Production of syndiotactic polystyrene powder for part manufacturing through SLS

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ABSTRACT: Selective laser sintering (SLS) is a well-established additive manufacturing (AM) process. While AM originally found its use as rapid prototyping technique, it is nowadays more and more considered for the production of actual end-use parts. A widely acknowledged hindrance in the evolution of this technology is the limited range of materials available for processing with SLS, making the application window rather small. Introducing new materials with the correct morphology and thermal requirements for SLS could broaden this window and give rise to new products. This research aims at identifying such promising materials, considering the relevant requirements for selecting and processing a new material. Considered foremost within this manuscript is the processability of syndiotactic polystyrene from pellet form into spherical particles of 50-90 μm without significantly changing their properties. Regarding processing methods, the focus of this work is on solution based techniques (single phase precipitation, emulsion precipitation) instead of more conventional mechanical processing methods (ball milling) as these are believed to be more accessible and more suitable as a precursor step for a wide range of processing techniques.

1. INTRODUCTION

Selective Laser Sintering (SLS) is an additive manufacturing (AM) technique which produces 3D objects by selectively fusing successive layers of polymer powders with a laser. In the past decade this technique has undergone a tremendous evolution towards actual end-use parts. This evolution brings with it an imposition of more stringent conditions on the properties of the materials used, as the resulting products need to be fully functional without any problems in their environment. For most applications, these conditions can not be met with the commercial powders available for SLS. Currently the market is dominated by PA-based materials which account for 95% of the SLS applications [1]. Research on the processing of other thermoplastic materials may broaden the application window and give rise to new products, for which other mechanical, thermal or electrical properties are required than those of the PA materials. In theory, any polymeric material available in powder form can be a candidate for SLS. In practice however, this is not the case due to a number of reasons. Firstly, most polymers are not available in a powder form with the desired particle size distribution and morphology. Optimum particle sizes have been found to be in the range of 45-90 μm [2] in order to produce parts with good densities (low porosity), low surface roughness and no electrostatic buildup. Secondly, the powders should have a high sphericity to facilitate flow and optimize packing efficiency [3, 4]. Finally, other relevant properties include a wide thermal processing window [5], thermal stability of the powder, good rheology of the polymer melt and control of the laser processing parameters. However, these are considered outside the scope of the current research. Instead, this manuscript will focus on the first aspect in selecting polymer candidates for SLS, namely the processability into fine powders of desired size and morphology. Syndiotactic Polystyrene (sPS) is selected as a testing material. It is a semi-crystalline polymer with much of the aforementioned desirable physical properties like high melt temperature (270°C), high crystallinity, near equal densities in crystalline and amorphous phases and good dimensional stability. This ensures not only that the material has a good chemical resistance but also that its mechanical performance stays relatively unchanged at elevated temperatures. Successfully preparing sPS powders for processing with SLS could enlarge the potential applications possible of this AM technique [6, 7].

There are two main methods for processing polymers into fine powders: the mechanical methods like (cryogenic) ball milling [8, 9], jet milling [10], (cryogenic) grinding, Solid State Shear Pulverization (SSSP) [11] and Spray Congealing [12] and the physicochemical methods like Thermal Induced Phase Separation (TIPS) [13-15], Diffusion Induced Phase Separation (DIPS) [15] and Evaporation Phase Separation (EPS) [15, 16]. In the latter processes, a precipitation of the polymer takes place out of solution by changing the polymer solubility in

regard to the solvent. This paper focuses on the solution based techniques - more precisely DIPS - as non-solvent aided precipitation. It will compare the formed particles in size and shape with those processed by conventional ball milling, which is most commonly used for the processing of polymers.

2. MATERIALS AND METHODS

2.1. Materials

The sPS material used is sPS F2250 B from Dow Chemical Company. CHCl₃ (purity ≥ 99%), EtOH (purity 96%), MeOH (purity 99,8%) were obtained from VWR. m-xylene (purity 98%) from Jansens Farmaceutica and n-hexane (purity 98%), n-heptane (purity 98%) and n-octane (purity 97%) from Fiers. Sodium dodecyl sulfate was obtained from Merck (purity > 99%).

