*Engineering Transactions*, **67**(2): 157–165, 2019, doi: 10.24423/EngTrans.983.20190301
Polish Academy of Sciences • Institute of Fundamental Technological Research (IPPT PAN)
Université de Lorraine • Poznan University of Technology


# Virtual Additive Manufacturing Based on Semicrystalline Polymer Polyetheretherketone (PEEK)

Paweł BAJERSKI[1)]*, Ryszard B. PĘCHERSKI[2)], Damian CHUDY[2)]

[1)] *ABB Sp. z o.o. Corporate Research Center*
Starowiślna 13A, 31-038 Kraków, Poland
*Corresponding Author e-mail: pawel.bajerski@pl.abb.com

[2)] *AGH University of Science and Technology*
*Faculty of Mechanical Engineering and Robotics*
Al. Mickiewcza 30, 30-059 Kraków, Poland
e-mail: rpe@agh.edu.pl, damlok24@gmail.com

Virtual additive manufacturing (AM) is one of the new directions of research that is necessary to improve AM technology. Abaqus/SIMULIA software allows to simulate the whole process using user subroutines to expand solver capabilities. Two of the most important subroutines are UepActivationVol and UMATHT. The UepActivationVol is related to an activation of elements in accordance with the defined path of the process. The second one the UMATHT is used to implement and combine thermal and crystallization process [2].

The presented investigations describe the dual crystallization kinetics model for considered high temperature thermoplastic material Polyetheretherketone (PEEK). Furthermore, it is shown how to analyse the overall process with use of Abaqus/SIMULIA software. The innovation of the presented approach lies in the proper interpreting of the G-Code from Computer-aided manufacturing software (CAM), which is an input for the real machines dedicated to AM. The path (coordinates of discrete points) and time of particular steps of the manufacturing process are extracted from the G-Code and are included as input parameters in the simulation code. The discretized part is simplification of the Computer-aided design (CAD) geometry. The final results show the effect implemented in user subroutines. Additionally, Differential Scanning Calorimetry (DSC) test results are presented in order to calculate crystallization and melting parameters.

The presented work is the basis of the following investigations covering prediction of residual stresses, volumetric shrinkage and deformations.

**Key words:** additive manufacturing (AM), Avrami model, dual crystallization, Differential Scanning Calorimetry (DSC), Fused Deposition Modeling (FDM), Fused Filament Fabrication (FFF), glass transition temperature, Polyetheretherketone (PEEK).

## 1. General

AM process is the most appropriate technique for fast producing of the complex geometries without preparing any special equipment and machines for a specific production line. It allows for building complex parts, which could not be created in the traditional technology like injection moulding, machining or milling processes. Many commercial companies started use of the manufactured components not only for prototypes but also as standard parts which cannot be manufactured by the traditional way or the present technology is too expensive. More and more visible expansion of the AM requires to predict and estimate the quality of the mechanical properties, e.g. stiffness, strength and deformations before producing. Recently, there are available tools that allow to perform simulations of the AM processes. Basing on these tools the user can perform simulations of the process for metals, thermosets or thermoplastic polymers. The analyses usually provide information about the defined paths of created parts, temperature distribution and residual stress for simple material models. Empirical investigations indicate that for the thermoplastic semi-crystalline polymers the crystallization kinetics has a strong influence on viscoelastic behaviour and consequently residual stresses, shrinkage and warpage of the manufactured components [2–4].

The considering of the fundamental process of crystallization and melting in AM for the thermoplastic parts is the basis to start working on calculations of deformation, to predict the orientation of the built part in the chamber, set correct process parameters and speed up the process before starting the final production stage. Abaqus/SIMULIA environment gives possibility of writing user subroutines [2], which will help to improve simulations of the whole process and the final assessment of the quality of the part, what is the goal of this work.

