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Exact solution for the problem of segregation of polymer spherulites

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ABSTRACT

The problem of segregation for non-crystallizable species, as a mass transfer problem during isothermal crystallization, is considered with a suitable boundary condition for the semicrystalline polymeric materials. The velocity of the growth front of an isolated spherulite is considered to be depressed as a result of segregation during crystallization and it is assumed to be inversely proportional to the square root of time. A self-similar solution has been found and shows that the species concentration, at the growth front, increases with increasing the growth-to-diffusion ratio but it is independent on the time of crystallization. The segregated species concentration in the diffusion layer, near the growth front, increases with crystallization time, this is considered to be the reason of depressing the growth velocity with time.

KEYWORDS

Segregation;
Crystallization;
Polymer;
Exact solution.

INTRODUCTION

In polymer crystallization field, the segregation is a well known phenomenon associated with crystallization of a crystallizable component from a system which contains also, impurities, or non-crystallizable species. When crystallization occurs below the melting point of the crystalline component, the process involves two types of material transport, namely, diffusion of the crystallizable component toward the moving crystal growth front and a simultaneous rejection of the non-crysallizable species. The segregated species accumulate at the growth front during crystallization and cause a depression of both the equilibrium melting temperature and the overall crystallization velocity[1,2]. Also, the properties of the final solid of the polymer product would be influenced by the concentration of the non-crystallizable species in the spherulitic boundaries[3]. It is useful then is to find out the concentration of segregated species both on the melt near and at the moving growth front during the time of crystallization.

The diffusion problem was solved generally and applied to phase growth controlled by both (either) heat and (or) solute[4], but this sort of wok has rarely been extended to polymer field, only numerical solutions were applied on the binary polymer blends[5,6]. Analytically, the problem was treated only for non-polymeric materials. In a previous work[7], by a moving plane front of phase transition, an exact solution was found for a constant growth rate for a problem of gas segregation during solidification of liquid. In a more recent work[8], the gas segregation problem has been treated mathematically by using both of a plane and a spherical growth front for both constant growth and a rate inversely proportional to the square root of time.

In this paper, the diffusion equation for moving spherical solid/melt interface, with initial and suitable boundary conditions for semicrystalline spherulitic growth, has been solved exactly. The isothermal crystallization is considered for a polymeric system of a crystallizable component contains an initial concentration of non-crystallizable species. The problem is solved here for a spherical moving growth front with a rate inversely proportional to the square root of time. This solution can be applied on spherulitic crystallization of polymers[9,10] of similar radial growth rate, as a second stage succeeds a first stage of constant growth rate[10]. The concentration of the non-crystallizable species at the growth front is found to be dependent on the growth-to-diffusion ratio and independent on time of crystallization, but the concentration in the diffusion layer, near the growth front, increases with crystallization time.

THEORETICAL ANALYSIS

During isothermal crystallization, consider a certain polymer spherulite of radius R at a certain crystallization time, t, as presented in Figure 1. The spherical growth front, or solid/melt interface, is moving through the melt with a velocity, V. The melt has an initial non-crystallizable species concentration C_o. As a result of segregation during the crystallization, the non-crystallizable species concentration, in the melt, is then changed and becomes, C(r,t), which can be described by the following equation:

$$\frac{\partial C}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) \qquad (1)$$

The initial and boundary conditions can be assumed as:

$$C = C_o \quad \text{for} \quad t = 0$$

$$-D\frac{\partial C}{\partial r} = V\psi\, C \ \text{for}\ r = R \qquad (2)$$

$$C \rightarrow C_o \quad \text{for} \quad r \rightarrow \infty$$

Where D is the diffusion rate of the non-crystallizable segregated molecules through the melt and ψ is a factor represents the volume crystallinity at the growth front.

