ANALYSIS OF VOID APPEARANCE IN ENDLESSFIBRE REINFORCED THERMOPLASTIC 3D-PRINTING FILAMENTS

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ABSTRACT

Composite materials are increasingly used in lightweight systems like the aeronautical and space industry (1). Especially, those industries require high quality (2). Thermoplastic polymers are foreseen to grow in market shares (1).
The high-performance polymers are typically highly viscous and hence, challenging to process without void generation. Void content is limited to pass the quality requirements (3,4,5,6). To reach this goal, the german aerospace center (DLR) performed several experiments on how to reduce the void content during the manufacturing of continuously reinforced 3D-prinitng filaments which is done in a co-extruding process.
This paper analyses the different types of voids and gives a first hypothesis od the correlation of those.

INTRODUCTION

Additive manufacturing (AM) is increasingly used in different markets. Numerous companies establish AM as one of their manufacturing processes. AM includes many different process types and material classes which can be used. These different methods and materials are diversely mature. AM is commonly used with virgin material but some contain reinforcement like short- or endless fibre reinforcement. The following paper focuses on the production of endless fibre reinforced filaments for Fused Deposit Molding (FDM) which can either be used for polymers or metals. Endless fibre reinforced filaments are currently not frequently used since there are very few filaments using high performance matrices and / or high reinforcement content.

It is common to use low melting, low performance polymers for AM, but high-performance polymers like polyphenylene sulfide (PPS), polyethyleneimine (PEI) or polyaryletherketone (PAEK) are gathering industrial importance as they are thermomechanical viable for the production of structural components and not only for rapid prototyping. A further aim is to reinforce these polymers with short or endless fibres with a fiber volume content of up to 50%. Short fibre reinforcement already increases the range for the usage of AM products by enhancing the stiffness to up to 90% compared to endless fibres (7). A different use-case is the reinforcement of conventionally manufactured shell structures by overprinting to functionalize the basic structure. Endless fibre reinforced filaments are able to increase the mechanical performance of a part even more, especially, if high strength and not only high stiffness is needed for the application. The investigated manufacturing technique, co-extrusion of a 12K roving, leads to voids which cause an unacceptable decrease in thermomechanical properties. Different evaluation methods for voids are available and are discussed within this paper. The occurrence of voids can be influenced during the manufacturing process; therefore, different parameter sets were used in order to reduce the overall void content.

The filaments that are used for the evaluated experiments contain 12.000 single carbon fibres and either use semi-crystalline PPS or amorph PEI. 50% fibre volume content (FVC) leads to a nominal diameter of 1,06 mm. Voids can be classified in different category systems which are mainly used in conventual manufacturing techniques but may be adapted for the co-extrusion process. Further details about the used theory as well as the utilized methods are given in the following section.

STATE OF THE ART

Thermoset infusion processes are well-known as they have been used for a long time. Therefore, the void formation process is well understood. Thermoplastic infusion and especially co-extrusion have not been of major interest in the past but they are increasingly focus of research and industry.

The infusion processes use a classification system to sort the voids in two or three categories (3). The largest voids are categorized as macro voids and are commonly defined as ‘larger’ dry areas. Micro voids are the smallest subtypes but they are not commonly defined in terms of sizes and location. Mostly they are referred to as inter tow voids. Meso voids are sometimes classed separately as the voids are larger than micro-Voids but smaller as macro voids. Some classification systems do not name this category but if they do, they are mainly referred to as intra tow voids. The evaluated composite system only uses one roving but similar behaviour can be identified as fibres are not homogeneously distributed (1). Hence, there are areas with higher and some with lower fibre volume content. Therefore, a new characterization method is given within this paper which is based on the well-known method but recognizes the specific conditions of the single tow filaments.

The overall contents can be evaluated using either optical microscopy (at least 20 pictures from each data set to be statistically correct) (8), ultrasound, micro CT or thermogravimetric analysis (TGA) in combination with a density analysis. The used methods are explained further in the methods sections, not all analysis methods are evenly viable for the experiment’s evaluation.

Implemented voids cause a change in mechanical as well as thermomechanical behaviour. Porosity influences mainly matrix properties. Especially, the shear strength decreases tremendously, 6% decrease in Void Volume Content (VCC) for 1% additional voids (3, 5). Further evaluations state a decrease in the Youngs modulus in all directions, especially, orthogonally to the fibres with reductions to up to 40% (5% Void increase). The pressure strength is reduced by 15% for 1% increase in VVC. Most evaluations lack the consideration of the void type and the location which causes the significant scattering of the data.

