International Journal of Chemical Engineering and Applications, Vol. 6, No. 1, February 2015

Phase-Field Simulation of Polymer Crystallization during Cooling Stage

Xiaodong Wang and Jie Ouyang

Abstract—**The phase-field method has been developed to simulate the crystal growth of semi-crystalline polymer during cooling stage by considering the effect of temperature on the nucleation density. It assumes that the nucleation mechanism is heterogeneous, and the relationship between the nucleation density and the temperature is described by an empirical function. The crystal growth after nucleation is modeled by a modified phase-field method which uses a non-conserved crystal order parameter to indicate whether the material is solid or liquid. By using the proposed model, the influence of cooling rate on the crystallization morphologies and crystallization kinetics has been investigated.**

Index Terms—**Polymer, crystallization, phase-field, cooling.**

I. INTRODUCTION

It is well known that polymer is one of the most important technical materials in our daily life. The cooling conditions imposed during polymer processing affect the crystallization morphologies of semi-crystalline polymers, thus determining the final properties of polymeric products. Therefore, the prediction of microstructure formation in semi-crystalline polymers during cooling stage is of great importance. For doing this, it is essential to establish an effective numerical model to predict the crystallization morphologies. The simulated results may supply theoretical basis for controlling or optimizing the fabrication procedures.

Earlier approaches to model the crystallization morphologies of semi-crystalline polymers during solidifications were discussed in detail by researchers. For instance, Micheletti and Burger [1] developed an efficient algorithm for simulating the stochastic birth-and-growth process of non-isothermal crystallization of polymers. They showed how non-isothermal crystallization can be simulated either by a stochastic or a deterministic approach. Raabe and Godara [2] studied the kinetics and topology of spherulite growth during crystallization of isotactic polypropylene (iPP) by using a three-dimensional cellular automaton model. The use of experimental input data for polypropylene was helpful for giving quantitative simulations. Huang and Kamal [3] proposed a physical model for multiple domain nucleation and growth, in order to perform cross-scale simulation on envelop profiles of the domain and the internal structure of spherulites. Ruan *et al.* [4] proposed a pixel coloring technique based on the Hoffman-Lauritzen theory to capture the crystallization morphology evolution and calculating the crystallization kinetics. According to coupling the temperature field, non-isothermal crystallizations of polymers with or without short fiber reinforced components were simulated.

Except the above mentioned approaches, the phase-field methods can also be used to model the crystallization morphologies of semi-crystalline polymers [5]-[9]. This kind of method has been successfully applied to simulate the polycrystalline growth of polymers and reveal the corresponding formation mechanisms under isothermal conditions. However, for the crystallizations under non-isothermal conditions, the phase-field methods have not yet been applied. In this paper, we are aim to develop a phase-field method to simulate the crystal growth of semi-crystalline polymers during cooling stage by considering the effect of temperature on the nucleation density.

II. THEORETICAL MODEL

A. Modeling of Nucleation

Nucleation is the first stage of polymer crystallization. It provides the template (nucleus) for further crystal growth. It starts with nanometer-sized areas where some chains or their segments occur parallel as a result of heat motion. Those seeds can either dissociate, if thermal motion destroys the molecular order, or grow further, if the grain size exceeds a certain critical value. The number of nuclei can be modeled by some empirical nucleation models in the cases of both heterogeneous nucleation and homogeneous nucleation [10], [11]. In this work, we assume that the nucleation mechanism is heterogeneous. The following equation reported in literature [10] is used to describe the relationship between the nucleation density and the temperature:

$$N(T) = N_0 \exp(\varphi(T_m^0 - T)), \tag{1}$$

where $N(T)$ is the temperature dependent nucleation density, T_m^0 is the equilibrium melting temperature, N_0 and φ are empirical parameters.

B. Modeling of Crystal Growth

According to our previous work [12], [13], the crystal growth of polymer can be modeled by a modified phase-field

---

Manuscript received May 31, 2014; revised July 7, 2014. This work was supported in part by supported by the National key Basic Research Program of China (973 Program) (No: 2012CB025903), the Northwestern Polytechnical University Foundation for Fundamental Research (JCY20130141), the Doctorate Foundation of Northwestern Polytechnical University (No: cx201019) and the Ministry of Education Fund for Doctoral Students Newcomer Awards of china.

