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PROCESS ROUTES TOWARDS NOVEL POLYBUTYLENE TEREPHTHALATE – POLYCARBONATE BLEND POWDERS FOR SELECTIVE LASER SINTERING

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Abstract

Additive manufacturing techniques, such as powder bed fusion (PBF) of polymers, often referred to as laser sintering (LS) or selective laser sintering (SLS), generate components directly from a CAD data set without using a specific mold. The range of materials commercially available for SLS merely includes some semi crystalline polymers, mainly polyamides. In this contribution two process chains to produce polybutylene terephthalate (PBT) – polycarbonate (PC) blend particles and the respective dependencies of product characteristics on process parameters are addressed. In the first recently proposed approach, blend powder systems are produced via co-comminution of PBT and PC in a planetary ball mill and subsequent thermal rounding of the obtained comminution product. This approach is compared to a route, where blend particles are obtained by agglomeration of comminution products of the respective polymers obtained by wet grinding and subsequent thermal rounding.

Introduction

Powder bed fusion processes (PBF) of polymers, such as selective laser sintering (SLS) or laser sintering (LS), allow the direct production of solid parts from a three-dimensional CAD model by selectively fusing powders without the need for any tools or molds. So far, materials for PBF of polymers are very limited [1, 2]; preferentially semi-crystalline thermoplasts, in particular polyamide (PA) powders are applied because of their favorable sintering behavior that allows for manufacture of parts of good mechanical part properties [1, 2]. Besides polyamide 12 (PA12) so far PA11, PA6 and some other materials like polystyrene (PS), polypropylene (PP), polyethylene (PE), thermoplastic elastomers (TPE) or polyether ether ketone (PEEK) are commercially available [1-3]. While several approaches to provide PBF one-component powders from other polymers have been reported in the literature, e.g. a process chain [4, 5] employing wet grinding of polymers [6] followed by thermal rounding of comminuted particles in a downer reactor 7], melt emulsification [8], spray agglomeration [9], spray drying [10] and precipitation-based processes [11, 12], strategies towards polymer blend systems, which might be beneficial with respect to novel material functionalities, have been rarely reported. For example, the addressed PBT-PC blend system made up of a semi-crystalline (PBT) and an amorphous (PC) component might be beneficial with respect to enhanced part properties and improved dimensional accuracy due to lower shrinkage during cooling. Moreover, the PBT-PC blend combines excellent mechanical properties with chemical resistance making it e.g. interesting for the automotive industries. In the majority of studies on PBF of blend systems, polymer powder mixtures were applied: Salmoria et al., for example, processed blends of PA12 / HDPE [13, 14], PA6 / PA12 [15] or PBT/ PA12 [16] in a SLS machine. Greiner et al. reported on SLS processing of a physical mixture of PBT and PC [17], although, there were already attempts to produce blend systems characterized by intra-particle mixing by cryogenic grinding and mechanical alloying [18-21]. A drawback of the comminution process, respectively, mechanical alloying by mills is that the obtained product particles typically are irregular shaped and, in consequence, often show poor flowability and low bulk density, which results in bad PBF processability of these materials [4, 5]; processability may be enhanced by thermal rounding of the particles and application of flowing aids [6, 7]. Two approaches towards intra-particle mixed PBT-PC blend particles with good flowability, namely dry co-comminution (mechanical alloying) in a planetary ball mill and subsequent thermal rounding in a heated downer reactor, respectively, (separate) wet comminution

of the two polymers, agglomeration of the obtained comminuted particles and rounding of the agglomerates in the heated downer are addressed in this contribution.

Materials

Commercial injection-grade polymer granules, namely polybutylene terephthalate PBT Ultradur B 4520 (BASF) and bisphenol-A-based amorphous polycarbonate PC Makrolon 2405 (Covestro) were used in this study. For wet comminution denatured ethanol (95 %, Carl Roth) was applied as solvent.

Methods

Comminution

PBT and PC particles of suitable size (< 0.5 mm) as feed materials for wet comminution and planetary ball milling in batch mode, respectively, were obtained by dry impact comminution using a rotary impact mill Pulverisette 14 (Fritsch). The feed granules of several millimeters size were pre-cooled with liquid nitrogen priot to stressing. A sieve ring of 0.5 mm mesh size was applied and the pin rotor rotational frequency was set to 20,000 min^{-1}. The obtained PBT and PC particles were subjected to (i) wet comminution in a stirred media mill PE5 (Netzsch), respectively, (ii) dry comminution in a planetary ball mill Pulverisette 7 classic line (Fritsch). For wet comminution grinding beads made of Yttrium-stabilized zirconium oxide (YTZ) of 2 mm diameter were applied; as solvent denatured ethanol was used. For planetary ball milling grinding beads of 5 mm diameter were used. Further details on chosen stressing conditions are given in the results and discussion section.

