Production of spherical wax and polyolefin microparticles by melt emulsification for additive manufacturing

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HIGHLIGHTS

- Melt emulsification of paraffin, PE and PP granules allows for microparticles.
- Production of spherical polymer particles in a single process step.
- Tailored product properties as function of process conditions (e.g. composition).
- Decreasing temperature and viscosity leads to smaller particles.

GRAPHICAL ABSTRACT
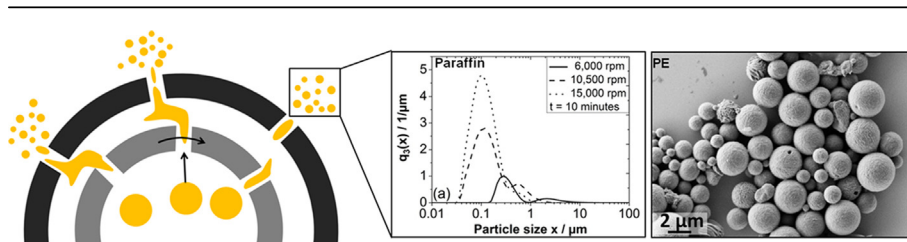
ABSTRACT

Melt emulsification is a top-down approach that so far has been applied in the food industries (cf. homogenization of milk) and in pharmaceutical applications. Within this contribution the applicability of the process for the production of spherical polymer microparticles will be outlined. Size reduction of the polymer raw melt emulsion was realized in a rotor–stator-device. The process is characterized for paraffin and polyethylene (PE) waxes in aqueous environment using Tween 85 as an emulsifier. Process temperature and dispersed phase viscosity have the largest impact on the particle size distribution (PSD): decreasing temperature and viscosity leads to smaller particles. The suitability of the melt emulsification process for technical polymers is demonstrated for polypropylene (PP) emulsified in a continuous hexadecane phase. Polymer particles obtained by the proposed method are promising candidates for advanced powders for additive manufacturing processes like selective laser beam melting (LBM) of polymers. The LBM processability of the obtained PP powders is demonstrated by production of sintered layers.

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1. Introduction

This study is motivated by the growing need for polymer powders which can be used for additive manufacture and 3D printing (Wohlers, 2014). The production of polymer microparticles using a top-down approach is quite challenging because of the viscoelastic behavior of the material at ambient temperature. To increase the efficiency of comminution of such materials the process temperature is reduced in order to increase the brittleness of the polymer. Typically, cryogenic dry grinding methods (Liang et al., 2002; Weber et al., 2006; Wilczek et al., 2004) i.e. impact milling in pin or jet mills as well as cutting mills are used. A recently proposed wet grinding method at reduced temperatures can be applied if products of small size ($< 5\,\mu m$) are needed (Schmidt et al., 2012; Wolff et al., 2014). In both processes irregular shaped particles with a rather broad particle size distribution (PSD) are obtained. For applications such as laser beam melting (LBM) of polymers, spherically shaped particles are required

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because of their improved flowability and dense packing, i.e. the irregular comminution products cannot be used without further modification. Spherical LBM powders of good flowability and processability, for example, from ground polymer powder can be produced in a heated downer reactor with subsequent dry coating (Schmidt et al., 2014). In this paper melt emulsification is discussed as an alternative approach to produce spherical polymer particles in suspension directly in a single process step which can be used in LBM after spray drying.

Melt emulsification has been applied for example to homogenize milk (Köhler et al., 2007, 2011), to obtain narrowly distributed spherical Sn–Cu alloy soldering particles (Hornig and Fritsching, 2014) or in pharmaceutical applications for solid lipid nanoparticles (SLN) (Mehnert and Mäder, 2001). In the field of polymers melt emulsification is patented for emulsions with dispersed phase fractions between 85% and 99.5% (Engel et al., 2011), for toner resins (Nair et al., 1989) as well as for polymer dispersions with particles composed of two or more phases that e.g. are applied as paints, coating agents or sealing agents (Mc Kee et al., 2002). In melt emulsification the dispersed phase is heated above its solidification temperature in the presence of a continuous phase and typically emulsifiers in a stirred tank. The pre-emulsion formed is transferred to a rotor–stator device where the product melt emulsion is formed due to shear and elongational stress. The product droplets are subsequently cooled, they solidify and a suspension of spherical particles is obtained. Besides rotor–stator devices (Engel et al., 2011; Grabnar et al., 1998) also nozzles (Köhler et al., 2011; Mehnert and Mäder, 2001), membranes (Hornig and Fritsching, 2014) or ultrasonic treatment (Mehnert and Mäder, 2001) have been reported for melt emulsification. Melt emulsification with a rotor–stator device at the lab scale was investigated by Grabnar et al. (1998) for different lipids of viscosities between 66 mPa s and 87 mPa s. Products of mean particle sizes of 120–220 nm have been obtained.

