Preparation and characterization of novel PA6/SiO₂ composite microsphere applied for selective laser sintering

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Received 19 June 2017; accepted in revised form 21 August 2017

Abstract. The high cost and less variety of raw materials has greatly restricted the wide application of selective laser sintering (SLS) technology. In order to make the material cheaper and more diverse, PA6 is the most preferable material. In this work, a new PA6/SiO₂ composite microsphere used for SLS was designed and fabricated. To construct the material, PA6 porous microspheres with diameters of 20–80 μm and a certain pore volume were firstly prepared by the dissolution precipitation method. Then, SiO₂ was generated *in situ* in the PA6 porous microsphere framework, thus achieving a special structured PA6/SiO₂ composite microsphere. These microspheres with much well dispersed SiO₂ in PA6 matrices formed a powder with high bulk density and good electron conductivity. The particle size and weight fraction of the two components can be well controlled by adjusting the experimental conditions. Differential scanning calorimetry (DSC) data showed that the composite powder had a larger sintering window, which would be beneficial for SLS processing. The introduction of SiO₂ reduced the rate of water absorption in the composite powder, which could improve the accuracy of SLS forming. This work has certain significance as a reference for the design and development of SLS polymer-based composite materials.

Keywords: polymer composites, PA6 microspheres, selective laser sintering, preparation and characterization

1. Introduction

SLS is one of the most developed and widely used 3D printing technologies [1, 2]. The laser sintering process allows complex 3D objects to be built by selectively fusing together successive layers of powdered material. Theoretically, the wide range of material choices is a major advantage of SLS technology, because any powder that can be bonded after heating can be applied in SLS technology, but in practical applications, powder materials that can be successfully used are scarce [3–8]. The main reason for this scarcity is that SLS technology requires high-performance powder materials. For example, in order to create molded parts with good dimensional accuracy and mechanical strength, the resin material used to prepare the powder should have an appropriate melting point, high thermal stability, small shrinkage

rate, and suitable melt viscosity. Furthermore, the prepared powder particles should have approximately spherical structures with diameters of 20–80 μm , permitting greater powder fluidity and higher bulk density [9, 10].

Polyamide-12 (PA12)-based powder is one of the only materials used for SLS technology because it has good dimensional stability, a low melting point, easy processing, and a small shrinkage rate [11–16]. However, the cost of PA12 powder is very high; even simple sintered parts with volumes of 10 cm^3 cost thousands of dollars for the raw material alone. In addition, the use of PA12 powders often creates unsatisfactory mechanical properties. The thermal stability of the material is decreased under strong irradiation with UV or long-term UV exposure, which makes both powder and sintered products prone to

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yellowing [17, 18]. Therefore, the development of new high-performance and low-cost polymer powders is urgent.

PA6 is the most widely and successfully used engineering polymer, with a price of only 1/5 of that of PA12. PA6 has a higher melting point, thermal deformation temperature, and thermal decomposition temperature than PA12 does [19–21]. The modification technology for PA6 is also more mature. The excellent bending strength, tensile strength, and notched impact strength allow widespread use of PA6 in personalized consumer goods, as well as the automotive, aerospace, and medical industries, among other fields. If PA6 could be used in SLS technology, not only would the material cost be effectively reduced, but also the application of SLS would be broadened into the fields of customization, aerospace, automotive, construction, and medicine. Nevertheless, the commercialization of PA6 powder material has not yet succeeded. The greatest obstacle is determining the preparation technique for high-quality PA6 microspheres. In addition to this, the high water absorption rate of the hydrophilic amide group in the PA6 polymer chain is a problem. For direct application in SLS processing, the water absorption rate greatly influences the powder in the molding process, as well as the thermal stability, size stability, and mechanical strength of the sintered product. Therefore, the preparation of SLS microsphere structures with the required 20–100 μm diameter and the reduction of the water absorption rate are the two crucial problems to solve before PA6 powder can be applied in SLS. Methods for synthesizing PA polymeric microspheres are seldom researched in recent documents [22–25]. Hou and Lobuglio [22] prepared uniform spheres of PA6/PA12 polymers from a 1 wt% theta solvent when cooling the solution rapidly to a point below the theta temperature. Li *et al.* [23] obtained high-crystallinity PA6 microspheres by a slow solvent evaporation method from a high-concentration PA6/formic acid solution. In the literature, the maximum size of PA6 microspheres is a few micrometers, and the preparation of PA6 microspheres with sizes of several tens of micrometers and applicability in SLS technology is rarely reported.

