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Edited by Maya J John and Sabu Thomas

Natural Polymers

Volume 1: Composites



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Natural Polymers
Volume 1: Composites

RSC Green Chemistry

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Natural Polymers

Volume 1: Composites

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Preface

Natural polymers offer an alternative solution to the growing environmental threat and looming petroleum crisis. The use of natural polymers for many applications would therefore contribute to creating a sustainable economy. In contrast, the feedstocks for polymers derived from petrochemicals will in the long run eventually perish. Polymer chemists, physicists and engineers show great interest in the development of eco-friendly micro- and nano-structured functional materials based on natural polymers. In recent years, natural polymers have generated much interest due to their unique morphology and physical properties. The growing interest among academics and industrial researchers in the field of natural polymers is the driving force behind the present book.

The book is divided into two volumes: the first covers natural polymer composites and the second deals with natural polymer nanocomposites. Volume 1 comprises two sections reviewing (1) natural fibres and composites and (2) protein fibres and composites. Under natural fibres and composites, the characterization and new sources of natural fibres are discussed. It also looks into whether natural fibres can indeed be a replacement for synthetic fibres in industrial applications. Under protein fibres and composites, important advancements in the field of silk, spider silk and mussel fibres are discussed. Volume 2 deals with the properties and characterization of cellulose, chitosan, furanic, starch and silk nanocomposites. A final chapter touches upon the industrial applications of natural polymer nanocomposites.

This book is unique in the sense that it deals exclusively with some of the important polymers found in nature, modifications of natural polymers and tailoring them into composites and nanocomposites. In addition, it covers novel topics related to the properties and characterization of mussel fibres and sea shells.

As the editors of this book, we have enjoyed working with the individual contributors from different parts of the world and appreciate their diligence and patience. We would also like to thank all the publishers who generously gave their permission to reprint material.

Maya Jacob John and Sabu Thomas

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CHAPTER 1

Natural Polymers: An Overview

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1.1 Introduction

The scarcity of natural polymers during the world war years led to the development of synthetic polymers like nylon, acrylic, neoprene, styrene–butadiene rubber (SBR) and polyethylene. The increasing popularity of synthetic polymers is partly due to the fact that there are unlimited and economic avenues for modification of chemical structures to obtain a product with specific properties. However, this rampant use of petroleum products has created a twin dilemma: depletion of petroleum resources (Figure 1.1) and entrapment of plastics in the food chain and environment.¹ The exhaustive use of petroleum-based resources has initiated efforts to develop biodegradable plastics. This is based on renewable bio-based plant and agricultural products that can compete in the markets currently dominated by petroleum-based products. Table 1.1 presents a selected list of the common synthetic polymers.

Another issue is that the disposal of plastics in landfills creates a serious aesthetic problem in large urbanized areas of the world. The chemical stability of plastic prevents plastic waste from decomposing into the environment at a

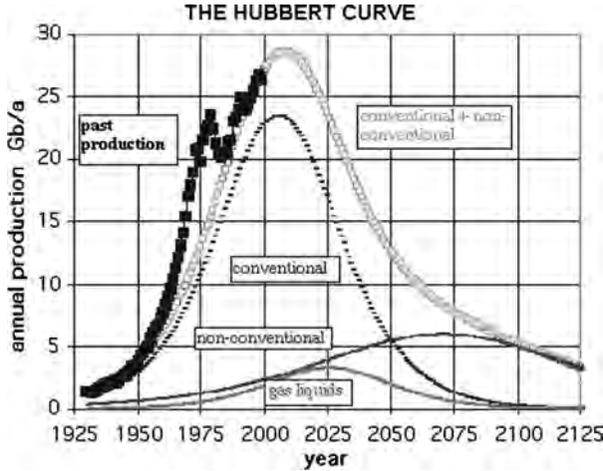


Figure 1.1 Chart of world oil reserves.

Table 1.1 List of selected synthetic polymers.

<i>Synthetic polymer</i>
Poly(ethylene terephthalate)
Polyethylene
Poly(vinyl chloride)
Polypropylene
Polystyrene
Poly(tetrafluoroethylene)
Polyurethane
Polyamide
Polyacrylamide

rate comparable to the rate of waste generation. In the long run, the incentive to preserve the local environment is reduced and the costs of cleaning and recovery of contaminated sites rise. Large streams can also transport excess plastic waste to other areas, creating a mobile contamination problem. Plastic waste comprises 60–80% of the marine debris litter accumulated in ocean shores. The problem of marine waste is aggravated by the low reliability of removal mechanisms aimed at reducing marine plastic residual concentration in the oceans. The effects of plastic waste on marine life include the entanglement and ingestion of harmful plastics by marine vertebrates and the bioaccumulation of toxicants along the food chain.

Natural polymers are those which are present in, or created by, living organisms. These include polymers from renewable resources that can be polymerized to create bio-plastics. There are two main types of natural polymers: those that come from living organisms (these include carbohydrates and proteins) and those which need to be polymerized but come from renewable

resources (e.g. lactic acid and triglycerides). Both types are used in the production of bio-plastics.

Among the different types of natural polymers, the best known resources capable of making biodegradable plastics are starch and cellulose. Cellulose is the most abundant carbohydrate in the world (40% of all organic matter is cellulose). It is the main constituent of plants, serving to maintain their structure, and is also present in bacteria, fungi, algae and even in animals. Cellulose from trees and cotton plants is a substitute for petroleum feedstocks to make cellulose plastics.

