Solidification behavior of high-density polyethylene (HDPE) during injection molding: Correlation between crystallization kinetics and thermal gradient field

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Abstract. This work mainly investigated the effect of thermal field on the crystallization kinetics of high-density polyethylene (HDPE) during injection molding (IM) process. The thickness $X = 0.4$ was found to be a crucial location heavily influenced by thermal conduction. The temperature decay tended to be stable, with limited variation of the crystallization rate when $X > 0.4$. It was observed that the crystallization rate was in good proportion to the cooling rate ($\phi$). Our experimental finding showed that the consequence of relative crystallinity ($\chi$) was in agreement with that of the secondary temperature difference (STD). This study is practically significant to the further investigation on the relationship among “processing-structure-property” of polymeric materials.

1. Introduction

The transient heat conduction problems (e.g., the ice formation), also referred to as the “Stefan problems” or “moving boundary problems”, were initially proposed by J. Stefan in 1981 [1]. Nowadays, issues of this kind still have practical significance in both engineering and industrial fields. Numerous methods have been proposed to numerically solve the multi-dimensional phase-change heat conduction problems, such as, the variational method [2, 3], the moving heat source method [4], the finite element method [5], the enthalpy method [6], the variable space-grid method [7, 8], the nodal...
integral method [9], and so forth.

Injection molding (IM) is one of the most commonly used fabricating techniques, accounting for about one third of all plastics processing [10, 11]. Generally speaking, an IM cycle consists of four stages, namely, filling, packing/holding, cooling and demolding (ejection) [12]. The product quality will also be considerably influenced by the operational parameters, mixing with another material, etc [13-15]. In spite of the significant improvement on modeling/simulation of the IM process of thermoplastic polymers over the past few decades, a reliable prediction of the viscoelastic response and microstructure development during real processing operation still remains challenging so far. In this study, the cooling stage of IM process was numerically studied using the enthalpy transformation methodology (ETM), which has been recently proved to be an efficient method to treat the phase-change heat conduction issues of crystalline polymers.

The degree of crystallinity is a vital parameter that basically dictates many end-use properties of polymers, including dimensional stability, mechanical, optical and thermal properties [16-18]. For instance, the difference in density between crystalline and non-crystalline regions leads to different refractive indices. The heat resistance always increases with the improvement of crystallinity. Besides, many defects of the injection-molded articles (e.g., warpage, shrinkage, dimensional instability, etc.) are usually associated with crystallinity, primarily owing to the improper selection of processing variables. As a result, the acquisition of desired material performance could also be realized by regulating the crystallinity via the optimization of process parameters, such as, melt temperature, mold temperature, injection speed, holding pressure, etc. [19-21]. Besides, recent findings have shown that the mold temperature has a tremendous influence on the product life-time [22].

In light of the importance of crystallinity to polymeric materials, a lot of literature has been already presented on the simulation and experimental studies of the polymer crystallization process [23-31]. Among them, the Avrami Equation is a widely established relationship between crystallinity and crystallization time especially under quiescent isothermal crystallization conditions. On this basis, a number of mathematical models and modifications have also been proposed for non-isothermal crystallization circumstances [23, 27-29]. The theoretical analyses generally showed good agreement with their resultant experimental data. As is known, real processing conditions (e.g., extrusion, blow molding, injection molding, etc.) are considerably different from the quiescent crystallization investigations (either isothermal or non-isothermal) since the polymers are actually subject to the varying mechanical and thermal fields simultaneously. More importantly, the liberation of latent heat due to polymer crystallization could remarkably alter the in-cavity temperature fields [32]. Nevertheless, the correlation between solidification kinetics and polymer crystallization is still unclear up to now.

