Dynamic local temperature control in micro-injection molding: effects on poly(lactic acid) morphology

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ABSTRACT

Microinjection molding is one of the most efficient processes for wide-scale production of thermoplastic polymer micro-parts. The injection molding process with a cold mold suffers from drawbacks, i.e. the premature solidification, caused by the small thickness and large temperature difference between the surface of the mold and the incoming polymer. In this work, an original and versatile system to dynamically control the local temperature of the cavity surfaces in microinjection molding was developed. The system was used to investigate the effects of rapid variations of the temperature of a 200 μm thick cavity on the reachable flow length and study the morphology of microinjection molded parts of poly(lactic acid). For the rapid mold temperature control, electrical resistive thin components are located very near the surface of the impression to change the temperature by some tens of degrees per second. This study also demonstrates that the system is able to influence the final morphology of the part with a semi-crystalline thermoplastic material. Changing the annealing time and temperature, the effects on the morphology of the part, in the mold and immediately after the injection, were investigated by microscopy analysis and X-ray diffraction.

Keywords: injection molding, crystallization, thermoplastics, biopolymers, differential scanning calorimetry (DSC)

INTRODUCTION

The microinjection molding (μIM) process is a commonly used technology for manufacturing components with dimensions or features in the micrometer scale. Because of the small part thickness, the process is subjected to filling difficulties caused by premature freezing of the polymer inside the cavity [1, 2]. Furthermore, high temperature and elevated injection speed are applied to reproduce small features in the conventional process to reduce melt viscosity [3-5]. Consequently, the materials experience high stresses and shear rates. This thermomechanical situation could have an influence on the nucleation and growth rate of crystalline entities as far as to material degradation [6-9].

In order to prevent the premature freezing and ensure an acceptable cycle time, the ideal molding condition is to have a hot mold during the injection stage and a cold mold during the cooling stage. An overview of the state of the art in the use of systems to rapidly change the temperature of the mold for microinjection molding is offered by Su et al. [10]. In this review, various heating methods are compared and it was highlighted that there is still not a proven method for an optimal use of microinjection molding. The heating techniques are more interesting, in particular, the electrically resistive heating in which the source is generated according to Joule effect. As a consequence, the temperature of the cavity can be controlled by regulating the power supply.

A novel system consisting in a mold with inserts and heating elements to control the temperature of the surface of a mold for microinjection molding was developed by De Santis et al. [11, 12]. The implemented heating structure is based on very thin and flexible wire resistances with a high power density. Furthermore, a thin insulation layer was used to separate the resistance layer from the mold. The system, able to increase the mold surface temperature of some tenths of Celsius degrees in a time of the order of one second, appears ideal for applications in which the conditioning of the mold is a crucial point in polymer processing. The temperature of the mold surface can affect the flow length [13], the replicability [14] the crystal formation and their morphological structures, in addition to mechanical and thermal properties [15]. In the case of PLA, having a very slow

crystallization time [16] an annealing step can enhance the crystallization of the polymer chains [17]. In the work of Harris et al. [18], significant improvements in the mechanical performance of PLA were achieved by increasing the overall material crystallinity. This was accomplished in several ways including the addition of nucleating agents, the post-annealing of injection molded samples, and the direct enhancement of crystallinity by injection molding into a preheated mold. The highly crystalline samples formed by these methods were shown to have enhanced flexural stiffness, strength, and heat deflection temperature.

In this study, the previous system developed by De Santis [11] was reorganized, measuring and independently controlling the temperature of four different heating elements, and applied to the microinjection molding of 200 μm thin parts of a commercial PLA grade. The effect of the temperature of the cavity surface on the flow length was investigated. Furthermore the effect of the isothermal time, after the filling, at a certain temperature, on the morphology of the products was studied. The differential scanning calorimetry was utilized to study the crystallization behavior of the material. The morphology of the injected parts were observed by optical microscopy and X-ray patterns.

