An Analytical Model for Spherulitic Growth in Fiber-Reinforced Polymers

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ABSTRACT: An analytical model for the isothermal crystallization of fiber reinforced polymers is presented. The model is based on approximate expressions for the volume of intersection between a sphere and cylinder. These expressions are used to account for the effect of the fibers on the overall crystallization process. Expressions for the average volume of spherulites truncated by the fibers are computed. The crystallization process is divided into time frames during which specific types of fiber truncations are encountered. Three different time sequences for the occurrence of the truncations are also derived according to the fiber volume fraction. The depressing effect of the fibers on the overall crystallization process is demonstrated with simple examples. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1677–1687, 1998

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INTRODUCTION

In polymer crystallization studies, it is generally observed that overall crystallization rates measured on bulk specimens are higher than those measured from thin films or fiber reinforced polymers. In these cases, the thinness of the film or the space occupied by the fibers, due to geometric considerations, reduce the overall rate of crystallization. Several studies were recently presented on the theoretical treatment of crystallization in thin films¹⁻⁴ and direct numerical simulations were performed to verify the models developed.¹⁻³ Similar numerical studies were performed on fiber-reinforced polymers but without the accompanying analytical studies. $^{5-8}$ It is therefore the purpose of this paper to present a theoretical treatment that explains the effect of the fibers on the overall crystallization rate.

Although we are concerned with fiber-reinforced polymers, it will be seen below that the main distinction between crystallization occurring in thin films, compared with crystallization in fiber-reinforced polymers, is due to geometrical considerations. A schematic representation of crystallization in fiber-reinforced polymers is shown in Figure 1. The top drawing of Figure 1 shows a crystallization process occurring in a composites with low fiber volume fraction. The bottom drawing of this figure shows a crystallization process occurring in a polymer with a high fiber volume fraction. The fibers are represented by large black circles. It is to be noted that the spherulites intersect frequently with the fibers and that the higher the fiber volume fraction, the more frequent the truncations (or intersections).

The objective of this work is to develop an analytical model for isothermal crystallization in semicrystalline polymer composites. An analytical model, when compared with a numerical model, has a number of advantages, namely ease

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Figure 1 Schematic representation of crystallization in fiber-reinforced polymers (a = fiber, b = spherulite, c = molten polymer); top schematic corresponds to a low-fiber volume fraction, bottom figure corresponds to high-fiber volume fraction.

of use, enhanced understanding of the phenomena, and rapidity in the computations. The method used for developing the model is based on the work of the group of Billon and associates^{1–3} and Escleine and coworkers.9 They extended and adapted to thin films the work of Evans¹⁰ and Avrami,^{11–13} and the same approach can be used to treat crystallization in fiber-reinforced polymers. Schultz⁴ also recently modified the constitutive equations in a different manner to account for the thinness of the polymer film, and the same technique can be also be adapted to treat fiberreinforced polymers. Presentation of the model begins with a brief review of the crystallization in neat polymers. The approach used in the model then follows.

GEOMETRICAL APPROACH BASED ON AVRAMI'S THEORY

During crystallization, at time t, the volume fraction of spherulites growing from a uniform distribution of potential nuclei is given by

$$\alpha(t) = 1 - \exp[-\alpha'(t)] \tag{1}$$

where $\alpha'(t)$ is the "extended" volume fraction. The concept of extended volume was introduced by Avrami.¹¹⁻¹³ It corresponds to the volume occupied by spherulites as if they grew unconstrained by each other, i.e., without impingement. It also implies that nuclei can be activated in already transformed regions (the so-called "phantom" nuclei). The model of Avrami given in eq. (1) relates crystallization in a real system, where impingement occurs, to the growth of hypothetical spherulites growing freely without impingement. To compute the actual crystallization rate, it is required to know only the nucleation and growth characteristics of the spherulites of a particular polymer system. The extended volume fraction can then be expressed as

$$\alpha'(t) = \int_0^t \dot{\eta}(\tau) \upsilon'(t, \tau) \ d\tau \tag{2}$$

which is simply the integral of the rate at which potential nuclei are activated at time τ multiplied by their volume at time t.

Computation of the Extended Volume for Neat Polymers

A brief review of well-known expressions used for describing crystallization in polymers is presented below. As mentioned above, the extended volume concept corresponds to spherulites that grow without constraints. In order to compute the actual crystallization rate, nucleation and growth characteristics of a polymer must be specified.

