Modeling of Crystallization Kinetics in Fiber Reinforced Composites

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SUMMARY: The kinetics of spherulitic crystallization in fiber reinforced thermoplastics was determined by means of the theoretical model based on the statistical approach and by and the computer simulation of spherulitic crystallization. The computer simulation of the spherulites nucleation and growth was performed to verify the derived expressions and to visualize the polymer morphology. The obtained results indicate that the classic Avrami equation is inappropriate for the description of systems with fibers serving as additional nucleation sites. The kinetics of crystallization is governed by the nucleation inside a polymer matrix and at fiber surfaces as well as by fibers content and fiber radius. The developed model permits to predict the half-time of crystallization in fiber reinforced systems

Introduction

The overall crystallization kinetics in materials crystallizing in the form of polycrystalline aggregates growing radially from nuclei is usually described by the model developed by Evans and Avrami. Further development of the theory [e.g.1,2] permits to consider the effects of polymer volume confinement and additional nucleation at sample surfaces. The experimental studies of fiber reinforced thermoplastics demonstrate the differences in the kinetics of crystallization between unfilled and filled systems[e.g.3,4]. Usually, the changes of the Avrami exponent and the half time of crystallization are reported. The influence of fibers on the overall crystallization kinetics was also investigated by means of computer simulation[5,6] and was discussed in terms of confinement of polymer between fibers and transcrystallinity caused by a strong nucleation of spherulites on fibers[7]. In the present paper the spherulitic crystallization kinetics in fiber reinforced thermoplastics is determined by means of the theoretical model and the computer simulation of spherulitic crystallization.

Mathematical model

The mathematical model is based on the statistical approach developed previously for unfilled

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polymers[2,8]. An arbitrarily chosen point A remains unoccluded by instantaneously nucleated spherulites until time t if none of them is nucleated within a sphere of radius r around that point. For constant growth rate, G, r= G*t. If the fibers volume is neglected the fibers are represented by lines. The probability p_0 that no nucleation event occurred within that sphere equals $p_i\ p_f$, where $p_i=\exp[-4\pi D(Gt)^3/3]$ is the probability that no nucleation event occurred within the polymer matrix (D is the density of instantaneous nucleation inside a matrix), and p_f is the probability that no nucleation event occurred on fibers. p_f is the sum of the two probabilities: 1. that no fiber enters the sphere and 2. that any number of fibers enter the sphere but no nucleation event occurs on parts of fibers enclosed in the sphere. Finally:

$$p_0=\exp\{-(4/3)\pi D(Gt)^3-\pi D_f(Gt)^2-0.5\pi D_f D_s^{-2}[(2GtD_s+1)\exp(-2D_sGt)-1]\} \quad (1)$$

where: D_s is the nucleation density on fibers, D_f is the length of fibers per unit volume of a composite. The conversion degree, $\alpha(t)$, equals $1-p_0$. For the intense nucleation on fibers D_s tends to infinity and p_0 equals $\exp\{-(4/3)\pi D(Gt)^3-\pi D_f(Gt)^2\}$.

To account for fibers volume a portion of composite is considered in the form of cylindrical polymer layer of outer radius r_g surrounding the fiber of radius r_f, where $(r_f/r_g)^2=v_f$, and v_f is the total fibers content. The conversion degree is then given by the equation:

$$\alpha(t)=1-2(r_g^2-r_f^2)^{-1}\int_0^{r_g-r_f}(s+r_f)p_0(s,t)ds \quad (2)$$

where $p_0(s,t)$ is the probability that a point in distance s from a fiber surface remains unoccluded by until time t (i.e if no nucleation event occurred within a sphere of radius r of volume $V=(4/3)\pi r^3$) and equals $\exp[-D(V-V_1)-D_sS_1]$, where: V_1 is the part of sphere overlapping the fiber, S_1 is the part of fiber surface within the sphere and D_s is the instantaneous nucleation density at fiber surface (Fig.1). If r is large enough only the part of that sphere, denoted as V_2, overlaps the considered portion of composite. Hence:

$$p_0(s,t)=\exp\{-[D(V_2-V_1)+D_sS_1]V/V_2\} \quad (3)$$

For r>s S_1 and V_1 are described by the equations:

