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On the Development of Polymer Particles for Laser Powder Bed Fusion via Precipitation

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Abstract

In this contribution, some aspects of the development of powder bed fusion (PBF) feedstock powders via the solution-dissolution process, also known as precipitation, are exemplarily addressed based on the authors' own work. The development is based on the selection of an appropriate polymer-solvent system, followed by the investigation of the cloud point diagram. After identification of a polymer-solvent system for precipitation, process-product relations, i.e. the influence of stirring, concentration and thermal regime on particle size distribution and shape, can be assessed. Via thorough product characterization concerning, amongst others, flowability and thermal properties, not only applicable PBF process parameters, but also necessary in-situ additive-enhancement with thermal stabilizers or post-processing with flow aids can be derived.

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1. Introduction

Additive manufacturing via powder bed fusion (PBF) of polymers yields parts of high mechanical strength, while offering large freedom of design. In PBF, the powder feedstock is spread as a homogeneous layer onto a building platform. Then, the contours of the part cross-section to be built are selectively fused by a CO₂ laser. Finally, the platform is lowered and the process is repeated. The process is run at elevated temperature (c.f. building chamber temperature), which typically lies between the onset of melting and the onset of crystallization, i.e. the so-called process window [1]. However, the powder feedstock applicable in PBF needs to be tailor-made for the application. The polymers need to exhibit a narrow particle size distribution, high flowability (spreadability), suitable rheological properties, high crystallinity for good detail precision (c.f. sharp solid melt transition), moderate isothermal crystallization kinetics at the building chamber temperature to prevent curling, a sufficiently

wide enough process window and PBF relevant optical properties (c.f. laser absorption), to only name a few [2,3]. Due to these rigid and demanding requirements, the choice of commercially available PBF feedstock materials is still limited. The market was and is dominated [4] by polyamide 12 (PA12) and its additive-enhanced variants, which are manufactured via the precipitation process in ethanol [5]. Other processes yielding PBF feedstocks include cryo-milling [6], co-extrusion [7], (thermal) rounding [8] and melt-based processes like emulsification [9] or fiber decomposition [10]. While there are other materials available, e.g. polypropylene, thermoplastic urethanes or other polyamides, they often appear less optimized for PBF as the PA12 material [1,2]. This can lead to diminished processability, resulting in build-jobs with low reproducibility and deviating part properties and tolerances, rendering such feedstock materials problematic for industrial applications [1,2,4]. Therefore, there is still a need for research on PBF feedstock materials and on processes to obtain them. For this purpose, we focused on the precipitation process, which is well-

known for PA12, with the aim to make it applicable to other thermoplastics. Interestingly, reports in the open literature on the application of liquid-liquid phase separation and precipitation for production of polymer PBF feedstock powders are scarce and virtually limited to the work of the authors and some other groups [1,10–17]. Though, in an academic environment, contrary to large chemical corporations, the full development control starting from petro or renewable raw feed material, over the polymerization, additive-enhancement and post-processing is lacking, there are still many insights able to be gained. In the following, we want to showcase important aspects of the PBF feedstock development, based on our own results. Starting from the selection of an appropriate polymer-solvent system, followed by the investigation of the cloud point diagram, the process-product dependencies, i.e. the influence of stirring, concentration and thermal regime on particle size distribution (PSD) and shape can be investigated. PBF process parameters, but also the possible need for in-situ additive-enhancement with e.g. thermal stabilizers or post-processing with flow aids can be derived, based on thorough powder characterization.

