semi-crystalline material into a final product, the injection molding technique needs particular caution. The cooling cycle should be controlled at or near the material's crystallization temperature (T_c). Cooling time should also be precisely handled following material properties, end product crystallinity with complete solidification, and acceptable dimensional stability. Nucleation and development of crystalline structures are both thermodynamic processes with time-temperature dependence. To achieve high crystallinity in the injection process, the cycle time must be extended beyond the norm[9]. Modifying the formulation of the material by adding nucleating agents is an effective way of enhancing crystallinity [10]. Moreover, increasing the shear rate during the injection cycle influences the crystallinity development of numerous polymeric materials [11,12].

2 EXPERIMENTAL INVESTIGATION

2.1 Material Selection

Poly-lactic acid (PLA) is a thermoplastic polyester generated from renewable sources that might replace some fossil-based plastics and is suitable for the injection molding process. The food packaging industry, where polymers are utilized and frequently disposed of in non-renewable ways, is where PLA is having the most impact.

PLA has become an adequate eco-friendly option for petroleum-based polymers to boost the sustainability of products and processes, from water bottles to shrink wrap and many new uses. However, it has drawbacks that limit its uses. As a result, additives are commonly employed to improve PLA's chemical and mechanical qualities, as well as its versatility and biodegradability, making it suitable for a wide range of applications. Nucleating agents help semi-crystalline materials crystallize by forming several nucleating sites that shape and extend the spherulites.

2.2 Sample Preparation

This study utilized 2500 HP PLA provided by NatureWorks. Initially, the material had the form of pellets. The pellets were dried at 40°C for 8 hours, as directed by the supplier, to reduce the amount of moisture. In addition, to optimize the crystallization kinetics, 97 percent anhydrous orotic acid (OA) from Alfa Aesar was utilized as a nucleating agent for PLA. The dried neat PLA was mixed with two different OA concentrations. A mixture of 0.7 and 0.3 percent orotic acid was extruded with a Brabender single screw extruder at 190°C nozzle temperature. The treated filaments have a diameter of 1 mm. It was then cut into 2 mm sections for further investigation.

2.3 Crystallization Investigation Under Quiescent Conditions

The effect of orotic acid on the crystallization behavior of PLA was examined using TA Instruments Q2000 Differential Scanning Calorimetry (DSC) equipment. DSC experiments including isothermal heating at various temperatures for extended periods used samples weighing 6 to 10 mg of PLA-OA blend filaments. The isothermal protocol utilized in all of the tests was the same and included the following measures.

Cycle 1: Samples were heated from 25°C to 220°C at a rate of 10°C/min with 3 minutes of isotherm at 220°C to ensure complete melting and remove thermal history.

Cycle 2: Rapid cooling to isotherm temperatures at 85°C and 100 °C.

Cycle 3: Samples are kept at these temperatures for 30 minutes to allow crystals to grow.

Cycle 4: The samples were heated from isotherm temperature to 220°C. The melting behavior was used to calculate the degree of crystallinity attained from the isotherm cycle.

2.4 Test procedure of crystallization through CIM and VAIM

A Nissei PS40E5A injection molding machine was used in this study. Different processing techniques were used to create dog-bone specimens that fulfilled the ASTM D638-01 standard. The temperature of the material in the injection unit was set at four points along the screw: the

nozzle, the front, the middle, and the back parts of the screw were kept at 215° C, 205° C, 195° C, and 175° C, respectively. In all cases, the total pressure was set at 64 and 36 MPa for the injection and packing periods, respectively. Each sample received a 15-second injection and packing time. The cycle time was the total of the cooling time and all of the preceding processes. Two mold temperatures were tested for both concentrations; cooling time reflects the shortest possible time to obtain a high-quality product; any shorter cooling time would result in defective parts due to the parts not having enough time to solidify. Tables 1 and 2 indicate the mold temperatures, type of injection molding, and cooling time that were studied.

