



## Crystallization Kinetics of Polyamide 2200 in the Modelling of Additive Manufacturing Processes by FE Analyses

Paweł BAJERSKI<sup>1</sup>\*, Ryszard B. PECHERSKI<sup>2</sup>), Damian CHUDY<sup>2</sup>)  
Leszek JARECKI<sup>3</sup>)

<sup>1</sup>) *ABB Sp. z o.o. Corporate Research Center*  
Starowińska 13A, 31-038 Cracow, Poland

\*Corresponding Author e-mail: pawel.bajerski@pl.abb.com

<sup>2</sup>) *AGH University of Science and Technology*  
*Faculty of Mechanical Engineering and Robotics*  
Al. Mickiewicza 30, 30-059 Cracow, Poland  
e-mail: rpe@agh.edu.pl, damlok24@gmail.com

<sup>3</sup>) *Institute of Fundamental Technological Research*  
*Polish Academy of Sciences*  
Pawińskiego 5B, 02-106 Warsaw, Poland  
e-mail: ljarecki@ippt.pan.pl

The thermoplastic polymers present amorphous or semi-crystalline structures which are very important factors in describing volumetric shrinkage. The thermoplastic materials are commonly used for production of daily life products, industrial or as the prototypes. Different techniques of manufacturing polymer structures are considered like: injection molding, extrusion, milling, additive manufacturing (AM). AM is a very fast developing field in the manufacturing and research. Unfortunately, components or prototypes made using the thermoplastic semi-crystalline materials in 3D techniques have quite low mechanical strength compared to the parts made by injection molding processes. It is caused by porosity obtained during the processing, as well as by fraction of crystallinity in the volume of the components. Additionally, the volumetric shrinkage is hard to predict without knowledge of its origin. Therefore, it is necessary to consider crystallization kinetics and the melting of the analysed materials. The investigations presented in this work concern the crystallization and melting model to be implemented in the finite element (FE) analyses. With use of the model, one can predict development of the structure during the real processes and, in the future, to control the warpage of the manufactured components.

**Key words:** additive manufacturing; Avrami model; crystallization; Differential Scanning Calorimetry (DSC); glass transition temperature; Hoffman-Lauritzen theory; melting; PA2200; van Krevelen empirical model.

## 1. GENERAL

Additive Manufacturing (AM) process is a very fast and promising technique to build various very complex prototypes and components in massive production. One of the most common techniques in AM for thermoplastic materials are Selective Laser Sintering (SLS) and Fused Filament Fabrication (FFF). The complexity of the AM processes and the behaviour of the materials in specific environment have a strong influence on the quality, strength and warpage of the obtained structures. The state of the art of the studies indicates that the morphology of the material and the crystallization processes influence the aforementioned characteristics of the created components. The accumulated for many years knowledge on the crystallization kinetics of polymers is still developing in order to get an adequate description of the behaviour of the materials under various thermodynamic conditions, isothermal and non-isothermal one. The type of the process and the conditions have an influence on the crystallinity and its progress. The description of the crystallization kinetics for thermoplastic materials in the literature concerns mainly the injection moulding or extrusion processes. The available tools dedicated to the finite element (FE) analyses allow to increase functionality and implementation of the own material models and techniques to perform the customize simulations. Based on the theory and the Differential Scanning Calorimetry (DSC) results, it is possible to predict the behaviour of the material and work on simulation of the virtual AM process, as it is shown in [1–4].

