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Effect of particle rounding on the processability of polypropylene powder and the mechanical properties of selective laser sintering produced parts

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Abstract

Common techniques for the production of polymer powders for selective laser sintering (SLS) involve the comminution of polymers. Comminution of polymers often results in powders made of irregular shaped particles with a low bulk density and a bad flow behavior. With the aim to improve the flowability of grinded powders and, thus, the SLS processability, a thermal process for particle shape modification was developed. This has been applied successfully for a broad variety of thermoplasts. In this contribution, a modified design of a rounding reactor with direct heating and optimized geometry is presented. The performance of the new design is assessed by the rounding of commercially available polypropylene powders. The influence of the rounding process on the packing density, flowability and particle size and shape distributions of the powders is investigated. Test specimens produced by SLS were tested to assess the effect of the rounding process on the mechanical properties of the produced parts.

Introduction

Selective laser sintering (SLS) of polymers is one of the additive manufacturing (AM) techniques, which allows the production of 3D functional parts with complex geometries without the need for tooling and assembly [1]. During the manufacturing process, consecutive layers of powder are applied with a blade or a roller and then sintered with a laser, before the next layer of powder is applied [2–4]. The mechanical properties and surface quality of the produced devices depend to a great extent on the intrinsic material (e.g. melting behavior, crystallization) and powder bulk (e.g. particle size and shape, flowability) properties [5–7]. Desirable powders are of narrow particle size distribution with volume-averaged mean particles sizes between 15 and 100 µm made of spherical or potato-shaped particles [8]. The choice of commercially available SLS materials is rather limited. Currently, the most widely used polymeric material for SLS is polyamide 12 (PA12) with a market share of around 90% [9]. Besides PA12, other types of polyamides (PA11 and PA6), polystyrene, polypropylene and polyether ether ketone are available in minor extent [9]. One popular process for the production of polymer powders for SLS is comminution [10,11]. Nevertheless, comminuted particles normally have an irregular shape with different aspects ratios, which results in powders with low flowability and packing density [11–13]. To improve the flowability of these powders, an additional step of shape modification is required. With this aim, a thermal process for shape modification was developed [10]. This process consists of the rounding of irregular polymer particles in a heated downer reactor. This process has been applied successfully for a broad variety of polymers [10,14,15], nevertheless, low yields due to particle build-up at the reactor walls [16], and agglomeration are the main drawbacks of the process. In this study, a modified rounding reactor concept is presented. The efficiency of the modified concept in terms of yield is analyzed by considering the rounding of commercial

polypropylene powders. Furthermore, the effect of the rounding process on the bulk properties and processability of polymer powders is investigated. With this aim, the untreated and rounded powders are characterized according to shape and size distribution, as well as packing density and flowability. Test specimens produced by SLS of the rounded and modified powders were tested to assess the effect of the rounding process on the processability of the powders and the mechanical properties of the produced parts.

Methods

Rounding reactor

A batch of 600 g of polypropylene (PP) powder (Coathylene® PD0580, Axalta polymer powders, Switzerland) was rounded in the downer reactor. The downer setup is composed of a stainless steel pipe (inner diameter =100 mm, length=600 mm), an aerosol generator unit, a cooling section, and a separation system to recover the rounded particles. The powder feed is dispersed in nitrogen (5.0, Air Liquide Deutschland GmbH, Germany) by means of a flat-tray feeder (ZD 22 FB-C-2M, Three-tec GmbH, Germany) equipped with a self-made powder venturi injector at a pressure of 6 bars and a flow rate of 6 Nm^3/h. In the current study, the powder feed rate was 100 g/h. The aerosol flow is heated to 120°C by using a heating band (HBS, Horst GmbH, Germany) wrapped around the aerosol pipe, which is centrally fed into the head of the reactor. A nitrogen sheath flow is heated to 210°C employing a gas heater (GA00565, Horst GmbH, Germany). The function of the sheath flow is to provide the energy necessary to melt the particles and to reduce the interactions of the particles and the wall [16]. The volumetric flow of the sheath gas was set at 7 Nm^3/h by a mass flow controller (EL-Flow, Wagner Mess-und Regeltechnik, Germany). The sheath gas is homogeneously distributed over the downer cross-section surrounding the aerosol gas by means of a sintered metal plate (SIKA-R20, GKN Sinter Metals GmbH, Germany). The molten particles acquire progressively a spherical shape driven by the minimization of surface energy (c.f. minimization of free surface) of the melt droplet. At the end of the reactor, the gas and particles are cooled by quenching with air at room temperature. Finally, the rounded solid particles are separated from the gas flow by means of a deflecting separator and cyclone. After the experiment, the mass of the product obtained was measured to determine the yield of the process.