Under isothermal conditions, the growth rate of the spherulites has been found to be constant and the radius of a spherulite varies linearly with time for several systems,¹⁴ i.e., $R(t) = G_o t$. Finding an appropriate nucleation law is more problematic, as nucleation can be homogeneous, heterogeneous, or a mixture of both. Nucleation is also characterized as being thermal or athermal. Homogeneous nucleation is directly linked to thermal nucleation. Het-

erogeneous nucleation, however, can be of either form, thermal or a thermal. $^{\rm 15}$

Avrami¹² presented an expression that allows description of the nucleation process in a general manner. This expression, which provides the number of potential nuclei per unit volume at a given time, is given by

$$N(t) = N_o \exp(-qt) \tag{3}$$

where N_o is the initial number of potential nuclei per unit volume and q is their activation frequency. It is assumed here that the number of nuclei activated decreases with time.

Equation (3) can be used to model an instantaneous nucleation process (often associated with heterogeneous nucleation) if q tends to infinity, as well as a homogeneous nucleation process if N_o is large and q is small. With eq. (3), the extended volume for an unfilled polymer is given by

$$\alpha'(t) = qN_o \int_0^t v'(t, \tau) \exp[-q\tau] d\tau \qquad (4)$$

where $v'(t, \tau)$ is the volume (without impingement) at time *t* for a spherulite that nucleated at time τ . Under isothermal conditions, $v'(t, \tau)$, is simply

$$v'(t, \tau) = \frac{4\pi}{3} G_o^3 (t-\tau)^3$$
 (5)

and substituting eq. (5) into eq. (4) gives the well-known expression

$$\begin{aligned} \alpha'(t) &= \frac{8N_o \pi G_o^3}{q^3} \left(\exp(-qt) - 1 \right. \\ &+ qt - \frac{-q^2 t^2}{2} + \frac{q^3 t^3}{6} \right) \end{aligned} \tag{6}$$

However, if homogeneous nucleation is suspected to occur, it is simpler to model the process with the expression

$$\dot{n}(t) = N_o \tag{7}$$

where N_o is then the steady nucleation rate. The extended volume is then given by

$$\alpha'(t) = N_o \int_0^t v'(t, \tau) \ d\tau = \frac{N_o \pi G_o^3 t^4}{3} \qquad (8)$$

If heterogeneous nucleation is the dominant factor, a delta function can be used to represent the nucleation rate, i.e.,

$$\dot{n}(\tau) = N_o \delta(\tau) \tag{9}$$

where N_o is the total number of nuclei. The extended volume is then given by

$$\alpha'(t) = N_o \int_0^t \delta(\tau) \upsilon'(t-\tau) \ d\tau \tag{10}$$

or

$$\alpha'(t) = N_o \upsilon'(t) = \frac{4\pi N_o G_o^3 t^3}{3}$$
(11)

for instantaneous nucleation. An induction time period can also be introduced and it then suffices to use $\delta(t - t_i)$, where t_i is the induction time period.

CRYSTALLIZATION RESTRICTED BY FIBERS

In calculating the overall crystallization rate of a volume limited by fibers we can use Avrami's equation, and the average volume fraction occupied by the spherulites must be known. The average volume must consider the interactions between the fibers and the growing spherulites, i.e., it must account for the truncations caused by the presence of fibers in the melt because they reduce the overall crystallization rate by intersecting with the spherulites. The crystallinity computed for an infinite volume must therefore be modified in order to account for the various geometrical effects. If the fibers are approximated as infinitely long cylinders, it is possible to correct the extended volume and account for their effect on the crystallization process.

Volume of Intersection Between a Cylinder and a Sphere

Finding an analytical expression for the volume of intersection for a cylinder with a sphere at an arbitrary distance from each other in three dimensions is not a trivial problem. An exact expression, valid in all cases, was presented only a few years ago by Lamarche and Leroy¹⁶ and involves the three standard elliptic integrals. Approximate expressions were also presented earlier by Gosset and colleagues.¹⁷ The approximate and exact solutions are presented as a function of b, the distance between the axis of the cylinder and the center of a sphere. They also involve R_{f} , the radius of the fiber, and R_s , the radius of the spherulite. Both the exact and approximate expressions are discussed below.

Exact Solution

The exact solution for the volume of a sphere intersecting with a cylinder is presented for nine possible cases in ref. 16. These nine cases are summarized with

$$(b < R_{\it f}, \ b = R_{\it f}, \ b > R_{\it f}) \cap (R_{\it s} < b + R_{\it f}, \ R_{\it s} = b + R_{\it f}, \ R_{\it s} > b + R_{\it f})$$

Of these nine cases, six are of interest in this work. Three correspond to spherulites nucleating on the fiber surface and three correspond to nucleation in the melt surrounding the fiber. The exact mathematical expressions for the volume of intersection are not reproduced here for the sake of brevity but can be found in ref. 16.

