Mechanical properties of load-bearing biological materials

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MECHANICAL PROPERTIES OF LOAD-BEARING BIOLOGICAL
MATERIALS

MAHAN QWAMIZADEH

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**SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
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**A thesis submitted to the Nanyang Technological University in partial fulfillment of the
requirement for the degree of Doctor of Philosophy**

2017

Dedication

To Mohammadreza Lahijanian, I started with your support and now you are not here to see my success. I would much prefer it if you were alive and well. I'll promise you will always be in my heart, my mind and my memories.

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Abstract

Bone, a typical load-bearing biological material, composed of ordinary base materials such as organic protein and inorganic mineral arranged in a hierarchical architecture, exhibits extraordinary mechanical properties. Up to now, most of previous studies focused on its mechanical properties under static loading. However, failure of the bone occurs often under dynamical loading. One of the key functions of load-bearing biological materials, is to protect their inside fragile organs by effectively damping dynamic impact. How those materials achieve this remarkable function remains largely unknown. An interesting question is: Are the structural sizes and layouts of the bone related or even adapted to the functionalities demanded by its dynamic performance?

In this thesis, systematic finite element analysis was performed on the dynamic response of nanoscale bone structures under dynamic loading. It was found that for a fixed mineral volume fraction and unit cell area, there exists a nanoscale staggered structure at some specific feature size and layout that exhibits the fastest attenuation of stress waves. Remarkably, these specific feature sizes and layouts are in excellent agreement with those at experimentally observed in the bone at the same scale, indicating that the structural size and layout of the bone at the nanoscale are evolutionarily adapted to its dynamic behavior.

Furthermore, This study shows that the nanostructure of bone very well synergizes the two mechanisms to achieve the fast stress wave attenuation which are stress wave scattering due to the protein-mineral interfaces and kinetic energy dissipation due to the viscosity of biopolymer components. Moreover, considering a self-similar hierarchical model, a theoretical approach was established to investigate the damping behavior of load-bearing biological materials in relation to the biopolymer viscous characteristics, the

loading frequency, and the geometrical parameters of mineral inclusions as well as the hierarchy number. It was found that the damping properties of biological materials are greatly tuned and enhanced by the staggered and hierarchical organization of the organic and inorganic constituents.

Finally, a theoretical framework was developed to establish the elastic bounds for the storage and loss moduli of various bioinspired staggered composites such as regular staggering, regular staggering with an offset, stairwise, herringbone and random staggering architectures. In a recursive way, the elastic bounds were further extended for bioinspired composites with multiple levels of structural hierarchy, and the effect of structural hierarchy was investigated; a theoretical approach was developed to estimate the damping properties of the hierarchical biocomposite at different length scales. It was found that, in comparison with other structural architectures, stairwise staggering structure generally gives higher loss viscoelasticity. The present work points out the importance of dynamic effect on the biological evolution of load-bearing biological materials.

List of Publications

- [1] **Mahan Qwamizadeh**, Zuoqi Zhang, Kun Zhou, and Yong Wei Zhang, “On the relationship between the dynamic behavior and nanoscale staggered structure of the bone”, *Journal of the Mechanics and Physics of Solids*, (2015) 78: 17-31.
- [2] **Mahan Qwamizadeh**, Zuoqi Zhang, Kun Zhou, and Yong Wei Zhang, “Protein viscosity, mineral fraction and staggered architecture cooperatively enable the fastest stress wave decay in load-bearing biological materials”, *Journal of The Mechanical Behavior of Biomedical Materials*, (2016) 60: 339-355.
- [3] **Mahan Qwamizadeh**, Zuoqi Zhang, Kun Zhou, and Yong Wei Zhang, “Hierarchical structure enhances and tunes the damping behavior of load-bearing biological materials”, *Journal of Applied Mechanics*, (2016) 83(5): 051009, 1-9.
- [4] **Mahan Qwamizadeh**, Kun Zhou, and Yong Wei Zhang, “Damping behavior investigation and optimization of the structural layout of load-bearing biological materials”, *International Journal of Mechanical Sciences*, (2017) 120: 263-275.
- [5] **Mahan Qwamizadeh**, Min Lin, Zuoqi Zhang, Kun Zhou, and Yong Wei Zhang, “Bounds for the dynamic modulus of unidirectional composites with bioinspired staggered distributions of platelets”, *Composite structures*, (2017) 167: 152-165.
- [6] Fei Shen, Shangqin Yuan, Yanchunni Guo, BO Zhao, Jiaming Bai, **Mahan Qwamizadeh**, Chee Kai Chua, Jun Wei, and Kun Zhou, “Energy absorption of thermoplastic polyurethane lattice structures via 3D printing: modeling and prediction”, published in *International Journal of Applied Mechanics*, (2016) 8(7): 1640006, 1-13.

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Nomenclature

AFM	Atomic Force Microscope
AR	Aspect Ratio
DB	Dugdale-Barenblatt
DEJ	Dentin-Enamel Junction
ESC	Equal Strength Criteria
FEA	Finite Element Analysis
FEM	Finite Element Method
FTIR-RM	Fourier-transform Infrared microspectroscopy in Reflectance Mode
GA	Genetic Algorithm
HOF	High Order Formulation
Lay	Layered
LB	Lower Bound
LOF	Low Order Formulation
MMC	Metal-Matrix Composite
MD	Molecular Dynamics
MTLT	Mineralized Turkey Leg Tendon
ODE	Ordinary Differential Equation
PBC	Periodic Boundary Condition
RVE	Representative Volume Element
SAXS	Small Angle X-Ray Scattering
SEM	Scanning Electron Microscope
Stag	Staggered
STC	Stress Transfer Criteria
TBI	Traumatic Brain Injury
TEM	Transmission Electron Microscopy
TGA	Termo Gravimetric Analysis
TP	Tropo-Collagen
TSC	Tension-Shear chain
UB	Upper Bound
VIB	Virtual Internal Bond
XRD	X-Ray Diffraction

List of Symbols

Alphabetical symbols

a	Vertical gap between the mineral platelets
A_{ei}	Area of the i^{th} element
c_0	Phase velocity of the laminated structure for the zero frequency limit
$c_{h,s}$	Wave speed in the hard and soft portions of the laminated structure, respectively
$c_{m,p}$	Wave speed in the mineral and protein, respectively
E	Elastic modulus
E^*	Complex elastic modulus
$E_{h,s}$	Elastic modulus of the hard and soft material, respectively
E_l	Composite loss modulus
$E_{m,p}$	Elastic modulus of the mineral and protein, respectively
E_s	Composite storage modulus
f	Loading frequency
g	Relaxation coefficient of protein
g_1	Relaxation coefficient of the material in the first term of Prony series
g_R	Dimensionless relaxation function
G	Shear modulus of the material
G_0	Instantaneous shear modulus of the material
G_{0P}	Instantaneous shear modulus of the protein
G_P	Shear modulus of the protein
G_P^*	Complex shear modulus of the protein
G_{sP}	Storage shear modulus of the protein
G_{lP}	Loss shear modulus of the protein
h	Half of the unit cell length in the laminated and staggered structures
$h_{h,s}$	Thickness of the hard and soft material in the laminated structure, respectively
$h_{m,p}$	Thickness of the mineral and protein in the layered and staggered biocomposite, respectively
k	Wave number
$k_{h,s}$	Wave frequency within the hard and soft material, respectively
L	Length of the hard inclusion
LN	Horizontal length of the layered or staggered composite

n	Stairwise or herringbone staggering arrangement parameter
N	Hierarchy number
s	Laplace parameter
t	Time
t_0	Duration of the impact pulse
t_c	Time that wave passes one unit cell
v	Particle velocity
$v_{h,s}$	Wave velocity in the hard and soft material, respectively
W	Vertical length of the layered or staggered composite
x	Horizontal direction index
y	Vertical direction index
Greek symbols	
α	First dimensionless parameter depending on the staggering pattern and the bound type
β	Second dimensionless parameter depending on the staggering pattern and the bound type
$\gamma_{h,s}$	Modulus index of the hard and soft material, respectively
$\gamma_{m,p}$	Modulus index of the mineral and protein, respectively
$\gamma^{U,L}$	Shear strain in the upper and lower portion of the soft matrix, respectively
δt	Small time scale
δ	Small longitudinal elongation
Δ	Small longitudinal elongation amplitude
λ	Impedance mismatch
ξ	Offset staggering arrangement parameter
φ	Mineral volume fraction of a self-similar hierarchical structure at each structural level
ϕ	Mineral volume fraction at macroscale
σ	Longitudinal stress
σ_0	Imposed stress on the vertical side of the unit cell
σ_{ave}	Average normal stress within the unit cell
$\sigma_{A,B}$	Normal stress at point A and B, respectively
σ_{ei}	Longitudinal stress at the i^{th} element
$\sigma_{h,s}$	Longitudinal stress in the hard and soft material, respectively
τ	Characteristic relaxation time of the protein
τ_1	Characteristic relaxation time of the material in the first term of Prony series
τ_{ave}	Average shear stress within the unit cell
$\tau_{C,D}$	Shear stress at point C and D, respectively

$\tau_{h,s}$	Viscoelastic characteristic time of the hard and soft material, respectively
$\tau_{m,p}$	Characteristic relaxation time of the mineral and protein, respectively
$\tau^{U,L}$	Shear stress in the upper and lower portion of the soft matrix, respectively
τ_{xy}	Shear stress at x - y plane
ε	Normal strain
ε_0	Longitudinal strain amplitude harmonically applied to the specimen
$\varepsilon_{h,s}$	Longitudinal strain in the hard and soft material, respectively
$\dot{\varepsilon}_{xy}$	Strain rate of the material
χ	Tension region correction factor
Π	Potential energy in the unit cell
Π_c	Complementary potential energy in the unit cell
ρ	Aspect ratio of the hard inclusion
$\rho_{h,s}$	Density of the hard and soft material, respectively
$\rho_{m,p}$	Density of the mineral and protein, respectively
$\rho_{opt}^{LOF,HOF}$	The optimal aspect ratio in each frequency for the Low and High Order Formulation, respectively
$\nu_{m,p}$	Poisson's ratio of the mineral and protein, respectively
ω	Angular loading frequency
ψ	Phase difference between the harmonic stress and strain

Chapter 1 Introduction

Load-bearing biological materials, such as bone, shell, tendon, possess outstanding mechanical properties with respect to their weak components from which they are formed. In general, these biological materials have seen with different and yet complicated layouts and structures, forming amazing composites with a combination of organic and inorganic materials through the millions of years of biological evolution.

1.1 Background

It is known that the structure of most of the biological materials typically possesses a number of hierarchical levels (Meyers et al., 2008). The number of hierarchical levels is very crucial in those materials because at different dimension scales, different damage and deformation mechanisms may occur. It should be noted that in biological materials there is an intrinsic hierarchical architecture with regard to the different combination of organic and inorganic portions. Thus, to understand how the structure and mechanical properties of these biological materials are related to each other, multi-scale modeling and simulations provide a powerful tool.

Fig. 1.1 (from (Zhang et al., 2011)) shows the hierarchical structures for different biological materials like bone (45% mineral volume fraction), mineralized tendon (15% mineral volume fraction) and shell (95% mineral volume fraction).

As it is seen, bone possesses seven hierarchical levels with an amazing self-similarity near the bottom levels. Mineralized tendon has four structural levels which are self-similar

in all the levels. Shell exhibits three levels of structural hierarchy with different structures in each level.

Fig. 1.1 Hierarchical structures of different biological materials, (a) bone (Jäger and Fratzl, 2000; Rho et al., 1998), (b) mineralized tendon (Puxkandl et al., 2002) and (c) shell (Menig et al., 2001).

Load bearing biological materials also have many other amazing features like the ability of self-healing, multifunctionality, self-assembly and self-organization. Self-healing is an extraordinary characteristic widely seen in natural materials brought about

from biological evolution, which allows them to repair themselves after injury. It is also noted that there are different exceptions for self-healing capability in natural materials such as teeth, cartilages and some cells of brains which are not able to heal themselves.

In addition, multifunctionality has been seen in most of the biological materials. There are many examples of different biological materials that can perform different functions such as:

- Bone: blood cell formation as well as providing the main structural support of the body as well as the mineral ion homeostasis (tendency to safeguard internal stability)
- Skin: environmental protection as well as regulating the body temperature
- Insect antennas: detecting thermal and chemical information as well as changing the orientation and shape to be more sensitive
- Sponge spicules: Structural support as well as light transmission
- Plant roots and vascular vessels: nutrition as well as structural support

Self-assembly and self-organization are used by biological materials to create their structures with optimized functionalities. Many researchers have focused on these two characteristics with aim to understand the driving forces for self-assembly and self-organization, and try to synthesize artificially similar structures with the same functionalities.

Most of the natural materials possess various common features at the smallest level of their hierarchical structures. In the primary level (molecular level), the amino acids are the main building blocks. There are about 22 different types of amino acids in nature which can link each other to form a chain, called protein. A combination of a small number of

amino acids can produce more than thousand different types of proteins which are the fundamental units of the primary level of the hierarchical structure of biological materials. Chitin, collagen, elastin and keratin are some of the principal types of protein existing in the structure of biological materials (Meyers et al., 2008).

Here, some examples of proteins used in biological materials are listed below:

- Chitin: insect exoskeletons and arthropods
- Collagen: organic portion of blood vessels, bone, dentine, muscles and tendons
- Elastin: skin, lungs
- Keratin: nail and hair

Minerals are another main building block of biological materials. Minerals, which are intrinsically harder than proteins, are nucleated and grown in the protein matrix, and form embedded crystals within the protein layers. These crystals have distinguished sizes, shapes and layouts. Some of the principal minerals are aragonite (calcium carbonate), calcite, hydroxyapatite (calcium phosphate) and silica. Here, there are some examples of minerals used in natural materials:

- Aragonite: shells and mollusks
- Calcite: bird eggs
- Hydroxyapatite: antlers, bones and teeth
- Silica: diatoms and spicules in sponges

In the first hierarchical level of load-bearing biological materials, protein portion is called the soft or organic tissue while the mineral portion is known as the hard or inorganic tissue. In fact, combination of these hard and soft tissues is the typical feature of the load-bearing biological materials. Generally, these biological materials have relatively

complicated structures systematized over several length scales (hierarchical structures) which are able to operate from larger length scales, down to the smallest length scale such as nanoscale (Ballarini et al., 2005; Barthelat et al., 2006; Gao et al., 2003). These multiscale structures are bountifully found in the nature, where they form a varied range of different materials which include antler, dentin, skin, cell and bone.

Wegst and Ashby (2004) classified the structural as well as mechanical properties of biological materials. Their classification has been done with regard to the relationship between the structure layouts of the materials and their mechanical responses. In this classification, the stiffness and toughness of different biological materials are compared together, which revealed that biological composites, like bone, dentin and tendon, are a reinforced combination of the stiff mineral and tough protein.

In this systematic arranging, there exist four principal categories for natural materials which are listed below:

- Biological ceramics and ceramic composites: In this category, mineral (hard portion) is dominant, and bones, shells and teeth fall into this category.
- Biological polymers and polymer composites: In this category, collagen (soft portion) is dominant, and ligaments, silk and tendons fall into this category.
- Cellular biological materials: This category of biological materials includes those with light weight, and examples of this category are feather or trabecular bone.
- Elastomers: These categories of biological materials are those that can experience large strains. Examples of this category are blood vessels, muscles and skin.

Fig. 1.2 depicts the toughness-stiffness relation of synthetic and biological materials.

(a)

(b)

Fig. 1.2 Toughness-stiffness relation in (a) synthetic materials such as metals, composites, and ceramics (Ashby et al., 1995), and (b) biological materials such as skin, dentin, shell and bone (Fratzl et al., 2004).

Fig. 1.2(a) shows that for a variety of synthetic materials ranging from alloys with high toughness to ceramics with high stiffness, by increasing the elastic modulus, the toughness will decrease. However, Fig. 1.2(b) shows that for biological materials with

high stiffness (the right side of the plot), a small increase in stiffness can cause a drastic decrease in their toughness. In the right lower corner of the plot, there are brittle minerals like hydroxyapatite while in the left upper corner, there are soft protein materials such as skin.

Nearly most of the load-bearing biological materials such as bone and mineralized tendon, which possess the functionality of structural support, are composed of proteins and brittle minerals (Currey, 1999). These load-bearing biological materials, which are the mixture of proteins and minerals, are seen in the upper right corner of Fig. 1.2(b). Generally, biological materials have a low density. It seldom goes beyond 3 g/cm^3 while a wide range from 3-10 g/cm^3 has been seen for synthetic materials such as metals, ceramics and composites. The stiffness of biological materials varies from 0.001 to 100 GPa, which is directly dependent on the basic constituents as well as the structure of the material. The strength in biological materials, which changes from 0.1-1000 MPa, shows a large variation for this amazing class of materials.

There are four main areas which have recently attracted great research attention. These four main areas are:

- Biological materials: In this area, materials, which can be found in nature like nacre, shell, dentin, skin and bone, are being studied, focusing on their mechanical properties as well as the interactions between the different levels of the material structure.
- Biomaterials: In this area, the focus is to find an optimized functionality for various biological systems specifically designated for particular purposes.

- Biomimicked materials: In this field, the focus is on using different approaches to synthesize materials inspired by biological systems.
- Functional biomaterials: In this area, biomaterials are designed to perform specific functionalities.

In the present work, we will study load-bearing biological materials, especially bone and bone-like materials, focusing on the relation between their internal structures and mechanical properties.

The main building blocks of the bone at its primary level are composed of collagen, mineral (hydroxyapatite) and non-collagenous organic proteins. The collagen contributes to the ductility while hydroxyapatite provides strength; meanwhile the mixture of these two components leads to a large amount of energy absorption before fracture or failure of the bone structure. To deeply understand the structure of the bone, it is necessary to understand its organic and inorganic components.

Collagen is the basic material of soft tissues in living organisms. Collagen is naturally a triple helix which is made of various chains of amino acid with approximate diameter of 1.5 nm. The amino acid chains will intercalate together to form the tropo-collagen molecules. The length of each collagen molecules is ~280 nm, which are arranged in a staggered pattern with a gap of 67 nm between them. The collagen molecules with staggered pattern are the basic matrix of the bone structure in the primary level. Intrafibrillar bonding makes these tropo-collagen molecules form collagen fibrils with diameter of approximately 50 nm, and these fibrils attach together to form collagen fibers with the diameter of ~1 μm .

The elastic modulus of the collagen is around ~1 GPa and its maximum strength is approximately 70-150 MPa. The density of the collagen is ~1 g/cm³ (Meyers et al., 2008). The maximum strain is also in the range of 10-20% (Meyers et al., 2008). Collagenous tissues have also been shown to exhibit viscoelastic properties under different creep and relaxation tests (Gautieri et al., 2013; Puxkandl et al., 2002; Shen et al., 2011).

Hydroxyapatite (calcium phosphate) is a naturally occurring mineral form of calcium apatite with the formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ but is usually written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ to denote the fact that the crystal unit cell comprises two entities. Hydroxyapatite is a hexagonal mineral crystal with elastic modulus around ~130 GPa and maximum strength of ~100 MPa. The density of the hydroxyapatite is ~2 g/cm³.

Hydroxyapatite is the basic material of the mineral component in the primary level of the bone structure that nucleates in the gap regions of the collagen molecules to form the mineralized collagen structure. The embedded hydroxyapatite crystals are plate-like in shape with the dimension of 15-150 nm in length, 10-80 nm in width and 2-10 nm in thickness (Meyers et al., 2008).

Bone, as a typical load-bearing biological material, composed of ordinary base materials such as organic protein and inorganic mineral arranged in a hierarchical architecture, exhibits extraordinary mechanical properties. In order to understand the mechanical properties of the bone, it is crucial to understand the hierarchical structure of the bone, and also the relationship between different levels of its structure. It is also important to understand the relation between the mechanical properties and the structure of the building blocks at each structural level of the bone and ultimately the mechanical properties of the whole bone.

Fig. 1.3 depicts the hierarchical structural levels of the bone in the macroscale level, microscale level and its sub-microstructure and also nanoscale and its sub-nanostructure.

Fig. 1.3 Bone hierarchical structure.

It is seen from Fig. 1.3 that the bone possesses different hierarchies in various size scales. At the smallest length scale, the bone consists of collagen molecules (~280 nm) and embedded mineral (hydroxyapatite) nanocrystals (~1-10 nm). In the next hierarchical level, the mineral and collagen are composed of mineralized collagen fibrils (~300 nm - 1 μm), which are stabilized by various enzymatic cross-links. At the next hierarchy, fiber arrays (~1-7 μm) form lamellae. At the next level, osteones (~100 μm) are the main part

of the bone structure. These osteones have central vascular holes (Haversian canals) enclosed by lamellae ($\sim 3 \mu\text{m}$). At the highest length scale, internal levels form the cortical bone (Hulmes, 2002; Jäger and Fratzl, 2000; Meyers et al., 2008; Puxkandl et al., 2002; Rho et al., 1998).

The structure of the bone can be also classified based on the following:

- Macrostructure: trabecular (cancellous) and cortical bone
- Microstructure: osteons, Haversian canals and lamellae (from 1 to $500 \mu\text{m}$)
- Nanostructure: collagen fibrils and mineralized collagen fibers (from 1 to a few hundreds of nm)

At the macrostructural level, the bone is recognized as cortical (compact) and trabecular (cancellous or porous) form. By examining the cross-section of a long bone, one will notice that the outer portion is dense like cortical bone and the inner part is porous like trabecular bone. In general, cortical bone is observed in long bone such as tibia and femur while trabecular bone is seen in bone core and flat bones.

In the microstructural level, lamellae play the key role in constructing the structure of the bone. Lamellae which are formed of the flat arrangement of the mineralized collagen fibers will concentrically wrap around a vascular canal (Haversian canals) to form the osteons. Osteons are similar to cylinders with diameter of approximately $200\text{--}250 \mu\text{m}$ that are organized parallel to the longitudinal axis of the bone.

In the nanostructural level, tropo-collagen molecules will form the staggered collagen matrix which is shown in Fig. 1.4. As it is seen, mineral crystals are embedded and grown in the gap regions of the collagen matrix to form the mineralized collagen structure. The

mineral crystals grow in the orientation of c-axis, which is parallel to the long axis of collagen fibrils.

The Young's modulus of the cortical and trabecular bone is dependent on the size and structural level. It was reported to be 14-20 GPa (Reilly et al., 1974) for macroscale level while in microscale level the Young's modulus of the cortical bone was 5.4 GPa (Choi et al., 1990). Recently, nanoindentation was used to measure the Young's modulus of osteon lamellar bone and it was reported to be around 22 GPa (Rho et al., 1997). In the primary level, it is almost impossible to perform mechanical testing because the size of the structures is too small. The only available information are the sizes and mechanical properties of the organic (collagen) and inorganic (hydroxyapatite) components that form the primary hierarchical level.

Fig. 1.4 Mineralized collagen structure.

In this work, firstly, the primary structural level of the bone will be studied with aim to investigate how nature selects the size of the bone structure at the nanoscale over the millions of years of evolution and how structural sizes and layouts of the bone are related or even adapted to the functionalities demanded by its mechanical response. To do so, it is important to understand the structure of the bone at its first hierarchical level. As it was shown in Fig. 1.3 and Fig. 1.4, the bone structure in the nanoscale level is a matrix of collagen in which small mineral crystals are embedded into the protein matrix. The arrangement of the hydroxyapatite crystals within the collagen matrix has been shown to follow a staggered arrangement shown in Fig. 1.5.

Fig. 1.5 Staggered arrangement of the mineralized collagen structure at the first hierarchical level of the bone.

To analyze the mechanical response of such a staggered structure (a composite made of organic and inorganic materials) depicted in Fig. 1.5, it is necessary to understand the mechanical properties of the mineral and protein components of the mineralized collagen structure. There is almost no analytical solution for the stress wave traveling procedure in the staggered structure as shown in Fig. 1.5. Thus, to analyze the dynamic response of the staggered structure, it is essential to start from the layered structure. There are several solutions for the wave traveling analysis of the layered composites. In the following chapters, we will discuss in-depth, the modeling procedure, methodology and analysis of the layered and staggered structures as well to report our findings in the investigation of the relationship between the structural level and mechanical properties of the bone.

1.2. Motivation and objectives

Load-bearing biological materials, which are composed of organic materials, such as proteins and inorganic materials, exhibit extraordinary mechanical properties. Examples of this class of materials are shells, antlers, teeth, tendons and bones. Structurally, these materials often have two or more hierarchical levels constructed based on their constituent materials. For example, bone, a composite consisting of ceramic (calcium phosphate, or hydroxyapatite) and protein (collagen), with several levels of hierarchy, is the most important structural component of the human body. It is well-known that their mechanical properties such as fracture strength and toughness are directly linked to their internal structures and loading conditions. Undoubtedly, the mechanical properties of these load-bearing biological materials cannot be fully understood without taking into account their structural hierarchies.

The present project will focus on the structure-property relations of this amazing class of biological materials. The main objective is to determine the relation between their mechanical properties and fascinating structural features, and uncover the origins of the superb mechanical properties of these load-bearing materials hierarchically constructed by using their constituent materials (proteins and biominerals) of relatively poor mechanical properties.

The research methodology adopted here is to combine analytical modeling and finite element method (FEM) to develop the structure-property relation of these load-bearing biological materials. Analytical modeling will be based on the composite model with simple linear elastic material properties and simple structure geometries, which can approximately take into account the bottom levels of the structure hierarchy in load-bearing biological materials. In this model, each structural level will be composed of both hard and soft portions of the materials. The characteristics of soft portion (protein layers) and hard portion (mineral layers) and their self-similar and hierarchical composite structures will be considered within the model. However, when the characteristics of component materials become structurally complex, or their material properties become visco-elastic-plastic or the interfaces between them can debond and fracture, numerical modeling, more specifically, finite element analysis (FEA) is needed. With this method, we will be further studying failure behaviors such as strength, ductility and toughness as well as dynamic behaviors such as mechanical wave traveling with the consideration of the hierarchical structure levels of the materials. The relation to be obtained between structure characteristics and mechanical properties of the biological materials will be validated with existing experimental data and their functionalities.

The objectives of the present work are outlined as follows:

- Almost all the previous studies on biological materials have focused on static loading conditions; however, in real circumstances, load-bearing biological materials are often subjected to dynamic loading conditions. This work will investigate the dynamic response of these materials.
- Numerical methods are to be used to construct the relation between structure and property of the load-bearing biological materials. These numerical solutions will be used to model the layered composite and generalize it to different arrangements of soft and hard portion like staggered arrangement (The arrangement of most of the load-bearing biological materials in their primary structural level) to investigate the failure as well as dynamic behavior of the load-bearing biological materials such as stress wave propagation.
- Most of the previous studies assumed that the individual components were linear elastic materials. In the present study, we will consider nonlinear behavior arising from the visco-elastic-plastic characteristics of the materials in our numerical analysis.
- In most of the previous studies, the interfaces between different components were assumed to be in the perfect bonding conditions. In the present work, we decide to consider interface delamination and fracture, by using a cohesive law to describe the interfaces between the soft and the hard portion of the biological materials.
- Since these biological materials often possess hierarchical structures, it is important to introduce hierarchy into the model for more realistic results.

In this work, we focus on bone as a model material to study the load-bearing biological materials. By electing bone as a research subject in the present work, we have two purposes:

- Firstly, although there has been intensive research on the bone structural features; the mechanical properties of bone have not been yet fully understood, especially at primary structural levels under dynamic loading conditions.
- Secondly, amongst almost all the load-bearing biological materials, bone has the most complex structure with a large number of hierarchical levels, presenting a great challenge.

It should be emphasized that accurate prediction of the bone mechanical properties is not possible without taking its complex structural hierarchies as well as the interactions between the organic and inorganic components into account. In the next section, the bone structure will be studied in detail.

1.3 Dissertation outline

This PhD dissertation contains eight chapters. Following the introduction chapter, a comprehensive literature review on the load-bearing biological materials, their mechanical properties, the fundamentals of their hierarchical architecture and the necessity of studying the dynamic behavior of load-bearing biological materials is given in Chapter 2. Chapter 3 deals with the stress wave traveling through the laminated structure. Chapter 4 investigates the dynamic response of the staggered nanostructure of load-bearing biological materials considering the elastic materials for the mineral and biopolymer counterparts. Chapter 5 focuses on the effects of viscoelastic characteristics of biopolymer

on the dynamic behavior of load-bearing biological materials. Chapter 6 presents dynamic properties of multi-level biological materials and points out the importance of the hierarchical architecture in natural materials. Chapter 7 is concerned about the dynamic properties of different bioinspired staggered structures of biological materials. Finally, conclusions are drawn and future works are recommended in Chapter 8.

Chapter 2 Literature Review

Load-bearing biological materials such as nacre, dentin and enamel, tendon and bone primarily made from organic and inorganic materials have been seen with superior mechanical characteristics. During the million years of evolution, nature has designed them in such a smart way that they develop amazing hierarchical structures which possess extraordinary mechanical behavior. Numerous studies have been done to investigate the composition, structure and importantly mechanical behavior of these materials.

Considering the fact that the field of biological materials is relatively new compared to mechanical and materials science, and detailed experimental works on the mechanical properties of biological materials only started from 1950s, many important issues on the structures and mechanical properties of biological materials remain unexplored. Previous studies conducted on the mineralized collagen nanostructure of biological materials and the relationship between their exceptional mechanical properties and the structure at nanoscale level are briefly reviewed in the following section.

2.1 Biological materials

The first studies of biological materials date back to the earlier part of the twentieth century. Thompson in 1917 published a book, which is one of the major principal works in the field of biological materials. His book was reprinted in 1968. In this book, he studied biological systems as engineering structures to find a way to describe the structure and composition of biological systems (Thompson, 1968). Currey in 1970s did more research on biological materials (Currey, 1977; Currey, 1984), which led to the publication of his well-known book named “Bone” (Currey, 2002). His book was

extremely populous among those who studied the bone structure and mechanical properties.

Recently, there are several review articles (Espinosa et al., 2009; Fratzl and Weinkamer, 2007; Meyers et al., 2008; Rho et al., 1998; Weiner and Wagner, 1998) and books (Currey, 1984, 2002; Ethier and Simmons, 2007; Lucas et al., 1999a) on the structures, functionalities and mechanical properties of biological materials. For example, Fratzl and Weinkamer (2007) reviewed biological materials like woods, tendons, sponges and bones as well as their multi-level structures. In their investigation, they studied the relation of the structural design and mechanical properties in biological materials and reviewed mechanical and biological principles that need to be taken into account in the hierarchical design of biological materials. They also considered remodeling of bone with *in vivo*, *in vitro* and *in silico* experiments (Fratzl and Weinkamer, 2007). Meyers et al. (2008) also reviewed biological materials and their superior extraordinary mechanical properties as well as their structural characteristics. In their work, they started from the main building blocks of the biological materials such as protein and minerals from their molecular level and then extended their work by introducing new concepts like biomineralization, nucleation as well as morphology to describe this intriguing class of materials. In their work, they studied various kinds of biological materials, such as shell and nacre, dentin and enamel, tendon, skin, feather, muscle, blood vessels and bone. They also considered bioinspired materials in their study as well (Meyers et al., 2008).

Wegst and Ashby (2004) inspired by the similar work done by Ashby (1993) for classifying the composite components in different groups based on their mechanical as well as material performance, characterized various biological materials and put them into

four principal groups, that is, ceramics, polymers, elastomers and cellular materials according to their density, strength and stiffness (Wegst and Ashby, 2004).

Gao and Ji (2003) used a virtual internal bond (VIB) method to model fracture in nanomaterials. When the characteristic size of the material is as small as nanometer scales, the fracture procedure becomes dominant by the surface energy in many cases. They used VIB method in their investigation. This method does not need a separate fracture criterion because a cohesive law has been combined with the constitutive model in this approach. They showed that in the length scale of the size of nanometer, the singularity of the displacement field is removed in the crack tip and the stress distribution tends to be uniform (Gao and Ji, 2003). In another work, VIB method was used to study the effect of interface of mineral and protein on the fracture of biomaterial nanostructures. It was shown that in such nanocomposites, with increasing the protein volume fraction, the damage of the mineral-protein interfaces occurring during impact loading can be effectively decreased (Ji and Gao, 2004b).