Scanning electron microscopy

Particle shape and surface morphology were characterized by scanning electron microscopy (SEM). A Gemini Ultra 55 (Zeiss) was used to take images of the coated particles using an SE2 detector at an acceleration voltage of 1kV.

Laser diffraction particle sizing

Particle size distribution (PSD) was determined by laser diffraction (Mastersizer 2000, Malvern Panalytical GmbH, Germany) according to ISO13320-1, using the dry dispersion unit Scirocco 2000 at 50% of the vibration amplitude of the feeding tray.

Light microscopy

Light microscopy was also used to determine the particle size and shape distribution of the feed and rounded powders. With this aim, a few milligrams of powder were applied on a microscope slide and were spread by friction with the help of another microscope slide, in order to reduce particle agglomeration. Images were taken by using an Axio Imager M1m light microscope (Carl Zeiss Microscopy GmbH, Germany) in transmitted light mode with a 10x objective. The motorized microscope stage allows to scan the complete slide generating an array of images, which were digitally analyzed in ImageJ software in order to determine the particle size and shape factor distributions of the powders. For the evaluation, at least 8000 particles were analyzed. The shape factor used in the image analysis was the circularity defined as [19]

$$Circularity = 4\,\pi\ * \frac{Area}{Perimeter^2}$$

, where a value of 1 indicates a perfect circle and a value nearing 0 represents a very elongated particle.

Flowability

A ring shear tester (RST-01.01, Dr. Dietmar Schulze Schüttgutmesstechnik, Germany) was used to measure the flow behavior of the plasma-treated powder. The powders are filled in the tester and the measuring device was prepared according to procedures indicated in ASTM D6773 – 02 [17]. The powders were subjected to consolidation stresses of 1450 Pa, 2500Pa and 5800 Pa. The unconfined yield strength (σ_c) and the major consolidation stress (σ_1) are derived from the two Mohr stress circles according to the procedure described by Jenike [18]. The ratio σ_1/σ_c is called the flow function ff_C. The flow function provides a measure of the flowability of the powder at a defined consolidation stress. In general, higher values of ff_C represent good flowability, while small values characterize cohesive materials. A value in the range of 1-2 corresponds to very cohesive, while a value larger than 4 to an easily or free flowing powder. The reported values of ff_c correspond to the mean value of three separated measurements [18].

Packing density

The packing density of the samples was determined by filling the powders into an aluminum cylinder with a previously calibrated volume of 243.46 mL. The cylinder was filled with the powders using a spoon until the powder is over the top of the cylinder wall in a way, that (consolidation) forces were omitted as far as possible. The excess of material was removed by scrapping the cylinder with a blade. The weight of powder filled in the cylinder was determined and the (loose) packing density was calculated. Measurements were repeated three times for each sample. Mean values and standard deviations are reported.

Laser sintering

To investigate the influence of the rounding on the SLS processability and mechanical properties of the produced devices, test specimens from the untreated and rounded powders were produced in a SnowWhite desktop SLS machine (Sharebot, Italy). The small building chamber (100x100x100 mm^3) allows for production of tensile strength specimens of type 5A according to DIN EN ISO 527-2 [20]. The geometry of the test specimens was sliced in 10 layers of 200 µm by using the freeware software Slic3r 69. The temperature in the machine was controlled by using the "Environment" mode, which controls the heaters by the environment temperature in the machine. The environment temperature was set to 126°C, which equals a powder bed temperature of 148°C. The laser power and scanning speed were set to 2.8 W and 1100 mm/s. The powder reservoir was elevated 290 µm after each layer in order to obtain homogenous and closed layers of powder. Six test specimens were produced from each powder sample.

Characterization of the dimension stability and mechanical properties of test specimens

All tensile tests of SLS produced specimen were performed on a Z050 (Zwick) tensile testing machine according to DIN EN ISO 527-1 [21]. The test speed was 20 mm/min, the clamping length 50 mm and the preload 0.1 N. The Young's modulus was determined at a speed of 0.5 mm/min with an elongation between 0.05 % and 0.25 %. Images of cross-section of the fracture region of the tensile strength specimens were taken with a Keyence VHX-1000 microscope equipped with a VH-Z20R objective, in order to determine the fracture area for the calculation of the mechanical properties.

