

THERMAL CHARACTERISTIC OF WASTE-DERIVED HYDROXYAPATITE (HA) REINFORCED ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) COMPOSITES FOR FUSED DEPOSITION MODELING (FDM) PROCESS

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Abstract— The present study provides a hydrothermal synthesis to obtain Hydroxyapatite (HA) powder from waste eggshells. This waste-derived HA has been characterized by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy analysis. Waste-derived HA will be reinforced the Ultra-High Molecular Weight Polyethylene (UHMWPE) to develop a material composite for biomedical applications because of impressive mechanical properties owned by UHMWPE. Main challenger is UHMWPE has an ultra-high viscosity that renders continuous melt-state processes including one of the additive manufacturing processes which is Fused Deposition Modeling (FDM). To develop this material as feedstock in FDM process, it has been overcome by blending UHMWPE with waste-derived HA as filler. It exhibit the inclusion of 50wt% HA has reduced the degradation temperature in TGA and DSC thus enhances the processability in FDM process.

1.0 Introduction

In a 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 using several kinds of materials. With this AM processes, it can make a porous scaffolds 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 additive manufacturing (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 additive manufacturing (AM) technologies and techniques have been developing due to extensively used in many industries.



One of additive manufacturing (AM) technologies is fused deposition modeling (FDM) process by layered deposition of polymer plastic on the platform in three dimensional objects [1]. Application of fused deposition modeling (FDM) in biomedical applications has shown its potential compared to the conventional manufacturing process where conventional manufacturing techniques process no control over the pore sizes, their distribution or their interconnectivity. FDM process as has shown in Figure 1 is one of AM technologies where 3D objects are built layer-by-layer from CAD file on a computer-controlled fixtureless platform. By using wire filament has been passes through a heated liquefier and continuous bead or road of materials through a nozzle and deposit onto a platform. Most challenge in the FDM process when to develop a new material of feedstock for this process is thermal characteristic of filament and surrounding environment [2]. Besides FDM process, there are others techniques that are most popular which are Stereo Lithography (SL), Laminated Object Manufacturing (LOM), Selective Laser Sintering (SLS), Solid Ground Curing (SGC), and Ink Jet Printing (IJP) [3] based on layered deposition of polymer plastic on the platform in three dimensional objects. Despite on each type of techniques are based on same concept to build a product, there are have different aspects and own characteristic which can indicates the user to choose of every technique on certain applications more than others [3]. The selection of the right technique for any field leads to better results. There has been a study that presenting about a systematic approach for selection of AM technology to help the user to select the applicable process technique technology. Selection of technology is a complex task because it depends on many criteria such as cost, flexibility, complexity, user friendliness, environmentally green as well as technical capabilities [4].

This paper selects the FDM process because it is potential to produce prototypes with locally controlled properties (porosity and mechanical properties). FDM is functional for use in design verification, prototyping, development and manufacturing. This kind of method also involves into making of three dimensional objects based upon design data which was provided from a computer aided design (CAD) system. Stratasys Inc. was known as a leading company to fabricate the FDM machine and also a manufacturer of 3D production systems which are based on rapid prototyping and solid free-form fabrication. In 1999, several inventors which were been assigned Stratasys Inc. has patterned first their FDM machine [5]. Nowadays, many industrial and manufacturer use Stratasys system to develop and produce parts which are having complex dimensions and shape in variety thermoplastic materials such as ABS, PPSF and PC. FDM process has been widely used in many industries including automotive, aerospace, biomedical, construction and also in manufacturing industries [6]. This FDM process is economical and quite. Thermoplastic extrusion is perfectly adequate fast for minor parts and those parts that have simple geometries.

