

The Effect of Binder on Hydroxyapatite (HAP) Properties and Surface Roughness when Machining

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Abstract

The increasing number of road accidents often leads to bone damage, which may require surgery. To help with bone replacement, hydroxyapatite (HAP), a bio ceramic that closely resembles the mineral found in human bone, has been used. To make the HAP hold together, water-soluble binders like PEG and PVA are added. Four different samples of hydroxyapatite, zinc and magnesium were made with different amounts of binder to study how the binders affect the mechanical properties and surface roughness of the bio ceramic. The samples were prepared by dry mixing the materials and compacting them. The amount of PEG and PVA used ranged from 1% to 4% by weight. All sample were containing 2.5% zinc and 2% magnesium.

1. Introduction

The Hydroxyapatite (HAP) composition denotes a substance specifically engineered for utilization within medical contexts, with the purpose of repairing, replicating, or substituting the structure of limbs or bones, thereby establishing a functional interface with living tissue. Biomaterial is a material designed to interface with biological systems to enhance, treat, or substitute any tissue, organ, or body function. Biomaterials are categorized based on their material properties, which are polymeric materials, biopolymers, and ceramic materials. Notably, biomaterials do not possess the capability to entirely supplant organ function.

Hydroxyapatite (HAP), a naturally occurring calcium phosphate mineral, holds immense significance in biomedical and materials science due to its exceptional biocompatibility, osteoconductive, and bioactivity. With a chemical composition closely resembling that of bone and teeth, HAP exhibits a remarkable ability to integrate seamlessly with living tissues, making it an ideal candidate for a wide array of applications in regenerative medicine, orthopaedics, and dentistry. In the realm of orthopaedics, HAP based implants and coatings offer promising solutions for bone repair and regeneration, while in dentistry, HAP based materials find applications in dental implants, bone grafts, and restorative dentistry. Moreover, the versatility of HAP extends beyond biomedical applications to include environmental remediation, where its adsorption properties make it effective for removing heavy metals and other pollutants from water and wastewater. Ongoing research continues to focus on refining synthesis techniques, enhancing mechanical properties and elucidating the underlying mechanisms of HAP's interactions with biological systems.

2. Biomaterial

Biomaterials are a diverse and interdisciplinary field that bridges materials science, biology, and medicine. These substances are carefully designed and engineered to perform specific roles within the human body, such as repairing damaged tissues or replacing entire organs. They form the foundation for various medical devices,

implants, and therapeutic solutions, making them essential to modern healthcare. Biomaterials are defined by their compatibility with the body, being non-allergenic, non-carcinogenic, and non-toxic. They release soluble chemical compounds that are safe for the body.

2.1 Bio-ceramic

Bioceramics are a specialized class of ceramic materials designed for biomedical applications. Renowned for their biocompatibility, these materials interact harmoniously with biological systems without causing adverse reactions. Bioceramics are widely used in medical fields such as orthopedic implants, dental prosthetics, bone grafts, and tissue engineering scaffolds. Among the most commonly used bioceramics is hydroxyapatite (HAP), a material that closely mimics the mineral composition of natural bone. HAP is frequently employed in medical implants due to its capacity to integrate with surrounding bone tissue, fostering osseointegration and ensuring long-term stability [23]. Other notable bioceramics include calcium phosphates like tricalcium phosphate (TCP) and calcium phosphate cements (CPCs), as well as bioactive glasses and glass-ceramics.

2.2 Hydroxyapatite (HAP)

Hydroxyapatite (HAP) is a calcium phosphate mineral with a complex crystalline structure that closely mimics the mineral phase of natural bone tissue. Its chemical formula, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})$, reflects its composition, consisting of calcium ions (Ca^{2+}), phosphate ions (PO_4^{3-}), and hydroxide ions (OH^-). These ions arrange themselves in a hexagonal crystal lattice, forming the characteristic hydroxyapatite structure. The inorganic phase consists of tiny hydroxyapatite (HAP) crystals, a mineral with an alkaline. In terms of human bone, the HAP crystals act as a bioactive ceramic that covers 65% to 70% by weight of the bone. Thus, these make the HAP is the main important component of hard tissue. HAP can be classified as a bioactive ceramic since it promotes bone ingrowth without degrading. There two (2) variants of synthetic HAP which ceramic and non-ceramic, and porous and non-porous. The presence of HAP in water solutions at pH levels between 4.2 and 8.0 minimizes the risk of implant corrosion [5].