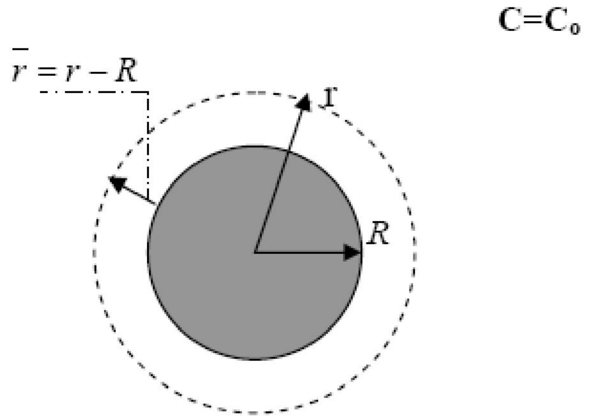

Figure 1 : Schematic diagram of the spherical growth front.

The factor ψ is inserted in the boundary condition because the crystallization front contains both of crystalline phase in the form of dominant lamellae and the interlamellar spacing of amorphous phase. It is assumed that crystalline lamellae are free from any non-crystallizable molecules. The interlamellar regions, at the growth front, have non-crysallizable species of concentration, C, the same as that in the melt at the growth front. This assumption is suitable for the semicrystalline polymeric material. We have to distinguish between the crystallinity at the growth front and the overall crystallinity after quenching. The later is quite higher because it includes, in addition to the first, the crystallization behind the growth front, which in the form of thickening and subsidiary lamellae, and crystallization during quenching. Simply, the factor $\psi = l_c/\,l_t$ where, l_c is the average dominant lamellar thickness and l_t is average distance between two neighbored dominant lamellae, both must be considered at the growth front.

Introducing the dimensionless concentration $\bar{C} = (C - C_o)/C_o$ and we can use the new coordinate system, $\bar{r} = r - R$ (Figure 1). The diffusion equation 1 can be rewritten as;

$$\frac{\partial \bar{C}}{\partial t} - V\frac{\partial \bar{C}}{\partial \bar{r}} = D\frac{1}{(\bar{r}+R)^2}\frac{\partial}{\partial \bar{r}}\left((\bar{r}+R)^2\frac{\partial \bar{C}}{\partial \bar{r}}\right) \qquad (3)$$

and the initial and boundary conditions are then:

$$\bar{C} = 0 \quad \text{for} \quad t = 0$$

$$-D\frac{\partial \bar{C}}{\partial \bar{r}} = \psi V(\bar{C}+1) \ \text{for}\ \bar{r} = 0 \qquad (4)$$

$\overline{C} \to 0 \quad \text{for} \quad \overline{r} \to \infty$

This problem has a self-similar solution, as the growth rate is inversely proportional to the square rote of time $V = K/\sqrt{t}$. This solution can be obtained by introducing the variable $\eta = \overline{r}/\sqrt{t}$. The diffusion equation can be reduced to the ordinary differential equation:

$$\frac{d^2\overline{C}}{d\eta^2} + \left[\frac{2}{\eta + 2K} + \frac{\eta + 2K}{2D}\right]\frac{d\overline{C}}{d\eta} = 0 \qquad (5)$$

The boundary conditions will be

$$-D\frac{d\overline{C}}{d\eta} = K\left(\overline{C} + 1\right)\psi \text{ at } \eta = 0 \qquad (6)$$

and $\overline{C} \to 0$ for $\eta \to \infty$

Using the variable $\gamma = \frac{\eta}{2\sqrt{D}} + k$, where $k = \frac{K}{\sqrt{D}}$. Substituting in equation 5 and rearranging, one can write the differential equation in the following form;

$$\frac{d^2\overline{C}}{d\eta^2} + \left[\frac{2}{\gamma} + 2\gamma\right]\frac{d\overline{C}}{d\eta} = 0 \qquad (7)$$

and the initial and the boundary conditions are:

$$\frac{d\overline{C}}{d\gamma} = -2k(\overline{C} + 1)\psi, \ \gamma = k \qquad (8)$$

and $\overline{C} \to 0$ for $\gamma \to \infty$

Integrating and substituting by the boundary condition, we can get the solution as

$$\overline{C} = \frac{f(\gamma)}{\frac{1}{\psi} - f(k)} \qquad (9)$$

The function $f(\gamma)$ is given as

$$f(\gamma) = 2k^2\left[k\frac{e^{k^2-\gamma^2}}{\gamma} - k\sqrt{\pi}e^{k^2}\operatorname{erfc}(\gamma)\right] \qquad (10)$$