2.2. Polymer solubility and solubility parameters

In the solution based precipitation techniques a polymer is first dissolved into a suitable solvent and then precipitated by either the addition of a non-solvent (DIPS), changing the temperature of the solution (TIPS) or evaporating the solvent in its whole (EPS, SD). A parameter based approach was selected based on the Hansen Solubility Parameter (HSP) model in order to find the most suitable solvents for dissolving the polymer [18].

The HSP model is an extension of the Hildebrand solubility parameter model. This model is based on the cohesive energy density or the energy necessary to completely remove all intermolecular forces in a unit volume of the material [19]. For a material to dissolve, these interactions need to be overcome. The parameter can be expressed as:

$$\delta = \left[\left(\Delta H_{vap} - RT \right) \middle/ V_m \right]^{1/2} \tag{1}$$

where ΔH_{vap} is the enthalpy of vaporization and δ has a dimension of $(cal/cm^3)^{1/2} = 2{,}046 \times 10^3$ $(J/m^3)^{1/2}$ or $2{,}046$ MPa$^{1/2}$. Dissolution will occur when the free energy of mixing ΔG_{mix} is negative in the Gibbs free energy equation:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{2}$$

Here ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} the entropy of mixing. Since latter is generally positive for the dissolution of polymers the sign of ΔG_{mix} is dependent on the value of ΔH_{mix}. For a binary mixture ΔH_{mix} can be written as:

$$\Delta H_{mix} = \left(\delta_s - \delta_p \right)^2 \phi_s \phi_p V_m \tag{3}$$

Where V_m is the volume of the mixture, ϕ_s and ϕ_p volume fractions of the solvent and polymer and δ_s and δ_p the solubility parameter of the solvent and polymer respectively. When the difference between solubility parameters is small (typically $\delta_s - \delta_p < 4$ MPa$^{1/2}$) miscibility occurs and dissolution takes place [20].

The predictions made with the Hildebrand solubility parameter however, do not account for any specific interactions like hydrogen bonds nor for any effects of morphology or crosslinking and can therefore be misleading. Hansen tried to overcome these inconsistencies in the Hildebrand Solubility Parameter by splitting it into three specific interactions (see equation 4); the dispersive interactions or non-polar interactions (δ_d) which are created by the electromagnetic field of an atom causing attraction between all atoms to one another regardless of direction, the polar cohesive interactions (δ_p) produced by permanent dipole-dipole moments of molecules and the hydrogen bonding interaction (δ_h). Hence the Hansen Solubility Parameter was defined (equation 4):

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

The Hansen parameters are in closer agreement with experimental data but can still not completely describe the solution thermodynamics for every system.

Using this parameter a list of solvents was screened of which a section is displayed in Table 1. From this list it was clear that chloroform and m-xylene were the most suitable solvents for experimentation and these were used for solubilizing the sPS.

2.3. Solution precipitation

As dispersing medium any liquid with significantly different cohesive energy density –and by extent solubility parameters-from the polymer

Table 1: Hansen Solubility Parameters (HSP) and Hildebrand parameters of representative solvents and anti-solvents at 25°C

Solvents	Hansen δ [MPa$^{1/2}$]			Hansen's total δ [MPa$^{1/2}$]
	δ_d	δ_p	δ_h	δ
sPS[18]	18,5	4,50	2,90	19,26
m-xylene[18]	17,8	0,82	2,66	18,01
Benzene[18]	18,4	0,00	2,00	18,51
Chloroform[18]	17,8	3,10	5,70	18,95
D-limonene[21]	16,4	0,20	0,20	16,40
Eucalyptol[21]	15,9	3,90	3,40	16,72
p-cymene[21]	16,5	0,60	0,00	16,52
Water[21]	15,6	16,0	42,3	47,83
Methanol[18]	15,1	12,3	22,3	29,61
Ethanol[18]	15,8	8,79	19,4	26,50
n-hexane[18]	14,9	0,00	0,00	14,90
n-heptane[18]	15,3	0,00	0,00	15,30
n-octane[18]	15,5	0,00	0,00	15,50

and solvent applied can be used. Depending on how great the difference is between both, the relevant mechanism will be either emulsion precipitation or single phase precipitation. The former denotes that solvent and non-solvent are immiscible while the latter means precipitation occurs in one single phase of mixed solvent and non-solvent. Thus, an analysis of the solubility parameters (Table 1) was performed to predict which anti-solvent would yield the best results regarding precipitation. Precipitation of the polymer took place by adding the polymer solution drop wise into a volume ratio of 1:20 solvent to non-solvent while stirring heavily on a magnetic plate. A 1:10 ratio solvent to non-solvent has also proven to be sufficient to prevent agglomeration and disperse the solution.

