

Influence Of ZrO₂ And TiO₂ Nanoparticle Reinforcement On The Microstructure And Mechanical Behavior Of Hap Nanocomposites

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In the present study, hybrid HAp nanocomposites reinforced with zirconia (ZrO₂) and titania (TiO₂) were developed to improve the mechanical performance of HAp while retaining its desirable biological characteristics. HAp/(ZrO₂ + TiO₂) nanocomposites containing different reinforcement concentrations were synthesized using a high-energy ball milling (HEBM) technique. The milled powders were compacted and subsequently sintered to obtain dense composite specimens. The structural and microstructural characteristics of the developed nanocomposites were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The influence of ZrO₂ and TiO₂ reinforcement on the mechanical properties of HAp was evaluated in terms of compressive strength, microhardness, Young's modulus, flexural strength, and fracture toughness. The results demonstrate the potential of ZrO₂-TiO₂ reinforced HAp nanocomposites as candidate materials for advanced biomedical and orthopaedic applications.

1. Introduction

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HAp) is one of the most extensively studied bioceramic materials for biomedical applications, particularly in orthopaedic and dental fields. Its chemical composition and crystal structure are closely related to the inorganic mineral component of human hard tissues, including bones and teeth. Consequently, HAp exhibits excellent biocompatibility, bioactivity, osteoconductivity, and the ability to support the formation of new bone tissue. These characteristics have made HAp an attractive material for bone substitutes, coatings, dental applications, and tissue-engineering scaffolds.

Despite its favorable biological properties, the practical application of HAp in load-bearing conditions is limited by its intrinsic brittleness, relatively low fracture toughness, and inadequate mechanical strength. Therefore, considerable research has been directed toward improving the mechanical performance of HAp through the incorporation of suitable reinforcing phases. Ceramic reinforcements with higher strength, elastic modulus, and wear resistance than the HAp matrix can effectively improve the mechanical characteristics of HAp-based composites.

The incorporation of secondary ceramic phases is one of the promising approaches for overcoming the mechanical limitations of HAp. In particular, zirconia (ZrO₂) and titania (TiO₂) have attracted significant interest because of their excellent mechanical properties, chemical stability, wear resistance, and biocompatibility. The combination of HAp with ZrO₂ and TiO₂ can potentially produce hybrid bioceramic composites exhibiting an improved balance between mechanical strength and biological compatibility.

Zyman et al. [1] reported that the incorporation of strong reinforcing phases can considerably enhance the mechanical properties of ceramic materials. Xihua et al. [2] developed cost-effective, high-performance HAp-based ceramic composites and investigated the effect of alumina addition on their properties. Lee et al. [3] reported that ZrO₂/Al₂O₃ systems exhibit improved biocompatibility, oxidation resistance, and wear resistance. Shi et al. [4] investigated the use of ZrO₂/La₂O₃ binders for improving the bending and tensile strength of HAp. Aminzare et al. [5] studied HAp-based nanocomposites with high density and investigated the influence of titania and alumina nanoparticles on their mechanical properties, microstructure, and phase stability.

Viswanath and Ravishankar [6] investigated the interfacial reactions in HAp/alumina nanocomposites and reported significant interaction between the alumina reinforcement and HAp matrix. Mobasherpour et al. [7] synthesized nanocrystalline HAp through a precipitation method and investigated the influence of ZrO₂/Al₂O₃ additions on the mechanical properties of HAp powders. Lee et al. [8] investigated a multi-pass extrusion process for improving the mechanical properties of HAp-(t-ZrO₂/Al₂O₃)-(m-ZrO₂) composites. Khalil and Almajid [9] developed Mg/HAp nanocomposites containing nanosized reinforcement and investigated their properties following high-frequency induction sintering. They reported microhardness and compressive-strength values of approximately 60 HV and 194.5 MPa, respectively.

Gain et al. [10] fabricated HAp-ZrO₂ nanocomposites using powder metallurgy and employed polymethyl methacrylate as a pore-forming agent. Their investigation demonstrated that the microstructure of the nanocomposites has a substantial influence on mechanical strength. Rapacz-Kmita et al. [11] studied the mechanical properties of zirconia-reinforced HAp and reported improved mechanical performance associated with needle-like grain structures at different temperatures. Choi et al. [12] investigated Al₂O₃- and Ni₃Al-reinforced HAp composites and observed improvements in fracture toughness and fracture strength following reinforcement. Morks et al. [13] investigated HA/SiO₂/TiO₂ plasma-sprayed coatings on SUS 304 substrates using a gas-tunnel plasma torch. Their results indicated that the incorporation of SiO₂ and TiO₂ significantly influenced the microstructure, mechanical properties, and corrosion resistance of the coatings.

The above studies demonstrate the potential of ceramic reinforcement for improving the mechanical characteristics of HAp-based materials. However, further investigation is required to understand the combined effect of multiple nanoscale ceramic reinforcements on the microstructure and mechanical behavior of HAp. In this context, ZrO₂ and TiO₂ are particularly promising reinforcement materials because of their high strength, hardness, wear resistance, thermal and chemical stability, and suitability for biomedical applications.

