

CHAPTER 1 INTRODUCTION

1.1 History of Engineering Materials

Engineering materials are substances or mixtures of substances utilized in the design and construction of components, structures, and systems in engineering. The materials are chosen for their qualities, performance characteristics, and adaptability for particular engineering tasks. Engineering materials can be categorized into many groups according to their composition, characteristics, and uses. Common engineering materials include metals, polymers, ceramics, composites, semiconductors, alloys, biomaterials, etc. Choosing the right material is crucial for obtaining the necessary performance, reliability, and lifetime in engineering applications.

Basically, a **composite material** is made up of two or more constituent materials having different physical or chemical qualities that, when combined, generate a material with better properties than the individual components alone. In other words, a composite material is created by mixing or integrating many components to produce a new material with unique properties not found in any single component alone. The composite material mainly comprises of two components, **i.e. matrix and reinforcement**. The continuous component that makes up the composite material is designated as the matrix. It combines the reinforcing elements and ensures a fair distribution of loads throughout the structure by acting as an adhesive. The matrix material is an important factor in influencing the mechanical properties, resilience to environmental changes, and processing properties of the composite. It can be polymer resin, metal, ceramic, or other materials. In composite materials, reinforcement improves desired properties like strength and stiffness. Reinforcement materials might

be fibers, particles, flakes, or various shapes that are frequently mixed in with the matrix material.

1.2 Evolution of Biomaterials

Ancient civilizations used biomaterials such as **wood, bone, and ivory for medical purposes**. The ancient Egyptians made use of linen and other natural fibers to cure wounds. Metals such as gold and silver were widely utilized in dentistry for fillings and prostheses during the Middle Ages. Nonetheless, these materials usually cause toxicity and inadequate biocompatibility. The Industrial Revolution in the early nineteenth century resulted in significant advances in biomaterials. Rubber and gutta-percha were used for dental prostheses and other medical applications. Synthetic polymers and ceramics have substantially changed the field of biomaterials science. In the early 1900s, materials like Bakelite, the first synthetic polymer, were used in medical equipment. The need for blood transfusions during World War II drove the development of blood bags and anticoagulants. Modern biomaterials research evolved in the 1950s and 1970s, with the development of materials such as silicone rubber and **polymethyl methacrylate (PMMA)**, which are used in medical implants and prosthetics. Biomaterials have improved rapidly because of the use of biodegradable polymers, tissue engineering, and nanotechnology. Advancements in material science, cell biology, and engineering have resulted in the development of advanced biomaterials utilized in a variety of applications, including drug delivery systems and artificial organs. Current breakthroughs in biomaterials research include the development of smart materials that respond to physiological signals, bio-inspired materials that mimic natural biological structures, and the use of stem cells and biologics in regenerative medicine.

1.3 Waste Eggshells

The eggshell serves as a hard and strengthening casing that surrounds the contents of the egg. The composition of the structure is primarily made up of crystalline calcium carbonate and is typically permeable. "Waste eggshell" refers to the outer covering of eggs that are no longer needed for their original purpose, such as being eaten or hatched. This term commonly denotes the eggshells that are disposed of from food preparation, cooking, or household activities. Eggshells that are no longer needed are commonly considered to be a type of garbage that can decompose naturally and be reused, recycled, or utilized for composting in many ways. These include applications in agriculture, gardening, the creation of calcium-rich substances, and industrial operations. Each eggshell contains traces of various elements like C, Ca, Na, Mg, Fe, Zn, P, etc. as shown Fig. 1.1.