EXPERIMENTAL SECTION

Injection molding machine

The injection molding machine used in this work is the HAAKE Minijet II by Thermo Scientific, designed as a piston injection molding system. The molds for the HAAKE Minijet II present a truncated cone shape, with a diameter that changes from 50 mm (at the gate side) to 35 mm over a length of about 90 mm. In addition, a modular system [11] consisting of mold inserts and heating elements near the cavity surface is created. The thickness of the rectangular cavity, wide 4 mm and long 35 mm, is 200 μm. Fig. 1a depicts the 3D model of the mold coupled with a picture of the cavity together used for the experiments, whereas Fig. 1b show a schematic of the heating system.

The insert-mold system is schematized as a multi-layer model [11] using electrical resistances as a heat source and insulating layers which limit the heat flow towards the mold. The electrical resistances are grids of constantan foil sealed in a polyimide film with a nominal resistance of 120 Ω. The grid covers an area of 22 mm^2 and is 20 μm thick.

The heating elements are placed symmetrically on both sides of the mold, between the cavity and the insulation layer that inhibits the heat dissipation towards the rest of the mold. On both side of the cavity, two resistances, arranged in sequence, cover a length of 8 mm. The temperature is measured using thin wire thermocouples (Type T, about 50 μm in diameter supplied by Omega Engineering Ltd.) which are positioned at the very center of each heating resistance, between the steel slab and the heating element. The system is able to control independently four areas, i.e. two on each cavity surface. A data acquisition board (DAQ NI-USB 6210 supplied by the National Instruments) is used to acquire the thermocouples measurements. In order to get the set point local temperature evolution, a dedicated software was developed. This system allows to control the evolution of the local mold temperature switching the linked relays and thus imposing a given heating and cooling rate (in the limit of the maximum values determined by the heating power and the ballistic cooling without power supply). Each test in this work was carried out by using a power supply equal to 12 V, and acquiring and controlling the temperature of four heating elements at 10 kHz (sampling time 10 ms).

In this work, three experimental protocols for conditioning the cavity surface were adopted. Fig. 2a, Fig. 2b, and Fig. 2c point out the set parameters for the various protocols, namely time and temperature.

In the first protocol, here called "*protocol 1*", just after starting the dynamic control system, the temperature of the cavity surface rises up to the set values, T_{cavity}, for the injection stage. Once the cavity temperature is reached, the injection is manually activated with the cylinder injection temperature of 180°C and a pressure of 10 MPa for 3 s, this pressure is that withstands by the polymer melt. At that moment, switching off the power supply, the system is cooled down to a

temperature that is lower than glass transition temperature, T_g, that allows the demolding of the solid sample. The effect of different values of the temperature of the cavity surface, T_{cavity} listed in Table 1, during the injection stage was explored.

In the "*protocol 2*" and the "*protocol 3*", the temperature of the cavity surface rises up to the set values, T_{cavity}=115°C, for the injection stage. This value of T_{cavity} was established because it is easily reached by the system, applying the voltage of 12 V and consequently a current that is not stressing the heating resistances, but permitted to mold a part of about 4 mm. For both these protocols, once the cavity temperature is reached, the injection is manually activated with the cylinder injection temperature of 180°C and a pressure of 13 MPa for 3 s.

In the case of "*protocol 2*", after the injection step, the cavity surface is cooled to a lower temperature, $T_{isotherm}$=105°C, for isothermal set time called isothermal time. This value for $T_{isotherm}$ was chosen after considering the crystallization half times, later discussed, and corresponding to the maximum crystallization rate. After this isothermal step, the power supply of heating elements is automatically switched off and the temperature of the cavity is lowered under T_g for part demolding.

In the case of "*protocol 3*", after the injection step, the cavity surface is immediately cooled under T_g. Subsequently, the cavity surface is heated again to $T_{isotherm}$=105°C, for the set isothermal time, and then cooled again for the part demolding.

The effect of time of the isothermal step, for both the "*protocol 2*" and the "*protocol 3*", is explored with times of 10 s, 100 s and 1000 s.

Material

Poly(lactic acid) 3251D, hereafter called PLA 3251D, supplied by NatureWorks LLC, was a grade designed for injection molding applications, having a number average molecular weight M_n of 83 kDa, dispersity of M_w/M_n = 1.6, and D-isomer content of 1.4%. As recommended by the supplier, before any test or processing, the material was dried for 24 h under vacuum at a temperature of 60°C to prevent viscosity degradation.