X. D. Wang and J. Ouyang are with the Department of Applied Mathematics, Northwestern Polytechnical University, Xi’an, 710129, China (e-mail: xiaodongwang@nwpu.edu.cn, jieouyang@nwpu.edu.cn).

DOI: 10.7763/IJCEA.2015.V6.445

model, which uses a non-conserved crystal order parameter ψ to indicate whether the material is solid or liquid. In phase field modeling, the value of ψ is usually bound between 0 and 1, where 0 represents the melt and 1 the crystal at equilibrium. The temporal evolution of the crystal order parameter can be modeled by the following non-conserved phase-field equation:

$$\frac{\partial\psi(\mathbf{x},t)}{\partial t} = -\Gamma\frac{\delta F(\psi)}{\delta\psi(\mathbf{x},t)}, \qquad (2)$$

where $\psi(\mathbf{x},t)$ representing the crystal order parameter at time t and position $\mathbf{x}$. Γ is the mobility which is inversely proportional to the viscosity of the melt. $F(\psi)$ is the total free energy of the crystallizing system defined as

$$F(\psi) = \int[f_{local}(\psi) + f_{grad}(\psi)]dV, \qquad (3)$$

where the local free energy density $f_{local}(\psi)$ and nonlocal free energy density $f_{grad}(\psi)$ are

$$f_{local}(\psi,T) = W\left(\frac{\zeta\zeta_0}{2}\psi^2 - \frac{\zeta+\zeta_0}{3}\psi^3 + \frac{\psi^4}{4}\right), \quad (4)$$

and

$$f_{grad}(\psi) = \frac{1}{2}\kappa_0^2(\nabla\psi)^2, \qquad (5)$$

respectively. Here, ζ_0 and ζ correspond to the stable solidification potential and unstable energy barrier, W is a dimensionless coefficient describing the height of energy barrier for surface nucleation, κ_0 is the coefficient of interface gradient. Substituting equations (3)-(5) into equation (2), one obtains

$$\begin{aligned}\frac{\partial\psi(\mathbf{x},t)}{\partial t} &= -\Gamma\frac{\delta F(\psi)}{\delta\psi(\mathbf{x},t)} \\ &= -\Gamma\left(W\psi(\psi-\zeta)(\psi-\zeta_0) - \kappa_0^2\nabla\cdot(\nabla\psi)\right)\end{aligned} \qquad (6)$$

From references [5], [12], [13], the model parameters can be calculated by

$$\zeta_0 = \frac{T_m}{T_m^0}, \qquad (7)$$

$$\zeta = \frac{4\zeta_0\hat{\psi} - 3\hat{\psi}^2}{6\zeta_0 - 4\hat{\psi}}\left(1.0 + \frac{2.0}{\pi}\arctan\left(k\frac{T-T_m}{T_m-T_c}\right)\right), \quad (8)$$

(here $\hat{\psi} = \frac{T_m^0 - T_m}{T_m^0 - T}\zeta_0$)

$$W = 6\frac{\Delta H}{RT\zeta_0^3}\left(\frac{T_m - T}{T_m^0}\right)\left(\frac{\zeta_0}{2} - \zeta\right)^{-1}, \qquad (9)$$

$$\kappa_0 = 6\frac{\sigma}{nRT}\left(\frac{2}{W}\right)^{1/2}, \qquad (10)$$

where T_m is the supercooling-dependent melting temperature, T_c is the experimental temperature of crystallization, ΔH is the latent heat, R is the gas constant, σ is the surface free energy per unit area, and n is the amount of substance of polymer monomers per unit volume.

C. Computational Form

In computations, dimensionless form is usually considered to be more convenient for applications. In order to write the phase field equation (6) in dimensionless form, the temporal and spatial variables are rescaled to $\tau = Dt/d^2$, $\tilde{x} = x/d$, $\tilde{y} = y/d$. Here d is the characteristic length for single crystals, D is the diffusion coefficient. The mobility Γ can be estimated from d and D as $\Gamma = D/d^2$. With these dimensionless variables, the final governing equations can be represented in the following dimensionless form:

$$\frac{\partial\psi}{\partial\tau} = -\left(W\psi(\psi-\zeta)(\psi-\zeta_0) - \tilde{\kappa}_0^2\tilde{\nabla}\cdot\left(\tilde{\nabla}\psi\right)\right), \qquad (11)$$

where

$$\tilde{\nabla} = \left(\frac{\partial}{\partial\tilde{x}}, \frac{\partial}{\partial\tilde{y}}\right), \quad \tilde{\kappa}_0^2 = \frac{\kappa_0^2}{d^2}. \qquad (12)$$