In the present investigation, HAp nanopowders with an average particle size of approximately 20–40 nm were used as the matrix material. Zirconia particles with an average particle size of 80–100 nm were selected as one of the reinforcement phases owing to their high strength,

fracture toughness, wear resistance, chemical and thermal stability, and bio-inert nature. Titania particles with an average particle size of 80–100 nm were employed as the second reinforcement because of their favorable mechanical properties, chemical stability, corrosion resistance, and biocompatibility. The combined use of ZrO₂ and TiO₂ is expected to enhance the mechanical performance of the HAp matrix while maintaining its suitability for biomedical applications.

Accordingly, the present study focuses on the fabrication and characterization of HAp-based hybrid nanocomposites reinforced with ZrO₂ and TiO₂. The reinforcement content was varied at 5, 10, 15, 20, and 25 wt.% to investigate its influence on the phase composition, microstructure, and mechanical properties of the resulting nanocomposites.

2. Experimentation

2.1 Sample Preparation

Hydroxyapatite (HAp) and HAp-based composite powders containing different weight percentages of ZrO₂ and TiO₂ reinforcement were prepared using the high-energy ball milling (HEBM) technique. The total reinforcement content was varied as 0, 5, 10, 15, 20, and 25 wt.%. ZrO₂ and TiO₂ nanoparticles were incorporated into the HAp matrix either individually or in combination to develop hybrid HAp-based nanocomposites.

The powder mixtures were subjected to high-energy ball milling using tungsten-carbide-hardened steel balls. Milling was performed for 1 h at a rotational speed of 300 rpm, while the ball-to-powder weight ratio was maintained at 20:1. The milling process facilitated uniform mixing and refinement of the constituent powders.

Following milling, the composite powders were compacted under a pressure of 100 bar with a holding time of 150 s. The compacted specimens were subsequently sintered at 1200 °C for 1 h. Cylindrical specimens with a diameter of 20 mm and a height of 5 mm were prepared for compressive-strength and hardness measurements. Rectangular specimens measuring 40 mm × 10 mm × 3 mm were fabricated for flexural-strength and fracture-toughness investigations. After reaching the specified sintering temperature, the holding time was recorded for 1 h. Following completion of the sintering cycle, the furnace was switched off and the specimens were allowed to cool naturally to room temperature. The sintered specimens were then prepared for subsequent structural, microstructural, and mechanical characterization.

2.2 Experimental Procedure

The phase composition and crystallographic characteristics of the HAp matrix and its composites were examined using an X-ray diffractometer equipped with Cu-K α radiation having a wavelength of $\lambda = 1.5406 \text{ \AA}$. XRD measurements were performed over a diffraction angle range of 6°–90° with a step size of 0.01°. The average crystallite size was estimated from the broadening of the diffraction peaks using Scherrer's equation [19].

The surface morphology and microstructural features of the sintered specimens were investigated using scanning electron microscopy (SEM). Elemental analysis was performed using an energy-dispersive X-ray spectroscopy (EDX) system attached to the field-emission scanning electron microscope (FE-SEM). The presence and distribution of elements such as Ca, P, O, Zr, and Ti were examined to verify the composition of the developed composites.

The compressive strength of the nanocomposite ceramics was evaluated using a universal testing machine (UTM). Cylindrical specimens measuring 20 mm in diameter and 5 mm in height were subjected to quasi-static compressive loading. The crosshead speed was calculated according to the relationship $v = \dot{\epsilon} h_0$, where h_0 represents the initial specimen height and $\dot{\epsilon}$ denotes the initial strain rate. A constant initial strain rate of 0.001 s^{-1} was employed during the test. The specimens were loaded until fracture [19].

The density of the sintered specimens was determined using the Archimedes principle with distilled water as the immersion medium. The measured density was used to evaluate the relative density of the fabricated nanocomposites.

Microhardness measurements were performed on polished HAp composite specimens using a Shimadzu HMV-2000 microhardness tester equipped with a Knoop indenter. The hardness measurements were conducted in accordance with ASTM E384. A load of 4.905 N was applied for a dwell time of 15 s. The Knoop hardness value was calculated from the applied load and the length of the longer diagonal of the indentation according to Eq. (1) [20].

$$H = 14229 \frac{L}{d^2} \quad (1)$$

In Eq. (1), d represents the longer diagonal of the indentation in millimetres, while L denotes the applied load in Newtons.

Young's modulus of the composites was determined using Eq. (2) [20]. In this equation, $B_1/A_1 B_2/A_2$ represents the indentation diagonal ratio, whereas $B/AB/A$ denotes the corresponding ratio for the Knoop indenter. The constant α was taken as 0.45.

$$\frac{B'}{A'} = \frac{B}{A} - \alpha \frac{E}{H} \quad (2)$$

The flexural strength of the fabricated nanocomposites was evaluated using a three-point bending test. Rectangular specimens measuring 40 mm in length, 10 mm in width, and 3 mm in thickness were polished to remove surface irregularities before testing. The specimens were positioned on a three-point bending fixture, and the load was applied at the midpoint of the specimen using a crosshead speed of 0.05 mm/min.