Starch is a condensation polymer made up of hundreds of glucose monomers, which release water molecules as they chemically combine. Starch is a member of the basic food group of carbohydrates and is found in cereal grains and potatoes. It is also referred to as a polysaccharide, because it is a polymer of the monosaccharide glucose. Starch molecules include two types of glucose polymers, *i.e.* amylose and amylopectin, the latter being the major starch component in most plants, making up about three-quarters of the total starch in wheat flour. Amylose is a straight-chain polymer with an average of about 200 glucose units per molecule. Starch is one of the least expensive biodegradable materials available in the world market today. It is a versatile polymer with immense potential for use in non-food industries. The annual world production of starch is well over 70 billion pounds weight, with much of it being used for non-food purposes, like making paper, cardboard, textile sizing and adhesives.

Chitin, a polysaccharide similar to cellulose, is Earth's second most abundant polysaccharide. It is present in the cell walls of fungi and is the fundamental substance in the exoskeletons of crustaceans, insects and spiders. The structure of chitin is identical to that of cellulose, except for the replacement of the OH group on the C-2 carbon of each of the glucose units with an -NHCOCH_3 group. The principal source of chitin is shellfish waste. Commercial uses of chitin waste include the making of edible plastic food wraps and the cleaning up of industrial wastewater.

Chitin is the main source of production of chitosan, which is used in a number of applications, such as a flocculating agent, a wound healing agent, a sizing and strengthening agent for paper, and a delivery vehicle for pharmaceuticals and genes. Chitin deacetylation leads to the formation of chitosan. The process involves the use of strong alkali solutions for the removal of *N*-acetyl groups, both at room and elevated temperatures. The amount of chitin obtained annually from harvested shellfish is estimated to be over 39 000 tonnes. At least 10 billion tonnes of chitin are produced in the biosphere each year, chiefly in marine environments.²

Collagen is one of the most plentiful proteins present in the bodies of mammals, including humans. In fact, it makes up about 25% of the total amount of proteins in the body. It has found increasing applications in tissue engineering and repair.³ The ability of collagen to polymerize into a three-dimensional fibrous matrix makes it an appealing material for extensive therapeutic applications, including medical implants.⁴

Table 1.2 List of common natural polymers.

<i>Natural polymer</i>
Polysaccharides
Starch
Cellulose
Chitin
Proteins
Collagen/gelatin
Casein, albumin, fibrogen, silks
Polyesters
Poly(hydroxyalkanoates)
Other polymers
Lignin
Lipids
Shellac
Natural rubber

Some of the other important natural polymers that are under scrutiny by the research community, but beyond the scope of this book, include lignin, shellac and natural rubber. In the category of natural polymers which need to be polymerized is the interesting development of biodegradable plastics from edible and non-edible vegetable oils like soybean oil, peanut oil, walnut oil, sesame oil, sunflower oil, tung oil and castor oil.

Table 1.2 presents a selected list of the common natural polymers.⁵

The production of 100% bio-based materials as substitutes for petroleum-based products is not an economical solution. Some of the possible solutions are blending biopolymers with synthetic polymers and reinforcing natural fibres with synthetic polymers (termed bio-composites), which are a viable alternative to glass fibre composites.

1.2 Natural Polymer Research

The aim of this book is to examine the research conducted worldwide on the use of different types of natural polymers. The book looks at the different processing techniques of natural polymers as well as applications in advanced industrial sectors. The structure, mechanical and thermal characteristics of selected natural polymers are highlighted.

1.2.1 Natural Fibres

The history of fibre-reinforced plastics began in 1908 with cellulose fibre in phenolics, later extending to urea and melamine and reaching commodity status with glass fibre-reinforced plastics. Natural fibres are subdivided based on their origins, coming from plants, animals or minerals. All plant fibres are composed of cellulose, while animal fibres consist of proteins (hair, silk and wool). Plant fibres include bast (or stem or soft sclerenchyma) fibres, leaf or

hard fibres, seed, fruit, wood, cereal straw and other grass fibres. Knowledge of the structure of natural fibres is crucial in understanding the structural parameters (number, size and shape of cells, chemical constituents) and fracture mechanisms in fibres.⁶

Some of the important natural fibres used as reinforcement in composites are listed in Table 1.3.

Over the last few years, a number of researchers have been involved in investigating the exploitation of natural fibres as load-bearing constituents in

Table 1.3 List of important natural fibres.

<i>Fibre source</i>	<i>Species</i>	<i>Origin</i>
Abaca	<i>Musa textilis</i>	Leaf
Agave	<i>Agave americana</i>	Leaf
Alfa	<i>Stippa tenacissima</i>	Grass
Bagasse	–	Grass
Bamboo	(> 1250 species)	Grass
Banana	<i>Musa indica</i>	Leaf
Broom root	<i>Muhlenbergia macroura</i>	Root
Cantala	<i>Agave cantala</i>	Leaf
Caroa	<i>Neoglaziovia variegata</i>	Leaf
China jute	<i>Abutilon theophrasti</i>	Stem
Coir	<i>Cocos nucifera</i>	Fruit
Cotton	<i>Gossypium</i> spp.	Seed
Curaua	<i>Ananas erectifolius</i>	Leaf
Date palm	<i>Phoenix dactylifera</i>	Leaf
Flax	<i>Linum usitatissimum</i>	Stem
Hemp	<i>Cannabis sativa</i>	Stem
Henequen	<i>Agave fourcroydes</i>	Leaf
Isora	<i>Helicteres isora</i>	Stem
Istle	<i>Samuela carnerosana</i>	Leaf
Jute	<i>Corchorus capsularis</i>	Stem
Kapok	<i>Ceiba pentrandia</i>	Fruit
Kenaf	<i>Hibiscus cannabinus</i>	Stem
Kudzu	<i>Pueraria thunbergiana</i>	Stem
Mauritius hemp	<i>Furcraea gigantea</i>	Leaf
Nettle	<i>Urtica dioica</i>	Stem
Oil palm	<i>Elaeis guineensis</i>	Fruit
Piassava	<i>Attalea funifera</i>	Leaf
Pineapple	<i>Ananas comosus</i>	Leaf
Phormium	<i>Phormium tenax</i>	Leaf
Roselle	<i>Hibiscus sabdariffa</i>	Stem
Ramie	<i>Boehmeria nivea</i>	Stem
Sansevieria	<i>Sansevieria</i>	Leaf
(bowstring hemp)		
Sisal	<i>Agave sisalana</i>	Leaf
Sponge gourd	<i>Luffa cylindrica</i>	Fruit
Straw (cereal)	–	Stalk
Sun hemp	<i>Crotalaria juncea</i>	Stem
Cadillo/urena	<i>Urena lobata</i>	Stem
Wood	(> 10 000 species)	Stem

