A Crystallization Kinetic Model for Long Fiber-Based Composite with Thermoplastic Semicrystalline Polymer Matrix

Nicolas Bigot[1,a*], M'hamed Boutaous[2,b], Shihe Xin[2,d], and Nahiène Hamila[3,c]

[1]Université de Lyon, LaMCOS UMR 5259, INSA-Lyon, F-69621, Villeurbanne, France

[2]Université de Lyon, CNRS, INSA-Lyon, CETHIL, UMR 5008, F-69621, Villeurbanne, France

[3]ENIB, IRDL UMR CNRS 6027, 945 Avenue du Technopôle, 29280 Plouzané

[a]nicolas.bigot@insa-lyon.fr, [b]mhamed.boutaous@insa-lyon, [c]nahiene.hamila@enib.fr, [d]shihe.xin@insa-lyon.fr

Abstract. A numerical model simulating the crystallization kinetics in fiber-based composites with a thermoplastic semicrystalline matrix is proposed. The model, based on Schneider's formalism, considers the specificity of crystalline entities (transcrystallinity) growing in a confined media such as fibrous composite. Indeed, transcrystallization has been experimentally observed many times and its effects on both kinetics and mechanical properties of polymers have been largely demonstrated. As an application, this paper aims at illustrating this former effect during the cooling step of a composite plate in thermoforming process. The simulated materials based on finite elements method (FEM) are polypropylene alone and a fiber-based composite with a polypropylene matrix. Information on the temperature, the rate of transformation and the microstructure are obtained from both materials and compared to emphasize the contribution of transcrystallization.

Introduction

Fiber-based composites with polymer matrix are largely used in industry. The control of the anysotropy of those materials, associated to a combination of low density and high rigidity enable to optimize the material parts quality. In this area, the use of thermoplastic semicrystalline polymer is of main interest. Nevertheless, the crystallization kinetics and the microstructure are relying on the conditions of the process, especially the temperature and the pressure kinetics. So, a profound knowledge of those conditions is required to efficiently control the mechanical properties of the composite parts.

The process of thermoforming comprises in four stages : the heating, the forming, the consolidation and the demoulding. Firstly, the thermoplastic matrix is heated up in an infrared (IR) oven to a temperature up to its melting temperature. The composite part is quickly brought to the mould with a robotic arm for the forming stage. During the consolidation, a growing pressure is applied in order to reduce the porosity of the sample being cooled in the mould. The cooling down of the material continues after the demoulding.

The mould is either at room temperature or pre-heated but the difference of temperature with the composite piece is important enough to generate a thermal shock when in contact. Therefore, as those materials exhibit very low thermal diffusivity, an important thermal gradient occurs in the thickness, leading to an important gradient in the material. With semicrystalline polymers, that means crystallization near the surface occurs with different thermal processing conditions than in the core. A gradient in microstructure itself arises which induces a gradient in mechanical properties.

Besides the processing conditions in temperature and pressure, the fibrous structure of thermoplastic composite must be considered. Indeed, fibers can modify the microstructure of semicrystalline matrix by inducing important nucleation rate. According to the processing conditions and the choice of the fiber/matrix couple, transcrystalline structures can grow up. Transcrystallization increases the rate of the global crystallization kinetics. During the forming phase, the gradient in microstructure between the surface and the core grows stronger. But, the development of transcrystallinity could be helpful for the reinforcement of the polymer/fiber interface, leading to mechanical properties enhancement.

All these considerations together emphasize that a crystallization kinetics model considering the transcrystallization is of main interest to simulate the structural conditions of a fiber-based composite with semicrystalline matrix during the thermoforming process.

Modeling

Crystallization in semicrystalline polymer takes place in two stages, the nucleation and the growth. A sample is set to be at a temperature up to the equilibrium melting temperature T_f^0, i.e. the temperature from which no active nucleus exist. When the temperature decreases, the nuclei, i.e. potential crystalline structures, pop up uniformly in the media in a proportion dependent on the temperature. This is the nucleation process.

From a nucleus, a crystalline structure grows at a rate dependent on the local temperature. This is the growth process. Considering that the temperature of the media is uniform, and since the rate is only dependent on the temperature, the crystalline entity grows at the same growth rate in every directions. A sphere is logically obtained which is called a "spherulite".