Fracture toughness (K_{IC}) was estimated using the indentation fracture technique. The calculated values were evaluated using Eq. (3) [21], which relates fracture toughness to Young's modulus, hardness, applied load, and the crack geometry generated by the indentation. In Eq. (3), K_{IC} represents fracture toughness, E is Young's modulus (GPa), H is hardness (GPa), P is the applied load (N), and ξ is a geometrical constant associated with the indenter, with a value of 0.008.

$$K_{IC} = \xi \left[\frac{E}{H} \right]^{2/5} \frac{P}{d^{1/2}} \quad (3)$$

3. Results and Discussion

3.1 X-Ray Diffraction Analysis of HAp/(ZrO₂ + TiO₂) (1:1) Powders

Figure 1 presents the X-ray diffraction (XRD) patterns of the HAp/(ZrO₂ + TiO₂) nanocomposite powders synthesized using the high-energy ball milling (HEBM) technique. The diffraction patterns confirm the presence of the constituent HAp, ZrO₂, and TiO₂ phases in the composite powders. The characteristic diffraction peaks of HAp are prominently

observed, with a strong reflection around $2\theta = 32.6^\circ$. With increasing ($\text{ZrO}_2 + \text{TiO}_2$) reinforcement content, changes in the intensity and broadening of the diffraction peaks are observed, particularly around $2\theta = 34.8^\circ$.

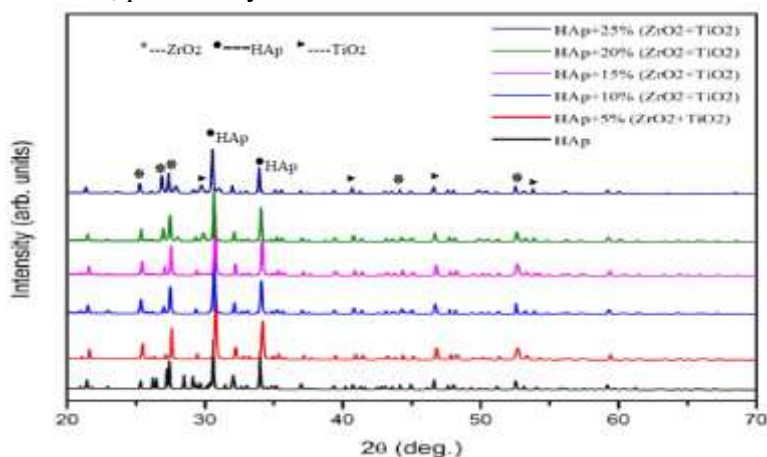


Figure.1 X-ray diffraction patterns of HAp/($\text{ZrO}_2 + \text{TiO}_2$)(1:1) Nano-composite powders

The observed peak broadening can be attributed to the refinement of the HAp crystallites during high-energy ball milling and the presence of ZrO_2 and TiO_2 particles, which can restrict grain growth within the HAp matrix. The reinforcement phases act as effective grain-growth inhibitors and contribute to crystallite refinement. No additional diffraction peaks corresponding to undesirable impurity phases are detected, indicating that the milling process produced chemically stable composite powders. The increase in peak intensity with reinforcement content also suggests an improvement in the crystallinity of the resulting composite system.

3.2 Microstructural Analysis of HAp/($\text{ZrO}_2 + \text{TiO}_2$) (1:1) Powders

The SEM micrographs of HAp/($\text{ZrO}_2 + \text{TiO}_2$) composite powders containing 5, 10, 15, 20, and 25 wt.% reinforcement are presented in Figure 2(a–e). The micrographs reveal significant changes in particle morphology and agglomeration behavior with increasing reinforcement content.

The incorporation of ZrO_2 and TiO_2 into the HAp matrix results in a reduction in the apparent particle size and a more uniform distribution of the constituent phases. The homogeneity of the powder mixture depends primarily on the particle size and the extent of unbroken agglomerates formed during the milling process. The addition of nanosized reinforcement particles contributes to the refinement and redistribution of the HAp particles.

The reduction in particle agglomeration can be attributed to the repeated impact, fracture, cold welding, and mechanical alloying effects occurring during high-energy ball milling. The severe plastic deformation and repeated collisions between the milling media and powders promote intimate mixing of HAp, ZrO_2 , and TiO_2 particles. However, excessive milling and cold welding may also influence powder packing characteristics and, consequently, the densification and microstructural homogeneity of the sintered composites.

