

OVERSHOOTS IN STRESS AND FREE ENERGY CHANGE DURING THE FLOW-INDUCED CRYSTALLIZATION OF POLYMERIC MELT IN SHEAR FLOW*

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Abstract The effect of pre-shear flow on the subsequent crystallization process of polymeric melt was investigated and a flow-induced crystallization (FIC) model based on the conformation tensor incorporating the pre-shear effect was proposed. The model is capable of predicting the overshoot phenomena of the stress and the flow-induced free energy change of the polymeric system at high pre-shear rates. Under the condition of flow, the increase in the activated nuclei number was contributed by the flow-induced free energy change, which showed an overwhelming effect on the nuclei formation during the pre-shear process at high shear rates. The half crystallization time ($t_{1/2}$) of polypropylene (PP) as functions of pre-shear rate and pre-shear time at different crystallization temperatures was predicted and compared with the experiment data. Both numerical and experimental results showed that $t_{1/2}$ of PP decreased dramatically when the flow started but leveled off at long times. It was found that two transformation stages in $t_{1/2}$ existed within a wide range of shear rates. For the first stage where the melting polymer experienced a relatively weak shear flow, the acceleration of crystallization kinetics was mainly contributed by the steady value of free energy change while in the second stage for high shear rates, strong overshoot in flow-induced free energy change occurred and the crystallization kinetics was thus significantly enhanced. The overshoots in stress and flow-induced free energy change reflected an important role of flow on the primary nucleation especially when the flow was strong enough.

Keywords: Crystallization kinetics; Half crystallization time; Flow; Model; Conformation tensor.

INTRODUCTION

The crystallization behavior of thermoplastic polymers is strongly affected by processing conditions. For example, the degree of crystallization and the size of the resulting spherulites depend on both the temperature and the rate of temperature change^[1–3]. It is also well known that the applied flow may significantly enhance the crystallization kinetics and also produce highly oriented morphologies^[4, 5]. The molecular orientation induced by the flow is found to be positive to improve the mechanical properties of the polymer materials. The effect of flow on crystallization is often referred to as flow-induced crystallization (FIC).

It is known that the polymer crystallization evolves two typical stages: the formation of stable nuclei and the subsequent process of crystallite growth^[6]. The effect of flow on crystallization kinetics is mostly attributed to a significant nucleation process^[7]. Martins *et al.*^[8] reported that the formation of the ordered regions between

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entangled polymer chains would lead to higher activation energies for critically sheared melts, which might prefer to form nuclei precursors. In spite of the relative simplicity of the underlying physics, modeling of the FIC process turns out to be a formidable task, even though only the very basic problem of isothermal crystalline nucleation under flow is addressed.

To get insight of the FIC phenomenon, there have been considerable literatures concerning prediction of the crystallization kinetics in a flow field based on different theories. Among them, some different quantitative predictions are carried out within a similar framework: first, the adopted rheological constitutive equations, including Doi-Edwards^[9], Upper Convected Maxwell^[10], Leonov^[11], Single-mode PTT model^[12], or conformational tensor model^[13, 14], and second, the correlation between the rheological equation and the nucleation rate; for example, based on the Hamiltonian/Poisson Bracket formalism combined with the Avrami equation, Doufas *et al.*^[14] developed a continuum model to simulate FIC of polymer melts in homogeneous flow fields under isothermal conditions. This model predicted the crystallization kinetics as well as the rheological and rheo-optical behavior of semi-crystalline systems. However, Tanner^[15] expressed doubts about the stress calculation in Doufas *et al.*'s work. He proposed a suspension-based theory whereby "rigid" crystals were considered to be embedded in an amorphous matrix, and pointed out a more complex stress calculation. In addition, based on a Leonov model Zuidema *et al.*^[11] regarded the recoverable strain as the driving force for FIC. More recently, much attention has been paid to construct more accurate micro-rheological models to describe the FIC phenomenon. For example, based on the classical thermodynamic theory, Coppola *et al.*^[9] considered that the inner structure of polymer melts was changed by the flow, which denoted that the free energy difference between the crystalline and amorphous phase was also changed by the flow field. They thereby proposed a nucleation equation, in which the flow-induced change of free energy was introduced into nucleation process, and a good agreement between model predictions and experimental data was obtained. Later, Zheng and Kennedy^[16] proposed a model that coupled the Eder's flow-induced nuclei formation equation^[17] with the dumbbell free energy expression, and they successfully predicted the half crystallization time ($t_{1/2}$) of polypropylene (PP) under pre-shear flow. Although the values of the predicted $t_{1/2}$ were somewhat overestimated for shear rate higher than 10 s^{-1} and the reason that $t_{1/2}$ dropped down dramatically at the instant once upon shearing was not clear, a relatively good agreement between predictions and the experimental data was achieved.