2. Identification of Polymer-Solvent Systems

First, a polymer, or to be more precise, a plastic has to be selected for PBF feedstock manufacturing. While, as outlined above, the formulation of a tailor-made PBF-grade plastic is most probably not an option, some reports suggest, that injection molding grade plastics are a good enough choice for the feed material [13,18]. The precipitation or solution-dissolution process requires so called ‘moderate’ solvents, which only act as solvents for the appropriate polymer at elevated temperatures. Upon cooling, the moderate solvent does not act as a solvent anymore. Fundamental to the process is the exploitation of a miscibility gap in the system [19]. After the polymer is fully dissolved, the system is cooled down and reaches the miscibility gap characterized by a binodal and a spinodal [20]. For the PBF feedstock production, especially the metastable area enclosed by the binodal and the spinodal is important, as, after a temperature-dependent induction time, liquid-liquid phase separation (LLPS) and subsequent nucleation and growth set in [21]. Small, polymer-rich droplets are forming and grow. The droplets are furthermore affected by coalescence, Ostwald ripening and, via stirring, shear-induced droplet breakup or collision [13]. Consequently, polymer solidification or crystallization begins in the polymer-rich droplets and micro particles are precipitated. In order to identify suitable moderate solvents, solubility parameters, especially Hansen solubility parameters [22] have proven to be useful as a criterion for the pre-selection of solvents prior to a screening study. The Hansen parameters give information on the interaction of the polymer with the solvent with respect to dispersion forces (c.f. dispersive Hansen parameter, δ_d), polar interactions (δ_p) and hydrogen bond interactions (δ_h). Based on these single contributions, the total Hansen parameter δ_t can be calculated and the difference in total Hansen parameter $\Delta\delta_t$ between the polymer and the respective solvent can be assessed. Based on this assessment, a threshold value for $\Delta\delta_t$ can be assigned, where polymer-solvent pairings outside this

threshold are ruled out. While e.g. a threshold of $\Delta\delta_t \leq 2.5 \text{ MPa}^{1/2}$ proved viable for poly(L-lactide) (PLLA) [23], the PA12-ethanol system exhibits a $\Delta\delta_t$ of $4.3 \text{ MPa}^{1/2}$. Furthermore, solvents known to act as a good solvent, i.e. dissolving the polymer at room temperature, should be ruled out. Additionally, the solvent hazardousness, cost, recyclability and vapor pressure should be considered. Since in the precipitation process, the particles need to be dried, higher volatility of the solvent renders the drying process more efficient. Considering these aspects, ethanol is a superb solvent for PA12, as, except for its high flammability, it is non-toxic, cheap, evaporates easily and can be re-used after purification via rectification. Each of the pre-selected potential solvents is then tested in a screening study, e.g. in autoclaves [23], and assessed according to whether particles are obtained. As an example, a TEAS plot of a screening study for polyvinylidene difluoride (PVDF), adapted from [17], with successful and non-successful solvents is displayed in Figure 1. Each solvent and PVDF are depicted in the ternary TEAS plot based on their Hansen parameters according to Eq. 1.

$$f(\delta_x) = 100 * \frac{\delta_x}{(\delta_d + \delta_p + \delta_h)} \quad (1)$$

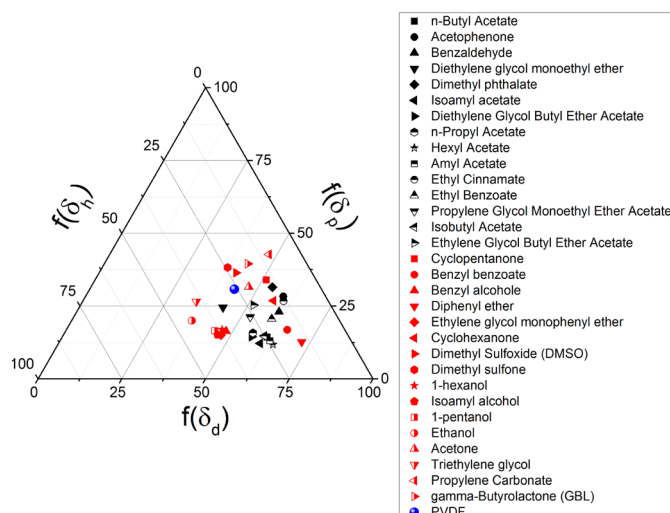


Fig. 1. TEAS plot for the screening study of moderate solvents yielding PVDF particles in the precipitation process; adapted from [17]. PVDF (blue symbol) particles could be successfully obtained from the solvents with black symbols, while the solvents with red symbols did not yield appropriate particles. Complete overview of displayed solvents is listed in [17].