Results

From the 600 g of raw material, 450 g of rounded product were obtained in the separator unit of the downer. This corresponds to a yield of 75 % in mass. The product was contaminated with large aggregates and agglomerates of particles, produced due to collisions between two or more particles during the rounding process. These agglomerates would affect negatively the packing density of powder. For that reason, the product was sieved by using sieve-wide of 200 μm, which correspond to the $x_{90,3}$ of the PSD of the feed material (see Figure 1). After sieving, a total mass of 380 g was obtained which is 63.3% of the fed mass of raw material.

Figures 1a and 1b show SEM images and Figures 1c and 1d show microscope images of the raw and rounded materials, respectively. The raw material is characterized by irregular shaped particles with a broad distribution of aspect ratios, sharp edges and relative rough surfaces. In the rounded product, the roughness of the particle surface decreased considerably and the edges were rounded. A complete spheroidization was only achieved for particles smaller than 30 μm. This fact indicates that particles smaller than 30 μm melted completely and for that form completely spherical drops. For particles sizes between 30 μm and 200μm, the process of shape transformation to spheres was incomplete, and only the region close to the surface of the particles was affected by the process. Particles larger than 200 μm were not modified after the rounding process, probably due to the very short residence time in the downer. Agglomeration as well as coalescence between two or more rounded particles can be observed. This explains the shift of the PSD of the powder towards higher values after rounding.

