PRODUCTION OF POLYBUTYLENE TEREPHTHALATE GLASS COMPOSITE POWDERS AND CHARACTERIZATION FOR PROCESSING IN SELECTIVE LASER SINTERING

Jochen Schmidt*‡, Juan Gómez Bonilla*‡, Marius Sachs*‡, Lydia Lanzl†‡, Katrin Wudy†‡, Karl-Ernst Wirth*‡, Dietmar Drummer†‡, Wolfgang Peukert*‡

* Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Cauerstraße 4, 91058 Erlangen, Germany
† Institute of Polymer Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Am Weichselgarten 6, 91058 Erlangen, Germany
‡ Collaborative Research Center 814 – Additive Manufacturing, Friedrich-Alexander-Universität Erlangen-Nürnberg, Am Weichselgarten 6, 91058 Erlangen, Germany

Abstract

Additive manufacturing techniques, such as selective laser melting of plastics, generate components directly from a CAD data set without using a specific mould. The range of materials commercially available for selective laser sintering merely includes some semi crystalline polymers, mainly polyamides. In this contribution a recently proposed process route (grinding and rounding) which allows for production of spherical polymer micro particles is applied to glass-filled polybutylene terephthalate. Composite powders of good flowability are obtained. Process relevant material characteristics like powder flowability and thermal properties are investigated. The influence of filler content on grinding behavior and resulting materials properties is discussed.

Introduction

Additive manufacturing technologies like selective laser sintering of thermoplastic powders generate components directly from a CAD dataset without needing a form or a mold. In selective laser sintering (SLS) a part is build up layer by layer in a powder bed. The cross section of the component is fused by a laser source, while the surrounding powder acts as supporting structure. Frequently semi-crystalline polymers are used and the process temperature is set between the melting and the crystallization temperature, i.e. polymer melt and powder coexist during the whole building process (quasi-isothermal laser sintering). In a first step the polymer powder is applied by a coating system (e.g. knife or roller) in the pre-heated building chamber. The layer thickness is set between 80 and 150 µm for commercial laser sintering powders of approximately 60 µm size. After laser exposure the building chamber is lowered by the thickness of one layer and another layer is applied. The process steps are repeated until the component is finished [1,2]. Selective laser sintering can process any polymer materials that tend to fuse or melt when heat is applied [3].

Typically polyamide (PA) powders (mostly PA12) are used in SLS of polymers [4,5] besides some polystyrene, polypropylene, thermoplastic elastomers or PEEK [6]. PA12 powders are produced by emulsion polymerization or precipitation processes. Besides these bottom-up routes also cryogenic grinding [7], wet grinding of polymers [8] with subsequent rounding of the fragments in a heated downer reactor [9], co-extrusion [5] or melt emulsification [10] have been proposed to produce novel polymer micro particles for SLS. Also composite materials like filled systems are of interest for SLS. Materials with advantageous mechanical properties may be obtained by applying fillers to the polymer matrix. Mazzoli et al. [11] characterized bulk properties, particles size distribution and several part properties of a composite material consisting of PA 12 and aluminum particles. The authors suggest using the developed material for stiff parts, with a metallic appearance in prototype construction. Nevertheless, there was neither a systematic change of material properties like filler concentration nor a variation of processing parameters to detect beam powder interaction. Forderhase et al. [12] analyzed the dependence of particle size, as well as filler form (spheres and fibers) of a glass filled PA12

powder on mechanical properties. They concluded that an optimal glass filled material for SLS applications is a mixture with 29 volume percent glass beads with a median particle size of 35 µm. Chung et al. [13] studied a polyamide 11 – silica nanocomposite in selective laser sintering.

Within this contribution a process chain to produce SLS polymer powders [9] is applied to glass-filled polybutylene terephthalate (PBT). The influence of the filler degree on the behavior during wet grinding (first step of the process chain) and rounding in a heated downer reactor (second step) is discussed and characteristics of the powders which are relevant to the beam melting process like e.g. flowability or thermal behavior are addressed.