Approximate Expressions

Approximate expressions are also available for computing the modified extended volume if it is assumed that no nucleation occurs on the fiber itself. The expressions presented in ref. 17 are for the following three cases:

- 1. A cylindrical hole of radius R_f is gouged by the fiber in the spherulite of radius $R_s(2R_f)$ $< R_{\circ}$).
- 2. A cylindrical channel is gouged by the fiber
- in the spherulite $(R_f < R_s)$. 3. A cylindrical channel of radius R_f is gouged in the spherulite of radius $R_s(R_f > R_s)$.

Cases 2 and 3 are both associated with a cylindrical channel. Different expressions must be used according to the size of the fiber radius with respect to the spherulite radius. The three cases are illustrated in Figure 2.

For each of the three cases considered, the volume of intersection can be approximated by ref. 17.



Figure 2 Three cases of interest in the interactions between spherulites and a fiber. Cases 1, 2, and 3 correspond respectively to a cylindrical hole, a cylindrical channel, and no fiber truncation.

$$\begin{split} V_3^i &= \frac{3}{4} (1-\nu)^{1/2} \left(\frac{1-\beta}{\nu}\right)^2 - \frac{1}{8} \\ &\times [3(1-\nu)^{1/2} - 1] \left(\frac{1-\beta}{\nu}\right)^3 \end{split}$$

where μ equals R_f/R_s , ν equals $R_s/(R_f + R_s)$, and β equals $b/(R_f + R_s)$. V_1^i , V_2^i and V_3^i are all normalized with respect to $\frac{4}{3}\pi R_s^3$. The superscript *i* is used to indicate that these expressions are for the volumes of intersection. The normalized volume of a sphere is then given by $1 - V_k$ (k = 1, 2, 3).

The exact and approximate solutions are compared in Figure 3 for three cases. The error intro-



Figure 3 Comparison between the exact (solid line) and approximate (dashed line) solutions for the volume of intersection between a cylinder and a sphere. Three cases are shown: (a) $R_f = 0.1$, b = 0.2; (b) $R_f = 0.3$, b = 0.4; (c) $R_f = 0.5$, b = 0.6.

duced by the approximate solution can be observed to be small for these cases.

Computation of the Average Volumes

The next step in accounting for the presence of fibers is to compute the average volume $\langle v \rangle$ for each type of truncation for various center-to-center distances *b*. The domain average volume is computed with

$$\langle v \rangle = \frac{1}{V} \int_{V} v dV$$
 (12)

where *V* is the total volume of the domain and v is the volume of the sphere. In considering the axisymmetry of the problem and assuming infinitely long fibers, this equation reduces to an integral on the distance from the fiber center, *b*:

$$\langle v \rangle = \frac{2\pi}{A} \int_{\Delta R} v b db \tag{13}$$

where ΔR is the interval on *b* that corresponds to the particular type of truncation being considered and *A* is the relevant surface area for a given interval ΔR . It is also assumed here that only one truncation occurs per spherulite.

In view of the unwieldy nature of the exact solution, we resorted to the approximate expressions of Gosset and coworkers¹⁷ to compute the average volume of the three possible cases. These expressions are provided in the Appendix. More than three expressions are found because the limits of integration may change according to the time interval considered during the crystallization process.

Unit Cells

In order to study the interaction between fibers and spherulites during crystallization in composites, it suffices to consider a representative volume of the overall structure, i.e., a unit cell. Possible unit cells are shown in Figure 4. Each one corresponds to a specific packing order of the fibers, e.g., triangular, square, Voronoi, or hexagonal packing. The unit cell chosen must satisfy two requirements: it must be sufficiently large to provide a faithful representation of the average microstructure, and it must also closely match the arrangement of the fibers in the polymer.

Each of the cells shown in Figure 4 possesses only one fiber at its center. These cells will therefore be valid as long as only one fiber truncation occurs per spherulite. If multiple fiber truncations occur, a larger unit cell that includes several fibers must be used. Also, the relevance of the shape of the cell arises in the calculations of the probabilities of occurrence of each truncation. The probability of occurrence is related to the respective area where each truncation is possible.

We consider in this work a unit cell with the outer boundary represented by a circular cylinder. This cell is the simplest case and approximates a hexagonal packing arrangement of the fibers.

