Preparation of polystyrene coated alumina powder via dispersion polymerization and precipitation with non-solvent for use in Selective Laser Sintering

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ABSTRACT: Two distinct methods to produce polystyrene coated alumina powder for Selective Laser Sintering (SLS) applications are presented. A first method is dispersion polymerization, a heterogeneous polymerisation technique. A second method is precipitation with non-solvent, a phase inversion technique. The preparation methods are described, the polystyrene binder amount is determined and further characterization of the polystyrene coated alumina powders with SEM, STA/TGA and DSC is discussed.

1 INTRODUCTION

For indirect Selective Laser Sintering (SLS), a powder-based additive manufacturing (AM) process, powders are coated with a polymeric binder (Subramanian et al. 1995, Liu et al. 2007). The binder will be sacrificed during the sintering of the green parts. To develop a polymer coated powder, several techniques can be applied. Polystyrene (PS) is compared to other semi-crystalline polymer materials suited because it is geometrically stable during the burning out step (Kruth et al. 2008).

A first class of techniques to prepare polymer coatings are the heterogeneous polymerisation techniques (Arshady, 1992). They exist of two phases, in which the starting monomers and/or the formed polymers are present in the form of a fine dispersion of non-mixable liquid phases. The two most frequently used polymerisation techniques to coat with PS are emulsion polymerization and dispersion polymerization. SiO_2 is most often used as inorganic core, due to its high surface energy and activity, which enhances the formation of core-shell structures (Bourgeat-Lami et al. 1998, Bourgeat-Lami et al. 1999, Wang et al. 2007). To enhance the interfacial interaction between inorganic particles and the organic polymer, molecules can be adsorbed or grafted onto the inorganic core. Ding et al. 2004 used emulsion polymerization to coat silica with PS. The silica was first grafted with oleic acid prior to emulsion polymerization with sodium dodecyl sulphonate surfactant. The disadvantage of such emulsifiers is their impact on the smoothness and morphology of the composites. Bourgeat-Lami and Lang 1999, Tianbin and Yangchuan 2006 and Liu et al. 2004 encapsulated silica beads by dispersion polymerization of styrene and modified the silica beads prior to dispersion polymerization by grafting the silica surface with a silane coupling agent. In all these studies polyvinylpyrrolidone (PVP) was used as stabilisator and 2,2'-azobisisobutyronitrille (AIBN) as the initiator. The preparation of silica/polystyrene core–shell composite nanospheres has also been reported by *in situ* radical dispersion polymerization in an ionic liquid (IL) (Haldorai et al. 2010).

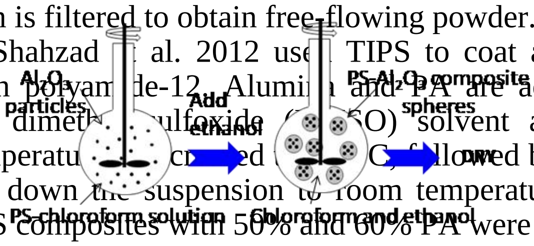
Zheng et al. 2006 coated alumina nanoparticles with polystyrene by emulsion polymerization (according to a similar method as Ding et al. 2004) and investigated the filled PS matrix in SLS. Both the impact and tensile strength of the sintered specimens were improved for the filled PS matrix with 5% PS coated nano-alumina particles compared to the PS matrix with pure nano-alumina particles. This can be explained by the enhanced interface adhesion of filler and matrix (Zheng et al. 2006).

A simple dispersion polymerization method was reported with Fe_3O_4, in which the Fe_3O_4 core was modified with divinylbenzene as cross-linking agent (Guo et al. 2007).

A second class of techniques to coat inorganic particles with a polymer phase are the phase inversion techniques. The polymer is first dissolved and through changing the conditions, phase separation occurs. Depending on how the phase separation is induced, one can distinguish the following phase inversion techniques: thermally induced phase separation (TIPS), immersion precipitation, solvent evaporation (air-casting) and precipitation with non-solvent (Freiberg and Zhu 2004, Haruma 2000, van de Witte et al. 1996).

Scarfato et al. 2011 make use of solvent evaporation to coat silica with polystyrene. The method exists of first dissolving the PS in chloroform, followed by addition of silica and placement in an ultrasonic bath. The solution is then emulsified in water with a small amount of polyvinylalcohol and the chloroform is evaporated. In a last step, the suspension is filtered to obtain free-flowing powder.