Thermal Rounding

Thermal rounding of the comminution products was performed in a heated downer reactor, which is described in great detail in e.g. [6] or [7]. Briefly, the reactor consists of a heated stainless steel pipe of 6 m length and 100 mm inner diameter, an aerosol generator (brush disperser RGB 100 (Palas), aerosol gas: nitrogen) to disperse the comminuted particles and a separation unit to recover the (spherical) product particles. Heating is accomplished by a three-stage oven (Thermal Technology) with a total length of 4.5 m. The aerosol is fed centrally into the head of the reactor and surrounded by a sheath gas (nitrogen) flow to minimize particle-particle and particle-wall interactions. Along the reactor coordinate a temperature profile is applied that allows for (complete) melting of the particles, rounding (due to action of the surface tension / minimization of total surface area) and finally solidification of the (spherical) polymer melt droplets resulting in spherical polymer particles. Typical residence times necessary for complete rounding of polymer particles of several 10 microns size are in the range of some seconds. The optimum temperature profile depends amongst others on particle size distribution of the feed, melt viscosity and surface tension, for details please refer to our previous work [6, 7].

Agglomeration

For agglomeration of the PBT and PC particles obtained by wet comminution a turbular mixer T2F (Willy A. Bachofen) was used. The device was operated at 49 min^{-1} for 100 minutes. For each agglomeration experiment, a total mass of 100 g polymer feed powder was applied. For mixing an aluminum bottle of a total volume of 500 mL was used and as mixing agent glass spheres were applied at a volume concentration of around 18 % (with respect to the volume of 500 mL).

Laser diffraction particle sizing

Particle size distributions (PSDs) were determined by laser diffraction sizing using a Mastersizer 2000 (Malvern) equipped with a wet dispersion unit Hydro 2000S. Small amounts of sodium dodecyl sulphate solution (SDS, 98% (Merck)) have been added to assure dispersion stability of aqueous polymer particle suspensions used for measurement. Prior to measurement the dispersions were ultrasonicated. In the following, the depicted volume-averaged particle sizes $x_{10,3}$, $x_{50,3}$ and $x_{90,3}$ are mean values calculated from five single measurements.

Scanning Electron Microscopy

The PBT-PC particle obtained after comminution and thermal rounding were stained with RuO_4 as described by Brown [51] and Trent [52], which allows assessment of the spatial distribution of the polymers via the material contrast. A scanning electron microscope (SEM) Gemini Ultra 55 (Carl Zeiss AG, Germany) operated at an acceleration voltage of 1.0 kV equipped with a SE2 detector and a through-the-hole detector was used.

Results and Discussion

Planetary ball milling and thermal rounding of PBT and PC

For planetary ball milling grinding chambers made of YTZ of 12 mL total volume were filled with 2 g of pre-comminuted PBT and PC, respectively, and 50 grinding beads (5 mm, YTZ). This mixture was co-comminuted for total process times of up to 16 hours at a rotational speed (of the sun wheel) of 600 min^{-1}.and cycles of 20 minutes followed by 2 minutes cooling time and reversal of the rotational direction of the mill at ambient atmosphere. Under these conditions, a stationary (global) temperature of around 40 °C was observed in the grinding chamber. The stress energy SE, being proportional to the kinetic energy of the grinding bead, was estimated to around 11.8 mJ under these conditions (see [22]). The comminution kinetics, i.e. the evolution of the volume-averaged particle sizes $x_{10,3}$, $x_{50,3}$ and $x_{90,3}$ observed for the co-comminution of the two polymers at a weight ratio of 1:1 is depicted in Figure 1.

