Research Article

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Analysis of the rheological property and crystallization behavior of polylactic acid (Ingeo™ Biopolymer 4032D) at different process temperatures

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Abstract: The aim of this study was to determine the rheological property and crystallization behavior of polylactic acid (PLA) with improved heat resistance (Ingeo™ Biopolymer 4032D) through investigation of the melt viscosity and crystallization kinetics of PLA at different process temperatures. The viscosity was measured using a rotational rheometer under conditions of shear rates of 0.01, 0.1, and 1/s. The obtained rheological data show that the viscosity tended to decrease slightly as the shear rate increases and decrease sharply as the temperature increases from 180°C to 210°C. To investigate the effect of the process temperature on the crystallization kinetics and final crystallinity of PLA, thermal analysis using isothermal differential scanning calorimetry (DSC) were also performed. The Avrami equation was successfully applied for the isothermal crystallization kinetics model. From crystallization temperature of 85°C to 120°C, we found that the Ingeo™ Biopolymer 4032D PLA had the fastest crystallization rate ($t_{1/2}$: 26.0 min) and the largest crystallinity (47.4%) at 100°C.

Keywords: PLA, rheology, DSC, crystallization kinetics, crystallinity

1 Introduction

Plastic materials are used in various industrial fields due to numerous advantages such as easy molding by heat and low price. However, most plastic materials are made from fossil fuels, non-renewable resource which are not easily decomposed. Consequently, they cause environmental pollution such as soil deterioration due to the various accumulated wastes and air pollution due to the environmental hormones and dioxin generated during incineration or landfill. To solve this problem, research on biodegradable polymer that can naturally decompose in a short time under specific conditions is essential (1–4). As demands for biodegradable materials increase due to environmental protection issues, the development of products using biodegradable plastic is also actively being conducted. Among the various biodegradable materials, the widely used polylactic acid (PLA) is an aliphatic polyester with a linear structure and is a biodegradable thermoplastic polymer synthesized using monomers obtained from corn, potato starch, etc. (5,6). When discarded, PLA is decomposed into carbon dioxide and water by the action of microorganisms in the soil. PLA not only has a high strength and good processability compared with other biodegradable polymers, but it also has various advantages such as transparency and biocompatibility accounting for most of the global biodegradable polymer production (7,8). Through these advantages, PLA is used for industrial applications instead of the conventional petrochemical base polymer or as a biomaterial for numerous applications in medicine (9,10). On the other hand, PLA has different mechanical properties depending on the polymerization environment. Therefore, studies are being conducted recently to improve the mechanical properties by finding the optimal process condition under various situations (10,11).

PLA can be synthesized in two ways: the first is direct condensation of lactic acid and the second is ring-opening

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polymerization of lactide using a catalyst (12,13). The PLA product was processed with PLA in the form of pellets or powders that have been polymerized in advance for convenience. Since the PLA in pellet or powder form has a high melting point and viscosity when melted, for successful molding, high process temperature and pressure are needed (14,15). Extrusion molding using an extruder, injection molding using a screw, and compression molding using a hot press are the general methods of processing the PLA. In such a molding process, depending on process variables such as temperature, pressure, and time, the viscosity of the PLA during the process and the degree of crystallinity of the final product change (16–18). Since the degree of crystallinity is directly related to the mechanical properties, and the melt viscosity and crystallization rate are directly related to the production efficiency, they are important properties to investigate (19–21). Several studies to investigate the degree of crystallinity and crystallization rate of PLA with additives are being conducted (11,22,23). In this study, we analyze the viscosity change in the PLA with enhanced heat resistance (Ingeo™ Biopolymer 4032D) from NatureWorks LCC according to the process variables at different shear rates and temperatures. In addition, by investigating the crystallization kinetics and the crystallinity through thermal analysis of differential scanning calorimetry (DSC), we tried to find out the optimal PLA molding process conditions.

2 Experiments

2.1 Materials

For PLA, we used Ingeo Biopolymer 4032D in the form of pellets from NatureWorks LCC. The PLA has the ratio of L- to D-lactide of 28:1 and the melting point of 170°C. All PLA samples for rheological and thermal analysis were used after drying for at least 12 h at 90°C under vacuum to remove moisture (22,23). The rotational rheometer (MCR 302 from the Anton Paar) was used to measure the viscosity with different shear rates and temperatures. For thermal analysis, we used the DSC (Q2000) from TA Instrument including a cooling function (50°C/min) with an operating range from –180°C to 725°C.