This solubility parameter approach has been successfully reported for the manufacture of particles comprising polypropylene (PP) [11], polyethylene terephthalate (PET) [16], polybutylene terephthalate (PBT) [16], PLLA [23], polycarbonate (PC) [14], polyoxymethylene (POM) [12] and will most probably also work for other polymers, e.g. polyetherimide (PEI) and many more.

3. Cloud Point Diagram

Once a suitable solvent is identified, knowledge on the temperature of dissolution and the cloud point, i.e. the temperature where LLPS sets in, depending on the system composition is needed, in order to transfer the process to a

reactor or autoclave system. The knowledge on the system behavior is important to derive suitable process temperature profiles and process control. While of course, also the full exploration of the phase diagram, which deviates strongly from the ideal binary phase diagram due to the heterogeneity in molecular weight of technical polymers, for a polymer-solvent system is possible (c.f. polystyrene / cyclohexane [20]), it is very tedious and cumbersome. Depending on the boiling point of the solvent, cloud points can be easily determined in open systems, e.g. in a beaker [23] or it might be necessary to investigate them in a pressure resistant optical cell as demonstrated for the PA11-ethanol system [13]. As an example, in Fig. 2, the cloud points and the approximate dissolution temperatures are given for PBT (Ultradrur B4520, BASF) in propylene carbonate, γ -butyrolactone and cyclopentanone.

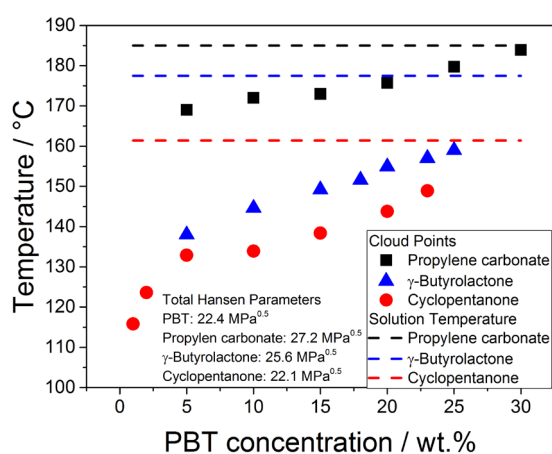


Fig. 2. Cloud points and approximate dissolution temperatures in dependence of PBT concentration in propylene carbonate, γ -butyrolactone and cyclopentanone. Dissolution temperatures indicate full dissolution of PBT feed granules. Also displayed are the δ_t values of the components.

It can be clearly observed, that dissolution temperatures and cloud points are a function of the respective solvent, i.e. these characteristic temperatures are directly linked to the compatibility of the polymer-solvent system as expressed by $\Delta\delta_t$. Higher compatibility results in lower temperatures of dissolution and, subsequently, lower cloud-points, which is well reflected for PBT in cyclopentanone, γ -butyrolactone and propylene carbonate with $\Delta\delta_t$ of 0.3 MPa^{1/2}, 3.2 MPa^{1/2} and 4.8 MPa^{1/2}. Another point, which should be considered as well, is the effect of the precipitation process on the molecular weight distribution (MWD). The solvent itself, potential contaminations and water, in combination with the minimum dissolution temperature predefined by the solvent, could contribute towards polymer chain degradation. For the systems depicted in Fig. 2 with the highest and lowest compatibility, a MWD degradation, assessed via gel permeation chromatography, from 43.39 kDa for the PBT feed material to 41.23 kDa and 17.99 kDa could be determined for PBT particles precipitated from cyclopentanone and propylene carbonate, respectively [16]. Therefore, cyclopentanone appears as a very favourable solvent for PBT PBF feedstock production, as it requires low dissolution temperatures, is non-toxic, shows no significant chain degradation, is obtainable in

large quantities and can be easily evaporated during particle drying.