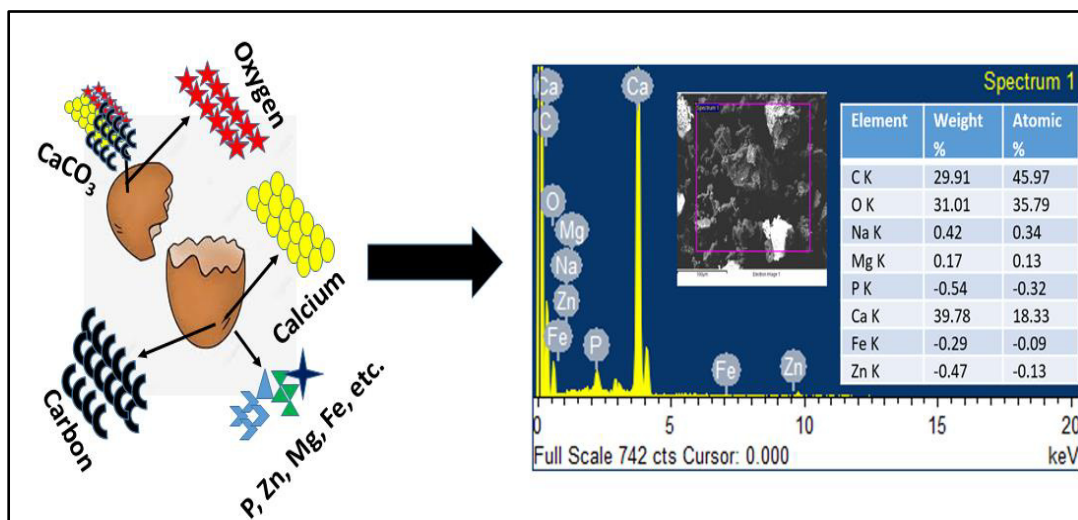


Fig. 1.1. Composition of Eggshell

According to **Food and Agriculture Organization of the United States (FAOSTAT)** production data (2022), **India ranks 3rd** in egg production in the world (Leading eggshell producing countries are China, USA and India.) [1]. The egg production in the country has increased from 16 billion eggs produced in fiscal year 1986 to 114.38 billion in 2019-20. Global egg production for the year 2018 was 78 million metric tons,

contributing approximately 8.58 million metric tons (around 858 crore kg, 11%) of eggshells which are being discarded mostly as waste. The data is not updated during covid- 19 (2020-21 and 21-22) but has surely risen. In the last three decades, global egg production has risen by 150 percent. A significant portion of this expansion has occurred in Asia, with manufacturing experiencing an almost fourfold increase. It is the need of the hour to convert waste into useful commodities for sustainable development. Applications of eggshell may include medicinal supplements, bone graft substitute and denture base, animal feed, plant fertilizer, batteries, inkjet printers, biodiesel production, Calcium synthesis and removal of heavy metals from soil and water, etc.

Each piece of Chicken egg contains almost **11% waste Eggshell, 86% eatable (albumen and yolk) and remaining 2 percent thin skin membrane** between hard eggshell and albumen which is also wasted and disposed [2,3].

1.4 What is Hydroxyapatite?

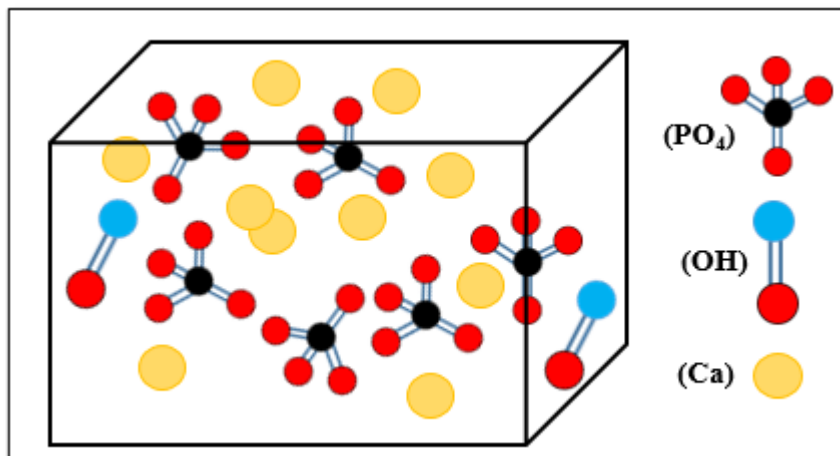


Fig. 1.2. Crystal Structure of Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$)

Hydroxyapatite (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 odourless,

tasteless, and insoluble in water and most organic solvents. It has a high melting point (about 1100 °C) and is stable under typical physiological conditions. Crystalline HAp has a hexagonal structure with approximate lattice parameters as $a = b = 9.372 \text{ \AA}$, $c = 6.88 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The skeleton of the unit cell is a tetrahedral arrangement of phosphate (PO_4^{3-}) that forms the HAp structure. Two of the oxygen are perpendicular to the c-axis, while the other two are in a horizontal plane [4]. Within the unit cell, phosphates are separated into two layers with corresponding heights of 1/4 and 3/4. The simple crystallite structure of HAp is shown in **Fig. 1.2**.

Since HAp is biocompatible and biodegradable, it is a desirable material for biomedical purposes. It is the principal mineral component of mammalian bone and teeth and plays a crucial role in their structural and functional qualities. **An inorganic phase of a natural bone consists of almost 65- 70% of the HAp along with 5 – 8% water.** HAp has a molecular weight of 1004.6 g/mol. Also, the organic phase of human bone consists of protein fiber, i.e. collagen, along with amino acid, which is responsible for the elastic resistance of the bone [5].

In addition to its use in bone and dental implants, HAp is employed in several other applications, including coatings for orthopaedic implants, drug delivery systems, and tissue engineering scaffolds.