composite materials. The use of such materials in composites has increased due to their relative cheapness, their ability to recycle and the fact that they can compete well in terms of strength per weight of material.

Volume 1 focuses on different sources and applications of natural fibres. One chapter deals with novel renewable sources from which natural fibres can be extracted. Another chapter looks at relating the structural anisotropy of natural fibres to mechanical properties. One of the challenges of using natural fibres in aerospace applications is the airworthiness requirements. Currently, natural fibres are being explored for use in secondary structures in aircraft for which flame, smoke and toxicity (FST) requirements are very stringent. This has led to a lot of developmental research being undertaken in this field. A further chapter therefore explores the flammability properties of natural fibre reinforced composites. A crucial problem associated with the use of natural fibres in composites is their hydrophilic properties. This aspect is dealt with in a chapter on probing the water sorption characteristics of natural fibres. The chemical modification of natural fibres has been well documented in the literature, but ideally it would also be desirable that the chemicals used for modification should also be from renewable resources as it would preserve the biodegradable nature of natural fibres. A chapter therefore focuses on environmentally friendly coupling agents for natural fibre-reinforced composites. Other chapters include examining the characterization techniques of the interfacial properties of natural fibre-reinforced composites and the increasing applications of natural fibre composites in the automotive sector.

1.2.2 Protein Fibres

The book also deals with the properties of selected protein fibres. Protein fibres are formed by natural animal sources through condensation of α -amino acids to form repeating polyamide units with various substituents on the α -carbon atom. The sequence and type of amino acids making up the individual protein chains contribute to the overall properties of the resultant fibre.⁷ In general, protein fibres possess moderate strength, resiliency and elasticity. They have excellent moisture absorbency and transport characteristics and do not build up static charge. Some of the common protein fibres include wool, spider silk, cashmere, *etc.* Among natural fibres, silk exhibits exceptional properties, especially in toughness and biocompatibility properties. A chapter therefore focuses on the studies and properties of silk fibre-reinforced composites. Other chapters include studies on collagenous waste-based composites and exploring the properties and applications of mussel byssus fibres. Important advancements in the field of zein fibres are also discussed in another chapter.

Volume 2 deals with the properties and characterization of selected natural polymer nanocomposites. Cellulose nanowhiskers (CNWs) have emerged as one of the most interesting bio-based nano-reinforcements in the last decade.^{8,9} Cellulose nanowhiskers can be generated from various plant sources with transverse dimensions as small as 3–30 nm, giving a high surface-to-volume ratio.

It has also been shown that since the nanowhiskers are rod-like, they can be self-assembled into chiral nematic liquid crystalline structures, not only in solution but also in the dry state. The volume begins by exploring nanocellulose as a potential reinforcement in composites. Chitosan (a natural polymer) is a good candidate for the development of conventional and novel drug delivery systems. Chitosan has been found to be used as a support material for gene delivery, cell culture, and tissue engineering. However, practical use of chitosan has been mainly confined to the unmodified forms. For a breakthrough in utilization, especially in the field of controlled drug delivery, graft copolymerization onto chitosan will be a key point, which will introduce desired properties and enlarge the field of the potential applications of chitosan by choosing various types of side chains. The properties and applications of chitosan and soy protein-based nanocomposites are discussed in subsequent chapters. Other chapters include studies on furanic-based nanocomposites, the characterization of molecular interactions in amylose/starch nanocomposites, and unique properties of nacre from mollusc shells.^{10,11} The last two chapters touch upon the industrial and biomedical applications of natural polymer nanocomposites.

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CHAPTER 2

Biomimetics: Inspiration from the Structural Organization of Biological Systems

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2.1 Introduction: Hierarchy and Structural Order

Structural materials found in nature exhibit hierarchical structures that span a structural order over length scales from molecular to macroscopic.¹⁻⁵ Optimization of properties and structural redundancy as well as growth are all ramifications of the hierarchical structures that result from eons of evolution. The following sections elucidate the hierarchical details of structure in bone, teeth, seashells and spider silk and fabrication attempts at duplication of these structures.

2.2 Biological Materials Systems

2.2.1 Bone

Bone is a remarkable biological material, providing skeletal stability, support and protection of vital organs. The structure of bone has been extensively

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studied historically as well as recently, owing to its perfect adaption of mechanical properties to metabolic functions. In addition, as a protein/mineral nanocomposite, bone combines the optimal properties of both components: stiffness and toughness. This rather unusual combination of material properties is a combination of rigidity and resistance against fracture.⁶ The unique mechanical properties of bone and the structure–property relationship have attracted significant attention.

