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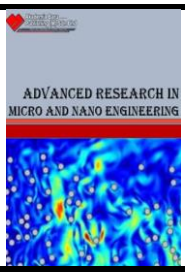

Preparation and Characterization of Hydroxyapatite Based Composite Material via Cold Sintering Process

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ABSTRACT

This study focuses on the synthesis of hydroxyapatite (HA) from bovine bones through calcination and subsequent combination with Polyvinyl Alcohol (PVA) using the Cold Sintering Process (CSP). The CSP, operating at lower temperatures than conventional methods, aims to preserve the bioactivity and biocompatibility of HA, crucial for biomedical applications. The research investigates the influence of HA composition, sintering temperature, and PVA content on the porosity and compressive strength of the HA-PVA composite. The Hydroxyapatite powder, obtained from calcinated bovine bones, exhibits irregular shapes and sizes with a maximum grain size of 10µm, confirmed by SEM analysis. XRD analysis validates the successful production of Hydroxyapatite, showcasing characteristic peaks. The HA/PVA composite's XRD pattern indicates the dominance of HA, with PVA present as well. The study produces 27 specimens through the CSP, varying HA composition and sintering temperature. Porosity increases with higher HA content and sintering temperature, attributed to the role of PVA in binding HA particles. Compressive strength rises with increased HA content, emphasizing HA's role in enhancing mechanical strength. The presence of porosity is mitigated by a strong bond between HA and PVA, contributing to structural integrity. This research provides insights into tailoring HA-PVA materials for biomedical applications, considering controlled porosity and mechanical strength. The CSP, with its unique advantages, emerges as a promising method for developing customized materials to meet diverse biomedical needs.

1. Introduction

Hydroxyapatite (HA) is a calcium phosphate compound that is similar to the primary mineral components found in human bones and teeth. It is widely used in biomedical applications, including the production of bone and dental implants, as well as tissue regenerative materials [1,2]. Advanced synthesis methods are required to meet specific requirements such as controlled porosity and

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suitable mechanical strength. HA is also a material commonly used as a catalyst [3], adsorption [4] and sensors [5].

Conventional sintering processes typically involve high temperatures, often exceeding 1000°C [6-8]. While these methods achieve material densification, they can pose challenges. For HA, exposure to such extreme temperatures can lead to undesired changes in crystal structure and composition, affecting bioactivity [9]. In contrast, the Cold Sintering Process allows synthesis at significantly lower temperatures, typically below 300°C or even at room temperature [10]. This preservation of HA's bioactivity and biocompatibility without risking alterations is facilitated by pressure-assisted densification in the Cold Sintering Process, enabling controlled material densification and porosity manipulation. The Cold Sintering Process is versatile in its application to polymer and ceramic materials, making it suitable for developing composite materials for biomedical applications [11-13].

Polyvinyl Alcohol (PVA) is a synthetic polymer formed from vinyl alcohol monomers through polymerization processes. Its distinctive chemical structure provides excellent water solubility, making it highly suitable for applications in the biomedical field. Additionally, PVA boasts advantages in terms of resistance to organic and chemical solvents, as well as good dimensional stability [14]. One of the main advantages of PVA is its high biocompatibility, meaning it can interact with biological tissues without inducing toxic or harmful immunological reactions. This makes PVA particularly suitable for manufacturing various medical implants, such as wound dressings, tissue scaffolds, and artificial blood vessels.

Furthermore, the ease of its manufacturing process is a crucial factor contributing to PVA's popularity in the biomaterial industry. PVA can be processed using various manufacturing methods, including 3D printing, extrusion, and moulding, allowing for the production of various shapes and structures tailored to specific application needs. Several previous studies have demonstrated the enhanced benefits of HA-PVA composites, as reported by Jalager, where PVA was able to improve mechanical strength and biocompatibility [15]. The addition of HA also altered the physical and chemical properties of PVA, enhancing its potential as artificial cartilage [16-18].