The cloud-point measurements are typically performed with continuous cooling after dissolution of the polymer. Therefore, the observed cloud points are close to the spinodal, i.e. the lower boundary of the metastable area. However, when the precipitation process is scaled up to several cubic meters of reactor volume, continuous cooling seems impractical. In this case, after dissolution of the polymer, it might be more reasonable to approach a certain temperature in the metastable area, or even two, where one acts as nucleating step [24]. There, LLPS sets in after a temperature dependent induction time, which is shorter for temperatures closer to the spinodal and longer for temperatures closer to the binodal. Above the binodal, no LLPS takes place. Knowledge of the induction times yields time-efficient process operation and can be obtained by isothermal cloud point experiments. In Fig. 3 (a), the cloud point diagram of a PA11-ethanol system, including isothermal cloud points and an estimate of the binodal is depicted. In Fig. 3(b) the obtained induction times are plotted and interpolated according to [21] for different PA11 concentrations. Via this plot, induction times for different concentrations at different temperatures in the metastable area can be approximated.

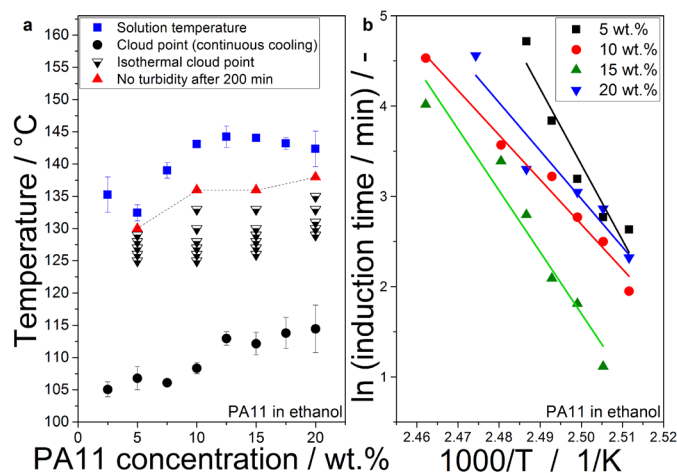


Fig. 3. (a) Cloud point diagram of a PA11-ethanol system, depicting cloud points obtained from continuous cooling, isothermal cloud points, an estimate of the binodal, where after waiting for 200 min no turbidity, i.e. cloud point, could be observed and, the dissolution temperature. (b) Plot of the determined induction times from the isothermal cloud point measurements.

4. Process-Product dependencies

Based on the cloud point diagram, the process can now be transferred to an autoclave or reactor system. Important process parameters governing the particle properties, c.f. PSD, shape, porosity etc., are stirring, temperature profile and initial polymer concentration. While many implications of the process parameters on the LLPS process, the formed droplets and subsequently the obtained particles, are discussed in detail in [13] and references therein, in this contribution we want to focus on the stirring conditions and give an example for a PBT-cyclopentanone system. The stirring conditions strongly affect the obtained PSD, as intense stirring leads to smaller particles. In Fig. 4, the PSDs of PBT particles precipitated from

cyclopentanone under varying stirrer speeds are displayed. Additionally, also the mean particle size $x_{50,3}$ and the distribution width, given as span, calculated according to Eq. 2, are displayed.

$$\text{span} = \frac{x_{90,3} - x_{10,3}}{x_{50,3}} \quad (2)$$

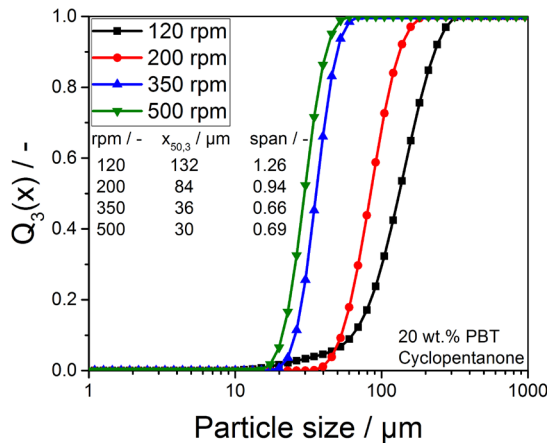


Fig. 4. PSDs of PBT particles precipitated from cyclopentanone under varying stirring conditions. Also given are the mean particle size $x_{50,3}$ and the span of the particles. The employed PBT concentration was 20 wt.%. The experiments were conducted in a 3L autoclave system (versoclave Typ 3E/3.0 Lt., 200 bar, 300°C)