$$V_1=2\int_0^{z_g}\{k\pi r_f^2+l[\beta r_f^2+\alpha(r^2-z^2)-R]\}\,dz$$

$$S_1=4\int_0^{z_g} r_f(k\pi+l\beta)\,dz$$

where: $z_g=[r^2-s^2]^{0.5}$

k=1 and l=0 for $z^2<r^2-(2r_f+s)^2$

k=0 and l=1 for $z^2>r^2-(2r_f+s)^2$

$\alpha=\arcsin[R(r_f+s)^{-1}(r^2-z^2)^{-0.5}]$

$\beta=\pi-\arcsin[R(r_f+s)^{-1}r_f^{-1}]$ for $z^2<r^2-(r_f+s)^2-r_f^2$

$\beta=\arcsin[R(r_f+s)^{-1}r_f^{-1}]$ for $z^2>r^2-(r_f+s)^2-r_f^2$

$R=0.5\{(r^2-z^2-s^2)[(2r_f+s)^2-r^2+z^2]\}^{0.5}$

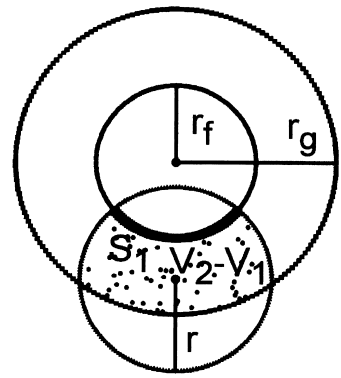

Fig.1.Scheme of fiber in polymer matrix.

while: $V_2 = 2\,{}_0\int^r \{k\pi r_f^2 + l\pi(r^2-z^2) + m[\beta_1 r_g^2 + \alpha_1(r^2-z^2) - R_1]\}dz$

where: k=1, l=0 and m=0 for $z^2 < r^2-(r_f+s+r_g)^2$, k=0, l=0 and m=1 for $r^2-(r_g-r_f-s)^2>z^2>r^2-(r_f+s+r_g)^2$,

k=0, l=1 and m=0 for $z^2>r^2-(r_g-r_f-s)^2$, α_1 =arc sin $[R_1(r_f+s)^{-1}(r^2-z^2)^{-0.5}]$ for $z^2 <r^2-r_g^2+(r_f+s)^2$,

$\alpha_1 = \pi$ - arc sin $[R_1(r_f+s)^{-1}(r^2-z^2)^{-0.5}]$ for $z^2 >r^2-r_g^2+(r_f+s)^2$,

$\beta_1 = \pi$- arc sin $[R_1(r_f+s)^{-1}r_g^{-1}]$ for $z^2<r^2-r_g^2-(r_f+s)^2$, β_1=arc sin $[R_1(r_f+s)^{-1}r_g^{-1}]$ for $z^2>r^2-r_g^2-(r_f+s)^2$

$R_1 = 0.5\{[(r^2-z^2)^{0.5}+r_f+s]^2-r_g^2\}^{0.5}\{r_g^2-[r_f+s-(r^2-z^2)^{0.5}]\}^{0.5}$

Computer simulation

The computer simulation of spherulitic crystallization was performed in a way similar to that described previously[2]. The coordinates of spherulites nuclei in a bulk of a polymer were generated by means of pseudorandom number generator. The fibers centers were randomly chosen as points on a plane. When the volume of fibers was accounted each new fiber overlapping already created fibers was rejected and another fiber was generated. In this case also the spherulites centers nucleated in bulk of a polymer were checked and rejected if chosen in fiber inhabited volume. The positions of nuclei along fibers and, if fibers volume was accounted, the positions on fibers circumferences were randomly generated. The sizes of simulated samples were adjusted to have at least 1000 spherulites and several tens of fibers in the sample. In order to determine the conversion degree 10^4 sampling pseudorandom points were chosen within the polymer matrix, outside fibers, and at distances from sample surfaces. For each point the time of

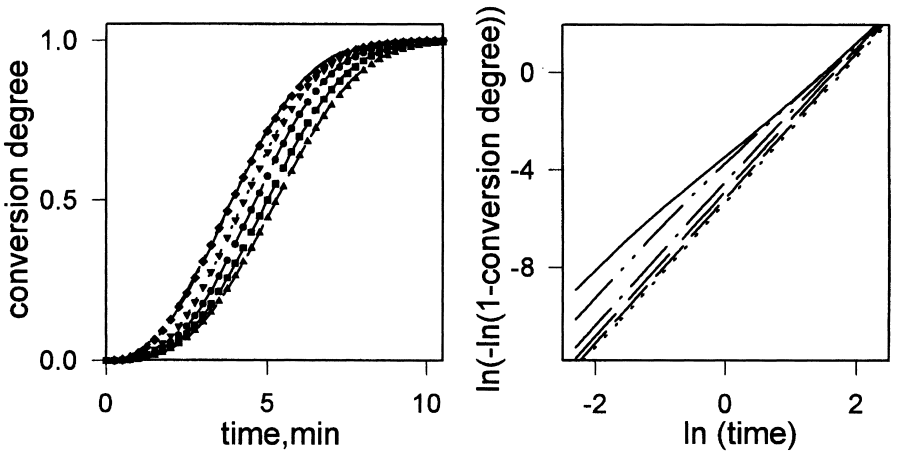

Fig.2. Kinetics of conversion in fiber reinforced systems: conversion degree vs.time (left) and the Avrami plot (right). D=9 10^{-6} vol.unit^{-1}, D_f=3.5 10^{-1} area unit^{-1}, G=5 length unit min^{-1} and D_s: 0.0, 0.005, 0.016, 0.04, 0.2, 1.0 length unit^{-1} from right to left.