More comprehensive research related to the utilization of HA-PVA composites as implant materials has also been conducted. However, its utilization is generally limited to gel forms, with very few reports on the preparation of these composites in solid forms. This limitation is understandable due to the significant difference in solidification temperatures between the two materials, making it difficult to form them into solid shapes using conventional methods. However, with the cold sintering process, this becomes feasible.

The objective of this research is to combine the advantages of the Cold Sintering Process with the development of customizable HA-PVA materials. By understanding the parameters in this process, this study aims to produce materials with controlled porosity and appropriate mechanical strength. These outcomes hold great relevance for the advancement of bone and dental implant technology, as well as other biomedical applications.

2. Materials and Method

The raw materials of the Hydroxyapatite in the form of bovine bones were processed using the calcination method at 800^{o}C for 1 hour inside an electric furnace, producing bones that are free from organic contaminants. After the calcination process was finished, the calcinated bones were then crushed with mortar and then sieved to reach the intended size.

The cold sintering process begins with mixing the pre-weighed HA (Hydroxyapatite) and PVA (Polyvinyl Alcohol) using a magnetic stirrer for 1 hour. Subsequently, the HA/PVA mixture is poured

into a molding for the sintering process, with a pressure of 600 MPa applied for 30 minutes, at temperature variations of 90, 100, and 120°C.

The X-ray Diffraction (XRD) analysis was employed to investigate the potential phase transformations that may occur during the sintering process, utilizing the Rigaku MiniFlex 600 X-Ray Diffraction equipment. The surface structure of the samples was observed using a scanning electron microscope (SEM), specifically the FEI Inspect S50. Porosity, specific mass, and water absorption characteristics of each sintered specimen were measured using the Archimedes method, particularly the water immersion technique. All the data presented represent the average values obtained from three measurements. Compression testing was performed using a Universal Testing Machine (UTM), with reference to the ASTM C 733 standard as the basis for calculations in measuring compressive strength.

3. Results and Discussion

The hydroxyapatite powder produced by the procedure is then analyzed using SEM as depicted at Figure 1. It shows an irregular shape and size with a maximum grain size of 10µm. The SEM images also show that there is a huge size disparity between the HA grains produced in this method.

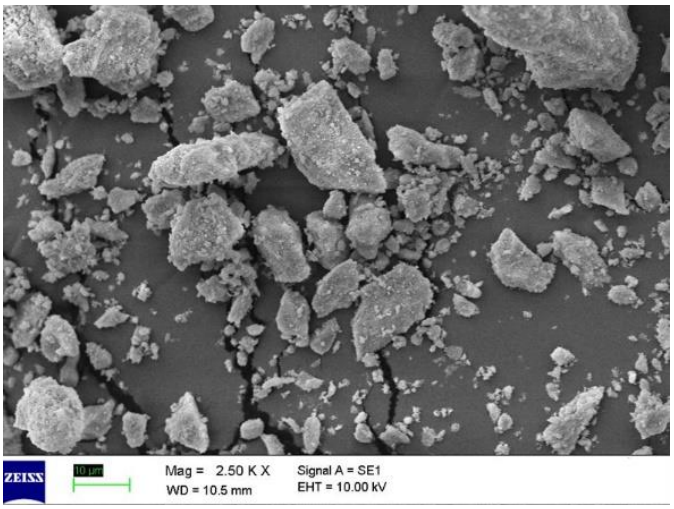

Fig. 1. SEM result of HA powder

The powder Hydroxyapatite from calcinated bovine bones was put into the XRD machine and the result in the form of intensities at certain angles (theta) was then compared to the ICDD 00-009-0432 standard of Hydroxyapatite (Figure 2). It is confirmed that the calcination process successfully created Hydroxyapatite from bovine bones. There are 5 notable peaks in the hydroxyapatite specimen at angles 2θ = 32.1, 26.3, 49.5, 47, and 40.1°.