Mold Temperature (°C)	Injection Molding	Cooling Time (s)
80	CIM	100
	VAIM	90
90	CIM	50
	VAIM	45

Table 1. Processing Parameter for PLA-0.3%OA

Mold Temperature (°C)	Injection Molding	Cooling Time (s)
80	CIM	90
	VAIM	80
90	CIM	50
	VAIM	40

Table 2. Processing Parameter for PLA-0.7%OA

A thin slice of the PLA dog-bone specimen was collected from the center; each sample weighs around 6-10 mg and contains the surface layers, intermediate layers, and core of the PLA dog-bone specimen. Only the first heating scan at 10°C/minute from 25°C to 220°C was collected to investigate the effect of molding parameters on the characteristics of the samples. The degree of crystallinity (X_C) was calculated using Equation (2).

$$X_C = \frac{\Delta H_m - \Delta H_c}{\Delta H_M} \times 100 \quad (2)$$

ΔH_m is the experimental melting enthalpy [J/g], ΔH_c is the experimental cold crystallization enthalpy [J/g], and ΔH_M is 93 J/g for a PLA.

3 RESULTS AND DISCUSSION

3.1 Crystallinity under quiescent conditions (Isothermal Crystallization)

Figure 2 shows the procedure of the isotherm DSC test at 100°C.

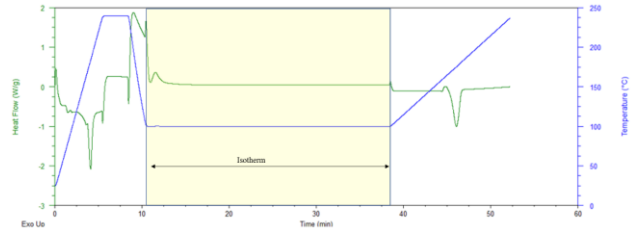


Figure 2. DSC isotherm test procedure.

During the isotherm cycle, the heat flow data were collected and normalized to sample weight. The heat flow per unit mass data was then treated and fitted into a modified Avrami Equation to replace the unreliable data during the beginning of the isotherm cycle. The treated data were integrated to obtain the total enthalpy during crystallization. The integrated values were then normalized to the degree of crystallinity calculated from the cycle [13].

A comparison of the kinetics of crystallization at two different temperatures of the PLA-0.3OA blend is presented in Figure 3. At 100°C, the initial crystallization rate was faster and the incubation time is significantly shorter as compared to samples tested at 85°C. However, after 25 minutes the same degree of crystallinity was observed in both samples.

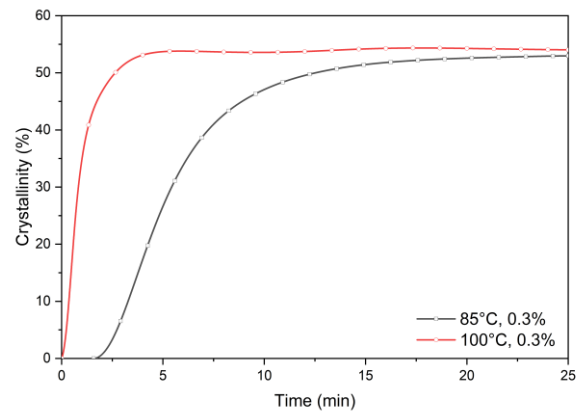


Figure 3. The crystallinity curve of the PLA-0.3OA blend.

Figure 4 shows a comparison of the kinetics of crystallization of the PLA-0.7OA blend at two different temperatures. The same trend was observed as compared to PLA-0.3OA samples on initial crystallization rate and incubation time. Furthermore, at 100°C samples reach the maximum crystallinity of ~65% within 5 minutes whereas it

required 20 minutes to reach the maximum crystallinity of ~60% for 85°C samples. Previous research showed that neat PLA 2500HP required >40 minutes to reach 50% crystallinity [13,14]. These results indicated that 0.3% and 0.7% orotic acid is sufficient in promoting crystallization kinetics under quiescent conditions.

