The Use of an *In-Situ* Measurement to Probe the Solidification Kinetics of Injection-Molded HDPE/PP Blends

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Abstract: The largest portion of an injection molding (IM) cycle is actually occupied by the melt cooling stage, which also significantly dictates many end-use properties of the final parts, especially for crystalline polymers which undergo both solidification and crystallization processes simultaneously. The solidification kinetics of HDPE/PP blends were investigated under injection molding conditions with the aid of an in-situ measurement of in-cavity temperature profiles throughout the IM process. The obtained experimental results were in good agreement with our previous theoretical predictions. The present study will be instructive to the optimization of processing variables, and supplies good insight into the formation of various crystalline structures in injection-molded articles.

Keywords: Solidification Kinetics, Crystallization, Injection Molding, Temperature Profile, Blend.

INTRODUCTION

The transient heat-transfer problems involving solidification or melting are also referred as the "moving-boundary problems" or "phase-change problems", which were initially raised by *J. Stefan* in early 1890s [1]. They are still of practical significance in modern industrial and engineering fields, e.g., the in-mold solidification of metal or polymer, the cooling of large masses, the freezing of food, and so forth. However, due to the very nature of non-linearity caused by the liquid/solid interface that is always moving with the latent heat liberated or absorbed, few exact closed-form solutions are currently available [2]. Thus, enormous solution methods (e.g., variational, nodal integral, boundary immobilization, enthalpy, etc.) were developed, among which the enthalpy transformation method (ETM) has recently proved an efficient method to treat the phase-change heat transfer issues of crystalline polymers [3-6].

Injection molding (IM), one of the most widely employed fabrication techniques for thermoplastic polymers, currently accounts for nearly one third of all plastics processed. During an IM cycle, the polymeric materials are subject to high pressure, high shear rate and high cooling rate, etc [7-9]. And all these factors will jointly dictate the final property distribution across the thickness of the injection-molded article [10, 11]. For crystalline polymers, crystallization always takes place during the solidification (i.e., melt cooling) stage, which generally affects both productivity and quality of the final products. With this respect, the optimization of the operational variables should also focus on the reduction of cooling time [12-14], which is of practical significance to the industrial injection-molded products, typically characterized by relatively large part thickness or shot volumes.

Polymer blend (also known as polymer mixture) is a member of a class of materials, in which at least two polymers are blended to create new materials with different physical properties. Polymer blends currently comprise 30~40 % of plastics products, and are increasingly employed in the design of novel materials primarily owing to the versatility in tailoring the end-use properties, improved biodegradability, as well as low investment costs in new materials design in comparison to copolymer solutions [8, 15, 16]. As compared to the blend systems containing amorphous components, the practical investigations on properties (esp. the crystallization and melting behavior, degree of crystallinity, solidification kinetics from melt of components) of those with crystalline components have received relatively less attention. Also, the understanding of the influence of blend compositions on the thermodynamic and kinetic quantities related to the crystallization process is still insufficient. High-density polyethylene (HDPE) and isotactic polypropylene (*i*PP) are both large volume commodity

polymers, and also crystallizable polymeric materials. It was reported that positive synergistic improvement in mechanical properties (e.g., modulus, ultimate tensile strength, heat distortion temperature, etc.) was observed for some blend compositions of HDPE/PP, which was found to be closely related to their thermal and pressure history during the processing operation [15, 16]. The further disclosure of the solidification phenomena and crystallization kinetics of HDPE/PP blend will surely be instructive to not only the theoretical research (e.g., the study of epitaxial crystallization in HDPE/PP blends under shear conditions), but also the engineering design in industrial applications (e.g., the selection of operational variables).

Different from small molecular substances, it is rather difficult for crystalline polymers to achieve 100 percent crystallinity. Besides, the polymer crystallization occurs within an extended temperature range [7, 16] (commonly known as "the crystallization temperature range"). Recent investigation suggests that the liberated latent heat during crystallization could result in an obvious increase in the melt temperature. Allowing for the variant factors that influence both morphologies and final properties simultaneously, to understand the global phenomenology involved during various stages of an IM process is obviously difficult [2, 13]. Thus, to investigate the solidification phenomena coupled with crystallization kinetics under processing conditions will be helpful to an improved understanding of the molecular orientation mechanism and microstructure evolution, as well as the further optimization of the pressure or thermal history during the IM process.