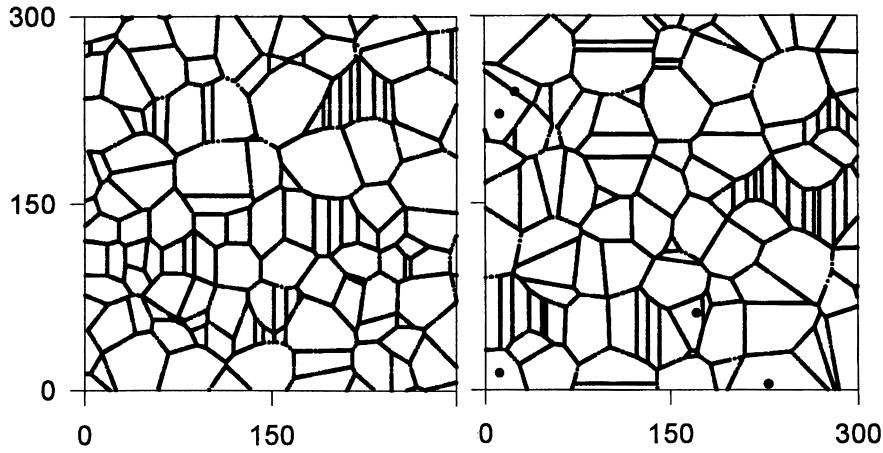

Fig.3. Cross-sections of computer simulated fiber reinforced samples: with fibers parallel to x-axis (left) and with fibers parallel to x,y and z-axes. Points - fibers perpendicular to the picture plane. D_s=0.04 length unit^{-1}, D_f, D and G as in Fig.2.

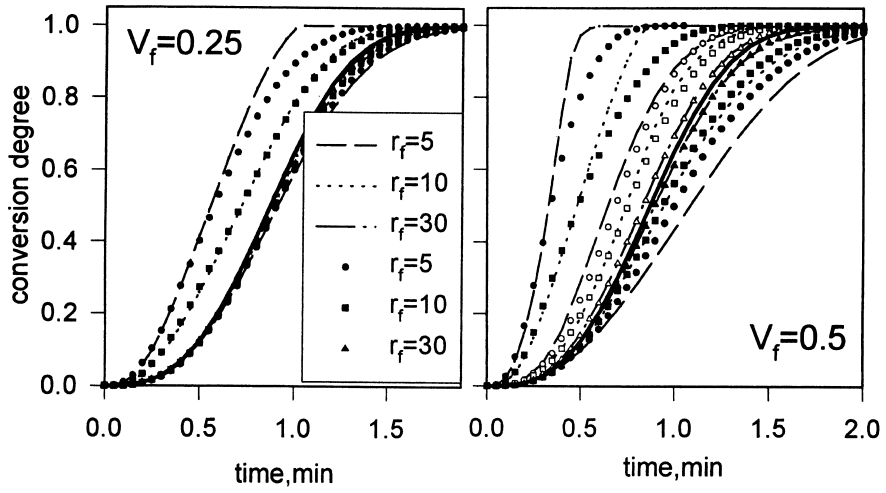

Fig.4. Model (lines) and computer simulation (symbols) predictions of conversion kinetics in fiber reinforced systems; G as in Fig.2, D=0.002 vol.unit^{-1}. Thick solid line - neat sample (V_f=0), on right side data for D_s=0, on left side data for D_s=0.013 area unit^{-1} (open symbols) and D_s=0.2 area unit^{-1} (filled symbols).

occlusion by spherulites growing radially at constant rate was determined. Also the programs for visualization of cross-sections of resulting structures were developed. The systems with various densities of bulk nucleation, fibers content, fiber radius and density of nucleation on fibers were simulated.

