

# Processing and characterization of Polysulfone to spherical powders for SLS purposes

N. Mys<sup>a</sup>, A. Verberckmoes<sup>b</sup>, L. Cardon<sup>a</sup>

<sup>a</sup>*Center for Polymer and Material Technologies (CPMT), Faculty of Engineering and Architecture, Ghent University, Tech Lane Science Park – Campus A, Technologiepark Zwijnaarde 915, 9052 Zwijnaarde, Belgium*

<sup>b</sup>*Industrial Catalysis and Adsorption Technology (INCAT), Faculty of Engineering and Architecture, Ghent University, Valentin Vaerwyckweg 1, 9000 Ghent, Belgium*

**ABSTRACT:** Polysulfone (PSU) has been processed into powder form by rotor milling and spray drying in an attempt to produce a new material for Selective Laser Sintering purposes. Both rotor milling and spray drying were adept to make spherical particles that can be used for this aim. Processing PSU pellets by rotor milling in a three-step process resulted in particles of 51,8  $\mu\text{m}$  mean diameter whereas spray drying could only manage a mean diameter of 26,1  $\mu\text{m}$ . The resulting powders were characterized using Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC) and X-Ray Diffraction measurements (XRD). DSC measurements revealed an influence for all processing techniques on the thermal behavior of the material. Glass transitions remained unaffected for spray drying and rotor milling. GPC measurements revealed that spray drying and rotor milling did not cause significant degradation.

## 1 INTRODUCTION

Selective Laser Sintering (SLS) is a versatile 3D printing technique which builds 3D objects by selectively fusing thin layers of polymer powders by the use of a CO<sub>2</sub> laser. In the last decades this technique has undergone a shift from Rapid Prototyping (RP) to Additive Manufacturing (AM) in which actual end-use parts can be produced (Hopkinson et al. 2006; Kruth et al. 1998). Complex tailor made products can be achieved as no support structures are needed since the powder itself acts as support. Furthermore tooling costs are greatly lowered and the surrounding powder can easily be recycled making this technique also interesting from an economical point of view. The benefits of SLS are somewhat overshadowed, however, by the critical shortage of materials processable with this technique. The increase in interest in SLS as AM technique brings a great demand for a variety of applications along with it. For the moment these applications are limited to those which fall within the properties of these processable materials. Presently Polyamide (PA) makes up the bulk of these available polymeric powders (Wohlers associates 2009). In order to broaden this Window, new materials should be added to this material palette in order to widen the range of mechanical and thermal properties. Research on the processing of other thermoplastic materials with different mechanical, electrical and thermal properties might be a solution to this obstacle. To our knowledge no suitable method exists yet to process commercially available polymers into powder form which meet the specific requirements for SLS. Goodridge et al. (2012) defined these powders to be spherical of nature with a mean diameter in the 45-90  $\mu\text{m}$  range. Powders should display a low surface

roughness in order to be able to spread easily and evenly over the build platform. The large range allows for better packing density leaving not too many air inclusions (Hopkinson et al. 2006; Yang & Evans 2007).

This paper will focus on two techniques as possible processing methods for polymer candidates for SLS; namely Spray Drying (SD) and Rotor Milling (RM). Spray drying was chosen as a physicochemical processing method as it is said to achieve more spherical particles and allows for higher weight percentages to be used than for example Thermal Induced Phase Separation (TIPS, Matsuyama 2000)

or Diffusion Induced Phase Separation (DIPS, van de Witte et al. 1996). What's more, it virtually eliminates agglomeration of which the aforementioned techniques often suffer and allows for better control over particle size and particle size distribution. Rotor Milling was chosen as a mechanical processing technique that may prove to be a reasonable alternative to the conventional milling techniques. Whereas conventional ball milling often results in drastic changes in the intrinsic properties of the polymer in question due to the long residence time in the crucible and high impact of the impact balls (Font et al. 2000; Castricum et al. 1996 & Ishida 1994), the semi-continuous rotor milling allows for a shorter residence time of the material as the material impacts quickly on the rotating blades and is transported outside via a cyclone system. This shortens processing time and minimizes the possibility of material degradation. Additionally, the material can be milled to a predefined particle size thanks to the use of internal sieves.