Production of composite material

PBT Ultradur B4520 HS (BASF) was filled with glass beads (SG3000 or SG5000, Potters Industries LLC) at different ratios. According to the manufacturers PBT and the glass spheres have a density of 1.3 g/cm^3 and 2.5 g/cm³, respectively. The particle diameter of the SG3000 and the SG5000 glass beads is given as 12-26 µm and 3.5-8 µm, respectively. The melting temperature of the polymer is 223 °C. The composite was compounded in a co-rotating twin screw extruder ZSE HE 27 (Leistritz). A gravimetric feeder was used for dosing the glass spheres as a filler and the PBT matrix material. The temperature was set to 250 °C. The extrudate was cooled on a cooling channel and is then granulated with a granulator by Rapid Granulator AG. The granules have been used as starting material to produce spherical polymer particles according to the approach proposed in [9].

Methods

Laser diffraction particle sizing

Laser diffraction particle sizing was applied to determine the particle size distributions of the ground and rounded product particles using a Mastersizer 2000 (Malvern) equipped with a Hydro 2000S wet dispersion unit. To obtain stable aqueous dispersions sodium dodecyl sulphate (SDS) has been used as stabilizer [9,10].

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to characterize the particles. A Gemini Ultra 55 (Zeiss) device equipped with a through-the-hole detector was used at an acceleration voltage of 1 kV.

Tensile strength of powders

A tensile strength tester [14,15] for powders was used to assess their flowability. The device measures the interparticulate forces necessary to separate two adjacent particle layers. For details on the experimental procedure and conditions see [9,16].

Helium pycnometry

The solid density of the comminuted and rounded materials was determined by helium pycnometry using the device AccuPyc 1330 (Micromeritics). The average value from three independent determinations is given.

Dynamic scanning calorimetry / Thermogravimetric analysis

For analyzing the melting and crystallization temperature of the samples, a Perkin Elmer DSC was used at a heating and cooling rate of 10 K min^{-1}. The measurements were done under nitrogen atmosphere. For thermogravimetric analysis (TGA) a TGA Q 5000 (TA Instruments) was used at a heating rate of 10 K min^{-1}.

Results and discussion

Comminution

To obtain a suitable feed material for wet grinding the glass-filled PBT granules (size: 2 … 3 mm) produced have been impact-comminuted using a rotary impact mill Pulverisette-14 (Fritsch). The feed material has been cooled by soaking in liquid nitrogen. The rotational frequency of the pin rotor was 20,000 min^{-1} and a sieve ring of 0.5 mm mesh size was applied.

Wet comminution of the polymer material [8,17] has been performed in a batch agitator bead mill PE5 (Netzsch) equipped with a three-disc stirrer. The feed mass fraction was approximately 18.5 % and denatured ethanol was the solvent. A stress energy SE [18] of 1.91mJ was selected by setting the stirrer speed to 800 min^{-1} which corresponds to a stirrer tip speed v_{tip} of 6.3 m s^{-1}. Yttria-stabilized ZrO_2 grinding media (YSZ, Tosoh, density: 6,050 kg m^{-3}) of diameter d_{GM} = 2.0 mm were used. Approximately 14.3 kg of grinding media were filled into the grinding chamber. The process temperature T was (20 +/- 2) °C. The effect of the volume fraction of the filler material (given as (nominal) polymer-to-filler-volume ratio) on the grinding kinetics at constant stressing conditions represented by the temporal evolution of the product particle size $x_{50,3}$ is exemplified for PBT filled with SG3000 glass beads in Figure 1. For comparison, the grinding kinetics of non-filled PBT are given as well (blue asterisks).

