## EXPLOITING DESIGN PRINCIPLES IN NATURE TO SYNTHETIC COMPOSITES

By

Abhishek Dutta

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Mechanical Engineering—Doctor of Philosophy

2013

#### ABSTRACT

#### EXPLOITING DESIGN PRINCIPLES IN NATURE TO SYNTHETIC COMPOSITES

### By

## Abhishek Dutta

The current need of technology demands the generation of light-weight, durable and energy efficient structural materials. In order to attain this goal, over the last few decades there has been an increasing trend towards understanding design guidelines existing in natural composites and to implement the same in the development of synthetic composites. Of the innumerable structural biological composites existing in Nature, the nacreous layer in the seashells has received significant attention owing to its unique architecture and exceptional mechanical properties. Over the past decade, researchers all over the globe have addressed the reasons which are responsible for this attribute, and also attempted to synthesize them in the laboratory. However from the perspective of structural application, it is imperative to understand the suitability/applicability of these type of composites, should they be subjected to a variety of loading rates. In our investigations, we have attempted to address as to why bioinspired nacre-mimetic composites are suited for impact loading conditions. We have also tried to understand the mechanics of these type of composites when subjected to impact loading and unearth the parametric attributes that are responsible for superior resistance. Additionally, we have also tried to interpret what does it take for the nacreous layer to promote not only significant fracture resistance but at the same time attain light-weight as well. Excerpts from our investigations provide beneficial guidelines in designing tough bio-inspired composites at any length scale.

### ACKNOWLEDGMENTS

The author would like to express his sincere gratitude to his advisor Dr. Srinivasan Arjun Tekalur for his persistent support, guidance, and critique throughout the duration of this research work. The author would also like to express his gratitude to Dr. Alfred C. Loos, Dr. Lawrence T. Drzal, and Dr. Gary J. Blanchard for all their valuable suggestions and associated help in each and every part associated with this research.

The author would also like to thank Dr. Parimal Maity for his continued encouragement. In addition to that, the author is also thankful to Wei Zhang, Oishik Sen, Andy VanderKlok, David Gonzalez and Aiswarya Venkadachalam for providing an amicable environment in the laboratory. The author also acknowledges the support of Gail Berry, Mike McClean, Adam and Todd for their help throughout the course of the research.

Last but not the least, the author would like to thank his parents, his elder brother & sister and his wife for their unabated belief in the author's capabilities and perennial support.

# TABLE OF CONTENTS

LIST	OF TABLES	vi
LIST	OF FIGURES	vii
KEY	TO SYMBOLS	xii
1.	<ul> <li>Synthetic Staggered Architecture Composites</li> <li>1.1. Introduction</li> <li>1.2. Materials and Methods</li> <li>1.3. Results and Discussion</li> <li>1.3.1. Effect on composite stiffness and strength</li> <li>1.3.2. Effect on composite toughness</li> <li>1.4. Conclusion</li> <li>REFERENCES</li> </ul>	<b>1</b> 2 6 8 12 16 21
2.	<ul> <li>High Strain Rate Mechanical Behavior of Seashell-Mimetic Composites:</li> <li>Analytical Model Formulation &amp; Validation</li> <li>2.1. Introduction</li> <li>2.2. Mathematical Formulation</li> <li>2.3. Materials and Methods</li> <li>2.3. Results and Discussion</li> <li>2.4. Conclusion</li> <li>REFERENCES</li> </ul>	29 34 42 45 54
3.	Optimal Overlap Length in Staggered Architecture Composites Under Dynamic Loading Conditions 3.1. Introduction 3.2. Mathematical Formulation 3.3. Results and Discussion 3.3.1. Limitations of the analytical model and future directions 3.4. Conclusion REFERENCES	<b>61</b> 65 80 96 100

4.	Enhancing Resistance and Load Transfer Via Choice of Optimal Overlap Length	106
	4.1. Introduction	107
	4.2. Analytical Model	110
	4.2.1. Solution scheme for elemental displacements	116
	<b>4.2.2.</b> Computation of crack driving force (CDF)	119

	4.2.3. Limitations associated with the analytical model	121
	4.3. Results and Discussion	123
	4.3.1. Validation by experimental data	135
	4.3.2. An illustrative example	137
	4.4. Conclusion	139
	REFERENCES	
5.	Conclusions	145
	5.1. Design Guideline	146
	<b>5.2.</b> Future Scope of Work	147

## LIST OF TABLES

- Table 1.1.Influence of starting powder size & metal (base) plate on ceramic10content and aspect ratios of the synthesized silica-SC 15 composites.
- **Table 2.1.**Results of dynamic compression experiments on SiO2 SC-15 composites.**51**
- Table 2.2.Results of dynamic compression experiments on Al2O3 SC-1552composites.
- Table 3.1.Comparison of experimentally measured joint strength against those88predicted by analytical model for varying overlap area and loading rates.
- Table 4.1.Recent advances on modeling staggered architecture biological108composites by various researchers.
- Table 4.2.Recent advances on investigating existence of characteristic overlap109length in staggered architecture biological composites by various<br/>researchers.

## **LIST OF FIGURES**

2

- **Figure 1.1.** Brick and mortar type structural arrangement observed in seashells.
- **Figure 1.2.** Microstructure of the synthesized composites (c, d) exhibiting staggered **9** arrangement (a, b)-shown as blown-out view to obtain aspect ratios associated with various samples.  $\rho$  and  $\Phi_w$  indicate the aspect ratio and ceramic content respectively in the synthesized composites.
- **Figure 1.3.** TGA curves of the samples identifying varying ceramic content  $(\Phi_w)$  in **10** the synthesized composites (a); blown-out view another sample to obtain aspect ratios associated with it.  $\rho$  indicates aspect ratio.
- Figure 1.4. Compressive stress-strain plots (a) for different sample ID's as indicated 13 in Table 1.1; variation of Young's modulus of elasticity (b) and maximum compressive strength (c) of silica-SC 15 epoxy staggered composites for varying ceramic content and aspect ratio; (d) sample used for compressive experiments (specimen dimensions mentioned in Materials and Methods); failure of the specimens along the interface (e).
- Figure 1.5. Dependence of stiffness of a staggered architecture composite as a 15 function of aspect ratio and ceramic content as investigated theoretically under quasi-static [Gao et al., 2003] and dynamic rates of loading [Dutta et al., 2013] (plot adapted from [Dutta et al., 2013]).
- Figure 1.6. Representative load-displacement curves obtained upon fracture testing 17 of samples in accordance with <u>ASTM C1421</u> (a), variation of fracture toughness of silica-SC 15 brick and mortar composites with varying ceramic content and aspect ratio and their comparison against the fracture toughness of silica (ceramic) and SC 15 (polymer) alone (b).
- Figure 2.1. Dependence of stiffness of biocomposites (exhibiting brick and mortar 31 type of architecture at its most elementary level) as a function of aspect ratio of ceramic bricks and volume fraction of ceramic as laid down by Gao et al., 2003. Inset shows the brick and mortar type microstructural arrangement observed in seashells, and microstructure of bone.

- Figure 2.2. (a) Schematic of the brick and mortar type structural arrangement 34 subjected to external loading; (b) load acting on the ceramic and transfer of load between ceramic platelets by shearing of the intermediate polymer layers; (c) variation of shear stress and displacement profile along the ceramic thickness for the outer ceramic; (d) variation of shear stress and displacement profile along the ceramic thickness for the inner ceramic.
- **Figure 2.3.** (a) Typical specimen and its representative microstructure (b, c); (d) **44** schematic showing distribution of ceramic platelets in polymeric matrix in brick and mortar type microstructural composites; (e) region under consideration highlighting the overlap region; (f, g) deformed platelets and intermediate polymer upon tensile and compressive loading respectively; (h) specimen for quasi-static experiments; (i) fractured specimen under quasi-static loading.
- Figure 2.4. (a) Schematic of a Split Hopkinson Pressure Bar (SHPB); (b) plot of pulses 48 traced in the oscilloscope based on the pulses recorded by the strain gages in the incident bar (solid pink) and transmission bar (solid yellow); (c) specimen for SHPB experiments; (d) fractured specimen upon impact loading; (e) ratio of force on the transmission face to the incident face over time; (f) plot of strain-rate versus time.
- **Figure 2.5.** Dynamic stress strain curves obtained for SiO<sub>2</sub> SC-15 ceramic polymer **50** composite (a) and Al<sub>2</sub>O<sub>3</sub> SC-15 ceramic polymer composite (b) corresponding to varying ceramic contents and strain-rates.
- **Figure 2.6.** Plot of (a) experimental stress, and (b) strains (at peak stress) for SiO<sub>2</sub> SC- **52** 15 ceramic polymer composite corresponding to varying ceramic contents at different strain-rates.
- **Figure 2.7.** Plot of (a) experimental stress, and (b) strains (at peak stress) for Al<sub>2</sub>O<sub>3</sub> **53** SC-15 ceramic polymer composite corresponding to varying ceramic contents at different strain-rates.

- Figure 3.1. (a) Schematic of brick-and-mortar microstructure identifying the overlap 65 region; Representative loading pulses obtained from SHPB experiments:
   (b) triangular pulse, and (c) half-sinusoidal pulse.
- **Figure 3.2.** Shear stress distribution profile over the overlap length at varying times **81** under the application of triangular loading pulse.
- **Figure 3.3.** Variation of shear stress at the extremities of the joint against overlap **83** length for nacre (a), and its dependence on loading rate (b).
- **Figure 3.4.** Variation of shear stress at the extremities of the joint against overlap **85** length for spider-silk (a), and its dependence on loading rate (b).
- Figure 3.5. Variation of shear stress at the extremities of the joint against overlap 86 length for collagen in tendon/bone (a), and its dependence on loading rate (b).
- Figure 3.6. Variation of elastic strain energy density against varying overlap length at 91 different intervals of time under the application of triangular pulse loading (a), and dependence of elastic strain energy density on loading rate, under the application of triangular pulse loading, shown via (1) varying max stress (keeping time at maximum stress fixed)-shown in red and (2) varying time at max stress (keeping maximum stress fixed)-shown in black; dependence of w<sub>eff</sub> is markedly pronounced towards increasing stress-levels than for time under the application of triangular pulse loading.
- Figure 3.7. Plot showing the dependence of maximum shear stress (at the ends of overlap) as a function of aspect ratio and volume fraction of the ceramic bricks for: aspect ratio varying between 4 to 200 (a) and, 4 to 800 (b) under the application of triangular pulse loading, corresponding to a given loading-rate.
- **Figure 3.8.** Plot showing the dependence of the ratio of composite modulus to **95** Young's modulus of the ceramic bricks for varying aspect ratio and volume fraction of the ceramic bricks: correlation between dynamic (a) and quasi-static (b) regime, corresponding to a given loading rate.

- Figure 3.9. Variation of shear stress at the interface as a function of overlap length 99 in a material (in the current case, nacreous layer in seashells) under (a) static, and (b) dynamic rates of loading.
- **Figure 4.1.** Toughening mechanisms associated with nacre and region under **111** consideration.
- Figure 4.2. (a) Schematic of staggered architecture of calcium carbonate bricks 113 (shown in green) in biopolymer matrix (shown in yellow); (b) expanded view of the 2-dimensional unit cell structure (with plane strain infinitesimal deformation) showing the pre-cracked length (L<sub>1</sub>) and instantaneous overlap length (L<sub>2</sub>) and coordinate systems; (c) expanded view of the 2-dimensional unit cell structure (with plane strain infinitesimal deformation) highlighting the elemental blocks and the original overlap length (L<sub>0</sub>); (d) splitting of parent crack tip for crack driving force calculations; (e) schematic identifying shear and normal force resultants N<sub>C</sub> and Q<sub>C</sub> respectively.
- **Figure 4.3.** Variation of interfacial shear stress (at the extremities of the overlap) as **124** a function of varying overlap length and pre-crack. The figure in the inset shows the expanded view for lower shear levels in the unit cell.
- **Figure 4.4.** Plot of crack driving force as a function of overlap length in nacre for **127** varying pre-crack lengths.
- Figure 4.5.Variation of crack driving force against applied stress for overlap length128on either end of the characteristic value in the nacreous layer.
- **Figure 4.6.** Mode mixity parameter as a function of overlap length for varying pre- **129** crack lengths.
- **Figure 4.7.** Variation of crack driving force upon overlap length for varying pre-crack **131** length associated with the primary crack. The figure in the inset identifies the angle ( $\theta$ ) at which crack driving force of the kinked crack attains a maximum value for varying pre-crack length (0.09-1.29µm).

- **Figure 4.8.** Variation of crack driving force upon overlap length for varying pre-crack **132** length associated with the primary crack. The figure in the inset identifies the angle ( $\theta$ ) at which crack driving force of the kinked crack attains a maximum value for a pre-crack length of 1.49 µm.
- Figure 4.9. (a) Schematic of staggered architecture of calcium carbonate bricks 133 (shown in green) in biopolymer matrix (shown in yellow); (b) expanded view of the 2-dimensional unit cell structure (with plane strain infinitesimal deformation) highlighting the elemental blocks and the original overlap length (L<sub>o</sub>); (c) crack trajectory through the overlap length and crack jump/deflection from one unit cell to another.
- Figure 4.10.Existence of optimal length scale, as predicted by the analytical model, 136<br/>for an Al99.5- Loctite 3421 single lap adhesive bonded joint.
- **Figure 4.11.** Existence of optimal overlap lengths for varying widths of composite **138** adherend (10 mm, 40 mm and 100 mm) and adhesive thickness (0.50 mm, 1.00 mm, 2.00 mm, 3.00 mm and 5.00 mm). The hollow and solid circles are representative of characteristic length with respect to minimization of crack driving force (a,c,e) and shear stress (b,d,f) respectively.
- **Figure 5.** Design guideline for synthetic composite showing the interplay of **146** optimization scheme and manufacturing technique.

# **KEY TO SYMBOLS**

Φ	Volume fraction of ceramic.
W	Inter-ceramic spacing.
V	Freeze front velocity.
Mm	Microns.
Φw	Weight fraction of ceramic.
E	Young's modulus of the composite (in <b>Chapter 1</b> )/ of the ceramic (in <b>Chapter 3</b> ).
E <sub>m</sub>	Young's modulus of the mineral/ceramic.
Sp	Strength of the polymer (or, polymer-ceramic interface).
S <sub>m</sub>	Compressive strength of the ceramic bricks.
Ρ	Aspect ratio (in <b>Chapter 1</b> )/density (in <b>Chapter 3</b> ) of ceramic bricks.
κ <sub>ic</sub>	Fracture toughness (MPa m <sup>0.5</sup> ).
a/W	Ratio of crack length to the width of specimen.
P <sub>max</sub>	Maximum load.
S	Span.
В	Specimen width.

J	Fracture energy.
Θ <sub>p</sub>	Effective strain to which the polymer can deform before failure.
Sp	Yield strength of the polymer.
S <sub>int</sub>	Ceramic polymer interface strength.
τ <sub>p</sub>	Polymeric shear strength (in <b>Chapter 1</b> )/shear stress (in <b>Chapter 2</b> ).
ε <sub>ρ</sub>	Strain in the polymer.
Gp	Protein (polymer) shear modulus.
Т <sub>о</sub>	Axial stress resultant in the outer ceramic.
Тi	Axial stress resultant in the inner ceramic.
a <sub>O</sub>	Average acceleration of the cross-section of the outer ceramic.
a <sub>i</sub>	Average acceleration of the cross-section of the inner ceramic.
Н	Thickness of the ceramic (in <b>Chapter 2</b> )/Polymer thickness (in <b>Chapter 3</b> ).
u <sub>O</sub>	Horizontal displacement of the outer ceramic brick.
u <sub>i</sub>	Horizontal displacement of the inner ceramic brick.
τ <sub>o</sub>	Shear stress in the outer ceramic.
τ <sub>i</sub>	Shear stress in the inner ceramic.

G <sub>m</sub>	Shear modulus of the ceramic.
γ <sub>o</sub>	Shear strain in the outer ceramic.
γ <sub>i</sub>	Shear strain in the inner ceramic.
z	Location of origin for the outer ceramic.
z"	Location of origin for the inner ceramic.
u <sub>op</sub>	Displacement of the ceramic at the interface between the outer ceramic block and the intermediate polymer.
u <sub>ip</sub>	Displacement of the ceramic at the interface between the inner ceramic block and the intermediate polymer.
γ <sub>p</sub>	Shear strain in the polymer.
tp	Thickness of the polymer.
2L*	Width of the ceramic layer.
C <sub>C</sub>	Wave velocity through the ceramic.
A	A parameter associated with structural and geometrical properties.
F(t)	Prescribed loading at the inner and outer ceramic.
$\overline{\gamma}_{p}$	Approximate shear strain.
N <sub>1</sub> (x), N <sub>2</sub> (x)	First order interpolation functions and correspond to weighted residuals in Galerkin method.
$\left[\kappa^{(e)}\right]$	Elemental stiffness matrix.

$\left[M^{(e)}\right]$	Elemental mass matrix.
C	Wave velocity in the incident bar (in <b>Chapter 2</b> )/through the ceramic (in <b>Chapter 3</b> ).
<sup>ɛ</sup> eff  <sub>o</sub>	Effective strain in the outer ceramic.
<sup>ɛ</sup> predicted	Predicted strain.
<sup>o</sup> predicted	Predicted stress.
Eb	Young's modulus of the transmission bar.
Ab	Cross-sectional area of the transmission bar.
A <sub>S</sub>	Instantaneous cross-sectional area of the specimen.
I <sub>S</sub>	Thickness of the specimen for SHPB testing.
J	Polar moment of inertia of the cross-section of the specimen.
ε <sub>i</sub>	Incident strain record.
٤ <sub>r</sub>	Reflected strain record.
ε <sub>t</sub>	Transmission strain record.
έ	Strain rate.
ε <sub>exp</sub>	Strain value obtained experimentally.
ɛcal	Calculated strain value.

$\sigma_1 \equiv \sigma_1(x,t)$	Normal stress developed in the upper ceramic brick.
$\sigma_2 \equiv \sigma_2(x,t)$	Normal stress developed in the lower ceramic bricks.
τ or, ζ	Shear stress developed in the polymer.
$u_1 \equiv u_1(x,t)$	In-plane displacement of the upper ceramic brick.
$u_2 \equiv u_2(x,t)$	In-plane displacement of the lower ceramic brick.
G	Shear modulus of the polymer.
В	Half the width of ceramic bricks.
т	Time.
$u_4 \equiv u_4(x,t)$	A variable dependent upon terms $u_1 \equiv u_1(x,t)$ and $u_2 \equiv u_2(x,t)$ .
w(x,t)	Smoothing function satisfying boundary conditions.
v(x,t)	A variable leading to solution for $u_4(x,t)$ .
$\sigma(t)$	External acting stress on the unit-cell structure.
К	A parameter dependent upon E, G, b and h.
p <sub>04</sub> ,p <sub>n4</sub>	Variables for computing another variable $p_4$ .
L	Overlap length.
$\lambda_{n4}$	Eigen values for $v(x,t)$ , $n \ge 1$ .
x <sub>n4</sub>	Eigen functions for $v(x,t)$ , $n \ge 1$ .
T <sub>04</sub> , T <sub>n4</sub>	Variables for computing temporal variation $T_{\rm 4}$ corresponding to $v(x,t).$

a <sub>n4</sub> ,e <sub>n4</sub>	Variables for computing $T_{n4}$ .
a <sub>04</sub> ,b <sub>04</sub> ,d <sub>04</sub>	Variables for computing $T_{04}$ .
$u_3 \equiv u_3(x,t)$	Another variable dependent upon terms $u_1 \equiv u_1(x,t)$ and $u_2 \equiv u_2(x,t)$ .
s(x,t)	Smoothing function satisfying boundary conditions.
r(x,t)	A variable leading to solution for $u_4(x,t)$ .
p <sub>03</sub> ,p <sub>n3</sub>	Variables for computing another variable p <sub>3</sub> .
λ <sub>n3</sub>	Eigen values for $r(x,t)$ , $n \ge 1$ .
x <sub>n3</sub>	Eigen functions for $r(x,t)$ , $n \ge 1$ .
T <sub>03</sub> , T <sub>n3</sub>	Variables for computing temporal variation $T_3$ corresponding to $r\bigl(x,t\bigr).$
a <sub>n</sub> 3,e <sub>n</sub> 3	Variables for computing $T_{n3}$ .
a <sub>03</sub> ,b <sub>03</sub>	Variables for computing $T_{03}$ .
σ <sub>max</sub> or, σ <sub>0</sub>	Maximum value of externally applied stress.
t <sub>a</sub> or t <sub>f</sub>	Time at which $\sigma_{max}$ occurs.
Ms	Micro-seconds.
• P	Loading rate (stress per unit time).
Nm	Nanometer.
c <sub>t</sub>	Wave velocity in the transmission bar.

A <sub>IS</sub>	Area of the adhesive lap joint.
ü <sub>1</sub>   <sub>avg</sub>	Average acceleration.
w <sub>eff</sub>	Elastic strain energy density.
$\sigma_{eff}$	Effective stress.
<sup>ɛ</sup> eff	Effective strain.
• <sup>ɛ</sup> s	Strain rate of the organic matrix.
L*	Characteristic length.
<sup>L</sup> optimal	Optimal overlap length.
L <sub>1</sub>	Pre-cracked length in the unit cell.
L <sub>2</sub>	Instantaneous overlap length in the unit cell.
Lo	Original overlap length.
N <sub>c</sub>	Shear force resultant.
Q <sub>c</sub>	Normal force resultant.
η	Thickness of the bio-polymer in nacre.
Z	Thickness direction of the ceramic bricks in nacre.
x, $x_1$ , and $x_2$	Horizontal axes with different origins.
a <sub>0</sub>	Void length.
da	Length of pre-existing incremental crack.

u <sub>X</sub> i	Displacement along the horizontal direction corresponding to block i (=1,4).
uz	Displacement along the thickness direction corresponding to block i (=1,4).
$\sigma^{i}_{XX}$	Axial stress corresponding to block i (=1,4).
$\sigma_{zz}^{i}$	Peeling stress corresponding to block i (=1,4).
$\sigma^{i}_{xz}$	Shear stress corresponding to block i (=1,4).
ε <sup>p</sup> zz	Axial strain in the biopolymer.
ε <sup>p</sup> zz	Normal (peel) strain in the biopolymer.
ε <sup>p</sup> xz	Shear strain in the biopolymer.
$\sigma^{p}_{zz}$	Normal (peel) stress in the biopolymer.
$\sigma^{p}_{xz}$	Shear stress in the biopolymer.
$c_{11}^{c}, c_{22}^{c}, c_{44}^{c}$	Orthotropic properties (stiffness) of ceramic bricks.
$c_{22}^{p}, c_{33}^{p}, c_{44}^{p}$	Material properties (stiffness) of the bio-polymeric matrix.
$M_1, M_2, M_3$	Variables computed from $C_{11}^{c}$ , $C_{22}^{c}$ , $C_{44}^{c}$ , $C_{22}^{p}$ , $C_{33}^{p}$ , $C_{44}^{p}$ .
$u_X^A$	Displacement along the horizontal direction corresponding to point A.
uzA	Displacement along the thickness direction corresponding to point A.

u <mark>B</mark>	Displacement along the horizontal direction corresponding to point B.
uz <sup>B</sup>	Displacement along the thickness direction corresponding to point B.
W	Work required to close the virtual crack.
Gl	Mode I crack driving force.
G <sub>II</sub>	Mode II crack driving force.
E <sub>1</sub> ,E <sub>2</sub> ,E <sub>3</sub>	Young's modulus along orthogonal directions for the mineral component in the nacreous layer.
G <sub>12</sub> ,G <sub>23</sub> ,G <sub>13</sub>	Shear modulus values for the mineral component in the nacreous layer.
E <sub>p</sub> ,G <sub>a</sub> ,υ <sub>a</sub>	Properties of biopolymer layer in nacre.
$L_{characteristic} (\equiv \tau_{min})$	Characteristic length on minimization of maximum shear stress.
$L_{characteristic} \equiv (CDF_{min})$	Characteristic length on minimization of crack driving force (CDF).

**CHAPTER 1: SYNTHETIC STAGGERED ARCHITECTURE COMPOSITES** 

## **1.1. Introduction**

Biological materials are composites structures synthesized by nature via bottom-up route and exhibit complex hierarchical design over several length scales. Nacre, or the mother-of-pearl, is one of the most widely studied biocomposites since it is inherently light weight and strong (high stiffness and specifically, superior toughness) [Jackson et al., 1988; Sarikaya et al., 1990; Menig et al., 2000; Kamat et al., 2000; Barthelat and Espinosa, 2007]. Nacre is composed of polygonal mineral tablets (width=5-10  $\mu$ m & thickness=0.4-0.5  $\mu$ m) of high weight fraction ( $\Phi$ =0.95) which are cemented together with very small amount of polymeric matrix (thickness=20-30 nm) which is composed of proteins and polysaccharides. Irrespective of the degree of hierarchical complexity exhibited by the biocomposites, at the most elementary level, they exhibit a generic microstructure comprising of nanometer sized inorganic crystals embedded in a soft organic matrix (biopolymers) in the form of a staggered architecture [Gao et al., 2003], otherwise known as a *brick-and-mortar type structural arrangement* (Figure 1.1).



Seashell (Gastropods)



**Figure 1.1.** Brick and mortar type structural arrangement observed in seashells. For interpretation of the references to the color in this and all other figures, the reader is referred to the electronic version of this dissertation.

Nature cleverly uses aspect ratio and ceramic content for fine tuning properties for functions. For instance, bone is primarily designed for withstanding time-dependent or, impact loading (for example, withstanding stresses while running, jumping, accidental fall) and hence the microstructure is designed primarily from enhanced toughness point of view and moderate stiffness. On the contrary, seashells (which lie in the abyss of oceans) apart from providing defense to the organism (it is hosting) against predatory attacks, is also subjected to quasistatic loading (for example, enormous hydrostatic pressure). Hence, emphasis on the shell structure evolution is directed primarily towards providing enhanced stiffness. Such an amazing capability of tuning properties based on a function has rarely been seen in synthetic composites. Although bone and nacre differ from each other in varying aspects, deformation and toughening mechanisms in both these materials are similar. Thus, in order to synthesize composites having brick and mortar architecture, freeze-casting technique can be used to first synthesize the ceramic relic. It consists of four principal steps: (1) ceramic slurry preparation, (2) freezing the ceramic-solvent system, (3) sublimation of the frozen solvent, and (4) sintering of the porous ceramic relic. A short summary of the recent work in the literature of freeze-casting is given as follows. Porous alumina  $(Al_2O_3)$  and silicon nitride  $(Si_3N_4)$  ceramics were produced using water as the carrier where growth of dendritic shaped ice crystals was observed upon freezing which produced elliptical pores (dendritic channel) having a lengths of major and minor axis equal to 500  $\mu$ m and 30  $\mu$ m respectively [Fukusawa et al., 2002]. Simultaneously, camphene (C<sub>10</sub>H<sub>16</sub>) was also being used as a freezing vehicle because of its environment

friendliness and its ability to cast at room temperatures dense Al2O3 ceramics [Sofie and Dogan, 2001]. Araki and Halloran, 2005 produced Al<sub>2</sub>O<sub>3</sub> ceramics by using an amine derivative of a fatty acid condensation polymer as a dispersant in addition to the Al<sub>2</sub>O<sub>3</sub>-C<sub>10</sub>H<sub>16</sub> slurry which was cast on polyurethane molds and subsequently sintered at 1600°C for 4 hours and obtained circular cross-sectional channels. Porous silica (SiO<sub>2</sub>) ceramics were produced using polyvinyl alcohol (PVA) as the binder by casting the slurry onto glass tubes which was subsequently immersed in liquid nitrogen at a controlled speed [Zhang et al., 2005]. Porous hydroxyapatite (HAP) scaffold were produced using glycerol as the carrier, PVA as a binder (1.5 wt%) and Dynol 604 as the dispersant (0.75 wt%) by casting the solutions on PVC tubes which was covered with polyurethane foam [Fu et al., 2008]. Similarly, porous HAP ceramic scaffold, titanium foam and HAP/tricalcium phosphate (TCP) ceramic scaffold respectively using camphene as the freezing vehicle [Chino and Dunand, 2008; Macchettaa et al., 2009; Yoon et al., 2007]. Pore channels generated were greater than 100  $\mu$ m which enabled their use for bone-tissue engineering applications. Porous HAP have been produced which were modified by silica [Blindow et al., 2009], with functionally graded core-shell structure (using camphene as the carrier) [Soon et al., 2011], and using distilled water as the carrier, PVA as a binder and ammonium polyacrylate as the dispersant [Zuo et al., 2011]. Titanium foams [Li and Dunand, **2011**] and porous Si<sub>3</sub>N<sub>4</sub> ceramics [Ye et al., 2010] have been produced using distilled water as the media and using a variety of compounds as an addition agent to observe subsequent pore

structure and geometry (for example, ammonium polymethacrylate anionic dispersant, polyacrylamide dispersion agent, etc). Macroporous alumina ceramics [Jing et al., 2010], Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> ceramic (20:80 with a 40-80 wt% solid loading) [Liu et al., 2010], and porous alumina ceramic using Al<sub>2</sub>O<sub>3</sub> sol [Yoon et al., 2010] as a substitute for water and as a medium for making ceramic slurry have also been produced. The authors [Yoon et al., 2010] also discussed the use of PVA both as a binder as well as an emulsifying agent to stabilize air bubbles during magnetic stirring. Following the manufacturing of the ceramic backbone, the ceramic-polymer composites can be synthesized via infusion of polymer into the porous ceramic. Deville and coauthors [Deville et al., 2006] were the first to produce Alumina epoxy lamellar composite by filling the porous IT scaffolds by epoxy. Al<sub>2</sub>O<sub>3</sub>-PMMA brick and mortar and lamellar composites [Launey et al., 2009] have been synthesized by introducing a polymeric phase (by free radical polymerization of methylmethacrylate (MMA) initiated by 2,2'-azobisisobutyronitrile (AIBN)) into the porous  $Al_2O_3$  freeze cast component. By grafting the  $Al_2O_3$  with another polymeric component [3-(trimethoxysilyl)propyl methacrylate (y-MPS)], significant improvement in mechanical properties have been obtained in comparison to the non-grafted, Al<sub>2</sub>O<sub>3</sub> and PMMA counterparts alone.