Research on the structure of bone dates back to the early 17th century, when the compound microscope was invented. Clopton Havers is generally credited with providing the first description of the porous nature of bone in 1691, but due to the poor quality of the magnifying lenses, the initial descriptions dealt primarily with the canal system and the “laminar” structure of bone without the presence of osteonal bone. In the 18th and 19th century, some observations were described and defined in detail, such as the Haversian system of lamellae, and the orientation and disposition of lacunae and canaliculi.⁷ By utilizing polarized light microscopy, Schmidt found that the crystallographic “*c*” axis of mineral in bone is well aligned with the collagen fibrils.⁸ Further detailed studies came after the invention of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in 1930, which enabled examination of structures on the nanometer scale. With the help of these high-resolution instruments and other techniques such as X-ray diffraction, polarized optical microscopy, sonic velocity, as well as mechanical tests, the hierarchical structure of bone was discovered and depicted. Atomic force microscopy (AFM), which appeared in 1980, made it possible to investigate the structure of bone in the ambient environment on the nanometer scale.^{9–11} Although the overall structure from nano to macro scales of bone has been extensively studied, more detailed research is also needed.

Bone refers to a family of materials having in common a basic building block, the mineralized collagen fibril; however, the structural organization of the fibrils is different in different bone types. The family of bone also contains dentin, cementum and mineralized tendon, which have various proportions of bone components.¹² Disregarding the different shapes, bone is generally mechanically divided into two types, compact bone and cancellous bone,¹³ which will be introduced later.

Primarily, bone tissue is composed of collagen fibres, crystals of a calcium phosphate complex also known as carbonated apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ (namely, mineral) and a cement containing mucopolysaccharides, among other biopolymers. The chemical analysis of bone shows that there are three primary components in bone: collagen, mineral and water. The collagen part accounts for nearly 1/3 and the mineral part accounts for nearly 2/3 of the dry weight of bone matrix.¹⁴ The water component is about 10–12 wt% of cortical bone and 20% of the bone matrix.¹⁵ The mineral crystals and grow in the triple helical collagen fibres and replace some of the water while mineralization takes place. The bone structure has been described in terms of up to six or seven hierarchical levels of organization from nanoscale collagen and mineral to macroscale femur bone (Figure 2.1).^{12,16,17} Recently, new studies indicate hierarchical

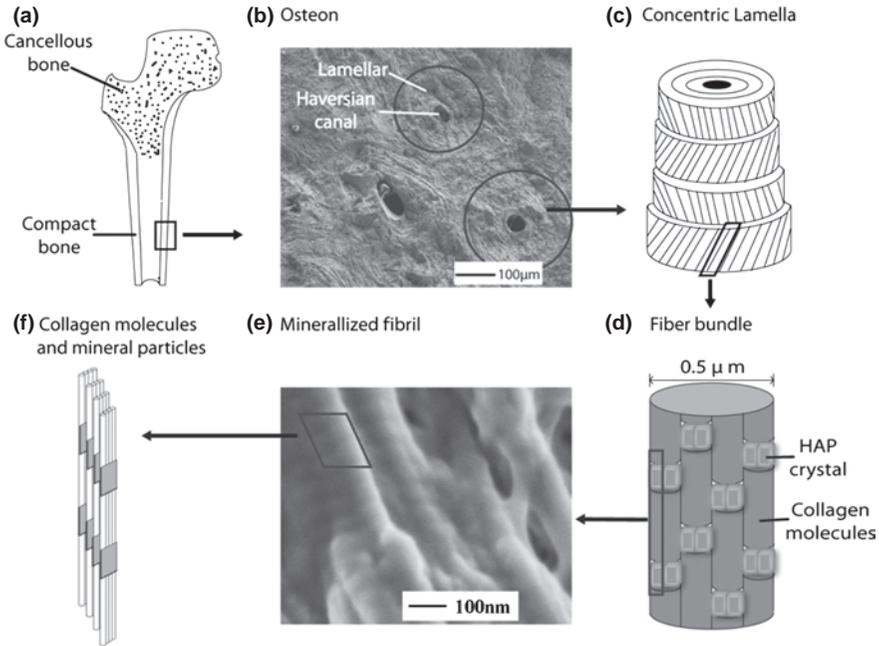


Figure 2.1 Hierarchical organization of a human femur bone from macro- to nanoscale. (a) Macroscale organ level: human femur bone. (b) Macroscale tissue level: osteon. (c) Microscopic level: bone lamellae (adapted from Giraudguille¹⁷). (d) Mesoscopic level: fibre bundle. (e) Nanoscale level: mineralized fibril. (f) Molecular level: collagen molecule and mineral particle. (Adapted from Fratzl.¹⁶)

structures in the collagen molecule in bone with three levels of hierarchy within the molecule.¹⁸

2.2.1.1 Level 1: Collagen Fibrils and Minerals

2.2.1.1.1 Collagen. Type I collagen molecules, also called triple helices, are supercoiled assemblies of three polypeptide chains, two identical $\alpha 1$ -chains and one $\alpha 2$ -chain, each with over 1000 amino acid residues. Collagen type I accounts for nearly 90% of its total organic content. The main part of a collagen chain consists of Gly-X-Y repeats, in which X and Y can be any amino acid but are frequently proline and hydroxyproline. A triple-helical molecule is cylindrically shaped, with an average diameter of about 1.5 nm and length of 300 nm.¹⁹ Besides the main helical part, collagen triple helices also comprise short nonhelical end sequences called telopeptides with both N- and C-terminal ends. Telopeptides account for 2% of the molecule and are critical for fibril formation in a self-assembly process.²⁰ Figure 2.2 shows a schematic of the general structure and triple helical motifs of the collagen molecules.

