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Selective laser sintering of hydroxyapatite reinforced polyethylene composites for bioactive implants and tissue scaffold development

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Abstract

Selective laser sintering (SLS) has been investigated for the production of bioactive implants and tissue scaffolds using hydroxyapatite (HA) reinforced polyethylene (HDPE) composites with the aim of achieving the rapid manufacturing of customised implants. Single layer and multilayer block specimens made of HA-HDPE composites with 30 vol% and 40 vol% HA were sintered successfully using a CO₂ laser sintering system. Laser power and scanning speed had a significant effect on the sintering behaviour. The degree of particle fusion and porosity were influenced by the laser processing parameters, hence control can be attained by varying these parameters. Moreover, the SLS processing allowed exposure of HA particles on the surface of the composites and thereby should provide bioactive products. Pores existed in the SLS fabricated composite parts and at certain processing parameters a significant fraction of the pores were within the optimal sizes for tissue regeneration. The results indicate that the SLS technique has the potential not only to fabricate HA-HDPE composite products, but also produce appropriate features for their application as bioactive implants and tissue scaffolds.

Keywords: Selective Laser Sintering, hydroxyapatite, polyethylene, bioactive implants, tissue scaffolds

1. INTRODUCTION

Hydroxyapatite (HA) is a ceramic to which bone bonds [1]. When combined at high filler levels with a binding polymer, the material forms a bioactive composite. HA particulate reinforced high density polyethylene (HDPE) composites (HA-HDPE) were developed by Bonfield and co-workers [2,3] and have been used clinically for bone augmentation for over 15 years [4]. The clinically used grade of HA-HDPE composite, known commercially as HAPEXTM, is an analogue material designed to replace bone. This material has been used for orbital floor implants for patients suffering from post-enucleation socket syndrome and in middle ear implants [5]. Presently, these implants are shaped by conventional techniques such as moulding and machining. These indirect techniques require more process steps, are less automated, have high material waste for machining techniques, and require individual tooling for one-off jobs for moulding technique. These conventional techniques also impose geometrical restrictions on the shapes that may be produced, i.e. undercut and re-entrant shapes are difficult to produce from moulds, the shape of articles produced by cutting techniques are restricted by the movements required by the cutting tool, and neither technique can produce internal structures. The limitations of conventional manufacturing methods therefore restrict the production and application of HA-HDPE.

Selective laser sintering (SLS) is an additive manufacturing process, which belongs to a family of techniques known as layer manufacturing (LM). The use of layer manufacturing allows physical parts to be created immediately, directly and automatically from a 3D representation known as a 3D computer-aided-designed [CAD] model, like the information obtained from a computed tomography (CT) or magnetic resonance imaging (MRI) scan. Layer manufacturing was used for rapid prototyping (RP) and has emerged as a key enabling technology for rapid manufacturing (RM) to produce directly useable products or parts. RP produces parts for prototyping or tooling purposes, while RM pursues the production of objects for long-term use. RM facilitates total customisation of products and one individual product to be manufactured as easily as millions of products (i.e. mass production). Therefore, layer based RM approach permits extremely complex shapes to be produced and enables the economically viable production of implants that are customised with respect to size and functionality for individual patients. Customised implants give the potential to improve bone defect repair methods and enhance the longevity of the implants by providing a more secure fit due to exact geometry [6]. For SLS fabrication of polymer/ceramic composite powders, the polymer serves as a binder which is activated at relatively low temperature, while the ceramic serves as a structural and/or a functional material. During the SLS process, powders are subjected to low compaction forces and thus fabricated objects are inherently porous, a key property requirement for some in vivo implantation devices. The nature and extent of this interconnected porosity may be tailored and controlled to meet application criteria through material selection, physical design and processing parameters. Furthermore, SLS has the potential capability to produce functionally graded materials

(FGM) which exhibit spatially inhomogeneous properties and microstructures and allows for the positional variation of physical properties and characteristics. This functional grading would allow new products of unique and customised characteristics to be produced. Functional grading is possible in SLS by varying the composition of two or more powdered materials across the surface, interface or bulk of the material during the build sequences. Possible applications include encouraging locational bone ingrowth by greater density of HA and providing different mechanical properties in the areas of high load bearing or wear by the use of different polymers.