The behaviour is highly non-linear and therefore dependent on the content range considered. Common values for the degradation of the properties is not yet established.

A second influence caused by the voids is the reduced thermal conductivity. This can cause local unproportional heating and hence, local polymer degradation which harms the material even more. Furthermore, increased porosity enhances the moisture absorption. Moisture acts as an emollient in polymers. The maximum acceptable moisture content is material dependent (9).

Permeability is a key parameter for the infiltration process of the polymer as it indicates the ability for a fluid (polymer) to penetrate through a porous medium (fibre). The permeability of fibres can be calculated using D'Arcy's law (3).

$$v = \frac{K}{\mu} * \nabla P \tag{1}$$

The velocity used in this concept is the global velocity through the semi-finished fibre product. K is the permeability, μ is the viscosity and P the hydrodynamic pressure. D'Arcy uses an absolute velocity which is material dependent. The concept of the capillary number (a dimension less speed) correlates the speed (V), the viscosity (μ), the surface tension (γ) and the fibre-polymer contact angle (φ) by giving the ratio between hydrodynamic and capillary forces (3).

$$Ca^* = \frac{\mu * V}{\gamma * \cos(\varphi)} \tag{2}$$

An optimum between these forces causes an evenly distributed speed in the different material phases and therefore a reduced void contend as phases are not infiltrated orthogonally to the fibre direction.

The theory proposes that different scale voids appear dominantly according to the capillary number. Capillary numbers smaller that the optimum value lead to meso voids, larger numbers cause dominantly micro-voids.

METHODS

Microscopy

Microscopy is used to analyse orthogonal cuts of the filaments optically. The resolution of the microscope needs to be set according to the size of the single fibres within the filaments. The specimen within this paper use fibres with a diameter of 7 µm. A magnification of 1000 is chosen to resolute the contact area between fibre and polymer. Microscopy pictures are transferred to a black and white image file. After this processing step a tool is used to analyse the different volume contents by automatically setting colour threshold values. The images are also used to analyse the void subtypes, the roundness and the fibre distribution of the filament. According to literature, 20 images are needed to evaluate statistically valid data (3).

Samples for microscopy images need to be well-prepared. Firstly, they are cut with a rotating saw to not damage the brittle material. Sputtering is the second step to provide some shielding against imbedding resin and to ease the automated edge detection for the analyzation software. After the sputtering process, the specimens are embedded with resin and grinded and polished before they are inspected with the microscope.

Thermogravimetrically analysis

Thermogravimetrically analysis (TGA), a process to measure material flow at temperature over time is normed to ASTM E1131 (10). 10-15mg are used for the evaluation process (11). The method is used to analyse the volume contents of the different properties. The first heating ramp is conducted in nitrogen environment. Polymer burns during this step but the carbon fibres do not, they ash and can be burned during a second heating ramp using oxygen. The reduction in mass is measured during the process. In combination with the total mass, and the overall density, it is possible to calculate the overall volume contents of the properties. This approach can be used to verify the estimated volume contents of the microscopic analysis (12).

Difference scanning caliometry

Difference scanning caliometry (DSC) is as well as TGA a thermal analyzation approach. The DSC measures the heat flow of a sample that is heated with a defined ramp. It enables the analyzation of glass transition temperatures, melting temperature, crystallinity as well as purity of the sample's material. Step ramps of the heat transition process indicate active process within the material. Endotherm or exotherm reactions display in the direction of the displayed peak (11, 12).

Each specimen needs to be prepared accurate to guarantee a good heat transition. Another important parameter is the gradient of the heating ramp to allow evenly distributed temperature in the sample. The analyzation is conducted in nitrogen or oxygen to analyse oxidization process. The heat transition is always measured in comparison to a reference sample of an empty probe. The results of the analysis are influenced by the thermal history of the specimen. Therefore, the analyzation cycle should always include a second temperature increase phase. The temperature gradient is a crucial factor for the accuracy of the results.

10-20 K/min is a recommended rate (11). The maximum temperature should be at least 20 K above the expected temperature of the highest ongoing process. The mass needs to be adjusted to the relevant evaluating reaction.