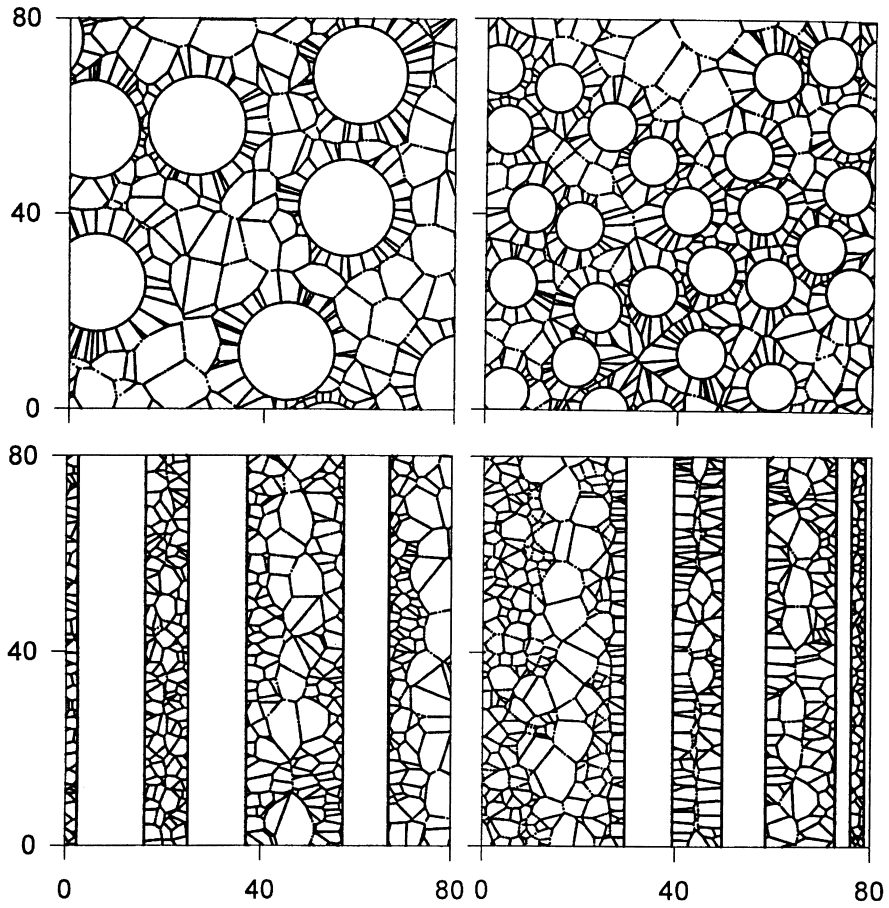

Fig.5. Cross-sections of computer simulated fiber reinforced samples. D and G as in Fig.4, D_S=0.2 area unit^{-1}, V_f=0.25, r_f=10 units (left) and r_f=5 units (right).

Model vs. computer simulation

Fibers volume neglected. The model predictions of the conversion degree in the presence of fibers are in a very good agreement with the computer simulation. The exemplary results are shown in Fig.2. The increase of fibers number and the density of nucleation on fibers speeds up the conversion of melt into spherulites. The Avrami plots resemble straight lines but with a decreased slope. The departure from linearity is seen for very dense nucleation on fibers. These observations are in agreement with the experimental results[3,4]. Exactly the same kinetics of conversion was obtained for the composites containing fibers aligned in 1 direction and with 1/3

of fibers aligned in each of 3 perpendicular directions although the spherulitic structures differ significantly (Fig.3). This observation points out that in the case of 3D crystallization the orientation of fibers serving as nucleation sites may influence the final structure but is unimportant for the kinetics of conversion.

Fibers volume regarded. The fibers can be obstacles for spherulitic growth and may cause the change of shape of growing front as it was observed in blends or even to stop the growth if the fibers confine pockets of melt. These effects could be of importance in the case of non-nucleating or weakly nucleating fibers. Since nor the model neither the simulation accounts for such effects, only such cases were considered in which spherulites radii are comparable or smaller than radii of fibers. The model predicts correctly the beginning of crystallization and it could be useful for foreseeing the half-time of crystallization (Fig.4). It fails, however, to predict the kinetics of the later stages of crystallization in the case of high contents of strongly nucleating fibers. The non-nucleating fibers slow down the conversion since the spherulites can not be nucleated in fiber volume while the fibers with nucleating ability speed up the conversion. Both, the model and the computer simulation indicate that the increase of number of fibers results in stronger changes in crystallization kinetics. In composites containing the same amount of fibers, the fibers of smaller radius stronger influence the kinetics of conversion and the resulting spherulitic structure, similarly as it was observed in ref.[5] This could be explained with the help of the visualization of cross-sections of resulting structures (Fig.5). If the fibers are large as compared to spherulites also the spaces between them are large and growth of spherulites nucleated in bulk of a polymer is less affected.

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