PA6 is a semi-crystalline material. The rate of water absorption therefore depends on the polar amide, amino, and carboxyl groups on the polymer chains in the amorphous regions [26]. Thus, the water absorption of PA6 can be reduced by improving the

degree of crystallinity to reduce the water absorption probability of the amorphous region or adding non-polar filler modification to inhibit water penetration. SiO_2 is cheap, easily obtained, and the most commonly used material for the modification of PA6 [27]. The silicon hydroxyl on SiO_2 and amide groups on the PA6 polymer chain can form stable intermolecular interactions, thereby significantly improving the material hydrophobicity, thermal stability, and mechanical properties [28, 29]. The sol-gel approach, used to synthesize PA6 nanomaterials has received considerable interest in recent decades. However, most previous studies investigated PA6 films or sheets with nanoscale SiO_2 mainly distributed on the surface of the PA6 matrices at low-volume loading [30–33]. The preparation of PA6/ SiO_2 composites, especially microspheres with high dispersion and high loading weight, is more challenging and rarely reported.

Particular interest in developing new materials used for SLS, a new special structured PA6/ SiO_2 was designed and fabricated in this study. To construct the material, PA6 porous microspheres with diameters of 20–80 μm and a certain pore volume were prepared by the dissolution precipitation method. High content of SiO_2 was generated and well dispersed *in situ* in the PA6 porous microsphere framework, thus achieving PA6/ SiO_2 composite microsphere with the mean diameter of 20–80 μm (Figure 1). By introducing the SiO_2 particles, the bulk density, electron conductivity, and laser sintering window of the PA6 composite powder were significantly improved. More importantly, the increased crystallinity and surface roughness of the PA6 matrix consequently decreased the water absorption rate of PA6/ SiO_2 composite powder.

2. Experimental

2.1. Materials

PA6 pellets with a type of B30S were purchased from BASF. Polyvinylpyrrolidone (PVP) with the molecular weight of $M_w = 40\,000$ g/mol (PVP-K30) was purchased from Guang Zhou Xilong Chemical Reagent Co., China. Formic acid and tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich. The polymers in this study were all commercial products and used without further purification or fractionation. Therefore, the molecular weight and chain length distributions can be assumed as broad.

Figure 1. Schematic of the preparation of PA6/SiO₂ composite microspheres

2.2. Instruments

The surface morphologies of the PA6 porous microspheres and the PA6/SiO₂ composites were examined by using a Hitachi S-4800 scanning electron microscope (SEM). The cross-sections of the PA6 porous microspheres and PA6/SiO₂ composite microspheres were detected by using a 3-in-1 multibeam ion microscope Orion NanoFab from Carl Zeiss Company. This system covers the complete range of micromachining to nanomachining applications using gallium, neon and helium ion beams integrated in a single instrument, as well as high resolution imaging capability in the same instrument. The optional gallium focused ion beam (FIB) column were used to cut off the target PA6 microparticles by removing one half of the massive material, then high resolution microscope system was used to characterized the other half of the particle. The bulk density was determined by measuring the volume of a known mass of sample powder that was passed through a screen into a graduated cylinder, according to the USP32 (616) standard (Method I). A dry 250 mL cylinder was used to test approximately 100 g of sample material; the measurement was repeated three times to obtain an average value. The pores volume and other pores properties were detected by using mercury porosimetry Pore Master GT 60.

The thermal stability and SiO₂ contents in the PA6 composite microspheres were determined using thermogravimetric analysis (TGA) with an SDTA 851

Thermobalance apparatus. The samples were heated to 800 °C with a heating rate of 10 °C/min for 90 min under a nitrogen atmosphere. The wt% of SiO₂ was calculated using curve plateaus. The thermal behaviors of the materials were characterized by differential scanning calorimetry (DSC) experiments. The first running of melt and crystalize behavior were detected using a Mettler-DSC1 at a heating rate of 10 °C/min and a cooling rate of –10 °C/min. The weight of each sample was 5.0 mg.

