Fused filament fabrication: Numerical adhesion modeling suitable for semicrystalline polymers

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Abstract. Numerous studies have been conducted to improve the adhesion quality at the interface between the filaments which remains one of the weak points in the FFF process. The interfacial adhesion of printed parts has already been investigated by several authors for amorphous polymers. However, for semicrystalline polymers, the influence of crystallization on adhesion kinetics as well as the description of partial melting at interfaces between filaments are not well taken into account in the models describing FFF process. The purpose of this work consists of proposing a predictive multiphysics model that enables the prediction of the adhesion degree for semi-crystalline polymers during FFF process. The coupling of a crystallization and melting model allows the estimation of the crystalline degree evolution at the interface. The use of a recent model predicting the molecular mobility as a function of temperature and crystallization makes it possible to estimate the degree of healing in anisothermal conditions. Finally, a parametric study is performed in order to propose process window improving the adhesion quality.

Introduction

In recent years, additive manufacturing has been the subject of many studies, regardless of the type of technology. The Fused Filament Fabrication (FFF) process being the most widespread, a great deal of attention has been paid to it. It is one of the affordable additive manufacturing technologies with a simple technology and a fast manufacturing speed. Nevertheless, one of the notable limitations of the FFF process is the decrease of the mechanical properties, compared to conventional processes like injection molding. These mechanical properties are low in the direction normal to the interfaces, resulting in high anisotropic properties [1]. The decrease in mechanical properties is related to the presence of porosities and the low interfacial strength between filaments. A lot of researches have been performed to improve the quality of the parts manufactured with this process [1,2].

Adhesion in the FFF process takes place in several steps. First, the material melted by the nozzle is deposited on the previous filament, intimate contact occurs and interfaces develop with the other filaments. This phenomenon called coalescence is strongly controlled by the rheological behavior of the material and the surface tension but also external pressures such as nozzle crushing. When coalescence begins, the healing process starts with the diffusion of polymer chains through the interfaces in order to create a real molecular bond with the others filaments [3].

Coalescence and healing are only possible if the chains present at the interfaces have sufficient molecular mobility [4]. Molecular mobility is governed by the thermodynamic state of the polymers, for the amorphous phase, mobility is restricted below the glass transition [5]. Finally, in the case of semicrystalline polymers, crystallization may limit the adhesion phenomenon. These mechanisms are therefore strongly dependent on the rheological behavior evolving with the temperature and the crystalline degree of the polymer [6].

Studies were conducted to predict the thermal history of the FFF process and its influence on interfacial adhesion. A large majority of the studies consider the heat transfer at the interface assuming a homogeneous temperature within the thickness of the filament [3,7]. But some studies have proposed thermal modeling at the filament scale in order to estimate more precisely the interface temperature [2]. From these works, numerical Finite Element Method (FEM) models were developed and showed good agreement with experimental tests in the case of amorphous polymers.

However, for semicrystalline polymers, even if some works take into account the influence of crystallization and melting enthalpies o heat transfer, none of them realize a real link with the adhesion physics [8]. The only studies that propose to predict the healing degree as a function of crystalline degree assume that adhesion stops abruptly at the beginning of crystallization [9]. In spite of this approximation the authors obtained consistent results with the experimental. Nevertheless, several studies showed that despite the presence of crystals, for low crystallinity degree, the adhesion mechanism can continue because the amorphous phase still has a certain level of mobility [10,11]. In recent years, a promising time-temperature-crystallization-superposition (TTCS) model has been studied in order to predict the evolution of molecular mobility as a function of temperature and crystallinity and could allow a better understanding of adhesion with semicrystalline polymer [10,12].

Multiphysics Modeling of FFF Process

In this work, heat transfers, phase transformations and adhesion physics are implemented in a coupled multiphysics model. The model does not represent the rheology of the deposited filament. Assuming an instantaneous flow, a non-deformable oblong section will be taken to build the model. The simulation is performed in a single computational step where the use of boolean conditions allows the model to evolve in order to represent the successive filaments deposition. This allows a strong coupling between heat transfers and phase transformations.