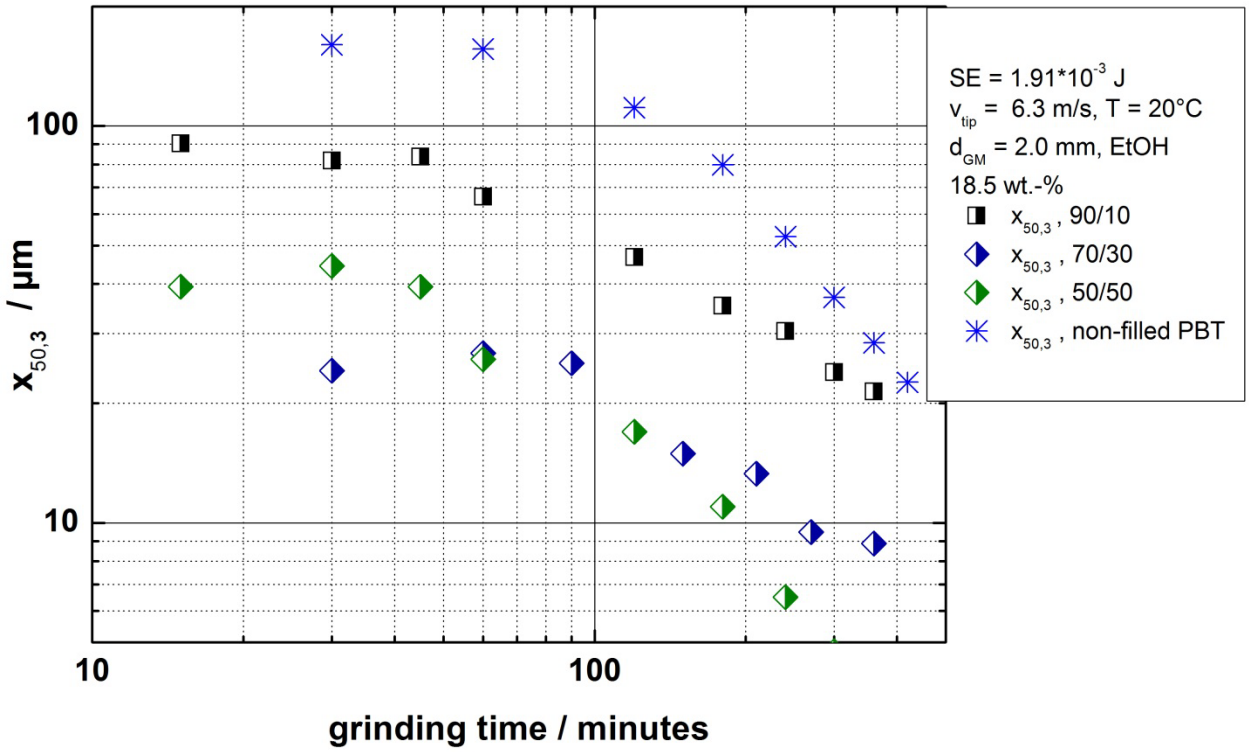

Figure 1: Evolution of product particle size $x_{50,3}$ during wet grinding of PBT-glass (SG3000) composite material in ethanol: influence of polymer-to-filler volume ratio on grinding kinetics.

Obviously the composite is not strengthened by the filler material (glass spheres of several 10 microns size) during wet comminution, on the contrary a weakening effect was observed: smaller product particle sizes are observed for larger filling degrees. Moreover, faster grinding kinetics were observed for the filled systems as compared to non-filled PBT. Similar dependencies were found for PBT / SG5000 systems, i.e.no remarkable influence of the filler particle size on the comminution behavior was found. The process was stopped after around 6 hours for the 90/10 and 70/30 (volume PBT / volume glass) and around 4 hours for the 50/50 system (because of the rapid size reduction in the latter case). The product particles were separated from the solvent by centrifugation. The comminution products have been characterized by SEM imaging and He pycnometry (see section ‘Characterization’).

Rounding

The rounding of the dried comminution product was done in a heated downer reactor. In the reactor the particles are molten, rounded due to the surface tension and finally solidified. For details on the experimental setup and the choice of appropriate process parameters, i.e. the residence time and temperature profile along the reactor coordinate, please refer to [9]. Heating is realized by a nine stage heating system (Thermal Technology) and the particles are introduced into the heated downer as an aerosol. For aerosol generation a Venturi disperser was used. The carrier gas was nitrogen (purity 5.0, Linde) and the aerosol gas flow was surrounded by a sheath gas flow (nitrogen) to minimize the contact between (molten) particles and the reactor wall. The temperature profile applied in the rounding experiments is depicted in Figure 2: The aerosol and sheath gas flow enter the reactor at its top section. The total gas flow first is heated to the process temperature necessary for rounding (> 230 °C) and then gradually reduced to allow for solidification. At the bottom of the reactor the (solid) rounded particles may be collected.