The rate of water absorption of the sample was determined according to the ASTM_D570 standard. The test specimens for homogeneous plastics measuring 60 by 60 by 1 mm were prepared directly by hot press molding. The specimens were firstly dried in an oven for 24 h at 50 °C, cooled in a desiccator, and immediately weighed to the nearest 0.001 g, before being placed in a container of distilled water maintained at a temperature of 23±1 °C, resting on edge while entirely immersed. After 24 h, the specimens were removed from the water one at a time, all water was wiped off the surfaces of the specimens with a dry cloth, and the specimens were weighed to the nearest 0.001 g immediately.

2.3. Procedures

2.3.1. Synthesis of PA6 porous microspheres

The procedure for preparing PA6 porous microspheres used three steps: First, we dissolved the PA6 pellets and PVP-K30 powder with concentrations of

12.5 and 8.0 wt%, respectively, in acetic acid under heating until a transparent homogeneous solution formed. Second, we added ethanol as the poor solvent 2 times the amount of acetic acid to the acetic acid solution with vigorous stirring until the PA6 was precipitated and dispersed as white particles in the mixture. Third, we filtered and washed the precipitate with ethanol and water until the acetic acid and PVP were removed. The resulting white powder was dried in an oven at 90 °C for direct testing and used without additional screening.

2.3.2. Synthesis of PA6/SiO₂ composites

To prepare the PA6/SiO₂ composite, the prepared PA6 porous microspheres were firstly added and dispersed in a mixed solvent of ethanol and ammonia water (NH₃·H₂O) under stirring. Then TEOS was added and heated to 40 °C for 20 h with vigorous stirring to finish the hydrolysis-condensation reaction. The resulting white powder was dried in an oven at 90 °C for direct testing without any other screening. The ethanol and PVP were recycled for further use.

3. Results and discussion

The preparation of PA6/SiO₂ composite microspheres was conducted by firstly preparing porous PA6 microspheres using a modified phase-separation process and then generating nanoscale SiO₂ within the PA6 porous microsphere framework, using a typical sol-gel technique. The preparation of the PA6 porous microspheres was conducted by a modified dissolution precipitation method. Compared to other methods in the literature, the advantages of this preparation process can be summarized as follows: 1) A low-boiling-point solvent could be applied as the good solvent, making the obtained powder easily dried. 2) A mild reaction temperature without pressure was applied during the preparation process, thus effectively preventing the polymer from decomposition at high temperatures. 3) The preparation process does not depend on the grade of the raw materials. The porous microspheres could be obtained by using different sources of raw materials. In addition, the powder can perform amplification in the 50 L reactor. 4) By controlling the experimental conditions, we can obtain PA6 microspheres with controlled sizes and bulk densities.

Figure 2a–2c depict SEM images of the PA6 porous microspheres. As shown, the porous microspheres

with average particle sizes of 50 μm exhibit spherical coil structures, intertwined by a ball of micrometer-scale lines with diameters of 1–3 μm, with many random pores of 1–5 μm on the surface. To examine the inside structure, the porous microspheres were cut with high energy gallium focused ion beam (FIB) and characterized by a high resolution microscope which integrated in a 3-in-1 multibeam ion microscope. The cross-section shows many through-holes inside the porous microsphere, which is similar to the surface pore structure. Obviously, the pores of the porous microspheres are interlinked (Figure 2g).

The porous microspheres can be directly used for the *in situ* growth of SiO₂ without further processing. It is gratifying that the SiO₂ grows selectively inside the PA6 porous microspheres, rather than in the outside solution. This high degree of selectivity may relate to the intermolecular hydrogen-bonding interactions between the hydroxyl groups on the surface of the SiO₂ and the amide groups of the PA6 chains. Because of this, the silica firstly selected to be deposited around the surface of nylon 6 micrometer-scale lines. In addition, due to the self intermolecular interaction of silica particles the generated SiO₂ accumulates continuously in the same place. This eventually results in the gradual filling of the surface and internal pores of the porous microspheres, which are intertwined by the micrometer-scale lines. However, when the pores of nylon 6 microspheres are gradually filled with silica, little space was left for the generation of SiO₂ in the inner of the microsphere, while SiO₂ tends to grow on the surface of microspheres.