Gao et al. (2003) showed that materials like bone, shell and tooth which are nanocomposites composed of mineral and protein exhibit exceptional strength. They demonstrated that the mineral crystal dimensions, which were designed by nature during the evolution process, are selected to guarantee the optimum strength and maximum robustness. They proved that materials become insensitive to flaws at the nanoscale. Their findings have revealed many interesting insights in the field of biological materials and their results were extensively used by those who study biological materials (Gao and Chen, 2005; Gao et al., 2004; Gao et al., 2003).

Gao and Yao (2004) did a research on the adhesion tools existing on the feet of insects and geckoes. They found that these complicated adhesion systems are based on nanostructures containing a lot of nanofibrils. They modeled the adhesion mechanism of the fibers similar to the layers using van der Waals electrostatic interactions to calculate the optimum size and shape of the adhesive fibers. Interestingly, their results showed that in smaller scales around 100 nm, the shape of the fibers is not as important as larger scales. This means that by decreasing the diameter of the fibers to hundreds of nanometers, it is possible to have an optimized design of shape-insensitive adhesion mechanism (Gao et al., 2005; Gao and Yao, 2004).

Ji and Gao (2004a) investigated the mechanical properties of biomaterials and the relationship between the structure, layout, size and mechanical properties of these nature-designed materials. They found that protein and its volume fraction in the structure of biomaterials as well as the arrangement of the mineral crystals in the protein matrix and their long aspect ratios play important roles in designing the mechanical properties of load-bearing biological materials. They also revealed the viscoelastic characteristics of protein using the tension-shear chain (TSC) model and investigated the efficient role of protein in making tough and smart biological materials. Subsequently, this TSC model has been widely used in studying the nanocomposite structure of load-bearing biological materials (Ji and Gao, 2004a).

Ji et al. (2004b) studied the flow stress of the nanoscale metal-matrix composites (MMC) composed of soft materials and hard inclusions to investigate the interfacial failure mechanism of MMCs. They showed that by increasing the inclusion's volume fraction, the interface tends to be more tolerant. Their results indicated that when the

aspect ratio of the inclusions in the MMC structure reaches a sufficient large value, the flow stress increases, leading to the reinforcement of the MMC. Under this condition, the MMC becomes insensitive to interfacial fracture and debonding (Ji et al., 2004b).

Ji et al. (2004a) studied the buckling of the mineral crystals embedded in the soft protein matrix in biological materials such as bones and teeth. Their investigation showed that protein plays a crucial role in making the nanostructure of the biological materials more resistant to buckling failure. At first, they modeled the buckling analysis of a slender mineral crystal limited by soft matrix and then extended their model to a staggered arrangement of mineral-protein nanocomposite. They found that the staggered arrangement of the mineral crystals within the protein matrix is another important factor in stabilizing the nanocomposite structure against buckling failure under the compressive loading conditions. They proved that despite the fact that the Euler buckling formula predicts the buckling critical load increases with decreasing the aspect ratio, in the nanocomposite structure of biological materials however, the critical buckling stress is not dependent on the aspect ratio of the mineral crystals. Their results illustrated that with regard to the huge differences in the elastic modulus of soft protein and hard minerals, confining the mineral crystal by protein matrix in a staggered layout makes the biological nanostructure more stable against buckling (Ji et al., 2004a).

Guo and Gao (2006) used genetic algorithm (GA) to find the optimum arrangement for nanostructures composed of mineral and protein with regard to the failure criteria and constitutive models of biological materials. Their investigation showed that the staggered structure, by setting the maximum ductility as an objective of the nature to form biological nanocomposites, is the most optimized arrangement that can exist for mineral-protein

combination at the nanoscale. The finding may be used to design synthetic materials inspired from natural materials (Guo and Gao, 2006).

Buehler (2006) studied the mechanical characteristics of tropo-collagen (TC) molecules and found how nature designs collagen. Analytical as well as molecular models were used to investigate the effects of collagen fibril nanostructure on its strength and toughness. A strong relationship was found between the chemical properties of the tropo-collagen molecules and mechanical performance of collagen microfibrils (Buehler, 2006).

Yao and Gao (2006) used a simple bottom-up model to calculate the geometrical and mechanical properties of the gecko hair structure in different levels of structural hierarchy. They tried to find an explanation for the advanced nature-designed adhesion system of gecko's feet which allows robust attachment and easy detachment. In addition to analytical modeling, they performed systematic finite element analysis to investigate the attachment as well as the release mechanism of the gecko's feet to such a rough surface. Using a bottom-up self-similar structure for the gecko's fibrils they illustrated that there exists a specific adhesion flaw tolerance in each different length scale which will leads to different characteristic sizes for the fibrils in each hierarchy based of flaw tolerant theory which had been developed in the author's previous works (Gao and Chen, 2005; Gao et al., 2004; Gao et al., 2003). They considered in their work that the particular arrangement of the gecko's hair will form such a strong anisotropic material with particular adhesion strength which will significantly be altered with the movement in upward and downward directions. In another work, the same investigators used cohesive law to study the hierarchical structure of gecko and bone (Yao and Gao, 2006, 2007).

Zhang et al. (2010) demonstrated that staggered arrangement can provide the best mechanical properties for biocomposites composed of protein and mineral. They investigated the stiffness, toughness as well as the strength and maximum strain of the mineralized collagen nanostructures and found out that not only the volume fractions of the organic and inorganic components and their shapes play an important role in estimating the mechanical properties of the hybrid mineral-protein nanostructure but also the arrangement and orientation of the mineral crystals within the protein matrix have significant effects on the mechanical properties of these nanocomposites (Zhang et al., 2010).

Liu et al. (2011) analytically calculated the stress and strain distributions of the mineralized collagen nanostructure under unidirectional tension. They studied the influence of aspect ratio, mineral volume fraction as well as mechanical properties of the organic and inorganic portions on the strain and stress fields of the mineral-protein nanocomposites. They demonstrated that the uniform shear stress assumption in the TSC model which was developed by Ji and Gao (2004a) before, is only valid in such particular conditions. They further proposed a dimensionless parameter based on the obtained stress and strain fields to determine when TSC model is truly applicable to the mineral-protein nanostructures (Liu et al., 2011).

Tang et al. (2005) used elasticity principles and performed numerical analysis as well as FEM calculations to study a generic fibrillar interface in elastic conditions. They built their model according to the Dugdale-Barenblatt (DB) model. They tested fibrillar as well as non-fibrillar interfaces in both flaw sensitive and insensitive modes. Their results

showed that the interface strength is stronger in fibrillar interface rather than the non-fibrillar one (Tang et al., 2005).

There are various investigations on the effects of dimensions and characteristics of the building blocks of connective tissues on their mechanical performance. Connective tissues like skin and cartilage are composed of water, collagen, other kinds of proteins and also minerals. They play a significant role in the human as well as animal bodies. The arrangement of the matrix structure and also the characteristics of the components of the connective tissues were shown to have strong effects on the tissue mechanical properties (Birk et al., 1991; Craig et al., 1989; Parry and Craig, 1984).

Almost all the investigations discussed above were analytical or numerical works, focusing on the mechanical properties as well as the structure of mineralized collagen structure at the nanoscale level. Load-bearing biological materials like sea shells (nacre), teeth, mineralized tendons and bones are an interesting class of biological materials which deserve special attention from a mechanical point of view.

2.2 Load-bearing biological materials

In the next sections, the structure as well as the mechanical characteristics of various load-bearing biological materials will be briefly reviewed.

2.2.1 Nacre

There are a lot of investigations focusing on the structure and mechanical properties of nacre (Kamat et al., 2000; Laraia and Heuer, 1989; Menig et al., 2000, 2001; Shao et al., 2014). Nacre is formed of a matrix of protein which is densely embedded by mineral

crystals. The mineral volume fraction in nacre is very high and the mineral shape is reported to be plate-like (with a large aspect ratio) with dimensions of a few microns in length and up to ~500 nm in thickness (Currey, 1977; Jackson et al., 1988).

Kessler et al. (1996) studied the toughness of the conch shells. They proposed a fracture mechanics model to investigate the energy dissipation using a multiple cracking approach. Their results showed that mutual actions between the cracks in the shell microstructure can protect the nacre structure from failure (by providing smaller stress intensity factors at the crack tips), which leads to toughness enhancement of the nacre structure (Kessler et al., 1996; Shao et al., 2012).

Smith et al. (1999) used atomic force microscope (AFM) to study the fracture resistance of nacre. They elongated the surface molecules of nacre with small load around 200 pN to investigate the toughness of biological adhesives (Smith et al., 1999).

Kamat et al. (2000) used transmission electron microscopy (TEM) to study the conch shell fracture toughness. They presented two energy dissipation mechanisms such as crack bridging and multiple microcracking which were proposed by previous researchers (Kessler et al., 1996). In their work, they found that both of the mechanisms can lead to the increase of fracture toughness of their selected shells. The results of their investigation can also help design synthesized tough microstructures (Kamat et al., 2000).

Menig et al. (2000) and Menig et al. (2001) did quasi-static as well as dynamic compression tests to investigate the mechanical performance of two different kinds of sea shells (abalone and conch). The strength magnitude in both types of shells showed surface orientation-dependence. Their results also revealed that there exists high strain-rate sensitivity in both kinds of shells (Menig et al., 2000, 2001). Other works were also done

by using the fracture mechanics to investigate the toughness of nacre (Okumura and De Gennes, 2001). Furthermore, there were other works on the different mechanisms of deformation in nacre and estimation of surface roughness of its mineral components (Wang et al., 2001). Moreover, it was shown that mineral bridges observed in the protein layers of nacre can affect its mechanical properties (Song et al., 2003). Similar to the work on bone by Fantner et al. (2004), other researchers studied the influence of organic phase of nacre on its mechanical properties in dry and wet conditions. They found that by drying (dehydration process) the shells, their microstructures do not change; however the strength is significantly reduced (Neves and Mano, 2005).

2.2.2 Dentin and enamel

Enamel is seen as a low protein volume fraction nanostructure with high aspect ratio mineral crystals inserted into its soft matrix. The mineral crystals in enamel nanostructure are needle-shape with dimensions of ~1 micrometer in length and up to ~20 nm in thickness (Ang et al., 2010; Bechtle et al., 2010b; Bechtle et al., 2010c; Jiang et al., 2005; Kinney et al., 2005; Warshawsky, 1989).

Tesch et al. (2001) used Fourier-transform infrared microspectroscopy in reflectance mode (FTIR-RM), small angle X-ray scattering (SAXS) and other types of electron imaging as well as nanoindentation to investigate the organic-inorganic microcomposite structure of dentin. They showed that the mineralized structure of dentin has specific localized mechanical properties. Their measurements demonstrated that the mineral volume fraction decreases in dentin structure by approaching to the dentin-enamel junction (DEJ); meanwhile, it was observed that towards DEJ, the thickness of the mineral

platelets is increased. They reported that at regions near DEJ, the Young's modulus and hardness of the dentin layers are minimum in value, which effectively prevents cracks from growth at DEJ region (Tesch et al., 2001). Recently, it was shown that because of existing nanoscale-sized mineral crystals within its protein matrix, the resistance of the nanocomposite structure of enamel to chemical dissolution effects is decreased. It was reported that dissolution of the crystals can be prevented if their dimensions were in the range of a few nanometers (Tang et al., 2004; Wang et al., 2005).

2.2.3 Mineralized tendon

Prostak and Lees (1996) studied the layout and arrangement of the mineral crystals in mineralized turkey leg tendon (MTLT) and bone after demineralization. Their results indicated that the periodic layout was not seen in the regions where mineral crystals were packed before demineralization. This means that the axial layout of the collagen molecules is changed significantly during the mineralization process (Prostak and Lees, 1996).

Landis et al. (1996b) used normal and high voltage electron microscopy to investigate the mineralization procedure in turkey leg tendons. They also employed three-dimensional image reconstruction techniques as well as tomography to make their results more accurate. They found that the mineral crystals in the turkey leg tendons are plate-like crystals which are arranged parallel to the direction of the collagen molecules (c-axis). These plate-shaped mineral crystals were observed to be nucleated on the collagen fibrils surfaces for the first time. They also reported that calcified crystals can also be nucleated in the collagen gap and overlap regions (Landis et al., 1996b).

High-voltage electron microscope tomography was also used to measure geometrical characteristics of the mineral crystals in tendon. The results obtained from electron microscope were extended to three-dimensional estimations by reconstruction image techniques and showed that the crystals are arranged in coplanar sheets and the distance between two mineral crystals is approximately 4.2 ± 1.0 nm (Landis et al., 1993). High-voltage electron microscopy also showed that the strength of the mineralized tissues is dependent on its layout (Landis, 1995).

Moradian-Oldak et al. (1991) used transmission electron microscope to estimate the dimension of hydroxyapatite crystals in bone and mineralized tendon. The results of electron diffraction indicated that the crystals are plate-shape inclusions with orientation parallel to the collagen fibril c-axis. They performed their experiments on both natural as well as synthesized materials and revealed that synthesized crystals are bigger in length (Moradian-Oldak et al., 1991; Sasaki and Odajima, 1996a).

2.2.4 Bone

Bone, a composite primarily consisting of mineral (calcium phosphate, or hydroxyapatite) and protein (collagen) in a hierarchical structure, is one of the most important structural components in the human body. Mechanically, bone not only provides a robust support for the whole human body, but also protects various organs from external impacts. Mechanical performance of the bone and bone-like materials are significantly related to their structural hierarchies. In the first level, the bone structure is a composite composed of protein and nanometer-sized mineral materials. The arrangement of the mineral crystals as well as the mechanical properties of each component have

strong effects on the mechanical properties of the bone (Fratzl et al., 2004). The mechanical properties of the bone are believed to be dictated by its structural architecture built hierarchically with strong and stiff mineral and weak and soft protein. It is known that the bone structure typically possesses seven hierarchical levels as schematically shown in Fig. 1.1 (Rho et al., 1998; Weiner and Wagner, 1998).

Previous works on the bone can be categorized into two major groups:

- Theoretical and/or experimental (AFM, SEM, SAXS, TEM and nanoindentation method) studies
- Numerical studies (finite element and molecular dynamics simulations)

In the next sections the investigations on the bone in each category will be reviewed.

Rho et al. (1998) and Weiner and Wagner (1998) reviewed bone, focusing on its structure and mechanical performance as well as the relationship between them. They studied the bone, its layout and the interaction of its soft and hard components as well as its exceptional characteristics in each level of the bone structural hierarchies (Rho et al., 1998; Weiner and Wagner, 1998).

Due to the importance of the bone as one of the most important materials in the human body, extensive studies have been performed to understand its composition, structure and the origins of its impressive mechanical properties (Akiva et al., 1998; Currey, 2003; Delmas et al., 1984; Dorozhkin and Epple, 2002; Ethier and Simmons, 2007; Nyman et al., 2006; Orgel et al., 2006). Different combinations of the building blocks of the bone can have significant effects on its elastic modulus, yield strain and stress. Currey (2003) showed in his investigation that the small changes in the collagen properties will lead to drastic changes in the mechanical properties of the whole bone. It also can change the

structure and layout of the bone as it can change the mineral amount and characterized arrangements of inorganic crystals (Currey, 2003).

Dorozhkin and Epple (2002) studied the important role of mineral component (calcium phosphate) in the inorganic tissue of biological materials such as bone and tooth. They studied hydroxyapatite crystals in a chemical point of view to investigate the effects of mineral component on the stiffness of the bone and tooth. They showed that because of the analogy of calcium phosphate to the natural calcified tissue, hydroxyapatite is chemically compatible with natural materials. In fact in a pathological view, normal bones and teeth mean crystallization of calcium phosphate while on the other hand, osteoporosis and dental cavities are demineralization of their structure (Dorozhkin and Epple, 2002). Other investigations were done to study the effects of organic and inorganic phase on the bone mechanical properties (Currey, 2003; Delmas et al., 1984; Orgel et al., 2006). Furthermore, using hydroxyapatite coatings in the implants to measure their mechanical properties like normal and shear strength under different loading conditions were studied (Geesink et al., 1987; Kroon and Freeman, 1992; Müller and Patsalis, 1997). Moreover, Nyman et al. (2006) reflected results of their experiment in which the dehydration effects of the human cortical bone on its stiffness and toughness had been studied. They developed a theory to investigate the separate interaction of the water with organic as well as that with inorganic portion of the bone. They found that each of water-protein or water-mineral interaction in the bone structure will separately make specific alterations in the stiffness and toughness of the bone. They performed their experiments in a wide temperature range from 21 (room temperature) to 110 centigrade degree and their results showed that in high temperature, the interaction of the water with mineral components of

the bone structure will be stopped. However, water-protein interaction can be continued in this condition. They understood that dehydration in the mineral phase will lead to the reduction of both strength and toughness in the bone while dehydration in organic phase decreases the bone toughness only and has no drastic effects on its strength (Nyman et al., 2006).

To understand the structure-property relationship of the bone, models focusing on an individual level of structural hierarchy as well as considering multiple levels together have been proposed (Currey, 2002; Ji and Gao, 2004a; Lipson and Katz, 1984; Lucas et al., 1999b; Ritchie, 2011; Zhang et al., 2010; Zhang et al., 2011). For example, a staggered arrangement was suggested for the primary hierarchical level of the bone structure (Jäger and Fratzl, 2000). In this arrangement, the structure of the bone is composed of a collagen matrix embedded with nano-sized hydroxyapatite crystals. Importantly, this primary structure has been supported by several experimental observations (Hassenkam et al., 2004; Landis et al., 1996b; Orgel et al., 2001; Orgel et al., 2000). Consequently, this model has been widely adopted to investigate the mechanical and failure behavior of biological materials (Gao, 2006; Lei et al., 2013; Lei et al., 2012; Yang et al., 2009). The bone structure, as well as its organic matrix, the arrangements of the mineral crystals within the protein matrix, mineralization and hydroxyapatite nucleation and different experimental methods to investigate the dimensions of the mineral components in nanosclae were reviewed (Olszta et al., 2007).

Gao (2006) in a review paper studied the load-bearing biological materials like bone using the concepts of fracture mechanics with ordinary analytical as well as numerical patterns. He applied fracture mechanics concepts to hierarchical bio-structures to answer a

lot of unsolved questions about the structure and mechanical properties of load-bearing biological materials. In his review paper he answered the questions like why the nanoscale size is crucial for the biological materials?, or why nature designs hierarchical structure for biological materials? He also investigated the stiffness and toughness of the biological materials and their relation with the protein and mineral volume fractions within the nanocomposite structure. Buckling stability as well as finding an optimized structure for biological materials which is to be compatible with nature design has been investigated. This review paper is an extensive work in the field of biological materials and its concepts were extensively used by other investigators to develop their research on the field of biological materials (Gao, 2006). In a similar work, Ji and Gao (2010) have reviewed the simple mechanical principles behind the characteristics of natural materials. In this work, the authors studied the mechanical properties of biological materials such as stiffness, toughness, strength and stability as well as hybrid interface characteristics (caused by protein-mineral interactions) of biological materials (Ji, 2008; Ji and Gao, 2010).

The staggered nanostructure has been rationalized in the perspective of mechanics and materials science by means of theoretical modeling, computational simulations, and relevant experiments on bio/biomimetic-materials, separately. A number of theoretical models including the tension-shear chain model and other similar ones, combined with finite element simulations, were built up to reveal the working mechanism of the staggered nanostructure. It was shown that the staggered structure, in which mineral platelets mainly bear tensile force and protein mainly transfers tensile force between neighboring mineral platelets via shear deformation, can synergize the advantages of both mineral and protein while avoiding their drawbacks, and thus provide good mechanical

properties in the terms of stiffness, strength and toughness (Jäger and Fratzl, 2000; Ji and Gao, 2004a; Lei et al., 2013; Lei et al., 2012; Zhang et al., 2010). Ji and Gao (2006) used TSC model that they had developed before (Ji and Gao, 2004a) to calculate the mechanical properties of the bone. In this investigation, they performed FEM and used analytical model to calculate the bone elastic properties like the Young's and shear modulus as well as its Poisson's ratio at the nanoscale level. Furthermore, they understood that the elastic behavior of the bone is so anisotropic at primary hierarchical level in nanometer dimensions. They tried to find out the relationship between the multiple structural hierarchies of the bone and its macrostructure mechanical properties. They believed that the mechanical behavior of the bone at macroscopic scales will be significantly affected by mechanical properties of the bone at nanoscale (Ji and Gao, 2006).

Interestingly, Guo and Gao (2006) speculated that the staggered arrangement should be a result of optimization and evolution in nature, and tried to prove it by finding the optimal distribution of a hard and brittle inorganic phase in a soft and ductile organic phase through a topological optimization procedure based on genetic algorithm (GA). Their results showed that the staggered arrangement is the stable solution for simultaneously optimizing the stiffness and toughness of the composites. In addition, there have been many successful biomimetic artificial composites with staggered nano-/micro-structure fabricated in the laboratory through the state-of-the-art fabrication technologies such as the layer-by-layer assembly (Tang et al., 2003), ice-templated method (Munch et al., 2008), and 3D printing (Dimas et al., 2013; Espinosa et al., 2011). These biomimetic materials all exhibited mechanical properties surpassing much their

conventional counterparts, which further validated the superiority of the staggered arrangement.

Yao et al. (2011) showed that the mechanical performance of the bone structure is directly dependent on its heterogeneous structure. They determined the heterogeneity of the bovine cortical bone in two different length scales from a hundred of nanometers to a few micrometers. Their results showed that there exists a characteristic length scale about ~200 nm that beyond this value such a heterogeneous size-dependency in the bone structure is not observed. Their numerical analysis and simulations verified that the effect of heterogeneous size-dependency is much stronger in inelasticity rather than the elastic deformation (Yao et al., 2011).

Zhang et al. (2011) proposed a quasi-self-similar hierarchical model in which the hard portion aspect ratio was been changing between the different structural levels. This assumption was not usual in the previous works using self-similar models to study the multiple hierarchical structures of biological materials (Gao, 2006; Yao and Gao, 2006). They suggested that optimal hierarchy numbers exist for bone and other load-bearing biological materials like shell and mineralized tendon to achieve maximum toughness and flaw-tolerance; it is worth noting that their predicted optimal hierarchy numbers are in good agreement with experimental observations for a variety of biological materials, respectively (Zhang et al., 2011).

Kotha et al. (2000) proposed a model based on the theory of shear-lag to investigate the effect of mineral crystal volume fraction, aspect ratio as well as the overlap region of these inorganic crystals on the mechanical properties of the protein-based composites containing mineral plate-shaped inclusions. They performed systematic finite element

method to compare their obtained simulation results with those obtained from their theoretical model. Their investigation demonstrated that the FEM results for the Young's modulus of the reinforced composite were greater than those derived from the analytical model; meanwhile both solutions showed the same axial stress transfer values. The presented shear-lag model can be used in analyzing the bone structure at nanoscale levels (Kotha et al., 2000).

Roschger et al. (2001) studied the nucleation and growth of mineral crystals within the human L4 vertebral body for a wide range of age from 15 weeks up to 97 years old. Two-dimensional histomorphometry as well as electron imaging and small angle X-ray scattering were used to track the orientation and thickness of the calcified crystals. In their investigation, tissue levels (cancellous arrangement) as well as the material levels (nanostructure) were studied and the results revealed that tissue levels will be developed through the whole life while the dimension and orientation of the mineral crystals have been formed after passing just one year. This means that in the first year of life the mineral crystals will grow in size and the growth will be fully completed after that (Roschger et al., 2001).

Similar to (Smith et al., 1999) investigation for nacre, Thompson et al. (2001) showed that a change in mechanical properties of protein portion have strong effects on fracture energy dissipation in bone. Using atomic force microscope and indentation tests, they showed that decreasing the number of collagen cross-links within the bone structure leads to a reduction in the strength of the bone. They concluded that these collagen cross-links can significantly affect the toughness and fracture energy dissipation of the bone (Thompson et al., 2001).

Oyen (2008) studied the bone mechanical properties, nanostructure, mineralization as well as the interactions between them in biomimetic material. It was shown that synthesizing biological materials with inspiration from nature can help understand the superior characteristics of biological materials (Oyen, 2008).

Weinkamer and Fratzl (2011) studied the adaption mechanism of two biological materials (bone and wood). They believed that in the biological materials, the capability of being positively responsive to the environment can cause changes in the structure as well as the performance of these kinds of materials. They found out that the biological materials tend to be adapted with their environment to efficiently recuperate their mechanical properties and this adaption tendency is existing in all of their structural levels from nanoscale to macroscale levels (Weinkamer and Fratzl, 2011).

Fantner et al. (2004) studied the effect of protein matrix of the bone nanostructure on its mechanical properties in different conditions using scanning electron microscopy (SEM), X-ray diffraction (XRD), thermo gravimetric analysis (TGA) as well as atomic force microscope (AFM). They tested the bone structure in boiled and baked conditions and found that the bone strength can be reduced by baking. They also reported that the strength of the normal bone (without any heat treatments) is greater than heat treated bone while the strength of the baked bone is less than that of the boiled one. Their results showed that the Young's modulus of baked bone is less than that of the normal bone, which is less than the elastic modulus of the boiled bone. They concluded that the fracture acting of the bone microstructure can be significantly changed by heat treatment (Fantner et al., 2004).

Furthermore, the size and layout for the primary hierarchical level have been measured experimentally over the past decades. Most of the previous works measured the dimensions of the bone nanostructure using electron microscopy (Ascenzi and Bonucci, 1966; Hulmes et al., 1989; Johansen and Parks, 1960; Lowenstam and Weiner, 1989; Molnar, 1960; Posner, 1969; Robinson, 1952; Robinson and Watson, 1952, 1955; Weiner and Price, 1986; Weiner and Traub, 1989). Fratzl et al. (1991) studied the mineralization procedure of the rat and mouse bone nanocomposite using Small angle X-ray scattering (SAXS) method. They speculated that measurement of bone mineral crystallites is not accurate enough using electron microscopy. They investigated the size as well as the shape and layout of the mineral crystals and also the direction of them within the bone nanostructure. Their results showed that the mineral crystals will be formed as slender layers of calcium phosphate within the gap regions of collagen fibrills. They also reported that the maximum grown thickness of the crystals is seen to be about 3 nm (Fratzl et al., 1991; Fratzl et al., 1992). SAXS was also utilized to study the crystal calcification after fluoride treatment in osteoporosis bone (Fratzl et al., 1994) and in horse radius (Fratzl et al., 1996).

Ziv and Weiner (1994) in two separate sets of experiments (TEM and SAXS) studied the mineral crystallite dimensions in rat bone in various range of ages. They also tested synthesized apatite crystals. TEM was used to measure the crystal length and width and SAXS was used to estimate the average mineralized crystals length. The results obtained from both experiments revealed that the synthesized crystals are much bigger than the natural mineral crystals (Ziv and Weiner, 1994). In another investigation high-voltage transmission electron microscopy was used to measure three-dimensional sizes of the

chick bone mineral crystals. The investigators reported the length ~80 nm, the width ~30 nm and the thickness ~8 nm for the mineral crystallite, respectively (Landis et al., 1996a). Eppell et al. (2001) measured the length, width and thickness of the plate-shaped mineral crystals in the bone using atomic force microscope (AFM). In their investigation, they reported the size of the crystal thickness from less than 2 nm to the mean value of 37 nm. Furthermore, they found out that approximately 98% of the total mineral crystals measured in their experiment have the thickness less than 10 nm. Interestingly, they have shown the histograms of aspect ratio of the mineral crystals for small and large crystals in their work. At first, they have calculated the aspect ratio for each mineral crystal and then they calculated the means to obtain the average aspect ratio values for thick and thin mineral crystals. Their calculation revealed that small crystals (thin plates) had the aspect ratio of 20 ± 5.6 while large crystals (thick plates) had an aspect ratio of 2.7 ± 1.1 . Their results show that in the bone structure at nanoscale levels, thick crystals have smaller aspect ratio and thin crystals have larger aspect ratio. Their results indicated that by increasing the mineral thickness, a smaller aspect ratio is needed for the bone structure (Eppell et al., 2001).

Rubin et al. (2003) used transmission electron microscope to study the difference of nanocomposite mineral crystals in the normal and osteoporosis bone. The results indicated that the mineral thickness does not change drastically (Rubin et al., 2003). Recently, high-resolution AFM imaging was also used to indicate the size and layout of the nanostructure of trabecular bone (Hassenkam et al., 2004).

The crystallite dimension measurements provide quantitative information for describing the bone structure at the nanoscale structural levels. Taking the multi-hierarchy

features into consideration, a self-similar hierarchical model was used to investigate the relationship between the mechanical properties of biological materials in different levels of structural hierarchy (Bechtel et al., 2010a). Furthermore, Zhang et al. (2011) in an analytical work, proposed a quasi-self-similar hierarchical model to study the mechanical properties as well as the characteristic dimensions of different load-bearing biological materials such as shells, mineralized tendons and bones in different structural levels. In the derivation of their analytical model to relate the different structural levels together, they used two basic principles, that is, flaw tolerance principle (Gao et al., 2004; Gao et al., 2003; Ji et al., 2004b) as well as equal strength and efficient stress transfer criteria (ESC and STC) (Gao et al., 2003; Liu et al., 2006). They also mixed both ESC and STC to gain a combined criterion to formulate their analytical model (Zhang et al., 2011).

Computer simulations have also been used to study the mechanical behavior of the bone by considering either single or multi-hierarchy. For example, finite element method (FEM) was used to study the mechanical and failure behavior of the bone using a model based on a structural hierarchy at higher levels (Borah et al., 2001; Gong et al., 2007).

At the primary hierarchical levels, FEM analysis was used to study the mechanical properties of the mineralized collagen structure, and the failure criteria of the bone at the nanoscale. Dong et al. (2009) used FEM analysis to study the effects of the characteristics of the bone nanostructure and mechanical properties of its hard and soft tissues on the microdamage procedure of the bone nanocomposite. The simulation results indicated that the microdamages will be occurred along the plane of the beginning defect (Dong et al., 2009). A similar FEM work using cohesive modeling approach was done to investigate the influence of organic-inorganic interface of the bone nanocomposite structure on the

growth of the microdamages within the structure. The results of the recent work showed that there is a particular type of damage failure for each interface characteristic (Luo et al., 2011). Barkaoui et al. (2011) performed FEM to study the fracture failure of mineralized collagen microfibrils. They showed that the strength of the bone is significantly affected by changing the characteristics of its organic and inorganic components. Their numerical results indicated that the mineral density as well as the number of cross-links between the mineral and collagen components can have drastic effects on the bone strength (Barkaoui et al., 2011; Barkaoui and Hambli, 2011, 2014; Hambli and Barkaoui, 2012). Yuan et al. (2011) used two-dimensional as well as three-dimensional representative volume elements (RVEs) to analyze the mechanical properties of mineralized collagen microfibrils. They verified the elastic modulus of the fibril which was obtained from FEM with those obtained by synchrotron X-ray diffraction method and showed that the mechanical properties of the fibril will be dominantly altered by changing the structural as well as the mechanical characteristics of the fibril organic and inorganic compounds (Yuan et al., 2011). The similar FEM analysis was done to study the bone structure at both micro and nano levels (Vaughan et al., 2012).

It should be noted that almost all the previous theoretical studies only focused on the mechanical behavior of the bone under static loading conditions. However, failure of the bone often occurs under impact or dynamic loading. It has been shown that natural materials, such as the bone, adopt an intriguing structure, which becomes insensitive to flaws at the nanoscale (Gao, 2006; Gao and Chen, 2005; Gao et al., 2003). This flaw-tolerant behavior allows the bone to be able to survive at extraordinarily high stress levels. However, it should be recognized that an important functionality of the bone is to protect

the various organs inside it, such as brain and marrow, from external impact. Hence, a fast stress wave attenuation of the bone under dynamic loading becomes vitally important. Therefore, a question arises naturally: Are the sizes and layouts of the bone structure related to or even adapted to the functionalities demanded by its dynamic performance?

