Tailored modification of flow behavior and processability of polypropylene powders in SLS by fluidized bed coating with in-situ plasma produced silica nanoparticles

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Abstract

The processability of selective laser sintering (SLS) powders and the characteristics of the generated parts depend amongst others on the flowability. To increase the flowability, SLS powders are usually functionalized with flowing agents. Flowing agents are typically applied by dry particle coating. The optimization of the process parameters necessary to achieve a homogenous coating avoiding segregation is still empirical. In this contribution, an alternative process to particle dry coating is presented. This process integrates the synthesis of silica nanoparticles via plasma enhanced chemical vapor deposition (PECVD) and coating of polymer host particles in a fluidized bed in a single process. The influence of the treatment time on the packing density and flow behavior of the powders is investigated. Test specimen are produced to assess the influence of the treatment on the processability of the powders and the mechanical properties of the produced parts.

Introduction

Selective laser sintering (SLS) of polymers is a powder-based technique, which allows the series production of 3D functional parts by sintering consecutive layers of powder with a laser from a CAD geometry without the need for tools or molds. The processability of the powders and the characteristics of the generated parts depend among others on the material and powder bulk properties [1,2]. Powder bulk properties such as the flowability, bulk density, particle size and particle size distribution have to be optimized in order to produce parts with high density, accuracy, and mechanical properties close to those obtained by conventional manufacturing techniques [3–5]. In general, spherical particles of narrow size distribution with a mean particle size between 50 μm and 100 μm are typically desired [6,7]. To increase the flowability, SLS powders are usually functionalized with flowing agents [5,8]. Flowing agents are nano-sized particles, which are deposited onto the surface of the polymer particles (host particles) where they adhere firmly due to van der Waals forces. These nanoparticles increase the distance between the host particles inducing a reduction of the cohesive van der Waals forces and, thus, improving the flowability of the powders [9,10]. Nevertheless, the addition of flowing agents can also influence the SLS-process negatively. Flowing agents also may act as heterogeneous nuclei for polymer crystals accelerating the crystallization [11,12] and narrowing in this way the process window (temperature distance between melting and crystallization points of the material) [13]. Thus, an optimum amount of flowing agents must be found to increase the flowability of powders and at the same time allowing the processability of the powders.

Flowing agents are typically applied by dry particle coating [5,8,14]. In this process, the host particles and nanoparticles are brought into contact by means of mechanical agitation. A broad range of devices can be used for dry particle coating including tumbling and ploughshare mixers, hybridizers, mechano-fusion machines and

rotating fluidized beds, which differentiate in the achieved mixing intensity. The degree of coverage and homogeneity of the coating depends on several operating conditions as the type of dry coating device, the time of mixing, amount of flowing agent and particle properties [10]. Despite the popularity of dry particle coating, the optimization of the mixing time and amount of flowing agent necessary to achieve an homogenous coating avoiding segregation and re-agglomeration of the nanoparticles of is still empirical [15,10]. Dry particle coating additionally required the production of nanoparticles in separated processes (e.g. gas phase [16], sol-gel [17] or crystallization processes [18]).

In this contribution, an alternative process to particle dry coating is presented. This process integrates the synthesis of silica nanoparticles with variable content of organic residues, in the following referred as to 'SiOx', via plasma enhanced chemical vapor deposition (PECVD) and posterior coating of polymer host particles in a fluidized bed in a single process. The influence of the treatment time on the bulk properties and processability of treated polymer powders is investigated. With this aim, the treated powders are characterized according packing density and flow behavior. Test specimen are also produced to assess the influence of the treatment on the processability of the powders and the quality, dimension stability and mechanical properties of the produced parts.

