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Simulating polymer crystallization in thin films: Numerical and analytical methods

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ABSTRACT

In this paper, a general numerical method to simulate polymer crystallization under various conditions is proposed. This method is first validated comparing its predictions with well-validated analytical models in infinite volumes. Then, it is compared to Billon et al. validated model for thin films, without or in presence of transcrystallinity on the films surfaces. It is also compared with Chenot et al. model for thin films, proposed in a conference in 2005 and never yet compared with other methods. Finally, it is also compared with an extension of this model for the transcrystalline case. These models are valid for general nucleation cases (not only sporadic or instantaneous), and can be used for any thermal conditions. All the numerical and analytical results are consistent, except in a case which is shown to be out of the validity domain of the transcrystalline case extension of Chenot et al. model.

1. Introduction

Many analytical and numerical modeling methods have been proposed to simulate the crystallization of polymers under different conditions and configurations, as in thin films or for non-isothermal conditions. Such simulations are very useful to understand DSC measurements, to predict the final microstructure and the physical properties of polymer parts or to compute temperature evolution in process simulations [1–6].

1.1. Global kinetic theories

Polymer crystallization can be described by overall crystallization kinetic theories. These models are based on a general description of the transformation of the polymers from the liquid to the solid state. From the molten state, many polymers develop a semi-crystalline spherulitic morphology. In this kind of microstructure, the crystallization starts at particular points of the volume: the nuclei. These are the starting points of mono-crystalline lamellae growing and multiplying in all directions of space, including between them some amorphous polymer. The combination of the crystalline lamellae and the amorphous polymer defines, in three dimensions, a spherical semi-crystalline entity: the spherulite. Spherulites tend to occupy the whole volume without covering each over. This description is the basic principle of the overall kinetic theories, neglecting the possibility of a secondary crystallization of the amorphous part. The studied quantity is generally the trans-

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formed fraction α, defined as the ratio of the volume occupied by spherulites to the total volume. This quantity is 0 at the beginning and reaches 1 at the end of the transformation. Thus, it has to be differentiated from the crystalline fraction, as this one will never be equal to 1.

One of the most used among the overall kinetics theories is Avrami's theory [7–9]. It is based on a number of hypotheses concerning nucleation and growth. There are pre-existing sites in the molten liquid, called potential nuclei, with an initial density N_0 (number per unit volume) function of temperature [10,11]. Each potential nucleus in a non-transformed area can be activated, *i.e.* generate an entity (e.g., a spherulite). On the other hand, a potential nucleus that has been absorbed by an entity before getting activated can no longer be activated. The activation frequency q is defined as the probability per unit time for any nucleus to be activated. The new entity generated by this activation immediately starts to grow. The spherulite growth rate G is the lamella growth rate. The impingement of two growing spherulites stops their growth at the contact point. G and q are only functions of temperature, as the crystalline growth is governed by secondary nucleation phenomena, and not by diffusion phenomena [12]. Therefore, their time dependence is only through the time variation of temperature. In the limiting case of instantaneous nucleation, all the potential nuclei are instantaneously activated and the number of spherulites per unit volume remains constant and equal to N_0. In the other limiting case of isothermal sporadic in time nucleation, the number of activated nuclei per unit time and unit volume is constant: $\frac{dN_a}{dt} = qN = cte$ (with N the number of remaining potential nuclei per unit volume). That implies that q is small and N_0 is high.

Sometimes, the presence of surfaces or inclusions will generate a fast and massive local nucleation. In this case, the numerous spherulites limit the growth of their neighbors and then oblige them to grow along one direction perpendicular to the surface on which they were generated. Then, they form a crystallization front propagating at the spherulite growth rate G. This phenomenon is called transcrystallinity and can lead to very different crystallization kinetics from those obtained in bulk infinite volume. Especially, it can play an important role in DSC measurement results, and thus has to be taken into account in their interpretations [1]. Sample geometry, especially volume restriction, as in thin films, can also lead to changes in crystallization kinetics, and models have to be adapted to the sample geometry to perform accurate predictions [13]. Furthermore, it has been shown that transcrystallinity and volume restriction effects are tightly connected [2,14].

If Avrami's theory [7–9] is very popular, there are other well-known theories [15–18], all of them based on statistical approaches allowing the calculation of the average transformed volume fraction α. For all of these models, there is only one kind of nuclei, uniformly distributed in an infinite volume. All the entities are growing at the same rate, and are spheres in 3D, disks in 2D and rods in 1D. A critical review of overall crystallization kinetics theories has been done by Piorkowska et al. [19]. It has been demonstrated that Evans' and Avrami's approaches are equivalent [20], whereas Tobin's one is generally recognized as incorrect [19]. Based on the hypothesis of an instantaneous or a sporadic in time nucleation, simplified formulations are frequently used either in isothermal (Avrami–Evans' simplified model) or in non-isothermal (Nakamura's and Ozawa's models) conditions. Their interest is to replace the three parameters (N_0, q, G) by two more easily measurable ones [7–9,21–24].

1.2. Extensions to non-isothermal and thin films cases

In their general form, the overall crystallization kinetics theories can be used or extended to treat non-isothermal crystallization, to consider a non-uniform distribution or several populations of nuclei [25] or to include the influence of parameters other than temperature (shear rate, for example) on the kinetic parameters (N_0, G, q). An important extension has been the modelling of the crystallization in thin films [13], with the possibility to consider transcrystallinity on the film surfaces [26] and non-isothermal cases [2,20,25]. In these models, transcrystallinity is introduced through a second set of parameters (number of potential nuclei per surface unit N_s (m^{-2}) and activation frequency s, equivalent to N_0 (m^{-3}) and q in the volume, G remaining the same), describing the behavior of nuclei generated on surfaces. These parameters are chosen so that the nucleation on the surfaces is faster than in the volume, in agreement with experimental observations. Some experimental methods, based on these simulations, have been proposed to find the overall kinetics parameters [11,27]. Some keys for the interpretation of DSC experiments have been highlighted using a thin film simulation method [1,14].

Piorkowska has also proposed another approach of analytical simulation, based on the spherulitic pattern, which can be characterized by the distance between the center of a spherulite and its boundary at the interface with another spherulite. This approach has been proposed for instantaneous and sporadic in time activations, for both isothermal and non-isothermal conditions, in infinite and finite volumes, and allows focusing on the structure weaknesses that are the spherulites boundaries [4–6,28,29].

In the present study, the focus is put on the model proposed by Chenot et al. in 2005 [30], which is an extension for thin films of the model proposed by Haudin and Chenot [10], and which till now, has been only presented in an international conference. Haudin–Chenot's model allows computing the evolution of the transformed fraction, the number of activated nuclei and the distribution of spherulite sizes during the crystallization, whatever the temperature conditions and for any type of nucleation *i.e.* not only for instantaneous or sporadic in time nucleation. In the case of non-isothermal conditions, most of the classical models neglect the possibility for new potential nuclei to appear during cooling. Monasse et al. [11], who have experimentally validated the model, proved that these appearances have an influence on the crystallization kinetics, justifying the need to take them into account. This model can also consider the influence of shear rate on the kinetic parameters [31]. In 2005, Chenot et al. [30] proposed a generalization of this model to thin film configuration. However, this