## 2. AM processes for thermoplastic materials

There are many methods of AM processes. Two of the most common techniques for producing components from the thermoplastics materials are Fused Deposition Modeling (FDM) and Selective Laser Sintering (SLS). FDM technology relays on selectively depositing melted material in a pre-determined path. The material is provided in a filament form. The built geometry requires the use of support that is the same or made of different material added and at the end removed from final geometry. In case of SLS technique, laser selectively sinters the particles of a polymer powder, fusing them together and manufacturing component layer by layer. In this process, the not sintered powder in a chamber is treated as the support. The schemas of the discussed processes are shown in Fig. 1 [2, 5].

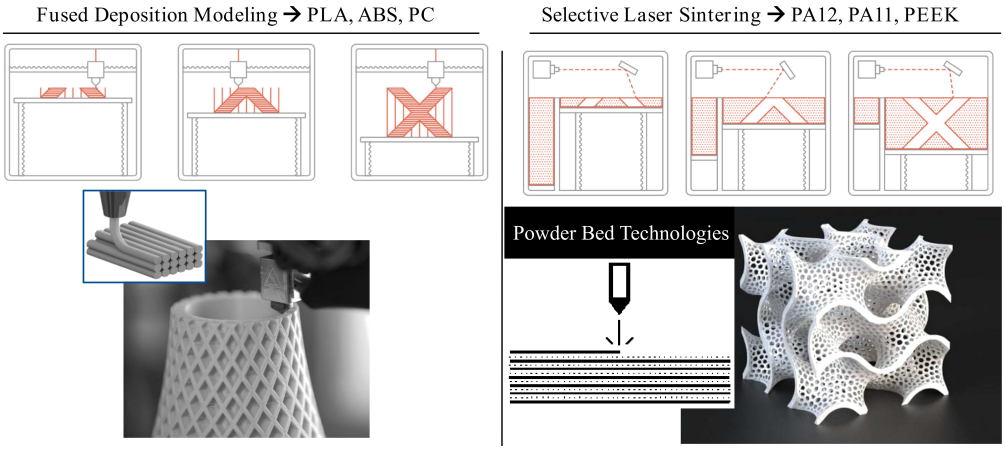


FIG. 1. Schemas of the FDM and SLS processes.

## 3. CRYSTALLIZATION AND MELTING MODEL

The polymers cannot be completely crystalline. One can select an amorphous and a crystal phase [1, 7, 8]. The crystallization in polymers consists basically of nucleation and growth [2, 7–9]. Overall crystallization for non-isothermal conditions is described by the VELISARIS and SEFERIS [1, 2, 8] who extended the fundamental Avrami model [4, 9] that is valid for isothermal crystallization of polymers. The proposed model describes two crystallization phenomena. It can be shown that the dual crystallization kinetics model finds the better confirmation in experiments. Absolute crystalline fraction degree is presented in Eq. (1) which represents two connected crystallization processes ($F_{vc1}$, $F_{vc2}$) [1, 2, 8] with the respective contributions $w_1$ and $w_2$. The sum of the contributions should be equal to 1. The crystallization process is described by equation (3) [1]. Each of the expressed processes is described in [1, 3] and [8]. The proposed model provides satisfactory prediction of the crystallization rate of high temperature thermoplastic polymers like PEEK, cf. Fig. 2a

$$X_{vc} = X_{vc\infty}(w_1 \cdot F_{vc1} + w_2 \cdot F_{vc2}), \tag{3.1}$$

$$w_1 + w_2 = 1, \tag{3.2}$$

$$F_{vc,i} = 1 - \exp\left[-C_{i1}\int_0^t T \cdot \exp\left\{\frac{-C_{i2}}{T - T_g + T_{add,i}} - \frac{C_{i3}}{T(T_{m,i} - T)^2}\right\} n_i t^{n_i - 1}\,\mathrm{d}t\right]. \tag{3.3}$$

The parameter $n_i$ denotes the Avrami exponent, which need to be determined by isothermal crystallization experiments [2]. Parameters $C_{i1}$, $C_{i2}$, $C_{i3}$ are obtained experimentally, $T_{m,i}$ – crystal melting temperature, $T_g$ – glass transition temperature, $T_{add,i}$ – correction parameter [1, 2, 8].