All the above mentioned researches have attempted to mimic lamellar/brick and mortar microstructure in its entirety. In our current investigation, we are not trying to mimic brick and mortar microstructure of nacre; rather, what we are interested is in drawing inspiration from

staggered architecture in biological composites at their elementary level (such as nacre: 0.90-0.95 ceramic content [**Jackson et al., 1988**], bone: 0.50 ceramic content [**Currey, 2002**], dentin: 0.43 ceramic content [**Currey, 2002**], etc.), we want to (a) synthesize synthetic ceramic-polymer composites with varying ceramic content and aspect ratio, and (b) experimentally understand the structure-property correlationship of these composites when subjected to external loading. Excerpts drawn from this investigation would thereby help in custom-design manufacture of hybrid bio-inspired composite materials.

### **1.2.** Materials and Methods

Sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S) was obtained from Sigma Aldrich (St. Louis, MO, USA). Poly (vinyl alcohol) [-CH<sub>2</sub>CH(OH)-]n 98% hydrolyzed having an average molecular weight M<sub>w</sub> 13,000-23,000 was obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) crystals were obtained from Roche Diagnostics Corporation (IN, USA). Two types of ceramic powders were purchased: Silica (SiO<sub>2</sub>) spheres of 8µm and 1µm diameter were obtained from Fiber Optic Center Inc (New Bedford, MA, USA). SC-15 epoxy resin (toughened two phase) was obtained from Applied Poleramic Inc. (Benicia, CA, USA).

The ceramic scaffolds were prepared following the sequence of steps as have been carried out by authors [**Deville et al., 2006; Launey et al., 2009**] and for brevity purposes not described in detail. Suspension of micrometer sized ceramic powders were prepared by dispersing ceramic powders of different concentrations (30 wt%, 40 wt%, and 50 wt%) into a solution composed of 2 wt% polyvinyl alcohol (PVA), 4 wt% sucrose and 5 wt% sodium dodecyl

sulfate (SDS) in order to produce ceramic scaffolds having varying porosity. The colloidal solutions were sonicated for 10 minutes duration (Fisherbrand, FB 11021) at 35W. The ceramic suspensions were casted in teflon (PTFE) molds on top of a metal plate which was cooled by liquid nitrogen. The frozen samples were subsequently transferred to a freeze dryer (Freeze Dryer 1.0, Labconco, Kansas City, MO) for a period of 48 hours which in turn promotes sublimation of ice and thereby, we are left behind with the ceramic green body. Densification of the ceramic was by obtained by sintering at 1550°C for 2 hours. The epoxy is prepared by mixing 100wt% SC-15 Part A (resin) and 30wt% of SC-15 Part B (hardener). The mixture is stirred gently for approximately 10 minutes followed by degassing for another 10 minutes. Finally, the scaffolds were infiltrated with the two-phase epoxy followed by curing of the epoxy at 60°C for 2 hours and 94°C for 4 hours.

Morphological features of the samples were acquired using a JEOL JSM-6400V scanning electron microscope (JEOL Ltd., Tokyo, Japan). Samples thermogravimetric analysis (TGA Q500 V20.10 Build 36, TA Instruments) were conducted at a heating rate of 20°C min<sup>-1</sup> up at temperatures up to 550°C. **ASTM D695** was followed for the determination of compressive strength of these ceramic polymer composites under quasi-static rates of loading. The specimen dimension chosen for testing was 5mm × 5mm × 10 mm and was performed in a MTS machine (10kN load cell) at a crosshead speed of 1mm/min. **ASTM C1421** was followed for the determination of the d

chosen for testing was 4mm × 4mm × 16 mm (with an initial crack length of 1.40 mm), and was performed in a MTS machine (10kN load cell) at a crosshead speed of 0.01 mm/s.

## **1.3.** Results and Discussion

The first task in the current investigation involves synthesizing composites with varying ceramic content and aspect ratio. As mentioned earlier, freeze-casting technique followed by infusion of polymer (into the porous ceramic) has been employed for synthesis of ceramic-polymer composites. The most critical stage of the entire freeze-casting process is the *controlled solidification of the slurry*. Formation of the structure and future porosity are determined in this step. The cooling rates, for freezing the water to ice, typically will range from  $0.1^{\circ}$ C min<sup>-1</sup> to  $10^{\circ}$ C min<sup>-1</sup>. Freezing front velocity, which is directly proportional to cooling rate, plays an important role in the final microstructure development. With reference to the basic crystallography of ice, water solidifies into anisotropic hexagonal ice crystals during freeze casting. Empirically, the inter-ceramic spacing *w* has been found to vary with freezing-front velocity *v* [**Deville, 2008**] as follows:  $w \propto \frac{1}{v^n}$ . In order to control the freezing rate and thereby,

the porosity of the ceramic, we employ a simple and fundamental approach. The ceramic suspensions are casted in PTFE molds on top of a metal plate which in-turn is cooled by liquid nitrogen. The freezing velocity or the solidification rate of the solution can be tuned by changing the base metal plate. In current experiments, we have employed two types of metal plate: aluminum and copper. Since, thermal conductivity of copper (401 W/m-K) is greater than the thermal conductivity of aluminum (167 W/m-K), for the same ceramic concentration in

solution, denser ceramic backbone (or, lower porosity ceramics) will be obtained which in-turn implies, higher weight fraction of ceramic content in synthesized ceramic-polymer composites. Additionally, the starting particle size is seen to have an effect on the solidification kinetics, and subsequently on the structural wavelength (or rather, the final thickness of the ceramic bricks). Hence, we employed two different sized powders (particle diameters of 8µm and 1µm) to control the structural wavelength and thereby, the aspect ratio of the ceramic blocks in the synthesized composite. Thus following this simple approach, both ceramic content and aspect ratio were controlled in the synthesized silica-SC 15 composites. **Figure 1.2(a,c)** and **Figure 1.3(b)** shows the staggered microstructure of a representative sample.



**Figure 1.2.** Microstructure of the synthesized composites (c,d) exhibiting staggered arrangement (a, b)-shown as blown-out view to obtain aspect ratios associated with various

Figure 1.2. (cont'd)





**Figure 1.3.** TGA curves of the samples identifying varying ceramic content ( $\Phi_w$ ) in the synthesized composites (a); blown-out view another sample to obtain aspect ratios associated with it.  $\rho$  indicates aspect ratio.

 Table 1.1. Influence of starting powder size & metal (base) plate on ceramic content and aspect

 ratios of the synthesized silica-SC 15 composites.

Ceramic Conc. in Solution	Plate Type	Initial Particle Size	Ceramic Content in composite (Φ <sub>w</sub> ) *From TGA	Aspect Ratio (ρ) *From SEM	ID
30%	Aluminum	1-µm	35%	15	Φ <sub>w</sub> =0.35/ρ=15
30%	Copper	1-µm	40%	15	Φ <sub>w</sub> =0.40/ρ=15
40%	Aluminum	8-µm	55%	10	Φ <sub>w</sub> =0.55/ρ=10
40%	Copper	8-µm	58%	10	Φ <sub>w</sub> =0.58/ρ=10

Table 1.1. (cont'd)

45%	Aluminum	8-µm	60%	10	Φ <sub>w</sub> =0.60/ρ=10
50%	Aluminum	8-µm	65%	7	Φ <sub>w</sub> =0.65/ρ=7
50%	Copper	8-µm	70%	6	Φ <sub>w</sub> =0.70/ρ=6

Table 1.1 lists the details of the above set of processes for different starting ceramic concentrations & powder size. Figure 1.3(a) demonstrates the TGA curves of different samples for subsequent evaluation of ceramic content in the samples, the values of which are tabulated in **Table 1.1**. Aspect ratio of the ceramic platelets is defined as the ratio of length to the width of the ceramic platelet. Corresponding to each sample ID, SEM was done to obtain the aspect ratio of the ceramic platelets. Figure 1.2(a-d) shows the microstructure of the synthesized samples which helps in identifying the aspect ratio of the ceramic platelets in the composite. For a given particle size as a precursor, as the ceramic content in the composite increases, the aspect ratio of the platelets decreases which is intuitive as the thickness of the platelets remains constant; however, the length of the platelets decreases owing to higher particle distribution in the interdendritic space [Deville, 2008]. Nevertheless, the aspect ratio of the ceramic platelets varied from 6-10 & 15-16 for 8µm and 1µm ceramic spheres respectively. Ceramic concentration in solution greater than 30wt% & 50 wt% for 1-µm and 8-µm were not probed into as it was difficult to maintain suspension of ceramic particles in solution under those conditions.

An integral part of understanding predator-prey interactions is to first understand the mechanisms operating in food web dynamics. For instance in a marine food chain, otters and crabs can be considered as the predators who use their molar tooth and claws respectively to

prey the protein-rich flesh of the organism (acting as the prey) hosted by seashells. Similarly, bone has to be durable enough to withstand high stresses associated with biting of tooth, sudden fall, etc. Predatory attacks involve application of compressive loads to the structural component associated with the prey that has to be not only durable but fracture-resistant as well. However, it can be pointed out that mechanical behavior of structural biocomposites is tuned predominantly for the function that it is specifically designed for. For instance, bone is primarily designed for withstanding time-dependent or, impact loading (for example, withstanding stresses while running, jumping, accidental fall) and hence the microstructure is designed primarily from enhanced toughness point of view and moderate stiffness. On the contrary, seashells (which lie in the abyss of oceans) apart from providing defense to the organism it is hosting against predatory attacks, is also subjected to quasi-static loading (for example, enormous hydrostatic pressure). Hence, emphasis on the shell structure evolution is directed primarily towards providing enhanced stiffness. In order to observe whether the synthesized composites also exhibit this variance in mechanical behavior for varying ceramic content and aspect ratio, quasi-static compression and fracture experiments were performed to better understand this aspect.

#### **1.3.1.** *Effect on composite stiffness and strength*

**Figure 1.4(a)** shows the representative stress-strain plots obtained upon quasi-static compressive loading of the synthesized composites. It has been shown theoretically, as shown in **Figure 1.5(a,b)**, that the stiffness of a staggered architecture composite can be tuned via

12

controlling its aspect ratio for a given ceramic content under both static [Gao et al., 2003] and dynamic rates [Dutta et al., 2013] of loading.



**Figure 1.4.** Compressive stress-strain plots (a) for different sample ID's as indicated in **Table 1.1**; variation of Young's modulus of elasticity (b) and maximum compressive strength (c) of silica-SC 15 epoxy staggered composites for varying ceramic content and aspect ratio;

### Figure 1.4. (cont'd)

(d) sample used for compressive experiments (specimen dimensions mentioned in **Materials and Methods**); failure of the specimens along the interface (e).

Indeed similar observations have been observed from experimentally obtained data as shown in **Figure 1.4(b,c)** where as the aspect ratio increases, the stiffness of the composite increases as well even if high polymeric content is present in the composite.

For a ceramic polymer composite having a staggered microstructure, the ceramic forms the load-bearing component and load transfer from one platelet to another is accomplished via shear-deformation of the polymer. Larger is the aspect ratio, larger will be the force that would be transmitted from one ceramic brick to another via the polymer matrix. Failure of the interfacial matrix is initiated at the extremities of the polymeric layer joint via nucleation and growth of plastic zone from either ends of the overlap length towards the center [**Apalak and Gunes, 2007; Ouinas et al., 2010; da Costa et al., 2012; Sayman et al., 2013**]. Indeed failure of the synthesized composite has been observed along the interfaces as shown in **Figure 1.4(e)**. Hence, aspect ratio of the ceramic platelets plays a superior role in its contribution to the composite's stiffness.

It might be speculated that the shear model might not be applicable under compressive loading scenario for staggered architecture composites, because microbuckling has been observed as the failure mode operational under quasi-static and dynamic rates of loading in seashells [Menig et al., 2000]. This aspect, however, can be addressed as follows [Dutta et al., 2012]:

14



Figure 1.5. Dependence of stiffness of a staggered architecture composite as a function of aspect ratio and ceramic content as investigated theoretically under quasi-static [Gao et al., 2003] and dynamic rates of loading [Dutta et al., 2013] (plot adapted from [Dutta et al., 2013]).

The ceramic backbone in a ceramic polymer composite is brittle in nature. Hence, in these composites failure initiates at the micro-scales in the form of interfacial matrix failure starting at the joint extremities. The nacreous layer in seashells is a exhibits a hierarchical architecture (2-3 levels) where the staggered architecture is exhibited only at the level of micro-scales; however, the meso-scale is representative of a lamellar architecture (equivalent to a fiber-reinforced composite structure) comprising of 300 µm layers between nearly 20 µm layers of viscoplastic material [Menig et al., 2000]. Plastic microbuckling is the dominant failure mechanism in fiber-reinforced composites under the action of compressive loads, and thereby based on this analogy, microbuckling was hence observed in seashells under compressive loading conditions. Similar inferences have been laid down [Menig et al., 2000] where it has been observed in the lamellar structures of seashells that cracks initiates first in the viscoplastic layers separating the mesolayers. Additionally, with reference to the microstructure of the

synthesized composites, ceramic bridges present amidst the ceramic layers (an attribute associated with nacre at micro-scales) also cripples Euler buckling of the ceramic layers at microscopic scales [**Deville et al., 2006**]. Similarly, buckling is restrained at micro-scales, under rapid-compression ballistic conditions, via synchronized deformation twinning of the nano-scale particles [**Huang et al., 2011**].

Similarly, for a staggered ceramic-polymer composite, the strength [Gao et al., 2003] can be expressed as follows:

$$S = \min\left(\frac{\rho\phi S_p}{2}, \frac{\phi S_m}{2}\right)$$
(1.1)

where, S<sub>p</sub> is the strength of the polymer (or, polymer-ceramic interface) and S<sub>m</sub> is the compressive strength of the ceramic bricks. Based on the experimentally obtained data and the theoretical foundation [Gao et al., 2003; Ji and Gao, 2010], it can be clearly seen from Figure **1.4(c)** that aspect ratio (p) plays a superior role than ceramic content in its contribution towards the strength of the staggered ceramic-polymer composite and confirms that fine tuning of properties can be obtained in synthetic composites by varying ceramic content and aspect ratio. Thus, from the point-of-view of stiffness and strength, the aspect ratio of mineral crystals significantly affects the mechanical properties of the composite materials in a number of aspects (for instance, microstructural load transfer) as is evident from established theoretical models [Ji and Gao, 2010] and current experimental observations.

**1.3.2.** *Effect on composite toughness*


**Figure 1.6.** Representative load-displacement curves obtained upon fracture testing of samples in accordance with <u>ASTM C1421</u> (a), variation of fracture toughness of silica-SC 15 brick and

## Figure 1.6. (cont'd)

mortar composites with varying ceramic content and aspect ratio and their comparison against the fracture toughness of silica (ceramic) and SC 15 (polymer) alone (b).

What makes bioinspired staggered architecture very promising from structural point of view is its unique structural arrangement which confers it superior toughness in comparison to its ceramic and polymer counterparts alone. Whether similar attributes exist in the synthesized composites, fracture toughness of the composites were measured to observe this effect and the results are shown in **Figure 1.6(a,b)**.

<u>ASTM C1421</u> was followed for the determination of fracture toughness of the synthesized composites. Figure 1.6(a) shows the representative load-displacement curves obtained during fracture testing of the samples in a three-point bending set up. As per <u>ASTM</u> <u>C1421</u>, determination of  $K_{IC}$ , as shown in Figure 1.6(b) is as follows:

$$K_{IC} = g \left[ \frac{P_{max}S}{BW^{3/2}} \right] \left[ \frac{3[a/W]^{1/2}}{2[1-[a/W]]^{3/2}} \right]$$
  
where,  
$$g = g \left( \frac{a}{W} \right) = \frac{1.99 - [a/W][1-a/W][2.15 - 3.93[a/W] + 2.7[a/W]^{2}]}{1+2[a/W]}$$
(1.2)

As it can be seen from **Figure 1.6(b)**, the measured fracture toughness of all the synthesized composites is significantly greater than the fracture toughness of the ceramic (silica: 0.64 MPa m<sup>0.5</sup>) and the polymer (SC 15: 1.54 MPa m<sup>0.5</sup>) [**Robinette et al., 2007**]. Once again, the effect of both aspect ratio and ceramic content of the ceramic can be seen to

contribute a superior role to the composite's fracture toughness even if high polymeric content is present in the composite. This can be explained as follows.

Dugdale's cohesive strip model [Gao et al., 2003; Ji and Gao, 2010] is given by the following equation,

$$J = (1 - \Phi) L \int \Gamma_{p} d\varepsilon_{p} = (1 - \Phi) L \Theta_{p} \min(S_{p}, S_{int}, \Gamma_{p})$$
(1.3)

where, J is the fracture energy,  $\Theta_p$  denotes the effective strain to which the polymer can deform before failure,  $S_p$  denotes the yield strength of the polymer,  $S_{int}$  denotes the ceramicpolymer interface strength, and  $\tau_p$  denotes shear strength of the polymer. With reference to equation (1.3), the expression under the integral is representative of the dissipation energy by the polymer per unit volume and thus,  $\Theta_p$  is a key parameter which contributes to fracture energy. The polymeric matrix is thereby essential for enhancing toughness via energy dissipation due to its viscoelastic nature that contributes to large deformation. Also it is discernible that inelasticity is a key material parameter that renders a material notch insensitive by enabling a material to eliminate stress concentration at strain concentration locales. However, the aspect ratio also plays an important role which is explained as follows. The staggered microstructure provides a strain amplification mechanism [**Ji and Gao, 2010**] and contributes to full utilization of large deformation capability of the polymer.

$$\varepsilon_{p} = \frac{\Phi}{2(1-\Phi)} \rho \left(\varepsilon - \frac{\Delta_{m}}{L}\right) \propto \rho \varepsilon$$
(1.4)

As it can be seen from equation (1.4), the capability of the polymeric matrix to be strained is magnified over composite strain by the aspect ratio of the ceramic platelets, thereby allowing the polymer to deform and dissipate energy at the microscopic level without giving rise to large deformation on the composite level. For composites having high ceramic content, fracture is often triggered before plastic instability inception via abrupt percolation of damage across the material [Mortensen and Llorca, 2010]. This explains, that why toughness decreases in composites with high ceramic content and lower aspect ratios. As is evident from Figure **1.4(c)** and Figure **1.6(b)**, higher toughness comes at a cost of decreasing strength; this is in agreement with analytical foundation [Zhang et al., 2010] where this behavior can be attributed to increasing difficulty in driving the polymeric matrix deformation unless smaller aspect ratios are used. Another way to enhance toughness of the composites is by grafting the ceramic platelets with polymeric chains. This in turn will lead to increase in S<sub>int</sub> which in current non-grafted synthesized composites is one of the most vulnerable entities under contemporary loading conditions.

From structural engineering application view point, a knowledge and an understanding of the synthesis-structure-property relationship in these composites is vital for the development of advanced ceramic-polymer composites with enhanced mechanical stiffness, strength and toughness. Based on the information obtained from experimental data, we can summarize our observations as follows. If high stiffness and strength is desired, it would be advantageous to have composites synthesized having low aspect ratios and high ceramic content. Similarly, if high toughness is desired, it would be advantageous to have composites

synthesized having high aspect ratios and low ceramic content. This is in agreement with Wilbrink and co-authors [Wilbrink et al., 2010] where they demonstrated, via development of a unit-cell model, that as the aspect ratio of the bricks increases, a trade-off exists between increasing strength and decreasing ductility. Indeed, the same set of phenomena can be observed in biological composites as well. As mentioned earlier, bone comprises of plate-like crystals (having an aspect ratio varying from 25-50) embedded in a collagen-rich protein matrix (~0.40) resulting in variation of elastic modulus from ~2–25 GPa and a strength varying from ~150–200 MPa. Similarly, nacre is made of enormously high ceramic content (~0.90-0.95) of plate-like inorganic tablets (having an aspect ratio from 10-20) resulting in variation of elastic modulus from ~40–70 GPa and a strength varying from ~20–120 MPa [Espinosa et al., 2009]. From literature, it can be recalled that toughening rate of bone is higher than that of nacre; corresponding to a crack extension of 0.6 mm, resistance increases to 30 kJm<sup>-2</sup> in bone but only to 1.5 kJm<sup>-2</sup> in nacre [Barthelat and Espinosa, 2007; Wang and Gupta, 2011]. Similarly, elk antler falls in the realm of tougher side of the bone family materials, exhibits a toughness increase of 60 kJm<sup>-2</sup> at a crack extension of 0.6 mm [**Wang and Gupta, 2011**].

# 1.4. Conclusion

'Mother Nature' cleverly uses the aspect ratio and content of inorganic matter to synthesize composites having varying degrees of stiffness, strength and toughness. Such an amazing capability of fine-tuning the properties for functions has rarely been demonstrated in synthetic composites. In this article, an attempt has been made to synthesize staggered

21

ceramic-polymer composites having varying ceramic content and aspect ratio using freezecasting technique. Inferences obtained from experimental investigation provides us useful information as to their effects on the mechanical properties of synthesized composites. This will in-turn help us in custom-design manufacture of hybrid bio-inspired composite materials. REFERENCES

### REFERENCES

Araki, K., Halloran, J.W. 2005. Porous ceramic bodies with interconnected pore channels by a novel freeze casting technique. *J. Am. Ceram. Soc.* 88, 1108–1114.

**Apalak, M.K., Gunes, R., 2007.** Elastic flexural behavior of an adhesively bonded single lap joint with functionally graded adherends. *Mater. Design* **28**(5), 1597-1617.

**Barthelat, F., Espinosa, H.D. 2007.** An Experimental Investigation of Deformation and Fracture of Nacre-Mother of Pearl. *Exp. Mech.* **47**, 311–324.

Blindow, S., Pulkin, M., Koch, D., Grathwohl, G., Rezwan, K. 2009. Hydroxyapatite/SiO<sub>2</sub> composites via freeze casting for bone tissue engineering. *Adv. Eng. Mater.* **11**(11), 875-84.

**Currey, J.D. 2002.** Bones: Structure and Mechanics, Princeton University Press, Princeton.

**Chino, Y., Dunand, D. 2008.** Directionally freeze-cast titanium foam with aligned, elongated pores. *Acta Mater.* **56**, 105–113.

**Deville, S., Saiza, E., Nalla, R.K., Tomsiaa, A.P. 2006.** Freezing as a path to build complex composites. *Science* **311**, 515–518.

**Deville, S. 2008.** Freeze-casting of porous ceramics: A review of current achievements and issues. *Adv. Eng. Mater.* **10**(3), 155-69.

Dutta, A., Tekalur, S.A., Miklavcic, M. 2013. Optimal overlap length in staggered architecture composites under dynamic loading conditions. *J. Mech. Phys. Solids.* **61**(1), 145-160.

Dutta, A., Vanderklok, A., Tekalur, S.A., 2012. High strain rate mechanical behavior of seashell-mimetic composites: Analytical model formulation and validation. *Mech. Mater.* 55, 102-111.

da Costa Mattos, H.S., Monteiro, A.H., Palazzetti, R., 2012. Failure analysis of adhesively bonded joints in composite materials. *Mater. Design* **33**, 242-247.

**Espinosa, H.D., Rim, J.E., Barthelat, F., Buehler, M.J. 2009.** Merger of structure and material in nacre and bone–Perspectives on de novo biomimetic materials. *Prog. Mater. Sci.* **54**, 1059–1100.

**Fukasawa, T., Deng, Z.-Y., Ando, M., Ohji, T., Kanzaki, S. 2002.** Synthesis of porous silicon nitride with unidirectionally aligned channels using freeze-drying process. *J. Am. Ceram Soc.* **85**, 2151–2155.

Fu, Q., Rahaman, M.N., Dogan, F., Bal, B.S. 2008. Freeze casting of porous hydroxyapatite scaffolds. I. processing and general microstructure. *J. Biomed. Mater. Res. B* **86**(1), 125-135.

Gao, H., Ji, B., J¨ager, I.L., Arzt, E., Fratzl, P. 2003. Materials become insensitive to flaws at nanoscale: lessons from nature. *P. Natl. Acad. Sci. USA* **100**, 5597–5600.

Huang, Z., Li, H., Pan, Z., Wei, Q., Chao, Y.J., Li, X. 2011. Uncovering high-strain rate protection mechanism in nacre. *Sci. Rep.* 1:148, 1-5.

Jackson, A.P., Vincent, J.F.V., Turner, R.M. 1988. The mechanical design of nacre. *P. R. Soc. London B.* 234, 415–440.

Jing, L., Zuo, K.H., Zhang, F.Q., Chun, X., Fu, Y.F., Jiang, D.L., Zeng, Y.P. 2010. The controllable microstructure of porous Al<sub>2</sub>O<sub>3</sub> ceramics prepared via a novel freeze casting route. *Ceram. Int.* **36**(8), 2499-2503.

Ji, B., Gao, H. 2010. Mechanical principles of biological nanocomposites. *Annu. Rev. Mater. Res.* 40, 77-100.

Kamat, S., Su, X., Ballarini, R., Heuer, A.H. 2000. Structural basis for the fracture toughness of the shell of the conch Strombus gigas. *Nature* **405**, 1036–1040.

Launey, M.E., Munch, E., Alsem, D.H., Barth, H.B., Saiz, E., Tomsia, A.P., Ritchie, R.O. 2009. Designing Highly Toughened Hybrid Composites Through Nature-Inspired Hierarchical Complexity. *Acta Mater.* 57, 2919-2932.

**Liu, G., Zhang, D., Meggs, C., Button, T.W. 2010.** Porous Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> composites fabricated by an ice template method. *Scripta Mater.* **62**(7), 466-468.

Li, J.C., Dunand, D.C. 2011. Mechanical properties of directionally freeze-cast titanium foams. *Acta Mater.* 59(1), 146-58.

Menig, R., Meyers, M.H., Meyers, M.A., Vecchio, K.S. 2000. Quasi-static and dynamic mechanical response of Haliotis rufescens (abalone) shells. *Acta Mater.* **48**, 2383–2398.

**Macchettaa, A., Turner, I.G., Bowena, C.R. 2009.** Fabrication of HA/TCP scaffolds with a graded and porous structure using a camphene-based freeze-casting method. *Acta Biomater.* **5**, 1319–27.

Mortensen, A., Llorca, J. 2010. Metal matrix composites. Annu. Rev. Mater. Res. 40, 243-270.

**Ouinas, D., Bouiadjra, B.B., Achour, T., Benderdouche, N., 2010.** Influence of disbond on notch crack behavior in single bonded lap joints. *Mater. Design* **31**(9), 4356-4362.

Robinette, J., Bujanda, A., DeSchepper, D., Dibelka, J., Costanzo, P., Jensen, R., McKnight, S. 2007. Nanosilica modification of elastomer-modified VARTM epoxy resins for improved resin & composite toughness. Aberdeen Proving Ground, MD : Army Research Laboratory, Report Number: ARL-TR-4084 (http://www.dtic.mil/cgibin/GetTRDoc?AD=ADA466485) [Access Date: August 17, 2012].

Sarikaya, M., Gunnison, K.E., Yasrebi, M., Aksay, J.A., 1990. Mechanical property-microstructural relationships in abalone shell. *Mater. Res. Soc.* 174, 109-116.

**Sofie, S.W., Dogan, F. 2001.** Freeze casting of aqueous alumina slurries with glycerol. *J. Am. Ceram. Soc.* **84**(7) 1459–1464.