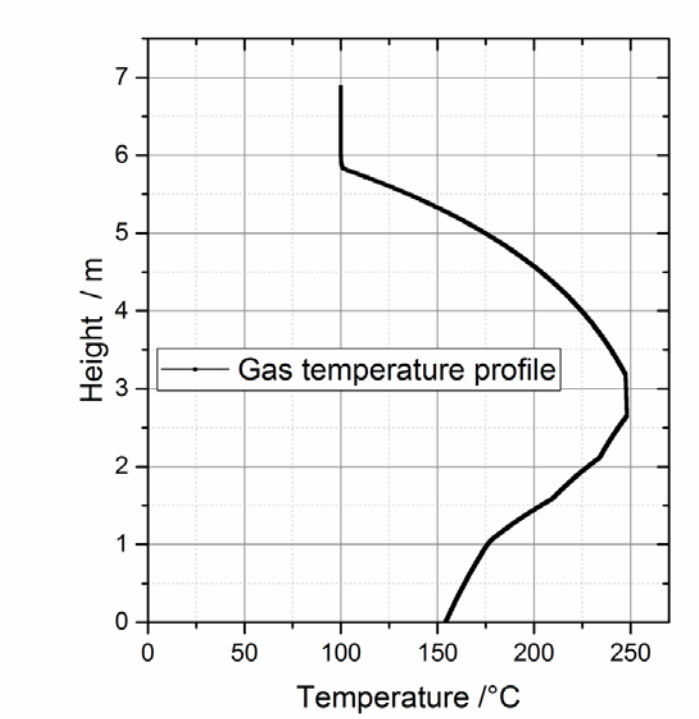

Figure 2: Temperature profile used for rounding of PBT-glass comminution products.

SEM images of PBT-glass (SG3000) comminution products of different polymer to glass volume ratio and the respective rounded particles obtained are shown in Figure 3: the comminution product consists of irregular shaped, plate-like particles (Figure 3, left). Disintegration of the composite (c.f. liberation of glass spheres, Figure 3, middle, left) and breakage of glass spheres occurs. Rounding of the comminution product was possible up to a PBT-glass-ratio of 70/30; for the 50/50 system the procedure was not successful anymore possibly due to the high fraction of nanoscale plate-like glass fragments [19,20] present hindering the coalescence of the polymer melt. The spatial distribution of the glass in the composite particles will be subject to future investigations.

