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CRYSTALLIZATION KINETICS OF COMMERCIAL PLA FILAMENT

The Poly-Lactic Acid (PLA), the often used material for 3D printing and the rapid prototyping is very important in development process in automotive industry, as well. The commercial PLA filament was chosen and isothermal melt-crystallization and melting behavior was investigated by the DSC (differential scanning calorimetry). The PLA is a semi - crystalline biopolymer but the crystallization process is slow and sensitive to the changing of the cooling rate. Avrami equation was applied to analyze the crystallization. Arrhenius equation was used to calculate the activation energy and the equilibrium melting temperature was determined by the Hoffman-Weeks linear method. These results are the basis for further experiments.

Keywords: 3D printing, PLA, isothermal crystallization, DSC

1. Introduction

The rapid prototyping is an important part of product development process in several industry sector include automotive. There are more 3D printing technologies, and they have become popular and available. Besides the multinational and small companies, everyone as a private person, can buy a 3D printer and make own products. One of the frequently used 3D printing technology is the fused deposition modeling (FDM), which is based on the melt extrusion. The FDM is a layer by layer method built by melted thermoplastic fibers [1]. A lot of polymers are optional for printing but there is one special type-the Poly-Lactic Acid, the PLA.

The PLA is a biodegradable and compostable polymer produced from renewable resources, such as starch and sugar. The PLA is thermoplastic, semi-crystalline polyester and it is based on the lactic acid (LA), which can be produced by fermentation or chemical synthesis. There are two polymerization routes, one is polycondensation from the LA, and the other is the ring-opening polymerization from lactide, it is the dimer of the lactic acid. The LA has two stereoisomers L-lactic acid and D-lactic acid. The commercial PLA are copolymers of PLLA, poly (L-lactic acid) and PDLA, poly (D, L-lactic acid), but the L-lactic is the main fraction. Depending on the copolymer ratio, properties, glass transition and the melting temperatures can be different.

Nowadays, the environmental protection is very important so the biopolymers as the PLA have become the center of interest. The elevated environmental awareness and the good

properties (high tensile strength and Young's modulus, good flexural strength) have resulted in an expanded use of the PLA for consumer goods and packaging applications; furthermore it is expected that novel technological advances will lead to the biopolymers market boom in transportation and automotive industry [2-4].

Unfortunately, there are some drawbacks, for example the PLA is brittle material and the crystallization process is slow. The mechanical, thermal and optical properties, depend on the crystallinity, so investigating the crystallization is very important [2-4].

In this work, the isothermal melt-crystallization and melting behavior of a commercial 3D printing filament from the PLA was investigated. The Avrami equation was applied to analyze the crystallization kinetics. This study will be of the basis for the further experiments like nucleation, to improve crystallization and provide better mechanical properties.

2. Experimental

2.1 Material

The used PLA is a filament with 1.75 mm diameter and metallic blue color from Orbi-Tech GmbH. The Orbi-Tech Company gives only general information. There is no datasheet. We know only the diameter and the color.

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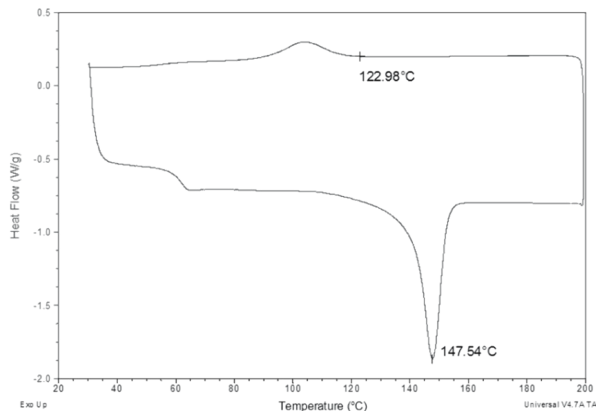


Figure 1 Heat -flow versus temperature, the starting temperature of crystallization and the melting peak temperature

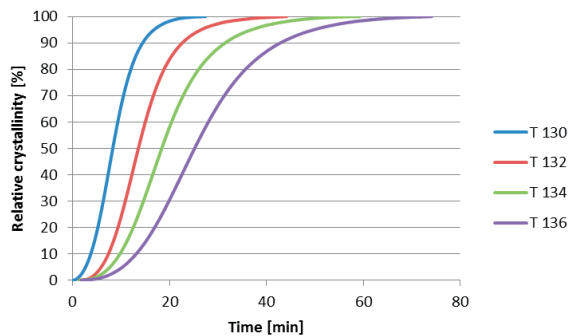


Figure 3 Relative crystallinity as a function of isothermal crystallization time

2.2 Method

The thermal behavior of the PLA was measured by differential scanning calorimeter (DSC), TA Q200 heat-flux DSC instrument, which was calibrated by Indium. The sample weight was 5.37 mg. The applied gas during the DSC scan was nitrogen; the using flowing rate was 50 ml/min. The temperature range was from 30 °C to 200 °C.