Based on our previous work [10, 33-37], the objective of the present study is to explore the effect of the initial temperature difference (ITD) and the secondary temperature difference (STD) on the solidification kinetics of HDPE, in an attempt to disclose the physical nature behind the phase-change heat conduction during injection molding process. Crystallization behaviors under different processing conditions were compared, with the degree of crystallinity obtained using the ETM coupled with the material P-V-T relationship [1, 8, 34]. The present work is of fundamental importance to the optimization of the process variables as well as the further investigation on the relationship among “processing-structure-property” of crystalline polymers.

2. Experimental

2.1. Material

The material used in present experiments was high-density polyethylene (HDPE), Model: 5000S, which was kindly supplied by the Daqing Petroleum Chemical Co., China, with a number-averaged molecular weight ($M_n$) of $5.30 \times 10^5$, and a melt flow rate (MFR) of 1.0 g/10 min (2.16 kg/190°C) according to ASTM D1238. Detailed material thermal parameters of HDPE had been presented elsewhere [10, 35].

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2.2. Rheological property characterization

Rheological behavior was examined using the melting index (MI) tester, Model: ZRZ-1452, provided by the SANS Instrument Co., China. The capillary diameter is 2.09 mm, with a capillary length of 8.0 mm. The logarithmic apparent viscosity (\( \eta_a \)) of the material used shows good linearity with the increase of the inverse absolute temperature (\( T^{-1} \)) under a constant load (2.16 kg) at various temperatures ranging from 150 to 230°C with an increment of 20°C, as demonstrated in figure 1. The melt flow activation energy (\( E_a \)) of the HDPE resin was 26.6 kJ/mol, evaluated using the Arrhenius Equation [38].

![Figure 1. Measured rheological curve of the HDPE resin used.](image)

2.3. In-cavity temperature measurement during IM process

IM experiments were carried out on a reciprocating screw precision injection-molding machine (Model: HYF-350, Haiying Plastic Machinery Manufacturing Co., China). The mold cavity utilized had its dimensions as follows: 175.0 mm in length, 12.0 mm in width, and 4.0 mm in thickness. The mold temperature was regulated through the use of circulating water. The injection time and packing time were 1.5 sec and 3.0 sec, respectively. Two armored copper-constantan micro-thermocouples (Model: TK-247, Anthone Electronics Co., China), with a 0.5 mm diameter sensor tip and measuring range from 35 to 350°C, were installed to monitor the temperature decays at specific positions. The insert depth of both thermocouples was adjustable so as to measure the in-cavity temperature profiles at different positions from the mold surface to the central plane of the cavity. The operation has been detailed in our previous studies [39]. The temperature changes throughout the injection molding cycles were recorded by a Keithley-2700 Data Acquisition System with a sampling time of 0.1 sec. In the present work, the injection molding experiments were conducted according to the processing conditions, as listed in table 1. For better comparison, four cooling conditions used in this study were denoted as Case A (\( T_0 = 190°C, T_w = 20°C \)), Case B (\( T_0 = 210°C, T_w = 40°C \)), Case C (\( T_0 = 210°C, T_w = 60°C \)) and Case D (\( T_0 = 230°C, T_w = 50°C \)), where \( T_0 \) and \( T_w \) represent the melt and mold temperatures, respectively.

| Processing parameters | Values                  |
|-----------------------|-------------------------|
| Melt temperature (°C) | 190, 210, 230           |
| Mold temperature (°C) | 20, 40, 50, 60          |
| Injection pressure (MPa) | 50.0                    |
| Packing pressure (MPa) | 35.0                    |
| Injection time (sec)  | 1.5                     |
| Packing time (sec)    | 3.0                     |
| Cooling time (sec)    | 120.0                   |
3. Results and discussion