Computation of the Probabilities

The probability of finding a sphere in a specific configuration with respect to the cylinder can be computed for the three cases shown in Figure 2 and the case of an untruncated spherulite. These probabilities are computed from the ratio of the areas where each type of spherulite can occur to the total space available for crystallization within the cell. For example, the absence of any fiber truncation on a spherulite can occur only between $R_f + R_s$ and R_o , and as long as $R_f + R_s < R_o$. These probabilities can be easily computed with the aid of Figure 5.

Three time sequences are possible for the occurrence of the truncations. The volume fraction is the determining factor of the time sequence for the truncation, i.e., the time frame in which a hole in the spherulite or a channel occur. The volume fraction at which the various truncation sequences and the probabilities differ is determined by comparing the fiber radius R_f to the polymer gap $R_o - R_f$. A first volume fraction is at $R_f = R_o$ $- R_f$ or $V_f = \frac{1}{3}$. Another volume fraction that will change the time sequence is at $2R_f = R_o - R_f$ or V_f $= \frac{1}{9}$. The various probabilities are shown in Tables I, II, and III for $V_f \leq \frac{1}{9}, \frac{1}{9} \leq V_f \leq \frac{1}{3}$, and $V_f \geq \frac{1}{3}$, respectively.



Figure 4 Illustration of possible unit cells that can be used to compute probabilities of occurrence of various truncations.



Figure 5 Areas used in computing the probability of occurrence of each of the three possible cases for R_s $> \ 2R_f$

Tables I, II, and III also show the probability of finding spherulites that do not have any truncation. Since this probability depends on the size of the spherulite with respect to the space between the limit of the cell and the fiber, it is also a function of time. The spherulites are initially very small, which results in high probabilities of no truncation. As the spherulites grow, the chance of a truncation to occur increases and the chance of no truncation decreases.

Furthermore, an entry could be made for the occurrence of $R_s > (R_o - R_f)$. This entry would indicate at which point in time multiple fiber truncations will start occurring. The importance of multiple fiber truncations depends on nuclei density with respect to the fiber volume fraction. If nucleation is profuse and a large number of spherulites are formed rapidly, a crystallinity close to 1 will be reached quickly and only one fiber truncation is expected to occur.

Spherulite Size	Distance from Fiber Center	Truncation Type	Probability
$0 < R_s < R_f$	$R_f < b < R_f + R_s$	channel (V_3^a)	$P_{1} = \frac{R_{s}(R_{s} + 2R_{f})}{R_{s}^{2} - R_{s}^{2}}$
	$R_f \ + \ R_s \ < \ b \ < \ R_o$	no truncation	$1 - P_1$
$R_f R_s < 2R_f$	$R_f < b < R_f + R_s$	channel (V_2^a)	${ m P_1} = rac{R_s(R_s+2R_f)}{R_s^2-R_s^2}$
	$R_f \ + \ R_s \ < \ b \ < \ R_o$	no truncation	$1 - P_1$
$2R_f < R_s < (R_o - R_f)$	$R_f < b < R_s - R_f$	hole (V_1^a)	$\mathrm{P}_{2}=rac{R_{s}^{2}-2R_{f}R_{s}}{R_{o}^{2}-R_{f}^{2}}$
	R_s – R_f < b < R_f + R_s	channel (V_2^b)	$\mathrm{P}_3=rac{4R_sR_f}{R^2-R_c^2}$
	$R_f \ + \ R_s \ < \ b \ < \ R_o$	no truncation	$1 - P_1$
$(R_o \ - \ R_f) \ < \ R_s$	$R_f < b < R_s - R_f$	hole (V_1^a)	$\mathrm{P_{2}}=rac{R_{s}^{2}-2R_{f}\!R_{s}}{R_{o}^{2}-R_{f}^{2}}$
	$R_s~-~R_f<~b~<~R_o$	channel (V_2^c)	$1 - P_2$

Table I Summary of Possible Spherulite Sizes and the Associated Probability of Occurrence for Various Truncations (for a Volume Fraction Smaller than $\frac{1}{9}$)

Modified Extended Volume for Crystallization with No Fiber Nucleation

Calculation of the crystallinity for a restricted volume due to fibrous reinforcements involves replacing the free volume of the growing entities with corresponding average values of the corrected volumes weighted by their probability of occurrence. Calculations of the modified extended volume fractions $\alpha'(t)$ are presented below for the case of an instantaneous heterogeneous nucleation process. The calculations use the average volume expressions that correspond to the different values of the spherulites radius $R(t, \tau)$ at time t, which have nucleated at time τ . The sequence of possible truncations, as the process evolves with time, depends on the fiber volume fraction. Expressions for the extended volume are presented below for $V_f > \frac{1}{3}$ because it is a common parameter encountered in composites.

