Development of nanocomposite powders for the SLS process to enhance mechanical properties

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Abstract

In an effort to fabricate prototypes with improved mechanical properties in the dual laser sintering process, functionalized graphite nanoplatelets were added to the PA-12 powder to produce a nanocomposite powder. The PA-12 powder was chosen as the matrix polymer because it has features conducive to laser sintering such as relatively low melting temperature and high mechanical properties. The GNPs were oxidized through a nitric acid treatment to improve the interfacial bonding. The resulting nanocomposite powder was layered and sintered by laser without any sign of agglomeration. Although the result is preliminary, it nevertheless shows the suitability of the nanocomposite powder for the laser sintering process.

Key Words : Rapid prototyping, Nanocomposite, Graphite nanoplatelets, Polyamide-12, Dual Laser Sintering process

Introduction

In recent years the product life cycle has become shorter than ever because of rapidly changing customer demands. Since it is almost impossible for conventional methods of product manufacturing to meet these demands, much research is being done to reduce the time and cost of product development when diverse models and frequent design changes are indispensable. The solid freeform fabrication (SFF) technology, also known as the rapid prototyping (RP) technology developed since the late 1980s, has established itself as part of CAD/CAM and is expected to cope with the dynamic manufacturing environment. RP is an additive manufacturing process, in which a 3-D computer model is sliced and reassembled in real space layer-by-layer [1-2].

There are many commercial SFF systems such as SLA (stereolithography apparatus), FDM (fused deposition modeling), SLS (selective laser sintering), LOM (laminated object Manufacturing), JP5 (JP System 5), 3DP (3D Printing) and some other processes [3]. However, all these processes are limited by the available materials although much research have been done to make available better materials.

Nanocomposites are composite materials where the reinforcement phase has at least one dimension in the range of 1-100 nm. There are many types of nanocomposites depending on the

matrix materials and nanofillers used. Integrating reinforcement particles in a polymer of choice to form a composite material has been practiced for decades [4]. They have attracted much interest due to their special physicochemical properties which may be quite different from their constituent materials'. These composite materials can offer potentially useful and unusual combinations of mechanical, electrical, magnetic and optical properties that are otherwise unachievable in conventional materials [5]. Due to many advantages of nanocomposites, the field of their application has been gradually expanding. The use of Nan composites in the SFF processes would be a timely development.

A few researchers have tried to apply nanocomposites to the SFF processes. In 1993, Manthiram et al. [6] developed a nanocomposite to optimize selective laser sintering (SLS) and selective laser reactive sintering (SLRS). They selected ceramic-ceramic and ceramic-metal nanocomposite systems in such a way that one nanosize component has a lower melting temperature than the other nanophase. The nanocomposite powders of Al2O3-CoO3, and Al2O3-NiO were synthesized by a sol-gel processing. In 2006, Ritzhaupt et al. [7] tailored the refractive index of polymethylmethacrylate (PMMA) using a UV-curable reactive resin and two different alumina powders and one nanosized silica. In the same year, Kim et al. [8] developed a nanocomposite deposition system (NCDS) to fabricate 3D nanocomposite parts. The NCDS uses a photo-curable polymer resin as the matrix and various nanoparticles to form a composite prototype. They used multi-walled carbon nanotubes (MWCNT) to improve electrical properties and hydroxyapatite particles to produce a biocompatible composite.

In most previous works, nanocomposites used in the SFF process were fabricated by simple mixing of nanoparticles and polymer. However, this results in poor bond between the filler and the polymer matrix, and introduces artificial defects, which can consequently be detrimental to the mechanical properties of the final nanocomposite [9].

In our work, a nanocomposite powder consisting of PA-12 (polyamide-12) powder and functionalized GNPs (graphite nanoplateletx) has been synthesized and evaluated for the dual laser sintering process. The PA-12 powder, which has good laser sintering characteristics such as relatively low melting temperature and good mechanical properties, was chosen as the matrix polymer. To improve the interfacial bonding the GNPs were oxidized through a nitric acid treatment. The resulting nanocomposite powder was used in the dual laser sintering process.