In order to the adequate description of the AM processes not only crystallization phenomenon is considered. The melting phenomenon has a strong influence on whole process. The crystallization is strictly connected with the melting. One should to underline that the crystallization process can be run between glass transition temperature ($T_g$) and melt temperature ($T_m$) [4, 7]. Greco and Maffezzoli [6] proposed statistical sigmoidal melting model that can be used to describe semi crystalline materials. The model is presented in Eq. (4), [6].

$$\frac{\mathrm{d}X_m}{\mathrm{d}T}(T) = a \cdot k_{mb} \left[\exp\left(-k_{mb}\left(T - T_c\right)\right)\right] \cdot \left[1 + (d-1) \cdot \exp\left(-k_{mb}\left(T - T_c\right)\right)\right]^{d/(1-d)}. \tag{3.4}$$

The proposed equation describing degree of melting $X_m$ is assumed as a sigmoidal growth curve, where the amplitude is tuned by factor $a$ which corresponds to the material. Parameter $T_c$ is a peak melting temperature, $k_{mb}$ is the intensity factor related to sharpness of the distribution and $d$ is a shape factor that controls the dispersion of melting temperature parameter $T_c$. If the $X_m = 1$, then material is fully molten [6].

## 4. Differential Scanning Calorimetry (DSC) test

DSC is a technique which measures the energy difference between a substance and a reference material in function of temperature or time when both,

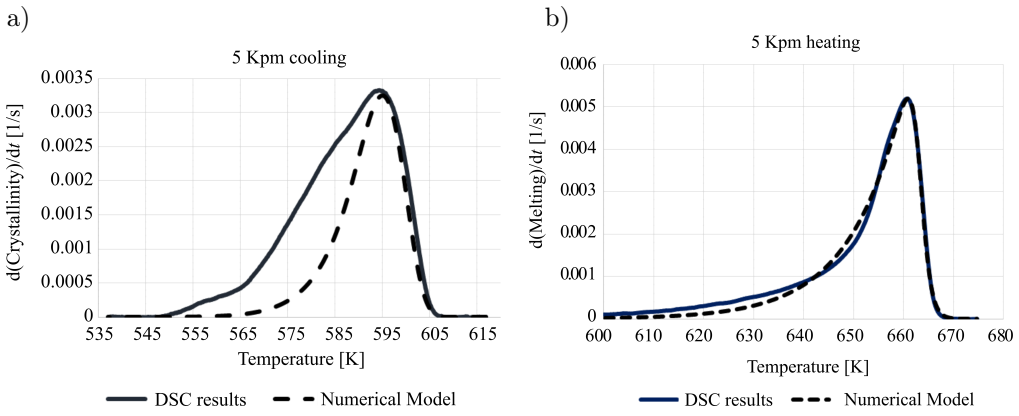


Fig. 2. a) Comparison of the model prediction with the DSC results, b) parameter adjustment of the melting model with use of the DSC results.

the sample and the reference, follow the controlled temperature program (ISO 11357, ASTM E 474) [4]. This is one of several methods of measuring the overall crystallization [4, 7]. The DSC output is expressed as power ($\mathrm{d}H/\mathrm{d}t$). The validated results of cooling and heating process for speed 5K per minute is presented in Fig. 2. The figure shows the matching numerical model to the results from DSC test. Based on the obtained and matched models, parameters to the crystallization and the heating processes were calculated [1, 2, 4, 7].

## 5. Finite element analysis

To realize the concept of virtual AM, several steps must be done. The created design in CAD software is going to the analysis in CAM environment. There G-Code is created. The basic information of the process is included in the file. Information from the G-Code file is translated into binary file that is the input for written user subroutines UMATHT and UepActivationVol. In the subroutines are included information about the methodology of building part and parameters for melting and crystallization process [2, 3]. The simulation is performed according to the path generation in real process. Definition of the path is created with respect to the G-code and to the characteristic mesh length. It is very important to provide adequate cooling process to the component as a thermal convection and optional as a thermal radiation. Based on the thermal aspects, the influence of crystallization and melting processes are included because of changing structure of crystallization inside the part. Consequently, the part is deformed. The visual procedure is presented in Fig. 3. and in Appendixes [2, 3, 5].