To date, medical applications of SLS have primarily concerned the production of physical models of human anatomy for surgical planning, training and design of customised implants. Berry et al. [7] built SLS models of two skulls and a normal femur using nylon with the dimensions being in good agreement with the CT data. However, commercially available SLS materials are not biocompatible and cannot be used for in vivo applications. Rimell and Marquis [8] demonstrated that SLS has the potential to fabricate linear continuous ultra high molecular weight polyethylene (UHMWPE) solid bodies for clinical application by using a non-commercial SLS machine without preheating the powders. During the laser processing material shrinkage caused problems in forming sheet-like structures and degradation of UHMWPE was unavoidable. Scaffolds with periodic cellular and biomimetic architectures were designed and fabricated by SLS by Das et al. [9] using Nylon-6. Williams et al. [10] fabricated porous polycaprolactone (PCL), a bioresorbable polymer, scaffolds with the potential application for bone and cartilage repair by SLS. The early application of SLS for composite implant fabrication using HA and other calcium phosphate materials [11,12] involved coating of the HA powder with a secondary polymeric binder, poly(methylmethacrylate) (PMMA). Problems were encountered by the use of organic solvents (diluted methanol) in coating and additional post debinding and sintering. Tan et al. [13] and Chua et al. [14] have investigated scaffolds produced with the physically blended HA/polyetheretherketone (PEEK) and HA/polyvinyl alcohol (PVA) composites using a commercial SLS system.

This work investigated the potential of SLS to fabricate parts using 30 vol% and 40 vol% HA-HDPE composites and analysed the effects of laser power and scanning speed on the sintered parts, the features of pores and the HA particle morphology.

2. METHODOLOGY

2.1 HDPE and HA raw materials

The HDPE (Rigidex HM4560XP) was supplied in pellet form by BP Chemicals Ltd. Synthetic HA particles (P218R, Plasma Biotal Ltd., UK) were used as the filler material. The particles had a median size ($d_{0.5}$) of 3.80 µm and a specific surface area of 13.54 m²g⁻¹, while the theoretical density was

3160 kg m⁻³ [15]. The melting temperature of the HA-HDPE composites was determined as 136 °C by thermal analysis using differential scanning calorimetry (DSC) (DSC 60, Shimadzu, Japan).

2.2 Production of HA and HDPE composite powders

As described in detail by Wang *et al* [16], the HA and HDPE powders were blended to produce mixtures with 30 vol% and 40 vol% HA. These mixtures were compounded in a twin screw extruder (Betol BTS40L, Betol, UK) to produce the HA-HDPE composites. The extruded composites were subsequently pelletized in a Betol pelletizer. The pelletized HA-HDPE composites were powderized in a Retsch ultra centrifugal mill (Retsch, German) using a sieve of 0.250 mm aperture size. Liquid nitrogen was used as a coolant to prevent temperature increases and to embrittle its material during milling. It should be noted that the compounded composites prepared in this study are matrix composites containing both the binder and structural material, not a distinct component mixture in which the binder is separate from the structure material. The sintering of matrix composites can avoid the segregation of the different elements that can occur with mixed element blends.

2.3 SLS Systems and Processing

Instead of using a commercial SLS system, an experimental SLS system was developed by incorporating an "experimental powder bed chamber" and a CO₂ laser system (Synrad Ltd, USA) which has an average output power between 0.2 and 10 W and can be driven at various can velocities between 0.2 and 10,000 mm s⁻¹. This system permits the economical use of the expensive material and greater variation of laser sintering parameters than commercial systems. A laser beam with a wavelength of 10.6 µm was focused to a spot size of 193 µm at a focal length of 491 mm and used to scan the powders. As shown in Figure 1, the "experimental powder bed chamber" simulates the commercial SLS processing chamber, but has a smaller powder bed volume (103 mm diameter cylinder for both operation and feed powder bed). During sintering, nitrogen gas filled the chamber to create an inert atmosphere and the oxygen content was maintained below 5%. One heater band enclosed both the feed and build cylinders and one overhead heater installed at the top of chamber preheated the powders to 110 °C. The dimension of the sintered specimens was 4 × 23 mm and laser scan space was 63 µm. To begin a detailed investigation, single layer specimens were built over a wide range of laser parameters to analyse the effects of laser power and scanning speed on the sintered HA-HDPE composite. Then, optimum parameters were used to build specimen blocks of 5 layers with a layer thickness of 0.4 mm.

