

# Exploring the Significance of Structural Hierarchy in Material Systems - A review

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## **Abstract**

Structural hierarchy and heterogeneity are inherent features in biological materials, but their significance in affecting the system behaviors is yet to be fully understood. In Section 1, this article first identifies the major characteristics that manifest, or are resulted from, such hierarchy and heterogeneity in materials. Then in Section 2, it presents several typical natural material systems including wood, bone and others from animals to illustrate the proposed views. The paper also discusses a man-made smart material, textiles, to demonstrate that textiles are hierarchal, multifunctional, highly complex and arguably the engineered material closest on a par with biological materials in complexity, and more importantly we can still learn quite a few new things from them in development of novel materials.

In Section 3, the paper summarizes several general approaches in developing a hierarchal material system at various scales, including structure thinning and splitting, laminating and layering, spatial and angular orientation, heterogenization and hybridization, and analyzes the advantages associated with them. It also stresses the adverse consequences once the existing structural hierarchy breaks down due to various mutations in biological systems. It discusses in particular the influences of moisture and air on material properties, given the near ubiquitousness of both air and water in materials.

It next deals with in Section 4 some theoretical issues in material research including packing and ordering, the bi-modular mechanics, the behavior non-affinities due to disparity in hierarchal levels, the importance of system dimensionality in a hierarchal material system, and more philosophically, the issues of Nature's wisdom versus Intelligent Design. Section 5 then offers some concluding remarks, including a recap of the major issues covered in this article, and some general conclusions derived from the analyses and discussions.

The main purpose of this paper is to make an effort to explore, identify, derive or theorize some generic principles based on the existing results, *not to offer another comprehensive review of current research activities in the fields for that there already exist some excellent ones*. This paper examines the related topics with several approaches to not only reveal the underlying geometrical and physical mechanisms, but also to emphasize the ways in which such mechanisms may be applied to developing engineered material systems with novel properties.

**Keywords:** Structural hierarchy; Heterogeneity; Material properties; Behavior non-affinities; System dimensionality.

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## I. INTRODUCTION

### A. Overview

Materials Science covers sizes over macro, meso, nano/molecular and atomic levels, and has branched from chemistry, physics into biology, thus turning increasingly into a multi-disciplinary research field<sup>1</sup>. Its focuses have grown over the years to embrace metals, inorganic, organic (and their mixtures or composites), and natural biological materials<sup>1</sup>. Although molecular biologists, material physicists, and polymer engineers are taking different approaches to the development of new materials with controlled properties<sup>2</sup>, there is an increasing understanding and shared appreciation of the significance of material morphological/topological structures, and the hierarchy organized at various scale levels: a partial list of major books and review articles on this topic includes<sup>1,3-12</sup>.

The term *hierarchy* is defined (*New Oxford American Dictionary*, 3<sup>rd</sup> ed. 2010) as “an arrangement or classification of things according to relative importance or inclusiveness”, whereas our worlds, both natural and social, are structured or arranged in a hierarchal format. For human society, such man-made hierarchies have evolved to be, presumably, beneficial to facilitating communication and management. However, for natural systems, such as a tree, a polymer gel, or a vascular system in a biological body, the significance or usefulness of a branched conformation is not always as obvious and has therefore attracted extensive research interests<sup>3,11,13-17</sup>.

It should be noted hereafter that researches on hierarchy and heterogeneity in material systems have been spectacularly escalating in recent years, mainly because of the huge interests in biological and nanoscale materials. The areas involved and the advances progressed span over such a tremendous range that it is difficult, if not impossible, for one review like this to cover and keep update with all the important findings and emerging topics. It should in fact be an on-going process and the main purpose of this paper is to make an effort to explore, identify, derive or theorize some of the generic principles embedded in the existing results, *not to offer another comprehensive review of current research activities in the fields for that there already exist some excellent ones as cited herein*. This paper examines the related topics with several approaches to not only reveal the underlying geometrical and physical mechanisms, but also emphasize the ways in which such mechanisms may be applied to developing engineered material systems with novel properties.

### B. Basic manifestations of system hierarchy

Hierarchy in a material system is reflected by several characteristics. The first lies in the form of multiscale, i.e., the system consists of different structural levels with gradual transition in sizes between them, and conversely the system behaviors can be controlled at length scales ranging from macro, meso, nano, to molecular levels. In that sense, hierarchy is always accompanied by this multi-scality.

Further, this multiscale frequently if not always brings in multiple phases (or heterogeneity) into the system where each phase occupies a structure level so as to distinguish one from another. It is thus assumed self-evident the term “phase” is used here more generally as representing a structural unit distinctive from its neighbors in any chemical, physical or geometrical attributes. It is obvious that this heterogenization will fundamentally change the overall properties of a material formed by the same substance but with such a multiphase

hierarchical structure. Particularly in all surface and interfacial phenomena, heterogeneities of the surfaces play even more dominant role that is only partially understood<sup>18, 19</sup>.

It may be added that as multiphase destroys system homogeneity, structural hierarchy often brings directionality into a system to render it anisotropic. Given the fact that many important mathematical laws and tools in material sciences assume a homogeneous and isotropic system, caution has to be taken when applying an existing theory to tackle a new material system. In fact, the influences of hierarchy permeate into various aspects of material properties and many supposedly intrinsic properties like the thermal and electric conductivities, elastic moduli and dielectric permittivity are actually functions of structural characteristics such as system dimensions, component shape, scale, orientation and interactions<sup>17, 20-25</sup>.

We will in this paper examine how such hierarchical, multi-scaled, heterogenized or multi-phased structures are advantageous or useful, by accounting for the associated unique functionalities in many materials systems. We will use mostly the biological natural materials, as well as some man-made hierarchical materials, as cases for studying so as to reveal or illustrate the principles underlying the observations.

Study of biological systems as structures dates back to the early part of the 20<sup>th</sup> century. The classic representative work on this subject by D'Arcy W. Thompson<sup>26</sup> was first published in 1917. The structure–function relationship has been one of the fundamental issues in biology<sup>14</sup> where, implicitly or explicitly, structural hierarchies have been extensively investigated and are believed to account for various unique attributes observed. As a well known example, geckos use fibrous adhesive on their feet to acquire superior surface attachment without losing their movement agility<sup>27-35</sup>. It was reported that the unique macroscopic orientation and preloading of gecko foot-hair increased the attachment force 600-fold above that of normal friction of the material<sup>28</sup>. Furthermore, in studying biological gels, Miyazaki et al reported that one of the reasons why synthetic polymer gels are deficient in mechanical toughness and quick responses is due to the fact that they “have no particular ordered structure at the molecular level,” whereas the “biological gels have an ordered aggregate state, which imparts living organisms sufficient mechanical toughness and smart functions<sup>36</sup>.” Fratzl and Weinkamer have reviewed some hierarchical biological structures and related their exceptional mechanical properties to a “functional adaptation of the structure at all levels of hierarchy”<sup>6</sup>.

In other words, one major advantage of hierarchical structuring is that a material can be made multifunctional and that a specific material property, such as fracture toughness, can be tuned, independent of other properties, by optimization at different size levels<sup>8</sup>. By combining this degrees of freedom of hierarchical structuring (inspired by biology) with the variety of materials offered by engineering, there is a huge potential to acquire new or unusual combinations of material functions/properties by structuring a given material, rather than changing its chemical composition<sup>37</sup>. This is a challenging yet potentially highly rewarding research topic<sup>8, 38</sup>.

### **C. System hierarchy and more properties**

We first present here briefly a few reported examples on the benefits associated with structural hierarchy, in either enhancing material performance or rendering new functionalities.

Starting from mechanical properties, impact of scale, heterogeneity or hierarchy on material strength has been the essential focus of fracture mechanics, where structural irregularities have

been established as the main cause for material failure. Lakes<sup>3</sup> studying material hierarchy, used the relative density  $\rho/\rho_o$  to reflect the structure efficiency ( $\rho$  the system bulk density and  $\rho_o$  the density of the material forming the system), for which the Eiffel Tower is  $1.2 \times 10^{-3}$  versus  $5.7 \times 10^{-3}$  for the late World Trade Center. This ratio (or the more commonly used volume fraction) has been widely used in characterizing multi-phased porous material systems. The fact that  $\rho/\rho_o \leq 1$  implied the fact that very often, like in these two cases, air makes up the additional volume in the structure. (*Actually the critical contribution of air residing in a material structure is often ignored or grossly underappreciated, as will be elucidated later in the present paper.*) Lakes also discussed the hierarchies existed in polymers, fibrous composites, biological materials and inorganic crystalline materials, and pointed out that the distributed interfaces and finer structural features give rise to desirable properties such as stress attenuation and damping, viscoelasticity, super-plasticity, increased toughness (fracture resistance) and other benefits. He also demonstrated that for honeycomb and foam systems, both specific strength  $\sigma_u/\rho$  and stiffness  $E/\rho$  increase with the system hierarchical order (number of hierarchical levels).<sup>3</sup>

Such explorations of influences due to hierarchy have also taken place in research on other material properties. For instance, surface hierarchy and morphologies are found responsible for super-hydrophobicity<sup>39-42</sup> and self cleaning – the lotus leaf effect<sup>43-49</sup>. Structural photonics employs differential structural scales or hierarchies to generate color without resorting to chemical dyeing<sup>50-61</sup>.

In addition, although the properties of nanomaterials are often superior to those of bulk materials, translating these advantages to macroscopic scales remains a challenge, for we are still in the process learning how to connect the disparate scales to form a macro system while maintaining their superior qualities found at the nanoscale<sup>62-66</sup>. At nanoscale, structural hierarchy and heterogeneity are reported<sup>67-70</sup> to be responsible for the improved elasticity, strength and fracture toughness of bones. Pereira et al<sup>71</sup> have demonstrated that geometrical and deformational surface topology of a graphene sheet significantly alter its mechanical and electronic properties. Nanoscale hierarchy is also found to control the stiffness, strength and mechanical toughness of silk<sup>31, 62, 72-75</sup>. So understanding of nanoscale structural hierarchies in natural biological materials is vital to shed light on the secret of their unique functionalities so that we can learn how to achieve the functionalities at larger scales<sup>70, 76-78</sup>.

Hierarchical *molecular* assembly has also drawn growing interest in recent years because of the possibility of fabricating highly ordered functional superstructures from the elemental building units. The multilevel assembling process is initiated by assembly of elemental units into clusters via chemical and physical bonding. Subsequently, these molecular clusters become the building blocks to form more complicated assembling structures<sup>79-81</sup>.

The importance of structure on material performance is probably best highlighted in the emerging metamaterials which are defined as materials that acquire their unique properties, nonexistent in nature, not through chemical modification but through structural scale and shape alternations<sup>82-85</sup>. In addition, the functionally graded materials are man-made systems with hierarchical structure as well<sup>86-88</sup>.

Accumulated research on hierarchal structure in material systems has led to a few general theoretical schemes, including the self-assembly theories<sup>89-91</sup>, and the fractal theories<sup>92, 93</sup>. Some

also explored certain underlying invariants in these systems in terms of allometric scaling laws<sup>94, 95</sup> to search for possible shared common features in biological materials at various structural scales. For instance, based on existing work on diverse structural systems, West et al<sup>94, 96</sup> proposed a few allometric scaling relations, including the 3/4 power law for metabolic rates derived from a general model. They believe that these laws are characteristic of all organisms and show how the essential materials are transported through space-filling fractal networks of branching tubes, as displayed in Figure 1<sup>94, 96</sup>. They also expanded their scaling laws to forests<sup>97</sup> and even human societies<sup>98</sup>.

(Fig. 1)

Still no general frame has been established for biomimetics, although some other theoretical attempts have been reported<sup>99-104</sup>. Pugno and colleagues<sup>105, 106</sup> developed mathematical models, force- or energy-based, for the design of nanoscale bio-inspired hierarchical materials, considering strong or weak interfaces, leading to formulas describing the dependence of strength, toughness and stiffness on the system scale. Gao and co-workers also proposed a theoretical model for a hierarchically built bone structure loaded in tension to calculate the mechanical properties at each level of hierarchy. The predicted strength values compared well with real biomaterials up to 5 hierarchical levels, yet the elastic modulus was overestimated at the third hierarchical level<sup>68, 69, 107</sup>. Wang et al<sup>108</sup> proposed a theoretical method based on the steady-state non-Fourier heat conduction principle to predict the effective thermal conductivities of materials over different scales down to nanosystems.

#### **D. About this review article**

As stated above, this article is another attempt to explore the advantages or added functionalities attributable to system hierarchy in a more systematic and explicit way, by analyzing the existing research results and grouping them into logical categories so as to establish some general rules for future researchers to build on. This paper examines these related topics from several different angles to not only reveal the underlying geometrical and physical mechanisms, but also to emphasize the ways in which such mechanisms may be applied to developing engineered material systems with novel properties.

We have used in this paper many examples from biological systems, polymers, fiber and composite material research fields mainly because of the long standing emphasis on phenomena associated with structural hierarchy in these areas. We even devoted one subsection to examine textiles from a materials science point of view, showing that textile materials are hierarchal, multifunctional by human design and yet comparable to biological materials in structural complexity. More importantly we can still learn quite a few things from textiles in development of advanced smart materials. We also include a subsection to discuss the limitations in biomimicry, and to caution about the differences between Nature's selection and evolution and the Intelligent Design.

Some guidance followed in writing this review article:

1. As stressed before, the main objective of this review article is to make an effort to induce or deduce or theorize some generic principles based on the existing results so as to push forward the studies, not to offer another comprehensive review of current research activities in the fields for that there already exist some excellent ones, for instance<sup>1, 3-10</sup>;
2. To focus on the targeted topics, even though there may be various improved forms of the original theory, for brevity we only use the one sophisticated enough, not necessarily the

most updated/accurate, to illustrate our point;

3. The division of sections in this paper is more or less arbitrary with main consideration of clearer organization and logical presentation of the contents. Cross-referencing is used occasionally when related subjects are discussed at different places, and as a result, certain degree of overlapping and repetition may be inevitable – as long as they don't appear to block the flow and become bothersome to the readers.

Structure-wise, this article is divided into five sections. The *first* section (Introduction) lies down some general descriptions about hierarchy in materials systems over various scales and the related major directions of research. The *second* section uses examples from typical materials groups to demonstrate the importance of structural hierarchy in both natural and man made systems. Based on those examples and practical cases, we have derived in section *three* several general rules with the potential to be applied in developing new materials. Then in section *four* we identify some theoretical issues that are critical in our understanding of materials behaviors and are not yet completely resolved. In the *final* section, we summarize the major topics dealt with in this article and highlight the conclusions with their practical significance.

## II. EXAMPLES OF STRUCTURAL HIERARCHY IN TYPICAL MATERIALS SYSTEMS

### A. Natural biological materials

Hierarchy is one of the basic attributes of biological materials whose shape, structure, and functions are primarily the results of highly complex interactions between its constituents at different scales and the environment during their growth and lifetime. “At a small scale, intermolecular forces are sufficient to convert the amino acid sequence of a protein into a shape, and these forces are probably sufficient to account for the structure of biological materials into the micrometer scale. Above this size, a major organizing principle is represented by liquid crystalline structure, which occurs in a wide range of systems in going from 1 to 500  $\mu\text{m}$  or more. Broadly speaking, in biological structures, there is a level of hierarchy at every order of magnitude in size”<sup>4</sup>.

As noticed in several papers, in biological materials, the hierarchical structural organization is inherent to the design, and the materials and design are intimately connected and inseparable. A further defining characteristic of biological systems is that they are “grown”, rather than “made”<sup>109</sup>. This is a direct result of self-assembly and has a profound effect on their formation, since biological systems can undergo structural adjustments as the loads change. For example, a bone will adjust the mass deposition in regions where the stresses are highest. The same happens in the growth of trees, and the trunk and branches will thicken where the stresses are highest. This feature is called “adaptive mechanical design”<sup>1</sup>.

This has not been the case in man-made materials. In our engineering practice, there is often a “disciplinary separation between materials (materials engineers) and structures (mechanical engineers)”<sup>1</sup>: using commercialized standard parts and assembling them into a functional material system is all dictated from a pre-designed blue print. We have produced many *synthetic* polymers, but none of them is as versatile or responsive as the two *biological* polymers, protein and polysaccharide<sup>1, 110</sup>. In our current technology, hierarchy mostly occurs by accident and is rarely designed into a structure, with an exception perhaps in textile materials. Also unlike in synthetic structural materials, the chemical compositions for natural materials are highly limited to surprisingly few chemical elements<sup>1, 110</sup>: the near complete absence of metals in forming natural materials may be responsible for their low density and easy formation at benign natural conditions.

Furthermore, natural materials rarely exist in pure form, i.e., they are more or less composite materials. Neville has even suggested treating biological materials as fibrous composite materials, “Fibrous composites occur in all skeletal systems, including plant cell walls, insect cuticles, moth eggshells, bone, and cornea. They function like industrial fiberglass, with fibers set in a matrix. The fibrous molecules are long, extracellular, and water insoluble, and to be effective they must be orientated strategically”, and “... the fibers are oriented by self-assembly just outside the cells during a mobile liquid crystalline phase prior to stabilization”<sup>4</sup>.

As mentioned before, multi-functionality is another particular characteristic of biological materials. The basis for achieving this attribute is usually a complex hierarchical architecture in which an adaptation to the function(s) is possible at different structural levels<sup>110</sup>. If function follows structure<sup>26</sup>, then a multitude of functions is possible by varying the structure of a composite with similar constituents. A consequence is the adaptivity of natural composites. Bone, for example, may have a wide range of (anisotropic) mechanical properties, following



different needs in the skull, the vertebra, or the femur<sup>111</sup>. Another example is wood, for each individual tree can tune the mechanical properties to a particular need, e.g., side winds by adaptive growth<sup>13</sup>. These aspects of multi-functionality, structural adaptation, and hierarchy are of particular interest for biomimetic materials research<sup>103, 112</sup>.

Wegst and Ashby<sup>113</sup> have classified biological materials into four groups:

- Ceramics and ceramic composites: biological materials where the mineral component is dominant, such as in shells, teeth, bones, diatoms, and spicules of sponges;
- Biopolymer and biopolymer composites: examples of these include the hooves of mammals, ligaments and tendons, silk, and arthropod exoskeletons;
- Elastomers: biological materials that can undergo large stretches (or strains). The skin, muscle, blood vessels, soft tissues in body, and the individual cells fall under this category;
- Cellular materials: the light weight materials prevalent in feathers, beak interior, cancellous bone, and wood.

Yet increasingly, another non-solid group, including gel<sup>36, 114, 115</sup>, wax<sup>14</sup>, glue<sup>116, 117</sup> and surface coatings<sup>118, 119</sup> should be added into the list.

Arzt<sup>120</sup> on the other hand has characterized the unique features of biological materials into five components: self assembly, ambient temperature and pressure processing, multi – functionality, structural hierarchy and self-healing/evolution/environmental effects. These are further specified by Tirrell<sup>5</sup> and are quoted below:

- Recurrent use of molecular constituents (e.g. collagen), such that widely variable properties are attained from apparently similar elementary units;
- Controlled orientation of structural elements;
- Durable interfaces between hard and soft materials;
- Sensitivity to—and critical dependence on—the presence of water;
- Properties that vary in response to performance requirements;
- Fatigue resistance and resiliency;
- Controlled and often complex shapes; and
- Capacity for self-repair.

We selected several examples from biological systems in this section and briefly review them to facilitate our analysis and discussion.

#### *a. Wood*

Figure 2 shows the hierarchical scale and complexity of wood<sup>5</sup>, with two significant characteristics: concentric layers and the cellular fibrils at helix angle.

(Fig. 2)

Wood is typically composed of cellulose fibrils embedded in an amorphous matrix of hemicellulose, lignin and other compounds. It is clearly visible from the figure that the cellulose fibrils follow a right-handed helix, and the angle has a major influence on the mechanical properties and can adjust locally to reflect some seasonal variations in plant growth<sup>121, 122</sup>. Such construction occurs in concentric growth layers to form the main composite structure. With the possibilities given by the hierarchical structure, a growing tree can include graded

properties into the stem or the branch, according to functional requirements which may change during its lifetime <sup>4</sup>.

The most remarkable property of wood is its fracture toughness that is 10 times greater than would be predicted from the fibers and matrix and their volume fractions in the fibrous composites <sup>5</sup>. “The cellulose fibrils made of high-modulus, high-strength, crystalline polysaccharide carry most of the load practically without deformation, while almost all of the deformation takes place by shearing of the hemicellulose/lignin matrix <sup>5</sup>”. More specifically, the main mechanism accounting for the high fracture toughness in wood is that the interfibrillar cracks due to shearing will open and propagate longitudinally while the cylindrical wall collapses inward, which allows each cell wall to be pulled apart without being broken into two <sup>123</sup>.

Meanwhile adjusting the bonding strength between the fibrils and the matrix alters the relative proportion between toughness and stiffness <sup>124</sup> and gluing of fibrils allows a tuning of the mechanical properties of the composite <sup>124</sup>. The data of Kohler and Spatz <sup>125</sup> and Keckes et al. <sup>126</sup> indicate that it is most likely that the hemicelluloses act as the glue between cellulose fibrils and allow deformation by shear <sup>124</sup>.