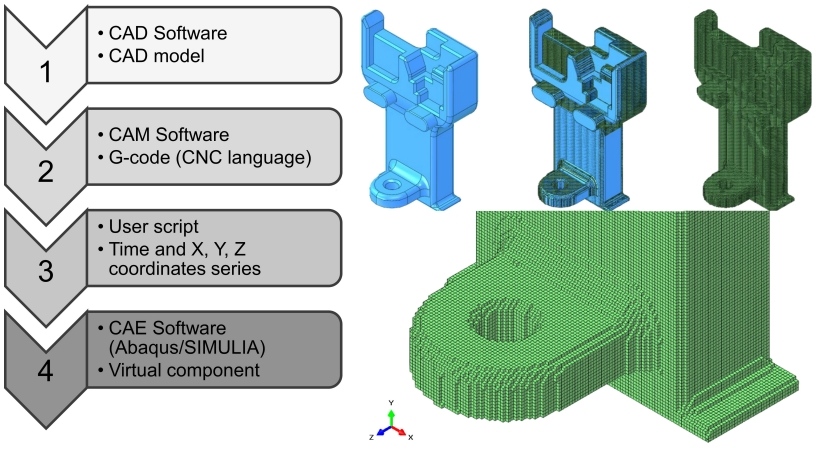


Fig. 3. Schema of the approach based on finite element analysis.

## 6. Simulation results

The interplay of melting and crystallization processes in AM is visible during the addition of the material in the strictly defined path at the built partially crystallized structure. The higher temperature close to $T_m$ causes remelting of the previous layer and merging of the new path to the built layer. The simulation results are presented in Fig. 4. There is shown temperature distribution in some specific frames. Figure 5 presents absolute crystalline fraction in the volume. Comparing the temperature distribution and fraction of crystallization, one can see the material transition from an amorphous phase to the semi-crystalline one. Irregular crystallization in the volume can be the reason of the non-regular shrinkage of the part. In such a case it is not possible to predict precisely the deformation of the manufactured element.

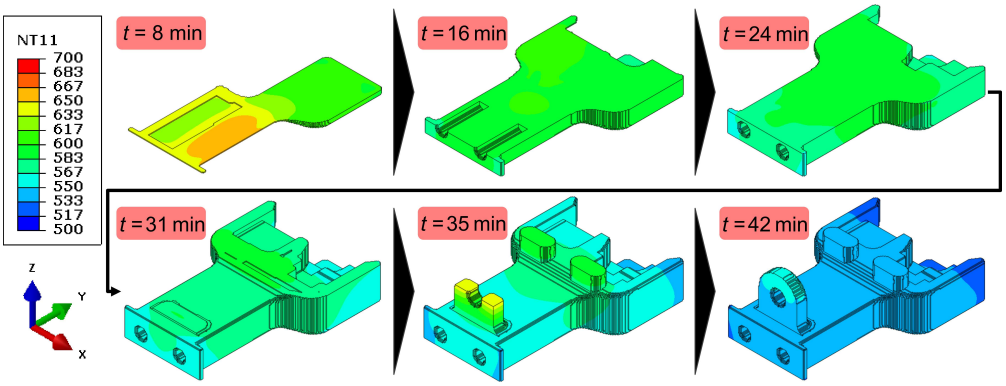


Fig. 4. Temperature [K] distribution during AM process.