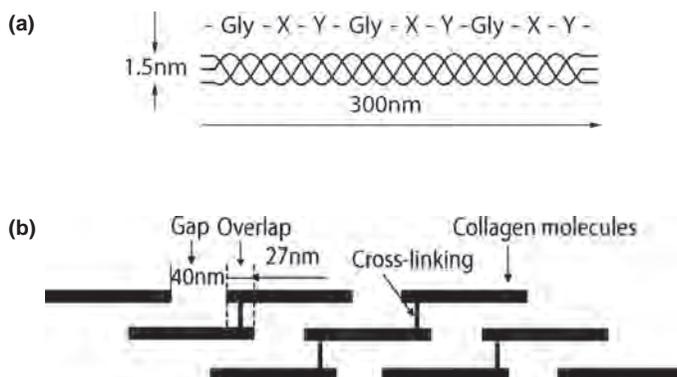


Figure 2.2 Collagen molecules and intermolecular cross-linking. (a) Triple-helical structural motif of collagen molecules (adapted from Giraud-Guille¹⁹). (b) Lysyl oxidase cross-linking. (Adapted from Kadler *et al.*²⁰)

During the formation of a fibril the collagen spontaneously self-assembles into cross-striated fibrils that occur in the extracellular matrix of connective tissues. The fibrils are stabilized by covalent cross-linking which is initiated by oxidative de-amination of specific lysine and hydroxylysine residues in collagen by lysyl oxidase.²⁰ The intermolecular cross-linking provides the fibrillar matrices with various mechanical properties, such as tensile strength and viscoelasticity. Both high-performance liquid chromatography (HPLC) and Fourier transform infrared spectroscopy (FTIR) have been frequently adopted to analyze the cross-links.²¹

2.2.1.1.2 Mineral. The mineral in bone primarily consists of poorly crystalline non-stoichiometric carbonated hydroxyapatite (dahllite), which has a plate-shaped hexagonal crystal structure. Bone crystallites are probably the smallest biogenic crystals. They are only 1.5–4 nm thick, 25 nm wide and 50 nm long on average,¹² but very little is understood about the atomic structure. The *c*-axis of the unit cells of these crystallites in bone is usually aligned parallel with the long axis of the adjacent collagen fibres.²² Studies using AFM indicate that many of these mineral plates appear to be aligned, forming larger aggregates (475–600 nm long \times 75–90 nm thick) that also retain collagen periodicity along their exposed edges.¹¹

2.2.1.2 Level 2: Mineralized Fibril

The triple-helical collagen molecules assemble into the fibril in a staggered arrangement. Within the fibril there is a linear shift of ~ 67 nm (D-period) between neighboring molecules. The D-period is divided by overlaps and gaps, where an overlap is around 27 nm and a gap is 40 nm (shown in Figure 2.2b). Robinson and Watson^{22,23} pioneered a TEM study and reported the 68-nm

banding pattern in collagen fibrils. The assembly of collagen molecules into fibrils is an entropy-driven process, driven by the loss of solvent molecules from the surface of protein molecules, resulting in assemblies with a circular cross-section, which minimizes the surface area/volume ratio of the final assembly.²⁰

Mineralized fibrils are the basic building blocks of bone. Minerals are intimately associated with the collagen framework in which they form, resulting in a highly complex but ordered mineral/organic composite material. Studies of crystal growth show that crystals are first formed in the gap, and then they continue to grow and penetrate into the overlap zone, thus pushing aside the triple-helical collagen molecules and even breaking cross-linking and other bonds.²⁴ Because the density of crystals is higher in the gap region, a periodic mineral density profile with around 67 nm spacing can be observed by electron microscopy. The width of a mineralized fibril is about 100 nm.

It is also important to mention that the spaces between mineralized collagen fibrils (extrafibrillar) are filled with non-collagenous macromolecules and minerals. The extrafibrillar volume is at least 60% of the total, while the fibrils are no more than 40%. More of the mineral appears to be extrafibrillar than within the fibrils, and is cemented together by non-collagenous organic matter.²⁵

2.2.1.3 Level 3: Fibrillar Arrays

The mineralized fibrils are self-organized into fibre bundles along their length and the bundles may fuse with neighboring bundles. How the mineralized fibrils are aligned is of great interest, which leads to a great difference in mechanical properties. Two arrangements have been suggested.¹² One is an arrangement of mineralized collagen fibrils aligned both with respect to the crystal layers and the fibril axes. The other arrangement of mineralized collagen fibrils is with only the fibril axes aligned. Sonic velocity measurements in three orthogonal directions of macroscopic specimens show significant differences,²⁶ implying that orthotropic order at the fibril level may well extend to millimeter distances.

2.2.1.4 Level 4: Fibrillar Array Patterns

The fibril bundles continue to be organized into layers or lamellae with a few microns thickness, and they in turn are arranged in a variety of ways into higher-order structures, depending on the bone type. Four of the most common patterns have been presented. In a parallel array pattern, all the fibrils are parallel to each other. In a woven array pattern, individual fibrils or fibril bundles are randomly organized. A radical fibril array is characteristic of the bulk of dentine, which also belongs to the bone family.¹² Further, plywood-like structures are common in nature, which is believed to have a structure–function relationship.¹⁹ SEM and TEM studies showed that lamellar bone is made up of alternating collagen-rich and collagen-poor layers, all having an interwoven arrangement of fibres.²⁷ The successive layers in a thin/thick lamellar unit proceed by an angle of roughly 30° from one layer to the next.²⁸

2.2.1.5 Level 5: Osteon

The osteon, also called the Haversian system, is the fundamental structural unit of compact bone. Each osteon consists of concentric layers or lamellae that surround a central canal, the Haversian canal. The Haversian canal, parallel to the long axis of the bone, contains the bone's nerve and blood supplies. Between adjoining osteons there are angular intervals that are occupied by interstitial lamellae. These lamellae are remnants of osteons, the greater parts of which have been destroyed.¹⁴ The osteon takes part in the remodeling process, whereby tunnels are eroded and then filled in again with cylinders of bone.