Polysulfone was selected as testing material due to its difference in characteristics from the conven-

tionally used PA. It is a rigid high-strength and transparent polymer which exhibits good chemical resistance over a broad pH-range and retains dimensional stability at elevated temperatures (Solvay 2014).

The authors will describe in this paper the processing methods as well as characterize the obtained powders in size and morphology. Next, the polymeric powders will be investigated on any change in intrinsic properties by the use of Differential Scanning Calorimetry (DSC) and Gel Permeation Chromatography (GPC).

## 2 MATERIALS AND METHODS

### 2.1 Materials

Polysulphone Udel P-1700 was provided by Solvay in the form of pellets and was used as-received. The pellets were dissolved in N,N-Dimethylformamide (DMF, purity 99+ %).

### 2.2 Solubility determination

Based on the Hansen Solubility Parameter (HSP, Hansen 2012) model the most suitable solvent to dissolve PSU was determined. The solubility of PSU was determined gravimetrically as the minimum amount of solvent necessary to completely dissolve the polymer. Polysulphone was refluxed in this regard at 153 °C until dissolved and left to cool at ambient temperature. The gravimetric experiments were replicated thrice.

### 2.3 Viscosity determination

Viscosity measurements were performed on a Thermo Scientific HAAKE viscotester 550 rotational viscosimeter according to ISO 3219. Samples were conditioned at constant temperature of 25 °C by a HAAKE K15 thermostatic bath and measured at 10 RPM using the MVI spindle. Each sample was measured at least three times. The results for the viscosity were then averaged.

### 2.4 Spray Drying

Spray drying was performed on a Buchi B290 equipped with a two-fluid nebulizer connected to pressurized air. The nozzle orifice size was 2,0 mm. The aspirator ran at a maximum air velocity of 40 m<sup>3</sup>/h. The heater inlet temperature, temperature of solution, solution feeding rate and gas flow rate were fixed factors in this article and were previously optimized by systematic approach. The optimization of the morphology of the particles lies beyond the scope of this article.

A PSU solution of 12 w% in DMF was heated to 150°C and fed to the nozzle at a feed rate of 7,4

mL/min. The prepared solution was heated to decrease the solution viscosity and hence increase the diffusion rate of the solutes during drying. The heated solution was then atomized by the two-fluid nozzle into the drying chamber where the droplets were dried by the use of dry air at 210°C.

### 2.5 Rotor Milling

Rotor milling was performed on a Fritsch Pulverisette 14 rotor mill to pulverize the polysulphone pellets in a three-step comminution process. The first step consists of comminution of the pellets to a coarse powder using a sieve with mesh size of 500 µm. In a second and third refinement step the coarse powder is further pulverized to a fine powder and sieved at 120 µm and 80 µm subsequently. A 12 ribbed rotor blade was used at 15000 RPM to achieve pulverisation. The resulting powder was sieved and isolated using a cyclone system. During the milling process the rotor mill was cooled by air at room temperature using an aspirator connected to the cyclone system.

### 2.6 GPC measurements

GPC was used as a direct way to measure degradation by calculating the molecular weight of the virgin and processed samples. GPC measurements were performed on a Waters Instrument, with RI detector (2414 Waters), equipped with three Polymer Standards Services GPC serial columns (1 x GRAM Analytical 30 Å, 10 µm and 2 x GRAM Analytical 1000 Å, 10 µm). PMMA standards (690 g.mol<sup>-1</sup> to 1944000 g.mol<sup>-1</sup>) were used for calibration and DMA containing LiBr (0.42 g.mL<sup>-1</sup>) was used as a solvent at a flow rate of 1 mL.min<sup>-1</sup>. Molecular weight and dispersities were determined using Empower software. Samples were injected with a PL-AS RT autosampler. Infrared measurements were carried out with an ATR Perkin Elmer FT-IR spectrum 1000 in a range of 4000 cm<sup>-1</sup> to 600 cm<sup>-1</sup>. Each sample was measured twice.