Density determination
The density evaluation of polymers is standardized in ISO 1183-1 (13). Firstly, the specimens' weight is measured in air before the same specimens' weight is measured in distilled water which has to have 23°C. The density of the specimen is calculated according to the following equation:

$$\rho_S = \frac{m_{S,A} * \rho_{IL}}{m_{S,A} - m_{S,IL}} \quad (3)$$

$m_{S,A}$ is the mass measured in air, $m_{S,IL}$ is the mass in the liquid. The density of the fluid is ρ_{IL}.

VOID CHARACTERIZATION

The characterization of the voids is crucial for the evaluation process and the results that are gained through it including the work of this paper. It is important to recognize all voids either in the volume using for example computer tomography or in the surface area, for example in cross-sectional microscopic pictures. Secondly, it is important to classify the pores according to their properties related to the specimens' properties.

As mentioned before, voids can be categorized according to their size and location. Different methods are used within the field of void detection in composite materials. Microscopy is well established and relatively easy to use, but a destructive method. The microscopic pictures lead to the established analyzation method of micrographs, where the pictures are transformed to a black-and-white image. The properties displayed in the picture are evaluated by the grey value of a pixel and sorting it to the property classes. If a region is classified as a void, the analyzation code evaluates the properties of each void region and compares its area to the surface area of an orthogonal cut of a fibre. A second parameter used is the actual perimeter of the void area in comparison to a circular area of the same size. Very small areas in which voids appear are not evaluated further as they are image and artefacts. This has been checked with high resolution high detailed microscopy and a height measuring mode of the microscope. Detected voids which possess less than 0.8 times of a fibre cross-sectional area are not considered in further evaluation. Meso voids are classified if the area exceeds 10 times the fibre diameter but does not exceed the area of 100 fibre diameter. Additionally, the perimeter of the void is only allowed to be 10 times as big as the optimal circular perimeter of this particular area. The remaining voids are labelled as dry areas. These parameters have been set manually after the evaluation of numerous pictures to suit the manual classification which have been conducted before. It has been tested on differently produced filaments with different material combination and is set to well-suit the average pictures.

The characterization of the voids as classification to three classes is based on the different type of pores resulting in the filaments. Small voids appear close to single fibres or in areas of high fibre-volume-content. Larger Voids appear in the larger polymer filled region with no or hardly any fibres in this particular section of the filament.

EXPERIMENTS & RESULTS

The DLR institute of lightweight systems in Brunswick designed a co-extrusion machine to produce endless fibre reinforced filament. This machine uses a miniaturized extruder to extrude the polymer into a fibre insertion tool. Downstream, two ultrasound introduction chambers are implemented as well as a nozzle concept using one main nozzle, a temperature tube and a second consolidation nozzle before a temperature guided outlet is attached. All sections of the machine are separately exchangeable. The experimental setup for the conducted experiments of this paper are manufactured using the basic setup of the ultrasound impregnation unit of the DLR (14).

The conducted coextrusion filament manufacturing test consists of changes in the line speed, the polymer pressure, frequency implementation in the ultrasound range as well as low frequencies. The used polymers were alternated between semi-crystalline and amorphous polymers. Fibres with and without sizing were used.

Each experiment changed only one parameter at the time in order to keep this parameter evaluable.

The parameter set for the filament velocity consist of three different line-speeds. 10, 20 and 50 mm/s were used to modify the production speed. Filaments were producible with all velocities without damaging the filament externally. The second boundary condition is the maximum polymer throughput of the extruder which is polymer dependent.

The overall void content changes with an increased speed.

Velocity (v)	**VVC**
10mm/s	12,45%
20mm/s	15,3%
50mm/s	14.7

An acceleration from 10mm/s to 20mm/s causes an increased void content of 3%. It is noticeable that this behaviour does not continue linear to a velocity of 50mm/s. Some filaments are displayed in figure 1.