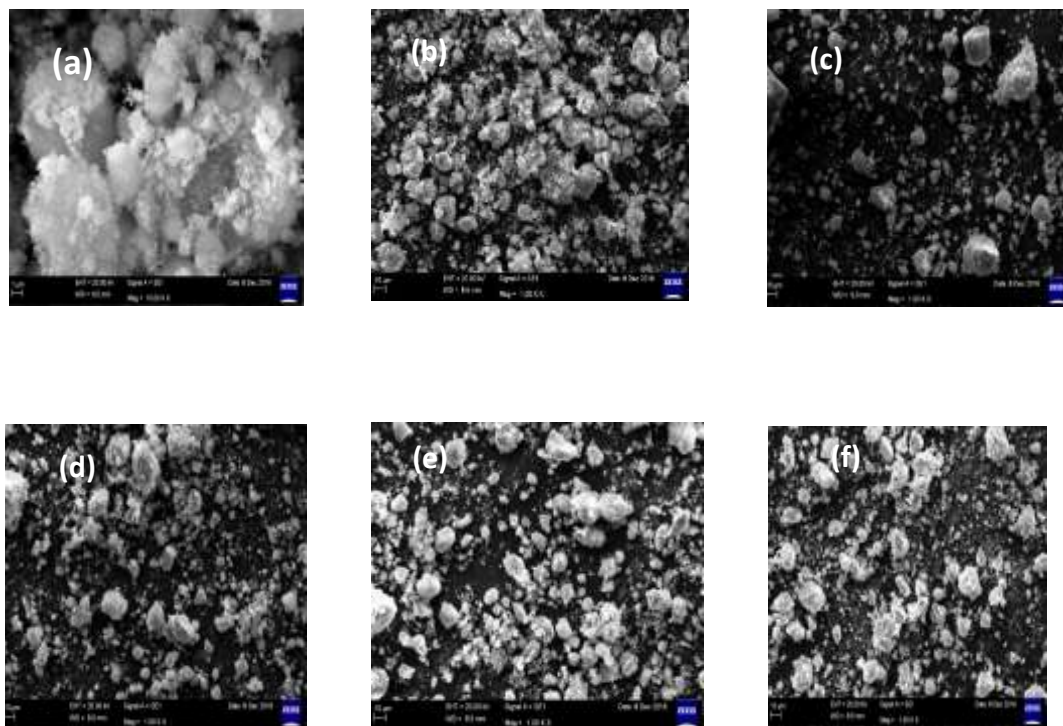


Figure. 2 SEM micrographs after ball milling (a) HAp (b) HAp /5 wt% (ZrO₂+ TiO₂) (c) HAp/10 wt% (ZrO₂+ TiO₂) (d) HAp/15 wt% (ZrO₂+ TiO₂) (e) HAp/20 wt% (ZrO₂+ TiO₂) (f) HAp/25 wt% (ZrO₂+ TiO₂)

3.3 X-Ray Diffraction Analysis of Sintered HAp/(ZrO₂ + TiO₂) (1:1) Nanocomposites

Figure 3 illustrates the XRD patterns of pure HAp and HAp/(ZrO₂ + TiO₂) composites after sintering at 1200 °C. The diffraction peaks correspond predominantly to the HAp matrix and the incorporated ZrO₂ and TiO₂ phases. No significant additional peaks associated with undesirable impurity phases are detected in the investigated compositions.

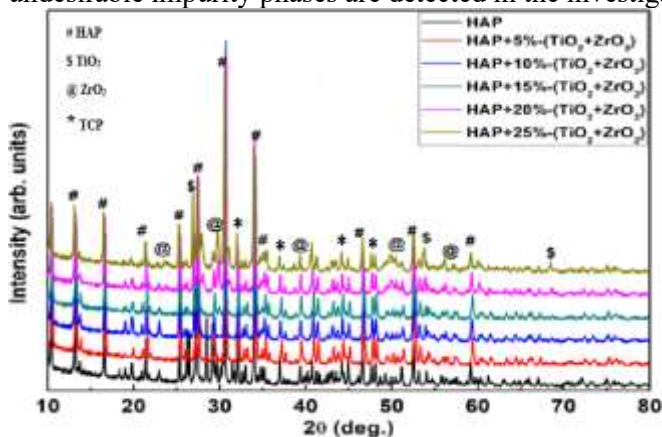


Figure 3 XRD pattern of HAp/(ZrO₂+TiO₂)

An increase in the intensity of the diffraction peaks is observed with increasing reinforcement content, indicating changes in the phase composition and crystallinity of the composites. The interaction between HAp and ZrO₂ during sintering may promote the formation of secondary calcium phosphate phases, particularly tricalcium phosphate (TCP). The formation of TCP at elevated temperatures can be associated with the thermal decomposition and interfacial reactions of HAp in the presence of reinforcing ceramic phases.

TCP-based biomaterials are of considerable interest in biomedical applications because of their favorable biocompatibility and osteoconductive characteristics. Colon et al. [22] reported the potential of calcium phosphate-based materials to promote bone regeneration.

The relative contributions of ZrO₂ and TiO₂ phases were further investigated through EDX and XRD analyses. The EDX spectra indicate relatively strong Zr and Ti signals in the projecting crystalline regions, whereas the background regions exhibit stronger Zr and comparatively weaker Ti signals. These observations suggest a non-uniform distribution of the reinforcement phases within the microstructure. However, EDX analysis alone cannot unambiguously identify crystalline phases because elemental analysis does not provide direct information regarding crystal structure. Therefore, XRD analysis was used to confirm the phases present in the sintered composites.