Soon, Y.M., Shin, K.H., Koh, Y.H., Lee, J.H., Choi, W.Y., Kim, H.E. 2011. Fabrication and compressive strength of porous hydroxyapatite scaffolds with a functionally graded core/shell structure. *J. Eur. Ceram. Soc.* **31**(1-2), 13-18.

Sayman, O., Ozen, M., Korkmaz, B., 2013. Elasto-plastic stress distributions in adhesively bonded double lap joints. *Mater. Design* **45**, 31-35.

Wilbrink, D.V., Utz, M., Ritchie, R.O., Begley, M.R. 2010. Scaling of strength and ductility in bioinspired brick and mortar composites. *Applied Physics Letters* **97**, 193701.

Wang, R., Gupta, H.S. 2011. Deformation and fracture mechanisms of bone and nacre. *Annu. Rev. Mater. Res.* 41, 41-73.

Yoon, B.H., Koh, Y.H., Park, C.S., Kim, H.E. 2007. Generation of large pore channels for bone tissue engineering using camphene-based freeze casting. *J. Am. Ceram. Soc.* **90**, 1744–1752.

Ye, F., Zhang, J.Y., Zhang, H.J., Liu, L.M. 2010. Pore structure and mechanical properties in freeze cast porous Si3N4 composites using polyacrylamide as an addition agent. *J. Alloy. Compd.* 506(1), 423-27.

Yoon, H.J., Kim, U.C., Kim, J.H., Koh, Y.H., Choi, W.Y., Kim, H.E. 2010. Macroporous alumina ceramics with aligned microporous walls by unidirectionally freezing foamed aqueous ceramic suspensions. *J. Am. Ceram. Soc.* **93**(6), 1580-1582.

**Zhang, H., Hussain, I., Brust, M., Butler, M.F., Rannard, S.P., Cooper, A.I. 2005.** Aligned two- and three-dimensional structures by directional freezing of polymers and nanoparticles. *Nature Mater.* **4**, 787–93.

Zhang, Z., Zhang, Y.-W., Gao, H. 2010. On optimal hierarchy of load-bearing biological materials. *Proc. R. Soc. B* 278, 519-525.

**Zuo, K.H., Zhang, Y.A., Zeng, Y.P., Jiang, D.L. 2011.** Pore-forming agent induced microstructure evolution of freeze casted hydroxyapatite. *Ceram. Int.* **37**(1), 407-10.

CHAPTER 2: HIGH STRAIN RATE MECHANICAL BEHAVIOR OF SEASHELL-MIMETIC

COMPOSITES: ANALYTICAL MODEL FORMULATION & VALIDATION

## 2.1. Introduction

Superior strength and light weightiness are two discernible facets in biological composites, like bone and nacre, and has caught substantial attention of the scientific community. Biological composites have been tried, tested and designed by the theory of evolution over millions of years. Nacre and bone exhibit high stiffness, strength and specifically, superior toughness [Barthelat and Espinosa, 2007; Jackson et al., 1988; Kessler et al., 1996; Kamat et al., 2000; Menig et al., 2000, 2001; Sarikaya et al., 1990] which is orders of magnitude higher with respect to its inorganic (brittle minerals) and organic (ductile polymers) components. The brittle minerals tend to have different structures and compositions. With specific reference to mollusks, the shell material is typically composed of aragonite and/or calcite where the orientation of the inorganic component may be prismatic, nacre, crossedlamellar or foliated in nature. Nacre is composed of mineral tablets (of high weight fraction  $\Phi$ ~0.95) and soft polymeric matrix, composed of proteins and polysaccharides, laid in a brickand-mortar structural arrangement. Significant macroscopic deformations have been observed in nacre in the form of high values of failure strains of the order of nearly 5%. Quasi-static compression tests [Menig et al., 2000], at loading rates of 1–500 MPas<sup>-1</sup>, were performed on nacre under two loading configurations: (a) load applied perpendicular to the lamellar bricks and (b) load applied along the plane of bricks. Probability estimation using Weibull function was employed which showed that there is a 50% chance of failure at stress levels of 450 MPa and 200 MPa for loading configurations (a) and (b) respectively. Similar observations (for static case only) were inferred in the works of [Barthelat et al., 2006; Barthelat and Espinosa, 2007;

Jackson et al., 1988; Sarikaya et al., 1990]. In nacre, a number of factors contribute to toughening mechanisms, namely (a) pull-out of tablets [Jackson et al., 1988], (b) crack deflection by the organic layers [Menig et al., 2000], (c) platelet interlocks [Katti et al., 2005], and (d) presence of nanoasperities & tablet waviness and sliding which results in high inelastic strains and hence whitening [Barthelat and Espinosa, 2007], which in-turn is responsible for its superior fracture resistance.

An underlying course in the evolutionary process of shells is shell-crushing predation by crustaceans [Kitching and Lockwood, 1974; Vermeij, 1976, 1977, 1978; Zipser and Vermeij, 1978]. Shell breaking methods is recognizable in other tropical and subtropical crab species [Rossi and Parisi, 1973; Shoup, 1968; Vermeij, 1976, 1978; Zipser and Vermeij, 1978]. Predatory attack by fishes on larger gastropods, living in the open, is also pretty common [Bertness and Cunningham, 1981]. Similarly, bone suffers fracture and failure due to impact loading from falls, accidents, ballistic impact and blast loading. Note that a number of the studies in literature are limited to quasi-static loading scenario. This is intriguing given the fact that both this material is fundamentally used as a basic structural material for synthesizing and in orchestrating complex load bearing/shielding structures against predatory attack. Understanding the mechanics of failure of the biological composites under such a wide range of impact loading will provide us design strategies for fabrication of hybrid bio-inspired composites.

Biological composites are synthesized by nature via bottom-up route exhibiting complex hierarchical design over nano-micro-meso-macro scales. For instance, seashells and bone

30

(vertebral) exhibit 2-3 [Currey, 1977; Jackson et al., 1988; Menig et al., 2000, 2001] and 7 levels [Currey, 1984; Landis, 1995; Rho et al., 1998; Weiner and Wagner, 1998] of hierarchy respectively. Biocomposites, notwithstanding the degree of hierarchical complexity, at the most elementary level, exhibit an analogous microstructure comprising of nanometer sized inorganic crystals reinforced in a soft biopolymer (organic) matrix in the form of a staggered architecture [Fratzl et al., 2004; Gao et al., 2003; Jager and Fratzl, 2000], otherwise known as a *brick-andmortar type structural arrangement* (shown in the inset in Figure 2.1).



**Figure 2.1.** Dependence of stiffness of biocomposites (exhibiting brick and mortar type of architecture at its most elementary level) as a function of aspect ratio of ceramic bricks and volume fraction of ceramic as laid down by **Gao et al., 2003**. Inset shows the brick and mortar type microstructural arrangement observed in seashells, and microstructure of bone.

Crystalline plate-like (2–4nm thick and up to 100nm long) reinforcements ( $\Phi$ ~0.50-0.67) in collagen-rich protein matrix [Landis, 1995; Landis et al., 1996; Roschger et al., 2001] are

present in bone and dentin. As discussed earlier, nacre is made of enormously high volume fraction (0.90-0.95) of plate-like inorganic tablets (0.4-0.5  $\mu$ m thick and 5-10  $\mu$ m long) with a small amount of soft matrix (thickness of around 20-30 nm) in between the platelets [Currey, 1977; Jackson et al., 1988; Kamat et al., 2000; Menig et al., 2000; Wang et al., 2001]. In the literature, there have been attempts to analyze the stiffness of the staggered nanostructure of bone [Jager and Fratzl, 2000; Kotha et al., 2000]. A mechanical model was proposed by Jager and Fratzl (2000), to estimate the maximum stress and strain of the composite, by advancing previously established models for the mechanical properties of mineralized collagen fibrils [Wagner and Weiner, 1992] by setting forth inorganic crystals in a staggered arrangement in agreement with the distribution of gaps in the collagen fibril [Hulmes et al., 1995; Landis, 1995; Veis and Sabsay, 1987]. Micromechanical model developed by Kotha et al. (2000) was based on shear-lag theory for deriving axial and shear stress distribution in platelets on the assumption of a fundamental basis that the load carried by the platelets remains constant and inter-platelet load transfer occurs via shear deformation of the matrix. Tension-shear chain (TSC) model developed by Gao et al., (2003) and Ji and Gao (2004), as shown in Figure 2.1. and given by equation (2.1) below, unraveled the reason for high stiffness of the biocomposites.

$$\frac{1}{E} = \frac{4(1-\Phi)}{G_{\rm p}\Phi^2\rho^2} + \frac{1}{\Phi E_{\rm m}}$$
(2.1)

On the basis of the mathematical expression as given by equation (1), the composite stiffness estimate (E) is dependent on factors, namely, mineral Young's modulus (E<sub>m</sub>), protein

shear modulus ( $G_p$ ), mineral volume fraction ( $\Phi$ ), and aspect ratio of the mineral crystals (p). Additionally, beyond a certain value of aspect ratio, the composite stiffness (E) becomes nearly constant. Also, the TSC model predicts the stiffness with a reasonable good accuracy. However, all the different theoretical models developed earlier predict material behavior under quasistatic loading conditions.

Several questions still remain unanswered when we shift our focus to the dynamic regime, such as (1) Is the material behavior better under dynamic loading conditions than its static counterpart? (2) what are the parameters that govern the material behavior of particulate composites under dynamic loading conditions? Menig et al. (2000, 2001) carried out dynamic compression test on abalone and conch shells in a Split Hopkinson Pressure Bar (SHPB) and found out that dynamic compressive strength of abalone is approximately 50% higher than static compressive strength. However, a theoretical analysis would provide guidance on the development of nanostructured materials by tailor-designing materials from a scale of nanometers and up. Currently we barely have any theoretical basis on how to design a hierarchical material to achieve a particular set of macroscopic properties. Recently, Wei et al. (2012) developed a continuum model, under static loading conditions, which communicates the existence of characteristic overlap length (a function of cross-linking chemistry of the matrix with its reinforcement and mechanical properties of reinforcement) which contributes to optimization of both strength and toughness in nacre, collagen molecules and spider-silk fibers. In order to understand the mechanical response of staggered and lamellar composites under dynamic rates of loading, in the current research we attempt to use the fundamental aspect of

shear-lag theory i.e., ceramic scaffold serves as the load-bearing member and the polymer contributes to transfer of load via shear, however applying it under compressive loading scenario en-route to the development of a theoretical model followed by subsequent experimental investigation in a SHPB.





**Figure 2.2.** (a) Schematic of the brick and mortar type structural arrangement subjected to external loading; (b) load acting on the ceramic and transfer of load between ceramic platelets by shearing of the intermediate polymer layers; (c) variation of shear stress and displacement

## Figure 2.2. (cont'd)

profile along the ceramic thickness for the outer ceramic; (d) variation of shear stress and displacement profile along the ceramic thickness for the inner ceramic.

**Figure 2.2.** shows the schematic of the representative element of a ceramic polymer composite having a brick and mortar structural arrangement at its elementary level. Following assumptions have been taken into consideration:

(a) ceramic blocks are linear elastic,

(b) constant axial stress distribution throughout the ceramic thickness,

(c) constant shear stress distribution throughout the polymer thickness, and

(d) inconsequential peeling thickness.

Performing force equilibrium on the outer ceramic and inner ceramic, we obtain

$$(T_{o} + \partial T_{o}) - T_{o} + 2\tau_{p}dx = \rho_{c}(hdx)a_{o}$$
(2.2)

$$\frac{\partial T_{0}}{\partial x} + 2\tau_{p} = \rho_{c}ha_{0} = \rho_{c}h\frac{\partial^{2}u_{0}}{\partial t^{2}}\Big|_{avg}$$
(2.3)

$$(T_{i} + \partial T_{i}) - T_{i} + 2\tau_{p}dx = \rho_{C}(hdx)a_{i}$$
(2.4)

$$\frac{\partial T_{i}}{\partial x} - 2\tau_{a} = \rho_{c}ha_{i} = \rho_{c}h\frac{\partial^{2}u_{i}}{\partial t^{2}}\Big|_{avg}$$
(2.5)

where, subscripts 'c', 'p', 'o, and' 'i' denotes the ceramic, polymer, outer (ceramic) and inner (ceramic) respectively. T represents the axial stress resultant (positive in tension) in the ceramic,  $\tau_p$  represents the shear stress in the polymer, a is the average acceleration of the

cross-section of the ceramic, h represents the thickness of the ceramic and u represents the horizontal displacement of the ceramic brick. Let  $\tau_0$  and  $\tau_i$  denote the shear stress in the outer and the inner ceramic respectively with z' and z'' as its origins. Assuming linear variation of shear stress through the ceramic thickness, we obtain

$$\tau_{\rm O} = \frac{2\tau_{\rm P}}{\rm h} z' \tag{2.6}$$

$$\tau_{i} = \tau_{p} \left( 1 - \frac{2z''}{h} \right)$$
(2.7)

If  $G_c$  denotes the shear modulus of the ceramic, then the shear strains in the outer ( $\gamma_0$ ) and inner ceramic ( $\gamma_i$ ) can be represented as

$$\gamma_{O} = \frac{2\tau_{P}}{G_{C}h}z'$$
(2.8)

$$\gamma_{i} = \frac{\tau_{p}}{G_{c}} \left( 1 - \frac{2z''}{h} \right)$$
(2.9)

Integrating shear strains given by (2.8) and (2.9) over the thickness of the ceramic, we obtain the following expressions for horizontal displacement of the outer ceramic ( $u_0$ ) and inner ceramic ( $u_i$ ), given by

$$u_{0}(x,z') = u_{0p}(x) + \frac{\tau_{p}(x)z'^{2}}{G_{c}h} - \frac{\tau_{p}(x)h}{4G_{c}}$$
 (2.10)

$$u_{i}(x,z'') = u_{ip}(x) + \frac{\tau_{p}(x)}{G_{c}} \left( z'' - \frac{z''^{2}}{h} \right)$$
 (2.11)

where  $u_{op}$  and  $u_{ip}$  represent the displacement of the ceramic at the interface between the outer ceramic block and the intermediate polymer and between the polymer and the inner ceramic respectively. The axial forces in the outer (T<sub>o</sub>) and inner ceramic (T<sub>i</sub>) is given by

$$T_{O} = E_{C} \int_{z'=\frac{h}{2}}^{\frac{h}{2}} \frac{\partial u_{O}}{\partial x} dz' = E_{C} h \left( \frac{du_{OP}}{dx} - \frac{h}{6G_{C}} \frac{d\tau_{P}}{dx} \right)$$
(2.12)

$$T_{i} = E_{C} \int_{z''=0}^{h} \frac{\partial u_{i}}{\partial x} dz'' = E_{C} h \left( \frac{du_{ip}}{dx} + \frac{h}{6G_{C}} \frac{d\tau_{p}}{dx} \right)$$
(2.13)

Assuming polymeric shear thickness to be constant throughout the thickness of the polymer layer, the shear strain in the polymer ( $\gamma_p$ ) may be expressed as follows

$$\gamma_{\mathbf{p}} = \frac{u_{\mathbf{i}\mathbf{p}} - u_{\mathbf{o}\mathbf{p}}}{t_{\mathbf{p}}} \tag{2.14}$$

where,  $t_{\mbox{p}}$  represents the thickness of the polymer. Thus, it can be shown that

$$\frac{\partial^2 \gamma_p}{\partial x^2} = \frac{1}{t_p} \left( \frac{\partial^2 u_{ip}}{\partial x^2} - \frac{\partial^2 u_{op}}{\partial x^2} \right)$$
(2.15)

Rearrangement of the terms in equation (2.12) and (2.13) yields

$$\frac{du_{OP}}{dx} = \frac{T_{O}}{hE_{C}} + \frac{h}{6G_{C}}\frac{d\tau_{P}}{dx}$$
(2.16)

$$\frac{du_{ip}}{dx} = \frac{T_i}{hE_c} - \frac{h}{6G_c} \frac{d\tau_p}{dx}$$
(2.17)

Substitution of equations (2.16) and (2.17) in equation (2.15) followed by rearrangement of the terms leads to the following expression

$$\frac{\partial T_{i}}{\partial x} - \frac{\partial T_{o}}{\partial x} = hE_{c} \left( t_{p} + \frac{hG_{p}}{3G_{c}} \right) \frac{\partial^{2} \gamma_{p}}{\partial x^{2}}$$
(2.18)

where  $G_p$  denotes the shear modulus of the polymer. The average accelerations of the outer and inner ceramic layers is given by

$$a_{0}(x,t) = \frac{\partial^{2}u_{0}}{\partial t^{2}}\Big|_{avg} = \frac{V_{j}^{*} - L_{z}^{*} z' = -\frac{h}{2}}{L_{j}^{*} - \frac{h}{2}} \frac{\partial^{2}u_{0}(x,y,z',t)}{\partial t^{2}} dz' dy}{\int_{j}^{*} - L_{z}^{*} z' = -\frac{h}{2}} = \frac{\partial^{2}u_{0p}}{\partial t^{2}} - \frac{hG_{p}}{6G_{m}} \frac{\partial^{2}\gamma_{p}}{\partial t^{2}}$$
(2.19)  
$$a_{i}(x,t) = \frac{\partial^{2}u_{i}}{\partial t^{2}}\Big|_{avg} = \frac{\int_{j}^{*} \int_{j}^{*} \frac{\partial^{2}u_{i}(x,y,z',t)}{\partial t^{2}} dz' dy}{\int_{j}^{*} \int_{j}^{*} \frac{\partial^{2}u_{i}(x,y,z',t)}{\partial t^{2}} dz' dy}{\int_{j}^{*} \int_{j}^{*} \frac{\partial^{2}u_{i}(x,y,z',t)}{\partial t^{2}} dz' dy} = \frac{\partial^{2}u_{ip}}{\partial t^{2}} + \frac{hG_{p}}{6G_{m}} \frac{\partial^{2}\gamma_{p}}{\partial t^{2}}$$
(2.20)

where, 2L\* represents the width of the ceramic layer. Combining equations (2.19) and (2.20) together, taking into account (2.14) and rearranging the terms, we get

$$a_{i} - a_{0} = \left(t_{p} + \frac{hG_{p}}{3G_{c}}\right) \frac{\partial^{2} \gamma_{p}}{\partial t^{2}}$$
(2.21)

Subtracting equation (2.3) from (2.5), we get

$$\left(\frac{\partial T_{i}}{\partial x} - \frac{\partial T_{0}}{\partial x}\right) - 4\tau_{p} = \rho_{c}h(a_{i} - a_{0})$$
(2.22)

Replacement of bracketed terms in the right-hand side and left-hand side of equation (2.22) by (2.18) and (2.21) respectively followed by rearrangement of the terms leads us to the generation of the governing differential equation of the system, given by

$$\frac{\partial^2 \gamma_p}{\partial x^2} - \frac{1}{c_c^2} \frac{\partial^2 \gamma_p}{\partial t^2} = \frac{1}{\alpha} \gamma_p$$
(2.23)

where  $c_c$  denotes the wave velocity through the ceramic  $c_c = \sqrt{\frac{E_c}{\rho_c}}$  and,  $\alpha$  is given by

$$\frac{1}{\alpha} = \frac{12G_pG_c}{E_c\left(3G_cht_p + h^2G_p\right)}$$
(2.24)

Combining equations (2.14), (2.16) and (2.17), we get

$$\left[1 + \frac{\Phi G_{p}}{3G_{c}(1 - \Phi)}\right]\frac{\partial \gamma_{p}}{\partial x} = \frac{\Phi}{h^{2}E_{c}(1 - \Phi)}(T_{i} - T_{o})$$
(2.25)

The initial conditions and the boundary conditions of the problem, given by equations (2.26-2.29), can be represented as

$$\gamma \big|_{t=0} = 0 \tag{2.26}$$

$$\left. \frac{\partial \gamma}{\partial t} \right|_{t=0} = 0 \tag{2.27}$$

At x = 0,  $T_i = 0$  and  $T_o = -F(t)$  (2.28)

At x = L,  $T_i = -F(t)$  and  $T_0 = 0$  (2.29)

where, F(t) is the prescribed loading at the inner and outer ceramic and the negative sign is representative sign of compressive load (as in a SHPB experiment) and L denotes the overlap length. Note that the prescribed loading is equal on both the ends which in turn ensures that the specimen is in a state of dynamic equilibrium with minimal wave propagation effects.

Solution of the governing equation is carried out using Galerkin method of weighted residuals [**Cook et al., 2007**] as follows:

For a finite element  $x_1 \le x \le x_2$ , the residual equation for the element is

$$\sum_{x_{1}}^{x_{2}} N_{i} \left[ \frac{\partial}{\partial x} \left( \frac{\partial \overline{\gamma}_{p}}{\partial x} \right) - \frac{1}{c^{2}} \frac{\partial^{2} \overline{\gamma}_{p}}{\partial t^{2}} - \frac{1}{\alpha} \overline{\gamma}_{p} \right] \partial x = 0, i = 1, 2$$

$$(2.30)$$

where  $~\overline{\gamma}_p~$  represents the approximate shear strain, given in equation (2.31) as

$$\overline{\gamma}_{p} = N_{1}(x)\gamma_{p_{1}} + N_{2}(x)\gamma_{p_{2}}$$
(2.31)

 $N_1(x)$  and  $N_2(x)$  are first order interpolation functions and correspond to weighted residuals in Galerkin Method. Substituting i =1,2 in equation (2.30) followed by rearrangement of the terms leads to the following equation, given as

$$\begin{bmatrix} x_{2} \\ \int \\ x_{1} \end{bmatrix} \left[ \frac{\partial N_{1}}{\partial x} \frac{\partial N_{1}}{\partial x} + \frac{1}{\alpha} N_{1} N_{1} \right] \partial x \quad \int \\ x_{1} \end{bmatrix} \left[ \frac{\partial N_{2}}{\partial x} \frac{\partial N_{2}}{\partial x} + \frac{1}{\alpha} N_{1} N_{2} \right] \partial x \quad \int \\ x_{1} \begin{bmatrix} \frac{\partial N_{2}}{\partial x} \frac{\partial N_{1}}{\partial x} + \frac{1}{\alpha} N_{2} N_{1} \\ \gamma_{p_{2}} \end{bmatrix} d x \quad \int \\ x_{1} \end{bmatrix} \left[ \frac{\partial N_{2}}{\partial x} \frac{\partial N_{2}}{\partial x} + \frac{1}{\alpha} N_{2} N_{2} \right] \partial x \quad \int \\ x_{1} \begin{bmatrix} \frac{\partial N_{2}}{\partial x} \frac{\partial N_{2}}{\partial x} + \frac{1}{\alpha} N_{2} N_{2} \\ \frac{1}{\alpha} \sum_{r_{1}} \frac{1}{c_{c}^{2}} N_{1} N_{1} \partial x \quad \int \\ x_{1} \sum_{r_{1}} \frac{1}{c_{c}^{2}} N_{1} N_{2} \partial x \\ \frac{1}{\gamma_{p_{1}}} \sum_{r_{1}} \frac{1}{c_{c}^{2}} N_{2} N_{2} \partial x \\ \frac{1}{\gamma_{p_{1}}} \sum_{r_{1}} \frac{1}{c_{c}^{2}} N_{2} N_{1} \partial x \quad \int \\ \frac{1}{\gamma_{p_{1}}} \sum_{r_{1}} \frac{1}{c_{c}^{2}} N_{2} N_{2} \partial x \\ \frac{1}{\gamma_{p_{1}}} \sum_{r_{1}} \frac{1}{c_{c}$$

which is equivalent to

$$\left[ \kappa^{(e)} \right] \left\{ \gamma_{p}^{(e)} \right\} + \left[ M^{(e)} \right] \left\{ \ddot{\gamma}_{p}^{(e)} \right\} = \left\{ f^{(e)} \right\}$$
(2.33)

where (2.32) can be simplified to obtain

$$\begin{bmatrix} \mathsf{K}^{(e)} \end{bmatrix} = \frac{1}{(x_2 - x_1)} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} + \frac{(x_2 - x_1)}{6\alpha} \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix}$$
(2.34)

$$\begin{bmatrix} \mathsf{M}^{(e)} \end{bmatrix} = \frac{(\mathsf{x}_2 - \mathsf{x}_1)}{2\mathsf{c}^2} \begin{bmatrix} \mathsf{1} & \mathsf{0} \\ \mathsf{0} & \mathsf{1} \end{bmatrix}$$
(2.35)

The elemental mass matrix given by equation (2.32-2.33) is consistent mass matrix and has been converted into diagonally lumped mass matrix, as shown in equation (2.35), using HRZ lumping scheme.

For the representative element, total displacement is the sum of deformation corresponding to the ceramic element and the deformation corresponding to the shear deformation of the protein, and thus strain can be expressed as given by equation (2.36).

$$\varepsilon_{\text{eff}}\Big|_{O} = \frac{\partial u_{O}\Big|_{avg}}{\partial x} + \frac{h(1-\Phi)}{\Phi} \frac{\partial \gamma_{P}}{\partial x}\Big|_{x=L}$$
(2.36)

Based on the condition of velocity compatibility on the specimen incident bar interface, it can be laid down that particle velocity of the specimen and that of the incident bar are equal. Thus, the predicted strain  $\varepsilon_{predicted}$ , as given by equation (2.37), can be computed as follows

$$\varepsilon_{\text{predicted}} c = \varepsilon_{\text{eff}} c_{\text{c}}$$
 (2.37)

where c represents stress-wave velocity in the incident bar. Taking into consideration our initial assumption that the load is carried by the ceramic skeleton, the stress in the specimen,  $\sigma_{\text{predicted}}$ , can be computed by taking into consideration, on the basis of similar grounds, strain continuity between adjacent elements and is given by equation (2.38) as

$$\sigma_{\text{predicted}} = \left(\frac{E_b A_b}{A_s}\right) \left(\frac{c_c}{c}\right) \frac{T_i}{hE_c}$$
(2.38)

where E<sub>b</sub>, A<sub>b</sub> and A<sub>s</sub> correspond to Young's modulus of the transmission bar, cross-sectional area of the transmission bar and cross-sectional area of the specimen respectively. Lamellar microstructure can be visualized as an extension of brick and mortar microstructure where inter-ceramic brick spacing in a given zero is essentially equal to zero (can be imagined as ceramic bricks in a given row are fused together and forming a rod). Note that this mathematical formulation is thereby equally applicable for composites having lamellar architecture as its elementary microstructure.

### 2.3. Materials and Methods

Sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S) was obtained from Sigma Aldrich (St. Louis, MO, USA). Poly (vinyl alcohol) [-CH<sub>2</sub>CH(OH)-]n 98% hydrolyzed having an average molecular weight  $M_w$  13,000-23,000 was obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) crystals were obtained from Roche Diagnostics Corporation (IN, USA). Two types of ceramic powders were purchased for synthesizing two types of ceramic polymer composite. Silica (SiO<sub>2</sub>) spheres having  $\Phi$  8µm were obtained from Fiber Optic Center Inc (New Bedford, MA, USA). Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) spheres having  $\Phi$  10µm were obtained from Sigma Aldrich (Milwaukee, WI, USA). SC-15 epoxy resin (toughened two phase) was obtained from Applied Poleramic Inc. (Benicia, CA, USA).

Ceramic-polymer composites were prepared by freeze-casting technique [**Deville et al.**, **2006; Launey et al.**, **2009**], as shown in **Figure 2.3(a,b,c)**. Samples thermogravimetric analysis (TGA Q500 V20.10 Build 36, TA Instruments) were conducted at a heating rate of 20°C min<sup>-1</sup> up at temperatures up to 600°C. **ASTM D695-10** was followed for the determination of compressive strength of these ceramic polymer composites under static rates of loading. The specimen dimension chosen for testing was 5mm × 5mm × 10 mm and was performed in a MTS machine (10 kN load cell) at a crosshead speed of 1mm/min. For dynamic compression behavior, material properties have been investigated using SHPB technique. A conventional SHPB or the Kolsky Bar [Kolsky, 1963, 1964)] consists of a striker bar, an incident bar and a transmitter bar, as illustrated in **Figure 2.4(a)**. The specimen is sandwiched between the

incident and transmitter bar (made of high strength aluminum alloy (alloy 7075), each of which was 6ft (1.8 m) long and 5/8 inch (15.9 mm) in diameter. The specimen dimension chosen for testing purpose was 11.22mm × 11.22mm × 9.161 mm. Choice of this dimension has been explained in the *Discussion* section. The responses were measured with electrical resistance strain gages, bonded to the middle of the incident and transmitter bars, connected to Vishay Signal Conditioning Amplifiers (Model 2310B), and the response from the strain gages were recorded using a LeCroy digital oscilloscope (Model354A). The specimen can be subjected to a wide range of strain rates by employing striker bars of various lengths. Performing one dimensional wave analysis on the strain signal obtained from the incident and transmitter bars, and coupling an important assumption that wave propagation effects within a short specimen may be neglected, we can obtain the stress-strain profile in the specimen as given below.