The usage of in-line and on-line techniques has currently turned out an effective way to investigate the solidification or crystallization phenomena during real processing operations, which offers deeper insight into the study on the structural development [9, 16, 17]. The experimental methods of in-mold transient temperature measurements are generally carried out *via* optical, infrared and ultrasound sensors or detection equipment [13]. It was found that the disappearance of the liquid

phase is mainly owing to the transient heat conduction through the thickness of the mold, and the difference in cooling rates is an important factor dictating the formation of various hierarchical structures in the injection-molded parts of crystalline polymers [18-20]. Nevertheless, studies on the transient heat transfer with phase-change effects (esp. for crystalline polymers or their blends) are still inadequate up to now.

On the basis of our previous work [3, 5, 13, 17], we further explored the solidification kinetics of HDPE/PP blends (with varying compositions) during IM process with the aid of an *in-situ* temperature measurement technique. The data on the cooling curves of crystalline polymers were also experimentally investigated and non-linearly fitted using a three-parameter model proposed recently. The obtained experimental results were in fair agreement with our previous studies. The present work is technologically significant to the optimization of processing variables, and supplies an insight into the formation of various crystalline structures in injection-molded polymer blends.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE, Model: 6098) used in the present study was obtained from *Qilu Petrochemical Co.*, with a weight-averaged molecular weight (M_w) of 5.63×10^5 kg/mol and polydispersity index (PDI) of 14.7. Isotactic polypropylene (*i*PP, Model: H-T022), was supplied by *Lanzhou Petrochemical Co.*, having a density of 0.910 g/cm^3, and a melt flow rate (MFR) of 2.5 g/10 min (2.16kg/230 °C). The thermophysical parameters of the HDPE and iPP used are presented in Table **1**.

Preparation of Polyolefin Blends

The PP/HDPE blends were prepared on a twin-screw extruder (Model: SJSH-30, *Nanjing Plastic & Rubber Machinery Co.*). The temperature profile from hopper to die was 145, 165, 190, 210 and 195 °C, respectively. Sample for rheological characterizations

Table 1: Material Thermophysical Parameters of HDPE (6098) and PP (H-T022)

Material code	k_s (W/m·°C)	C_p (J/m·°C)	α_s (m²/s)	T_f (°C)	n^a
6098	0.347	2.25×10^3	1.4×10^{-7}	116.4	0.581
H-T022	0.221	2.40×10^3	8.5×10^{-8}	88.0	0.670

[a]Determined by non-linearly fitting the *Carreau*-A model.

was prepared through compression molding it into a disc of 1.5 mm in thickness and 25 mm in diameter under 10 MPa at 190 °C.