The numerical resolution was performed on a 2D model simulated by FEM on COMSOL® software. In agreement with the work of [2], we develop a dimensionless modelling with the simplifying hypothesis that the thermal exchanges occur mainly in the plane orthogonal to the deposition direction. A comparison between 2D and 3D models validated this assumption. The deposition is simulated by the domain activation method and the boundary conditions change according to the deposition steps.

Heat transfer and phase transformation are computed on the whole domain. At each calculation step, the healing degree is evaluated on filaments interfaces in order to predict their evolution over time as a function of temperature and crystalline degree.

The driving mechanisms of coalescence are more difficult to quantify and can make the simulation complex. Indeed, some authors agree that the phenomenon is driven only by viscous effects and surface tension [2,13]. While others describe a strong influence of the printing nozzle pressure on the filament geometry [3].

Based on these studies, our model will consider an oblong geometry with a constant and homogeneous section without defects. The oblong geometry allows to take into account the porosities present between the filaments. The fillet size will be based on micrographic observations of a printed part. An 8 filament high wall was simulated in one step. The model being adaptive, it is possible to simulate a wall of several filaments wide as shown Fig. 1.

Heat transfer.

The thermal model is represented in Fig. 1. In the domain, we solve the energy equation coupled with crystallization and melting. The source term present in the energy equation term depends on ΔH the crystallization and melting enthalpies and α the crystalline degree. In order to represent the effects of the heating nozzle, the initial temperature of each new filament is considered uniform and set to T_{NOZZLE} to represent the extrusion set point. The bottom surface of the first filament is fixed at the temperature T_{BED} throughout the simulation process in order to represent the printing plate setting. Heat transfer between the environment and the deposited filaments are considered only convective. It is considered a constant chamber temperature $T_{Chamber}$ throughout the deposit. The boundary conditions are re-evaluated at each deposit thanks to boolean variables in order to make the model evolve with the deposit. Thermal contact resistances (TCR) were applied between the filaments to represent contact imperfection [2].

The characterizations of thermal conductivity k, heat capacity Cp and density ρ were performed on PAEK (Polyaryletherketone). The thermal property measurements were performed above the glass transition in the semi-crystalline solid state taking into account the influence of temperature. We will consider a linear variation of the thermal properties with temperature and will realize the simplifying assumption that the values are identical whatever the crystalline degree.

Model parameters such as layer thickness, printing speed, nozzle temperature are chosen as representative of real process [14].

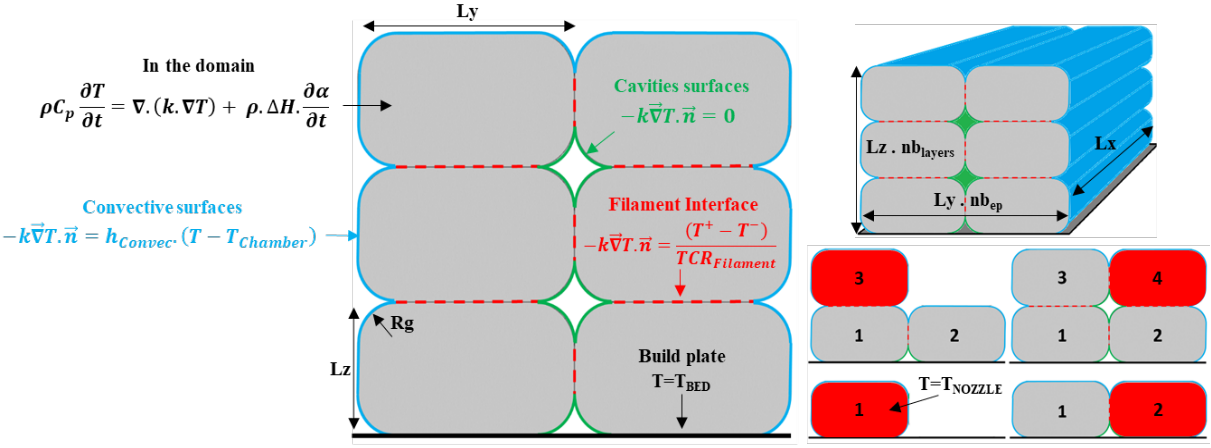

Fig. 1. Schematic representation of the case study.