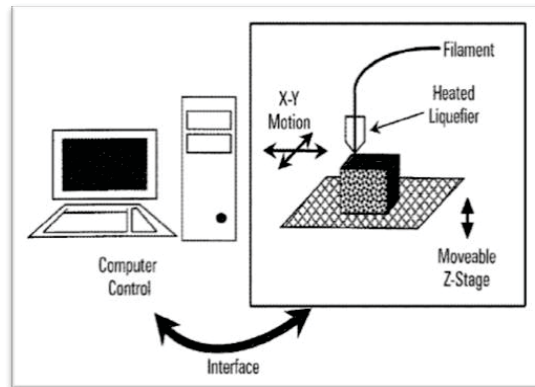


Figure 1. Schematic of fused deposition modeling (FDM) process. [5]

1.1 FDM Material

As we known, feedstock material for FDM process is in filament wire formed which need to deposit in a semi-melted phase and solidifies under jurisdiction of the platform temperature. In generally, the researchers in this field believe that the filament material for FDM process needs to consider two factors which are nozzle temperature and platform temperature. This parameter plays a significant role that affected the properties of the final product. A process parameter optimization for FDM process was conducted by Peng et al. (2014) inappropriate temperature applied in the nozzle temperature can cause the nozzle clogging [7]. Therefore, a melting point temperature of material needs to know and concern. It applies in all material including metal, polymer, ceramic and composite for the engineering application or biomedical application because it is influenced the interlayer bonding thus determine the strength of the material. Nowadays, there are only few material for FDM technology that has been commercialized regardless for engineering applications or biomedical applications due to heating temperature are available ranges within around 120 until 210 °C [8]. This caused FDM technologies suffer limitations of new materials. However with this kind of circumstances, polymers and some low melting point of metals are more suitable for the FDM technologies thus attract many researchers to explore the possibility to process new materials by using FDM process. Most problem faces by the researchers are to study the durability of the material during heating process in FDM. To produce a polymer and some low melting point suitable for FDM process, they have to be thermoplastics that become molten at reasonably low heating temperature usually not above 250 °C [8] and solidify fast enough (decently high glass transition temperature) so that they becomes hardened [9] and hold their shape rather than remaining soft and droopy. This is a very different requirement as compared to injection molding which could literally accept any molten plastics, as long as they can be removing from the mold relatively easily after cooling.

Type of FDM materials application can be divided to two type which are engineering and biomedical applications. In the engineering applications, FDM technology produces strong parts and prototypes and is known to accurately produce feature details [10]. The final parts usually renowned because it is well to being drilled threaded and painted. This technology has entered various types of industries such as aerospace, automotive and manufacturing. Thus, the expanding material will give

benefit for the FDM process to evolve and improve. Stratasys's founder, Scott Crump invented FDM Technology more than 20 years ago, and Stratasys has continued to study ever since, developing a range of systems that appeal to large manufacturers, designers, engineers, educators and other professionals [5]. Many researchers usually have focused on processing polymers using FDM process but to expand FDM benefits; there are also has been reported work that has been carried out using low melting alloys [11]. It has been mentioned that it has posses more strength than polymers. Alloy is a mixture of metals or with another element and has been characterized by metallic bonding character. According to Mirelles et al. (2013), the main factors controlling the depositing metal alloys using FDM were the melting temperature and phase transition characteristics based on alloy composition [11]. Besides of polymer and some of the low melting point metal alloys, there are also researchers who are attempts to mix between of metal and polymer [12] and nowadays it has been used in several applications.

In the scope of FDM material for biomedical application, the researchers need to emphasize the characteristic selection of material by selecting the suitable implant materials that have good biocompatibility and supporting mechanical properties with human body. Although metals became regular choice as biomaterial in biomedical applications by manufacturer and designer but polymer has been explored by many researchers and scientist as another option [13]. By using FDM process as manufacturing process, polymer or thermoplastic polymer can become a significant biomaterial for biomedical applications with high biocompatibility and suitable strength of mechanical properties. In this paper, researcher are intend to make HA/UHMWPE as feedstock material for FDM process. UHMWPE as we know is ultra high molecular weight polyethylene that has extremely long chains of polyethylene with molecular mass which has proven has impressive mechanical strength. The main challenge to use UHMWPE as biomedical application material is it difficult to process and needed the incorporation of the other material as binder system. Therefore, the presence of HA in UHMWPE will be expected shows the better thermal stability of the composites. Further discussion about HA, UHMWPE and previously study on HA/UHMWPE will be discussed in the next topic.