## 2. POLYMER CRYSTALLIZATION

The crystallization kinetics theory describes the evolution of the degree of crystallization  $\alpha(t)$  as a function of time  $t$  and time-dependent temperature  $T(t)$ . The models of crystallinity evolution include information on the kinetics of crystal nucleation and growth in the bulk of material. The polymers cannot be fully crystalline. It means that the amorphous and crystallite fractions can coexist. The progress of crystallization is described by the Avrami equation for isothermal conditions, Eq. (2.1), where  $\alpha(t)$  is a fraction of the material transformed at time  $t$  [1],  $k$  – the Avrami constant,  $n$  – the Avrami exponent (see Table 1)

$$(2.1) \quad \alpha(t) = 1 - \exp[-k(T)t^n].$$

The Avrami exponent  $n$  is equal to the growth dimensionality in the case of heterogeneous nucleation or to the dimensionality increased by unity in the case of sporadic homogeneous nucleation,  $k(T)$  is the isothermal crystallization rate dependent on temperature and the geometry of crystal growth [1–3, 7].

**Table 1.** Avrami parameters [7].

Form of growth	$n$	$k$	$n$	$k$
Spherulitic (spheres)	3	$\frac{4}{3}\pi\vartheta^3 N\rho^*$	4	$\frac{1}{3}\pi\vartheta^3 J\rho^*$
Discoid (platelets)	2	$\pi b\vartheta^2 N\rho^*$	3	$\frac{1}{3}\pi b\vartheta^2 J\rho^*$
Fibrillar (rodlets)	1	$f\vartheta\pi N\rho^*$	2	$\frac{1}{2}f\vartheta J\rho^*$

$N$  – number of predetermined nuclei per unit volume,  $J$  – nucleation rate density,  $\vartheta$  – crystal growth rate,  $b$  – growth nucleus thickness,  $f$  – rodlet cross section,  $\rho^*$  – relative crystalline density [7].

Nakamura expanded the isothermal Avrami equation for non-isothermal crystallization [2, 3]. See Eqs (2.2) and (2.3).

$$(2.2) \quad \alpha(t) = 1 - \exp \left[ - \left\{ \int_0^t K [T(\tau)] d\tau \right\}^n \right],$$

$$(2.3) \quad \frac{d\alpha}{dt} = nK [T(t)] (1 - \alpha) \left[ \ln \left( \frac{1}{1 - \alpha} \right) \right]^{\frac{n-1}{n}},$$

where  $K(T)$  is a crystallization rate function dependent on the actual temperature. The Nakamura and Avrami theories can be directly related to the crystallization half time  $t_{1/2}(T)$  expressed by the Hoffman-Lauritzen theory [5, 7] (Eq. (2.4)). The material parameters needed in the crystallization model, such as the constants present in the rate function  $K(T)$ , i.e. the glass transition and equilibrium melting temperatures, specific heat of melting, heat capacity and other constants are determined from the DSC tests:

$$(2.4) \quad K(T) = k(T)^{1/n} = \ln(2)^{1/n} \left( \frac{1}{t_{1/2}} \right).$$

The crystal growth rate  $G(T)$  is described by the modified Hoffman-Lauritzen formula, e.g. Eq. (2.5). Determination of constants  $G_0$  and  $K_G$  requires to know  $G(T)$ , while the other parameters are assumed as constants or taken from literature. The temperature  $T$  and crystallization half-time  $t_{1/2}$  are determined with use of the DSC tests.  $T_\infty$  is the temperature at which transport of the chain segments stops, estimated as  $T_g - 30$  [K],  $T_m^0$  is the equilibrium melting temperature,  $U$  activation energy of molecular motion,  $R$  – gas constant,  $D = [\ln 2 / (C \cdot N_{\text{pred}})]^{1/n}$ , where  $N_{\text{pred}}$  is density of predetermined nuclei,  $C$  is the geometric constant of the order of unity [2–4]

$$(2.5) \quad G(T) = D \cdot \left( \frac{1}{t_{1/2}} \right) = G_0 \exp \left[ \frac{-U}{R(T - T_\infty)} \right] \exp \left[ \frac{-K_G(T + T_m^0)}{2T^2(T_m^0 - T)} \right].$$