2.3 Characterisation

The height of sintered single layer specimens was measured by Vernier calipers. The mean value of three measurements was recorded. The particles of HA-HDPE composite powders, surface morphologies of sintered single layers and the cross-section of scalpel cut sintered blocks were

examined using scanning electron microscope (SEM) (LEO 440, UK). All samples were sputter coated with gold prior to imaging.

3. RESULTS AND DISCUSSION

3.1 Microscopic examination of HA-HDPE composite powders (non-sintered)

Figure 2 shows the HA-HDPE composite particles of 30 vol% and 40 vol% HA. It can be seen that most of its particles were of irregular shape and demonstrated a wide range of particle sizes. Some elongated filaments are present as well as amongst on the particles. There are no substantial differences in the shape between the composite particles of 30 vol% HA and those of 40 vol% HA.

3.2 Effect of SLS parameters on the sintering of HA-HDPE composites

3.2.1 Visual effects of laser scanning speed and laser power

The quality of SLS fabricated parts are influenced by many factors such as materials properties, powder bed characteristics and process parameters. Of the process parameters, laser power and scanning speed were found to be the two most influential parameters. Williams and Dechard [17] studied the sintering height/depth of powders following single pass laser scanning and showed that there is a minimum power necessary to induce sintering and a maximum scanning speed above which sintering does not occur. The sintering height to which the laser is able to sinter determines the maximum layer thickness that can be used to construct a part. In order to investigate the effect of the laser scanning speed, the speed was varied from 300 mm s⁻¹ to 4800 mm s⁻¹, while the laser power was fixed at 3.6 W and 7.2 W. As is shown in Figure 3, the scanning speed had a significant effect on the height of single sintered layer and decreased with increasing laser scanning speed. This result may be because at lower scanning speed a relatively longer interaction time leads to greater energy absorption and more time for particle interaction and fusion. The surface of the single layer sintered at the scanning speed of 300 and 600 mm s⁻¹ changed colour from white (colour of HA-HDPE powders) to dark brown colour, indicating that the HDPE on the composite surface had degraded. At low scanning speeds, the composite powders experienced longer interaction time which would result in the degradation of the composite powders even in the low oxygen environment. For the high laser scanning speed of 4800 mm s⁻¹, no single layer could be sintered under 3.6 W and the single layer sintered under 7.2 W was fragile. Due to the short interaction time at the high scanning speed, the particles did not have enough time to interact and fuse. Therefore, these initial tests demonstrated that it was better to use a relatively moderate scanning speed to sinter HA-HDPE composites.

The laser scanning speed of 1200 mm s⁻¹ was chosen to investigate the effect of laser power over a wider power range, owing to the success of layers being sintered at this speed at both 3.6 W and 7.2 W. As shown in Figure 4, the height of a single layer increased with increasing laser power. At the

same scanning speed, higher laser power lead to more energy absorbed in the composite powders and thus a higher degree of sintering. At a laser power of 1.2 W, the particles were not well sintered and a continuous single layer was not produced. At a laser power of 2.4 W, a continuous single layer was produced, but resulting in a fragile specimen. When the laser power was above 3.6 W, the single sintered layers were strong enough to be handled. At laser powers between 3.6 W and 6.0 W, the colour of the single layer remained similar to that of original composite powders. However, when the laser power was increased to the 7.2 W, the colour became brown which was more pronounced with increasing laser power, indicating that the powders are likely to have degraded during processing at the higher laser power. A brown colour has also been observed in previous work on SLS sintered PVA at differing processing parameters [14].