1.2 *HA/UHMWPE Composites as Feedstock for FDM Process*

1.2.1 Hydroxyapatite (HA). For a numbers of years, a various synthetic implant materials have been routinely utilized as replacement for biomedical applications. Bioactive apatite such as Hydroxyapatite (HA) has been extensively investigated for biomedical applications due to its excellent biocompatibility and tissue bioactivity properties. HA is a natural occurring mineral from calcium apatite with the usually written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and has similarity in chemical composition to the inorganic matrix of bone [20]. HA is a natural occurring mineral from calcium apatite with the usually written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. HA has been widely used as an implant material because its close similarity in composition to natural bone. Based on the previous study, biologically derived natural material such as corals [14], fish bone [15] and eggshells [16] have been converted into useful biomaterials like HA. One of these natural materials is eggshell has most composition similar with the human bone. Everyday millions of tons of eggshells are produced as biowaste around the world. Most of this waste is disposed of in landfills without any pretreatment. Eggshells in landfills produce odors and promote microbial growth as they biodegrade. The eggshell contributes by 11% of the total weight of the egg and has been composed of calcium carbonate

(94%), calcium phosphate (1%), organic matter (4%) and magnesium carbonate (1%). The natural biological origin of eggshells results in HA with a crystalline structure and composition similar to that of human bone.

1.2.2 HA reinforced UHMWPE. By using only Hydroxyapatite (HA) as biomaterial to make scaffolds or load-bearing applications is not much suitable due to its poor mechanical properties. Therefore, a study conducted by Bonfield et al., in 1981 shown about HA reinforced polyethylene for bone replacement, it shown that this composite of HA and polymer has potential to improve the mechanical properties and has both the porous structure and the chemical structure of bone [17]. 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. UHMWPE has extremely long chains of polyethylene with molecular mass which all align in the same direction. UHMWPE has been long used in biomedical applications as biomaterial due to its impressive mechanical strength. Recently, many applications were directed towards the development of polymer composites for load-bearing orthopedic applications. The advantage of using composite material for such application is due to the fact that by varying the amount and type of reinforcing material such as Hydroxyapatite (HA), the mechanical and biological properties can be tailored for specific applications [18]. Furthermore, the low processing temperature of the composites prevents phase and compositional changes of the HA.

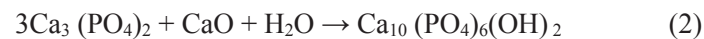
Among the wide choice of polymer matrix that have been widely promoted, UHMWPE and its composites have been highlighted as having the potential for such application [18]. Thermal and chemical stability of ceramics, high strength, wear resistance and durability. These characteristic contribute to making ceramics good candidate materials for bones implant and UHMWPE as a composite matrix has these entire characteristic. UHMWPE is a high performance thermoplastic which have to date been associated with high performance devices, structural and load-bearing biomaterials in various fields including electronic and automotive industries [19]. It is best suited for medium mechanical duties in water, oil hydraulics, pneumatics and unlubricated applications. It has a good abrasion resistance but is better suited to soft mating surfaces. It is anticipated that by incorporating particulate HA into UHMWPE matrix, the mechanical performance of the material, particularly the Young's modulus could be improved considerably [20]. Reinforcing UHMWPE with HA could potentially reduce the risk for infection due to wear particles. Because of it, this could help to increase the osseointegration (bone growth onto the acetabular cup) [21]. This HA/UHMWPE composite shown many benefit and can help the growth of cells of bones. Therefore, the presence of bioactive HA would subsequently enhance implant fixation with proper provision for their interactions with the host tissue [22]. A study by Panin et al. in 2012 shows that the role of HA in HA/UHMWPE composite to increase the wear resistance in 3.5 times compared to the pure UHMWPE polymer [23]. Thus, in the FDM process it will be advantages to solve the problem with the conventional manufacturing is that it takes an amount of processing time for the whole process to complete and producing a part. Besides that, FDM process has control over the pore sizes, their distribution or their interconnectivity with the help of HA within UHMWPE composites towards cell culture of bones. Thus, introduction of HA/UHMWPE composites as a new biomaterial shows a promising potential to be study for biomedical applications like bone grafting and orthopedic implants. As

mentioned previously, this paper has been proposed a suggestion to use HA/UHMWPE composites as feedstock for FDM process. FDM process is an easy as long the material made in form of filament wire. Due of certain circumstances, FDM process suffer a limitation of material and it is worth extending the FDM material list with materials/composites. Although FDM process has extensively used in engineering application such as manufacturing industry and construction but it has proven that FDM process can make a significant useful in biomedical application. In this present paper, waste-derived-HA from eggshell and ultra high molecular weight polyethylene (UHMWPE) has been used and formed as feedstock for FDM process. Therefore, a quick brief review about HA and previous study HA reinforced UHMWPE as biomaterial in biomedical applications has been taken.