2.2 Rheological analysis

The melt viscosity of PLA was measured using a rotational type viscometer to determine the changes in viscosity with

different shear rates and process temperatures. A 55-mm diameter parallel plate was used, and the gap was maintained at 1 mm under constant shear rate. The steady-state melt viscosity of PLA at each temperature was measured. The melted PLA is known as a non-Newtonian fluid exhibiting the shear-thinning behavior, which shows the decrease in viscosity as the shear rate increase (1). The general viscosity equation for non-Newtonian fluid is as follows (24):

$$\tau = k \cdot \dot{\gamma}^n \quad (1)$$

$$\eta = k \cdot \dot{\gamma}^{n-1} \quad (2)$$

where τ is the shear stress, k is constant, $\dot{\gamma}$ is the shear rate, η is the viscosity, and n is the power-law parameter. Parameter n has a value of 1 when the fluid acts as a Newtonian fluid. Considering the melting point of PLA pellets (170°C or higher), the change in PLA viscosity was measured for four process temperature conditions: 180°C, 190°C, 200°C, and 210°C.

2.3 Thermal analysis

Two types of DSC analysis were performed. The first is dynamic scanning to examine the heat flow with temperature under constant heating rate and the second is isothermal scanning to examine the heat flow with the time under a constant temperature. In dynamic scanning, to remove the heat history of the PLA, the sample was heated from 25°C to 200°C at 50°C/min, and maintained at 200°C for 5 min and then cooled down (10°C/min) to 25°C. Afterward, the sample was heated up at a heating rate of 10°C/min from 25°C to 200°C, and the heat flow changes were obtained. For isothermal scanning, as in dynamic scanning, to remove the heat history of the sample first, the sample was heated from 25°C to 200°C at 50°C/min, maintained for 5 min and then proceeded to the cooling step with 50°C/min from 200°C to each set temperature (85–120°C). After cooling down to the set temperature, the sample was held at isothermal set temperature for 120 min, allowing crystallization. After the isothermal procedure, the sample was reheated up to 200°C at 10°C/min to observe the melting behavior and the degree of crystallinity. The formula to obtain crystallinity (X_c) from DSC reaction heat is as follows (22):

$$\text{Crystallinity } (X_c) = \frac{\Delta H}{\Delta H_m^0} \times 100 (\%) \quad (3)$$

($\Delta H = \Delta H_c$ at cooling curve and $\Delta H = \Delta H_m - \Delta H_{cc}$ at heating curve) where ΔH is the melting enthalpy of the

Figure 1: ΔH_{cc} and ΔH_m from the isothermal DSC results (cooling down to the set temperature of 95°C).

sample, ΔH_m^0 is the melting enthalpy of the 100% crystalline PLA (93 J/g) (25,26), ΔH_c is the crystallization enthalpy of the sample, and ΔH_m and ΔH_{cc} represent the measured endothermic and exothermic enthalpies generated by crystallization of the sample before melting, respectively (Figure 1). In isothermal scanning, we calculated the crystallinity with eight cases of the set temperature from 85°C to 120°C at 5°C intervals.

3 Results and discussion

3.1 Rheological property

The viscosity was measured under the constant shear rate at each process temperature, as shown in Figure 2 and

Table 1. Results were obtained at shear rates of 0.01, 0.1, and 1/s. The results of the experiment denote that the viscosity decreases slightly as the shear rate increases at all temperatures, and as can be seen from other references measured by capillary and rotational rheometer, it is consistent with the results that PLA exhibits almost Newtonian fluid behavior at less than 1/s near 180°C (1,27). Through this experiment, it was found that this trend of Newtonian behavior was maintained even when the process temperature was raised to 210°C. Looking at the viscosity for each process temperature, it shows that the viscosity at all shear rates decreases as the temperature increases, which can be explained as due to that the molecular movement of polymer becomes easier as the temperature increases, as in the general tendency of polymer resins (24). A similar trend was observed in Biopolymer 4032D having a viscosity between 720 and 3,050 Pa s depending on the temperature. Especially, it was found

Figure 2: Viscosity versus shear rate at each temperature.