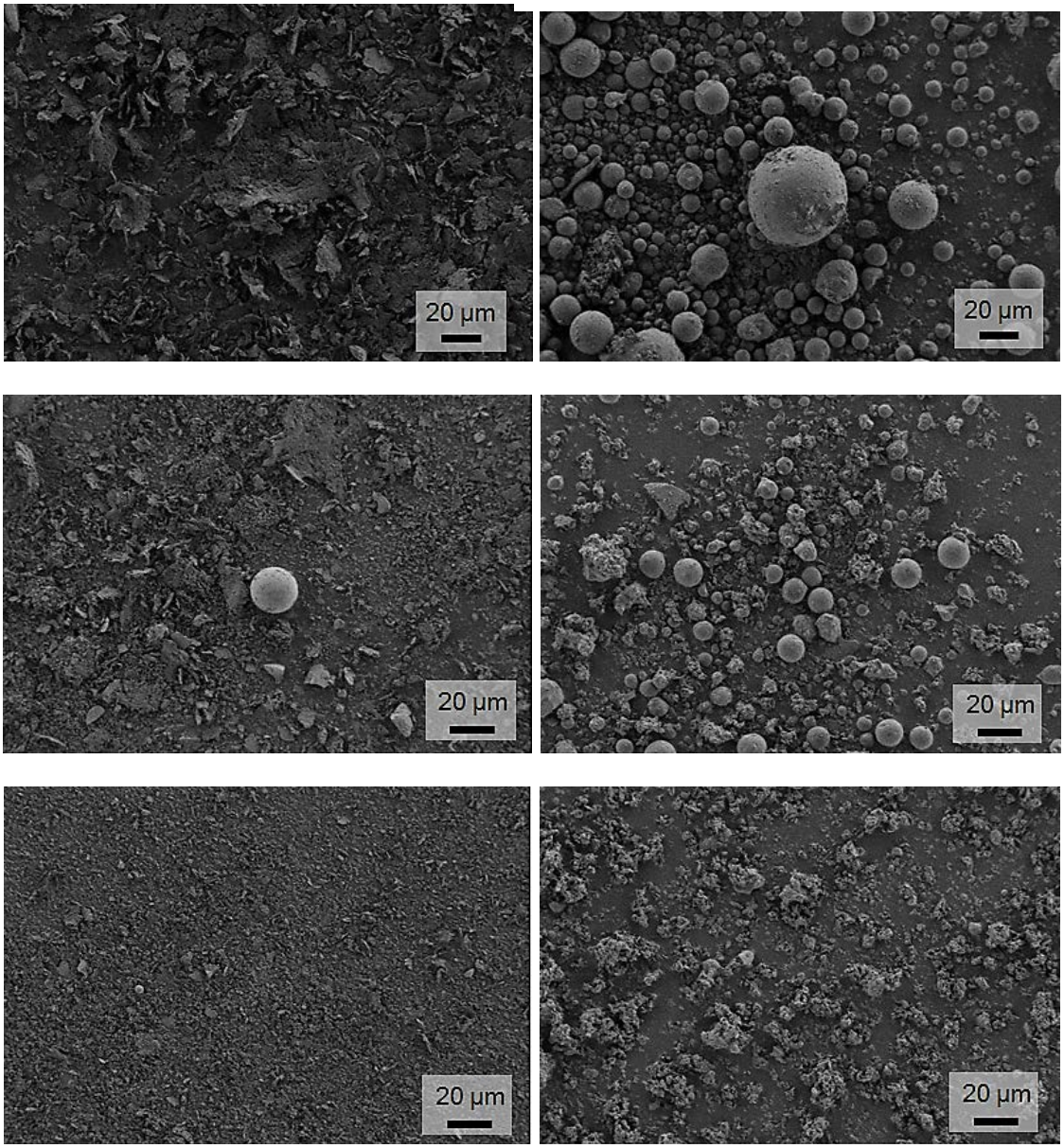

Figure 3: SEM images of the comminuted (left) and rounded (right) PBT-glass composite powders: 90/10 (top), 70/30 (middle), 50/50 (bottom).

Characterization of material properties

Solid density of the powders

Solid densities of the PBT-glass comminution products and the rounded particles of different polymer to glass ratio are summarized in Table 1. Moreover, the amount of glass in the composite powder was calculated from the measured He densities using 1.3 g/cm^3 and 2.5 g/cm^3 for the densities of PBT and SG 3000, respectively. For nominal glass concentrations of more than 30 vol.-% a slight reduction of the amount of glass in the rounded composite material was noted. Although some glass seems to get lost during rounding, presumably due to adhesion to the reactor walls, the approach of subsequent grinding and rounding of a PBT-glass composite allows for production of spherical composite particles.

Label	Solid density / g/cm^3	Amount of glass (calculated) / vol.-%
PBT / SG3000 90/10 (comminuted)	1.51	17.5
PBT / SG3000 90/10 (rounded)	1.51	17.5
PBT / SG3000 70/30 (comminuted)	1.71	34.2
PBT / SG3000 70/30 (rounded)	1.66	30.0
PBT / SG3000 50/50 (comminuted)	1.92	51.7
PBT / SG3000 50/50 (rounded)	1.85	45.8

Table 1: Solid densities of the produced PBT-glass composite as determined by helium pycnometry.