After the *in situ* growth of SiO₂, the surface porous structure is completely filled with SiO₂, although the particle size of the composite microspheres does not obviously change as shown in Figure 2d–2f. Scanning electron microscope energy dispersion spectra of PA6/SiO₂ composite confirmed the existence of SiO₂ (Figure 2i). The cross-section obtained after FIB cutting shows that most of the pores within the microsphere are filled effectively. Importantly, the SEM images of the PA6/SiO₂ composite microspheres are clearer (Figure 2h) than those of the PA6 microspheres, indicating that the electrical conductive properties of the composite microspheres are significantly improved compared with that of pure PA6. It is reasonable to believe that good electrical conductivity can effectively reduce the electrostatic adsorption capacity of powder in the powder-laying device during SLS processing.

Figure 2. a–c) SEM photographs of PA6 porous microspheres at different magnifications; d–f) SEM photographs of PA6/SiO₂ composite microspheres at different magnifications; g) cross-sectional image of PA6 porous microsphere; h) cross-sectional image of PA6/SiO₂ composite microsphere; i) scanning electron microscope energy dispersion spectra of PA6/SiO₂ composite carried

The properties of the PA6 porous microspheres were important for the construction of the PA6/SiO₂ composites. These properties are strongly dependent on the preparation conditions. Among these conditions, the PVP concentration is especially crucial as PVP acts as a dispersant in preparation. When no PVP is used, only random powder can be obtained. The size and diameter of the porous microspheres is significantly changed when different weight ratios of PVP are introduced. With the increase of PVP content to 4, 8, and 12 wt%, the diameter of the microspheres decreases to 75, 50, and 18 μm, respectively, while the pore volume decreases to 9.84, 6.83, and 5.70 mL/g, respectively, as shown in Figure 3 and Table 1.

The PA6 porous microspheres have large porosities and specific surface areas with large load capacities, suitable for application in the field of painting.

However, the bulk density of the powder is low and the mobility is poor, so such microspheres are unsuitable for SLS. In order to improve the sintering properties of the powder, the porous PA6 spheres of 50 μm in particle size were used as templates, and SiO₂ at weight ratios of 5, 27, 32, and 65% is introduced to the porous microspheres by *in situ* hydrolysis. As the SiO₂ content increases, the pore volume and porosity of the composite microspheres decrease significantly, while the bulk density and flowability are greatly improved, as shown in Table 2 and Figure 4.

The thermal stability of materials is characterized by TGA, in which the weight loss is monitored as a function of the temperature. TGA measurements of neat PA6 and its composites with varying amounts of SiO₂ were performed, and the SiO₂ content determined in each composite microsphere from TGA is

Figure 3. SEM photographs of PA6 porous microspheres precipitated from solution with PVP added at concentrations of a) 0 wt%; b) 4 wt%; c) 8 wt%; d) 12 wt%

Table 1. Conditions of phase separation procedures and the resulting particle sizes, bulk densities, and pore properties

Powder No.	PVP [wt%]	Diameter, $d(0.5)$ [μm]	Bulk density [g/cm^3]	Pore volume [mL/g]	Mean diameter of pore [μm]	Porosity [%]
1	0	<10.0	–	–	–	–
2	4	75.0	0.12	9.84	1.23	85.1
3	8	50.0	0.19	6.83	1.53	79.9
4	12	18.0	0.23	5.70	0.99	77.1

Table 2. Properties of PA6/SiO₂ composite microspheres with different concentrations of SiO₂

Powder No.	SiO ₂ , calculated [wt%]	Bulk density [g/cm^3]	Pore volume [mL/g]	Mean diameter of pore [μm]	Porosity [%]
1	0	0.19	6.83	1.53	85.1
2	5	0.21	5.96	1.45	81.5
3	17	0.23	2.99	1.15	77.5
4	32	0.29	2.07	0.44	67.8
5	65	0.42	1.72	0.39	51.9

The weight content of SiO₂ was calculated by the weight of feeding TEOS and the conversion rate of SiO₂ synthesized by TEOS.

