Feasibility of Waste-Derived Hydroxyapatite Mixed with Ultra High Molecular Weight Polyethylene Composites for Fused Deposition Modeling Process

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A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master of Mechanical Engineering

Faculty of Mechanical and Manufacturing Engineering
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SEPTEMBER 2018

Special dedication to my beloved parents, wife and family….

Thanks for the love, support and memories

ACKNOWLEDGEMENT

First and foremost, I am thankful to The Almighty God for establishing yours truly to bring this study to a completion.

I wish to express my sincere appreciations to my supervisor, Prof. Madya Dr Mohd Halim Irwan Bin Ibrahim for his generous guidance and introduced me to the fantastic world of biomaterials and build my interest throughout the study. His suggestion and evaluation help me a lot during the study to develop the understandable effort.

I take this opportunity to record my sincere gratitude to all faculty member, especially the technicians involved namely En. Anuar, En. Tarmizi, En. Shahrul and En.Fazlanuddin, technicians of Material Science Lab, Polymer and Ceramic Lab from the Faculty of Mechanical and Manufacturing Engineering, University Tun Hussein Onn Malaysia. I am really grateful and appreciative for their proficient, detailed and patient instruction to me. Special thanks and give appreciation to the following person who generously contributed in helping me to complete the study especially Najwa binti Mustafa, Thoufelli bin Taufek and Nurmina Abdullah.

Finally, I'd like to give my warmest appreciation to my parents for their unceasing support encouragement and inspiration during the study and completion of this thesis. Last but not least, my friends that give ideas, support and cooperation in order to complete the study.

ABSTRACT

In this study, feasibility of waste-derived hydroxyapatite (HAp) reinforced UHMWPE composites for Fused Deposition Modeling (FDM) process was investigated. Compared to the commercial HAp, derived from natural resources such as corals, fish bone and eggshells have been converted into HAp and show the similarity with the commercial HAp. Ca/P ratio was so important to human body because Ca influence growth of human bones and P play a role in immune system activation. This research has used waste eggshell has been used to synthesize HAp by using hydrothermal synthesis. The Ca/P ratio was investigated by using SEM/EDS and XRD test. By using these test, it revealed Ca/P ratio of waste-derived HAp has shown 1.69 approximately with the standard Ca/P ratio (1.67). HAp/UHMWPE composites formulation samples were prepared by mixed between HAp and UHMWPE using Brabender Mixer. HAp/UHMWPE composite formulation samples were characterized by their weight percentage. The feasibility of each HAp/UHMWPE composite samples has been studied by their morphology, thermal and rheology properties by using SEM/EDS, TGA/DSC and Rheology test. Formulation sample U50H50 with 50 wt.% of HAp has shown the homogenous mixture, 1.69 Ca/P ratio, lowest melting point and good pseudo-plastic behavior compared to other formulation samples. Therefore, this formulation samples has been used in single screw extruder to fabricate diameter size of 1.75±0.05 mm filament wire for FDM process. DOE has been developed by using Taguchi method with the parameter controlled were die temperature and screw frequency. The optimum parameter setting to produce the diameter of 1.75±0.05 mm filament wire was successfully found at screw frequency of 2.5 Hz and die temperature of 190 ºC. The characteristic of the FDM process shows the samples with optimum dimensional accuracy and relative density was found at 245 ºC of temperature nozzle and 130 ºC of temperature platform. This result shown Hap/UHMWPE composite has potential to become material filament wire feedstock for FDM process.