3.2.2 Surface morphology of single sintered layers

Figure 5 shows the surfaces of the single sintered specimens built with different power densities at scanning speed of 1200 mm s⁻¹. The typical surface morphologies of sintered single layers are described in Table 1. Generally, the fusion of particles increased with increasing power. The more energy was induced to the powder, the greater particle fusion. Individual particles and a few incidences of contact necking were observed at a power of less than 4.8 W, conversely, complete fusion made the boundaries of particles indistinguishable at the power above 7.2 W. Pores occurred in the layers and the amount of the pores decreased as the degree of particle fusion increased. At power of 2.4 W, a number of pores were observed of 200 to 400 µm across. When the laser power was increased to 6.0 W, the particle boundaries fused together and pore size considerably decreased, implying that the particles would have experienced melting and the particles coalesced during the laser sintering. However, large voids, which may have been caused by shrinkage accompanied with the fusion of neighbouring particle,s were observed at some areas of the layers sintered at high powers, such as 7.2 W, as shown in Figure 5 (e). Some large HA particles were exposed on the surface of the layer sintered at high power such as 9.6 W, revealing that the HDPE would have been vaporised partially during the processing leaving HA particles on the surface. It was found by Rimell and Marquis [8] that the laser sintering of UHMWPE at high laser power resulted in volatilization due to a major physical breakdown of the polymer chains to a lower weight material, of which some vaporizes.

That size and number of the pores in the composite layer varied with the laser power and that generally the porosity decreased with the increasing laser power implies that the porosity of HA-HDPE composite parts could be controlled by the energy imparted on the powder surface. A number of other parameters such as scanning speed, scan space, scan pattern, beam spot size and layer thickness may also be methods of controlling this feature and extent of the pores in HA-HDPE as these parameters would also influence the energy imparted on the powder surface. Such SLS

processing parameters were described by the Leong *et al.* [18] as a potential means to fabricate porous polymeric matrix drug devices. Determining the effect of the other parameters is the subject of further work.

3.3 The morphology of HA particles in the composite following laser sintering

For HA reinforced HDPE composites, the HDPE provides a binding matrix and the HA provides the bioactivity of the composites. Hence, it is essential to expose HA materials on the surface of the sintered products to allow the biological tissue to interact with them when the composite products are used as bioactive implants or tissue scaffolds. Figure 6 shows the morphology of HA particles on the surface of sintered composite particles. At a laser power of 2.4 W, many small particles were observed on the surface of the sintered products, but most of them seemed to be entrapped or embedded in sintered surface (Figure 6 (a)). With the laser power increased to 3.6 W, some HA particles appeared on the surface (Figure 6 (b)). A large HA particle with dimension of approximately 20 µm was exposed. It is believed that laser sintering resulted in the partial surface melting of the composite matrix with HA particles exposed at the surface. At 4.8 W, a lot of HA particles were observed on the surface (Figure 6 (c)), the surface of the composite has melted completely. At 9.6 W, large amounts of small and numerous larger HA particles are visible (Figure 6 (d)), indicating that the HDPE may have degraded and vaporised exposing the HA particles. Therefore, it has been shown that the SLS can expose the HA particles on the sintered products. In the SLS process, the high power intensity focus provided by a small laser beam spot and overlapping of the beam tracks on the surface could result in local effects on the substrate material, dependent on the laser power intensity. At relative low power, the effect induced by the laser may occur mainly on the surface of the particles or cause partially melting of the matrixes. With increased laser power, the local heat induced by the laser could cause complete melting and generate an effect on the whole of the composite particles. When the laser power is too high, it could result in the degradation or vaporisation of the polymer (HDPE). A previous study by Rimell and Marquis [8] showed that ultra high molecular weight polyethylene (UHMWPE) underwent degradation following the SLS process. However, the nature of the degradation of the UHMWPE is comparable to that produced by irradiation sterilization and may not degrade the properties to an unacceptable level for some applications. In addition, the air trapped inside the particles and between the particles would be released during the evaporation and would undergo a high temperature exothermic reaction resulting in local burn sites, this could result in the vaporisation of the HDPE and expose the HA particles on the surface.