2.3 Binder

Binders are substances that effectively hold together various components to create a compact structure. The binder's properties are critical in determining particle movement, shaping, and precise measurements of the final shape [23]. The presence of the binder contributes to the formation of strong connections in the green body structure prior to sintering. These connections make the sintering process run more smoothly. By enhancing the physical and rheological characteristics, a binder can facilitate the utilization the material without reducing the performance. [23] The effect of the binder can also improve the microstructure and mechanical properties of HAP bones. Thus, the binding agent can provide a level of quality that allows it to effectively counteract the occurrence of flaws [23].

To make a good HAP bone, an ideal combination of HAP powder and a suitable binder formulation must be determined, as this will influence the mechanical properties and microstructure. The binder is necessary to produce HAP bone because HAP powder has a low reactivity to water. [16] However, if a water-based binder is added, the water becomes reactive with water. Aside from that, the binder used must be long-lasting, prompt, require little effort, have low water absorption, and be protected prior to molding

2.4 Polyvinyl Alcohol(PVA)

Polyvinyl Alcohol, also known as PVA, is a synthetic polymer that dissolves in water, and it consists of numerous connected molecules, characterized by the theoretical formula $[-\text{CH}_2\text{CH}(\text{OH})-n]$ PVA is very suitable for medical use since its attributes of minimal protein attraction, compatibility with living systems, extensive solubility in water, and resistance to chemicals. Thus, PVA is extensively employed in medical applications such as soft contact lenses, ocular solutions, particles used for embolization, barriers preventing tissue adhesion, and as substitutes for artificial cartilage and meniscus PVA's acute oral toxicity is extremely low, with LD_{50} s ranging from 15-20 g/kg. [6]

Nevertheless, PVA is not limited to medical applications, it is also soluble in water and is frequently used as a thin, single-use plastic wrapper in dishwasher. PVA was chosen for this investigation due to its robust hydrophilic properties, which are a consequence of the hydroxyl group present in each repetition module.

2.5 Polyethylene Glycols(PEG)

Polyethylene glycol (PEG) is a synthetic polyether compound known for its biocompatibility and hydrophilic nature, and it is widely used in medical, chemical, and industrial applications [12]. The structure of PEG is represented as $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$. Its production involves the polymerization of ethylene oxide, a key component in antifreeze, using the ring-opening technique. This method allows for the creation of PEGs with different

molecular weights and distributions to suit various applications. The variations in molecular weight can affect PEG's properties, including its shape and physical attributes [19].

PEG possesses numerous defining characteristics. It is colourless, non-toxic, inert, odorless, and non-volatile [19]. Moreover, it exhibits remarkable solubility in water and organic solvents such as benzene, carbon tetrachloride, and chloroform. Creating PEG variants with different molecular weights depends on constructing chains of varying lengths. Larger PEG molecules contain a greater number of repetitions of their structural units compared to their smaller counterparts.

2.6 Zinc (Zn)

Zinc is a chemical element with the atomic number 30 and symbol Zn on the periodic table. It is primarily obtained from zinc sulphide minerals such as sphalerite and zinc oxide ores such as zincite. [19]. Zinc is a bluish-white metal with a low melting point of 420 °C. It is a necessary trace element for the proper functioning of the human body and other biological processes. Zinc's biocompatibility and antimicrobial properties make it indispensable for medical applications, from surgical tools to implants. Zinc improves safety, minimizes infection risks, and promotes healing. Zinc plays essential roles in numerous biological processes and is crucial for the proper functioning of the human body. It is also a cofactor for enzymes that is involved in metabolic pathways, including DNA and protein synthesis, immune function, wound healing, and antioxidant defence mechanisms [14]. Zinc is also necessary for the proper growth and development of cells, tissues, and organs, making it indispensable for overall health and well-being. Low elastic modulus and open-cellular interconnecting porous structures resembling those of natural bone are drawing more attention to Zn-based scaffold materials as biodegradable scaffold materials for biomedical applications [14].