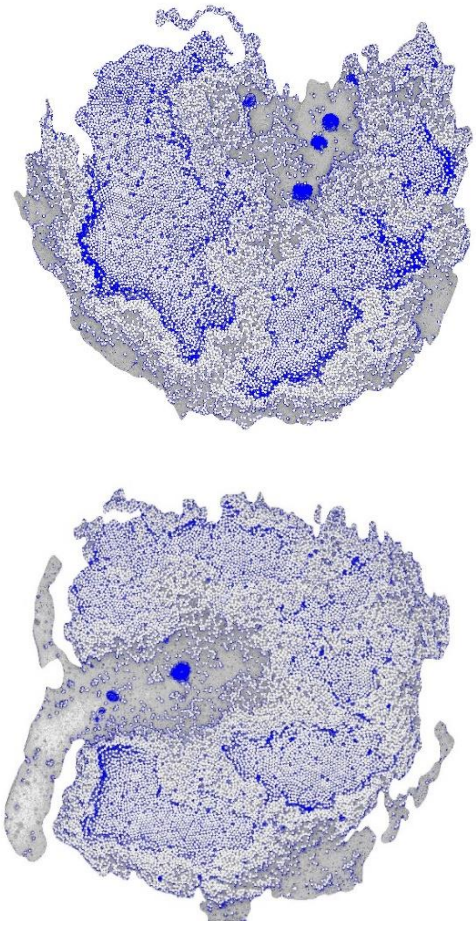


Figure 1: Sections of filament with different line speeds: upper figure-10mm/s, lower figure-20mm/s

The second changed manufacturing parameter is the impregnation pressure. The pressure is measured upstream of the impregnation zone. The extruder is controlled to the set pressure. Pressures of 20 bar, 25 bar and 30 bar were used as they are capable of infiltrating the roving and the extruder is capable of delivering enough power to maintain the proposed pressure. A change in impregnation pressure causes a change in void content as well. But, it is noticeable, that increased pressure does not always causes a reduced VVC. Some specimens display the opposite behaviour and cause even more voids. This behaviour can be explained with the concept of the optimum capillary number. The hydrodynamic melt flow is dominated by the overall pressure but the capillary flow is not (figure 2). As explained in the methods section, both flows need to be equally fast to infiltrate the roving ideally.

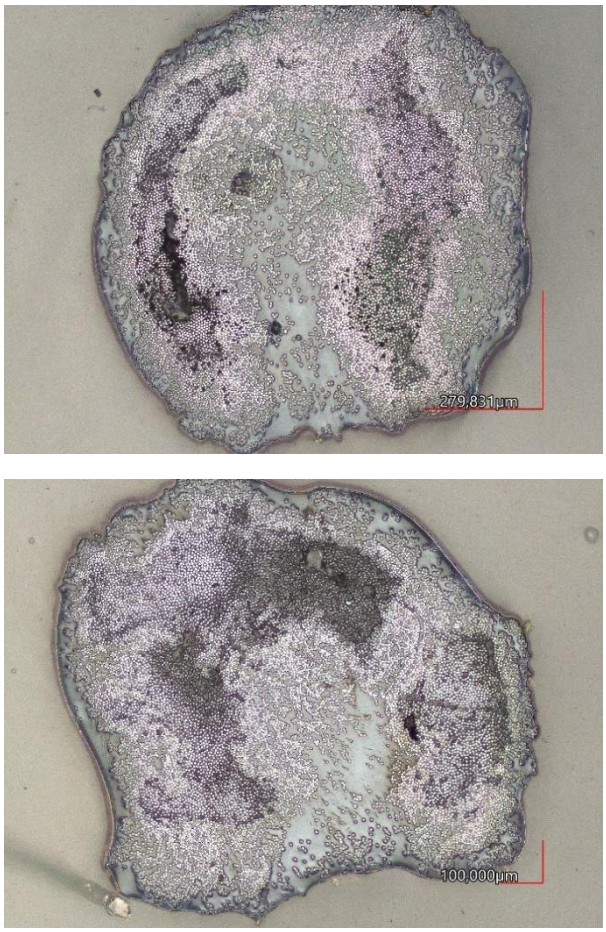


Figure 2: Filaments with a melt pressure 30 bar, 11,6%VVC (upper figure) and melt pressure 20bar, 14,9% (lower picture)

Another possible parameter in the DLR machine is the influence of frequency caused by two different mechanisms, reducing viscosity through shear forces and a change of the flow field of polymer in the impregnation chamber. Frequency is applied to reduce the viscosity of the polymer, enabling it to flow in the smaller channels and establishing a second direction of the melt flow. Experiments show increased performance of the filaments which have been manufactured with ultrasound which is due to the better impregnation of the single fibres (figure 3). Micrographs display larger dry spot for the filaments produced with ultrasound and with the broad band excited nozzle, which is even larger if both mechanisms were uses simultaneously. This behaviour is again related to the ratio of the two flow mechanisms. Both methods for the frequency implementation tend to strengthen the capillary flow and harm the hydrodynamic flow as the other parameters have been kept the same.