**Figure 2.3.** (a) Typical specimen and its representative microstructure (b, c); (d) schematic showing distribution of ceramic platelets in polymeric matrix in brick and mortar type

### Figure 2.3. (cont'd)

microstructural composites; (e) region under consideration highlighting the overlap region; (f, g) deformed platelets and intermediate polymer upon tensile and compressive loading respectively; (h) specimen for quasi-static experiments; (i) fractured specimen under quasistatic loading.

The specimen strain is calculated from the reflected pulse which is as follows:

$$\varepsilon_{s}(t) = \frac{-2c}{l_{s}} \int_{0}^{t} \varepsilon_{r}(t) dt$$
(2.39)

where, c and  $I_s$  denote the wave speed in the bar and the thickness of the specimen respectively. The average stress in the specimen is given by

$$\sigma_{\rm S} = E_{\rm b} \frac{A_{\rm b}}{A_{\rm S}} \varepsilon_{\rm t} \tag{2.40}$$

where,  $A_s$  is the instantaneous cross sectional area of the specimen.

# 2.4. Results and Discussion

Typically, cylindrical samples are employed for determination of mechanical behavior of specimens under dynamic rates of loading. Specimen design in a cylindrical specimen is governed by choice of an appropriate slenderness ratio (which is the ratio of the length to diameter of the sample). However, for non-cylindrical specimens, corresponding slenderness-ratio has not been defined. In recent studies [**Sen, 2011**], a general design criterion for non-cylindrical samples, as given by equation (2.41), has been proposed by suggesting an

appropriate cross-sectional dimension and a slenderness ratio for a specimen with arbitrary cross-sectional geometry.

$$1.4 \le \frac{l_{s}}{\sqrt{\frac{J}{A_{s}}}} \le 2.8 \tag{2.41}$$

where J denotes the polar moment of inertia of the cross-section of the specimen. In our current investigation, we chose a ratio of 2 and cross-sectional dimension of 11.22 mm× 11.22mm, which in turn based on the design criterion, gives  $I_s = 9.161$ mm.

A composite having a brick and mortar type of architecture at its most elementary level can be visualized as an adherend (the ceramic) held together by an adhesive (the polymer). In our model, we have combined the effects of both inelastic deformation of the polymer and shear deformation of ceramic by including the effects of shear strain acceleration of the polymer and out-of-plane thickness of the ceramic. **Figure 2.3(d)** shows the schematic of the distribution of ceramic platelets in the polymeric matrix as observed in staggered architecture composites. The overlap region, as shown in **Figure 2.3(e)**, is responsible for inter-platelet load transfer via shear deformation of the polymer under the action of tension (**Figure 2.3(f)**) and compressive (**Figure 2.3(g)**) loading respectively. One might speculate micro-buckling of the platelets to be the dominating deformation mechanism in compression based on compressive experiments on nacre by **Menig et al., 2000**. It is to be noted that the basic load transfer mechanism at the micro-scales still remains the same as is depicted in **Figure 2.3(g)**. The inorganic matter associated with nacreous layer (or, ceramic in a ceramic polymer composite) is brittle and inflexible in nature. Hence, failure initiates in these types of composites in the interfacial matrix at the extremities of the joint at micro-scales; the coordinated sliding of layer segments of the same approximate length produces an overall rotation of the specimen in the region with a decrease in length and hence, it appears to be buckled at meso-scales. The following points illustrate this aspect further: (a) seashell is a hierarchical material which exhibits brick and mortar construction of ceramic and biopolymer is exhibited in the microscale, whereas a lamellar architecture is exhibited in the meso-scales as shown in the figure below (comprising of 300 µm thick layers, spaced apart by layers of viscoplastic material of thickness of about 20  $\mu$ m); (b) under compressive loading conditions, microbuckling governs failure mechanism of fiber-reinforced composites [Espinosa et al., 1998] when loading is in a direction parallel to reinforcements, and hence based on the similarity of mesostructure in seashells against that of fiber-reinforced composites, microbuckling was thereby observed under compressive loading conditions in nacre. In the lamellar structures associated with the mesostructure in seashells, cracks initiate first in the at the viscoplastic material layers separating the mesolayers [Menig et al., 2000; Su et al., 2012]. Presence of ceramic bridges in between the ceramic layers (an attribute associated with nacre at micro-scales) also hinders Euler buckling of the ceramic layers at micro-scales [Deville, 2006]. Similarly, as was postulated by **Huang et al., 2011**, under rapid-compression ballistic conditions, buckling of the material is restrained at micro-scales via deformation twinning of the coordinated nano-scale particles. Under the application of an external loading, hence the failure of the specimen is pronounced along the interface for both static, as shown in Fig. 3(i), and under dynamic loading conditions

via nucleation and growth of plastic zone from either ends of the overlap length towards the center.



**Figure 2.4.** (a) Schematic of a Split Hopkinson Pressure Bar (SHPB); (b) plot of pulses traced in the oscilloscope based on the pulses recorded by the strain gages in the incident bar (solid pink) and transmission bar (solid yellow); (c) specimen for SHPB experiments; (d) fractured specimen upon impact loading; (e) ratio of force on the transmission face to the incident face over time; (f) plot of strain-rate versus time.

With reference to studies [Gao et al., 2003; Ji and Gao, 2004], for a brick and mortar type of composite, the strength of the staggered composite is dependent on the strength of the

ceramic-polymer interface, yield strength of the polymer, shear strength of the polymer and maximum compressive strength of the ceramic bricks. Typically, in a ceramic-polymeric composite, the most vulnerable entity under loading conditions (both, static and dynamic) is the interfacial ceramic-polymer strength which in turn is thus representative of the ceramicpolymer joint strength. Note that, the ceramic in the current synthesized ceramic-polymer composites were not grafted. Thus, dynamic compression experiments on these type of composites would provide us ceramic-polymer interfacial strength of the composite under high rates of loading.

Two types of ceramic-polymer composites were synthesized: (a) SiO<sub>2</sub>-SC 15 epoxy resin, and (b) Al<sub>2</sub>O<sub>3</sub>-SC 15 epoxy resin. Furthermore, corresponding to each type, (a) & (b), ceramicpolymer composites were synthesized having varying weight fractions ( $\Phi_w$ ) of the ceramic content in them. **Figure 2.4(b)** shows a typical plot of pulses obtained during dynamic compressive loading on the ceramic-polymer composites. The solid pink line represents the incident record ( $\varepsilon_i$ ) and reflected record ( $\varepsilon_r$ ). The solid yellow line represents transmitted record ( $\varepsilon_t$ ). Note that, a large opposite unloading wave can be observed in the later part of the reflected wave. This is a very special phenomenon and this can be attributed to occurrence of an elastic hysteresis effect, which may be caused by viscoelastic response of this kind of polymer [**Hao et al., 2005**]. **Figure 2.4(e,f)** shows a typical force-equilibrium and strain rate vs. time plot obtained under these strain rates. As it can be seen from **Figure 2.4(e,)**, reasonable

equilibrium was attained. Figure 2.4(f) shows a plot of strain-rate versus time. Constant strain



rate was achieved, however for a short period of time. Corresponding value was thereby chosen as the representative strain-rate corresponding to a given loading condition.

**Figure 2.5.** Dynamic stress strain curves obtained for SiO<sub>2</sub> SC-15 ceramic polymer composite (a) and  $Al_2O_3$  SC-15 ceramic polymer composite (b) corresponding to varying ceramic contents and strain-rates.

The dynamic stress-strain curves for SiO<sub>2</sub> SC-15 & Al<sub>2</sub>O<sub>3</sub> SC-15 composite systems are shown in **Figure 2.5(a,b)** respectively. Post peak stress, the stress-strain data is representative of the unloading behavior. **Figure 2.4(c)** shows the specimen used for testing in SHPB. Failure of the specimens, as shown in **Figure 2.4(d)** initiates at the peak stress. **Table 2.1** and **Table 2.2** lists the results obtained from dynamic compression experiments using SHPB on SiO<sub>2</sub> SC-15 &

 $Al_2O_3$  SC-15 composite systems respectively. Static compressive strengths of SiO<sub>2</sub> SC-15 composite system having ceramic weight fractions of 0.45, 0.55 & 0.60 (as determined from TGA) were found out to be 134 MPa, 170 MPa and 213 MPa respectively. Similarly, Static compressive strengths of  $Al_2O_3$  SC-15 composite system having ceramic weight fractions of 0.45, 0.55, 0.60 & 0.70 (as determined from TGA) were found out to be 105 MPa, 108 MPa, 115 MPa and 130 MPa respectively.

Φ <sub>w</sub>	έ <sub>max</sub> (s <sup>-1</sup> )	σ <sub>predicted</sub> (MPa)	σ <sub>experiment</sub> (MPa)	Error (%)	ε <sub>cal</sub>	ε <sub>exp</sub>	Error (%)
0.45	1310	165.11	167.02	1.15	0.0344	0.0354	2.70
0.45	1580	176.06	189.79	7.23	0.0388	0.0425	8.61
0.45	1640	175.99	182.21	3.42	0.0409	0.0431	5.01
0.55	1200	191.51	198.27	3.41	0.0291	0.0310	6.22
0.55	1330	198.23	208.99	5.15	0.0354	0.0371	4.61
0.55	1500	195.78	202.47	3.30	0.0372	0.0412	9.81
0.60	1140	197.91	203.57	2.78	0.0263	0.0292	9.90
0.60	1160	203.20	211.64	3.99	0.0308	0.0321	4.01
0.60	1250	210.24	219.71	4.31	0.0290	0.0308	5.88

Table 2.1. Results of dynamic compression experiments on SiO<sub>2</sub> SC-15 composites.

Φw	ἑ <sub>max</sub> (s <sup>-1</sup> )	σ <sub>predicted</sub> (MPa)	σ <sub>experiment</sub> (MPa)	Error (%)	ε <sub>cal</sub>	ε <sub>exp</sub>	Error (%)
0.45	1170	165.30	169.40	2.42	0.0345	0.0373	7.41
0.45	1230	171.23	175.77	2.58	0.0364	0.0402	9.54
0.45	1490	174.84	172.10	1.59	0.0379	0.0406	6.64
0.55	860	162.81	173.39	6.10	0.0229	0.0245	6.59
0.55	890	162.93	168.61	3.37	0.0230	0.0256	10.21
0.55	1120	195.73	196.97	0.63	0.0266	0.0287	7.38
0.60	1160	182.13	190.15	4.22	0.0294	0.0319	7.76
0.60	1180	184.98	189.01	2.13	0.0277	0.0297	6.60
0.60	1190	195.63	201.90	3.11	0.0251	0.0276	8.96
0.70	960	217.63	232.01	6.20	0.0228	0.0240	4.98
0.70	1070	213.77	230.34	7.19	0.0257	0.0267	3.58
0.70	1100	210.17	224.07	6.20	0.0165	0.0186	11.06

Table 2.2. Results of dynamic compression experiments on Al<sub>2</sub>O<sub>3</sub> SC-15 composites.



Figure 2.6. Plot of (a) experimental stress, and (b) strains (at peak stress) for SiO<sub>2</sub> SC-15 ceramic

polymer composite corresponding to varying ceramic contents at different strain-rates.


**Figure 2.7.** Plot of (a) experimental stress, and (b) strains (at peak stress) for Al<sub>2</sub>O<sub>3</sub> SC-15 ceramic polymer composite corresponding to varying ceramic contents at different strain-rates.

As it can be seen from **Table 2.1.** and **Table 2.2.**, the peak stresses and strains ( $\varepsilon_{cal}$  - at peak stress) as predicted by the analytical model are in reasonable agreement with the experimentally obtained stresses and strains. Dynamic compressive strength of ceramic-polymer composites is significantly higher than its static counterpart (especially, for Al<sub>2</sub>O<sub>3</sub> SC-15 composite) and this large discrepancy in fracture strength values is indicative of a strong strain-rate dependence of the mechanical properties of this type of ceramic polymer composites. However maximum strains, as it can be seen from **Figure 2.5(a,b)**, in dynamic regime (~5%-6%) are approximately the same with respect to its static counterpart (~6%-6.5%). From microstructural point of view, this could possibly be attributed to the occurrence of two deformation mechanisms, under high strain-rate loading, in the ceramic bricks: (a) partial dislocation emission, and (b) deformation twinning as it can be inferred from the recently

conducted studies [Huang et al., 2011] on their outlook towards uncovering high-strain rate protection mechanism in nacre. In fact, an additional observation can be noted from Table 2.1 and Table 2.2. It can be seen that for a fixed ceramic weight fraction strain levels increase, though minimal, with increasing strain-rate (shown in Figure 2.6(b) and Figure 2.7(b) for SiO<sub>2</sub> SC-15 & Al<sub>2</sub>O<sub>3</sub> SC-15 composite system respectively), which again follows the reasoning stated above. Also, it can be seen that ceramic-polymer composites having 0.55-0.60 weight fraction of ceramic provide the optimal performance in terms of stresses and strains (at peak stress). The current model predicts failure strength within ±10%. Nevertheless, future studies will be undertaken towards understanding the effect of kinking in these type of composites to determine if it plays a major role in strength determination.

Typically, ceramics exhibit rate-insensitive or even negative rate dependence behavior. If compared against the mechanical behavior obtained by brick-and-mortar ceramic-polymer composites, these composites exhibit dynamic self-stiffening behavior [**Huang et al., 2011**], which is similar to that observed in nacre. This kind of self-stiffening behavior under dynamic rates of loading will find particular relevance in application of these types of composites on their usage as protective materials when subjected to ballistic impact. The outcome of the current research will provide highlights on the applicability of hybrid bio-inspired composites as body armored materials.

### 2.5. Conclusion

Investigation on the mechanical behavior of ceramic-polymer composites, having brick and mortar structure as its most elementary level of architecture, under dynamic rates of loading have been performed in a SHPB. An analytical model has been formulated, for dynamic rates of loading, based on the mechanism that mineral platelets serve as the principle load bearing member & intermediate polymeric layer serve to transfer load between the platelets following shear deformation) and considering the fact that a composite having a brick and mortar type of architecture can be visualized as an adherend (the bricks/ceramic) held together by an adhesive (the mortar/polymer). In a ceramic-polymeric composite, the interfacial ceramic-polymer strength is representative of the ceramic-polymer joint strength and the analytical model attempts to predict the same. The results obtained from the analytical model are in reasonable agreement with the experimentally obtained stresses and strains. It was found that dynamic compressive strength of ceramic-polymer composites is significantly higher than its static counterpart and this can be attributed to strong strain-rate dependence of the mechanical properties of this type of ceramic polymer composites. From microstructural point of view, this could possibly be attributed to the occurrence of two deformation mechanisms, under high strain-rate loading, in the ceramic bricks: (a) partial dislocation emission, and (b) deformation twinning. Additionally, it was seen that for a fixed ceramic weight fraction, strain levels increase with increasing strain-rate which follows the justification stated above. Thus, these composites exhibit dynamic self-stiffening behavior which will find particular relevance in application of these types of composites as protective material when subjected to ballistic impact.

REFERENCES

#### REFERENCES

**ASTM D695-10:** Standard Test Method for Compressive Properties of Rigid Plastics, ASTM International.

Bertness, M.D., Cunningham, C. 1981. Crab shell-crushing predation and gastropod architectural defense. J. Exp. Mar. Biol. Ecol. 50, 213-230.

Barthelat, F., Li, C-M, Comi, C., Espinosa, H.D. 2006. Mechanical properties of nacre constituents and their impact on mechanical performance. *J. Mater. Res.* 21, 1977-1986.

**Barthelat, F., Espinosa, H.D. 2007.** An Experimental Investigation of Deformation and Fracture of Nacre-Mother of Pearl. *Exp. Mech.* **47**, 311–324.

**Currey, J.D. 1977.** Mechanical properties of pearl in tension. *P. R. Soc. London B* **196**, 443-463.

**Currey, J.D. 1984.** The Mechanical Adaptations of Bones. Princeton University Press, Princeton, NJ, pp 24–37.

**Cook, R.D., Malkus, D.S., Plesha, M.E., Witt, J.R. 2007.** Concepts and applications of finite element analysis. 4th edition. India:Wiley.

**Deville, S., Saiza, E., Nalla, R.K., Tomsiaa, A.P. 2006.** Freezing as a path to build complex composites. *Science* **311**, 515–518.

**Espinosa, H.D., Lu, H.C., Xu, Y. 1998.** A Novel Technique for Penetrator Velocity Measurement and Damage Identification in Ballistic Penetration Experiments. *J. Comp. Mater.* **32**(8), 722-743.

**Fratzl, P., Gupta, H.S., Paschalis, E.P., Roschger, P. 2004.** Structure and mechanical quality of the collagen–mineral nano-composite in bone. *J. Mater. Chem.* **14**, 2115–2123.

Gao, H., Ji, B., J¨ager, I.L., Arzt, E., Fratzl, P. 2003. Materials become insensitive to flaws at nanoscale: lessons from nature. *P. Natl. Acad. Sci. USA* 100, 5597–5600.

Hulmes, D.J.S., Wess, T.J., Prockop, D.J., Fratzl, P. 1995. Radial packing, order and disorder in collagen fibrils. *Bioph. J.* 68, 1661–1670.

Hao, X., Gai, G., Lu, F., Zhao, X., Zhang, Y., Liu, J., Yang, Y., Gui, D., Nan, C-W 2005. Dynamic mechanical properties of whisker/PA66 composites at high strain rates. *Polymer* 46, 3528-3534.

Huang, Z., Li, H., Pan, Z., Wei, Q., Chao, Y.J., Li, X. 2011. Uncovering high-strain rate protection mechanism in nacre. *Sci. Rep.* 1:148, 1-5.

Jackson, A.P., Vincent, J.F.V., Turner, R.M. 1988. The mechanical design of nacre. *P. R. Soc. London B.* 234, 415–440.

Jager, I., Fratzl, P. 2000. Mineralized collagen Fibrils: a mechanical model with a staggered arrangement of mineral particles. *Biophys. J.* 79, 1737–1746.

Ji, B., Gao, H. 2004. Mechanical properties of nanostructure of biological materials. J. Mech. Phys. Solids 52, 1963–1990.

Kolsky, H. 1963. Stress Waves in Solids. Publisher: Dover Publications, Inc., New York, N.Y.

Kolsky, H. 1964. Stress Waves in Solids. J. Sound Vib. 1, 88-110.

**Kitching, J.A., Lockwood, J. 1974.** Observations on shell form and its ecological significance in thaid gastropods of the genus Lepsiella in New Zealand, Marine Biology, **28**, 131-141.

**Kessler, H., Ballarini, R., Mullen, R.L., Kuhn, L.T., Heuer, A.H. 1996.** A biomimetic example of brittle toughening: (I) steady state multiple cracking. *Comp. Mater. Sci.* **5**, 157–166.

Kamat, S., Su, X., Ballarini, R., Heuer, A.H. 2000. Structural basis for the fracture toughness of the shell of the conch Strombus gigas. *Nature* **405**, 1036–1040.

Kotha, S.P., Kotha, S., Guzelsu, N. 2000. A shear-lag model to account for interaction effects between inclusions in composites reinforced with rectangular platelets. *Compos. Sci. Technol.* 60, 2147–2158.

Katti, K.S., Katti, D.R., Pradhan, S.M., Bhosle, A. 2005. Platelet interlocks are the key to toughness and strength in nacre. *J. Mater. Res.* 20, 1097-1110.

Landis, W.J. 1995. The strength of a calcified tissue depends in part on the molecular structure and organization of its constituent mineral crystals in their organic matrix. *Bone* 16, 533–544.

Landis, W.J., Hodgens, K.J., Song, M.J., Arena, J., Kiyonaga, S., Marko, M., Owen, C., McEwen, B.F. 1996. Mineralization of collagen may occur on fibril surfaces: evidence from conventional and high voltage electron microscopy and three dimensional imaging. *J. Struct. Biol.* **117**, 24–35.

Launey, M.E., Munch, E., Alsem, D.H., Barth, H.B., Saiz, E., Tomsia, A.P., Ritchie, R.O. 2009. Designing Highly Toughened Hybrid Composites Through Nature-Inspired Hierarchical Complexity. *Acta Mater.* 57, 2919-2932.

Menig, R., Meyers, M.H., Meyers, M.A. & Vecchio, K.S. 2000. Quasi-static and dynamic mechanical response of Haliotis rufescens (abalone) shells. *Acta Mater.* **48**, 2383–2398.

Menig, R., Meyers, M.H., Meyers, M.A. & Vecchio, K.S. 2001. Quasi-static and dynamic mechanical response of Strombus gigas (conch) shells. *Mater. Sci. Eng. A* 297, 203–211.

**Rossi, A.C., Parisi, V. 1973.** Experimental studies of predation by the crab Eriphia verrucosa on both snail and hermit crab occupants of conspecific gastropod shells. *Bollettino di Zoologia* **40**, 117-135.

**Rho, J.Y., Kuhn-Spearing, L., Zioupos, P. 1998.** Mechanical properties and the hierarchical structure of bone. *Med. Eng. Phys.* **20**, 92–102.

Roschger, P., Grabner, B.M., Rinnerthaler, S., Tesch, W., Kneissel, M., Berzlanovich, A., Klaushofer, K., Fratzl, P. 2001. Structural development of the mineralized tissue in the human L4 vertebral body. *J. Struct. Biol.* **136**, 126–136.

Shoup, J.B. 1968. Shell opening by crabs of the genus Calappa. Science 160, 887-888.

Sarikaya, M., Gunnison, K.E., Yasrebi, M., Aksay, J.A., 1990. Mechanical property-microstructural relationships in abalone shell. *Mater. Res. Soc.* 174, 109-116.

Sen, O., Tekalur, S.A., Jilek, C. 2011. The determination of dynamic strength of single lap joints using the split Hopkinson pressure bar. *Int. J. Adhes. Adhes.* **31**, 541-549.

**Sen, O. 2011.** Radial Inertia in Non-cylindrical Specimens in a Kolsky Bar. Conference Proceedings of the Society for Experimental Mechanics Series **17**, 169-170.

**Vermeij, G.J. 1976.** Interoceanic differences in vulnerability of shelled prey to crab predation. *Nature* **260**, 135-136.

Vermeij G.J. 1977. Patterns in crab claw size: the geography of crushing. *Syst. Zool.* 26, 138-152.

**Vermeij, G.J. 1978.** Biogeography and adaptation: patterns of marine life, Harvard University Press. Cambridge, Page: 416.

**Veis, A., Sabsay, B. 1987.** The collagen of mineralized matrices. In Bone and Mineral Research/5, W. A. Peck, editor. Elsevier Science Publications, New York, Amsterdam, Tokyo. pp: 1-63.

**Wagner, H.D., Weiner, S. 1992.** On the relationship between the microstructure of bone and its mechanical stiffness. *J. Biomech.* **25**, 1311–1320.

Weiner, S., Wagner, H.D. 1998. The material bone: structure–mechanical function relations. *Annu. Rev. Mater. Sci.* 28, 271–298.

Wang, R.Z., Suo, Z., Evans, A.G., Yao, N., Aksay, I.A. 2001. Deformation mechanisms in nacre. J. Mater. Res. 16, 2485–2493.

Wei, X., Naraghi, M., Espinosa, H. 2012. Optimal Length Scales Emerging from Shear Load Transfer in Natural Materials--Application to Carbon-Based Nanocomposite Design, ACS Nano 6(3), 2333–2344.

**Zipser, E., Vermeij, G.J. 1978.** Crushing behavior of tropical and temperate crabs. *J. Exp. Mar. Biol. Ecol.* **3I**, 155-172.

# CHAPTER 3. OPTIMAL OVERLAP LENGTH IN STAGGERED ARCHITECTURE COMPOSITES UNDER

# DYNAMIC LOADING CONDITIONS

### **3.1. Introduction**

Nacre refers to the inner shining layer in seashells. Microstructure of nacre reveals the existence of mineral tablets in a soft polymeric matrix in a brick-and-mortar structural arrangement [Jackson et al., 1988; Sarikaya et al., 1990]. Two of the most discerning aspects of nacre are exhibition of superior strength and synergistic toughness [Barthelat and Espinosa, 2007; Jackson et al., 1988; Kessler et al., 1996; Kamat et al., 2000; Menig et al., 2000, 2001; Sarikaya et al., 1990]. Multifarious factors contribute to toughening mechanisms, namely tablet pull-out [Jackson et al., 1988], crack deflection by the polymeric matrix [Menig et al., 2000], platelet interlocks [Katti et al., 2005], presence of nanoasperities [Evans et al., 2000; Wang et al., 2001], diffusive tablet sliding [Barthelat and Espinosa, 2007] arising from tablet waviness, aragonite bridge reinforcements at interface [Song et al., 2003], and re-locking of tablets [Meyers et al., 2008] due to persistent contact of broken aragonite bridges, all contribute to interfacial strengthening and thereby, superior fracture resistance.

So far, literature studies have addressed the interdependence of material properties and geometrical parameters on mechanical behavior of the staggered architecture materials under quasi-static loading conditions. Analytical model proposed by Jaeger and Fratzl (2000) estimated the maximum stress and strain of the composite, by advancing previously established models for the mechanical properties of mineralized collagen fibrils [Wagner and Weiner, 1992] by setting forth inorganic crystals in a staggered arrangement in agreement with the distribution of gaps in the collagen fibril [Hulmes et al., 1995; Landis, 1995; Veis and Sabsay, 1987]. Micromechanical model developed by Kotha et al. (2000) derived axial and shear stress distribution in platelets on the assumption of a fundamental basis that the load carried by the platelets remains constant and inter-platelet load transfer occurs by shear. Tension-shear-chain (TSC) model postulated by Gao et al. (2003) established the relationship between stiffness, aspect ratio of minerals, mineral volume fraction and material properties. Additionally, a critical overlap length, using Griffith's fracture criterion, was developed which attributed to the existence of an optimal aspect ratio of mineral crystals in biological composites. Shuchun and Yueguang (2007) used shear-lag model to study the interdependence of the overall elastic modulus and number of hierarchical levels in bone-like materials, and compared their results against TSC model and finite element simulations. Investigations by **Chen et al. (2009)** were directed towards understanding characteristic length for efficient stress transfer in staggered biocomposites via derivation of an analytical model followed by numerical simulations. Zhang et al. (2010) employed homogenization method to investigate the effect of platelet distribution (regular, stairwise, random), in staggered architecture materials, on the stiffness, strength, failure strain and energy storage capacity. Zhang et al. (2011) developed a quasi-self-similar hierarchical model to investigate the cause responsible for determination and existence of optimal number of hierarchical levels in staggered architecture materials, for varying mineral content, to obtain maximal toughness. Liu et al. (2011) used perturbation method to obtain analytical expressions for displacement and stress fields in the staggered nanocomposite structure, under quasi-static loading conditions, when subjected to uniaxial tension. Recently, Wei et al. (2012) laid down a criterion which reveals the existence of a

unique overlap length in biological composites that contributes to an optimization on both, strength and toughness fronts.

Resistance to crushing against crustacean predators is an integral part of shell evolution. Shell breaking methods by predators is representative of a dynamic loading event. It has been observed that under high strain-rates (using a Split-Hopkinson Pressure Bar(SHPB)), nacre exhibits superior damage tolerance and elevated fracture strength [**Huang et al., 2011**]. This behavior has been attributed to, based on electron microscopic analyses, on the existence of phenomenon's like partial dislocation emission and the onset of deformation twinning within the mineral crystals. However, minimal literature exists which addresses analytically the factors responsible for this behavior under dynamic rates of loading.

The following sections attempt to investigate and answer the following questions with regards to composites having staggered microstructure as its most elementary level of architecture under impact loading conditions. (1) Does there exist a structure-property correlationship for these materials under dynamic events? (2) Critical overlap length exists under quasi-static loading conditions which optimizes both strength and stiffness; is there any associated critical overlap length involved in load transfer mechanism between the adjacent reinforcements in dynamic regime? (3) As had been postulated by **Gao et al. (2003)**, building blocks in biological composites are at nanometer scales under quasi-static loading conditions; is the same argument true under impact loading? In order to address these questions, we based our analyses in the following manner: (a) Analytical model development for staggered microstructural materials under time dependent loading considering linear elastic behavior, (b)

identification of the critical overlap length criterion involved in these events, (c) predicting overlap lengths for other biocomposites exhibiting staggered microstructure as its most elementary level of architecture, for example nacre, spider-silk and collagen in bone/tendon, (d) predicting & validating the joint strength, using the analytical model, of aluminum-Loctite lap joint under impact loading using SHPB [**Sen et al., 2011**], (e) provide an explanation, based on the analytical model, for superior damage tolerance and elevated dynamic compressive strength of nacre, and (f) insights into the effect of loading rate.