Methods

PECVD treatment

Batches of 300g of polypropylene (PP) powder (Coathylene® PD0580, Axalta polymer powders) were processed in the fluidized bed depicted in Figure 1. The fluidized bed consists of a stainless steel pipe with an inner diameter of 0.1 m and a height of 0.8 m. In the bottom of the fluidized bed a sintered metal plate (SIKA-R20, GKN Sinter Metals Engineering GmbH, Germany) is used to support the powders and distribute the fluidization gas (Nitrogen, N_2, 5.0, Linde AG, Germany) through the whole cross-section. The volumetric flow rate of the fluidization gas was determined by means of a rotameter (DK800, KROHNE Messtechnik GmbH, Germany) and set to 1.8 Nm^3/h.
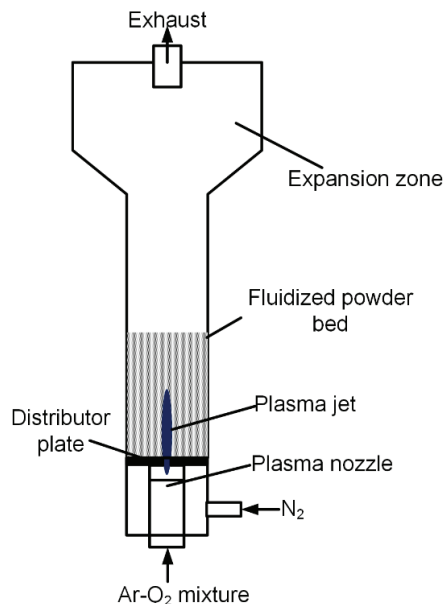

Figure 1. Schematic representation of the fluidized bed reactor used for plasma treatment of polymer powders.

An atmospheric DBD plasma jet is produced by using a commercial plasma nozzle (Openair PFW10, Plasmatreat GmbH, Germany). The plasma was ignited using a frequency of 21 kHz at 280 V and 17.5 A resulting in a power of 4.9 kW. The plasma nozzle is connected to the precursor reaction section, which is shown in detail

in Figure 2. The reaction section consists of a crosspiece of stainless steel. The plasma jet is fed in the lower end while a nitrogen flow of 600 cm^3/min saturated at room temperature with hexamethyldisiloxane (HMDSO, 98% purity, Alfa Aesar) is fed on both lateral sides of the crosspiece directly into the plasma jet. In this section the precursor decomposes by the heat and energy liberated by the plasma, generating primary particles. At supersaturation conditions, the primary clusters start to grow by nucleation, agglomeration and aggregation producing nanoparticles of SiOx [19,20]. The nanoparticles leave the reaction section at the upper end and are fed in the fluidized bed through a centered orifice in the sintered plate. Through the intensive mixing provided by the fluidization, the nanoparticles deposit onto the surface of host particles.
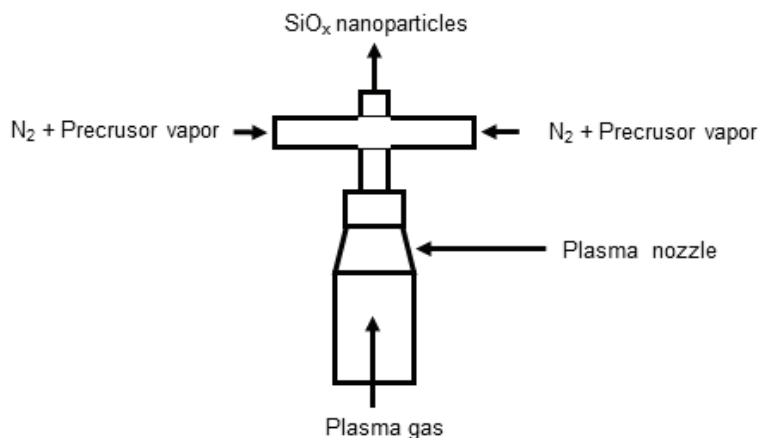

Figure 2. schematic representation of the precursor reaction zone

An Ar-O_2 mixture (quality 5.0, Linde AG Germany) with a volume concentration of oxygen of 5 vol.-% was used as plasma gas. The volumetric concentration was controlled by mass flow controllers (MFC, EL-FLOW®, Wagner Mess- und Regeltechnik GmbH, Germany), such that the total volumetric flow rate of the plasma gas was set at a constant value of 1.8 Nm^3/h. In order to avoid the thermal degradation and melting of the polymer particles, the treatment is conducted in cycles: the plasma was ignited for 60 s and then switched off for a cooling period of 180 s. Samples were treated for 2, 4, 6, 8, 10 and 15 cycles in order to investigation the influence of the treatment time on the bulk properties and processability of the powders.