Based on the DSC results for measured several different rates of cooling in the range of 0.2–40 K/min, it was determined average parameter  $D = 7.65 \cdot 10^{-3}$  cm and  $N_{\text{pred}} = 3.69 \cdot 10^5$  cm<sup>-3</sup>. The growth rate function  $G(T)$  is usually determined through the optical methods. However it is difficult to measure  $G(T)$  by optical methods because the samples need to be transparent during crystallization. One can applied an alternative way by using van Krevelen's empirical Eq. (2.6) that relates growth rate to the equilibrium melting temperature  $T_m^0$  and the glass transition temperature  $T_g$  [7]. The parameter  $G_K$  is the van Krevelen growth rate constant equal to  $7.75 \cdot 10^8$   $\mu\text{m/s}$ :

$$(2.6) \quad \log \frac{G(T)}{G_K} = -2.3 \cdot \frac{T_m^0}{T} \left( \frac{T_m^0}{T_m^0 - T_g} + \frac{50}{T_m^0 - T} \right).$$

The parameters taken from literature and calculated by the comparison of the modified Hoffmann-Lauritzen Eq. (2.5) with the empirical van Krevelen Eq. (2.6) are presented in Table 2.

**Table 2.** Parameters for the crystallization model.

Parameters from the literature [2, 3, 5, 7]		Parameters calculated by optimization [7]	
$T_m^0$ [K]	466.15	$G_0$ [ $\mu\text{m/s}$ ]	4.003e4
$T_g$ [K]	315.82	$K_G$ [K <sup>2</sup> ]	1.86e5
$U$ [J/mol]	6270		
$R$ [J/(mol·K)]	8.314		
$G_K$ [ $\mu\text{m/s}$ ]	7.75e8		
$T_\infty$ [K]	285.82		

The adjustment of the parameters for the crystallization model based on the empirical van Krevelen Eq. (2.6) and modified Hoffman-Lauritzen approach (2.5) is illustrated in Fig. 1. The parameter adjustment based on the matching curves is realized using the optimization methods utilizing the evolution solvers [3, 5, 7].

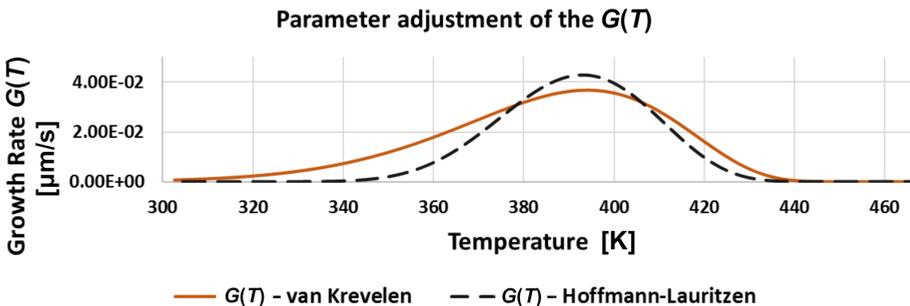


FIG. 1. Parameter adjustment of the growth rate  $G(T)$  models: van Krevelen and Hoffman-Lauritzen.

3. DIFFERENTIAL SCANNING CALORIMETRY (DSC) TEST

The fraction of crystallinity in the volume of material and the melting behaviour has been measured by DSC using STA 449 F1 Jupiter apparatus. The samples of polyamide PA 2200 in this study were obtained by the AM process in the SLS technique. Analysis of the crystallization kinetics of PA 2200 achieved with the DSC testing (solid lines) and comparison with the numerical approaches (dashed lines) are presented in Figs 2 and 3. One can see, that the numerical model presented in Sec. 2 describing the rate and fraction of crystallinity shows quite good approximation of the real crystallinity progress.