It was found that small weight percentages were best for experimentation; above 1w% the risk at agglomeration of the particles greatly increased and faster gelation upon cooling would occur.

Furthermore, the viscosity of the non-solvent is best not much lower than that of the polymer solution as the required energy for splitting droplets must be transferred from the stirrer to the non-solvent.

The interface tension of the dispersing phase was varied by adding SDS (Sodium Dodecyl Sulfate), a surface active agent, both in the single phase experiments and in the emulsion precipitation experiments, in an attempt to control the particle size and minimize agglomeration.

Based on these initial findings an experimental setup was established. The obtained precipitates, both in dried form and in solution were examined with an optical microscope (Keyence digital microscope VHX-500F) on morphology and size.

2.3.1. Single phase precipitation

Two polymer solutions were made of 1w% syndiotactic polystyrene in m-xylene and chloroform respectively. Depending on the solvent used different dissolution methods were performed. In the case of m-xylene it was refluxed at 140°C for 3h until a clear solution was obtained. In the case of chloroform the polymer was placed in a closed vial and agitated in an ultrasonic bath at 50°C. Both solutions were cooled to room temperature at ambient conditions before further experimentation.

After cooling the solutions were added dropwise in a 20-fold excess ethanol, which fulfilled the role as non-solvent, while stirring vigorously. The resultant precipitate was filtered off and washed thoroughly with cold EtOH in order to prevent agglomeration during the drying process. A separate experiment was executed in which a surfactant was added to the solution in an attempt to decrease agglomeration by electrostatic repulsion of the particle carrying micelles. As the CMC (Critical Micelle Concentration) of SDS in organic solvents is higher than that of pure water (due to the partial dissolution of SDS) a saturated solution was used. This was done by dissolving 0,1 g SDS in EtOH prior to precipitation. The obtained precipitates for all experiments, both in dried form and in solution, were examined by optical microscope on morphology and size.

2.3.2. Two- phase precipitation (emulsion precipitation)

A solution of 0,5 w% sPS in $CHCl_3$ was made and left to cool. Afterwards the polymer solution was added dropwise to a 20-fold excess of an aqueous SDS-solution while stirring vigorously. Different concentrations of SDS in H_2O were investigated, each time the concentration of SDS was above its CMC (8,27 mM or 23,8 mg per 10 mL H_2O). A range of 8,27 mM-0,52 M (0,1-1,5 g/10mL) was investigated.

2.4. Ball milling

As a basis for comparison, the conventional ball milling technique was utilized. For this study, a planetary ball mill with ceramic balls of 25 mm diameter was employed. 10 g of sPS pellets were loaded in the ceramic cup and subjected to the mechanical milling procedure at 300 RPM. Samples were taken at different times and examined on size and morphology by taking images with an optical microscope and analyzing them by software. In this manner the minimal time span needed to obtain particles in the desired range was investigated. A Keyence digital microscope VHX-500F was used for this purpose at 100x magnification. Image J served as an analyzing software for particle size distribution measurement.