*b. Bone and others from animals*

(Fig. 3)

Bone too, as illustrated in Fig. 3 <sup>1</sup>, is a hierarchically structured material consisting of platelike nanoparticles of hydroxyapatite embedded within a proteinaceous matrix of collagen, some noncollagenous proteins, and water <sup>6 111 127 128</sup>. That is, at the lower levels of hierarchy, bone is already a composite of collagen and mineral nanoparticles made of carbonated hydroxyapatite. Collagens are tough but not very stiff. Mineral, on the contrary, is stiff but not very tough, and is considered to dominate the stiffness of bone <sup>111</sup>. The toughness of the system is thought to arise mainly from the hierarchical structure of bone and the numerous associated interfaces, imparting the ability to dissipate deformation energy without propagation of the crack <sup>6 127, 129-133</sup>. Different toughening mechanisms have been identified in bone <sup>134</sup>, and its nanoscale heterogeneity leads to markedly different biomechanical properties compared with a uniform material <sup>67</sup>.

It is known that a superior stiffness typically comes at the cost of reduced toughness, as a high elastic modulus implies strong bonds that do not allow for much energy dissipation. The stiffest materials are those based essentially on mineral with little amounts of organic materials, such as sea shells <sup>135</sup>, glass sponges <sup>136</sup>, and tooth enamel <sup>137</sup>, whereas tiny amounts of organic phase are sufficient to increase the toughness of an brittle mineral by factors of more than 1,000 <sup>110, 138</sup>.

In contrast, the beak of the giant squid is a fascinating example of organic-organic composite, that contains no hard substance like minerals and yet has a hardness and stiffness above those of polymeric engineering composites <sup>139</sup>. The beak material is a fiber composite containing approximately 15–20% chitin fibers embedded within a 40–45% histidine- and glycine-rich protein matrix, along with water <sup>140</sup>. This composite has an excellent wear resistance, and the beak tip is very stiff, having a modulus of approximately 5 GPa, ideal for a cutting surface to penetrate foods <sup>140</sup>. Direct contact between the tissues of different moduli would potentially give rise to harmful interfacial stresses, and but in the squid beak, this danger is minimized by the presence of a stiffness gradient of approximately two orders of magnitude from the beak tip to

the base<sup>9, 140</sup>.

Another recent example for a natural composite that uses interfacial architecture to control structural stiffness is the suture found in the carapace of the red-slider turtle<sup>1, 141</sup>. The structure is held together solely through the geometric constraints between the bricks, and this intricate construction allows for a combination of both flexibility at low strains and stiffness at large strains<sup>9, 141</sup>. An additional advantage of such a system is that, even if bricks damaged, the structure remains load bearing. In addition, cracks formed in one brick are not able to propagate, giving rise to a system that has “paradoxically been toughened by fragmentation<sup>9, 141</sup>”.

Given the discussions above, we can identify the main themes known in engineering composite mechanics yet with remarkable sophistication from the natural materials. In biological composites, there exist three indispensable components in a single system, the fibrous phase, the matrix, and the glue phase to collectively form the system. The fibril phase is to provide strength while reducing the system bulkiness, the matrix supports the fibrils while transmitting stress to them: the matrix also imparts compressive and shear stiffness and strengths to the system. The functions of the glue phase are more extensive than appeared – the toughness and strengths of the entire system can be tuned by adjusting the glue bonding strength.

### **B. Revisit of textile materials - man made hierarchal materials**

Textiles are a subgroup of fibrous materials with special purposes, mainly and originally, in providing body protection and decoration for human beings, and are among the first groups of human engineered and industrially manufactured materials. Textiles are hierarchal, multifunctional, and arguably the manmade materials closest on a par with biological materials in terms of structural complexity (Figure 4). It is therefore surprisingly puzzling that the materials are so critically indispensable to us, and yet have been so taken for granted that many rarely pause to think about textiles from a materials science point of view. Textiles in fact remain to be poorly understood in terms of materials sciences vigor, when we can actually learn from them for development of advanced smart materials.

(Fig. 4)

Understandably, we can only provide here a very brief overview of textile materials to facilitate our investigation on structural hierarchy, and for more comprehensive treatment of the subject, we suggest the following works<sup>142-148</sup>. In addition, since we used several examples of textile structures in other sections of this paper, only more general considerations are offered below.

#### *a. Textile as “smart” materials*

It doesn't take a thorough examination to realize that textiles have to satisfy an extensive array of often competing functions to fulfill the clothing purpose:

- Flexibly and pliable to conform to human body, yet with desirable durability under various loading types and intensities for body protection;
- Soft and smooth to touch but resistant enough to abrasion and punctuation;
- Permeable for body perspiration and breath, while with sufficient proof to liquid penetration;
- Biocompatible to human body yet chemically active for dyeing and printing;
- Light weight to reduce wearing burden but rigid enough for body shaping;
- ...

Now there may be a need to (re)examine textiles using a more vigorous materials science scheme. This is partly because textiles have found increasingly expanding and burgeoning applications in areas beyond clothing, such as fiber reinforced composites in engineering applications, and fiber-based products in medical and biological fields. Also, textiles have been considered brilliant results of human biomimicry, likely inspired originally by nature<sup>10</sup>, and hence can serve as examples for developing other bio-inspired materials. Textiles, just like the biological natural materials of plants and animals, can be viewed as fibrous composites if we consider the indispensable air and moisture in textiles as the matrix phase, and a better and deeper understanding of the mechanisms for their versatile multi-functionality can be highly beneficial for research into other novel materials. Another advantage in studying textiles is that unlike most of its counterparts in biomaterials, *textile is made from a human design so that its macro properties allow for alternation or optimization*; which in turn enables them to serve as a potential sample for studying other natural biomaterials, or as tools to validate the theoretical models developed for complex materials.

*b. Making textiles – friction only*

Friction is the *only* mechanism by which textiles are formed, through entangling, twisting or interlacing between the structural elements. In that sense, textile is the most efficient and convenient material to fabricate. In ropes or yarns for example, the friction is brought into play via tension on fibers of helical conformation due to twist as seen in Fig. 5. Galileo<sup>149</sup> was fascinated by the fact that short fibers can form a long and strong rope via friction between fibers induced by twisting, although a relatively rigorous account for the mechanism has not been available until not long ago<sup>150</sup>. Extensive theoretical treatments of yarn mechanics can be found in<sup>146-148 151-154</sup>.

(Fig. 5)

Staple (short) fibers are assembled into a continuous strand (yarn) by virtue of frictional twist, which leads to a spatial helical conformation of individual fibers in the yarn. Upon stretching, the tension on the helical fibers will generate lateral pressure to bind the fibers together so as to sustain the loading, as described by Hearle<sup>146</sup> and Carnaby<sup>148</sup> and shown in Fig. 5(B). That is, if the external stretching is non-existent, the yarn is just a loose assembly of fibers held together by the weak inter-fiber adhesion, in addition to some fiber entanglements; the yarn has virtually no strength. So it is truly fascinating that the very force attempting to break the yarn is simultaneously the sole mechanism reinforcing it, or *a yarn is strengthened by being stretched*.

Considering inside the yarn a fiber of length  $l$  with slipping length  $\frac{1}{2}\lambda l$  at both ends, Pan<sup>155</sup> developed a relationship between the slipping proportionality  $\lambda$  and other related factors as

$$\lambda = \frac{\text{Tanh}(\mu n \bar{s})}{\mu n \bar{s}} \quad (1)$$

where  $n$  is a factor representing the twisting level in a given yarn and hence termed the dimensionless twist; the revised fiber aspect ratio  $\bar{s} = s(1 - \lambda)$ , with the fiber aspect ratio  $s = \frac{l}{D}$ ; the fiber diameter is  $D$ , and the fiber-fiber frictional coefficient  $\mu$ . In a stretched yarn and if  $\lambda$  equaling to 1, the fiber is completely slipping. As soon as the yarn twist level  $n$  increases to a critical point, the  $\lambda$  value will drop, revealing that the central portion of the fiber is now gripped

tightly, which in turn triggers further reduction of  $\lambda$  until the whole fiber is held over its entire length and a self-locking mechanism forms. This whole process occurs abruptly as predicted by Eqn. 1 and plotted in Figure 6.

(Fig. 6)

Whereas in a piece of fabric, the friction takes place mainly at the interlacing points between yarns crimped after weaving process to accommodate the perpendicular counterparts. This crimp in a fabric serves the same critical purpose as the helices in a yarn to provide pressure upon stretching so as to enhance the fabric<sup>156, 157</sup>.

Such unique friction mechanism imparts distinctive features in the materials. For instance, no other solid sheets or films can fit on a human body or on a solid object as elegantly as textile fabrics (Fig. 7). Several factors, all resulted from this structural mechanism, contribute to this trait. First, the relative movement of the structural components over each other during fabric deformation allows the multi-curvature bending, clearly distinctive in fabrics and critical for its formability, as studied by Hearle<sup>146</sup> and Postle<sup>148</sup>. Another important factor is the unique response of fabrics to different types of stresses. Since fibers are best in carrying tension, when a fabric starts to break, at the micro level, fibers break almost exclusively due to extension, regardless of the nature of the macro deformation, the structure allows fibers to reorient to and retreat from the loading so as to enhance simultaneously the fabric flexibility, toughness and strength.

### *c. Textiles – hierarchical and porous media*

Textile materials are undeniably hierarchical, even whose structural components such as yarns and individual fibers are themselves structured materials with several scale levels (Fig. 4). As a result, treating the materials from a structural perspective has long been the tradition in textile mechanics<sup>146-148</sup>.

From time to time, there has been question on the difference between a material and a structure. For instance, should a piece of a cloth or a trestle be treated as a material or a structure? The answer to it seems to be more or less artificial, not much to do with the object itself but largely by human expedience: it often depends on the size of the object relative to our own body. For example, we rarely if ever consider a high-rise building or a huge foothill as a material so as to derive its elastic modulus, but often contemplate to do so to a piece of wood or a pill of sand. In other words, we tend to consider objects much larger than our body as structures, those smaller as materials. Yet given the increasing trend to develop engineering materials with more sophisticated sub-structures, this argument about the difference between a material and a structure may gradually diminish.

From materials science, textiles can be viewed as a multi-phase mixture of fiber and air, dry or moistured, and are inherently heterogeneous due to the existence of the macro-pores. Owing to the large disparity in physical and geometrical features of the distinct phases, they serve different purposes. Fibers provide structural integrity and strength; air and moisture contribute to the system flexibility and high deformation, thermal and moisture transfer, and antistatic properties, and air also reduces the system weight.

Furthermore textiles are rarely isotropic, behaving differently when viewed at different directions. They can display huge deformation even at load as small as its own weight (Fig. 7). In fact, unlike other engineering materials, exhibiting large deformation is the indispensable attribute of textiles so they can cover our body intimately without failure or without hindering our daily movement, i.e., *excessive deformation is its normal state in service*. The frictional mechanism also implies non-linearity and hysteresis, and being polymeric materials associates their behaviors to time and rate changes. Vast structural and property variability introduce statistical, and stochastic considerations in the analyses. All of these lead to technical challenges. For instance, for an isotropic material, its strength remains constant regardless of direction, represented by a circle when plotted against directions, as in Fig. 8 (owing to symmetry, only a quarter is drawn); whereas the strength direction relationship for an anisotropic material can be illustrated by an ellipse. However, this relationship for a woven fabric is much more complex as seen in the figure, because of the different degrees of internal yarn re-orientation and movement when stretched in different directions of the fabric<sup>158</sup>. Moreover, this yarn re-orientation to self-reinforce the resistance in the loading direction reveals the adaptive nature of textile materials. Finally, analyses of wrinkling or crumpling of such flexible sheets have been proven to be hugely sophisticated<sup>159-163</sup>.

(Fig. 7)

(Fig. 8)

#### *d. Textiles – as precursors in composite study*

Textile are fibrous composites, and many theoretical advances in composite science can be rooted back to textile research. The following are just some examples:

- The Weakest link theorem about scale effect in material strength proposed by Peirce in 1926<sup>164</sup> when analyzing yarn failure;
- Study on mechanical behaviors of blended yarns, highly relevant to mechanics of composite and hybrid composites<sup>165, 166</sup>;
- The shear lag theory – stress transfer between matrix and fibers<sup>167-171</sup>;
- Fragmentation process and hybrid effect during fracture of a fibrous material (Fig. 9)<sup>168-171</sup>.

(Fig. 9)

Here is an interesting and revealing experimental work of blended yarn tensile strength tests<sup>168, 169</sup>. The authors prepared blended yarns with two components of low (LE) and high (HE) breaking elongations, and at both sufficient (Fig. 9(A)) and larger (Fig. 9(B)) twist levels. Upon stretching the system beyond the breaking elongation of the LE components, they will break, often multiple times due to the frictional constraints from their HE neighbors, a phenomenon known as the fragmentation process<sup>172-174</sup>. It is shown in Fig. 9 that when twist level increases:

- the fragment lengths of LE components decrease, i.e., broken further, due to increasing internal friction from the twist (Fig. 9(A)) ;
- the fragment lengths of LE components are shorter when closer to the yarn axis due to higher internal friction there (Fig. 9(A));
- the crack initiated in LE can propagate through the HE components at larger twist level, so the yarn behaves more like a brittle material (Fig. 9(B)).

*e. Textile processing – its potential and limits in novel structural material development*

Textile manufacturing involves processes that manipulate tiny individual fibers into complex, highly detailed and hierarchal macro-structures with multi-functionalities. Its major limit for nano-scale manufacturing lies clearly in the difficulty of handling nano-scale objects. However there are exceptions. The first is the electrospinning process originally proposed for textile (fiber) manufacturing<sup>175</sup>, but now flourished as the most widely used process in generating nano structures, especially in organic or polymeric areas<sup>176-178</sup>.

Surface printing could be another example of textile process extended to areas dealing with novel nano and delicate substances such as fabrication of biosensors and biodevices<sup>179</sup>, formation of nano/bio interfaces and architectures with living cells<sup>180</sup> and other soft media<sup>181, 182</sup>.

In general, textile processing can play an important role in manufacturing new materials with constituents at  $\mu\text{m}$  scale, as also recommended by Vincent<sup>8</sup>. Inherent limits exist when dealing with even finer scales.

### **C. Consequence of destroying hierarchy in materials**

A forceful way to illustrate the importance of structural hierarchy in a material system is to show the outcome if a system suddenly loses its structural hierarchy. When this happens at macro-scale level, it is self-evident that the system will simply fall into pieces, once the internal structural connections disappeared along with its structural hierarchy. It is however far more dramatic when this happens at molecular level.

Mutations in general refer to changes in the DNA sequence of a cell's genome, leading to damaged cells, and are caused by radiation, viruses, and transposons, as well as errors that occur during meiosis or DNA replication<sup>183</sup>. Buehler's group<sup>76, 184</sup> has showed the deterioration of system performance once its hierarchical designs break down due to mutation. In their study on the quantitative effects of osteogenesis imperfecta-related glycine replacement mutations on the molecular, intermolecular and collagen fibril mechanical properties, they demonstrated that such mutations caused poor fibril packing, changes in mineral crystals size and shape, and decrease of cross-links density.

## **III. SOME GENERAL MOTIFS**

From the examples of hierarchical multiscale materials, including those illustrated in this article, some general, simple yet effective rules can be drawn as discussed below. Note that complex systems are often resulted from combination of simple constituents following simple rules.

### **A. Thinning and splitting**

Natural materials grow into branches (branching) in most cases. To facilitate the analysis below, we can also view the materials forming along the reverse direction, i.e., all the grown plants are made of split components.

It is clear that such splitting as depicted in Fig. 1(A) is to divide an originally unified body into pieces – a process actually “destroying” the inter-connectivity or the system integrity at least in the transverse direction of the original system - it is almost counter-intuitive to think such a process can be beneficial to the functions of a material system. However, simple examination can reveal that such splitting processes actually impart desirable attributes to the material.

First take the simple structures in Figure 1 as examples and assume the two structures made of

the same material: a solid rod of radius  $R$  in Figure 1(A), and a bundle of total nominal radius  $R$  but with  $N$  circular branches each of radius  $r$  in Figure 1(B). When  $N \rightarrow \infty$  so that  $R \gg r$ , it is readily demonstrated

$$R = \sqrt{Nr} \quad (2)$$

These two structures ( $R$  and  $Nr$ ) and Equation 2 connecting the radii will be used repeatedly in our illustrations below. A word of caution is that comparison of these two cases is the examination of the structural hierarchy more in the transverse (radial) direction, not the length direction – the difference between the two is discussed later after Equation 9.

*a. Maximizing the specific area*

A system has to interact with its surroundings. Most such interactions are conducted through its surface, and a larger surface area facilitates more active interactions. Therefore maximizing surface area at a given mass or volume may be one of the advantages in forming a branched conformation.

The specific surface area is the total surface area over its volume, and it is easy to show that, when  $N$  is large enough, the ratio of the specific areas (lateral only for simplicity) between the two cases of  $R$  and  $Nr$  is

$$\frac{A_{Nr}}{A_R} = \frac{\sum_N A_{ri}}{A_R (R = \sqrt{Nr})} = \sqrt{N} \quad (3)$$

Where the subscript  $R$  represents the rod,  $Nr$  the fiber bundle and  $ri$  a single fiber  $i$ . That is, as  $N$  grows ( $r$  reduces), the specific surface area of the fiber bundle  $A_{Nr}$  increases, compared with  $A_R$  and approaches infinity as  $N \rightarrow \infty$  or  $r \rightarrow 0$ . In other words, the structure hierarchy directly increases the system specific area.

This simple illustration can be very useful, for an enlarged specific surface will increase the capacity in physical and chemical activities of the system, *which is likely responsible for many of the extraordinary active behaviors observed at nano scales*, as reported for example by Cervantes-Sodi *et al.* The team found that the specific surface area of a catalyst particle is more important than generally appreciated, and the smaller size of a catalyst will lead to a faster reaction than if a larger version of the same catalyst is used<sup>185</sup>.

As another example, Mahadevan<sup>186</sup> examined the effect of bundle number  $N$  on the behaviors of molecular fibril bundles made of keratin, collagen, elastin etc., and demonstrated that as the number of filaments increases, the morphology of the filament bundle, the strain field distribution, and the deformation modes all changed over a wide spectrum from essentially a discrete case into continuum.

Note that the volumes for the two cases are identical as  $N \rightarrow \infty$  or  $r \rightarrow 0$ , for the amount of mass remains the same. The specific area of a system reduces when the system size increases, as the system volume (cubic of the length) grows faster with the size than its surface area (square of the length) – implying a fact that increasing a system size diminishes its activity. Now that splitting the system into smaller parts solves the problem, thus enhancing any processes involving specific



surface area or interface between a large system and the surroundings.

*b. Arresting cracks – light from Griffith’s theory*

Besides the relationship between material strength and the internal crack, Griffith also dealt with in his seminal paper<sup>187</sup> the connection between strength and sample size, aka the scale effect. Based on his criterion, the fracture strength  $\sigma$  of a “cracked” plate can be expressed as<sup>133</sup>

$$\sigma = \alpha \sqrt{\frac{E\gamma}{h}} \quad (4a)$$

where  $E$ ,  $\gamma$  and  $h$  are the material tensile modulus, the surface energy, and the thickness of the plate, respectively, and  $\alpha$  is the crack geometry parameter.  $\sigma$  increases with the decreasing plate thickness  $h$ , i. e., smaller sample size results in a higher strength.

Although Eq. 4a was derived for a flat plate with infinite area so as to achieve uniform plane stresses, we have strong reason, sustained fully by experimental results, to believe that the trend predicted in Equation 4a is also valid for an axially loaded filament of diameter  $2r$  and infinite length so as to maintain the original uniform stress, just as Griffith stated that “very small solids of given form, e.g., wires or fibres, might be expected to be stronger than large ones, as there must in such cases be some additional restriction on the size of the flaws”<sup>187</sup>. We even suspect this can be proved theoretically using a cylindrical coordinate system. Therefore, the fiber strength  $\sigma$  can be obtained as:

$$\sigma = \alpha \sqrt{\frac{E\gamma}{2r}} \quad (4b)$$

and increases with the decreasing diameter  $2r$ . Then for the bundle in Figure 1(A) with  $N$  fibers of equal strength and the same cross sectional area  $A$ , its total breaking load from Equation 4b would be

$$\sigma_{Nr} = NA\alpha \sqrt{\frac{E\gamma}{2r}} \quad (5a)$$

Of course, this result can be further improved by taking into account the difference in strengths between a fiber bundle and its constituent fibers, but that will not affect the conclusion below. For the rod of radius  $R = \sqrt{N}r$  in Figure 1(B), its breaking load  $\sigma_R$  will be

$$\sigma_R = A_R\alpha \sqrt{\frac{E\gamma}{2\sqrt{N}r}} \quad (5a)$$

It is easy to prove that the cross sectional area for the rod  $A_R = NA$ . The ratio of Eqs 5a and 5b,

$$\frac{\sigma_{Nr}}{\sigma_R} = \sqrt[4]{N} = N^{\frac{1}{4}} \quad (6)$$

is always great than 1 as  $N > 1$ , and grows with number  $N$ . That is, by dividing a large piece into smaller ones, the resulting overall strength is always higher.

Physically, it is known that in a continuous larger rod, once a crack is propagating, it will go all the way through the whole body without requiring much additional effort. Whereas in an assembly of smaller fibers, the same crack propagation can only travel through the single fiber in which it was initiated. Once reaching the boundary between the fibers, the crack will stop and new load is needed to create new breaking surface for the crack to trek into another member: one of the main principles why fibers can reinforce a matrix.

Note however that the original Griffith's theory, therefore the above analysis, is mainly for brittle materials where crack propagation is the chief cause for failure. Equation 6 may be invalid for biological materials in which pre-existing cracks may not propagate even as the material is stretched to near its limiting strength, as reported by Gao et al<sup>133, 188</sup>.

