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A new method to prepare composite powders customized for high temperature laser sintering

Bahareh Yazdani, Binling Chen, Luiza Benedetti, Richard Davies, Oana Ghita, Yanqiu Zhu*

College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter, EX4 4QF, UK

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ABSTRACT

Composites have the potential to enhance the mechanical properties of components fabricated by additive manufacturing; however, the bottleneck is the limited number of polymeric composite powders available for this manufacturing process. This paper describes a generically new method to create composite powders that are suitable for High Temperature Laser Sintering (HT-LS). C-coated Inorganic Fullerene-like WS_2 (IF-WS_2) nanoparticles and graphene nanoplatelets (GNPs) have been chosen to demonstrate their incorporation into a high performance polymer matrix: Poly Ether Ether Ketone (PEEK). The morphological and physical property investigations have confirmed that the resulting composite powders exhibit the desired particle morphology, size, distribution and flowability for HT-LS applications. Further preliminary sintering results have demonstrated that they are comparable to the currently available commercial grade of PEEK powder HT-LS applications in terms of powder packing properties and flow ability. The new strategy reported here brings in great potential for the additive layer manufacturing of high performance polymeric composite components with improved mechanical and added functionalities by choosing the proper matrix and filler combination.

1. Introduction

Laser Sintering (LS) can produce complex parts directly from computer-aided design data, without the involvement of any expensive mould tooling [1], thus this technology has attracted great research attention. One of the key bottlenecks for the wider development and application of this technology is the lack of available powder materials. For a long time, polyamides (PA11 and PA12) have predominantly been used for a standard LS process, due to their excellent processability. The incorporation of reinforcement to polyamides can lead to composite components with improved performance and widened applications [2–4]. However, for harsh environments such as aerospace, defence and gas applications, the currently available polymers for LS cannot meet these requirements. High performance polymeric materials that are suitable for LS processing need to be developed.

PEEK is indeed one of such best candidates, due to its high melting point, good biocompatibility, high mechanical properties and chemical resistance [5–7]. However, due to the high melting temperature, it was not possible to process PEEK with standard LS systems with operating temperature only up to 200 °C until the High Temperature Laser Sintering (HT-LS) system, EOSINT P800 was introduced to the market. Berretta et al. have successfully applied the commercial grade PEEK (450PF Victrex) to the HT-LS system [8].

Incorporating various nanofillers into the PEEK matrix during HT-LS could further improve the mechanical properties and introduce crucial functionalities for different advanced applications. Yuan et al. physically added 5 wt% of graphite platelets into PEEK150PF powder and achieved a 40% increase in tensile strength, however for concentrations above 5%, in this case 7.5 wt%, the Micro-CT analysis revealed porosity in the microstructure [9], which was related to the poor powders flow and uneven heating absorption between the graphite platelets and PEEK powder during the HT-LS. One of the conventional ways to incorporate fillers into a polymer matrix is direct melt-compounding [10,11], however the high cohesive forces between nanofillers cause their severe agglomeration and poor dispersion inside the polymer matrix [12], which significantly limits the full potential of the nanofillers. Furthermore, modifying the melt compounded polymer into powder form with appropriate particle size and morphology requires following up milling or other size reduction processes that are very energy consuming and costly, needless to say the huge challenges for obtaining powders of round shape and proper size distribution by milling, especially for high performance polymers, such as PEEK [13]. Therefore, investigation to develop new strategies for making composite powder in a suitable morphology and cost-effective way is of highly importance.

Graphene nanoplatelet (GNP) is one of the best nanofillers in

* Corresponding author.
E-mail address: Y.Zhu@exeter.ac.uk (Y. Zhu).

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polymer-based composites, because of its excellent mechanical, electrical and thermal properties. Inorganic fullerene-like tungsten disulphide (IF-WS_2) is another interesting nanoparticles with hollow core and layered shell morphology. Such a unique microstructure brings in exceptional lubricating and wear resistant properties, and extraordinary shock-absorbing properties for ultimate protections, triggered us to incorporate it as nanofiller into the PEEK matrix. Previous studies have shown that adding 5 nm carbon coating on the surface of IF-WS_2 nanoparticles (C-coated IF-WS_2) can improve their thermal stability against oxidation [14].

We herein describe a completely new and cost-effective method for the preparation of composite PEEK powders using GNPs and C-coated IF-WS_2 as the nanofillers. We used salt template as a spacer and adapted a partial melting process to purposely create a 'weak' porous composite block. After leaching out the salt, the porous block can be easily broken into powder form. A number of researchers have used salt to produce porous PEEK structure for PEEK bioactivity improvement and better implant-bone contact [15,16]. However, to the best of our knowledge, this is the first time that this method is used to prepare composite powders suitable for Laser Sintering. Several types of near spherical-shaped composite powders with desirable particle size, distribution and flowability have been achieved. Finally, we will further demonstrate their suitability for HT-LS.