### **3.2.** Mathematical Formulation

We begin our analysis by taking into consideration the simplified 2D unit cell, as shown in **Figure 3.1(a)**, and by employing 'shear-lag theory' [**Volkersen, 1938**].



**Figure. 3.1.** (a) Schematic of brick-and-mortar microstructure identifying the overlap region; Representative loading pulses obtained from SHPB experiments: (b) triangular pulse, and (c) half-sinusoidal pulse.

Applying force equilibrium to the upper and lower ceramic bricks, we obtain

$$\frac{\partial \sigma_1}{\partial x} - \frac{\tau}{b} = \rho \frac{\partial^2 u_1}{\partial t^2}$$
(3.1)

$$\frac{\partial \sigma_2}{\partial x} + \frac{\tau}{b} = \rho \frac{\partial^2 u_2}{\partial t^2}$$
(3.2)

where,  $\sigma_1 = \sigma_1(x,t)$  and  $\sigma_2 = \sigma_2(x,t)$  denotes the normal stress developed in the upper and lower ceramic bricks,  $\tau$  denotes the shear stress developed in the polymer, b denotes half the ceramic brick width and h, the polymeric thickness. Assuming a state of pure shear in the polymer, we have  $\tau = G\left(\frac{u_1 - u_2}{h}\right)$  where,  $u_1 \equiv u_1(x,t)$ ,  $u_2 \equiv u_2(x,t)$  denotes in-plane displacement of the upper and lower ceramic bricks respectively and G denotes the shear modulus of the polymer. Assuming linear elastic behavior of the ceramic bricks, i.e.,  $\sigma = E \frac{\partial u}{\partial x}$ , where E denotes Young's modulus of elasticity of the ceramic, equations (3.1) and (3.2) can we rewritten as equations (3.3) and (3.4), to obtain the governing differential equation of the system, given by

$$\frac{\partial^2 u_1}{\partial x^2} - \frac{G}{Ebh} (u_1 - u_2) = \frac{1}{c^2} \frac{\partial^2 u_1}{\partial t^2}$$
(3.3)

$$\frac{\partial^2 u_2}{\partial x^2} + \frac{G}{Ebh} (u_1 - u_2) = \frac{1}{c^2} \frac{\partial^2 u_2}{\partial t^2}$$
(3.4)

where  $c = \sqrt{\frac{E}{\rho}}$  denotes the wave velocity through the ceramic and,  $\rho$  denotes the density of the

ceramic. The boundary conditions of the system are given by

$$\sigma_{2}(0,t) = \sigma(t) \Longrightarrow \frac{\partial u_{2}}{\partial x} \Big|_{(0,t)} = \frac{\sigma(t)}{E}$$
(3.5)

$$\sigma_{1}(0,t) = 0 \Longrightarrow \frac{\partial u_{1}}{\partial x} \bigg|_{(0,t)} = 0$$
(3.6)

$$\sigma_{2}(L,t) = 0 \Longrightarrow \frac{\partial u_{2}}{\partial x} \Big|_{(L,t)} = 0$$
(3.7)

$$\sigma_{1}(L,t) = \sigma(t) \Longrightarrow \frac{\partial u_{1}}{\partial x} \Big|_{(L,t)} = \frac{\sigma(t)}{E}$$
(3.8)

The initial conditions of the system are given by

$$u_1(x,0) = 0$$
 (3.9)

$$u_2(x,0) = 0$$
 (3.10)

$$\frac{\partial u_1}{\partial t}\Big|_{(\mathbf{x},\mathbf{0})} = 0 \tag{3.11}$$

$$\frac{\partial u_2}{\partial t}\Big|_{(\mathbf{x},\mathbf{0})} = 0 \tag{3.12}$$

We thus have coupled partial hyperbolic differential equations subjected to non-homogenous boundary conditions. Given the nature of the problem, we employed advanced separation of variables technique coupled with rearrangement of terms to obtain a closed-form solution for the displacements in the ceramic blocks.

We now introduce a variable,  $u_{4}\equiv u_{4}\left(x,t\right)$  which is defined as follows:

$$u_4(x,t) = u_1(x,t) - u_2(x,t)$$
 (3.13)

Additionally, we define  $u_4 \equiv u_4(x,t)$  in an alternative manner as follows:

$$u_4(x,t) = v(x,t) + w(x,t)$$
 (3.14)

where w(x,t) represents a smoothing function satisfying only the boundary conditions, i.e.,

$$\frac{\partial w}{\partial x}\Big|_{(0,t)} = -\frac{\sigma(t)}{E}$$
(3.15)

$$\frac{\partial \mathbf{w}}{\partial \mathbf{x}}\Big|_{\left(\mathsf{L},\mathsf{t}\right)} = \frac{\sigma(\mathsf{t})}{\mathsf{E}}$$
(3.16)

Subtracting equation (3.4) from equation (3.3) and substituting equation (3.14), we obtain another governing differential equation of the system, given by

$$\frac{\partial^2 v}{\partial x^2} - kv - \frac{1}{c^2} \frac{\partial^2 v}{\partial t^2} = -\frac{\partial^2 w}{\partial x^2} + kw + \frac{1}{c^2} \frac{\partial^2 w}{\partial t^2}$$
(3.17)

where,  $k = \frac{2G}{Ebh}$ , and is subjected to boundary conditions and initial conditions, given by

equations (3.18-3.21) respectively.

$$\left. \frac{\partial \mathbf{v}}{\partial \mathbf{x}} \right|_{\left(0,t\right)} = 0 \tag{3.18}$$

$$\frac{\partial \mathbf{v}}{\partial \mathbf{x}}\Big|_{\left(\mathbf{L},\mathbf{t}\right)} = 0 \tag{3.19}$$

$$v(x,0) = -w(x,0)$$
 (3.20)

$$\frac{\partial \mathbf{v}}{\partial t}\Big|_{(\mathbf{x},\mathbf{0})} = -\frac{\partial \mathbf{w}}{\partial t}\Big|_{(\mathbf{x},\mathbf{0})}$$
(3.21)

Since boundary conditions are to be satisfied, choice of w(x,t) is made on the basis of Neumann boundary conditions, and is thus represented by

$$w(x,t) = \frac{\sigma(t)}{E} \left( \frac{x^2}{L} - x \right)$$
(3.22)

Substituting equation (3.22) into right hand side of equation (3.17), we thus have the following differential equation of the system, given by

$$\frac{\partial^2 v}{\partial x^2} - kv - \frac{1}{c^2} \frac{\partial^2 v}{\partial t^2} = p_4(x, t) = p_{04}(t) + \sum_{n \ge 1} p_{n4}(t) \cos\left(\frac{n\pi x}{L}\right)$$
(3.23)

where,

$$p_{4}(x,t) = \left[-\frac{2}{L} + k\left(\frac{x^{2}}{L} - x\right)\right]\frac{\sigma(t)}{E} + \frac{1}{c^{2}E}\left(\frac{x^{2}}{L} - x\right)\frac{d^{2}\sigma(t)}{dt^{2}}$$
(3.24)

$$p_{04}(t) = \frac{1}{L} \int_{x=0}^{L} p_4(x,t) dx = -\left(\frac{12 + kL^2}{6EL}\right) \sigma(t) - \left(\frac{L}{6c^2E}\right) \frac{d^2\sigma(t)}{dt^2}$$
(3.25)

$$p_{n4}(t) = \frac{2}{L} \int_{x=0}^{L} p_4(x,t) \cos\left(\frac{n\pi x}{L}\right) dx = \left(\frac{2LK}{E}\right) \left(\frac{1+\cos(n\pi)}{n^2 \pi^2}\right) \sigma(t) + \left(\frac{2L}{c^2 E}\right) \left(\frac{1+\cos(n\pi)}{n^2 \pi^2}\right) \frac{d^2 \sigma(t)}{dt^2}, n \ge 1$$
(3.26)

Assume,  $v(x,t) = X_4(x)T_4(t)$ . The Eigen values and functions are thus given by

$$\lambda_{n4} = \left(\frac{n\pi}{L}\right)^2, n \ge 0 \tag{3.27}$$

$$X_{n4}(x) = \cos\left(\frac{n\pi x}{L}\right), n \ge 0$$
(3.28)

Hence the formal solution of the problem is given by formal Fourier series, as

$$v(x,t) = \sum_{n \ge 0} T_{n4}(t) \cos\left(\frac{n\pi x}{L}\right) = T_{04}(t) + \sum_{n \ge 1} T_{n4}(t) \cos\left(\frac{n\pi x}{L}\right)$$
(29)

Substituting equation (3.29) into left hand side of equation (3.23) and equating both sides, we get

$$\frac{d^{2}T_{n4}}{dt^{2}} + \left[c^{2}\left\{k + \left(\frac{n\pi}{L}\right)^{2}\right\}\right]T_{n4} = -c^{2}p_{n4}(t), n \ge 1$$
(3.30)

$$\frac{d^2 T_{04}}{dt^2} + kc^2 T_{04} = -c^2 p_{04}(t)$$
(3.31)

The initial conditions, equations (3.20, 3.21), can be rewritten as follows:

$$v(x,0) = T_{04}(0) + \sum_{n \ge 1} T_{n4}(0) \cos\left(\frac{n\pi x}{L}\right)$$
  
=  $-w(x,0) = -\left(\frac{x^2}{L} - x\right) \frac{\sigma(0)}{E}$  (3.32)  
 $\Rightarrow T_{04}(0) = \frac{L\sigma(0)}{6E}, T_{n4}(0) = -\frac{2L\sigma(0)}{E} \left(\frac{1 + \cos(n\pi)}{n^2 \pi^2}\right)$ 

$$\begin{aligned} \frac{\partial v}{\partial t} \Big|_{(\mathbf{x},0)} &= \frac{dT_{04}(0)}{dt} + \sum_{n \ge 1} \frac{dT_{n4}(0)}{dt} \cos\left(\frac{n\pi x}{L}\right) \\ &= -\frac{\partial w}{\partial t} \Big|_{(\mathbf{x},0)} = -\frac{1}{E} \frac{d\sigma(0)}{dt} \left(\frac{x^2}{L} - x\right) = q_4(x) = q_{04} + \sum_{n \ge 1} q_{n4} \cos\left(\frac{n\pi x}{L}\right) \\ &\Rightarrow \frac{dT_{04}(0)}{dt} = q_{04} = \frac{1}{L} \int_{\mathbf{x}=0}^{L} q_4(x) dx = \frac{L}{6E} \frac{d\sigma(0)}{dt}, \text{and} \\ &\Rightarrow \frac{dT_{n4}(0)}{dt} = q_{n4} = \frac{2}{L} \int_{\mathbf{x}=0}^{L} q_4(x) \cos\left(\frac{n\pi x}{L}\right) dx = -\frac{2L}{E} \left(\frac{1 + \cos(n\pi)}{n^2 \pi^2}\right) \frac{d\sigma(0)}{dt}, n \ge 1 \end{aligned}$$
(3.33)

Equation (3.30) can be rewritten as follows:

$$\frac{d^2 T_{n4}}{dt^2} + e_{n4}^2 T_{n4} = -c^2 a_{n4} \left( \frac{k\sigma(t)}{E} + \frac{1}{c^2 E} \frac{d^2 \sigma(t)}{dt^2} \right), n \ge 1$$
(3.34)

where,  $a_{n4} = 2L\left(\frac{1+\cos(n\pi)}{n^2\pi^2}\right)$ , and  $e_{n4} = c\sqrt{k+\left(\frac{n\pi}{L}\right)^2}$ . Equation (3.34) can be rearranged

further to obtain equation (3.35) as follows:

$$\left[ \frac{d^2 T_{n4}}{dt^2} + \frac{a_{n4}}{E} \frac{d^2 \sigma(t)}{dt^2} \right] + e_{n4}^2 \left[ T_{n4} + \frac{a_{n4}}{E} \sigma(t) \right] =$$

$$- \frac{c^2 a_{n4} k \sigma(t)}{E} + \frac{e_{n4}^2 a_{n4} \sigma(t)}{E} = \frac{a_{n4}}{E} \left( \frac{n \pi c}{L} \right)^2 \sigma(t)$$

$$(3.35)$$

Equation (3.35) can be written in a simplified manner to obtain equation (3.36) as follows:

$$\Rightarrow \frac{d^{2}y_{4}(t)}{dt^{2}} + e_{n4}^{2}y_{4}(t) = g_{4}(t)$$
(3.36)

where,

$$y_{4}(t) = T_{n4} + \frac{a_{n4}}{E}\sigma(t), \text{and}$$

$$g_{4}(t) = \frac{a_{n}}{E} \left(\frac{n\pi c}{L}\right)^{2} \sigma(t)$$
(3.37)

We use Laplace Transform to solve equation (3.36). Let us denote  $L\{y_4(t)\}=Y_4(s)$ , and  $L\{g_4(t)\}=G_4(s)$ . Thus, we obtain

$$s^{2}Y_{4}(s) - sy_{4}(0) - \frac{dy_{4}(0)}{dt} + e_{n4}^{2}Y_{4}(s) = G_{4}(s)$$

$$\Rightarrow Y_{4}(s) = \left(\frac{s}{s^{2} + e_{n4}^{2}}\right)y_{4}(0) + \left(\frac{1}{s^{2} + e_{n4}^{2}}\right)\frac{dy_{4}(0)}{dt} + \left(\frac{1}{s^{2} + e_{n4}^{2}}\right)G_{4}(s) \qquad (3.38)$$

$$\Rightarrow y_{4}(t) = y_{4}(0)\cos(e_{n4}t) + \frac{dy_{4}(0)}{dt}\frac{\sin(e_{n4}t)}{e_{n4}} + \int_{\tau=0}^{t}\frac{1}{e_{n4}}\sin(e_{n4}(t-\tau))g_{4}(\tau)d\tau$$

Note that,

$$y_{4}(0) = T_{n4}(0) + \frac{a_{n4}}{E}\sigma(0) = -\frac{2L\sigma(0)}{E} \left(\frac{1+\cos(n\pi)}{n^{2}\pi^{2}}\right) + \frac{2L\sigma(0)}{E} \left(\frac{1+\cos(n\pi)}{n^{2}\pi^{2}}\right) = 0, \text{ and}$$

$$\frac{dy_{4}(0)}{dt} = \frac{dT_{n4}(0)}{dt} + \frac{a_{n4}}{E}\frac{d\sigma(0)}{dt} = -\frac{2L}{E} \left(\frac{1+\cos(n\pi)}{n^{2}\pi^{2}}\right) \frac{d\sigma(0)}{dt} + \frac{2L}{E} \left(\frac{1+\cos(n\pi)}{n^{2}\pi^{2}}\right) \frac{d\sigma(0)}{dt} = 0$$
(3.39)

and thus, using equations (3.37-3.39), we finally obtain

$$T_{n4}(t) = -\frac{a_{n4}}{E}\sigma(t) + \frac{a_{n4}}{Ee_{n4}} \left(\frac{n\pi c}{L}\right)^2 \int_{\tau=0}^{t} \sigma(\tau) \sin(e_{n4}(t-\tau)) d\tau, n \ge 1$$
(3.40)

Lets us now solve equation (3.31). We proceed as follows. Equation (3.31) can be rewritten as follows:

$$\frac{d^2 T_{04}}{dt^2} + d_{04}^2 T_{04} = -c^2 \left( a_{04} \sigma(t) + b_{04} \frac{d^2 \sigma(t)}{dt^2} \right)$$
(3.41)

where,  $a_{04} = -\left(\frac{12 + kL^2}{6EL}\right)$ ,  $b_{04} = -\left(\frac{L}{6c^2E}\right)$ , and  $d_{04} = c\sqrt{k}$ . Equation (3.41) can be rearranged

further to obtain equation (3.42) as follows:

$$\begin{bmatrix} \frac{d^{2}T_{04}}{dt^{2}} + c^{2}b_{04}\frac{d^{2}\sigma(t)}{dt^{2}} \end{bmatrix} + d_{04}^{2} \begin{bmatrix} T_{04} + c^{2}b_{04}\sigma(t) \end{bmatrix} = -c^{2}a_{04}\sigma(t) + d_{04}^{2}c^{2}b_{04}\sigma(t) = \begin{bmatrix} \frac{2c^{2}}{EL} \end{bmatrix} \sigma(t)$$

$$(3.42)$$

Equation (3.42) can be written in a simplified manner to obtain equation (3.43) as follows:

$$\Rightarrow \frac{d^{2}m_{4}(t)}{dt^{2}} + d^{2}_{04}m_{4}(t) = f_{4}(t)$$
(3.43)

where,

$$m_{4}(t) = T_{04} + c^{2}b_{04}\sigma(t), \text{and}$$

$$f_{4}(t) = \left(\frac{2c^{2}}{EL}\right)\sigma(t)$$
(3.44)

We use Laplace Transform to solve equation (3.43). Let us denote  $L\{m_4(t)\}=M_4(s)$ , and  $L\{f_4(t)\}=F_4(s)$ . Thus, we obtain

$$s^{2}M_{4}(s) - sm_{4}(0) - \frac{dm_{4}(0)}{dt} + d^{2}_{04}M_{4}(s) = F_{4}(s)$$

$$\Rightarrow M_{4}(s) = \left(\frac{s}{s^{2} + d^{2}_{04}}\right)m_{4}(0) + \left(\frac{1}{s^{2} + d^{2}_{04}}\right)\frac{dm_{4}(0)}{dt} + \left(\frac{1}{s^{2} + d^{2}_{04}}\right)F_{4}(s) \qquad (3.45)$$

$$\Rightarrow m_{4}(t) = m_{4}(0)\cos(d_{04}t) + \frac{dm_{4}(0)}{dt}\frac{\sin(d_{04}t)}{d_{04}} + \int_{\tau=0}^{t}\frac{1}{d_{04}}\sin(d_{04}(t-\tau))f_{4}(\tau)d\tau$$

Note that,

$$m_{4}(0) = T_{04}(0) + c^{2}b_{04}\sigma(0) = \left(\frac{L}{6E}\right)\sigma(0) - \left(\frac{L}{6E}\right)\sigma(0) = 0, \text{ and}$$

$$\frac{dm_{4}(0)}{dt} = \frac{dT_{04}(0)}{dt} + c^{2}b_{04}\frac{d\sigma(0)}{dt} = \left(\frac{L}{6E}\right)\frac{d\sigma(0)}{dt} - \left(\frac{L}{6E}\right)\frac{d\sigma(0)}{dt} = 0$$
(3.46)

and thus, using equations (3.44-3.46), we finally obtain

$$T_{04}(t) = -c^{2}b_{04}\sigma(t) + \frac{2c^{2}}{ELd_{04}}\int_{\tau=0}^{t}\sigma(\tau)\sin(d_{04}(t-\tau))d\tau$$
(3.47)

Substituting the expressions  $T_{n4}$ ,  $T_{04}$  obtained from equations (3.40, 3.47) into equation (3.29) and finally into equation (3.14), we finally get

$$u_{4}(x,t) = u_{1}(x,t) - u_{2}(x,t) = T_{04}(t) + \sum_{n \ge 1} T_{n4}(t) \cos\left(\frac{n\pi x}{L}\right) + \frac{\sigma(t)}{E}\left(\frac{x^{2}}{L} - x\right)$$
(3.48)

We now introduce another variable,  $u_3 \equiv u_3(x,t)$  which is defined as follows:

$$u_3(x,t) = u_1(x,t) + u_2(x,t)$$
 (3.49)

Additionally, we define  $u_3 \equiv u_3(x,t)$  in an alternative manner as follows:

$$u_3(x,t) = r(x,t) + s(x,t)$$
 (3.50)

where s(x,t) represents a smoothing function satisfying only the boundary conditions, i.e.,

$$\frac{\partial s}{\partial x}\Big|_{(0,t)} = \frac{\sigma(t)}{E}$$
(3.51)

$$\frac{\partial s}{\partial x}\Big|_{(L,t)} = \frac{\sigma(t)}{E}$$
(3.52)

Adding equations (3.3) and (3.4), and substituting equation (3.50), we obtain another governing differential equation of the system, given by

$$\frac{\partial^2 \mathbf{r}}{\partial \mathbf{x}^2} - \frac{1}{c^2} \frac{\partial^2 \mathbf{r}}{\partial t^2} = -\frac{\partial^2 \mathbf{s}}{\partial \mathbf{x}^2} + \frac{1}{c^2} \frac{\partial^2 \mathbf{s}}{\partial t^2}$$
(3.53)

subjected to boundary conditions and initial conditions, given by equations (3.54-3.57) respectively.

$$\left. \frac{\partial \mathbf{r}}{\partial \mathbf{x}} \right|_{(0,t)} = 0 \tag{3.54}$$

$$\frac{\partial \mathbf{r}}{\partial \mathbf{x}}\Big|_{\left(\mathbf{L},\mathbf{t}\right)} = 0 \tag{3.55}$$

$$r(x,0) = -s(x,0)$$
 (3.56)

$$\frac{\partial \mathbf{r}}{\partial t}\Big|_{(\mathbf{x},\mathbf{0})} = -\frac{\partial \mathbf{s}}{\partial t}\Big|_{(\mathbf{x},\mathbf{0})}$$
(3.57)

Since boundary conditions are to be satisfied, choice of s(x,t) is made on the basis of Neumann boundary conditions, and is thus represented by

$$s(x,t) = \frac{x\sigma(t)}{E}$$
(3.58)

Substituting equation (3.58) into right hand side of equation (3.53), we thus have the following differential equation of the system, given by

$$\frac{\partial^2 \mathbf{r}}{\partial x^2} - \frac{1}{c^2} \frac{\partial^2 \mathbf{r}}{\partial t^2} = \mathbf{p}_3(\mathbf{x}, t) = \mathbf{p}_{03}(t) + \sum_{n \ge 1} \mathbf{p}_{n3}(t) \cos\left(\frac{n\pi x}{L}\right)$$
(3.59)

where,

$$p_{3}(x,t) = \frac{x}{c^{2}E} \frac{d^{2}\sigma(t)}{dt^{2}}$$
 (3.60)

$$p_{03}(t) = \frac{1}{L} \int_{x=0}^{L} p_3(x,t) dx = \left(\frac{L}{2c^2 E}\right) \frac{d^2 \sigma(t)}{dt^2}$$
(3.61)

$$p_{n3}(t) = \frac{2}{L} \int_{x=0}^{L} p_3(x,t) \cos\left(\frac{n\pi x}{L}\right) dx = \left(\frac{2L}{c^2 E}\right) \left(\frac{\cos(n\pi) - 1}{n^2 \pi^2}\right) \frac{d^2 \sigma(t)}{dt^2}$$
(3.62)

Assume,  $r(x,t) = X_3(x)T_3(t)$ . The Eigen values and functions are thus given by

$$\lambda_{n3} = \left(\frac{n\pi}{L}\right)^2, n \ge 0 \tag{3.63}$$

$$X_{n3}(x) = \cos\left(\frac{n\pi x}{L}\right), n \ge 0$$
(3.64)

Hence the formal solution of the problem is given by formal Fourier series, as

$$r(x,t) = \sum_{n\geq 0} T_{n3}(t) \cos\left(\frac{n\pi x}{L}\right) = T_{03}(t) + \sum_{n\geq 1} T_{n3}(t) \cos\left(\frac{n\pi x}{L}\right)$$
(3.65)

Substituting equation (3.65) into left hand side of equation (3.59) and equating both sides, we

get

$$\frac{d^{2}T_{n3}}{dt^{2}} + \left(\frac{n\pi c}{L}\right)^{2} T_{n3} = -c^{2}p_{n3}(t), n \ge 1$$
(3.66)

$$\frac{d^2 T_{03}}{dt^2} = -c^2 p_{03}(t)$$
(3.67)

The initial conditions, equations (3.56, 3.57), can be rewritten as follows:

$$\begin{aligned} r(x,0) &= T_{03}(0) + \sum_{n \ge 1} T_{n3}(0) \cos\left(\frac{n\pi x}{L}\right) \\ &= -s(x,0) = -\frac{x\sigma(0)}{E} \\ &\Rightarrow T_{03}(0) = -\frac{L\sigma(0)}{2E}, T_{n3}(0) = -\frac{2L\sigma(0)}{E} \left(\frac{\cos(n\pi) - 1}{n^2 \pi^2}\right) \end{aligned}$$
(3.68)

$$\begin{aligned} \frac{\partial r}{\partial t} \Big|_{(\mathbf{x},0)} &= \frac{dT_{03}(0)}{dt} + \sum_{n \ge 1} \frac{dT_{n3}(0)}{dt} \cos\left(\frac{n\pi x}{L}\right) \\ &= -\frac{\partial s}{\partial t} \Big|_{(\mathbf{x},0)} = -\frac{x}{E} \frac{d\sigma(0)}{dt} = q_3(\mathbf{x}) = q_{03} + \sum_{n \ge 1} q_{n3} \cos\left(\frac{n\pi x}{L}\right) \\ &\Rightarrow \frac{dT_{03}(0)}{dt} = q_{03} = \frac{1}{L} \int_{\mathbf{x}=0}^{L} q_3(\mathbf{x}) d\mathbf{x} = -\frac{L}{2E} \frac{d\sigma(0)}{dt}, \text{and} \\ &\Rightarrow \frac{dT_{n3}(0)}{dt} = q_{n3} = \frac{2}{L} \int_{\mathbf{x}=0}^{L} q_3(\mathbf{x}) \cos\left(\frac{n\pi x}{L}\right) d\mathbf{x} = -\frac{2L}{E} \left(\frac{\cos(n\pi) - 1}{\pi^2 n^2}\right) \frac{d\sigma(0)}{dt}, n \ge 1 \end{aligned}$$
(3.69)

Equation (3.66) can be rewritten as follows:

$$\frac{d^2 T_{n3}}{dt^2} + e_{n3}^2 T_{n3} = -c^2 a_{n3} \frac{d^2 \sigma(t)}{dt^2}, n \ge 1$$
(3.70)

where,  $a_{n3} = \left(\frac{2L}{c^2E}\right) \left(\frac{\cos(n\pi) - 1}{n^2\pi^2}\right)$ , and  $e_{n3} = \left(\frac{n\pi c}{L}\right)$ . Equation (3.70) can be rearranged

further to obtain equation (3.71) as follows:

$$\left[\frac{d^{2}T_{n3}}{dt^{2}} + c^{2}a_{n3}\frac{d^{2}\sigma(t)}{dt^{2}}\right] + e_{n3}^{2}\left[T_{n3} + c^{2}a_{n3}\sigma(t)\right] = e_{n3}^{2}c^{2}a_{n3}\sigma(t), n \ge 1$$
(3.71)

Equation (3.71) can be written in a simplified manner to obtain equation (3.72) as follows:

$$\Rightarrow \frac{d^2 y_3(t)}{dt^2} + e_{n3}^2 y_3(t) = g_3(t)$$
(3.72)

where,

$$y_{3}(t) = T_{n3} + c^{2}a_{n3}\sigma(t), \text{and}$$
  

$$g_{3}(t) = e_{n3}^{2}c^{2}a_{n3}\sigma(t)$$
(3.73)

We use Laplace Transform to solve equation (3.72). Let us denote  $L\{y_3(t)\}=Y_3(s)$ , and  $L\{g_3(t)\}=G_3(s)$ . Thus, we obtain

$$s^{2}Y_{3}(s) - sy_{3}(0) - \frac{dy_{3}(0)}{dt} + e_{n3}^{2}Y_{3}(s) = G_{3}(s)$$
  

$$\Rightarrow Y_{3}(s) = \left(\frac{s}{s^{2} + e_{n3}^{2}}\right)y_{3}(0) + \left(\frac{1}{s^{2} + e_{n3}^{2}}\right)\frac{dy_{3}(0)}{dt} + \left(\frac{1}{s^{2} + e_{n3}^{2}}\right)G_{3}(s) \qquad (3.74)$$
  

$$\Rightarrow y_{3}(t) = y_{3}(0)\cos(e_{n3}t) + \frac{dy_{3}(0)}{dt}\frac{\sin(e_{n3}t)}{e_{n3}} + \int_{\tau=0}^{t}\frac{1}{e_{n4}}\sin(e_{n3}(t-\tau))g_{3}(\tau)d\tau$$