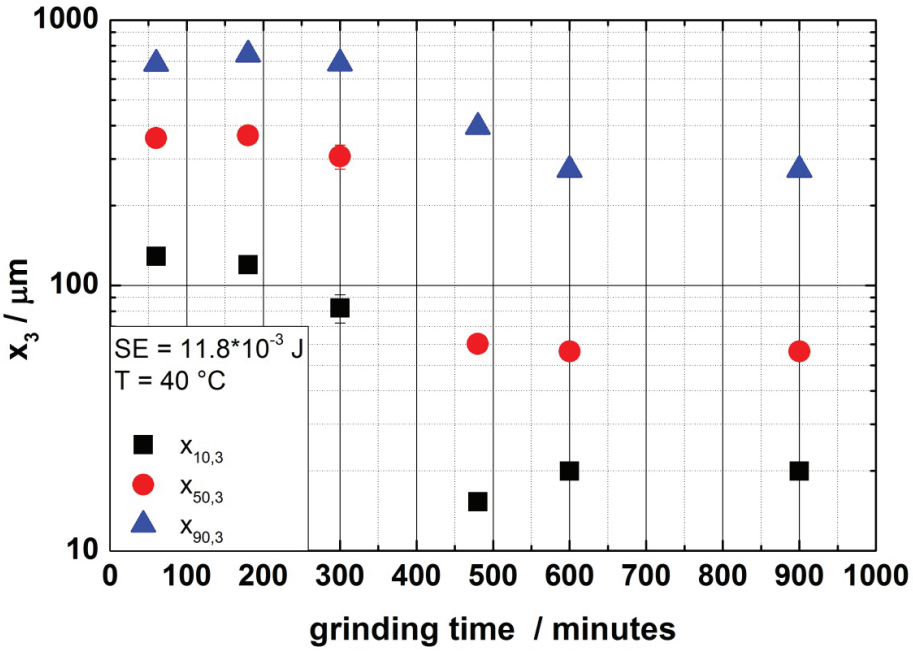


Figure 1: Evolution of particle sizes $x_{10,3}$, $x_{50,3}$ and $x_{90,3}$ over process time during co-comminution of a PBT-PC mixture (1:1 (wt./wt.); feed mass load: 2 g).

Particle with an average size between 50 and 60 microns, i.e. a size range where particles are known to be usable in PBF, are obtained after a process time of around 600 minutes ($x_{10,3}$ = 20.0 µm, $x_{50,3}$ = 56.5 µm, $x_{90,3}$ = 272.7 µm). In the further course of the process, under the chosen conditions, no further size reduction could be observed. The co-comminution product obtained in this batch process has a rather broad distribution width as expressed by a span ($x_{90,3}$ - $x_{10,3}$) / $x_{50,3}$ of 4.46. To get information on the shape of the obtained particles, scanning electron microscopy was performed. A SEM image of the co-comminuted particles is depicted in Figure 2, left. Obviously, the obtained product particles are of irregular and somewhat flattened shape. The morphology suggests, that the polymers were jointly kneaded as characterized by the many boundaries being visible. As grinding products typically show non-favorable flowability and packing density due to their irregular shape, thermal rounding of co-comminution products was performed in a heated downer reactor. On these products, staining with in-situ formed RuO_4 was performed, which allows to assess the spatial distribution of the two polymers in the particle. A SEM image of RuO_4 stained spherical PBT-PC particles is depicted in Figure 2,

right. The material contrast being due to the different entrapment of Ru into PC and PBT, respectively, confirms crescent shaped PC domains on the particle surface and, thus, the successful formation of an intra-particle PBT-PC blend powder via this approach. Further characteristics of the obtained materials including thermal properties, polarization microscopy to assess polymer distribution in the volume and vibrational spectroscopy are given in detail in [22].