### 2.7 DSC measurements

The intrinsic properties of the produced powders were analyzed using a Netzsch DSC 204F1 under N<sub>2</sub>-atmosphere. Samples were contained in an open Al pan and referenced against an empty open Al pan. A heating rate of 10 °C/min was used to heat the DSC to 450 °C to determine the effects of degradation and thermal history imparted during processing. A second heating run under the same conditions was performed to determine if any change in thermal properties had occurred. A baseline subtraction was done to correct for any slope or variation in heat transfer effects. The sample material never exceeded 1,2 % of initial sample weight (25,8 mg).

## 2.8 Particle size distribution (PSD)

The morphology of the produced particles was investigated using a scanning electron microscopy (JEOL JSM-7600F) at low voltage (2 kV) and working distance of 8mm. Samples were sputtered shortly with gold using a BAL-TEC SCD 005 Sputter Coater at 25 mA. Obtained micrographs were then analyzed using the software program Image J and further investigated using the statistical program SPSS.

## 3 RESULTS

### 3.1 Solubility determination

The HSP model is correlated to the cohesive energy density; the energy necessary to completely remove all intermolecular forces in a unit volume. The parameter can be expressed as:

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

Where  $\Delta H_{vap}$  is the enthalpy of vaporization and  $\delta$  has a dimension of  $(\text{cal}/\text{cm}^3)^{1/2} = 2,046 \times 10^3 (\text{J}/\text{m}^3)^{1/2}$  or  $2,046 \text{ MPa}^{1/2}$ . For dissolution to occur the Gibbs free energy of mixing needs to be negative. As the entropy of dissolution of a polymer generally tends to be positive the Gibbs free energy equation in (2) can be rewritten as (3):

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (2)$$

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

Where  $V_m$  is the volume of the mixture,  $\phi_s$  and  $\phi_p$  the volume fractions for solvent and polymer respectively and  $\delta_s$  and  $\delta_p$  the HSP for solvent and polymer respectively. When the difference in solubility parameters is small, miscibility takes place and dissolution will occur.

Using the HSP several solvents were screened of which DMF was experimentally determined to be the most suitable solvent. Gravimetric experiments revealed a maximum weight percentage of 18,18 w% or a solubility of 0,21 g/mL could be attained. Table 1 displays the aforementioned HSP values.

Table 1. Hansen Solubility Parameters of Polysulfone and N,N-dimethylformamide.

Solvents	$\delta_t$	$\delta_d$	$\delta_p$	$\delta_h$
	$(\text{MPa})^{1/2}$	$(\text{MPa})^{1/2}$	$(\text{MPa})^{1/2}$	$(\text{MPa})^{1/2}$
PSU	23,6	19,8	11,2	6,2
DMF	24,9	17,4	13,7	11,3

\*(Hansen 2012).

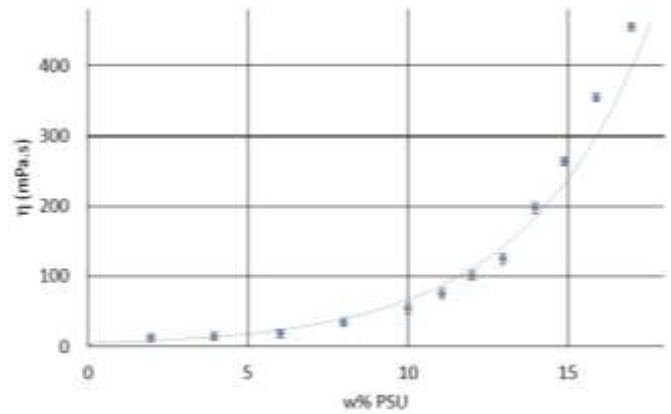


Figure 1. Viscosity curve of PSU concentration range in DMF measured at 25 °C.

### 3.2 Viscosity determination

In order to determine the maximum weight percentage that could be sprayed on the spray dryer a viscosity measurement was performed on a concentration range of PSU in DMF. Figure 1 shows the viscosity curve or the resulting analysis. The two-fluid nozzle can handle viscosities up to 300 mPa.s (Arpagaus et al. 2010) which is depicted as the horizontal line in Figure 1. Solutions with higher viscosities would not jet well due to viscous dissipation and simply drop off due to mass buildup at the nozzle orifice. For this reason solutions sprayed never exceeded 14 w%. In this article, optimum conditions for spray drying were found at a solution concentration of 12 w%.

