

# ABSTRACT

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As I embark on presenting this thesis, the current work represents the culmination of extensive research, experimentation, and collaboration aimed at addressing a pressing global issue: **waste management**. Throughout history, people have utilized stone, wood, bone, and clay to make tools, weapons, shelter, and art. The major transformation in the technology of material synthesis has generated a sense of revolution that has led to the formation of advanced composites, alloys, blends, etc, that are application-specific. In the current thesis, the motivation of waste management is restricted to the conversion of waste eggshells to valuable Hydroxyapatite (HAp). HAp is a naturally occurring calcium apatite mineral, chemically termed as Penta calcium triphosphate hydroxide with the formula  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  or in a molecular form as  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . It is a white powder that is odorless, tasteless, and insoluble in water and most organic solvents. HAp is biocompatible and an inorganic phase of a natural bone consists of almost 65- 70% of the HAp so it is well used in orthopedic applications. Other applications include **dental implant, membranes for bone regeneration, implant coating, orthopedic implants, pharmaceuticals, drug delivery system, cosmetology, fertilizers, toothpastes** etc. The HAp samples are synthesized using a modified synthesis route, i.e., multistage calcination followed by a chemical precipitation method. The synthesis was performed at varying stirring timings (6, 12, 18 and 24 h) and then the best composition was identified based on the flowability, density and mechanical characterization. Furthermore, to enhance the antibacterial characteristic of the synthesized HAp, the varying weight percentage of silver doping (0, 0.1, 0.2 and 0.5 wt%) was done. Then, physical, mechanical, flowability, morphological, thermal, etc, characterizations are performed on the

samples and analyzed. Later, the PMMA/ HApAg composites were developed using the cold moulding method with varying wt% of HApAg (0, 2.5, 5 and 7.5 wt%) in PMMA and the prepared samples were tested for the mechanical, wettability and tribological characterization. Also, the pellets of PMMA and HApAg were blended to form sol containing 0, 10, 15 and 20 wt% of HApAg in PMMA, dissolved using toluene. The prepared sol was dip coated on Ti6Al4V substrate and adhesion, morphological, antibacterial and surface characteristics were analyzed. The main focus of the current research was to develop a biocompatible and antibacterial material from waste eggshell with high level of purity. The task was structured in 8 chapters starting with Introduction followed by Literature review, materials and methods, Synthesis and Characterization of Eggshell-derived Hydroxyapatite, Physiomechanical, Flowability and Antibacterial characterization of silver-doped eggshell-derived hydroxyapatite for biomedical applications, Synthesis and characterization of PMMA/ HApAg coating on Ti6Al4V substrate, Tribological behavior of PMMA/ HApAg composite and finally conclusions & future scope. Ultimately, the outcome of thesis was to develop a biomaterial from livestock waste, characterize it for analysing its purity, strength and compatibility, and to generate a “**waste to wealth**” mindset. The future scope of the current work is to convert the technology from educational scale to commercial scale.

**Keywords:** Hydroxyapatite, Eggshell waste, Silver-doping, Antibacterial Characterization, Biocompatibility, Coating, Tribology, Physiomechanical, Poly (methyl methacrylate)

## **Organization of the current thesis**

The thesis is organized as follows:

### **Chapter 1. Introduction**

The chapter briefs about the title of the thesis, including basic introduction to history of materials, materials involved in current research, synthesis methods, coating methods, characterizations, etc. The systematic streamline in the form of a flowchart was added to highlight the workflow in the current thesis without any ambiguity. The chapter also discusses the advantages, disadvantages, limitations, and applications related to current research. The research gaps and the objectives of the thesis are also discussed.

## **Chapter 2. Literature Review**

This chapter highlights the selective review related to the selection of material, methods, characterization, and its applications. The main motive of the current literature was to converge the existing research and to investigate the research gaps systematically. The comparative and bibliometric analysis was performed, and the outcomes are interpreted. The literature review also helped to point out the hypotheses in our research area. Finally, based on the identified research gaps and hypotheses, the research objectives are defined and executed.