The stress overshoot at the start of shear flow at sufficiently high shear rates is an important rheological phenomenon and has been noticed in many experiments and theories^[18–20]. Stress overshoot results in the shear stress increasing with time, passing through a maximum, and leveling off at long times. Doufas *et al.*^[14] captured a stress overshoot during the initial stages of the melt deformation and considered that the overshoot was a consequence of the nonlinear rheological behavior of the amorphous melt before the start of crystallization. Kumaraswamy *et al.*^[20] reported that the high shear stresses imposed on PP melt gave rise to the nonlinear overshoot phenomenon, which led to an acceleration of crystallization kinetics. Taking into account the relationship between the nucleation and viscoelastic response of polymer melts, it is necessary to interpret this stress overshoot phenomenon with a more precise rheological consideration.

In the present work, a rheological model with regard to the overshoot during FIC in polymer melts was employed under homogeneous flow in isothermal conditions, in which two relevant stages, nucleus generation and crystal growth, were coupled with the pre-shear treatment. This model was primarily concerned with the effects of flow on the nucleation process of polymer melts, in which some factors that evidently contributed to flow-enhanced crystallization such as shear rate, shearing time as well as the stress overshoot were investigated.

MODELS

Similar to many authors' work^[14, 21–23], the crystalline polymer system is treated as a two-phase system of amorphous and semi-crystalline phases. Based on the following assumptions, the rheologically FIC model is constructed.

- (1) The physical properties of the amorphous phase are independent of the crystallinity.
- (2) Once the activated nuclei form, they need a very long relaxation time to disappear, which means that the number of nuclei per unit volume almost does not change after the shear is stopped.
- (3) The crystallizing system is regarded as a suspension system with the semi-crystalline entities growing and spreading in the amorphous matrix.

Following previous work^[15, 16], the general nucleus generation N of the semi-crystalline polymer can be separated into two parts: the number of activated nuclei in the quiescent condition, denoted as N_q , and the number of activated nuclei induced by the flow, N_f , scilicet:

$$N = N_q + N_f \quad (1)$$

N_q can be expressed directly as^[24]

$$N_q = \exp(a \cdot \Delta T + b) \quad (2)$$

where ΔT is the temperature difference between the equilibrium melting temperature of the polymer melt and the experimental temperature, *i.e.*, the degree of supercooling, and a and b are two constants.

As for the influence of shearing on N_f , the same expression as Zheng and Kennedy's^[16] is used. This expression was previously proposed by Eder and Janeschitz-Kriegl^[17] and shown as follows:

$$\dot{N}_f + \frac{1}{\lambda_N} N_f = f \quad (3)$$

where λ_N is the temperature-dependent relaxation time and always possesses a large value, which corresponds to the second assumption as above mentioned. f is considered to be dependent on the flow variables as well as temperature, and is written as^[16]:

$$f(\Delta G_f, T) = C_0 \cdot k_b \cdot T \cdot \exp\left(-\frac{U^*}{R_g \cdot (T - T_\infty)}\right) \cdot \left\{ (\Delta G_q + \Delta G_f) \cdot \exp\left(-\frac{K_g}{T \cdot [(1 + \theta \cdot \Delta G_f) \cdot T_m^0 - T]}\right) - \Delta G_q \cdot \exp\left(-\frac{K_g}{T \cdot \Delta T}\right) \right\} \quad (4)$$