### c. Increasing contact adhesion

The adhesion of solid elastic bodies has been extensively studied in the past. Two general models of the contact behavior have been proposed: the Derjagin-Muller-Toporov (DMT) approach<sup>189</sup> for small, stiff and low surface energy systems and the Johnson-Kendall-Roberts (JKR) theory<sup>190</sup> for large, soft and high surface energy systems<sup>191</sup>. In both theories nonetheless, it is predicted that splitting up a large contact into finer sub-contacts can increase the total adhesion. This results in a scaling effect, i.e., finer structures exhibiting stronger adhesion<sup>192</sup>.

Again it has been demonstrated in<sup>193</sup> that compared to the rod of radius  $R$  in Figure 1(A), the pull-off force for simultaneous detachment of the bundle with  $N$  fibers of radius  $r$  in Figure 1(B) will be enhanced by a factor of  $\sqrt{N}$ . That is, thinner spatulas (decreasing  $r$  and thus increasing the number  $N$  of the spatulas) lead to stronger adhesion, as long as high fiber modulus and aspect ratio with small inter-fiber spacing are maintained<sup>10, 194</sup>.

Peressadko and Gorb have provided the first experimental verification of such adhesion enhancement by division of contact areas. A patterned surface made out of polyvinylsiloxane (PVS) has exhibited significantly higher adhesion on a glass surface than a smooth continuous sample made of the same material, and this effect is even more pronounced on curved substrate<sup>195</sup>. Gao and Yao have also reported<sup>196</sup> that when the diameter of fibers is reduced to length scales on the order of 100 nm, an optimal fibrous system can be designed where the fiber pull-off force achieves its theoretical value.

### d. Improving structural flexibility, property synergy and processibility

Again from Figure 1, the ratio of the bending moment of inertia between the bundle in Figure 1(B) and the trunk in Figure 1 (A) with  $R = \sqrt{N}r$  is

$$\frac{I_{Nr}}{I_R} = \frac{\sum_N I_{ri}}{I_R} \rightarrow \frac{N\zeta \frac{\pi r^4}{4}}{\pi(\sqrt{N}r)^4} = \frac{\zeta}{N} \quad (7)$$

The coefficient  $\zeta$  is introduced to reflect the constraint between the members in the bundle, hindering the individual fiber from moving or bending over its own axis freely. However, as long as such constraint remains constant or at least not growing at the same rate as the number of branches  $N$ , increasing  $N$  will considerably *reduce* the ratio of bending stiffness, i.e., relative to a rod of the same size, the more members in the bundle, the more flexible the system at a given

constraint  $\xi$  - the advantages of a rope over a rod. By branching out, as opposed to being a single trunk, a tree indeed becomes more springy or resilient against wind. Note the heterogenization during the process by bringing air into the tree as a buffer also improves the system resilience and hence its fracture resistance.

This reduction in material bending stiffness due to structural hierarchy also works for shear load. Consider two pieces of samples shown in Figure 10, where Fig. 10(A) is a homogeneous and isotropic membrane, and Fig. 10(B) a piece of woven fabric with finer components.

(Fig. 10)

According to continuum theory, for the uniform membrane Fig. 10(A), the ratio between its tensile modulus  $E$  and shear modulus  $G$  is related to its Poisson's ratio  $\nu$  as:

$$\frac{E}{G} = 2(1 + \nu) \quad (8)$$

For normal materials,  $0 < \nu < 0.5$  so that  $2 < (E/G) < 3$ . In other words, for ordinary isotropic materials, the tensile and shear moduli are of the same order of magnitude, i.e., shearing the material is not much easier than stretching it. This is not the case for the fabric in Fig. 10(B), its ratio of  $E/G \rightarrow 200$ , depending on the type of weave structure<sup>197</sup>. In fact, a fabric will fortunately shear easily even under its own weight: once a fabric is laid onto an object, it will deform in complex strain state including bending and shear until it covers the object to the degree allowable by this  $E/G$  ratio – making woven fabrics irreplaceable as *the* material for comfortable and elegant apparels (Fig. 7).

The main physics for such excellent formability of a fabric is due of course to the easy relative movement of individual components (yarns) in the fabric, reflected by the unusually small fabric shear modulus  $G$  value. The frictional constraint is the mechanism here in controlling the relative movement between the individual yarns and thus the overall compliance to deformation. In general, ability to accommodating complex stress fields is the main mechanism in buckling or wrinkling of membranes<sup>198</sup>, including facial skin<sup>199</sup>. It was a pleasant surprise therefore to see in a paper on studying the mechanical properties of silk. It reported that silk is formed at finer scale with the so-called  $\beta$ -nano crystals sheets shown in Figure 10(C), found responsible for the excellent strength and fracture toughness of spider silk fibers, due mainly to the ability of such a flexible nano structure in accommodating various local stresses<sup>200</sup>.

Such inter-coupling was also reported that cytoskeletal microtubules can bear enhanced compressive loads in living cells because of lateral reinforcement provided by the cytoskeletal actin network<sup>201</sup> – an effect similar to changing the constraint  $\xi$  in Equation 6. In addition, the silica skeleton of the deep-sea sponge *Euplectella aspergillum* was recently shown to be structured over at least six levels of hierarchy, and the presence of organic interlayers is not only deviating cracks but lowering the overall stiffness and hardness of the composite<sup>202</sup>.

Essentially structural hierarchy with its attendant interfaces allows the origins of stiffness and toughness in a material to be separated, and thus offers the possibility of independent control. This is impossible in most solid materials, for which one has to sacrifice stiffness for toughness, or vice versa as mentioned before. For instance, in a woven structure like Figure 10(B), its

tensile moduli in the two orthogonal directions  $E_{xx}$  and  $E_{yy}$  can be adjusted independently as long as:

$$\frac{\nu_{xy}}{E_{xx}} = \frac{\nu_{yx}}{E_{yy}} \quad (9)$$

where  $\nu_{xy}$  and  $\nu_{yx}$  are the associated Poisson's ratios<sup>203</sup>. This seemingly simple relationship reveals the unique nature of the interconnectivities that exist in the hierarchical systems and is responsible for the advantageous functionalities exhibited by many membranes in biological systems (like in bird's wings and duck's feet), but difficult to achieve in regular solid engineering materials.

Furthermore, a recent theoretical work on fiber bundle structures by Bosia et al<sup>17</sup> has demonstrated that increasing the number of hierarchy levels in such a structure results in a decreased overall material strength, whereas incorporating different fiber types into a bundle, i.e., increasing the *lateral hierarchy*, can enhance the strength. They hence concluded that "both hierarchy and material "mixing" are necessary ingredients to obtain improved mechanical properties".

For a deeper exploring on the significance of structural hierarchy, let's turn to another investigation on spider silk whose superior mechanical properties formed at room temperature and ambient pressure have fascinated generations of materials scientists. Researches by Buehler and colleagues<sup>62, 204-206</sup> may cast promising light on the secrets. Amyloids, the main building blocks for spider silk and most natural protein materials, are found to possess an innate capacity to self-assemble into hierarchical structures (Fig. 11) through a process called amyloidogenesis. Because the fundamental interactions in the amyloids are of largely weak hydrogen bonds in forming the nanosized beta-strand clusters in Fig. 10(C), the intrinsic weakness of hydrogen bonds is overcome during the process so that these bonds work cooperatively to provide maximum strength and toughness. More importantly, the dominance of weak hydrogen bonds in building the amyloid structure is considered by the researchers to be responsible for the processibility of spider silk at benign conditions. Furthermore, the structure becomes self-healing because broken bonds can be easily reformed into a fully functional state.

(Fig. 11)

## B. Laminating or layering

Layered or laminated structure is a frequent structural motif in hierarchical biological composites as exemplified in wood and bone in Figures 2 and 3. Trees and plants grow thicker by adding more rings (layers), and maintain their desirable shapes and properties by layering accordingly in the internal structures during growth. Extensive theoretical analysis on layered structures has been made available in engineering composite study, and should be used more extensively to explore the layering mechanics in biological materials.

### a. Basic theories of laminated structures<sup>203</sup>

For a composite formed by multiple layers of different physical, geometrical and orientational properties, its constitutive, or load and deformation, relation can be in general expressed in a matrix form as

$$\begin{Bmatrix} N \\ M \end{Bmatrix} = \begin{Bmatrix} A & B \\ B & D \end{Bmatrix} \begin{Bmatrix} \epsilon \\ K \end{Bmatrix} \quad (10)$$

Where  $N$  and  $M$  are the tensors of forces and bending moments exerted on the composite, and  $\varepsilon$  and  $K$  are the strains and curvatures caused.  $A$ ,  $B$  and  $D$ , all themselves 3x3 square matrices, are the comprehensive mechanical properties of the system, reflecting the contributions from all the constituent layers, where:

$A$ : termed extensional stiffness matrix – relating the resultant forces to composite strains;  
 $B$ : coupling stiffness matrix – reflecting the *coupling* between bending and extension;  
 $D$ : bending stiffness matrix – connecting the moments to the plate curvature.

#### *b. Design strategies*<sup>203</sup>

It is known in composite mechanics that,  $A$ ,  $B$  and  $D$  matrices, are determined by the properties, the thickness and numbers of individual layers and the way such layers are arranged relative to each other. By manipulating all these factors, we can construct laminates that possess special characteristics – the advantages of laminating or layering. Some of the examples using layering technique include:

- Making up the required total thickness;
- Tailoring the properties of individual layers to tune the matrices  $A$ ,  $B$  and  $D$  so as to achieve synergistic overall performance;
- Arranging each layer tactically so that the most durable side is deployed in the direction with most severe loading;
- Properly choosing and positioning the layers, a composite with other peculiar behaviors can also be achieved.

More specifically, by selecting and stacking layers strategically so as to make the coupling stiffness matrix  $B \rightarrow 0$ , we can attain symmetric laminates with no undesirable bending-stretching coupling once loaded; that is, normal or shear stress only generate corresponding normal or shear strains. Also by altering the bending stiffness matrix  $D$ , we can eliminate coupling between bending and twisting moments to avoid adverse buckling and wrinkling.

#### *c. Layering in biological systems*

Conversely, we can generate bending, stretching, twisting actions via linear forces, and this has been found as the main actuating mechanism in biological systems. It is recently demonstrated that during the blooming process of the *asiatic lily Lilium Casablanca*, linear motion or force leads to bending, and twisting actions so the flower petals can open<sup>207</sup>. Other similar examples include muscles growth<sup>208</sup>, venus flytrap snapping<sup>209</sup>, leaf expansion<sup>210</sup> and flowers blossoming<sup>207-209, 211, 212</sup>.

Moreover, alternate layering of soft and stiff materials (at the nanoscale) has been shown to result in considerable synergy in toughness in bones and woods<sup>1, 6, 132, 133</sup>. Also layered assemblies of mesoporous materials<sup>213</sup> have recently been developed in creating advanced functions including highly selective sensing and auto-modulated drug release.

### **C. Spatial and angular orientation**

As mentioned previously, the twisted helicoidal principle of fiber composite in biomaterials has been proposed as a major unifying concept across different species<sup>4, 91, 214</sup>. Angular orientation of a structural unit in a material, such as fibrils in wood and collagen fibers in bone, twisted or in helical conformation as shown in Figures 2 and 3, can be abstracted into Figure 5(B) for easy analysis.

*a. Reinforcement at selected directions*

The first clear benefit of fibril orientation is that a material can be selectively reinforced at the most desirable direction – the primary design principle in fabricating fiber reinforced composites. Also the distribution of microfibril angles is used by the plants to introduce property gradients into the material and to tune the mechanical properties according to needs<sup>4</sup>.

*b. Reduction in system stiffness*

In Figure 5(B), the relationship between the fibril oblique angle  $q$ , its tensile modulus  $E_f$  and the system effective tensile modulus  $E_e$  can be easily obtained using tensorial transformation:

$$E_e = E_f \cos^4 q \quad (11)$$

That is, because of the orientation angle  $q$ , the system is less stiff or more stretchable than the fibril by a factor  $\cos^4 q$ . There are many illustrations in nature using this principle. For instance, it was reported that the constituent mineralized collagen fibrils, spiral around the central axis with varying degrees of tilt, led to higher extensibility of the osteon<sup>215</sup>.

*c. More known functions of helicity*

As analyzed above, in an assembly of helical fibers, a yarn or a muscle bundle, upon stretching, the tension on the helical fibers will generate lateral pressure to bind the fibers together to sustain the stretching – a smart and easy way to reinforcing the assembly. In addition, “The bilateral, helical-ortho/axial-para structure (in wool fiber) leads to the crimp that provides bulk in coats, whether worn by sheep or people<sup>216</sup>”.

Interestingly, Mahadevan and Rica<sup>217</sup> reported a novel process to spontaneously induce helicity into a *synthetic* polymeric nanobristle assembled in an evaporating liquid. The process can be controlled “to yield highly ordered helical clusters with a unique structural hierarchy that arises from the sequential assembly of self-similar coiled building blocks over multiple length scales, leading to a system having previously unseen structures with uniform, periodic patterns and controlled handedness for efficient particle-trapping and adhering”. More recently, Clark and Prabhakar reported<sup>218</sup> that in both singly- and multiply-flagellated organisms, filament helicity may confer significant advantages to micro-swimmers by eliminating the bistability associated with the wrapping transition.

Research on twist and helix formation in biomaterials seems to pick up some momentum recently with the publication of several interesting papers on the subject. Twist configuration has been considered a critical feature in self-assembly of materials<sup>12, 219, 220</sup>. Also, based on the continuum analysis, Grason and Bruinsma<sup>221</sup> showed that chirality is a key thermodynamic parameter in forming and controlling the aggregation of biopolymers. Gibaud et al experimentally demonstrated<sup>91, 222</sup> that molecular chirality can control the interfacial tension, thus “allowing precise assembly and nanosculpting of highly dynamical and designable materials with complex topologies”.

## **D. Heterogenization or hybridization**

The effect of system heterogeneity is the central theme in dealing with composite structures<sup>223-228</sup>. Given the fact that materials exist rarely in pure form and composition, the term composite actually covers many more types of materials including biological materials systems. In a composite system, interactions between the distinctive components through interfaces are chiefly

responsible for the complex system performance, which becomes difficult to explain if only based on the behaviors and fractions of individual constituents forming the system. The critical importance of geometrical arrangement of and interfacial interactions between the constituents has been made fairly known through extensive research.

It is apparent that many advantages arise from heterogeneity via blending substances of different types to form a single hybrid material. First and foremost, such hybridization can impart synergistic system behaviors by compensating the property deficiency among the constituents. Also it can improve the compatibility of the ingredients to be mixed into one system.

*a. Property compensation*

The toucan beak, formed by a stiff sheath covering a soft porous core as shown in Fig. 12 (A), can serve as a good example in illuminating the property superposition and compensation in a hybrid system. Individually, the sheath exhibits a respectable performance under tension but inferior in compression as depicted in Fig. 12 (B), and the core does that almost in opposite as in Fig. 12 (C). However properly combining the two to form the beak, a behavior superior in both loading situations can be resulted as in Fig. 12 (D).

(Fig. 12)

As repeatedly demonstrated, biological composites are based on polymers and sometimes mineral. Nevertheless, their overall mechanical properties are usually significantly superior to those of the components, which can mostly be attributed to hierarchical structuring plus hybridization. For instance, high stiffness is readily achieved by the incorporation of mineral phases (e.g., calcite and hydroxyapatite) and of stiff, fibrous elements (cellulose or chitin) through extensive cross-linking<sup>1,6 229</sup>. Tiny amounts of organic phase are sufficient to increase the toughness of an inherently brittle mineral by factors of more than 1,000<sup>138</sup>.

Moreover, the presence of a large number of interfaces between the mineral platelets forces cracks to be deflected as they propagate across the structure and also allows for crack bridging and plate pullout to increase energy dissipation<sup>230</sup>. Nanoasperities<sup>231,232</sup> and mineral bridges<sup>233</sup> found between and on the surfaces of the mineral platelets may also give rise to strengthening interactions between platelets<sup>18</sup>. Indeed, the crack driving force essentially vanishes in the valleys of a periodically varying modulus, “if the difference between high modulus and low modulus is large enough (typically more than a factor of 5), ... the crack driving force also depends on the gradient of the modulus and decreases with a positive modulus gradient between platelets<sup>234,</sup>”.

As a unique case of hybridization, bio-mineralization is the formation of inorganic minerals in a biological environment, which generally occurs under strict morphological and structural control through the interaction of a variety of biomolecules. There are over 60 different biominerals existing in natural systems, including oxides, sulfides, carbonates, phosphates, oxalates as well as silicates<sup>235</sup>. Extensive research by biologists, archeologists, physicists and chemists has revealed a large number of functions for these hybrid materials, such as mechanical support and protection, gravity sensing, magnetic perception, light amplification and transmission, and metabolic energy generation<sup>236</sup>.

*b. Compatibility improvement and new functionalities*

Direct contact between the tissues of different moduli would potentially give rise to harmful interfacial stresses. In the squid beak mentioned before, this danger is minimized by the presence of a stiffness gradient of approximately two orders of magnitude from the beak tip to the base, as measured by tensile and nanoindentation measurements<sup>140</sup>. Similar case was found in the combination of hard enamel on softer dentin in teeth<sup>237</sup>. Also "...composite fibril/ matrix structure in animal hair allows it to recover elastically after being extended by up to 40%..." as reported by Hearle<sup>216</sup>.

Two recent review papers by Buehler<sup>7, 62, 204</sup> have further demonstrated that, hierarchies formed via self-assembly in some biological materials have demonstrated two important advantages: first they turned weakness of the building blocks to strength via the interplay of universality and diversity in the evolutionary process, and also they create materials with a vast range of functional properties based on a limited set of universal elements, such as proteins or more fundamentally, the natural amino acids.

*c. Multi-state: air and moisture and material properties*

A particularly common group of hybrid materials is the mixtures with moisture or air. Because of the omnipresence of air and moisture, they often constitute, not by design, individual phases in a system. Although the mechanical resistance of air when confined in a tire or a basketball, and the associated importance is hard to deny, air or moisture is still more often viewed as "emptiness" or "nothingness". However, if indeed ignored, it will frequently led to erroneous predictions in analyzing the host systems.

Table 1 Properties comparison

property	polymer s	water	air
Density (g/cm <sup>3</sup> )	0.8	1	0.001
Bulk modulus (GPa)	5	2.2	1x10 <sup>-4</sup>
Thermal conductivity (W/m·K)	0.03~ 0.3	0.6	0.025
Electrical Conductivity (S·m <sup>-1</sup> )	< 10 <sup>-6</sup>	5*10 <sup>-4</sup> ~5*10 <sup>-2</sup>	~ 0
Shear modulus (GPa)	0.8	$\mu / t$	$\mu / t$

- $\mu$  is the viscosity of the fluids and  $t$  the time.
- The data in the table are estimations for discussion only and more specific ranges can be readily obtained.



Water is ubiquitous in biological materials, and so is air if pores exist. While frequently unintentioned, their existence in materials can play deciding roles in determining the behaviors of the system under various external stimuli, especially in properties with huge extremity as exemplified in Table 1. Figure 13 shows, for instance, the initial Young's modulus of the hoof wall plotted as a function of water content and the modulus directly reduces as water content increases.

(Fig. 13)

Many naturally occurring materials are not fully dense, i.e. they possess internal cavities. This type of design can be intentional, since it reduces the material density. Examples are plenty, including cork, bones, wood, sponge, and plant stalks<sup>238</sup>. Modern synthetic materials have also adopted this type, such as metallic, ceramic, and polymeric foams. Some are of common and every day usage, and others are quite esoteric, like the Space Shuttle tiles, which have a density of 0.141 g/cm<sup>3</sup> and a maximum temperature capability of 1260 C<sup>o</sup><sup>1</sup>, air/gas is deliberately introduced for thermal property improvement.

Heterogenization in material design to more purposely include air and/or moisture can be highly effective and efficient in achieving otherwise unattainable functions - the superior thermal and electric insulation of air has already found extensive applications, as detailed in next section. Note in particular from Table 1 the time dependent nature of the shear moduli for both air and water, just like other shear thickening fluids<sup>239, 240</sup>, which can increase the design sophistication in material performance if used properly.

Of course, the reason why moisture or water plays important role in determining material properties is far from merely mechanical or physical. Being a chemical agent itself, water affects system behaviors more fundamentally by forming weak secondary bonds, thus interacting chemically with other constituents in the system<sup>241, 242</sup>. Corresponding approaches have to be taken to investigate that part of the influence water imparts on material properties<sup>243, 244</sup>.

## E. Hierarchy, geometry and other material properties

### a. Scale and geometry effects on material wetting and moisture transport properties

It is easy to demonstrate that hierarchy improves wettability of a material<sup>245, 246</sup>. We can use the Harkinson spreading parameter<sup>246</sup> for this purpose, which for a given multiphase material is defined as:

$$S = \gamma_s + \gamma_{sl} - \gamma_l \quad (12)$$

where  $\gamma_s, \gamma_{sl}, \gamma_l$  are the surface tensions between solid-air, solid-liquid and liquid-air, respectively. The material will be wetted if its *critical* Harkinson spreading parameter  $S_c \leq S$ . This critical parameter for the fiber bundle in Figure 1(C) can be expressed as<sup>245</sup>:

$$S_c = \frac{R - Nr}{Nr} \gamma_l = \frac{\sqrt{Nr} - Nr}{Nr} \gamma_l = \left( \frac{1}{\sqrt{N}} - 1 \right) \gamma_l \quad (13)$$

and it decreases as  $N$  increases. That is, for a given mass of material, making a material into a bundle containing fine fibers will significantly enhance its wettability- the secret of a terry towel!