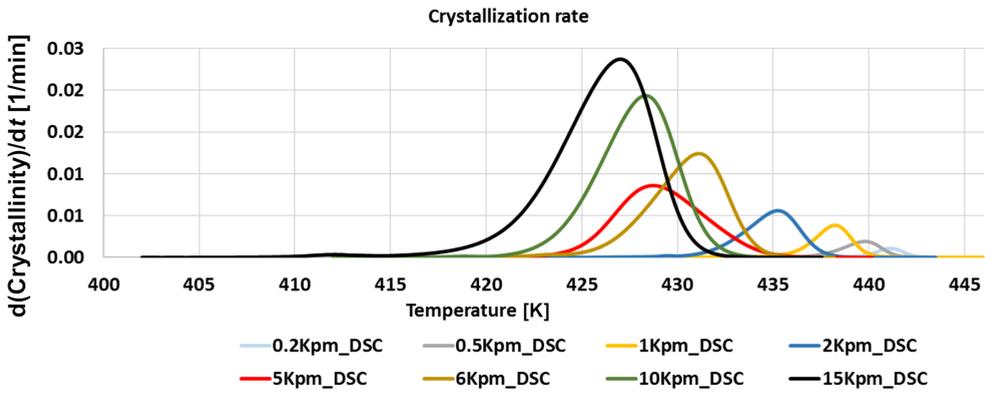


FIG. 2. DSC curves of the crystallization rate of PA 2200 at several cooling rates.

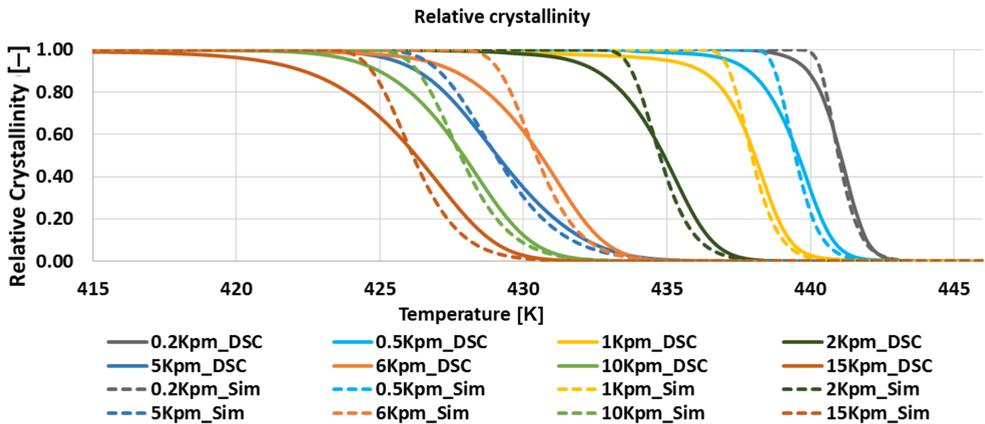


FIG. 3. Numerically simulated curves of the relative crystallinity of PA 2200 at several cooling rates (dashed lines,  $n = 3$ ) and the DSC curves (solid lines).

## 4. MELTING MODEL

In order to implement the AM process in the FE analysis, it is also necessary to consider a correct melting model. The AM process is based on cooling and melting of the material. After adding new layers of the melted material, the solidified structure undergoes re-melting in local areas. For that reason, Greco and Maffezzoli proposed a statistical sigmoidal model that could describe melting in semi-crystalline materials [6]. The degree of melting,  $X_m$  is described by Eq. (4.1). The parameter  $T_m$  corresponds to endothermic melting peak extracted from the DSC results. One should underline that  $T_m$  is not the equilibrium melting temperature  $T_m^0$ . Generally  $T_m$  is always below  $T_m^0$ . The degree of melting can be related to the volume of crystallinity by assuming that in a fully molten material the crystallinity degree is zero. In order to determine constant parameters like  $k_{mb}$ ,  $d$ , and  $a$ , the numerical model was tuned up to the DSC results. The parameter adjustment of the numerical model with use of the DSC results is shown in Fig. 4 [2, 6].