Different from static loading, dynamic loading is able to generate stress waves which can bring the kinetic energy from the loading boundary deep inside and even throughout bone. A negative but obvious example is traumatic brain injury (TBI) which results from mechanical loads in the brain, often without skull fracture. TBI in civilians is usually caused by head impacts in motor vehicles and sports accidents, while TBI among military combat personnel is caused by blast waves (Taber et al., 2006; Viano et al., 2006; Zhang et al., 2004). Hence, under dynamic loading, one of the main functionalities of bone is to dissipate the kinetic energy and attenuate the stress wave so as to protect its inside fragile organs such as brain and marrow (Fratzl and Weinkamer, 2007; Meyers et al., 2008). One of our recent studies on the dynamic behavior of bone (Qwamizadeh et al., 2015) showed that the fast stress wave attenuation occurs due to the wave refraction and reflection at the interfaces of the hard (inorganic) and soft (organic) phases of the bone structure. It was also found that a staggered structure with specific layout and dimensions can most efficiently attenuate the stress wave, which again highlights from the dynamic perspective why the staggered structure has been selected by nature for the bone nanostructure during millions of years of biological evolution. However, the viscous behavior of organic phase (proteins like collagen, and some other biopolymers) was not considered in that study in order to simplify the problem to better focus on the effect of the staggered structure. Various works have been done to calculate the dynamic modulus of the polycrystals or

multiphase materials using homogenization approaches (Gibiansky and Lakes, 1993; Hashin, 1970a, b; Hashin and Shtrikman, 1962; Hashin and Shtrikman, 1963; Mori and Tanaka, 1973; Rho et al., 1993; Zhao and Weng, 1990).

In the macroscopic scales, stress wave propagation in bone was widely studied (Fellah et al., 2004; Lakes et al., 1986; Lowet and Van der Perre, 1996; Pelker and Saha, 1975; Pelker and Saha, 1983; Qing et al., 2008; Schraad and Harlow, 2006; Van der Perre and Lowet, 1996; Yoon and Katz, 1976; Yoon and Lawrence Katz, 1976) while in nanoscopic scale, the field remains open. As the structure of the bone is known to have a staggered arrangement in nanoscale levels, wave propagation analysis of composites with staggered layouts can help reveal the mechanisms of wave traveling in the bone nanostructure. However, there is almost no analytical solution for the staggered structure under impact loading conditions; meanwhile there are various works on dynamic response of the layered structures due to impact loading (Chen and Clifton, 1975; Clements et al., 1996; Kanel et al., 1995; Karagiozova and Alves, 2015; Lundergan and Drumheller, 1971; Oved et al., 1978; Sve, 1972; Ting, 1980). Recently, experimental (Zhuang et al., 2003) as well as numerical and analytical solutions were done to study the effects of heterogeneity on the dynamic response of the layered structures (Chandra et al., 2002; Chen and Chandra, 2004; Chen et al., 2004). Therefore, with regard to the lack of analytical solutions for staggered layouts, numerical analysis is necessary to investigate the wave traveling mechanism within the composites with staggered arrangement.

It is well known that biopolymers like collagenous proteins in bone usually exhibit significant viscous feature (Lakes and Katz, 1979a, b; Lakes et al., 1979; Puxkandl et al., 2002; Shen et al., 2011; Smith Jr and Keiper, 1964) that constitutes another important

mechanism to damp stress waves and dissipate kinetic energy (Bouchbinder and Brener, 2011). Experimental and modeling works have been conducted to study the viscoelastic properties of collagen fiber and related tissues (Gibson et al., 1999; Kawakami et al., 2006; Purslow et al., 1998; Puxkandl et al., 2002; Sanjeevi et al., 1982; Sasaki et al., 1993; Shen et al., 2011; Silver et al., 2002), and showed that the viscoelasticity can effectively increase the slope of stress-strain curve and damp the elastic stress waves (Bozec and Horton, 2005; Chandran and Barocas, 2004; Chaudhry et al., 2009; Kadler et al., 2007; Kawakami et al., 2005; Kumar et al., 2003; Liu et al., 2006). Recently, molecular dynamics simulations unveiled the characteristic relaxation time of collagen molecules to be in the range of 0.13-0.27 and 0.24-0.64 ns for dry and solvated collagen molecules, respectively (Gautieri and Buehler, 2013; Gautieri et al., 2013; Vesentini et al., 2013). The average characteristic time of the collagen molecule was reported to be around 0.5 ns from the atomistic creep test (Gautieri et al., 2012). Zhang and To demonstrated that a multilayered model with bioinspired hierarchical design may achieve a broadband wave filtering function (Zhang and To, 2013), and they also calculated the figure of merit of the composites with a hierarchical staggered microstructure inspired by bone, and suggested that the bioinspired hierarchical design can enhance the figure of merit significantly (Zhang and To, 2014).

Davies et al. proposed that the heterogeneous and hierarchical structures of bone and nacre may simultaneously localize a broad wavelength of phonons and cut off the energy flow from the process zone to crack tip, and thus significantly increase the fracture toughness (Davies et al., 2014). Their works illustrate in principle the possible benefits of the bioinspired hierarchical designs in acoustic filtering and dynamic energy dissipation,

but did not explore the physical details about how a wave is attenuated as it propagates in these composites with bioinspired structural design.

2.3 Summary

In the present work, FEM analysis is used to examine the dynamic response of the bone at the primary level, that is, at the nanoscale, under impact loading. To do so, we first validate our mechanical model and FEM procedure by comparing the model predictions with the existing analytical solution for a layered structure, and then perform systematic FEM analysis to investigate the stress wave traveling across different staggered structures.

It is expected that the staggered structure is able to significantly reduce the magnitude of the stress wave compared to the layered structure, explaining why the bone has chosen a staggered structure as its first hierarchical level. In addition, for a fixed mineral volume fraction and unit cell area, there does exist an optimal staggered structure of the bone at the nanoscale with specific feature size and layout that can lead to the fastest attenuation of stress waves. Importantly, the specific sizes and layouts are to be in excellent agreement with those obtained from experiments at the same level, indicating that the size and layout of the bone structure are adapted to the functionalities demanded by its dynamic performance.

Chapter 3 Layered Structures

In the previous chapters, load-bearing biological materials were extensively reviewed and their fascinating characteristics as well as intriguing hierarchical structure were discussed. Importantly, the main research methodology of the project has been presented and both analytical and numerical models have been proposed to analyze the mineralized collagen structure.

The present work will focus on the dynamic response of load-bearing biological materials. For this purpose, it is important and necessary to start from a heterogeneous layered composite material and then by imposing gradual changes in the geometry and material properties of the layered model, the staggered structure of the mineralized collagen will be produced. For the current section, all materials are assumed to be linear elastic at first step and then viscoelastic properties will be taken into account and for both models the dynamic response of the layered composite structure to the step loading condition will be investigated. By comparing the characteristics of the mechanical wave traveling in the layered and staggered media, we will examine the difference between these two different arrangements in the future. In the following section, the dynamic response of a layered structure will be studied.

3.1 Wave traveling in elastic laminate

Chen and Clifton (1975) proposed an analytical solution in which the stress in the layered composite structures can be calculated under unit step loading conditions. In their model, it was assumed that the composite structure is formed of two different materials which are periodically repeated during the whole structure (Fig. 3.1) and both materials

have been assumed to be linearly elastic and then viscoelastic with damping effects. The stress wave propagating through the laminate under the step load σ_0 , which is imposed on the left vertical side ($x = 0$) of the model (refer to Fig. 3.1).

Fig. 3.1 Geometrical condition of the layered structure.

To calculate the stress traveling through the elastic and viscoelastic layered media with infinitesimal assumption it is necessary to start from the momentum balance relation as

$$\rho_i \frac{\partial v(x,t)}{\partial t} - \frac{\partial \sigma(x,t)}{\partial x} = 0, \quad (3-1)$$

The continuity condition can be written as

$$\frac{\partial \varepsilon(x,t)}{\partial t} = \frac{\partial v(x,t)}{\partial x}, \quad (3-2)$$

The constitutive equation for the elastic material is to be defined as

$$\sigma(x,t) = E_i \varepsilon(x,t), \quad (3-3a)$$

The constitutive equation for the viscoelastic material can be written as

$$\sigma(x, t) = \int_{0^-}^t E_i(x, t - \eta) d\varepsilon(x, \eta), \quad (3-3b)$$

in which $E_i(x, t) = E_i(x, \infty) + [E_i(x, 0) - E_i(x, \infty)]e^{-t/\tau_i}$. It should be noted that $E_i(x, \infty)$ is the long-term modulus of the viscoelastic material and is related to its instantaneous modulus $E_i(x, 0)$ with $\gamma_i = \sqrt{E_i(x, 0)/E_i(x, \infty)}$. Index i can select h, s that will distinguish the hard or soft layer of the laminate during the formulation, respectively.

Having the relation between the longitudinal displacement and velocity as

$$v(x, t) = \frac{\partial u(x, t)}{\partial t}, \quad (3-4)$$

One can readily rewrite the momentum balance equation in the form below

$$\rho_i \frac{\partial^2 u(x, t)}{\partial t^2} - \frac{\partial \sigma(x, t)}{\partial x} = 0, \quad (3-5)$$

The initial as well as the boundary conditions for $0 < x < \infty$ are assumed to be as

$$\begin{cases} \sigma(x, 0) = 0 \\ u(x, 0) = 0 \\ \varepsilon(x, 0) = 0 \\ v(x, 0) = 0 \end{cases}, \quad (3-6)$$

where $\sigma(x, t)$, $\varepsilon(x, t)$, $v(x, t)$ and $u(x, t)$ are longitudinal stress, strain, velocity and displacement within the media, respectively. Furthermore, $\rho_i(x, t)$ and $E_i(x, t)$ are the density and Young's modulus of each material.

The stress as well as the velocity continuity should be considered at all interfaces between the hard and soft portion. Stress as well as velocity conditions at interface $x = h_h + qh$ (q is an integer that $q \geq 0$) are

$$\begin{cases} \sigma_h(h_h + qh, t) = \sigma_s(h_h + qh, t) \\ v_h(h_h + qh, t) = v_s(h_h + qh, t) \end{cases} \quad (3-7)$$

Similarly, the continuity of the stress and velocity at interface $x = qh$ (q is a positive integer) are as

$$\begin{cases} \sigma_h(qh, t) = \sigma_s(qh, t) \\ v_h(qh, t) = v_s(qh, t) \end{cases} \quad (3-8)$$

To calculate the late-time solution for Eq. (3-5), it is very simple to take the Laplace transform from Eq. (3-2), (3-3a), (3-3b) and (3-5).

$$\frac{\partial v(x, s)}{\partial x} - s\varepsilon(x, s) = 0, \quad (3-9)$$

for elastic material one can write

$$\sigma(x, s) = E_i \varepsilon(x, s), \quad (3-10a)$$

for viscoelastic material one can write

$$\sigma(x, s) = sE_i(s) \varepsilon(x, s), \quad (3-10b)$$

$$\frac{\partial \sigma(x, s)}{\partial x} = \rho_i s v(x, s), \quad (3-11)$$

Solving the Eq. (3-9) and (3-11) will lead to

$$\sigma(x, s) = A_i \left(\frac{s\rho_i}{k_i} \right) e^{k_i x} + B_i \left(-\frac{s\rho_i}{k_i} \right) e^{-k_i x}, \quad (3-12)$$

$$v(x, s) = A_i e^{k_i x} + B_i e^{-k_i x}, \quad (3-13)$$

where k_i denotes the wave frequency within the hard and soft layers of the laminate and can be easily calculated for the elastic and viscoelastic materials as

$$k_i(s) = \frac{s}{c_i}, \quad (3-14a)$$

$$k_i(s) = \sqrt{\frac{\rho_i s}{E_i(s)}}, \quad (3-14b)$$

It should be noted that c_i is the velocity of the wave within the elastic laminate in hard and soft layers (dependent on the index i that can be h for hard layer and s for soft layer) which can be obtained by

$$c_i = \sqrt{\frac{E_i}{\rho_i}}, \quad (3-15)$$

Floquet theory can be applied to ordinary differential equations (ODEs) with periodic coefficients (Chen and Clifton, 1975) as

$$\begin{cases} \sigma(x, s) = e^{kh} \sigma(x - h, s) \\ v(x, s) = e^{kh} v(x - h, s) \end{cases}, \quad (3-16)$$

where k is the effective wave number for the laminate.

Applying the boundary conditions shown in Eq. (3-7) and (3-8), the continuity conditions for the stress and velocity at the interface of hard and soft layer within the first unit cell ($q = 0$) can be written as

$$\begin{cases} A_h e^{k_h h_h} + B_h e^{-k_h h_h} = A_s e^{k_s h_h} + B_s e^{-k_s h_h} \\ A_h \left(\frac{\rho_h}{k_h} \right) e^{k_h h_h} - B_h \left(\frac{\rho_h}{k_h} \right) e^{-k_h h_h} = A_s \left(\frac{\rho_s}{k_s} \right) e^{k_s h_h} - B_s \left(\frac{\rho_s}{k_s} \right) e^{-k_s h_h} \end{cases}, \quad (3-17)$$

Similarly, the stress as well as the velocity continuity conditions at the interface of the first and second unit cells ($q = 1$) can be written as

$$\begin{cases} A_h e^{k_h h} + B_h e^{-k_h h} = A_s e^{k_s h} + B_s e^{-k_s h} \\ A_h \left(\frac{\rho_h}{k_h} \right) e^{k_h h} - B_h \left(\frac{\rho_h}{k_h} \right) e^{-k_h h} = A_s \left(\frac{\rho_s}{k_s} \right) e^{k_s h} - B_s \left(\frac{\rho_s}{k_s} \right) e^{-k_s h} \end{cases} \quad (3-18)$$

Considering Eq. (3-16) to (3-18), a system of equation will be created that can have non-trivial solutions only when the coefficient determinant is equal to zero which finally will lead to the dispersion relation as below

$$\cosh kh = \cosh k_h h_h \cosh k_s h_s + \frac{1}{2} \left(\frac{\rho_h c_h}{\rho_s c_s} + \frac{\rho_s c_s}{\rho_h c_h} \right) \sinh k_h h_h \sinh k_s h_s, \quad (3-19)$$

For steady wave with frequency s and using Eq. (3-14a) and (3-14b) for the elastic as well as the viscoelastic material, simply one can rearrange Eq. (3-19) as

$$\cosh kh = \cosh \frac{s}{c_h} h_h \cosh \frac{s}{c_s} h_s + \frac{1}{2} \left(\frac{\rho_h c_h}{\rho_s c_s} + \frac{\rho_s c_s}{\rho_h c_h} \right) \sinh \frac{s}{c_h} h_h \sinh \frac{s}{c_s} h_s, \quad (3-20a)$$

$$\cosh kh = \cosh \sqrt{\frac{\rho_h s}{E_h(s)}} h_h \cosh \sqrt{\frac{\rho_s s}{E_s(s)}} h_s + \frac{1}{2} \left(\frac{\rho_h c_h}{\rho_s c_s} + \frac{\rho_s c_s}{\rho_h c_h} \right) \sinh \sqrt{\frac{\rho_h s}{E_h(s)}} h_h \sinh \sqrt{\frac{\rho_s s}{E_s(s)}} h_s, \quad (3-20b)$$

Finally c_0 , which is the phase velocity for the zero frequency limit, can be calculated as

$$c_0 = \frac{h_h + h_s}{\sqrt{\left(\frac{h_h}{c_h} \right)^2 + \left(\frac{h_s}{c_s} \right)^2 + \left(\frac{\rho_h c_h}{\rho_s c_s} + \frac{\rho_s c_s}{\rho_h c_h} \right) \frac{h_h h_s}{c_h c_s}}}, \quad (3-21)$$

in which $c_i = \sqrt{E_i / \rho_i}$ and $c_i = \sqrt{E_i(\infty) / \rho_i}$ for the elastic and viscoelastic laminate, respectively.

It should be noted that Eq. (3-21) is obtained for late time solution, which means that it is valid only for large propagation distance. The boundary condition for the left vertical side ($x = 0$) of the model (refer to Fig. 3.1) is in the form of

$$\sigma(0, t) = \sigma_0 u(t), \quad (3-22)$$

By taking Laplace transform and applying Floquet theory to Eq. (3-22), one can write

$$\sigma(qh, s) = e^{\frac{kqh}{2}} \frac{\sigma_0}{s}, \quad (3-23)$$

Therefore, the late time asymptotic solution in the time domain can be obtained as below

$$\sigma(qh, t) = \frac{1}{2\pi i} \int_{\zeta-j\infty}^{\zeta+j\infty} \sigma(2qh, s) e^{st} ds, \quad (3-24)$$

Introducing a small time scale as

$$\delta t = t - \frac{x}{c_0}, \quad (3-25)$$

and substituting Eq. (3-25) and (3-23) into Eq. (3-24), the stress function with respect to t

and δt will be in the form of

$$p(t, \delta t) = \frac{\sigma_0}{2\pi i} \int_{\zeta-j\infty}^{\zeta+j\infty} \frac{e^{-\delta t \cdot g(s)} e^{t \cdot h(s)}}{s} ds, \quad (3-26)$$

where

$$g(s) = k(s)c_0, \quad (3-27)$$

$$h(s) = g(s) + s, \quad (3-28)$$

The asymptotic solution for $p(t, \delta t)$ by letting $t \rightarrow \infty$ for a fixed δt will be obtained. Such asymptotic solution can be calculated by letting the integration path follow the steepest descent path though the saddle point (s_0 at which $h'(s) = 0$) which will be occurred when $s \rightarrow 0$. Therefore, expanding $h(s)$ of Eq. (3-26) through the saddle point ($s = 0$) for the elastic and viscoelastic case gives the following

$$h(s) \approx \frac{h'''(0)}{3!} s^3, \quad (3-29a)$$

$$h(s) \approx \frac{h''(0)}{2!} s^2, \quad (3-29b)$$

where

$$h'''(0) = \frac{c_0^2}{(h_h + h_s)^2} \left(\frac{h_h}{c_h} \right)^2 \left(\frac{h_s}{c_s} \right)^2 \left[\frac{1}{4} \left(\frac{\rho_h c_h}{\rho_s c_s} + \frac{\rho_s c_s}{\rho_h c_h} \right)^2 - 1 \right], \quad (3-30a)$$

$$h''(0) = \frac{c_0^2}{(h_h + h_s)^2} \left\{ (\gamma_h^2 - 1) \frac{h_h}{c_h} \left[\tau_h \frac{h_h}{c_h} + \tau_s \frac{h_s}{c_s} \frac{\rho_h c_h}{\rho_s c_s} \right] + (\gamma_s^2 - 1) \frac{h_s}{c_s} \left[\tau_s \frac{h_s}{c_s} + \tau_h \frac{h_h}{c_h} \frac{\rho_s c_s}{\rho_h c_h} \right] \right\}, \quad (3-30b)$$

Eq. (3-26) can be written using Eq. (3-29a) and (3-29b) in the form of

$$p(t, \delta t) = \frac{\sigma_0}{3} + \frac{\sigma_0}{2\pi i} \int_{\Gamma} \frac{e^{\delta t \cdot s} \frac{h'''(0)}{3!} s^3}{s} ds, \quad (3-31a)$$

$$p(t, \delta t) = \frac{\sigma_0}{2} + \frac{\sigma_0}{2\pi i} \int_{\Gamma} \frac{e^{\delta t \cdot s} \frac{h''(0)}{2!} s^2}{s} ds, \quad (3-31b)$$

Finally, Eq. (3-31a) and (3-31b) will be calculated by evaluating the integral along the steepest descent path Γ as

$$\sigma(x, t) = \sigma_0 \left[\frac{1}{3} + \int_0^B \text{Airy}(-s) ds \right], \quad (3-32a)$$

$$\sigma(x, t) = \frac{\sigma_0}{2} \left[1 + \text{erf} \left(\frac{t - x/c_0}{\sqrt{2th''(0)}} \right) \right], \quad (3-32b)$$

where

$$B = \left(t - \frac{x}{c_0} \right) \left(\frac{2}{h'''(0)t} \right)^{1/3}, \quad (3-33)$$

The plots of stress versus time obtained from analytical solution for elastic and viscoelastic materials are shown in Fig. 3.2(a, b), respectively. It is obvious that the wave

profile is raised to its maximum peak after passing the distinguished distance and then goes through the media by oscillating around the magnitude of applied stress at the boundary of the laminate with elastic hard and soft components.

Fig. 3.2 Wave profile passing through the laminated structure at $x = 15h$ for (a) elastic and (b) viscoelastic laminate; and at $t = 5\mu s$ for (c) elastic and (d) viscoelastic material ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = E_h(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μs , $\tau_s = 0.75$ μs).

It is clear that the magnitude of the stress decreases when passing through the media because of wave reflections and refractions occurred between the interfaces of two

different materials. However, for the laminate with viscoelastic materials, the oscillations will be removed due to damping effects of the materials.

Fig. 3.2(b, d) depicts the wave profile versus distance from the origin of the laminate in a particular time for the elastic and viscoelastic materials, respectively. It is seen that the wave propagates through the composite structure and starts vanishing after passing distinguished distances.

Fig. 3.3(a, b) depicts the effect of impedance mismatch ($\lambda = \rho_h c_h / \rho_s c_s$) on the wave profile of the elastic and viscoelastic layered structure, respectively. As it is shown for a larger impedance mismatch, the wave needs more time to pass the distance between those laminates with strong mechanical properties.

Fig. 3.3 Wave profiles at $x = 15h$ for different impedance mismatch values of (a) elastic and (b) viscoelastic laminated structure ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $c_h = 6000$ m/s, $c_s = 9000$ m/s).

The three-dimensional wave profiles of the elastic and viscoelastic laminated structure are plotted in Fig. 3.4 with respect to time and length of the laminate. As it is seen, for a

particular time or distance from the origin of the laminate, two-dimensional profiles similar to those plotted in Fig. 3.2(a, b) will be obtained.

Fig. 3.4 Three-dimensional wave profile passing through the laminated structure at $x = 15h$ for the (a) elastic and (b) viscoelastic materials ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = E_h(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μ s, $\tau_s = 0.75$ μ s).

To make a better sense, various case studies have been done in the next sections to illustrate the effects of different parameters on the wave profile passing through the layered composite.

3.1.1 Effect of time

Fig. 3.5 shows the wave profile going through the length of the layered structure in different times. To do so, at three different time values such as 1 μ s, 5 μ s and 10 μ s the stress wave profile propagating through the laminated structure has been plotted for elastic and viscoelastic materials to show how the wave profile will be changed due to traveling through the structure.

It is obvious that in smaller time, the wave tends to vanish faster while large time allows the wave to travel through longer distances within the laminates. Additionally, it is clear that for viscoelastic materials, the wave oscillations around the imposed loading have been removed due to the intrinsic damping effects of the hard and soft components with viscoelastic properties.

Fig. 3.5 The effect of time on the stress wave within the length of the laminated structure for (a) elastic and (b) viscoelastic materials ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = E_h(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μ s, $\tau_s = 0.75$ μ s).

3.1.2 Effect of elastic modulus and density

Fig. 3.6(a, b) shows that by increasing the elastic modulus of one of the layers (here the hard layer), the wave profile can be changed for both the elastic and viscoelastic laminated structures.

Fig. 3.6 The effect of mechanical properties on wave profile of the layered structure at $x = 15h$ by changing Young's modulus for (a) elastic and (b) viscoelastic materials; and changing the density for (c) elastic and (d) viscoelastic materials ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_{h0} = E_{h0}(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μs , $\tau_s = 0.75$ μs).

It is seen that by increasing the Young's modulus of the hard layer the wave profile will reach its peak at a smaller time. On the other hand, Fig. 3.6(c, d) shows that by increasing the density of one layer (here the hard layer), the profile of the wave will be effectively delayed in the striped structures.

3.1.3 Effect of the layer thickness

Fig. 3.7 shows the effect of the thickness ratio on the stress. It is seen that by increasing the layer thickness (here the hard layer), the wave profile will reach its maximum value in longer time. All the aforementioned results were obtained using analytical analysis of layered heterogeneous material systems. In the next section, numerical simulation of layered structures under step loading conditions will be studied and the simulation results will be compared with the analytical solution. After verifying the results for the layered media, the simulation will be continued for staggered structure to investigate the dynamic response of the staggered arrangement, which is the basic structure of the bone as a load-bearing biological material in the first level of its hierarchy.

Fig. 3.7 The effect of layer thickness on the wave profile of the (a) elastic and (b) viscoelastic laminated structure at $x = 15h$ ($h_{h0} = 1.5$ mm, $h_s = 1.2$ mm, $E_h = E_h(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μs , $\tau_s = 0.75$ μs).

3.2 Numerical analysis of layered structures

Regarding the structure of heterogeneous layered composites, a model composed of two different materials was used (refer to Fig. 3.1) to simulate the dynamic response of the structure in the step loading condition.

Fig. 3.8 Comparison of the wave profiles obtained from the analytical solution (Chen and Clifton, 1975) and the present FEM solution at (a) $x = 15h$ (b) $x = 25h$ and (c) $x = 35h$ for the elastic media ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = 108$ GPa, $E_s = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³).

Fig. 3.8 shows the comparison of wave profile passing through the layered structure with elastic materials versus time in both analytical and FEM approaches. As it is seen, there is a good agreement between the results obtained from both methods in the wave front. It should be noted that the analytical solution proposed by Chen and Clifton (1975) is an asymptotic solution in nature and is only valid in small time. This means that the analytical solution is the dominant solution for the wave front. However, for large time beyond the wave front, the dominant solution will be FEM. Thus, because of the good

agreement between the FEM results with those obtained from analytical solution, one can conclude that FEM solution will be the dominant solution for the whole time domain.

Fig. 3.9 The effect of distance on the normalized stress at different time: (a) $t = 5.3\mu s$ (b) $t = 14.7\mu s$ and (c) $t = 21\mu s$ for elastic laminate ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = 108$ GPa, $E_s = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³).

Furthermore, in our FEM calculations, the degrees of freedom of the simulation cell along the right boundary ($x = LN$) are fixed in all the directions, and those at the top boundary ($y = L$) and the bottom boundary ($y = 0$) are fixed only along the y direction;

meanwhile in the analytical solution the layered strip is assumed to be geometrically infinitesimal.

Fig. 3.10 Comparison of the wave profiles obtained from the analytical solution (Chen and Clifton, 1975) and the present FEM solution for the viscoelastic laminate at different (a) time and (b) distances from the origin of the laminate. ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = E_h(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μs , $\tau_s = 0.75$ μs).

(a)

(b)

(c)

(d)

Fig. 3.11 The wave profile passing through the layered composite versus time for (a) elastic and (b) viscoelastic materials; and versus distance for (c) elastic and (d) viscoelastic materials in different element sizes ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = E_h(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μ s, $\tau_s = 0.75$ μ s).

Fig. 3.9 compares the wave profiles within the layered structure with elastic materials versus distance from the origin of the laminate in both analytical and FEM solutions. In this condition, the wave profile starts vanishing after passing specific distances for each time. For the small time, the stress will decrease fast and for the large time the stress will start decreasing after passing a long distance. It is shown that the results obtained by the present simulation become compatible with those obtained from analytical solution for the wave front. Similarly, Fig. 3.10(a, b) shows the wave profile passing through the viscoelastic laminated structure in different times and distances from the origin of the laminate. It is clear that the findings here are quite similar to those obtained for the layered structure with elastic components; however, for the viscoelastic strip, the oscillations are removed due to internal damping properties of the viscous materials.

Before starting the simulation for the staggered material, there is need to investigate the effect of element numbers and homogenous as well as non-homogeneous mesh on the results obtained by numerical simulation to ensure the correct convergence of the solution.

For this purpose, the number of the elements in the model was increased to investigate the mesh dependency of the model. Also a homogeneous mesh was generated on the model to study the effect of using fine mesh on the stress. Fig. 3.11 shows that the mesh does not affect the stress results significantly. Fig. 3.11(a, b) shows the wave profile versus time and Fig. 3.11(c, d) depicts the wave profile versus distance for different element sizes. It is seen that the results for using non-homogeneous mesh are in good agreement with those obtained using homogeneous mesh. Obviously there is no marked effect on the magnitude of stress with any increase in the element numbers for the present case studies. This means that generating small enough elements will lead to sufficiently accurate results.

Table 3.1 Wave velocities in different element sizes using FEM ($h_h = 1.5$ mm, $h_s = 1.2$ mm, $E_h = E_h(\infty) = 108$ GPa, $E_s = E_s(\infty) = 20.25$ GPa, $\rho_h = 3$ g/cm³, $\rho_s = 0.25$ g/cm³, $\gamma_h = 1.2$, $\gamma_s = 1.6$, $\tau_h = 0.75$ μ s, $\tau_s = 0.75$ μ s).

Mesh size	c_0 (mm/s)	c_0 calculated from analytical solution (mm/s)
1.0 mm	4.70423×10^6	4.5566×10^6
0.8 mm	4.70361×10^6	
0.6 mm	4.70339×10^6	
0.4 mm	4.70327×10^6	
0.2 mm	4.70318×10^6	
0.1 mm	4.70313×10^6	

Table 3.1 shows the wave velocities obtained from our FEM simulations using different element sizes. It is seen that the FEM results at different element sizes are nearly

the same, indicating the convergence of the finite element discretization. However, the calculated values are slightly higher than the theoretical one.

It should be noted that this difference arises from the fact that c_0 is the phase velocity which is obtained from dispersion relation (Chen and Clifton, 1975), and Eq. (3-21) is obtained by letting $t \rightarrow \infty$, which means that it is valid only for a large propagation distance.

3.3 Summary

In this chapter, the dynamic response of the layered composites under the step loading conditions was studied. Systematic finite element calculations were performed to analyze the laminated composites under the dynamic loading conditions. The results obtained from FEM were compared with those obtained from analytical solution and the comparison showed a good agreement between the results from the two approaches. Different element sizes were also used in the FEM analysis to investigate the mesh dependency and check the solution convergence of the layered composite FEM model. It is known that the nanostructure of the bone has a staggered arrangement. The structure with the staggered arrangement is composed of a basic matrix and hard platelets which are periodically embedded into the matrix. In this case, the analytical solution for the dynamic response due to the imposed loading is not yet available. In these staggered structures, it is necessary to perform numerical simulations to investigate the dynamic response of the structure under the different geometry and loading conditions. Here, importantly, we have validated the numerical model and method by the analytical results of the layered arrangement. In the next chapter, we extend the model and method used here to

investigate the bone staggered structure at the first level of its structural hierarchy under dynamic loading conditions.

Chapter 4 Dynamic Behavior of the Nanoscale Staggered Structure of the Bone with Elastic Protein

Bone, a typical load-bearing biological material, composed of organic and inorganic mineral arranged in a hierarchical architecture, exhibits superb mechanical properties. The hierarchical structure of the bone has been shown in Fig. 1-3. Here, we focus on the bone structure at the primary level. At this level, the structure of the bone is made of a soft protein matrix and embedded hard mineral crystals. As a result, the bone structure at the primary hierarchical level is often called mineralized collagen structure. In the current chapter, the dynamic response of the bone mineralized collagen nanostructure will be studied.

4.1 Mechanical and FEM modeling

The staggered structure model proposed by Jäger and Fratzl (2000) has been widely accepted as the first-level hierarchical structure of the bone. In the present chapter, we also adopt this structure to study the behavior of stress wave propagation.

We would like to study the elastic wave travelling along the x and y directions for both the layered and staggered structures shown in Fig. 4.1(a) and (b), respectively. The geometrical dimensions are also marked in these figures. The dashed red square defines the unit cell in the staggered structures. In the present setting (Fig. 4.1(b)), when the dynamic impact load is applied along the x direction, the structure is called “vertically staggered”; while along the y direction “horizontally staggered”.

Fig. 4.1 Geometrical properties of structure models: (a) layered, (b) staggered arrangements.