Next, based on Kelvin – Cohan Equation for pore analysis<sup>247-249</sup>, the vapor pressure on a curved solid surface is different from that on a flat surface, so the vapor pressure  $P$  of a liquid dispersed

as a droplet to fit into the surface curvature of radius  $r$  is

$$\frac{P}{P_o} = e^{\frac{\gamma_l V_m}{rRT}} \quad (14)$$

where  $P_o$  is the saturation vapor pressure,  $\gamma_l$  is the liquid surface tension,  $V_m$  the molar volume, and  $R$ ,  $T$  are the gas constant and temperature. Hence the Kelvin-Cohan equation establishes the connection between the pore scale  $r$  and the pore condensation pressure  $P$ , and predicts that pore condensation shifts to a higher relative pressure with decreasing pore size  $r$ . Considering all moisture/liquid transfer process takes place at the interfaces seldom plainly flat, the implication of the geometry curvature is profound.

De Gennes <sup>250</sup> also summarized the size effect in fluid transport. Length scales in liquid transport include macroscopic scales for liquid thicknesses larger than a few thousand angstroms; mesoscopic scales for liquid thicknesses between 10 and 1000 Å; and microscopic scales at the molecular level. At the macroscopic level a liquid is characterized by its thermodynamic quantities, and its spreading kinetics is described as a hydrodynamic process. At the mesoscopic level however the properties of a thin liquid film are explained by continuum theories that ignore the molecular nature of the liquid, and the long range character of the molecular interactions is then taken into account through the disjoining pressure. Furthermore, the viscous effects predominate over inertial effects when length scale becomes sufficiently small, so that the dissipative mechanism in destabilizing liquid becomes dominant and has to be considered <sup>251, 252</sup>.

#### *b. Scale and geometry effects on material thermal behaviors*

The thermal properties of a material system can also be impacted by altering the structural constituents in both scale and shape as shown in Figure 14 <sup>20, 253</sup> where at the same volume fraction, the constituents of different shapes and size lead to significantly distinctive effective thermal conductivities for the system.

(Fig. 14)

Moreover, Donadio and Galli <sup>254</sup> in their study of the thermal properties of silicon nanowire reported that the dependence of the thermal conductivity on the nanowire thickness becomes considerably less significant for crystalline morphology than for amorphous samples.

#### *c. Scale effects on optical properties*

Optical properties of a material are the results of interactions between the material and the incident light, and the exact numerical correspondence between colors and the wavelengths in visible light stresses a direct scale effect between size in the material and the resulting colors. For instance, the blue color of *Morpho* butterfly comes from its wings with ridges of multiple slits spaced 200 nm apart, and such periodic nano-structures interact with the sunlight and reflect wavelength of blue light, ranging from 400 nm to 480 nm <sup>1, 56, 255</sup>.

In addition to controlling the scattering and reflection of light from surfaces, Nature also uses composite structures to control the transmission and focusing of light for signaling and vision. A fascinating example is the complex calcitic skeletal plates of the brittle star *Ophiocoma* <sup>256</sup>. These plates are covered in an array of lenses that focus light onto photosensitive nerve bundles, enabling the brittle stars to respond with color changes from night to day. The silica spicules that make up the architectural elements of *Euplectella* also display remarkable optical properties. They consist of a high-refractive index core of Na-doped silica whose refractive index is controlled for optimal waveguide behavior through the gradient in Na content and organic cover

layers<sup>9, 136, 257</sup>.

Moreover, Knowles and colleagues<sup>258</sup> have demonstrated that similar structure alternation can be employed to control the optical properties of biological materials. They used amyloid proteins to create multifunctional macroscopic materials by carefully organizing a few protein constituents to achieve the necessary diversity at each level of the hierarchy so the optical behavior of the resulting system can be tuned via a polarizer.

*d. Hierarchy diminishing the scale effect in mechanical strength*

Another interesting feature attributable to the fine local hierarchy is the *diminishing* scale effect in mechanics. In materials science, the scale or size effect on material strength has been a subject of extensive research<sup>259</sup>, and it has been widely accepted that at macro scale level, such effect is monotonic: the longer the material length, the weaker the strength as dictated by Griffith's theory. However studies have shown that such size effect is suppressed by increased material local hierarchy, i.e., the ones with finer structural details exhibit more stable strength value, and are less sensitive to their size change<sup>170, 171, 260</sup>.

Results from another study on collagen fibrils<sup>261</sup> also show that the elastic strength of the fibrils increases to a finite value with the molecular length, but levels off with further increase in molecular size as seen in Fig. 15. "Materials become insensitive to flaws at nanoscale" as concluded by Gao et al<sup>133</sup>.

(Fig. 15)

#### IV. A FEW THEORETICAL ISSUES

From our own research and literature study, we have identified/collected a few theoretical issues that are useful for better understanding of material performance, yet still unsettled and elusive, pending for further study.

##### A. Packing and ordering

Broadly speaking, materials properties are determined, intrinsically, by two major factors, i.e., the chemical compositions of the constituents and the structural morphology of the system. In that sense, once the material constituents are given, the behaviors of the new material formed are essentially dependent on the way the components are assembled – the internal structures, the interfaces and the interactions among the components. That is, the manner how individual parts are assembled into a structure, i.e., the packing order, becomes a critical question.

*a. Materials as from packing of the components*

Consequently and from a physicist's point of view, a material system can be studied by focusing on the geometrical shapes, relative positions and spatial constraints of the internal components and the interactive forces between them<sup>262-264</sup>. Such geometric relationship between the components in a closed volume is called in mathematics the packing problem and is a phenomenon easily visualized and commonplace in everyday experience. The interaction among the components is dominated by the strong repulsion between atoms that approach each other too closely, i.e., a short-range phenomenon which allows a more local treatment considering only the surrounding neighbors<sup>265</sup>. Onsager's seminal analysis of the effect of shape on the interaction between colloidal particles<sup>264</sup> has been considered the first such effort to treat materials structure explicitly as a packing problem.

Thereafter, particle packing has been used to study the structures of liquid, glassy and crystalline states of matter<sup>266-268</sup>, granular media<sup>267</sup>, heterogeneous materials<sup>267</sup>, polymer chains<sup>269</sup> and biological systems<sup>220, 270-274</sup>. Other fundamental mechanisms investigated along this line include the liquid crystal phase formation<sup>275</sup>, the effects of range and geometry of a simple attractive square-well on the phase diagram of hard ellipsoids and hard spherocylinders<sup>263</sup>.

Another pioneer work was done by Richards to explore the importance of close-packing in protein structure<sup>276, 277</sup> and his work has become increasingly recognized, as partly reflected by whopping citations of 641 and 1,824 times respectively for his two papers cited here. It was further reported that the last stage of protein folding, the “endgame,” involves the ordering of amino acid side-chains into a well defined and closely packed configuration, considered critical to the most important characteristics of native protein structures<sup>265</sup>. Attention was also focused on the type of packing observed in proteins and on the prediction of side chains packing, and on the more difficult problem of generating main-chain conformations close enough to make side-chain packing predictions possible<sup>265</sup>.

#### *b. Mathematics of packing and the Kepler Conjecture*

The packing of shapes has drawn the attention of humankind since ancient times. A Sanskrit work from 499 AD reveals the first-known mathematical study of the face-centered cubic arrangement of spheres, later known as the Kepler problem after the question put forth in 1611 by the astronomer Johannes Kepler<sup>138, 278-281</sup>, who speculated that the densest way to pack spheres is to place them in a pyramid arrangement known as the *face centered cubic* packing (**Figure 16(A)**). This statement has become known as the "Kepler's conjecture" or simply the sphere packing problem. To mathematically solve the sphere packing problem has been an active area of research for mathematicians ever since, and Hales only recently proved computationally the sphere-close packing fraction of  $\phi = \pi/\sqrt{18} \approx 0.7405$  achieved by face-centered cubic and its stacking variations<sup>282, 283</sup>.

(Fig. 16)

Yet, the sphere packing is the simplest packing case, for we only need to consider one characteristic size, i.e., the sphere diameter. Much less is known about the packing of other shapes<sup>284</sup>. In the case of ellipsoids, periodic arrangements were found with packing fractions up to  $\phi = 0.7707$ <sup>285</sup>. The recent progress in the synthesis of non-spherical particles of sizes ranging from nanometers to micrometers has focused attention on the problem of packing such three-dimensional shapes as tetrahedral<sup>286, 287</sup>. In a recent paper, Bruss and Grason analyzed the packing of twisted filament bundles. They concluded that the problem of twisted bundle packing can be mapped onto the problem of disc packing on a curved surface (**Fig. 16 (B)**). They also found that the “packing of any twisted bundle is geometrically frustrated, ... and the underlying non-Euclidean geometry of twisted fiber packing disrupts the regular lattice packing of filaments above a critical radius, proportional to the helical pitch”.

Given the mathematical challenges encountered, it is unlikely that major breakthrough on this topic would be achieved soon so that more pertaining theoretical tools are made available in guarding new material designs<sup>281, 288, 289</sup>.

#### *c. Growth, shape and self-assembly*

More generally, the connection between shape, form and its performance of a material system has long mesmerized scientists. Again if function is dictated by structure<sup>26, 229</sup>, then a multitude

of functions is possible by varying the structure of a composite formed by the same constituents.

In natural materials, shape and microstructure are intimately related due to their common origin - the growth of the organism. This has been discussed in detail by Jeronimidis in his introductory chapters to a book on “Structural Biological Materials”<sup>109</sup>. Growth implies that “form” and “microstructure” are created in the same process, i.e., the shape of a tree branch is formed by the assembly of molecules to cells, and of cells to wood with a specific shape. Hence, at every size level, the branch is “both the form and the material, and the structure becomes hierarchical”<sup>109</sup>.

The fact that natural materials are growing rather than being fabricated leads to unique advantages, as illustrated by Fratzl and Weinkamer<sup>6</sup>, that “biological structures and materials must not be thought as statically determined by the genetic blueprint but rather as systems actively responding to the biophysical stimuli of their environment”<sup>6</sup>. Firstly, it permits adaptation during growth to improve their functionality according to external constraints. Secondly, it allows the growth of hierarchical materials, where the microstructure at each position of the part is adapted to the local needs<sup>109</sup>. Thirdly, the processes of growth and “remodeling” (a combination of growth and removal of old material) allow a constant renewal of the material, thus reducing problems of material fatigue<sup>6</sup>. In addition to adaptation, “growth and remodeling processes enable healing for self-repair in biological materials”<sup>6</sup>.

Self-assembly as used now can be defined as the “spontaneous and reversible organization of molecular units into ordered structures”<sup>290</sup>, *a process equivalent to growth in natural biological systems*. The key feature this definition suggests is the spontaneity of the self-assembly process: the interactions responsible for the formation of the self-assembled system act on a strictly local level—in other words, the nanostructure builds itself. Three factors characterize a self-assembling process, i.e., order, interactions and building blocks<sup>291</sup>. The obvious challenges in synthetic self-assembly to imitate natural growth include controlling the size and shape to desirable ranges, and imparting differential growth rates and growth gradients for different parts of a structure<sup>292</sup>.

## **B. Bi-modular mechanical behaviors**

Anisotropy is responsible for many of the difficulties in dealing with hierarchical materials. However, even in the same direction of line deformation, materials often behave differently, depending on the sign of the force. In other words, for some materials, the Young’s modulus, strength, as well as the entire stress-strain relationship, are quite dissimilar when under tension versus under compression. Such “bi-modular” behavior is prevalent in biomaterials, and Figure 12 depicts a typical bi-modular behavior under tension and compression in the longitudinal direction. The pioneering work in this area was done mainly by Ambartsumyan and his collaborators and they further expanded the problem to two- and three- dimensional cases<sup>293-295</sup>. The research has picked up new momentum as interest in biomaterials increases in recent years<sup>296, 297</sup>. Also, in the current research on material mechanics at nano scale, one can only resort to nano-indentation approach, clear a compression test, assuming both compression and tensile mechanical behaviors of nano scale materials are the same. This expedient yet questionable approach is simply because the obvious problem that samples are just too tiny to grip for a normal tensile test<sup>298, 299</sup>.

Two issues are to be tackled. First, the current approach and its consequence in treating materials as inherently identical in both compression and in tension have to be reexamined. Also any

proposed solution still needs to be evaluated to satisfy the following criteria: (1) The compliances  $S_{ij}$  or the moduli (stiffness) must be symmetric in any coordinate systems in order for the strain energy to be positive, and therefore a potential function exists; (2) The values of the compliances are restricted in relation to one another such that the compliance matrix is positive; (3) The compliance matrix must be transformable between coordinate systems, i.e., it has to remain a tensor<sup>300-302</sup>.

### C. Behavior non-affinities between different hierarchal levels

#### a. Behavior non-affinities

Once hierarchy develops in a material system, other complications emerge. One of them concerns the issue of non-affinity, i.e., seemingly disconnection between the macro-properties of the system and the corresponding properties of its constituents. Just as nanoparticles display properties that differ from those of the bulk samples of the same material, ensembles of nanoparticles, or nano-structured materials, can have collective performance that deviates from that displayed by *both* the individual nanoparticles and the bulk samples<sup>64, 65, 80, 303</sup>. Such non-affinity is in fact the inherent consequence of the structural hierarchy, and is clearly an important issue for any theoretical attempt to predict materials properties over the full range of scales.

#### b. Examples and possible causes

On the material thermal performance from our daily experience, the same cotton fibers can be made into a thin and cool T-shirt for summer, or a thick and warm flannel coat for winter. That is, the thermal attributes of the final products seem to be independent of the thermal properties of its components (the fibers). Further analysis however reveals that our sensed warmth is actually related to a composite parameter termed the thermal effusivity  $\varepsilon$ <sup>304</sup>, defined as:

$$\varepsilon = \sqrt{k\rho c_p} \quad (15)$$

where  $k$  is the thermal conductivity,  $\rho$  the specific heat capacity and  $c_p$  the specific heat capacity of the material. By comparing the thin T-shirt and thick flannel coat, the first thing we notice is the huge difference in their bulk density  $\rho$ . In general, the  $\rho$  value in such textiles can vary from 1.0 to 200 (kg/m<sup>3</sup>)<sup>305</sup> by a few orders of magnitude, accountable by itself for the distinctive thermal feelings (thermal effusivity  $\varepsilon$  values) perceived when touching them. That is, the perceived thermal sensation is nearly independent of the fiber thermal properties, i.e., the thermal non-affinity. The secret of the heat retention lies of course in the still air contained in the much more porous flannel coat, for still air is the best thermal insulator. Enclosing air and keeping it still is the most effective way to generate super thermal protection, a very plausible explanation for the hollow fibers seen in Figure 17 forming the fur for polar bears.

(Fig. 17)

(Fig. 18)

Following is another example of the non-affinity, and also how air plays a dominant role in determining material performance. For the cushion under compression in Figure 18(A), the compressive stiffness  $E_c$  is known<sup>306, 307</sup> to scale to the cubic of the fiber volume fraction  $V_f$  as:

$$E_c \rightarrow E_f V_f^3 \quad (16)$$

where  $E_f$  is the axial tensile modulus of the solid fiber itself. Equation 16 suggests that by building a fibrous cushion to incorporate large amount of air so that  $V_f \ll 1$ , and the unconfined air there presents very low compression resistance, the macro compression resistance  $E_c$  is markedly reduced comparing to the fiber modulus  $E_f$ . A closer observation discloses that because of the existence of pores between fibers, when the cushion is under macro-compression, individual fibers are in fact experiencing *bending* deformation – another example of the behavior non-affinity. Because of its thin thickness, the bending (buckling) resistance of the fibers is very low, leading to the soft cushioning effect, something seemly manifested in fruit flies feet illustrated in the photo of Figure 18(B)<sup>308</sup>, cushioning could be one of the benefits when the fly lands on a hard surface.

Additionally, Hepworth *et al* recorded a non-affine relationship between the collagen fibers and ground substance in soft biological tissues like skin: at a micrometer scale, a pressed skin is under compression, whereas the fibers contained exhibited reorientation and stretching<sup>309</sup>.

Again, this non-affinity issue is clearly resulted from structural hierarchy. In a hierarchal material system, different structural components are connected in many ways at various levels; their behaviors are thus often not entirely synchronized, bringing, intended or not, such consequences discussed above.

#### D. Importance of dimensionality in a hierarchal system

##### a. System dimensionality

A material regardless of its size is a three-dimensional object in reality. However, in scientific study, simplification is often made to consider for example a particle as zero dimensional; a fiber as one dimensional; and a slab as two dimensional if a geometrical symmetry in the remaining dimension exists, as done repeatedly in theoretical treatment of mathematics and physics. Such simplification is often necessary and generally very effective in rendering a problem more tractable.

Question remains however on the impact of such treatment – if everything else is the same, will it make any difference to consider a uniform material slab a mere planar one or with thickness. If difference does exist, how much it imparts on the final results? To answer this question, let's start from the fiber composite theory. Since as mentioned before all heterogeneous materials can be viewed as composites by substituting the fiber and matrix with different types of constituents in the materials, the analysis below should have wider implications.

##### b. Theoretical descriptions

For a fiber reinforced composite system with fiber volume fraction  $V_f$ , the orientation of an arbitrary fiber in the system is uniquely defined by a pair  $(\theta, \phi)$  where  $\theta, \phi$  are the base and polar angles the fiber makes with the  $z$  axis and the  $xy$  plane, respectively. The system fiber orientation probability density function (*pdf*) can be in general expressed as  $\Omega(\theta, \phi)$ , and mathematically there is

$$\int_0^\pi \int_0^\pi \Omega(\theta, \phi) \sin \theta d\theta d\phi = 1 \quad (17)$$

The fiber volume fraction  $V_f$  for a given system of course remains constant. However, if we cut a cross section on the composite, the fiber *area* fractions (the ratio of the areas occupied by the fiber and the composite) of different such cross sections will in general not equal to the overall fiber volume fraction, nor will they be a constant, dependent on the location of the cross section. Then if we use another pair  $(\Theta, \Phi)$  to represent the direction of the cross section with  $\Theta, \Phi$  being the orientation angles of the normal of the plane as seen in Figure 19. Pan<sup>310</sup> has demonstrated that both the fiber volume and area fractions are related by the system *pdf* as

$$A(\Theta, \Phi) = \Omega(\Theta, \Phi)V_f \quad (18)$$

where  $\Omega(\Theta, \Phi)$  is the corresponding value of the *pdf* at the plane direction  $(\Theta, \Phi)$ . This connection and indeed the difference between the fiber volume and area fractions in Equation 18 are useful. First it provides a tool to predict the anisotropy of the material system – the behaviors of the material as a function of the direction concerned. It meanwhile suggests that the fiber orientation is the cause for the anisotropy. Furthermore, it indicates that to ignore the difference due to system dimensionality here is to assume that  $A(\Theta, \Phi) \equiv V_f$  or  $\Omega(\Theta, \Phi) \equiv 1$ , that is, to assume the system to be of both isotropy and homogeneity. Actually, derivation of the widely known Rule of Mixtures in composites required that  $A(\Theta, \Phi) = \text{const.} = V_f$ , which happens to be true only in the unidirectional fiber reinforced composites at the cross sections perpendicular to fiber orientation where there is indeed  $\Omega(\Theta, \Phi) \equiv 1$ . For heterogeneous and anisotropic materials, the impact of system dimensionality is easier to see now: clearly Equation 18 only works for 3D cases, for it becomes dependent only on one angle in 2D systems. So for 2D and 3D cases of otherwise identical systems, the normalization condition Equation 17 will require different values for the *pdf*  $\Omega(\theta, \phi)$ , thus resulting in different outcomes.

(Fig. 19)

### c. *Experimental verifications and their ramifications.*

Experimental verification of this dimensionality influence is more difficult because of the thorny issue of differentiating 2D from 3D settings in practice. Kirkpatrick however, in studying the conductance of mixed porous systems, reported such a difference between 2D and 3D cases from numerical results in his widely cited paper<sup>311</sup>. Wang and Li<sup>312, 313</sup> also noted that theoretically predicted 3D transport phenomena often differ from their 2D counterparts of identical boundary conditions, and attributed this to the difference in surface-to-volume ratios. More recently we performed the effective thermal conductivity modeling in both 2D- and 3D cases<sup>314</sup>. We maintained the identical length and height of 2D cell domains but added the cell number along the *third* dimension to develop a 3D case. Our predicted effective thermal conductivities as in Figure 20 are always smaller at 2D cases than at 3D ones, consistent with the conclusion by Kirkpatrick<sup>311</sup>. The difference diminished at both ends when system porosity is zero or 100%, i.e., *this dimensionality effect exists only in porous media.*

(Fig. 20)

## E. Wisdom of Nature versus Intelligent Design

### a. *Attraction to (or temptation from) Biomimetics*

There are ample examples, including those mentioned in this article, supporting the commonly accepted opinion that Nature can offer solutions for many problems plaguing our modern society: “After 3.8 billion years of evolution, nature has learned: What works. What is



appropriate. What lasts”<sup>315</sup>. As more expressly stated by Ruiz-Hitzky, Darder *et al* that “Biological systems usually adopt an intelligent combination of many parallel functional processes, which are mutually and dynamically connected to each other in optimized harmony”<sup>316</sup>.

Biomimetics (aka biomimesis, biomimicry, bionics, biognosis, biologically inspired design) is seen as an effective conduit from Nature to synthetic systems. Vincent<sup>100</sup> reviewed some successful cases of biomimetics including in flight, plant expansion, bio-sensing, materials toughness in wood, and nacre, and made the differentiation between biomimetics (copying the Nature), and bio-inspired developments where some human alternations have been done during the process. The view is widely shared that learning from nature is a highly valuable approach for human creativity<sup>6, 317, 318</sup>, since for the ever-increasing demand of changing environment and competition for survival, biological systems have evolved to improve their functionality, and the resulting hierarchies in plants, animals, physiological systems are logical manifestation of high efficiency and adaptability. It is therefore up to us to explore, decode and understand the accumulated efficiency embedded in such systems, and to apply the learned new knowledge for society’s benefit. One added advantage in bionics is that “... the design rules from Nature can be extended into non-biological environments once moved into a laboratory setting and less constrained by the requirements for survival of living organisms<sup>319</sup>.”