$$(4.1) \quad \frac{dX_m}{dT}(T) = a \cdot k_{mb} \{ \exp[-k_{mb}(T - T_m)] \cdot \{1 + (d - 1) \exp[-k_{mb}(T - T_m)]\}^{\frac{d}{1-d}} \}$$

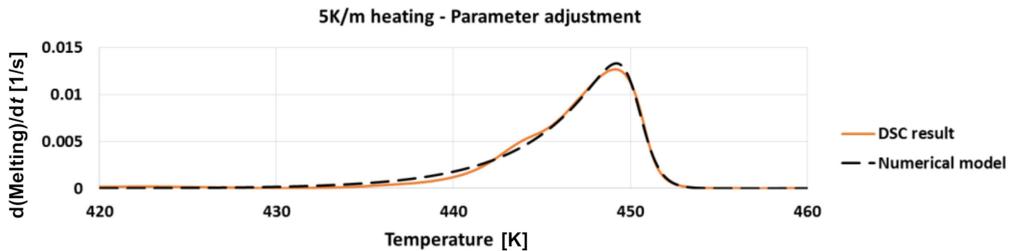


FIG. 4. Parameter adjustment of the numerical melting model to the DSC results.

## 5. IMPLEMENTATION CRYSTALLIZATION MODEL AND MELTING MODEL IN FE ANALYSES

Based on the theoretical and empirical models of the crystallization kinetics, melting description and the DSC results, one can implement the crystallization process of each of the analysed materials in the FE approach. The method is the first step to predict the structure formation during the AM process. The AM process was implemented in the FE analyses. The FE simulation results based on the numerical model and DSC tests performed in Abaqus/SIMULIA software

is presented in Fig. 5. The G-code of the manufacturing process of the thermo-plastic component needed to be interpreted in FE analysis was generated by SOFT-SHAPER software. The arrangement of the specimen in the machine chamber and process parameters are presented in Fig. 6. The temperature distribution

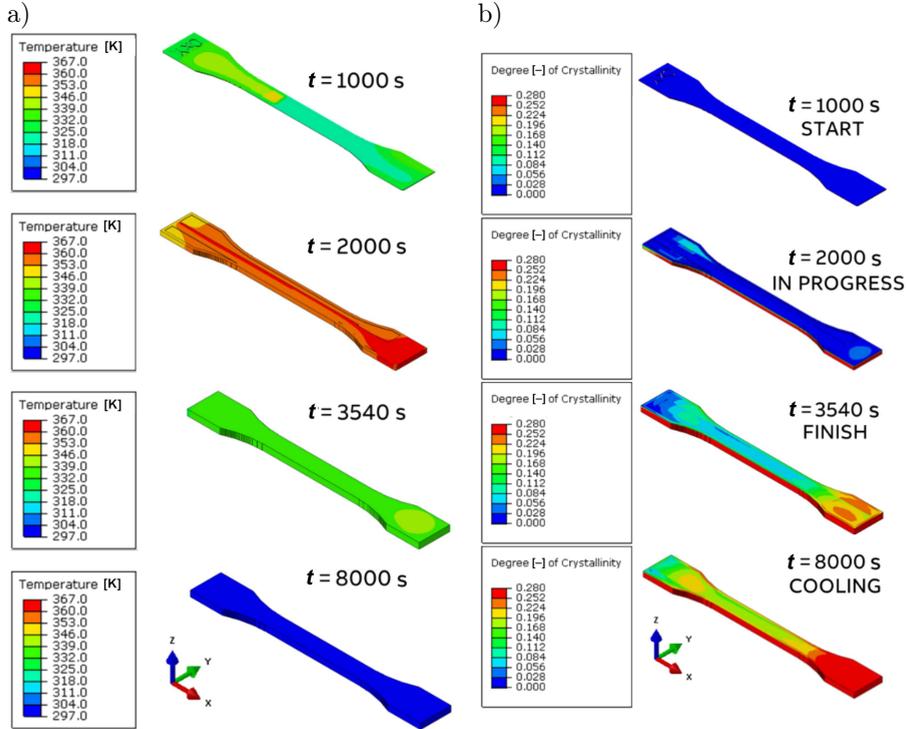


FIG. 5. a) Temperature [K] distribution during AM process; b) degree [-] of crystallinity during AM process.

