Wet grinding of thermoplastics

Jochen Schmidt[1,*], Florentin Tischer[1], Wolfgang Peukert[1]

[1]Institute of Interfaces and Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Abstract. Fine microparticles made from engineering and high-performance thermoplastics are of great interest for modern manufacturing methods of Industry 4.0, i.e. additive manufacturing processes, such as powder bed fusion of polymers with a laser beam (PBF-LB/P). The production of very fine polymer particles with a size of less than 10 micrometers via dry grinding is difficult for amorphous plastics and nearly impossible for engineering and high-performance thermoplastics, such as polybutylene terephthalate, polyoxymethylene, or polyaryl ether ketone. However, fine polymer microparticles of the aforementioned plastics can be easily produced by wet grinding addressed here. For PBF-LB/P, in addition to flowability, the thermal properties of the thermoplastic, i.e. its melting and solidification temperatures as well as melt crystallization kinetics are crucial. Therefore, damage to the polymer during the comminution process and contamination of the product due to grinding media wear should be minimized. The ground products are thoroughly characterized using vibrational spectroscopy, X-ray diffraction, and differential scanning calorimetry. The dependency of product properties on stressing conditions and system composition is discussed in view of the necessary mass specific comminution energy and in view of minimization of grinding media wear. Experimentally determined grinding limits are discussed in relation to the mechanical properties of thermoplastics.

1. Breakage of plastics

Polymers are materials that are difficult to grind due to their viscous or viscoelastic properties. Size reduction of plastics or rubber by comminution is necessary, for example, in recycling or for polymer-based particulate products such as toner systems, powder coatings or powders used in laser powder bed fusion additive manufacturing of polymers (PBF-LB/P). In order to break a particle, the elastically stored energy within the material must be greater than the critical energy required for crack propagation [1]. The behaviour of viscoelastic materials can be described by the complex Young's modulus (E*), which is made up of the elastic storage modulus (E') and the loss modulus (E”). Therefore, to efficiently break a viscoelastic material, it is necessary to ensure that the energy introduced into the particle by stressing in a mill is stored elastically rather than dissipated. Furthermore, a minimum stress energy must be applied to the material to allow for crack propagation. As E' and E" of a polymer depend significantly on temperature and stressing velocity, fine comminution of thermoplastics is usually performed at reduced temperatures and high stressing velocity. Under these conditions, viscous dissipation can be significantly reduced. To improve the grindability of visco-elastic materials such as polymers or other organic matter, they can be pre-cooled using liquid nitrogen or carbon dioxide. Pre-cooling is particularly important for the comminution of rubber-elastic materials, especially for fine comminution. Impact mills, cutting mills, pin mills, jet mills or pan mills are employed for the comminution of viscoelastic materials to account for high impact velocities. Pin mills and counter-rotating pin mills are recommended for fine comminution of polymers. The fine comminution of viscoelastic materials such as polymers is particularly costly: the mass-specific energy input required for a product fineness below 100 µm is estimated to be 10 to 50 times higher than that required for a brittle material of the same size.

Despite the widespread use of plastics, including fine polymer powders, few studies have systematically investigated the effect of process temperature on breakage and the size reduction process of thermoplastics. For dry comminution, for example, bin Ahmad and Ashby [2] investigated the failure mode of polymers in dependence on temperature and stress. They compiled fracture maps of failure for PMMA, PS, polyisobutylene and an epoxy resin, enabling the prevailing fracture mode in compression and tension to be assessed as a function of temperature (normalised to the respective glass transition temperature). They identified four modes of deformation and fracture: brittle fracture, ductile fracture, cold drawing, and viscous flow. Brittle fracture occurs at high stresses and low temperatures. Green et al. [3] exploited the temperature dependence of the failure mode of thermoplastics in impact comminution of PET-PVC mixtures in a hammer mill. PET and PVC flakes measuring between 4.6 and 7.4 mm in diameter and around 0.7 mm in thickness were subjected to dry comminution under identical stressing conditions at ambient temperature and at liquid nitrogen temperature.