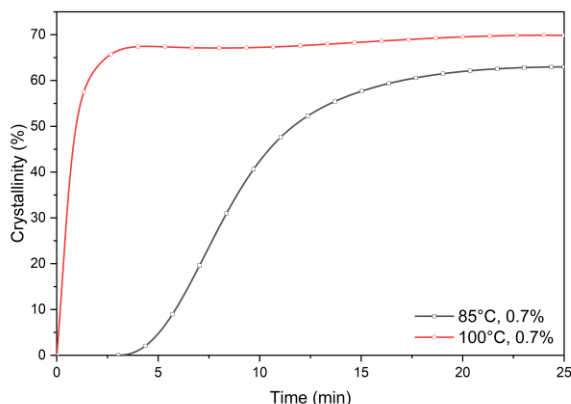


Figure 4. The crystallinity curve of the PLA-0.7OA blend.

Overall, the results for both concentrations showed significant development in the crystallization kinetics by increasing the crystallinity and reducing the incubation time compared to neat PLA, the crystallinity of neat PLA under quiescent conditions was previously investigated at the Manufacturing Science Laboratory at Lehigh University [12-15].

3.2 Crystallinity after injection molding (Non-isothermal crystallization)

Table 3 shows the crystallinity obtained from the first heating cycle of the DSC curve for the CIM and VAIM samples molded by using the PLA-0.3OA at mold temperatures of 80°C and 90°C. Molded samples using PLA-0.3OA at 80°C achieved 61% crystallinity with CIM in 100 seconds of cooling time and achieved 58% crystallinity utilizing VAIM with 10 seconds less cooling time. At 90°C, samples achieved 50% crystallinity with CIM in 50 seconds of cooling time and achieved 49% crystallinity utilizing VAIM with 5 seconds less cooling time.

Mold Temperature (°C)	Type	Cooling Time (s)	Crystallinity (%)
80	CIM	100	61
	VAIM	90	58
90	CIM	50	50
	VAIM	45	49

Table 3. Molded samples results for PLA-0.3% OA

Table 4 shows the crystallinity obtained from the first heating cycle of the DSC curve for the CIM and VAIM samples molded by using the PLA-0.7OA at mold temperatures of 80°C and 90°C. PLA with a small amount ~ 0.7wt.% of OA molded at 80°C accomplished 51% crystallinity with CIM in 90 seconds of cooling time and achieved higher to this crystallinity 53% by VAIM with 10 seconds less cooling time. At 90°C, samples accomplished 46% crystallinity with CIM in 50 seconds of cooling time and achieved higher to this crystallinity 58% by VAIM with 10 seconds less cooling time.

Mold Temperature (°C)	Type	Cooling Time (s)	Crystallinity (%)
80	CIM	90	51
	VAIM	80	53
90	CIM	50	46
	VAIM	40	58

Table 4. Molded samples results for PLA-0.7% OA

Overall, VAIM samples show higher crystallinity than samples molded utilizing CIM for the PLA-0.7OA blend with a shorter cycle time. On the other hand, the PLA-0.3OA blend of both samples fabricated with VAIM and CIM shows almost the same crystallinity but with a shorter cooling time when VAIM was utilized.

4 CONCLUSIONS

In this research, the effect of adding OA on the crystallinity development of PLA was investigated under quiescent conditions and on the injection molding samples using CIM and VAIM techniques. The conclusions are as follows:

Under quiescent conditions, both blends PLA-0.3OA and PLA-0.7OA showed increased initial crystallization rate and reduced incubation time for 100°C tests as compared to 85°C.

The maximum crystallinity increased from 55% to 63% as orotic concentration increased from 0.3% to 0.7% during 100°C isotherm DSC tests. At 85°C, PLA-0.3OA and PLA-0.7OA samples showed similar crystallinity due to a slow initial crystallization rate and lack of molecular movements.

Vibration-assisted injection molding is capable of reducing the cycle time significantly by reducing the required cooling time by 10 seconds for both concentrations of PLA-OA blend. The degree of crystallinity is maintained using the VAIM technique with reduced cycle time at both 80°C and 90°C mold temperatures.

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