In-Cavity Temperature Measurement During IM Process

Injection molding experiments were carried out on a reciprocating-screw precision injection molding machine (Model: HYF-350, *Haiying Plastic Machinery Co.*). A laboratory-built injection mold, with its dimensions of 160 mm in length, 12 mm in side width, was utilized. The mold temperature was regulated *via* circulating water. The injection time and packing time were set as 1.2 s and 3.0 s, respectively. Two armoring copper-constantan micro-thermocouples (Model: TK-235, *Anthone Electronics Co.*), with sensor tip of 0.7 mm in diameter, were instrumented into the cavity so as to monitor the temperature traces at specific positions (*cf*. Figure **1**). For the sake of simplicity, they were denoted as TC1 (in the middle of cavity) and TC2 (in the end of cavity, omitted in Figure **1**), respectively. TC1, whose insert depth was adjustable, was responsible for the in-cavity transient temperature measurements at different positions from the mold surface to the central plane of the cavity, with TC2 used as a reference. The temperature changes throughout the whole injection molding cycle were recorded by Keithley-2700 Data Acquisition System (DAS) with a sampling time of 0.1 s. In the present work, injection molding operations were performed using the process parameters as listed in Table **2**.
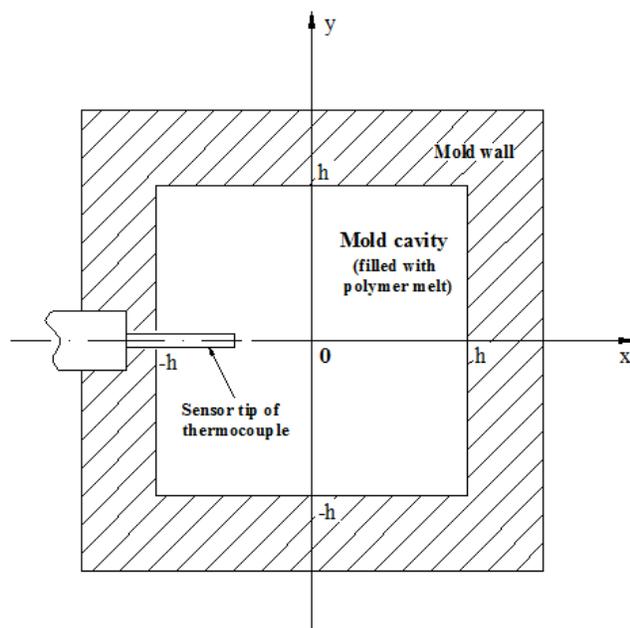
Figure 1: Schematic of the cross section of the experimental set-up (h=6 mm).

Table 2: Processing Variables Used in Injection Molding Experiments

Operational variables	Values
Melt temperature (°C)	220
Mold temperature (°C)	30
Injection speed (cm^3/s)	25
Injection pressure (MPa)	50
Injection time (s)	1.2
Packing time (s)	3.0
Cooling time (s)	120

RESULTS AND DISCUSSION

Figure **2** illustrates the temperature decay curves during the IM cooling stage of PP, HDPE as well as their blends. The cooling profile could be remarkably divided into three sections, i.e., the liquid, mushy as well as solid stages. It should also be mentioned that the temperatures had been normalized for better comparison, with the dimensionless form [3, 4, 13] defined as $\theta = (T-T_w)/(T_0-T_w)$ where T_0 and T_w are the initial melt temperature and the mold wall temperature, respectively. With this treatment, all cooling curves displayed an obvious phase-transition plateau (*ca.* θ = 0.44). Besides, with decreasing HDPE content, the onset of the phase-transition plateau was shifted to larger value, especially during the later stage of the solidification process.
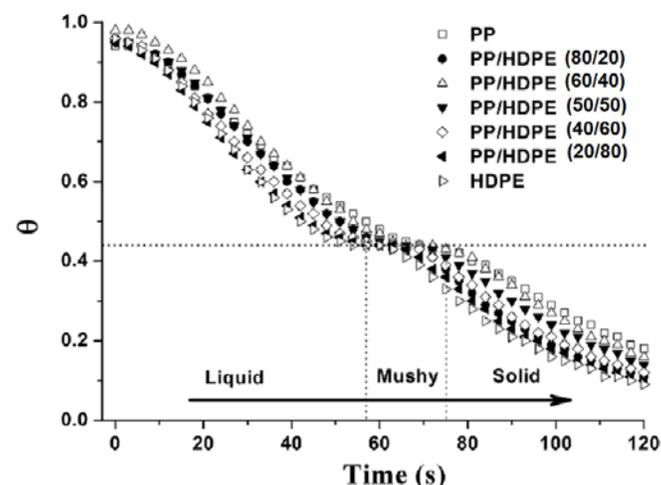
Figure 2: Evolution of dimensionless temperature (θ) versus cooling time of PP, HDPE and their blends.