### 3.3 Morphology

Micrographs taken from the powders obtained via spray drying revealed an overall good morphology. Upon inspection of the micrographs, depicted in Figure 2, one can remark that a small part of the particles exhibits either a collapsed or a string like structure. The latter can be ascribed to a too high viscosity of the solution while jetting causing incomplete atomization while the former is related to the low diffusion rate of the polymers causing bad skim or shell formation which collapses under further drying. Vehring et al. (2007) described these effects at length by means of both an analytical and a numerical model. When inspecting the samples obtained by rotor milling one can clearly see the effect the multiple comminution steps have on the powder morphology. In the first step the powders are processed to a coarse powder of very irregular structures with little to no sphericity (Figure 3a). Large thread-like structures are found due to the impact and shearing forces the pellets undergo in their first reprocessing step. Structures were found to have dimensions around 500 μm with occasionally some spherical particles. The following refinement steps further reduce the particle size and improve morphology visibly though inconsistencies in shape

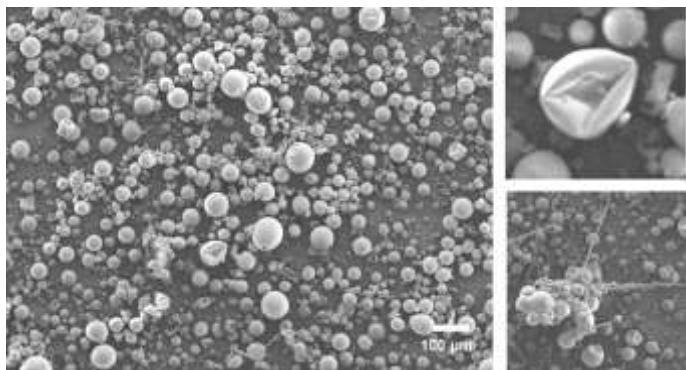


Figure 2. Micrograph of spray dried PSU at optimal conditions. Insets show a magnification of a collapsed structure above and string-like structure below.

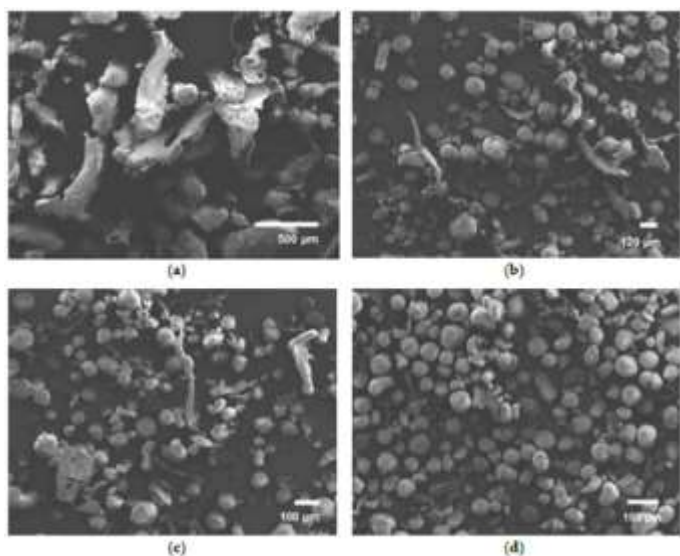


Figure 3. Micrographs of the PSU pellets subjected to a three-step refinement process. (a) Processing to a coarse powder of 500 µm, (b) refinement to 120 µm, (c) further refinement to 80 µm and (d) after additional sieving at 80 µm