Influence of shape on tensile strength of powders

The following characterization has been done for the PBT/SG5000 90/10, since a better mechanical performance as compared to the PBT/SG3000 system is assumed. The tensile strengths of comminuted and rounded powders produced from PBT/SG5000 90/10 were (13.7 +/- 1.6) Pa and (4.5 +/- 1.4) Pa, respectively. A small tensile strength corresponds to good powder flowability. The comminuted product is cohesive. The rounding step leads to a remarkable improvement of flowability which should be reflected by better processability of the rounded material. For commercially available PA12 materials used in SLS tensile strengths of 2 to 3 Pa are found. Moreover, rounding leads to an increase in bulk density of powders [9] which is advantageous for the additive manufacturing process as well.

Thermal characterization

The thermal values of the rounded powder are analyzed by a DSC measurement. The first heating run of the unmilled material shows a melt temperature of 221.6 °C and a crystallization temperature of 203.9 °C in the cooling run, which can be seen in Figure 4. The melting temperature of the rounded particles is 222.5 °C in the first heating run. A distinctive characteristic is the shoulder in the crystallization peak at 206.1 °C of the rounded sample, which cannot be observed for the unmilled sample. The crystallization temperature (main peak) is found at 200.1 °C. The double peak could be due to different polymorphic structures formed during powder processing. The difference between the onset temperature of the crystallization peak ($T_{c,onset}$ = 206°C) and the melting peak ($T_{m,\ onset}$ = 210 °C) reveals a small process window of around 5 °C.

The second heating run, see Figure 5, also shows a double peak in the melting peak of the rounded particles in contrary to the non-milled sample. The change in the crystallization in the cooling run implies two different crystal modifications und results in a double peak in the melting peak as well. Since the particles are remolten in the downer reactor for rounding the particles, the glass spheres or contamination in the reactor may act as nucleating agents and lead to two different crystal modifications.

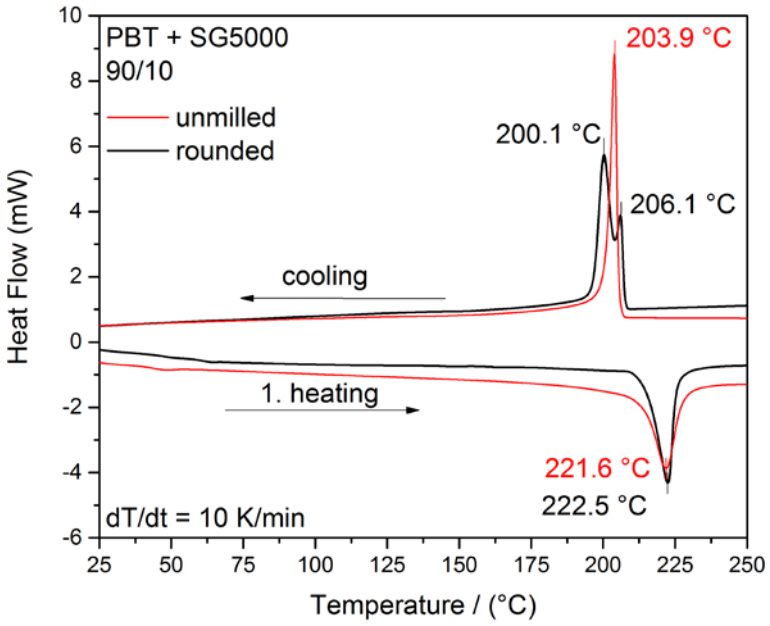

Figure 4: DSC curve of the first heating and cooling run of PBT+SG5000 in a ratio of 90/10 in the unmilled and rounded state.

