CHAPTER 8 CONCLUSIONS AND FUTURE SCOPE

8.1 Conclusions

The experimental investigation on the eggshell-derived HAp, silver-doped eggshell-derived HAp, HAPAg/PMMA composite and PMMA/ HAPAg sol. dip coating on Ti6Al4V substrate was performed in the current research. The results were analyzed and discussed in the previous chapters. Here, the final summary of each chapter is highlighted. The conclusions derived from each objective are individually elaborated in the subsequent sub-sections below.

8.1.1 Conclusion: Synthesis and characterization of HAp

In summary, synthesis of HAp from waste eggshell using multistage calcination and chemical precipitation method provides high level of crystallinity, purity, yielding and stability. The results obtained from the physical and morphological tests confirm the effective synthesis of HAp. From the results it can be concluded that,

- ❖ Average tap density and average bulk density increase with increase in chemical precipitation reaction timings which is almost 50% of the compact mass density. For HAP06Hr, HAP12Hr, HAP18Hr and HAP24Hr samples, values of Hausner ratio (1.21, 1.21, 1.18 and 1.16), Carr's Index percent (17.65%, 17.26%, 15.0% and 13.73%) and average angle of repose (37.45^0, 36.40^0, 35.06^0 and 35.06^0) shows good flow property for HAP18Hr and HAP24Hr. Also, fair flow property with no external effort is achieved for the crystallite samples HAP06Hr and HAP24Hr.

- Scanning Electron Microscopy shows the uniform morphology and agglomerated crystalline powder samples. The average particle size of the crystalline powder evaluated using histogram obtained from SEM images magnified at 10,000 X reveals that the average particle size of HAP06Hr, HAP12Hr, HAP18Hr and HAP24Hr samples are 1085.3nm, 965.45nm, 809.55nm and 808.05nm.
- Averaging the magnitude of crystallite size (calculated using Scherrer's formula shown in equation (k)) at multiple 2 theta positions and FWHM values shows the average crystallite size equals to 555.54Å, 537.09Å, 505.09Å and 513.54Å and average lateral strain shows 0.2964%, 0.2697%, 0.3050% and 0.3012% change for HAP06Hr, HAP12Hr, HAP18Hr and HAP24Hr, respectively. Results show minimum average crystallite size for HAP18Hr with maximum average lateral strain.
- FTIR spectroscopy verifies the presence of OH^- functional group near 3330 cm^{-1} and PO_4^{3-} functional group with asymmetric bending at 1165 ±1cm^{-1} and asymmetrical stretching at 568±1cm^{-1}. The combined results approve the presence of synthesized HAp derived using waste eggshell. HAP18Hr with comparatively low wave number value interprets the optimum reaction timing for HAp synthesis.
- The stirring timing shows a marginal downturn in wettability (≈17^0 between HAP06Hr and HAP24Hr) but concludes the hydrophilic nature of all the HAp samples.
- A slight variance in the maximum compressive strength was observed for samples prepared with 6- 24 h stirring. However, the magnitude is associated

with the natural HAp and commercially available HAp prepared by different synthesis routes and precursors.

- ❖ An increase in surface hardness of the eggshell-derived HAp correlates with a reduction in particle size[126], increase in porosity %, increased homogeneity of precipitation and densification of the structure. Also, the reported hardness of HAP18Hr and HAP24Hr, i.e., 25.63 ± 0.568 and 26.10 ± 0.870 HVN, respectively, is associated with the hardness of radius bone.
- ❖ The thermal analysis concludes the minimum engrossment of stirring timing on the decomposition rate of HAp and reports 8% decomposition of HAp when heated to 1000 ^{0}C.

HAP18Hr and HAP24Hr show effective and almost similar results of characterization and thus we can select process involved with synthesis of HAP18Hr as one with optimum timing and morphology. Further, the implementation and in vivo characterizations can be done to confirm the applications of HAp in biomedical applications.

8.1.2 Conclusion: Synthesis and characterization of HAPAg

Synthesis and characterization of eggshell-derived silver-doped hydroxyapatite have led to the following salient conclusions:

- ❖ The inclusion of silver ions in the eggshell-derived hydroxyapatite upsurges the density of the powdered and compacted samples. The powder bulk density increases from 1.24 ± 0.08 g/cm^3 (HAP0.0Ag) to 1.34 ± 0.21 g/cm^3 (HAP0.5Ag), while the experimental density of the compacted sample increases from 2.84 ± 0.12 g/cm^3 (HAP0.0Ag) to 2.96 ± 0.2 g/cm^3

(HAP0.5Ag). However, the maximum relative density of 92.03 % and minimum porosity of 7.97 % were observed in HAP0.2Ag.

- ❖ Flowability analysis of powdered sample reports good (HAP0.0Ag and HAP0.1Ag), fair (HAP0.2Ag) and travelable (HAP0.5Ag) flow characteristics and clinches the application of modified HAp in biopaste, biocreams, implant coatings and bone-gap filling applications.
- ❖ The maximum compressive strength (146.4 MPa) and Vickers microhardness (31.70 ± 0.989 HVN) for HAP0.2Ag composition correlate directly with the relative density and porosity of the sintered samples. Moreover, the variation in relative density ratifies the disparity in HVN and MCS with 23.68 % and 5.52 % increase in magnitude compared to undoped HAp.
- ❖ The Ag doping inhibited the growth of all types of bacteria and enhanced the antibacterial characteristics with a maximum DoI of 16.68 ± 0.21 mm for *S. Aureus* microorganism. The investigation concludes that even a minimal amount of Ag doping can give surface capping with antibacterial surrounding without impairing the formation and crystallography of the molecule.
- ❖ Silver-doped HAp shows reduction in the water absorption % but has minimal wettability change as compared to undoped HAp.
- ❖ HAP0.1Ag sample has comparatively higher thermal stability then undoped HAp and almost 92% mass loss is retained till 1000 ^{0}C heat treatment.
- ❖ Finally, the synthesized powder can be applicable as a cost effective, biocompatible and antibacterial material for implant fabrication and coating.