2.0 Methodology

2.1 Synthesis of HA

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. A study by Hui et al proves that HA powder has been successfully synthesized from waste chicken eggshell [24]. First steps to the method of synthesis of HA from waste chicken eggshell by using hydrothermal synthesis are waste of chicken eggshell was collected and crushed into small piece. After that, surface of eggshell was mechanically cleaned by distilled water and boiled in water about 20 minutes. Next, they were placed in a three-stage thermal treatment of furnace machine. In first-stage thermal treatment, the temperature was set from 0°C until 450°C with the heating rate per minute was 7°C and the soaking time was 2 hours. For the second-stage thermal treatment, the temperature was set from 450°C till 600°C with the heating rate per minute was 5°C and the soaking time was 2 hours. Finally in the third-stage, temperature was set from 600°C till 900°C with the heating rate per minute was 4°C and the soaking time was 1 hour. At the temperature 900°C, calcium oxide will be formed by releasing carbon dioxide (CO₂) from the waste chicken eggshells. The chemical equation is shown in equation (1) and by obtained CaO from the eggshells, it will transform into HA powder by mixing with Tri-Calcium Phosphate (Ca₃(PO₄)₂) to following procedure by Rivera et.al [25]. The equation will be expected reacted like equation (2) below:



2.2 Blend Formulations

In this research, ultra high molecular weight polyethylene (UHMWPE) will be incorporating with derived pure Hydroxyapatite (HA) powder to become HA/UHMWPE composites and investigate on their characteristic as a candidate for wire filament feedstock of fused deposition modeling (FDM) machine. Step of procedure for this mixing process will be follow as Mirsalehi et. al., 2015 which are resulting the increase in HA content leads to an increase of the interfacial bonding between HA and UHMWPE thus as a result can reduce viscosity of UHMWPE and help the improvement of UHMWPE polymer as a bone substitute material rather than pure UHMWPE alone. At first a sufficient amounts of UHMWPE will be

determine by their weight and hand-mixer it with paraffin oil at 100°C. Paraffin oil will act as surfactant and lubricant to the UHMWPE for improving processing the powder [26] After a certain time, the compounding of HA powder and swelled UHMWPE will be mixing by using Brabender Plastograph mixer type W50. UHMWPE will be feed into mixer at range of 230°C with rotation speed of 10rpm for 5 minutes. After that, HA will be adding into mixer for 10 minutes. Then, the compounding samples are cooling down to the room temperature. Besides that, it is important to remove the paraffin oil for HA/UHMWPE further analysis. The removing paraffin oil will by carry out by using hot press at 100°C at pressure 3.8 MPa for an hour. Then, the samples will be extracting by soaking in hexane for 24 hours to remove the remaining paraffin oil after hot press process. Subsequently, the samples then dry in an oven at 80°C overnight. The characterization of each sample was shown in the Table 1.

Table 1. Blend formulations of HA/UHMWPE composites samples

Designation	UHMWPE (%wt)	HA(%wt)
U100	100	0
U90H10	90	10
U80H20	80	20
U70H30	70	30
U60H40	60	40
U50H50	50	50

2.3 Morphology Properties on waste-derived HA from eggshell

2.3.1 SEM/EDS Analysis. To study the material composition of the samples, Scanning Electron Microscope (SEM) tool has been chosen because the ability to perform on-site analysis of the selected point in the specimen to determine the chemical composition of the specimen through the use software Energy Dispersive Spectroscopy (EDS) in the SEM tool. In the SEM tool has the electron beam which is functional to scan across a sample's surface. When the electrons beam focus on the samples, a variety of signals can be generated and detection of specific area of samples can resulting an image or composition of the samples. The three signals which provide the greatest amount of information in SEM are the secondary electrons, backscattered electrons and X-rays. In a previous study, SEM/EDS analysis has been used almost for every research and experiment to study the relation of viscosity and shear rate inside the element [27]. Scanning electron microscopy SEM studies have demonstrated that the morphology of structure inside the materials or element. Therefore, the application of SEM/EDS analysis was used in this experiment to analysis the morphological properties of synthesized of HA. Thus, the application of SEM/EDS analysis could be important because the analysis can determined the successfully research to achieve the objective that has been assigned.