reported in Table 3 and Figure 5, along with the theoretical SiO₂ content and the temperatures at which 10, 50%, and the fastest weight losses occur. The thermal degradation temperatures of the PA6 nanocomposites are decreased significantly compared to

that for neat PA6, suggesting that the thermal stability of the nanocomposites is decreased compared to that of neat PA6. Compared with the pure PA6 powder, SiO₂ in PA6 nanocomposites cannot be decomposed under the experimental temperature. Thus, the

Figure 4. SEM photographs of PA6/SiO₂ composite microspheres with SiO₂ prepared at concentrations of a–b) 5 wt% when the growth temperature is 30 °C; c–d) 17 wt% when the growth temperature is 30 °C; e–f) 32 wt% when the growth temperature is 70 °C; g–h) 65 wt% when the growth temperature is 80 °C

Table 3. The thermal stability of PA6 and its composites containing 5–65% SiO₂, characterized by TGA

Powder No.	SiO ₂ , calculated [wt%]	SiO ₂ , TGA [wt%]	T _{10%} [°C]	T _{50%} [°C]	T _f [°C]
Pellets	0.0	0.0	408.2	443.5	451.7
1	0.0	0.0	403.1	441.2	449.1
2	5.0	4.9	397.6	431.1	438.9
3	17.0	16.7	396.0	428.6	433.8
4	32.0	30.5	374.8	417.1	438.2
5	65.0	63.8	367.1	405.8	410.8

T_{10%} and T_{50%} indicate the temperatures at which 10 and 50% weight loss of PA6 occur, respectively. T_f indicates the temperature at which the fastest weight loss of PA6 occurs.

TGA curve of composite powder shows a plateau at a certain weight percentage. The weight loss before this plateau represents the content of PA6 in PA6/SiO₂ composite. The actual SiO₂ content, can be determined by weight percentage at this plateau represents, which appears only slightly lower than the theoretical

Figure 5. TGA thermogram comparison of raw PA6 pellets and the experimentally prepared PA6/SiO₂ composite microspheres with SiO₂ prepared at concentrations of 5, 17, 32 and 65 wt%

amount given in Table 3. This shows that the sol-gel reaction is almost complete in all cases. The decreases in the thermal stability of the PA6/SiO₂ composites is consistent with other reports [33], in which the thermal decomposition temperature reaches the maximum value as the SiO₂ content reaches ~3 wt%, probably because of strong secondary interactions between PA6 chains and SiO₂. When the SiO₂ content is increased more, the thermal conductivity of the large amount of inorganic powder renders the complex more easily decomposed.

During SLS processing, the larger sintering window can ensure better controllability of the powder. Accordingly, we studied the thermal and crystallization properties of the PA6/SiO₂ composite microspheres by DSC. As shown in Figure 6 and Table 4, pure PA6 pellets have melting and crystallization peaks at 222.5

Figure 6. DSC thermogram comparison of raw PA6 pellets and the experimentally prepared PA6/SiO₂ composite microspheres with SiO₂ prepared at concentrations of 0, 17, 32 and 65 wt%**Table 4.** Melting and crystallization characteristics for raw PA6 pellets and prepared PA6 powder

Powder No.	SiO ₂ , TGA [wt%]	Peak T _m [°C]	Onset of T _m [°C]	Melting enthalpy, ΔH _f ^a [J/g]	Peak T _c [°C]	Onset of T _c [°C]	Crystallinity ^a	Sintering window ^b [°C]
Pellets	0.0	222.5	217.3	−65.5	192.9	197.5	34.8	—
1	0.0	216.5	212.9	−94.6	192.6	195.7	50.3	17.2
2	4.9	216.7	212.7	−75.9	190.8	194.4	42.5	18.3
3	16.7	216.9	212.6	−67.4	190.2	193.9	43.2	18.7
4	30.5	217.1	212.3	−62.8	189.5	193.6	49.1	18.7
5	63.8	216.9	213.2	−37.8	189.6	193.3	57.4	19.9

^aCrystallinity was calculated as $X_c = \frac{\Delta H_f}{[(1 - \Phi)\Delta H_f^*]} \cdot 100\%$, where ΔH_f is the heat of fusion of the PA6 nanocomposite samples, is the heat of fusion of 100% crystalline PA6, taken as 188 J/g, and Φ is the weight fraction of SiO₂ in the composite sample.