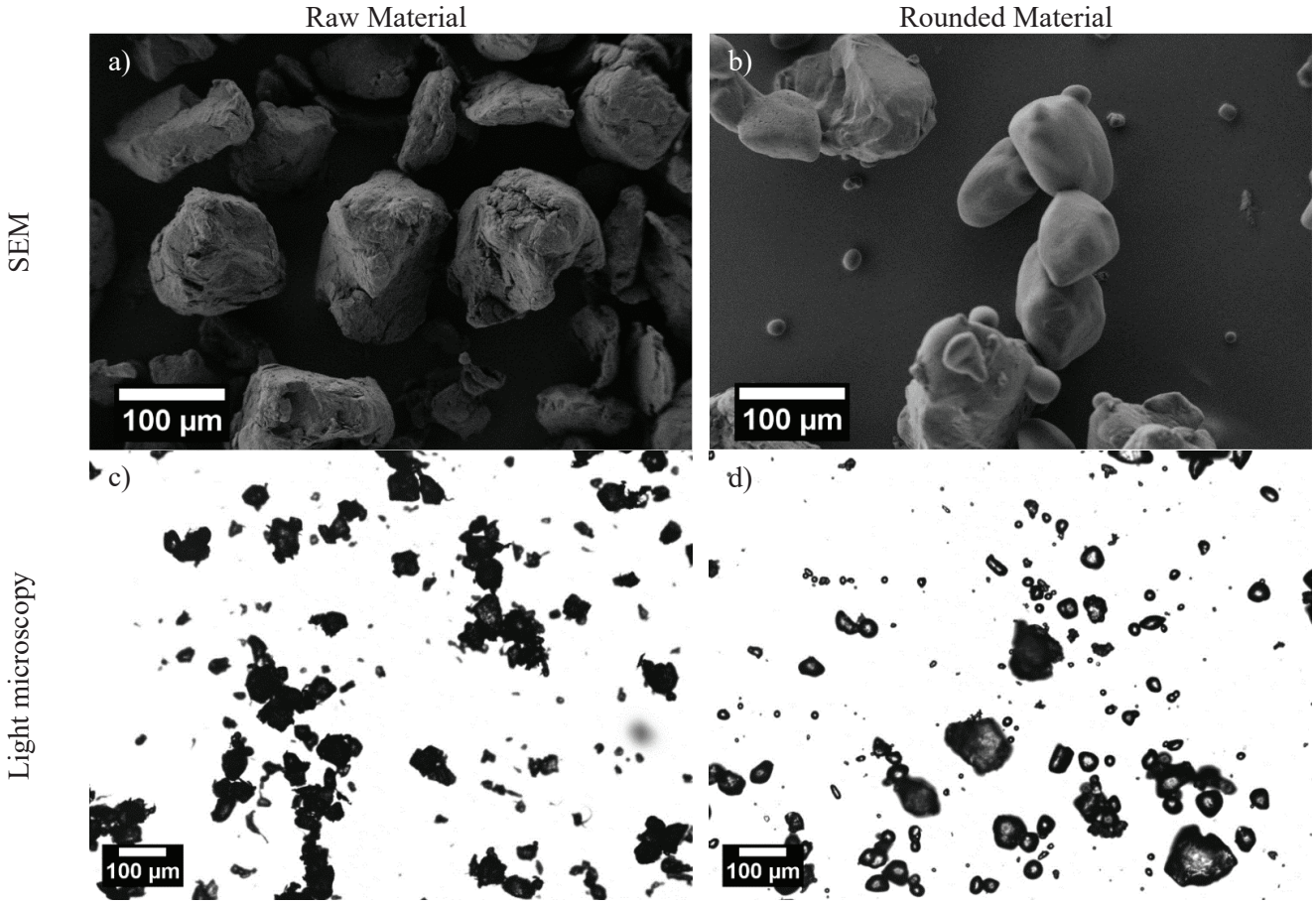

Figure 1. Scanning electron and light microscope images of the raw and rounded powders.

The volume and number-averaged particle size distributions (PSDs) of the raw and rounded powders determined by laser diffraction and light microcopy are shown in Figure 2. The volume and number-averaged PSDs of the raw material, determined by laser diffraction (Figure 1a and 1b, respectively) reveal a broad bi-modal distribution with modes at 20 μm and 100 μm respectively. The mean volume and number-averaged particle size

distribution of the raw material $x_{50,3}$ and $x_{50,0}$ are 120 µm and 20.9 µm, respectively. After rounding the particle size distribution was shifted towards coarse fractions due to agglomeration. The first mode remained constant, while the second mode increased to 120 µm. Accordingly, the volume-averaged mean particle size increases to 132 µm while the number-averaged mean particle size remains unchanged. These facts indicate that the small particles predominantly agglomerate to the larger particles.