2.3.2 X-ray powder diffraction (XRD) Analysis. X-ray diffraction (XRD) is a tool used for recognized the atomic and molecular structure of a crystal, which by the crystalline atoms can result a beam of incident X-ray to cause an undergo diffraction into many specific area of directions. In this research, XRD analysis needed to study the synthesized HA powder produced from waste eggshell.

2.4 Thermal analysis on different formulation of HA/UHMWPE composites

2.4.1 Differential Scanning Calorimeter (DSC). Differential scanning calorimeter is a thermo-analytical tool in which the difference in the amount of heat needed to increase the temperature of a sample. The instrument used in this study was TGA4000-Perkin Elmer. The references and the samples are sustained at closely the same temperature during the experiment. The basic principle in this technique is that when the sample undergoes physical transformation, heat is needed to flow to the sample than the reference to maintain both at same temperature. By observing the difference in heat flow, differential scanning calorimeter is able to detect the amount of heat absorbed or released throughout the transitions. DSC can be applied in measure a number of characteristic properties of a sample. This technique is possible to observe fusion and crystallization as well as glass transition temperature. This ability of examine the transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems. The heat of fusion pure UHMWPE, ΔH_f° is 291 J/g, therefore by using below equation (3), we can obtained the degree of crystallinity. ΔH_f is the enthalpy of each sample.

$$x_c = \frac{\Delta H_f}{\Delta H_f^\circ} \times 100\% \quad (3)$$

2.4.2 Thermo-gravimetric Analysis (TGA). Thermo-gravimetric analysis (TGA) is commonly used to determine selected characteristics of materials that display either mass loss or gain due to decomposition. In this study, TGA4000-Perkin Elmer was used in examination of materials characterization through analysis of characteristic decomposition patterns and determination of organic content of a sample. The methods of using this instrument is by continuously weighs a sample as it is heated to temperatures for coupling with FTIR and mass spectrometry gas analysis. As the temperature increases, various components from the sample decomposed and weight percentage for resulting change in mass can be measured. The thermo-gravimetric analysis data results in the effect of temperature change affect the relatively weight loss rate. Thermo-gravimetric analysis (TGA) was performed from the ambient temperature of 50 °C – 700°C of under a controlled environment with a heating rate of 10 °C /min by using TGA4000-Perkin Elmer to determine the thermal degradation behavior of the composites.

2.5 Pre-processing on FDM

The samples of HA/UHMWPE composites that has best thermal properties will be chosen to undergo a preliminary test in FDM process. First, the sample will go through the extruder process by using single screw extruder machine. By having the sample in the form of filament, a preliminary test was carried out using Flashforge 3D Printer machine to evaluate the extrudability through the print head nozzle of 0.4 mm diameter. The nozzle temperature and platform temperature will be set at 230°C and 110°C respectively.

3.0 Result and Discussions

3.1 Morphology properties of waste-derived HA from eggshell

3.1.1 XRD Analysis. The structural characterization of HA was done by using X-ray Diffraction with Cu-K α of 1.5406Å radiation that generated at generator setting of 40kV and 40mA. The samples of HA with calcined temperature of 900°C. The data was collected in the range of 10-70°, with step size of 0.020°. Phase identification for the sample was observed by comparing the diffraction pattern of HA obtained in laboratory with JCPDS standards. Figure 2 shows the XRD pattern of HA after calcined at 900°C. The phase of derived HA was confirmed with XRD analysis. The result was obtained from mixing of CaO and tri-calcium phosphate under several process followed by calcination at 900°C. The peaks were very sharp and clearly reveal the identity and strong broadening of lines. The formation of hydroxyapatite Ca₅(PO₄)₃(OH) was confirmed by study of X-ray diffraction (XRD). From the results obtained, the sample was recognized as hydroxyapatite in monoclinic phase with JCPDS standard pattern 01-089-4405 and the spectrum matched with the standard JCPDS pattern with reference code of 00-055-0592. From the figure shown, the peak start rising at 10.27° and attained highest peak at 31.71°.