Scanning electron microscopy

The coating of the particles was characterized with 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 1keV.

ICP-Optical emission spectroscopy

The amount of SiO_x deposited on the samples as a function of the number of cycles was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES, Thermo Scientific iCAP 6500) using Ar as plasma (flow rate 10 L/min) and nebulizer gas (0.6 L/min). The auxiliary gas (0.2 L/min) was N_2. The aqueous calibration and sample solutions were fed to the nebulizer at a flow rate of 3 mL/min. The plasma power was 1500 W and a 6-point calibration was performed for Si the concentration range between 1 mg/L and 100 g/L. The intensities at the emission lines at 251.611 nm and 212.412 nm were evaluated for quantification. The calibration solutions were obtained by dilution of respective 1000 mg/L Si standard solution specified for ICP-OES (Carl Roth, Germany). The aqueous solutions for measurement were prepared from ashed polymer residues which were dissolved in diluted hydrofluoric acid.

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 is prepared according to procedures indicated in ASTM D6773 – 02 [21]. The powders were subjected to a consolidation stress of 1450 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 [22]. 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 powders. An increase in value of ff_C corresponds to an increase in flowability. A value in the range of 1-2 corresponds to very cohesive, while a value larger than 10 to an easily or free flowing powder. The reported values of ff_C correspond to the mean value of three separated measurements.

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 powders were filled with a spoon in a way, such as that consolidation of the powder was avoided. The excess of material was removed by scrapping the cylinder with a blade. After filling the cylinder, the weight of powder filled into the cylinder was determined and the packing density was calculated. Measurements were repeated three times for each sample.

Laser sintering

To investigate the processability of the PECVD treated powders in SLS, test specimens type in a SnowWhite desktop SLS machine (Sharebot S.R.L., Italy). Due to the small building chamber (100x100x100 mm^3) tensile strength specimens type 5A according to DIN EN ISO 527-2 [23] were produced. 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 control the heaters, by the environment temperature in the machine. The environment temperature was set to 126 °C, which produced a powder bed temperature of 148 °C. The laser power and scanning speed were set at 2.8 W and 1100 mm/s. The powder reservoir was raised by 290 μm after each layer in order to obtain homogenous and closed layers of powder. 6 test specimens were produced from each sample. As result, the mean value and the standard deviation of the measurements are presented.

Characterization of the 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 [24]. 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%. The reported values consider the mean value and the standard deviation of 5 different measurements.

Results and discussion

Figure 3a shows the coating achieved after treatment with 2, 6 and 15 PECVD cycles. The results show that the in situ production of silica nanoparticles and coating of the polymer particles was successful. It is also possible to observe an increase in the coverage degree of the coating with increasing number of treatment cycles.
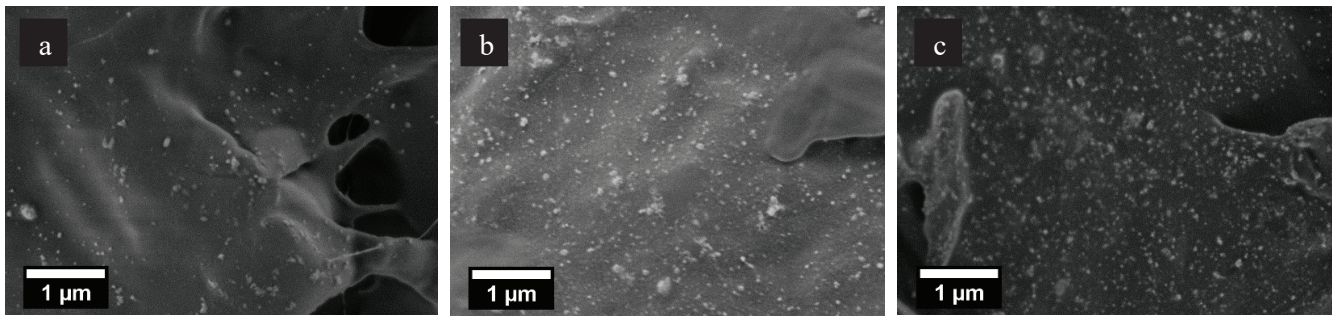
Figure 3. SEM images of coated PP samples after a) 2 cycles b) 6 cycles and d) 15 cycles of PECVD treatment