III. RESULTS AND DISCUSSION

Simulations are carried out in two-dimension for the models presented above. The model parameters for nucleation are $N_0 = 1.74\times10^9/m^3$ and $\varphi = 0.155$ [10]. For crystal growth, the model parameters can be calculated using a set of material parameters of isotactic polystyrene (iPS) from references [12], [13]. According to these data, a set of model parameters are calculated and specified in Table I. In the simulations, a square lattice of size 512×512 is employed. The dimensionless temporal step size and spatial step size are chosen as $\Delta\tau=0.2$ and $\Delta x = \Delta y = 2.0$, respectively.

TABLE I: MODEL PARAMETERS OF IPS AT A GIVEN EXPERIMENTAL TEMPERATURE OF 200 ℃

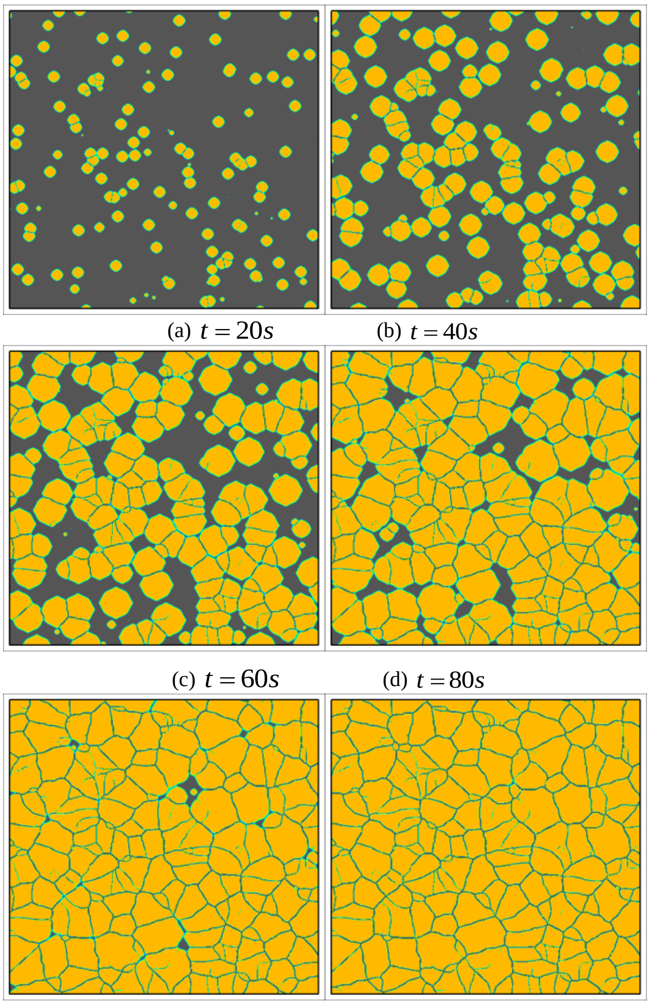
Symbol	Data set	Symbol	Data set
T_m^0	242^oC	ζ_0	0.95
T_m	230^oC	ζ	0.167
T_c	200^oC	W	15.43
Γ	10^5	$\tilde{\kappa}_0^2$	0.916

In this work, the material temperature is assumed to be uniformly reduced from T_m to T_c with a constant cooling rate c. That is the temperature at time instant t can be directly calculated by $T = T_m - ct$. In simulations, the initial data of ψ and T are prescribed as 0 and T_m, respectively. The simulations include repeating the following three steps before the temperature reaches to a given experimental temperature T_c and only the third step after the temperature reaches to T_c.

Step 1: calculate the temperature by $T = T_m - ct$.

Step 2: calculate the nucleus number by equation (1) and create new nuclei randomly in the material domain (ψ is prescribed as ζ_0 at nuclei).

Step 3: solve equation (11) over the rectangular material domain with homogeneous Neumann boundary conditions $\partial\psi/\partial\tau = 0$.