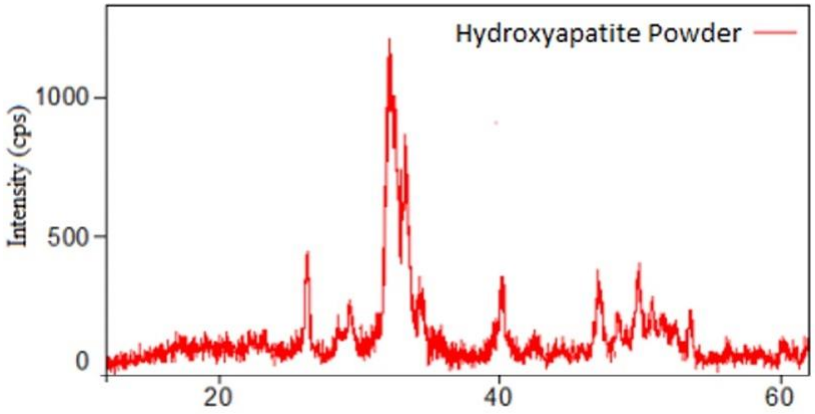

Fig. 2. XRD pattern of bovine bone powder

Based on the X-ray diffraction pattern formed, it can be observed that in this specimen (Figure 3), there are two main phases, namely hydroxyapatite (HA) and Polyvinyl Alcohol (PVA). There are 12 peaks in the X-ray diffraction pattern associated with HA. This indicates that HA is the dominant component in this sample. There are 7 peaks in the X-ray diffraction pattern associated with PVA. Although PVA is present in the sample, its presence is less compared to HA.

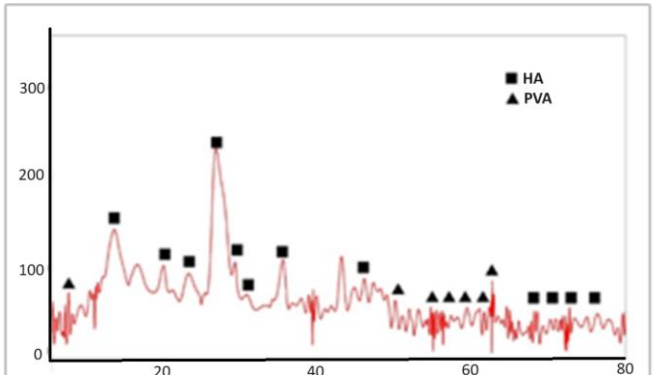

Fig. 3. XRD Pattern of HA/PVA composite

The specimens are in the form of a cylinder with a diameter of 12 mm (Figure 4). The compaction process faces some difficulty in maintaining the pressure set for each specimen because even a tiny mistake can melt the entire composite.

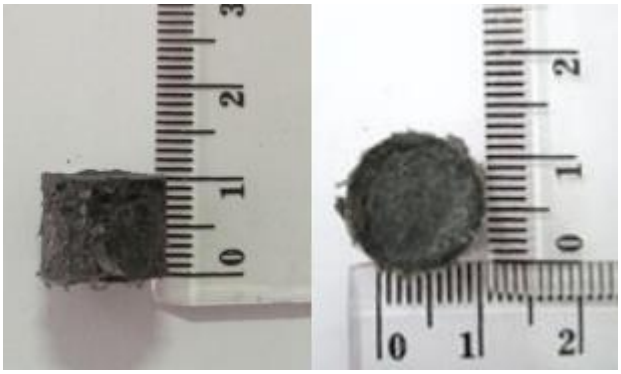

Fig. 4. Specimen from compaction process

There is a clear trend observed in the data, where an increase in the hydroxyapatite (HA) content within the composite results in higher porosity levels (as shown in Figure 5). This phenomenon can be attributed to the inherent characteristics of HA as a denser and more resistant material when subjected to pressure, in contrast to PVA. Consequently, a higher HA content leads to fewer voids or pores being formed during the sintering process.