2.2.1.6 Level 6: Compact and Cancellous Bone

Compact bone is solid, with the only porosities existing for canaliculi, osteocyte lacunae, blood channels and erosion cavities, while cancellous bone has porosity that is easily visible to the naked eye. Overall, bone serves a protective function by the construction of two compact plates separated by intervening cancellous (spongy or trabecular) bone. This construction is beneficial for the maximum absorption of energy with the minimum trauma to the bone itself.

2.2.1.7 Mechanical Advantages of the Hierarchical Structure

As pointed out by Gao *et al.*,²⁹ bone is much less sensitive to flaws because of its hierarchical structure. The hierarchical design distributes stresses throughout the levels of a structure, thereby minimizing dangerous stress concentrations that could precipitate failure and fracture. The hierarchical feature of bone controls the fracture properties, particularly the toughness.¹³ Because the collagen fibres in neighboring lamellae are oriented at some angle to each other, fracture surfaces show considerable roughness. The work of driving a crack across the interfaces consisting of the plates, sheets and Haversian systems of bone is much greater than it would be if the material were homogeneous.³⁰ Recently, many efforts have been made to model the structure of bone and its constituents through continuum and molecular modeling methods. The mechanical properties of bone and the relationship of the properties to the hierarchical structural organization have been extensively investigated.^{29,31-41} Continuum methods, using finite element modeling (FEM), are used to calculate the fundamental mechanical properties of bone.⁴²⁻⁴⁵ Attempts at multiscale modeling techniques for collagen have been made.^{18,36,46-50} Recent experimental studies using fluorescence resonance energy transfer has indicated molecular interactions between apatite and collagen. Simulations using steered molecular dynamics have indicated the nature of the interactions (primarily non-bonded), as well as their role on mechanics of the collagen molecule.^{50,51} In addition, it has been shown that the load-deformation of tropocollagen interacting with HAP⁵⁰ is significantly influenced by water. Molecular and nanomechanics of bone have also been described in a number of studies^{5,18,34,52-55} and different nanoscale deformation mechanisms have been

proposed in the literature. It has also been shown recently that the collagen molecule, when observed in its full length through simulations, exhibits a new level of hierarchy of structure which has significant contributions to the mechanics. The three levels are: level 1, the helicity of the individual polypeptide chain; level 2, the helical organization of the three peptide chains; and a third new hierarchy, the helicity of the overall triple helix that can only be observed in a full length collagen molecule.¹⁸

2.2.2 Teeth

Teeth are small, calcified, structures found in the jaws (or mouths) of many vertebrates that have the primary function of breaking down food. Teeth are anchored within alveolus bone sockets and are held in place by a thin cementum interlayer adjoining the periodontal ligament. The part of the tooth that projects into the mouth is called the tooth crown, while the part that is set into the jaw is called its root.⁵⁶ The tooth interior generally consists of three layers. The outer layer of enamel (96 wt% mineral), which is the hardest tissue in the body, covers part or all of the crown of the tooth. The middle layer of the tooth is made up of dentine (or dentin), with an enamel/dentine junction (EDJ) several micrometers thick separating it from enamel. Dentine is less hard than enamel and similar in composition to bone (70 wt% mineral, 20% organic, 10% water). The third and the innermost layer is pulp, containing blood vessels and nerves. The hard, brittle enamel coat protects the soft, tough dentine and pulp interior.⁵⁷

Enamel is not only hard (resistant to permanent surface deformation), but also very tough (resistant to crack propagation and brittle fracture).⁵⁸ Unlike bone, which is a collagen-based ceramic composite, enamel is a tissue mineralized with calcium phosphate, containing no collagen or cells, but rather having long, thin strands of hydroxyapatite (HAP) that are woven into a fabric-like ceramic. Enamel retains less than 0.5% protein and a very small amount of water and holds the mineral fibres together.⁵⁹ Additionally, in contrast to bone, enamel is not remodeled during its lifetime since the ectodermally derived cells that create enamel are lost once the tooth erupts into the oral cavity.⁶⁰

2.2.2.1 Hierarchical Structure of Enamel

The enamel mineral is a form of non-stoichiometric carbonated calcium hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$. The Ca/P ratio of enamel apatite is slightly lower than that of hydroxyapatite.⁶¹ Enamel exhibits a hierarchical organization that spans nanoscale to macroscale levels. Some literature regards the nanospheres as the first level, virtually as the first step of biomineralization. At the nanoscale, amelogenin molecules undergo self-assembly to form 15–20 nm spheres.⁶⁰ In mature teeth, apatite crystallites are the least complex and smallest structural unit.⁵⁸ The crystals resemble long bars with a hexagonal cross-section at a final size of about 30–40 nm across.⁵⁶ Here we list the five specific levels of structure based on structural complexity of mature teeth.⁶² These orders of

scale are interdependent and coalesce with one another, thereby creating a structural continuum in the tooth organization.