Figure 2 shows the temperature profiles obtained via ETM through the part thickness under the processing conditions of Cases A-D from $\ln t = 0$ to $\ln t = 4$, where $t$ is the cooling time. Two horizontal imaginary lines of $T = 110^\circ C$ and $T = 120^\circ C$ were portrayed so as to indicate the region representing the mushy zone, which consists of both liquid and solid phases [33]. For simplicity, the thickness is presented in the form of normalized distance ($X$), which is defined as $X = x/b$ with $b$ denoting the reference length (i.e., $b = 2$ mm in the present work) [36]. It can be seen from the comparison among figures 2a-2d that the temperature at $X = 0$ (i.e., the position closest to the mold wall) falls sufficiently rapidly to the wall temperature ($T_w$) from the initial melt temperature ($T_0$), suggesting the existence of a large cooling rate. At a specific time, the cooling rate decreases gradually with the increasing $X$ from the mold wall surface. As compared with the outer parts of the injection-molded article, the inner parts maintain relatively high temperature. This could be due to the fact that the latent heat released during the melt crystallization could not be transferred away timely in the central area. The vertical distance between two neighboring curves at a specific location can be adopted to be an estimate of the cooling rate. For instance, at $X = 0.5$, the time when the temperature drops from $T_0$ to the range of mushy zone $T_1$ to $T_2$ [34, 39] (i.e., $T_1 = 115.1^\circ C$ and $T_2 = 118.2^\circ C$ for the present case), can be employed to compare the cooling rate under various cooling conditions. For brevity, ITD and STD were defined as $\text{ITD} = T_0 - T_w$ and $\text{STD} = T_f - T_w$, respectively, with the reference phase transition temperature ($T_f$) given by $T_f = (T_1 + T_2)/2$ [34, 36]. The values of both ITD and STD are presented in table 2. The cooling rate ($\phi$) was estimated in the following order: $\phi_{\text{Case A}} > \phi_{\text{Case B}} > \phi_{\text{Case D}} > \phi_{\text{Case C}}$, which is consistent with the consequence of STD [39]. Both Cases A and B have the same ITD of 170$^\circ C$ but $T_w$ of Case A < $T_w$ of Case B, which also indicated that mold temperature exerted greater influence on the controlling of the cooling rate [11, 33]. It was shown that at a given location, when $X < 0.4$, the cooling speed increased firstly and then decreased; while $X \geq 0.4$, the cooling speed increased continuously. At $X = 1.0$, it was not until $\ln t = 2$ that the temperature began to change, suggesting that it took some time for heat to be transferred out.

![Figure 2](image-url)  

**Figure 2.** Temperature profiles across the part thickness direction (evaluated via ETM) under various cooling conditions: (a) $T_0 = 190^\circ C$, $T_w = 20^\circ C$, (b) $T_0 = 210^\circ C$, $T_w = 40^\circ C$, (c) $T_0 = 210^\circ C$, $T_w = 60^\circ C$, (d) $T_0 = 210^\circ C$, $T_w = 80^\circ C$. 

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**Table 2.** Values of both ITD and STD for various cooling conditions.
$T_W=60^\circ$C and (d) $T_W=50^\circ$C.

Table 2. Comparison of ITD and STD values under various cooling conditions (unit: $^\circ$C).

| Temperature Difference | Case A | Case B | Case C | Case D |
|------------------------|--------|--------|--------|--------|
| ITD                    | 170.0  | 170.0  | 150.0  | 180.0  |
| STD                    | 96.7   | 76.7   | 56.7   | 66.7   |