2. Experimental

2.1. Materials

PEEK 450PF was supplied by Victrex. Graphene nanoplatelets (GNPs, 6–8 nm thick × 5 μm wide) were purchased from ABCR GmbH& Co, Germany. NaCl (BioXtra grade with 99.5% purity) was purchased from Sigma Aldrich, UK. Full preparation details of the C-coated IF-WS_2 have been described in our previous papers [17,18].

2.2. Mixing the PEEK with nanofillers

C-coated IF-WS_2 particles were dispersed in water/ethanol solvent and probe sonicated for 5 min to obtain a stable suspension. 1 and 5 wt % of C-coated IF-WS_2 nanoparticles were further mixed with PEEK 450PF in the suspension, and subjecting to another 10 min sonication a well-dispersed composite suspension was obtained. The mixture suspension was placed on a hot plate at 150 °C, to dry under continuous magnetic stirring. The PEEK-GNP composite powder was prepared by following the same process, using the same GNP nanofiller amounts of 1 and 5 wt%.

2.3. Fabrication of PEEK-IF-WS_2 and PEEK-GNP composite powders for HT-LS

All composite powders were dry mixed with NaCl powder, with an optimised NaCl/powder ratio of 6/1, and the mixture was then placed in a mould for cold press. After pressing, the mould was heated up in a cubic furnace at 400 °C, just above the melting point of PEEK, for a given time depending on the mould size to allow for the PEEK to melt and mix with the nanofillers. The salt particles were used as a spacer to generate and regulate the porous structure in the sintered blocks. After cooling, the salt was leached away by immersing the blocks in water under magnetic stirring for 3 h, leaving behind porous composite blocks.

The porous blocks were crushed using a simple food blender in distilled water for 5 and 10 min, to assess any effects of milling time on the particle size and morphology. After milling, the suspension was filtered and washed with water to remove any trace of salt, and the resulting composite powder was left for 24 h in an oven for drying. The dried powder was sieved using 212 μm and 125 μm meshes, separately. In each sample, around 80% of the total powder passed through the 125 μm mesh and it was collected for further characterization.

2.4. Fabrication of PEEK-IF-WS_2 and PEEK-GNP composites by HT-LS

The HT-LS process was carried out in a reduced build mode using the EOSINT P800 system [8]. Four different composites including two PEEK-IF-WS_2 composites with 1 and 5 wt% IF-WS_2 nanofiller and two PEEK-GNP composites with 1 and 5 wt% GNPs were synthesized. The samples are one layer thick and each sample was repeated three times with 1 exposure, 2 exposures and 3 exposures of laser beam with the laser power of 15 W, using a scan speed of 2550 mm/s and scanning interval of 0.2 mm in order to get a robust sample.

2.5. Structure and morphology characterization

Micro-CT (X-TEC Bench top CT 160 XI) was used to analyse the 3D structure of the porous blocks. An SEM (NOVALAB 600) was used to investigate the morphology and size of the powders, and the fracture surfaces of the sintered samples. To visualise the dispersion of nanofillers inside the PEEK matrix before and after the melting process, a JEM2100 TEM (operated at 200 kV) was used. TEM samples were prepared by dispersing a small amount of powder into acetone and drop casting on a holey carbon Cu grid.

2.6. Particle size distribution

A Saturn DigiSizer 5200 Micrometrics was used to measure the particle size distribution. To carry out the measurement, the target particles were dispersed in deionized water to form a suspension, which will be sampled at certain concentration to obtain the particle size distribution.

2.7. Powder rheology

To characterise the flow properties of the composite powder, a Freeman FT4 powder Rheometer was used to measure powder stability and flowability. The powder is placed inside a standard 25 ml split vessel and a 22 mm diameter twisted blade rotates and moves simultaneously into the powder sample, firstly to condition the environment, which aims to remove any undesired air trap and powder agglomeration, then to perform the test. The parameters are measured by means of torque, which is applied by the simultaneous counter-clockwise rotation of the blade at 100 mm/s whilst moving downwards. The energy necessary to displace, lift, promote stability or flow of the powder are respectively associated with Basic Flow Energy (BFE), Specific Energy (SE), Stability Index (SI) and Flow Rate Index (FRI); these values are obtained from the stability and flow rate test using the following equations:

$$SI = \frac{Energy\ Test\ 7}{Energy\ Test\ 1} \tag{1}$$

$$BFE = Energy\ Test\ 7 \quad (mJ) \tag{2}$$

$$SE = \frac{\frac{Up\ Energy\ Test\ 6 + Up\ Energy\ Test\ 7}{2}}{Split\ Mass}\ (mJ/g) \tag{3}$$

$$FRI = \frac{Energy\ Test\ 4}{Energy\ Test\ 1} \tag{4}$$

In the Stability Test, the blade was performed seven successive cycles with a constant speed of 100 mm/s throughout the pre-conditioned powder and by analysing the difference in the energy required for each cycle by means of SI, the Stability Test data were obtained.

The difference between BFE and SE is that the BFE refers to energy measured when the blade is rotating anti-clockwise into the pre-conditioned powder from the top of the vessel to the bottom, whilst the SE