Description of the dual laser sintering process

Kim et al. [12] has developed the dual laser sintering process to increase the efficiency of laser sintering. The dual laser system which can scan two separate regions individually should be employed in a SFF system capable of large size fabrication (e.g., 500x800x600 mm). The dual laser scanners improve the precision and efficiency of the SLS machine.

As illustrated in Fig. 1, the dual laser sintering system consists of a laminating module that supplies and transfers the powder, a heating module to preheat the powder, a nitrogen supply module to create a nitrogen atmosphere, a dual laser module that supplies the laser energy to a large area, and a control module to control the entire system.

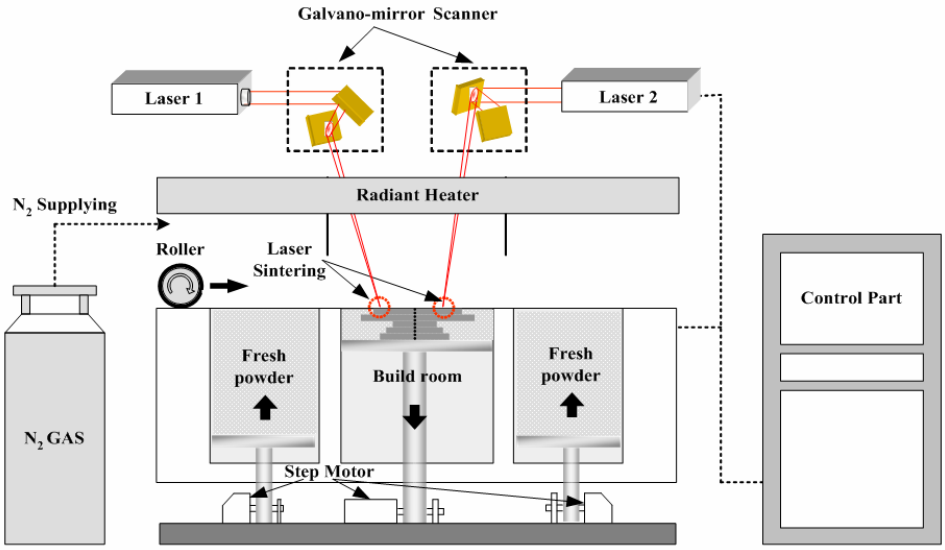


Fig. 1 Schematic diagram of SFF system

The powder is deposited layer by layer and a structure is constructed through sintering of the powder by the laser. Precise controls for powder deposition in the z axis and powder transfer in the x axis by a roller are critical to the precision of a 3D structure. The layer deposition cycle starts with the powder being moved up to the feeding room. The powder is then spread over the support by a roller in the building room. The roller mechanism has several specially designed features that influence the roughness of the powder surface and the porosity of the interior. The critical parameters include the linear and rotational speeds of the roller, the feed ratio, the roller roughness, and the deposition layer thickness.

Laser sintering of a polyamide powder in the SLS process requires a build room temperature of 150 $\pm 1\,^{o}C$ or higher to preheat the powder. The current machine utilizes a radiant heating system for preheating. The preheat temperature should be controlled precisely because any overshoot may cause curling or over-melting of the prototype.

The nitrogen supply module is used to produce a nitrogen atmosphere in the work room and for the scanner lens. The nitrogen atmosphere prevents the soot formation resulting from micro explosions that can occur during laser sintering and prevents the powder from exploding and sticking to the scanner lens. The nitrogen module maintains over 95 % nitrogen concentration in the build room during operation.

The laser head unit has been designed for the dual laser sintering. The laser module was manufactured using a 3-axis, dynamic focusing lens such that a 500×800×500 mm prototype could be fabricated using two laser beams. As shown in Fig.2, the laser module consists of a CO_2 laser engine, beam expanders, reflection mirrors, a three-axis dynamic scanner, and an x-y galvano mirror. The three-axis dynamic scanner system is employed instead of an f_θ lens especially for sintering large objects. This scanner system has the ability to prevent spot distortion by applying a focal distance function when the laser is used to irradiate large areas. This three-axis dynamic scanner contains an objective lens and a concave lens located in front of the x-y galvano mirror. The laser module with dual lasers is thus able to sinter large objects.

