CRYSTALLIZATION KINETICS OF POLYAMIDE 2200 IN THE MODELING OF ADDITIVE MANUFACTURING PROCESSES BY FE ANALYSES

P. Bajerski¹, R.B. Pęcherski², D. Chudy², L. Jarecki³

 ¹⁾ ABB Sp. z o.o. Corporate Research Center, Krakow, Poland
²⁾ Faculty of Mechanical Engineering and Robotics, AGH University of Science and Technology, Krakow, Poland
³⁾ Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw, Poland e-mail: pawel.bajerski@pl.abb.com

1. Introduction

Additive Manufacturing (AM) process is a very fast and promising technique to build various very complex prototypes and components directly in the industry. One can choose different techniques of AM like Selective Laser Sintering (SLS), Fused Filament Fabrication (FFF) dedicated for thermoplastic materials or Direct Laser Metal Sintering (DMLS) for powder metals, or Stereolitography Apparatus (SLA) for thermosets. One of the most common techniques in AM are SLS and FFF for thermoplastic materials. The complexity of the 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 morphology of the material and the crystallization processes influence the aforementioned characteristics of the created components. The knowledge on the crystallization kinetics of polymers is known since many years but it is still developing in order to get an adequate description of the behaviour of the materials in isothermal and non-isothermal conditions. Furthermore, it is needed to predict the warpage of manufactured components based on the virtual AM process in order to decrease the costs. The available tools dedicated for FE analyses allow to increase functionality and implementation of own material models and techniques to perform the customize simulations. Based on the theory and Differential Scanning Calorimetry (DSC) results it is possible to predict the behaviour of the materials and start working on simulation of the virtual AM process [1-4]. The extracted curves of the velocity of material crystallization in temperature domain with different cooling rate obtained in FE simulations are shown in Fig. 1. The simulated curves are confronted with the DSC experimental results.

2. Theoretical and experimental background

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 crystal nucleation and growth kinetics in the bulk of material. The general Avrami equation for the isothermal crystallization reads [1].

(1)
$$\alpha(t) = 1 - \exp(-k(T)t^n)$$

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 constant dependent on temperature and the geometry of crystal growth [1-3]. Nakamura expanded the isothermal Avrami equation for non-isothermal crystallization [2, 3].

(2)
$$\alpha(t) = 1 - \exp\left[-\left(\int_{0}^{t} K(T(\tau))d\tau\right)^{n}\right]$$

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

Based on the theoretical and empirical models of the crystallization kinetics and 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 structure formation during the AM process. The example of the curves of the velocity of

crystallization obtained for the considered Polyamide 2200 at several constant cooling rates in FE simulations is presented in Figure 1.

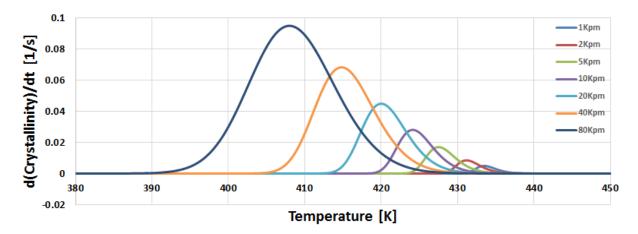


Figure 1: The simulated numerically curves of the velocity of crystallization of Polyamide 2200 at several constant cooling rates.

3. Implementation of polymer crystallization in the FE method

Available commercial finite element (FE) tools like Abaqus/SIMULIA offer to perform customization by expanding the solver. The user-subroutines can be written and implemented to standard analysis in order to calculate non-standard cases. The software dedicated to the prediction of the residual stresses and temperature distributions is available on the market but it is limited to metallic materials. The user-subroutines in Abaqus system offer good alternative and allow to create models for various non-metallic materials used in simulations of the AM processes.

In order to model the AM process for polymers and predict the progress of crystallization, the following evolution equation proposed by Nakamura for non-isothermal crystallization [2, 3] is used.

(3)
$$\frac{d\alpha}{dt} = nK(T(t))(1-\alpha)\left[\ln\left(\frac{1}{1-\alpha}\right)\right]^{\frac{n-1}{n}}$$

4. Further investigations

Crystallization of polymers has a strong influence on the strength and warpage structure obtained at the AM process. Furthermore, the complexity of the material behaviour at crystallization under non-isothermal conditions causes that the AM process is difficult to control and optimize. One has also to underline that after addition of new layers during the component manufacturing, the last built layer is partially melted in order to merge a new layer. It causes locally the change of material properties. The implementation of the crystallization process 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.

5. References

- [1] G. H Michler, F. J. Balta-Calleja. *Mechanical Properties of Polymers Based on Nanostructure and Morphology*. CRC Press, 2005.
- [2] J. M. Schultz. Polymer Crystallization. The Development of Crystalline order in Thermoplastic Polymers. Oxford University Press, 2001.
- [3] A. Amado, K. Wegener, M. Schmid, G. Levy. 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] L. Jarecki, R. B. Pęcherski, Kinetics of oriented crystallization of polymers in the linear stress-orientation range in the series expansion approach, *EXPRESS POLYMER LETTERS*, 12, No.4, pp. 330-348, 2018.
- [5] J. D. Hoffman., G. T. Davis, J. I. Jr. Lauritzen. The rate of crystallization of linear polymers with chain folding. *Treatise on Solid State Chemistry*, vol. 3 (ed.: Hannay N. B.) Plenum, New York, 1976.