2.7 Magnesium (Mg)

Magnesium (Mg) is a chemical element with the atomic number 12 and symbol Mg on the periodic table. It is lightweight, has low structure density and high damping capacity. [23] Magnesium is highly reactive, and in its pure form it is not found naturally on Earth due to its tendency to react with oxygen and other elements. Magnesium is not present in its pure elemental state; it is only found in the form of compounds. The minerals mentioned are $MgCO_3$, which is known as magnesite, $KCl \cdot MgCl_2 \cdot 6H_2O$, which is called carnallite, and $MgCO_3 \cdot CaCO_3$, which is referred to as dolomite [23]. High pure magnesium (Mg) exhibits less corrosion due to the presence of alpha Mg in its microstructure. Magnesium plays a crucial role in numerous biological processes and is essential for the proper functioning of the human body. It is involved in over 300 enzymatic reactions, including those related to energy metabolism, protein synthesis, muscle and nerve function, and the regulation of blood pressure and glucose levels [16]. Magnesium is also a cofactor for enzymes involved in DNA and RNA synthesis. Table 1 shows the mechanical properties of pure Mg at 20 °C.

Table 1 Mechanical Properties of pure Mg at 20 °C [16]

Mechanical Property	Annealed Sheet	Hand Rolled Sheet	Sand Cast	Extruded
Compressive Yield Strength (MPa)	69 to 83	105 to 115	21	34 to 55
Tensile Yield Strength (MPa)	90 to 105	115 to 140	21	69 to 105
Ultimate Tensile Strength (MPa)	160 to 195	180 to 220	90	165 to 205
Hardness (HB)	40 to 41	45 to 47	30	35

2.8 Surface Roughness

Surface roughness is a crucial aspect of material surface texture. It refers to the slight irregularities and variations that impact the functionality, performance, and appearance of materials and objects in engineering and manufacturing [4]. These irregularities, often likened to peaks and valleys on the surface, can vary in size, shape, and distribution, affecting key characteristics such as friction, wear resistance, and the ability of surfaces to adhere or bond in mechanical assemblies. Controlling surface roughness is essential for maximizing operational efficiency and long-term performance [4]. Smooth surfaces with controlled roughness levels can minimize frictional losses, thereby improving energy efficiency and prolonging the lifespan of material.

3. Methodology

The flowchart in Figure 1 illustrates the process of completing the project from start to finish. Hydroxyapatite and binders are employed in this experiment, and the mechanical properties are determined through the experiment.