Shahzad et al. 2012 used TIPS to coat alumina with polyamide-12. Alumina and PA are added to the dimethyl sulfoxide (DMSO) solvent and the temperature increased to [illegible]°C, followed by cooling down the suspension to room temperature. For SLS composites with 50% and 60% PA were tested.



In this paper, we developed a method for the preparation of polystyrene coated alumina particles using (1) dispersion polymerization and (2) precipitation with non-solvent (Lintacker 2012).

Combined TG and DSC measurements provide a good indication of the percentage of polystyrene binder coating. Microscopy is used to characterize the morphology and size of the composites and by STA heat treatments of the powders, SLS simulations are performed to check for neck formation.

2 MATERIALS AND METHODS

2.1 *Dispersion polymerization method*

A 500 ml synthesis was performed in a three-neck flask equipped with a thermometer and a reflux condenser. The flask was covered with aluminium foil and immersed in a water bath that was placed on a heating plate with magnetic stirrer capacity. First a water-ethanol mixture was heated to above 50°C and then styrene (99,5%, Acros Organics, USA), divinylbenzene (DVB) (98% DVB, Merck Millipore, USA) and α-alumina (grade SM8, Baikowski, France) were poured into the solution and stirred with magnetic stirrer agitation. Azobisisobutyronitrile (AIBN, Acros Organics, USA) was added when the mixture reached 65°C and the heating continued for 6.5 hours upon magnetic stirring. Product was cooled and the day after filtered and three times washed with water and dried at 50°C in a vacuum oven. A 2L synthesis was performed in a 3L three-neck reactor covered with aluminium foil and equipped with a thermometer, a reflux condenser and a mechanical stirrer. The preparation, sequence of addition and timing was similar as for the 500 ml preparation and the polymerization was executed at a temperature of 65-67°C for 6.5 hours upon mechanical stirring. The powder was grinded in a ball mill (Fritsch, Germany) followed by sieving (Retsch, Germany) with a mesh size sieve of 160 µm.

2.2 *Precipitation with non-solvent*

A schematic representation of the dissolution-precipitation method or precipitation method with non-solvent is illustrated in Figure 1.

First the PS (143E crystal clear, BASF) was dissolved in a solvent. In the initial experiments carbon tetrachloride was used as solvent, but mostly chloroform was the solvent used. Secondly, the alumina was added and the solution was stirred, in ultrasonic bath, magnetically or mechanically. Then ethanol, a non-solvent for PS, was added to allow the precipitation of the PS onto the alumina. The solution was again stirred. The chloroform or carbon tetrachloride and ethanol were removed by filtration or centrifugation. Finally, the alumina/PS composite particles were washed and dried in an oven at 75°C to remove the remaining solvent by evaporation.

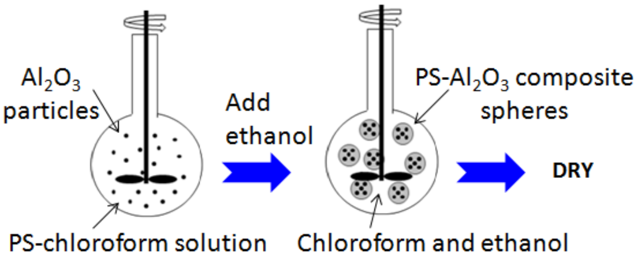


Figure 1. Scheme of the precipitation with non-solvent or dissolution-precipitation method.

Syntheses were performed at different scales from 10 ml up to 1L of starting PS-solvent solution. For the small scale experiments 30 ml vials were used and for the 1L experiments, a 3L stirred reactor was used (Figure 2).

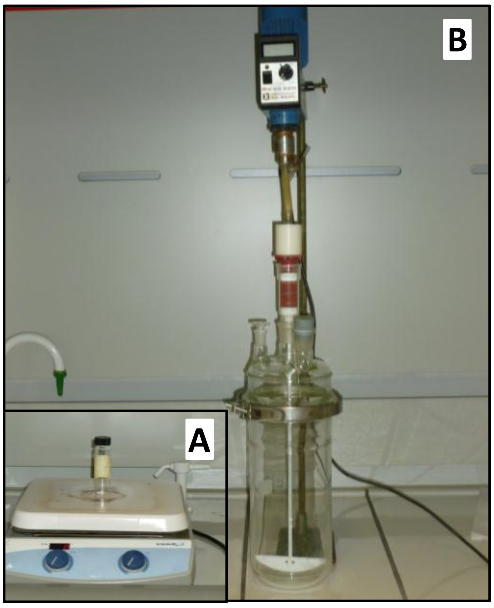


Figure 2. Different set-ups (empty) for the precipitation with non-solvent syntheses. A. 30 ml vials with magnetic stirring. B. 3L mechanically stirred reactor.