3. RESULTS AND DISCUSSION

3.1. Solution Precipitation

3.1.1. Single phase precipitation

Both solutions showed the similar results, for this reason the discussion will limit itself to the solution precipitation performed in $CHCl_3$ solution. With both methods, polymer agglomeration did occur during the drying step. This can be attributed to a remaining solvent phase that persisted during subsequent washing and drying. Changing the non-solvent showed little improvement on the tendency to agglomerate. As illustrated in Figure 1 A-E, ethanol was found to be the best dispersing medium. Although methanol was initially believed to be better because of its smaller size and better diffusion into the polymer chains, its fast evaporation rate caused a greater flux at the surface of the solution

making the particles collide and stick against each other fiercely. Hexane and octane showed large clumps when precipitated and heptane showed many smaller agglomerations. Provided some adjustments are made to the precipitation process heptane may still qualify as a valid anti-solvent, but it will not be further considered within this research. All further experiments were carried out with EtOH as anti-solvent. The observed agglomerations consisted of small spherical particles of 1-3 μm all sticking together (see Figure 1 F).

In an attempt to reduce the agglomeration and increase the particle size a surfactant was used to shield the particles from each other by electrostatic repulsion. Agglomerations were still present yet they now consist of smaller spherical clusters, all differing in size (from 5-50 μm, see Figure 2). These clusters were built up of the same spherical particles of 1-3 μm obtained by the surfactant free preparation method. These particles would then agglomerate into spherical clusters guided by the micelles formed by the SDS-molecules. It seems that because of the high nucleation rate of sPS [22, 23], it has the tendency to form small particles no larger than 3 μm instead of growing to a larger size. The use of stronger surfacantia might increase repulsion between clusters and remove the agglomeration structures that hold the separate clusters together.

3.1.2. Two- phase precipitation (emulsion precipitation)

Figure 3 shows the results of the performed experimentation. The same conclusions can be made as with the case of surfactants in EtOH. It was clear that a higher concentration of SDS resulted in a better dispersion of the polymer particles though agglomerations were still a problem. The clusters that made up the agglomerations were spherical in morphology and differed in size (Figure 3 F); the gross of the clusters had a size between 17-110 μm; which comes close to the 45-90 μm range. With increasing concentration of SDS a trend towards a larger spread on particle size was noticed. This seems logical as more SDS, molecules are free to form micelles when increasing the concentration above its CMC. Additionally, cluster size increases with higher SDS concentration, this can also be deemed relevant to the possibility for SDS to form more micelles upon higher concentration. It is highly plausible, based on the current observations, that a surfactant with higher charge density would be able to diminish the agglomeration even more. Also one might think of changing the ionicity of your solvent as a way of influencing the particle size and its distribution.

3.2. Ball milling

The results are depicted in Figure 5. One can see that between 300 to 580 minutes, particles with fitting size are obtained. The powders obtained after this time limit had a mean diameter of 78 μm, which falls in the desired range. After 580 minutes (sample 9 in Figure 4), a limit is reached where the size of the particles is no longer further reduced; instead the fraction of the small particles is observed to grow (see insets Figure 4). One can greatly improve the milling procedure by sieving the milled powder at a desired mesh and refeeding the larger particles back into the bulk. In this way, particles of desired size are not subjected to further fractionation - increasing the yield substantially. These procedures are already applicable thanks to the use of industrial (continuous) ball mills. Analysis of the microscopic images revealed that particles were not spherical at all. Rough angular structures were created as a result of the harsh impact of the ceramic balls which is more or less to be expected. The technique however proved to be the most efficient in creating particles in the right size range and in larger amount keeping in mind that the solution techniques required to work with smaller weight percentages leading to a smaller yield.