As can be seen, depending on the stirring conditions, larger, broader distributed particles or smaller, narrowly distributed particles can be obtained. Typically, particles in the size range 30 μm to 90 μm with a span below 1 are favored for PBF, as they exhibit high packing density and ensure homogenously spread layers [2].

5. Particle characterization

In order to assess the suitability of the precipitated particles, thorough characterization is needed. Next to the PSD, imaging of the particles via electron microscopy gives insight on the particle shape and especially the particle surface and morphology. Fig. 5 (a-d) shows exemplary PBT particles, PET particles precipitated using PET beverage bottles as feed material [16], PVDF particles and PLLA particles, respectively. In addition to the relative spherical particle shape, the precipitation process yields particles with very high degrees of crystallinity [13,23] and can yield even semi-crystalline particles for polymers which are typically hard to crystallize, as e.g. PC [14].

This high crystallinity, which can be determined by the melt enthalpy or solid density [23], is often unmatched by cryo-milled feedstock. However, it offers a sharp transition from solid to melt, which leads especially at the boundaries of the part to fewer sticking particles, which increases the surface properties and the detail precision. Further characterization should include measurement of flowability, by e.g. a ring shear tester [13], a powder tensile strength tester [23] or a rotating drum. Also, amongst others, the thermal properties, i.e. process window and isothermal crystallization kinetics, the mass-specific surface area and structural properties, e.g. obtainable

via X-ray diffraction, should be assessed. A comprehensive characterization of a precipitated PBF feedstock is outlined in [13].

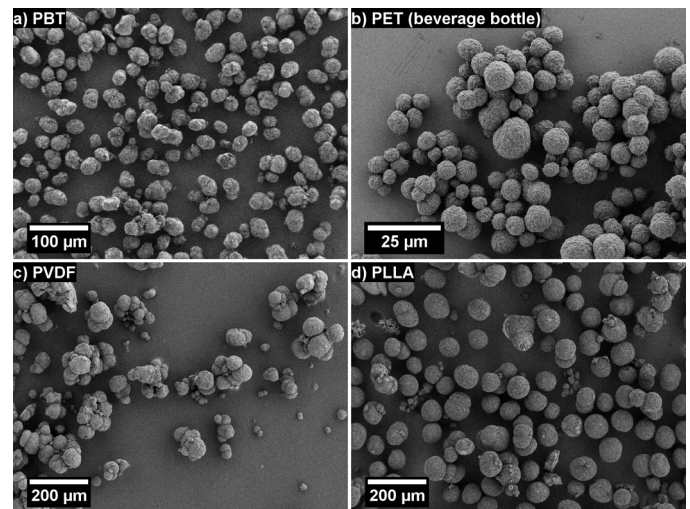


Fig. 5. (a) PBT particles precipitated from cyclopentanone [16]. (b) PET particles precipitated from cyclopentanone using a PET beverage bottle as feed material [16]. (c) PVDF particles precipitated from diethylene glycol n-butyl ether acetate [17]. (d) PLLA particles precipitated from triacetin [23].

6. Post-processing and PBF application

Based on the performed characterization, the need for post-processing and a range of suitable PBF parameters can be derived. The most widespread post-processing operations for PBF feedstock are sieving and classifying of the particles in order to optimize the PSD and dry coating with nanoparticles to increase the flowability [2]. Especially dry coating can drastically enhance powder flowability and spreadability in the PBF process, which is why commercial PBF feedstocks are typically dry coated [13]. Suitable PBF process parameters, which can be easily obtained from the powder characterization, are e.g. the layer height, which is reflected in the PSD, the building chamber temperature, which can be derived from the determined process window, the isothermal crystallization kinetics, and, to some degree, the laser power or energy input, which should in any case surpass the melt enthalpy to ensure full melting of the powder. Further details on the PBF processing itself are not addressed here, but can be found elsewhere, see e.g. [25].