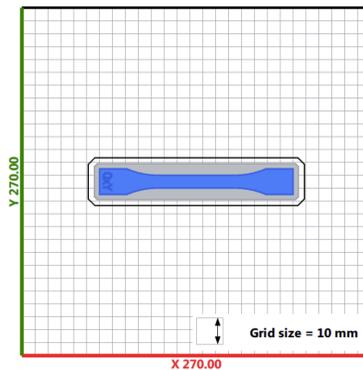


FIG. 6. Arrangement of the specimen in the printer chamber. Process parameters: print time: 59 min, print size: (X 167.600 mm Y 37.600 mm Z 10.000 mm), mass: 8.4 g, models: 8.4 g, filament length: 3316.4 mm.

and degree of crystallinity can be presented for each printing layer. One can see that the crystallization process is depended on the temperature distribution. Furthermore, the crystallinity in the volume of the structure is strongly related on the method of adding new layers. Consequently, the crystallinity can be non-uniform in the volume what can result in unpredictable volumetric shrinkage in the whole manufactured structure [8].

## 6. SUMMARY AND CONCLUSIONS

Prediction of the volumetric shrinkage of the structures in AM processes for the thermoplastic polymers requires knowledge of the crystallization behaviour and melting. The complexity of the material behaviour at crystallization under non-isothermal conditions causes that the AM process is difficult to control and optimize. After addition of new layers during the manufacturing of the component, the last built layer is partially melted in order to merge a new layer. It causes locally the changes in the material properties. The implementation of the crystallization and melting processes in the FE computations makes the first step in the analyses of the residual stresses and strength of the structures obtained during the technological tests. Each family of the thermoplastic polymers should be considered separately. Crystallization of polymers has a strong influence on the strength and warpage structure obtained at the AM process.

## REFERENCES

1. MICHLER G.H., BALTA-CALLEJA F.J., *Mechanical properties of polymers based on nanostructure and morphology*, CRC Press, 2005.
2. SCHULTZ J.M., *Polymer crystallization. The development of crystalline order in thermoplastic polymers*, Oxford University Press, 2001.
3. AMADO A., WEGENER K., SCHMID M., LEVY G., *Characterization and modelling of non-isothermal crystallization of Polyamide 12 and co-Polypropylene during the SLS process*, 5th International Polymers & Moulds Innovations Conference, Ghent, 2012.
4. JARECKI L., PECHERSKI R.B., *Kinetics of oriented crystallization of polymers in the linear stress-orientation range in the series expansion approach*, Express Polymer Letters, **12**(4): 330–348, 2018.
5. HOFFMAN J.D., DAVIS G.T., LAURITZEN J.I., JR., *The rate of crystallization of linear polymers with chain folding*, Treatise on Solid State Chemistry, vol. 3 (N.B. Hannay, ed.), Plenum, New York, 1976.
6. GRECO A., MAFFEZZOLI A., *Statistical and kinetic approaches for linear low-density polyethylene melting modeling*, Applied Polymer Science, **89**: 289–295, 2003.

7. VAN KREVELEN D.W., TE NIJENHIUS K., *Properties of polymers*, Elsevier, 4th completely revised edition, 2009.
8. BRENKEN B., BAROCIO E., FAVALORO A.J., PIPES R.B., *Simulation of semi-crystalline composites in the extrusion deposition additive manufacturing process*, Science in the Age of Experience, pp. 90–102, Chicago, IL, 2017.

*Received December 30, 2018; accepted version July 6, 2019.*

---

*Published on Creative Common licence CC BY-SA 4.0*