where C_0 is a coefficient involving the energetic and geometrical constants of the crystals. k_b is the Boltzmann constant. U^* is related to the activation energy of the supercooled liquid nucleus interface. R_g is the universal gas constant. $T_\infty = T_g - 30$, where T_g is glass transition temperature. K_g is a constant containing energetic and geometrical factors of the crystalline nucleus^[25]. ΔG_f is the free energy change of the polymeric system due to the pre-shear flow. The free energy change for the quiescent crystallization, ΔG_q , which accounts for the volumetric free energy difference between the liquid and crystalline phase, can be expressed to an approximation as^[9]

$$\Delta G_q = \Delta H_0 \cdot \Delta T / T_m^0 \quad (5)$$

where ΔH_0 is the latent heat of crystallization, T_m^0 represents the equilibrium melting temperature and in Eq. (4), $\theta = T_m^0 (\Delta H_0 \cdot \Delta T)$ ^[16].

The unknown variable, ΔG_f , corresponding to the flow-induced free energy change of polymeric melt before crystallization, is considered to be strongly related to the change of the inner molecular structure caused by the imposed macroscopic flow. Based on the concept of conformation tensor, the following equations are adopted to account for the effect of the inner structure change on the free energy of the liquid phase^[26, 27]:

$$\Delta G_f = \zeta G_c \left[\text{tr} \left(\frac{\delta - C}{2} \right)^2 \right] \quad (6)$$

where ζ is a constant, which is related to the material properties and is chosen as adjustable parameter in the calculation. The value of ζ ranges from 10 to 100. In the present work its value is *ca.* 82. G_c is the elastic

modulus of the material, δ is a unity tensor, and $\text{tr}(\cdot)$ represents the trace operator of a tensor. The phenomenological conformation tensor $\mathbf{C}$ is the internal structure tensor^[26, 27] and illustrated as:

$$\frac{\partial \mathbf{C}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{C} = \mathbf{C} \cdot \nabla \mathbf{u} + (\nabla \mathbf{u})^T \cdot \mathbf{C} - \frac{G_c}{\eta_0} (\mathbf{C} \cdot \mathbf{C} - \mathbf{C}) \quad (7)$$

where t is time; $\mathbf{u}$ is the velocity field; η_0 is the zero-shear viscosity; and superscript T denotes a tensor transpose. G_c is described as^[26–28]

$$G_c = G_0 \cdot h(\mathbf{C}) = \frac{G_0}{|\mathbf{C}|^{n+1}} \quad (8)$$

where G_0 is the shear modulus at rest, $h(\mathbf{C})$ is the damping function, and n is the flow index of the power-law model.

The stress tensor after the shear but before the crystallization can be derived from the calculation of the conformation tensor under flow^[26–28]:

$$\boldsymbol{\tau} = G_c \cdot (\mathbf{C} \cdot \mathbf{C} - \mathbf{C}) \quad (9)$$

Combining Eqs. (1)–(8), the evolution of the number of activated nuclei induced by the flow with time can be calculated. Then the volume fraction of the crystals, α_f changing with time during the isothermal crystallization process is obtained by Eq. (10) when impingement and swallowing are disregarded, which means that the nucleation rate does not depend on the volume fraction of the crystallized material^[15]:

$$\alpha_f = C_m \int_0^t \dot{N}(s) [G(T)(t-s)]^{m-1} ds \quad (10)$$

where $m = 3$ and $C_m = 4\pi/3$, corresponding to a three-dimensional growth of crystallites. $G(T)$ denotes the growth rate of spherulites, which will be discussed later.

Considering the pre-shear process, both the quiescent crystallization and FIC contribute to the degree of space filling. Therefore, the volume fraction of the crystals during and after shearing treatment is finally expressed as^[10]:

$$\alpha_f = C_m \pi G(T)^3 \left[N_q t^3 + \int_0^{t_s} \dot{N}(s)(t-s)^3 ds + N_f(t-t_s)^3 \right] \quad (11)$$

where t_s is the shearing time.