Differential Scanning Calorimetry

A differential scanning calorimeter DSC 822e from Mettler Toledo was used for the characterization of the thermal behavior of PLA 3251D. The DSC was calibrated with the extrapolated onset temperature of the melting phase transition of indium. The pellets with a weight of less than 10 mg were put into an aluminum pan and hermetically sealed. In order to prevent oxidative degradation at high temperatures, all the experiments were carried out in nitrogen atmosphere with a flow rate of 50 ml min^{-1}. The crystallization kinetics was investigated in isothermal conditions starting from the melt and then holding it at 200°C for 5 min in order to erase the effect of previous thermomechanical history. The glass transition temperature, T_g, measured by DSC is about 60°C. The melting temperature, T_m, measured as the peak of the melting endotherm during DSC heating ramp at 10°C min^{-1}, is about 170°C.

Furthermore, the differential scanning calorimetry was used to mimic the thermal history of the "*protocol 2*" and the "*protocol 3*" experienced by the material in the injection molding. In the first case, after melting, the pellet is cooled to the isothermal temperature, 105°C and held for 10, 100 and 1000 s. In the second case, after melting the sample is cooled under T_g, then heated to 105°C and held for 10, 100 and 1000 s.

Characterization of injection molded parts

The stereomicroscope LEICA MZ6 was used for morphological investigation and each sample was observed from the gate to the tip in polarized light. The thickness of the samples is 0.2 mm, the width is 4 mm and the length is about 4 mm. Wide-angle X-ray diffraction (WAXD) patterns were obtained by an automatic Bruker D8 Advance diffractometer, in reflection, at 35 kV and 40 mA, using the nickel filtered Cu-Kα radiation (1.5418 Å).

RESULTS AND DISCUSSION

Material characterization: DSC

In order to study melt isothermal crystallization, the sample was cooled from 200°C directly to isothermal test temperature (crystallization temperature), with a cooling rate of 10 K min^{-1} [19].

As a result, the specific heat flow evolutions were obtained (Fig. 3a) at different isothermal temperatures. This investigation pointed out that the narrowest crystallization peak is at 105°C, i.e. it requires the shortest time at this temperature to complete the crystallization. The semi-crystallization time, i.e. the time necessary for half crystallization of the material $t_{1/2}$, was evaluated from isothermal DSC experiments as shown in Fig. 3b. The shortest semi-crystallization, at the temperature of 105°C, is about 1000 s [19]. The numerical data results obtained from DSC experiments are showed in Table 2.

In order to highlight the effect of the annealing isothermal step, in the injection molding tests, this temperature, 105°C, was chosen with time up to 1000 s.

Injection molding tests: "protocol 1"

Using the aforementioned experimental "*protocol 1*", during the injection step only cavity surfaces were heated. A rate of 10°C s^{-1} was set for the subsequent cooling step, after which the sample was extracted. Fig. 4a shows the results of two of the tests performed with the surface temperature of 120°C and 150°C, respectively, adopting the "*protocol 1*". The cycle requires less than 60 s, taking into account the duration of the injection and the cooling steps. The flow length of the final part, obtained for each molding test varying the surface temperature during injection, is reported in Fig. 4b. The flow length obviously increases with increasing temperature of the cavity. As shown in Fig. 4b, when the cavity surface was 25°C, the material hesitated to enter and the length was 0.8 mm, as the molten polymer solidified just after the gate. The material never filled the entire cavity, like a spiral flow test in which the influence of the operational parameters is investigated. A significant effect on the final length was observed when the mold surface temperature was increased up to 160°C.

Injection molding tests: "protocol 2" and "protocol 3"

By using the system for the rapid control of temperature, according to experimental protocols, tests were conducted to investigate the effects of the holding temperature 105°C on the morphology of the injected samples. Fig. 5a and Fig. 5b show the temperature evolutions of the experiments following the *"protocol 2"* and the *"protocol 3"*.

The temperature evolutions perfectly reproduced the set values. In all cases, a length of about 4 mm was obtained, since the injection conditions were the same for all the samples.

The microscopy images, with crossed polarizers, of the parts are shown in Fig. 6. The differences in the morphology of the parts are quite evident. While samples experienced an isothermal time of 10 s present weak bands, clear fringes are observed after 100 s, indicating orientation. The molded parts with the highest time of isotherm, 1000 s, are opaque because they are more crystalline.