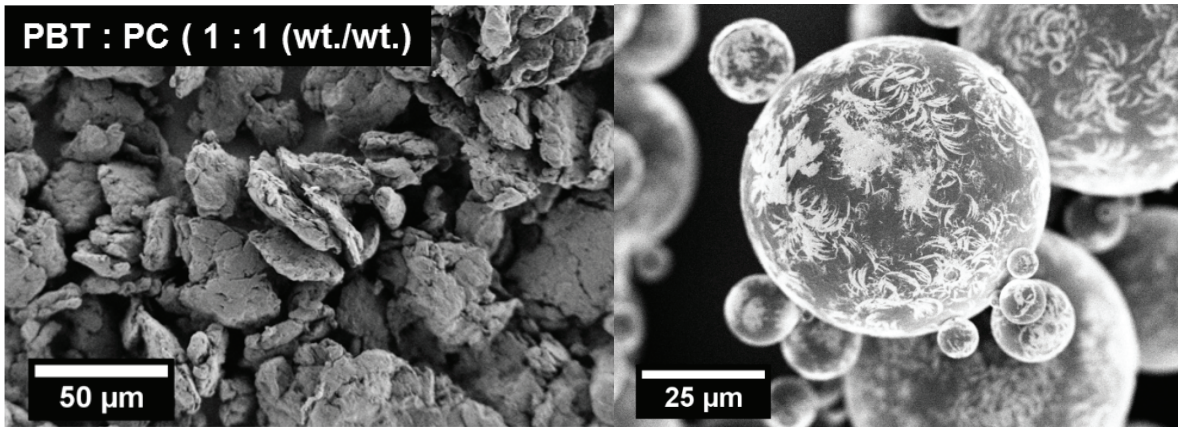


Figure 2: left: SEM image of PBT-PC particles obtained by co-comminution for 10 hours in a planetary ball mill, right: spherical PBT-PC particles obtained by thermal rounding of a sample co-comminuted for 15 hours; staining with RuO_4 confirms formation of an intra-particle blend powder.

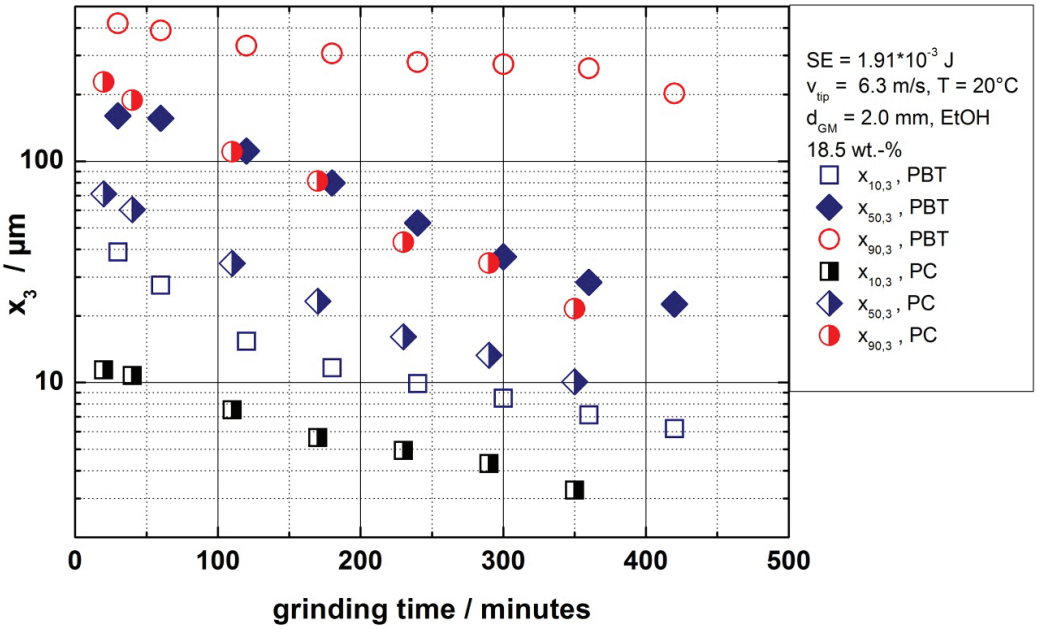


Figure 3: Evolution of particle sizes $x_{10,3}$, $x_{50,3}$ and $x_{90,3}$ over process time during wet grinding of PBT and PC in ethanol.

Wet comminution, agglomeration and thermal rounding of PBT and PC

As an alternative approach for PBT-PC blend particles a three stage process was studied, namely the wet comminution of PBT and PC in ethanol in separate processes followed by the agglomeration of the polymer particles in a turbular mixer and subsequent thermal rounding of the agglomerates in the heated downer reactor. The comminution kinetics for PBT and PC are summarized in Figure 3. There, a polymer feed concentration of 18.5 wt.-% was chosen. The solvent was denatured ethanol and the stress energy was set to 1.9 mJ by using YTZ grinding beads of 2 mm diameter and a rotational speed of 800 min^{-1} of the stirrer corresponding to a circumferential speed of 6.3 m/s. As compared to the co-comminution of the PBT-PC mixture, more efficient grinding kinetics, i.e. smaller product particles at shorter process times (and smaller (estimated stress energies))

are observed. That wet comminution allows for finer products as compared to dry comminution is well-known, see e.g. [5] and references therein. After 420 minutes PBT particles of $x_{10,3}$ = 6.2 µm, $x_{50,3}$ = 22.6 µm, $x_{90,3}$ = 202.0 µm and after 350 minutes PC particles of $x_{10,3}$ = 3.3 µm, $x_{50,3}$ = 10.1 µm and $x_{90,3}$ = 21.6 µm are obtained. While the span of the wet comminuted PC product is 1.81 and, thus, quite narrow, the wet-comminuted PBT shows a rather broad size distribution with a span of 8.66. The shape of the wet-comminuted particles was assessed by SEM as well, see Figure 4 for PBT: as compared to the co-comminuted product, the product is characterized by an even broader shape distribution and way finer particles. These fine cohesive particles were used to produce agglomerates in the turbular mixer, which have been subjected to thermal rounding in the downer reactor. Again, staining with RuO_4 was used to assess the spatial distribution of PBT and PC in the obtained, rounded particles. Results are depicted in Figure 5.