The role of PVA in acting as a binding agent is significant in reducing porosity, particularly when the PVA content in the composite is sufficiently high. During the sintering process, PVA effectively binds HA particles together, thereby mitigating the formation of pores. When PVA softens or undergoes partial decomposition near the sintering temperature, it can effectively occupy the interstitial spaces between HA grains, leading to a reduction in overall porosity. At the sintering temperature of approximately 120°C, PVA may undergo partial decomposition [19]. This decomposition process results in the release of gases, which subsequently create pores within the sample, ultimately leading to an increase in porosity. This effect is clearly demonstrated in the composition containing 10% PVA, where the porosity is significantly higher compared to the composition with 30% PVA.

In the composition with 30% PVA, a greater quantity of PVA is available to fill the voids between HA grains, resulting in a lower overall porosity. Conversely, in the composition with only 10% PVA, the reduced quantity of PVA diminishes its capacity to effectively bind HA particles together, consequently leading to higher porosity. Furthermore, the application of high pressure during the sintering process plays a vital role in compacting the material particles, thereby minimizing pore formation [20]. This pressure-related effect holds true for both compositions, although the varying PVA content may exert a more dominant influence in determining the final porosity.

The analysis results underscore the significance of several factors, including the material composition, the role of PVA as a binding agent, the partial decomposition of PVA, and the application of pressure during the sintering process, all of which collectively contribute to the observed levels of porosity in the hydroxyapatite/PVA composite. Lower porosity levels are associated with higher HA content and the effective role of PVA in occupying interstitial spaces between HA grains, while higher porosity levels are linked to PVA decomposition and its reduced presence within the composite composition.

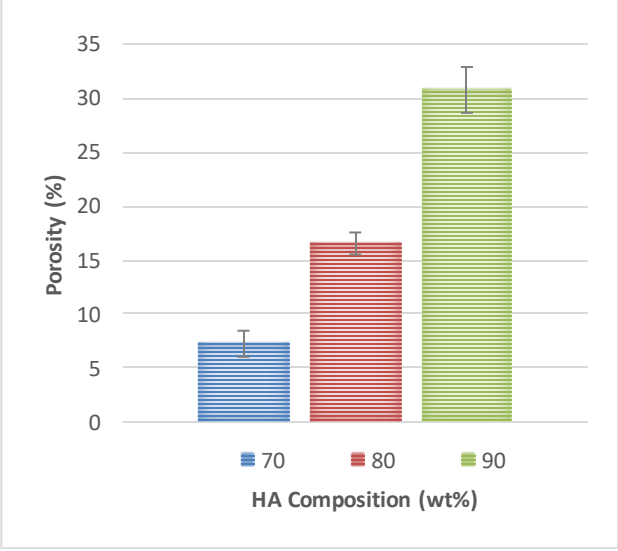

Fig. 5. Porosity of each HA Composition

The data, as illustrated in Figure 6, clearly indicates that porosity within the composite increases proportionally with the elevation of sintering temperature. At lower sintering temperatures, such as 90°C, PVA maintains its solid state, effectively functioning as a binding agent. This solid-state characteristic serves to mitigate the formation of pores, thereby accounting for the lower porosity observed at this temperature.