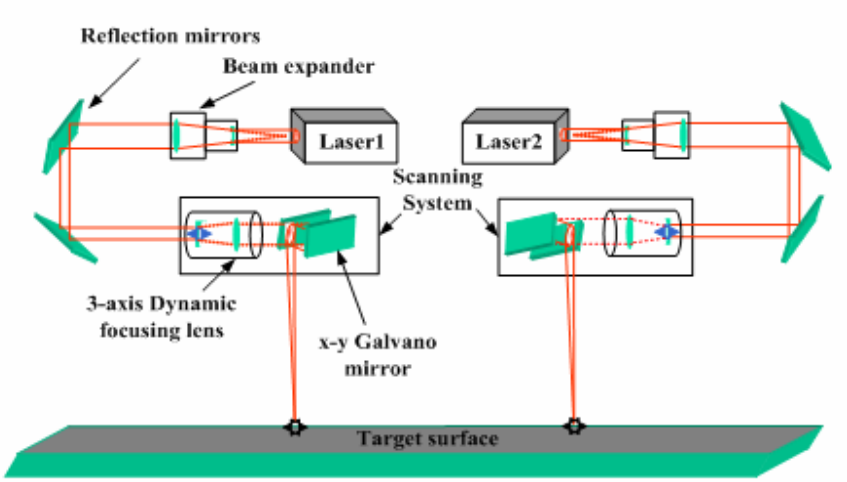


Fig. 2 Dual laser scanning system

Preparation of nanocomposite powder for the dual laser sintering process

Synthesis of polyamide-12 powder

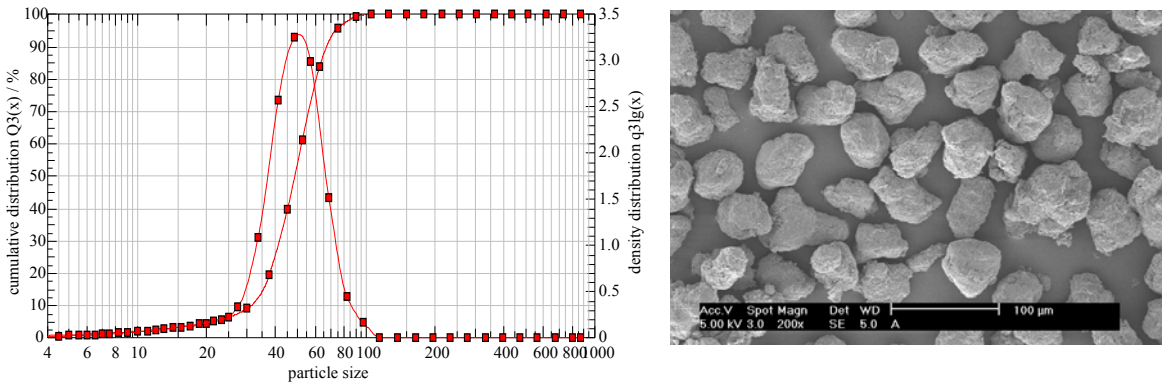
As the polymer matrix, polyamide-12 (PA-12) was chosen because of their good thermal stability and mechanical properties. Material properties of polyamide-12 are shown in Table 1.

Table 1. Material properties of polyamide-12

Density	1.01 g/cm^3
Tensile strength	35 Mpa
Elastic modulus	1100 Mpa
Melting temperature	179 ^{o}C
Glass transition temperature	115 ^{o}C

To process a large amount of the PA-12 powder that is smaller 100 μm in diameter, a wet process was employed. Compared with dry grinding process, the wet process can introduce additives to improve both the properties and manufacturability of the powder, where over 95% of particles have diameter less than 100 μm. Furthermore, the wet process can also control the particle shape.

The procedure of the wet process is as follows. PA-12 (50 g) pellets (EMS-Grivory) are dissolved in a mixture of benzyl alcohol (300 g) and Xylene (100 g) in a container where a stirrer and a condenser are installed. A 2% volume fraction of dispersing agent and stabilizer are added to the solution of PA-12. The temperature of the solution is increased to 140 ± 5^o C for 1 h while being stirred to fully dissolve PA-12. When the solution cools down to 115 ± 2^o C, PA-12 begins to crystallize in the solution. When the crystallization ends, the solution is cooled down below 50 ^{o}C to separate out the PA-12 crystals by a filter installed in a vacuum pump. The residue solvent in the container is completely evaporated in the vacuum oven. Finally the desired PA-12 powder is obtained by sieving the crystallized particles smaller than 100 μm in diameter.