4. CONCLUSIONS AND OUTLOOK

In conclusion, it could be posed that the upcoming techniques which are meant to replace ball milling still need some optimization. Generally solution-precipitation is used as alternative technique to create polymer powders. These techniques have the advantage of creating spherical particles as this is the most stable form in solution. Nevertheless, the low yield and high amount of agglomeration looms over these processing methods. A possible method to overcome this is the use of ionic surfactantia that can electrostatically stabilize the dispersion by encapturing the particles in the micelles formed. Though agglomerations were still a problem with this technique, larger spherical clusters of desirable size were visible, making further studies in this field very interesting. Finally, the conventional ball milling technique has also been investigated. Balancing the benefit of being a relatively fast and easy technique, a significant downside is found its inability (up to date) to produce the spherical particles which are required for the SLS process. From the particle size-time curve, one can see that particles of desired size are obtained after 300 minutes: a mean size of 78 μm is reported. After 580 minutes particle size does not diminish further but rather the fraction of small particles increases. The use of a ball mill with multiple chambers separated by screens of certain mesh size could prove
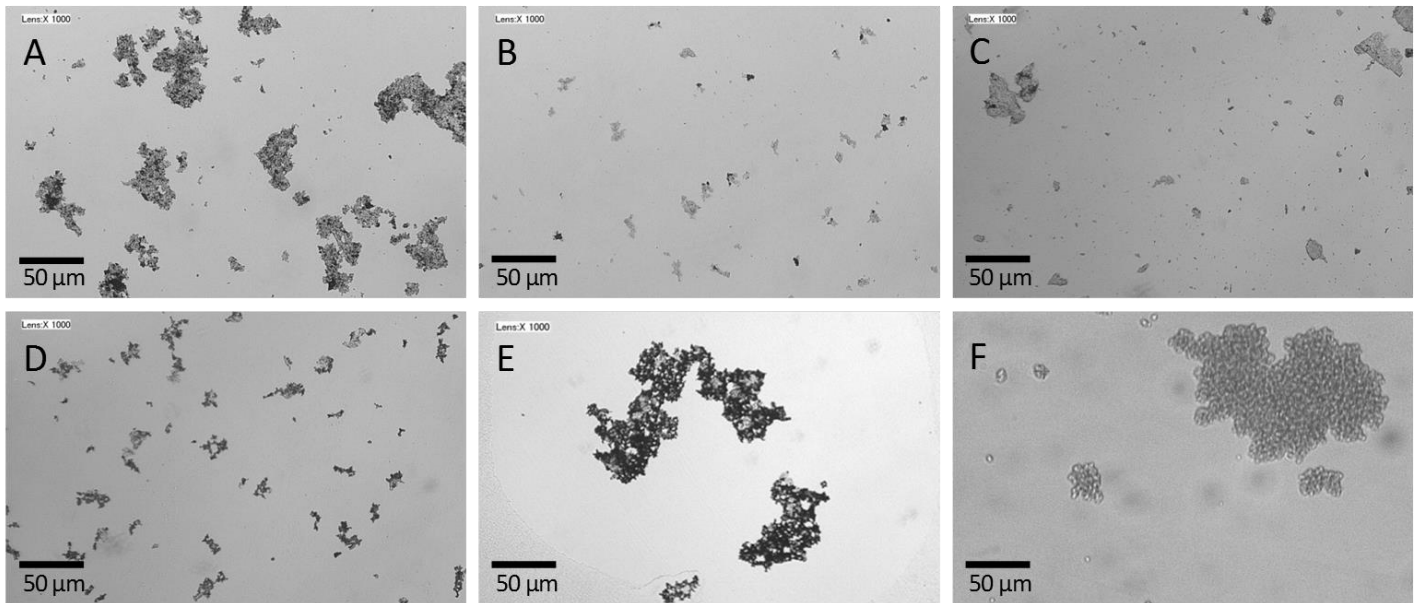
Figure 1: Evaluation of anti-solvent (precipitation experiments with 1w% sPS in $CHCl_3$): (A) n-hexane, (B) n-heptane, (C) n-octane, (D) ethanol, (E) methanol, (F) enlargement of an agglomeration structure in n-hexane
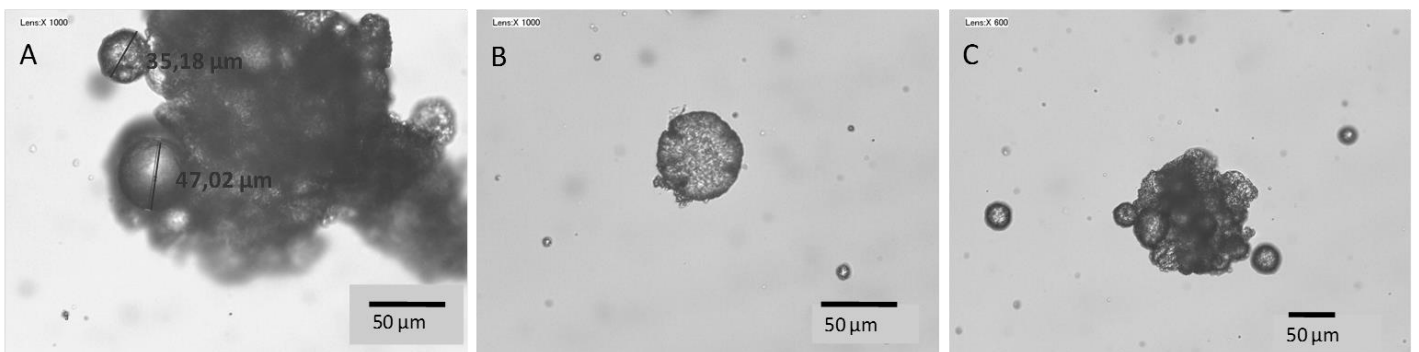