Crystalline HAp has a high level of thermal stability with a Ca/P ratio of 1.67 [6,7] It enhances osteoconduction [8–11], Osteointegration [12,13], bioactivity[14], etc. It has biocompatibility with several types of biocells like osteoblast, osteoclast, fibroblasts, periodontal ligament cells and macrophage [8,15]. It is, therefore, the first choice of several researchers working in the field of artificial implants [16]. Other than bioimplants, additional applications of HAp includes the pharmaceutical sector, water treatment, protein chromatography and fertilizer [17]. HAp can also be used for

coating purposes on a large variety of substrates due to its effective adhesive nature and blending ability. High Strength and good surface morphology can be achieved by coating HAp based composite with metallic substrates. Some resorbable polymers and inorganic compound-based HAp reinforcement composites are gaining popularity in biomedical applications. Apart from the coating of HAp and its composites, a small amount of doping in HAp also improves the characteristics and the desired outputs can be achieved. For example, coating of silver or copper doped HAp on any bioimplant improves the antibacterial nature of the coating material [18]. HAp delivers numerous applications in biomedical fields. Artificial limbs, joints, part replacements, prosthesis, soft tissue placements, resorbable surgery and drug delivery with HAp material is possible, and its in-vivo and in-vitro characteristics are also verified [19]. Based on the application and requirements, biodegradable and non-biodegradable composites are being developed using HAp material.

1.4.1 Applications of Hydroxyapatite

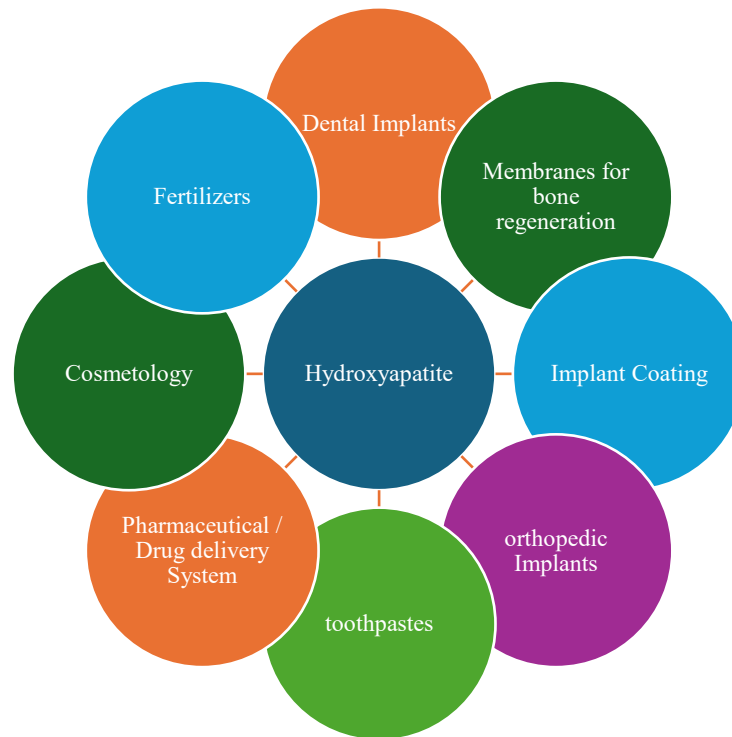


Fig. 1.3. Applications of Hydroxyapatite material

Apart from all the main areas of application of calcium and phosphorous, HAp has several proven applications as shown in **Fig. 1.3**. Presence of calcium and phosphorous apatite leads it to use in the arenas of dental, fertilizers, cosmetics, implants coating, bone regeneration, toothpastes etc. Converging the review on use of hydroxyapatite in biomedical applications [20], artificial HAp is considered as the most trusted bioimplant material with the mirror imaged characteristics as the natural composition of bone.

The in- vivo and in- vitro research of the HAp composites are characterized by various researchers and the closeness to exactness is observed [21]. The availability of calcium content in waste eggshells, bones of dead mammals, etc motivated us for synthesizing HAp from the waste precursors. The lifesaving material is synthetically produced and has several other applications like in dental implant, membranes for bone regeneration [22], implant coating [5,23–25], orthopedic implants [26],

pharmaceutical [27], drug delivery system [28], cosmetology [29,30], fertilizers [31], toothpastes [32] etc.

Application of artificial HAp with high level of non-toxic and biocompatible characterization leads it to the first choice in coating and composite reinforcements. HAp accelerates its usage in **bone fixation, bone repair, bone implant, prosthesis, artificial limbs**, etc. as it has high biocompatibility, Osteointegration and characteristics mirrored as the natural orthopedics [33]. Nano-sized, metallic doped HAp as reinforcement in the biocomposite material helps in the development of **non-flammable, anti-bacterial and ecofriendly** bio material [34].

HAp shows promising results as a filling material for bone and creates an effective physiochemical links around the bone tissue. Also, the osteoconductive nature of HAp material provides high affinity with bone material which accelerates the formation of new tissue. The HAp can be applied using plasma spray coating for this application [35]. Coating on metallic prosthesis provides recognizable characteristics and further research are being going to improve the thickness and adhesively of the material.