In this study it is demonstrated that melt emulsification can be applied also for technical polymers of higher viscosity such as polypropylene. As continuous phase hexadecane was used acting as a plasticizer, i.e. melt emulsification can be applied for dispersed phases of viscosities up to 11 times ($\eta = 1$ Pa s) higher than reported by Grabnar et al. (1998). Challenges of this approach, especially for highly viscous dispersed phases, are the realization of sufficiently high energy input for breakup of viscous droplets, stabilization against coalescence and scaling in reactors and pipes. The stabilization of the newly formed droplet surface is important to avoid coalescence. Droplet stabilization under process conditions is complex and specific emulsifier conditions are needed that cannot be deduced from experiments at ambient temperature (Schubert, 2010). The emulsifier must be effective during the whole process to ensure colloidal stability after droplet breakup, during phase change from liquid to solid and after cooling. Furthermore, the emulsifier must not decompose at process temperature and has to assure long-term stability against agglomeration during storage. Saito and Shinoda (1970) and Chen and Tao (2005) studied emulsification processes for temperatures up to 80 °C and 70 °C, respectively, in a cyclohexane–water system stabilized with polyoxyethylene nonylphenylether and diesel–water systems stabilized with sorbitan monooleate. Moreover, temperature-dependent characteristics of nonionic emulsifiers have been addressed in studies on emulsification using phase inversion temperature approaches (Förster et al., 1992; Izquierdo et al., 2002; Schubert, 2010).

2. Materials and methods

2.1. Materials

Paraffin wax (Aldrich) with a melting point of 53–57 °C, partially oxidized polyethylene (PE) wax EO 40 (melting point 97–105 °C, melt viscosity 120 mPa s (at 140 °C; manufacturers' instruction)) and Polyethylene (PE) wax EO 42 (melting point 106–114 °C, melt viscosity 300 mPa s (at 140 °C, manufacturers' instruction)) from Deurex were used as dispersed phases in the melt emulsification experiments. Deionized water was the continuous phase. For emulsion stabilization polyoxyethylene sorbitan trioleate (Tween 85; Sigma Aldrich) was applied. For experiments with polypropylene (PP, PP 520P, melting point 140–170 °C, Sabic), n-hexadecane (Alfa Aesar) as a continuous phase and sodium dioctyl sulfosuccinate (AOT; Acros Organics) as emulsifier/stabilizer were applied. The PP particles obtained were separated by centrifugation, dispersed in n-hexane (Alfa Aesar) and spray-dried using a Büchi B-290 spray dryer with Inert Loop B-295 (inlet temperature 90 °C, aspiration rate 80%, gas N₂) prior to usage in selective laser beam melting (LBM) of polymers. Coarse PP particles with $x_{50,3} = 29.8$ μm were obtained in the hopper of the spray tower and fine PP particles $x_{50,3} = 17.2$ μm in the cyclone. All chemicals were used without further purification. Melt viscosities of the dispersed phases studied are summarized in Table 1. In this study the melt viscosity of PP is reduced by a factor of around 3000 as compared to the typical literature value because hexadecane acts as a plasticizer (see Sections 2.2.3 and 3.4).

2.2. Characterization methods

2.2.1. Laser diffraction particle sizing

PSDs of the product suspensions have been obtained by laser diffraction particle sizing using a Mastersizer 2000 with a Hydro 2000S wet dispersion unit (Malvern). The concentrated suspensions have been diluted with deionized water. To prevent agglomeration of product particles during size measurements sodium dodecyl sulfate (SDS, 98%; MERCK) was added and the resulting dispersion was ultrasonicated prior to measurement.

2.2.2. Scanning electron microscope (SEM)

For characterization of particle size and shape a Gemini Ultra 55 (Zeiss) scanning electron microscope (SEM) with an InLens detector was applied. An acceleration voltage of 1.0–1.2 kV has been used.

2.2.3. Viscosimetry

For the determination of the viscosity of molten paraffin wax a Physica UDS 200 rotational viscometer (Anton Paar) equipped with a double gab measuring system (Z1 DIN) was used. The system was thermostated by a compact recirculating cooler FC 1600 T (Julabo Labortechnik).

The melt viscosity of solvent-swollen polypropylene containing about 85 wt% hexadecane was measured using a Brookfield DV-II

Table 1
Melt viscosity of different dispersed phases.

	Temperature (°C)	Melt viscosity (Pa s)
Paraffin	70	$6.0 \cdot 10^{-3}$
Polyethylene EO 40	140	$120 \cdot 10^{-3}$
Polyethylene EO 42	140	$300 \cdot 10^{-3}$
Pure polypropylene	220	$3 \cdot 10^{3}$ (Wu, 1982)
(PP in hexadecane)	(190 ± 1 °C)	(~1)