ABSTRAK

Dalam kajian ini, perlaksanaan HAp dari penguraian bahan buangan diperkuatkan dengan UHMWPE komposit untuk proses pemodelan pemendapan bersatu (FDM) telah dikaji. Dibandingkan dengan HAp komersial, penguraian bahan semulajadi seperti batu karang, tulang ikan dan kulit telur telah diubah menjadi HAp menunjukkan persamaan dengan HAp komersial. Bagi kajian ini, sisa kulit telur telah digunakan untuk mensintesis HAp dengan menggunakan hidroterma sintesis. Nisbah Ca/P disiasat dengan menggunakan ujian SEM/EDS dan XRD. Dengan menggunakan ujian ini, ia menunjukkan nisbah Ca /P yang diperolehi dari HAp telah menunjukkan 1.69 hampir menyamai dengan nisbah standard Ca/P (1.67). Sampel formulasi HAp/UHMWPE disediakan dengan campuran antara HAp dan UHMWPE di dalam Brabender Mixer. Sampel formulasi komposit HAp/UHMWPE dicirikan oleh peratusan berat badan kedua-dua bahan tersebut. Pencirian sampel komposit HAp/UHMWPE telah dikaji oleh sifat morfologi, terma dan reologi dengan menggunakan ujian SEM/EDS, TGA/DSC dan rheologi. Sampel sampel U50H50 dengan 50% berat HAp telah menunjukkan campuran homogen, nisbah 1.69 Ca/P, takat lebur yang terendah dan perilaku pseudo-plastik yang baik berbanding sampel formulasi yang lain. Oleh itu, sampel perumusan ini telah digunakan dalam mesin penyemperitan skru tunggal untuk menghasilkan wayar filament berdiameter 1.75 + 0.05 mm untuk proses FDM. DOE telah dibangunkan dengan menggunakan kaedah Taguchi dengan parameter yang dikawal adalah suhu acuan dan kelajuan skru. Pengaturan parameter yang optimum untuk menghasilkan wayar filamen berdiameter 1.75 + 0.05 mm berjaya dijumpai pada kelajuan skru 2.5 Hz dan suhu acuan 190 ºC. Ciri-ciri proses FDM menunjukkan sampel dengan ketepatan dimensi optimum dan ketumpatan relatif didapati pada suhu muncung 245 ºC dan suhu platform 130 ºC. Hasil keputusan menunjukkan Hap/UHMWPE komposit berpotensi menjadi wayar filamen untuk proses FDM.

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LIST OF SYMBOLS AND ABBREVIATIONS

AM	- Additive Manufacturing
ABS	- Acrylonitrile Butadiene Styrene
PC	- Polycarbonate
PS	- Polystyrene
UHMWPE	- Ultra High Molecular Weight Polyethylene
HAp	- Hydroxyapatite
Ca/P	- Calcium to Phosphate
SL	- Stereolithography
SLS	- Selective Laser Sintering
3DP	- 3D printing
CAD	- Computer Aided Design
ASTM	- American Society for Testing and Materials
HDPE	- High Density Polyethylene
SEM	- Scanning Electron Microscope
EDS	- Energy Dispersive Spectroscopy
XRD	- X-Ray Powder Diffraction
TGA	- Thermogravimetric Analysis
DSC	- Differential Scanning Calorimetry
FDM	- Fused Deposition Modeling

CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent years, additive manufacturing (AM) has been used extensively in biomedical applications such as bone implantation and dental application. AM processes have shown significant potential for developing patient-specific scaffolds with different structural properties by using several kinds of materials. With the AM processes, it can make a porous scaffold to make an augment in tissue regeneration and bone repair. AM normally refers to techniques that have the ability to fabricate physical objects automatically through continual build-up or creation of solid material through additive manufacturing. Applications of AM in tissue engineering offer the pledge of growing these regenerative tissues and functional organs. AM has been effective in integrating structural architecture and assimilation of hormones in scaffolds. In these recent years, there are many AM technologies and techniques that have been developed due to their extensive uses in many industries. One of AM technologies was fused deposition modelling (FDM) process by layered deposition of polymer plastic on the platform in three-dimensional objects (Kalita, 2010). Application of FDM in biomedical applications has shown its potential compared to the conventional manufacturing process, where conventional manufacturing techniques has no control over the pore

sizes, their distribution or their interconnectivity. FDM process was one of AM technologies where 3D objects are built layer-by-layer from CAD file on a computer-controlled fixtureless platform. In this FDM process, their feedstock material was in filament wire form. Filament wire feedstock material has been passed through a heated liquefier and continuous bead or road of materials through a nozzle and deposited onto a platform. The most challenging step in the FDM process to develop a new material of feedstock for this process was thermal characteristic of filament and surrounding environment (Torres *et al*., 2011). Besides FDM process, there are other techniques that are more popular, namely Stereo Lithography (SL), Laminated Object Manufacturing (LOM), Selective Laser Sintering (SLS), Solid Ground Curing (SGC), and Ink Jet Printing (IJP) (Kruth *et al*., 1998) based on layered deposition of polymer plastic on the platform in three-dimensional objects. Although each type of techniques was based on the same concept to build a product, there are different aspects and characteristics which can be guided for the users to choose every technique on certain applications over the others (Kruth *et al*., 1998). The selection of the right technique for any field leads to better results. There was a study that presents a systematic approach to selecting AM technology to help users select the applicable process technique technology. Selection of technology was a complex task because it depends on a number of criteria including cost, flexibility, complexity, user friendliness, environmentally green as well as technical capabilities (Lokesh & Jain, 2010).