Currently, the development of novel ceramics must strike a balance between the aforementioned factors, attempting to increase the mechanical properties for improved implant performance in vivo while also controlling the level of material-tissue interaction. Developing the thin film coating [36] on the electrical and thermal appliances provides high insulation characteristics. Thin film deposition advanced many new areas of research in solid state physics and chemistry.

Researchers can explore each application of HAp in detail using vast literature available in the research database. As mentioned above, the presence of calcium and phosphate diversifies the applications of HAp. Bioimplant companies are

manufacturing the implants using HAp as a powder and as a coating material in various metallic and non-metallic substrates.

1.5 Silver-Doped Hydroxyapatite

Silver-doped hydroxyapatite (HAPAg) is a type of HAp that has been modified by the addition of silver ions (Ag^+). HAPAg is of interest because it combines the properties of HAp with the antimicrobial properties of silver, making it a promising material for various biomedical applications. HAPAg can be used in a variety of biomedical applications, including as a coating material for orthopedic implants, as a bone graft material, and as a filler material for dental applications. The antimicrobial properties of silver can help prevent infection at the implant site or in the oral cavity, while the HAp component provides mechanical strength and biocompatibility.

The properties of HAPAg can be tuned by varying the concentration of silver ions added during synthesis. However, excessive silver doping can lead to cytotoxicity and other unwanted effects, so the concentration must be carefully controlled to ensure biocompatibility.

1.6 Advantages of Eggshell-derived Silver-doped Hydroxyapatite

Eggshell-derived hydroxyapatite is an attractive biomaterial due to its **biocompatibility, biodegradability, and structural similarity to human bone**. Eggshells are a readily available and inexpensive source of calcium and phosphorus, which are the main components of HAp.

Silver-doped HAp has received increasing attention in biomedical applications due to its antimicrobial properties. Silver ions can effectively inhibit the growth of bacteria, viruses, and fungi, making it an attractive option for implants and medical devices, where infection is a significant concern. The addition of silver to HAp can also improve the mechanical properties and biocompatibility of the material.

The combination of eggshell-derived HAp and silver doping can result in a biomaterial with enhanced antimicrobial properties, biocompatibility, and mechanical strength. Eggshell-derived HAp can serve as a natural and sustainable source of calcium and phosphorus, while the addition of silver can provide an effective means of preventing infection. This material may have potential applications in the development of implant coatings, bone substitutes, and other medical devices.

1.7 What is PMMA (poly methyl methacrylate)?

PMMA stands for poly methyl methacrylate. It is a synthetic resin made from the polymerization of methyl methacrylate monomer. PMMA is a transparent thermoplastic material that has high impact resistance, good chemical resistance, and is easy to process. It is commonly known by trade names such as Acrylic, Lucite, and Plexiglas.

1.8 PMMA –HAp coating on Ti6Al4V alloy

PMMA HAp coating on titanium alloy is a potential approach to improve the bioactivity and biocompatibility of titanium implants for orthopedic and dental applications. The process involves depositing a layer of PMMA on the surface of the titanium alloy, followed by the deposition of a layer of HAp on top of the PMMA layer. The PMMA layer acts as an adhesion promoter, allowing the HAp layer to bond more strongly with the titanium alloy. The HAp layer provides a surface that is more biologically active and can support the growth of bone cells, leading to improved implant integration and better long-term outcomes.

1.9 Tribology of biomaterials

The term "**tribology**" was introduced by **Dr. H Peter Jost** in **1966** when he presented a report to the UK government that discussed the economic consequences of **friction, wear, and lubrication**. This publication prompted a surge in global research and

investment in the field of tribology. Tribologists investigate different phenomena such as friction, wear, and lubrication on microscopic and nanoscopic scales. **Applications include automotive and aeronautical engineering, as well as biomedical implants and nanotechnology.** Tribological analysis in biomedical applications is highly efficient in designing safer, more effective medical devices and implants that improve patient outcomes and quality of life. The complicated challenges of engineering biomaterials for medical applications necessitate interdisciplinary collaboration among engineers, materials scientists, biologists, and medical specialists. Tribological investigations of HAp/PMMA composites are being carried out in order to comprehend the materials' frictional behavior and wear resistance when employed in orthopedic implants. **Surface roughness, contact pressure, and lubrication** are all factors that influence friction and wear. Researchers are looking for ways to reduce wear on HAp/PMMA implants, which may result in particle production and undesirable biological reactions in the body. Furthermore, the tribology offers a wide range of biological applications, including orthopedics, dentistry, biomechanics, prosthetics, drug delivery, tissue engineering, and ophthalmology. Also, the continuous improvement in medical equipments, therapies, and patient outcomes in a variety of healthcare sectors are been observed by studying the friction, wear, and lubrication behavior of biological systems.