(a) $t = 20s$ (b) $t = 40s$

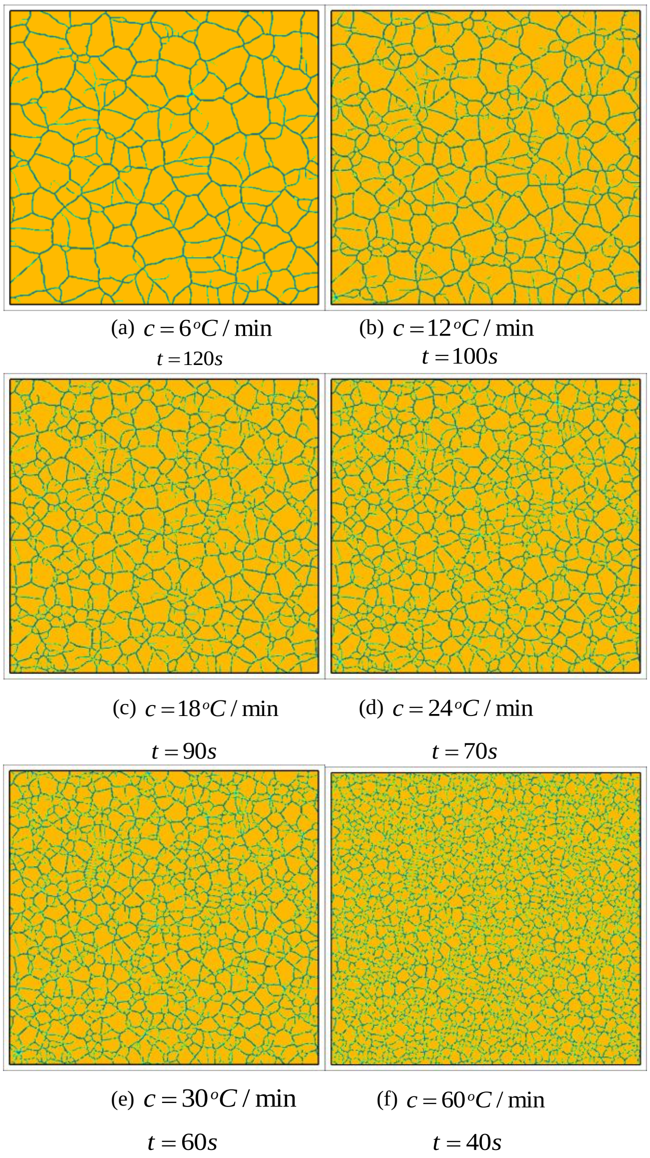
(c) $t = 60s$ (d) $t = 80s$

(e) $t = 100s$ (f) $t = 120s$

Fig. 1. Crystal growth with a constant cooling rate $c = 6^oC/\text{min}$.

Fig. 1 shows the simulated crystal growth with a constant cooling rate $c = 6^oC/\text{min}$. As can be seen, nucleation events take place successively as the temperature reduces. The shapes of the crystals are approximately spherical at the very early stage. As time elapses, the crystals impinge on their neighbors when they grow to certain sizes. Once the impingement occurs, the growth of the crystal in the impingement direction will be restricted. Thus, the crystals eventually exhibit polyhedral shapes, and neighbouring crystals are separated by curved grain boundaries.

Fig. 2 shows the crystalline morphologies with different cooling rates. It is obvious that the average size of the crystals is dependent on cooling rate. Generally, rapid cooling produces small crystals and slower cooling produces larger ones. What's more, the larger the cooling rate, the narrower the range of crystal size distribution. Besides, the growth rate increases as the cooling rate increases. This can be seen more clearly from Fig. 3. It is also illustrated that the crystallinity is a decreasing function of cooling rate.


(a) $c = 6^oC/\text{min}$ $t = 120s$ (b) $c = 12^oC/\text{min}$ $t = 100s$

(c) $c = 18^oC/\text{min}$ $t = 90s$ (d) $c = 24^oC/\text{min}$ $t = 70s$

(e) $c = 30^oC/\text{min}$ $t = 60s$ (f) $c = 60^oC/\text{min}$ $t = 40s$

Fig. 2. Crystalline morphologies of different cooling rates.

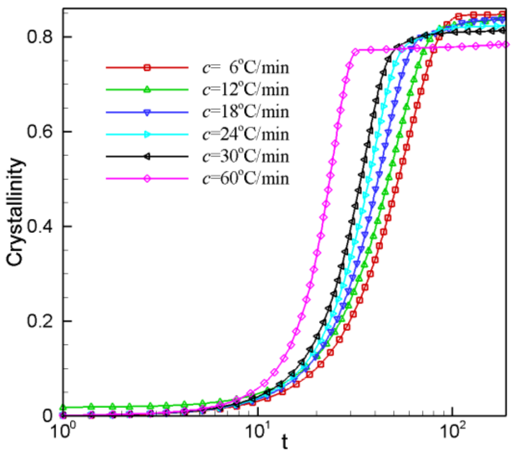


Fig. 3. Comparison of crystallinity with different cooling rates.