There are many type of material for feedstock in FDM process such as Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC), Polystyrene (PS) and rubber. The aim of this research was to use the waste-derived Hydroxyapatite (HAp) from eggshell and ultra-high molecular weight polyethylene (UHMWPE) as feedstock in FDM process. For a numbers of year, various synthetic implant materials have been routinely utilized as replacement for biomedical applications. Bioactive apatite, such as Hap, has been frequently investigated for biomedical applications due to its excellent biocompatibility and tissue bioactivity properties. HAp was a naturally occurring mineral from calcium apatite usually written $Ca_{10}(PO_4)_6(OH)_2$ and has similarity in chemical composition to the inorganic matrix of bone. This ceramic has also been widely used as an implant material because of the similarity in composition to natural

bone. Based on the previous study, biologically derived natural material such as corals, fish bone and eggshells have been converted into useful biomaterials like HAp. One of these natural materials was eggshell has consists most composition similar to the human bone between the other derived natural material (Gergely *et al.,* 2010). Every day, millions ton of eggshells are produced as waste that was composed chiefly of organic matter around the world. Most of this waste was disposed into the landfills without any pre-treatment. Eggshells in landfills produce odours and promote microbial growth as they biodegrade. The eggshell contributes by 11% of the total weight of the egg and was composed of calcium carbonate (94%), calcium phosphate (1%), organic matter (4%) and magnesium carbonate (1%) (Maxwell *et al*., 2012).

A study conducted by Bonfield *et al*. in 1981 about HAp reinforced polyethylene for bone replacement revealed that the incorporation of HAp and polyethylene has potential to improve the mechanical properties and has both the porous structure and the chemical structure of bone (Bonfield *et al*., 1981). Composite blending with a polymeric material such as ultra-high-molecular-weight polyethylene (UHMWPE) indicate its potential to improve the mechanical and biological properties of bio-composites which is can be adapted to use as implant material for biomedical applications. Figure 1.1 below shows the hip joint replacement implant produced by an orthopaedic company, Wright Medical Technology Inc. The arrow indicates an acetabular cup of hip joint replacement was made by UHMWPE and coated with HAp.

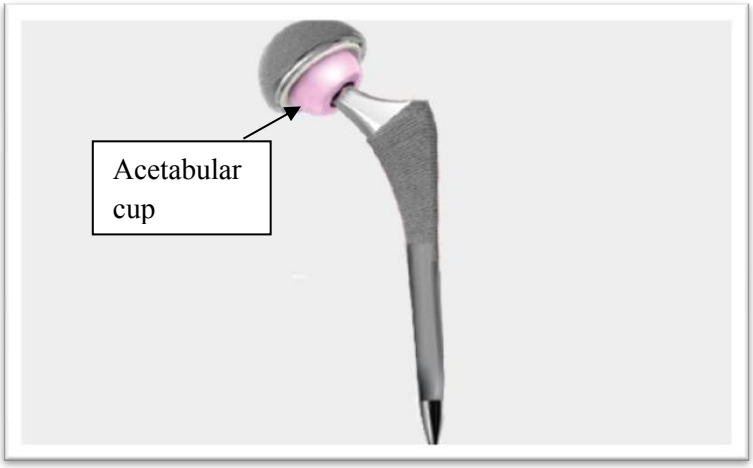

Figure 1.1: Hip joint replacement (Kuhn, 2005)

1.2 Problem Statement

The aim of this research was to use HAp to become the material feedstock in FDM process in produce a product for biomedical engineering applications. The development of the synthetic and the commercialize HAp has been shown to have the similarity composition of bones and can provide a better integrated interaction with the host and can provide a more integrated interaction with the host. However the problem was the synthetic and the commercialize HAp that have been produced were very expensive and limited because of the time consuming and very complicated process. Many equipment and expensive material such as ultrasonic equipment, plasma-spray coating and expensive reagent chemical like calcium nitrate tetrahydrate, potassium phosphate and sodium hydroxide have been used to produce synthetic and the commercialize Hap (Oktar *et al*., 2007). Therefore, the introduction of synthesize Hap from natural resources like eggshell by using hydrothermal synthesis could reduce the time consuming and complicated process.