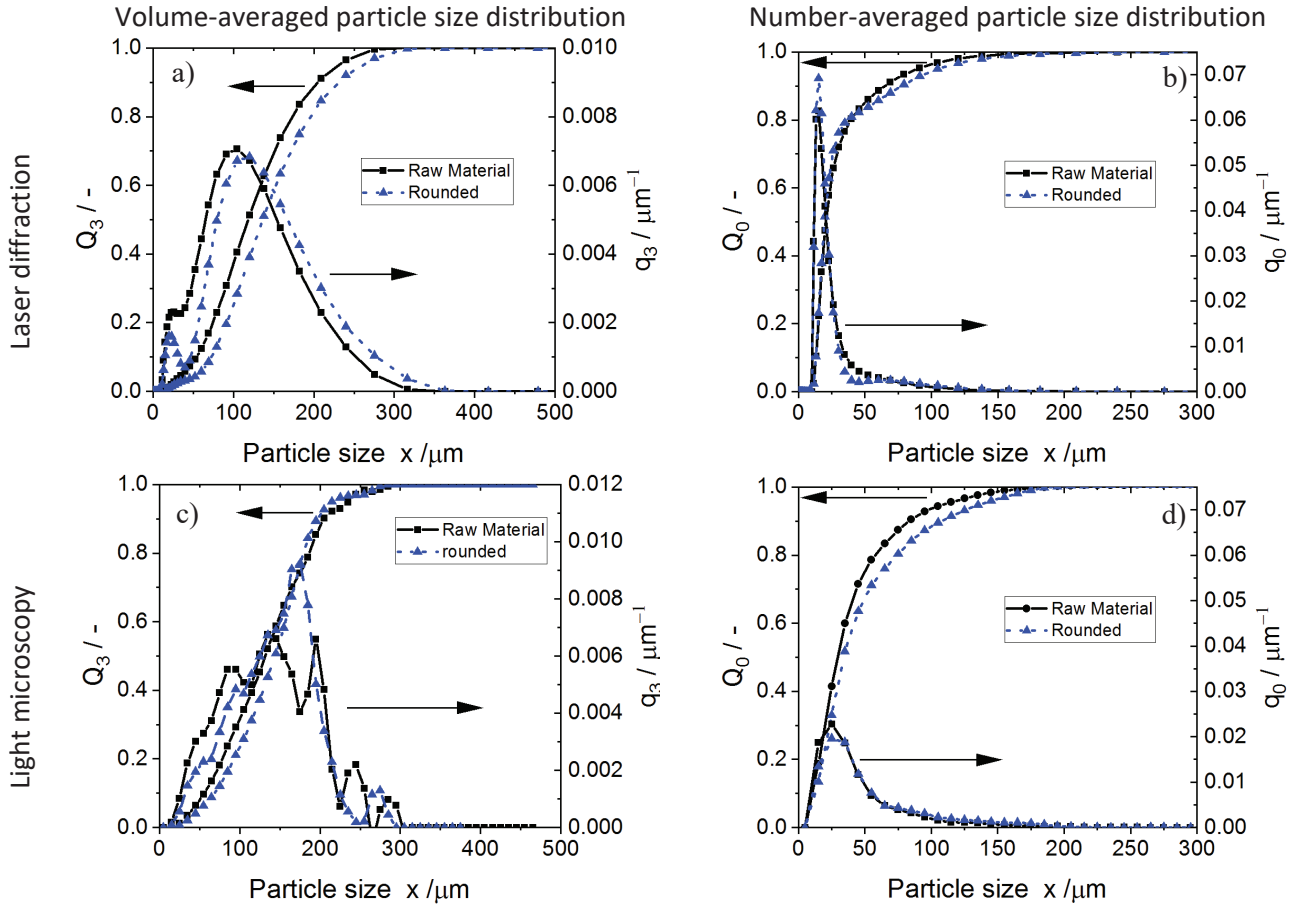

Figure 2. Volume-averaged (a and c) and number-averaged (b and d) particle size distributions of the raw and rounded powders determined by laser diffraction (a and b) and light microscopy (b and d).

The number-averaged PSDs determined by light microscopy (Figure 2d) present a mode at approximately 25 µm for both, the raw and rounded powders. The number-averaged mean particle sizes of the raw and rounded powders are 30.4 µm and 34.5 µm, respectively. In the case of the volume-averaged particle size distributions (Figure 2c), no clear modes could be identified, as the image analysis resulted in several peaks. The volume averaged mean particle sizes of the raw and rounded powders are 133 µm and 143.5 µm, respectively. The results also suggest that the particle size of the raw material was slightly shifted towards higher values after rounding as consequence of agglomeration. The distributions obtained by image analysis slightly overestimate the values obtained by laser diffraction. However, the results obtained by the two techniques are in good agreement.

The number (Figure 3a) and volume-averaged (Figure 3b) particle circularity distributions of the raw and rounded powders are shown in Figure 3. The circularity distributions of the raw material reveals a broad distribution of particle shapes which agrees with the images depicted in Figure 1. The number and volume-averaged mean circularity of the raw material are 0.7 and 0.65, respectively. After rounding, the number-averaged circularity distribution was shifted considerable towards higher values while the volume-averaged was only slightly affected. This indicates a considerable increase of the circularity of the small particles, which represent the majority of the particles, but only a slight change of shape of the large particles, which represent most of the

total volume of particles. This fact can be observed more clearly in Figure 4, which shows the number-averaged mean circularity for 6 different intervals of particles sizes for both the raw and rounded materials.