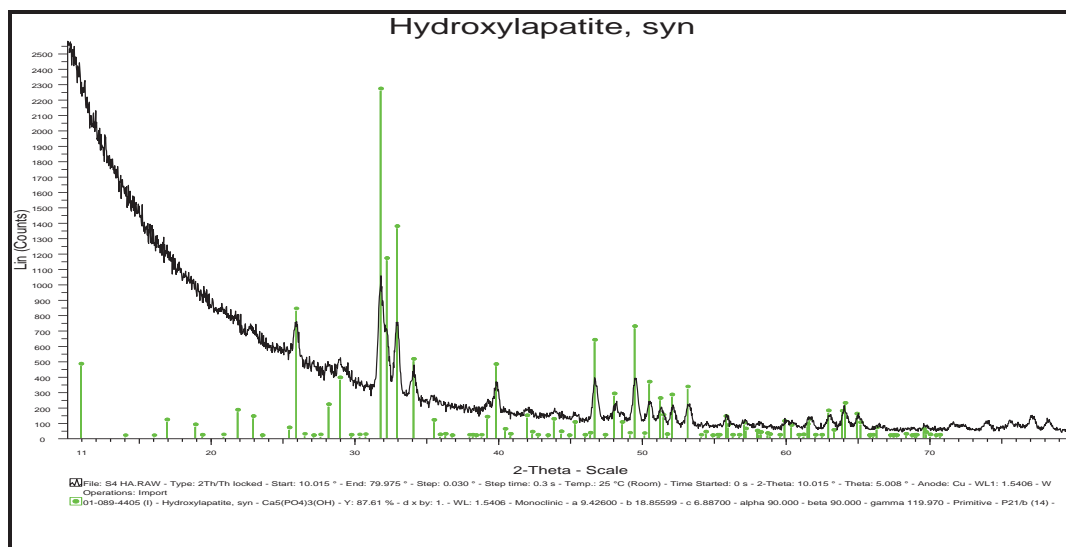


Figure 2. XRD pattern of HA

3.1.2 SEM/EDS Analysis. The surface morphology and crystal size of the derived HA which have been milled, sieved and calcined were investigated under SEM. Figure 3 shows the SEM images of waste-derived HA at 900°C. The HA samples were scaled for resolution of 30µm at 10kV. The results of the images were magnified to 1000X for 30µm for the whole field to view. The z-axis of the between the sample holder and detector was set to 10mm before scanning. The SEM images of the HA powder in

Figure 3 revealed that the produced HA microstructures are less spherical. The HA microstructure ascertain high porous in calcined HA powder. Before calcined, HA particle size was extremely small and the agglomerates are hard to disperse due to the small particle size. Formation of the calcined HA microstructures contributed to the ability of the particles to crystallize and form agglomeration at high temperature [28]. Electron dispersive X-ray spectroscopy was used for the elemental analysis of chemical composition for the HA samples. Based on the EDS analysis, the Ca/P ratio for the calcined HA was calculated and found to be 1.69 at 900 °C as shown at the Figure 4 below. The previous study reports that Ca/P ratio for HA is 1.67 thus the results of HA synthesized from eggshell could be considered successful because the result is approximately close to the standard Ca/P ratio.

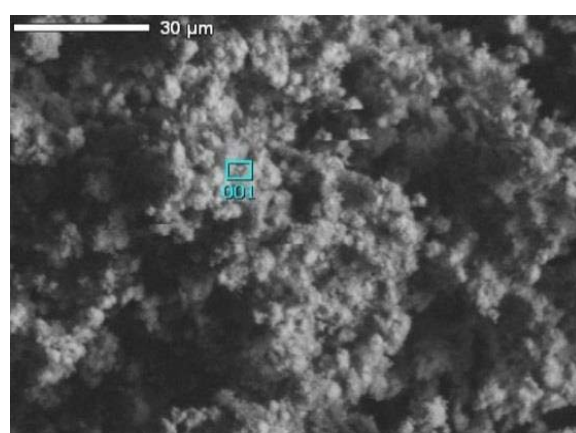


Figure 3. SEM images of waste-derived HA powder. The blue form box indicates the area of the element analysis.