The second problem that has been found was incorporating between biomaterial of implant and human bone inside human body. The main important to develop biomaterials for biomedical applications where it can be used to make devices that can replace a part or a function of the body in a safe, reliable, economic and physiologically acceptable manner. A biomaterial also has been recognized as a synthetic material used to replace part of a living system or to function in inmate contact with living tissue. The brittleness of biomaterial, which are much stiffer than human cortical bone lead to mechanical mismatch problems between the existing implant and bone. This mismatch of stiffness between the bone and the metallic or ceramic implants may lead to lower bone density, and altered bone architecture (Ramakrishna *et al*., 2004). A composite biomaterial always has been seen as alternative solution to overcome this problem but a study of thermal analysis and rheology test on the composite material need to be carried out.

Lastly, the problem that can be stated was the limitations of material feedstock in FDM process. Material feedstock for FDM process was in filament wire form. FDM process was so effective and economic because any material can be the material feedstock as long as it can be formed into a filament wire but the material need to have

the ability to melt and solidify in the short time before it deposits a thin bead of extruded material to form each layer. Other than that, the extruded material may can be prone to become shrinkage thus would lead the accuracy of the printed material. Therefore, the degradation of high melting point material would be a crucial thing before it can be used in FDM process.

1.3 Objective

This study embarks on the following objectives:

i. To synthesise hydroxyapatite (HAp) from waste eggshell by using hydrothermal synthesis
ii. To determine the processability of waste-derived HAp incorporated UHMWPE as material feedstock for FDM process by using thermal analysis and rheological test.
iii. To optimize the parameter of HAp/UHMWPE filament wire fabrication process for FDM process.

1.4 Scope

The scopes of this study were:

i. Synthesizing the hydroxyapatite (HAp) powder from waste chicken eggshell.
ii. Using ball milling to reduce waste chicken eggshell into average size of 10 µm till 50 µm.
iii. Using hydrothermal synthesis to extract pure and compatible HAp powder by using temperature until 900ºC.
iv. Analysis of waste-derive-HAp only focusing on morphology properties and Ca/P ratio after the hydrothermal synthesis.
v. Using Brabender Plastograph Mixer to blend HAp powder and UHMWPE.
vi. Acceptable range for Ca/P ratio for synthesized HAp in this study is 1.65 to 1.69.
vii. Analysis of the samples HAp/UHMWPE composites focus on the mixture composition, degradation temperature and melting point.
viii. Producing final parts of HAp/UHMWPE composites using FDM process only.

1.5 Significance of the Study

From this study, the introduction of waste derived-hydroxyapatite (HAp) reinforced UHMWPE composite can exhibit a promising potential towards biomedical applications such as for bone implant and can help the cell culture growth in human bones with the help of bioactive friendly like HAp. So far, there are no composite developed by using the mixture of HAp and UHMWPE into filament wire to be a feedstock material in FDM process due to limitation processibilty of UHMWPE. Therefore, this new development composite is expected to contribute to the improvement of its mechanical properties and reduce the risk for infection towards human body due to wear particles with the introduction of UHMWPE. Besides that, the result of this study will attract the researchers to explore the possibility HAp/UHMWPE composite usage in other additive manufacturing technologies.