4.2 FEM validation

Currently, there is no analytical solution for the wave traveling through the staggered structures under impact loading. As a result, it is necessary to resort to numerical (finite element) method to study the dynamic behavior of the staggered structure. Nevertheless, it is noted that there is an analytical solution for stress wave traveling through a layered composite upon a step load discussed in the previous chapter. Therefore, we validate our numerical procedure by using the solution for the layered structure and comparing our numerical predictions with the analytical solution. It should be noted that this analytical solution is an asymptotic one, which is only able to predict the wave profile accurately at the wave front (Chen and Clifton, 1975). The stress wave traveling through the layered media in the form of airy function under the step load σ_0 , which is imposed on the left vertical side ($x = 0$) of the model (refer to Fig. 4.1(a)), has the following form as

$$\sigma(x, t) = \sigma_0 \left[\frac{1}{3} + \int_0^B \text{Airy}(-s) ds \right], \quad (4-1)$$

in which the Airy function for the real value of x can be defined as

$$\text{Airy}(x) = \frac{1}{\pi} \int_0^\infty \cos\left(\frac{t^3}{3} + xt\right) dt, \quad (4-2)$$

and $y = \text{Airy}(x)$ satisfies the equation $y'' - xy = 0$.

$$B = \left(t - \frac{x}{c_0} \right) \left(\frac{2}{h'''(0)t} \right)^{1/3}, \quad (4-3)$$

$$h'''(0) = \frac{c_0^2}{(h_m + h_p)^2} \left(\frac{h_m}{c_m} \right)^2 \left(\frac{h_p}{c_p} \right)^2 \left[\frac{1}{4} \left(\frac{\rho_m c_m}{\rho_p c_p} + \frac{\rho_p c_p}{\rho_m c_m} \right)^2 - 1 \right], \quad (4-4)$$

where c_m and c_p are the wave velocities in the hard (mineral) and the soft (protein) component, respectively; c_0 is the phase velocity at the zero frequency limit for the laminated system and can be calculated by the following relations

$$c_m = \sqrt{\frac{E_m}{\rho_m}}, c_p = \sqrt{\frac{E_p}{\rho_p}}, \quad (4-5)$$

$$c_0 = \frac{h_m + h_p}{\sqrt{\left(\frac{h_m}{c_m} \right)^2 + \left(\frac{h_p}{c_p} \right)^2 + \left(\frac{\rho_m c_m}{\rho_p c_p} + \frac{\rho_p c_p}{\rho_m c_m} \right) \frac{h_m h_p}{c_m c_p}}}, \quad (4-6)$$

where E_m and ρ_m are the elastic modulus and the density of the hard component, respectively; E_p and ρ_p are those of the soft component. In the analytical solution, the laminate is subjected to a unit step load on its left vertical side (see Fig. 4.1(a)).

Subsequently, the wave starts to travel within the layered structure. Both components are assumed to be linear elastic with no viscous effects.

Fig. 4.2 Comparison of the wave profiles obtained from the analytical solution Chen and Clifton (1975) and the present FEM solution at $x = 35h$ ($h_m = 1.5$ mm, $h_p = 1.2$ mm, $E_m = 108$ GPa, $E_p = 20.25$ GPa, $\rho_m = 3$ g/cm³, $\rho_p = 0.25$ g/cm³).

In our FEM calculations, the degrees of freedom of the simulation cell along the right boundary ($x = LN$) are fixed in all the directions, and those at the top boundary ($y = L$) and the bottom boundary ($y = 0$) are fixed only along the y direction. In both analytical and numerical solutions, the mechanical properties of the hard and soft layers are taken from the work by Chen and Clifton (1975). The finite element analysis showed that the phase velocity of the wave is mesh-independent and the simulation results are in good agreement with those obtained from the previous analytical solution (Chen and Clifton, 1975). However, the calculated values are slightly higher than the theoretical one. This is because c_0 is the phase velocity which is obtained from dispersion relation (Eq. (4-6)). It

should be noted that Eq. (4-6) is obtained by letting $t \rightarrow \infty$, which means that it is valid only for large propagation distance.

Fig. 4.2 compares the wave profiles obtained from the analytical solution with those obtained from our FEM simulations. While both results show the same trend for the wave traveling through the laminated structure, there are distinguished differences between them beyond the traveling wave front. These differences are due to the fact that the analytical solution is asymptotic in nature and its results are only accurate in describing the traveling wave front. It can be readily seen from Fig. 4.2 that at the traveling wave front, the two solutions match exactly. However, away from the wave front, the deviation is apparent. The good agreement between our FEM results and the analytical ones at the traveling wave front validates our FEM model and numerical procedure. Meanwhile, it also highlights that the analytical solution is no longer valid for the wave behavior away from the traveling wave front due to its asymptotic nature. Therefore, our FEM approach is able to provide a reliable solution for the whole wave traveling process. In the following, we will employ the FEM model to study the dynamic behavior of the structures shown in Fig. 4.1(a, b).

4.3 Bone staggered structure at primary level

Before presenting our numerical results, we discuss the typical ranges for various geometrical parameters of the bone obtained in previous studies. The volume fraction of the mineral portion in the structure can be calculated from the unit cell as shown in Fig. 4.1(b) by using the following formulation as

$$\varphi = \frac{Lh_m}{(L+a)(h_m + h_p)}, \quad (4-7)$$

For the primary hierarchical structure, the mineral volume fraction is still currently unknown. However, for the whole bone, it was reported to be in the range of 30-50% (Lowenstam and Weiner, 1989) for different kinds of the bone. The value of 42% has been widely used for the bone mineral volume fraction (Jäger and Fratzl, 2000) and importantly this value has been experimentally verified for the whole bone (Lozano et al., 2003).

Since the bone exhibits seven hierarchical levels, the volume fraction at the primary level in general should be greater than that for the whole bone. In addition, the length of the tropo-collagen molecules was measured to be about 280 nm (Hulmes, 2002; Puxkandl et al., 2002), the unmineralized collagen structure which is composed of the tropo-collagen molecules typically was shown to have an axial period of about 67 nm (Jäger and Fratzl, 2000; Orgel et al., 2000), and the ratios for the gap and overlapping region in the axial period were found to be about 60% and 40%, respectively (Jäger and Fratzl, 2000).

The thickness of the mineral platelets was reported to be in a range from 2 nm to 10 nm (Eppell et al., 2001; Hassenkam et al., 2004; Moradian-Oldak et al., 1991; Posner, 1969; Robinson and Watson, 1952; Rubin et al., 2003), and the horizontal distance between the plates was reported to be in the same range as the thickness (Lowenstam and Weiner, 1989; Rubin et al., 2003). According to the model proposed by Jäger and Fratzl (2000), the axial period of the mineralized collagen structure is $(L+a)/2 = 67$ nm.

From the above discussion, it is seen that there is a wide range for values of mineral platelet dimensions reported in the literature: The length of the mineral plate is in the

range of 15-150 nm, its thickness 2-10 nm (Hassenkam et al., 2004; Moradian-Oldak et al., 1991; Rubin et al., 2003; Yuan et al., 2011), and the horizontal distances between the mineral platelets in the mineralized collagen matrix 2-4.5 nm (Lowenstam and Weiner, 1989). As a result, in the present work, parametrical studies were performed on the layered and staggered structures in the primary hierarchy.

Relevant information about all the parametrical study cases (the mineral volume fraction, structure layout, unit cell area, mineral plate thickness and aspect ratio (AR)) can be calculated from Eq. (4-7) in such a way that for a specific mineral volume fraction and a consistent unit cell area, by selecting the mineral platelet thickness within the range of experimental observations we choose all possible structural component dimensions which are limited within the experimentally reported ranges. For simplicity, in all the figure legends, layered and staggered structures are abbreviated as lay. and stag., respectively.

The material properties of the individual hard and soft components in the mineralized collagen structure have been widely studied (Gilmore and Katz, 1982; Gupta et al., 2005; Heim et al., 2006; Koch et al., 2007; Meyers et al., 2008). The reported elastic modulus of the collagen is about 1 GPa (Heim et al., 2006; Meyers et al., 2008), and that of the mineral crystals is in the range of 100-130 GPa (Koch et al., 2007; Meyers et al., 2008). The Poisson's ratio is in the range of 0.25-0.28 for both mineral and collagen components (Gilmore and Katz, 1982; Meyers et al., 2008). The reported density of the collagen is about 1 g/cm³ (Meyers et al., 2008) and the density of the mineral portion is nearly twice than that of the collagen.

In this chapter, the typical values for the elastic modulus, the Poisson's ratio and the density of the mineral and collagen component are respectively chosen as: $E_m = 130$ GPa, $E_p = 1$ GPa, $\nu_m = \nu_c = 0.28$, $\rho_m = 2$ g/cm³, $\rho_p = 1$ g/cm³

In the following, we first analyze the stress wave traveling in the vertically layered and vertically staggered structures as shown in Fig. 4.1(a) and (b), respectively. Fig. 4.3(a-c) shows the wave profiles for two different points at different distances from the impact surface with respect to time when passing through the vertically layered structure, the collagen portion and the mineral portion of the vertically staggered structure, respectively. It is seen from Fig. 4.3(a) that the stress wave profiles passing through the vertically layered structure are similar at different distances from the impact surface of the laminate. However, the transition times are different for different distances, causing the waves to start at different times. This means that for a larger distance from the impact surface of the layered structure, the wave needs more time to reach that position. It is seen from Fig. 4.3(b, c) that for the staggered structures, the stress peaks are not the same in the mineral and collagen components. Clearly, the magnitude of the stress in the mineral portion is greater than that in the collagen zone.

By comparing the stress wave profiles between the layered and staggered structures and between the different staggered structures, we find that the stress wave profiles clearly depend on the structure layouts. This dependence naturally raises a couple of interesting questions: Why does the bone take a staggered structure rather than a layered structure? How do the staggered structures adopt their geometrical dimensions at the primary hierarchy? To answer these questions, we perform systematic FEM simulations to

study the effect of staggered arrangement on the attenuation of wave travelling in the mineralized collagen structure.

To analyze the stress wave attenuation, we impose a unit pulse load on the vertical left side of the structure ($x = 0$), that is, the impact surface (see Fig. 4.1(b)), and the duration for the unit load is taken to be the time that the wave needs to pass one unit cell. Then, we plot the average stress of each unit cell with respect to the distance from the impact surface to study the wave attenuation.

The average stress is derived from the following procedure: We first extract the stress in each element within the unit cell through time. With the coordinates of each element within the unit cell, the area of each element can be calculated. Then, at each time t_j , the average stress in the unit cell can be found based on the current stresses in its elements using the following formulation as

$$(\sigma_{ave})_{t_j} = \left(\frac{\sum_{i=1}^n \sigma_{ei} \times A_{ei}}{\sum_{i=1}^n A_{ei}} \right)_{t_j}, \quad (4-8)$$

where σ_{ei} and A_{ei} are the stress and the area of the element i , respectively. Finally, the maximum of the average stresses for a particular unit cell during the time history is used as the average stress within the unit cell. It should be noted that in the present work, the decreasing rate of stress over distance is used as a measure for stress attenuation.

Fig. 4.4 depicts the plots of the average stress versus the number of the unit cells for various mineral volume fraction ratios. For each plot, the layered arrangement is also included for comparison. The mineral volume fractions are taken to be the same for the layered and also all the staggered structures for consistency.

(a)

(c)

(d)

Fig. 4.3 Wave profiles passing through two different points at different distances from the origin of the mineralized collagen structure in the x direction: (a) layered structure, (b) the collagen zone in the staggered structure, and (c) the mineral zone in staggered structure. Here, $h_m = 6$ nm and $h_p = 4.5$ nm for layered structure and $h_m = 6.5$ nm and $h_p = 4$ nm for staggered structure.

It shows that for the incidence of the elastic wave in the x direction, the stress in the layered arrangement is greater than that in all the chosen staggered structures with the same mineral volume fraction and unit cell area, which may provide a cogent explanation on why the staggered arrangement rather than the layered arrangement is taken by nature

for load-bearing biological materials. It should be noted that the layered structure and the staggered structure which shows the fastest stress wave decay have been plotted with narrow lines.

Fig. 4.4 Comparison of stress wave attenuation (in the x direction) for the layered and different staggered arrangements with a mineral volume fraction of (a) 53%, (b) 57%, (c) 61%, and (d) 64%.

Among all these staggered structures studied here, we find that the stress attenuation levels are different (Fig. 4.4). For all the mineral volume fractions, the last staggered cases show the fastest stress wave attenuation. For example, for the mineral volume fractions of 64% (see Fig. 4.4(d)), the case with $h_m = 10$ nm shows the fastest attenuation. It should

be noted that the cases with mineral thickness larger than 10 nm is geometrically not allowed for this mineral volume fraction. Hence, an important point that we would like to make is that for each mineral volume fraction and unit cell area, there is a specific staggered structure which leads to the fastest attenuation of the stress wave. Interestingly, for each mineral volume fraction and unit cell area, the last case stands out robustly as the optimal staggered arrangement.

In the above, we have studied the wave attenuation in the layered and staggered structures for the incidence of the elastic wave along the x direction. In the following, we analyze the stress wave attenuation in the layered and staggered structures as shown in Fig. 4.1(a, b) along the y direction.

Fig. 4.5 plots the average stress versus the number of the unit cells for the incidence of the elastic wave along the y direction in the layered and staggered structures at different mineral volume fractions. For comparison, the mineral volume fractions here are taken to be the same as that for the incidence of the elastic wave along the x direction in the layered and staggered structures. It should be noted that the layered structure and the staggered structure which shows the fastest stress wave decay have been plotted with narrow lines.

Fig. 4.5 shows again that the stress wave attenuation in all the staggered arrangements is much faster than that in the layered structure with the same mineral volume fraction and unit cell area, which again highlights the fact that the staggered arrangement rather than the layered arrangement is chosen by nature for the bone nanostructure.

(a)

(b)

(c)

Fig. 4.5 Comparison of stress wave attenuation (along the y direction) for the layered and different staggered arrangements with a mineral volume fraction of (a) 53%, (b) 57%, (c) 61% and (d) 64%.

Among all the staggered structures studied here, we find that the stress attenuation levels along the y direction are different from those of their staggered counterparts along the x direction: there is a specific staggered structure for each mineral volume fraction and unit cell area which leads to the fastest attenuation of the stress wave. For example, for the mineral volume fraction of 53%, the fast attenuation of stress wave occurs at $h_m = 6.5$ nm; for the mineral volume fraction of 61%, the fast attenuation of stress wave occurs at $h_m = 8$ nm. These results indicate that with a higher mineral volume fraction, the fastest attenuation of stress wave demands a larger mineral plate thickness. As a result, the aspect ratio decreases.

To understand the mechanistic origin of the presence of the optimal staggered structures, we further examine the stress distributions of both the layered and staggered structures for incidence of the elastic wave in the x and y directions with a mineral volume fraction of 57%.

Fig. 4.6 depicts the distribution contours of the normal stress along the impact of the layered and optimal staggered structures ($h_m = 8.5$ nm) in x direction (Fig. 4.6(a, b)) as well as that of the layered and optimal horizontally staggered structures ($h_m = 6.5$ nm) in y direction (Fig. 4-6(c, d)). For comparison, a unit cell at the same position (that is, the 10th unit cell) in these mineralized collagen structures was selected. For the incidence of the elastic wave in x direction, it is seen that the stress levels in both mineral and collagen zones of the layered structure as shown in Fig. 4.6(a), are uniform along the vertical direction. However, for the staggered structure as shown in Fig. 4.6(b), one can readily see the non-uniform distribution of stress level, that is, a decrease in the stress in the collagen zone and an increase in the stress in the mineral zone.

S, S11
(AVG: 75%)

(c)

S, S11
(AVG: 75%)

(d)

Fig. 4.6 Stress wave contour of the 10th unit cell for the incidence of the elastic wave in x direction for (a) layered structure, (b) staggered structure; and for the incidence of the elastic wave in y direction for (c) layered and (d) staggered (all with a mineral volume fraction of 57%).

Overall, a staggered structure can cause a reduction of the average stress in the whole unit cell with respect to the layered structure. We also found that with increasing the thickness of the mineral platelets, the vertical distance (here the protein gap) between the mineral platelets in the unit cell increases and the low stress region widens, leading to lower average stress; thus explaining the reason why the last case (the largest mineral plate thickness within the allowed experimental range) shows the fastest stress wave attenuation for the staggered arrangements in x direction.

For the incidence of the elastic wave in y direction, it is seen that the stress in collagen portion of the layered structure as shown in Fig. 4.6(c) is much lower than its mineral part. For the staggered structure shown in Fig. 4.6(d), it is seen that the stress distribution becomes highly non-uniform, in general, with the stress in the mineral portion being decreased and that in the protein portion being increased. Overall, the average stress within the whole unit cell for the staggered structure is lower than its layered counterpart.

Next, we compare both normal and shear stress wave attenuations for the incidence of the elastic wave along the x and y directions in both the layered and staggered structures (Fig. 4.1(a, b)). To analyze the stress wave attenuation, we impose a unit pulse normal stress of 1 MPa on the vertical left side of the structures, that is, the impact surface. In all the calculations, the mineral volume fraction is fixed at 57%.

Fig. 4.7(a, b) plots the normal and shear stress attenuations in the x direction, respectively, within the mineralized collagen structure for the layered and different staggered structures. It is seen that the layered arrangement shows a very high normal stress, but nearly zero shear stress while the staggered structures show both moderate normal and shear stresses. Among the staggered structures, with increasing the mineral platelet thickness, the normal stress decreases while the shear stress increases.

The above analysis clearly demonstrates that the decrease in the normal stress in the staggered structure is at the expense of the increase in the shear stress. The same observation was also reported by previous investigation under static loading (Jäger and Fratzl, 2000).

Fig. 4.7(c, d) shows the same plots for the incidence of the elastic wave along the y direction in layered and staggered structures (Fig. 4.1(a, b)). Again, the layered structure

shows a very high normal stress and nearly zero shear stress; while the staggered structures show both moderate normal and shear stress.

Fig. 4.7 Comparison of layered and staggered structures (Fig. 4.1(a, b)) for (a) normal and (b) shear stress decay in the incidence of the elastic wave along the x direction; (c) normal and (d) shear stress decay in the incidence of the elastic wave along the y direction. (All structures are of a mineral volume fraction of 57%).

It is known that all structure materials have certain capacity to resist both normal and shear stresses. In general, to avoid failure, the normal as well as shear stresses of a material should be lower than its respective normal and shear strength. It was reported that the tensile and shear strengths of mineral component (hydroxyapatite) are ~ 40 -100 and

~18-40 MPa, respectively (Gupta et al., 2005); and the tensile and shear strengths of the collagen are about 50 and 30 MPa, respectively (Meyers et al., 2008). These data clearly show that the soft (collagen) and hard (mineral) components in the mineralized collagen structure can resist both normal and shear stress. Hence, the staggered arrangement is more effective in exploiting the capacity of mineralized collagen structure than the layered arrangement.

Next, we examine the normal as well as shear stress profiles within a unit cell. To examine the normal stress profiles of the layered and staggered structures for the incidence of the elastic wave in x direction, we pick some representative points, that is, point A and point B in the 10th unit cell as shown in Fig. 4.8(a). It is noted that point A is the mineral material for all the structures, and its stress wave profiles for these different structures are shown in Fig. 4.8(b). It is seen that the mean stress at point A in the staggered structures is higher than their layered counterpart. In the layered structure, point B is positioned within the hard (mineral) material; while in the staggered structures, point B falls into the collagen gap in between the mineral components, and thus becomes the soft material.

(a)

(b)

(c)

(d)

Fig. 4.8 (a) The positions of the representative points (A, B, C and D) within the 10th unit cell for the incidence of the elastic wave in x direction; the normal stress wave profiles in the layered and different staggered structures at (b) point A and at (c) point B; the shear stress wave profiles in the layered and different staggered structures at (d) point C and at (e) point D. (The mineral volume fraction is 57 % for all the vertical layered and vertical staggered cases).

From Fig. 4.8(c), it is seen that the stress at point B in the staggered structures decreases drastically with respect to their layered counterpart. Hence, for point B, not only the maximal tensile stress is reduced, the average stress level is also reduced as well. In particular, the vertically staggered structure with $h_m = 8.5$ nm, the mean stress at point B is the lowest, providing a level of explanation why it is the optimal structure.

To examine the shear stress profiles within a unit cell in the layered and staggered structures for the incidence of the elastic wave in x direction, two more points were picked, that is, point C and D (see Fig. 4.8(a)).

Fig. 4.8(d) shows different shear stress profiles for point C. It is seen that the shear stress at the layered structure is close to zero while all staggered cases show the finite values of shear stress. Fig. 4.8(e) shows that by increasing the length of the platelets in the

staggered structure, the shear stress at point D will be increased. The maximum value of the shear stress is seen for the vertically staggered structure with $h_m = 8.5$ nm, which corresponds to the case with the highest shear stress.

Fig. 4.9 shows the normal as well as shear stress profiles within a unit cell in the layered and staggered structures for the incidence of the elastic wave in y direction. Similarly, to examine the normal stress profiles, we pick some representative points, that is, point A and point B in the 10th unit cell as shown in Fig. 4.9(a). Point A is in the mineral material for all the structures, and its stress wave profiles for these different structures are shown in Fig. 4.9(b). It is seen that the mean stress at point A in the staggered structures increases by increasing the width of the mineral plate (here by increasing the horizontal protein gap between the platelets).

In particular, for the staggered structure with $h_m = 6.5$ nm, the mean stress at point A is the lowest, providing a level of explanation why it is the optimal structure. In the layered structure, point B is the hard (mineral) material; while in the staggered structures, point B is within the soft (protein) material. From Fig. 4.9(c), it is seen that the stress at point B in the staggered structures decreases drastically with respect to their layered counterpart. Also by increasing the horizontal protein gap, both the maximal and also the average stress decrease. In both Fig. 4.9(b) and (c), the layered structure profiles look different comparing to those of the horizontally staggered. That is because of the different values of the wave velocity within these geometrically different structures.

To examine the shear stress profiles within the unit cell, two more points were selected, that is, point C and D.

Fig. 4.9 (a) The positions of the representative points (A, B, C and D) within the 10th unit cell for the incidence of the elastic wave in y direction; the normal stress wave profiles in the layered and different staggered structures at (b) point A and at (c) point B; shear stress wave profiles in the layered and different staggered structures at (d) point C and at (e) point D. (The mineral volume fraction is 57 % in all layered and staggered cases).

Fig. 4.9(d) shows different shear stress profiles for point C. Similar to the layered structure, the shear stress at the horizontal layered structure is close to zero while all the staggered cases show finite values of shear stress. Further, Fig. 4.9(e) shows that by

increasing the horizontal protein gap in the staggered structures, the shear stress at point D increases.

Fig. 4.10 shows the predicted aspect ratio and thickness of mineral crystals that lead to the fastest stress wave decay at different mineral volume fractions for the incidence of the elastic wave along (a) x and (b) y directions in staggered structures. Both plots show that for a constant mineral volume fraction, by increasing the mineral crystal thickness, a smaller aspect ratio is needed for the structure to exhibit the fastest stress wave decay. Although the exact value for the mineral volume fraction for the bone nanostructure is still unknown, our simulation results clearly show that for all the mineral volume fractions ranging from 42% to 68%, a similar decay trend is found between the aspect ratio and the thickness of mineral plates for the fastest stress wave attenuation. It is noted that this geometrical relation is derived purely from the dynamic behavior of wave traveling in staggered structures.

We note that many experimental works were done to measure the size of the nanoscale mineral crystals in the bone mineralized collagen structures by using different methods, such as electron-microscopy and X-ray diffraction (Johansen and Parks, 1960; Landis, 1995; Landis et al., 1993; Molnar, 1960; Moradian-Oldak et al., 1991; Posner, 1969; Robinson, 1952; Robinson and Watson, 1952, 1955; Weiner and Traub, 1989), small angle X-ray scattering (SAXS) (Fratzl et al., 1991; Fratzl et al., 1992; Fratzl et al., 1994; Fratzl et al., 1996), atomic force microscope (AFM) imaging (Eppell et al., 2001; Hassenkam et al., 2004) and transmission electron microscopy (TEM) (Landis et al., 1996a; Probst and Lees, 1996; Rubin et al., 2003; Weiner and Price, 1986; Ziv and Weiner, 1994). We have extracted the measured aspect ratio and also the thickness of the

bone mineral crystals from these experiments. Fig. 4.10(c) depicts the aspect ratio of mineral crystals versus their thickness for those experimental works. It is seen that the decreasing trend of the aspect ratio with the mineral plate thickness is in good agreement with our simulation results.

Fig. 4.10 Plot of the aspect ratio and thickness of the mineral crystal that leads to the fastest stress wave decay at different mineral volume fractions for the incident wave along the: (a) x and (b) y directions in the staggered structures. (c) Plot of the aspect ratio of the mineral plate versus its thickness from different experimental measurements. The same exponential fitting curve is plotted in (a), (b) and (c).

The simulation results for both incident waves along the x and y directions in the staggered structures shown in Fig. 4.10(a) and (b) and also the experimental results shown in Fig. 4.10(c) are fitted by the exponential function, $\rho(h_m) = Ae^{-Bh_m}$, where A and B are fitting parameters and $\rho = L/h_m$ is the aspect ratio of the mineral platelets. It is found that $A=77.95$ and $B= 0.2441 \text{ nm}^{-1}$. The same fitting curve is also shown in Fig. 4.10(a)-(c). It is seen remarkably that the fitting curve is in good agreement with all the three sets of data. It should be emphasized that for all the predicted staggered structures that exhibit the fastest wave decay, their layouts are consistent with experimental observations, their dimensions are all within the ranges observed experimentally, and most importantly, the predicted trend for the aspect ratio vs. mineral crystal thickness is also in good agreement with experimental results. Therefore, our work here demonstrates that the dimensions and layouts of the bone at the nanoscale are not only related but also evolutionarily adapted to the functionality demanded by the dynamic behavior of the bone.

4.4 Summary

We performed systematic finite element analysis to study the dynamic response of the bone at its first hierarchical level. The simulation results approved that the staggered structure can attenuate the stress wave faster than the layered structure with the same mineral volume fraction and the average normal stress in the staggered arrangement is smaller than that of the layered structure. On the other hand, the shear stress in the staggered structure is larger than that in the layered one. Regarding the fact that collagen and mineral can resist both tensile and shear stress, the staggered arrangement can employ its capacity to resist both tensile and shear stress; meanwhile, the layered arrangement

cannot effectively use its capacity to resist shear loading. Interestingly, the corresponding geometrical characteristics as well as the layout for the nanostructure that shows the fastest stress wave attenuation at primary level, are in good agreement with the previous experimental measurements.

The results of the current chapter have been published as a research paper (Qwamizadeh et al., 2015).

Chapter 5 Dynamic Behavior of the Nanoscale Staggered Structure of the Bone with Viscoelastic Protein

One of the key functions of load-bearing biological materials, such as bone, dentin and sea shell, is to protect their inside fragile organs by effectively damping dynamic impact. How those materials achieve this remarkable function remains largely unknown. Using systematic finite element analyses, in this chapter we decide to study the stress wave propagation and attenuation in cortical bone at nanoscale as a material model to examine the effects of protein viscosity, mineral fraction and staggered architecture on the elastic wave decay. The findings here not only significantly add to our understanding of the structure-function relationship of load-bearing biological materials, but also provide useful guidelines for the design of bioinspired materials with superior resistance to external impact loading.

As discussed above, one of the most crucial functionalities of the load-bearing biological materials is to protect its inside sensitive and fragile organs from external impact, and thus a fast stress wave attenuation over its propagation in these materials is vitally necessary and important.

The staggered arrangement of the hard inorganic phase embedded in the soft organic phase can effectively block and scatter stress waves with soft/hard interfaces, and the viscosity of the organic phase can effectively damp stress waves by dissipating kinetic energy through inelastic processes (Grant et al., 2012; Zhang and To, 2014). Obviously, both the staggered structure and the biopolymer viscosity play an important role in damping the stress waves originated from external dynamic loadings, and positively contribute to the protection functionality of load-bearing biological materials.

Nonetheless, several fundamental and interesting questions arise from the two factors: the staggered structure and the biopolymer viscosity.

These interesting questions are: How is the synergistic effect of the two factors in damping stress waves? Which factor plays a dominant role? Given material constituents, how should we optimize a structural arrangement to get such a fast stress wave decay? Clearly, answers to these questions are of great value not only for understanding the protection behavior of typical load-bearing biological materials under dynamic loading but also for guiding the design of bioinspired synthetic materials with outstanding protection functionality.

Numerous theoretical models on wave dispersion and attenuation in laminate and fiber-reinforced composites have been developed, but all of them have considered only the aligned continuous laminates or fibers (Chen and Clifton, 1975; Chen et al., 2004; Ting, 1980). With respect to the staggered composite here, the discontinuity due to the finite length of mineral platelets makes it a great challenge to derive an analytical model depicting the scattering and attenuation of stress waves in the composites, if not impossible.

Thus, the finite element method analyses were performed in the present work to study the dynamic response of the staggered nanostructure under the impact loading conditions. The FEM model was first validated using the theoretical solution for laminated structure considering viscosity, and then systematic analyses were conducted to investigate the stress wave attenuation for different staggered arrangements and different viscosities of biopolymers.

5.1 Mechanical and FEM modeling

This chapter focuses on the nanostructured composite at the primary level of bone known as mineralized collagen which features a protein matrix filled with nanometer-sized platelet-shape crystals in a staggered pattern. The staggered nanostructure was well described by the model proposed by Jäger and Fratzl (2000) and the tension-shear chain model by Gao and his co-workers (Gao et al., 2003; Ji and Gao, 2004a, b; Ji et al., 2004a). One of the major concerns to choose the staggered nanostructure for investigation here is that it is the most fundamental and typical structural organization of material constituents in bone as well as other load-bearing biological materials; therefore, the findings and conclusions from this investigation can be generally extended to other types of load-bearing biological materials, and also pave the way to study the dynamical responses of the hierarchical structures of biological materials based on self-similar or quasi-self-similar simplifications.

A two-dimensional plane strain model is used for all the dynamic analyses in the current study. The geometrical characteristics of the staggered structure are the same as those illustrated in Fig. 4.1(b), with a representative unit cell outlined by the dash box. In the staggered structure, a and h_p denote the longitudinal and horizontal spacing between the neighboring mineral platelets, respectively; L and h_m represent the length and width of the mineral platelet, respectively.

For comparison purpose, the corresponding layered structure is illustrated in Fig. 4.1(a). The periodic width of the layered structure is given by $h = h_m + h_p$. LN and W , respectively, are the horizontal and vertical lengths of the staggered composite, which have been assigned a large enough value in our computed samples to avoid the influence

of reflective waves at the loading-free end. In order to investigate the wave traveling through the structure, an impact pulse is prescribed normal to the left ($x = 0$, for horizontal propagation and attenuation) or top ($y = 0$, for vertical propagation and attenuation) boundary of the staggered model.

$$\sigma(t) = \sigma_0 S(t), \quad (5-1)$$

$$S(t) = \begin{cases} 1 & 0 < t < t_0 \\ 0 & t > t_0 \end{cases}, \quad (5-2)$$

where $S(t)$ is a Heaviside step function and t_0 is the duration of the impact pulse. As we know that the characteristic time (e.g., resonant period) and the characteristic length are closely correlated with each other in the dynamic behaviors of heterogeneous materials. In the current study, the size of the unit cell is a characteristic length, and thus the impact duration t_0 is assumed in the same order with the time t_c for a stress wave passing through a unit cell. For simplicity, $t_0 = t_c$ is adopted unless otherwise stated.

In the mechanical model for loading in the x direction, the problem is mirror symmetrical about both the upper ($y = L+a$) and lower ($y = 0$) edge and therefore mirror symmetrical boundary conditions are applied to the two edges, i.e., only necessary equations are defined to make the nodes on each of them always move together in the vertical (y) direction so that the upper and lower edges always keep horizontal during the analysis. Since the length LN is chosen to be large enough to avoid the occurrence of reflection at the right end, the boundary condition at the right edge ($x = LN$) has little influence on our results. For simplicity, here the right edge ($x = LN$) except the upper and lower end (on the upper and lower edge, respectively) is fixed in all directions. Similarly,

in the model for loading in the y direction, only necessary equations are prescribed to both the left and right edges to keep them always vertical due to the mirror symmetry of the problem, while the bottom edge except the left and right ends are simply fixed in all directions.

All the FEM simulations were performed via ABAQUS/Explicit. A linear elastic model is chosen for the mineral material while a linear viscoelastic model for the biopolymer material is defined by

$$\tau_{xy}(t) = 2G_0 \int_0^t g_R(t-\eta) \dot{\epsilon}_{xy}(\eta) d\eta, \quad (5-3)$$

where G_0 and $\dot{\epsilon}_{xy}$ are the instantaneous shear modulus and shear strain rate of the material and g_R is the dimensionless relaxation function having a general form of Prony series as below

$$g_R(t) = 1 - \sum_{m=1}^M g_m (1 - e^{-t/\tau_m}), \quad (5-4)$$

Note that, for simplicity purpose, only one term ($M = 1$) is kept in the Prony series model of viscoelasticity, and so Eq. (5-4) is simplified to be $g_R(t) = 1 - g_1 (1 - e^{-t/\tau_1})$ with $g_R(0) = 1$, $g_R(\infty) = G(\infty)/G(0)$ and $g_1 = 1 - g_R(\infty)$ for each of the hard or soft layer material. Here, $G(0)$ and $G(\infty)$ are the instantaneous and long-term shear modulus, respectively. For simplicity, the relaxation ratio g_1 and the characteristic relaxation time τ_1 can be considered here as g and τ for protein, respectively.