IV. CONCLUSION

In this work, we have extended the phase-field method to simulate the crystal growth of semi-crystalline polymer during cooling stage. The proposed model can be used to illustrate how the cooling rate at which the polymer cools affects the crystallization morphology. The simulation results showed that rapid cooling produces small crystals and slower cooling produces larger ones. Besides, the growth rate increases as the cooling rate increases. It is also illustrated that the crystallinity is a decreasing function of cooling rate.

REFERENCES

[1] A. Micheletti and M. Burger, "Stochastic and deterministic simulation of nonisothermal crystallization of polymers," *Journal of Mathematical Chemistry*, vol. 30, pp. 169-193, 2001.

[2] D. Raabe and A. Godara, "Mesoscale simulation of the kinetics and topology of spherulite growth during crystallization of isotactic polypropylene (iPP) by using a cellular automaton," *Modeling and Simulation in Materials Science and Engineering*, vol. 13, pp. 733-751, 2005.

[3] T. Huang and M. R. Kamal, "Morphological modeling of polymer solidification," *Polymer Engineering and Science*, vol. 40, pp. 1796-1808, 2000.

[4] C. L. Ruan, J. Ouyang, and S. Q. Liu, "Multi-scale modeling and simulation of crystallization during cooling in short fiber reinforced composites," *International Journal of Heat and Mass Transfer*, vol. 55, pp. 1911-1921, 2012.

[5] H. J. Xu, R. Matkar, and T. Kyu, "Phase-field modeling on morphological landscape of isotactic polystyrene single crystals," *Physical Review E*, vol. 72, p. 011804, 2005.

[6] M. Asanishi, T. Takaki, and Y. Tomita, "Polymer Spherulite Growth Simulation during Crystallization by phase-field method," in *Proc. AES – ATEMA' 2007 International Conference,* Montreal, Canada, 2007, pp. 195-203.

[7] L. Gránásy, T. Pusztai, D. Saylor, and J. A. Warren, "Phase field theory of heterogeneous crystal nucleation," *Physical Review Letters*, vol. 98, no. 3, p. 035703, 2007.

[8] D. Wang, T. F. Shi, J. Z. Chen, L. J. An, and Y. X. Jia, "Simulated morphological landscape of polymer single crystals by phase field mode," *Journal of Chemical Physics*, vol. 129, 194903, 2008.

[9] D. Wang, Z. K. Jin, Y. Xing, H. Gao and X. K. Wang, "Simulated rhythmic growth of targeted single crystal by polymer phase-field model," *Computational Materials Science*, vol. 68, pp. 23-26, 2013.

[10] R. Pantani, I. Coccorullo, V. Speranza, and G. Titomanlio, "Modeling of morphology evolution in the injection molding process of thermoplastic polymers," *Progress in Polymer Science*, vol. 30, pp. 1185-1222, 2005.

[11] R. Pantani, I. Coccorullo, V. Speranza, and G. Titomanlio, "Morphology evolution during injection molding: Effect of packing pressure," *Polymer*, vol. 48, pp. 2778-2790, 2007.

[12] X. D. Wang, J. Ouyang, J. Su, and W. Zhou, "Investigating the role of oriented nucleus in polymer shish-kebab crystal growth via phase-field method," *Journal of Chemical Physics*, vol. 140, p. 114102, 2014.

[13] X. D. Wang, J. Ouyang, J. Su, and W. Zhou, "A phase-field model for simulating various spherulite morphologies of semi-crystalline polymers," *Chinese Physics B*, vol. 22, p. 106103, 2013.

Xiaodong Wang was born in Shaanxi province, northwest of China in 1986. He received the B.S degree in computational mathematics in 2007, the M.S degree in applied mathematics in 2010, and the Ph.D degree in applied mathematics in 2014, all from Northwestern Polytechnical University (NPU), Xi'an, China. He is currently a lecturer with the Department of Applied Mathematics of NPU. His research interests include simulation of crystal growth, computational fluid mechanics, computational rheology and numerical methods for PDEs.