1.6 Expected Result

The result of this study expected can:

i. Explore the useful of eggshell thus can reduce the odours and air pollution caused by waste eggshell.
ii. Explore the potential of mixture between using waste-derived HAp and UHMWPE thus enhance the processability of UHMWPE for biomedical applications.
iii. Optimize the processing parameters of HAp/UHMWPE composites into filament wire during extruder process by using extruder machine.
iv. Introduce a new material feedstock from HAp/UHMWPE composites for FDM process.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This research focuses more on the development of new biomedical material for an orthopaedic implant in human body. Orthopaedic implant was one of biomedical applications that has attracted many researchers to study their functional and possibility to help tissue growth in human body. An implant was a medical devices made to replace and act as a missing biological structure. It was different than the transplant because it was more to the biomedical tissue. In general, an orthopaedic implant was used more predominantly to treat bone fractures, prosthetic joint replacements and fracture fixation implants. Biomedical materials used for orthopaedic implant were generally considered to be biocompatible. Some examples used for orthopaedic implant were titanium alloys and stainless steel. These orthopaedic implants or devices were commonly being manufactured by high-tech manufacturing process and technology such as Computer Numerical Control (CNC) milling and Electrical Discharge Machining (EDM) wire cut. When a new device needs to be developed, it often goes to a design engineer within the company who deals with the overall structure of the device. The design engineer will build a prototype to get a better idea of its physical properties before being approved by the company and sent to the manufacturer. The manufacturer would produce the product from a single block of metal or PEEK composite plastic. These blocks were secured into the large industrial multi-axis CNC milling machines which consist of a number of

robotic arms and drilling tips that can carve into very fine features. Even though milling has been done with the industrial robots, most of the remaining tasks were done by the hands of skilled machinists and technicians. If the implant or instrument requires a dull or matte finish, then it goes to the sandblaster to remove the metal's shine. Technicians also used a rotary sander to deburr and finish the part. Finally, all the parts are then cleaned ultrasonically using water, and then passivated using nitrate or citrate to prevent corrosion. Therefore, additive manufacturing would be introduced and discussed in the next topic to replace the conventional manufacturing process of orthopaedic implant to reduce cost and time of processing of the product.

2.2 Additive Manufacturing (AM)

In biomedical application, the manufacturing of orthopaedic implant usually has interior complex mechanical attributes and material variations. This limitation can give a difficulty and need a lot of time processing to fabricate by using conventional manufacturing method (Gu & Li, 2002). Thus, many researchers shifted to the AM to overcome this limitation from conventional manufacturing method such as injection molding and machining. AM normally refers to techniques that have the ability to fabricate physical objects automatically through continual build-up or creation of solid material through additive manufacturing. There is another old term called rapid prototyping (RP). RP usually refers to the fast manufacture of prototypes with different functions and AM was more often used in industry because it fabricates an actual production process, for example, the parts generated were meant for a true product life-cycle like hip implantation (Kruth *et al*., 1998). One of the useful of AM was during fabrication process of final parts, no mold or tooling required. AM would also reduced cost and time of processing parts and products. From the study conducted, AM processes can be divided into five categories. There were VAT Photopolymerisatio, Material Extrusion, Powder Bed Fusion, Sheet Lamination and Directed Energy Deposition (Chua *et al*., 2003). The next section would be discussing about the types of AM process that were widely used nowadays for commercial and biomedical applications.

2.2.1 Stereolithography (SL)

According to Hutmacher *et al*., (2004) SL first commercial system was introduced in 1988 by 3D Systems Inc. and it was considered as the pioneering RP technique (Hutchmacher *et al*., 2004). This technique was under VAT Photopolymerisation category and uses a UV laser that was vector scanned over the top of a bath of a photopolymerisable liquid polymer material. The laser beam create a first solid plaster layer and just below the surface of the batch when the polymerisation was initiated. This laser polymerisation process then has been repeated in order to generate subsequent layers by tracing the laser beam along the design boundaries and filling in the 2D cross section of the model. The platform was raised out of the vat and the excess resin was drained when the model has been completed. Then, the model was cured in a UV oven and finished by smoothing the surface irregularities. Standard resolution of SL layer was determined by the elevator layer resolution up to 1.3µm and 80-250 µm for laser spot size.

However, the application of SL in the biomedical industry was limited to the creation of anatomical models for surgical teaching or planning because curing and shrinkage after post-processing a shortfall of the SL model compromise resolution. Besides that, due to scattering and absorption of the laser beam, deformation happened when smaller and more intricate objects were fabricated. The manufactured part was weak and needs post-processing for further curing (Hutmacher *et al.,* 2004).