The first the sample was heated to 200 °C at a heating rate of 20 °C/min to eliminate any thermal history. Then the sample was cooled (by 5 °C/min) to the crystallization temperatures, which were 130, 132, 134 and 136 °C. After the set time of crystallization, heating scan of 20 °C/min was used. This heating rate is too fast, so there is no time for recrystallization [5-8].

3. Results and discussion

Determination of temperatures and the holding times of the isothermal crystallization can be quite difficult. Prior to the isothermal measurements, it is necessary to perform an anisothermal scan (Figure 1) to determine the starting temperature of crystallization. The endotherm curve shows the

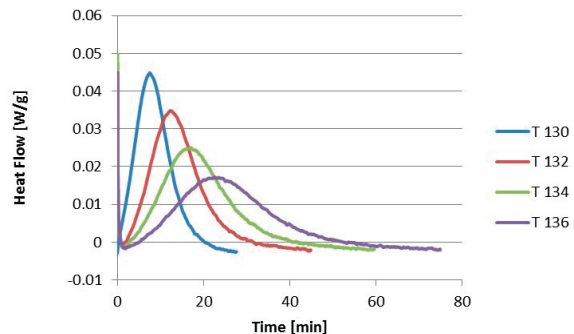


Figure 2 Heat-flow versus time during isothermal crystallization

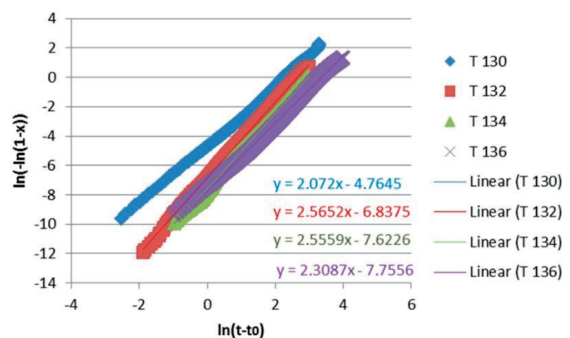


Figure 4 Straight lines obtained by the Avrami equation

melting, and the exotherm curve shows the crystallization. On the exotherm curve, when the line begin to change, it is the starting temperature of the crystallization.

The isotherm temperatures need to be higher than the start temperature of crystallization, but lower than the melting temperature. Several pre-tests were used to find the correct data, so in this work the first holding temperature was 130 °C. The applied temperature step was 2 °C from 130 to 136 °C.

Figure 2 shows the change of the heat flow versus isothermal crystallization time. The time zero (t_0) is that point when the real temperature reaches the setting temperature.

The asymmetrical shapes of the exothermic peaks suggest that the crystallization process presents some secondary crystallization. When the isothermal temperature was increased, the maximum of the heat flow was lower and the time of the crystallization was longer.

Figure 3 shows the relative crystallinity as a function of isothermal crystallization time.

The time to reach the end of the crystallinity increases with the increase of crystallization temperature. The change of the relative crystallinity with time can show the rate of the crystallization. The slope of the curve is reduced when the isothermal temperature increased and it means that the rate of the crystallization became lower.

Table 1 Avrami exponent, rate constant and melting temperature versus crystallization temperature

$T_{c\text{ iso}}$ [°C]	$T_{c\text{ iso}}$ [1/K]	n	ln K	T_m [°C]
130	0.00363343	2.072	- 4.765	155.31
132	0.003626973	2.562	- 6.8375	156.71
134	0.003627052	2.556	- 7.6226	158.11
136	0.003630318	2.308	- 7.7556	159.22

Table 2 Relationship between Avrami exponent and geometry of crystallite [9]

Dimension	Geometry	n	
		athermic nucleation	thermic nucleation
1	Fibril (cylinder)	1	2
2	Lamella (disk)	2	3
3	Spherulite (orb)	3	4

The Avrami equation (1) was used to analyze the increment of the relative crystallinity with time (Figure 3):

$$x(t) = 1 - \exp(-Kt^n) \quad (1)$$

where x is the relative crystallinity, K is the rate constant of crystallization, t is the time and n is the Avrami exponent. The values K and n are considered to be diagnostic for the mechanism of crystallization [6-9].

After the relative crystallinity was transformed by the Avrami equation, almost the straight lines were obtained (Figure 4). The equation of the linear lines can show the Avrami exponent, which is the steepness and rate constant of the crystallization is the intersection of the y axis.

Table 1 summarizes the result derived from the Avrami analysis and the melting peak temperatures after the isothermal crystallization. The heating rate was 20 °C/min.