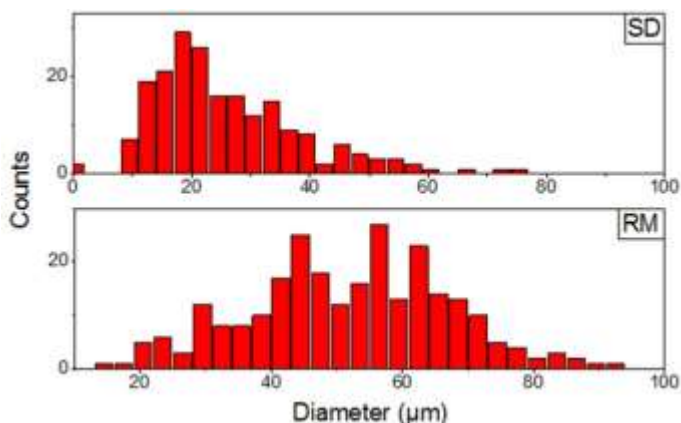


Figure 4. Particle Size Distribution of spray dried (SD) sample at optimum conditions and rotor milled (RM) sample after final sieving step

remain present. The coarse powder is again subjected to the shearing force of the turning rotor causing the material to slightly heat up and plasticize with every run, making the material to round off. A final sieving step using a vibratory sieve at 80 micron fur-

ther reduces the number of irregular particles impressively.

### 3.4 Particle Size Distribution

The micrographs depicted above were subsequently analyzed using Image J and statistically evaluated using SPSS to determine a particle size distribution of the produced powders. The PSD of the respective powders are given in Figure 4. Although the spray dried particles are largely spherical, the mean diameter of the particles remains smaller than the desired range for SLS applications. A mean particle size of 26,1 µm is reported with standard deviation of 12,8 µm. The PSD curve is skewed towards larger diameters. In order to further enhance the size of the particles a larger nozzle aperture and drying chamber is advised. A scale up to larger semi-industrial apparatuses is for this matter suggested at similar parameter settings.

In the case of rotor milling a constant decrease in particle size and standard deviation is reported with every sequence of the milling procedure. The final product displayed a mean particle size of 51 µm with a standard deviation of 15,15 µm. the spread on the particle size is much more outspoken than is the case with spray drying yet the fraction lies very well within the desired range.

### 3.5 Gel permeation chromatography

In order to investigate if any degradation had occurred due to the processing methods used GPC measurements were performed. The GPC curves are depicted in Figure 5. No significant shift in elution peaks is apparent suggesting no significant degradation that has occurred in both methods due to the powderization methods used. When looking at the molecular weights calculated from these chromatograms one can see that there is a slight increase in molecular weight for the spray dried sample (approximately 2% and 3% for weight and number average molecular weight respectively). Although this increase is rather small it could be suggestive of degradation by crosslinking due to the two thermal treatments the PSU has undergone (dissolution by reflux and spray drying). The molecular weights are displayed in Table 2.

### 3.6 Differential scanning calorimetry

DSC was performed in order to investigate the influence the processing methods impart on the polymer. As PSU is an amorphous polymer one would expect to find the curves to be quite flat with the only significant change in baseline the glass transition temperature ( $T_g$ ) at 189 °C. Any deviations could therefore be ascribed to the processing method as such.

The thermograms of the first and second heating run are depicted in Figure 6 and 7 and show that indeed for the virgin PSU primarily a glass transition

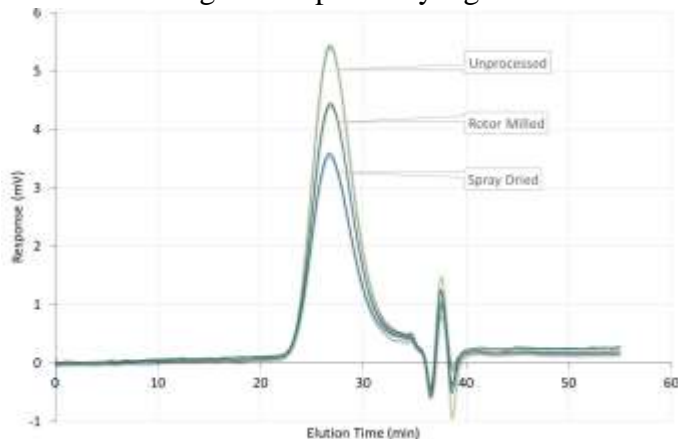


Figure 5. GPC measurements performed on the processed powders compared to the unprocessed PSU: Rotor milled powder subjected to the three step refinement process and spray dried PSU at best parameter settings

Table 2. Number average and weight average molecular weight and polydispersity of virgin and processed samples.