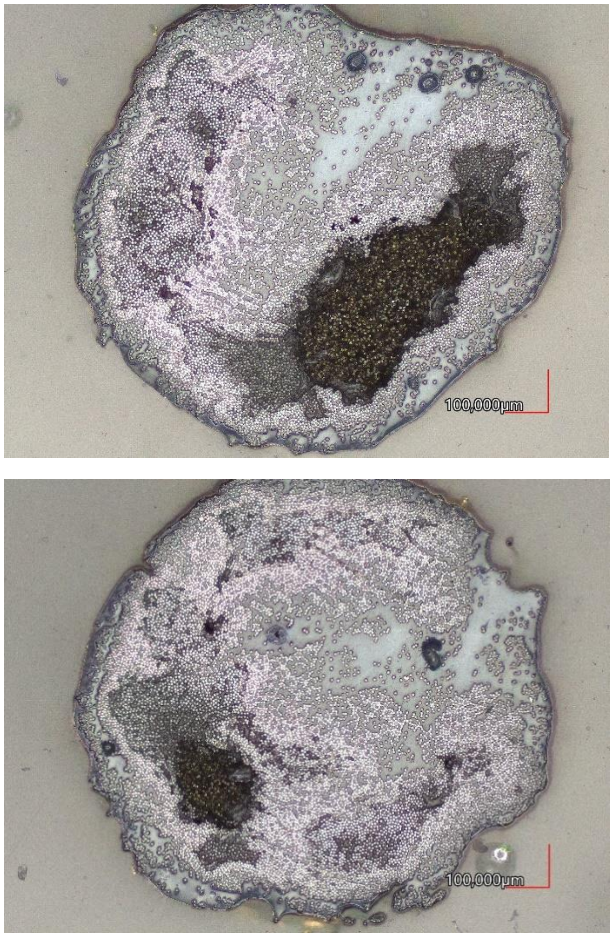
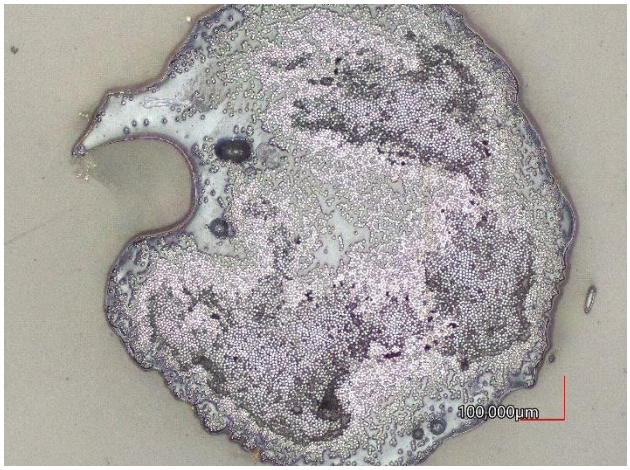


Figure 3: Filaments with ultrasound (upper figure) and without ultrasound (lower figure)

The amount of influence of all parameters is always dependent on the line speed and therefore, the time for the interaction process between fibre and polymer. In order to increase this time, an ironing zone was implemented into the process to validate this influence. The ironing zone possesses a fixed length of 45mm. Different line speed were tested but the filaments showed only improvement for 10mm/s (figure 4). The ironing zone would possibly needed to be designed differently for every speed.



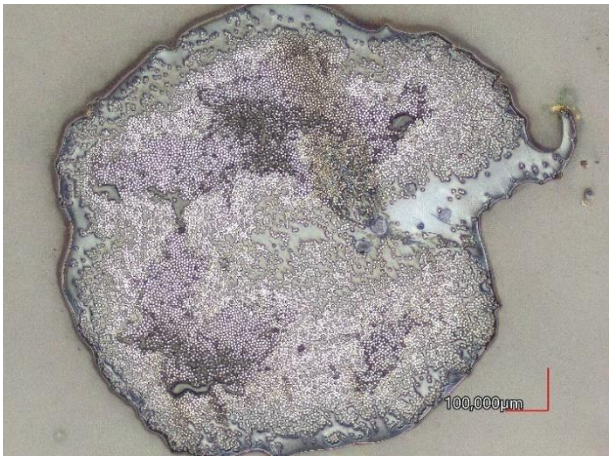


Figure 4: Filaments with ironing zone (upper figure) 13,3% VVC and without ironing zone (lower figure), 17,8% VVC, line speed 10mm/s

Further experiments showed that sized fibres result in an increased VVC as the sizing demotes. Even in areas with low fibre content there was always a small boundary layer of voids at the interface of fibre and polymer. This behaviour was supported by DSC results, which indicated a second peak at a different temperature as sizing usually derogates at the process temperatures of high-performance polymers.