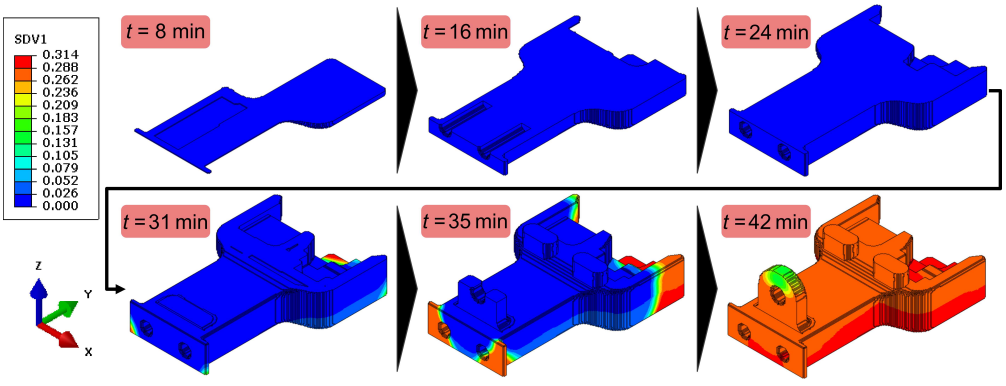


Fig. 5. Degree [–] of crystallinity during AM process.

## 7. Summary and conclusions

The presented investigations of the virtual AM show that the introduction of fundamental information about the crystallization of the polymers in non-isothermal condition is necessary. Furthermore, the procedure of the process in CAE software was implemented. In order to analyze the real process one should extract the information from G-Code file about path definition and apply it in simulation. The presented simulations are the first step to calculate residual stress, volumetric shrinkage and deformations of the analyzed structures. It can give comparison with the real manufactured components. The virtual AM approach will allow performing mechanical simulations and improve quality of manufactured structures made of the thermoplastic polymers. This approach can be used to create standard parts in industry, not only treated as prototypes.

## Appendix

Implementation of the presented material models (crystallization and melting) for PEEK in Abaqus/SIMULIA software requires to use of incremental versions of the models. See Eqs (A1) and (A2). The Eq. (A1) is based on the Eq. (3.1). The incremental integral contribution of a certain time step can be estimated as in Eq. (A3) [2]

$$X_{vc} = X_{vc\infty} w_1 \left[1 - \exp\left(-I_1\right)\right] + w_2 \left[1 - \exp\left(-I_2\right)\right], \tag{A1}$$

$$I_i = C_{i1} \int_0^t T \cdot \exp\left\{\frac{-C_{i2}}{T - T_g + T_{add,i}} - \frac{C_{i3}}{T\left(T_{m,i} - T\right)^2}\right\} n_i t^{n_i - 1}\, \mathrm{d}t, \quad i = 1,\, 2, \tag{A2}$$

$$\Delta I_i \approx C_{i1} T \cdot \exp\left\{\frac{-C_{i2}}{T - T_g + T_{add,i}} - \frac{C_{i3}}{T\left(T_{m,i} - T\right)^2}\right\} n_i t^{n_i - 1} \Delta t, \quad i = 1,\, 2. \tag{A3}$$

Below, one can see the general procedure of implementation crystallization and melting material models. Furthermore, procedure of simulation process like activation elements and sharing data is presented.

1) Thermal Constitutive Material Model Definition Subroutine – **UMATHT**
   a) Calculation of mid step temperature and material life time.
   b) **IF** element is active and $T$ is greater than $T_g$ (considered region)
      **IF** $T$ is decreasing and is less than $T_m$ (process crystallization)
      Calculation of $I_1$ and $I_2$ (Eq. (A3))
      Calculation of the degree of crystallinity $X_{vc}$ (Eq. (A1)) and melting parameters
      Update of the maximum crystallinity $X_{\max} = X_{vc}$ parameter

**ENDIF**
**IF** $T$ is increasing (melting process)
Calculation of melting coefficient (Eq. (3.4))
Calculation of new $X_{vc}$
Update of $I_1$ and $I_2$
**ENDIF**
**ENDIF**

c) Implementation of typical thermally isotropic material constitutive model.

2) Element Activation Subroutine – **UepActivationVol**
**IF** element is not active
**IF** element is on the layer which is activated
**LOOP** for path point close to analysis time
Calculation of the distance between point from path and element
**IF** the distance is in defined range
Activate element
Save the activation time
**ENDIF**
**ENDLOOP**
**ENDIF**
**ENDIF**

3) Subroutine control – **UExternalDb**
a) Open and read file with path of AM process – file is based on G-Code definition.
b) Definition of layer for activation in each time increment.
c) Definition of point from path definition in order to use in each time increment.

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*Received November 14, 2018; accepted version January 23, 2019.*

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