From equation 9, if we put $\eta = 0$ or $\gamma = k$, the species concentration, $\overline{C}_f$ at the growth front is in the form

$$\overline{C}_f = \frac{f(k)}{\frac{1}{\psi} - f(k)} \qquad (11)$$

and the function $f(k)$ is given as:

$$f(k) = 2k^2\left[1 - k\sqrt{\pi}e^{k^2}\operatorname{erfc}(k)\right] \qquad (12)$$

RESULTS AND DISCUSSION

Figure 2 shows the species concentration in the melt at and near the growth front with different values of *k*. The parameter *k* can be considered as a suitable indication of growth-to-diffusion ratio, where, $k = K/\sqrt{D}$. For higher values of *k*, i.e. at relatively higher supercooling or relatively lower crystallization temperature, within certain limits of temperature range[1], a more increasing in species concentration is expected at the growth front.

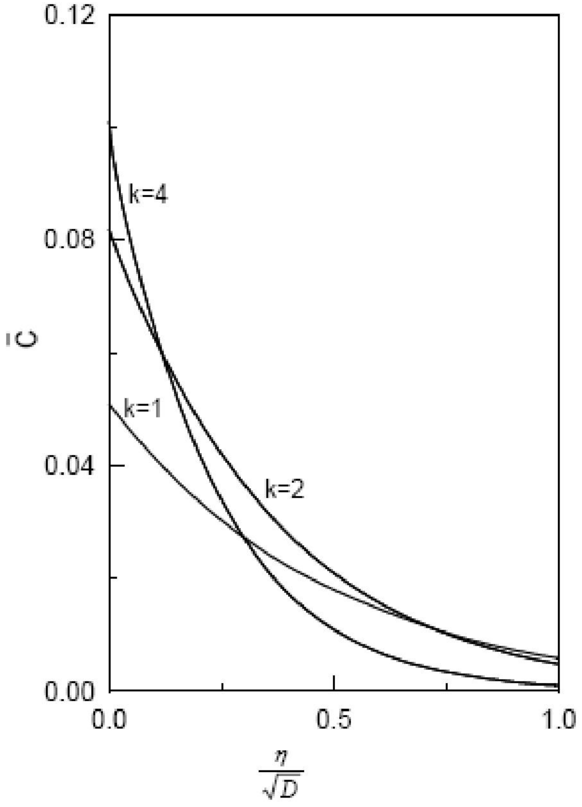

Figure 2 : The dimensionless concentration $\overline{C}$ of the non-crystallizable species versus $\eta/\sqrt{D}$ at different three values of the parameter k, $\psi = 0.1$.

The graphs of figure 3 show the species concentration in the melt at and near the growth front at different crystallization times. Here k is constant, the case of isothermal crystallization. The situation here according to equation 11, the species concentration at the growth front, $\overline{C}_f$ is instantly established and remains constant during the whole process. In fact our mathematical solution here satisfied a second stage of crystallization at which the growth velocity is inversely proportional to the square root of time. It is assumed that this stage follows a first stage, according to the previous works[9,10], at which the growth rate is constant and the species concentration increases to a specific value which may be near to that represented in figure 3. However, the concentration near the growth front, within a certain diffusion layer, increases with time (Figure 3). This may be depresses the equilibrium melting temperature[1,2] near the growth front, decreases the supercooling which can be considered the reason of depressing the crystallization rate from linearity at the first stage to inversely proportional to square root of time at the second stage.