As Kasemo and Lausmaa [19], among others, have described, biological tissues interact mainly with the outermost atomic layers of an implant. The ideal implant should present a surface conductive to bone growth or that will induce osseointegration that provide a direct structural and functional connection between ordered living bone and the surface of a load-carrying implant, regardless of

implantation site, bone quantity, bone quality, etc. The surface of HA is highly bioactive, and thus can stimulate bone to bond with it, thus can be said to be osseoconductive [20]. HA particles are exposed on the surface of SLS sintered articles and thus may be able to provide the functions of bioactivity and osseoconductivity. Further analysis is needed to confirm these functions. The large degree of HA exposure with the use of compounded matrix composite materials is in contrast to the results of a study using physically blended materials. A previous study of SLS sintering of PEEK-HA composite blends by Tan *et al.* [13] resulted in the HA particles being only partially exposed. In addition, the HA particles used in this study had a median size of 3.80 µm and extensive exposure of such size particles provided the large surface areas to facilitate osseoconductive functions. For the blended HA composites study by Tan *et al.* [13], the size of HA particles was 10 to 50 µm and thereby provided lower surface areas exposure compared with that provided by the smaller HA particles.

3.4 The effects of HA content on the laser sintering of HA-HDPE

As shown in Figure 7, composites with 30 vol% HA produced a thicker layer than 40 vol% HA for the same processing parameters. At 2.4 W, composite powders with 30 vol% HA were successfully sintered, while composite powders with 40 vol% HA were not sintered. This finding indicates that the lower HDPE content of the composite powder (higher HA content) resulted in a lesser sintering due to lower binder content. Figure 8 shows the surface morphology of a single sintered layer with 40 vol% HA content at laser powers of 3.6 W and 9.6 W. Similar to the sintered layer with composite powders of 30 vol% HA as shown in Figure 5, the sintered layer with the powders of 40 vol% HA exhibited more pores at low laser power (Figure 8 (a)) and became denser at high laser power (Figure 8 (b)).

3.5 Specimen building and cross-section analysis

A scanning speed of 1200 mm s⁻¹, and laser powers of 3.6 W, 4.8 W, 7.2W, 9.6 W were selected to build block specimens with 5 layers with a 0.4 mm layer thickness. Under all these parameters, the blocks were built with varying degrees of success using powders of both 30 vol% and 40 vol% HA content. At 3.6 W and 4.8 W, the colour of the block remained white in colour the same as thes original powder. At 7.2 W and 9.6 W, the colour of the sample became darker indicating some degradation had occurred. However, the layers still bonded. Figure 9 (a) and (b) shows cross-sections of the 30 vol% HA laser sintered block. A number of pores were observed from the cross-section of the block, indicating that pores existed inside of the block and might be interconnected.

At a laser power of 4.8 W, the block with 40 vol% HA could be built and pores existed within the block (Figure 9 (c)), however, delamination was noted between the layers as shown in Figure 9 (d). The delamination was also observed in the blocks with the composite of 40 vol% HA powder sintered at other power densities. This delamination suggests that the fusion between the layers with composite powders of 40 vol% HA was not as good as that with 30 vol% HA due to lower HDPE content. The

fusion between the laser sintered layers depends on the depth of the laser sintered layer and the layer thickness of the deposited loose powder. The depth of the laser sintered layer should be higher than the layer thickness of the deposited loose powder to allow an overlap between the newly sintered layer and the previous layer, thereby building a fusion interface between the layers. As shown in the Figure 7, the HA content influences the height of the laser sintered layer. The same laser power intensity under the same processing parameters generates a thicker layer of 30 vol% HA composite than 40 vol% HA composite, showing that the composition of the composite and the content of the binder play a role on the penetrating depth of laser beam and the height of the laser sintered layer. To provide better fusion between the layers and prevent delamination occurring in the sintered composites with 40 vol% HA, high laser power could have been used to provide enough energy to penetrate deeper than the layer thickness and remelt the previous layer and thus allow enough fusion at the interface between the new layer and the previous layer.