(a) Particle analysis data (b) SEM image

Fig. 3 Evaluation of the PA-12 powder

Figures 3 (a) and (b) respectively show the particle analysis data and an SEM micrograph of PA-12 powder manufactured by the above procedure. The average particle diameter is 49.06 μm

and the particles have a fairly uniform size. As shown in Fig. 3 (b), particles are almost spherical, the desired shape to ensure uniform layering and precise sintering.

Functionalization of graphite nanoplatelets

Graphite nanoplatelets (GNPs) are disk-shaped graphite particles of nanometer scale thickness. GNPs are attractive as fillers because they offer high strength, stiffness, and electrical and thermal conductivities. Compared with carbon nanofibers or nanotubes, GNPs provide reinforcement in two directions and are expected to be more efficient in improving mechanical properties.

As-received GNPs (ASBURY graphite mills Inc., grade 3775) do not have optimum interfacial bonding in the polymer composites. However, the interfacial bonding can be improved by chemically or physically modifying the surface of GNPs. Recent publications show that by functionalizing the surface of GNPs via a nitric acid oxidation process one can substantially increase the tensile strength and modulus of the resulting nanocomposite. The nitric acid oxidation leaves carboxylic acid groups on the surface that chemically bonds with the epoxy [10, 11].

The procedure used for the surface functionalization of GNPs is as follows [11]. As-received GNPs were chemically treated with 67% of nitric acid, HNO_3, at 83 °C. The platelets were then rinsed with de-ionized water for 2 hours and dried in an oven at 200 °C for 24 hours to remove residual acid and water. The GNPs produced were approximately 3 μm in diameter and 25 nm in thickness as shown in Fig. 4.

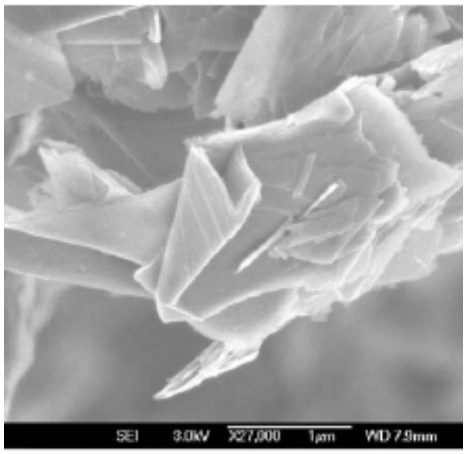
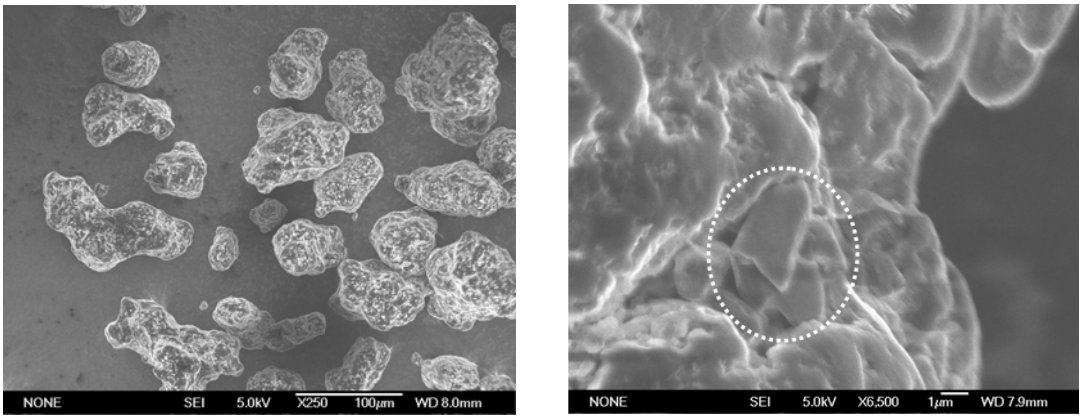


Fig. 4 SEM image of Nitric acid treated GNPs

Mixing of GNPs and PA-12 powder

GNPs were mixed with the PA-12 powder using a Thinky mixer (THINKY CORP., AR200) to achieve uniform dispersion for 1 hour and a sieve shaker (Retsch, AS200) to eliminate agglomerates. The mixer employs cup's dual high speed spinning motions that create forces of over 400 G's to accomplish powerful mixing and de-aerating simultaneously.