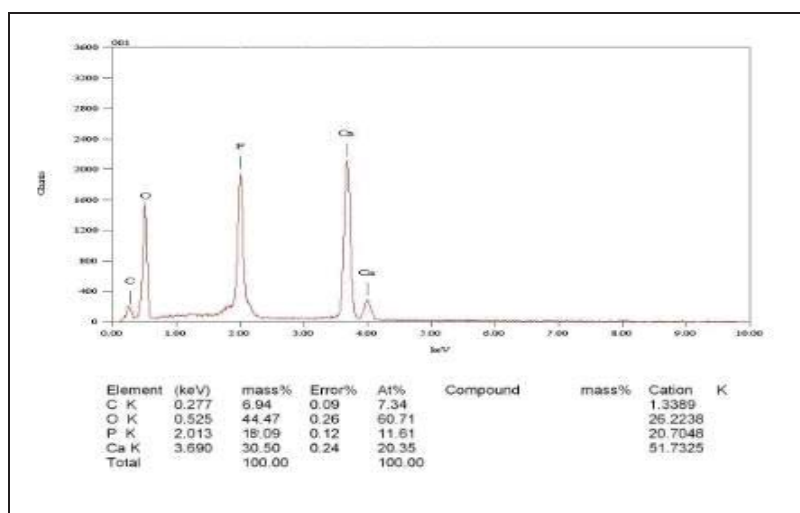


Figure 4. EDS results of HA powder eggshell.

3.2 Thermal properties of HA/UHMWPE composites

3.2.1 Thermo-gravimetric Analysis (TGA). TGA of pure UHMWPE and HA/UHMWPE blends was carried out to assess the effects of blend composition on the thermal stability of the polymers. The TG curves are shown in Figure 5 where as the degradation temperature of each sample blends obtained are shown in Table 2. The initial thermal stability is categorized by temperatures at 10% weight loss, which referred as $T_{10\%}$. The incorporation of HA into UHMWPE as polymer matrix has the ability to reduce the decomposition temperature of pure UHMWPE and HA/UHMWPE composites. In the Table 2 shown the initial decomposition temperature ($T_{10\%}$) for U50H50 has start at 232.255 °C and the peak of decomposition temperature (T_p) is 320.472°C. It shown the significant changes from result obtained by the pure UHMWPE by adding HA as filler. This results was also consistent with a previous study that adding HA reinforced UHMWPE up until 50 wt% has reduces UHMWPE chain mobility allowing HA particle to penetrate inside the composites thus can enhanced the processability of the HA/UHMWPE composites by the degradation of melting temperature.