Figure 2: Spherical clusters of sPS particles formed by micelles of SDS molecules in saturated EtOH solution (from a $CHCl_3$ polymer solution)
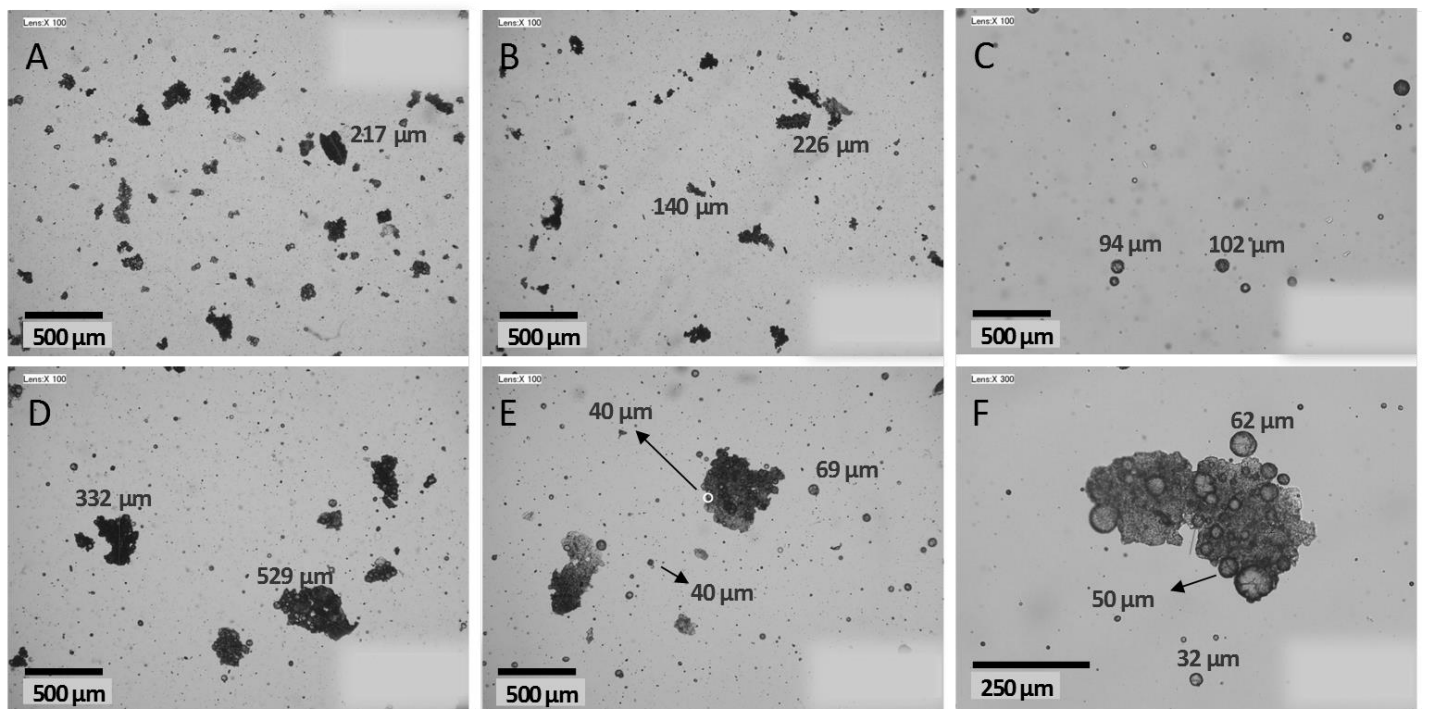