Phase transformation: Crystallization/melting.

In order to predict the evolution of the crystalline degree as a function of the thermal history, a phase change model including crystallization and melting was added to the model.

Given the high heating rates of the interface during deposition, we will consider that the material undergoes a simple melting without simultaneous melting and recrystallization [15]. It is therefore possible to model the two mechanisms separately by considering a transition temperature $T_{Transition}$ at 300°C.

- Crystallization kinetics

In the case of the FFF process, crystallization generally takes place in non-isothermal conditions. In order to model the formation and growth of crystals we chose the Nakamura model Eq. (1) which is the most widely used in the literature [16].

$$\frac{d\alpha}{dt} = K_{NAK}(T).G(\alpha) \quad , \qquad with\ G(\alpha) = n\,(1-\alpha)[-\ln(1-\alpha)]^{1-\frac{1}{n}} \tag{1}$$

where α is the relative crystalline degree, $K_{NAK}(T)$ the Nakamura kinetics coefficient calculated by $K_{NAK}(T) = K_{AVRAMI}(T)^{1/n}$ obtained in isothermal conditions and n the Avrami index [17].

Furthermore, in the FFF process, when the previously crystallized filament is heated due to the new deposit, it is possible that at low interfacial temperatures the polymer is partially melted. The kinetics of crystallization from a partially melted state is not well explored and no model is available in the literature. We will therefore assume that during a recrystallization from a partial melt, the kinetics is not impacted and therefore the polymer behaves as if it had simply stopped the crystallization. As our PAEK has too high crystallization kinetics to be characterized by differential scanning calorimetry (DSC), a test campaign was performed on fast scanning calorimeter (FSC) to estimate the thermal dependency of the isothermal Avrami coefficients $K_{AVRAMI}(T)$ over the large temperature range [160°C – 300°C].

- Melting kinetics

The melting kinetics has been further explored in the case of thermoplastic polymers. It has been shown that the thermo-kinetic models available in the literature taking into account the heating rate only allow to represent a restricted range of rates [8]. Moreover, these models cannot predict the interruption of melting during isotherm or cooling.

In several works, authors made the assumption that the melting behavior depends only on the temperature by considering an instantaneous mechanism independent of the heating rate over a certain range [18]. In this study, we also have chosen this approach by taking a statistical distribution model of the crystalline lamellae thickness which is temperature dependent Eq. (2).

$$\alpha = \alpha_{max}.Melting(T) \tag{2}$$

Melting function was estimate by temperature integration of the melting peak measured on DSC and weighting α_{max} in order to represent the melting under conditions of incomplete crystallization, case where $\alpha_{max} < 1$.

Implementation of the melting and crystallization models in the same simulation model allows to predict the melting zone and time available for the interfacial healing. For example, it can be seen in Fig. 2 that the interface melted during the deposition because of the heat provided by the hot filament.

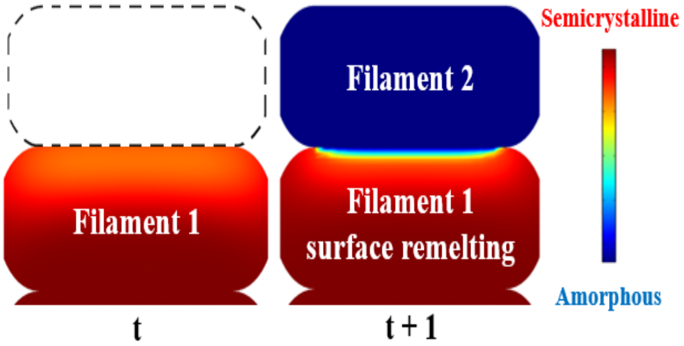

Fig. 2. Remelting of the filament surface after a second hot filament deposition.

Healing coupled with crystallization degree.

Prediction of healing at interfaces was also added in the modelling taking into account the coupling of an anisothermal healing model and a time-temperature-crystallization-superposition model

- Healing model.