## **Chapter 3. Materials and Methods**

In this chapter, discussion on the materials, synthesis methods, and various characterization techniques used in the current research work was done. The brief description about the instruments and the testing standards are also discussed in brief.

## **Chapter 4. Synthesis and Characterization of Eggshell-derived Hydroxyapatite**

In this chapter, the synthesis and characterization of novel bioceramic material i.e., hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HAp) derived from waste eggshell is experimentally accomplished. Materials and methods are discussed. Powder flow analysis using tap density, bulk density, angle of repose, Hausner ratio and Carr's Index are experimentally determined. SEM, XRD and FTIR at different stirring timings

justify the morphological characteristics of HAp. Average particle size, crystallite size and lateral strain are identified. The composition optimizations are also discussed.

### **Chapter 5. Physiomechanical, Flowability and Antibacterial characterization of silver-doped eggshell-derived hydroxyapatite for biomedical applications**

This chapter includes the synthesis of HAp powder from the waste eggshells using a modified synthesis route, i.e., multistage calcination preceded by a chemical precipitation method for process optimization. Secondly, the silver-doped HAp was synthesized with varying weight percent (0.0, 0.1, 0.2 and 0.5 wt %) of silver nitrate ( $\text{AgNO}_3$ ) in HAp. The compressive strength and Vickers microhardness tests are performed to interpret adhesion and bonding strength of the sintered samples. Later, the porosity, flowability and antibacterial properties are diagnosed. Inductively Coupled Plasma Mass Spectroscopy (ICPMS), X-Ray Diffraction Technique (XRD), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) verifies the morphology, chemical composition, bonding strength, crystallite size, particle size, lattice strain and phase purity. Six different bacteria strains, i.e., *S. epidermidis*, *S. aureus*, *B. subtilis*, *E. Coli DH5 $\alpha$* , *P. aeruginosa* and *E. Coli* were employed for antibacterial characterization confirm the antibacterial nature of silver-doped HAp. Results obtained accentuate the antibacterial nature of silver-doped HAp and its utility in biomedical applications.

### **Chapter 6. Synthesis and characterization of PMMA/ HAPAg coating on Ti6Al4V substrate**

This chapter intends to analyze the properties and potential applications of a novel composite coating composed of poly (methyl methacrylate) (PMMA) and silver-doped hydroxyapatite (HAPAg) produced from waste eggshells, which was dip-coated onto Ti6Al4V substrates. In order to add antibacterial and osteoconductive characteristics,

silver-doped hydroxyapatite nanoparticles are dispersed within a PMMA matrix to create the PMMA/HAPAg composite coating. The contact angle and total surface free energy (SFE) was investigated. The surface morphology of the defective zones was examined using scanning electron microscopy (SEM), and information on the elemental composition of synthesized was obtained using Inductively Coupled Plasma Mass Spectroscopy (ICPMS), Fourier Transform Infrared spectroscopy (FTIR) and X-ray diffractogram (XRD). Atomic force microscopy (AFM) reveals the surface roughness, root mean square roughness, roughness profile, skewness, and kurtosis of the coated samples. Finally, the results are interpreted and discussed.

### **Chapter 7. Tribological behavior of PMMA/ HAPAg composite**

This chapter includes the wettability and tribological characterization of the novel hybrid biocomposite of PMMA reinforced with eggshell-derived, silver-doped hydroxyapatite (HAPAg). Varying wt% of HAPAg in PMMA are analyzed using a ball-on-disk Tribometer. The coefficient of friction (COF), wear rate, porosity and Vickers microhardness are investigated. The XPS, FTIR, SEM, Stereo zoom microscopy and 3D surface profilometer are used for the characterization. The application of developed biocomposite material in dental and orthopedic applications are highlighted.

### **Chapter 8. Conclusions and Future Scope**

The chapter summarizes the overall progress of the current thesis. The converged conclusions are drawn from the outcomes of all the experimental tests and characterizations. Finally, the future scope of the current research are highlighted to motivate other researchers working in the similar field.

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