* Corresponding author: jochen.schmidt@fau.de

While PVC stressed at room temperature exhibited ductile fracture and a bimodal product particle size distribution, the lN_2 pre-cooled PVC exhibited brittle fracture and a monomodal product particle size distribution shifted towards smaller particle sizes. A more detailed discussion on breakage mechanism of polymers can be found in [4].
In own work wet comminution of thermoplastics in stirred media mills was investigated for amorphous plastics, such as polystyrene (PS) and semi-crystalline engineering and high performance thermoplastics including polybutylene terephthalate (PBT), polyoxymethylene (POM) and polyether ether ketone (PEEK) [5-8]. Depending on the thermoplastic and the mode of stressing, either a brittle or a ductile fracture was observed. In the case of PEEK, graze formation occurred prior to breakage. This increased the fracture toughness and led to unusual grinding kinetics [5]. The formation of crazes and viscous energy dissipation explain why polymers are harder to break than inorganic (brittle) matter. Upon reduction of the temperature, the formation of crazes is less pronounced, i.e. the material behaves more brittle leading to improved grindability. An advantage of the wet comminution process compared to dry grinding of thermoplastics is that it allows for very fine product particles at moderately reduced temperatures, which amongst other is due to the higher stress numbers [9] stirred media mills provide compared to impact comminution. In the case of PS product particles as small as 2 micrometers ($x_{50,3}$) could be obtained [5]. Within the conference contribution the process parameter dependencies during wet grinding of thermoplastics will be discussed in greater detail.
For this extended abstract we limit the discussion to the grinding limit of thermoplastics and the effect of grinding media wear on product properties relevant for PBF additive manufacturing of polymers, first and foremost the effect of grinding media wear on melt crystallization.

2. Grinding limit of plastics

There are different model pictures for the grinding limit of brittle matter. Brittle materials are known to become more ductile as the particle size decreases, cf. the brittle-ductile transition. Thus, the grinding limit can be defined as the critical particle size at which the brittle-ductile transition occurs. Another widely accepted explanation of the grinding limit for brittle materials is that the minimum size of a particle produced via comminution is given by the distance between two adjacent cracks. Kniecke et al. [10] have demonstrated that for brittle materials the ultimate grinding limit is independent of stressing conditions, but dependent on defect storage. In this model, size reduction continues until single-crystalline, defect-free nanoparticles are produced. For polymers, i.e. materials exhibiting viscous and plastic behaviour, the extension of the plastic zone δ_c according to Dugdale [11, 5] may serve as an estimate for the limiting particle size obtainable by grinding:

$$\delta_c = \frac{K_{Ic}^2}{2 \cdot \sigma_F \cdot E} \qquad (1)$$

Here K_{Ic} is the fracture toughness, σ_F is the yield stress and E the Young's modulus. Particles of a size being smaller than δ_c were expected not to break in the model picture, but only be deformed plastically. The extension of the plastic zone according to Dugdale for the thermoplastics considered in own work and calculated for 20°C taking typical material parameters into account is summarized in Table 1. While the experimentally observed grinding limit for PS is close to the extension of the plastic zone, remarkably, for the semi-crystalline thermoplastics grinding products smaller than that characteristic length could be produced.

Table 1. Extension of the plastic zone δc calculated according to eq. 1 (at 20°C) and observed minimal product particles sizes ($x_{50.3,\,min}$) in wet comminution of selected thermoplastics in ethanol (at given process temperature). The Young's modulus is between 2500 MPa and 3200 MPa for the investigated polymers.