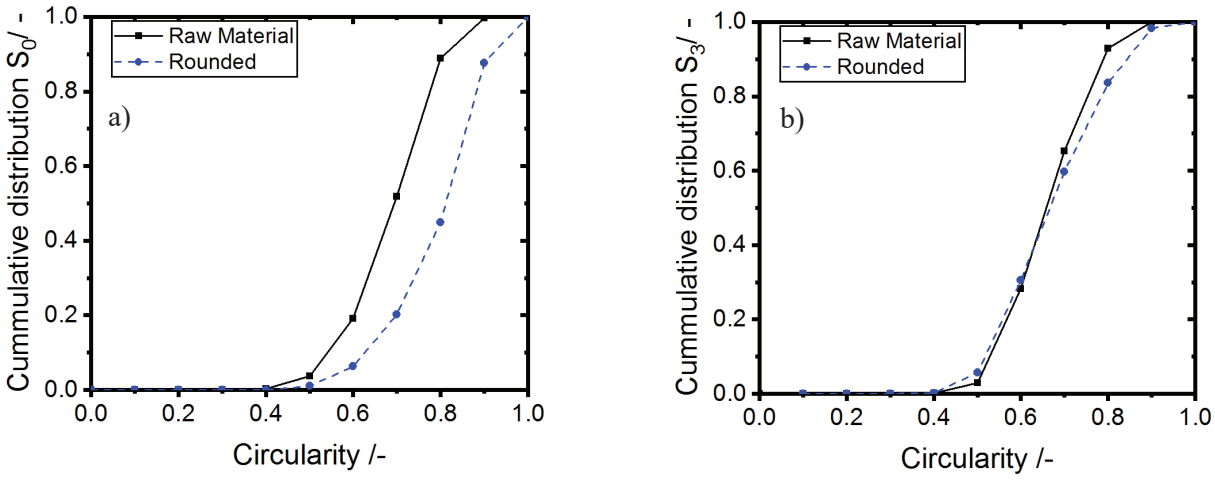

Figure 3. Number (a) and volume-averaged (b) circularity distributions of the raw and rounded powders.

The mean circularity of the particles between 0 and 60 µm increases considerably after rounding. However, for particles sizes between 60 µm and 90 µm the mean circularity remains unchanged and for particles larger than 90 µm the circularity decreases after the rounding process. The reduced change of shape was due to the fact, that large particles only melt completely at the surface, such that the shape of the particles was not highly influenced by the process. The formation of agglomerates during the rounding process, causing structures with low circularity (see Figure 1), contributed to a reduced rounding effect. Control of agglomeration and shape transformation require a more in-depth look into the occurring micro-processes and is the topic of separate, on-going work.

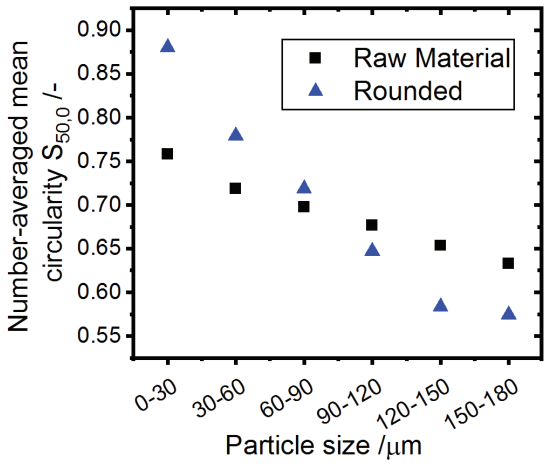

Figure 4. Number-average mean circularity as a function of particle size.

After rounding, the packing density of the powder remains unaltered at a value of 0.340 ±0.002 g/cm^3 indicating none or only a minor effect of the rounding process on the packing density. The flowability (flow function ff_c) of the raw and rounded powders are depicted in Figure 5. The flowability of the powder was improved at all the tested consolidation stresses. At low consolidation stresses (1450 Pa) the flow function increases from 1.5 to 1.8, which correspond to an increase of 21%. The improved flowability is attributed to the rounded particle edges obtained after rounding. Rounded edges would reduce the number of contact points between the particles, thus reducing the friction and resistance to flow [23,24].

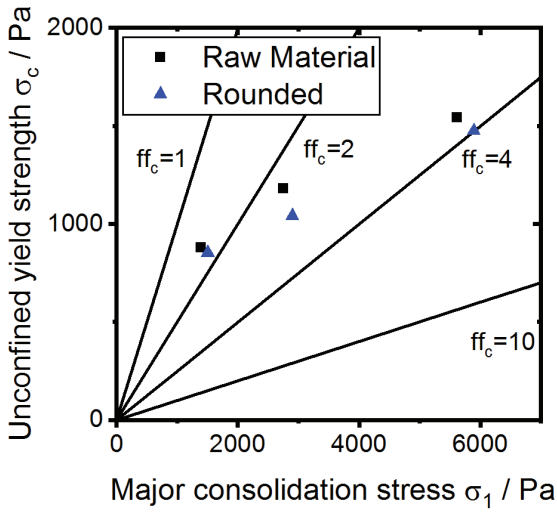

Figure 5. Influence of particle rounding process on flowability.

Figures 6a and 6b present the images of single-layer and tensile test specimens produced from the raw and rounded polypropylene powders. Single-layers produced from the rounded powders resulted in considerably less defects and lower porosity in comparison to the single-layers from the raw materials. The rounding process also leads to test specimens with higher surface quality (lower surface roughness) based on qualitative observation.