For the composite containing 25 wt.% (ZrO₂ + TiO₂) and sintered at 1200 °C, the diffraction pattern indicates the presence of rutile TiO₂ and zirconia-related phases. The addition of TiO₂ and ZrO₂, together with the sintering temperature, significantly influences the grain-growth behavior of the composite.

Up to 20 wt.% reinforcement, the particle/grain size of the background phase, predominantly associated with ZrO₂, decreases progressively. However, at 25 wt.% reinforcement, an increase in grain size is observed. This behavior may be attributed to accelerated grain growth at higher reinforcement concentrations. The limited solubility of TiO₂ in ZrO₂ and the increased diffusion activity during sintering may contribute to this grain-growth phenomenon. In addition, interactions between HAp and ZrO₂ may promote the formation of secondary calcium phosphate phases and enhance mass transport during sintering.

The average crystallite size of the HAp/(ZrO₂ + TiO₂) nanocomposites was calculated using the Debye–Scherrer equation [19].

3.4 Microstructural Analysis of HAp/(ZrO₂ + TiO₂) Nanocomposites after Sintering

The SEM micrographs of the sintered HAp/(ZrO₂ + TiO₂) composites containing 5, 10, 15, 20, and 25 wt.% reinforcement are presented in Figure 4(a–e). The micrographs indicate relatively high densification and low residual porosity after sintering at 1200 °C.

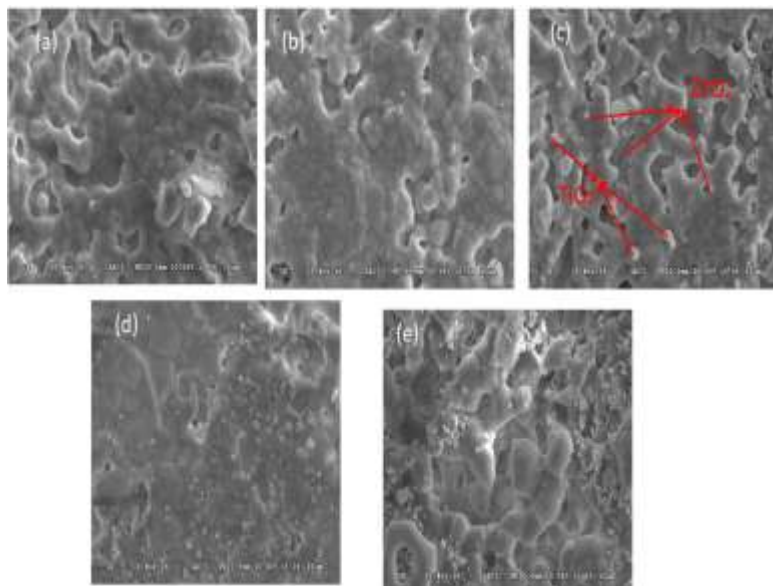


Figure 4 SEM micrographs of HAp/(ZrO₂+TiO₂) composites (a) 5 wt% (b) 10 wt% (c) 15 wt % (d) 20 wt% and (e) 25 wt%

The microstructure changes progressively with increasing reinforcement concentration. In addition to changes in densification, a distinct modification in the morphology and distribution of the ZrO₂ and TiO₂ phases is observed. The interaction between the HAp matrix and the reinforcement phases during sintering contributes to the development of a heterogeneous multiphase microstructure.

At 25 wt.% reinforcement, a distinct protruding crystalline structure, attributed to a TCP-rich phase, can be observed in Figure 4(e). The SEM observations are consistent with the XRD results and indicate the development of secondary phases during high-temperature sintering. The microstructural evolution also suggests that the influence of ZrO₂ becomes more pronounced relative to TiO₂ at higher reinforcement concentrations, particularly beyond 20 wt.%. The elemental composition of Ca, P, Zr, and Ti was investigated using EDX, as shown in Figure 5. The EDX results confirm the presence of the principal elements associated with the HAp matrix and the ceramic reinforcements.

The grain size of the sintered HAp/(ZrO₂ + TiO₂) composites was determined using the ASTM linear-intercept method. The corresponding microstructures used for grain-size measurements are presented in Figure 6. The grain size decreases progressively with increasing reinforcement content up to 20 wt.%, reaching a minimum value of approximately 15.9 nm. A subsequent increase in grain size is observed at 25 wt.% reinforcement.

The initial grain refinement can be attributed to the pinning effect of the dispersed ZrO₂ and TiO₂ nanoparticles, which restrict grain-boundary movement and inhibit grain growth. At higher reinforcement concentrations, however, particle agglomeration and enhanced diffusion during sintering may promote grain coarsening, resulting in the observed increase in grain size at 25 wt.%.