Note that,

$$\begin{split} y_{3}(0) &= T_{n3}(0) + c^{2}a_{n3}\sigma(0) = \\ &- \frac{2L\sigma(0)}{E} \left( \frac{\cos(n\pi) - 1}{n^{2}\pi^{2}} \right) + \frac{2L\sigma(0)}{E} \left( \frac{\cos(n\pi) - 1}{n^{2}\pi^{2}} \right) = 0, \text{and} \\ &\frac{dy_{3}(0)}{dt} = \frac{dT_{n3}(0)}{dt} + c^{2}a_{n3}\frac{d\sigma(0)}{dt} = \\ &- \frac{2L}{E} \left( \frac{\cos(n\pi) - 1}{n^{2}\pi^{2}} \right) \frac{d\sigma(0)}{dt} + \frac{2L}{E} \left( \frac{\cos(n\pi) - 1}{n^{2}\pi^{2}} \right) \frac{d\sigma(0)}{dt} = 0 \end{split}$$
(3.75)

and thus, using equations (3.73-3.75), we finally obtain

$$T_{n3}(t) = -c^{2}a_{n3}\sigma(t) + e_{n3}c^{2}a_{n3}\int_{\tau=0}^{t}\sigma(\tau)sin(e_{n3}(t-\tau))d\tau, n \ge 1$$
(3.76)

Lets us now solve equation (3.67). We proceed as follows. Equation (3.67) can be rewritten as follows:

$$\frac{d^2 T_{03}}{dt^2} = -c^2 a_{03} \frac{d^2 \sigma(t)}{dt^2}$$
(3.77)

where,  $a_{03} = \left(\frac{L}{2c^2E}\right)$ . Equation (3.77) can be rearranged further to obtain equation (3.78) as

follows:

$$\left[\frac{d^{2}T_{03}}{dt^{2}} + c^{2}a_{03}\frac{d^{2}\sigma(t)}{dt^{2}}\right] = 0$$
(3.78)

Equation (3.78) can be written in a simplified manner to obtain equation (3.79) as follows:

$$\Rightarrow \frac{d^2 m_3(t)}{dt^2} = 0 \tag{3.79}$$

where,

$$m_3(t) = T_{03} + c^2 b_{03} \sigma(t)$$
(3.80)

We use Laplace Transform to solve equation (3.79). Let us denote  $L\{m_3(t)\}=M_3(s)$ . Thus, we obtain

$$s^{2}M_{3}(s) - sm_{3}(0) - \frac{dm_{3}(0)}{dt} = 0$$
  

$$\Rightarrow M_{3}(s) = \left(\frac{1}{s}\right)m_{3}(0) + \left(\frac{1}{s^{2}}\right)\frac{dm_{3}(0)}{dt}$$
  

$$\Rightarrow m_{3}(t) = m_{3}(0) + t\frac{dm_{3}(0)}{dt}$$
(3.81)

Note that,

$$m_{3}(0) = T_{03}(0) + c^{2}a_{03}\sigma(0) = -\left(\frac{L}{2E}\right)\sigma(0) + \left(\frac{L}{2E}\right)\sigma(0) = 0, \text{ and}$$

$$\frac{dm_{3}(0)}{dt} = \frac{dT_{03}(0)}{dt} + c^{2}a_{03}\frac{d\sigma(0)}{dt} = -\left(\frac{L}{2E}\right)\frac{d\sigma(0)}{dt} + \left(\frac{L}{2E}\right)\frac{d\sigma(0)}{dt} = 0$$
(3.82)

and thus, using equations (80-82), we finally obtain

$$T_{03}(t) = -c^2 a_{03}\sigma(t)$$
 (3.83)

Substituting the expressions  $T_{n3}$ ,  $T_{03}$  obtained from equations (3.76, 3.83) into equation (3.65) and then into equation (3.50), we finally get

$$u_{3}(x,t) = u_{1}(x,t) + u_{2}(x,t) = T_{03}(t) + \sum_{n \ge 1} T_{n3}(t) \cos\left(\frac{n\pi x}{L}\right) + \frac{x\sigma(t)}{E}$$
(3.84)

Thus, we have

$$u_{1}(x,t) = \frac{u_{3}(x,t) + u_{4}(x,t)}{2}, \text{and}$$

$$u_{2}(x,t) = \frac{u_{3}(x,t) - u_{4}(x,t)}{2}$$
(3.85)

## 3.3. Results and Discussion

As mentioned earlier, the current formulation has been derived with respect to any arbitrary pulse loading. In SHPB experiments, obtained loading pulses typically exhibit either triangular  $\sigma(t) = \frac{\sigma_{max}}{t_a} t$  or, half-sinusoidal  $\sigma(t) = \sigma_{max} \sin\left(\frac{\pi t}{2t_a}\right)$  waveforms. Both type of loading pulses were applied to the staggered composite. As per the formulation carried out by Wei et al. (2012), under quasi-static loading conditions, shearing stress at the ends of the overlap ( $\tau_{max}$ ) is given in terms of the maximum applied stress ( $\sigma_0$ ) as follows:

$$\tau_{\max} = \tau \Big|_{x=0} = \tau \Big|_{x=L} = \frac{\sigma_0 b}{2} \sqrt{\frac{2G}{Ebh}} \operatorname{coth}\left(\frac{L}{2} \sqrt{\frac{2G}{Ebh}}\right)$$
(3.86)

Substitution of the geometrical and material properties of nacre [Barthelat et al., 2005; Espinosa et al., 2011, Meyers et al., 2008, Jackson et al., 1988] into equation (3.85), results in  $\sigma_0$ =133 MPa. In order to visualize the variation of shear strength in the joint throughout the overlap length and over time, a maximum stress ( $\sigma_{max}$ ) of 133 MPa is hence applied and the time taken to attain this stress level ( $t_a$ ) is chosen to be 133 µs. Shear stress distribution profiles obtained were almost identical corresponding to both types of loading. **Figure 3.2** shows the shear stress distribution profile. As it can be seen from **Figure 3.2**, the shear stresses are maximum at the either ends of the overlap. With progressing time, sliding between the ceramic bricks continues to increase and thereby, shear stress at the ends continues to increase along with increasing stress levels toward the center of the joint. Indeed similar behavior has been observed under quasi-static loading conditions [**Wei et al., 2012**] as well as under finite element (FE) simulations [**Sen et al., 2011**] which justifies the efficacy of the analytical model.



**Figure 3.2**. Shear stress distribution profile over the overlap length at varying times under the application of triangular loading pulse.

Biological composite structures such as nacre, bone, etc. exhibit a generic microstructure (brick and mortar) at their most elementary level of architecture [Gao et al., **2003**] where inorganic reinforcements serve as the load bearing member and the organic matrix mediates the load between adjacent ceramic bricks via shear. Under impact loading conditions, the total time for the event is in the order of tens of microseconds. Experimental studies [Sen et al., 2011] on adhesively bonded lap-joints account shearing failure of the adhesive as the predominant mode of failure under high-strain rate loading. Therefore, optimization of overlap length to provide maximum shearing resistance (at the ends) under dynamic loading conditions is a decisive parameter in the evolution of shells. Once the inorganic and organic constituents are fixed, nature cleverly chooses a characteristic overlap length such that shearing stress is a minimum and is thus, below or at par with the shear strength of the organic matrix. In order to prove this hypotheses, three natural materials were chosen (nacreous layer in abalone shell, spider silk and collagen in tendon/bone) and their characteristic overlap length scales were predicted based on this hypothesis. Figure 3.3-3.5. identifies those critical overlap length scales for nacreous layer in abalone shell, spider silk and collagen in tendon/bone respectively.



**Figure 3.3**. Variation of shear stress at the extremities of the joint against overlap length for nacre (a), and its dependence on loading rate (b).

In nacre, microscopic observations [**Meyers et al., 2008**] reveals the existence of 0.5µm ( $\equiv$  2b) thick aragonite bricks bonded together by 25 nm ( $\equiv$  h) thick organic matrix and, an average overlap length of 1.6 µm [**Barthelat et al., 2005; Espinosa et al., 2011**]. The Young's modulus of elasticity ( $\equiv$  E) of the aragonite bricks is chosen to be 105.39 GPa and the shear modulus of the biopolymer matrix ( $\equiv$  G) is approximately 1.4 GPa [**Wei et al., 2012**]. As it can be seen from **Figure 3.3(a)**, shear stress at the ends is minimum for an overlap length of ~2.5 µm. Note that the predicted value is reasonably close to the value observed in nature and that predicted by critical length scales [**Wei et al., 2012**] (of approximately 1.69 µm) under quasi-static loading scenario. Additionally, this critical overlap length remains constant even under increasing rates of loading as shown in **Figure 3.3(b)** and clearly justifies why this particular overlap length is chosen by nature once the material parameters (E, G) and geometrical parameters (b, h) are fixed. Also, note that shear stress distribution profile, as shown in **Figure** 

**3.2**, was developed for an overlap length of 1.6  $\mu$ m and interestingly, the maximum shear stress at the extremities at the end of the event matches exactly with the average shear strength of the polymer (= 37 MPa) [**Jackson et al., 1988**], which justifies the choice of this overlap length by nacreous layer corresponding to time-dependent loading event.

Next the analytical model is applied to identify the critical overlap length between  $\beta$ -sheets in spider silk, the constituents of which are in nanometer scale levels. The building blocks for spider silk fibrils are  $\beta$ -sheets. Molecular dynamic simulations [Keten and Buehler, **2008; Keten et al., 2010**] report an elastic modulus ( $\equiv$  E) of approximately 22.6 GPa, and shear modulus ( $\equiv$  G), which is representative of the crosslinking between b-sheets, of 4.6 GPa.  $\beta$ -sheet has a thickness ( $\equiv$  2b) of about 1 nm, and the distance between  $\beta$ -sheets (equal to the length of H-bond), is approximately 0.3 nm ( $\equiv$  h). Experimental studies have revealed  $\beta$ -sheet length in the range from 2 to 8 nm [Penel et al., **2003**]. Once again, substitution of these values predicts the critical overlap length of ~5 nm (shown in Figure 3.4) for dynamic loading event, which is in good agreement with experimental data. Additionally, the observed value is also in close agreement with those obtained by Wei et al. ( $\approx$  5.7 nm) [Wei et al., **2012**] in their analyses under quasi-static loading conditions.

Finally, we apply the analytical model to identify the critical overlap length of collagen fibrils in tendon/bone. Experiments on tropocollagen molecules [**Sun et al., 2002**] reveal a wide distribution of elastic modulus ranging from 0.35-18 GPa has been attributed probably to varied strain rates used in the studies. An elastic moduli ( $\equiv$  E) of approximately 1 GPa was chosen for the tropocollagen molecule corresponding to the current scenario. For wet environmental

conditions, over the overlap length, crosslinking shear modulus ( $\equiv$  G) in collagen fibrils was chosen to be approximately 3.4 MPa following measurements by micromechanical bending [Yang et al., 2008].



**Figure 3.4.** Variation of shear stress at the extremities of the joint against overlap length for spider-silk (a), and its dependence on loading rate (b).

Tropocollagen molecule has a diameter ( $\equiv$  2b) of about 1.23 nm, and intra-tropocollagen molecular gap ( $\equiv$  h) is about 0.24 nm [Landis et al., 1993]. Electron microscopy 3-D reconstruction technique identifies an overlap length of 27 nm [Landis et al., 1993].

Substitution of the above mechanical and geometrical parameters into the analytical model predicts the critical overlap length of ~36 nm (shown in **Figure 3.5**) for dynamic loading event, which once again is in close agreement with experimental data and also in close agreement with those obtained for characteristic length scales (≈ 31 nm) [**Wei et al., 2012**] under quasistatic loading conditions.



**Figure 3.5**. Variation of shear stress at the extremities of the joint against overlap length for collagen in tendon/bone (a), and its dependence on loading rate (b).

Next, we utilize our analytical model to predict the joint strength of an aluminum-Loctite adhesively bonded lap joint under impact loading conditions. Experiments, using SHPB, were carried out under high rates of loading for these lap joint specimens [**Sen et al., 2011**]. In order to predict the joint strength we proceeded as follows:

$$\varepsilon_{\mathbf{X}} = \frac{\partial \mathbf{u}_{\mathbf{1}}}{\partial \mathbf{x}} \Big|_{\left(\mathbf{L}, \mathbf{t}_{\mathbf{f}}\right)}$$
(3.87)

$$v_{x}(L,t_{f}) = v_{t}$$

$$\Rightarrow \varepsilon_{t} = \left(\frac{c}{c_{t}}\right)\varepsilon_{x}$$

$$\Rightarrow \sigma_{\text{predicted}} = \frac{A_{b}E_{b}\varepsilon_{t}}{A_{ls}}$$
(3.88)

where, c, c<sub>t</sub> represent stress-wave velocity in the aluminum, and wave velocity through the transmission bar (Aluminum alloy 7075) respectively. Transmitted strain is calculated on the basis of velocity compatibility condition at the specimen transmission bar interface. A<sub>b</sub>, A<sub>ls</sub> represent the cross-sectional area of the transmission bar, and area of the adhesive lap joint respectively. E<sub>b</sub>, t<sub>f</sub> denotes the Young's modulus of elasticity of the transmission bar and failure time of adhesively bonded lap joint. **Table 3.1** lists the predicted joint strength against experimentally measured data and they are found to be in reasonably close agreement with each other. Based on this observation, the efficacy of our analytical model can be validated.

**Table 3.1.** Comparison of experimentally measured joint strength against those predicted by analytical model for varying overlap area and loading rates.

Loading Rate (kN/µs)	σ <sub>Maximum</sub> (MPa)	t <sub>f</sub> (μs)	Overlap Length (mm)	Overlap Area (mm <sup>2</sup> )	σ <sub>Experimental</sub> (MPa)	σ <sub>Predicted</sub> (MPa)
0.64	27.68	12	10	158.75	34.62	33.78
	37.77	24			47.24	40.44
1.08	40.51	16	10	158.75	50.67	49.44
	38.22	18			47.80	46.64
0.87	41.08	16	10	158.75	36.29	35.38
	38.22	12			47.51	46.32
	38.22	18			34.91	34.03
0.65	21.22	12	15	238.5	17.67	17.22
	25.67	18			21.37	20.83
	30.76	20			25.61	24.96
1.08	43.59	13	15	238.5	36.29	35.38
	57.07	18			47.51	46.32
	41.94	20			34.91	34.03
1.52	72.42	16	15	238.5	60.29	58.77
	66.04	16			54.98	53.59

E = 71.7 GPa, G = 1.2 GPa, h = 0.5 mm, 2b = 15.9 mm

Thus, once the material properties and geometrical parameters are fixed, choice of overlap length can be based upon the essence of minimization of shear stress at the extremities to promote maximum load transfer by polymer via shear and to withstand the entire dynamic event. Too far a deviation from the optimal length will raise shear stress at the ends appreciably, which will in-turn will result in premature failure of the joint (will not be able to withstand the whole incident pulse) and thereby, reduce joint efficiency. Thus, perspectives drawn from this point-of-view can be utilized as a vital design guideline in tailoring adhesively bonded single lap composite joints (at micro/meso/macro scales). Note that, the current observations are based on triangular pulse loading. However, similar set of observations are
encountered if a half-sinusoidal pulse loading is applied, and for brevity purposes are not discussed here.

Based on fracture mechanics concepts, **Gao et al. (2003)** postulated the adoption of nanometer sized inorganic reinforcements in order to achieve a state of flaw-intolerance. Presence of nanometer sized inorganic crystals can be visualized from another point-of-view. Shear transfer efficiency of staggered architectural composites can be qualitatively interpreted by consideration of elastic strain-energy density via shear transfer mechanism. The effective strain,  $\varepsilon_{eff}$ , and the effective stress,  $\sigma_{eff}$ , can be written as

$$\varepsilon_{\text{eff}} \equiv \lim_{t \to t_a} \frac{2u_1}{L} \Big|_{(L,t)}$$
(3.89)

$$\sigma_{\text{eff}}(\mathbf{x}, \mathbf{t}) = \lim_{\mathbf{t} \to \mathbf{t}_{a}} \frac{\mathbf{b}\sigma(\mathbf{t}) - \rho \mathbf{b}(\mathbf{L} - \mathbf{x})\ddot{\mathbf{u}}_{1}|_{avg}}{(2\mathbf{b} + \mathbf{h})}$$
(3.90)

and the elastic strain energy density, w<sub>eff</sub>, is thus given by

$$w_{eff} = \int \sigma d\varepsilon = \frac{1}{2} \sigma_{eff} \varepsilon_{eff}$$
(91)

for triangular loading pulse loading. Similar to our previous analyses, once the material properties and geometrical parameters are fixed, w<sub>eff</sub> becomes a function of overlap length (L). A plot of elastic strain energy density variation against overlap length is shown in **Figure 3.6(a)**. As it can be seen from **Figure 3.6(a)**, as the length of the overlap decreases and reaches nanoscale dimensions, elastic strain energy density of the staggered composite increases. Note that, the plot in **Figure 3.6(a)** corresponds to dimensions and properties for nacreous layer in

seashell. In fact, this phenomena has been observed experimentally (for macro-scale specimens) where for a given loading rate, joint-strength increases with decreasing overlapping area [Sen et al., 2011]. It has been observed that the toughening rate (tearing modulus) in bone is higher than in nacre [Wang and Gupta, 2011], which can be inferred from Figure 3.6(a). and attributed to the presence of nanometer sized building blocks in its staggered architecture. This explains why nature chooses nano-sub-micrometer scale overlapping feature for biocomposites structural integrity.

One of the other interesting outcomes of the current analytical model is that as the loading rate increases, the elastic strain energy density (w<sub>eff</sub>) of the staggered composite increases as well. As it can be seen from **Figure 3.6(b)**, dependence of w<sub>eff</sub> is markedly pronounced towards increasing stress-levels than for time rise of the loading pulse. Thus, staggered composites showed increasing energy absorption behavior with increasing loading-rates and thereby, exhibit dynamic self-stiffening behavior [**Huang et al., 2011**]. This aspect of self-stiffening behavior under impact loading conditions will find particular relevance in application of these types of composites as protective materials under impact.

90



**Figure 3.6**. Variation of elastic strain energy density against varying overlap length at different intervals of time under the application of triangular pulse loading (a), and dependence of elastic strain energy density on loading rate, under the application of triangular pulse loading, shown via (1) varying max stress (keeping time at maximum stress fixed)-shown in red and (2) varying time at max stress (keeping maximum stress fixed)-shown in black; dependence of w<sub>eff</sub> is markedly pronounced towards increasing stress-levels than for time under the application of triangular pulse loading.

Note that, based on the current model, we can also explain the reason as to why the dynamic compressive strength of abalone nacre is nearly 50% higher than its static counterpart, as observed from SHPB experiments by **Menig et al. (2000)** and **Huang et al. (2011)**. As was postulated by Gao and coworkers [**Gao et al., 2003; Gao, 2006**], under quasi-static conditions, nature uses, particularly, aspect ratio of the mineral crystals to promote strain amplification mechanism and thereby obtain an optimal balance for deformation in organic and inorganic

components to obtain maximum potential. de Gennes and Okumura (2000) and Okumura and de Gennes (2003) presented an analytical solution for a layered system, based on laminar architecture of the seashells, and accounted the existence of weaker stress concentration ahead of the crack tip in these materials in comparison to traditional isotropic elastic materials, under quasi-static loading conditions. In our current investigation, we have attempted to establish a link between superior strength of nacre, under impact loading conditions for a given loading-rate, and its microstructural dependence, via the existence of an optimum overlap length during shear-transfer. The loading rates applied for dynamic compression testing [Menig et al. (2000)] of abalone nacre varied from 15-25 GPas<sup>-1</sup>. Corresponding to loading rates of 15 GPas<sup>-1</sup>, 20 GPas<sup>-1</sup> and, 25 GPas<sup>-1</sup>, the current analytical model predicts an effective strain of 0.0070, 0.0090, and 0.0117 respectively, which are in reasonable agreement with the experimentally observed values of 0.008, 0.0095, and 0.0145 respectively, obtained by Menig et al. (2000). Additionally, the predicted maximum compressive strength is approximately 450 MPa which is again in reasonable agreement with experimentally obtained strengths of nearly 500 MPa [Menig et al., 2000; Huang et al., 2011]. Predicted shear strains corresponding to loading rates of 15 GPas<sup>-1</sup>, 20 GPas<sup>-1</sup> and, 25 GPas<sup>-1</sup> were 0.178, 0.237, and 0.297 respectively which is less than experimentally obtained maximum shear strains of approximately 0.45 [Menig et al., 2000]. This accounts for the reason as to why staggered architecture composites exhibit elevated compressive strength under time-dependent loading conditions. Additionally, under the current model, the elastic strain energy density (weff) will thereby turn out to be

higher for dynamic loading than for quasi-static loading conditions, which can explain the reason for superior damage tolerance of staggered architecture composites. The outcome of the current research will thus provide beneficial guidelines in custom-design manufacture of hybrid bio-inspired protective composite materials.



**Figure 3.7.** Plot showing the dependence of maximum shear stress (at the ends of overlap) as a function of aspect ratio and volume fraction of the ceramic bricks for: aspect ratio varying

#### Figure 3.7. (cont'd)

between 4 to 200 (a) and, 4 to 800 (b) under the application of triangular pulse loading, corresponding to a given loading-rate.

Ji and Gao (2004, 2010) and Ji (2008) had analyzed the staggered arrangement of the biological structure previously under quasi-static loading conditions. They postulated that under quasi-static conditions, two parameters play a significant role: (a) presence of nanometer-sized crystals to obtain a state of maximum flaw tolerance and, (b) presence of an optimum aspect ratio of the mineral crystals to promote strain amplification mechanism and thereby obtain an optimal balance for deformation in organic and inorganic components to obtain maximum potential. Apart from visualizing the design in staggered architecture materials from optimal overlap length point of view, the current model can also be visualized from aspect ratio and volume fraction of the ceramic point of view, for a given thickness of the ceramic brick.

Under time-dependent loading conditions, optimum aspect ratios exist for varying volume fractions of ceramic in staggered architecture materials, as shown in **Figure 3.7(a,b)**. For lower volume fractions of the ceramic, a wide range of optimal aspect ratio exists which would correspond to maximum load transfer capability of the joint via attainment of a state of minimum shear. For example, bone and dentin comprise of plate-like crystals having aspect ratio varying from 25-50 and a volume fraction of 0.40-0.55 [**Ji and Gao (2004)**]. For very high volume fraction of the ceramic, the range of aspect ratio available to obtain a state of minimum

shear is narrow, as shown in **Figure 3.7(a)**. Similarly, nacre comprises of ceramic bricks having an aspect ratio varying from 10-16 and a volume fraction of nearly 0.95 [**Ji and Gao (2004)**].



**Figure 3.8.** Plot showing the dependence of the ratio of composite modulus to Young's modulus of the ceramic bricks for varying aspect ratio and volume fraction of the ceramic bricks: correlation between dynamic (a) and quasi-static (b) regime, corresponding to a given loading

rate.

In order to obtain a more clearer understanding of the interdependence of aspect ratio, volume fraction of the ceramic, and constituent material properties under impact loading conditions, a plot of ratio of composite modulus to the ceramic Young's modulus as a function of aspect ratio and volume fraction is shown in **Figure 3.8(a)**. **Figure 3.8(b)** shows the dependence obtained under quasi-static conditions using the Tension-Shear-Chain (TSC) model as was postulated by **Ji and Gao (2004)**.

It should be noted that extensive literature exists quantifying role of microstructure and material parameters on the behavior of staggered architecture, however under quasi-static loading conditions. Note that, in our current investigations, what we are trying to establish is that staggered architecture in biological composites is designed in such a unique manner that the structure would be able to provide maximum resistance both under quasi-static loading conditions, and when subjected to severe dynamic loads when attacked by predators (as resistance to shell crushing is an integral part of shell evolution process).

## **3.3.1.** *Limitations of the analytical model and future directions*

Formulation of the model is laid on the foundation of linear elastic material behavior only, i.e. the stresses are linearly dependent on strain only (via material properties E,G which are considered constant); however, the organic matrix being a visco-elastic material, under

dynamic loading conditions, strain-rate (  $\epsilon_{\text{S}}$  ) of the organic matrix is expected to play a key role

in load transfer via shear. Incorporation of strain-rate ( $\varepsilon_{s}$ ) dependent terms and large-scale deformation aspects would help in understanding mechanical behavior of these composites under very high-strain rate loading; for example under blast loading conditions. Additionally, incorporation of plastic behavior of the intermediate matrix is also expected to contribute to the cause. This could possibly account for the difference obtained between experimentally observed and theoretically predicted overlap length values in nacre as shown previously. Work is in progress in this direction. To further and better understand this aspect, the model can be extended to include strain-rate dependence and large-scale deformation of the intermediate polymer, effect of alignment (regular, stairwise, random), number of hierarchical levels, etc. These can be identified as future directions of the current work. Additionally, the current model is restricted to the scenario where adherends are made of same materials. Work is in progress to understand the behavior of staggered architecture composites where adherends are made of dissimilar materials.

Under static loading conditions, characteristic lengths predicted were essentially based on (a) stress transfer point of view,  $L^* = \sqrt{\frac{2Ebh}{G}}$ , as was postulated by **Chen et al. (2009)** and, (b) an optimization on both strength and toughness fronts,  $L^* = 2.318 \sqrt{\frac{Ebh}{G}}$ , as postulated by **Wei et al. (2012)**. Under dynamic rates of loading, the shear stress developed at the interface is also a function of the overlap length (L). If a joint has to withstand the entire dynamic event, critical overlap length exists based on the essence of minimization of shear stress at the extremities to promote maximum load transfer capability by polymer via shear (once the material properties and geometrical parameters are fixed). Thereby, in order to obtain optimum joint efficiency, an optimal overlap length is evaluated as follows:

$$L_{optimal} \equiv Minimize \left[ \tau(x,t) \right]_{L} = Minimize \left[ \frac{G}{h} \times u_{4}(x,t) \right]_{L} = \left[ \left\{ \begin{array}{c} \frac{\sigma(t)L}{6E} + \frac{2c^{2}}{ELd_{04}} \int_{\tau=0}^{t} \sigma(\tau) \sin(d_{04}(t-\tau)) d\tau \\ \int_{\tau=0}^{t} \frac{G}{E} \left[ \frac{1+\cos(n\pi)}{n^{2}\pi^{2}} \right] \sigma(t) + \\ \frac{G}{h} \times \left\{ + \sum_{n\geq 1} \left[ \frac{2c}{E} \left( \frac{1+\cos(n\pi)}{\sqrt{kt^{2}+n^{2}\pi^{2}}} \right) \int_{\tau=0}^{t} \sigma(\tau) \sin\left(c\sqrt{k} + \left(\frac{n\pi}{L}\right)^{2}(t-\tau)\right) d\tau \right\} \right\} \\ \frac{\cos\left(\frac{n\pi x}{L}\right)}{\cos\left(\frac{n\pi x}{L}\right)} \\ + \frac{\sigma(t)}{E} \left[ \frac{x^{2}}{L} - x \right] \right] L (3.92)$$

It is to be noted that there does not exist a direct relationship between dynamic overlap length and static overlap length. This can be better addressed with reference to the figure shown below.



**Figure 3.9.** Variation of shear stress at the interface as a function of overlap length in a material (in the current case, nacreous layer in seashells) under (a) static, and (b) dynamic rates of loading.

Under static loading conditions, the shear stress (at the extremities of the interface) [Wei et al. (2012)] as given by the equation below, decreases till a critical value is attained and remains constant thereafter.

$$\tau_{\text{static}}\Big|_{\mathbf{X}=\left(0,\frac{\mathsf{L}}{2}\right)} = \frac{\sigma b\lambda}{2\sinh\left(\frac{\lambda\mathsf{L}}{2}\right)}\cosh\left(\frac{\lambda\mathsf{L}}{2}\right); \lambda = \sqrt{\frac{2\mathsf{G}}{\mathsf{Ebh}}}$$
(3.93)

On the contrary, it can be clearly seen (**Figure 3.9**) that critical overlap length exists under dynamic rates of loading, and thus addresses the vitality of optimal overlap length under dynamic rates of loading.

Under quasi-static loading conditions, choice of critical overlap length in staggered biocomposites attempts to optimize mechanical performance on both strength and toughness fronts. However under impact loading conditions, since shear transfer mechanism is the most versatile parameter, choice of critical overlap length is mainly directed towards minimization of peak shear stresses at the extremities of the joint. However, nature simultaneously addresses the nano-sub-micro overlap length scales in an attempt to improve on toughness perspective as well. This feature can be adapted as an important guideline in the design of adhesively bonded lap joints, gradient microstructural composites, etc. under dynamic rates of loading. The outcome of the current research will thus provide beneficial guidelines in custom-design manufacture of hybrid bio-inspired protective composite materials.

#### **3.4.** Conclusions

In our current investigation, we have addressed the following aspects with regards to materials exhibiting staggered microstructure as its most elementary level of architecture under impact loading conditions, by considering a triangular loading pulse: (1) Identifying the structure-property correlationship for these materials, (2) existence of a critical overlap length which optimizes load transfer mechanism between the adjacent reinforcements, (3) ratify the choice of nanometer building blocks in biological composites under time-dependent loading, (4) generalizing the application of the concept to the case of macro-scale adhesively bonded lap joints, (5) explaining the reason behind superior damage tolerance and elevated dynamic compressive strength of nacre, and (6) theoretically justify the applicability of staggered microstructural composites under impact loading conditions. The outcome of the current research will provide beneficial guidelines in custom-design manufacture of hybrid bio-inspired protective composite materials.