Furthermore, when the impingement of crystals is considered, we can get the relative crystallinity α according to the Avrami model^[29]:

$$\alpha = 1 - \exp(-\alpha_f) \quad (12)$$

Considering the short-term pre-shear treatments, the influence of pre-shear on the growth rate of spherulites $G(T)$ can be regardless^[10]. Therefore, according to the Hoffman-Lauritzen theory^[25], the following equation should be available for the pre-shear experiments:

$$G(T) = G_a \exp \left[-\frac{U^*}{R_g(T-T_\infty)} \right] \exp \left(\frac{-K_g}{T\Delta T} \right) \quad (13)$$

where G_a is a constant.

The variations of viscosity and relaxation time with temperature are modeled by using a temperature shifting function α_T :

$$\eta(T) = \eta(T_0)\alpha_T(T); \quad \lambda(T) = \lambda(T_0)\alpha_T(T) \quad (14)$$

where $\eta(T_0)$ and $\lambda(T_0)$ are the viscosity and the relaxation time at the reference temperature T_0 , respectively. For

the temperature shifting function α_T , an Arrhenius type equation is used:

$$\alpha_T(T) = \exp\left[\frac{E_a}{R_g}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (15)$$

where E_a/R_g is a constant.

RESULTS AND DISCUSSION

Typical Results of Model Prediction

To investigate the model predictions for the various FIC experiments of semi-crystalline polymer systems, the model proposed in the previous section was constructed numerically. The necessary parameters regarding the material properties and model variables were obtained from references^[10, 16] and summarized in Table 1, which corresponded to the crystallization process of typical semi-crystalline materials such as PP. The rheological parameters in Table 1 were determined through the dynamic rheological experiments^[10] and the crystallization parameters were obtained from thermal experiments by the calorimeter and Linkam shearing hot stage^[16].

Table 1. Typical material properties and model parameters (after refs. [10], [16])

Symbol	Unit	Value
G_0	Pa	8.98×10^4
ζ	—	82
λ_a	s (at T_0)	4×10^{-2}
η_0	Pa·s (at T_0)	3.42×10^3
T_0	K	476.15
G_a	m·s ⁻¹	2.83×10^2
K_g^*	K ²	5.50×10^5
U^*	J·mol ⁻¹	6.27×10^3
T_g	K	2.69×10^2
λ_N	s	10^6
C_0	J ⁻² ·s ⁻¹	5.06×10^{34}
K_b	J·K ⁻¹	1.38×10^{-23}
a	m ⁻³ ·K ⁻¹	1.56×10^{-1}
b	m ⁻³	1.51×10^1
ΔH_0	J·m ⁻³	1.44×10^8
T_m^0	K	483.15
R_g	J·mol ⁻¹ ·K ⁻¹	8.314
E_a/R_g	K	5.602×10^3

According to the above equations, the crystallization process of PP under pre-shear treatment could be estimated. At a given pre-shear rate, the conformation change of polymer melt could be solved according to Eqs. (7) and (8). The absolute values of flow-induced free energy change $|\Delta G_f|$ were then obtained based on Eq. (6). Here ζ was treated as an adjustable parameter with a value of 82. Combining with Eq. (5), f in the expression of nuclei formation equation (Eq. 3) was available. By solving Eq. (3), the time evolution of N_f was obtained. Finally, according to Eq. (11), the volume fraction of crystallization α_f during and after shear treatment could be calculated. α_f could be transformed into the relative crystallinity α of the semi-crystalline system through Eq. (12). Moreover, spherulite impingement was able to be taken into account by comparison of α_f and α .

In our FIC model, both the absolute values of flow-induced free energy change $|\Delta G_f|$ and macroscopic stress τ were considered to depend on the conformation tensor, *i.e.*, inner structure of polymer melts, but their dependences were different in comparison with Eq. (6) and Eq. (9). The time evolution of shear stress of the polymer melt during the pre-shear process is shown in Fig. 1. When the pre-shear rate was low enough ($< 3 \text{ s}^{-1}$), the shear stress transited from zero to a steady plateau smoothly and no overshoot in stress was observed.