Table II Summary of Possible Spherulite Sizes and the Associated Probability of Occurrence for Various Truncations (for a Volume Fraction Between $\frac{1}{9}$ and $\frac{1}{3}$)

Spherulite Size	Distance from Fiber Center	Truncation Type	Probability
$\overline{0\ <\ R_s\ <\ R_f}$	$R_f < b < R_f + R_s$	channel (V_3^a)	$\mathbf{P_1} = \frac{R_s(R_s+2R_f)}{R_o^2-R_f^2}$
	R_f + R_s < b < R_o	no truncation	$1 - P_1$
$R_f < R_s < (R_o - R_f)$	$R_f < b < R_f + R_s$	channel (V_2^a)	${ m P_1} = rac{R_s(R_s+2R_f)}{R_o^2-R_f^2}$
	$R_f \ + \ R_s \ < \ b \ < \ R_o$	no truncation	$1 - P_1$
$(R_o \ - \ R_f) \ < \ R_s \ < \ 2R_f$	$R_f < b < R_o$	channel $({\cal V}_2^d)$	1
$2R_f < R_s$	$R_f < b < R_s - R_f$	hole (V_1^a)	${ m P}_2 = rac{R_s^2 - 2R_f\!R_s}{R_o^2 - R_f^2}$
	R_s – R_f < b < R_o	channel (V_2^c)	$1 - P_2$

		•	
Spherulite Size	Distance from Fiber Center	Truncation Type	Probability
$0 < R_s < (R_o - R_f)$	$R_f < b < R_f + R_s$	channel (V_3^a)	$\mathbf{P_1} = \frac{R_s(R_s+2R_f)}{R_o^2-R_f^2}$
	R_f + R_s < b < R_o	no truncation	$1 - P_1$
$(R_o \ - \ R_f) \ < \ R_s \ < \ R_f$	$R_f < b < R_o$	channel (V_3^b)	1
$R_f < R_s < 2R_f$	$R_f < \ b \ < \ R_o$	channel (V_2^d)	1
$2R_f < R_s < (R_o + R_f)$	$R_f < b < R_s - R_f$	hole (V_1^a)	${ m P}_2 = rac{R_s^2 - 2R_f R_s}{R_o^2 - R_f^2}$
	$R_s\ -\ R_f\ <\ b\ <\ R_o$	channel (V_2^c)	$1 - P_2$
$(R_o + R_f) < R_s$	$R_f < b < R_o$	hole (V_1^b)	1

Table III Summary of Possible Spherulite Sizes and the Associated Probability of Occurrence for Various Truncations (for a Volume Fraction Greater than $\frac{1}{r}$)

Modified $\alpha'(t)$ for Spherulites Nucleating at $t < (R_o - R_f)/G_o$

In this case, for all τ , $R_s(t, \tau) = G_o(t - \tau)$ is smaller than $(R_o - R_f)$ because $V_f > \frac{1}{3}$. The extended volume fraction can be written with a Dirac delta function which is used to represent the nucleation process, i.e., $\dot{n}(t) = N\delta(\tau)$, which gives simply

$$\begin{aligned} \alpha_{het}'(t) &= N_o \int_0^t \left[\left(1 - \frac{R_s(R_s + 2R_f)}{R_o^2 - R_f^2} \right) \frac{4}{3} \ \pi R_s^3 \\ &+ \frac{R_s(2R_f + R_s)}{R_o^2 - R_f^2} \frac{4}{3} \ \pi R_s^3 (1 - \langle V_3^{ia} \rangle) \right] \delta(\tau) d\tau \\ &= N_o \int_0^t \left[(1 - P_1 \langle V_3^{ia} \rangle) \frac{4}{3} \ \pi R_s^3 \right] \delta(\tau) d\tau \\ &= N_o \frac{4}{3} \ \pi R_s^3 (1 - P_1 \langle V_3^{ia} \rangle) \quad (14) \end{aligned}$$

Modified $\alpha'(t)$ for Spherulites Growing at $t > (R_o - R_f)/G_o$

The extended volume fraction at instants greater than (R_f/G_o) is simply given by the number of spherulites that nucleated at an earlier time multiplied by the probability of occurrence for the various types of truncation. No nucleation occurs during these time intervals because we are assuming heterogeneous nucleation represented by a delta function.