Moisture is an additional cause for increased voidage as moisture becomes gas at the elevated temperatures of the polymer. This gas becomes fluid again after the solidification of the polymer which uses less space, causing vacuoles. Moisture also acts as a plasticizer for polymers.

Semi-crystalline as well as amorphous polymers were used. The experiments show the importance for semi-crystalline polymers to be cooled under controlled circumstances. The line speed and the temperature profile need to allow the polymer to reach the designated crystallinity level as amorphous phases may crystalline after the manufacturing causing even more voids than crystallinity does during the manufacturing process.

DISCUSSION

The manufacturing of filaments with different parameter sets shows the complexity to find a good indicator to enable a choice for the correct parameter to reduce the overall VVC. The parameters tend to influence the appearance of the different subtypes of voids which superpositions to the overall void content. This really is a finding that was not specifically investigated for the specific kind or semi-finished product. Even if the overall VVC stays similar, changing a parameter, the content of the different subtypes changed significantly. It could be shown that the main evaluation factor is not necessarily referring to the actual capabilities of the material. As explained before, many studies come to different results evaluating the influence of a change in VVC to a change in thermomechanical properties. The

underestimation of the significance of the kind of void is the most likely explanation for this scattering. Size and location of the voids indicate a different thermomechanical behaviour. Additionally, the shape of the void may influence the filaments as well and therefore, should be investigated in the future.

The experiments display the need for combined parameter changes. All manipulation methods of the parameters need to be set to reach the optimal capillary number. It is important to focus on the parameters which really influence the filaments void content and find correlation between the parameters which are used by D'Arcy or the concept of the optimal capillary number and the results of the quality analysis. The current results indicate a co-dependency of the void subtypes. In the future, correlation between the parameters and the void subtypes need to be found to be able to choose the correct parameters. It is going to be particularly important to choose the minimum void content of the most concerning subtype. Therefore, further studies need to be conducted in order to evaluate the most significant kind of void for the reinforced filaments and how they migrate through the print head into the final part. The resulting voids in a printed part are the relevant voids but the occurrence depends on the raw material and every non-existing defect in this raw material is not a defect in the printed parts.

The conducted experiments led additionally to further influencing parameters. These influences for the appearance of voids like moisture, polymer type and fibre-sizing need to be chosen wisely to get an optimal result. It is important to note that these secondary parameters are not directly influenced by the process but by the choice of the initial experimental setting. These parameters should be managed accordingly to not initiate further defects.

The research already outlined the need for optimal flow behaviour in the filament. The introduced capillary number needs to be set appropriately which demands a dedicated relation between capillary and hydrodynamic flow. In a prime situation an optimal capillary number can be held if one parameter like the speed is changed if the other parameters are changed accordingly. This behaviour shows highly non-linear in the first stage and demands further evaluation as well. A huge challenge is the non-uniform distribution of fibres which cause different channel sizes and forms. Every channel would need a different pressure to keep a uniform melt-flow line across the cross-section. As long as there is not possibility to achieve 100% heterogenic fibre-distribution, void-free filaments will not be reached with a co-extrusion process with highly viscous polymers.

CONCLUSION

The demonstrated work shows insightfully that the void content is superposed by the content of the different void types. Void subtypes are produced by different mechanisms of formation. These mechanisms may cause opposite effects for the different subtypes and result in a necessity of the analysis of the parameter influence of the different subtypes. Unlike most of the current work, it is not sufficient to evaluate voids in the context of filaments, it is necessary to evaluate the appearance mechanisms for every type of voids and reduce the type that is most unwanted. It may be an option to leave some type of voids in the filament for certain tasks in order to reduce the density and hence, the weight of the material.

The demonstrated study is based on the void characterization process which was build up on a subjective classification. The process is automated in a dedicated code for the cross-sectional image analysis. Future studies need to be aware of the possible shift of thresholds that may be necessary but the major dependencies are clearly outlined in this article.

It is advised to evaluate the interdependency of the subtypes in the future and evaluate the thermomechanical influence of the different subtypes. A major following research project is the more detailed evaluation of the influence of the modified capillary number and the permeability in terms of the evaporation of voids.

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