It was also pointed out by Eadie and Ghosh<sup>10</sup> that nature follows the path of least resistance (least expenditure of energy), while often using the most common materials to accomplish a task. Following is a brief summary of more examples. The mechanism of pine cone opening relies on the humidity sensitive outer layer of the ovuliferous scales “to expand or shrink in response to moisture in the atmosphere, while the inner layer remains relatively unresponsive<sup>320</sup>”. Theoretical analyses as well as experimental data point to the fact that Nature uses high modulus fibers of high aspect ratio with small inter-fiber spacing to achieve good adhesion<sup>194</sup>. The water repellency of the bird feather in general is attributed to the “trapped air space in the multi-scale texture formed by the barbs, barbules and tomenta with nano-sized grooves, forming an air cushion at the feather–water interface thereby keeping the feather from being wet<sup>321</sup>”. The thermal-insulating property of duck feathers is attributed to the trapped air in their nanoscaled, hierarchical and fractal structures<sup>322</sup>. Stegmaier *et al.*<sup>323</sup> reported the development of a solar thermal collector, based on the supposed solar function of the polar bear fur and skin, with high light-transmission capability using a spacer fabric with translucence coatings on both sides<sup>10</sup>. Additional instances include structural or physical coloring from butterflies<sup>53</sup>, extreme water repellency and self-cleaning from plants and animals<sup>14, 42</sup>, fouling resistance from marine organisms<sup>324</sup>, novel materials by silk proteins from silkworms and spiders mixed with other polymers (both natural and synthetic) and/or inorganic particles<sup>325</sup>, a new family of artificial polymer nanocomposites that mimic the architecture and the mechanic adaptability of the sea cucumber dermis<sup>326</sup>, dynamic hydrogels for biosensing, actuation, and tissue engineering applications<sup>327</sup>, artificial muscles<sup>328</sup> etc. Perhaps the list can culminate at this one - “Bacteria such as *Colon bacillus* have flagella and swim by the high-speed rotation of the flagella, which is driven by an ultras-small motor. The flagellar motor with a diameter of 30nm can rotate 1,500 times per minute and can change rotational direction within 1 ms: the size and functions of this are far beyond the level of man-made machines. These amazing bio-machines are assembled of numerous protein parts surprisingly by a spontaneous low-energy process”<sup>316</sup>.

Even more amazingly, as added by Fratzl and Weinkamer<sup>6</sup> “...biological materials may also serve as ion reservoirs (bone is a typical example), as chemical barriers (like cell membranes),

have catalytic function (such as enzymes), transfer chemical into kinetic energy (such as the muscle), etc.” Of further interest is “to implement the ability to switch the structure of the material at different levels of the hierarchy using external signals such as temperature, pH, magnetic or electric fields, and thereby direct a change in a material’s properties” — an attribute referred to as mutability<sup>76</sup>. The significance in understanding such mechanisms from biological materials is profound in enhancing our capability of designing new generation of smart materials. Finally biomimetics should promote sustainability much like Nature does from ‘cradle to grave’, from raw material usage to recyclability<sup>10</sup>.

Giving the fascinating and even seemingly mystical power of nature, a few cautionary words may be in order here so we don’t fall into the trap of Intelligent Design in our pursuing bio-inspiration.

*b. Evolution not optimization*

To start, Darwin himself<sup>329</sup> already warned “natural selection will not produce absolute perfection”. As we all know that natural selection in simple term is “a process where organisms passes on to the next generations only those heritable traits that give them an advantage over their competitors<sup>330</sup>.” But there is a competing factor in the process termed genetic drift, a process in which “there are *random* changes to a generation’s genes during reproduction<sup>183</sup>.” and “there is absolutely no way in which biological systems could be immune from the stochasticity that is inherent in Brownian motion itself<sup>331</sup>.” In other words, biomimetics can go astray and there is risk with it.

First, it is usually difficult to measure the relative importance of the selection and drift<sup>332</sup> and the comparative importance of these two forces in driving evolutionary change is still an area of current research<sup>333</sup>. In other words, it is not always self-evident whether a trait is advantageous or not. A good example is the “loss of pigments from animals that live in caves, a change that produces no obvious advantage or disadvantage in complete darkness<sup>334</sup>.” The central concept of natural selection is the evolutionary fitness of an organism<sup>335</sup>, and the fitness is measured by an organism’s ability to survive and reproduce. However, a fitness for a particular species is not guaranteed beneficial to human needs, as cautioned by Fratzl and Weinkamer that “it is not evident at all that the lessons learned from biological materials will be directly applicable to the design of new engineering materials. This implies that we might be fooled, if we just take solutions found by Nature as optimal for a certain requirement which we hardly know<sup>6</sup>.”

Another issue is related to the so-called exaptations, structures originally adapted for one function, but coincidentally became somewhat useful for other function in the process. One example is the African lizard *Holaspis guentheri*, “which developed an extremely flat head for hiding in crevices. However, in this species, the head has become so flattened that it assists in gliding from tree to tree—an exaptation”<sup>336</sup>.

One more layer of complexity has to do with a common misconception that evolution has goals or long-term plans. However sufficient evidence has shown this is not the case<sup>337</sup>. Evolution is more of a passive reaction to the environment due to survival instinct, instead of a proactive exploration with clear overall purpose required in an optimization process.

Finally “One of the major problems confronting modern biology is to understand how complex morphological structures arise during development and how they are altered during evolution”<sup>338</sup>. In other words, our current knowledge about biological systems is still rather limited.

*c. Define and identify the traits for inspiration*

Less philosophically and more to our topic, natural biological materials have their share of weaknesses, especially from human perspective. Slow growth and low temperature resistance are apparently the first set of them.

A simple imitation of a biological system is rarely successful and some revisions from human are required. “ More often than not, the technical abstraction is possible only because a biologist has pointed out an interesting or unusual phenomenon and has uncovered the general principles behind its functioning (e.g. the self-cleaning lotus effect). Only then does the biological principle become available outside biology for biomimetic use. The result is often unexpected and seldom resembles the biological prototype <sup>102</sup>”.

Vincent also provided some warning remarks <sup>102</sup> that “illustrate some of the dangers involved in copying from nature without thorough mechanistic understanding”. First, natural materials are often multifunctional and we should not copy the undesirable functions. Also, although natural composites exhibit outstanding combinations of properties, these properties are usually limited to narrow temperature range, and subject to moisture hysteresis as noted in <sup>339</sup> that the moisture influences the mechanical behavior of rigid composites, but these effects are often not reversible upon removal of moisture. Finally, because of limited raw chemical compositions, the natural constituents themselves have deficiencies in levels of properties.

Just as importantly, biomimicry is often a tedious and demanding process, particularly so when dealing with a complex biological system. The nacre structure in Figure 21 can serve as an example. The toughening mechanisms in the nacre consist of crack blunting and branching; microcrack formation; sliding and pullout of aragonite plates; polymeric ligament formation into craze to bridge cracks; and possible strain hardening and shearing of the organic material, and have been well studied and understood <sup>5, 340</sup>. However if our goal is to design synthetic laminates that bear the attributes, and thus the architecture shown in Figure 21, the technical challenges would include, as outlined in <sup>5</sup>, “(1) lamination of the component phases should form a highly ordered microstructure; (2) the thick phase should have high hardness and be surrounded by the thin phase, which should be softer, tenacious, highly plastic, and capable of strain hardening; (3) interfaces should be strong but tailored so that delamination occurs before cracking across the stiff, brittle component; and, (4) no continuous path for easy fracture should be presented (no interfaces should line up along directions of loading).”

(Fig. 21)

## **V. CONCLUDING REMARKS**

### **A. Major issues covered in this article**

Instead of offering another comprehensive review of current research activities in the fields, this paper represents mainly an effort to derive or theorize some generic principles based on the existing research results.

It first listed the major characteristics resulted from, or associated with, structural heterogeneity and hierarchy in materials. It then presented several typical biological natural material systems

including wood, bone and others to illustrate the proposed views. The paper also discussed the man-made smart material – textiles to demonstrate that textiles are hierarchal, multifunctional, highly complex and arguably the engineered material closest on a par with biological materials in structural complexity, and more importantly we can still learn quite a few new things from them in development of novel materials.

In Section 3, the paper summarized several general approaches in developing a hierarchal material system at various scales, including structure thinning and splitting, laminating and layering, spatial and angular orientation, heterogenization and hybridization, shape and geometrical features, and analyzed the advantages associated with them. It also stressed the adverse consequences once the existing structural hierarchy breaks down, especially in biological systems due to various mutations. It further discussed the influences of moisture and air on material properties, giving that both air and water are omnipresent in biological materials.

It then dealt with in Section 4 some related theoretical issues including packing and ordering, the bi-modular mechanics, the behavior non-affinities due to disparity in hierarchal levels, the importance of system dimensionality in a hierarchal material system, and more philosophically, the issues of Nature's wisdom versus Intelligent Design.

## **B. Conclusions and their practical significance**

Hierarchy, multiphase and multiscale observed in natural materials occur not by accident but a manifestation of adaptation and improvement through the evolution process. It should be better studied, understood and more importantly utilized in our engineering designs for more efficient materials with novel properties.

In our analysis, we have demonstrated that structural hierarchy in a material system always or nearly produces multiple phases (or heterogeneity) in the system, and often brings directionality to render it anisotropic. Such complexities inevitably lead to more intricate behaviors of the material.

By looking into the existing research results on such biological materials as wood, bone and a few others, we have demonstrated how such hierarchal, multi-scaled, heterogenized or multi-phased structures are advantageous. Also new research has confirmed a deterioration of biological system performance once its hierarchical structure breaks down due to mutation. Additionally, textiles are hierarchal, multifunctional, and highly similar to biological materials in complexity; but unlike biomaterials, *textile is made from a human design so that its macro properties allow for alternation or optimization*. Another interesting feature of textile is that *any force that stresses a textile is, at the same time, reinforcing it*. Therefore a better and deeper understanding of the intrinsic mechanisms in textile behaviors and the manipulation process of tiny fibrous components in textile processing can be beneficial for research into other novel materials.

We have more explicitly and systematically demonstrated that structure hierarchies can be manifested in several features and each one improves the system performance in different ways. For instance, by branching out or splitting a material, we can maximize the specific area, arrest the cracks in the system, increase the contact adhesion, improve the structural flexibility, and promote the property synergy and processibility. Next, by employing layered structures and introducing spatial and angular orientations, we can design material systems with tailed performance and functionalities. It becomes much easier in a hierarchical system to adjust

individual properties independently so as to tailor to our needs. Lastly, blending or hybridization is a well known technique to achieve property compensation and compatibility for synergy. Because of the distinctions in properties of the constituents in different phases in a composite system, one can manipulate the distribution and relative proportion of each phase to optimize the system behavior. On the other hands, the omnipresence of air and moisture in materials, and their often significant impact on system properties should not be underestimated.

In our dealing with the theoretical issues, we stressed the importance of fundamental research of packing and ordering problem on such processes as material mixing, forming and assembling. We pointed out that synthetic self-assembly is *a process equivalent to growth in natural biological systems*. We then showed, in addition to the anisotropy, the so-called “bi-modular” behavior is prevalent in biomaterials such that their entire stress-strain relationship is quite different when under tension load versus under compression. Consequently, the validity of nano-indentation technique is rather limited when dealing with the mechanics of hierarchical material at nano scale.

Furthermore, we confirmed an interesting phenomenon in multiphase hierarchical material structures, i.e., seemingly disconnection between the macro-properties and the corresponding properties of its constituents, and concluded that such non-affinities are caused by structural hierarchy - in a hierarchal material system. Different structural components are connected in many ways at various levels and their behaviors are thus often not entirely synchronized, bringing significant inconsistency. In addition, we illustrated the importance of system dimensionality and demonstrated that when all other conditions are the same, there exists a difference in material behaviors when treated as a 2D versus a 3D case. This difference vanishes in homogeneous systems.

At the end, giving the fascinating and even seemingly mystical power of Nature, a few cautionary words are given so we don't fall into the trap of Intelligent Design in our pursuing bio-inspiration. First Darwin himself already stated, “natural selection will not produce absolute perfection”. Evolution is more of a passive reaction to the environment due to survival instinct than a proactive exploration with clear overall purpose required in an optimization process. During the evolution process, there are always two competing factors, the selection for the fitness and the drift by random factors in driving the outcome. Also our current knowledge about biological systems is often limited in understanding the mechanisms involved in a desirable function we want to imitate from a natural system. Furthermore, natural systems have their share of weakness, including slow growth and low temperature resistance, yet some of them may not be as apparent. Finally biomimicry is often a tedious and demanding process, and a simple copy of a biological system is rarely successful.

### **C. Outlook**

It is obviously a daunting task for anyone to attempt to propose even a relatively comprehensive list of pending problems in such an enormously huge field. Instead, we just offered some personal thoughts in this paper on some of the major issues, theoretical, numerical and experimental, in the hope that they can invite more discussion.

Regardless, one thing clear is that future for materials science and engineering is growingly more bright and promising, and its prime time is still yet to arrive. Material science has turned increasingly into a multi-disciplinary area involving all of the fundamental sciences, and

therefore the major breakthroughs in materials research were, have been and will continuously be, cultivated and impelled by the advances in those fundamental science fields.

Classic mathematical approaches, such as boundary problems of differential equations, have clearly encountered major challenges in their effectiveness in dealing with complex hierarchical composites materials - they even don't have a well defined boundary to begin with. While waiting for new and more systematic mathematical frame tools, computational methodologies based on, for instance, the first principles, molecular dynamics, and other lattice discrete methods have demonstrated their power in tackling extremely intricate problems in materials science. Computer simulations have also led the way in dealing with nonlinearities, statistical variations, irregularities, and probabilistic, stochastic and chaotic issues involved in such material systems. More advanced methods and instruments are also emerging constantly to provide more effective means in experimentally exploring the related phenomena. In other words, both challenges and opportunities are laid ahead in our pursuing for knowledge on new and novel materials.

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## References:

1. M. A. Meyers, P. Y. Chen, A. Y. M. Lin and Y. Seki, *Progress in Materials Science* **53** (1), 1-206 (2008).
2. A. E. Barron and R. N. Zuckermann, *Current Opinion in Chemical Biology* **3** (6), 681-687 (1999).
3. R. Lakes, *Nature* **361** (6412), 511-515 (1993).
4. A. C. Neville, *Biology of Fibrous Composites: Development beyond the Cell Membrane* (The University Press, Cambridge, UK, 1993).
5. D. A. Tirrell, *Hierarchical Structures in Biology as a Guide for New Materials Technology*. (National Research Council, Washington, D.C., 1994).
6. P. Fratzl and R. Weinkamer, *Progress in Materials Science* **52**, 1263–1334 (2007).
7. M. J. Buehler, S. Ketten and T. Ackbarow, *Progress in Materials Science* **53** (8), 1101-1241 (2008).
8. J. F. V. Vincent, *Journal of Materials Research* **23** (12), 3140-3147 (2008).
9. J. W. C. Dunlop and P. Fratzl, *Annual Review of Materials Research* **40**, 1-24 (2010).
10. L. Eadie and T. Ghosh, K. , *J. R. Soc. Interface* **8**, 761-775 (2011).
11. Z. Q. Zhang, Y. W. Zhang and H. J. Gao, *Proceedings of the Royal Society B-Biological Sciences* **278** (1705), 519-525 (2011).
12. A. H. Groschel, F. H. Schacher, H. Schmalz, O. V. Borisov, E. B. Zhulina, A. Walther and A. H. E. Muller, *Nature Communications* **3** (2012).
13. C. Mattheck, Kubler, H. , *The Internal Optimization of Trees*. (Springer Verlag, Berlin, 1995).
14. H. Bargel, K. Koch, Z. Cerman and C. Neinhuis, *Functional Plant Biology* **33** (10), 893-910 (2006).
15. B. J. Enquist, G. B. West, E. L. Charnov and J. H. Brown, *Nature* **408** (6813), 750-750 (2000).
16. K. Balani, R. R. Patel, A. K. Keshri, D. Lahiri and A. Agarwal, *Journal of the Mechanical Behavior of Biomedical Materials* **4** (7), 1440-1451 (2011).
17. F. Bosia, T. Abdalrahman and N. M. Pugno, *Nanoscale* **4** (4), 1200-1207 (2012).
18. N. Yao, A. K. Epstein, W. W. Liu, F. Sauer and N. Yang, *Journal of the Royal Society Interface* **6** (33), 367-376 (2009).
19. D. Stelitano and D. H. Rothman, *Physical Review E* **62** (5), 6667-6680 (2000).
20. M. Wang and N. Pan, *Materials Science & Engineering R-Reports* **63** (1), 1-30 (2008).
21. M. R. Wang, J. K. Wang, N. Pan and S. Y. Chen, *Physical Review E* **75**, 3 (2007).
22. Q. Chen and N. M. Pugno, *Journal of the Mechanical Behavior of Biomedical Materials* **19**, 3-33 (2013).
23. M. De Volder and A. J. Hart, *Angewandte Chemie-International Edition* **52** (9), 2412-2425 (2013).
24. B. Fang, J. H. Kim, M. S. Kim and J. S. Yu, *Accounts of Chemical Research* **46** (7), 1397-1406 (2013).
25. K. Johnston and V. Harmandaris, *Soft Matter* **9** (29), 6696-6710 (2013).
26. A. W. Thompson, *On Growth and Form: The Complete Revised Edition*. (Dover, New York, 1992 ).
27. K. Autumn and N. Gravish, *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences* **366** (1870), 1575-1590 (2008).
28. K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing and R. J. Full, *Nature* **405** (6787), 681-685 (2000).
29. A. K. Geim, S. V. Dubonos, I. V. Grigorieva, K. S. Novoselov, A. A. Zhukov and S. Y. Shapoval, *Nature Materials* **2** (7), 461-463 (2003).
30. W. R. Hansen and K. Autumn, *Proceedings of the National Academy of Sciences of the United States of America* **102** (2), 385-389 (2005).
31. J. P. O'Brien, S. R. Fahnstock, Y. Termonia and K. C. H. Gardner, *Advanced Materials* **10** (15), 1185. (1998).

32. Y. Tian, N. Pesika, H. B. Zeng, K. Rosenberg, B. X. Zhao, P. McGuiggan, K. Autumn and J. Israelachvili, *Proceedings of the National Academy of Sciences of the United States of America* **103** (51), 19320-19325 (2006).
33. H. B. Zeng, N. Pesika, Y. Tian, B. X. Zhao, Y. F. Chen, M. Tirrell, K. L. Turner and J. N. Israelachvili, *Langmuir* **25** (13), 7486-7495 (2009).
34. B. X. Zhao, N. Pesika, H. B. Zeng, Z. S. Wei, Y. F. Chen, K. Autumn, K. Turner and J. Israelachvili, *Journal of Physical Chemistry B* **113** (12), 3615-3621 (2009).
35. E. Arzt, S. Gorb and R. Spolenak, *Proceedings of the National Academy of Sciences of the United States of America* **100** (19), 10603-10606 (2003).
36. T. Miyazaki, K. Yamaoka, J. P. Gong and Y. Osada, *Macromol. Rapid Commun.* **23**, 447-455 (2002).
37. M. F. Ashby and Y. J. M. Brechet, *Acta Materialia* **51** (19), 5801-5821 (2003).
38. N. D. Petkovich and A. Stein, *Chemical Society Reviews* **42** (9), 3721-3739 (2013).
39. M. H. Sun, C. X. Luo, L. P. Xu, H. Ji, O. Y. Qi, D. P. Yu and Y. Chen, *Langmuir* **21** (19), 8978-8981 (2005).
40. N. Zhao, X. Y. Lu, X. Y. Zhang, H. Y. Liu, S. X. Tan and J. Xu, *Progress in Chemistry* **19** (6), 860-871 (2007).
41. D. T. Fullwood, S. R. Niezgodna, B. L. Adams and S. R. Kalidindi, *Progress in Materials Science* **55** (6), 477-562 (2010).
42. B. Bhushan and Y. C. Jung, *Progress in Materials Science* **56** (1), 1-108 (2011).
43. Z. Burton and B. Bhushan, *Nano Letters* **5** (8), 1607-1613 (2005).
44. A. B. D. Cassie and S. Baxter, *Transactions of the Faraday Society* **40**, 0546-0550 (1944).
45. R. Furstner, W. Barthlott, C. Neinhuis and P. Walzel, *Langmuir* **21** (3), 956-961 (2005).
46. L. C. Gao and T. J. McCarthy, *Langmuir* **22** (14), 5998-6000 (2006).
47. K. Koch, B. Bhushan and W. Barthlott, *Soft Matter* **4** (10), 1943-1963 (2008).
48. M. L. Ma and R. M. Hill, *Current Opinion in Colloid & Interface Science* **11** (4), 193-202 (2006).
49. A. Marmur, *Langmuir* **20** (9), 3517-3519 (2004).
50. C. W. Mason, *Journal of Physical Chemistry* **30** (3), 383-395 (1926).
51. E. J. Denten, *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences* **258** (824), 285-313 (1970).
52. R. O. Prum, R. H. Torres, S. Williamson and J. Dyck, *Nature* **396** (6706), 28-29 (1998).
53. M. Srinivasarao, *Chemical Reviews* **99** (7), 1935-1961 (1999).
54. S. Kinoshita, S. Yoshioka and K. Kawagoe, *Proceedings of the Royal Society of London Series B-Biological Sciences* **269** (1499), 1417-1421 (2002).
55. A. R. Parker, V. L. Welch, D. Driver and N. Martini, *Nature* **426** (6968), 786-787 (2003).
56. P. Vukusic and J. R. Sambles, *Nature* **424** (6950), 852-855 (2003).
57. J. Zi, X. D. Yu, Y. Z. Li, X. H. Hu, C. Xu, X. J. Wang, X. H. Liu and R. T. Fu, *Proceedings of the National Academy of Sciences of the United States of America* **100** (22), 12576-12578 (2003).
58. A. R. Parker, *Philosophical Transactions of the Royal Society of London Series A-Mathematical Physical and Engineering Sciences* **362** (1825), 2709-2720 (2004).
59. S. Kinoshita and S. Yoshioka, *Chemphyschem* **6** (8), 1442-1459 (2005).
60. S. Kinoshita, S. Yoshioka and J. Miyazaki, *Reports on Progress in Physics* **71**, 7 (2008).
61. Y. P. Yi, L. Y. Zhu and Z. G. Shuai, *Macromolecular Theory and Simulations* **17** (1), 12-22 (2008).
62. M. J. Buehler, *Nature Nanotechnology* **5** (3), 172-174 (2010).
63. C. S. Du, D. Heldbrant and N. Pan, *Materials Letters* **57** (2), 434-438 (2002).
64. C. S. Du, D. Heldebrant and N. Pan, *Journal of Materials Science Letters* **21** (7), 565-568 (2002).
65. Y. W. Su, B. H. Ji, K. Zhang, H. J. Gao, Y. G. Huang and K. Hwang, *Langmuir* **26** (7), 4984-4989 (2010).
66. Y. W. Su, B. H. Ji, Y. Huang and K. C. Hwang, *Langmuir* **26** (24), 18926-18937 (2010).
67. K. Tai, M. Dao, S. Suresh, A. Palazoglu and C. Ortiz, *Nature Materials* **6** (6), 454-462 (2007).
68. B. H. Ji and H. J. Gao, *Annual Review of Materials Research* **40**, 77-100 (2010).
69. H. J. Gao, *International Journal of Fracture* **138** (1-4), 101-137 (2006).