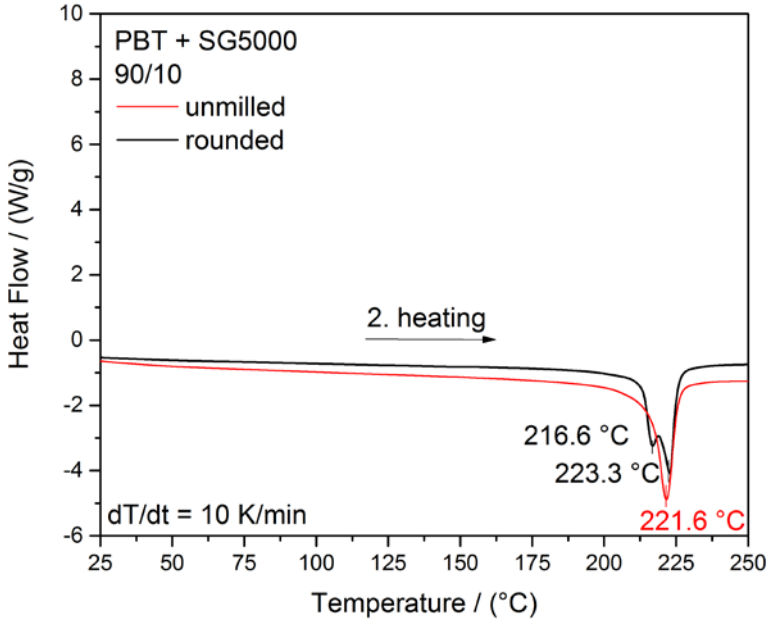

Figure 5: DSC curve of the second heating run of PBT+SG 5000 in a ratio of 90/10 in the unmilled and rounded state.

In Figure 6 the results of the thermogravimetric analysis is shown. By this investigation the real filler content can be compared to the set value. The unmilled sample reveals a residue of 18.3 wt.-% and is similar to the filler content of the rounded sample being 18.0 wt.-%. This value is in good agreement with the nominal filler amount of 10 vol.- %. No filler material is lost during rounding of systems with moderate filler concentration.

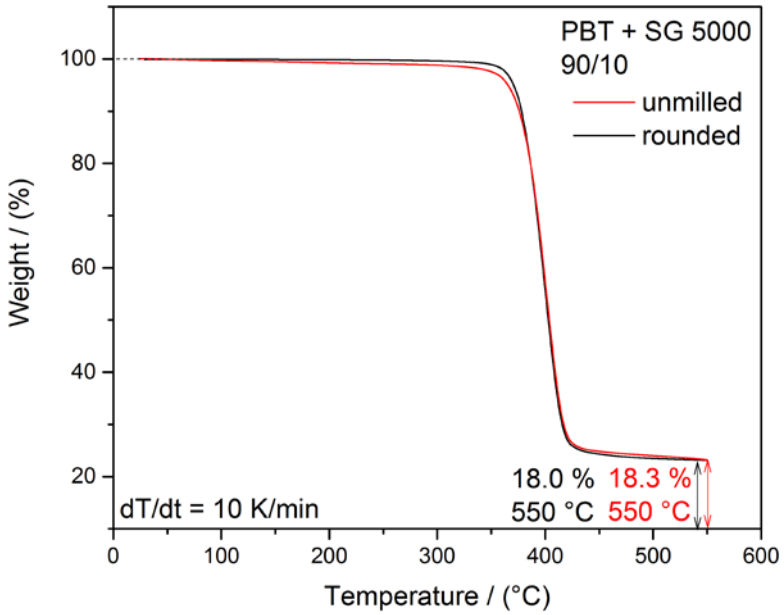

Figure 6: TGA curve of PBT+SG 5000 in a ratio 90/10 of the unmilled and rounded state.

Conclusions

Within this contribution an approach to produce PBT-glass composite powders by wet grinding and subsequent rounding was addressed. Wet comminution allows to tailor the product particle size. The flowability of the cohesive comminution product is remarkably improved by rounding as proven by tensile strength measurements of powders. Although disintegration of the composite during wet grinding takes place, rounded PBT-glass composite powders may be obtained and no pronounced de-mixing of matrix and filler material due to processing was observed. The processes applied are scalable, i.e. the approach could be transferred to the plant scale for production. Moreover it is applicable to a wide range of thermoplasts and therefore an option to produce novel SLS powders including filled systems.

Acknowledgements

The authors thank the German Research Foundation (DFG) for funding of their studies within Collaborative Research Center 814, sub-projects A2 and A3 as well as Bayerisches Laserzentrum for assistance.