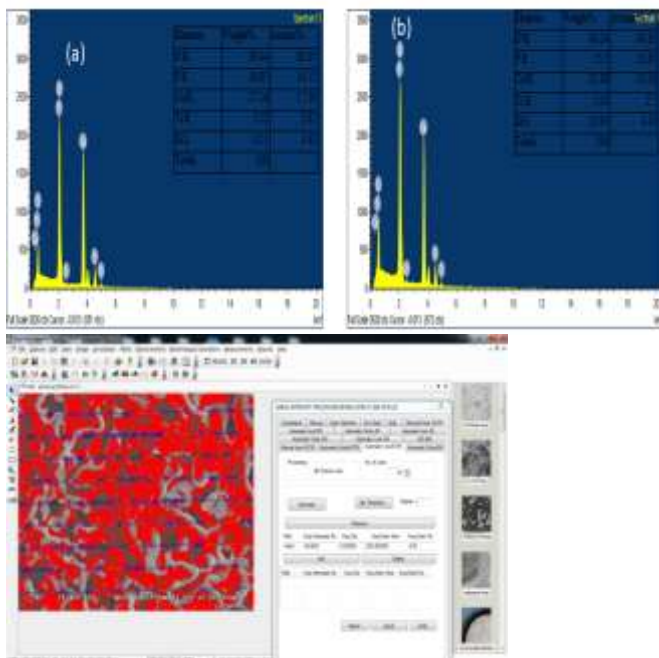


Fig 5.EDX (a) 10wt% (b) 20wt% HAp/(ZrO₂+TiO₂)

Fig 6. Grain size at 10 wt%

3.5 Mechanical Properties

3.5.1 Effect of (ZrO₂ + TiO₂) (1:1) Content on the Mechanical Properties of HAp Nanocomposites

The crystallographic structure of hydroxyapatite is similar to that of the mineral phase present in natural bone, making it an attractive candidate for biomedical applications, particularly bone replacement and implant coatings. However, the relatively low fracture toughness, brittleness, and fatigue resistance of sintered HAp restrict its application under high or cyclic loading conditions.

The incorporation of mechanically stronger ceramic reinforcements provides an effective approach for overcoming these limitations. In the present investigation, ZrO₂ and TiO₂ were incorporated into the HAp matrix in a 1:1 ratio to improve the mechanical performance of the resulting hybrid nanocomposites. The effects of reinforcement content on density, porosity, hardness, Young's modulus, fracture toughness, compressive strength, and flexural strength were therefore evaluated.

3.5.1.1 Porosity and Density

Figure 7 presents the variation in density and porosity of the HAp/(ZrO₂ + TiO₂) composites as a function of reinforcement content. All specimens were sintered at 1200 °C for 1 h. The measured densities of the composites were compared with their corresponding theoretical densities.

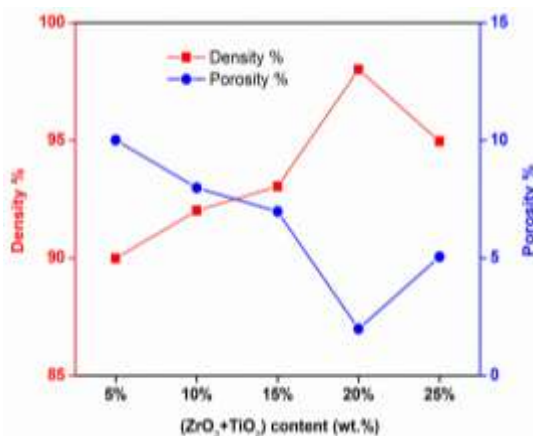


Figure 7. Variation of density and porosity

The density increases progressively with increasing (ZrO₂ + TiO₂) content up to 20 wt.%. The maximum density is obtained at 20 wt.% reinforcement. Beyond this concentration, a slight reduction in density is observed at 25 wt.%. The increase in density up to 20 wt.% can be attributed to the improved packing and dispersion of the reinforcing particles within the HAp matrix, together with enhanced densification during sintering.

In contrast, the reduction in density at 25 wt.% may be associated with particle agglomeration and the development of localized pores or microstructural heterogeneities at higher reinforcement concentrations.

A corresponding decrease in porosity is observed with increasing reinforcement content up to 20 wt.%. The minimum porosity is obtained at 20 wt.% reinforcement, indicating that this composition provides the most favorable combination of particle packing and sintering-induced densification. The subsequent increase in porosity at 25 wt.% may be related to reinforcement agglomeration and reduced packing efficiency.

3.5.1.2 Effect of Grain Size on Microhardness

Figure 8 illustrates the variation in grain size and microhardness of the HAp/(ZrO₂ + TiO₂) nanocomposites as a function of reinforcement content. The microhardness of the composite increases from 8.60 GPa for pure HAp to a maximum value of 14.01 GPa at 20 wt.% (ZrO₂ + TiO₂).

The progressive increase in hardness up to 20 wt.% can be attributed primarily to grain refinement, improved densification, and the presence of hard ZrO₂ and TiO₂ ceramic particles. The uniformly dispersed reinforcement particles restrict grain-boundary movement and contribute to strengthening of the HAp matrix.