Figures 5 (a) and (b) show the nanocomposite powder thus produced smaller than 100 μm in diameter. Figure 5 (b) shows GNPs with sharp edges, shown inside the circle, adhering on a polymer particle. The nanocomposite powder used in the dual laser sintering process contains 0.5% weight fraction of GNPs.



(a) Nanocomposite particles (b) GNP on a polymer particle

Fig. 5 SEM images of the nanocomposite powder

Evaluation of the nanocomposite powder via the laser sintering process

To evaluate the prepared nanocomposite powder, layering and laser sintering tests were carried out in the dual laser sintering system. Based on the previous experiments, the process parameters were set to be as shown in Table 2.

Table 2. Process parameters for the laser sintering test

Layering parameters	Roller feed rate	110 mm/s
	Roller rotary speed	100 mm/s
Sintering parameters	Temp. in the build room	135 ^{o}C
	Temp. in the feed room	110 ^{o}C
	Interval of laser scanning	0.3 mm
	Scanning speed	3.0 m/s
	Laser power	35 W

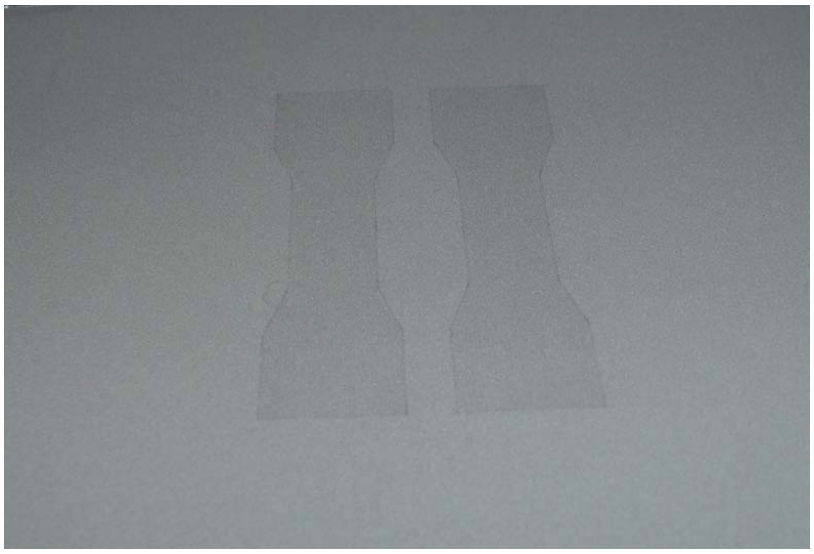


Fig. 6 Sintering of the nanocomposite in the dual laser sintering

Before laser sintering begins, the powder was predried at 110 ^{o}C for 4 hours to avoid the agglomeration by moisture. In the current test, the powder was sintered in the shape of a tensile specimen in one layer. Figure 6 shows no sign of agglomeration without irregular melting. Although the result is preliminary, the synthesized nanocomposite powder is thus believed to have good processability in the SLS process. Work is continuing to demonstrate that the nanocomposite powder can be used to fabricate products with better mechanical and electrical properties.

Conclusions

A nanocomposite powder based on graphite nanoplatelets (GNPs) and PA-12 particles has been synthesized for use in the selective laser sintering process. To improve interfacial bonding, the GNPs were functionalized by a nitric acid oxidation treatment. The two types of particles were mixed in a rotary Thinky mixer. The resulting nanocomposite powder indicates uniform mixing without agglomerations. The preliminary result on laser sintering experiment indicates the suitability of the nanocomposite powder for use in the laser sintering process. Efforts are underway to confirm better mechanical properties expected of the prototypes made of the nanocomposite powder.

Acknowledgements

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