1. Introduction

The rapid prototyping is an important part of product development process in several industry sectors including 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 technologies 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 PDLLA, 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. 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

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.
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.

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 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.

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The activation energy of this PLA is 670.324.5 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):

\[ T_m = T_{m0} \left(1 - \frac{c_1}{b_1 + c_2 T_c}\right) \]

where \( T_m \) is the melting temperature, \( T_{m0} \) is the equilibrium melting temperature, \( T_c \) is the crystallization temperature and \( \gamma \) 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 \( T_{m0} \) (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...
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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