ABAQUS/Explicit solver was used for the FEM analysis and element CPE4R was chosen for both mineral and biopolymer regions. The mesh sensitivity has been verified and the element size was checked to be fine enough to get convergent results.

As aforementioned, it is a great challenge in mathematics to get an analytical solution for the stress wave travelling and attenuation through the staggered structure, and thus we turn to FEM simulation instead. Nonetheless, we would like to first benchmark our FEM model by comparing the numerical results and the theoretical solution for layered structure as shown in Fig. 4.1(a), under a unit step loading (Chen and Clifton, 1975; Ting, 1980). In addition, the results of the layered structure also provide a reference for the following studies on the staggered structure. For the layered structure with alternative hard and soft materials under a step load σ_0 on the left boundary ($x = 0$ in Fig. 4.1(a)), the analytical solution of normal stress with viscoelastic characteristics is in the form of error function as

$$\sigma(x, t) = \frac{\sigma_0}{2} \left[1 + \operatorname{erf} \left(\frac{t - x/c_0}{\sqrt{2th''(0)}} \right) \right], \quad (5-5)$$

in which the error function can be defined as

$$\operatorname{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-\eta^2} d\eta, \quad (5-6)$$

and

$$h''(0) = \frac{c_0^2}{(h_m + h_p)^2} \left\{ (\gamma_m^2 - 1) \frac{h_m}{c_m} \left[\tau_m \frac{h_m}{c_m} + \tau_p \frac{h_p}{c_p} \frac{\rho_m c_m}{\rho_p c_p} \right] + (\gamma_p^2 - 1) \frac{h_p}{c_p} \left[\tau_p \frac{h_p}{c_p} + \tau_m \frac{h_m}{c_m} \frac{\rho_p c_p}{\rho_m c_m} \right] \right\}, \quad (5-7)$$

where $c_{[.]} = \sqrt{E_{[.]}(\infty)/\rho_{[.]}}$ is the wave velocity, $\gamma_{[.]} = \sqrt{E_{[.]}(0)/E_{[.]}(\infty)}$ is the square root of the ratio between the instantaneous and long-term elastic modulus, $\tau_{[.]}$ is the

characteristic relaxation time, $E_{[.]}$ is the elastic modulus, and $\rho_{[.]}$ is the mass density, with the subscript $[.] = m, p$ denoting the hard (mineral) and soft (protein) materials, respectively; c_0 is the phase velocity at the zero frequency limit for the laminated system and can be calculated by Eq. (4-6). Note that both soft and hard components are viscoelastic and with the same characteristic relaxation time in the benchmark case. It should also be noted that the analytical solution is asymptotic in nature and is only valid for the wave front.

Fig. 5.1 shows the comparison of stress wave profiles obtained from our FEM simulation with those calculated from the analytical solution at two different distances (e.g., $x = 20h$ and $x = 90h$) away from the loading boundary of the laminated structure (Fig. 4.1(a)). Here $E_m(\infty) = 108 \text{ GPa}$, $E_p(\infty) = 20.25 \text{ GPa}$, $\rho_m = 3 \text{ g/cm}^3$, $\rho_p = 0.25 \text{ g/cm}^3$, $\gamma_m = 1.2$, $\gamma_p = 1.6$, $\tau_m = \tau_p = 0.75 \text{ } \mu\text{s}$. In our FEM simulations, mirror symmetrical conditions are prescribed to both the upper ($y = 0$) and lower ($y = L$), fixed boundary conditions are applied to the right edge ($x = LN$), and a unit step loading is prescribed normal to the left edge ($x = 0$) (Fig. 4.1(a)). LN is large enough to avoid the influence of the reflective wave at the right end during our observation period (about $80 \text{ } \mu\text{s}$).

Comparing the numerical and analytical results, one can see that they are in excellent agreement with each other in the propagating wave front profile. However, beyond the traveling wave front there are some slight discrepancies between the FEM and analytical results. This is mainly due to the fact that the analytical solution here is an asymptotic one in nature which means that its results are accurate only near the traveling wave front. In a

word, the FEM model and procedure adopted here is validated by comparison to the analytical results in the wave front domain, and furthermore, it could provide more reliable results beyond the wave front domain. In the remaining part of this chapter, all results are from FEM model unless otherwise stated.

Fig. 5.1 Comparison of the wave profiles obtained from the analytical solution by Chen and Clifton (1975) and our FEM simulations for the layered structure ($h_m = 1.5$ mm, $h_p = 1.2$ mm) under a unit step loading. The two observation points are at $x = 20h$ and $x = 90h$, respectively.

5.2 Physical and geometrical parameters

The physical properties for both mineral and biopolymer components are taken based on the measurements on mineral and protein portions of mineralized collagen in the literature. Specifically, the density of the mineral crystals was reported to be about 2 g/cm³ while that of the collagen was approximately half of the density of the mineral portion (Meyers et al., 2008). The elastic modulus of the mineral portion was reported to be in the range of 100-130 GPa (Koch et al., 2007; Meyers et al., 2008) while 0.1-1GPa was reported for that of collagen (Grant et al., 2012; Heim et al., 2006; Katz, 1971; Mano,

2005; Meyers et al., 2008; Sasaki and Odajima, 1996b; Van Der Rijt et al., 2006). The Poisson's ratios for both the mineral and protein components were reported to be in the range of 0.25-0.28 (Gilmore and Katz, 1982; Meyers et al., 2008). In this work, the typical values for the elastic modulus, Poisson's ratio and the density of the hard and soft components are respectively chosen as: $E_m = 130 \text{ GPa}$, $E_p = 1 \text{ GPa}$, $\rho_m = 2 \text{ g/cm}^3$, $\rho_p = 1 \text{ g/cm}^3$, $\gamma_p = 4$. The characteristic relaxation time of biopolymer has been studied as a varying factor in this work. As mentioned in the introduction section, the relaxation time of collagen molecules estimated by MD (Molecular Dynamics) simulations is less than 1 nanosecond, and therefore several typical values between 0.005 to 0.24 ns were adopted in the following studies. It is worth noting that here in this model, the mineral platelets are assumed to be elastic with no viscoelastic characteristics; however, protein has viscoelastic properties. Therefore, Eq. (5-4) is only valid for the protein and the parameters g_1 and τ_1 define the protein relaxation ratio and characteristic time for the Prony series with just one term ($M = 1$), respectively. Thus, for simplicity here g and τ were used instead of g_1 and τ_1 to show the relaxation properties of the protein matrix.

According to Fig. 4.1(a), the mineral volume fraction can be calculated using Eq. (4-7). However, the exact value of mineral volume fraction in the staggered nanostructure of bone is still unknown. For the whole bone, its value is in the range of 30-48% (Lowenstam and Weiner, 1989), with a typical value of 42% (Lozano et al., 2003) that has been used widely in the literature (Jäger and Fratzl, 2000; Yuan et al., 2011). Due to the hierarchical structure of bone, the mineral volume fraction at the bottom level should be much higher than that of the whole bone. It should be noted that mineral volume fraction plays a significant role in shaping the mechanical properties, and in turn the major

functions of load-bearing biological materials. Generally, those with higher volume fraction of mineral are expected to own higher stiffness and strength to mainly provide mechanical support and protection for soft bodies, among which sea shell is a typical representative with around 99% volume fraction of mineral; on the other hand, those with lower volume fraction of mineral tend to be more resilient and tough to experience large deformation, transfer force and absorb kinetic energy, the typical example of which is mineralized tendon with a mineral volume fraction of about 15%. To some extent, the superiority of an inferior mineralized biological materials in absorbing and dissipating kinetic energy should be attributed to the viscoelastic properties of biopolymers such as collagen (Lakes, 2001; Sasaki et al., 1993). In the present work, several typical values of mineral volume fraction, 53%, 57%, 61%, and 64% are chosen for the staggered nanostructure in order to check their influence on the stress wave attenuation.

The length of collagen molecules was found to be approximately 280 nm (Hulmes, 2002; Puxkandl et al., 2002) and the overlapping period along the axial arrangement is 67 nm (Jäger and Fratzl, 2000; Orgel et al., 2000). The ratio of the gap and overlapping region in the axial period was found to be around 3 to 2. The thickness of these mineral platelets was reported to be in the range of 2-10 nm (Eppell et al., 2001; Hassenkam et al., 2004; Moradian-Oldak et al., 1991; Posner, 1969; Robinson, 1952; Rubin et al., 2003) and the distance between two plates in the transverse direction was reported to be in the same order of their thickness from 2 to 4.5 nm (Lowenstam and Weiner, 1989; Rubin et al., 2003). The mineral platelet length was reported in a wide range from 15 to 150 nm in different load-bearing biological materials (Lowenstam and Weiner, 1989; Rubin et al., 2003). According to the model proposed by Jäger and Fratzl (2000) for the nanostructure

of bone, the axial period of the mineralized collagen structure is $(L+a)/2 = 67$ nm. In this work, parametric studies were carried out on the mineralized collagen structure of the biological materials with staggered arrangement. It should be noted that in the current work, the dynamic responses of different staggered structures are used for comparative study. Therefore, during the numerical analysis, the mineral volume fraction φ , the thickness of the mineral plates h_m , the longitudinal and horizontal gaps between the neighboring mineral platelets a and h_p , and the unit cell area $2(a+L)(h_m+h_p)$ will be varied to do the parametric study. As soon as the mineral volume fraction φ , the mineral platelet thickness h_m , and the longitudinal gap a (in the same order of the experimental range of platelet thickness, $\approx h_m$) are chosen from their ranges, respectively, all the other geometrical parameters in Fig. 4.1(b), i.e., L , h_p can be determined immediately, as well as the platelet aspect ratio L/h_m . Therefore, in the following sections, the combination of φ and h_m is used to uniquely denote a staggered structure. Moreover, to make the study of more practical interest, all the geometrical parameters are set, respectively, to be within their experimentally observed ranges.

5.3 Results and discussion

In this chapter, the decrease of peak stress over the distance from the impact surface is used as an index for measuring the stress wave attenuation. To reflect the stress wave attenuation, the maximum average stress within each unit cell has been plotted with respect to the sequence number of the unit cell along the stress wave traveling direction.

Under the same impact loading, the plot is lower, the stress attenuation is faster. The maximum average stress σ_{ave} in a unit cell is derived from Eq. (4-8).

To demonstrate the effect of the viscosity of collagenous protein, comparisons of the stress wave attenuation in both x and y direction were carried out between the staggered structures with elastic and viscoelastic soft matrix.

Fig. 5.2 Comparison of stress wave attenuation (a) in the x direction and (b) in the y direction for different staggered structures with elastic and viscoelastic matrix. (All structures are of the same mineral volume fraction of 57%). The viscoelastic characteristic time for collagen is $\tau = 0.24$ ns.

As can be seen from Fig. 5.2, the peak stress decreases as the stress wave travels over a number of unit cells for all cases, but the plots for the staggered structures with viscoelastic matrix are distinctly below their counterparts of the staggered structures with elastic matrix, respectively. This clearly shows the significant contribution of the matrix viscoelasticity to the stress wave attenuation via kinetic energy dissipation. In another word, in addition to the interface scattering mechanism based on the staggered arrangement of hard phase in soft phase, the matrix viscosity induced kinetic energy dissipation is also an important mechanism for load-bearing biological materials to damp

the stress wave. Actually, for bone it is the synergism of the two mechanisms to achieve a fast decay of stress wave.

Fig. 5.3 Comparison of stress wave attenuation in the staggered structures with varying characteristic relaxation time as the elastic wave traveling in the x direction (a) and the y direction (b), respectively. (All structures are of the same mineral volume fraction of 53%).

Comparing Fig. 5.2(a) and (b), it can be seen that the peak stress of the elastic wave in the x direction is generally smaller than that of the stress wave in the y direction. This should be attributed to two aspects: 1) the effective Young's modulus of the staggered structure in the x direction is lower than that in the y direction and lower modulus

generates lower peak stress under dynamic loadings; 2) a larger area of soft-hard interface normal to the x direction scatters the stress wave more efficiently and thus reduces the peak stress faster.

Different types of biopolymer may have different extent of viscosity, and thus it is of practical interest to unveil how a varying viscosity influences the stress wave attenuation for staggered structures. To this end, the plots of stress wave decay in two typical staggered structures ($h_m = 6$ nm and 7.5 nm) with varying viscoelasticity (measured by the characteristic relaxation time τ) were made in Fig. 5.3(a, b), in which the stress wave propagates in the x and y direction, respectively.

First, it can be seen that, as the characteristic relaxation time τ decreases from infinity (pure elasticity) to 0.005 ns (i.e., the biopolymer viscosity increases gradually), the stress wave decay becomes faster for both of the staggered structures regardless of the loading direction. It further confirms that the viscosity of soft phase in bone plays a crucial role in mitigating dynamic impacts and protecting inside vulnerable tissues or organs. Furthermore, let us check the difference between the plots of $h_m = 6$ nm and $h_m = 7.5$ nm. It can be found that the difference is distinct when τ is not so small (for instance, $\tau=0.24$ ns and 0.1 ns), but becomes smaller and smaller as τ decreases, and completely disappears when τ reduces to 0.005 ns. It indicates that, regarding the staggered nanocomposites, there is a critical value of the characteristic relaxation time of soft matrix, below which the viscous effect is so strong that the viscosity-induced energy-dissipation is predominant in damping the stress wave and the incremental contribution by optimizing the staggered arrangement (e.g., from $h_m = 6$ nm to $h_m = 7.5$ nm as seen in Fig. 5.3) is negligible, whereas above which both the structure-based interface scattering

mechanism and the viscosity-induced energy-dissipation mechanism play a significant role and they work together to effectively attenuate the stress wave. In another word, there are two strategies for a staggered composite to most effectively attenuate stress wave: one is to choose a matrix material of especially high viscosity with a simply arbitrary staggered design, no much effort needed to optimize the staggered structure; the other is to delicately optimize the staggered design with a matrix material of mild viscosity.

From Fig. 5.3 and the above analysis, we have known that there exists a critical characteristic relaxation time of the soft matrix, below which the plots of average stress over number of unit cell is almost the same for different staggered structures, but above which an optimization of the staggered layout and arrangement becomes vital to achieve a faster stress wave attenuation. For the typical parameters of bone, the critical value of the characteristic relaxation time is between 0.005 ns and 0.1 ns (see Fig. 5.3).

The characteristic relaxation time of collagen has been reported in the range of 0.24-0.64 ns and 0.13-0.27 ns respectively for dry and solvated collagen molecule (Gautieri et al., 2013; Gautieri et al., 2011), obviously greater than the critical value observed in Fig. 5.3. Therefore, it can be inferred that for bone it is still important to optimize the staggered structure to realize its most efficient stress wave decay, even in the presence of viscoelastic collagen. In the following, a typical value of 0.24 ns is chosen as the characteristic relaxation time of collagen, and systematic FEM simulations are conducted to find out the optimal staggered structure for the stress wave decay along the y direction as well as along the x direction.

Fig. 5.4 shows the plots of stress wave decay for a group of staggered structures with a mineral volume fraction of 53% (Fig. 5.4(a)), 57% (Fig. 5.4(b)), 61% (Fig. 5.4(c)) and 64% (Fig. 5.4(d)), under loading in the y direction.

Fig. 5.4 Comparison of stress wave attenuation (along the y direction) for different staggered arrangements with a mineral volume fraction of (a) 53%, (b) 57%, (c) 61% and (d) 64%. The viscoelastic characteristic time for collagen is $\tau = 0.24$ ns.

It can be seen that for each mineral volume fraction, there exists an optimal staggered structure (with particular geometrical parameters, h_m and etc.) leading to the fastest stress wave attenuation. For instance, for the mineral volume fraction of 53%, the staggered

structure with a mineral platelet thickness of 6.5 nm shows the fastest decrease of stress over the unit number of cell (travelling distance). As the mineral volume fraction increases from 53% in Fig. 5.4(a) to 64% in Fig. 5.4(d), the curves for different staggered structures become closer and closer to each other, indicating that the effect of the optimization of staggered structure on the stress decay becomes smaller.

Fig. 5.5 Comparison of stress wave attenuation (in the x direction) for different staggered arrangements with a mineral volume fraction of (a) 53%, (b) 57%, (c) 61%, and (d) 64%. The viscoelastic characteristic time for collagen is $\tau = 0.24$ ns.

It should be noted that the staggered case that shows the fastest stress wave attenuation is denoted by thin line within the plots. Similarly, Fig. 5.5 shows the plots of stress wave decay for these staggered structures with a mineral volume fraction of 53% (Fig. 5.5(a)), 57% (Fig. 5.5(b)), 61% (Fig. 5.5(c)) and 64% (Fig. 5.5(d)), under loading in the x direction, and the similar phenomena can be seen.

Interestingly, it is observed that for stress wave travelling in the x direction, the staggered structures with larger h_m (correspondingly, smaller aspect ratio of mineral platelet) always leads to faster stress wave decay. This is in good agreement with the analysis by Ji and Gao (2004a) suggesting that decreasing the aspect ratio of mineral platelets can effectively increase the viscoelastic dissipation of the staggered composites under dynamic loading in the x direction.

It is worth noting that the impact duration t_0 in Eq. (5-2) is a characteristic time of the incident waves, and hence is an important factor affecting the results of stress wave attenuation. As discussed before, the characteristic time (or frequency) and the characteristic length are closely correlated with each other in the dynamic behaviors of heterogeneous materials. In the current study, the size of the unit cell is a characteristic length, and thus the time t_c for a stress wave passing through a unit cell is chosen as a typical value of the impact duration. However, in order to gain an insight of the effect of the impact duration, a variation in the impact duration (e.g., $t_0 = 0.5t_c$ and $t_0 = 2t_c$, still on the same order of t_c) has been investigated.

With the same geometrical structure and material parameters with Figs. 5-4(b) and 5-5(b), Fig. 5.6(a) and Fig. 5.6(b) show the stress wave attenuation under an impact pulse of

duration $t_0 = 0.5t_c$, loading in the x and y direction, respectively, while Fig. 5.6(c) and Fig. 5.6(d) plot the stress wave attenuation under an impact pulse of duration $t_0 = 2t_c$, loading in the x and y direction, respectively.

Fig. 5.6 Comparison of the stress wave attenuation for the different impact duration: $t_0 = 0.5t_c$ in the (a) x and (b) y direction, and $t_0 = 2t_c$ in the (c) x and (d) y direction.

Comparing the plots of stress wave decay in Figs. 5-4(b), 5-6(b) and 5-6(d) for different impact duration in the y direction, and those plots in Figs. 5-5(b), 5-6(a) and 5-6(c) for different impact duration in the x direction, respectively, one can see that, there is

no difference in the basic trend of stress wave decay over distance for different impact durations, and the optimal structural arrangements obtained from $t_0 = t_c$ are still effective for $t_0 = 0.5t_c$ and $t_0 = 2t_c$. Considering the specific values, we can find that larger impact duration usually leads to higher average stress at the same distance away from the loading boundary. The stress enhancement is mainly attributed to the interferences of more reflective waves from neighboring unit cells with incident waves.

From Fig. 5.4 to Fig. 5.6, the optimal staggered structures (represented by the optimal values of h_m) with different volume fractions of mineral are obtained for the fastest stress wave decay in the y and x directions, respectively. Hence, the thickness and aspect ratio of mineral platelet in the optimal staggered structures can be immediately derived based on our simulations, as shown in Fig. 5.7.

Fig. 5.7 The optimal aspect ratio and thickness of mineral platelet predicted by our simulations together with the data from experimental measurements (Hassenkam et al., 2004; Johansen and Parks, 1960; Landis et al., 1993; Landis et al., 1996b; Molnar, 1960; Moradian-Oldak et al., 1991; Robinson, 1952; Rubin et al., 2003; Ziv and Weiner, 1994). The viscoelastic characteristic time for collagen is $\tau = 0.24$ ns.

Recently, the feature sizes and layouts of bone at the nanoscale have been measured in various experimental investigations involving the state-of-the-art technologies such as X-ray diffraction and electron microscopy (Johansen and Parks, 1960; Landis, 1995; Landis et al., 1993; Molnar, 1960; Moradian-Oldak et al., 1991; Posner, 1969; Robinson, 1952; Robinson and Watson, 1952, 1955; Weiner and Traub, 1989), small angle X-ray scattering (Fratzl et al., 1991; Fratzl et al., 1992; Fratzl et al., 1994; Fratzl et al., 1996), transmission electron microscopy (Landis et al., 1996a; Probst and Lees, 1996; Rubin et al., 2003; Weiner and Price, 1986; Ziv and Weiner, 1994), and Atomic force microscopy (Eppell et al., 2001; Hassenkam et al., 2004; Rho et al., 1998).

The aspect ratios of mineral platelets in relation to their thicknesses are collected from these experimental studies and also shown in Fig. 5.7. It can be found that the optimal aspect ratios predicted by our FEM simulations, especially the varying trend (the fitted curve) with respect to the mineral platelet thickness, agree very well with the experimental results.

(a)

Fig. 5.8 Comparison of stress wave decay between two staggered structures for varying polymer viscosity and mineral volume fractions, (a) 57%, (b) 61% and (c) 64%; the elastic wave travels along the y direction.

As aforementioned, with a typical value of collagen viscosity, the larger is the volume fraction of mineral, the smaller is the difference between different staggered structures in attenuating the stress wave, which suggests that the stress wave decay becomes structure-insensitive as the mineral volume fraction increases.

To further validate the effect of mineral content on the structure-sensitivity of stress wave decay in the staggered nanocomposites, we designed the following studies:

1) choose two staggered structures for each mineral volume fraction of 57%, 61% and 64%, and for comparison purposes, make the same difference in h_m (1.5 nm here) between the two staggered structures for all the mineral volume fractions of 57% (Fig. 5.8(a) and Fig. 5.9(a)), 61% (Fig. 5.8(b) and Fig. 5.9(b)) and 64% (Fig. 5.8(c) and Fig. 5.9(c)).

2) study the stress wave attenuation in these staggered structures with a variety of characteristic times of viscoelasticity.

3) check how the difference of stress wave decay plot between the two staggered structures varies along the increasing mineral volume fraction, with different levels of viscosity of the matrix protein. The results for the incident elastic waves along the y direction are shown in Fig. 5.8 and for the incident elastic waves along the x direction are shown in Fig. 5.9, respectively.

(b)

(c)

Fig. 5.9 Comparison of stress wave decay between two staggered structures for varying polymer viscosity and mineral volume fractions, (a) 57%, (b) 61% and (c) 64%; the elastic wave travels along the x direction.

We can see that, regardless of the incident direction of the stress wave, the gap between the two staggered structures is always narrowing down for each individual mineral volume fraction as the biopolymer viscosity goes up (i.e., the characteristic time τ

goes down), and the gap is also always narrowing down for each individual viscosity level (i.e., each individual τ) as the mineral volume fraction increases. Especially, when the stress wave travels in the y direction, the curves for the two different staggered structures almost collapse together for all mineral volume fractions when τ goes down to 0.005 ns, and for all levels of viscosity when the mineral volume fraction goes up to 64%. These results suggest that if taking the biopolymer viscosity and the mineral volume fraction as two varying factors (as conceptually illustrated in Fig. 5.10(a)), there are two regimes regarding the stress wave decay in staggered nanocomposites: one is structure-sensitive regime where the structural arrangement has important effect on the stress wave decay, while the other is structure-insensitive regime where the structural arrangement has little effect on the stress wave decay. From the perspective of composite design, the former regime especially asks for structure optimization to achieve superior capability of stress wave attenuation, while the latter does not.

Mineral volume fraction, biopolymer viscosity and structural arrangement all play important roles in the stress wave decay of load-bearing biological materials, but they seem having different levels of dominance. As is seen in Fig. 5.8 and Fig. 5.9, both the effect of biopolymer viscosity and that of structural arrangement on stress wave decay become more and more insignificant when the mineral volume fraction increases, indicating that the mineral volume fraction is on the primary level of dominance. This is also consistent with the traditional theory of composites, i.e., the mixture rule, in which the volume fraction is the primary factor in determining the composite properties. Furthermore, given a moderate value of mineral volume fraction, we can see that the effect of structural arrangement becomes weaker and weaker as the biopolymer viscosity

goes stronger and stronger. Therefore, it can be inferred that the biopolymer viscosity is on the secondary level of dominance while the structural arrangement is on the tertiary level. However, it is worth noting that the structural arrangement plays a significant role in stress wave attenuation in most load-bearing biological materials including bones, since both the mineral volume fraction and the biopolymer viscosity are in the moderate range.

Fig. 5.10 (a) Conceptual illustration of the roles of the mineral volume fraction ratio, biopolymer viscosity and structural arrangements in the stress wave attenuation of load-bearing biological materials and (b) the correlation between the mineral volume fraction and hierarchy number (structure complexity) in typical load-bearing biological materials revealed from experimental observations, in which the fitted curve is to show the varying trend.

Now let us discuss in a more general scenario about the roles of mineral volume fraction, biopolymer viscosity and structural arrangement on the stress wave attenuation of load-bearing biological materials as shown in Fig. 5.10. Based on our proceeding simulation results, Fig. 5.10(a) gives a conceptual illustration about the roles of mineral volume fraction, biopolymer viscosity and structural arrangement on the stress wave attenuation. In the structure-sensitive regime, structural arrangement of mineral platelets plays a significant role in enhancing the stress wave attenuation, and hence a detailed

optimization of structural arrangement is needed to acquire a superior capability in attenuating stress waves. On the contrary, in the structure-insensitive regime, structural arrangement of mineral platelets plays a trivial role, and thus a detailed optimization of structural arrangement is unnecessary.

It is worth noting that, in Fig. 5.10(a), both extremely high and low mineral volume fractions would lead to the structure-insensitivity of stress wave decay while the evidences (see Fig. 5.8 and Fig. 5.9) are only shown for the former case in the current work. Only the cases of high mineral volume fraction have been studied here because the mineral volume fraction for bone is around 45% and the exact value at the bone primary level should be much higher than 45%. However, with the structure-insensitivity at extremely high mineral volume fraction, it can be inferred with ease that the structure-insensitivity should also hold for extremely low mineral volume fraction according to the simple rule of mixture. In another word, with an extremely low mineral volume fraction (close to zero), the composite would become close to the homogeneous biopolymer and the structural arrangement is certainly expected to take little effect. To rephrase the point from the standpoint of a composite designer, a delicate and expensive inner architecture after optimization is required in the structure-sensitive regime to produce a composite with superior protection capability, while a relatively simple and cheap inner structure without optimization is sufficient in the structure-insensitive regime. According to this general rule, the complexity of the inner architecture is expected to strongly correlate with the mineral volume fraction in load-bearing biological materials, since the viscosity of typical biopolymers (e.g., collagen) in load-bearing biological materials is located in a quite narrow range. Specifically, the inner architectures are expected be delicate and

complicate in the load-bearing biological materials of low volume fraction of mineral, whereas the inner architectures are expected to be relatively simple in those of high volume fraction of mineral. To verify our inference, let us check the correlation between structure complexity and mineral volume fraction in several typical load-bearing biological materials including bone (Jäger and Fratzl, 2000; Launey et al., 2010a; Lowenstam and Weiner, 1989; Lozano et al., 2003; Meyers et al., 2008; Rho et al., 1998; Weiner and Wagner, 1998), antler (Chen et al., 2009; Launey et al., 2010b), enamel (Nanci, 2007; Ten Cate, 2003) and shell (Barthelat et al., 2006; Epple and Bäuerlein, 2009; Jackson et al., 1988; Kamat et al., 2004; Mayer, 2005; Menig et al., 2001; Meyers et al., 2008). Structural hierarchy is a common feature of different types of load-bearing biological materials and well represents the delicacy and complexity of their inner architectures. Therefore, the number of structural hierarchies is adopted here to represent the structure complexity of each individual load-bearing biological material.

As shown in Fig. 5.10(b), with the mineral volume fraction increasing from around 40% (for cortical bone, antler, etc) to 95% (for shell, etc), the number of structural hierarchies decreases from 7 to 2, i.e., the structural complexity decreases significantly. The varying trend is in good agreement with our prediction, the higher the mineral volume fraction, the simpler the inner architecture. In this regard, it further confirms our findings and conclusions above. On the other hand, the findings and discussions here provide a possible explanation on the correlation between the hierarchy number and the mineral volume fraction in typical load-bearing biological materials from the perspective of dynamic mechanics, and also shed some useful light on the design of composites with superior capability of attenuating, filtering or blocking stress waves.

5.4 Summary

In this chapter, studies on the stress wave travelling and attenuation in the staggered nanostructure of load-bearing biological materials were conducted via the finite element method (FEM) to investigate the roles of biopolymer viscosity, structural arrangement and mineral volume fraction. The main findings and conclusions are summarized below:

- 1) First it is worth to note that there are two basic mechanisms for a typical biological material to fast attenuate stress wave over its travelling distance: one is stress wave scattering due to the soft-hard interfaces, and the other is kinetic energy dissipation due to the viscosity of biopolymer components. Our study here suggests that the nanostructure of bone very well synergizes the two mechanisms to achieve fast stress wave attenuation.
- 2) Adopting the characteristic relaxation time to measure the viscoelastic property of biopolymer matrix (like collagen), we found that, given a specific volume fraction of mineral (biopolymer), there is a critical characteristic relaxation time, below which the viscosity-based energy-dissipation mechanism predominantly dictates the stress wave attenuation so that the contribution from the structure-based interface scattering mechanism is trivial, whereas above which, structure optimization (from a layered structure to an optimal staggered in the current chapter) will be important and necessary to enhance the stress wave attenuation as the contribution from the structure-based interface scattering mechanism is nontrivial and crucial. The principle applies to bone soundly: the typical characteristic relaxation time of collagen is above the critical value, and bone

adopts the delicate staggered structure even in the presence of viscous protein. On the other hand, our finding here rationalizes the staggered arrangement widely seen in load-biological materials in the perspective of dynamics.

- 3) Regarding the staggered nanocomposites in bone, we found that an optimal staggered structure with specific feature sizes and geometrical layouts exists, leading to the fastest wave decay. Importantly, the optimal feature sizes and geometrical layouts predicted by our simulations are in excellent agreement with the experimental observations in the literature.
- 4) The roles of biopolymer viscosity, mineral volume fraction and structural arrangement are examined regarding the capability of stress wave attenuation of load-bearing biological materials, and it is found that the stress wave attenuation would gradually become structure-insensitive as the biopolymer viscosity or the mineral volume fraction increases. In the structure-sensitive regime, structural arrangement of mineral platelets plays a significant role in enhancing the stress wave attenuation, and hence a detailed optimization of structural arrangement is needed to acquire a superior capability in attenuating stress waves. In contrary, in the structure-insensitive regime, structural arrangement of mineral platelets plays a trivial role, and thus a detailed optimization of structural arrangement is unnecessary. As the viscosity of typical biopolymers in load-bearing biological materials is located in a quite narrow range, it is inferred that the mineral volume fraction has a strong correlation with the structural complexity in load-bearing biological materials, i.e., the higher the mineral volume fraction, the simpler the inner architecture. This agrees very well with experimental observations on the

correlation between the architecture and mineral volume fraction in typical load-bearing biological materials such as bone, antler, enamel and shell, in which the number of structural hierarchies decreases from 7 to 2 as the mineral volume fraction increases from 40% to 99%. Therefore, the present work may provide a logical explanation from the perspective of dynamic mechanics, on why biological materials with a higher mineral content exhibit a smaller number of structural hierarchies and vice versa.

In addition, there are also some limits about the current work worth to be noted. The stress waves on macroscopic bone are usually with frequencies less than 100 Hz, which should be of more practical interest. However, the current chapter mainly focuses on the stress wave attenuation at the bottom hierarchical level of bone, whose characteristic length scale is around tens of nanometers and whose target wave should be with much higher frequencies. Actually, one significant advantage of the hierarchical architecture of load-bearing biological materials like bone is their hierarchical-structure-based multimodal damping mechanism, i.e., lower levels (with smaller characteristic length) of hierarchy targeting at stress waves of higher frequencies and vice versa. The advantage of hierarchical design in damping and dissipating dynamic energy has attracted some research attentions (Davies et al., 2014; Zhang and To, 2013, 2014), but most of the details are still unknown. To reveal how load-bearing biological materials achieve the multimodal damping mechanism via hierarchical structures will be the focus of our next chapter in this work. Another limit is that the correlation between the mineral volume fraction and the structural complexity (measured by hierarchy number) proposed here is still a hypothesis before more detailed studies are able to provide more direct evidences.