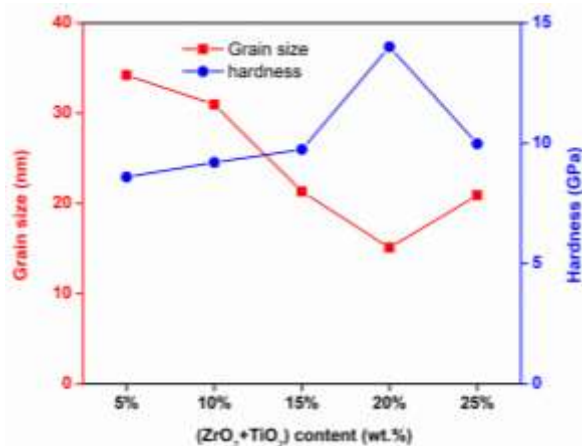


Figure 8. Variation of Hardness and Grain size

The simultaneous decrease in grain size and increase in density with increasing reinforcement concentration contribute to the improvement in hardness. The minimum grain size of approximately 15.9 nm at 20 wt.% reinforcement corresponds to the maximum hardness of 14.01 GPa.

At 25 wt.% reinforcement, however, the hardness decreases significantly to approximately 9.98 GPa. This reduction is consistent with the observed increase in grain size and decrease in density. At higher reinforcement concentrations, particle agglomeration and non-uniform distribution may introduce microstructural defects that adversely affect the load-bearing capacity of the composite.

The results indicate that 20 wt.% (ZrO₂ + TiO₂) provides the optimum reinforcement concentration for achieving enhanced hardness in the investigated HAp nanocomposite system.

3.5.1.3 Young's Modulus and Fracture Toughness

The Young's modulus of the HAp/(ZrO₂ + TiO₂) composites varies from 126.2 to 236.8 GPa, depending on the reinforcement concentration. Figure 9 presents the variation in Young's modulus and fracture toughness of the sintered composites.

The incorporation of ZrO₂ and TiO₂ results in a substantial improvement in the stiffness of the HAp matrix. The increase in Young's modulus can be attributed to the intrinsically high elastic modulus of the ceramic reinforcement phases and the improved densification of the composite. The fracture toughness of the composites also increases with reinforcement content and reaches its optimum value at 20 wt.% reinforcement. The fracture toughness of pure HAp is approximately 2.4 MPa·m^{1/2}, whereas the reinforced composites exhibit improved resistance to crack propagation.

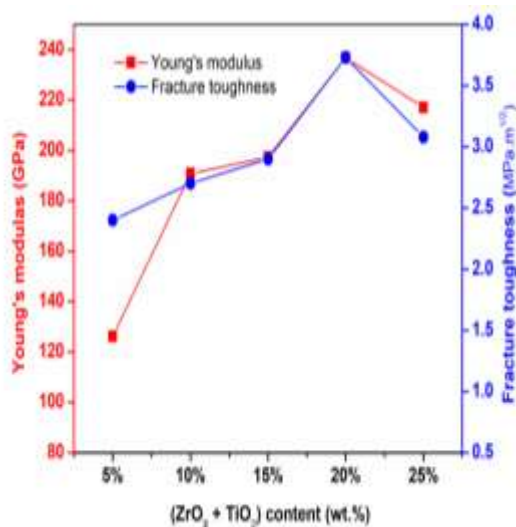


Figure 9 Variation of Young's modulus and Fracture toughness

The maximum improvement at 20 wt.% can be attributed to the combined effects of grain refinement, improved densification, crack deflection, crack bridging, and the presence of hard reinforcement particles. These mechanisms can increase the energy required for crack initiation and propagation through the composite.

At 25 wt.% reinforcement, both Young's modulus and fracture toughness show a slight decline. This behavior may be associated with grain coarsening, increased porosity, and possible agglomeration of the reinforcing particles. Based on the experimental results, the 20 wt.% HAp/(ZrO₂ + TiO₂) composition provides the most favorable combination of stiffness and fracture resistance.

3.5.1.4 Compressive Strength and Flexural Strength

Figure 10 presents the compressive and flexural strengths of the HAp/(ZrO₂ + TiO₂) composites containing different reinforcement concentrations. Pure HAp exhibits the lowest compressive strength, approximately 54.72 MPa, after sintering. With increasing (ZrO₂ + TiO₂) content, the compressive strength increases substantially and reaches a maximum value of approximately 230.6 MPa at 20 wt.% reinforcement.

The significant improvement in compressive strength can be attributed to the combined effects of reinforcement strengthening, grain refinement, improved densification, and reduced porosity. The hard ZrO₂ and TiO₂ particles effectively restrict deformation of the HAp matrix and enhance its load-bearing capability.