$$\begin{aligned} \alpha_{het}'(t) &= N_o \frac{4}{3} \, \pi R_s^3 \{ 1 - \langle V_3^{ib} \rangle \} \\ & \text{for } (R_o - R_f) / G_o < t < R_f / G_o \quad (15) \end{aligned}$$

$$\begin{aligned} \alpha_{het}'(t) &= N_o \frac{4}{3} \pi R_s^3 \{1 - \langle V_2^{id} \rangle \} \\ & \text{for } R_f / G_o < t < 2 R_f / G_o \quad (16) \end{aligned}$$

$$\begin{aligned} \alpha'_{het}(t) &= N_o \frac{4}{3} \pi R_s^3 \{ P_2(1 - \langle V_1^{ia} \rangle) + (1 - P_2) \\ &\times (1 - \langle V_2^{ic} \rangle) \} = N_o \frac{4}{3} \pi R_s^3 \{ 1 - (1 - P_2) \langle V_2^{ic} \rangle \\ &- P_2 \langle V_1^{ia} \rangle \} \text{ for } 2R_f / G_o < t < (R_o + R_f) / G_o \quad (17) \end{aligned}$$

$$lpha_{het}'(t) = N_o \frac{4}{3} \pi R_s^3 \{1 - \langle V_1^{ib} \rangle\}$$

for $(R_o + R_f)/G_o < t$ (18)

where $R_s = G_o t$.

Results for Crystallization with No Fiber Nucleation

For illustrative purposes, two examples are used for various volume fractions. In the first example the following parameters are used in the calculations: an isothermal growth rate of $G = 1 \mu$ m/s, a fiber radius of $R_f = 7 \mu$ m, and a cell outside radius of $R_o = 8.32 \mu$ m. This corresponds to a volume fraction of $V_f = (R_f/R_o)^2 = 0.71$, and a nucleation $N = 10^{15}$ nuclei/m³ is assumed to occur at t = 0. The average radius of the spherulites will therefore be of about 13 μ m at the end of the crystallization process. Comparison between the crystallization rate in neat polymer and the crystallization rate in a fiber-reinforced polymer is shown in Figure 6. The crystallinity profile is built by the evaluation of the extended volume within a specific time frame and the overall crystallization profile is obtained by assembling the profiles to obtain a description of the process at any time. It can also be observed that not all functions are relevant to every time frame. For example, eq. (14), when used to compute the actual crystallinity, gives a very small crystallinity, near 0. On the other hand, using eq. (18) gives a crystallinity of 1. The relevance of each equation is related to the growth rate, the number of nuclei, and the volume fraction.

It can also be observed in Figure 6 that the difference between the filled and unfilled polymer crystallization rates is not large, though not negligible either. The cell considered allows for only one fiber truncation per spherulite. For the volume fraction of fiber chosen in this example, double or triple truncations could occur, reducing the crystallization rate even more. The present treatment does not allow double or triple truncations. This effect of multiple fiber truncations will be present in polymer systems with low nuclei counts. Strictly speaking, there is no unit cell large enough to model the process accurately because the spherulites grow unimpeded in the extended volume and each spherulite can grow unbounded. For this reason, the degree of crystallinity computed with the Avrami equation will never reach the value of 1, but will approach it in an asymptotic manner. This is true for unfilled and filled polymers.



Figure 6 Resulting crystallinity profile and comparison with the unreinforced polymer (dashed line) for $G = 1 \ \mu \text{m/s}, R_f = 7 \ \mu \text{m}, R_o = 8.32 \ \mu \text{m}, \text{and } N = 10^{15} \text{ nuclei/m}^3$.



Figure 7 Resulting crystallinity profile and comparison with the unreinforced polymer (dashed line).

A second example is presented here with $G = 1 \ \mu \text{m/s}$, $R_f = 6 \ \mu \text{m}$, and $R_o = 9.4 \ \mu \text{m}$, which gives a volume fraction of $V_f = 0.41$, and a nucleation $N = 10^{14}$ nuclei/m³ was selected. The average radius of the spherulites at the end of the crystallization process will therefore be about 30 μ m. The construction of the crystallinity profile can be done with the equations relevant to the time interval considered; the resulting profile is also shown in Figure 7.

CONCLUSIONS

This article presented an analysis that allows for an analytical treatment of the phenomena of isothermal crystallization in reinforced polymers. The analytical model is based on the use of approximate expressions for the volume of intersection between a sphere and cylinder. The approach consists simply of first computing the average volumes related to the possible types of truncations that can be encountered. Once this is known, the crystallization process is divided into time frames during which specific types of truncations are encountered. Since the radii of the spherulites change with time, the possible types of truncations will also change with time. Although the resulting equations are somewhat complicated, they can be computed fairly easily with a symbolic computations package. Three different time sequences can be derived according to the fiber volume fraction. Furthermore, the effect of the fibers on the overall crystallization process was demonstrated with simple examples. It was also found that a larger unit cell should be used to account for the multiple fiber truncations that can occur near the end of the crystallization process, when large spherulites are encountered combined with a high fiber volume fraction.