8.1.3 Conclusion: Synthesis and characterization of PMMA/HAPAg coating on Ti6Al4V substrate

The characterization of deposited PMMA/HAPAg on Ti6Al4V using the dip coating method reveals the following conclusions:

- The reduction in the average contact angle from $75.27^0 \pm 1.69^0$ (for PMMA-coated samples) to $70^0 \pm 1.44^0$ (for PMMA/H20-coated samples) indicates a subtle increase in hydrophilicity for the coated samples which can enhance the osseointegration when used for implant coating.
- The average range of total SFE lying between 35-50 mJ/m^2 promotes the adhesion between substrate and coating material and thus concludes better coating characteristics of silver-doped HAp reinforced PMMA with Ti6Al4V.
- Surface morphology reveals pinholes, blisters and sol accumulation defects in dip-coated samples due to environmental factors and improper mixing of precursors in solvents.
- The 2D/ 3D topography of the coated samples endorses the reduced roughness with minimal increase in average roughness and root mean square roughness between PMMA/H0 and PMMA/H20. However, the magnitude skewness and kurtosis revealed the nano-fluctuation in the surface roughness.
- The prepared composite samples exhibits acceptable antibacterial characteristics, where *S. aureus* has a maximum DoI of 14.44 ± 0.32 mm.

Overall, the dip coating of PMMA/ HAPAg on Ti6Al4V provides effective biocompatibility, wettability, less stress shielding, improved antibacterial characteristics and minimum surface roughness. **Comparatively, PMMA/ H20 has a higher critical load and, therefore, was considered more stable compared to other**

compositions. However, the durability and adhesion strength of coating material on the substrate needs further investigation.

8.1.4 Conclusion: Synthesis and characterization of PMMA/ HAPAg composite

- ❖ The experimental investigation of the biocomposite material composed of a PMMA matrix and eggshell-derived HAPAg reinforcement reveals that the inclusion of HAPAg in PMMA possesses better wear resistance, strength and wettability compared to the pure sample.
- ❖ The identification of high-intensity peaks at calibrated binding energies via XPS verifies that the organic-inorganic components of the samples are uniformly bonded.
- ❖ The observed 15.16% variation in CA between PHA0 (96.300 ± 2.110) and PHA7.5 (81.700 ± 1.010) indicates that the HAPAg reinforcement causes the composites to undergo a surface transformation from hydrophobic to hydrophilic.
- ❖ The PHA5 sample exhibited the highest relative density of 92.09%. Additionally, the increase of 18.11% in Vickers hardness and the decrease of 2.86% in porosity from PHA0 to PHA7.5 indicate a significant likelihood of consistent dispersion of reinforcing HAPAg within PMMA.
- ❖ Furthermore, as the reinforcement content rises to 5% (PHA5), the steady-state COF experiences an initial surge, followed by an abrupt decline at PHA7.5. This can be attributed to the running-in mechanism that occurs between the chrome steel ball and the composite samples at PHA7.5.
- ❖ Possible causes for the abrupt decrease in wear rate at PHA7.5 include an increase in surface hardness and the development of flattened asperities during

sliding. Profilometer and SEM were utilized to examine the depth and morphology of the wear tracks.

- ❖ The findings indicate that the synthetic composite dentures are comparable to natural dentures in terms of wettability and wear resistance.

8.2 Future Scope

After the successful accomplishment of the current objectives in the thesis, new lacunas were identified that could be listed as a future scope of the current work.

- ❖ The main aim of the current research was to transform the synthesized HAp from a **laboratory scale to a commercial scale**. i.e., strive to acquire regulatory approval for utilizing HAp generated from waste eggshells in biomedical applications and investigate opportunities for commercialization through partnerships with industry collaborators or knowledge transfer programs.
- ❖ Examine the practicality of utilizing discarded eggshell-derived hydroxyapatite (HAp) as a raw material for 3D printing of customized biomedical structures, such as scaffolds for tissue engineering or implants for bone regeneration.
- ❖ Parametric optimization based on pH, temperature, precursors, environment, etc. can be further explored and analyzed.
- ❖ Effect of other metals doping (apart from Ag^{+}) can be done in hydroxyapatite and characterized for other specific applications.
- ❖ Other natural waste materials can be explored for deriving useful output.

- ❖ Examine the feasibility of integrating HAp derived from waste eggshells into composite materials comprising polymers, ceramics, or other bioactive substances (except PMMA). The objective is to develop hybrid biomaterials that exhibit improved mechanical, biological, and degradation properties.
- ❖ Synthesize and explore other methods of coating and analyze the compatibility, adhesion strength and other characteristics.
- ❖ The **computational analysis** on the synthesized HAp can be performed.