To get further information of crystallization, the crystalline nature of the injected samples was checked by X-ray diffraction. Fig. 7a and Fig. 7b reveal the X-ray diffraction profiles of PLA and injected parts. The pellet and the samples kept at 105°C for 1000 s presented two peaks at 16.7° and 19.0° that are characteristic peaks of crystalline PLA which represent (200)/(110) and (203) reflections of stable α-crystals [20, 21]. The parts obtained by holding for 100 s present a lower peak at 16.7°. Vice versa, patterns of samples kept at 105°C for only 10 s did not present any peak, resulting in an amorphous material. Consequently, the degree of crystallinity is negligible for the samples obtained after 10 s of isotherm. However, as the isothermal time rises to 100 and 1000 s, for protocols 2 and 3, the crystallinity increases up to 8% (±3%) and 18% (±3%), respectively.

Mimicking the same thermal history experienced by the samples in "*protocol 2*" and "*protocol 3*", the calorimetric analysis was performed on a piece of pellet of the virgin PLA.

In particular, the effect of the isothermal time at 105°C is analyzed in the subsequent heating up to 200°C. The differences in the specific heat flow released during the melting of the samples are quite evident, as shown in Fig. 8a and Fig. 8b, corresponding in the previous crystallization of the

sample. The analysis confirms that the length of the isothermal step promotes the crystallization, in particular for the "*protocol 3*" with the annealing of the solid part [19].

CONCLUSIONS

In this work, a novel system for dynamic control of the temperature of the mold surfaces was used to investigate the effects of rapid temperature variations on the final length. Furthermore, the resulting morphology from different isothermal steps on the final length of microinjection molded parts of poly(lactic acid) in a thin cavity was studied. The electrical resistive components used were able to change the temperature by some tens of degree per second allowing reaching values close to the melting temperature in the injection step. This idea allowed to analyze the effect of the temperature change on the filling capability of poly(lactic acid) during injection molding. When the system is used to realize the highest temperature of the cavity during the injection, an increase in the length of ten times is obtained. Furthermore, this study demonstrates that the system can tune the morphology of semi-crystalline thermoplastic materials. Microscopy and X-ray diffraction analysis demonstrate that the application of an annealing step, after the injection, affects the morphology of the samples indicating an enhancement of the mechanism of the crystallization on a resin that has a slow crystallization kinetics.

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Table 1. Temperature of the cavity surface, T_{cavity}, during the injection stage of "*protocol 1*"

$\boldsymbol{T_{cavity}}$ [°C]	25	120	125	135	140	150	160	165

Table 2 Crystallization half times evaluated from the DSC isothermal tests

T [°C]	85	90	95	100	105	110	115	120
$t_{1/2}$ [s]	6023	2756	1561	1109	1035	1303	1762	3028

LIST OF FIGURE CAPTIONS

FIG. 1. Representation of the system used in this work: a) mold and cavity, b) heating assembly

FIG. 2. Schematic of the protocols "*protocol 1*" a); "*protocol 2*" b) and "*protocol 3*" c).

FIG. 3. Specific heat flow rate a) varying isothermal step temperature, Crystallization half-time b) evaluated from isothermal DSC tests (the line is a guide for the eye).

FIG. 4. Temperature evolution a) during two experiments with "*protocol 1*"; final part length b) as a function of the temperature of the cavity during the injection (the line is a guide for the eye).

FIG. 5. Temperature evolutions during experiments following a) the "*protocol 2*", and b) the "*protocol 3*".

FIG. 6. Microscopy images, with crossed polarizers, of the injected samples obtained with "*protocol 2*", isothermal time (a) 10 s, (b) 100 s, (c) 1000 s; obtained with "*protocol 3*", isothermal time (d) 10 s, (e) 100 s, (f) 1000 s.

FIG. 7. X-ray diffraction patterns of a) neat pellet and injection molded parts of "*protocol 2*", b) neat pellet and injection molded parts of "*protocol 3*".

FIG. 8. Effect of the isothermal time: melting following the crystallization with (a) "*protocol 2*", and with (b) "*protocol 3*".