For better comparison, the dimensionless temperature ($\theta$) was also introduced by $\theta=(T-T_W)/(T_0-T_W)$ [33, 37]. The phase transition occurred at $\theta=0.56$–0.58, 0.44–0.46, 0.50–0.52, 0.36–0.38, respectively, under various cooling conditions from Case A to Case D. Two horizontal lines (also given in dimensionless form) were depicted in figure 3 to distinguish the area that underwent the phase-transition process. It can be observed that no phase-transition platform was displayed at $X=0.1$ under Case C. The onset time when phase-change platform occurs at the locations of $X=0.1$ and $X=0.3$ ranks as, Case C < Case A < Case B < Case D, which is generally in accordance with the rank of ITD. At $X=0.3$, the length of phase-transition plateau ($L_{pc}$) ranks as $L_{pc}$ Case C < $L_{pc}$ Case B < $L_{pc}$ Case D < $L_{pc}$ Case A, which is different from our previous finding that $L_{pc}$ is merely indicated by STD [39]. It was thus suggested that $L_{pc}$ is more relevant to the initial melt temperature ($T_0$) instead of the STD. It is obvious that the closer to the center, the slower cooling rate (that is to say, the longer time the polymers stay within the crystallization temperature range $T_1$–$T_2$). The cooling rates at the occurrence of the phase-change transition are summarized in table 3. At $X=0.7$, the sequence of cooling rate is consistent with that of ITD, indicating that when $X > 0.4$ the influence of various factors (such as, shear force, mold temperature, etc.) tends to be stable. But at $X = 0.3$, Cases D and A are on the contrary, since Case A has relatively low mold temperature as compared to Case D, which also suggests that the mold temperature displays greater influence on the cooling rate [33].

Figure 3. Temperature traces with elapsed time under various cooling conditions: (a) $T_0=190^\circ$C, $T_W=20^\circ$C, (b) $T_0=210^\circ$C, $T_W=40^\circ$C, (c) $T_0=210^\circ$C, $T_W=60^\circ$C and (d) $T_0=230^\circ$C, $T_W=50^\circ$C.
### Table 3. Comparison of cooling rates at the occurrence of phase transition under various cooling conditions (unit: °C/s).

| Location | Cooling rate at the occurrence of phase transition |
|----------|---------------------------------------------------|
|          | Case A | Case B | Case C | Case D |
| X=0.3    | 1.35   | 1.04   | 2.84   | 0.65   |
| X=0.7    | 0.91   | 0.70   | 1.29   | 0.51   |

As can be seen in figure 4, the length of the phase transition ($L_{pc}$) close to the mold surface is much shorter than that far away from it. At all positions in the cavity, $L_{pc}$ ranks as $L_{pc}$ | Case A | $< L_{pc}$ | Case B | $< L_{pc}$ | Case D | $< L_{pc}$ | Case C, indicating that the cooling speed ranks as, Case A > Case B > Case D > Case C. That is to say, the larger the $L_{pc}$ value, the slower the cooling rate, which is consistent with the result from STD. In Case A, at $X = 0.4$–0.6, the $L_{pc}$ value approximately remains constant. Generally speaking, the length of phase transition platform tends to share similar value when $X \geq 0.4$, for instance, Case B: $X = 0.4$–0.7, Case C: $X = 0.5$–0.7, and Case D: $X = 0.6$–0.7.

**Figure 4.** Position dependence of the phase-change plateau length ($L_{pc}$).

**Figure 5.** Distribution of crystallinity ($\chi$) across the part thickness direction: (a) $T_0=190$ °C,
$T_W=20 \, ^\circ C$, (b) $T_0=210 \, ^\circ C$, $T_W=40 \, ^\circ C$, (c) $T_0=210 \, ^\circ C$, $T_W=60 \, ^\circ C$ and (d) $T_0=230 \, ^\circ C$, $T_W=50 \, ^\circ C$.

Figure 5 shows the variation of crystallinity ($\chi$) of injection-molded articles as a function of position. It should be mentioned that the degree of crystallinity ($\chi$) can be calculated by using the following equation:

$$
\chi = \frac{\rho_c}{\rho} \cdot \frac{\rho - \rho_a}{\rho_c - \rho_a} \times \frac{100\%}{\frac{V_a - V}{V_a - V_c}} \times 100\% \tag{1}
$$

where $\rho_c$ and $V_c$ are the density and specific volume of the crystalline phase, respectively; while $\rho_a$ and $V_a$ are the density and specific volume of the amorphous phase of polymers, respectively. According to literature [40], $\rho_c = 1.014 \, g/cm^3$, $\rho_a = 0.854 \, g/cm^3$, for HDPE. With the aid of the 2d-Tait equation (see the Appendix), the specific volume can be estimated when the temperature and pressure are known. Then, the crystallinity ($\chi$) can be readily calculated using equation (1).