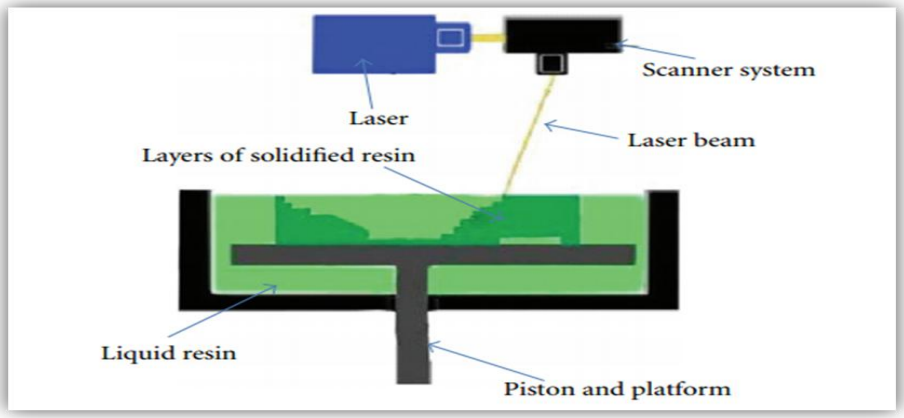

Figure 2.1: Schematic diagram of Stereolitography (SL) process
(Wong & Hernandez, 2012)

2.2.2 Selective Laser Sintering (SLS)

SLS falls under powder bed fusion category. SLS uses a laser beam directed by a computer onto the surface of non-metallic and metallic powders to produce surface models rapidly or copies of solid. SLS was first developed in 1987/88 by Carl Deckard at the University of Texas at Austin, TX to produce plastic parts. There were two types of SLS, namely indirect and direct SLS. The prototypes produced were capable of withstanding high heat and chemical exposure and can be made to snap, bend and bolt together, and form flexible hinges (Venuvinod & Ma, 2004). According to Jessica M. Williams, SLS can also be applied in medical application as it helps to create bone tissue engineering constructs. This was because it provides efficient method by which to construct scaffolds to match the complex anatomical geometry besides an effective cost (Williams *et al*., 2005). The scaffolds were constructed by SLS from 3D digital data by sequentially fusing regions in a powder bed, layer by layer. Compared to other methods of AM, SLS can produce parts from a relatively wide range of commercially available powder materials. These include polymers such as nylon (neat, glass-filled, or with other fillers) or polystyrene, metals including steel, titanium, alloy mixtures, and composites and green sand. Layer by layer fabrication in SLS allowed construction of scaffolds with complex external and internal geometries.

In addition, there was no use of the organic solvents for SLS, it can be used to make intricate biphasic scaffold geometries and does not use of a filament as in FDM (Williams *et al*., 2005). SLS technique does not require supports when printing overhanging, unsupported structures because the powder itself provides the necessary support and parts can be created out of a wide selection of materials. However, fabricated parts produced by SLS can be porous and/or have a rough surface depending on the used materials. Another problem for polymer parts was thermal distortion. This can caused shrinkage and warping of fabricated parts.

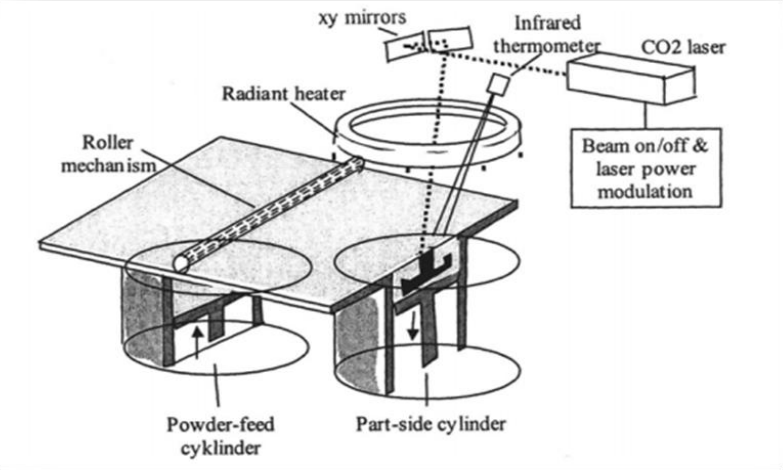

Figure 2.2 : The principle of Selective Laser Sintering (SLS) (Venuvinod & Ma, 2004)