7. Additive-enhancement and functionalization

Lastly, we want to address the unique possibilities the precipitation process offers concerning the additive-enhancement and in situ functionalization of the particles, i.e. during the precipitation process. By adding fibers, e.g. glass [26] or carbon, to the plastic feed material and the moderate solvent, manufacturing of fiber filled particles for PBF [15], yielding fiber-reinforced parts, is possible. Furthermore, also nanoparticle-filled particles are obtainable, via addition of dispersed nanoparticles to the moderate solvent [27]. Depending on the choice of nanoparticles, a wide range of functionalization is accessible, e.g. enhanced mechanical properties, whitening or increased thermal stability. Another

very interesting possibility is the addition of specific plastic additives to the process. Fig. 6 shows exemplary the effect of added antioxidants to the precipitation. Naturally, also the addition of flame retardants, anti-static agents, pigments, colors and many more, solely or together, can be imagined.

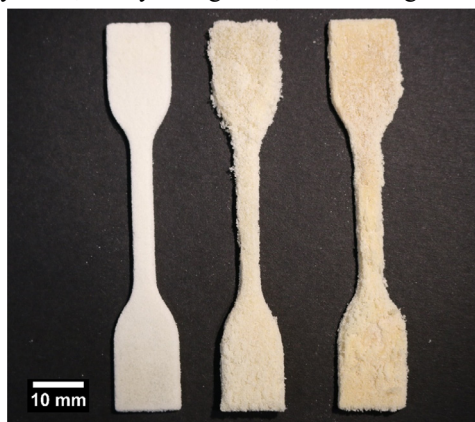


Fig. 6. Image of PA11 tensile test specimens manufactured via PBF with a Sharebot SnowWhite desktop device using PA11 feedstock with 0.5 wt.% primary and 2 wt.% secondary antioxidant (left), 0.05 wt.% primary and 0.2 wt.% secondary antioxidant (middle), without any antioxidants (right).

8. Conclusion

In this contribution, we highlighted important aspects of the development of PBF polymer feedstocks, based on the precipitation process investigated in our group. From solvent selection, cloud point determination, process-product dependencies, product characterization, functionalization and application, the precipitation process offers huge possibilities to produce tailor-made PBF feedstock materials.