The crystallinity of the polymer decreased from the mold surface to the core, as shown in figure 5. As the cooling time elapsed, the crystallinity of the polymer increased. The change of crystallinity at the central region was more obvious than that at the cortical region where the crystallinity hardly varied. Since there exist multi-scale structures as well as amorphous fractions within the macromolecules (unlike the ideal small molecular substances), polymer crystallization is quite difficult to achieve one hundred percent at all positions across the part thickness direction. In figure 6, the red curve is a master curve obtained via non-linear curve fitting technique, with the fitting curve being expressed as $t_{1/2}^{-1} = 0.0061 \cdot X^{-2.188}$. It can be readily seen that the experimental data under various cooling conditions have a relatively good fit to it. Since the value of $t_{1/2}^{-1}$ reflects the average crystallization rate [41, 42], the larger the value of $t_{1/2}^{-1}$, the greater the average crystallization rate of polymers. It can be seen that the crystallization rate considerably slows down with the decrease of cooling rate.

**Figure 6.** Position dependence of crystallization rate (as evaluated by $t_{1/2}^{-1}$).

Figure 7a suggests that the values of crystallinity at $\log t=0$ (namely, $\chi|_{\log t = 0}$) are quite similar under various cooling conditions for a given position (esp. in the inner locations). At $X = 0.1$, when $\log t = 0$, the crystallinity ranks as $\chi|_{\text{Case A}} > \chi|_{\text{Case B}} > \chi|_{\text{Case C}} > \chi|_{\text{Case D}}$, which could be primarily dictated by the melt temperature ($T_0$). Under different conditions, the evolution of crystallinity with time generally takes an "S" shape, which is also in accordance with the non-isothermal crystallization kinetic studies [23, 42, 43]. However, a remarkable distortion on the kinetic curves is observed roughly at $X = 80\%$, and the phenomenon could possibly be associated with the existence of shear flows during the melt post-filling stage. The start-stop time of phase transition can be readily acquired from the first derivation of the $\chi$ vs. $\log t$ curves. From the comparison, it can be concluded that the start time at $X=0.1$ is earlier than that at $X=0.3$ and $X=0.7$. At the position quite close to the mold surface, there exists large thermal gradient, which acts as the driving force of heat transfer [38], leading to the occurrence of phase transformation at the polymer/mold interface. Moreover, due to the thermal protection effect of the outer polymer (allowing for the poor thermal conductivity of...
polymers), the inner parts of the injection-molded article show relatively slower response to heat, thus these kinetic curves change slightly at the beginning of crystallization.

**Figure 7.** Evolution of relative crystallinity ($\chi$) as a function of cooling time under various processing conditions: (a) $T_0=190^\circ$C, $T_W=20^\circ$C, (b) $T_0=210^\circ$C, $T_W=40^\circ$C, (c) $T_0=210^\circ$C, $T_W=60^\circ$C and (d) $T_0=230^\circ$C, $T_W=50^\circ$C.

**Figure 8.** Variation of relative crystallinity ($\chi$) versus cooling time at various locations (a) $X=0.1$, (b) $X=0.3$, (c) $X=0.7$, and (d) comparison of crystallinity evolution with time between experimental and
calculated data at $X=0.5$ and $X=1.0$ (under Case D).