	K_{Ic} [MPa*m$^{0.5}$]	σ_F [MPa]	δ_c [µm]	$x_{50.3,\,min}$ [µm]
PS	0.80	55	1.8	1.9 (-40°C)
PEEK	5	100	32.9	4.2 (-30°C)
POM	4	65	45.6	5.0 (-30°C)
PBT	5	55	37.7	8.0 (15°C)

3. Influence of grinding media material on wear and melt crystallization kinetics of the thermoplastic comminution products

In laser powder bed fusion of polymers the feedstock powders do not only have to fulfil certain demands with respect to particle and bulk solid characteristics, such as dense packing and good flowability during the additive manufacturing process, which can be controlled by a narrow particle size distribution and particles of (close to) spherical shape, which e.g. can be produced by a thermal rounding process and the application of flowing aids [6], but also thermal -cf. the so-called 'sintering window', which is the difference between melting and solidification onset temperatures or the melt crystallization kinetics- and rheological material properties have to be well-tuned and ideally should not deteriorate during powder formulation. In a study by Tischer et al [8], PBT was wet ground in a stirred media mill at 20°C using ethanol as the dispersing medium at identical mass-specific energy inputs by applying grinding beads of 2 mm size of different materials, namely silica (SiO_2), chrome steel, cerium-stabilised (ZrO_2 (Ce)) and yttrium-stabilised (ZrO_2 (Y)) zirconia. The product particle size showed the same dependence on the mass-specific energy input irrespective of the used grinding media material. Figure 1 a shows the portion of grinding media wear caused by abrasion during the grinding process for products recovered after 15 hours process time. The (maximum) stress energy SE_{max} (stress intensity) [9] was 0.9 mJ for all experiments.

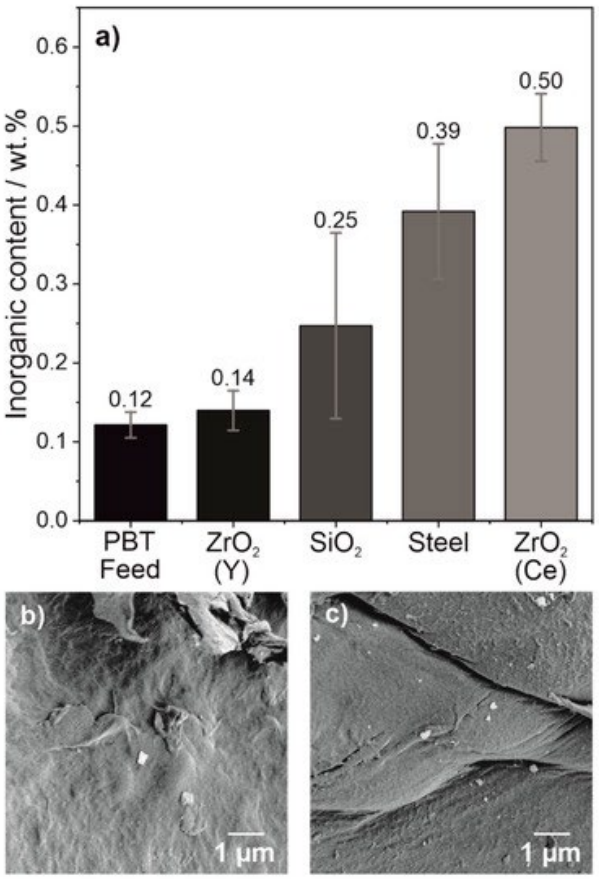

Figure 1. Inorganic content of (a) wet ground PBT particles (SE_{max} = 0.9 mJ, 20 °C, 15 h) using different grinding media as determined by TGA with representative SEM images of the abrasion on the PBT particle surface comminuted with (b) ZrO_2 (Y) and (c) ZrO_2.(Ce). Average of three measurements and standard deviation are shown. Reproduced from Tischer et al. [8] under the CC-BY 4.0 license.

Obviously, the abrasion content in the PBT product particles ground with yttrium-stabilized zirconia media (ZrO_2 (Y)) was the least and could not be discriminated from that of the feed material, which was 0.12 wt.-% (PBT Feed). Both, ceria-stabilized zirconia and steel media lead to substantial grinding media wear in the product and discolouration. The abrasion particles are sub-micron sized as confirmed by scanning electron microscopy (Figures 1 b and 1 c). In all cases the degree of crystallinity or the phase morphology did not change, as confirmed by differential scanning calorimetry (DSC) and X-ray diffraction.