70. B. Bar-On and H. D. Wagner, *Journal of Structural Biology* **183** (2), 149-164 (2013).
71. V. M. Pereira, A. H. C. Neto, H. Y. Liang and L. Mahadevan, *Physical Review Letters* **105** (15), 156603-156604 (2010).
72. F. Vollrath and D. P. Knight, *Nature* **410** (6828), 541-548 (2001).
73. H. M. Zhang and J. Y. Liu, *Progress in Natural Science* **15** (9), 769-776 (2005).
74. M. Heim, L. Romer and T. Scheibel, *Chemical Society Reviews* **39** (1), 156-164 (2010).
75. R. V. Lewis, *Chemical Reviews* **106** (9), 3762-3774 (2006).
76. M. J. Buehler and T. Ackbarow, *Materials Today* **10** (9), 46-58 (2007).
77. G. Bratzel and M. J. Buehler, *Biopolymers* **97** (6), 408-417 (2012).
78. D. E. Aston, J. R. Bow and D. N. Gangadear, *International Materials Reviews* **58** (3), 167-202 (2013).
79. Y. L. Yang and C. Wang, *Chemical Society Reviews* **38** (9), 2576-2589 (2009).
80. G. Bratzel and M. J. Buehler, *Journal of the Mechanical Behavior of Biomedical Materials* **7**, 30-40 (2012).
81. E. Bini, D. P. Knight and D. L. Kaplan, *Journal of Molecular Biology* **335** (1), 27-40 (2004).
82. C. Caloz, *Materials Today* **12** (3), 12-20 (2009).
83. M. H. Lu, L. Feng and Y. F. Chen, *Materials Today* **12** (12), 34-42 (2009).
84. D. R. Smith, J. B. Pendry and M. C. K. Wiltshire, *Science* **305** (5685), 788-792 (2004).
85. W. J. Padilla, D. N. Basov and D. R. Smith, *Materials Today* **9** (7-8), 28-35 (2006).
86. M. Hosseini, S. A. Fazlzadeh and P. Marzocca, *International Journal of Bifurcation and Chaos* **21** (3), 931-954 (2011).
87. Z. H. Jin and R. C. Batra, *Journal of the Mechanics and Physics of Solids* **44** (8), 1221-1235 (1996).
88. W. Y. Lee, D. P. Stinton, C. C. Berndt, F. Erdogan, Y. D. Lee and Z. Mutasim, *Journal of the American Ceramic Society* **79** (12), 3003-3012 (1996).
89. S. Srivastava, A. Santos, K. Critchley, K. S. Kim, P. Podsiadlo, K. Sun, J. Lee, C. L. Xu, G. D. Lilly, S. C. Glotzer and N. A. Kotov, *Science* **327** (5971), 1355-1359 (2010).
90. G. M. Whitesides and B. Grzybowski, *Science* **295** (5564), 2418-2421 (2002).
91. V. Schaller and A. R. Bausch, *Nature* **481** (7381), 268-269 (2012).
92. G. B. West, J. H. Brown and B. J. Enquist, *Science* **284** (5420), 1677-1679 (1999b).
93. J. H. Brown, V. K. Gupta, B. L. Li, B. T. Milne, C. Restrepo and G. B. West, *Philosophical Transactions of the Royal Society B-Biological Sciences* **357** (1421), 619-626 (2002).
94. G. B. West, J. H. Brown and B. J. Enquist, *Science* **276** (5309), 122-126 (1997).
95. C. Kuhnert, D. Helbing and G. B. West, *Physica a-Statistical Mechanics and Its Applications* **363** (1), 96-103 (2006).
96. G. B. West, J. H. Brown and B. J. Enquist, *Nature* **400** (6745), 664-667 (1999a).
97. G. B. West, B. J. Enquist and J. H. Brown, *Proceedings of the National Academy of Sciences of the United States of America* **106** (17), 7040-7045 (2009).
98. L. M. A. Bettencourt, J. Lobo and G. B. West, *European Physical Journal B* **63** (3), 285-293 (2008).
99. J. van Leeuwen and P. Aerts, *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences* **358** (1437), 1427-1428 (2003).
100. J. F. V. Vincent, *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences* **358** (1437), 1597-1603 (2003).
101. J. F. V. Vincent, *Science* **304** (5670), 520-520 (2004).
102. J. F. V. Vincent, O. A. Bogatyreva, N. R. Bogatyrev, A. Bowyer and A. K. Pahl, *Journal of the Royal Society Interface* **3** (9), 471-482 (2006).
103. P. Fratzl, *Journal of the Royal Society Interface* **4** (15), 637-642 (2007).
104. K. Konopka, *Archives of Metallurgy and Materials* **53** (3), 767-781 (2008).
105. N. M. Pugno, *Journal of Physics-Condensed Matter* **19**, 39 (2007).
106. N. M. Pugno and A. Carpinteri, *Philosophical Magazine Letters* **88** (6), 397-405 (2008).
107. H. M. Yao and H. J. Gao, *International Journal of Solids and Structures* **44** (25-26), 8177-8193 (2007).

108. M. R. Wang, N. Yang and Z. Y. Guo, *Journal of Applied Physics* **110** (6) (2011).
109. G. Jeronimidis, in *Structural biological materials*, edited by E. M (Pergamon, New York, 2001).
110. J. W. C. Dunlop and P. Fratzl, *Annu. Rev. Mater. Res.* **40**, 1-24 (2010).
111. J. D. Currey, *Bones. Structure and Mechanics*. (Princeton Univ. Press, Princeton, 2002).
112. J. Aizenberg and P. Fratzl, *Advanced Materials* **21** (4), 387-388 (2009).
113. U. G. K. Wegst and M. F. Ashby, *Philosophical Magazine* **84** (21), 2167-2181 (2004).
114. J. Kopecek, *Biomaterials* **28**, 5185-5192 (2007).
115. S. Banerjee, R. K. Das and U. Maitra, *Journal of Materials Chemistry* **19** (37), 6649-6687 (2009).
116. V. Sahni, T. A. Blackledge and A. Dhinojwala, *Nature Communications* **1** (2010).
117. J. H. Waite and M. L. Tanzer, *Science* **212** (4498), 1038-1040 (1981).
118. H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science* **318** (5849), 426-430 (2007).
119. H. Lee, *Nature* **465** (7296), 298-299 (2010).
120. E. Arzt, *Materials Science & Engineering C-Biomimetic and Supramolecular Systems* **26** (8), 1245-1250 (2006).
121. H. F. Jakob, P. Fratzl and S. E. Tschegg, *Journal of Structural Biology* **113** (1), 13-22 (1994).
122. R. Wimmer, G. M. Downes and R. Evans, *Tree Physiology* **22** (7), 449-457 (2002).
123. G. Jeronimidis, *Proceedings of the Royal Society of London Series B-Biological Sciences* **208**, 447 (1980).
124. P. Fratzl, I. Burgert and H. S. Gupta, *Physical Chemistry Chemical Physics* **6** (24), 5575-5579 (2004).
125. L. Kohler and H. C. Spatz, *Planta* **215** (1), 33-40 (2002).
126. J. Keckes, I. Burgert, K. Fruhmman, M. Muller, K. Kolln, M. Hamilton, M. Burghammer, S. V. Roth, S. Stanzl-Tschegg and P. Fratzl, *Nature Materials* **2** (12), 810-814 (2003).
127. P. Fratzl, H. S. Gupta, E. P. Paschalis and P. Roschger, *Journal of Materials Chemistry* **14** (14), 2115-2123 (2004).
128. S. Weiner and H. D. Wagner, *Annual Review of Materials Science* **28**, 271-298 (1998).
129. P. Fratzl, *Nature Materials* **7** (8), 610-612 (2008).
130. J. D. Currey, *Journal of Experimental Biology* **202** (23), 3285-3294 (1999).
131. J. D. Currey, *Journal of Bone and Mineral Research* **18** (4), 591-598 (2003).
132. B. H. Ji and H. J. Gao, *Journal of the Mechanics and Physics of Solids* **52** (9), 1963-1990 (2004).
133. H. J. Gao, B. H. Ji, I. L. Jager, E. Arzt and P. Fratzl, *Proceedings of the National Academy of Sciences of the United States of America* **100** (10), 5597-5600 (2003).
134. H. Peterlik, P. Roschger, K. Klaushofer and P. Fratzl, *Nature Materials* **5** (1), 52-55 (2006).
135. S. Kamat, X. Su, R. Ballarini and A. H. Heuer, *Nature* **405** (6790), 1036-1040 (2000).
136. J. Aizenberg, J. C. Weaver, M. S. Thanawala, V. C. Sundar, D. E. Morse and P. Fratzl, *Science* **309** (5732), 275-278 (2005).
137. B. R. Lawn and J. J. W. Lee, *Acta Biomaterialia* **5** (6), 2213-2221 (2009).
138. X. D. Li, W. C. Chang, Y. J. Chao, R. Z. Wang and M. Chang, *Nano Letters* **4** (4), 613-617 (2004).
139. A. Miserez, Y. L. Li, J. H. Waite and F. Zok, *Acta Biomaterialia* **3** (1), 139-149 (2007).
140. A. Miserez, T. Schneberk, C. J. Sun, F. W. Zok and J. H. Waite, *Science* **319** (5871), 1816-1819 (2008).
141. S. Krauss, E. Monsonogo-Ornan, E. Zelzer, P. Fratzl and R. Shahar, *Advanced Materials* **21** (4), 407-412 (2009).
142. J. L. Hu and J. G. Teng, *Finite Elements in Analysis and Design* **21** (4), 225-237 (1996).
143. G. Indelicato and A. Albano, *Journal of Elasticity* **94** (1), 33-54 (2009).
144. N. Pan and P. Gibson, *Thermal and Moisture Transport in Fibrous Material*. (Woodhead Publishing Ltd., Cambridge, 2006).
145. J. Hu, *Structure and mechanics of woven fabrics*. (Woodhead Publishing Ltd, Cambridge, 2004).
146. J. W. S. Hearle, P. Grosberg and S. Backer, *Structural Mechanics of Yarns and Fabrics*. (Wiley-Interscience, New York, 1969).

147. J. W. S. Hearle, J. J. Thwaites and J. Amirbayat, *Mechanics of flexible fibre assemblies* (Sijthoff & Noordhoff, Germantown. MD, 1980).
148. R. Postle, G. A. Carnaby and S. D. Jong, *The Mechanics of Wool Structures*. (Ellis Horwood, 1988).
149. G. Galileo, *Dialogue Concerning Two New Sciences*. (Evanston, Leyden, 1914).
150. N. Pan and D. Brookstein, *Journal of Applied Polymer Science* **83** (3), 610-630 (2002).
151. L. R. G. Treloar, *British Journal of Applied Physics* **13** (7), 314 (1962).
152. S. L. Phoenix, *International Journal of Engineering Science* **13** (3), 287-304 (1975).
153. B. D. Coleman, *Journal of the Mechanics and Physics of Solids* **7** (1), 60-70 (1958).
154. H. E. Daniels, *Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences* **183** (995), 405-435 (1945).
155. N. Pan, *Textile Research Journal* **63** (9), 504-514 (1993).
156. N. Pan, *Composites Science and Technology* **56** (3), 311-327 (1996).
157. A. A. Shahpurwala and P. Schwartz, *Textile Research Journal* **59** (1), 26-32 (1989).
158. N. Pan and M. Y. Yoon, *Textile Research Journal* **66** (4), 238-244 (1996).
159. E. Cerda and L. Mahadevan, *Physical Review Letters* **90**, 074302 (2003).
160. D. Breid and A. J. Crosby, *Soft Matter* **7** (9), 4490-4496 (2011).
161. E. Cerda, K. Ravi-Chandar and L. Mahadevan, *Nature* **419** (6907), 579-580 (2002).
162. V. Kantsler, E. Segre and V. Steinberg, *Physical Review Letters* **99**, 17 (2007).
163. E. Sharon, B. Roman, M. Marder, G. S. Shin and H. L. Swinney, *Nature* **419** (6907), 579-579 (2002).
164. F. T. Peirce, J., *J. Textile Inst.* **17**, T355-368 (1926).
165. G. N. Haddad and J. E. Sutton, *Textile Research Journal* **42** (8), 452 (1972).
166. T. V. Ratnam, Shankara.Ks, Underwoo.C and Govindar.K, *Textile Research Journal* **38** (4), 360-365 (1968).
167. H. L. Cox, *British Journal of Applied Physics* **3** (3), 72-79 (1952).
168. C. J. Monego, S. Backer, Y. P. Qui and K. Machida, *Composites Science and Technology* **50** (4), 451-456 (1994).
169. C. J. Monego and S. Backer, *Textile Research Journal* **38** (7), 762-766 (1968).
170. N. Pan, K. H. Chen, C. J. Monego and S. Backer, *Proceedings of the Royal Society of London Series A: Mathematical Physical and Engineering Sciences* **454** (1972), 1109-1127 (1998).
171. N. Pan and R. Postle, *Philosophical Transactions of the Royal Society of London Series A: Mathematical Physical and Engineering Sciences* **354** (1714), 1875-1897 (1996).
172. W. A. Curtin, *Journal of the American Ceramic Society* **74** (11), 2837-2845 (1991).
173. W. A. Curtin, *Journal of Materials Science* **26** (19), 5239-5253 (1991).
174. H. D. Wagner, O. Lourie, Y. Feldman and R. Tenne, *Applied Physics Letters* **72** (2), 188-190 (1998).
175. P. K. Baumgart, *Journal of Colloid and Interface Science* **36** (1), 71 (1971).
176. D. Li and Y. N. Xia, *Advanced Materials* **16** (14), 1151-1170 (2004).
177. T. J. Sill and H. A. von Recum, *Biomaterials* **29** (13), 1989-2006 (2008).
178. S. Ramakrishna, K. Fujihara, W. E. Teo, T. Yong, Z. W. Ma and R. Ramaseshan, *Materials Today* **9** (3), 40-50 (2006).
179. L. Gonzalez-Macia, A. Morrin, M. R. Smyth and A. J. Killard, *Analyst* **135** (5), 845-867 (2010).
180. H. K. Baca, E. C. Carnes, C. E. Ashley, D. M. Lopez, C. Douthit, S. Karlin and C. J. Brinker, *Biochimica Et Biophysica Acta-General Subjects* **1810** (3), 259-267 (2011).
181. M. Shimomura and T. Sawadaishi, *Current Opinion in Colloid & Interface Science* **6** (1), 11-16 (2001).
182. B. Michel, A. Bernard, A. Bietsch, E. Delamarche, M. Geissler, D. Juncker, H. Kind, J. P. Renault, H. Rothuizen, H. Schmid, P. Schmidt-Winkel, R. Stutz and H. Wolf, *Ibm Journal of Research and Development* **45** (5), 697-719 (2001).
183. D. J. Futuyma, *Evolution*. (Sinauer Associates, Inc. , Sunderland, Massachusetts, 2005).
184. M. J. Buehler and Y. C. Yung, *Nature Materials* **8** (3), 175-188 (2009).

185. F. Cervantes-Sodi, T. McNicholas, J. Simmons, J. Liu, G. Csnyai, A. Ferrari and S. Curtarolo, *ACS Nano* **4**, 6950–6956 (2010).
186. L. Mahadevan, *Faraday Discussions* **139**, 9-19 (2008).
187. A. A. Griffith, *Philosophical Transactions of the Royal Society of London. Series A*, **221**, 163-198 (1921).
188. H. J. Gao and S. H. Chen, *Journal of Applied Mechanics-Transactions of the ASME* **72** (5), 732-737 (2005).
189. B. V. Derjaguin, V. M. Muller and Y. P. Toporov, *Journal of Colloid and Interface Science* **53** (2), 314-326 (1975).
190. K. L. Johnson, K. Kendall and A. D. Roberts, *Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences* **324** (1558), 301-& (1971).
191. D. Maugis, *Journal of Colloid and Interface Science* **150** (1), 243-269 (1992).
192. M. Varenberg, A. Peressadko, S. Gorb and E. Arzt, *Appl. Phys. Lett.* **89**, 121905 121901-121903 (2006).
193. R. Spolenak, S. Gorb, H. J. Gao and E. Arzt, *Proceedings of the Royal Society of London Series A-Mathematical Physical and Engineering Sciences* **461** (2054), 305-319 (2005).
194. B. Aksak, M. P. Murphy and M. Sitti, *Langmuir* **23** (6), 3322-3332 (2007).
195. A. Peressadko and S. N. Gorb, *Journal of Adhesion* **80**, 247-261 (2004).
196. H. J. Gao and H. M. Yao, *Proceedings of the National Academy of Sciences of the United States of America* **101** (21), 7851-7856 (2004).
197. R. J. Bassett, R. Postle and N. Pan, *Textile Research Journal* **69** (11), 866-875 (1999).
198. L. Pocivavsek, R. Dellsy, A. Kern, S. Johnson, B. H. Lin, K. Y. C. Lee and E. Cerda, *Science* **320** (5878), 912-916 (2008).
199. S. McCormick, *Science* **317** (5838), 605-606 (2007).
200. S. Ketten, Z. P. Xu, B. Ihle and M. J. Buehler, *Nature Materials* **9** (4), 359-367 (2010).
201. C. P. Brangwynne, F. C. MacKintosh, S. Kumar, N. A. Geisse, J. Talbot, L. Mahadevan, K. K. Parker, D. E. Ingber and D. A. Weitz, *Journal of Cell Biology* **173** (5), 733-741 (2006).
202. A. Woesz, J. C. Weaver, M. Kazanci, Y. Dauphin, J. Aizenberg, D. E. Morse and P. Fratzl, *Journal of Materials Research* **21** (8), 2068-2078 (2006).
203. B. D. Agarwal and L. J. Broutman, *Analysis and Performance of Fiber Composites*, 2nd ed. (Wiley-Interscience, New York, 1990).
204. M. J. Buehler, *Nano Today* **5**, 379-383 (2010).
205. S. Ketten and M. J. Buehler, *Nano Letters* **8** (2), 743-748 (2008).
206. A. Tarakanova and M. J. Buehler, *Jom* **64** (2), 214-225 (2012).
207. H. Y. Liang and L. Mahadevan, *Proceedings of the National Academy of Sciences of the United States of America* **108** (14), 5516-5521 (2011).
208. L. A. Hirano, M. T. Escote, L. S. Martins, G. L. Mantovani and C. H. Scuracchio, *Artificial Organs* **35** (5), 478-483 (2011).
209. Y. Forterre, J. M. Skotheim, J. Dumais and L. Mahadevan, *Nature* **433** (7024), 421-425 (2005).
210. H. Y. Liang and L. Mahadevan, *Proceedings of the National Academy of Sciences of the United States of America* **106** (52), 22049-22054 (2009).
211. R. Bieleski, J. Elgar and J. Heyes, *Annals of Botany* **86** (6), 1175-1183 (2000).
212. W. G. van Doorn and U. van Meeteren, *Journal of Experimental Botany* **54** (389), 1801-1812 (2003).
213. Q. Ji, M. Miyahara, J. P. Hill, S. Acharya, A. Vinu, S. B. Yoon, J. S. Yu, K. Sakamoto and K. Ariga, *Journal of the American Chemical Society* **130** (8), 2376-2377 (2008).
214. G. M. Grason, *Physical Review Letters* **108** (5) (2012).
215. W. Wagermaier, H. S. Gupta, A. Gourrier, M. Burghammer, P. Roschger and P. Fratzl, *Biointerphases* **1** (1), 1-5 (2006).
216. J. Hearle, *Physics World* (November ), 22 (2010).
217. L. Mahadevan and S. Rica, *Science* **307** (5716), 1740-1740 (2005).
218. S. Clark and R. Prabhakar, *Soft Matter* **7**, 5536 (2011).
219. T. Yue and X. Zhang, *Journal of Physical Chemistry B* **115** (40), 11566-11574 (2011).