Figure **3** presents the temperature and respective cooling rate (-dT/dt) as a function of cooling time. It can be seen that there existed a valley on the curve of cooling rate vs. time, which corresponded to the
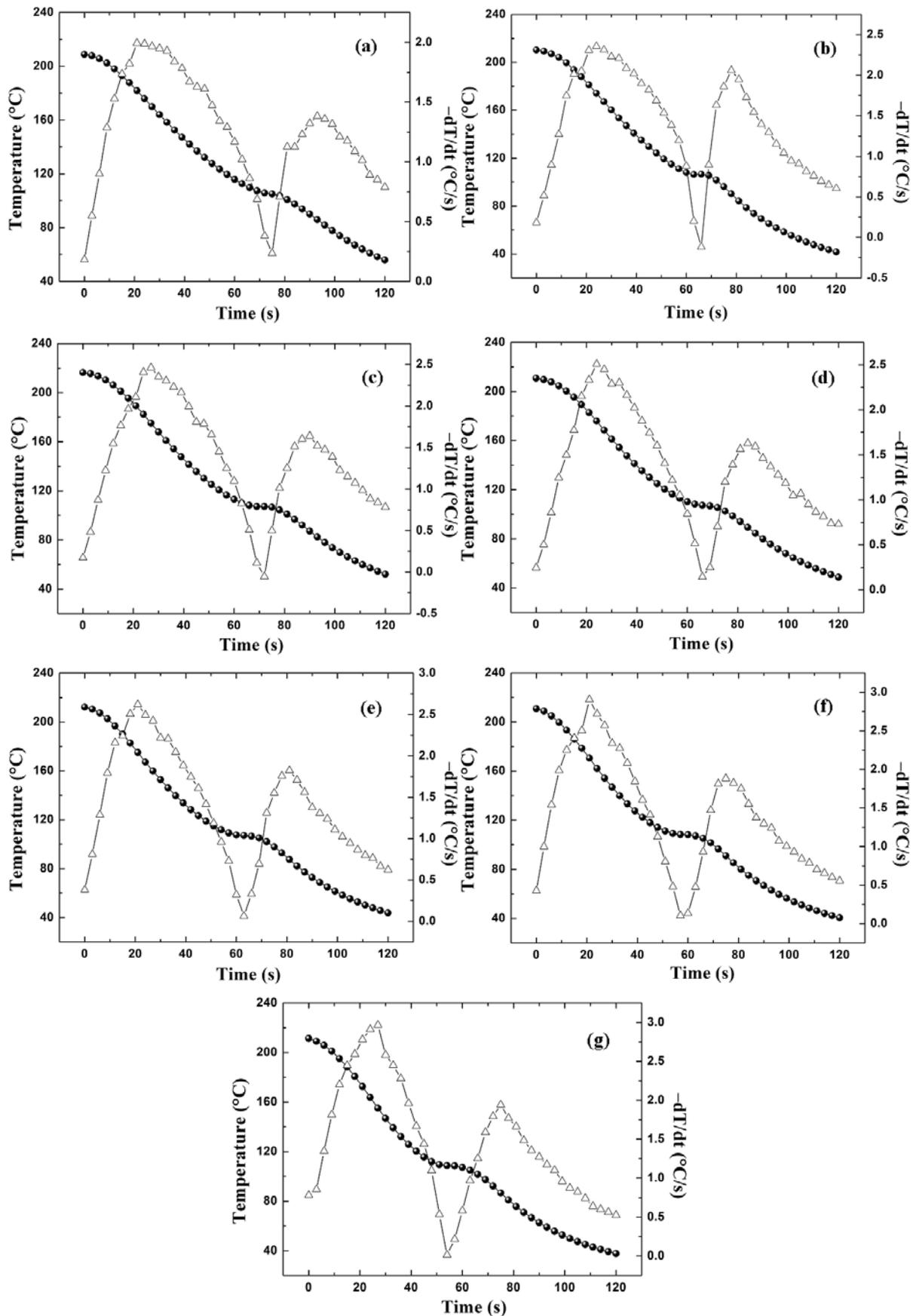
Figure 3: Correlation of cooling curves and associated cooling rate (-d*T*/d*t*) versus time: (**a**) PP; (**b**) PP/HDPE (80/20); (**c**) PP/HDPE (60/40); (**d**) PP/HDPE (50/50); (**e**) PP/HDPE (40/60); (**f**) PP/HDPE (20/80); (**g**) HDPE.
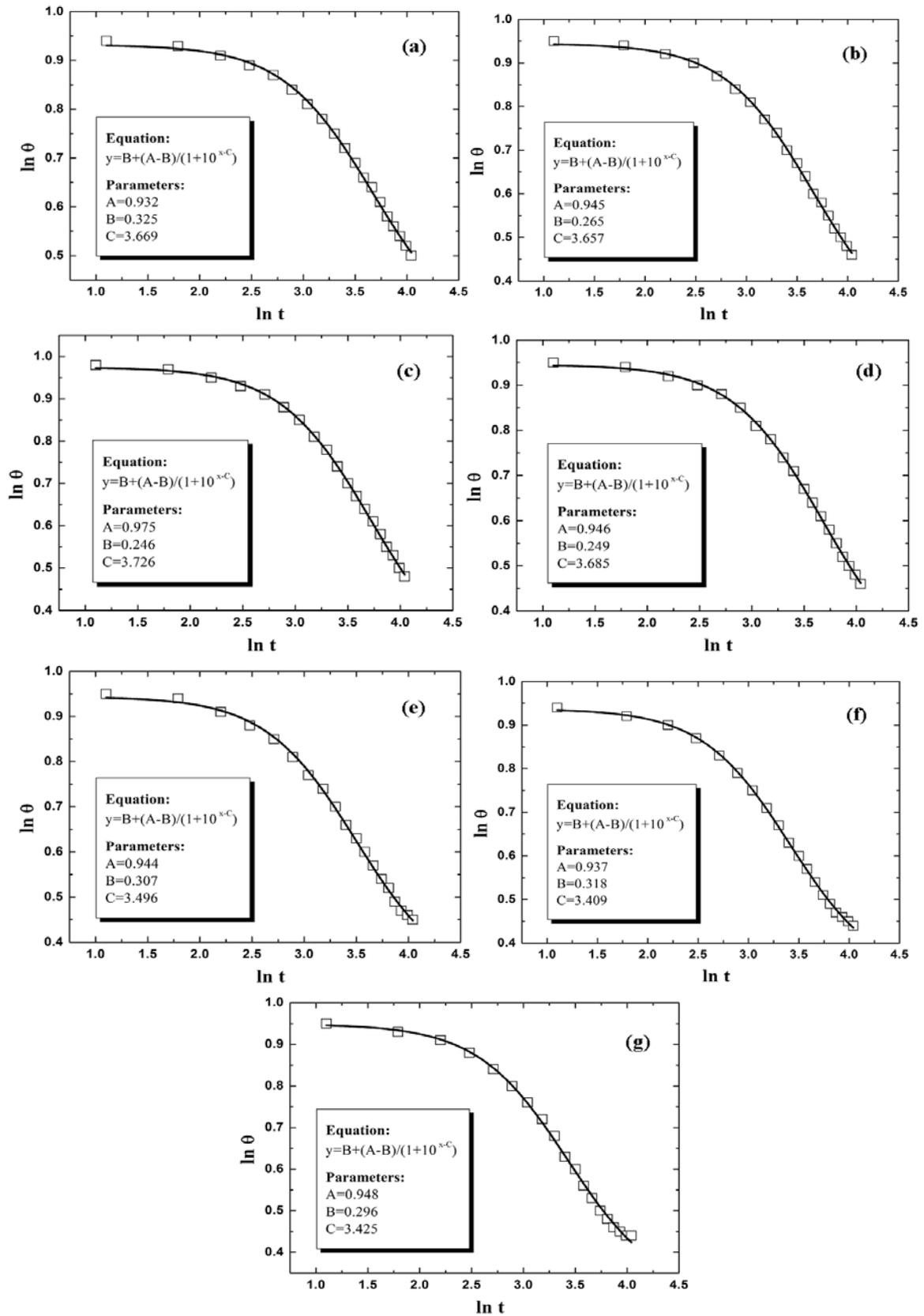
Figure 4: Non-linear curve fitting of experimental data using the three-parameter model: (**a**) PP; (**b**) PP/HDPE (80/20); (**c**) PP/HDPE (60/40); (**d**) PP/HDPE (50/50); (**e**) PP/HDPE (40/60); (**f**) PP/HDPE (20/80); (**g**) HDPE.