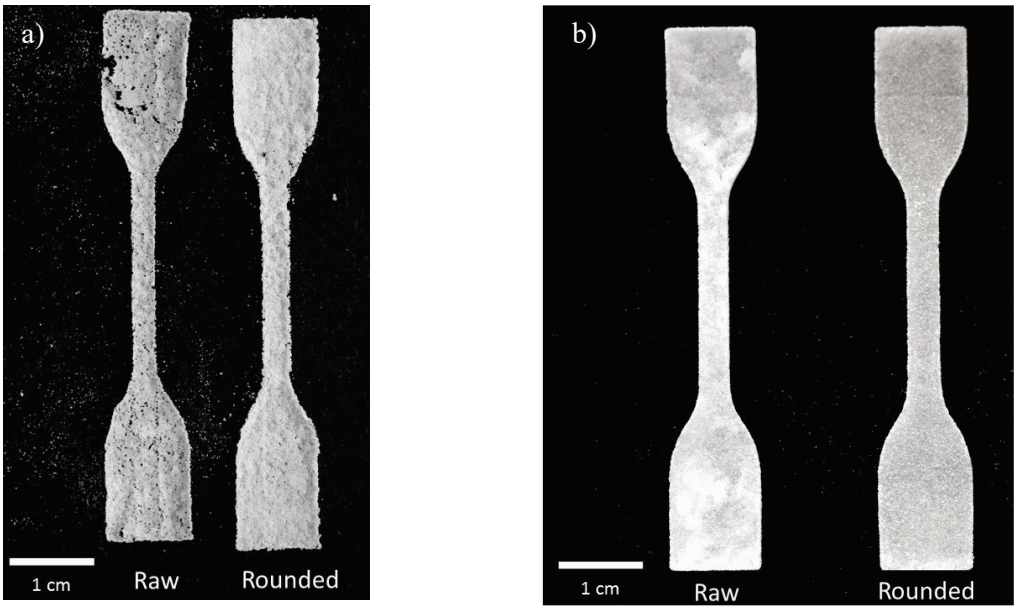

Figure 6. Influence of rounding process on a) defects of single-layer specimens and b) surface quality of tensile specimens.

The results of the tensile strength test on the produced samples are depicted in Figure 7. Both, the Young´s modulus and the stress at break increased pronouncedly after rounding. The Young´s modulus and stress at break increases by 166% and 113% respectively after rounding. The reduction of defect on single-layer specimens and the improvement of the surface quality and mechanical properties of the test specimens is associated with the improvement of the flowability of the powders after particle rounding, which allows the spreading of more homogenous layers of powders.

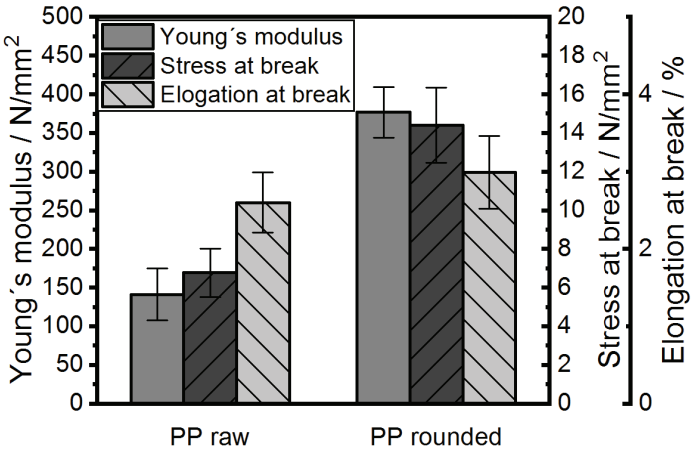

Figure 7. Tensile properties of SLS produced test specimens.

Conclusions

In this work, we presented an experimental study on the rounding of commercial polypropylene powders using a modified downer reactor. The process result in a slight shift of the particle size distribution towards higher particle sizes as consequence of agglomeration. The rounding process mainly affected the surface of the particles rather than the shape: Produced particles show a shape like the feed, however, with rounded edges. The modification of the surface of the particles contributed to an improvement of the flowability of the powder. The surface quality and tensile properties of the produced test specimens was considerably improved after the rounding process.

Acknowledgements

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