In a fibrous media, the fiber surface appears to be a nucleating agent. On the surface, the nuclei density is higher than the one in the surrounding bulk polymer. During the growth stage, on the surface of a fiber, because of the proximity of each nucleus, a spherulite can only grow in one direction, radially to the fiber's surface. This is the "transcrystallization" phenomenon. Since the nucleation is quasi-instantaneous and the temperature is locally uniform, a cylindrical crystal can be seen growing around the fiber (Fig. 1). However, this is only a macroscopic observation. In fact, this is thousands of confined spherulites, born at the same instant and growing at the same rate.
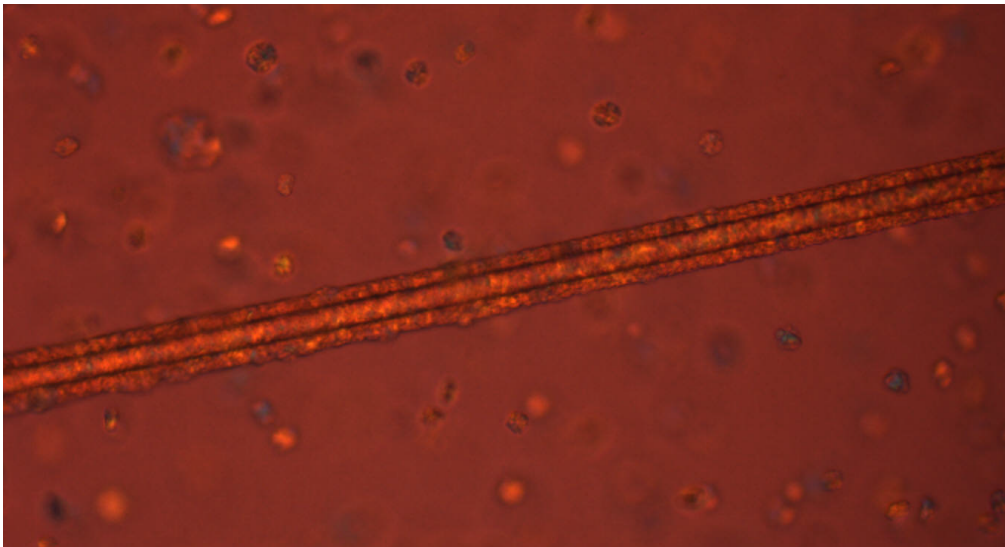

Fig. 1: Transcrystalline structure growing around a glass fiber in polypropylene in isothermal condition at 135°C

Several crystallization kinetics models already exist. The first approach was to consider how the presence of fibers influences the shape of the spherulites. Bernard and Advani [1] determined the subtracted volume of a spherulite depending on its distance from the fiber. Piorkowska and al. [2] developed a probabilistic approach. They determined the probability that a random point of the media is located in a crystallized region. Their approach was initially used for bulk polymer and then extented to fibrous media. Durin and al. [3] used the Haudin and Chenot's model [4] adding a correction to the density of nuclei. Indeed, in the material, the fibers overlap the volume initially occupied by bulk polymer and so, by nuclei. However, those three models did not consider the transcrystallization phenomenon.

Recent models tried to deal with transcrystallization and its impact on overall crystallization kinetics. Durin an al. [3] worked on continuous fibers. They split the composite material into two sub-spaces. Close to the fiber, transcrystallization occurs and is described as a growing cylinder surrounding the fiber. Far from the fiber, crystallization occurs like in bulk polymer. Therefore, usual crystallization kinetics models can be applied as in Haudin and Chenot's model [4]. In Frang and al. work on short fibers [5, 6], spherulites and transcrystalline cylinders are assumed growing in the same space. The rate of transformation is obtained from Kolmogoroff's equations [7].

In this wor, the proposed model of crystallization in confined long fiber composite material is based on the experimental observations shown in Fig.1. Following the same concept as in [3], the media is divided into two sub-spaces. Near the fiber, crystallization is described by the growth of a cylinder. In the surrounding bulk polymer, spherulites are growing without considering the presence of fibers (Fig. 2).