Figure 8 shows that under the four different cooling conditions, the crystallinity ($\chi$) ranks as $\chi_{\text{Case A}} > \chi_{\text{Case B}} > \chi_{\text{Case C}} > \chi_{\text{Case D}}$ at the beginning; while $\chi_{\text{Case A}} > \chi_{\text{Case B}} > \chi_{\text{Case D}} > \chi_{\text{Case C}}$ at the later stage of the IM cooling process. The exchange of sequence in crystallinity under Cases C and D can be explained by the crystallinity being primarily influenced by $T_0$ at the beginning (high $T_0$ is unfavorable to the crystal nucleus formation). Subsequently, the crystallinity shows the same trends with STD. The variation of crystallinity versus location ranks as, $\chi_{X=0.1} > \chi_{X=0.3} > \chi_{X=0.7}$, which indicates that the position close to the mold wall achieves higher crystallinity. Consistent with figure 7, the curve becomes complicated when the crystallinity is close to 80%, which might be caused by the effect of shear stress. When $\log t = 0$, an obvious degree of crystallinity ($\chi$) can be obtained only at $X=0.1$; while its value is close to zero at the locations of $X=0.3$ and $X=0.7$. Through the comparison among figures 8a-c, it is seen that there exists an induction time before the jump of crystallinity, the length of which depends heavily on the melt temperature, since the melt temperature is too high to form the crystal nucleus. Figure 8d shows the theoretical and experimental kinetic curves at $X=0.5$ and $X=1.0$ under Case D, where the trends of both experimental curves are generally in reasonable agreement with those obtained from theoretical prediction using the Avrami Equation. Anyway, investigation on quantitative relationship between crystallization kinetics and cooling rate is an ongoing subject in our group.

4. Conclusion
The work further explores the correlation between crystallization kinetics and thermal gradient field on the basis of our previous studies. It is found that the thickness $X = 0.4$ is a crucial position heavily influenced by the thermal conduction. When $X > 0.4$, the temperature decay tends to be stable, and the phase-change plateau lengths share quite similar values within a specific range (cf. figures 2 and 4). In addition, the crystallization rate, which is in proportion to the cooling rate, hardly changes after $X = 0.4$ (cf. figure 6). The crystallization rate is higher at the location close to the mold wall than that in the core region during the IM cooling process, primarily due to the temperature difference between the melt temperature and the mold temperature. At a later stage of melt cooling, the consequence in relative crystallinity is in agreement with that in STD (cf. figure 8). The present study is of practical significance to the optimization of cooling parameters and the further investigation on the correlation among “processing-structure-property” of polymers and their composites.

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Appendix
The P-V-T relation of polyethylene is presented as below:

$$V(T, P) = V_0(T) \cdot [1 - C_0 \cdot \ln(1 + \frac{P}{B(T)})] + V_i(T, P);$$

$$V_0(T) = b_{im} + b_{2m} \cdot (T - b_3); B(T) = b_{3m} \cdot \exp[-b_{4m} \cdot (T - b_5)]; V_i(T, P) = 0, T > T_i(P);$$

$$V_i(T, P) = b_{1s} + b_{2s} \cdot (T - b_3); B(T) = b_{3s} \cdot \exp[-b_{4s} \cdot (T - b_5)];$$

$$V_i(T, P) = b_{1s} \cdot \exp[b_{5s} \cdot (T - b_3) - b_3 \cdot P], T < T_i(P);$$

where $T_i(P) = b_3 + b_6 \cdot P$ and $C_0 = 0.0894$

The values of the material parameters are listed as follows: $b_{im}=0.001274$ m$^3$·kg$^{-1}$; $b_{1s}=0.0001075$ m$^3$·kg$^{-1}$; $b_{2m}=1.026 \times 10^{-6}$ m$^3$·kg$^{-1}$·K$^{-1}$; $b_{3s}=3.324 \times 10^7$ Pa; $b_{4m}=0.004941$ K$^{-1}$; $b_{5s}=2.46 \times 10^{-6}$ K$^{-1}$; $b_{6s}=414.5$ K; $b_{7s}=1.543 \times 10^{-7}$ K·Pa$^{-1}$; $b_{7s}=0.0001872$ m$^3$·kg$^{-1}$;
$b_8=0.05158 \text{ K}^{-1}$; $b_9=1.023 \times 10^{-8} \text{ Pa}$.

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