REFERENCES

#### REFERENCES

**Barthelat, F., Espinosa, H.D., 2007.** An Experimental Investigation of Deformation and Fracture of Nacre-Mother of Pearl. *Exp. Mech.* **47**, 311–324.

Barthelat, F., Tang, H., Zavattieri, P., Li, C.M., Espinosa, H., 2007. On the Mechanics of Mother-of-Pearl: A Key Feature in the Material Hierarchical Structure. *J. Mech. Phys. Solids* 55, 306-337.

Chen, B., Wu, P.D., Gao, H., 2009. A characteristic length for stress transfer in the nanostructure of biological composites. *Compos. Sci. Technol.* 69, 1160-1164.

de Gennes, P.G., Okumura, K., 2000. On the toughness of biocomposites. C. R. Acad. Sci. Paris, t.1, Ser. IV, 257-261.

Evans, A., Suo, Z., Wang, R., Aksay, I., He, M., Hutchinson, J., 2001. Model for the Robust Mechanical Behavior of Nacre. *J. Mater. Res.* **16**, 2475-2484.

**Espinosa, H.D., Juster, A.L., Latourte, F.J., Loh, O.Y., Gregoire, D., Zavattieri, P.D., 2011.** Tablet-Level Origin of Toughening in Abalone Shells and Translation to Synthetic Composite Materials. *Nature Comm.* **2**, 173.

Gao, H., Ji, B., Jäger, I., Arzt, E., Fratzl, P., 2003. Materials Become Insensitive to Flaws at Nanoscale: Lessons from Nature. *Proc. Natl. Acad. Sci. U.S.A.* 100, 5597-5600.

**Gao, H., 2006.** Application of fracture mechanics concepts to hierarchical biomechanics of bone and bone-like materials. *Int. J. Fracture*, **138**, 107-137.

Hulmes, D.J.S., Wess, T.J., Prockop, D.J., Fratzl, P., 1995. Radial packing, order and disorder in collagen fibrils. *Bioph. J.* 68, 1661–1670.

Huang, Z., Li, H., Pan, Z., Wei, Q., Chao, Y.J., Li, X., 2011. Uncovering high-strain rate protection mechanism in nacre. *Sci. Rep.* **1**, 148; DOI:10.1038/srep00148.

Jackson, A.P., Vincent, J.F.V., Turner, R.M., 1988. The mechanical design of nacre. *P. R. Soc. London B.* 234, 415–440.

Jager, I., Fratzl, P., 2000. Mineralized collagen Fibrils: a mechanical model with a staggered arrangement of mineral particles. *Biophys. J.* **79**, 1737–1746.

Ji, H., Gao, H., 2004. Mechanical properties of nanostructure of biological materials. J. Mech. Phys. Solids 52, 1963-1990.

Ji, B.H., 2008. A study of the interface strength between protein and mineral in biological materials. J. Biomech. 41, 259–266.

Ji, B., Gao, H., 2010. Mechanical principles of biological nanocomposites. *Annu. Rev. Mater. Res.* 40, 77-100.

**Kessler, H., Ballarini, R., Mullen, R.L., Kuhn, L.T., Heuer, A.H., 1996.** A biomimetic example of brittle toughening: (I) steady state multiple cracking. *Comp Mater Sci.* **5**, 157–166.

Kamat, S., Su, X., Ballarini, R., Heuer, A.H., 2000. Structural basis for the fracture toughness of the shell of the conch Strombus gigas. *Nature*, 405, 1036–1040.

Kotha, S.P., Kotha, S., Guzelsu, N., 2000. A shear-lag model to account for interaction effects between inclusions in composites reinforced with rectangular platelets. *Compos. Sci. Technol.* 60, 2147–2158.

Katti, K.S., Katti, D.R., Pradhan, S.M., Bhosle, A., 2005. Platelet interlocks are the key to toughness and strength in nacre. *J. Mater. Res.* 20, 1097-1110.

Keten, S., Buehler, M.J., 2008. Asymptotic Strength Limit of Hydrogen-Bond Assemblies in Proteins at Vanishing Pulling Rates. *Phys. Rev. Lett.* 100, 198301.

Keten, S., Xu, Z., Ihle, B., Buehler, M.J., 2010. Nanoconfinement Controls Stiffness, Strength and Mechanical Toughness of -Sheet Crystals in Silk. *Nature Materials* 9, 359-367.

Landis, W., Song, M., Leith, A., McEwen, L., McEwen, B., 1993. Mineral and Organic Matrix Interaction in Normally Calcifying Tendon Visualized in Three Dimensions by High-Voltage Electron Microscopic Tomography and Graphic Image Reconstruction. *J. Struct. Biol.* **110**, 39-54.

Landis, W.J., 1995. The strength of a calcified tissue depends in part on the molecular structure and organization of its constituent mineral crystals in their organic matrix. *Bone* 16, 533–544.

Liu, G., Ji, B.H., Hwang, K.C., Khoo, B.C., 2011. Analytical solutions of the displacement and stress fields of the nanocomposite structure of biological materials. *Compos. Sci. Technol.* **71**, 1190-1195.

Menig, R., Meyers, M.H., Meyers, M.A., Vecchio, K.S., 2000. Quasi-static and dynamic mechanical response of Haliotis rufescens (abalone) shells. *Acta Mater.* **48**, 2383–2398.

Menig, R., Meyers, M.H., Meyers, M.A., Vecchio, K.S., 2001. Quasi-static and dynamic mechanical response of Strombus gigas (conch) shells. *Mater. Sci. Eng. A* **297**, 203–211.

Meyers, M., Lin, A., Chen, P., Muyco, J., 2008. Mechanical Strength of Abalone Nacre: Role of the Soft Organic Layer. *J. Mech. Behav. Biomed. Mater.* **1**, 76-85.

**Okumura, K., de Gennes, P.-G., 2001.** Why is nacre strong? : Elastic theory and fracture mechanics for biocomposites with stratified structures. *Eur. Phys. J. E* **4**, 121-127.

**Penel, S., Morrison, R.G., Dobson, P.D., Mortishire Smith, R.J., Doig, A.J., 2003.** Length Preferences and Periodicity in Strands. Antiparallel Edge Sheets Are More Likely to Finish in Non Hydrogen Bonded Rings. *Protein Eng.* **16**, 957.

Sarikaya, M., Gunnison, K.E., Yasrebi, M., Aksay, J.A., 1990. Mechanical property-microstructural relationships in abalone shell. *Mater. Res. Soc.* 174, 109-116.

Sun, Y.L., Luo, Z.P., Fertala, A., An, K.N., 2002. Direct quantification of the flexibility of type I collagen monomer. *Biochemical and Biophysical Research Communications* 295, 382-386.

**Song, F., Soh, A., Bai, Y., 2003.** Structural and mechanical properties of the organic matrix layers of nacre. *Biomaterials* **24**, 3623-3631.

Shuchun, Z., Yueguang, W., 2007. Effective elastic modulus of bone-like hierarchical materials. *Acta Mech. Solida Sin.* 20, 198-205.

Sen, O., Tekalur, S.A., Jilek, C., 2011. The determination of dynamic strength of single lap joints using the split Hopkinson pressure bar. *Int. J. Adhes. Adhes.* **31**, 541-549.

**Volkersen, O., 1938.** Die Nietkraftverteilung in zugbeanspruchten Nietverbindungen mit konstanten Laschenquerschnitten, *Luftfahrtforsch* **15**, 41.

**Veis, A., Sabsay, B., 1987.** *The collagen of mineralized matrices*. In Bone and Mineral Research/5, W. A. Peck, editor. (Elsevier Science Publications, New York, Amsterdam, Tokyo). pp. 1-63.

**Wagner, H.D., Weiner, S., 1992.** On the relationship between the microstructure of bone and its mechanical stiffness. *J. Biomech.* **25**, 1311–1320.

Wang, R., Suo, Z., Evans, A., Yao, N., Aksay, I., 2001. Deformation mechanisms in nacre. J. Mater. Res. 16, 2485-2493.

Wang, R., Gupta, H.S., 2011. Deformation and fracture mechanisms of bone and nacre, *Annu. Rev. Mater. Res.* 41, 41-73.

Wei, X., Naraghi, M., Espinosa, H.D., 2012. Optimal length scales emerging from shear load transfer in natural materials: application to carbon-based nanocomposite design. ACS Nano 6(3), 2333-2344.

Yang, L., Van Der Werf, K.O., Fitié, C.F.C., Bennink, M.L., Dijkstra, P.J., Feijen, J., 2008. Mechanical Properties of Native and Cross-Linked Type I Collagen Fibrils. *Biophys. J.* 94, 2204-2211.

Zhang, Z.Q., Liu, B., Huang, Y., Hwang, K.C., Gao, H., 2010. Mechanical properties of unidirectional nanocomposites with non-uniformly/randomly staggered platelet distribution. *J. Mech. Phys. Solids* **58**, 1646-1660.

Zhang, Z., Zhang, Y.-W, Gao, H., 2011. On optimal hierarchy of load-bearing biological materials. *Proc. R. Soc. B*, 278, 519-525.

CHAPTER 4. ENHANCING RESISTANCE AND LOAD TRANSFER VIA CHOICE OF OPTIMAL

**OVERLAP LENGTH** 

#### 4.1. Introduction

Over the past decade, increasing attention has been focused towards producing composites that are both light-weight and durable via extracting design principles from structural biological composites for example, nacre. The inner shining layer in seashells is referred to as the nacreous layer and exhibits a staggered architecture in the form of an overlapping arrangement of mineral tablets in a soft polymeric matrix [Jackson et al., 1988; Sarikaya et al., 1990]. What confers nacre an ideal model for biomimetic inspiration are two promising aspects: light weight and superior toughness [Barthelat and Espinosa, 2007; Jackson et al., 1988; Kessler et al., 1996; Kamat et al., 2000; Sarikaya et al., 1990]. Light weight is accomplished via embedding a polymeric matrix in a network of ceramic/mineral bricks, whereas toughness has been attributed to existence of a multitude of toughening mechanisms, namely tablet pull-out [Jackson et al., 1988], crack deflection through the biopolymer [Menig et al., 2000], platelet interlocks [Katti et al., 2005], presence of nanoasperities [Evans et al., 2000; Wang et al., 2001], diffusive tablet sliding [Barthelat et al., 2007] arising from tablet waviness, aragonite bridge reinforcements at interface [Song et al., 2003], re-locking of tablets [Meyers et al., 2008] due to persistent contact of broken aragonite bridges, and synchronized deformation twinning of the nano-scale particles in ceramic bricks [Huang et al., 2011]. All the aforementioned factors contribute to both interfacial strengthening and fracture resistance in varying degrees of resistance.

Till date, a number of literature studies have attempted to address the behavior of the staggered architecture materials on the basis of interdependence of material properties and

geometrical parameters. Table 4.1 provides the references and the approach adopted by

various researchers with reference to modeling of biological composites, in a brief manner.

Table 4.1. Recent advances on modeling staggered architecture biological composites by

various researchers.

Authors	Description
Jaegar and Fratzl,	Predicted modulus of staggered architecture composites along the
2000; Kotha et	longitudinal direction of the inclusions as a function of aspect ratio and
al., 2001	concentration of the inclusions.
de Gennes and Okumura, 2000; Okumura and de Geness, 2003	Developed an analytical model based on laminar architecture of seashells
	to account for the existence of weaker stress concentration ahead of the
	crack tip in these materials in comparison to traditional isotropic elastic
	materials along with an examination of the effect of differential stiffness
	of inclusions and interfaces.
Gao et al., 2003	Developed the Tension-shear-chain (TSC) model to describe the
	mechanics of staggered architecture composites and study the
	mechanical properties of these type of biological composites.
Shuchun and Yueguang, 2007	Studied the interdependence of the elastic modulus of the composite
	and number of hierarchical levels in bone-like materials via comparison
	of their results against TSC model and FE (finite element) simulations.
Zhang et al., 2010	Investigated the effect of platelet distribution (regular, stairwise,
	random) on stiffness, strength, failure strain and energy absorption
	capability in materials exhibiting staggered architecture.
Zhang et al., 2011	Used a guasi-self-similar hierarchical model to comprehend the existence
	of an optimal number of hierarchical levels in biological composites.
Liu et al., 2011	Provided analytical expressions for displacement and stress fields in
	staggered nanocomposite structures under static loading conditions
	under uniaxial tension
Barthelat and	Developed a micromechanical model taking into consideration the effect
Rahiei 2011	of toughening associated with the process zone
Navici, 2011	or toughening associated with the process zone.

The nacreous layer can be visualized as translation of unit cell structure in 2-dimensions comprising of overlapping mineral tablets having distinct overlap and core regions. The overlap region is responsible for inter-mineral load transfer via shear deformation of the polymer. One might consider what could possibly be the reason associated with the existence of specific overlap length in the nacreous layer in seashells. Analytical models and numerical simulations

have been developed and certain criterion been proposed to address this aspect as listed in

Table 4.2 below.

**Table 4.2.** Recent advances on investigating existence of characteristic overlap length in staggered architecture biological composites by various researchers.

Authors	Description
	Under static rates of loading, the existence of characteristic length was
Chen et al., 2009	attributed to attainment of efficient stress transfer in staggered
	biocomposites.
	Under static rates of loading, the existence of unique overlap length in
	biological composites was attributed to an attempt to optimize both
Wei et al., 2013	strength and toughness frontiers in staggered architecture biological
	composites. Note that, the toughness in their investigations was
	defined in terms of elastic strain energy density.
	From the perspective of impact rates of loading, existence of optimal
Dutta et al., 2013	overlap length was attributed to an attempt to obtain maximum shear
	transfer efficiency.

What contributes to the superior load-transfer and energy dissipative capabilities of the nacreous layer is the meandering nature of the crack path throughout its architecture. Higher is the level of tortuousness associated with the crack path, higher will be the energy required to drive the crack throughout the individual microscopic unit cells and thereby, superior will be the toughness of the nacreous layer on a macroscopic level. Note that, the current scenario under consideration is representative of an interface fracture problem. On a conservative approach, it is opportune to consider that an interface is as much fracture resistant as the least tough participating component in the system. As per Griffith criterion, cracks will initiate and delamination or cohesive failure will occur in the unit-cell once the crack driving force (rate of energy input) ahead of the crack tip exceeds the fracture resistance (rate of energy dissipated)

of either the biopolymer itself, or that of the interface. The objective thus is to find out how structural overlap length is responsible for minimizing this event to the maximum extent possible. Under given set of loading conditions, if overlap length is adopted such that crack tip driving forces required for crack initiation can be kept to a minimum, higher will be load that further needs to be applied to elevate the energy required to attain the fracture resistance of the barrier(s) to promote delamination (shown later in **Figure 4.5**) in the unit-cell. This would in-turn raise the toughness associated with the individual unit-cells which would contribute to global toughness of the composite. The main outcome of the developed analytical model in the current study is to obtain a simplified expression for crack driving force in terms of local finite stress concentrations in the biopolymer layer of nacre. This would in-turn provide an insight into the severity of load carried and transferred by the joint. Finally, the article concludes with validation of the hypothesis against previously published experimental data followed by proposing a design guideline to guide staggered architecture composite development to obtain optimized performance in terms of stiffness, load-transfer and toughness.

# 4.2. Analytical model

The remarkable macroscopic toughness of nacre is as a result of all the microstructural mechanisms taking place ahead of the crack tip (otherwise referred to as intrinsic toughening), behind the crack tip (otherwise referred to as extrinsic toughening), around the crack tip and at the crack tip [Launey and Ritchie, 2009] as shown in Figure 4.1. Extrinsic toughening is associated with mechanisms such as crack-bridging and in-situ phase transformations. On the contrary, intrinsic toughening is associated with the role of type, size, distribution of

reinforcement and it's interfacial properties with the binding matrix. Crack growth ensues from extrinsic toughening whereas crack initiation is primarily dependent upon intrinsic toughening. So, the question is how does the nacreous layer allay crack initiation in its micro-architecture? In the current study, we will try to better understand the design principle in the nacreous layer from a fracture mechanics perspective from the point-of-view of intrinsic toughening.



Figure 4.1. Toughening mechanisms associated with nacre and region under consideration.

In order to address this, we develop our analytical model by taking into consideration a unit cell with plane strain infinitesimal deformations, as shown in **Figure 4.2**. Following are the assumptions associated with the analytical model:

- (1). One-dimensional analysis.
- (2). Participating members exhibit linear elastic behavior (ceramic bricks, bio-polymer).
- (3). Normal stress distribution in the ceramic bricks (no bending).

(4). Shear stress distribution in the bio-polymer.

(5). Since the bio-polymer is very thin in comparison to the brick thickness, the stress distribution is considered constant throughout the joint thickness [Luo and Tong, 2004].

(6). There is no rotation of the transverse normal about the y-axis, which is directed into the plane of the paper.

The unit cell has been discretized into four elemental blocks (labeled 1 to 4). The total width of the mineral tablets is 2b and thickness of the biopolymer is given by  $\eta$ . Local rectangular Cartesian coordinate system for elemental blocks 1-4 have been defined as shown in **Figure 4.2**. It has also been assumed that there is no rotation of the transverse normal about the y-axis.



**Figure 4.2.** (a) Schematic of staggered architecture of calcium carbonate bricks (shown in green) in biopolymer matrix (shown in yellow); (b) expanded view of the 2-dimensional unit cell structure (with plane strain infinitesimal deformation) showing the pre-cracked length ( $L_1$ ) and instantaneous overlap length ( $L_2$ ) and coordinate systems; (c) expanded view of the 2-dimensional unit cell structure (with plane strain infinitesimal deformation) highlighting the elemental blocks and the original overlap length ( $L_0$ ); (d) splitting of parent crack tip for crack driving force calculations; (e) schematic identifying shear and normal force resultants  $N_C$  and  $Q_C$  respectively.

With reference to **Figure 4.2**, x,  $x_1$ , and  $x_2$  represents horizontal axes with different origins (along the longitudinal direction of the bricks) and the z direction is associated in the thickness direction. With reference to **Figure 4.2(b)**, as a starting point, it has been considered that there is a pre-existing void (of length,  $a_0$ ), an incremental crack (of length, da) in the cell. Subsequent analyses are based on the value of that instantaneous crack length. The displacements are denoted by u and are associated with a subscript and superscript. The subscript corresponds to direction of displacement (either x,  $x_1$ ,  $x_2$ , or z) whereas the superscript corresponds to elemental block number (labeled 1 through 4). We assume that in all the elemental blocks, the variation of displacements is a function of either x,  $x_1$ , or  $x_2$ . The elemental strains are thus defined as follows:

# Elemental block #1:

$$\varepsilon_{XX}^{1} = \frac{du_{X}^{1}}{dx_{1}}$$
(4.1)

$$\varepsilon_{ZZ}^1 = 0 \tag{4.2}$$

$$\gamma_{XZ}^{1} = \frac{du_{Z}^{1}}{dx_{1}}$$
(4.3)

Elemental block #2:

$$\varepsilon_{XX}^2 = \frac{du_X^2}{dx_2} \tag{4.4}$$

$$\varepsilon_{ZZ}^2 = 0 \tag{4.5}$$

$$\gamma_{xz}^2 = \frac{du_z^2}{dx_2} \tag{4.6}$$

Elemental block #3:

$$\varepsilon_{XX}^3 = \frac{du_X^3}{dx}$$
(4.7)

$$\varepsilon_{ZZ}^3 = 0 \tag{4.8}$$

$$\gamma_{XZ}^3 = \frac{du_Z^3}{dx}$$
(4.9)

Elemental block #4:

$$\varepsilon_{XX}^{4} = \frac{du_{X}^{4}}{dx}$$
(4.10)

$$\varepsilon_{ZZ}^4 = 0 \tag{4.11}$$

$$\gamma_{xz}^{4} = \frac{du_{z}^{4}}{dx}$$
(4.12)

The stresses in the elemental blocks (i = 1..4) have been computed as follows:

$$\sigma_{\mathbf{X}\mathbf{X}}^{\mathbf{i}} = \mathsf{C}_{11}^{\mathsf{C}} \varepsilon_{\mathbf{X}\mathbf{X}}^{\mathbf{i}} + \mathsf{C}_{22}^{\mathsf{C}} \varepsilon_{\mathbf{Z}\mathbf{Z}}^{\mathbf{i}} \tag{4.13}$$

$$\sigma_{zz}^{i} = C_{22}^{c} \varepsilon_{xx}^{i} + C_{33}^{c} \varepsilon_{zz}^{i}$$

$$(4.14)$$

$$\sigma_{XZ}^{i} = C_{44}^{C} \gamma_{XZ}^{i} \tag{4.15}$$

The strains and the stresses in the biopolymer are obtained as follows:

$$\varepsilon_{XX}^{p} = \frac{1}{2} \left( \frac{du_{X}^{3}}{dx} + \frac{du_{X}^{4}}{dx} \right)$$
(4.16)

$$\gamma_{XZ}^{p} = \frac{1}{\eta} \left( u_{X}^{4} - u_{X}^{3} \right)$$
(4.17)

$$\varepsilon_{ZZ}^{p} = \frac{1}{\eta} \left( u_{Z}^{3} - u_{Z}^{4} \right) \tag{4.18}$$

$$\sigma_{zz}^{p} = C_{22}^{p} \varepsilon_{xx}^{p} + C_{33}^{p} \varepsilon_{zz}^{p}$$

$$\tag{4.19}$$

$$\sigma_{xz}^{p} = C_{44}^{p} \gamma_{xz}^{p} \tag{4.20}$$

where,  $\sigma_{zz}^p$  and  $\sigma_{xz}^p$  denotes the normal (peel) stress and shear stress in the polymer respectively.

# **4.2.1.** Solution scheme for elemental displacements

Force equilibrium on the elemental blocks leads to the development of following governing differential equations of the system, given by

$$\frac{d^2 u_x^1}{dx_1^2} = 0$$
(4.21)

$$\frac{d^2 u_z^1}{dx_1^2} = 0$$
(4.22)

$$\frac{d^2 u_X^2}{dx_2^2} = 0$$
 (4.23)

$$\frac{d^2 u_z^2}{dx_2^2} = 0$$
 (4.24)

$$\frac{d^{2}u_{x}^{3}}{dx^{2}} - M_{1}\left(u_{x}^{3} - u_{x}^{4}\right) = 0$$
(4.25)

$$\frac{d^2 u_x^4}{dx^2} + M_1 \left( u_x^3 - u_x^4 \right) = 0$$
(4.26)

$$\frac{d^{2}u_{z}^{3}}{dx^{2}} - M_{2}\left(\frac{du_{x}^{3}}{dx} + \frac{du_{x}^{4}}{dx}\right) - M_{3}\left(u_{z}^{3} - u_{z}^{4}\right) = 0$$
(4.27)

$$\frac{d^{2}u_{z}^{4}}{dx^{2}} + M_{2}\left(\frac{du_{x}^{3}}{dx} + \frac{du_{x}^{4}}{dx}\right) + M_{3}\left(u_{z}^{3} - u_{z}^{4}\right) = 0$$
(4.28)

where 
$$M_1 = \frac{C_{44}^p}{b\eta C_{11}^c}$$
,  $M_2 = \frac{C_{22}^p}{2bC_{44}^c}$ , and  $M_3 = \frac{C_{33}^p}{b\eta C_{44}^c}$ . The boundary conditions of the

system are given by

$$u_{z}^{1}\Big|_{x_{1}=0} = 0$$
 (4.29)

$$|u_{x}^{2}|_{x_{2}=0} = 0$$
 (4.30)

$$\frac{du_{x}^{1}}{dx_{1}}\bigg|_{x_{1}=0} = 0$$
(4.31)

$$\left. \frac{\mathrm{d}u_{z}^{1}}{\mathrm{d}x_{1}} \right|_{x_{1}=0} = 0 \tag{4.32}$$

$$\frac{du_z^4}{dx}\bigg|_{x=L_2} = 0$$
 (4.33)

$$\frac{du_{X}^{3}}{dx}\bigg|_{x=L_{2}} = \frac{\sigma}{c_{11}^{c}}$$
(4.34)

$$\frac{du_X^2}{dx_2}\bigg|_{x_2=0} = \frac{\sigma}{c_{11}^c}$$
(4.35)

$$\frac{\left. \frac{du_{X}^{4}}{dx} \right|_{x=L_{2}} = 0 \tag{4.36}$$

$$\frac{\mathrm{d}u_{z}^{2}}{\mathrm{d}x_{2}}\bigg|_{x_{2}=0} = 0 \tag{4.37}$$

$$\frac{du_z^3}{dx}\bigg|_{x=L_2} = 0$$
(4.38)

where,  $L_1 = a_0$  and  $L_2 = L_0 - a_0$ . The continuity equations for forces across the element

boundaries are thus given by

$$\frac{du_{x}^{1}}{dx_{1}}\bigg|_{x_{1}=L_{1}} = \frac{du_{x}^{3}}{dx}\bigg|_{x=0}$$
(4.39)

$$\frac{\mathrm{d}u_{z}^{1}}{\mathrm{d}x_{1}}\bigg|_{x_{1}=L_{1}} = \frac{\mathrm{d}u_{z}^{3}}{\mathrm{d}x}\bigg|_{x=0}$$
(4.40)

$$\frac{du_{x}^{2}}{dx_{1}}\bigg|_{x_{1}=L_{1}} = \frac{du_{x}^{4}}{dx}\bigg|_{x=0}$$
(4.41)

$$\frac{\mathrm{d}u_{z}^{2}}{\mathrm{d}x_{1}}\Big|_{x_{1}=L_{1}} = \frac{\mathrm{d}u_{z}^{4}}{\mathrm{d}x}\Big|_{x=0}$$
(4.42)

The continuity equations for displacements across the element boundaries are defined as follows:

$$u_{x}^{1}\Big|_{x_{1}=L_{1}} = u_{x}^{3}\Big|_{x=0}$$
 (4.43)

$$u_{z}^{1}\Big|_{x_{1}=L_{1}} = u_{z}^{3}\Big|_{x=0}$$
 (4.44)

$$u_{x}^{2}\Big|_{x_{2}=L_{1}} = u_{x}^{4}\Big|_{x=0}$$
 (4.45)

$$u_{z}^{2}\Big|_{x_{2}=L_{1}} = u_{z}^{4}\Big|_{x=0}$$
 (4.46)

We thus have coupled second-order linear differential equations subjected to homogenous boundary conditions. The governing equations corresponding to each elemental blocks are solved first which results in 16 constants of integration. The unknown constants of integration are determined from the boundary conditions and continuity conditions of the system to finally obtain the generalized displacements associated with each elemental block.

#### **4.2.2.** Computation of crack driving force (CDF)

As per linear elastic fracture mechanics, energy released from the propagation of a crack is equivalent to work needed to close that small crack propagation. The energy release rate (or rather, rate of energy input) is representative of the severity of load acting on the infinitesimal crack in the biopolymer layer. It is also representative of energy-flux to crack tip which acts a driving force for quasi-static advancement of crack and subsequently fracture. Thus in our present analyses energy release rate ahead of the crack tip will be henceforth perceived as crack driving force.

As mentioned previously, considering plane strain conditions, we assume a virtual crack tip displacement by an amount da. The parent crack tip at point C splits into points A and B, and translates to point C'. Crack driving force ahead of a crack-tip due to an incremental increase in crack length is equivalent to work (or rather, energy) required to close that infinitesimal increment and is thus computed as follows [Yang et al., 2008]:

$$G = \frac{W}{da} = \frac{1}{2da} \left[ N_C \left( u_X^B - u_X^A \right) + Q_C \left( u_Z^B - u_Z^A \right) \right]$$
(4.47)

where, W represents the work required to close the virtual crack. As shown in **Figure 4.2(d,e)**, shear and normal force resultants  $N_c$  and  $Q_c$  respectively can be computed as follows:

$$N_{\rm C} = -\int_{x=0}^{da} \sigma_{\rm XZ}^{\rm p} dx \tag{4.48}$$

$$Q_{c} = \int_{x=0}^{da} \sigma_{ZZ}^{p} dx$$
(4.49)

 $\sigma_{XZ}^{p}$  and  $\sigma_{ZZ}^{p}$  are obtained from the solution of the problem prior to virtual crack-tip extension.  $u_{X}^{A}$ ,  $u_{Z}^{A}$ ,  $u_{X}^{B}$  and  $u_{Z}^{B}$  are found out by solving the problem by substitution of overlap length  $L_{2} = L_{0} - a_{0}$  by  $L_{2} = L_{0} - a_{0} - da$  and by using the following relations:

$$|u_{x}^{A} = u_{x}^{2}|_{x_{2} = a_{0} - da}$$
 (4.50)

$$u_{z}^{A} = u_{z}^{2} \Big|_{x_{2} = a_{0} - da}$$
 (4.51)

$$u_{X}^{B} = u_{X}^{1} \Big|_{x_{1} = a_{0} - da}$$
 (4.52)

$$u_{z}^{B} = u_{z}^{1} \Big|_{x_{1} = a_{0} - da}$$
 (4.53)

Practically speaking the unit-cell structure in the nacreous layer of seashells is representative of an adhesive joint and in order to better understand the crack initiation and growth process, it is imperative to extract the crack driving force contributions associated with both mode-I and mode-II, and thus we introduce the mode-mixity parameter. In order to investigate the effect of components of crack driving force that contributes to crack initiation, Equation (4.47) can alternatively be written as

$$G_{II} = \frac{1}{2da} \left[ N_C \left( u_X^B - u_X^A \right) \right]$$
(4.54)

$$G_{I} = \frac{1}{2da} \left[ Q_{C} \left( u_{Z}^{B} - u_{Z}^{A} \right) \right]$$
(4.55)

$$MMP = \tan^{-1} \left( \frac{G_{II}}{G_{I}} \right)$$
(4.56)

where,  $G_{II}$ ,  $G_{I}$  and MMP denotes mode I crack driving force, mode II crack driving force and mode mixity parameter respectively. For pure mode I failure, MMP=0 and for pure mode II failure, MMP =  $\frac{\pi}{2}$ .