2.2.2.1.1 Level 1: HAP Crystallites, a Few Ångstroms Wide. Unlike the minute, short crystallites of bone, the crystallites of dahllite in enamel are needle-like, narrow and extremely long. Reports of crystallite length vary from a fraction of a micron to 100 μm . Each crystallite is surrounded by nanospheres favoring growth on their *c*-axis and proper spacing among the crystallites.⁶⁰

In the early mineralized enamel crystals, ribbon-like crystals appear near the ameloblast at the DEJ. As maturation occurs, the enamel crystals become more densely packed and more highly oriented.⁶³ Cross sections of fully mineralized crystallites are usually hexagonal⁶⁴ or rhomboidal.⁶⁵ Many other growth habits, including rectangular or irregular crystals (30–40 nm in width) which contain “notches”, have also been observed.⁶⁴ Simmer proposed a three-stage enamel crystal growth mechanism which involved a crystal precursor, octacalcium phosphate (OCP). The three-stage mechanism includes: (1) formation of the incipient seed of the crystals; (2) two-dimensional growth of the seed (*a*- and *b*-axes); (3) three-dimensional growth, which involves growth along the *c*-axis and then one-unit-cell thickness of OCP hydrolyzes to a two-unit-cell thickness of HAP, thereby leading to a contraction of the lattice in one direction and growth in the *c*-axis produces a regular hexagonal prism. Further, enamel incorporates some ions in its apatite lattice, such as HPO_4^{2-} , CO_3^{2-} , Na^+ , F^- , *etc.*, different from ideal hydroxyapatite. Therefore, some ions fit in the interstices and cause distortions in the close-packed lattice.⁶⁵

2.2.2.1.2 Level 2: Prisms. Concerning the arrangement and orientation of crystallites, two major classes of mammalian enamel are defined: prismless (also named as aprismatic, nonprismatic or preprism in various publications) and prismatic enamel.⁵⁸ Prismless enamel refers to a discontinuous structure separated by distinct boundary planes, and prismatic enamel has the cross-sections of prisms that are demarked by sheaths that usually have curved outlines.⁶² In primates, as in most mammals, prismatic enamel is the dominant component of enamel patterns and the ameloblast cells weave the hydroxyapatite crystallites into bundles called “rods” that decussate one another.⁶⁰ The diameter of a prism ranges from 2 to 10 μm .⁵⁸ The sheath, where protein and water accumulate, is approximately 100 nm thick.⁵⁷ The cross-sectional morphology of the prism sheath was determined by the shape of the Tomes process on the tip of the ameloblast,⁶² and various morphologies were shown, such as circular prisms with complete sheaths, highly derived prisms with key-hole cross-sections, *etc.*, but it is still not known if the differences in morphology of the prism cross-sections affect functions.

2.2.2.1.3 Level 3: Enamel Types. Units of enamel in which the prisms have similar orientations are defined as enamel types. The orientations of prisms are independent of their cross-section morphology. In order to study the

orientation of prisms, the enamel/dentine junction (EDJ) is regarded as a reference plane.⁶² The two prismatic enamel types that occur in primate enamel are radial enamel and decussating enamel.

In radial enamel, all prisms are roughly parallel to one another as they rise radially from the enamel/dentine junction and occlusally toward the enamel surface.⁵⁸ Radial enamel can be distinguished into different subtypes by differences in orientation of the interprismatic matrix (IPM) crystallites relative to the prisms, which can vary from almost parallel to intersections at angles of approximately 90° .⁶²

In decussating enamel, prisms are arranged in regularly organized, alternating layers or groups that rise from the enamel/dentine junction to the surface at different orientations.⁵⁸ Decussation is manifested optically in tooth sections as so-called Hunter–Schreger bands (HSBs), due to variations in light reflection from differently oriented prism bundles. Hunter–Schreger bands, like radial enamel, are commonly observed in mammalian enamel but vary in degree from species to species.⁵⁷ Complete crossing of prisms at 90° to those in adjacent groups (“true decussation”) does not occur in all species. More often, the angle between prisms in adjacent bands is less than 90° , and changes as prisms pursue a slightly sinuous course from the enamel/dentine junction to the outer tooth surface. In primates and most other mammals the layers are usually several prisms thick, but in some rodents each layer is only one prism thick. The most common type of decussating enamel is horizontal decussation, in which HSBs are stacked on top of one another from crown to root, with long axes of prisms in adjacent horizontal layers of prisms extending toward the outer enamel surface at different angles. This is the type of decussating enamel found in primate teeth.⁵⁸ Tangential enamel and irregular decussation of prism bundles were also recognized in some molars of rodents.⁶²

2.2.2.1.4 Level 4: Enamel Patterns. Enamel patterns refer to the arrangement of the enamel types within a tooth. Normally, mammalian teeth are capped with enamel that is composed of two or more enamel types and have a characteristic distribution through the enamel of the crown. The enamel pattern was designated “schmeltzmuster” by Koenigswald in 1977.⁶² In rodents, the enamel pattern regularly includes an inner layer of HSBs and the outer layer of radial enamel. In molars of small-bodied primates the enamel pattern usually consists of an inner layer of radial enamel and a much thinner outer layer of prismless parallel crystal. In larger primates the enamel pattern is usually composed of an inner layer of horizontal HSBs, a middle radial layer and an outer prismless layer.⁵⁸

2.2.2.1.5 Level 5: Dentition. Dentition is the most complex and largest-scale hierarchical level that describes the variation of enamel patterns from tooth to tooth. Animals whose teeth are all of the same type, such as most non-mammalian vertebrates, are said to have homodont dentition, whereas those whose teeth differ morphologically are said to have heterodont

dentition. At the dentition level, primates appear to have relatively little variation in enamel microstructure in comparison with rodents.⁵⁸ In human teeth, enamel is the most dense (96% mineral) close to the outer surface and less dense (84% mineral) near the enamel/dentine junction.⁶⁶

Further, each level of complexity only provides limited information on one aspect of the total structure. The thorough analysis should also take the study of systematic interrelationships and biomechanical functions into account.