Evident stress overshoots were observed when the shear rate increased to some critical value: obviously above 3 s^{-1} the stress growth in start-up of the shear flow exhibited a stress overshoot before a steady-state value was reached. The higher the shear rate was, the earlier the stress overshoot occurred and the larger the peak and steady values of the shear stress were. Such behavior predicted by the model is typical as the rheological response of a polymer melt when subjected to shear flow^[19, 30], consistent with the reported work^[18–20]. Figure 2 shows the predicted absolute value of flow-induced free energy change with the pre-shear time at different shear rates. The overshoot in $|\Delta G_f|$ was also evident for large shear rates ($> 3 \text{ s}^{-1}$), and with increasing shear rate the peak value of flow-induced free energy change $|\Delta G_f|^{\text{overshoot}}$ appeared at short shearing time, in the same way as the peak value of shear stress did in Fig. 1. However, taking into account the steady value of $|\Delta G_f|$ (denoted as $|\Delta G_f|^s$) at different shear rates, it was found that the values of $|\Delta G_f|^s$ were not so different when the imposed pre-shear rates were larger than a critical value of 5 s^{-1} comparing with those at lower shear rates. It indicated that $|\Delta G_f|^s$ after overshoot remained almost invariable if the pre-shear rates applied were high enough, which may be attributed to that the deformation or the degree of stretch of the polymer coils induced by flow was limited even though the shearing was strong^[26]. Based on the theory of Lauritzen and Hoffman^[31], Coppola and Grizzuti^[9] thought that the effect of the macroscopic flow on the free energy would lead to a change of nucleation rate ultimately. Therefore, the evolution of $|\Delta G_f|$ with shearing time reflected a great effect of shear on the formation of the activated nuclei and then the subsequent crystallization process.

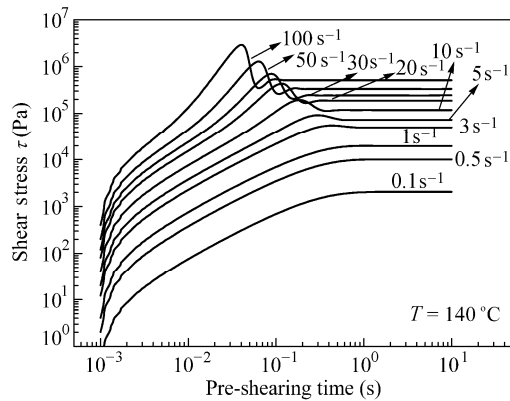


Fig. 1 Time evolution of shear stress during pre-shearing for the different shear rates at 140°C

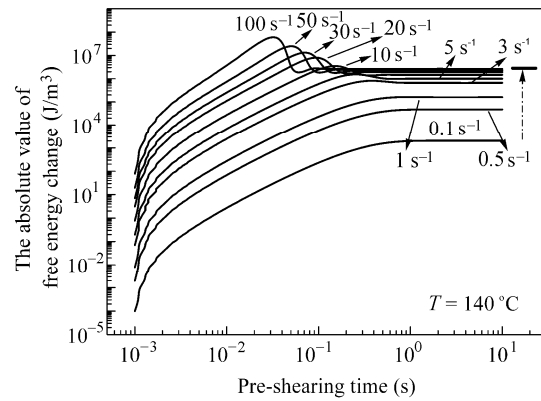


Fig. 2 Time evolution of the absolute value of flow induced free energy change for the different shear rates at 140°C

Shearing promotes the occurrence of nuclei^[7]. When higher shear rate is imposed, the larger number of nuclei is expected. As shown in Fig. 3, the final steady number of activated nuclei increased sharply with the pre-shear rate. Noting that all the values of N in Fig. 3 started from the same value, corresponding to the number of nuclei caused by super-cooling under the quiescent condition as described in Eq. (1), and the rise in N from the base line was undoubtedly caused by the effect of pre-shearing. In contrast with Fig. (2), two different kinds of effect of shearing or flow-induced free energy change on the nucleation process of the system could be found. First, $|\Delta G_f|^s$ was dominant for weak shearing without overshoot in stress or $|\Delta G_f|$. In the range of low shear rate below 3 s^{-1} , the number of activated nuclei increased with time smoothly and gently, consistent with the results in Figs. 1 and 2. Second, both $|\Delta G_f|^s$ and $|\Delta G_f|^{\text{overshoot}}$ co-dominated the nucleation process when the shear rate was larger than 3 s^{-1} . In this regime, a very sharp increase in the number of the activated nuclei resulting from the free energy overshoot was first observed, and a relatively gentle rise followed until the shearing was stopped