The number-averaged particle size distribution Q_0 of the generated nanoparticles was determined by particle counting using the software ImageJ taking a sample of 500 primary nanoparticles. The results are depicted in Figure 4. The produced silica nanoparticles have a number-averaged mean particle size of about 50 nm.
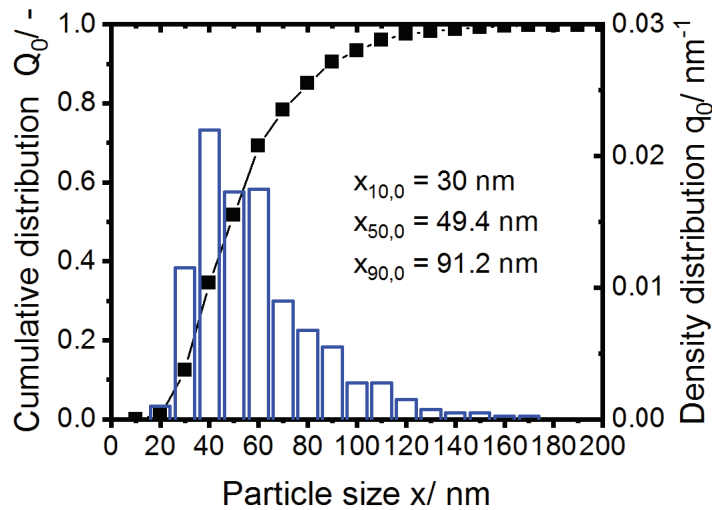

Figure 4. Number averaged particle size distribution of deposited silica nanoparticles

The polypropylene host particles were homogenously coated by the silica nanoparticles achieving results comparable to the achieved by using other types of dry particle coating devices. The structures of nanoparticles deposited on the surface of the polypropylene particles are mainly primary silica nanoparticles as well as some few agglomerates of primary nanoparticles in some regions.

The amount of silica deposited on the polymer particles as a function of number of PECVD cycles is shown in Figure 5. The amount of silica increase linearly with increasing number of PECVD cycles with a slope of about 0.005 wt % per cycle. Thus, the amount of silica deposited on the polymer particles can be controlled by the number of cycles.
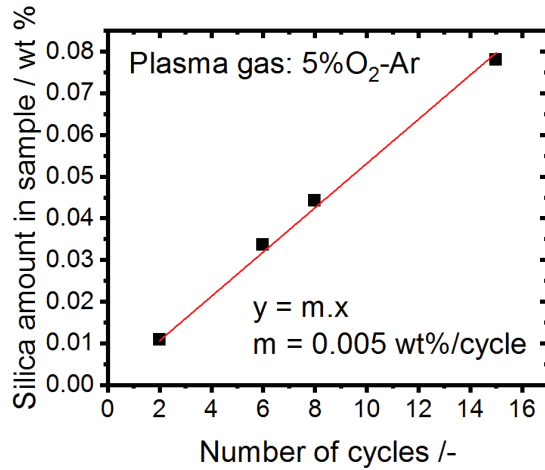
Figure 5. Amount of silica deposited on PP powder as a function of number of PECVD cycles