2.3 *STA /DSC analysis*

The STA analysis of the developed PS coated alumina powder is done using Netzsch 449 F3 Jupiter STA equipment under protective nitrogen atmosphere measuring combined TGA and DSC. Samples were heated to 1500°C at a heating rate of 10°C/min. Mass change (%) was determined via Netzsch Proteus TA software providing the wt% PS coated on the Al_2O_3 particles.

Differential scanning calorimetry (DSC) was performed using a Netzsch 204 F1 equipment under nitrogen atmosphere. Approximately 25 mg of sample material in an open aluminum pan was referenced against an empty open aluminum pan. Samples were heated to 150 °C at a heating rate of 10°C/min.

2.4 *Digital Microscopy / SEM*

Digital microscope pictures of the powders after powder production and samples after burning out the polymer within the STA equipment were taken using a Digital Microscope VHX-500 F from Keyence.

Scanning electron microscopy of the coated powders was performed on a Quanta 200FEG FEI scanning electron microscope.

3 RESULTS AND DISCUSSION

3.1 *Dispersion polymerization*

Recipes were optimized and developed at 500 ml and 2L scale using the amounts given in Table 1.

Table 1. Dispersion polymerization synthesis experiments.

		500 ml	2L
Al_2O_3	g	30.11	120.44
Styrene	g	55.58	222.32
DVB	g	0.58	2.32
AIBN	g	0.565	2.26
Ethanol	g	283.5	1134
Water	g	16.5	66

From the mass loss around 400°C due to the decomposition of the polystyrene, the amount of PS coated on the alumina particles can be calculated from the first derivative of the mass loss with temperature. Thermo Gravimetric Analysis indicated 30 wt% PS for the 500 ml recipe and 39 wt% PS for the 2L recipe. From the 2L powder, some powder material was heated in the STA equipment to burn out the polymer. After cooling down of the sample, the powder remains bound, as is illustrated in Figure 3.

Details on the characterization of the PS/Al_2O_3 particles is given elsewhere (Cardon et al. 2012) and SLS tests on the PS/Al_2O_3 materials have been executed and reported (Cardon et al. 2012, Deckers et al. 2012).

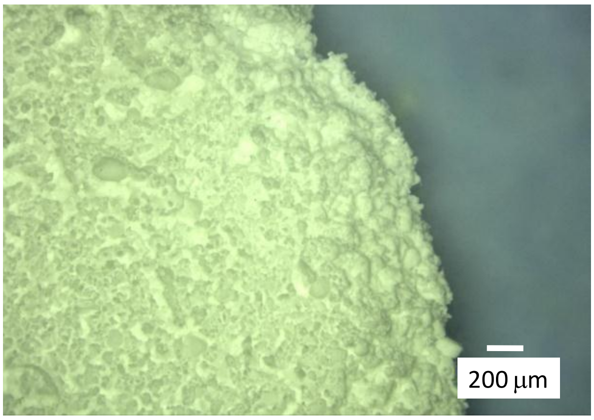


Figure 3. Digital microscope picture of bound powder after STA analysis.

3.2 *Precipitation with non-solvent (Dissolution-precipitation)*

In Table 2 the parameters are shown for the precipitation experiments with non-solvent. The different time parameters are the time the solution was placed in an ultrasonic bath (t1), the time the solution was stirred before addition of ethanol (t2) or after the addition of ethanol (t3) and the ageing time without stirring (t4).