2.2.3 Fused Deposition Modelling (FDM)

FDM process was a common material extrusion process and has been trademarked by the company Stratasys Inc. FDM was used in design verification, prototyping, development and manufacturing. This kind of method also involves making of three-dimensional objects based on the design data provided from a computer aided design (CAD) system. Stratasys Inc. was known as the leading company to fabricate the FDM machine and also a manufacturer of 3D production systems based on rapid prototyping and solid free-form fabrication. It was started by S.S. Crump and his wife when the idea to fabricate small toys for their child leads to innovation of small printing machine by using plastic as the material (Crump, 2013). In 1999, several inventors assigned by Stratasys Inc. have patterned their first FDM machine and it has been the best-selling rapid prototyping system in 2003 (Nelson, 2004). Nowadays, many industries and manufacturers use Stratasys system to develop and produce parts with complex dimensions and shape in a variety of thermoplastic materials such as Acrylonitrile Butadine Styrene (ABS), polyphenylsulfone (PPSF), polycarbonate (PC) and ULTEM 9085.

Through the study and observation of this company profile, several commercial materials were available for the process. Most widely used material was ABS because it offers good strengths for the parts while the introduction of PPSF, PC and ULTEM 9085

materials can increase the capacity of this method in the area of range of strength and temperature machine. FDM process has been widely used in many industries including automotive, aerospace, biomedical, construction and also in manufacturing industries (Chua *et al*, 2003). FDM process was economical and quiet. Thermoplastic extrusion was perfectly adequate for minor parts and those parts that have simple geometries. It can also take time for the difficult geometries and wide cross section in comparison to conventional manufacturing method which required mold and another tooling for the finish parts.

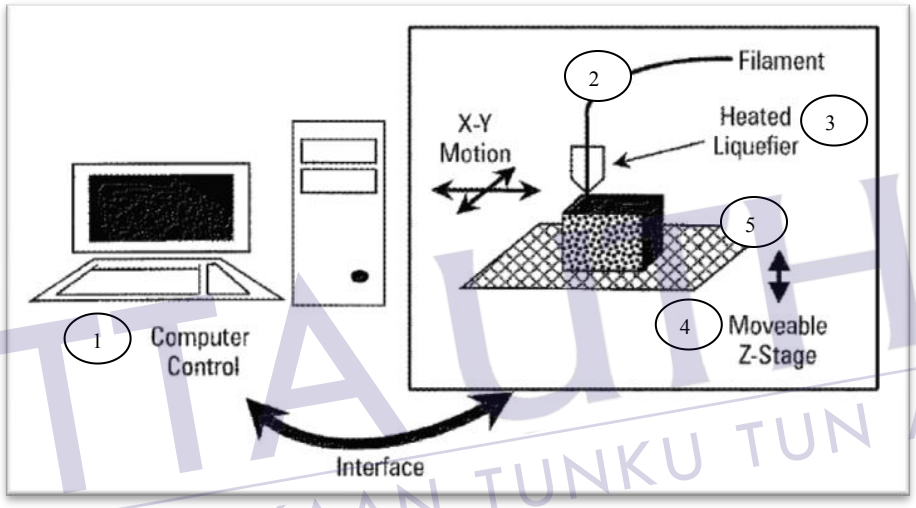

Figure 2.3: Schematic of fused deposition modelling (FDM) process.

Basic concepts of this FDM method were shown below:

i. FDM begins with a software process which processes CAD file to transfer the program into FDM machine for the build process.

ii. An extrusion nozzle moves in vertical (X-axis) and horizontal (Y-axis) directions over a height-adjustable work platform.

iii. Then, the nozzle was heated to melt the thermoplastic filament and has a mechanism like spool or coil which allows the flow of the melted plastic to be turned on and off. If needed, support structures will be generated. Therefore, the machine would be dispensing a layer to make a support structure before constructing required three-dimensional parts.

iv. As the nozzle was moved over the table in the required geometry, it deposits a thin bead of extruded plastic to generate a layer by layer from 3D CAD file. The

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