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References

- [1] Ligon SC, Liska R, Stampfl J, Gurr M, Mülhaupt R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem Rev* 2017;**117**:10212–90.
- [2] Schmid M. Laser Sintering with Plastics München: Carl Hanser Verlag GmbH & Co. KG; 2018.
- [3] Schmid M, Amado A, Wegener K. Polymer powders for selective laser sintering (SLS). *Proc PPS-30 30th Int Conf Polym Process Soc – Conf Pap* 2015:160009.
- [4] Wohlers TT. Wohlers Report 2016 Fort Collins, Col.: Wohlers Associates; 2016.
- [5] Monsheimer S, Grebe M, Baumann F-E, von der Bey E. DE102004010160 (A1) — 2005-09-15 2005.
- [6] Gayer C, Ritter J, Bullemer M, Grom S, et al. Development of a solvent-free polylactide/calcium carbonate composite for selective laser sintering of bone tissue engineering scaffolds. *Mater Sci Eng C* 2019;**101**:660–73.
- [7] Kleijnen R, Schmid M, Wegener K. Production and Processing of a Spherical Polybutylene Terephthalate Powder for Laser Sintering. *Appl Sci* 2019;**9**:1308.
- [8] Schmidt J, Sachs M, Fanselow S, Zhao M, et al. Optimized polybutylene terephthalate powders for selective laser beam melting. *Chem Eng Sci* 2016;**156**:1–10.
- [9] Fanselow S, Emamjomeh SE, Wirth KE, Schmidt J, Peukert W. Production of spherical wax and polyolefin microparticles by melt emulsification for additive manufacturing. *Chem Eng Sci* 2016;**141**:282–92.
- [10] Zhou Y, Xi S, Huang Y, Kong M, et al. Preparation of near-spherical PA12 particles for selective laser sintering via Plateau-Rayleigh instability of molten fibers. *Mater Des* 2020;**190**:108578.
- [11] Wang S-J, Liu J-Y, Chu L-Q, Zou H, et al. Preparation of polypropylene microspheres for selective laser sintering via thermal-induced phase separation: Roles of liquid-liquid phase separation and crystallization. *J Polym Sci Part B Polym Phys* 2017;**55**:320–29.
- [12] Dechet MA, Baumeister I, Schmidt J. Development of Polyoxymethylene Particles via the Solution-Dissolution Process and Application to the Powder Bed Fusion of Polymers. *Materials (Basel)* 2020;**13**:1535.
- [13] Dechet MA, Goblirsch A, Romeis S, Zhao M, et al. Production of polyamide 11 microparticles for Additive Manufacturing by liquid-liquid phase separation and precipitation. *Chem Eng Sci* 2019;**197**:11–25.
- [14] Kloos S, Dechet MA, Peukert W, Schmidt J. Production of spherical semi-crystalline polycarbonate microparticles for Additive Manufacturing by liquid-liquid phase separation. *Powder Technol* 2018;**335**:275–84.
- [15] Yan C, Hao L, Xu L, Shi Y. Preparation, characterisation and processing of carbon fibre/polyamide-12 composites for selective laser sintering. *Compos Sci Technol* 2011;**71**:1834–41.
- [16] Dechet MA, Kloos S, Schmidt J, Peukert W. WO2019185582 2019.
- [17] Dechet MA, Kloos S, Schmidt J, Peukert W. WO2019185583 2019.
- [18] Haworth B, Hopkinson N, Hitt D, Zhong X. Shear viscosity measurements on Polyamide-12 polymers for laser sintering. *Rapid Prototyp J* 2013;**19**:28–36.
- [19] van de Witte P, Dijkstra PJJ, van den Berg JWAW a, Feijen J. Phase separation processes in polymer solutions in relation to membrane formation. *J Memb Sci* 1996;**117**:1–31.
- [20] Rehage G, Möller D, Ernst O. Entmischungserscheinungen in Lösungen von molekularuneinheitlichen Hochpolymeren. *Die Makromol Chemie* 1965;**88**:232–55.
- [21] van Emmerik PT, Smolders CA. Liquid-liquid phase separation by nucleation and growth in solutions of poly(2,6 dimethyl-1,4 phenylene oxide) in toluene. *Eur Polym J* 1973;**9**:931–40.
- [22] Hansen CM. Hansen Solubility Parameters, 2nd ed. Boca Raton: Taylor & Francis; 2007.
- [23] Dechet MA, Demina A, Römling L, Gómez Bonilla JS, et al. Development of poly(L-lactide) (PLLA) microspheres precipitated from triacetin for application in powder bed fusion of polymers. *Addit Manuf* 2020;**32**:100966.
- [24] Baumann FE, Wilczok N. DE19708946 1998.
- [25] Drummer D, Rietzel D, Kühnlein F. Development of a characterization approach for the sintering behavior of new thermoplastics for selective laser sintering. *Phys Procedia* 2010;**5**:533–42.
- [26] Dechet MA, Lanzl L, Werner Y, Drummer D, et al. Manufacturing and Application of PA11-Glass Fiber Composite Particles for Selective Laser Sintering. *Proc 30th Annu Int Solid Free Fabr Symp* 2019:1022–30.
- [27] Dechet MA, Lanzl L, Wilden A, Sattes M, et al. Manufacturing of Nanoparticle-Filled PA11 Composite Particles for Selective Laser Sintering. *Proc 30th Annu Int Solid Free Fabr Symp* 2019:1031–40.