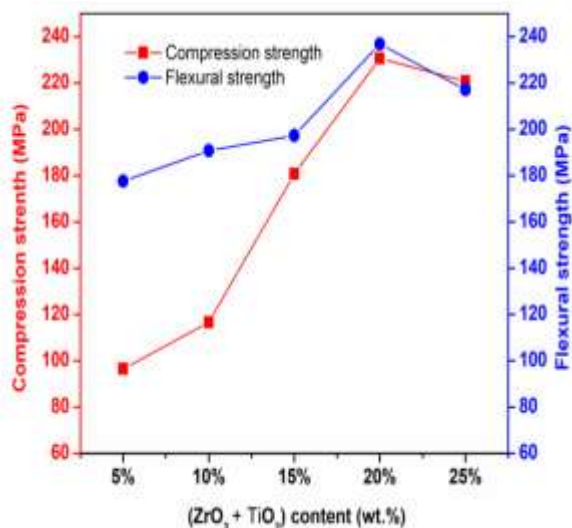


Figure 10 Variation of compression strength and flexural strength

The flexural strength of the HAp/(ZrO₂ + TiO₂) composites ranges from approximately 177.63 to 236.8 MPa. The maximum flexural strength is obtained at 20 wt.% reinforcement, followed by a reduction at 25 wt.%.

The improvement in flexural strength up to 20 wt.% can be associated with the uniform dispersion of the reinforcement particles, improved interfacial bonding, reduced porosity, and grain refinement. These factors contribute to improved resistance to crack initiation and propagation under bending loads.

At 25 wt.% reinforcement, the reduction in flexural strength may be attributed to grain coarsening, increased porosity, and localized agglomeration of ZrO₂ and TiO₂ particles. Such microstructural heterogeneities can act as stress-concentration sites and facilitate crack initiation.

Overall, the results indicate that the incorporation of ZrO₂ and TiO₂ in a 1:1 ratio significantly improves the mechanical performance of HAp. Among the compositions investigated, 20 wt.% (ZrO₂ + TiO₂) provides the most favorable combination of density, grain refinement, hardness, Young's modulus, fracture toughness, compressive strength, and flexural strength.

4. Conclusions

HAp/(ZrO₂ + TiO₂) hybrid nanocomposites with a 1:1 reinforcement ratio were successfully fabricated using the high-energy ball milling (HEBM) technique and subsequently sintered. The influence of ZrO₂ and TiO₂ reinforcement content on the microstructure and mechanical properties of the HAp matrix was systematically investigated. The results demonstrate that the incorporation of ZrO₂ and TiO₂ significantly improves the mechanical performance of HAp, primarily due to enhanced densification, grain refinement, and the strengthening effect of the ceramic reinforcement phases.

The major conclusions of the study are as follows:

- The microstructure of the HAp/(ZrO₂ + TiO₂) nanocomposites undergoes progressive grain refinement with increasing reinforcement content up to 20 wt.%. The minimum grain size of approximately 15.9 nm is obtained at 20 wt.% reinforcement. Beyond this concentration, particularly at 25 wt.%, grain coarsening is observed, which is accompanied by a reduction in density and mechanical properties.
- The microhardness of the composites increases from 8.60 to 14.01 GPa with increasing reinforcement content up to 20 wt.%. The maximum hardness of 14.01 GPa is obtained for the composite containing 20 wt.% (ZrO₂ + TiO₂), demonstrating a significant improvement compared with the reported value for pure HAp.
- The fracture toughness of the composites increases with reinforcement content, reaching a maximum reported value of 3.73 MPa·m^{1/2} at 20 wt.% (ZrO₂ + TiO₂). This improvement can be attributed to grain refinement, increased densification, and mechanisms such as crack deflection and crack propagation resistance provided by the dispersed ceramic reinforcement phases.
- The Young's modulus increases from 126.2 to 217.1 GPa with increasing reinforcement content. The enhanced stiffness is attributed to the higher elastic modulus of ZrO₂ and TiO₂ and the improved densification of the composite structure.
- The compressive strength increases significantly with reinforcement content and reaches a maximum value of 230.6 MPa at 20 wt.% (ZrO₂ + TiO₂). Further addition of reinforcement to 25 wt.% results in a reduction in compressive strength to 220.07 MPa, which is consistent with the observed grain coarsening and reduction in density.
- The flexural strength follows a similar trend, attaining a maximum value of 236.8 MPa at 20 wt.% reinforcement. At 25 wt.%, the flexural strength decreases to 217.1 MPa, possibly due to increased grain size, particle agglomeration, and residual porosity.
- Overall, the mechanical properties of HAp/(ZrO₂ + TiO₂) nanocomposites improve progressively with increasing reinforcement content up to 20 wt.%. The composite containing 20 wt.% (ZrO₂ + TiO₂) in a 1:1 ratio exhibits the most favorable combination of microstructural and mechanical properties among the investigated compositions.

Therefore, 20 wt.% (ZrO₂ + TiO₂) is identified as the optimum reinforcement concentration for the HAp-based hybrid nanocomposites investigated in the present study. Further addition of reinforcement to 25 wt.% adversely affects the microstructure and mechanical performance, indicating that excessive reinforcement may lead to grain growth, reduced densification, and the formation of microstructural defects.

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