Additionally, the correlation between mineral volume fraction and hierarchy number in real load-bearing biological materials may be much more complicated, especially considering that many other biological factors and function requirements are also involved in a complicate way. From the perspective of protection function against impacts, the current study suggests that the structural complexity should decrease as the mineral volume fraction goes up from a moderate value, which is in agreement with experimental observations on typical mineralized biological materials from bone, dentine, to sea shell and etc. Hopefully, the preliminary discussions here could inspire more works to rationalize the correlation between structural complexity and mineral volume fraction in typical load-bearing biological materials.

The results of this chapter have been published as a research paper (Qwamizadeh et al., 2016b).

Chapter 6 Damping Properties of Hierarchical Load-Bearing Biological Materials with Staggered Architectures

One of the most crucial functionalities of load-bearing biological materials such as shell and bone is to protect their interior organs from damage and fracture arising from external dynamic impacts. However, how this class of materials effectively damp stress waves traveling through their structure is still largely unknown. In this chapter, with a self-similar hierarchical model, a theoretical approach was established to investigate the damping properties of load-bearing biological materials in relation to the biopolymer viscous characteristics, the loading frequency, and the geometrical parameters of reinforcements as well as the hierarchy number. It was found that the energy dissipation originates from the viscous characteristics of the organic (biopolymer) constituents and is greatly tuned and enhanced by the staggered and hierarchical organization of the organic and inorganic constituents. For verification purpose, numerical experiments via Finite Element Method (FEM) have also been conducted and obtained results are consistent with the theoretical predictions.

6.1 Modeling

Load-bearing biological materials such as bone, mineralized tendon and shell that are made from soft organic and brittle inorganic materials, exhibit extraordinary mechanical properties (Meyers et al., 2008). These biological materials usually contain several internal levels of structural hierarchy with length scale varying from nanoscale to macroscale (Rho et al., 1998; Weiner and Wagner, 1998). For instance, bone is seen with seven levels of structural hierarchy (Rho et al., 1998), mineralized tendon shows six levels

of hierarchy (Kastelic et al., 1978; Puxkandl et al., 2002; Screen, 2009), and sea shells are observed with two to three hierarchical levels (Menig et al., 2001). It is believed that such hierarchical design is an effective strategy selected by nature through millions of years of evolution to develop biological materials with superb properties and functionalities, especially from relatively weak constituent materials. Even though the hierarchical structures of different types of load-bearing biological materials are quite different, all of them are made of a biopolymer matrix with buried platelet-shape mineral crystals at their primary level (Jäger and Fratzl, 2000; Meyers et al., 2008).

Numerous studies have been performed to investigate the structure-property relationship of the load-bearing biological materials (Gao, 2006; Gao et al., 2003; Ji and Gao, 2004a; Lei et al., 2013; Lei et al., 2012; Zhang et al., 2010; Zhang et al., 2011), mostly under static loading conditions. However, one of the crucial functionalities of these load-bearing biological materials is to protect their inside fragile tissues via damping the impact waves, since, in reality, they are frequently exposed to dynamic loadings (Lakes, 2002; Meyers et al., 2008) and it is well known that dynamic loadings are more dangerous than static ones from mechanics perspective. Therefore, it is both necessary and important to study how these biological materials effectively damp stress wave and dissipate dynamic energy.

Several recent studies focused on investigating the damping behavior of the biological materials at the primary level as well as the higher structural levels (Qwamizadeh et al., 2015; Zhang et al., 2015; Zhang and To, 2013). Zhang and To (2014) considered the protein viscosity and calculated the damping figure of merit in the hierarchical structure of typical load-bearing biological materials. However, in their study, they only considered

dynamic loadings in a narrow frequency window which is close to the static loading condition. In reality, routine loadings exerting on the load-bearing biological materials like bone are often dynamic and their frequency can be varied in a wide range.

In general, the damping behavior of a material can be characterized by the complex modulus (Lakes, 2009), $E^*(\omega) = E_s(\omega) + iE_l(\omega)$, where $i = \sqrt{-1}$, the real part E_s is the storage modulus, the imaginary part E_l is the loss modulus, and $\omega = 2\pi f$ is the angular frequency of harmonic loadings, with f being the loading frequency.

The storage modulus and loss modulus, respectively, measure how much energy can be stored and dissipated by the material. It is worth noting that both of them are a function of loading frequency, i.e., frequency-dependent. Since the organic (protein) portion generally shows a viscoelastic behavior (Christensen, 1982; Gautieri et al., 2012; Sanjeevi et al., 1982; Sasaki et al., 1993; Shen et al., 2011; Svensson et al., 2010; Yoon et al., 2014), an interesting question here is: what is the role of biopolymer viscosity in damping behavior of a load-bearing biological material? More specifically, how does viscous biopolymer work together with pure elastic mineral through the staggered and hierarchical organization to realize the protective functions of load-bearing biological composites?

Based on a self-similar hierarchical model, an analytical model is developed in the present work to probe the damping properties of typical load-bearing biological materials in relation to the material characteristics of biopolymer, the loading frequency, the geometrical parameters of reinforcements as well as the hierarchy number. In the addition, numerical experiments via Finite Element Method (FEM) have also been carried out for verification purposes.

6.1.1 Mathematical modeling

In describing the damping mechanism and energy dissipation through a load-bearing biological material, a harmonic test with small strain is considered as

$$\varepsilon(t) = \varepsilon_0 e^{i\omega t}, \quad (6-1)$$

where ε_0 is the strain amplitude harmonically applied to the specimen. Then, the stress response is in the form of

$$\sigma(t) = \sigma_0 e^{i(\omega t + \psi)} = E^*(\omega) \varepsilon_0 e^{i\omega t}, \quad (6-2)$$

where ψ is the phase difference between the stress and strain, which is related to the ratio of the loss modulus to the storage modulus via $\tan\psi = E_l/E_s$.

The self-similar hierarchical model (Ji and Gao, 2004a) for load-bearing biological materials is schematically shown in Fig. 6.1. In the model, each level consists of hard reinforcements aligned in a staggered pattern in a soft biopolymer matrix, and the composite of one level comprises the reinforcements of its immediate neighbor of higher levels. The arrangement pattern, the volume fraction and the aspect ratio of reinforcement are the same through different levels, which is just what the “self-similar” means.

It is worth noting that the reinforcements in higher levels (Level 2 and above) are heterogeneous, made of the composite of its immediate neighbor of lower levels. In another word, at the first (bottom) level, the structure is composed of a viscous matrix of biopolymer (homogeneous and viscous) and staggering aligned elastic mineral platelets (homogenous and elastic); however, at the higher levels, the structure consists of the homogeneous biopolymer matrix and the heterogeneous reinforcement (the composite of a lower level), and both of them have viscous characteristics.

Fig. 6.1 The self-similar hierarchical model for typical load-bearing biological materials (Ji and Gao, 2004a).

Fig. 6.2 shows the unit cell of the regular staggered structure and the stress as well as the strain fields within the unit cell due to imposing a small longitudinal elongation Δ to the unit cell. It should be noted that L is the hard inclusion length, and h_m is the hard inclusion thickness and is related to the soft matrix thickness h_p with mineral volume fraction relation as $\phi = h_m / (h_p + h_m)$.

According to Fig. 6.2, the hard inclusions are assumed to experience ε_m , then the shear strain in the soft matrix will be in the form of

$$\begin{Bmatrix} \gamma^U \\ \gamma^L \end{Bmatrix} = \frac{\Delta - L\varepsilon_m}{h_m} \begin{Bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{Bmatrix}, \quad (6-3)$$

Therefore, the total strain energy stored in the mineral platelets is $E_m \varepsilon_m^2 h_m L$ and that for the soft protein can be obtained as below

$$2 \left[G_p (\gamma^L)^2 h_p (L/2) / 2 + G_p (\gamma^U)^2 h_p (L/2) L / 2 \right] = G_p L (\Delta - L \varepsilon_m)^2 / 4 h_p, \quad (6-4)$$

$$\Pi = \left[E_m \varepsilon_m^2 h_m L + \frac{G_p L (\Delta - L \varepsilon_m)^2}{4 h_p} \right], \quad (6-5)$$

Fig. 6.2 Generalized staggered structure. (a) Schematic nanostructure of bio-composite; (b) the unit cell (solid box) with staggering number n , (c) the assumed balanced stress field under a longitudinal elongation Δ ; and (d) the assumed kinematically admissible strain field under a longitudinal elongation Δ (Zhang et al., 2010).

The potential energy in the unit cell can be written as:

Minimization of the potential energy with respect to ε_m gives the effective elastic modulus of the composite as

$$E = \frac{d^2 [\Pi / 2L(h_m + h_p)]}{d\Delta^2} \cdot L^2 = \left[\frac{1}{\phi E_m} + \frac{4(1-\phi)}{\rho^2 \phi^2 G_p} \right]^{-1}, \quad (6-6)$$

where $\rho = L/h_m$ is the aspect ratio of the mineral inclusion.

Therefore, according to the correspondence principle of viscoelasticity, substitute the complex modulus into the stiffness formulation of the self-similar hierarchical model developed in (Ji and Gao, 2004a; Zhang and To, 2014), and the following recursive formulae can be derived for the complex dynamic modulus of the composite at every level as

$$\frac{1}{E_i^*(\omega)} = \frac{1}{E_{i-1}^*(\omega)\varphi} + \frac{4(1-\varphi)}{\chi\rho^2\varphi^2G_p^*(\omega)}, \quad i = 1, 2, \dots, N, \quad (6-7)$$

where N is the total hierarchy number of the composite, and the subscripts i and $i-1$ denote the sequence number of structural hierarchy; ρ and φ are, respectively, the aspect ratio and volume fraction of the hard inclusion at each individual level, and φ is related to the mineral volume fraction of the hierarchical composite, ϕ , by $\varphi = \sqrt[N]{\phi}$; $G_p^* = G_{sp} + iG_{lp}$ is the complex shear modulus of viscoelastic biopolymer, and χ is the tension region factor derived in (Zhang and To, 2014), representing the stiffness contribution of the matrix in the connecting regions between neighboring reinforcements in the longitudinal direction. It should be noted that the biopolymer characteristic is assumed to be the same for different levels of structural hierarchy, i.e., only one type of biopolymer (for example the protein of Type I collagen) is adopted as the soft matrix in the hierarchical model. This is a reasonable simplification, as, for instance, in bone Type I collagen is the major component of biopolymer matrix, occupying about 90% in mass (Zhang et al., 2011). Another point worth to mention is that $E_0^*(\omega) = E_m$, the purely elastic modulus of mineral material. Insert the complex form of E^* and G_p^* into Eq. (6-7) and do the mathematical

operations to separate the real and imaginary parts, the storage and loss modulus of different hierarchical levels can be obtained in a bottom-up sequence. Zhang and To (2014) used the same approach to calculate the storage and loss moduli of the composite structure as

$$E_{s(i)}^{LOF} = \frac{\chi^2 \rho^4 \phi G_{sP}^2 E_{s(i-1)} + 4 \chi \rho^2 (1 - \phi) E_{s(i-1)}^2 G_{sP}}{[\chi \rho^2 G_{sP} - 4(1 - 1/\phi) E_{s(i-1)}]^2}, \quad (6-8)$$

$$E_{l(i)}^{LOF} = \frac{\chi^2 \rho^4 \phi G_{sP}^2 E_{l(i-1)} + 4 \chi \rho^2 (1 - \phi) E_{s(i-1)}^2 G_{lP}}{[\chi \rho^2 G_{sP} - 4(1 - 1/\phi) E_{s(i-1)}]^2}, \quad (6-9)$$

However, the solutions above ignored the higher order terms of loss modulus, and thus are referred to as Lower-Order-Formulae (LOF) in the present work. Here we would like to provide a complete solution for the dynamic modulus. Therefore, all the higher order terms of the loss modulus have been kept in deriving the solutions of storage and loss modulus. The obtained full solutions are shown as below

$$E_{s(i)}^{HOF} = \frac{\chi^2 \rho^4 \phi (G_{sP}^2 E_{s(i-1)} + E_{s(i-1)} G_{lP}^2) + 4 \chi \rho^2 (1 - \phi) (E_{s(i-1)}^2 G_{sP} + G_{sP} E_{l(i-1)}^2)}{[\chi \rho^2 G_{sP} - 4(1 - 1/\phi) E_{s(i-1)}]^2 + [\chi \rho^2 G_{lP} - 4(1 - 1/\phi) E_{l(i-1)}]^2}, \quad (6-10)$$

$$E_{l(i)}^{HOF} = \frac{\chi^2 \rho^4 \phi (E_{l(i-1)} G_{sP}^2 + E_{l(i-1)} G_{lP}^2) + 4 \chi \rho^2 (1 - \phi) G_{lP} (E_{s(i-1)}^2 + E_{l(i-1)}^2)}{[\chi \rho^2 G_{sP} - 4(1 - 1/\phi) E_{s(i-1)}]^2 + [\chi \rho^2 G_{lP} - 4(1 - 1/\phi) E_{l(i-1)}]^2}, \quad (6-11)$$

referred to the Higher-Order-Formulae (HOF) hereafter. It is obvious that Eqs. (6-10) and (6-11) are, respectively, the same as Eqs. (6-8) and (6-9), except containing the higher terms of loss modulus. Then, an interesting question arises: Is it important and necessary to include these higher order terms of the loss modulus? In the following section, we will show that the high order term is important and necessary to correctly predict the

composite responses to dynamic loadings, especially for those of relatively high frequency.

6.1.2 FEM modeling

In this chapter, all the FEM simulations were performed via ABAQUS/CAE, steady-state dynamics, direct solver. At the first hierarchical level, a linear elastic material model has been used for the mineral while a linear viscoelastic model for the protein. In the higher levels, for example Level i , $i > 1$, a linear viscoelastic material model with effective parameters extracted from FEM simulations on Level $i-1$ is used for the reinforcements. For the regular staggering structure at every hierarchical level, a representative volume element prescribed with periodic boundaries is modeled to represent the composite, and the two-dimensional plane stress element is used for the meshes of both the hard and soft regions. The mesh sensitivity has been checked within the FEM model and the element size has been proved fine enough to get convergent results. The harmonic cyclic loading defined in Eq. (6-1) is prescribed in the longitudinal direction, with $\varepsilon_0 = 0.001$ adopted.

6.2 Results and discussion

First of all, it should be noted that Prony series have been used to model the viscoelastic properties of the viscoelastic matrix material, i.e., collagenous protein here. The shear modulus of the material in the time domain can be presented as

$$G(t) = G_0 \left[1 - \sum_{m=1}^M g_m \left(1 - e^{-t/\tau_m} \right) \right], \quad (6-12)$$

where M is the number of terms in the Prony series and g_m , τ_m , $m = 1, 2, 3, \dots, M$, are material constants and G_0 is the instant shear modulus of the material as $G_0 = G(t=0)$. It should be noted that in the current model, it is assumed that just protein has viscoelastic properties. Therefore, $G(t) = G_p(t)$ and $G_0 = G_{0P} = G_p(t=0)$. Performing Fourier transforms, the shear modulus in time domain can be simply written into the form of complex modulus as $G_p^*(\omega) = G_{sP}(\omega) + iG_{lP}(\omega)$ in the frequency domain. The storage and loss moduli are in the following forms, respectively as

$$G_{sP}(\omega) = G_{0P} \left[1 - \sum_{m=1}^M g_m \right] + G_{0P} \sum_{m=1}^M \frac{g_m \tau_m^2 \omega^2}{1 + \tau_m^2 \omega^2} = G_{0P} \left[1 - \sum_{m=1}^M g_m \right] + G_{0P} \sum_{m=1}^M \frac{g_m}{1 + (\tau_m \omega)^{-2}}, \quad (6-13)$$

$$G_{lP}(\omega) = G_{0P} \sum_{m=1}^M \frac{g_m \tau_m \omega}{1 + \tau_m^2 \omega^2} = G_{0P} \sum_{m=1}^M \frac{g_m}{(\tau_m \omega)^{-1} + \tau_m \omega}, \quad (6-14)$$

From the equations above, we can infer that the storage modulus monotonically increases with the loading frequency and is gradually saturated to the instant modulus G_{0P} , while the loss modulus is a multimodal function of the loading frequency, with multiple peaks at $\omega_m = \tau_m^{-1}$, which is named as peak frequency in this chapter. For simplification purposes, only one term ($M = 1$) is kept for protein in this chapter so that there are only three independent parameters G_{0P} , g_1 and τ_1 for the viscoelastic matrix. For consistency, these three independent parameters for protein will be considered as G_{0P} , g and τ .

To verify our HOF formulae and show their advantages compared to the previous LOF formulae, let us focus on a single-level composite ($N = 1$) first. For a single-level composite, the Eq. (6-8) to (6-11) can be rewritten to be in the form of

$$E_{s(1)}^{LOF} = \frac{\chi^2 \rho^4 \phi G_{sP}^2 E_m + 4\chi \rho^2 (1-\phi) E_m^2 G_{sP}}{[\chi \rho^2 G_{sP} - 4(1-1/\phi) E_m]^2}, \quad (6-15)$$

$$E_{l(1)}^{LOF} = \frac{4\chi \rho^2 (1-\phi) E_m^2 G_{lP}}{[\chi \rho^2 G_{sP} - 4(1-1/\phi) E_m]^2}, \quad (6-16)$$

$$E_{s(1)}^{HOF} = \frac{\chi^2 \rho^4 \phi (G_{sP}^2 E_m + E_m G_{lP}^2) + 4\chi \rho^2 (1-\phi) E_m^2 G_{sP}}{[\chi \rho^2 G_{sP} - 4(1-1/\phi) E_m]^2 + [\chi \rho^2 G_{lP}]^2}, \quad (6-17)$$

$$E_{l(1)}^{HOF} = \frac{4\chi \rho^2 (1-\phi) E_m^2 G_{lP}}{[\chi \rho^2 G_{sP} - 4(1-1/\phi) E_m]^2 + [\chi \rho^2 G_{lP}]^2}, \quad (6-18)$$

with $E_{s(0)}(\omega) = E_m$ and $E_{l(0)}(\omega) = 0$ utilized.

Fig. 6.3 (a) Theoretical and FEM results for the variation of the storage modulus and (b) the loss modulus with the aspect ratio of the mineral platelet in the single-level staggered composite ($N = 1$) at oscillatory loadings of low frequency ($f = 1 \text{ Hz}$) and high frequency ($f = 200 \text{ Hz}$).

Given the typical geometrical and constituent material parameters $\phi = 0.45$, $E_m = 100 \text{ GPa}$, $\nu_m = 0.27$ (the Poisson's ratio of mineral), $G_{0P} = 1 \text{ GPa}$, $\nu_p = 0.4$ (the Poisson's ratio of protein), $g = 0.9$ (the relaxation coefficient of the protein in the Prony

series) and $\tau = 0.0002\text{s}$ (the viscoelastic characteristic time of the protein in the Prony series), Fig. 6.3(a) and Fig. 6.3(b), respectively, show the storage and loss moduli of the single-level staggered structure ($N = 1$) varying against the aspect ratio of mineral platelet at oscillatory loadings of low frequency (e.g., $f = 1\text{Hz}$) and high frequency (e.g., $f = 200\text{Hz}$). For verification purpose, the data points from FEM simulations have also been included.

From the plots in Fig. 6.3, it is evident that the complex modulus (i.e., the dynamic responses) of the composite is quite different in response to dynamic loadings of low and high frequencies. For low frequency ($f = 1\text{Hz}$), there is no distinct difference between the moduli predicted by the HOF and LOF, and both of them are in good agreement with the results from FEM simulations. However, for the high frequency ($f = 200\text{Hz}$), HOF's predictions on both the storage and loss modulus still agree very well with the FEM results, while LOF significantly underestimate the storage modulus and overestimate the loss modulus. Up to now, the advantage of the HOF is evident, and the high order terms in the formulae are important and necessary to reflect the composite responses to dynamic loadings of relatively high frequency. In addition, it can be seen from Fig. 6.3(a) that, as the aspect ratio of the mineral platelet increases, the composite stiffness (storage modulus) is always increasing and gradually approaches the Voigt limit, approximately $\phi E_m = 0.45 E_m$, which is consistent with the previous statics studies (Zhang et al., 2010). More interestingly, Fig. 6.3(b) shows that the loss modulus initially increases with the platelet aspect ratio and then decreases beyond a critical value of the aspect ratio, implying that there is an optimal aspect ratio of hard platelet for the composite to achieve the best damping performance against the dynamical loading of a certain frequency. In

addition, the predicted range of optimal aspect ratio is between 20-40, in good agreement with that from previous studies (Bai et al., 2016; Su et al., 2012).

According to Eqs. (6-10) and (6-11), the storage and loss moduli of a hierarchical composite with an arbitrary hierarchy number N can be obtained once the geometrical and constituent material parameters are known. Adopting the same set of geometrical and constituent material parameters, the storage and loss moduli for hierarchical composites with different hierarchy number N are plotted with respect to the aspect ratio of reinforcement in Fig. 6.4, in response to a oscillatory loading of low frequency, $f = 1\text{ Hz}$.

Fig. 6.4 (a) Storage and (b) loss modulus of the self-similar hierarchical composites with different hierarchy number N in response to an oscillatory loading of relatively low frequency ($f=1\text{ Hz}$).

As is seen in Figs. 6-4(a) and (b), the varying trend of either the storage modulus or the loss modulus does not change significantly with the hierarchy number N increasing from 1 to 7. However, as the hierarchy number increases, the optimal aspect ratio for the maximum loss modulus slightly decreases while the maximum loss modulus remains the same (see Fig. 6.4(b)). Regarding the recursive formulations derived in Eqs (6-8) to (6-

11), one can efficiently find the optimal aspect ratio in which the loss modulus is maximal. To do so, one can start from the following rigorous formulae as

$$\frac{\partial E_{l(i)}^{HOF, LOF}(\rho)}{\partial \rho} = \lim_{\Omega \rightarrow 0} \frac{E_{l(i)}^{HOF, LOF}(\rho + \Omega) - E_{l(i)}^{HOF, LOF}(\rho)}{\Omega}, \quad (6-19)$$

It can be seen that for the primary level ($N = 1$) the optimal aspect ratio as well as the maximum loss modulus can be obtained for the LOF formulation as below

$$\left. \frac{\partial E_l^{LOF}}{\partial \rho} \right|_{N=1} = 0 \rightarrow \rho_{opt}^{LOF} \Big|_{N=1} = \sqrt{\frac{4(1-\phi)E_m}{\chi\phi G_{sP}}}, \quad (6-20)$$

$$E_l^{LOF} \Big|_{N=1}^{\max} = \frac{E_m G_{lP} \phi}{4G_{sP}}, \quad (6-21)$$

Similarly, one can calculate the same for the HOF formulation as

$$\left. \frac{\partial E_l^{HOF}}{\partial \rho} \right|_{N=1} = 0 \rightarrow \rho_{opt}^{HOF} \Big|_{N=1} = \sqrt{\frac{4(1-\phi)E_m}{\chi\phi \sqrt{G_{sP}^2 + G_{lP}^2}}}, \quad (6-22)$$

$$E_l^{HOF} \Big|_{N=1}^{\max} = \frac{E_m G_{lP} \phi (\phi - 1)^2 \sqrt{G_{sP}^2 + G_{lP}^2}}{\left[G_{lP}^2 (\phi - 1)^2 + \left[(\phi - 1) \left(G_{sP} + \sqrt{G_{sP}^2 + G_{lP}^2} \right) \right]^2 \right]}, \quad (6-23)$$

Using the same approach and after doing several mathematical simplifications, finally, it is possible to calculate the optimal aspect ratio and the maximum loss modulus of the staggered structure at N^{th} hierarchical level for both the LOF and HOF approaches as below

$$\rho_{opt}^{LOF} \Big|_N = \sqrt{\frac{4(1-\phi)E_m}{\chi\phi^{1/N} G_{sP}}}, \quad (6-24)$$

$$E_l^{LOF} \Big|_N^{\max} = \frac{E_m G_{lP} \phi}{4G_{sP}}, \quad (6-25)$$

$$\rho_{opt}^{HOF} \Big|_N = \sqrt{\frac{4(1-\phi)E_m}{\chi\phi^{1/N}\sqrt{G_{sp}^2 + G_{lp}^2}}}, \quad (6-26)$$

$$E_l^{HOF} \Big|_N^{\max} = \frac{E_m G_{lp} \phi (\phi - 1)^2 \sqrt{G_{sp}^2 + G_{lp}^2}}{\left[G_{lp}^2 (\phi - 1)^2 + \left[(\phi - 1) \left(G_{sp} + \sqrt{G_{sp}^2 + G_{lp}^2} \right) \right]^2 \right]}, \quad (6-27)$$

Interestingly, it is confirmed from Eqs. (6-20) to (6-27) that increasing the hierarchy level N does not increase the loss modulus obtained from either LOF or HOF formulations, but it is able to reduce the aspect ratio leading to the maximum energy loss as well. These findings have been shown in Fig. 6.4(b) earlier. Therefore, based on the recursive formulae and the self-similar hierarchical model, it seems that the structural hierarchy has a minor effect to enhance the damping capacity of the composite. Nonetheless, it is worth noting that this may be partially attributed to that the recursive formulae are based on the principle of homogenization, which is not able to properly account for the stress wave interaction with detailed nano/micro-structures inside the composites. Hence, a finer theoretical or computational model is needed to further clarify the role of hierarchical structure in damping capacity of load-bearing biological materials, which will also be the focus of our next work in the field.

Most of the previous works assumed that load-bearing biological materials like bone and shell are exposed to loadings which are with either zero or rather low frequencies, i.e., static or quasi-static situations. Actually, dynamic loadings acting on load-bearing biological materials are quite common in reality, and the loading frequency may vary from several hertz, for example, the loadings from our daily walking and jogging, to several hundred hertz, for instance, the stress wave loadings from motor vehicle accidents or explosions. Thus, it is important to unveil how the damping property of load-bearing

biological materials varies in response to a broad range of loading frequencies. As discussed above, when the frequency of loading is high, the HOF is needed to correctly characterize the responses of the composites, and hence all the theoretical results shown hereafter are from HOF unless otherwise stated. Fig. 6.5(a) plots the storage and loss shear moduli of the homogeneous protein matrix and Fig. 6.5(b) shows the storage and loss moduli of the single-level composite ($N = 1$) varying with respect to the loading frequency, so that the enhancement in damping property can be clearly seen.

Fig. 6.5 (a) The storage and loss shear moduli of the homogenous protein against the loading frequency, and (b) the plots of storage and loss moduli of the single-level staggered composite ($\rho = 100$) with respect to loading frequency, in comparison with the data points from FEM simulations.

In Fig. 6.5(b), the theoretical predictions are shown together with the FEM results for comparison purpose. The geometrical and material parameters are the same as those in the last example, and the platelet aspect ratio $\rho = 100$ is chosen in the example. First of all, it can be seen that the HOF predictions agree very well with FEM results, and HOF model is validated again.

Secondly, we can see that, as the loading frequency increases, the storage modulus first increases from around 32GPa and then gradually saturates around 42GPa; on the other hand, the loss modulus first increases and then gradually decreases, the maximum loss modulus is around 6GPa and the peak frequency is about 75Hz. Comparing to the protein matrix whose instant shear modulus is about 1GPa, maximum loss shear modulus is about 440MPa and peak frequency is about 1000Hz, the staggered structured composite greatly and simultaneously enhances the stiffness and capacity of energy dissipation while effectively reduces the peak frequency close to that daily loading on human bones.

As discussed earlier, upon loading of relatively high frequency, HOF can provide correct predictions of the dynamics modulus while LOF (Zhang et al., 2015; Zhang and To, 2014) neglecting the higher order terms of loss modulus cannot. Now let us check the variation of storage and loss moduli with loading frequency for self-similar hierarchical composites of different hierarchy number N .

Fig. 6.6 shows the storage and loss moduli of self-similar hierarchical composites (N from 1 to 7 and $\rho=100$) for a wide frequency range of oscillatory loading, with the predictions by HOF, LOF and the FEM results together for comparison. Over the broad range (0-500 Hz) of loading frequency, the predictions of both storage and loss moduli given by HOF are always in good agreement with FEM results. In contrary, the LOF only provides comparable predictions at extremely low frequency (several Hz), and gives distinct under-estimation about the storage modulus and over-estimation about the loss modulus for relatively high frequency.

Additionally, as the hierarchy number increases from 1 to 7, the plot of storage modulus is seen shifting upward, indicating the storage modulus grows faster to

saturation, while the plot of loss modulus is seen lowering down, with the maximum loss modulus slightly being decreased while the peak frequency almost being unchanged. Therefore, the hierarchical design seems mainly to enhance the composite stiffness rather than the capacity of energy dissipation, according to the homogenization-based recursive formulae.

Fig. 6.6 Comparison of the (a) storage and (b) loss modulus of the self-similar hierarchical composites ($\rho = 100$) with different hierarchy number N .

Figs. 6-7(a) and (b) show the effect of the characteristic relaxation time τ of protein on its frequency-dependent storage and loss shear modulus, respectively, while Figs. 6-7(c) and (d) show the corresponding effects on the storage and loss moduli of the single-level staggered composite ($N=1$).

Fig. 6.7 Effects of the characteristic relaxation time of protein on the (a) storage and (b) loss moduli of the homogeneous protein, and its effects on the (c) storage and (d) loss moduli of the single-level staggered composite ($N=1$, reinforcement aspect ratio $\rho=100$).

It is found that, as the characteristic relaxation time of the soft matrix becomes smaller, both the peak frequencies of the protein (see Fig. 6.7(b)) and the composite (see

Fig. 6.7(d)) become higher, and higher frequencies are needed for the storage modulus to increase from its long-term value to the instantaneous value.

However, it is worth noting that, regardless of the homogenous or composite materials, the characteristic relaxation does not affect the maximum value of the storage or loss modulus at all. These phenomena can be easily understood according to Eqs. (6-12) and (6-13).

The protein viscous ratio $g = [G_p(t=0) - G_p(t=\infty)]/G_p(t=0)$, is an important parameter to measure the magnitude of the viscoelasticity.

Figs. 6-8(a) and (b) present the effect of the protein viscous ratio g on the storage and loss moduli of homogeneous protein, respectively, and Figs. 6-8(c) and (d) show the effect of g on the storage and loss moduli of the single-level ($N=1$) staggered composite. For the homogenous protein, the results suggest that increasing g leads to decreasing in storage modulus while increasing in loss modulus; nevertheless, the peak frequency does not change at all because the peak frequency is governed by the protein characteristic relaxation time τ .

For the single-level staggered composite, it is seen that the storage modulus at the frequency of $f=0$ (i.e., the long-term modulus) decreases with the viscous ratio of protein, but the storage modulus reaches its upper limit (the instantaneous modulus) almost at the same frequency. Furthermore, with the protein viscous ratio increasing, the loss modulus of the single-level staggered composite significantly increases and the peak frequency reduces slightly. Hence, choosing matrix materials with large viscous ratio may be an effective strategy to design composites with larger loss modulus, i.e., better capability of dissipating dynamic energy.

Fig. 6.8 Effects of the protein viscous ratio on the (a) storage and (b) loss moduli of the homogeneous protein, and its effects on the (a) storage and (b) loss moduli of the single-level staggered composite ($N = 1$, reinforcement aspect ratio $\rho = 100$).

Fig. 6.9 shows the contour plot of the storage and loss moduli with respect to the aspect ratio of mineral platelet and the loading frequency for the single-level and multi-level (here $N = 7$) staggered structure.

(a)

(b)

(c)

Fig. 6.9 Contour plots of the (a) storage and (b) loss moduli for the single-level and (c) storage and (d) loss moduli of a multi-level ($N = 7$) staggered composites versus varying loading frequency and reinforcement aspect ratio.

It can be seen that, for each loading frequency there is a specific aspect ratio where the loss modulus gets maximized, and the aspect ratio is named as the optimal aspect ratio for the loading frequency; for each aspect ratio there is a specific loading frequency where the loss modulus reaches its maximum, and the frequency is termed as the peak frequency for the aspect ratio of reinforcement.