In order to represent the adhesion kinetics in the anisothermal case, we proposed to use the empirical model largely defined in Eq. (3).

$$D_{Healing}(t) = \sqrt[4]{\int_0^t \frac{dt}{t_{welding}}} \tag{3}$$

where $D_{Healing}$ is the healing degree and $t_{welding}$ the experimental measured welding times to achieve complete welding of an interface under isothermal conditions.

Several authors showed that in the case of several thermoplastics, the welding times can be considered as equal to the molecule reptation times $t_{reptation}$ [19] with a good agreement with the experiment. In order to simplify the numerical solution, an integrative form was proposed by [2]. Taking into account the assumption that the relaxation times are equal to welding time, we obtain Eq. (4) with Δt the calculation step, and *t* the simulation time step.

$$[D_{Healing}]_{t+1} = \left(\frac{\Delta t}{t_{reptation}} + [D_{Healing}]_t^4\right)^{\frac{1}{4}} \tag{4}$$

- Time / Temperature / Crystallization Superposition (TTCS).

In order to represent the evolution of the molecular mobility during the process, it is necessary to know the relaxation time of the polymer according to its local environment. To our knowledge, no study takes into account the crystalline degree in its adhesion model. Indeed, while the evolution of molecular mobility as a function of temperature is well known with the time-temperature-superposition TTS, few studies focus on the influence of the presence of crystals on polymer diffusion.

But recently, some studies have converged to present a time-temperature-crystallization-superposition TTCS principle Eq. (5) based on experimental approaches [12].

$$\tau(T,\alpha) = \underbrace{a_t(T_{REF},\alpha_0,T)}_{\textbf{Thermal shift factor}} \,.\, \underbrace{a_\xi(T_{REF},\alpha_0,\alpha)}_{\textbf{Cristalline shift factor}} \,.\, \underbrace{\tau(T_{REF},\alpha_0)}_{\textbf{Reference time}} \qquad (5)$$

where T_{REF} and α_0 are respectively the temperature and crystalline degree reference and τ the reptation time.

The model proposes a shift of rheological properties similar to thermal shift but with the crystalline degree. The postulated TTCS is very promising and has shown its consistency on several polymers. Moreover, several previous studies have shown that the evolution of rheological properties is proportional to the volume of crystallites and not to the shape or size of crystals [20]. These observations suggest that they can be applied to all types of crystallization. Moreover, the principle of TTCS allows to correctly represent the state of molecular mobility in cases of isothermal and anisothermal crystallization. Its general validity must be evaluated in order to apply it widely to all polymer families. Nevertheless, being the only model available in the literature, we will use it to predict the evolution of the mobility depending on the temperature and the crystalline degree. The thermal shift factors were fitted using the Williams-Landel-Ferry equation (WLF) [21] and the crystalline shift factors using a power law as proposed by defined [10] in Eq. (6).

$$\ln[a_t(T_{REF},\alpha_0,T)] = \frac{-C1(T-T_{REF})}{C2+(T-T_{REF})} \qquad and \qquad a_\xi(T_{REF},\alpha_0,\alpha) = 10^{\,B1.\alpha^{B2}} \qquad (6)$$

where C1, C2, B1 and B2 are fitting coefficients.

Rheological measurements were carried out in our laboratory between 360°C and 400°C under nitrogen in the amorphous state in order to estimate the thermal shift factor. The model coefficients of the crystallinity shift factor are taken from the literature [10].

As previously explained, by integrating all these models in the same study, the multiphysics model is able to predict the evolution of reptation time as a function of temperature and crystalline degree in anisothermal condition. In order to explain the model, we have calculated the evolution of the relaxation time for several constant cooling rates. The results are shown in Fig. 3.