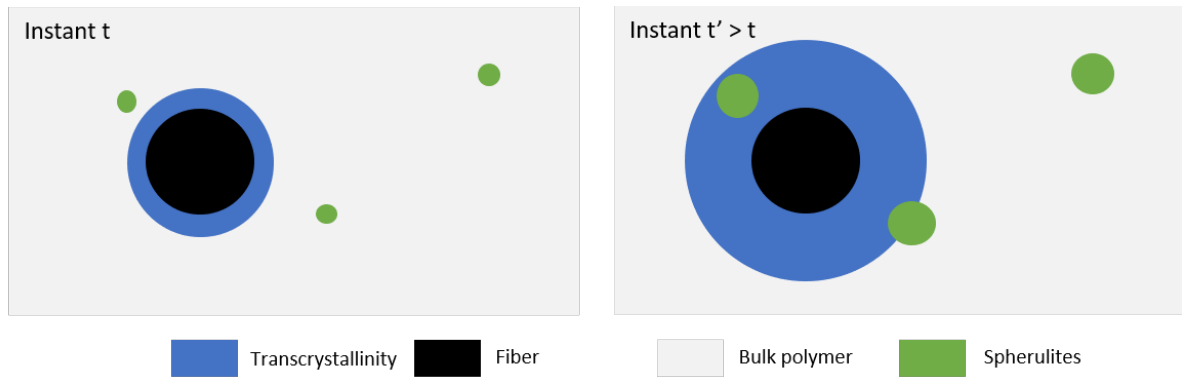| Transcrystallinity | Fiber | Bulk polymer | Spherulites |

Fig. 2: Schema of the crystallization in confined media

In this framework, a conventional crystallization kinetics model can be applied. Schneider's formalism [8] is used. Indeed, this formalism considers spherulites as geometrical objects. So, the volume of the crystalline phase is equal to the total volume occupied by the spherulites.

$$V_{tot}(t) = \sum_i (\frac{4}{3}\pi R_i^3(t)) = \frac{4}{3}\pi \sum_i R_i^3(t) = \varphi_0(t) \tag{1}$$

With $R_i(t)$ the radius of a spherulite at time t. By successive derivation the total volume with respect of time, the total area, then the total radius and finally the density of crystalline entities N are obtained as in the following equations:

$$\frac{d\varphi_0(t)}{dt} = (4\pi \sum_i R_i^2(t)).\frac{dR}{dt} = S_{tot}(t)G(t) \tag{2}$$

$$\frac{d\varphi_1(t)}{dt} = 4\pi(\sum_i \frac{dR_i^2(t)}{dt}) = 8\pi R_{tot}(t)G(t) \tag{3}$$

$$\frac{d\varphi_2(t)}{dt} = 8\pi(\sum_i \frac{dR_i(t)}{dt}) = 8\pi N_{tot}(t)G(t) \tag{4}$$

$$\frac{d\varphi_3(t)}{dt} = 8\pi \dot{N}(t) \tag{5}$$

The empirical expressions for the density of nuclei function of the temperature are taken from [9, 10], and the total volume can be deduced by successively integrating with respect of time. However, Schneider's formalism stands out the other kinetics models thanks to an easy to solve differential system.

$$\dot{\varphi}_0 = G(t)\varphi_1(t) \tag{6}$$
$$\dot{\varphi}_1 = G(t)\varphi_2(t) \tag{7}$$
$$\dot{\varphi}_2 = G(t)\varphi_3(t) \tag{8}$$
$$\dot{\varphi}_3 = 8\pi\dot{N}(t) \tag{9}$$

With G is the growth rate of spherulites whom a theoretical expression based on thermodynamical considerations exists [11].The impingement of spherulites is considered thanks to Avrami's correction [12] :

$$V_{real} = 1 - \exp(-\varphi_0) \tag{10}$$

Where φ_0 is the total extended volume of the spherulites.
Schneider's formalism also exhibits a great modularity for the description of supplementary phenomena such as shearing [13] and flow [14] conditions. Since shearing induced an additional nuclei density (Eq. 11), the previous differential system can be divided into two sub-systems, one identical to the previous static one and the other associated to the shear (Eq. 15,16,17), see details in [13, 14, 15]

$$N(t) = N_0(t) + N_f(t) \tag{11}$$

The flow is considered with advection term dependent on the flow velocity :

$$\dot{\varphi_{20}} + v.\nabla\varphi_{20} = G(t)\varphi_{30}(t) \tag{12}$$
$$\dot{\varphi_{10}} + v.\nabla\varphi_{10} = G(t)\varphi_{20}(t) \tag{13}$$
$$\dot{\varphi_{00}} + v.\nabla\varphi_{00} = G(t)\varphi_{10}(t) \tag{14}$$

$$\dot{\varphi_{2f}} + v.\nabla\varphi_{2f} = G(t)\varphi_{3f}(t) \tag{15}$$
$$\dot{\varphi_{1f}} + v.\nabla\varphi_{1f} = G(t)\varphi_{2f}(t) \tag{16}$$
$$\dot{\varphi_{0f}} + v.\nabla\varphi_{0f} = G(t)\varphi_{1f}(t) \tag{17}$$