It is clear that by increasing the frequency, the aspect ratio for the maximum loss modulus decreases. Therefore, to fast damp the dynamic effect of loadings, those structures with smaller aspect ratios are more effective for high loading frequencies while the structures with larger aspect ratios are more effective for relatively low loading frequencies. In Figs. 6-9(b) and (d), the dashed black line shows the variation of peak frequency versus the aspect ratio while the solid black line presents the variation of optimal aspect ratio with respect to the loading frequency. It can be seen more clearly that

larger aspect ratios of hard reinforcements have lower peak frequencies, while higher loading frequencies ask for smaller aspect ratios of hard reinforcements.

Moreover, it is seen that for a single-level staggered structure with very small mineral platelet's aspect ratio, the maximum energy loss occurs at very large frequencies; however, for multi-level staggered structure, the loading frequencies leading to the maximum loss modulus in very small inclusion's aspect ratio are much less than those of the single-level bio-composite. It means that bottom-levels of the staggered architectures of the hierarchical bio-composites are much more effective in damping the dynamic energy than the higher structural levels. These provide useful guidelines for composite selection and design for protection applications to effectively resist external impact loadings. Using the self-similar hierarchical model, the effects of reinforcement aspect ratio and loading frequency are shown in Figs. 6-10(a), (b) and (c), respectively, for the hierarchical composites similar to sea shell (Mineral volume fraction $\phi = 0.95$, Hierarchy number $N = 3$), bone ($\phi = 0.45$, $N = 7$) and mineralized tendon ($\phi = 0.15$, $N = 6$).

Fig. 6.10 Plots of the loss modulus for the self-similar hierarchical structure of (a) shell (Hierarchy number $N = 3$, Mineral volume fraction $\phi = 0.95$), (b) bone ($N = 7$, $\phi = 0.45$) and (c) mineralized tendon ($N = 6$, $\phi = 0.15$).

The corresponding FEM results are also included for verification purpose. It can be found that the maximum loss modulus for sea shell happens with the optimal aspect ratio $\rho = 10$ and the peak frequency $f = 140$ Hz, for bone the optimal aspect ratio $\rho = 20$ and the peak frequency $f = 260$, and for mineralized tendon $\rho = 30$ and the peak frequency $f = 250$.

The predicted optimal aspect ratios of reinforcement for sea shell, bone and mineralized tendon are well comparable to those observed in experiments, about 10 for sea shell (Kamat et al., 2000; Wang et al., 2001) and 20-30 for bone and mineralized tendon (Hassenkam et al., 2004; Johansen and Parks, 1960; Landis et al., 1993; Molnar, 1960; Moradian-Oldak et al., 1991; Ziv and Weiner, 1994). Notice that for these self-similar hierarchical composites, the peak frequencies are also seen slightly going down with the aspect ratio increasing, reminiscent of the single-level staggered composites discussed above. In addition, once again all the plots by our theoretical model are verified well by comparing with FEM results, for the self-similar hierarchical composites here.

6.3 Summary

Load-bearing biological materials are distinguished for their multifunctional characteristics. One of the most important functionalities of them is to fast attenuate stress wave and dynamic energy to protect their inner soft tissues from impact or dynamic loading. This functionality originates from the viscous properties of the biopolymer which is the major component constituting the extraordinary structure of biological materials. Based on a self-similar hierarchical model, the present work has probed the damping properties of typical load-bearing biological materials in relation to the material characteristics of biopolymer, the loading frequency, the geometrical parameters of the reinforcements as well as the hierarchy number. The major contributions and findings include:

- A set of high order formulae were developed for the dynamic modulus of self-similar hierarchical composites, and validated by FEM simulations. Importantly, they can

- correctly depict the frequency-dependent damping properties of biological and bioinspired composites while the low order formulae significantly underestimate the storage modulus and overestimate the loss modulus for dynamic loadings with relatively high frequencies.
- Regardless of a single-level staggered composite or a self-similar hierarchical composite, there is a peak frequency for each aspect ratio of reinforcement, where the loss modulus gets its maximum, i.e., the aspect ratio is most efficient to attenuate the loadings of this frequency. On the other hand, for each loading frequency, we may figure out an optimal aspect ratio of reinforcement where the loss modulus of composites gets maximized. According to our theoretical model and FEM simulations, larger aspect ratios usually work better for lower frequencies, and higher loading frequencies normally ask for smaller aspect ratios.
 - Mixture of hard and elastic mineral reinforcements can significantly enhance the storage and loss moduli of viscoelastic biopolymers simultaneously, and can also reduce the peak frequency and make it closer to those of daily loadings on the load-bearing biological materials. The characteristic relaxation time τ of biopolymer has important effect on the peak frequency of the composites while having little effect on the magnitude of loss modulus. In contrary, the viscous coefficient g has distinct effect on the magnitude of loss modulus of the composites and also has a little effect on the peak frequency.

In summary, the present study provides not only new insights into the damping behaviors of load-bearing biological materials but also useful guidelines for constituent material selection and microstructural design in developing protective composites to resist

dynamic loadings. In addition, it is worth noting that the recursive model developed here is a homogenization-based approach in nature, and thus it is unable to exactly account for the synergistic effects of multiple levels of structural hierarchy in damping dynamic loadings. Developing such a cross-scale hierarchical model to consider the synergistic effects is one of our foci in the future studies in this field.

The results of the current chapter have been published as a research paper (Qwamizadeh et al., 2016a).

Chapter 7 Damping Properties of Hierarchical Load-Bearing Biological Materials with Different Bioinspired Staggered Architectures

Load-bearing biological materials like bone, nacre and tendon are biocomposites with superior mechanical properties to resist static and dynamic loadings and thus have been intensively studied not only for exploring the structure-property relationship but also for developing novel bioinspired materials. Here a theoretical framework was developed to establish the bounds for the storage and loss moduli of the bioinspired staggered composites. The bounds were first verified by the Finite Element Method (FEM). Then, the framework was utilized to study how the storage and loss moduli of the bioinspired composites vary against a series of geometrical and constituent material parameters including the distribution, volume fraction, and aspect ratio of the mineral platelets, as well as the loading frequency. In a recursive way, the bounds were further extended for bioinspired composites with multiple levels of structural hierarchy, and the effect of structural hierarchy was investigated, a theoretical approach was developed to estimate the damping properties of the hierarchical biocomposite at different length scales. Numerical method based on the Finite Element Analysis (FEA) was also carried out to verify the derived elastic bounds for the biocomposite storage and loss moduli. It is found that, in comparison with other structural architectures, stairwise staggering structure generally gives higher loss viscoelasticity. The bounds derived in the present chapter not only add insights into the damping behaviors of load-bearing biological composites but

also provide a useful tool to estimate and help design the dynamic moduli of bioinspired composites.

7.1 Modeling

Load-bearing biological materials like bone, sea shell, tooth, antler and mineralized tendon, in nature can be found as composites of organic and inorganic materials (Currey, 1977; Landis, 1995; Landis et al., 1996b; Meyers et al., 2008; Rho et al., 1998; Weiner and Wagner, 1998). They are well known for their complicated layouts and organizations of stiff mineral reinforcements in soft protein matrices, and thereby have been recruited as a remarkable source of inspiration to develop novel synthetic composites with excellent mechanical properties and extraordinary functionalities. The biological materials usually include several internal levels of structural hierarchy with length scales from a few nanometers to a few centimeters (Kastelic et al., 1978; Menig et al., 2001; Puxkandl et al., 2002; Rho et al., 1998; Screen, 2009; Weiner and Wagner, 1998). The well-organized hierarchical structures of biological materials are believed to be taken into account for their great functionalities and superior properties with respect to their relatively weak constituents. Regardless of the various types of structural hierarchy in different biological materials, all of them have a common feature, that is, the staggered arrangement of stiff mineral inclusions within the organic matrices at nanoscale (Jäger and Fratzl, 2000; Meyers et al., 2008).

Recently, many efforts have been done to study the structure-property relation of biological materials (Gao, 2006; Gao et al., 2003; Jäger and Fratzl, 2000; Lei et al., 2013; Lei et al., 2012; Meyers et al., 2008; Zhang et al., 2011), especially focusing on the

microscale and nanoscale, and a number of physical principles and mechanisms have been proposed to help understand the superior mechanical properties and functions of these materials (Anup et al., 2007; Currey, 1984; Fratzl et al., 2004; Gupta et al., 2004; Gupta et al., 2006; Jackson et al., 1988; Ji and Gao, 2004b; Kamat et al., 2000; Liu et al., 2009; Liu et al., 2006; Nukala and Šimunović, 2005; Weiner and Wagner, 1998). For instance, the staggered arrangement of reinforcements in matrices (also known as “brick-and-mortar” structure) widely seen in load-bearing biological materials is shown synergizing the advantages of both stiff reinforcements and soft matrices while avoiding their weaknesses simultaneously (Ji and Gao, 2004a; Zhang et al., 2010), and thus accounts for the outstanding integrative properties of these biological composites, i.e., achieving the high stiffness, strength and toughness simultaneously. (Jackson et al., 1988; Kotha et al., 2001). The hierarchical architecture bottomed up from nanoscale is another distinct feature in load-bearing biological materials, which has been shown contributing greatly to the fracture toughness and flaw-tolerance capacity of these biological composites at different length scales (Gao, 2006; Gao et al., 2003; Zhang et al., 2011).

In addition, these findings have also driven material scientists and engineers with an attempt to develop biomimetic artificial composites with nano-/micro-structures similar to their biological counterparts. Several successful trials in laboratories have been reported, in which bioinspired synthetic materials were fabricated through the state-of-the-art manufacturing technologies such as the layer-by-layer assembly (Tang et al., 2003), ice-templated method (Munch et al., 2008), and 3D printing (Dimas et al., 2013; Espinosa et al., 2011), and exhibited excellent mechanical properties as expected. In turn, these successes also demonstrate clearly and straightly the superiority of the biological design.

To facilitate and speed up the development of bioinspired composites, several frameworks have also been developed to guide and optimize the bioinspired designs (Begley et al., 2012; Lei et al., 2013). Nevertheless, most of the aforementioned works were focused on static loading conditions, while load-bearing biological materials in reality are mainly exposed to dynamical loadings like external impact (Lakes, 2002; Meyers et al., 2008). For example, loadings on bones are often dynamic arising from jumping, running, sporting and fighting activities as well as impacting from external objects.

Unlike static loadings, dynamic loadings generate stress waves which can transmit the kinetic energy from the loading boundary deep inside and even throughout bone to cause damage to the inside fragile tissue. Traumatic brain injury (TBI) is just a good example which results from stress waves reaching brain but often without breaking skull (Taber et al., 2006; Viano et al., 2006; Zhang et al., 2004). Therefore, it is expected that high loss viscoelasticity should be an important property for these load-bearing biological materials to efficiently damp stress wave and protect their inside soft organs from various external dynamic loads. Exploring the damping behaviors and their relations with the architectures in these load-bearing biological materials not only can add insights into their protection functions, but also can provide useful guidelines for developing high loss viscoelastic composites which are highly desired in many industrial areas including vehicle, military, and etc.

The dynamic energy dissipation and stress wave decay within load-bearing biological materials are attracting more and more research efforts (Qwamizadeh et al., 2016a; Qwamizadeh et al., 2015, 2016b; Zhang et al., 2015; Zhang and To, 2013, 2014). Biopolymers like collagenous proteins in bone usually exhibit significant viscous

characteristic, an important origin of the outstanding damping properties of load-bearing materials. Investigations on tropo-collagen molecules, collagen fiber and related tissues all show that their viscoelasticity can effectively increase the slope of stress-strain curve and damp the elastic stress waves (Puxkandl et al., 2002; Sanjeevi et al., 1982; Shen et al., 2011).

Davies et al. (2014) suggested that the heterogeneous and hierarchical structures of bone-like biological materials may simultaneously localize a broad wavelength of phonons and cut off the energy flow from the process zone to the crack tip, and thereby enhance the fracture toughness. Zhang and To (2013) showed with a multilayered model that a bioinspired hierarchical design may achieve a broadband wave filtering function. They also calculated the figure of merit of the bioinspired composites with a hierarchical staggered microstructure, and indicated that the bioinspired hierarchical design can effectively enhance the figure of merit.

One of our previous work showed that the staggered nanostructures of load-bearing biological materials could effectively damp the stress waves passing through them by reflecting and refracting the stress waves at the hard and soft phase interface (Qwamizadeh et al., 2015). Recently, we also investigated the effects of the protein viscosity and found that there exists two different regimes (structure-dependent regime in presence of protein with low viscoelastic properties and structure-independent regime in presence of protein with high viscoelastic properties) for damping the stress waves in the nanostructured level of biological materials (Qwamizadeh et al., 2016b). Furthermore, our recent study considered with a multi-level staggered model the effects of hierarchical design on the damping properties of biological and bioinspired composites and found that

the hierarchical design can enhance and tune the damping behaviors of these biological and bioinspired composites, i.e., increasing the loss modulus and reducing the peak frequency (Qwamizadeh et al., 2016a). However, it is worth noting that there exist different patterns of staggered architecture in different types of load-bearing biological materials, for example, regular staggering in shell, and stairwise staggering in nanoscale bone, etc (Bonderer et al., 2008; Fratzl et al., 2004; Meyers et al., 2008; Meyers et al., 2006; Rho et al., 1998; Tang et al., 2003).

Fig. 7.1 shows the regular staggering, regular staggering with an offset and stairwise staggering patterns which are seen in natural biological materials. As seen in Fig. 7.1(a), for the regular staggering pattern (also known as “brick-and-mortar structure”), the mineral platelets are regularly shifted by a half of the platelet length L relative to its immediate neighbors.

Similarly, the regular staggering pattern with an offset is almost the same as the regular staggering pattern except that the relative shift between two neighboring platelets is not $0.5L$ but ξL where $0 \leq \xi < 1$ is defined as the offset parameter, as seen in Fig. 7.1(b). One can see that the regular staggering can be regarded as a special case of the regular staggering with an offset and the specific offset parameter is equal to 0.5.

Fig. 7.1(c) shows the stairwise staggering pattern in which a representative periodic unit cell is composed of n aligned platelets and each platelet has an upward shift of L/n relative to its left neighbor. Note that the regular staggering can also be regarded as a special case of the stairwise staggering with $n = 2$.

Fig. 7.1 The illustrations of three typical staggering patterns seen in load-bearing biological materials; (a) regular staggering, (b) regular staggering with an offset and (c) stairwise staggering (Zhang et al., 2010).

A series of questions arise here: why do these different staggered architectures co-exist in natural load-bearing biological composites, what are their respective strengths and weaknesses, which pattern should be chosen when one would like to fabricate bioinspired composites in laboratory?

Answers to these questions are important not only for understanding the structure-property relationships of natural load-bearing biological materials but also for guiding the development of artificial biomimetic materials. To this end, previous works from our group from the static point of view studied the effects of non-uniform or random staggering alignment of the mineral platelets on the mechanical properties of the biocomposite and found that the regular and stairwise staggering can provide better integrative mechanical properties compared to other distributions (Zhang et al., 2010). Furthermore, we also established the lower and upper bounds of the effective longitudinal

modulus of the regular and stairwise staggering composites in order to provide useful estimations and guidelines for the design of relative bioinspired composites (Lei et al., 2013). However, these questions are still unanswered in the perspective of dynamics, especially considering that these load-bearing biological materials are usually exposed to dynamic loadings in reality. Thus, it is necessary to develop a dynamic framework to probe how efficient these biological architectures dissipate dynamic energy and damp the stress waves.

In this chapter, based on the principles of minimum potential energy, minimum complementary energy and correspondence, bounds of the dynamic modulus of typical staggered composites are established to estimate and compare the dynamical properties (storage and loss moduli) of bioinspired composites with different staggered microstructures.

The following part of the chapter shows the mathematical derivation of the upper and lower bounds, and then the bounds are extended in a recursive way to account for the effect of structural hierarchy, and the Finite Element Method (FEM) is also included for verification purposes; the theoretical as well as FEM results are listed and discussed in the future sections to summarize the major findings and conclusive remarks.

7.2 Mathematical and FEM Modeling

For self-completeness, the mathematical derivation of the elastic bounds (statics) is first briefed in this section. Then, the bounds for dynamic modulus are derived based on the principle of correspondence, and the recursive formulae are also obtained with ease. Finally, the FEM models adopted to validate our theoretical models are explained.

7.2.1 Derivation of elastic bounds in static loading conditions

According to theory of elasticity, the principles of minimum potential energy and complementary energy can provide the upper and lower bounds of elastic modulus of a structure, respectively, with an assumed allowable displacement fields and stress fields. Based on these principles, the elastic bounds for the composites with different staggering structures including the regular staggering, the regular staggering with an offset and the stairwise staggering can be derived in a uniform framework, in which the different patterns are characterized by two dimensionless parameters.

Fig. 7.2 schematically shows a composite with the generalized regular staggering pattern of reinforcements, and its representative unit cell, as well as the hypothetical balanced stress field and the kinematically admissible strain fields within the unit cell under an infinitely small longitudinal elongation Δ . L and h_m are the length and thickness of hard platelets, respectively. h_p denotes the thickness of soft matrix layer. The mineral volume fraction can be approximated to $\phi = h_m / (h_p + h_m)$, since the longitudinal gap between neighboring platelets is quite small compared to the platelet length.

In addition, it should be noted that the basic simplifications or assumptions for “tension-shear chain model” (Ji and Gao, 2004a; Zhang et al., 2010) are still utilized in the derivation of the elastic bounds. For instance, since the Young’s modulus of mineral reinforcements is usually 2-3 orders of magnitude higher than that of protein matrices, the mineral inclusions are assumed to mainly resist tensile loading while the protein matrices mainly transfer loading between mineral inclusions via shear stress; the effects of the

stress and deformation in transversal direction are neglected due to the large aspect ratio of mineral platelets.

Fig. 7.2 Schematics of the regular staggering with an offset. (a) The composite with bioinspired microstructure; (b) the representative unit cell (solid box); (c) the assumed kinematically admissible strain field under a longitudinal elongation Δ ; and (d) the assumed balanced stress field under a longitudinal elongation Δ (Zhang et al., 2010).

According to Fig. 7.2(c), the average strain in the mineral inclusions is assumed to be ε_m , and the shear strain in the soft matrix can be obtained from geometrical relations as

$$\begin{Bmatrix} \gamma^U \\ \gamma^L \end{Bmatrix} = \frac{\Delta - L\varepsilon_m}{h_m} \begin{Bmatrix} \xi \\ 1 - \xi \end{Bmatrix}, \quad (7-1)$$

Then, the total strain energy stored in the mineral platelets and the soft matrix can be expressed as $E_m \varepsilon_m^2 h_m L$ and $G_p L (\Delta - L\varepsilon_m)^2 \xi(1 - \xi) / h_p$, respectively, and the total potential energy in the unit cell of the staggered structure can be easily written as

$\Pi = [E_m \varepsilon_m^2 h_m h_p L + G_p L (\Delta - L \varepsilon_m)^2 \xi (1 - \xi)] / h_p$. Finally, minimization of the potential energy with respect to ε_m gives the solution of ε_m . The effective elastic modulus of the composite can be calculated by the average stress over the average strain of the unit cell as

$$E = \left[\frac{1}{\phi E_m} + \frac{(1 - \phi)}{\xi(1 - \xi) \rho^2 \phi^2 G_p} \right]^{-1}, \quad (7-2)$$

where $\rho = L/h_m$ is the aspect ratio of the mineral platelet. As aforementioned, the effective modulus from the principle of minimum potential energy is an upper bound.

According to Fig. 7.2(d), one can readily write out the following relations from the force equilibrium of mineral platelets in the longitudinal direction as

$$\begin{Bmatrix} \tau^U \\ \tau^L \end{Bmatrix} = \tau_{mp} \begin{Bmatrix} \xi \\ 1 - \xi \end{Bmatrix}, \quad (7-3)$$

where τ_{mp} is a parameter awaiting to be determined. From the equilibrium analysis on the mineral platelets, the normal stress distribution with respect to axial coordinate z within the mineral platelets can be obtained immediately, and subsequently the energy stored in the mineral platelets and the total elongation force on the unit cell can be derived as $(4L^3 \xi^2 (1 - \xi)^2 / 3E_m h_m) \tau_{mp}^2$ and $2L \tau_{mp} \xi (1 - \xi)$, respectively. Including the strain energy stored in the protein matrix, $(1 - \phi) h_m L \tau_{mp}^2 \xi (1 - \xi) / \phi G_p$, the complementary energy within the unit cell can be written as

$$\Pi_c = n \left[\frac{4L^3 \tau_{mp}^2 \xi^2 (1 - \xi)^2}{3E_m h_m} + \frac{(1 - \phi) h_m L \tau_{mp}^2 \xi (1 - \xi)}{\phi G_p} - 2L \tau_{mp} \xi (1 - \xi) \Delta \right], \quad (7-4)$$

Minimization of the complementary energy with respect to τ_{mp} gives us the solution of τ_{mp}

. Again, the effective elastic modulus of the composite can be obtained to be as below

$$E = \left[\frac{4}{3\phi E_m} + \frac{(1-\phi)}{\xi(1-\xi)\rho^2\phi^2 G_p} \right]^{-1}, \quad (7-5)$$

Fig. 7.3 Schematics of stairwise staggering structure. (a) Composite with a stairwise staggering microstructure; (b) the representative unit cell (solid box) with periodic number n , (c) the assumed kinematically admissible strain field under a longitudinal elongation Δ ; and (d) the assumed balanced stress field under a longitudinal elongation Δ (Zhang et al., 2010).

Note that the effective modulus derived from the principle of minimum complementary energy above is a lower bound.

Following the similar process, the upper and lower bounds of the effective modulus of the stairwise staggered composites in Fig. 7.3 can be derived with ease. The assumed strain and stress fields can be written as

$$\begin{Bmatrix} \gamma^U \\ \gamma^L \end{Bmatrix} = \frac{\Delta - L\varepsilon_m}{h_m} \begin{Bmatrix} \frac{1}{n} \\ \frac{n-1}{n} \end{Bmatrix}, \quad \begin{Bmatrix} \tau^U \\ \tau^L \end{Bmatrix} = \tau_p \begin{Bmatrix} \frac{1}{n} \\ \frac{n-1}{n} \end{Bmatrix}, \quad (7-6)$$

And, the upper and lower bounds are, respectively:

$$E = \left[\frac{1}{\phi E_m} + \frac{n^2(1-\phi)}{(n-1)\rho^2\phi^2 G_p} \right]^{-1}, \quad (7-7)$$

$$E = \left[\frac{n(3n-4)}{3(n-1)^2\phi E_m} + \frac{n^2(1-\phi)}{(n-1)\rho^2\phi^2 G_p} \right]^{-1}, \quad (7-8)$$

Table 7.1 The dimensionless parameters for the typical staggering patterns as well as the layered structure of load-bearing biological materials.

$E = \left[\frac{\alpha}{\phi E_m} + \frac{\beta(1-\phi)}{\rho^2\phi^2 G_p} \right]^{-1}$	Upper bound		Lower bound	
	α	β	α	β
Regular staggering	1	4	4/3	4
Offset regular staggering	1	$1/\xi(1-\xi)$	4/3	$1/\xi(1-\xi)$
Stairwise staggering	1	$n^2/(n-1)$	$n(3n-4)/3(n-1)^2$	$n^2/(n-1)$
Continuous layering	1	-	1	-

The upper and lower bounds can be reformatted into a united form, respectively as

$$E = \left[\frac{\alpha}{\phi E_m} + \frac{\beta(1-\phi)}{\rho^2\phi^2 G_p} \right]^{-1}, \quad (7-9)$$

where α and β are two dimensionless parameters, dependent on the type of bound (upper or lower) and staggering pattern.

Table 7.1 summarizes the expressions of α and β for the upper and lower bounds of different types of staggering patterns. The α and β for the continuous layering structure are also provided for comparison purposes, as it is known that the layered structure corresponds to the Voigt limit (an upper limit).

7.2.2 Derivation of the bounds of dynamic elasticity

Generally the damping behavior of a material can be measured by its dynamic modulus $E^*(\omega) = E_s(\omega) + jE_l(\omega)$, where $j = \sqrt{-1}$, the real part E_s is the storage modulus, the imaginary part E_l is the loss modulus, and $\omega = 2\pi f$ is the angular frequency of harmonic loadings, with f is the loading frequency. Note that the dynamic modulus as well as its real and imaginary parts are all frequency dependent. The storage modulus and loss modulus, respectively, measure the energy stored and dissipated by the material. The damping mechanism in these load-bearing biological materials originates from not only the viscoelasticity of biopolymer matrices (like protein) but also the staggered organization of two highly mismatched constituent materials (with high stress wave impedance ratio) (Sanjeevi et al., 1982; Shen et al., 2011; Svensson et al., 2010).

According to the correspondence principle, the dynamic modulus of a composite has the same form as the elastic modulus, with only the elastic moduli of viscoelastic constituents being replaced with the corresponding complex moduli. Thus, the dynamic modulus of the staggered composites can be formulated as

$$E^*(\omega) = \left[\frac{\alpha}{\phi E_m} + \frac{\beta(1-\phi)}{\rho^2 \varphi^2 G_p^*(\omega)} \right]^{-1}, \quad (7-9)$$

where $G_p^*(\omega) = G_{sp}(\omega) + jG_{lp}(\omega)$ is the frequency dependent complex shear modulus of the viscoelastic biopolymer (Qwamizadeh et al., 2016a). The mineral constituent is still considered to be purely elastic. Performing mathematical operations to separate the real and imaginary parts, the storage and loss moduli of the staggered structures can be obtained as below

$$E_s = \frac{\rho^2 \phi^2 E_m^3 [\alpha \rho^2 \phi (G_{sP}^2 + G_{lP}^2) + \beta (1 - \phi) E_m G_{sP}] (G_{sP}^2 + G_{lP}^2)}{[\alpha \rho^2 \phi E_m (G_{sP}^2 + G_{lP}^2) + \beta (1 - \phi) E_m^2 G_{sP}]^2 + [\beta (1 - \phi) E_m^2 G_{lP}]^2}, \quad (7-10)$$

$$E_l = \frac{\beta \rho^2 \phi^2 (1 - \phi) G_{lP} E_m^4 (G_{sP}^2 + G_{lP}^2)}{[\alpha \rho^2 \phi E_m (G_{sP}^2 + G_{lP}^2) + \beta (1 - \phi) E_m^2 G_{sP}]^2 + [\beta (1 - \phi) E_m^2 G_{lP}]^2}, \quad (7-11)$$

It is obvious that Eqs. (7-10) and (7-11) for very large aspect ratio of the platelet will be converted to $E_s \approx \phi E_m / \alpha$ and $E_l \approx 0$, respectively, which are similar to those of the continuous layering structure by choosing the coefficient α from the upper bound solution. It can be seen that the layering pattern, in comparison with the staggering patterns, is not effective in exploiting the capacity of the biocomposite to attenuate the dynamic energy in the longitudinal direction, since the continuous layers of elastic mineral provide channels for stress wave passing through with little energy dissipation. This provides a new perspective to understand why natural load-bearing biological materials prefer the staggered patterns rather than the layered one.

To investigate the effect of structural hierarchy, it is convenient to take a self-similar hierarchical structure as an example. The effective modulus of the self-similar hierarchical composites (refer to Fig. 6.1) at different levels can be obtained in a recursive fashion, similar to the recursive stiffness formulation that was used in the previous chapter for regular staggering pattern. Consequently, the general recursive formulae of effective modulus for any staggering pattern can be written as

$$E_{(i)} = \left[\frac{\alpha}{\phi E_{(i-1)}} + \frac{\beta (1 - \phi)}{\rho^2 \phi^2 G_P} \right]^{-1} \quad i = 1, 2, 3, \dots, N \quad (7-12)$$

where ϕ is related to the mineral volume fraction of the hierarchical composite, ϕ , by $\phi = \sqrt[N]{\phi}$.

Substitute the dynamic tensile and shear moduli $E_{(i-1)}^*(\omega) = E_{s(i-1)}(\omega) + jE_{l(i-1)}(\omega)$ and $G_{P(i-1)}^*(\omega) = G_{sP(i-1)}(\omega) + jG_{lP(i-1)}(\omega)$ into Eq. (7-12), the effective dynamic modulus of the self-similar hierarchical composite can be calculated according to the following recursive formulae

$$E_{(i)}^*(\omega) = \left[\frac{\alpha}{\phi E_{(i-1)}^*(\omega)} + \frac{\beta(1-\phi)}{\rho^2 \phi^2 G_{P(i-1)}^*(\omega)} \right]^{-1} \quad i = 1, 2, 3, \dots, N \quad (7-13)$$

Doing mathematical operations to separate the real and imaginary parts, the storage and loss moduli of the hierarchical composite can be got in a bottom-up sequence as

$$E_{s(i)} = A_{(i)} J_{(i)} / (C_{(i)}^2 + D_{(i)}^2), \quad (7-14)$$

$$E_{l(i)} = B_{(i)} J_{(i)} / (C_{(i)}^2 + D_{(i)}^2), \quad (7-15)$$

where $i = 1, 2, 3, \dots, N$, and

$$A_{(i)} = \phi^2 \rho^2 [\phi \rho^2 \alpha (E_{s(i-1)} G_{sP(i-1)}^2 + E_{s(i-1)} G_{lP(i-1)}^2) + \beta(1-\phi)(G_{sP(i-1)} E_{s(i-1)}^2 + G_{sP(i-1)} E_{l(i-1)}^2)], \quad (7-16)$$

$$B_{(i)} = \phi^2 \rho^2 [\phi \rho^2 \alpha (E_{l(i-1)} G_{sP(i-1)}^2 + E_{l(i-1)} G_{lP(i-1)}^2) + \beta(1-\phi)(G_{lP(i-1)} E_{s(i-1)}^2 + G_{lP(i-1)} E_{l(i-1)}^2)], \quad (7-17)$$

$$C_{(i)} = [\phi \rho^2 \alpha (E_{s(i-1)} G_{sP(i-1)}^2 + E_{s(i-1)} G_{lP(i-1)}^2) + \beta(1-\phi)(G_{sP(i-1)} E_{s(i-1)}^2 + G_{sP(i-1)} E_{l(i-1)}^2)], \quad (7-18)$$

$$D_{(i)} = [\phi \rho^2 \alpha (E_{l(i-1)} G_{sP(i-1)}^2 + E_{l(i-1)} G_{lP(i-1)}^2) + \beta(1-\phi)(G_{lP(i-1)} E_{s(i-1)}^2 + G_{lP(i-1)} E_{l(i-1)}^2)], \quad (7-19)$$

$$J_{(i)} = (E_{s(i-1)}^2 + E_{l(i-1)}^2)(G_{sP(i-1)}^2 + G_{lP(i-1)}^2), \quad (7-20)$$

The coefficients α and β can be calculated from Table 1 for the upper bound and lower bound solutions. For example, taking α and β for the upper bound of the regular staggering from Table 7.1, the effective storage and loss moduli for a single-level composite are as below

$$E_{s(1)} = \frac{\rho^4 \phi (G_{sP}^2 E_m + E_m G_{lP}^2) + 4\rho^2 (1 - \phi) E_m^2 G_{sP}}{[\rho^2 G_{sP} - 4(1 - 1/\phi) E_m]^2 + [\rho^2 G_{lP}]^2}, \quad (7-21)$$

$$E_{l(1)} = \frac{4\rho^2 (1 - \phi) E_m^2 G_{lP}}{[\rho^2 G_{sP} - 4(1 - 1/\phi) E_m]^2 + [\rho^2 G_{lP}]^2}, \quad (7-22)$$

Similarly, for a multi-level regular staggering, the storage and loss moduli for the upper bound solution can be obtained as

$$E_{s(i)} = \frac{\rho^4 \phi (G_{sP}^2 E_{s(i-1)} + E_{s(i-1)} G_{lP}^2) + 4\rho^2 (1 - \phi) (E_{s(i-1)}^2 G_{sP} + G_{sP} E_{l(i-1)}^2)}{[\rho^2 G_{sP} - 4(1 - 1/\phi) E_{s(i-1)}]^2 + [\rho^2 G_{lP} - 4(1 - 1/\phi) E_{l(i-1)}]^2}, \quad (7-23)$$

$$E_{l(i)} = \frac{\rho^4 \phi (E_{l(i-1)} G_{sP}^2 + E_{l(i-1)} G_{lP}^2) + 4\rho^2 (1 - \phi) G_{lP} (E_{s(i-1)}^2 + E_{l(i-1)}^2)}{[\rho^2 G_{sP} - 4(1 - 1/\phi) E_{s(i-1)}]^2 + [\rho^2 G_{lP} - 4(1 - 1/\phi) E_{l(i-1)}]^2}, \quad (7-24)$$

Since the mineral inclusions at the first level are purely elastic, $E_{s(0)}(\omega) = E_m$ and $E_{l(0)}(\omega) = 0$. As is seen, Eqs. (7-21 to 7-24) are exactly the same as those for the regular staggering pattern in the previous chapter.