at 10 s, and then the number of the activated nuclei leveled off. The sharp increase in the nuclei number was due to the overshoot and the fact that once the activated nuclei formed, they needed a very long time to disappear. Especially, the overshoot would be overwhelming when the pre-shear rates were high enough (larger than 20 s^{-1}). In such cases $|\Delta G_f|^{\text{overshoot}}$ was much higher than $|\Delta G_f|^s$ (Fig. 2); the contribution of $|\Delta G_f|^s$ to the nuclei number was thus tiny. This could be further interpreted as shown in Fig. 4, the time evolution of nucleation rate for different pre-shear rates during pre-shearing for 10 s. The nucleation rate sharply increased with time at the start of shear flow, passed through a maximum, and leveled off at some time, after which the nucleation rate did not change. The degree of overshoot on the nucleation rate at high shear rates (larger than 20 s^{-1}) was much higher than those at low shear rates.

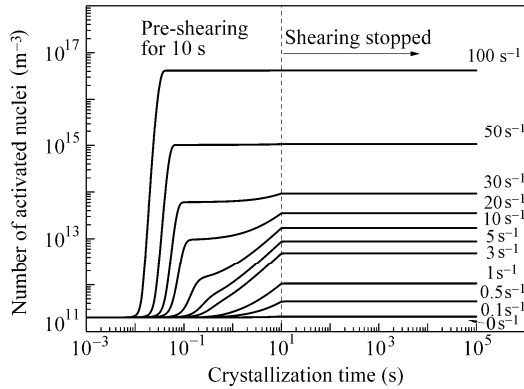


Fig. 3 Time evolution of activated nuclei for different pre-shear rates at 140°C (pre-shear time for 10 s)

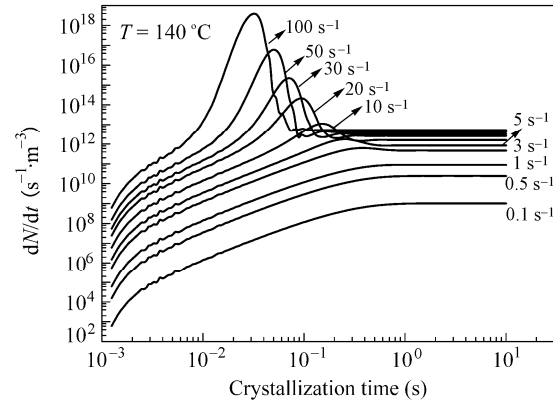


Fig. 4 Time evolution of nucleation rate for different pre-shear rates at 140°C during pre-shearing for 10 s

Comparison with Experimental

As a demonstrating example of our model, the crystallization kinetics of PP was focused and calculated. Here the half crystallization time $t_{1/2}$ was chosen as a key macroscopic experimental parameter to characterize the crystallization kinetics. The experimental data used in this work was obtained from Koscher and Fulchiron's work^[10], in which $t_{1/2}$ of PP was determined by averaging the experimental data measured through three different methods including DSC, rheometry, and microscopy. At the same time, numerically, the plot of $t_{1/2}$ versus shear rate was obtained by solving Eq. (12) in the case of $\alpha_f = \ln 2$ ^[10].