Table 1: Viscosity versus shear rate at each process temperature

Sample	Temperature (°C)	Shear rate, $\dot{\gamma}$ (/s)	Viscosity, η (Pa s)
PLA	180	0.01	3,037
		0.1	2,931
		1	2,796
	190	0.01	2,360
		0.1	2,356
		1	2,273
	200	0.01	1,232
		0.1	1,227
		1	1,216
	210	0.01	733
		0.1	730
		1	725

Figure 3: Plot of $\ln(\text{viscosity})$ versus $1/T$ for the PLA at 0.01/s shear rate.

that the viscosity at 210°C was four times lower than the viscosity at 180°C. To investigate the tendency of viscosity change with temperature more deeply, the experimental values were fitted using the Arrhenius equation; the results are shown in Figures 3–5. As the result of curve fitting shows, in all cases, the error r^2 was above 0.96, indicating that the viscosity of PLA follows well the Arrhenius equation depending on the temperature.

3.2 Thermal properties

3.2.1 Dynamic analysis

Figure 6 shows the dynamic DSC results. The upper graph shows the heat flow when the PLA sample is cooled to room temperature (25°C) at 10°C/min after being maintained at

Figure 4: Plot of $\ln(\text{viscosity})$ versus $1/T$ for the PLA at 0.1/s shear rate.

Figure 5: Plot of $\ln(\text{viscosity})$ versus $1/T$ for the PLA at 1/s shear rate.

200°C for 5 min. The lower graph shows the heat flow of the sample while heating up from 25°C to 200°C. The cooling graph did not show a distinct peak, which means that neat PLA does not crystallize dramatically during the cooling process at cooling rate of 10°C/min. The 2nd heating graph shows the glass transition period, melting temperature, cold crystallization enthalpy (ΔH_{cc}), and melting enthalpy (ΔH_m) of the sample. The values are listed in Table 2, where the cold crystallization enthalpy and the melting enthalpy are almost the same. This indicates that crystallization of PLA does not occur during cooling in this procedure and mostly occurs (more than 99%) during the heat up process.

3.2.2 Isothermal analysis

The results were obtained by performing isothermal DSC analysis according to the procedure introduced in Section 2.3.

Figure 6: Dynamic DSC results (1st cooling and 2nd heating process).

Table 2: DSC results of dynamic scanning

Sample	T_g (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_c (%)
PLA	59	174	23.2	24	0.9

To reflect the general molding process temperature, the eight cases of tests were performed from 85°C to 120°C at 5°C intervals, and it was held for 120 min allowing crystallization of sample at each temperature. Figure 7 shows the exothermic curves during crystallization at several representative temperatures, and as can be seen from the Figure 7, up to 100°C, as crystallization temperature increases, the maximum heat flow of curves increases with narrower peak which means that crystallization occurs in a short time. The curves show the narrowest peak and largest maximum heat flow at 100°C, and at a temperature higher than 100°C, it flattened again and also had a small maximum heat flow.

To investigate the crystallization behavior deeply, the kinetics of isothermal crystallization were studied by Avrami Equation (28,29). A relative volumetric crystallinity at time t ($X(t)$) for isothermal crystallization can be expressed as below:

$$X(t) = 1 - \exp(-kt^n) \quad (4)$$

$$\log[-\ln(1 - X(t))] = \log k + n \log t \quad (5)$$

where t is the time, k is the overall crystallization, and n is the Avrami exponent which is related with the nucleation and growth mechanism of the crystal (15,22). The relative volumetric crystallinity at time, $X(t)$ can be calculated as follows:

Figure 7: Isothermal DSC results obtained from crystallization at different set temperatures (85°C, 90°C, 100°C, 110°C, and 120°C). **Figure 8:** Plots of $\log[-\ln(1 - X(t))]$ vs $\log(t)$ for isothermal crystallization.

$$X(t) = \frac{\Delta H(t)}{\Delta H_{\text{total}}} \quad (6)$$

The $\Delta H(t)$ is the enthalpy calculated by integrating the curve at selected time at given isothermal crystallization temperature, and ΔH_{total} is the total enthalpy value at the end of the crystallization process at given temperature. Parameters n and k can be determined by curve fitting the plot of $\log[-\ln(1 - X(t))]$ versus $\log(t)$ as shown in Figure 8. In Figure 8, parameters n and k can be obtained from the slope and the intercept of the linear regression, respectively. According to other studies, the initial data points less than 3% of $X(t)$ may not be accurate due to experimental errors, hence a relative volumetric crystallization range of 3–40% is used in linear regression (30). The calculated values of n and k for isothermal crystallization kinetic of PLA are listed in Table 3. It can be seen from the Figure 8 and the r^2 value in Table 3 that the calculated results fit well with experimental data. Generally, parameter n has an integer value between 1 and 4 including dimension of the crystal growth and nucleation constant. The value of n is 4 means that it has three dimensions of growth and one nucleation