Although protein and water occur only a very small amount in enamel, they are crucial to the development and toughness of bone. Amelogenin and enamelin are the main proteins present in enamel. Initially, amelogenins make up about 90% of the protein and are most important. They are hydrophobic and probably control crystal size and orientation.⁵⁶ As the mineral crystals grow in size during maturation, amelogenins disappear and then suck out vast amounts of protein (degraded with proteases) and water. Enamelin is the largest known enamel protein and its expression is highly restricted to developing teeth. There are also some other proteins that have been observed, such as tuftelin, which may play a role in the nucleation of enamel crystallites.⁶⁷ Enamelins and tuftelins in the spaces between mineral crystals also serve as a “glue”,⁶⁸ and some other proteins such as ameloblastin and enamelysin are believed to be essential for proper enamel mineral formation.⁶⁹ The water in enamel was found to be bound in two different ways. A small part is very loosely bound, whereas the greater part is firmly bound to the mineral phase.⁷⁰

2.2.2.1.6 Dentine. Dentine forms most of the volume of the tooth (as shown in Figure 2.3). Dentine contains tubules that intersect the EDJ

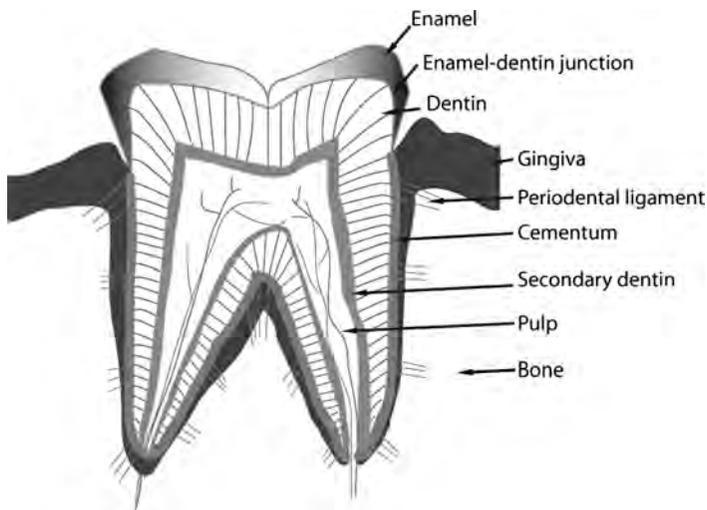


Figure 2.3 Schematic representation of the basic structure of the human tooth. (Adapted from Lawn *et al.*⁵⁷)

approximately perpendicularly, enabling transport of nutrients from the pulp through the tooth interior.⁵⁷ Dentine is rather like bone, with about 48% of its volume composed of mineral and has an organic matrix based on type I collagen fibres.

The microstructure of dentine was also suggested to be hierarchical. The mineral crystallites are needle-like near the pulp and the shape continuously progresses to be plate-like near the DEJ.⁷¹ The edge view of plate-like mineral crystallites in dentine is as long as in enamel (up to 100 nm),⁷² and with thickness in the range 2–3.5 nm. The collagen fibrils, approximately 30% by volume, are roughly 50–100 nm in diameter; they are randomly oriented in a plane perpendicular to the direction of dentine formation. The whole orientation of collagen seems to determine that of the crystals which initiate within and around them. Like bone structure, distinct bands from collagen fibrils in longitudinal sections of dentine were also seen by TEM^{72,73} and AFM.⁷⁴

At a higher level of organization, dentine is regarded as a composite, with the intertubular dentine as the matrix and the tubule lumens with their associated cuffs of peritubular dentine forming the cylindrical fibre reinforcement. Peritubular dentine exhibits hardness close to that of enamel.⁵⁶ At the greatest length scale are the effective, or continuum, properties of dentine.⁷⁵

2.2.2.1.7 Mechanical Advantages of the Hierarchical Structure. From a micro-structural point of view, enamel and dentine are both very heterogeneous tissues. There are obvious mechanical advantages of their intricate make-up. At the cost of a low stiffness and the loss of some compressive “strength”, dental tissues have much greater toughness than plain ceramics and survive much repeated loading.⁵⁶ Cracks spreading between adjacent prisms may be stopped if the rods change direction periodically (decussation).⁷⁶ The complex fabric that dissipates forces traveling through teeth also protects them from fracture.⁵⁸

Many studies have been done on the hierarchical complexity of enamel and dentine. However, there is still a lot that remains to be done if we are to understand the adaptive significance of mammalian dental form and the relations between the hierarchical structure and function; a better understanding of their structure could definitely contribute to improving the processing of artificial composite materials.

2.2.3 Seashells

Seashells are natural mineralized nanocomposites with hierarchical structures. There are a large variety of seashells found in nature and they possess many different morphological types of shell structures,^{77,78} but most of them are built of two CaCO₃ polymorphs, *viz.* an outer prismatic layer of rhombohedral calcite and an inner nacreous layer of orthorhombic aragonite, which are sandwiched by an organic matrix containing glycine- and alanine-rich proteins and polysaccharides, thus forming complicated multilayered microstructures.⁷⁹