The model prediction of PP crystallization kinetics was shown in Fig. 5, in which the experimental data and the predictive curves by Zheng and Kennedy^[16] were also shown for comparison. Our predictive curves, $t_{1/2}$ versus pre-shear rate at different crystallization temperatures, showed a reasonable agreement with experimental data. Especially, it should be pointed out that two transition shear rates were observed in each curve, which was essentially different from Zheng and Kennedy's simulated results^[16] as well as that of Koscher and Fulchiron's^[10]. In Fig. 5, an evident decrease in $t_{1/2}$ was not observed until the shear rate increased up to *ca.* 0.3 s^{-1} , indicating that the effect of flow on crystallization kinetics was not significantly enhanced when the shear rate was too small. After passing the first transition shear rate, the $t_{1/2}$ decreased dramatically with increasing shear rate up to about 20 s^{-1} , *i.e.*, the second transition shear rate, indicating that the whole crystallization kinetic was enhanced remarkably under moderate shear flow. Above 20 s^{-1} , strong shearing gave rise to a further acceleration of crystallization kinetics. The reason for the existence of two transition shear rates may lie in the different nucleation rates in the two stages. According to Fig. 2, it was known that the flow-induced free energy change did not show overshoot when the shear flow was weak (shear rate $< 3 \text{ s}^{-1}$ in Fig. 2), or only show a weak overshoot for shear rates below 20 s^{-1} . For low shear rates, the maximum of the free energy change didn't show until the steady state was reached. In these cases, the number of activated nuclei was mainly determined by the magnitude of the steady value of the free energy change. However, when the shear rate was higher than 20 s^{-1} , there existed a maximum difference of free energy change between the peak and steady

values. The overshoot in $|\Delta G_f|$ thus became a decisive factor in primary nucleation. As abovementioned, the crystallization rate of PP was mainly determined by the number of activated nuclei, so the change of the nucleation rate would result in a variation of crystallization kinetics. Therefore, the overshoot in $|\Delta G_f|$ played an important role in second acceleration stage of crystallization kinetics. These results indicated the validity of the present FIC model which emphasized the effect of overshoot of the flow induced free energy change on the crystallization kinetics.

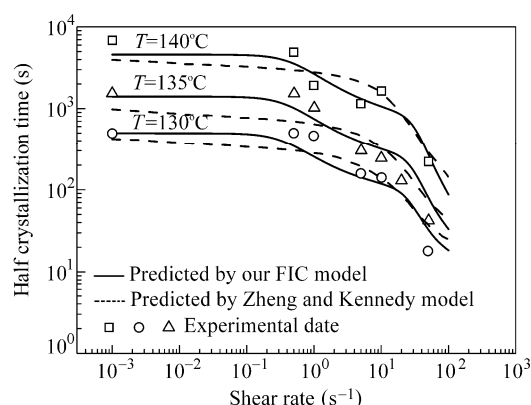


Fig. 5 The half crystallization time versus shear rate at different crystallization temperatures after 10 s pre-shear treatment in comparison with experimental data and Zheng and Kennedy's results^[16]

The effect of pre-shear time on the crystallization kinetics was shown in Fig. 6, in which the experimental data and the fitting curves by Zheng and Kennedy^[16] were also shown for comparison. Once upon shearing, $t_{1/2}$ dropped down dramatically. A further increase of the shearing time seemed to play a tiny role on the enhancement of the crystallization. By contrast, our prediction seemed to show a better agreement with the experimental data at both testing temperatures.

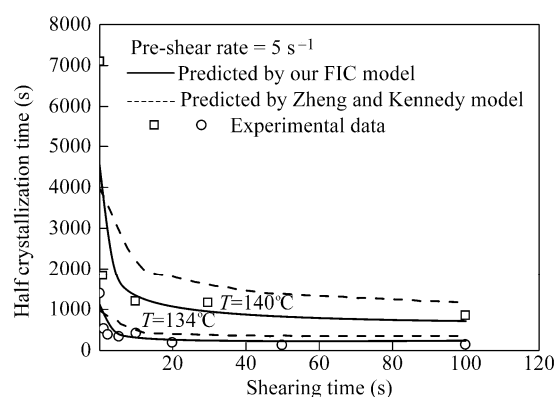


Fig. 6 The half crystallization time versus pre-shear time at different crystallization temperatures and a pre-shear rate of 5 s^{-1} and in comparison with experimental data and Zheng and Kennedy's results^[16]