It should be noted that the aspect ratio in which the loss modulus has its maximum value can be obtained based on the recursive formulations shown in Eqs. (7-14 to 7-20). It can be seen that for the primary level ($N = 1$) the optimal aspect ratio as well as the maximum loss modulus can be obtained as below

$$\left. \frac{\partial E_l}{\partial \rho} \right|_{N=1} = 0 \rightarrow \rho_{opt} \Big|_{N=1} = \sqrt{\frac{\beta(1 - \phi) E_m}{\alpha \phi \sqrt{G_{sP}^2 + G_{lP}^2}}}, \quad (7-25)$$

$$E_l \Big|_{N=1}^{\max} = \frac{E_m G_{lP} \phi (\phi - 1)^2 \sqrt{G_{sP}^2 + G_{lP}^2}}{\alpha \left[G_{lP}^2 (\phi - 1)^2 + \left[(\phi - 1) \left(G_{sP} + \sqrt{G_{sP}^2 + G_{lP}^2} \right) \right]^2 \right]}, \quad (7-26)$$

Similarly, using the same approach, it is possible to calculate the optimal aspect ratio and the maximum loss modulus of the staggered structure at N^{th} hierarchical level as below

$$\rho_{opt}|_N = \sqrt{\frac{\beta(1-\phi^{1/N})E_m(\alpha^{N-1} + \alpha^{N-2}\phi^{1/N} + \dots + \alpha\phi^{N-2/N} + \phi^{N-1/N})}{\alpha^N \phi^{1/N} \sqrt{G_{sP}^2 + G_{lP}^2}}}, \quad (7-27)$$

$$E_l|_N^{\max} = \frac{E_m G_{lP} \phi (\phi - 1)^2 \sqrt{G_{sP}^2 + G_{lP}^2}}{\alpha^N \left[G_{lP}^2 (\phi - 1)^2 + \left[(\phi - 1) (G_{sP} + \sqrt{G_{sP}^2 + G_{lP}^2}) \right]^2 \right]}, \quad (7-28)$$

7.2.3 FEM model and validation of the elastic bounds

ABAQUS/CAE was used to carry out FEM simulations. A plane stress condition was prescribed to the FEM models. The element sizes were selected to be fine enough to avoid mesh sensitivity issue. At the primary level, a linear elastic material model was adopted for the hard inclusions while a linear viscoelastic model for the soft matrix.

At higher levels, for example Level i , $i > 1$, a linear viscoelastic material model with effective parameters extracted from FEM simulations on Level $i-1$ was used for the reinforcements. For each hierarchical level, a representative unit cell with periodic boundaries was modeled to represent the composite of infinitely large size. A harmonic small elongation $\delta = \Delta e^{j\omega t}$ with amplitude $\Delta = 0.001 L$ was applied to the FEM model in longitudinal direction.

7.3 Results and discussion

In this chapter, given the typical geometrical and constituent material parameters $\phi = 0.45$, $E_m = 100\text{GPa}$, $\nu_m = 0.27$ (the Poisson's ratio) for the mineral inclusions and $G_{0P} = 1\text{GPa}$, $\nu_p = 0.4$ (the Poisson's ratio), $g = g_1 = 0.9$ and $\tau = \tau_1 = 0.0002\text{s}$, for the time-dependent shear relaxation behavior of the soft matrix

$$G_p(t) = G_{0p} \left[1 - \sum_{m=1}^M g_m (1 - e^{-t/\tau_m}) \right] \text{ with just one term } (M = 1) \text{ in the primary level, the}$$

results have been provided.

Fig. 7.4 shows the plots of the storage and loss moduli bounds of different single-level staggered distributions varying against the mineral platelet aspect ratio at low ($f = 1$ Hz) and high ($f = 100$ Hz) loading frequencies.

(a)

(b)

(c)

(d)

Fig. 7.4 Comparison of the theoretical bounds of storage (a) and loss (b) modulus with FEM results for low loading frequency ($f = 1$ Hz); and (c) and (d) are for high loading frequency ($f = 100$ Hz).

To verify the theoretical bounds, FEM results (scattered data points) are also included in the figures. The LB and UB in the figure legends refer to the lower bound and upper bound shown by thick and thin lines, respectively. As it is seen, the FEM results are well sandwiched by the theoretical bounds for all these staggered patterns and loading frequencies, and hence our theoretical model is well validated.

Regardless the staggering pattern and loading frequency, as the aspect ratio of mineral platelet increases, the storage modulus first goes up and then gradually saturates (see Fig. 7.4(a) and (c)) while the loss modulus first increases and then decreases after a maximum (see Fig. 7.4(b) and (d)), indicating that there is an optimal aspect ratio of mineral platelet generating the maximum loss modulus for each staggering pattern. According to the FEM results, it can also be found that there exist different levels of storage and loss moduli for different staggered architectures with the same mineral volume fraction. With the same aspect ratio of mineral platelet, Fig. 7.4(a) shows that under the low loading frequency (e.g., 1 Hz) the regular staggering (the offset $\xi = 0.5$) gives the largest storage modulus, the offset regular staggering ($\xi = 0.9$) gives the smallest, while those of the stairwise staggering (e.g., $n = 6$ and 8) lie between of them.

However, when the aspect ratio of mineral platelet is large (for instance, $\rho > 150$), the storage modulus by the stairwise staggering (e.g., $n = 6$) gradually catches up and surpasses that of the regular staggering, especially under the high loading frequency (e.g., 100 Hz), see Fig. 7.4(c). Regarding the loss modulus varying against the mineral platelet aspect ratio in Fig. 7.4(b) and (d), we can see that the results of regular staggering reaches its peak first, which indicates its optimal aspect ratio for maximum loss modulus is the smallest among these typical examples. However, the maximum value of loss modulus for the staggering pattern is significantly lower than those of stairwise staggering patterns, and even slightly smaller than that of the offset regular staggering. Therefore, with relatively small aspect ratio of mineral platelet, the regular staggering tends to give higher storage and loss moduli while the stairwise staggering would result in higher storage and loss moduli with relatively large aspect ratio of mineral platelet. It is also worth noting

that the bound gaps for both the storage and loss moduli are narrowing down as the period n of stairwise staggering pattern is increasing ($n = 2$ for the regular staggering pattern).

With Fig. 7.5 the dynamic moduli of a single-level offset staggering are investigated with the varying offset parameter ξ . All the plots in Fig. 7.5 are symmetrical about $\xi = 0.5$ due to the reflection relation between the structures ξ and $1-\xi$. Fig. 7.5(a) and (b), respectively, plot the storage and loss modulus bounds of a single-level offset staggering pattern changing over the offset parameter for different loading frequencies, where a typical mineral platelet aspect ratio $\rho = 100$ is adopted as an example.

It can be found from Fig. 7.5(a) that the maximum storage modulus occurs at $\xi = 0.5$ (i.e., the regular staggering), but there is a quite large range around $\xi = 0.5$ achieving the storage modulus close to the maximum value. In contrary, with $\rho = 100$, the regular staggering pattern ($\xi = 0.5$) leads to a local minimum value of loss modulus, and the offset regular staggering with $\xi = 0.08$ and 0.92 give the maximum loss modulus. In addition, both the predicted storage and loss moduli under the loading frequency $f = 100$ Hz are larger than those under $f = 1$ Hz, and the gap between the upper and lower bounds are also a little larger.

Fig. 7.5(c) and (d), respectively, plot the storage and loss modulus bounds of a single-level offset staggering pattern changing over the offset parameter for different aspect ratio of hard inclusion, with the loading frequency $f = 1$ Hz kept as a constant.

It can be seen that the basic trends of the storage and loss moduli in Fig. 7.5(c) and (d) varying with the offset parameter are, respectively, the same with those in Fig. 7.5(a) and (b) except that the loss modulus reaches its maximum at $\xi = 0.5$ for the relatively

small aspect ratio of hard inclusion, for instance $\rho = 20$ and 50 (see Fig. 7.5(d)). It is also distinguished from Fig. 7.5(c) that the larger is the mineral platelet aspect ratio, the more both upper and lower bounds of the storage modulus are shifted upward. Interestingly, Fig. 7.5(d) shows that the shape of plots changes distinctly as the aspect ratio of mineral platelet increases beyond 50, with the maximum loss modulus moves sideways from the middle region.

Fig. 7.5 Plot of the (a) storage and (b) loss modulus of an offset regular staggering against the offset parameter ξ for different frequencies; (c) and (d) are for different aspect ratios.

Fig. 7.6 Plots of the (a) storage and (b) loss modulus of a single-level stairwise staggering pattern over the period n for different loading frequencies; plots of the (c) storage and (d) loss modulus over the period n for different aspect ratios of mineral platelet.

This is consistent with our previous findings in Fig. 7.4 that the regular staggering ($\xi = 0.5$) gives the larger loss modulus if the aspect ratio of mineral platelet is relatively small; otherwise the offset regular staggering or stairwise staggering provides the maximum loss modulus. It is also worth noting that, as the mineral platelet aspect ratio increases from 20 to 100, the plots of loss modulus are generally shifted upward, but they

turn to lower down as the aspect ratio is beyond 100, confirming again that there is an optimal aspect ratio for the maximum loss modulus of each staggering pattern.

Fig. 7.7 Plots of the (a) storage and (b) loss modulus of the offset staggering with different offset parameters; and the (c) storage and (d) loss moduli of the stairwise staggering with different period n .

Now let us study how the period n of single-level stairwise staggering pattern affects the storage and loss moduli of the staggered composites.

Fig. 7.6 shows the storage and loss moduli of a single-level stairwise staggering pattern over the period n for different loading frequencies and hard inclusion's aspect ratios. The plots show that both the storage and loss moduli first increase to a peak and then gradually

decrease. As observed above, it can also be seen here that for small aspect ratio of the hard inclusions, the maximum value for both storage and loss moduli happens at $n = 2$, i.e., the regular staggering pattern, while for large aspect ratios of the mineral platelets, the maximum value of both storage and loss moduli are obtained from the stairwise staggering with the period $n > 2$.

Specifically, the optimal period n is around 2 for the aspect ratio $\rho = 20$ and 50, 8 for $\rho = 100$, and 18 for $\rho = 150$. Note that the values of storage and loss moduli are significantly different in response to the different loading frequencies, but the optimal period for each aspect ratio of mineral platelet seems independent of the loading frequency.

To probe into the loading frequency dependence of the storage and loss moduli of different staggering patterns, in Fig. 7.7 the storage and loss moduli of several typical staggering patterns are plotted against the loading frequency.

First of all, both the storage and loss moduli of these staggering structures are frequency dependent. The storage modulus is always increasing with the loading frequency while the loss modulus first increases and then decreases after a peak. Therefore, there is a peak frequency for each staggered composite to dissipate dynamic energy most efficiently (due to the maximum loss modulus). In another word, the peak frequency of a structured composite is just the ideally targeted loading frequency for it to damp.

It can also be found that the peak frequency increases with the offset parameter ξ increasing from 0.5 to 0.9. The same trend can be observed for the stairwise staggering with the period n increasing from 2 to 10. This should be attributed to the characteristic

overlap length decreasing with respect to the increasing ξ and n with a constant aspect ratio of hard inclusion.

According to Eqs. (7-14 to 7-20), the storage and loss moduli of a hierarchical composite with an arbitrary hierarchy number N can be obtained, provided that the geometrical and constituent material parameters are known. If the structural organization and relative geometrical parameters are utterly the same through all the hierarchical levels, the hierarchical composite is referred as the self-similar hierarchical composite (Gao, 2006). If the structural organization is the same but the relative geometrical parameters are different, the hierarchical composite is named as the quasi-self-similar hierarchical composite (Zhang et al., 2011).

For simplicity, here self-similar hierarchical composites are utilized to demonstrate the effect of the level number of structural hierarchies. Note that the constituent materials and their total volume fraction are kept the same in all the hierarchical materials studied here. In another word, the hierarchical number N is the sole variable.

The storage and loss moduli of the hierarchical composites with different hierarchy number N have been plotted in Fig. 7.8 for the offset staggering $\xi = 0.9$. Figs. 7-8(a) and (b), respectively, show the curves of the storage and loss moduli versus the reinforcement aspect ratio for the loading frequency $f = 1$ Hz. Figs. 7-8(c) and (d) present the curves of the storage and loss moduli with respect to the loading frequency for the reinforcement aspect ratio $\rho = 50$. First of all, we can see that the basic trends of these curves of hierarchical composites are, respectively, similar to their counterparts of the single-level composites.

Fig. 7.8 The plots of (a) the storage and (b) loss modulus versus the reinforcement aspect ratio of the hierarchical composite of offset regular staggering for different hierarchy number N ; (c) the storage and (d) loss modulus versus the loading frequency. FEM results for $N = 7$ are also included.

Furthermore, we can see that the plots of upper bound generally move upward while those of lower bound usually move downward as the hierarchy number N increases from 2 to 7.

To some extent, the enlarging gap between upper and lower bounds with N should be attributed to the accumulation effect of the recursive formulae Eqs. (7-14) and (7-15). Moreover, as the hierarchy number increases, the optimal aspect ratio of reinforcements

and the peak frequency of targeted loadings would decrease to the ranges of practical interest.

Fig. 7.9 The plots of (a) the storage and (b) loss modulus versus the reinforcement aspect ratio of the hierarchical composite of stairwise staggering for different hierarchy number N ; (c) the storage and (d) loss modulus versus the loading frequency. FEM results for $N=7$ are also included.

Fig. 7.10 Contours of the lower bound (a) and upper bound (b) of the storage modulus for the single-level offset staggering composites versus varying loading frequency and offset parameter; and the lower bound (c) and upper bound (d) storage modulus for the hierarchical ($N = 7$) offset staggering composites versus varying loading frequency and offset parameter.

As it is well known that the aspect ratio of mineral crystals and the peak frequency of biopolymers at nanoscale are both pretty large while the aspect ratio of reinforcement available and the loading frequency at macroscale are usually small, hence the hierarchical design is critically important for biological materials to achieve their

protection function and efficiently damp the dynamic loadings in their practical working environment.

For comparison purposes, FEM results for $N = 3$ and 7 are also included, from which we can also see that the larger N corresponds to smaller optimal aspect ratio of reinforcement and lower peak frequency. Fig. 7.9 shows the effects of structural hierarchy on the storage and loss moduli of a stairwise staggering pattern with period $n = 8$. The findings here are similar to those explained in Fig. 7.8. However, it can be seen that for relatively small aspect ratio of reinforcement (e.g., no larger than 50) and relatively low loading frequency (e.g., no larger than 100 Hz), the curves of storage modulus for different hierarchy number N in Fig. 7.9 are closer to each other than those in Fig. 7.8, indicating that the storage modulus is not so sensitive to the hierarchy number. The finding and conclusion applies to the loss modulus as well. Further, it can be inferred that for the hierarchical composites of stairwise staggering with relatively small aspect ratio of reinforcement and low loading frequency, a large number of structural hierarchies is unnecessary from mechanics point of view.

Up to now, with the theoretical model of bound we have studied the effects of staggering pattern, reinforcement aspect ratio, loading frequency, hierarchy number and etc. For a composite designer to design a high loss composite, an interesting question is what staggering pattern one should choose for a targeted loading given the constituent materials and volume fractions, and etc. Further, it is important to know how much the designed composite is able to store the dynamic energy. To help answer these questions, the contours of Figs. 7-10 to 7-17 are presented to illustrate how our theoretical model can help the design of efficient composites.

Fig. 7.11 Contours of the lower bound (a) and upper bound (b) of the loss modulus for the single-level offset staggering composites versus varying loading frequency and offset parameter; and the lower bound (c) and upper bound (d) loss modulus for the hierarchical ($N = 7$) offset staggering composites versus varying loading frequency and offset parameter.

Fig.7-10 and Fig 7-11 show the contours of storage and loss moduli of the biocomposite with an offset for a single-level and multi-level staggered structure ($N = 7$). As can be seen in Fig. 7.10, the storage modulus shows the same trend for both lower and upper bound solutions; however, the results obtained from the UB solution are larger than

the LB solution. Similarly, Fig. 7.12 shows the same findings for stairwise staggered structure.

Fig. 7.11 is aimed to help determine which offset regular staggering (defined by ξ) should be chosen for a targeted loading frequency, and Fig. 7.13 is for determining which stairwise staggering (defined by n) is best for a targeted loading frequency. Note that only ξ between 0 and 0.5 is shown in Fig. 7.11 due to the reflection relationship between the structures ξ and $1-\xi$. Figs. 7-11(a) and (b), respectively, show the contours of the lower and upper bound of the loss modulus for a single-level offset regular staggering. Note that the reinforcement aspect ratio $\rho = 100$ is chosen as an example. The ordinate is the offset parameter ξ , the abscissa is the targeted loading frequency, and the color map denotes the lower bound of loss modulus. Thus, for a given combination of (ξ, f) , it is convenient to get the lower and upper bounds, respectively, from the contours in Fig. 7.11(a) and (b), and an estimated range of the loss modulus can be obtained immediately for the staggered composite working under the loading frequency.

To facilitate the high loss composite design, the optimal offset parameter ξ is plotted as a function of loading frequency f , see the solid lines, and the targeted loading frequency f is also plotted as a function of offset parameter ξ , see the dotted lines. Actually, they are two ridges on the contour. Therefore, the optimal design of offset regular staggering can be determined based on the solid lines, and the targeted peak frequency can be known on basis of the dotted lines; at the same time, their loss moduli can also be estimated conveniently. Further checking the lines, a general trend can be spotted that the larger ξ matches the smaller f for achieving high loss modulus.

Fig. 7.12 Contours of the lower bound (a) and upper bound (b) of the storage modulus for the single-level stairwise staggering composites versus varying loading frequency and stairwise parameter; and the lower bound (c) and upper bound (d) storage modulus for the hierarchical ($N = 7$) stairwise staggering composites versus varying loading frequency and stairwise parameter.

Figs. 7-11(c) and (d) present the contours of the lower and upper bounds of the loss modulus for multi-level hierarchical composites ($N = 7$) with an offset regular staggering, respectively. We can find that all the remarks for the single-level case still hold true here. The point worth noting is that here the line of optimal design (solid) and the line of

targeted peak frequency (dotted) are both shifted to the left comparing to their counterparts in the single-level case, again suggesting that the introduction of structural hierarchy can effectively reduce the targeted peak frequency.

Fig. 7.13 Contours of the lower bound (a) and upper bound (b) of loss modulus for the single-level stairwise staggering composites versus varying loading frequency and the period; and the lower bound (c) and upper bound (d) of loss modulus for the hierarchical ($N = 7$) stairwise staggering composites versus varying loading frequency and the period.

Similar to Fig. 7.11, Fig. 7.13 shows the contours of the lower and upper bounds of the loss modulus for the stairwise staggered composites, and thus the ordinate as the design variable is replaced with the period n of stairwise staggering. The reinforcement aspect ratio is still fixed to be $\rho = 100$. Then, for single-level stairwise staggering composites, given a combination of (n, f) , it is convenient to get the lower and upper bounds, respectively, from the contours in Fig. 7.13(a) and (b), and an estimated range of the loss modulus can be obtained immediately.

To facilitate the high loss composite design, the line (solid) of optimal period n is plotted against loading frequency f , while the line (dotted) of targeted loading frequency f is plotted against the period n . Hence, the best choice of stairwise staggering can be determined based on the solid lines, and the targeted peak frequency can be obtained on basis of the dotted lines; at the same time, their loss moduli can also be estimated conveniently. Furthermore, it can be found that here the stairwise staggering of larger n is better to damp the dynamic loading of higher f .

Figs. 7-13(c) and (d) present the contours of the lower and upper bounds of the loss modulus for 7-level hierarchical composites with a stairwise staggering, respectively. The remarks for the single-level case still hold true here. It can also be observed that the introduction of structural hierarchy effectively reduces the targeted peak frequency.

To study the effects of the aspect ratio of the mineral platelets on the storage and loss moduli of the biocomposite, Fig. 7.14 and Fig. 7.15 show the contour plots of the storage and loss moduli with respect to the aspect ratio of mineral platelet and the loading frequency for the single-level and multi-level (here $N = 7$) staggered structure with an offset.

Fig. 7.14 Contour plots of the lower bound (a) and upper bound (b) of storage modulus for the single-level offset staggering composites versus varying loading frequency and the platelet's aspect ratio; and the lower bound (c) and upper bound (d) of storage modulus for the hierarchical ($N = 7$) offset staggering composites versus varying loading frequency and the platelet's aspect ratio.

It should be noted that the offset parameter $\xi = 0.9$ is chosen here as an example. As can be seen, Figs. 7-14(a) and (b) present the contours of the lower and upper bounds of

the storage modulus for single-level hierarchical composites with an offset regular staggering, respectively.

Fig. 7.15 Contour plots of the lower bound (a) and upper bound (b) of loss modulus for the single-level offset staggering composites versus varying loading frequency and the platelet's aspect ratio; and the lower bound (c) and upper bound (d) of loss modulus for the hierarchical ($N = 7$) offset staggering composites versus varying loading frequency and the platelet's aspect ratio.

Similarly, 7-14(c) and (d) show the contour plots of the storage modulus for 7-level hierarchical composites for lower and upper bound solutions, respectively. It is obvious

that the storage modulus obtained from the lower bound solution is less than those calculated from the upper bound solution.

Fig. 7.16 Contour plots of the lower bound (a) and upper bound (b) of storage modulus for the single-level stairwise staggering composites versus varying loading frequency and the platelet's aspect ratio; and the lower bound (c) and upper bound (d) of storage modulus for the hierarchical ($N = 7$) stairwise staggering composites versus varying loading frequency and the platelet's aspect ratio.

Fig. 7.15 helps determine which offset regular staggering feature size (aspect ratio ρ) should be chosen for a targeted loading frequency. It can be seen that, for each loading

frequency there is a specific aspect ratio at which the loss modulus gets maximized. Interestingly, for larger loading frequencies, regular offset staggering structures with smaller platelet's aspect ratios contribute to the maximum energy loss.

Fig. 7.17 Contour plots of the lower bound (a) and upper bound (b) of loss modulus for the single-level stairwise staggering composites versus varying loading frequency and the platelet's aspect ratio; and the lower bound (c) and upper bound (d) of loss modulus for the hierarchical ($N = 7$) stairwise staggering composites versus varying loading frequency and the platelet's aspect ratio.

Further, it can be seen from Fig. 7.15(c) and (d) that for a multi-level (here $N = 7$) staggered structure, the targeted peak frequency will be decreased by considering the structural hierarchy within the model.

Similar to Fig. 7.14, Fig. 7.16 compares the contour plots of the storage modulus of the stairwise staggering pattern for both lower and upper bound solutions versus varying loading frequency and mineral platelet's aspect ratio, respectively. Again it can be seen that the contours of the storage modulus are similar for both the lower and upper bound solutions.

Finally, similar to Fig. 7.15, Fig. 7.17 is for determining which feature size (aspect ratio ρ) of the stairwise staggering pattern is efficient for a targeted loading frequency. As shown in Fig. 7.17(a) and (b), for a single-level stairwise staggered structure there exists a specific aspect ratio at which the loss modulus is maximum. Moreover, it can be found that here the stairwise staggering patterns with smaller platelet's aspect ratios are better to damp the dynamic loading of higher frequencies. Surprisingly, taking a look at Figs. 7-17(c) and (d), it can also be observed that the introduction of structural hierarchy efficiently reduces the targeted peak frequency for the stairwise staggering architectures as well.

7.4 Summary

In the chapter, a theoretical model has been developed to derive the upper and lower bounds for the storage and loss moduli of the unidirectional composites with bioinspired staggered distributions of platelet reinforcements. For verification purposes, numerical analyses based on the finite element method (FEM) have also been carried out and the

results validate our bound model. Then, with the theoretical predictions and FEM results, the effects of staggering pattern, reinforcement aspect ratio, loading frequency and structural hierarchy on the storage and loss moduli of composites have been explored systemically. Finally, we demonstrated via several examples how the bound model can be utilized to aid and guide the design of high loss composites.

The major findings can be summarized as below:

- 1) Explicit and analytical formulations have been derived for the dynamic moduli of the unidirectional composites with bioinspired staggered distributions of platelet reinforcements, available for both single-level and hierarchical. FEM simulations with help of intuitive homogenization method validate that the theoretical model can give good estimation about the frequency-dependent damping properties of biological and bioinspired composites.
- 2) Generally, the regular staggering pattern ($\xi = 0.5$, $n = 2$) can give higher storage and loss moduli when the reinforcement aspect ratio is small, while the stairwise staggering ($n > 2$) can generate higher storage and loss moduli when the reinforcement aspect ratio is relatively large. With fixed aspect ratio of reinforcement, the further is the offset parameter ξ away from 0.5, or the larger is the period n , the higher is the peak frequency of loss modulus, since the characteristic length of overlap is smaller. Hierarchical design can effectively reduce the peak frequency of the loss modulus of composites with given viscoelastic constituent materials.
- 3) Besides the hard inclusion's shape, alignment and volume fraction, its distribution also plays a significant role in the damping properties of the biological and bioinspired composites. The present model can help composite scientists and engineers compare

different microstructure designs and find out the optimal bioinspired design of high loss composites.

The results of the current chapter have been published as research papers (Qwamizadeh et al., 2017a; Qwamizadeh et al., 2017b)

Chapter 8 Conclusions and recommendations

As discussed in the previous chapters, the main objective of the present work is to study the mechanical properties of load-bearing biological materials under dynamic loading conditions. We hypothesized that there is a close relation between the dynamic response of the material and its layout in different structural hierarchies. In the current chapter, the works performed in the previous chapters will be summarized as conclusion part and then followed by the future work.

8.1 Conclusions

During this work, firstly, FEM simulations have been performed to study the dynamic response of the bone at its primary hierarchical level. Both layered and staggered arrangements have been analyzed to show the advantages of the staggered structure over its layer counterpart. Our stress wave analysis shows that the average normal stress in the staggered arrangement is smaller than that of the layered structure for the same mineral volume fraction, while the shear stress in the staggered structure is larger than that in the layered structure. Since soft collagen and hard mineral can resist both tensile stress and shear stress, the staggered structure is more effective in utilizing the capacity to resist both tensile and shear loads.

Secondly, the viscoelastic properties of the protein counterpart were added to the model to investigate the effects of biopolymer viscosity on the stress wave attenuation of the nanostructure of load-bearing biological materials. Adopting the characteristic relaxation time to measure the viscoelastic properties of protein counterpart, it was found

that there is a critical characteristic relaxation time, above which, structure optimization will be crucial to enhance the stress wave attenuation and surprisingly it was found that a staggered arrangement with specific size and layout can most effectively damp the stress wave, which highlights another important advantage of the staggered structure. Importantly, the corresponding geometrical dimensions and layout for the mineral platelets are in good agreement with previous experimental measurements. However, whereas below the critical characteristic relaxation time, the viscosity-based energy-dissipation mechanism predominantly dictates the stress wave attenuation so that the contribution from the structure-based interface scattering mechanism is negligible.

Thirdly, a self-similar hierarchical structure was assumed to investigate the effects of structural levels on the damping properties of load-bearing biological materials with regular staggering pattern. Regardless of a single-level staggered structure or a self-similar hierarchical composite, there exists a peak frequency for each aspect ratio of reinforcement, at which the loss modulus gets its maximum. On the other hand, for each loading frequency, there is an optimal aspect ratio of reinforcement at which the loss modulus of composites gets maximized. Furthermore, as the hierarchy number increases, the storage modulus was seen to be shifted upward, indicating the storage modulus grows faster to saturation. However, the loss modulus was seen lowering down, with the maximum loss modulus slightly decreased while the peak frequency almost unchanged. Therefore, the hierarchical structure is able to chiefly increase the stiffness rather than the capacity of energy damping in load-bearing biological materials, with regard to the homogenization-based recursive formulae.

Finally, different distributions of staggered structures such as offset and stairwise staggering patterns were considered in the previous self-similar hierarchical model to study the effect of distribution of the mineral reinforcements on the damping properties of the biocomposite. It was shown that besides the mineral reinforcement's shape and volume fraction, its distribution also plays a significant role in the damping behavior of the biological and bioinspired composites. The findings here will help engineers to design and find out different microstructure with optimal bioinspired distribution of mineral platelets leading to high loss composites. The present work highlights the importance of dynamic properties in the evolution for load-bearing biological materials.

8.2 Recommendations

Up to now, we have studied various staggered structures of the load-bearing biological materials from the nanoscale to macroscale levels, and shown that these structures may exhibit the fastest wave decay, and the corresponding geometrical characteristics and layout are selected by nature through evolution for these load-bearing biological materials.

Regarding the fact that the biological materials often possess hierarchical structures, it is crucial to introduce the hierarchy into the model for more practical results. We used a self-similar hierarchical model to study the effect of structural level on the damping properties of biocomposite. However, most of the load-bearing biological materials are not noticeably self-similar in the structures far from the bottom levels like bone and bone-like materials. For our future study, we recommend to consider a quasi-self-similar or general (non-self-similar) hierarchical structure model to investigate the effects of

hierarchy on the mechanical properties of the biological materials. To do so, at the first, it is necessary to develop an analytical solution to obtain the wave traveling mechanism for each separate level of the biocomposite to be able to reflect the precise mechanical properties of the structure. Then, to simulate the staggered structure, it is necessary to find the hard and soft portion's material properties at each level. There are various existing experimental works that have investigated the properties of the collagen in different length scales. We should start from the bottom level (nanostructure) which has been well analyzed in the present work. Then, using the characteristic length and the material properties of the load-bearing biological material in each level obtained from the experimental results, the geometry as well as the mechanical properties of the hard inclusions and soft matrix of the structure will be determined. Subsequently, systematic finite element analysis will be used to investigate the dynamic response of the structure at each hierarchical level and find the relationship between the hierarchical structure and mechanical properties of the load-bearing biological material.

There are enough drawbacks that the bone is so anisotropic at primary hierarchical level. To efficiently find the relationship between the multiple structural levels of the bone and its mechanical properties, it is highly recommended to consider a model for bone with anisotropic component materials. This model will help researchers to approach one more step to the complicated natural design of the bone created during the long era of evolution process.

For another part of our future work, it is recommended to consider interface fracture and delamination in the model. Applying the cohesive law, we will be able to study the interface delamination between the collagen and mineral components of the load-bearing

biological material. The effect of the interface on the wave energy dissipation will be studied and the wave propagation through the nanostructure can be compared with that in the perfect bonding conditions (the current assumption).

Up to now, the findings of the present thesis were based on the theoretical approach and simulation. To create a novel method for synthesizing various hierarchical, low-cost structures composed of two different types of materials (one very stiff as the hard inclusion and the other one very soft with viscous characteristics as the matrix) in both layered and staggered patterns, it is necessary to use 3D printers to manufacture the composites in different length scales to perform impact tests (time domain dynamic analysis) in different directions. The 3D printing techniques offer a digitized and materialized fabrication for advanced structural composite with novel architectures. The 2D or 3D staggered structures in the multi-scale will be fabricated through lab-based and commercialized inkjet printing approaches.

The fabricated high-damping polymer composites will be used to validate the proposed design and theory for hierarchical structures. Experimentally, 3D printers, specifically inkjet printing using two different materials as the hard and viscous soft portions of the composite, are the prerequisite for the fabrication of laminated and staggered structures in bottom level. During the experiments, different samples with various geometrical parameters like thickness and aspect ratio of the hard inclusions, their volume fraction within the soft matrix as well as the horizontal and longitudinal gap between the inclusions should be tested to find the optimum structural parameters in which the fastest stress wave attenuation will occur. Then, by changing the loading amplitudes and frequencies, the optimal frequency in which the structure shows the maximum energy

dissipation can be measured. The measurements of the bottom level can be used in fabricating the structure in the next hierarchy to find the structure-property relation of load-bearing biological materials.

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