References

References

[1] A. Gebhardt, Generative Fertigungsverfahren: Additive manufacturing und 3D-Drucken für Prototyping - Tooling - Produktion, 4th ed., Hanser, München, 2013.

[2] B. Wendel, D. Rietzel, F. Kühnlein, R. Feulner, G. Hülder, E. Schmachtenberg, Additive Processing of Polymers, Macromol. Mater. Eng. 293 (2008) 799–809.

[3] J.P. Kruth, X. Wang, T. Laoui, L. Froyen, Lasers and materials in selective laser sintering, Assembly Automation 23 (2003) 357–371.

[4] T.T. Wohlers, Wohlers report 2014: 3D printing and additive manufacturing state of the industry annual worldwide progress report, Wohlers Associates, Fort Collins, Col., 2014.

[5] M. Schmid, Selektives Lasersintern (SLS) mit Kunststoffen: Technologie, Prozesse und Werkstoffe, Hanser, München, 2015.
[6] R.D. Goodridge, C.J. Tuck, R. Hague, Laser sintering of polyamides and other polymers, Progress in Materials Science 57 (2012) 229–267.
[7] M. Wilczek, J. Bertling, D. Hintemann, Optimised technologies for cryogenic grinding, International Journal of Mineral Processing 74 (2004) S425-S434.
[8] J. Schmidt, M. Plata, S. Tröger, W. Peukert, Production of polymer particles below 5µm by wet grinding, Powder Technology 228 (2012) 84–90.
[9] J. Schmidt, M. Sachs, C. Blümel, B. Winzer, F. Toni, K.-E. Wirth, W. Peukert, A novel process route for the production of spherical LBM polymer powders with small size and good flowability, Powder Technology 261 (2014) 78–86.
[10] S. Fanselow, S.E. Emamjomeh, K.-E. Wirth, J. Schmidt, W. Peukert, Production of spherical wax and polyolefin microparticles by melt emulsification for additive manufacturing, Chemical Engineering Science 141 (2016) 282–292.
[11] A. Mazzoli, G. Moriconi, M.G. Pauri, Characterization of an aluminum-filled polyamide powder for applications in selective laser sintering, Materials & Design 28 (2007) 993–1000.
[12] P. Forderhase, K. McAlea, R. Booth, The development of a SLS® composite material. University of Texas, Austin, Texas, Solid freeform fabrication proceedings (1995) 287–297.
[13] H. Chung, S. Das, Functionally graded Nylon-11/silica nanocomposites produced by selective laser sintering, Materials Science and Engineering: A 487 (2008) 251–257.
[14] A. Schweiger, I. Zimmermann, A new approach for the measurement of the tensile strength of powders, Powder Technology 101 (1999) 7–15.
[15] K. Meyer, I. Zimmermann, Effect of glidants in binary powder mixtures, Powder Technology 139 (2004) 40–54.
[16] C. Blümel, M. Sachs, T. Laumer, B. Winzer, J. Schmidt, M. Schmidt, W. Peukert, K.-E. Wirth, Increasing flowability and bulk density of PE-HD powders by a dry particle coating process and impact on LBM processes, Rapid Prototyping Journal 21 (2015) 697–704.
[17] M. Wolff, S. Antonyuk, S. Heinrich, G.A. Schneider, Attritor-milling of poly(amide imide) suspensions, Particuology 17 (2014) 92–96.
[18] A. Kwade, Determination of the most important grinding mechanism in stirred media mills by calculating stress intensity and stress number, Powder Technology 105 (1999) 382–388.
[19] S. Romeis, J. Schmidt, W. Peukert, Mechanochemical aspects in wet stirred media milling, International Journal of Mineral Processing (2016).
[20] S. Romeis, A. Hoppe, C. Eisermann, N. Schneider, A.R. Boccaccini, J. Schmidt, W. Peukert, Enhancing In Vitro Bioactivity of Melt-Derived 45S5 Bioglass ® by Comminution in a Stirred Media Mill, J. Am. Ceram. Soc. 97 (2014) 150–156.