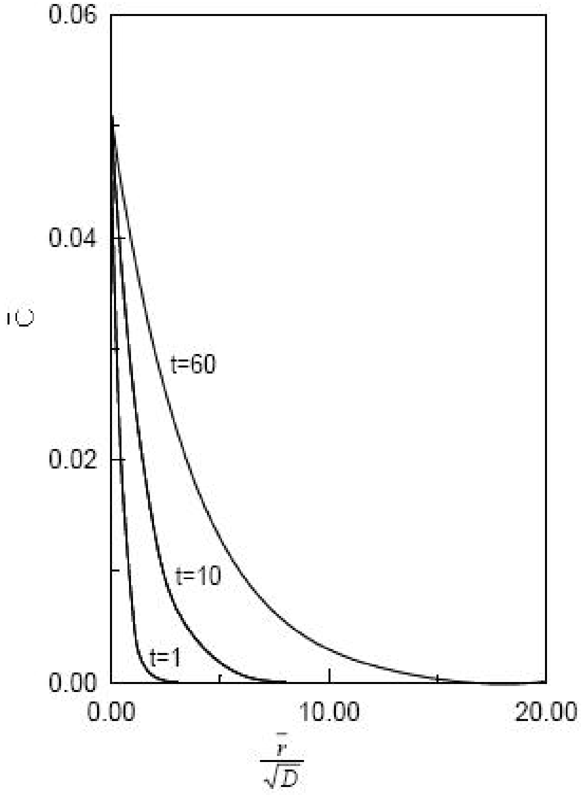

Figure 3 : The dimensionless concentration $\bar{C}$ of the non-crystallizable species versus $\bar{r}/\sqrt{D}$ at three different times, $k = 1, \psi = 0.1$.

It is also useful to find out the diffusion layer thickness δ which grows through the melt as the solid/melt interface grows. The diffusion layer thickness δ can be defined from the relation: $\bar{C}(t,\delta)/\bar{C}_f = 1/e$. Hence, using the equations 9-12 one can find;

$$\delta = \alpha\sqrt{Dt} \tag{13}$$

and the factor α can be determined from the following relation:

$$\frac{ke^{k^2-(\alpha/2+k)^2}/(\alpha/2+k)-\sqrt{\pi}ke^{k^2}\operatorname{erfc}(\alpha/2+k)}{1-\sqrt{\pi}ke^{k^2}\operatorname{ercf}(k)}=\frac{1}{e}$$

At large values of *k*, using asymptotic representation of the additional integral of errors, near the growth front we obtain:

$$\bar{C} \approx \bar{C}_f \exp\left(-\frac{\bar{r}}{\delta}\right) \text{ and } \delta = \frac{D}{V} \tag{14}$$

Equation 14 gives an approximate relation which gives the general behavior of the species diffusion, in consistent with the mostly known and interested work presented in the phenomenological theory of spherulitic crystallization[11].

This work is an attempt to formulate the segregation problem mathematically in polymer field. Although it does not give a complete view for the whole process but it describes and formulates a second stage of growth at which the interface velocity is inversely proportional to the square root of time. In fact, there are three mutually-interactive parameters, the species concentration at the growth front, the equilibrium melting temperature and the growth velocity. The constant growth rate can be obtained, for homopolymer, in isothermal crystallization according to Lauritzen-Hoffman theory[12]. This can not be observed for a system including sensible content of non-crystallizable species at segregation conditions. In these, the more expected is that the equilibrium melting point and the growth rate are depressed as a result of segregation[1,2]. Also, it is not expected, in this system, to find a constant species concentration unless steady-state conditions have been reached near the end of crystallization time at which a nearly constant growth rate can be observed[13]. A more complete view, as it can be suggested in future work, would cover the whole crystallization process smoothly and gives more proper interpretations on the relation between the three mutually-interactive parameters.

CONCLUSIONS

The problem of segregation for non-crystallizable species, as a mass transfer problem during isothermal crystallization, is considered with a suitable boundary condition for the semicrystalline polymeric materials. The growth velocity is taken as to be inversely proportional to the square root of time, the case at which a self-similar solution has been found. The species concentration, at the growth front, is found to be dependent on the growth-to-diffusion ratio and independent on time of crystallization. But the concentration in the diffusion layer, near the growth front, increases with the crystallization time. This increasing in concentration near the growth front can be considered the reason of depressing the growth velocity with time.

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