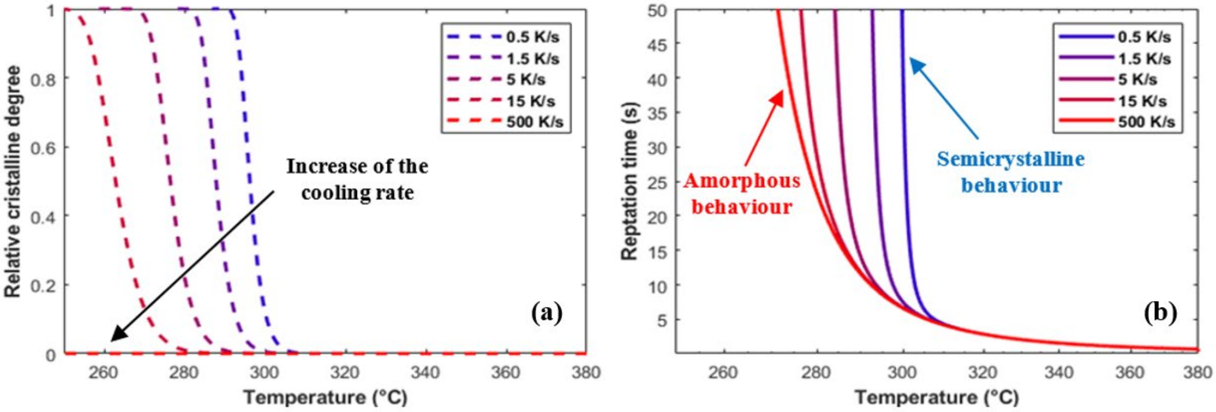

Fig. 3. (a) Relative crystalline degree and (b) the reptation time evolution under different cooling rate.

Fig. 3B represents the evolution of the creep time as a function of temperature and crystalline degree Fig. 3A. We notice that at high speed, the polymer remains amorphous during the cooling and the material follows the TTS law. But when the speed decreases and the material crystallizes, the reptation time increases quickly from the first moment of crystallization.

Results and Discussion

As said previously, a wall of 8 filaments high and 1 filament wide is simulated. All results are evaluated in the middle of the interface between the 5th and 6th layer so the results will begin at 32s. The simulations carried out from the multiphysics model allow to estimate the evolution of the crystallinity rate and the degree of healing according to the thermal history at the interface.

Simulations were performed with the TTCS model and with the TTC model in order to show the importance of taking into account the crystallization on the adhesion. Both cases were simulated with the same parameters except that the crystalline shift factor was numerically fixed at 1 to model the TTS.

With the conditions used in the simulation, it can be seen in Fig. 4, that the 5th filament crystallizes rapidly during cooling. During the next deposition, the heat generated by the upper filament partially melts the interface. The difference in the evolution of the degree of healing between the TTCS and TTS models describes the low molecular mobility of the chains due to the presence of crystals at the interface. Indeed, the final degree of healing is divided by 10.