APPENDIX: AVERAGE VOLUME EXPRESSIONS

The average volumes required to compute the extended volume fractions are provided below. Eight expressions are required because the intervals for the integration vary. The subscripts 1a, 1b, 2a, 2b, 2c, 2d, 3a, and 3b are used to distinguish the possible cases.

$$\begin{split} \langle V_{1a}^{i} \rangle &= \frac{2}{R_{s}(R_{s}-2R_{f})} \int_{R_{f}}^{R_{f}-R_{s}} V_{1}^{i} b d b \\ &= \frac{2\pi}{R_{s}-2R_{f}} \bigg[-\frac{1}{3} \left(\frac{R_{f}(2R_{s}-R_{f})}{R_{s}^{2}} \right)^{3/2} \\ &\times \bigg[R_{s}^{2} + \sqrt{1 - \frac{R_{f}^{2}}{R_{s}^{2}}} \left(R_{f}^{2} - R_{s}^{2} \right) \bigg] \\ &+ \frac{(R_{f}^{2} - R_{s}^{2})^{3} + \sqrt{1 - \frac{R_{f}^{2}}{R_{s}^{2}}} R_{s}^{4}(R_{s}^{2} - R_{f}^{2})}{3R_{s}^{4}} \end{split}$$
(A.1)

$$\begin{split} \langle V_{1b}^{i} \rangle &= \frac{2}{(R_{o}^{2} - R_{f}^{2})} \int_{R_{f}}^{R_{o}} V_{1}^{i} b d b \\ & 2 \left(\frac{(R_{f}^{2} - R_{s}^{2})^{3}}{R_{s}^{4}} + \sqrt{1 - \frac{R_{f}^{2}}{R_{s}^{2}}} \left(R_{s}^{2} - R_{f}^{2} \right) \right. \\ & + \left(\left(1 - \frac{R_{f}^{2}}{R_{s}^{2}} \right)^{3/2} - 1 \right) \\ & = \frac{\sqrt{1 - \frac{R_{o}^{2}}{R_{s}^{2}}} \left(R_{s}^{2} - R_{o}^{2} \right) \right)}{3(R_{o}^{2} - R_{f}^{2})} \end{split}$$
(A.2)

$$\begin{split} \langle V_{2a}^{i} \rangle &= \frac{2}{R_{s}(2R_{f}+R_{s})} \int_{R_{f}}^{R_{s}+R_{f}} V_{2}^{i} b d b \\ & \sqrt{\frac{R_{f}(2R_{s}-R_{f})}{R_{s}^{2}}} R_{s}(5R_{f}+R_{s}) \\ & \times \left[R_{s}^{2} + \sqrt{1 - \frac{R_{f}^{2}}{R_{s}^{2}}} \left(R_{f}^{2} - R_{s}^{2} \right) \right] \\ & + \frac{R_{f}^{5/2}(40R_{f}^{2} - 5R_{f}R_{s} - 3R_{s}^{2})}{\sqrt{R_{f} + R_{s}}} \\ & = \frac{-\frac{R_{f}^{5/2}(40R_{f}^{2} - 5R_{f}R_{s} - 3R_{s}^{2})}{80R_{f}^{3}(2R_{f} + R_{s})} \end{split}$$
(A.3)