The experiments are performed in 30 ml vials containing a magnet that are placed on a plate with magnetic stirrer capacity (Figure 2A). Either carbon tetrachloride or chloroform was used as solvent. Stock solutions were prepared beforehand in which 50 g PS was dissolved in 1L solvent. 10 ml of this stock solution was taken and filled in the vial. Then respectively 0.5, 0.25 or 0.33 g alumina was added to obtain a theoretical ratio of PS/Al_2O_3 of resp. 1.0, 2.0 or 1.5. The amount of ethanol (V_{Et}) added to obtain a phase inversion was either 2 or 4 ml. In the last column of Table 2 the wt% PS measured with STA is given. After the dissolution-precipitation procedure, all powders were filtered, washed with ethanol and dried in an oven for 1h at 75°C.

Table 2. Syntheses with (A) CCl_4 (S1-S5) and $CHCl_3$ (S6-S10) in 30 ml vials.

		t1	t2	t3	t4	V_{Et}	Ratio	PS
		min	min	min	h	ml		wt%
S1	A	0	300	30	0	2	1.0	5.0
S2	A	0	30	300	0	2	1.0	14.3
S3	A	0	300	30	16	2	1.1	7.8
S4	A	30	10	30	0	2	1.0	15.3
S5	A	30	240	30	0	2	1.0	6.0
S6	B	30	10	270	0	2	2.0	7.0
S7	B	30	10	240	0	4	2.0	38.0
S8	B	30	10	30	0	2	2.0	36.1
S9	B	30	10	30	0	4	2.0	32.4
S10	B	30	10	30	0	2	1.5	44.3

From experiments S1-S3 in Table 2 it can be observed that the highest %PS (14.3 wt%) was obtained with long stirring time (t3 = 5h) after the addition of ethanol. It is not necessary to stirr long (t2 = 300 min, S1 and S3) before the addition of ethanol. In experiments S4-S5 the additional effect of an ultrasonic treatment of the PS and alumina in solution was examined. The best combination was for experiment S4 which resulted in 15.3 wt% PS.
As from experiment S6, solvent was changed from carbon tetrachloride to chloroform for health reasons. When starting with an ultrasonic treatment of 30 minutes, long stirring times after addition of ethanol are not necessary. In exp. S7-S10, t1 and t2 were kept constant and t3, the volume of ethanol and the ratio PS/Al_2O_3 were varied. Several combinations with a ratio of PS/Al_2O_3 of 2 resulted in high %PS values (32-38 wt%). The highest value was obtained for combination of S10 with 1.5 PS/Al_2O_3.

To verify the robustness of the recipe at somewhat larger scale, the ingredients of synthesis S8 were scaled up with a factor 12 and 20, holding identical times as for S8, but using adjusted glass flasks of resp. 250 ml and 500 ml containing a magnet and that were placed on a plate with magnetic stirrer capacity. The parameters used in syntheses S11 and S12 are shown in Table 3. With higher scale, it became more difficult to filter the powder. According to STA, %PS of resp. 35.9 and 10.6 were obtained, indicating that the %PS diminished at higher scale.

Table 3. Syntheses with $CHCl_3$ scaled up with a factor of 12 and 20.

	Vsolvent	PS g	Al_2O_3 g	Vethanol ml	Ratio	%PS wt%
S11	120	6	3.0	20	2.0	35.9
S12	200	10	5.0	40	2.0	10.6

t1 = 30 min, t2 = 10 min, t3= 30 min.

In a next step, syntheses were performed in a 3L reactor with mechanical stirring (see Figure 2B). The starting volume of the PS-chloroform solution was always 1L. The concentration of PS in chloroform was either 50g/L or 100g/L. After the dissolution-precipitation procedure, all powders were centrifuged to remove the chloroform-ethanol solvent, further washed with ethanol and centrifuged, dried in air overnight, followed by drying in the oven at 75°C for 1 hour. The syntheses are given in Table 4. The time in ultrasonic bath (t1) was for all experiments 30 minutes and the stirring time before addition of ethanol (t2) was 10 minutes. The time (t3) of stirring after the addition of ethanol is 4 or 5 hrs. Experiment S13 resulted in an amount of PS (wt%) of 14. The volume of ethanol was increased in experiment S14 and two phases were obtained: (1) a fine powder and (2) a fraction of powder that was tightened together to form a large lump, however both phases had similar amounts of PS (14.5 and 15.2).

Table 4. Syntheses with $CHCl_3$ at 1 L scale.