The pores observed from both surface and cross-section images confirmed that the SLS fabricated HA-HDPE parts could be porous, which may enable their use as tissue scaffolds. Ideally, scaffolds must possess an interconnected open-pore geometry and microstructure that permits cell in-growth and reorganization during the *in vitro* phase and provides the necessary space for neovascularization from the surrounding tissues in vivo. A highly porous microstructure and interconnected porous network are critical in ensuring spatially uniform cell distribution, cell survival, proliferation and migration. The scaffold's porosity and degree of pore interconnectivity directly affect the diffusion of physiological nutrients and gases to and the removal of metabolic waste and by-products from cells that have penetrated the scaffolds [21,22]. A tissue scaffold is required to provide optimal pore sizes and a suitable microenvironment for biological tissue. In regenerating bone tissue in vitro, bone cells are sensitive to the gross morphology of a material and have a preferred pore size of 200 - 400 μm for encouraging migration, attachment and proliferation. This size range may be because the curvature of these pores provides optimum compression and tension on the cell's mechanoreceptors [23]. The surface microscopy images (Figure 5) and cross-section microscopy images (Figure 9) illustrate that the SLS fabricated HA-HDPE composite layers under certain processing parameters had considerable numbers of pores within the optimal size for bone regeneration. It is speculated that the pores inside the SLS fabricated parts were not enclosed at certain processing parameters under which the particles were partially fused and thus the pores between them would be interconnected. Future work will be conducted to characterise the open porosity and interconnectivity and optimise the SLS processing to obtain the suitable porosity by adjusting processing parameters or the characteristics of powders to produce tissue scaffolds.

4. CONCLUSIONS

The results presented in this work show that SLS is not only capable of building HA-HDPE products, but also brings about necessary features for their application as bioactive implants and tissue scaffolds.

The laser power and scanning speed were found to have a significant effect on the sintering of HA-HDPE composites and influence the degree of fusion between the particles and the porosity existing in the composite layers. Control over the structure and its porosity could be achieved by varying processing parameters. Besides laser power and scanning speed, a number of other processing parameters can also be adjusted and may further control the feature and extent of the pores and therefore would have great potential to optimise pore size in HA-HDPE for tissue scaffolds.

In addition, SLS enabled a good number of HA particles to be exposed on the surface of HA-HDPE composites and may provide a higher level of bioactivity to the products. The compounded HA-HDPE particles used in this study allow the HA embedded on the composite surface to be exposed following the surface melting induced by laser irradiation. The exposure of the HA particles would provide bioactivity and osseoconductivity to the SLS fabricated implants or tissue scaffolds. Moreover, the HA particles exposed are generally small (median size of $3.80~\mu m$) and provide large bioactive surface areas.

Under the same processing parameters, a lesser degree of sintering was observed for less HDPE (higher HA content) in the composite powders due to the lower binder content. Since HA plays the bioactive function in the composite parts, this could compromise the effects of the HA content on the sintering and its functions of bioactivity.

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Figure 1. Photograph of the experimental chamber showing the build and feed cylinders and feed mechanism



Figure 2. SEM micrograph of (a) 30 vol% HA content, (b) 40 vol% HA content composite powders $(marker\ bars=100\ \mu m)$

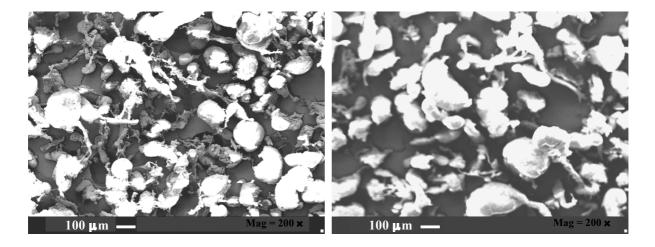


Figure 3. The effect of laser scanning speed on the height of sintered single layers at 3.6 and 7.2 W power density (30 vol% HA composite powder)

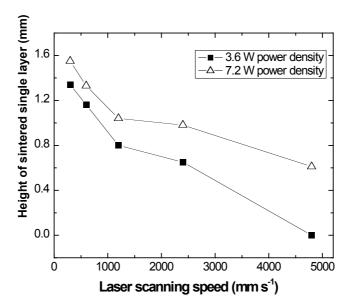


Figure 4. The effect of laser power on the height of sintered single layers (30 vol% HA composite powder)

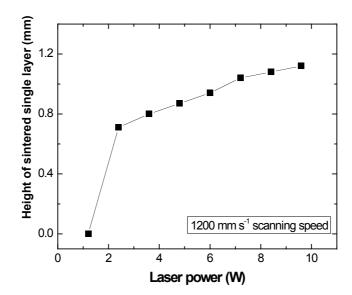


Figure 5. SEM micrograph of the surface of a sintered single layer with 30 vol% HA composite and laser power of (a) 2.4 W, (b) 3.6W, (c) 4.8W, (d) 6.0W, (f) 7.2W and (e) 9.6 W at the scanning speed of 1200 mm s⁻¹ (marker bars = $100 \mu m$).