$$\begin{split} \langle V_{2b}^{i} \rangle &= \frac{1}{2R_{s}R_{f}} \int_{R_{s}-R_{f}}^{R_{s}+R_{f}} V_{2}^{i} b d b \\ & \left(R_{f}(5R_{s}-3R_{f}) \sqrt{\frac{R_{f}(2R_{s}-R_{f})}{R_{s}^{2}}} \\ & \times \left[R_{s}^{2} + \sqrt{1 - \frac{R_{f}^{2}}{R_{s}^{2}}} (R_{f}^{2} - R_{s}^{2})} \right] \\ &= \frac{-\frac{R_{f}^{7/2}(R_{f}-5R_{s})}{\sqrt{R_{f}+R_{s}}} \right) \\ \langle V_{2c}^{i} \rangle &= \frac{2}{(R_{o}^{2} - (R_{f}-R_{s})^{2})} \int_{R_{s}-R_{f}}^{R_{o}} V_{2}^{i} b d b \\ &= \sqrt{-\frac{R_{f}(R_{f}-2R_{s})}{R_{s}^{2}}} \left[49R_{f}^{5} - 75R_{f}^{4}R_{s} \\ &- 10R_{f}^{2}(R_{o}^{2} - R_{s}^{2}) \\ &+ 10R_{f}^{2}(R_{o} - R_{s})^{2}(2R_{o} + R_{s}) \\ &- 5R_{f}(R_{o} - R_{s})^{3}(3R_{o} + R_{s}) \\ &+ (R_{o} - R_{s})^{4}(4R_{o} + R_{s}) \right] \\ &\times \left[1 + \frac{\sqrt{1 - \frac{R_{f}^{2}}{R_{s}^{2}}} (R_{f} - R_{s})}{R_{s}^{2}} \\ &\times (23R_{f}^{3} - 3(R_{o} - R_{s})^{2}\sqrt{\frac{1}{R_{f} + R_{s}}} \\ &\times (23R_{f}^{3} - 3(R_{o} - R_{s})^{2}(4R_{o} + R_{s}) \\ &- R_{f}^{2}(46R_{o} + 9R_{s}) \\ &+ R_{f}(R_{o} - R_{s})(39R_{o} + 11R_{s})) \right] / \\ &\left\{ 160R_{f}^{3}((R_{f} - R_{s})^{2} - R_{o}^{2}) \right\} \quad (A.5) \\ \langle V_{2d}^{i} \rangle &= \frac{2}{(R_{o}^{2} - R_{f}^{2})} \int_{R_{f}}^{R_{o}} V_{2}^{i} b d b \\ &= \frac{A(R_{s}^{3} - \sqrt{(R_{s}^{2} - R_{f}^{2})}(R_{s}^{2} - R_{f}^{2}))}{80R_{f}^{3}R_{s}^{4}(R_{f} + R_{o})} \\ &+ B[(7R_{f}^{4} + R_{f}^{2}(7R_{o} + 25R_{s}))] \\ &+ B[R_{f}^{2}(-23R_{o}^{2} + 25R_{o}R_{s} + 30R_{s}^{2}) \quad (A.6) \\ \end{array}$$

where

$$\begin{split} A &= \sqrt{(R_f(2R_s-R_f))} \{ (R_f-R_o)^3 (R_f+4R_o) \\ &+ 5(R_f-R_o)^2 (R_f+3R_o) R_s + 10 (R_f-R_o) \\ &\times (R_f+2R_o) R_s^2 + 10 (R_f+R_o) R_s^3 \} \quad (A.7) \end{split}$$

$$B = \frac{\sqrt{\frac{1}{R_f + R_s}}}{80\sqrt{R_f}R_s^2(R_f + R_o)}$$
(A.8)

$$\begin{split} \langle V_{3a}^{i} \rangle &= \frac{2}{R_{s}(2R_{f}+R_{s})} \int_{R_{f}}^{R_{s}+R_{f}} V_{3}^{i} b db \\ &= \frac{5R_{f}+R_{s}+\sqrt{\frac{R_{f}}{R_{f}+R_{s})}} \left(25R_{f}+7R_{s}\right)}{80(2R_{f}+R_{s})} \ \ (A.9) \end{split}$$

$$\begin{split} \langle V_{3b}^i \rangle &= \frac{2}{(R_o^2 - R_f^2)} \int_{R_f}^{R_o} V_3^i b \, db \\ & = \frac{10(R_f - R_o)(R_f + 2R_o)R_s^2 \bigg(1 + \sqrt{\frac{R_f}{R_f + R_s(t)}}\bigg)}{-5(R_f - R_o)^2(R_f + 3R_o)R_s \bigg(-1 + \sqrt{\frac{R_f}{R_f + R_s}}\bigg)} \\ &= \frac{-5(R_f - R_o)^2(R_f + 3R_o)R_s^2\bigg(-1 + \sqrt{\frac{R_f}{R_f + R_s}}\bigg)}{80(R_f + R_o)R_s^3} \end{split}$$

$$+ \frac{10(R_f + R_o)R_s^3 \left(1 + 3\sqrt{\frac{R_f}{R_f + R_s}}\right)}{-(R_f - R_o)^3(R_f + 4R_o)\left(-1 + 3\sqrt{\frac{R_f}{R_f + R_s}}\right)}{80(R_f + R_o)R_s^3}$$
(A.10)

 $\langle V_1^i \rangle$, $\langle V_2^i \rangle$, and $\langle V_3^i \rangle$ are all normalized with respect to $(\frac{4}{3})\pi R_s^3$.

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