220. G. M. Grason, Physics Reports-Review Section of Physics Letters **433** (1), 1-64 (2006).
221. G. M. Grason and R. F. Bruinsma, Physical Review Letters **99** (9), 098101 (2007).
222. T. Gibaud, E. Barry, M. J. Zakhary, M. Henglin, A. Ward, Y. Yang, C. Berciu, R. Oldenbourg, M. F. Hagan, D. Nicastro, R. B. Meyer and Z. Dogic, Nature **481** (7381), 348-U127 (2012).
223. B. W. Rosen, AIAA Journal **2** (11), 1985-1991 (1964).
224. C. Zweben and B. W. Rosen, Journal of the Mechanics and Physics of Solids **18** (3), 189 (1970).
225. L. S. Sutherland, R. A. Shenoi and S. M. Lewis, Composites Science and Technology **59** (2), 209-220 (1999).
226. J. Weiss, Engineering Fracture Mechanics **68** (17-18), 1975-2012 (2001).
227. A. Carpinteri, P. Cornetti and S. Puzzi, Applied Mechanics Reviews **59** (1-6), 283-305 (2006).
228. L. Y. Sun, R. F. Gibson, F. Gordaninejad and J. Suhr, Composites Science and Technology **69** (14), 2392-2409 (2009).
229. S. A. Wainwright, W. D. Biggs, J. D. Currey and J. M. Gosline, *Mechanical Design in Organisms*. (Princeton Univ. Press, Princeton, 1982).
230. R. Menig, M. H. Meyers, M. A. Meyers and K. S. Vecchio, Acta Materialia **48** (9), 2383-2398 (2000).
231. A. G. Evans, Z. Suo, R. Z. Wang, I. A. Aksay, M. Y. He and J. W. Hutchinson, Journal of Materials Research **16** (9), 2475-2484 (2001).
232. R. Z. Wang, Z. Suo, A. G. Evans, N. Yao and I. A. Aksay, Journal of Materials Research **16** (9), 2485-2493 (2001).
233. F. Song, A. K. Soh and Y. L. Bai, Biomaterials **24** (20), 3623-3631 (2003).
234. P. Fratzl, H. S. Gupta, F. D. Fischer and O. Kolednik, Advanced Materials **19**, 2657 (2007).
235. S. W. a. H. A. Lowenstam, *On Biomineralization*. (Oxford University Press Inc., Oxford, UK, 1989).
236. A. Dey, G. de With and N. Sommerdijk, Chemical Society Reviews **39** (2), 397-409 (2010).
237. P. Zaslansky, R. Shahar, A. A. Friesem and S. Weiner, Advanced Functional Materials **16** (15), 1925-1936 (2006).
238. L. J. Gibson and M. F. Ashby, *Cellular solids: structure and properties*, 2nd ed. (Cambridge University Press, Cambridge, 1997).
239. S. Majumdar, R. Krishnaswamy and A. K. Sood, Proceedings of the National Academy of Sciences of the United States of America **108** (22), 8996-9001 (2011).
240. R. P. Wool, Soft Matter **4** (3), 400-418 (2008).
241. D. S. Fudge, K. H. Gardner, V. T. Forsyth, C. Riekel and J. M. Gosline, Biophysical Journal **85** (3), 2015-2027 (2003).
242. N. B. Hatzigrigoriou, S. N. Vouyiouka, C. Joly, P. Dole and C. D. Papaspyrides, Journal of Applied Polymer Science **125** (4), 2814-2823 (2012).
243. D. B. Staple, M. Loparic, H. J. Kreuzer and L. Kreplak, Physical Review Letters **102** (12), 128302 (2009).
244. J. Wu, W. Lin, Z. Wang, S. Chen and Y. Chang, Langmuir **28** (19), 7436-7441 (2012).
245. D. Lukas and N. Pan, Polymer Composites **24** (3), 314-322 (2003).
246. F. Brochard, Journal of Chemical Physics **84** (8), 4664-4672 (1986).
247. F. Casanova, C. E. Chiang, C. P. Li, I. V. Roshchin, A. M. Ruminski, M. J. Sailor and I. K. Schuller, Nanotechnology **19** (31), 315709 (2008).
248. S. P. Rigby, P. I. Chigada, E. L. Perkins, M. J. Watt-Smith, J. P. Lowe and K. J. Edler, Adsorption-Journal of the International Adsorption Society **14** (2-3), 289-307 (2008).
249. A. Wongkoblap, D. D. Do, G. Birkett and D. Nicholson, Journal of Colloid and Interface Science **356** (2), 672-680 (2011).
250. P. G. De Gennes, F. Brochard-Wyart and D. Quere, *Capillarity and Wetting Phenomena: Drops, bubbles, pearls, waves*. (Springer, New York, 2003).
251. W. W. Schultz and S. H. Davis, Journal of Rheology **26** (4), 331-345 (1982).
252. J. Eggers, Reviews of Modern Physics **69** (3), 865-929 (1997).
253. M. R. Wang, J. H. He, J. Y. Yu and N. Pan, International Journal of Thermal Sciences **46** (9), 848-855 (2007).

254. D. Donadio and G. Galli, *Nano Letters* **10** (3), 847-851 (2010).
255. K. Nassau, *The physics and chemistry of color*, 2 ed. (Wiley, New York, 2001).
256. J. Aizenberg, A. Tkachenko, S. Weiner, L. Addadi and G. Hendler, *Nature* **412** (6849), 819-822 (2001).
257. V. C. Sundar, A. D. Yablon, J. L. Grazul, M. Ilan and J. Aizenberg, *Nature* **424** (6951), 899-900 (2003).
258. T. P. J. Knowles, T. W. Oppenheim, A. K. Buell, D. Y. Chirgadze and M. E. Welland, *Nature Nanotechnology* **5** (3), 204-207 (2010).
259. C. Tekoglu, L. J. Gibson, T. Pardoen and P. R. Onck, *Progress in Materials Science* **56** (2), 109-138 (2011).
260. N. Pan, S. M. Zhao and T. Hua, *Polymer Composites* **21** (2), 187-195 (2000).
261. M. J. Buehler, *Proceedings of the National Academy of Sciences of the United States of America* **103** (33), 12285-12290 (2006).
262. D. Frenkel, *Theoretical Chemistry Accounts* **103** (3-4), 212-213 (2000).
263. E. Garcia, D. C. Williamson and A. Martinez-Richa, *Molecular Physics* **98** (3), 179-192 (2000).
264. L. Onsager, *Ann. NY Acad. Sci.* **51**, 627-659 (1949).
265. M. Levitt, M. Gerstein, E. Huang, S. Subbiah and J. Tsai, *Annual Review of Biochemistry* **66**, 549-579 (1997).
266. R. T. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
267. S. Torquato, *Random Heterogeneous Materials: Microstructure and Macroscopic Properties* (Springer, 2002).
268. P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge Univ. Press, 2000).
269. L. N. Zou, X. Cheng, M. L. Rivers, H. M. Jaeger and S. R. Nagel, *Science* **326** (5951), 408-410 (2009).
270. J. Liang and K. A. Dill, *Biophysical Journal* **78** (1), 197 (2000).
271. J. Liang and K. A. Dill, *Biophysical Journal* **81** (2), 751-766 (2001).
272. P. K. Purohit, M. M. Inamdar, P. D. Grayson, T. M. Squires, J. Kondev and R. Phillips, *Biophysical Journal* **88** (2), 851-866 (2005).
273. J. L. Gevertz and S. Torquato, *Plos Computational Biology* **4**, 8 (2008).
274. S. Torquato and Y. Jiao, *Nature* **460** (7257), 876 (2009).
275. S. P. De Gennes and G. Prost, *The Physics of Liquid Crystals*. (Clarendon Press, Oxford, 1995).
276. F. M. Richards, *Annual Review of Biophysics and Bioengineering* **6**, 151-176 (1977).
277. F. M. Richards, *Journal of Molecular Biology* **82** (1), 1-14 (1974).
278. T. C. Hales, *Discrete & Computational Geometry* **36** (1), 5-20 (2006).
279. D. A. Weitz, *Science* **303**, 968-969 (2004).
280. I. Peterson, *Science News* **154** (7), 103 (1998).
281. R. O. Erickson, *Science* **181** (4101), 705-716 (1973).
282. T. C. Hales, *Annals of Mathematics* **162** (3), 1065-1185 (2005).
283. T. C. Hales, J. Harrison, S. McLaughlin, T. Nipkow, S. Obua and R. Zumkeller, *Discrete & Computational Geometry* **44** (1), 1-34 (2010).
284. A. Haji-Akbari, M. Engel, A. S. Keys, X. Y. Zheng, R. G. Petschek, P. Palffy-Muhoray and S. C. Glotzer, *Nature* **462** (7274), 773-777 (2009).
285. A. Donev, F. H. Stillinger, P. M. Chaikin and S. Torquato, *Physical Review Letters* **92** (25), 255506 (2004).
286. Z. Y. Tang, Z. L. Zhang, Y. Wang, S. C. Glotzer and N. A. Kotov, *Science* **314** (5797), 274-278 (2006).
287. S. C. Glotzer and M. J. Solomon, *Nature Materials* **6** (8), 557-562 (2007).
288. A. Donev, I. Cisse, D. Sachs, E. Variano, F. H. Stillinger, R. Connelly, S. Torquato and P. M. Chaikin, *Science* **303** (5660), 990-993 (2004).
289. G. N. Meng, N. Arkus, M. P. Brenner and V. N. Manoharan, *Science* **327** (5965), 560-563 (2010).
290. G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science* **254** (5036), 1312-1319 (1991).

291. G. M. Whitesides and M. Boncheva, Proceedings of the National Academy of Sciences of the United States of America **99** (8), 4769-4774 (2002).
292. E. C. R. Reeve and J. S. Huxley, in *Assays on Growth and Form presented to D'arcy Wentworth Thompson*, edited by W. E. Clark and P. B. Medawar (Clarendon Press, Oxford, 1945).
293. S. A. Ambartsumyan and A. A. Khachatryan, Mechanics of Solids **1**, 29-34 (1966).
294. S. A. Ambartsumyan, Mechanics of Solids **4**, 48-56 (1969).
295. S. A. Ambartsumyan, Izv. Akad. Nauk. SSSR Mekh., **4**, 77-85 (1965).
296. K. Bertoldi, D. Bigoni and W. J. Drugan, Composites Science and Technology **68** (6), 1363-1375 (2008).
297. J. Y. Sun, H. Q. Zhu, S. H. Qin, D. L. Yang and X. T. He, Journal of Mechanical Science and Technology **24** (9), 1845-1854 (2010).
298. B. J. Briscoe, L. Fiori and E. Pelillo, Journal of Physics D-Applied Physics **31** (19), 2395-2405 (1998).
299. J. Malzbender, J. M. J. den Toonder, A. R. Balkenende and G. de With, Materials Science & Engineering R-Reports **36** (2-3), 47-103 (2002).
300. D. Bruno, S. Lato and R. Zinno, Composites Engineering **3** (5), 419-435 (1993).
301. W. W. Eltahan, G. H. Staab, S. H. Advani and J. K. Lee, Journal of Engineering Mechanics-ASCE **115** (5), 963-981 (1989).
302. E. Sacco and J. N. Reddy, Journal of Applied Mechanics-Transactions of the ASME **59** (1), 220-221 (1992).
303. Z. H. Nie, A. Petukhova and E. Kumacheva, Nature Nanotechnology **5** (1), 15-25 (2010).
304. A. Mandelis, Journal of Thermal Analysis **37** (5), 1065-1101 (1991).
305. N. Pan, Int. Journal of Nature & Design **1**, 48-60 (2007).
306. G. A. Carnaby and N. Pan, Textile Research Journal **59** (5), 275-284 (1989).
307. C. M. van Wyk, Journal of Textile Institute **37**, 282 (1946).
308. S. Niederegger, S. Gorb and Y. Jiao, J. Comp Physiol A **187**, 961-970 (2002).
309. D. G. Hepworth, A. Steven-fountain, D. M. Bruce and J. F. V. Vincent, Journal of Biomechanics **34** (3), 341-346 (2001).
310. N. Pan, Journal of Composite Materials **28**, 1500-1531 (1994).
311. S. Kirkpatrick, Rev. Mod. Phys. **45**, 574-588 (1973).
312. M. Wang and Z. X. Li, Microfluidics and Nanofluidics **1**, 62-70 (2004).
313. M. Wang and Z. X. Li, J. Eng. Thermophys. **25**, 840-842 (2004).
314. M. Wang, J. Wang, N. Pan, S. Chen and J. He, J. Phys. D: Appl. Phys. **40**, 260-265 (2007).
315. J. M. Benyus, *Biomimicry: Innovation inspired by nature*. (William Morrow and Company, Inc., New York, 1997).
316. E. Ruiz-Hitzky, M. Darder, P. Aranda and K. Ariga, Advanced Materials **22** (3), 323-336 (2010).
317. T. X. Fan, S. K. Chow and Z. Di, Progress in Materials Science **54** (5), 542-659 (2009).
318. B. Bhushan, Progress in Materials Science **53** (4), 585-710 (2008).
319. C. M. Li and D. L. Kaplan, Current Opinion in Solid State & Materials Science **7** (4-5), 265-271 (2003).
320. J. Dawson, J. F. V. Vincent and A. M. Rocca, Nature **390** (6661), 668-668 (1997).
321. E. Bormashenko, Y. Bormashenko, T. Stein and G. Whyman, Journal of Colloid and Interface Science **311** (1), 212-216 (2007).
322. J. Gao, N. Pan and W. D. Yu, International Journal of Nonlinear Sciences and Numerical Simulation **7** (1), 113-116 (2006).
323. T. Stegmaier, M. Linke and H. Planck, Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences **367** (1894), 1749-1758 (2009).
324. A. J. Scardino and R. de Nys, Biofouling **27** (1), 73-86 (2011).
325. J. G. Hardy and T. R. Scheibel, Progress in Polymer Science **35** (9), 1093-1115 (2010).
326. K. Shanmuganathan, J. R. Capadona, S. J. Rowan and C. Weder, Progress in Polymer Science **35** (1-2), 212-222 (2010).
327. W. L. Murphy, Soft Matter **7**, 3679-3688 (2011).
328. P. Brochu and Q. B. Pei, Macromolecular Rapid Communications **31** (1), 10-36 (2010).

329. C. Darwin, *The Origin of Species, Chapter 6*, 150th Anniversary Edition ed. (Signet Classic, Penguin Publishing Group, New York, 2003).
330. L. D. Hurst, *Nature Reviews Genetics* **10** (2), 83-93 (2009).
331. D. Noble, *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences* **368** (1914), 1125-1139 (2010).
332. T. Mitchell-Olds, J. H. Willis and D. B. Goldstein, *Nature Reviews Genetics* **8**, 845-856 (2007).
333. M. Nei, *Molecular Biology and Evolution* **22** (12), 2318-2342 (2005).
334. M. Protas, I. Tabansky, M. Conrad, J. B. Gross, O. Vidal, C. J. Tabin and R. Borowsky, *Evolution & Development* **10** (2), 196-209 (2008).
335. H. A. Orr, *Nature Reviews Genetics* **10** (8), 531-539 (2009).
336. S. J. Gould and E. A. Lloyd, *Proceedings of the National Academy of Sciences of the United States of America* **96** (21), 11904-11909 (1999).
337. M. J. Dougherty, *Scientific American* (July 20), <http://www.scientificamerican.com/article/is-the-human-race-evolvin/> (1998).
338. W. R. Atchley and B. K. Hall, *Biological Reviews of the Cambridge Philosophical Society* **66** (2), 101-157 (1991).
339. J. F. V. Vincent, *Advances in Botanical Research Incorporating Advances in Plant Pathology* **17**, 235-287 (1990).
340. J. Y. Sun and B. Bhushan, *Rsc Advances* **2** (20), 7617-7632 (2012).
341. M. Spinderellas, <http://www.Spinderellas.com> (2014).
342. I. R. Bruss and G. M. Grason, *Proceedings of the National Academy of Sciences of the United States of America* **109** (27), 10781-10786 (2012).



## LIST OF FIGURE CAPTION

Fig. 1. Diagrammatic examples of segments of biological distribution networks.

(A) mammalian circulatory and respiratory systems composed of branching tubes;

(B) plant vessel-bundle vascular system composed of diverging vessel elements;

(C) cross section of (B).

(A) and (B) From G. B. West, J. H. Brown and B. J. Enquist, A General Model for the Origin of Allometric Scaling Laws in Biology, *Science* **276** (5309), 122-126 (1997)<sup>94</sup>. Reprinted with permission from AAAS.

Fig. 2. Hierarchical structure of cellulose in wood.

From D. A. Tirrell, Hierarchical Structures in Biology as a Guide for New Materials Technology, Washington, DC: National Academy Press, NMAB-464, p25 (1994)<sup>5</sup>. Reprinted with permission from NAS.

Fig. 3. Hierarchical structure of a bone.

Reprinted from M. A. Meyers, P. Y. Chen, A. Y. M. Lin and Y. Seki, Biological materials: Structure and mechanical properties, *Progress in Materials Science* **53** (1), 1-206 (2008)<sup>1</sup>, with permission from Elsevier.

Fig. 4. Hierarchical structures of textiles

(A) A piece of a fabric;

(B) A yarn from the fabric;

(C) A single fiber from the yarn;

(D) Hierarchical structure of a wool fiber. Reprinted from [www.spinderellas.com](http://www.spinderellas.com) with permission from Spinderellas Creations and Fiber Mill<sup>341</sup>.

Fig. 5 Twisted yarn and a helical model

(A) A twisted yarn;

(B) A helical model.

Fig. 6. Fiber slippage and yarn twist level.

Reprinted from N. Pan, Development of a Constitutive Theory for Short-Fiber Yarns .2. Mechanics of Staple Yarn with Slippage Effect, *Textile Research Journal* **63** (9), 504-514 (1993)<sup>155</sup> with permission from SAGE Publications.

Fig. 7. Draping and formability of textiles.

Fig. 8 Direction dependence of failure behaviors.

Fig. 9 Fragmentation in a blended textile yarn.

(A) The fragmentation pattern of cotton yarns embedded in a cotton/polyester strand with 11% of cotton and 1.1TM when extended to a strain of 30%. The fragments are longer in outer layers.

(B) A single crack fragmentation pattern of cotton yarns embedded in a cotton/polyester strand with 44% cotton and 4.4 TM when extended to a strain of 13-8%.

Reprinted from C. J. Monego, S. Backer, Y. P. Qui and K. Machida, Illustration of stress/strain behavior and yarn fragmentation in a pseudo-hybrid Composite system, *Composites Science and Technology* **50** (4), 451-456 (1994)<sup>168</sup>, with permission from Elsevier.

Fig. 10. Hierarchy brings in system flexibility and controlled stiffness.

- (A) an isotropic plastic sheet;
- (B) a woven fabric;
- (C)  $\beta$ -nano crystals sheets in silk. Reprinted from S. Keten, Z. P. Xu, B. Ihle and M. J. Buehler, Nanoconfinement controls stiffness, strength and mechanical toughness of beta-sheet crystals in silk, *Nature Materials* 9 (4), 359-367 (2010)<sup>200</sup>, with permission from Macmillan Publishers Ltd.

Fig. 11. Hierarchical structures of amyloid protein materials

Reprinted from M. J. Buehler, Nanomaterials: Strength in numbers *Nature Nanotechnology* 5 (3), 172-174 (2010)<sup>62</sup>, with permission from Macmillan Publishers Ltd.

Fig. 12. Bird beak as a composite structure

- (A) The structure of a bird beak;  
Reprinted from M. A. Meyers, P. Y. Chen, A. Y. M. Lin and Y. Seki, *Biological materials: Structure and mechanical properties*, *Progress in Materials Science* 53 (1), 1-206 (2008)<sup>1</sup>, with permission from Elsevier.
- (B) The stress-strain curve for the bird beak;
- (C) The stress-strain curve for the core;
- (D) The stress-strain curve for the sheath.

Fig. 13 Tensile modulus of a hoof wall as function of water content.

Reprinted from M. A. Meyers, P. Y. Chen, A. Y. M. Lin and Y. Seki, *Biological materials: Structure and mechanical properties*, *Progress in Materials Science* 53 (1), 1-206 (2008)<sup>1</sup>, with permission from Elsevier.

Fig. 14 Effects of components size and shapes on the system effective thermal conductivity:

- (A) The effective thermal conductivity versus volume fractions of different component shapes; Reprinted from M. Wang and N. Pan, Predictions of effective physical properties of complex multiphase materials, *Materials Science & Engineering R-Reports* 63 (1), 1-30 (2008)<sup>20</sup>, with permission from Elsevier.
- (B) Composite effective thermal conductivity versus fiber length.  
Reprinted from M. R. Wang, J. H. He, J. Y. Yu and N. Pan, Lattice Boltzmann modeling of the effective thermal conductivity for fibrous materials, *International Journal of Thermal Sciences* 46 (9), 848-855 (2007)<sup>253</sup>, with permission from Elsevier.

Fig. 15 Elastic strength and energy dissipation of the collagen fibril

Reprinted from M. J. Buehler, Nature designs tough collagen: Explaining the nanostructure of collagen fibrils, *Proceedings of the National Academy of Sciences of the United States of America*, 103 (33), 12285-12290, Copyright (2006)<sup>261</sup> National Academy of Sciences, U.S.A., with permission from NAS.