	Conc. PS g/L	Al_2O_3 g	t3 min	V_{Et} ml	Ratio	%PS wt%
S13	50	29.2	240	200	1.7	14
S14	50	25	300	300	2.0	14.5 15.2
S15	100	50	270	250	2.0	17.6
S16	100	50	300	500	2.0	13.2 58.3

Vsolvent = 1 L, t1 = 30 min, t2 = 10 min.

In syntheses S15 and S16, the concentration of the PS in the stock solution was doubled from 50 to 100 g/L to increase the precipitation power upon addition of ethanol. The main difference between S15 and S16 is the doubling of the amount of ethanol from 250 to 500 ml. The higher the amount of ethanol, the faster and more efficient the precipitation will be, expecting to result in higher amounts of %PS.The STA results are shown in the last column. S15 resulted in a single phase of 17.6 wt% PS, whereas S16 resulted in two phases with very different amounts of %PS, respectively 13.2% and 58.3%. The STA curves of experiments S15 (17.6 wt% PS) and S16 (phase 2, 58.3 wt% PS) are shown in Figures 4 and 5.

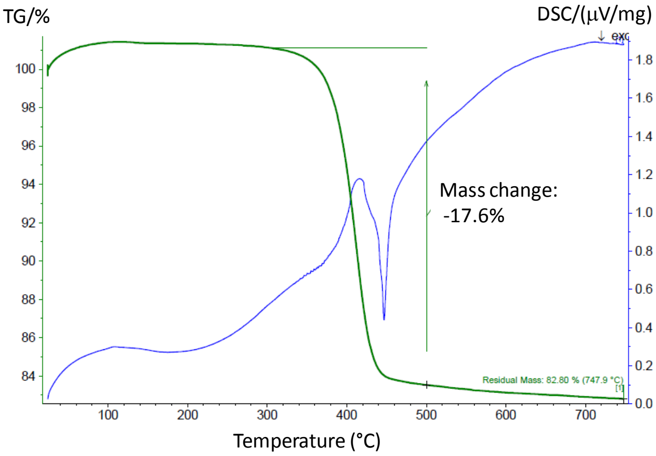


Figure 4. STA results of S15 (17.6 wt% PS).

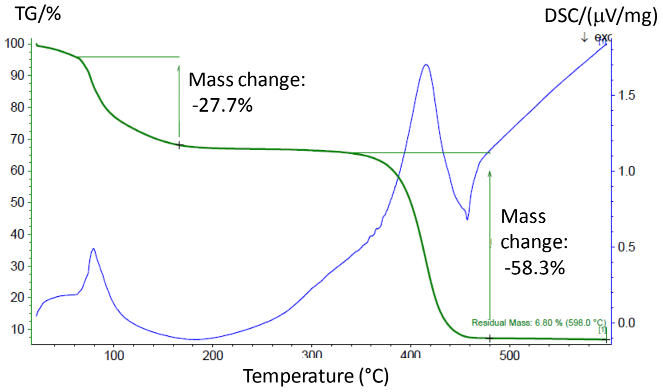


Figure 5. STA results of S16 (phase 2, 58.3 wt% PS).

Figure 4 shows a single mass change of 17.6% that occurs at the decomposition temperature of PS at 400°C. The STA curve of 58.3% (Figure 5) is unusual, because a first mass change of 27.7% is observed with a DSC peak before 100°C. This mass change of 27.7% could be explained by inclusion of chloroform-ethanol in this fraction. The large amount (500 ml) of ethanol made the polystyrene completely insoluble in the chloroform-ethanol mixture. The polystyrene started to massively precipitate on the alumina particles with inclusion of some of the chloroform-ethanol. This was not yet removed upon drying in the oven, but is released upon the treatment in STA. An additional mass change of 58.3 % around 400°C points towards the high loading of the PS coating in this phase.