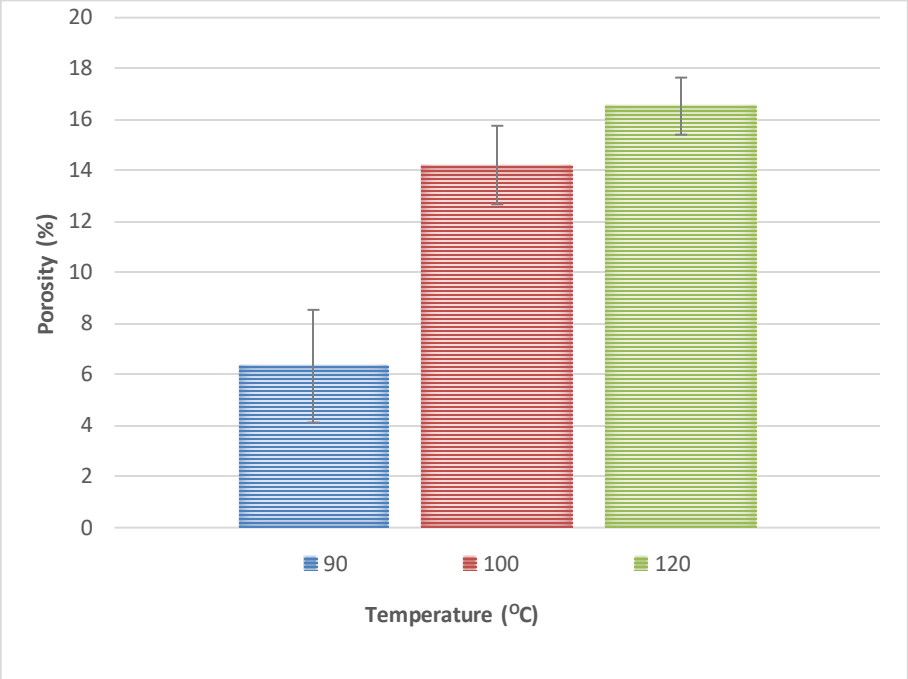

Fig. 6. Porosity of HA80/PVA20 at various sintering temperature

Conversely, as the temperature nears or exceeds the melting point of PVA—where PVA initiates melting or experiences partial decomposition—partial melting occurs, accompanied by the release of gas. This phenomenon subsequently intensifies the creation of pores, elucidating the heightened porosity evident at 100°C and 120°C. The elevated melting point of PVA ensures its solidity at lower sintering temperatures, like 90°C, permitting PVA to act as a proficient binding agent. Nevertheless, at 100°C and 120°C, it is plausible that PVA commences partial melting or decomposition, thereby contributing to the formation of substantial pores.

The porosity data is intrinsically intertwined with sintering temperature, with the melting point of PVA playing a pivotal role in this intricate relationship. At lower temperatures, PVA retains its solid form and effectively fulfils its role as a binder [21], whereas, at higher temperatures, the potential occurrence of partial melting or decomposition in PVA leads to an augmentation of porosity.

The data reveals a noticeable trend: a higher proportion of HA in the composite leads to increased compressive strength in the samples. This observation strongly suggests that HA plays a significant role in enhancing the material's compressive strength, as demonstrated in Figure 7. Conversely, PVA, as another component, seems to exert a relatively minor influence on compressive strength.