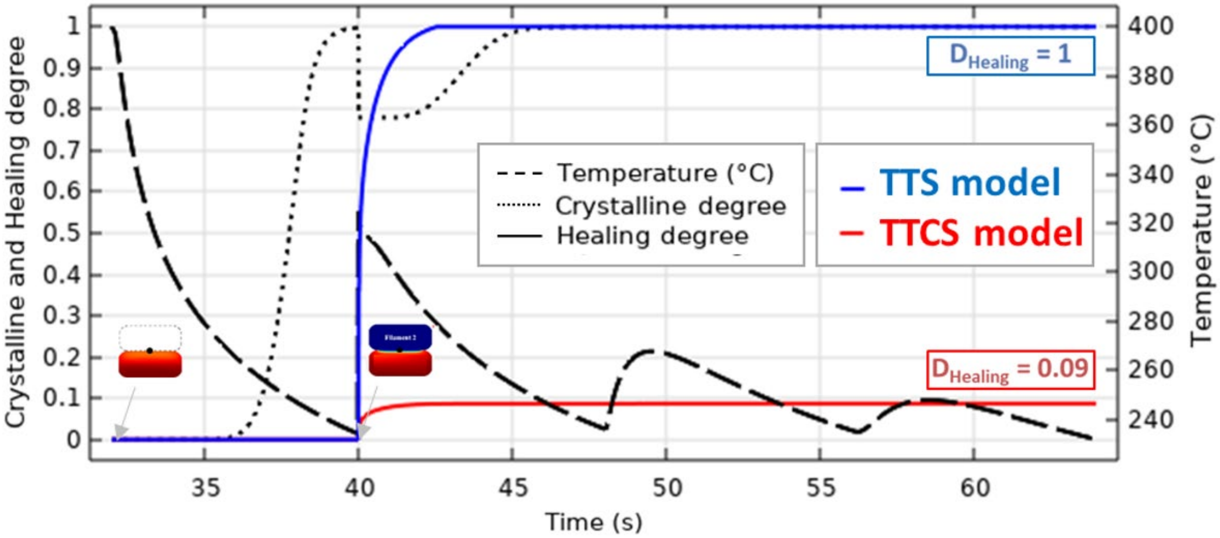

Fig. 4. Evolution of computed temperature, crystalline and healing degree with TTS and TTCS model.

To show the influence of the thermal environment on the adhesion degree, we varied the chamber and bed temperatures between 150°C and 270°C as shown Fig. 5. It is first noticed for temperatures lower than 200°C, *i.e.* where the cooling is fast, that the filament crystallizes completely before the next deposition. In these cases, only melting can allow a noticeable decrease of crystalline degree and thus a better adhesion. Because during deposition the interface temperature is not high enough to allow a total fusion, the healing degree are very low (<0.09). At high temperatures, the crystals are not yet formed at the time of deposition (T≥250°C) therefore a better healing degree is obtained.

This numerical study allows to estimate the process range in order to obtain a correct interface with a complete crystallization at the end of printing. Other parameters such as nozzle temperature, printing speed, number of beads per layer, deposit order can be tested to evaluate their influence on crystallization and adhesion.

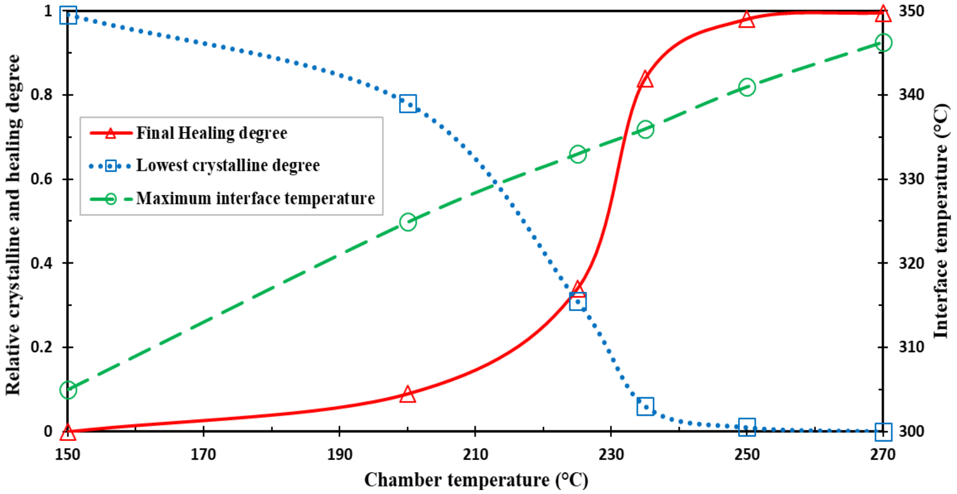

Fig. 5. Evolution of computed maximum interfacial temperature, lowest crystalline degree and final healing degree reaches after deposition as function of chamber temperature.

Summary

A multiphysics model was developed to represent the thermal history, crystalline and adhesion degree evolution at the filament scale in the FFF process. Modeling development allowed to calculate the evolution of the crystalline degree on the whole domain and in particular at the interfaces. Indeed, the model describes crystalline degree remaining after the melting generated by the deposit and the time before recrystallization. A brief parametric analysis demonstrates the non-negligible influence on the crystalline evolution on interfacial adhesion. In fact, it is shown that complete healing is only possible if the crystalline degree is close to zero. This model allows us to understand the influence of many printing parameters on adhesion and therefore to propose groups of parameters in order to improve the printing quality.

In order to confirm that the model correctly predicts the evolution of the crystalline degree as well as the effective adhesion degree of the printed part, an experimental study will have to be carried out and the adhesion values confronted with mechanical tests. Moreover, a next study will aim to model more finely the melting kinetics as well as the recrystallization kinetics through an experimental campaign.

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