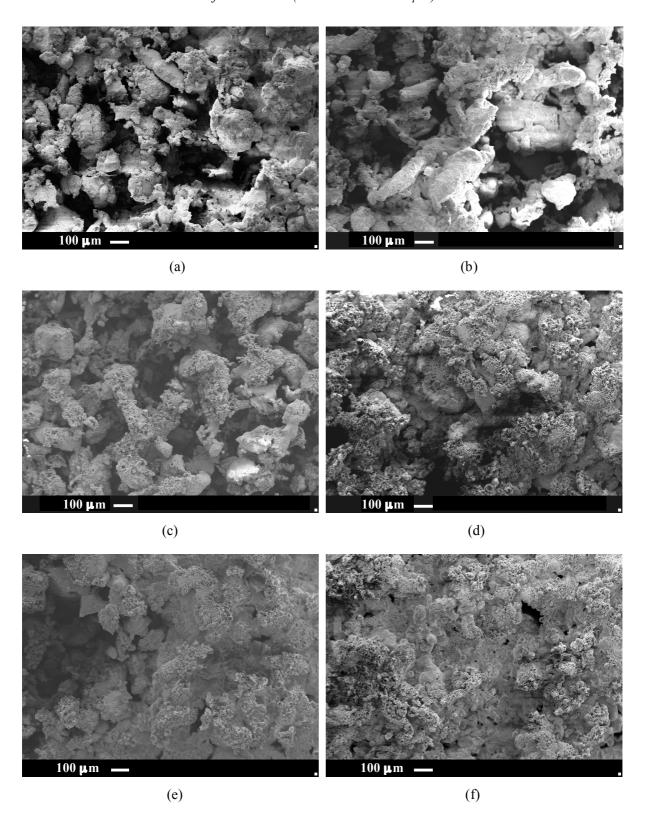


Figure 6. SEM micrograph of the morphology of HA on the surface of sintered particles with 30 vol% HA composite and laser power of (a) 2.4 W, (b) 3.6W, (c) 4.8W, (d) 9.6 W at the scanning speed of 1200 mm s^{-1} (marker bars = 20 μ m)

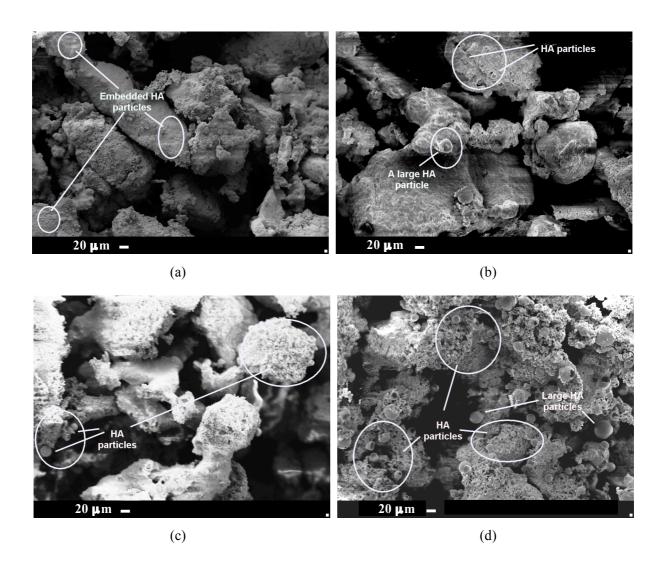


Figure 7. The effect of HA content on the height of sintered single layers at laser scanning speed of 1200 mm s^{-1}

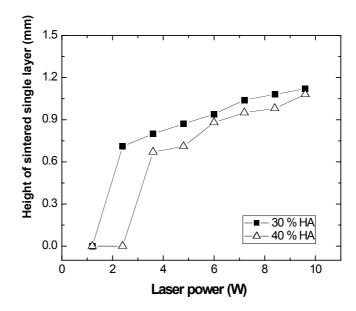


Figure 8. SEM micrograph of sintered single layer surfaces with 40 vol% HA ratio composite and laser power of (a) 3.6W and (b) 9.6 W at scanning speed of 1200 mm s⁻¹ (marker bars = $100 \mu m$).