The measured flow function and packing density of the treated PP powders as a function of the amount of silica deposited are depicted in Figure 6. Both the flow function and packing density show similar trends: an initial increase of flowability and packing density with increasing amount of silica until reaching a plateau at approximately 0.044 wt %. This amount was reached after 8 PECVD cycles. The improvement of the flowability and packing density is the result of the reduction of the cohesive van der Waals forces as consequence of the surface roughness produced after PECVD treatment [10]. For larger amounts of silica than 0.0044 wt % no further improvement of powder flowability and packing density was observed.
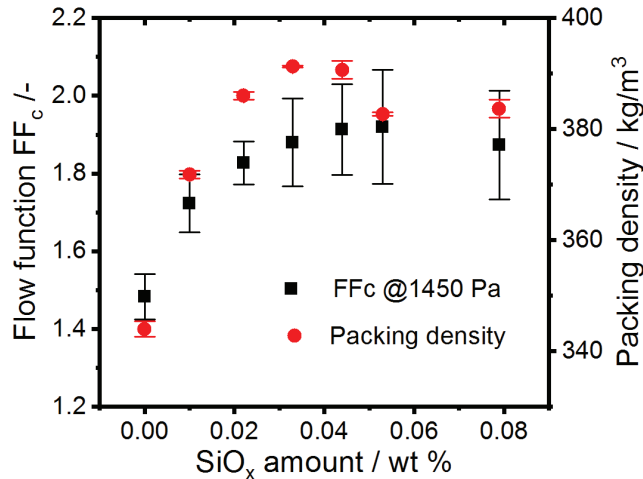

Figure 6. Influence of amount of silica deposited on flowability and packing density of the powders

Figure 7a shows single-layer specimens obtained from the treated PP powders at different PECVD cycles. As evidenced in the figure, the deposited silica contributed to a premature crystallization during SLS processing resulting in curling. The magnitude of curling increases with increasing amount of silica on the sample. For the samples treated with more than 8 cycles (silica amount >0.044 wt%) the produced single-layer were always removed by the blade when the next layer of powder was applied and for that reason could not be processed.
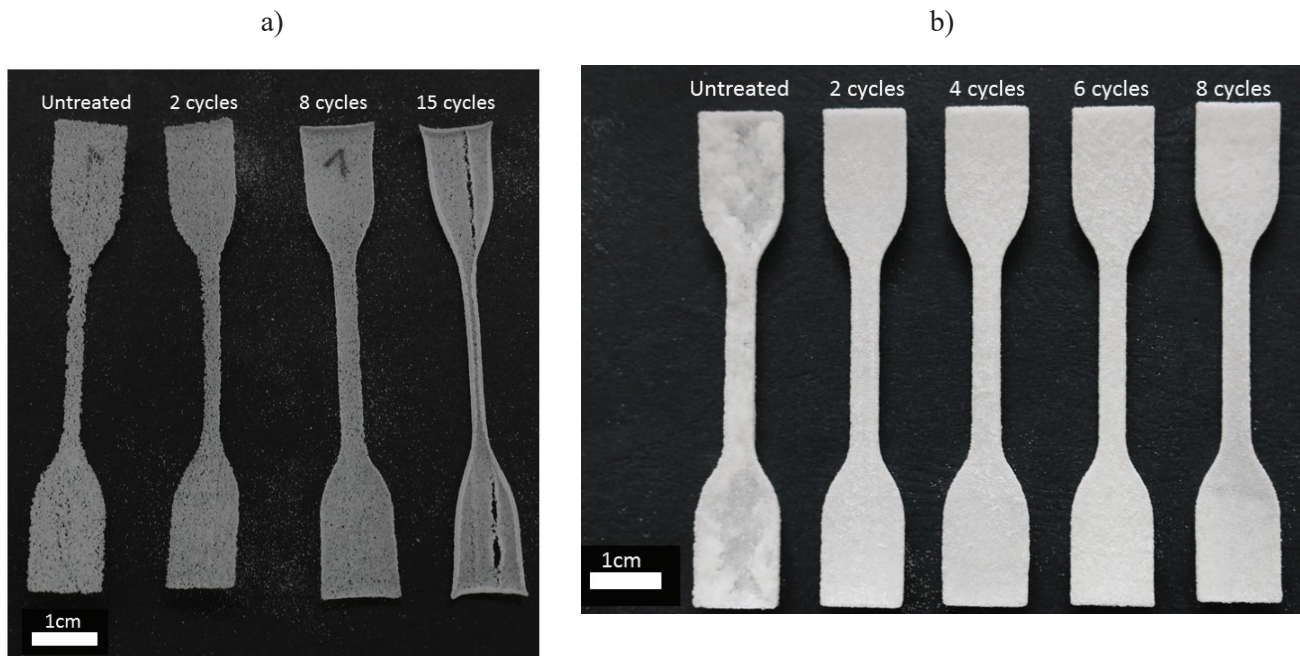
Figure 7. Influence of PECVD treatment on the processability and surface quality of the test specimen