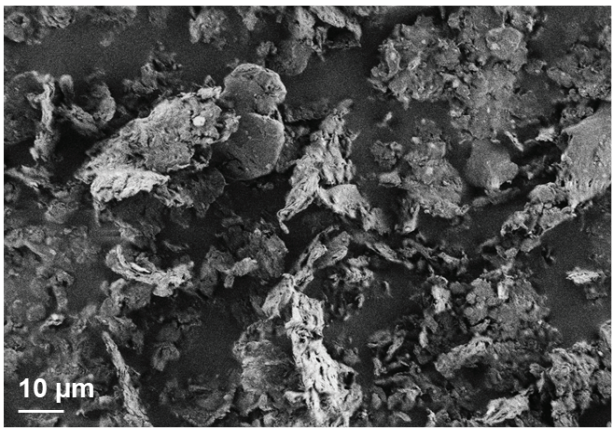
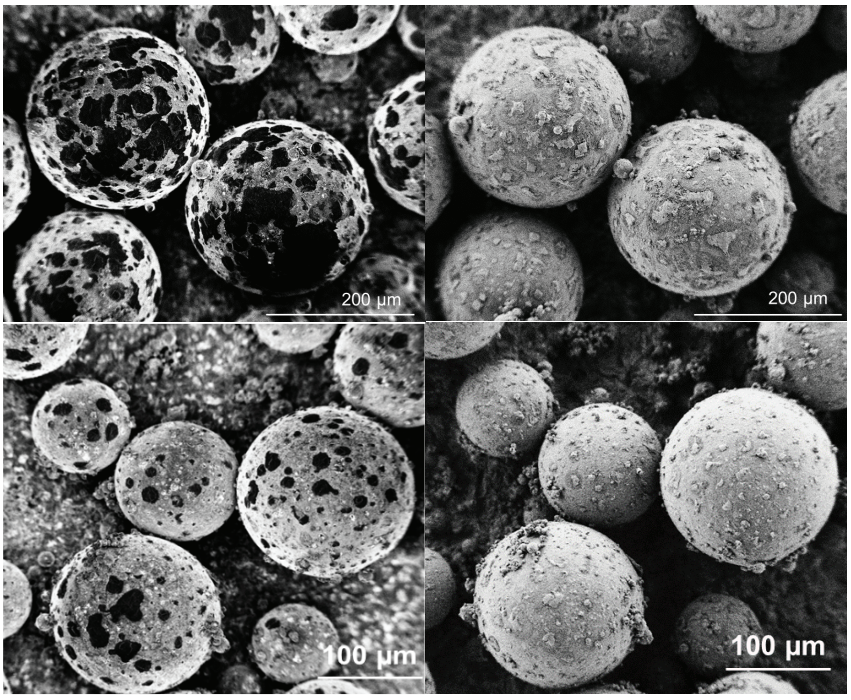


Figure 4: SEM image of PBT particles obtained by wet comminution in ethanol.



generation step, as confirmed by vibrational spectroscopy on the feed material and the obtained rounded powders.

Conclusions

Co-comminution in a planetary ball mill followed by thermal rounding allows for successful production of intra-particle-mixed, spherical PBT-PC blend powders as confirmed by SEM imaging of RuO_4 stained samples. Thus, this approach gives the possibility to obtain micro-heterogeneous blend systems [22] in contrast to physical powder mixtures applied so far. The approach was compared to an alternative process route, where the first step is wet comminution of the polymer. While wet comminution allows for finer, cohesive particles that can be successfully agglomerated, the blend particles obtained by thermal rounding show less inter-mixing of the polymers and seem to be made up of a PBT-rich core and a shell being enriched in PC as confirmed by electron microscopy. A more detailed analysis of the spatial distribution of PBT and PC in the particles obtained by the later approach is subject to future work, as well as a comparison of further material characteristics of the powders produced by the two approaches of nominal same composition and studies on PBF processability of these powders.

Acknowledgements

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