## **4.2.3.** *Limitations associated with the analytical model*

In our current study, the microstructural resistance to crack initiation has been associated from a local perspective in terms of crack driving force. Lower the value of crack driving force, higher is the microstructural resistance associated with the unit-cells to crack initiation. At this stage, we would like to point out that applied stress levels responsible for crack initiation could possibly be higher than the strength of the nacreous layer. Since the foundation of the model is based upon linear elastic deformation conditions, specific levels of external energy needed to be applied to generate appropriate level of rate of energy input (CDF) to surpass corresponding fracture resistance might possibly be over predicted. As we know, inelastic energy dissipation associated in the process zone [**Barthelat and Espinosa**, **2007**], viscoplastic deformation and microvoid coalescence mechanisms do contribute to a significant extent on the rate of energy dissipation in the forward zone associated with the crack-tip (as was shown in **Figure 4.1**).

However, note that under quasi-static rates of loading, the precursor to inelastic deformations is tablet sliding where the tablets start to slide upon one another once the shear strength of the material has been reached and is subsequently accompanied by interface strengthening. Additionally, under high strain-rate loading, the bio-polymer in the nacreous layer is expected to behave in a hard and brittle manner [Zachary and Burger, 1980] which would lead to conditions favoring brittle fracture and thereby, linear elastic conditions can be assumed without significant loss of fidelity.

The question that can be posed at this stage is under either of those scenarios what is that optimal overlap length which would delay this event (crack initiation following tablet sliding) and enhance interface strengthening to the maximum extent possible? It can be envisaged that a crack will advance only if the crack driving force (rate of energy input) associated with the local crack tip exceeds the fracture toughness (rate of energy dissipated) of (a) the bio-polymer, and/or (b) the interface. Thus, in our analyses we have focused our attention to the abovementioned perspective only.

# 4.3. Results and Discussion

It has already been reported in the past by Jackson et al., 1988 that approximately a third of the toughness of wet nacre samples has been associated with tablet pull-out. As per the TSC model postulated by **Gao et al., 2003** the inter-platelet load transfer occurs via shearing deformation of the polymer in its existing overlap length. The question is whether this length scale is just an arbitrary random number chosen by Nature or, is it associated with optimizing the structure-property correlationship? If the latter one, what are those mechano-biological principles that are operating underneath?

In order to test the validity of the analytical model, the variation of shear stress at mineral biopolymer interface is plotted for varying overlap lengths and pre-crack in the unit cell as shown in **Figure 4.3**. The properties of the mineral component in the nacreous layer [**Barthelat et al., 2006**] are:  $E_1$ =144 GPa,  $E_2$ =76 GPa,  $E_3$ =82 GPa,  $G_{12}$ =47.2 GPa,  $G_{13}$ =25.6 GPa,  $G_{23}$ =41.3 GPa,  $v_{12}$ =0.44,  $v_{13}$ =-0.06,  $v_{23}$ =0.18, 2b=0.5 µm. The properties of the biopolymer layer in nacre [**Xu et al., 2011**] are:  $E_p$ =10.57 GPa,  $G_a$ =1.4 GPa,  $v_a$ =0.45,  $\eta$ =20 nm. The observed overlap length in the nacreous layer is reported to be 1.67µm [**Espinosa et al., 2011**].



**Figure 4.3.** Variation of interfacial shear stress (at the extremities of the overlap) as a function of varying overlap length and pre-crack. The figure in the inset shows the expanded view for lower shear levels in the unit cell.

When an external load is applied, interfacial shear stress attains a maximum value at the extremities of its overlap. As it can be seen from **Figure 4.3**, the maximum interfacial shear stress (at the ends of the joint) attains a minimum value for overlap length exceeding 2-2.5  $\mu$ m and reaches the shear strength of the biopolymer  $\equiv$  37 MPa [Jackson et al., 1988]. This observation is in direct agreement with those obtained by **Dutta et al., 2013** in their estimation of characteristic overlap length in nacre under dynamic rates of loading respectively. The region to the right-hand side of 2-2.5  $\mu$ m might be considered as the preferred zone as it contributes
to a minimization of shear stress at the interface and optimizes intertablet load transfer via shear deformation of the intermediate biopolymer.

Resistance to crack advancement is an attribute associated with extrinsic toughening that takes place in the wake of the crack, and thus is responsible for R - curve. On the contrary, microstructural damage mechanisms in the cohesive zone and in bounded material are responsible for crack initiation which can be attributed to intrinsic toughening. Intrinsic toughening is dependent upon material properties and independent of length of crack or geometry of test specimen (except plane stress/plane strain). This brings into forefront that crack driving force to initiate fracture is a result of dissipation mechanism associated with intrinsic toughening. The current scenario under consideration is representative of an interface fracture problem. Note that an interface is as much fracture resistant as the least tough participating component in the system. As per Griffith criterion, cracks will initiate and delamination or cohesive failure will occur in the unit-cells once the crack driving force (rate of energy input) ahead of the crack tip exceeds the fracture resistance (rate of energy dissipated) of either the biopolymer itself, or that of the interface. The objective at present is to find out how structural overlap length is responsible for minimizing delamination in the unit-cells to the maximum extent possible.

Fracture toughness of the organic matrix varies between 20-160 mJ/m<sup>2</sup> [Song et al., 2003] whereas intrinsic fracture toughness of the organic interface has an upper limit varying between 400-1000 mJ/m<sup>2</sup> [Rabiei et al., 2012]. This value is comparable to the mineral toughness in the nacreous layer. This wide variation can be associated with viscoelastic nature

of the biopolymer, presence of nanoasperities, mineral bridges or a combination of all the modes. Once the crack driving force ahead of the crack-tip reaches fracture resistance of the biopolymer and/or the interface, the crack will initiate and start to grow in the unit-cell.

Resistance to crack advancement is an attribute associated with extrinsic toughening that takes place in the wake of the crack, and thus is responsible for R - curve. On the contrary, microstructural damage mechanisms in the cohesive zone and in bounded material are responsible for crack initiation which can be attributed to intrinsic toughening. Intrinsic toughening is dependent upon material properties and independent of the length of the crack or geometry of the test specimen (except plane stress/plane strain). This brings into forefront that crack driving force to initiate fracture is a result of dissipation mechanism associated with intrinsic toughening. Under a given set of loading conditions, if overlap length is adopted such that crack tip driving forces required for crack initiation can be kept to a minimum, higher will be load that further needs to be applied to elevate the energy required attain the fracture resistance of the barrier(s) to promote delamination in the unit-cell. This would in-turn raise the toughness associated with the individual unit-cells which would contribute to global toughness of the composite. **Figure 4.4** shows the variation of crack driving force against overlap length for varying pre-crack lengths in the nacreous layer.



**Figure 4.4.** Plot of crack driving force as a function of overlap length in nacre for varying precrack lengths.

As it can be seen from **Figure 4.4**, under the application of a given stress, crack driving force is limited to a minimum value for an overlap length of approximately 1.6-2.5µm. In fact, the crack driving force value corresponding to this overlap length scale range is less than or comparable to the fracture resistance of the biopolymer. Thus it can now be clearly understood as to why nacre adopts 1.69µm as its characteristic overlap length, not only to maximize its load-transfer capability but at the same time provide resistance to crack initiation to the maximum extent possible via minimization of crack driving force.



**Figure 4.5.** Variation of crack driving force against applied stress for overlap length on either end of the characteristic value in the nacreous layer.

In order to better understand the influence of overlap length on the response associated with the unit cells, **Figure 4.5** highlights the effect of stress levels needed to generate appreciable crack driving force for crack initiation corresponding to values of overlap length on either side of the characteristic length in the nacreous layer. Clearly it can be seen that if overlap lengths are smaller than characteristic length, significantly lower stress levels are sufficient to reach crack driving force values to surpass biopolymer fracture resistance (horizontal dotted blue line). Similarly, if the overlap lengths are larger than characteristic length, it does not contribute to any additional property enhancement; it simply increases the weight of the entire bonded unit. That explains the reason behind choice of characteristic length scales by Nature in the nacreous layer. Additionally, at this stage we would like to highlight the fact the stress levels that are needed to be actually applied would be less than those reported above. This can be explained as follows. Energy input to initiate and drive the crack is obtained from the energy that is applied to the system externally. Since linear elastic deformation was a key assumption en route to model development, corresponding stress values are thereby very large. In reality, the same energy is input to the system via elasticplastic deformation (shown in the inset) and thereby stress levels required for crack initiation would be less than those predicted above.



Figure 4.6. Mode mixity parameter as a function of overlap length for varying pre-crack lengths.

As mentioned previously, the unit-cell structure in the nacreous layer of seashells is representative of an adhesive joint and in order to better understand the crack initiation and growth process, it is imperative to extract the crack driving force contributions associated with both mode-I and mode-II, and thus we introduce the mode-mixity parameter. Clearly it can be seen with reference to **Figure 4.6** that the relative magnitude associated with mode-I and mode-I and the overlap length in a premeditated manner. For pure mode-I failure, MMP=0° and for pure mode-II failure, MMP=90°.

With reference to **Figure 4.6**, substantial contributions from mode-II component are likely to ensue crack initiation and subsequent growth via interfacial failure within the unit cell. The inset in **Figure 4.6** shows the strength of the nacreous layer under different loading configurations [**Menig et al., 2000**]. Of all the loading configurations, it can be seen that the nacreous layer is extremely weak under peeling. In order to provide maximum resistance against peeling, choice of overlap length is kept at a characteristic value ( $\equiv 1.6-2.5\mu$ m) in order to promote maximum resistance against peeling and thereby ensuing initiation and propagation via shear within the unit cells.

Existing literature in the experimental work on the nacreous layer associates toughness with significant contribution of inelastic deformations [Barthelat and Espinosa, 2007] and occurrence of 'process zone' [Barthelat and Rabiei, 2011]. Nonetheless, these events are associated with sliding of ceramic bricks in a large region around the vicinity of cracks. The crack trajectory is extremely meandering. Upon the application of external loading, numerous microcracks/voids are generated in all the unit-cells associated with the forward region in the damage zone as shown in **Figure 4.1**. With progressive loading, these micro-voids coalesce together thereby rendering the crack path through the damage zone extremely tortuous. The question posed at this juncture how do these dispersed cracks in the unit-cells join together?



**Figure 4.7.** Variation of crack driving force upon overlap length for varying pre-crack length associated with the primary crack. The figure in the inset identifies the angle ( $\theta$ ) at which crack driving force of the kinked crack attains a maximum value for varying pre-crack length (0.09-1.29µm).

The current problem at hand represents mixed-mode crack propagation. Taking into consideration Griffith's energy theory as the valid criteria which explains crack growth, kinking of the crack will take place and the crack will grow in the direction ( $\theta$ ) along which the elastic

energy release per unit crack extension attains a maximum value. As it can be seen from **Figure 4.7** and **Figure 4.8**, the initiation and propagation of the crack in the unit-cells is primarily shear dominated throughout a majority of the overlap length. As the overlap length narrows down appreciably, the crack kinks at an angle through the biopolymer at an angle of approximately 75°. This probably accounts for the reason as to why the crack does not run through completely in a given row.



**Figure 4.8.** Variation of crack driving force upon overlap length for varying pre-crack length associated with the primary crack. The figure in the inset identifies the angle ( $\theta$ ) at which crack driving force of the kinked crack attains a maximum value for a pre-crack length of 1.49 µm.

By the time crack driving force attains a value which is comparable to the fracture resistance associated with the mineral or tablet, it has almost reached the very edge of the joint. The sharp kinking angle thereby is responsible for connecting associated cracks in unit-cells of other columns, and thereby rendering the overall trajectory extremely tortuous as shown in **Figure 4.9**.



**Figure 4.9**. (a) Schematic of staggered architecture of calcium carbonate bricks (shown in green) in biopolymer matrix (shown in yellow); (b) expanded view of the unit cell structure (with plane strain infinitesimal deformation) highlighting the elemental blocks and the original overlap length (L<sub>0</sub>); (c) crack trajectory through the overlap length and kinking of the crack from one unit cell to another.

The current analytical model is only an approximate model for the nanocomposite structure. It should be noted that crack propagation process is inelastic in nature (associated

with molecule bond breaking process); however in a simplified manner, growth of bondline crack can be perceived as alteration of geometry associated with the overlap to account for changes in the load path and thereby, this approach was followed to get a preliminary understanding of the crack propagation process.

Under static loading conditions, characteristic lengths predicted were essentially based on (a) stress transfer point of view,  $L^* = \sqrt{\frac{2Ebh}{G}}$ , as was postulated by **Chen et al., 2009** and, (b) maximizing elastic strain energy density,  $L^* = 2.318\sqrt{\frac{Ebh}{G}}$ , as postulated by **Wei et al., 2012.** Similarly under dynamic rates of loading, characteristic length was predicted based on maximum shear transfer efficiency point of view,  $L_{optimal} \equiv Minimize[\tau(x,t)]_L$ , as was postulated by **Dutta et al., 2013.** In this article, we have shown using fracture mechanics concepts (under quasi-static rates of loading) that characteristic length exists in the nacreous layer in seashells which is based upon the existence of upper and lower bounds as given by equation (4.57) below:

$$L_{characteristic} (\equiv CDF_{min}) \leq L_{optimal} \leq L_{characteristic} (\equiv \tau_{min})$$
(4.57)

Too far a deviation of optimal length on the right hand bound of equation (57) would provide no additional structural property enhancement, but would only add to weight of the adhesively bonded unit. Similarly, too far a deviation of optimal length on the left hand bound of equation (4.57) might produce a further light weight design; however, it would at the same time reduce the load withstanding capability rendering it more prone to fracture via increasing crack driving force ahead of the crack tip and simultaneously raising the shear stress in adhesive beyond its allowable limit/strength. Thus, the optimal length scale criterion, as given by equation (4.57), serves as an important design guideline in the not only in synthesizing adhesively-bonded structures but staggered architecture composites which would not only be light-weight but tough as well. In order to validate our claim, in the subsequent paragraphs we illustrate the unanimity that exists between our model predictions against previously published experimental data followed by additional illustrative example.

#### **4.3.1.** Validation by experimental data

Lucic et al., 2006 investigated the existence of optimal overlap length in single lap adhesive bonded joint comprising of *Al99.5* as the adherend material and *Loctite 3421* as the (two-component) structural adhesive. The thickness and width of the adherend was 30 mm and 1.95 mm respectively. The thickness of the adhesive was 0.15 mm. The overlap length was varied from 15 - 60 mm to explore optimal overlap length which corresponds to maximizing the joint strength. Using the same geometrical and material parameters as were used in their investigation, in our current analysis we tried to explore whether our model predictions, as per our design criterion as given by equation (4.57), gave similar results against their experimental observations. As it can be seen from **Figure 4.10**, optimal length scale predicted by the model lies in the range of 30-35 mm.



**Figure 4.10.** Existence of optimal length scale, as predicted by the analytical model, for an *Al99.5-Loctite 3421* single lap adhesive bonded joint.

Optimal length observed experimentally by Lucic et al., 2006 lie in the range of 35-50 mm and thus, model predictions are in reasonable agreement with previously reported experimental data and thus, justifies the efficacy of our proposed design guideline. Note that, the unit for change in shear stress and CDF in Figure 4.10 and Figure 4.11 is MPa and J/m<sup>2</sup> respectively.

## **4.3.2.** An illustrative example

Consider the adherend material in single-lap adhesive joint to be made of plain weave S2-glass/SC-15 epoxy laminate (Deka et al., 2007: E1=24.85 GPa, E2=24.85 GPa, E3=11.04 GPa, G<sub>12</sub>=2.67 GPa, G<sub>13</sub>=1.97 GPa, G<sub>23</sub>=1.97 GPa, v<sub>12</sub>=0.11, v<sub>13</sub>=0.18, v<sub>23</sub>=0.18) and adhesive to be SC-15 epoxy resin (Applied Poleramic Inc.: E<sub>p</sub>=2.00 GPa, G<sub>a</sub>=1.40 GPa, v<sub>a</sub>=0.35). Fracture toughness of cured SC-15 epoxy resin, S2-glass/SC-15 epoxy laminate for initiation and propagation are 0.989 kJ/m<sup>2</sup>, 0.688 kJ/m<sup>2</sup> and 1.104 kJ/m<sup>2</sup> respectively. Figure 4.11 shows the variation of optimal overlap lengths for varying widths of adherend (10 mm, 40 mm and 100 mm) and adhesive thickness (0.50 mm, 1.00 mm, 2.00 mm, 3.00 mm and 5.00 mm) where the hollow and solid circles are representative of characteristic length with respect to minimization of crack driving force, as shown in Figure 4.11(a,c,e), and shear stress, as shown in Figure 4.11(b,d,f) respectively. With increasing adhesive thickness, crack driving force increases, interfacial shear stress decreases and bounds of characteristic overlap length shift toward higher numbers.



**Figure 4.11.** Existence of optimal overlap lengths for varying widths of composite adherend (10 mm, 40 mm and 100 mm) and adhesive thickness (0.50 mm, 1.00 mm, 2.00 mm, 3.00 mm and

#### Figure 4.11. (cont'd)

5.00 mm). The hollow and solid circles are representative of characteristic length with respect to minimization of crack driving force (a,c,e) and shear stress (b,d,f) respectively.

Clearly, optimal overlap lengths exists in adhesively bonded structures which are governed by characteristic overlap length as given by equation (57). Note that in **Figure 4.11**, the hollow and solid circles are representative of characteristic length with respect to minimization of crack driving force and shear stress respectively. Thus under quasi-static loading conditions, choice of characteristic overlap length ensures optimal combinations both from the perspective of weight reduction, maximum interfacial shear resistance, resistance to crack initiation, and consequently superior toughness. In our current investigation, nacre has been chosen as the structural biological composite for illustrative purposes. Feature drawn from current analysis can be adapted as an important guideline for designing adhesive bonded structures and staggered architecture materials at any level of scale. The outcome of the current research will thereby provide beneficial guidelines in designing hybrid bio-inspired protective composite materials [**Dutta et al., 2012**].

### 4.4. Conclusions

In our current investigation, we showed the influence of structural overlap length on minimizing delamination in the unit-cells to the maximum extent possible via development of an analytical model. The main outcome of the developed analytical model was to provide a simplified expression for crack driving force in terms of local finite stress concentrations in the biopolymer layer of nacre. Based on the above analysis, we have attempted to address that the 'well-made' structure of the nacreous layer is built with respect to two bounds: a lower-bound based on an energy criteria (to allay crack-initiation) and an upper-bound based on stress criterion (to improve load-transfer/shear-transfer efficiency). Excerpts drawn from the current study would provide beneficial guidelines in designing light-weight and tough adhesively bonded structures and staggered architecture composites. REFERENCES

#### REFERENCES

**Barthelat, F., Li, C.-M., Comi, C., Espinosa, H.D. 2006.** Mechanical properties of nacre constituents and their impact on mechanical performance. *J. Mater. Res.* **21**(8), 1977-1986.

**Barthelat, F., Espinosa, H.D., 2007.** An Experimental Investigation of Deformation and Fracture of Nacre-Mother of Pearl. *Exp. Mech.* **47**, 311–324.

Barthelat, F., Tang, H., Zavattieri, P., Li, C.M., Espinosa, H., 2007. On the Mechanics of Mother-of-Pearl: A Key Feature in the Material Hierarchical Structure. *J. Mech. Phys. Solids* 55, 306-337.

Barthelat. F., Rabiei, R., 2011. Toughness amplification in natural composites. J. Mech. Phys. Solids 59, 829-840.

Chen, B., Wu, P.D., Gao, H., 2009. A characteristic length for stress transfer in the nanostructure of biological composites. *Compos. Sci. Technol.* 69, 1160-1164.

de Gennes, P.G., Okumura, K., 2000. On the toughness of biocomposites. C. R. Acad. Sci. Paris, t.1, Ser. IV, 257-261.

**Deka, L.J., Bartus, S.D., Vaidya, U.K., 2007.** Numerical modeling of simultaneous and sequential multi-site impact response of S-2 glass/epoxy composite laminates. In: Proceedings of Composites and Polycon. American Composites Manufacturers Association, Tampa, Florida USA, October 17-19.

**Dutta, A., Vanderklok, A., Tekalur, S.A., 2012.** High strain rate mechanical behavior of seashell-mimetic composites: Analytical model formulation & validation, *Mech. Mater.* **55**, 102-111.

**Dutta, A., Tekalur, S.A., Miklavcic, M., 2013.** Optimal length scales in staggered architecture composites under dynamic loading conditions, *J. Mech. Phys. Solids* **61**(1), 145-160.

Evans, A., Suo, Z., Wang, R., Aksay, I., He, M., Hutchinson, J., 2001. Model for the Robust Mechanical Behavior of Nacre. *J. Mater. Res.* **16**, 2475-2484.

**Espinosa, H.D., Juster, A.L., Latourte, F.J., Loh, O.Y., Gregoire, D., Zavattieri, P.D., 2011.** Tablet-Level Origin of Toughening in Abalone Shells and Translation to Synthetic Composite Materials. *Nature Comm.* **2**, 173. Gao, H., Ji, B., Jäger, I., Arzt, E., Fratzl, P., 2003. Materials Become Insensitive to Flaws at Nanoscale: Lessons from Nature. *Proc. Natl. Acad. Sci. U.S.A.* 100, 5597-5600.

Huang, Z., Li, H., Pan, Z., Wei, Q., Chao, Y.J., Li, X., 2011. Uncovering high-strain rate protection mechanism in nacre. *Sci. Rep.* **1**, 148; DOI:10.1038/srep00148.

Jackson, A.P., Vincent, J.F.V., Turner, R.M., 1988. The mechanical design of nacre. P. R. Soc. London B. 234, 415–440.

Jager, I., Fratzl, P., 2000. Mineralized collagen Fibrils: a mechanical model with a staggered arrangement of mineral particles. *Biophys. J.* **79**, 1737–1746.

**Kessler, H., Ballarini, R., Mullen, R.L., Kuhn, L.T., Heuer, A.H., 1996.** A biomimetic example of brittle toughening: (I) steady state multiple cracking. *Comp Mater Sci.* **5**, 157–166.

Kamat, S., Su, X., Ballarini, R., Heuer, A.H., 2000. Structural basis for the fracture toughness of the shell of the conch Strombus gigas. *Nature*, 405, 1036–1040.

Kotha, S.P., Kotha, S., Guzelsu, N., 2000. A shear-lag model to account for interaction effects between inclusions in composites reinforced with rectangular platelets. *Compos. Sci. Technol.* 60, 2147–2158.

Katti, K.S., Katti, D.R., Pradhan, S.M., Bhosle, A., 2005. Platelet interlocks are the key to toughness and strength in nacre. *J. Mater. Res.* 20, 1097-1110.

Luo, Q., Tong, L., 2004. Linear and higher order displacement theories for adhesively bonded lap joints. *Int. J. Solids Struct.* **41**(22-23), 6351-6381.

Launey, M.E., Ritchie, R.O. 2009. On the fracture toughness of advanced materials. *Adv. Mater.* 21, 2103-2110.

Liu, G., Ji, B.H., Hwang, K.C., Khoo, B.C., 2011. Analytical solutions of the displacement and stress fields of the nanocomposite structure of biological materials. *Compos. Sci. Technol.* 71, 1190-1195.

Menig, R., Meyers, M.H., Meyers, M.A., Vecchio, K.S., 2000. Quasi-static and dynamic mechanical response of Haliotis rufescens (abalone) shells. *Acta Mater.* **48**, 2383–2398.

Meyers, M., Lin, A., Chen, P., Muyco, J., 2008. Mechanical Strength of Abalone Nacre: Role of the Soft Organic Layer. *J. Mech. Behav. Biomed. Mater.* **1**, 76-85.

**Okumura, K., de Gennes, P.-G., 2001.** Why is nacre strong? : Elastic theory and fracture mechanics for biocomposites with stratified structures. *Eur. Phys. J. E* **4**, 121-127.

Sarikaya, M., Gunnison, K.E., Yasrebi, M., Aksay, J.A., 1990. Mechanical property-microstructural relationships in abalone shell. *Mater. Res. Soc.* 174, 109-116.

**Song, F., Soh, A., Bai, Y., 2003.** Structural and mechanical properties of the organic matrix layers of nacre. *Biomaterials* **24**, 3623-3631.

Shuchun, Z., Yueguang, W., 2007. Effective elastic modulus of bone-like hierarchical materials. *Acta Mech. Solida Sin.* 20, 198-205.

Wang, R., Suo, Z., Evans, A., Yao, N., Aksay, I., 2001. Deformation mechanisms in nacre. J. Mater. Res. 16, 2485-2493.

Wei, X., Naraghi, M., Espinosa, H.D., 2012. Optimal length scales emerging from shear load transfer in natural materials: application to carbon-based nanocomposite design. ACS Nano 6(3), 2333-2344.

Xu, Z.-H., Yang, Y., Huang, Z., Li, X. 2011. Elastic modulus of biopolymer matrix in nacre measured using coupled atomic force microscopy bending and inverse finite element techniques. *Mat. Sci. Eng. C* **31**(8), 1852-1856.

**Yang, C., Chadegani, A., Tomblin, J.S., 2008.** Strain energy release rate determination of prescribed cracks in adhesively-bonded single-lap composite joints with thick bondlines. *Composites Part B: Engineering* **39**(5), 863-873.

Zhang, Z.Q., Liu, B., Huang, Y., Hwang, K.C., Gao, H., 2010. Mechanical properties of unidirectional nanocomposites with non-uniformly/randomly staggered platelet distribution. *J. Mech. Phys. Solids* **58**, 1646-1660.

Zhang, Z., Zhang, Y.-W, Gao, H., 2011. On optimal hierarchy of load-bearing biological materials. *Proc. R. Soc. B*, 278, 519-525.

# **CHAPTER 5: CONCLUSIONS**

## 5.1. Design Guideline

In the current study, an attempt was made to understand the mechano-biological principles existing in structural biological composites in Nature exhibiting staggered architecture. As mentioned previously, Nature optimizes stiffness, strength and toughness by fine tuning the ceramic content and aspect ratio of ceramic platelets.



**Figure 5**. Design guideline for synthetic composite showing the interplay of optimization scheme and manufacturing technique.

If the same strategy were to be applied to synthetic composite design, choice of participating materials and manufacturing technique need to go hand-in-hand so that an optimized performance can be attainable in synthetic composites. **Figure 5** shows the design guideline that can be adopted from the current study with the help of an associated example. Assuming that epoxy matrix, reinforcement material, starting particle size and volume fraction are known (fixed) beforehand, based on structural property enhancement desired, different optimized aspect ratios exist based on either stiffness, load-transfer and toughness via maximization of Young's modulus, minimization of maximum shear stress and minimization of crack driving force respectively. Based on a judicial choice of aspect ratio, the manufacturing technique (in the current case, freeze casting) technique can be adjusted accordingly to vary the cooling rate and/or freezing time to regulate the aspect ratio in the final composites and thereby, obtain optimized performance.

#### **5.2.** Future Scope of Work

Optimization scheme with respect to toughness carried in the current study addressed it from a quasi-static point of view. As a extension of the current work, it would be opportune to unravel the corresponding parameter and associated criterion for toughness optimization under dynamic rates of loading. In the current study, the ceramic material was same throughout and had the same thickness. As a future work, it would be interesting to investigate material response and establish a design criterion for gradient architecture (dissimilar materials and/or dissimilar thickness) materials. The manufacturing technique needs to be tuned accordingly to custom-design manufacture functional gradient architecture materials.