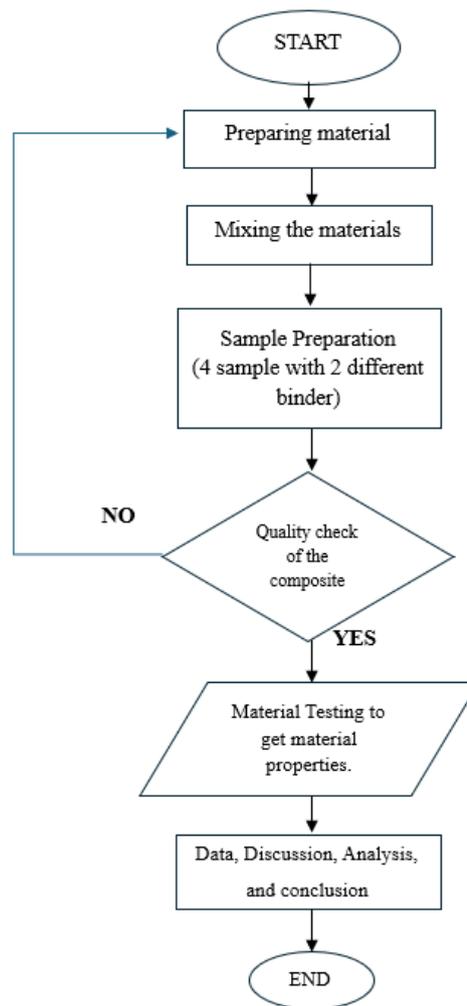


Fig. 1 Experiment flowchart

4. Results and Discussion

Two test categories have been completed. The first involves the characterization of hydroxyapatite powder, serving as a preliminary evaluation. The second test, conducted after machining, focuses on further analysis. To characterize the hydroxyapatite powder, the following tests were performed: X-ray diffraction, scanning electron microscopy (SEM), modulus of rupture (MOR), surface roughness, density, porosity, and evaluations after sintering shrinkage. All collected data were thoroughly analyzed for discussion and conclusions.

4.1 Mechanical Properties Test

4.1.1 Shrinkage

A shrinkage test was conducted to better understand the behavior of the composite and to enhance its mechanical strength and bioactivity. The process began with preheating the HAP sample at 56°C for 24 hours to remove the water. This was followed by sintering at 1200°C with a holding time of 120 minutes. To measure shrinkage, the length of the HAP sample was recorded both before and after sintering using vernier calipers, which have an accuracy of ± 0.005 mm. These measurements, summarized in Table 2, were then used to calculate the percentage of shrinkage (Table 3).

Table 2 Sample dimension before and after sintering

Mixture Ratio		Weight (g)		Length (mm)		Width (mm)		Thickness (mm)	
PEG	PVA	Before	After	Before	After	Before	After	Before	After
1%	4%	14.73	12.60	102	79.30	13	9.74	9.45	7.33
2%	3%	13.56	11.64	102	78.66	13	9.38	8.98	6.89
3%	2%	14.47	12.06	102	78.70	13	9.42	9.20	6.78
4%	1%	14.22	11.77	102	79.02	13	9.68	9.24	5.95

Table 3 Percentage of Shrinkage

Sample		Percentage of Shrinkage (%)	
PEG	PVA	Weight	Length
1%	4%	14.43	22.43
2%	3%	14.15	23.27
3%	2%	16.64	26.30
4%	1%	17.22	35.61

4.1.2 Flexural Test

The Modulus of Rupture (MOR) test was done to indicate the highest level of stress that a substance can withstand before fractures under bending loads. Thus, the mechanical properties of HAP sample can be determined as presented in Table 4. The Stress of HAP samples were plotted as shown in Figure 2.

Table 4 Max Stress and Strain obtained from testing

Sample		Max Stress (N/mm ²)	Max Strain (%)
PEG	PVA		
1%	4%	11.7224	0.82667
2%	3%	9.85368	1.01454
3%	2%	13.3948	0.63765
4%	1%	5.09953	0.93890