In all cases, a consequence of the media wear particles being present in the PBT comminution product was a decrease of the 'sintering window' (difference between melting and solidification onset temperatures as determined by dynamic DSC) from around 21 K (PBT Feed) to 17 K to 13 K, where the smallest thermal process window was observed for the product obtained with steel grinding media. For PBF-LB/P a wide sintering window is desired. A too small thermal process window makes it more challenging to assure a stable manufacturing process. In the worst case a too narrow sintering window can lead to distorted parts or cause a termination of the building process. That using steel grinding media is unfavourable in terms of the desired product properties and a stable PBF-LB/P process, also becomes obvious from isothermal DSC measurements (Figure 2).

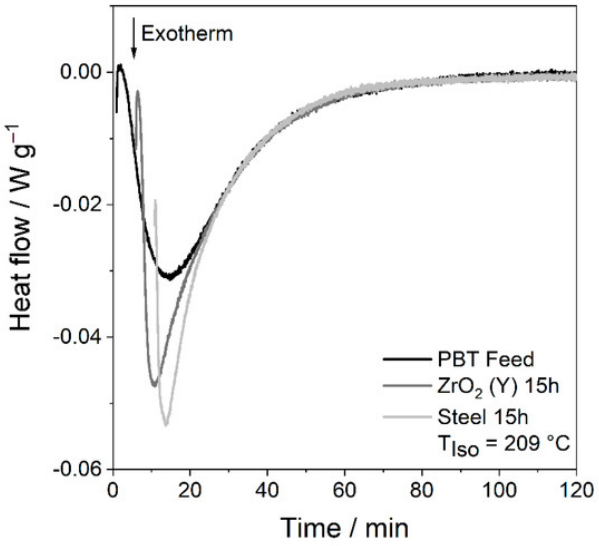

Figure 2. Isothermal crystallisation at 209°C of PBT feed material and wet ground powder with steel and ZrO_2 (Y) grinding beads (SE_{max} = 0.9 mJ, 20 ◦C, 15 h), where wet ground samples have a time off-set. Reproduced from Tischer et al. [8] under the CC-BY 4.0 license.

Figure 2 shows the time course of the isothermal crystallisation of the PBT feed material and the wet ground PBT material with steel and ZrO_2 (Y) after 15 hours. The thermograms of PBT stressed with ZrO_2 (Y) and steel media have a given temporal offset, with the aim of overlapping the latter part of the thermogram where crystal growth occurs. This clearly illustrates that although nucleation is accelerated, crystal growth is hardly affected. In the case of wet ground PBT, the time taken to reach the peak is greatly reduced, as can be seen from the large temporal offset required. However, the thermogram behind the peak is almost identical to that of the PBT feed material. This proves that only nucleation, which takes place in the early stage of the crystallisation process, is accelerated. Crystal growth, which determines the later course of the thermogram, remains unchanged. A more detailed discussion and explanation can be found in [8]. An accelerated melt crystallization kinetics is undesired for PBF-LB/P feedstock powders, as it negatively can affect the process and lead to premature melt crystallization causing warpage and, consequently, in the worst case the abortion of the building process.

4. Conclusions

Within this contribution we will discuss wet comminution of various thermoplastics in stirred media mill from a fundamental perspective (grinding limit, process parameter dependencies) and from practical considerations in view of (undesired) changes of product properties being relevant for powder bed fusion additive manufacturing based on own work [4-8]. Wet

comminution of thermoplastics is especially interesting, if very fine product particles below 10 microns size are desired, which are hard to obtain by dry impact comminution. In wet comminution of thermoplastics, yttrium-stabilized zirconia media are recommended. Powders comminuted with ZrO_2 (Y) grinding beads exhibited reduced abrasion and slower accelerated crystallisation kinetics compared to ZrO_2 (Ce). Consequently, yttrium-stabilised ZrO_2 grinding media were found to be the most effective for the wet comminution of polymers amongst the tested materials, as they exhibited rapid comminution kinetics, no discolouration, and the least altered thermal properties of the ground thermoplastic in terms of dynamic and isothermal crystallisation.

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