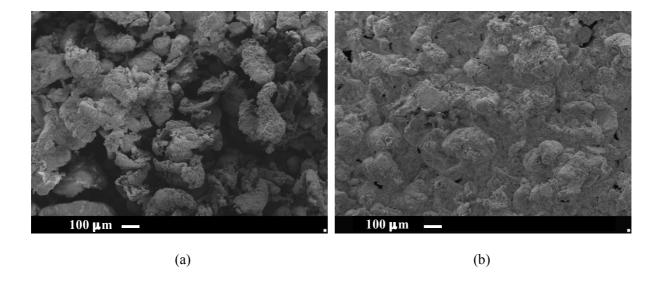


Figure 9. SEM micrograph of the cross-section of sintered blocks (a) at 3.6W and (b) at 4.8W power with 30 vol% HA composite, (c) at 4.8 W power with 40 vol% HA composite and (d) delaminated area in this place at 4.8 W power with 40 vol% HA composite with the scanning speed of 1200 mm s⁻¹ (marker bars = 100 µm).

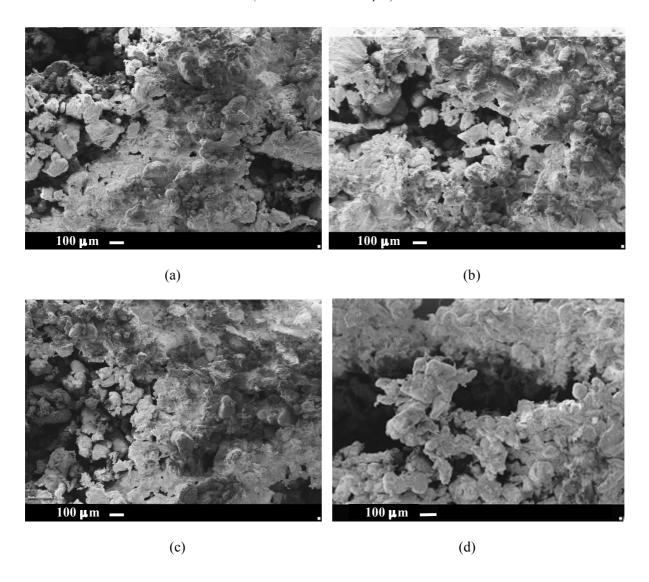


Table 1. Descriptions of Surface Morphology of single sintered HA-HDPE layers under different laser power at scanning speed of 1200 mm s $^{-1}$

Laser power (W)	Figures	Surface morphology of single sintered layers
1.2		No layer was sintered
2.4	Figure 5 (a)	Individual particles could be identified; particles fused partially; a few incidences of contact necking were observed between the particles; a large number of pores were seen between the particles; size of these pores were irregular and varied from small to as large as 200 to 400 µm.
3.6	Figure 5 (b)	Some individual particles could be identified; most of particles fused with other particles and partial boundaries between the particles were not distinguishable; large number of pores existed.
4.8	Figure 5 (c)	Some individual particles could be identified; most of particles fused and inter-necked with each other; large amounts of the boundaries between the particles were fused; pores presented between the particles and inter-necking.
6.0	Figure 5 (d)	Few individual particles could be identified; most of particles fused together; a few pores were observed.
7.2	Figure 5 (e)	Individual particles could not be identified; all particles fused together; boundaries between most particles became undistinguishable; large voids were observed.
8.4		Similar to that observed for a power of 7.2 W.
9.6	Figure 5 (f)	Individual particles could not be identified; all particles fused together; boundaries between particles became indistinguishable.