Figure 7b shows the produced multi-layer test specimens. It is possible to observe differences on the quality of the single-layers as well as the multiple-layer test specimens comparing untreated and treated powders. In first place, when considering the single-layer specimens, the porosity decreased while the sharpness of the edges increased after treatment with PECVD. In the case of the tensile test specimens, it is possible to observe that the roughness of the surface decreased considerably after treatment. Neither trend nor significant differences could be observed between the samples treated at different PECVD cycles. The aforementioned differences are due to the improvement of the flowability and packing density of the powders after the coating with silica nanoparticles discussed above, which allows the spreading of more homogenous and dense layers of powders.

The results of the tensile strength test on the produced samples are depicted in Figure 8. As the produced test specimens do not correspond to the standard Type 1 according the DIN EN ISO 527-2, the results cannot be compared directly with results obtained by injection molding or SLS reported in literature, where Type 1 test specimens were used. Nevertheless, as the produced test specimens were produced under the same parameters, the results can be compared between each other in order to assess the influence of the PECVD treatment. The results shows that both the Young´s modulus and stress at break increased pronouncedly after treatment with PECVD. The Young´s modulus and the stress at break of the test specimens increased by 160% and 67% respectively, by treating the PP powders with 2 cycles of PECVD (deposition of 0.01wt% SiO_x). The improvement of the mechanical properties is associated to the increase on the flowability and packing density of the powders after PECVD treatment. No clear trend could be observed between the treated samples considering the mean value of the results. However, the interval defined by the error bars of the different samples overlaps implying that the effect of longer PECVD treatment on the mechanical properties of the test specimens is negligible. The elongation at break of the produced specimens was not affected by the PECVD treatment.
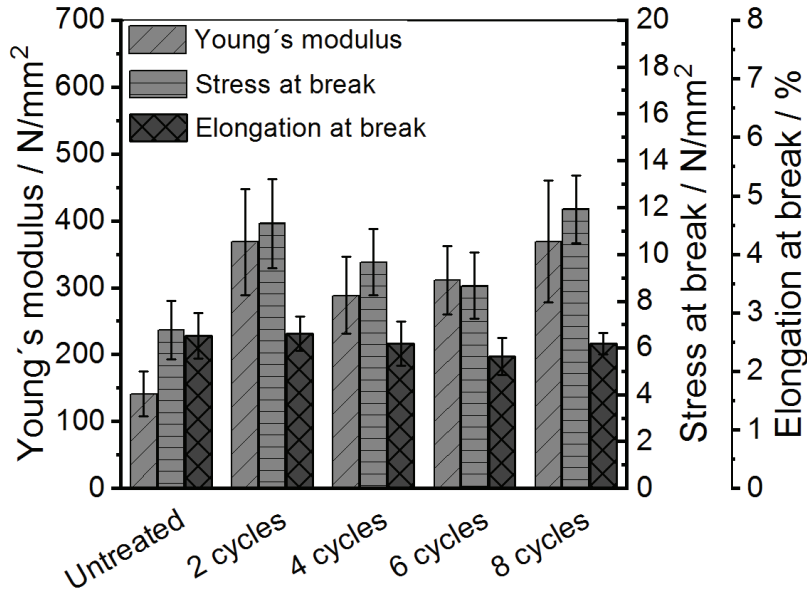
Figure 8. Mechanical properties SLS produced test specimens

Conclusions

In this work, we presented an experimental study on the coating of polymer particles in a fluidized bed with in situ produced silica nanoparticles using plasma-enhanced chemical vapor deposition. This new process allows to combine the generation of nanoparticles and coating of micron-size polymer particles in a single process step. We showed that the production of silica nanoparticles and coating was successful and that the treatment lead to and improved flowability and packing density of the powders after the deposition of a small amount of silica nanoparticles. This result also was reflected in the quality and mechanical properties of test specimens compared with those produced from untreated powders.

Acknowledgements

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