Figure 3: Spherical clusters of sPS particles formed by micelles of SDS in H_2O (from a $CHCl_3$ polymer solution); (A) in 8,27 mM, (B) in 0,035 M, (C) in 0,17 M, (D) in 0,35 M, (E) in 0,52 M and (F) an enlargement of an agglomeration structure in 0,52 M
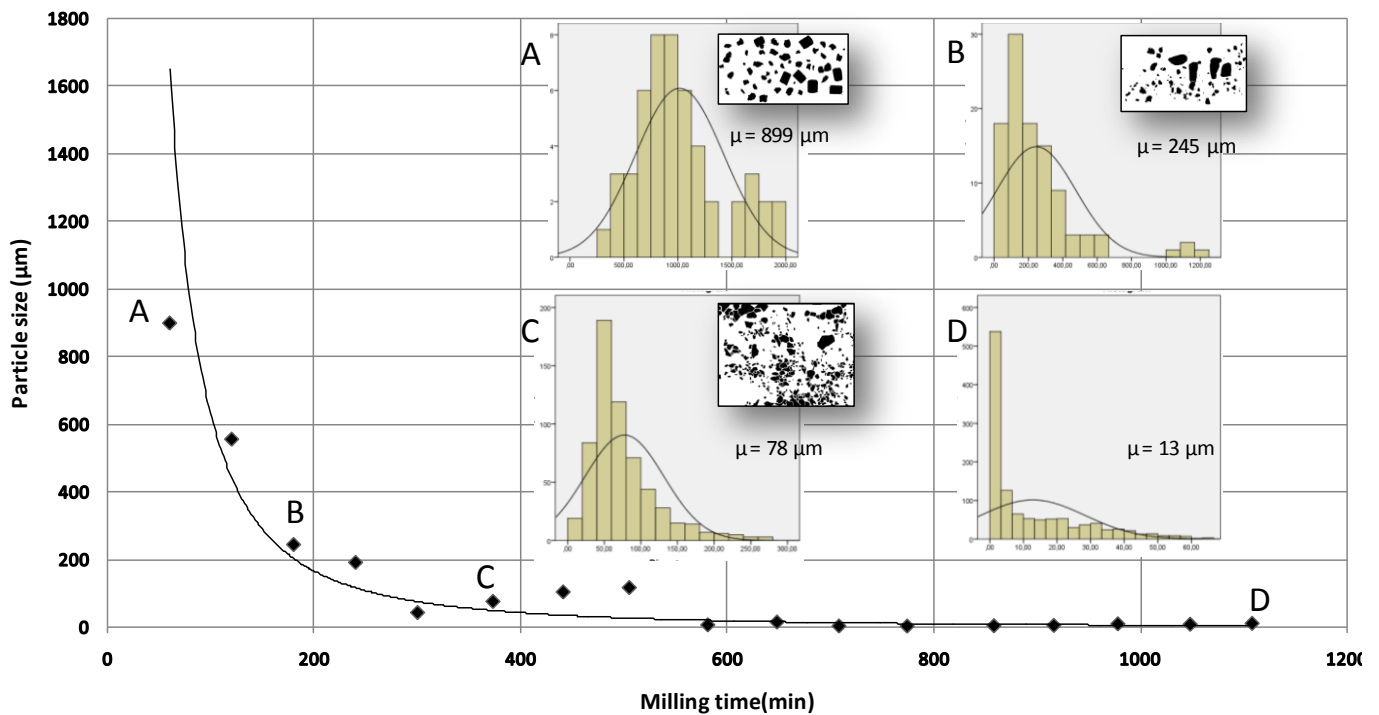
Figure 4: Particle size – time graph with PSD calculations in inset. A clear shift of particle size to the smaller diameters is visible with time.

interesting as it would make the milling process continuous by filtering out the particles of right size and continue milling the bigger particles. Testing of the powder flow seems a logical next step in the characterization of this powder.

5. ACKNOWLEDGEMENTS

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