Table 3: Properties and parameters of isothermal crystallization kinetics

Sample	T (°C)	n	k	r^2	$t_{1/2}$ (min)
PLA	90	3.86	4.42×10^{-8}	0.9987	72.9
	100	3.96	1.75×10^{-6}	0.9992	26.0
	110	3.76	9.72×10^{-7}	0.9989	35.9
	120	3.97	1.06×10^{-7}	0.9952	51.9

Figure 9: Plots of relative degree of crystallinity vs time for isothermal crystallization (symbols: experiment data and solid lines: calculated using parameters n and k in Table 3).

constant. Figure 9 shows the plots of relative degree of crystallinity with time, and experimental values are represented by symbols and Avrami equation using calculated n and k are represented by solid lines. From the graphs of Figure 9 it can be seen that they also fit well with calculated Avrami equation. To determine the crystallization rate, the half crystallization time $t_{1/2}$ which is defined as the time at $X(t) = 50\%$ was calculated and listed in Table 3. The results show that the $t_{1/2}$ decreases as the temperature increases, and then have the minimum time (26 min) at 100°C and decreases again above 100°C.

In all cases, the 2nd heating graph was obtained by reheating introduced in Figure 6, and through this graph, the crystallinity (X_c) of PLA at different crystallization temperature conditions could be derived. The results are shown in Table 4. As can be seen from the table, the crystallinity increases as the holding temperature increases from 85°C, with the maximum value at 100°C, and then decreases slightly to 120°C. Crystallinity at 100°C is 47.4%, which is more than twice larger than

that at 85°C. Since it is known that the higher the crystallinity, the better the mechanical properties of thermoplastic (19–21,31), the temperature of 100°C can be said to be the optimum temperature for the holding time of 120 min. of the process. In addition, it can be seen that there is no significant difference compared to different kinds of PLA that was subjected to annealing as a post-process after the molding process (11).

4 Conclusion

In this study, for optimizing the general molding process of PLA with improved heat resistance, the viscosity and thermal properties of PLA in different temperature conditions were investigated. The steady-state viscosity was measured for each temperature for shear rates of 0.01, 0.1, and 1/s. As a result, it was confirmed that the viscosity decreases slightly as the shear rate increases where the temperature was kept constant, whereas in different temperature conditions, the viscosity tended to decrease dramatically as the temperature increased. To quantify this trend, the experimental data were subjected to linear curve fitting using the Arrhenius equation, and it was confirmed that the experimental results follow the equation well. Using this derived trend, the viscosity at other temperatures can also be inferred and used. Through thermal analysis, we investigated the dynamic and isothermal DSC analyses to determine the optimum molding process temperature, and the crystallinity of each case was also evaluated. From the results of isothermal scanning, in the case of crystallization temperature of 100°C, it has the largest maximum heat flow of curve and the narrowest peak which means that the crystallization rate is the fastest in the range from 85°C to 120°C. The Avrami equation described the isothermal crystallization kinetics very well, and they have similar Avrami exponent n in all crystallization temperature ranges, which means that they have the same dimensions of growth and nucleation

Table 4: Crystallinity calculated by Isothermal DSC results (2nd heating)

Temperature (°C)	PLA sample							
	85	90	95	100	105	110	115	120
ΔH_{cc} (J/g)	18.32	43.46	47.85	46.36	41.2	42	42.11	42.3
ΔH_m (J/g)	0.26	2.8	2.9	1.3	0.7	0	0	0
ΔH (J/g)	18.06	40.66	44.95	45.06	40.5	42	42.11	42.3
X_c (%)	19.4	43.7	45.1	47.4	43.8	45.2	45.3	45.5

constant. The crystallinity of the PLA also has a similar tendency. It increases as the holding isothermal temperature increases up to 100°C, and the maximum crystallinity was shown at 100°C, and then decreases above 100°C. Using the above information, we can set the optimal temperature of the mold during injection molding or compression molding process. Furthermore, by using the optimum temperature, the process time can be reduced to increase production efficiency.

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