Sample		Stress (N/mm ²) vs Stroke strain (&)
PEG	PVA	
1%	4%	
2%	3%	

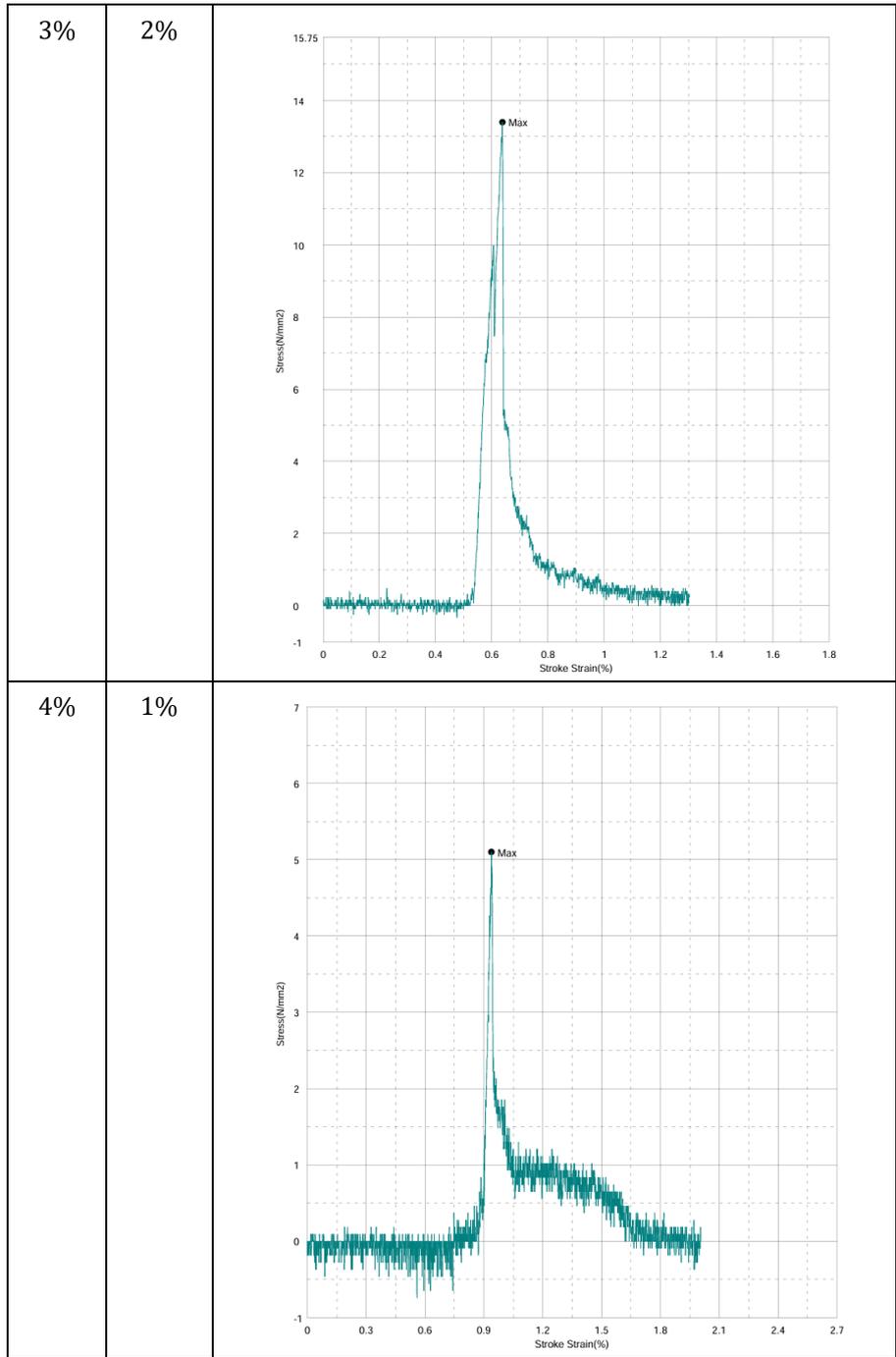


Fig.2 Max Stress of HAP samples graph

5. Conclusion

The binder used has a significant impact on the surface roughness of bioceramic materials milled with a ball nose end mill. Hydroxyapatite (HAP) samples were prepared through mixing, compressing, sintering, and machining, followed by tests to find the best binder percentage for smooth surfaces. Two binders, polyvinyl alcohol (PVA) and polyethylene glycol (PEG), were tested at different percentages. The results showed that the binder type and amount affected HAP's properties. Surface roughness was evaluated using tests like shrinkage, strength, microscopy, hardness, porosity, and density, all performed on sintered HAP samples.

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Conflict of Interest

The authors declare no conflict of interest regarding the paper's publication.

Author Contribution

The authors confirm contribution to the paper as follows: **study conception and design:** Ezzra Epoi Wan, Noor Hakim Rafai; **data collection:** Ezzra Epoi Wan; **analysis and interpretation of results:** Ezzra Epoi Wan; **draft manuscript preparation:** Ezzra Epoi Wan, Noor Hakim Rafai. All authors reviewed the results and approved the final version of the manuscript.

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