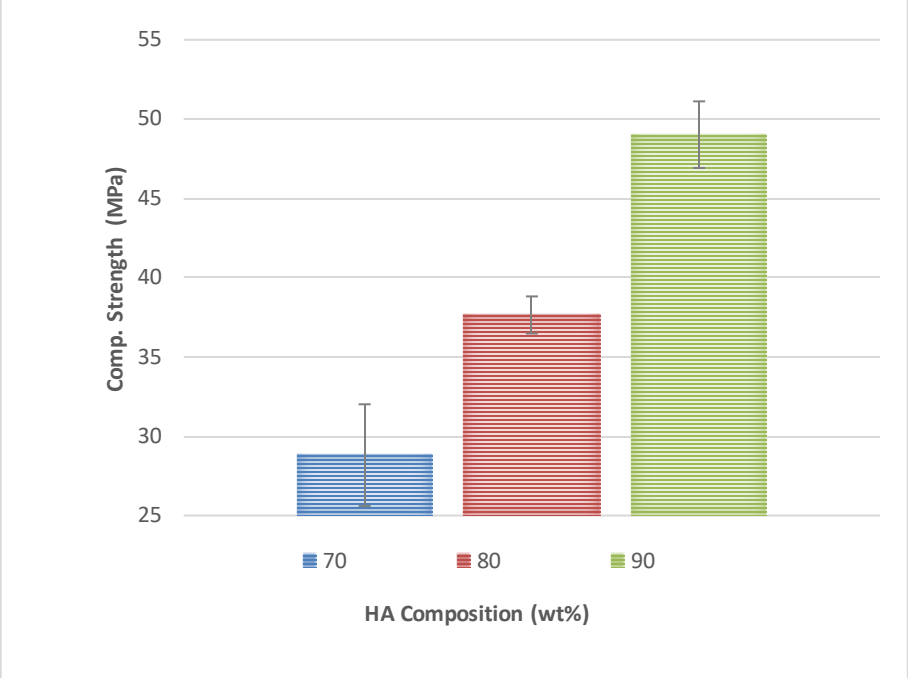

Fig. 7. Compressive Strength of each HA Composition

Moreover, the presence of a robust bond between HA and PVA can uphold material strength even when porosity is present. This phenomenon is achievable through meticulous sintering processes or alternative manufacturing techniques that establish a robust interconnection between the composite components [22]. Such interconnections enable mutual support and compensation, mitigating the impact of porosity.

Additionally, the distinct structural arrangement within the composite can be a contributing factor. For example, if porosity is evenly and precisely distributed within the matrix, it may have minimal adverse effects on mechanical strength. In fact, when porosity takes the form of a well-organized structure, akin to a sponge-like configuration, it can contribute to enhanced strength [23]. This is attributed to its role in redistributing loads and reducing stress concentration points. Furthermore, well-structured porosity can effectively minimize stress concentration, thereby reducing the risk of material failure.

Figure 8 clearly shows porosity on the surface of the HA90/PVA10 specimen. The size of the porosity is ±4µm and correlates to the result of the validation experiment which has the material at an average of 30.75% porosity. The SEM (Scanning Electron Microscope) image reveals that densification has occurred within the specimen. This suggests that during the manufacturing process, diffusion between the HA and PVA components took place, resulting in the creation of bonds between the particles. This bonding is a positive aspect as it can enhance the material's structural integrity and strength.

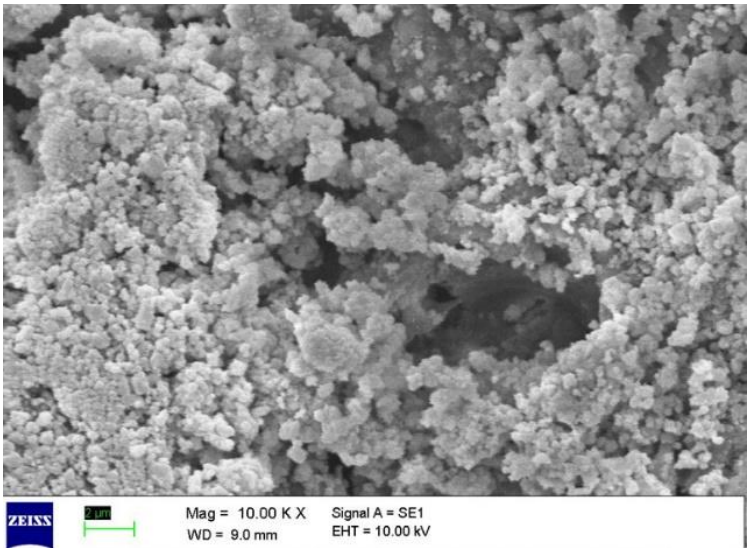

Fig. 8. The SEM image of HA90/PVA10 specimen

4. Conclusions

The Hydroxyapatite (HA) powder obtained from bovine bones exhibits irregular shapes and sizes, with a maximum grain size of 10µm. The X-ray diffraction (XRD) analysis confirms the successful conversion of bovine bone into HA. The study demonstrates a clear trend where an increase in HA content within the composite leads to higher porosity levels. This is primarily due to the denser and more resistant nature of HA compared to PVA under pressure, resulting in fewer voids formed during the sintering process. PVA plays a significant role as a binding agent, reducing porosity, especially when its content in the composite is high. During sintering, PVA effectively binds HA particles together, reducing the formation of pores. However, PVA may undergo partial decomposition during sintering, leading to gas release and increased porosity. The data suggests that HA content significantly influences compressive strength, with higher HA content contributing to increased strength. Strong bonds between HA and PVA can also maintain strength even in the presence of porosity. The composition, the role of PVA, sintering temperature, and structural organization collectively contribute to the observed properties of the material.

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