Finally, both contributions are represented in the final volume V_{real}, the one due to the temperature φ_{00} and the other due to shear conditions φ_{0f} :

$$V_{real}(t) = 1 - \exp(-\varphi_{00} - \varphi_{0f}) \tag{18}$$

For the transcrystallization, the growth rate of the transcristalline cylinders and the spherulites are set to be the same. Schneider's formalism is applied in a similar way than Eq. 18. The impingement between spherulites, between spherulites and transcristalline cylinders and between transcrystalline cylinders are considered with Avrami's correction :

$$V_{real} = 1 - \exp(-\varphi_{0_{tr}} - \varphi_{0_{sph}}) \tag{19}$$

with $\varphi_{0_{tr}}$ and $\varphi_{0_{sph}}$ the extented volume of the transcristalline and the spherulitic entities respectively.

Numerical Simulation and Analysis

The present work is based on a home-made finite element solver derived from [16] and run on python. A 2mm plate, initially at 200° C, is cooled down. The studied material will be either a polypropylene or a fiber-based composite with polypropylene matrix. Heat exchange takes place between a face of the plate and the outside, characterized by a external temperature T_{ext} and a heat exchange coefficient h. The other side of the plate is insulated. The problem is reduced to a 1D transient heat problem (Eq. 20). Since the crystallization is an exothermic reaction, a heat source term Φ_{cr} is added in every equations :

$$\rho(T,\alpha)c_p(T,\alpha)\frac{\partial T}{\partial t} = \lambda(T,\alpha)\frac{\partial^2 T}{\partial z^2} + \Phi_{cr}(T,\alpha) \tag{20}$$

$$\Phi_{cr}(T,\alpha) = \rho(T,\alpha)\Delta H_\infty \frac{\partial \alpha}{\partial t} \tag{21}$$

With the enthalpy of crystallization ΔH_∞, the density ρ, the thermal conductivity λ and the specific heat c_p depending on both temperature T and the rate of transformation α.

The crystallization kinetics is modeled with Schneider's formalism as presented previously. The values of the φ_i are obtained by solving Schneider's differential system with a second order Runge-Kutta scheme. Deriving Eq. 10, an explicit form of Eq. 21 can be written, based on the φ_i functions :

$$\frac{\partial \alpha(t)}{\partial t} = \frac{\partial \varphi_0(t)}{\partial t}\exp(-\varphi_0(t)) = G(t)\varphi_1(t)\exp(-\varphi_0(t)) = G(t)\varphi_1(t)(1-\alpha(t)) \tag{22}$$

A generalized trapezoidal scheme is used :

$$\frac{T(t+\Delta t) - T(t)}{\Delta t} = (1-\nu)\dot{T}(t) + \nu\dot{T}(t+\Delta t) \tag{23}$$

And the value $\nu = 1$ is applied to obtain an Euler implicit scheme. The non-linearity of the problem is treated with a Raphson-Newton algorithm. The expressions of the material parameters for both thermal and crystallization aspects are detailed in [14].

After validation of the model based on comparison of result with the literature , a parametric study is performed to simulate mainly temperature, crystallization and material structure (spherulite distribution) in the material under severe processing conditions. Fig.3 summarizes some original results like the temperature evolution at different location, the crystallization rate and the mean size of the crystalline structures in a polymer (polypropylene) without fibers. In Fig.3.a, the temperature evolution at three different locations in the thickness shows clearly the important thermal gradient experienced by the material during the process. Note the importance of exothermal energy developed by the material due to the crystallization, represented by the inflexion of the curves at different times for different locations. This is confirmed by the different crystallization rates presented in Fig.3.b, where clearly, the core exhibits a delay in the heat crystallization compared to the surface line where the cooling process is faster. More interesting, as a consequence of such thermal gradient, an important structure gradient is induced in the material thickness. As shown in Fig.3.c, the mean size of these spherulites is higher in the core zone where the material experiences a soft cooling kinetics compared to the surface, where the interaction with the mould leads to a sudden cooling and relative small size of crystallite. Those results will be helpful to build constitutive models to describe the mechanical behaviour of such material in connection to their real structure.