Method	Mw	Mn
Virgin	60318 ± 283	29805 ± 146
Rotor Milling	60293 ± 217	30298 ± 1272
Spray drying	61662 ± 110	30804 ± 1769

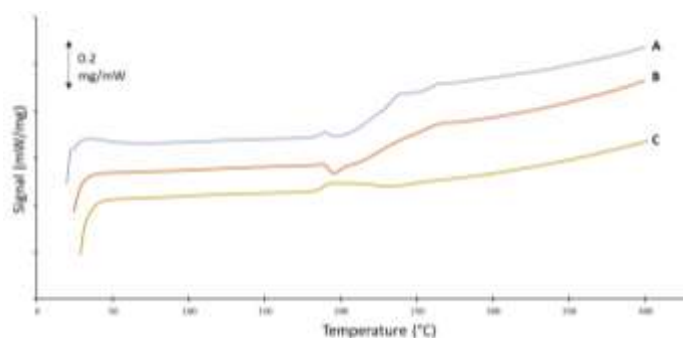


Figure 6. First heating run on (A) spray dried powder obtained at best parameter settings, (B) rotor milled powder after final sieving and (C) virgin PSU.

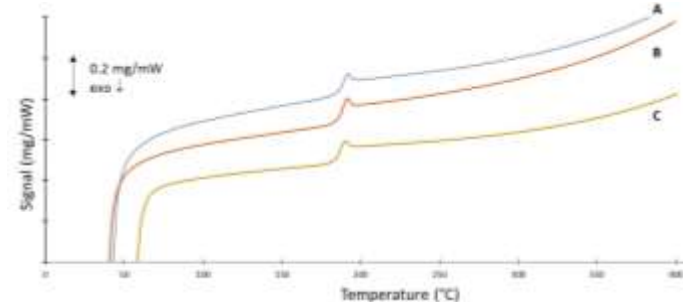


Figure 7. Second heating run on (A) spray dried powder obtained at best parameter settings, (B) rotor milled powder after final sieving and (C) virgin PSU.

can be detected around 189 °C followed by enthalpic relaxation. This can also be seen in the second heating run.

When looking at the rotor milled sample a slight endothermic peak can be seen going from 210 °C to 236 °C. The peak disappears in the following ther-

mal loop and suggests orientation in the polymer chains imposed by the processing method. This is not unusual as the PSU pellets (and powders in a first and second refinement step) impact at high velocity on the rotor miller's blades and get partially sheared apart. The Tg, however, does not differ significantly from that of the virgin polymer and remains stable upon the second heating process indicating no severe degradation.

Before analysis of the spray dried particles the sample has been dried in a vacuum oven for two days at 50 °C in order to remove any residual solvent that might have been left from spray drying. A clear Tg is visible at 188 °C with two small exothermic peaks at 237 °C and 262 °C in the first heating run. These peaks also disappear in the second thermal run and also suggest a form of orientation imposed by the processing method. The second heating curve shows a clear Tg at 189 °C again in resemblance to the virgin PSU suggesting no major changes in intrinsic properties due to the processing method.

#### 4 CONCLUSION

Polysulfone pellets were processed into powder form by both rotor milling and spray drying. Of both methods, rotor milling provided the best results yielding particles of reasonable sphericity and mean diameter within the desired range. Spray drying has the benefit of generating more spherical particles yet the particle size remains too small. A scale-up of the current equipment is advised in order to increase particle size to the desired range. GPC measurements revealed no significant change in molecular weight for both processed powders though DSC measurements did reveal an influence imparted by both processing methods on the thermal properties of PSU. In the first heating run of the DSC analysis endothermic peaks were noticeable which could be ascribed to some orientation in the polymer chains due to the processing method. These influences however disappeared upon the second thermal run and reveal no changes to the intrinsic properties of the polymer.

#### ACKNOWLEDGEMENT

An extensive version of this research has been published in *Polymers* (Mys et al. 2016). It contains additional processing techniques as well as additional characterization techniques to examine the changes in intrinsic properties.

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