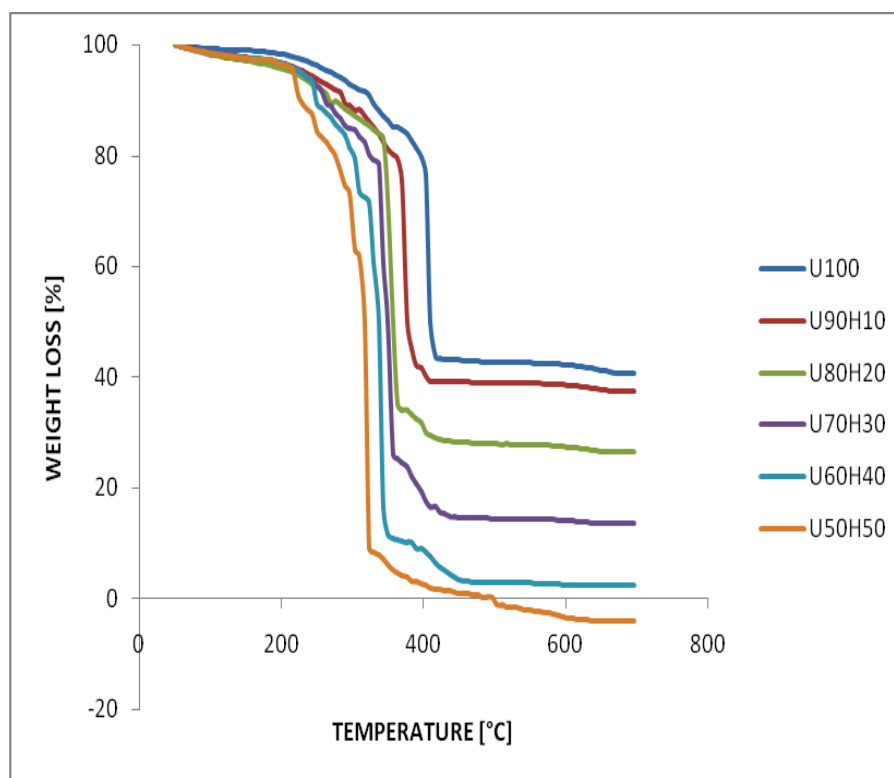


Figure 5. Thermograms of HA/UHMWPE Composites

Table 2. Degradation temperature of components and UHMWPE/PEG blends obtained from TG and DTG curves.

Formulation	Percentage composition (wt %)		Initial decomposition temperature, $T_{10\%}$ (°C)	Peak of decomposition temperature, T_p (°C)
	UHMWPE	HA		
U100	100	0	333.151	421.352
U90H10	90	10	292.446	394.898
U80H20	80	20	272.462	361.296
U70H30	70	30	265.929	354.378
U60H40	60	40	252.735	340.746
U50H50	50	50	232.255	320.472

3.2.2 Differential Scanning Calorimeter (DSC) Analysis. Table 3 below shown the result obtained by DSC analysis which has melting temperature, heat fusion and degree of crystallinity. By addition of HA, it induce of the decreasing of the melting point, heat fusion and crystallinity. Therefore the incorporation of HA can help the processability of HA/UHMWPE composites for FDM process. It also exhibit by introducing of HA as filler can also decrease the degree of crystallinity (χ) of the composites. It shown that increasing HA reinforced UHMWPE can cause the composites hinder the polymer macromolecules to rearrange regularly to form crystals. These results are consistently with the previous study by increasing HA particles in the polymer matrix decreasing the decomposition of crystal formation [29]. However, it shown that degree of crystallinity of HA/UHMWPE composites don't show significant of changes thus the incorporation of HA in UHMWPE can't affect the mechanical properties of the composites.

Table 3. The melting temperature, heat fusion and degree of crystallinity for pure UHMWPE and HA/UHMWPE composites

Designation	Melting point, T_m (°C)	Heat fusion, ΔH_f (J/g)	Crystallinity, χ (%)
U100	326.3	174.89	60.1
U90H10	312.7	170.82	58.7

U80H20	305.1	166.74	57.3
U70H30	285.3	155.98	53.6
U60H40	271.4	152.48	52.4
U50H50	244.7	147.54	50.7

4.0 Conclusion

The present study successfully synthesis of Hydroxyapatite (HA) from waste eggshell by using hydrothermal synthesis method and exhibit the result of Ca/P ratio is approximately with the standard Ca/P ratio of HA. By using this waste-derived HA to incorporate with UHMWPE, the degradation temperature of HA/UHMWPE composites is successfully reduced significantly rather than pure UHMWPE with the incorporation of waste-derived HA as filler. Paraffin oil also plays a significant role to reduce the viscosity of UHMWPE before mix with the waste-derived HA. By result from TGA and DSC, this research successfully reduces the HA/UHMWPE composites of melting point by increasing the waste-derived HA as filler thus enhances the processability in FDM process. By increasing HA content up till 50wt%, it will be expected that the HA /UHMWPE composites allows the HA content to the level of cortical bone without the brittleness problems. In the pre-processing on FDM process, HA/UHMWPE composites by using U50H50 formulation is showing a promising results where the composites able to extrude with a constant diameter of 1.80mm. Further study will be about optimization parameter in extruder process to fabricate wire filament feedstock for FDM process with application of U50H50 formulation HA/UHMWPE composite by using Taguchi method because Taguchi method has been proved by its ability to improve the quality of product with the lesser experiment [30]. Overall, the viscosity of UHMWPE is successfully reduced to become a feedstock material in FDM process with the degradation temperature by using waste-derived HA as filler and also with the help of paraffin oil.

5.0 References

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