Similar results and analysis are valid in case of composite materials where fibers are added to the polymer matrix. As the fibers are thermally more conductive than the matrix, the composites material exhibits faster thermal kinetics. In fact, Fig.4 represents the mean size of the crystalline structures. Only the crystalline part in the bulk zone far from the fiber is presented. The spherulites in the core
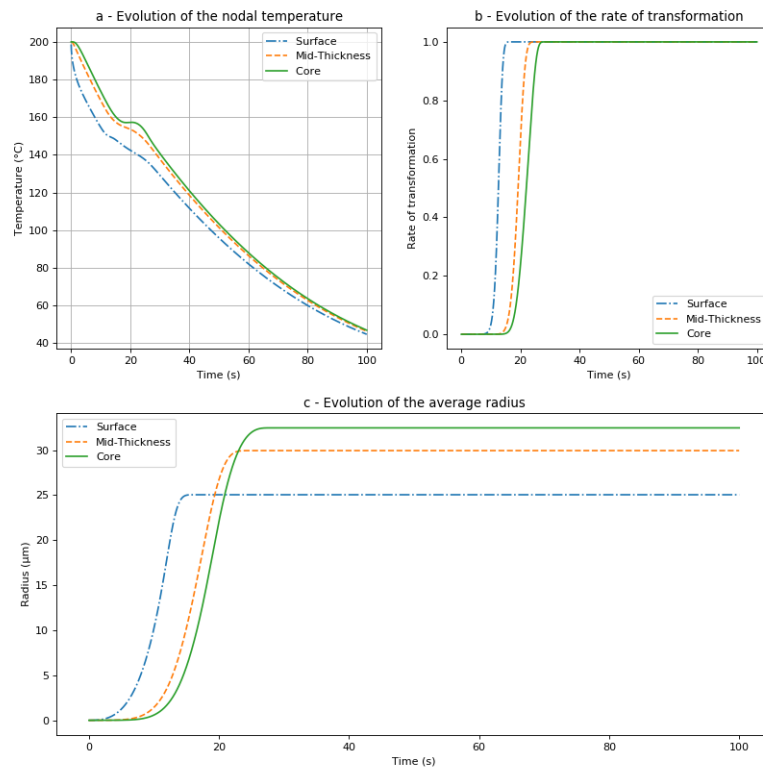
Fig. 3: Evolution of the temperature, the rate of transformation and the radius of the spherulites in a polypropylene plate

are smaller than those near the surface, which is the opposite trend observed in Fig.3.c. The transcrystallization occurs first. By the beginning of the spherulites growth, the media is already crowded by the transcrystalline structures. The remaining space does not allow the spherulites to reach a higher radius. Inversely, near the surface, as the contact with the cold mold imposes a sudden decrease of the material temperature, the crystalline nucleation starts early in both the polymers matrix and on the fiber surface. Hence, the growing spherulites in the polymer are in real competition with the creation of the transcrystallinity in this zone, leading to relative higher size than those in the core.

Conclusion

The presented work belongs to a larger framework. A crystallization kinetics model considering transcrystallization should be able to provide for a realistic description of the microstructure of the semicristalline matrix. So, the numerical simulation of composite material during processing should be based on a realistic estimation of the thermo-physical properties evolution. In this article, the proposed crystallization kinetic model relies on Schneider's extended formalism. The model is expanded to the crystallization in fibrous media, considering the transcrystallization. The results demonstrate and quantify the known effects of transcrystallization, i.e. a speed up of the overall crystallization kinetics. The model is able to provide for spherulites and transcrystallines microstructures. Based on this information, it will be of main interest to simulate the mechanical behaviour of composite material during and after the thermoforming process, and hence propose constitutive laws based on the real description of the material structure (work in progress).
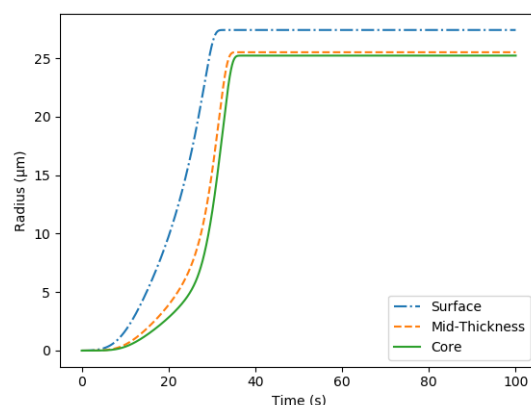
Fig. 4: Evolution of the radius of the spherulites in a fibrous composite plate with a polypropylene matrix and glass fibers

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