Table 1 Avrami exponent, rate constant and melting temperature versus crystallization temperature

The Avrami exponents were in the range of 2.1-2.6 for the temperature range of 130-136 °C, suggesting a change in crystal growth from two to three dimensional with athermic nucleation. The rate constant is reduced as expected by increasing the isothermal crystallization temperature [4, 6-9].

The activation energy of the crystallization process was determined from the rates of crystallization by the Arrhenius equation (2):

$$K = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where K is the rate of crystallization, A is a constant, T is the crystallization temperature, R is the universal gas constant and E_a is the activation energy. The activation energy can be obtained from the slope of the plot of K as a function of reciprocal of crystallization temperature in Kelvin (Figure 5) [6-9].

The activation energy of this PLA is 670324.5 J/mol.K. The four points in Figure 5 are not collinear, so this activation energy is just an approximate value and further experiments are required.

After the isothermal crystallization, there were heating scans and the melting temperatures were measured. The applied heating rate was 20 °C/min. Figure 6 shows that if the isothermal crystallization temperature was higher, the melting peak temperature was higher too, because the crystallites became bigger and contain less mistakes [6-9].

The equilibrium melting temperature can be determined from the change of melting temperature. It is based on the linear method of Hoffman-Weeks (3):

$$T_m = T_m^0 \left(1 - \frac{1}{\gamma}\right) + \frac{T_c}{\gamma} \quad (3)$$

where T_m is the melting temperature, T_m^0 is the equilibrium melting temperature, T_c is the crystallization temperature and γ is the lamella thickening factor. The linear method means that it is assumed that there is no lamella thickening. The equilibrium melting temperature was determined by the relationship between the apparent melting temperature and the crystallization temperature. The plot of T_m as function of T_c gives straight lines whose intersection points with the line $T_m = T_c$ determine T_m^0 (Figure 7) [5-9].

The equilibrium melting temperature of the PLA filament is 203.85 °C.

4. Conclusion

The commercial PLA filament was measured by the isothermal DSC method. The crystallization temperature range was between 130 and 136 °C using 2 °C steps. The Avrami equation was applied to analyze the crystallization process. The Avrami exponent showed that the nucleation is athermic and the geometry can

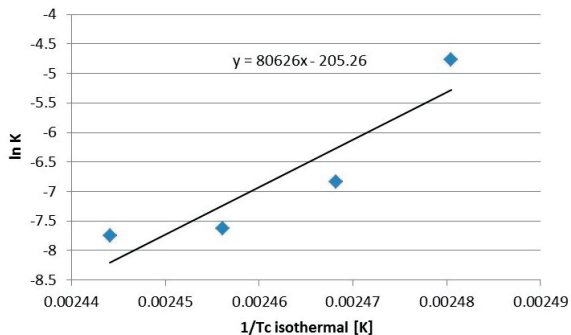


Figure 5 Rate constant versus reciprocal of isothermal crystallization temperature in Kelvin

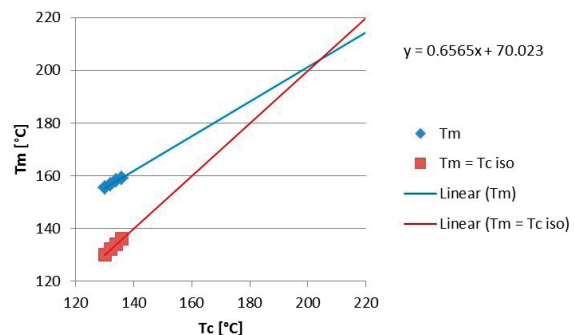


Figure 7 Determination of the equilibrium melting temperature

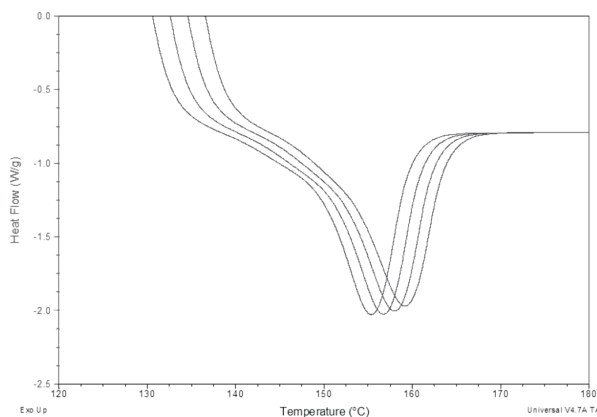


Figure 6 Changing of the melting peak temperatures

be change from 2 dimension to 3, but the transformation is not complete. The activation energy was calculated from the

change of rate constant by the Arrhenius equation. Finally, the equilibrium melting temperature was determined from the melting temperature by the Hoffman-Weeks linear method. These results are the basis for further experiments, like nucleation to improve crystallization and provide better mechanical properties for the 3D printing model.

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