occurrence of phase transition. The valley value of each cooling curve was close to zero, but only on that point the cooling rate was the lowest, which was totally different from the situation of small molecules at the occurrence of phase transformation [5, 8, 15]. In addition, there were double peaks on each cooling curve, which was considered to be closely related to the maximum cooling rate during the liquid (melt) cooling and solid cooling stages, respectively. Besides, it was interesting that the time with respect to the second peak on the cooling curve was gradually shifted to larger value as the HDPE content was increased; while the time with respect to the first peak almost remained constant. Thus, the composition of the polyolefin blends apparently exerted more significant influence on the solid cooling stage than the melt cooling stage.

The double logarithmic plots of the dimensionless temperature (θ) versus the elapsed time (t) were presented in Figure **4**. It was readily seen that all materials displayed quite similar trend (also in agreement with the ETM prediction [6]), which could be non-linearly fitted using a three-parameter model [13] $y = B+(A-B)/(1+10^{x-C})$, with $x = ln\ t$ and $y = ln\ \theta$. Parameter A is primarily determined by the initial temperature (T_0). Parameter B is dictated by the mold temperature (T_w). And a small value of C always indicates shorter time for the melt to reach the extended phase-change temperature range [13].

Figure **5** demonstrates the variations of the parameters A, B and C with increasing HDPE content. It was obvious that A and B nearly remained a constant value ($A{\approx}0.95$ and $B{\approx}0.30$, respectively) when the HDPE content was varied. As for C, the situation was
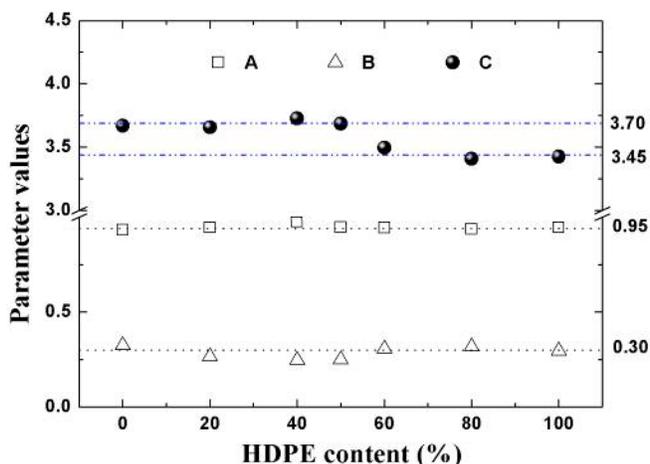
Figure 5: Variation of A, B and C as a function of HDPE content.

relatively complex: $C{\approx}3.70$ when HDPE% $\leq$ 50%; while $C{\approx}3.45$ with higher HDPE content. The varied value of C with HDPE content could be associated with the phase inversion occurring in the HDPE/iPP blends, which will be further investigated in our ongoing work.

CONCLUSION

In this article, we experimentally investigated the solidification kinetics of HDPE/PP blends with varying compositions during injection molding process using an in-situ temperature measurement technique. The experimental results fairly agreed with the theoretical predictions using the enthalpy transformation method (ETM) reported recently. However, a quantitative analysis of the correlation between shear-induced molecular orientation and thermal gradient is in progress. The present study will be crucial to the disclosure of physical nature behind the phase-change heat transfer during real processing operations, and will provide improved understanding of the formation mechanisms of various hierarchical structures in the injection-molded articles, as well as the forecast of cooling time of injection moldings for crystalline polymers.

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