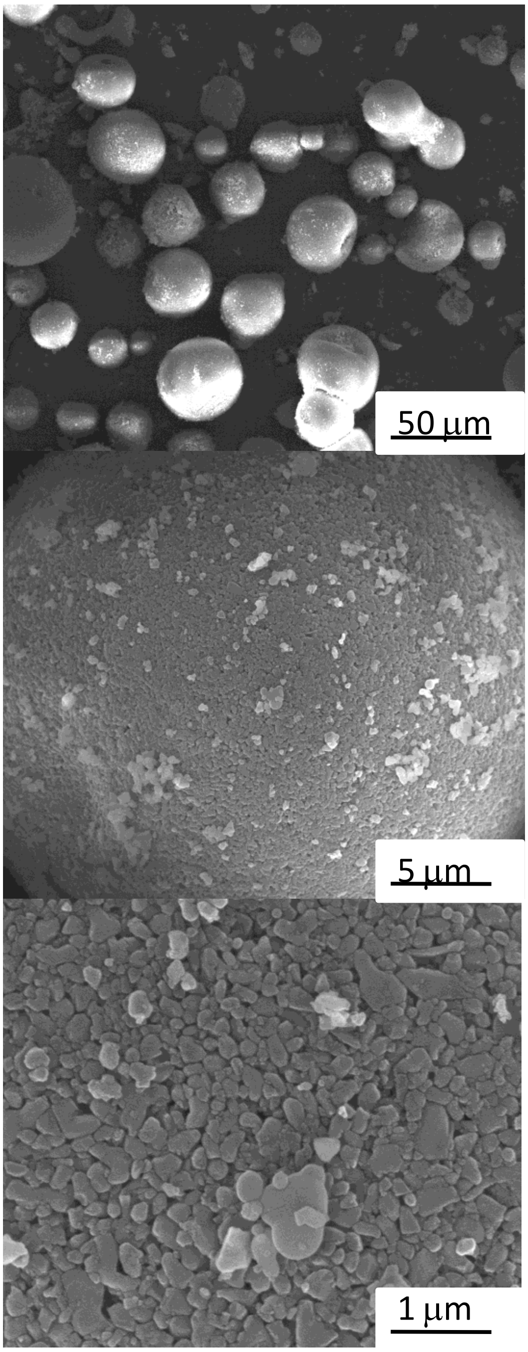


Figure 6. SEM pictures of the powder of experiment S14.

This shows it is possible to increase the amount of polystyrene on the alumina particles by conditioning (1) the amount of ethanol and (2) controlling the addition rate of the ethanol.

The morphology of sample S14 is illustrated with SEM (Figure 6) and clearly shows the formation of PS-alumina microspheres with a size of about 10-60 µm. The SEM picture below with the largest magnification demonstrates the good coverage of the alumina surface with polystyrene particles of about 0.1-1 µm.

An SLS simulation experiment was performed by mixing the powders of experiments S14 and S15, grinding the mixture in a mortar and heating 30 mg of the fine powder in the STA equipment to 1500°C. The powder was examined by digital microscopy (Figure 7) and also with this synthesis method to prepare a PS/Al_2O_3 composite the neck formation can be observed. This is promising for further SLS tests.

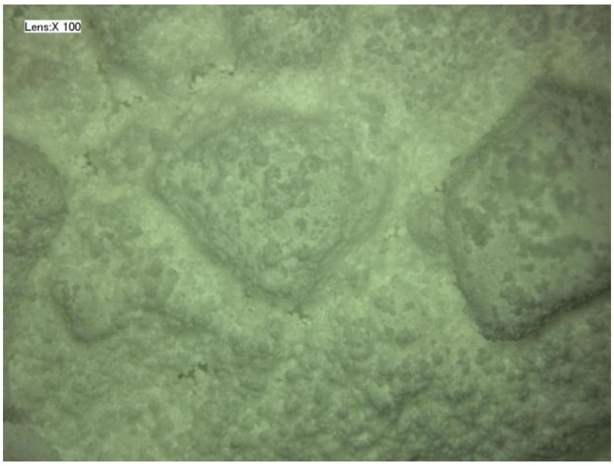


Figure 7. Digital microscopy picture of bound powder of a mixture of powders from experiments S14 and S15 (magnification x100).

4 CONCLUSIONS

Two strategies have been demonstrated to prepare PS/Al_2O_3 composite powders for application in SLS. A first method is dispersion polymerization. The recipe has been scaled-up to 2L with 39 wt% PS/Al_2O_3 composite particles. A second method is via dissolution-precipitation, dissolving polystyrene in preferably chloroform and precipitating the PS on alumina upon addition of ethanol to the solution. Recipes have been demonstrated prepared from 10 ml up to 1L PS-chloroform solutions. For the 10 ml and 120 ml preparations PS loadings up to 30-40 wt% were obtained. A homogeneous 1L preparation of 17 wt% PS/Al_2O_3 spherical composite particles was obtained with mechanical stirring. Both preparation methods are promising for use in SLS.

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