To further elucidated the effect of pre-shear time on the crystallization kinetics, Fig. 7 illustrated the predicted relative crystallinity as a function of crystallization time at 140°C for different pre-shear times. The shear rate of 5 s^{-1} was chosen because the experimental data could be available only. In the case of applying shearing for 10 s, the crystallization time was shortened significantly compared with that without shearing. With increasing pre-shear time, the crystallization time decreased gradually. However, as the pre-shear time further increased, the difference between the relevant crystallization times trended to be negligible as seen for the cases

of shearing for 90 and 100 s. This predicted result was consistent with that in Fig. 6, in which the crystallization times were almost unchanged at long times. According to Martins *et al.*^[8, 30], the molecular chains in shear flow could not be fully stretched, and the nucleation density could not increase infinitely, therefore the crystallization must be saturated under some critical conditions. Kumaraswamy *et al.*'s work^[20] also indicated that shearing above a critical stress for a time longer than a critical value, would lead to a saturation of crystallization (limiting crystallization kinetics), and both the stress and strain could be considered as controlling factors for this saturation. By comparing the curves for pre-shear time of 90 and 100 s, the nucleation capability of PP could be considered to be saturated in such a strain range since the two curves for relative crystallinity were close. Figure 8 showed the number of activated nuclei per unit volume, N , as a function of crystallization time for different shear rates at 140°C. Comparing the number of activated nuclei after pre-shear treatments with shearing time of 90 and 100 s, it was also found that the numbers for the two cases were very close, again indicating that the nucleation capability of PP was saturated.

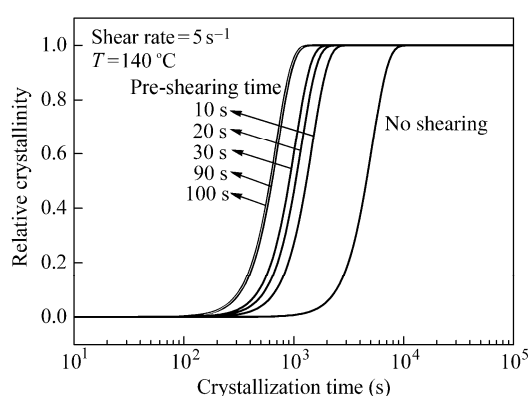


Fig. 7 Evolution of relative crystallinity with time at 140°C for different shearing time at a shear rate of 5 s^{-1}

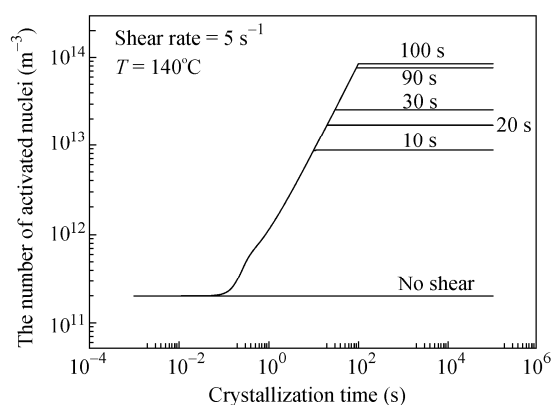


Fig. 8 Evolution of activated nuclei with time at 140°C for different shearing time at a shear rate of 5 s^{-1}

CONCLUSIONS

The present work dealt with the overshoot phenomena during flow-induced crystallization in polymer melts. The influences of overshoots in stress and in free energy change of the polymeric system induced by the pre-shear flow were discussed based on a FIC model. It was found that when the pre-shear rates were low enough, the shear stress and the flow-induced free energy change increased to a steady plateau without overshoots, whereas evident overshoot phenomena were observed for shear rates larger than some critical values. The higher the shear rate was, the earlier the overshoot occurred and the larger the peak and steady values of the shear stress and the flow-induced free energy change were. The flow-induced free energy change played an overwhelming role in the nucleation process during the pre-shear process when the shear flow was strong enough. The strong overshoot in flow-induced free energy change prompted the number of activated nuclei to reach the steady value much more rapidly. The acceleration of crystallization kinetics exhibited different features depending on the shear rate. The comparison of the predicted half crystallization time of PP with experimental data and other reported fitting data indicated the validity of the proposed FIC model.

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