^bThe ‘sintering window’ for SLS processing was calculated as ΔT = (T_m − T_c).

and 192.9 °C, with melting enthalpy and crystallinity of –65.5 J/g and 34.8%, respectively. In the powder preparation process, the arrangement of the molecular chains is more regular, which resulted in a higher melting enthalpy and crystallinity of –94.6 J/g and 50.3%, respectively. On the other hand, because pure PA6 recrystallized at a lower temperature, the size of the crystal decreases relatively in the powder preparation process. Thus, the melting temperature of PA6 powder is lower than the pellets and the crystallization temperature remains constant.

After the introduction of SiO₂, SiO₂ was polymerized on the template of the PA6 porous microsphere, with no influence on the PA6 matrix structure. Thus, when the content of SiO₂ is increased in the range of 27–65%, the melting temperature is slightly increased from 216.5 to 217.1 °C when SiO₂ content is 32%. More importantly, the introduction of SiO₂ have significant effect on the PA6 crystallization process. On the one hand, the introduction of inorganic powders may promote the crystal nucleation process thus lead a more rapid crystallization process and higher crystallization temperature. On the other hand, the introduction of inorganic powders may increase the overall thermal conductivity of composite powders, thus hindering the crystallization process and reducing the crystallization temperature on the contrary [34]. Because of the combined effect of these two aspects, the crystallization temperature of composite powders decreases from 192.6 to 189.5 °C with the increase of SiO₂ content, while the crystallinity calculated from the melting enthalpy decreased first and then increased. More importantly, the sintering window which represent the gap between the onset of melting and crystallization temperature are increased to 18.3, 18.7, 18.7, 19.9 °C, respectively. Therefore, the composite powder has a wider sintering window than the PA6 pure pellet does. The material prepared by the dissolution precipitation method first forms a porous powder with a high melting enthalpy, and then the sintering window is increased by the method of *in situ* introduction of SiO₂. The composite material prepared by our method has a wider sintering window, which permits improved controllability of the sintering process.

The water absorption rate of the PA6 powder is another important factor affecting the forming precision of sintered parts. Accordingly, the water absorption rates of the PA6 pellets, porous powder, and composite powders were tested. According to the

test standard, the pellets and powders were first hot-pressed into shells and then immersed in water for 24 h; the water absorption rate was calculated according to the quality of the shells before and after water immersion. The pure PA6 powder and pellets have similar water absorption rates of 4.1 and 4.3% respectively. After the introduction of SiO₂, the water absorption of the shell of the composite powder decreases obviously, and the water absorption rate continues to decrease as the SiO₂ content increases. When the SiO₂ content in the composite powder is 5, 17, 32, and 65%, the corresponding water absorption rate is 3.1, 1.8, 0.81, and 0.35%, respectively. The decrease of water absorption of the composite microspheres should be analyzed from the following two aspects, one is the hydrophilic amide groups in the PA6 polymer chain decrease significantly because the intermolecular hydrogen-bonding interactions between the hydroxyl groups on the surface of the SiO₂ and the amide groups of the PA6 chains. The other is SiO₂ inside the PA6 porous microspheres occupied most innerspace of composite microspheres, so there is no enough space for water molecules absorption.

4. Conclusions

In this study, a new kind of PA6/SiO₂ composite microsphere structure is designed and constructed by *in situ* generation of SiO₂ within a PA6 porous microsphere framework, thus achieving good dispersion of many SiO₂ particles in the PA6 matrix. The *in situ* preparation technology and the effect of the structure on the powder properties are investigated to obtain controllable properties of the composite microspheres by manipulating the preparation process. The bulk density, conductivity, and mobility of the composite powders were effectively improved by the introduction of SiO₂. Simultaneously, the crystallinity of PA6 in the composite powder was improved, which decreased the crystallization temperature and broadened the sintering window. The filling of the PA6 matrix and the improvement of the degree of crystallization by the SiO₂ decrease the water absorption of the composite material. This polymer-based composite material preparation technique may provide new ideas for adjusting the functionality of materials, as well as enabling low-cost and high-performance SLS technology with polymer powders prepared by this new technique.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (Project No. 51603212 and 51473175), and the Hangzhou City Economic and Technological Development Zone for financial support.

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