Fig. 16 (A). The *face centered cubic* packing of spheres.

(B) The horizontal cross section of a twisted bundle, where circular filament sections become distorted, “stretched” along the azimuthal direction, depending on the tilt and curvature of the filament backbones. Reprinted from I. R. Bruss and G. M. Grason, Non-Euclidean geometry of twisted filament bundle packing, *Proceedings of the National Academy of Sciences of the United States of America*, 109 (27), 10781–10786 (2012)<sup>342</sup>, with permission from NAS.

Fig. 17. The cross sections of hollow fibers in polar bear fur.

Fig. 18. Hierarchy brings in system softness.

- (A) A fibrous cushion;
- (B) A portion of the foot of a fruit fly. Springer and the original publisher J. Comp Physiol A

187:961-970, (2002) S. Niederegger, S. Gorb, Y. Jiao, Contact behaviour of tenent setae in attachment pads of the blowfly *Calliphora vicina* (Diptera, Calliphoridae) <sup>308</sup>, is given to the publication in which the material was originally published, with kind permission from Springer Science and Business Media.

Fig. 19 A cross section cut from a fiber reinforced composite

Fig. 20. Dimension dependence of material thermal properties.

Reprinted from M. Wang, J. Wang, N. Pan, S. Chen and J. He, Three-dimensional effect on the effective thermal conductivity of porous media *J. Phys. D: Appl. Phys.* 40, 260–265 (2007) <sup>314</sup>, with permission from IOP Publishing Ltd.

Fig. 21 Challenges in imitating a nacre structure <sup>5</sup>

(A) Clockwise from top left: entire shell; mesostructure with mesolayers; microstructure with aragonite tiles; nanostructure showing organic interlayer.

Reprinted from M. A. Meyers, P. Y. Chen, A. Y. M. Lin and Y. Seki, Biological materials: Structure and mechanical properties, *Progress in Materials Science* 53 (1), 1-206 (2008) <sup>1</sup>, with permission from Elsevier.

(B) Scales and compositions. Reprinted from D. A. Tirrell, Hierarchical Structures in Biology as a Guide for New Materials Technology, Washington, DC: National Academy Press, NMAB-464, p42 (1994) <sup>5</sup>, with permission from NAS.

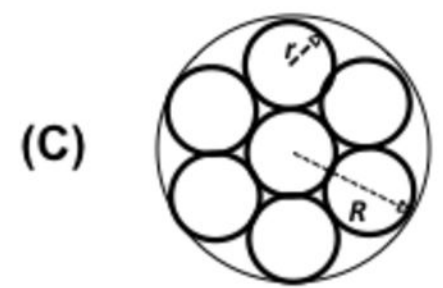
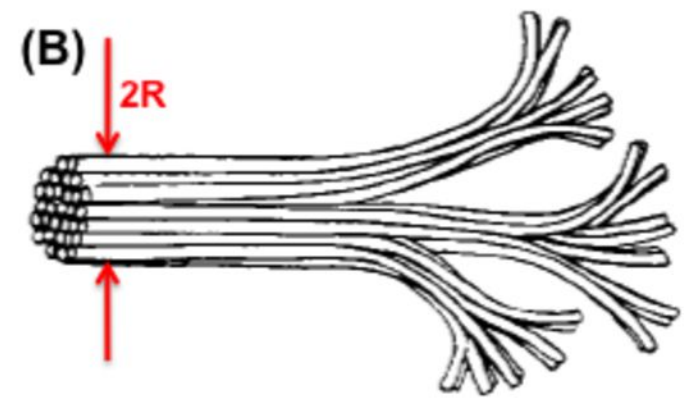
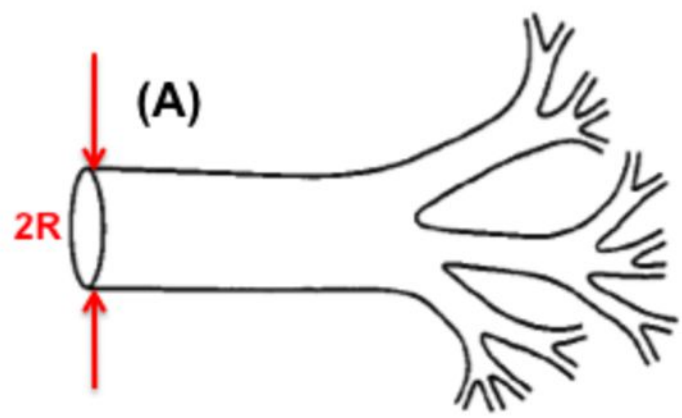


Fig. 1.

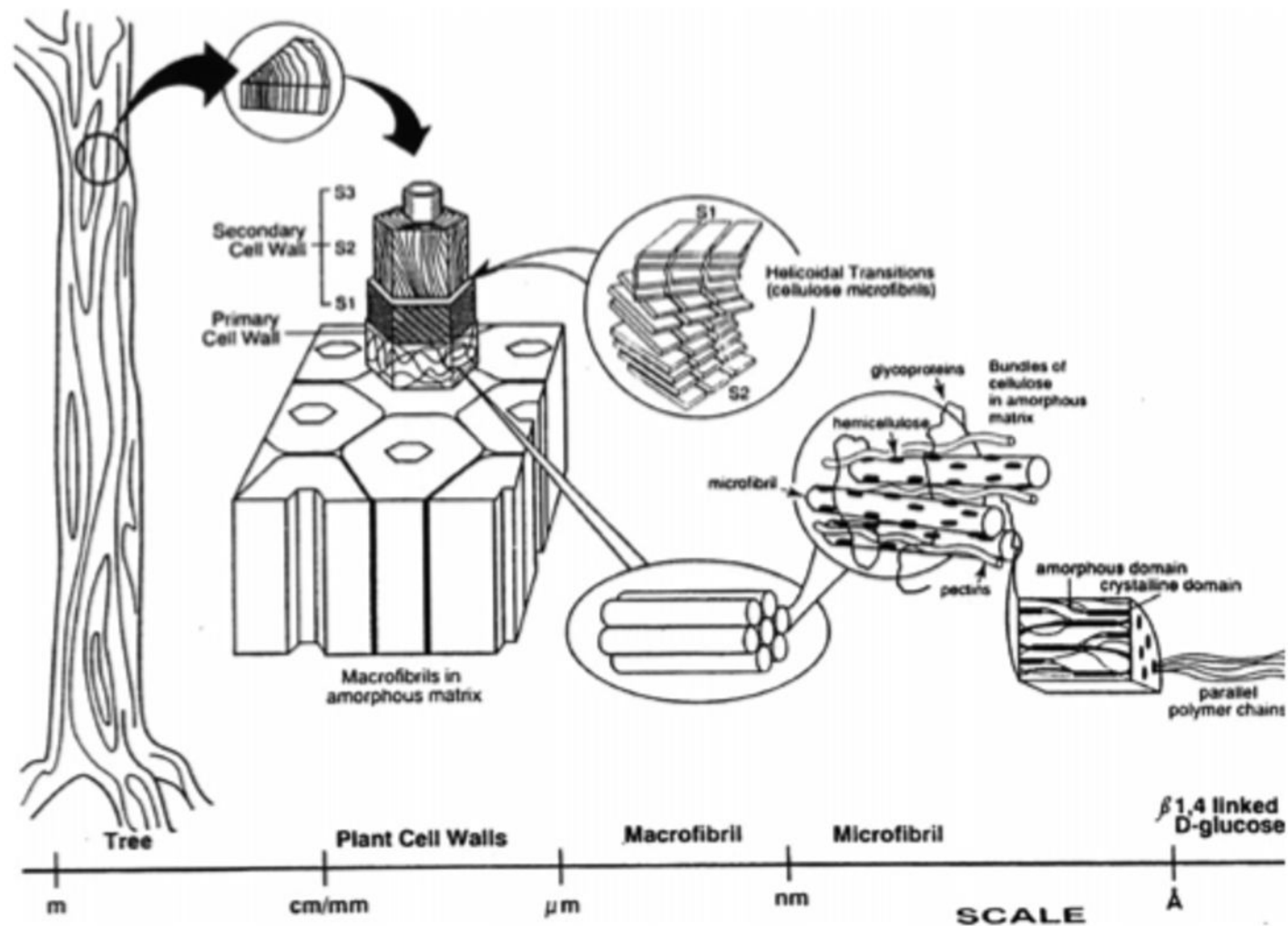


Fig. 2.

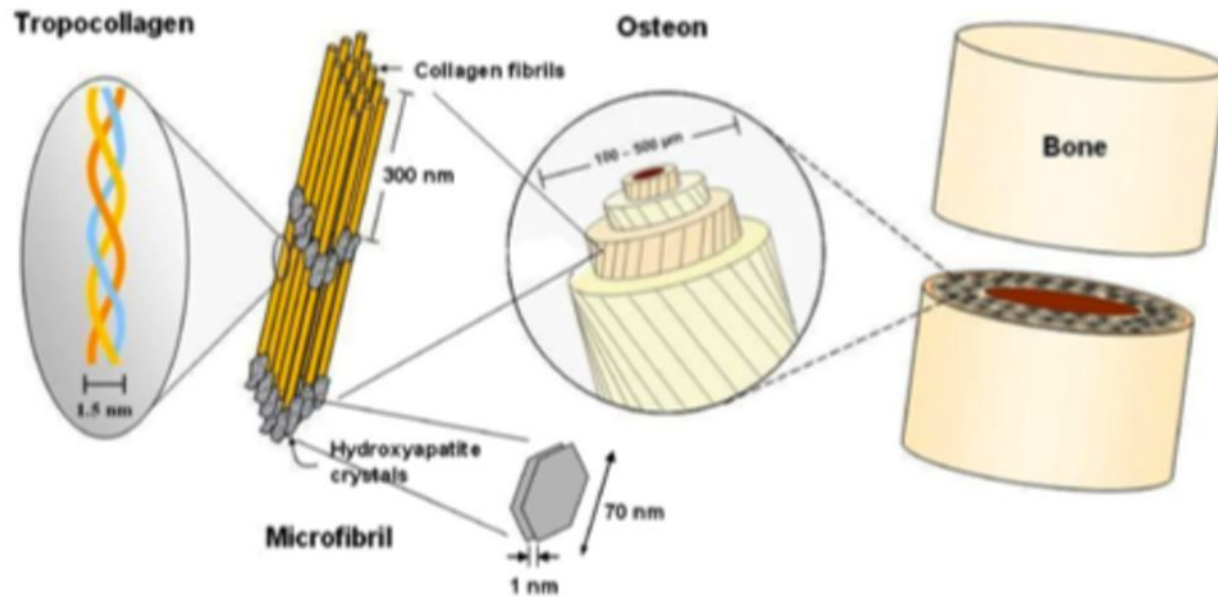
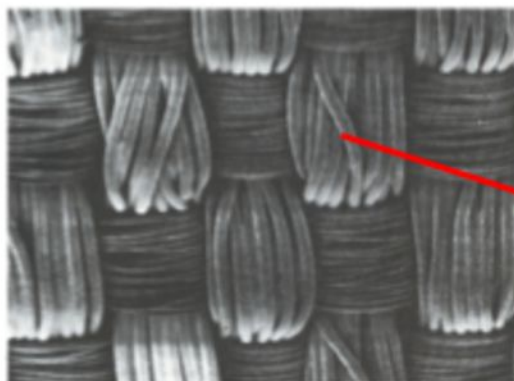
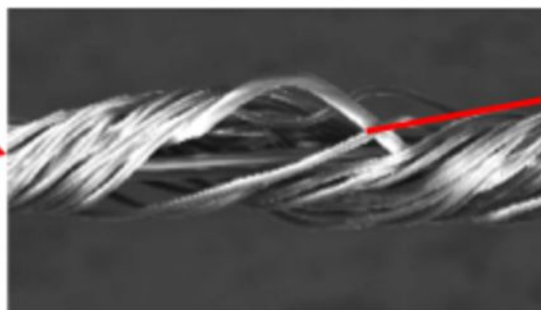


Fig. 3.

**(A) A fabric**



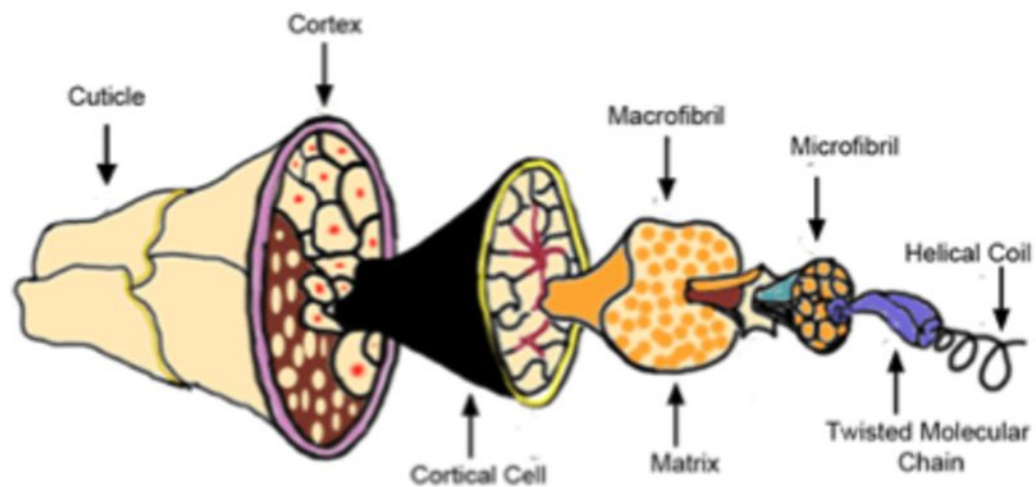
**(B) A yarn**



**(C) A single wool fiber**



**(D) Hierarchy of wool fiber**



**Fig. 4.**

(A)



(B)

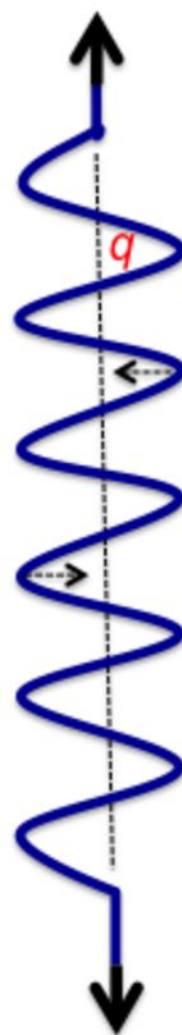


Figure 5



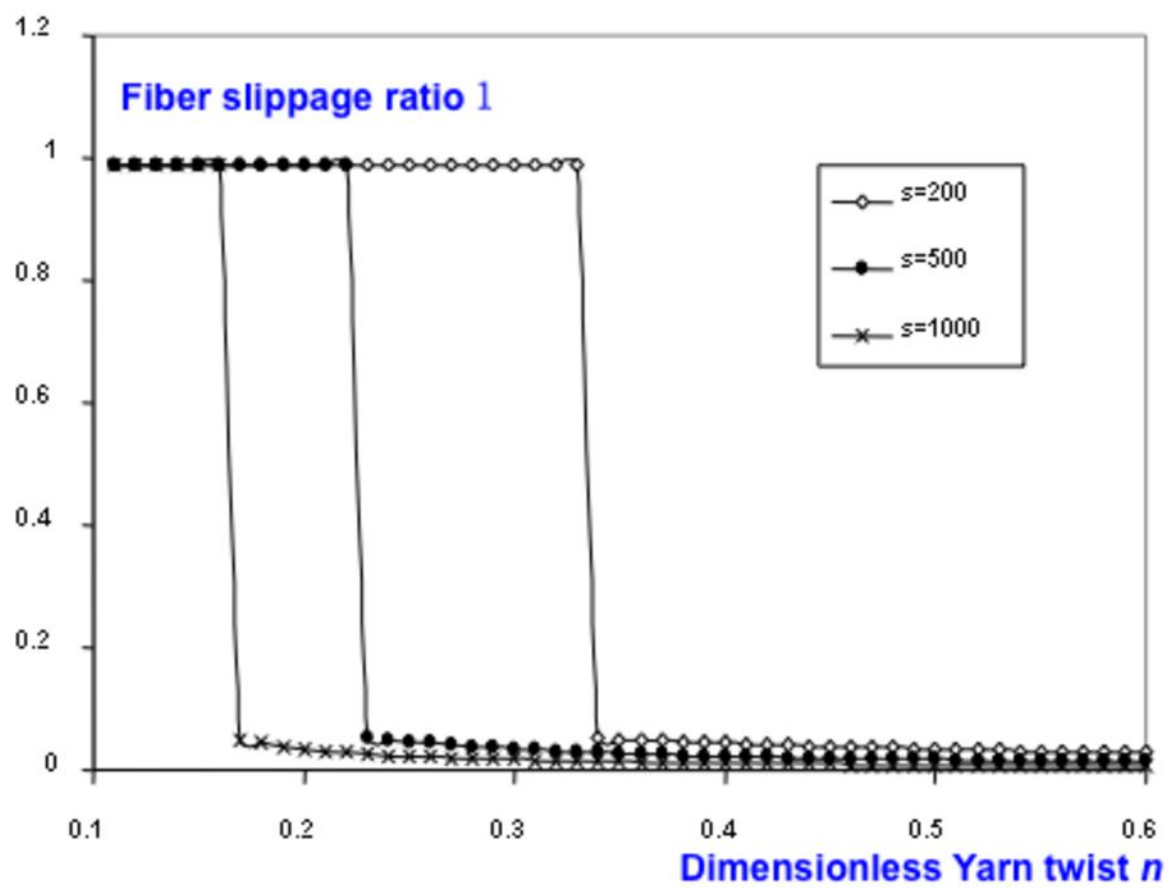


Fig. 6.



Figure 7

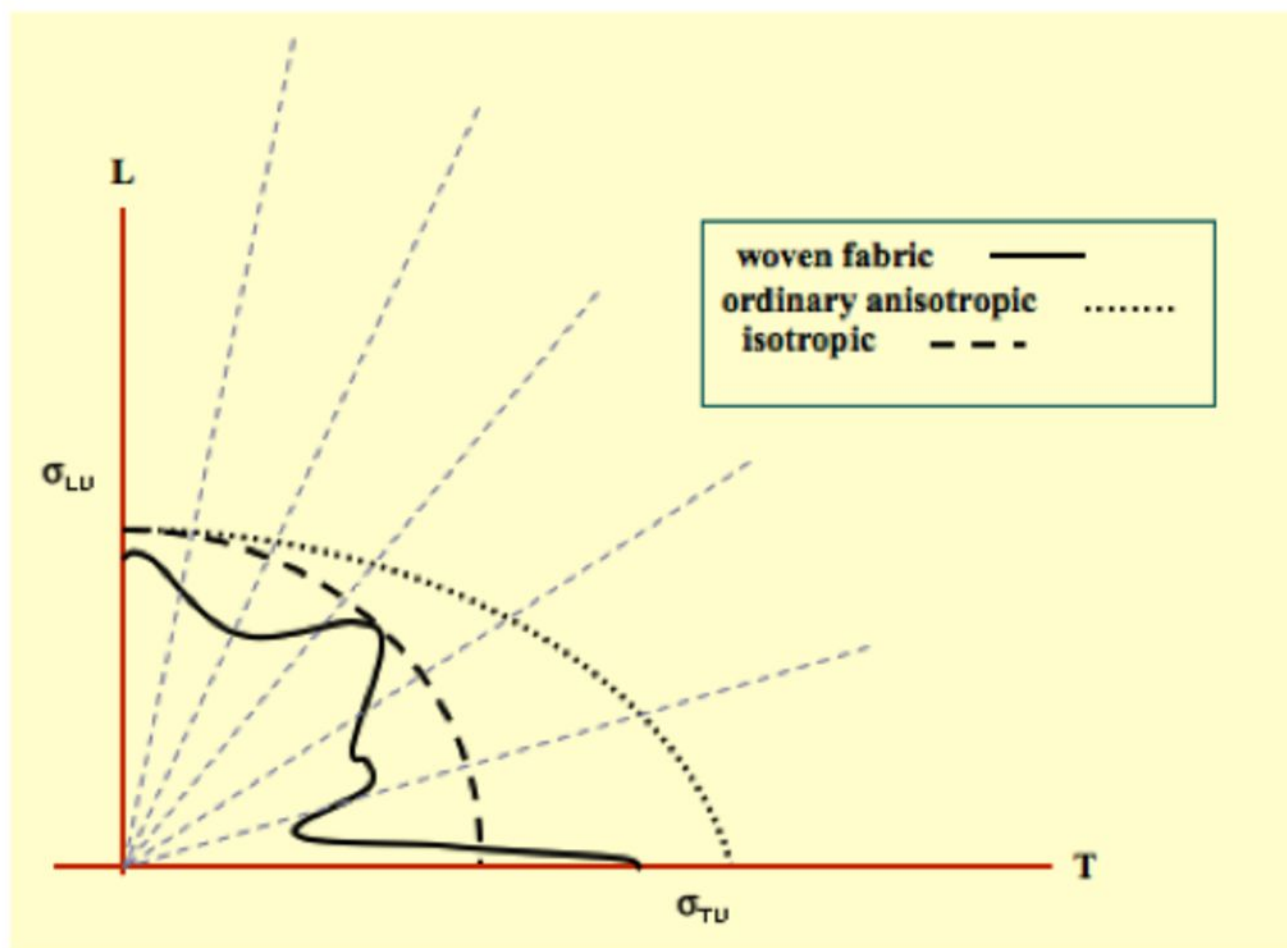


Figure 8

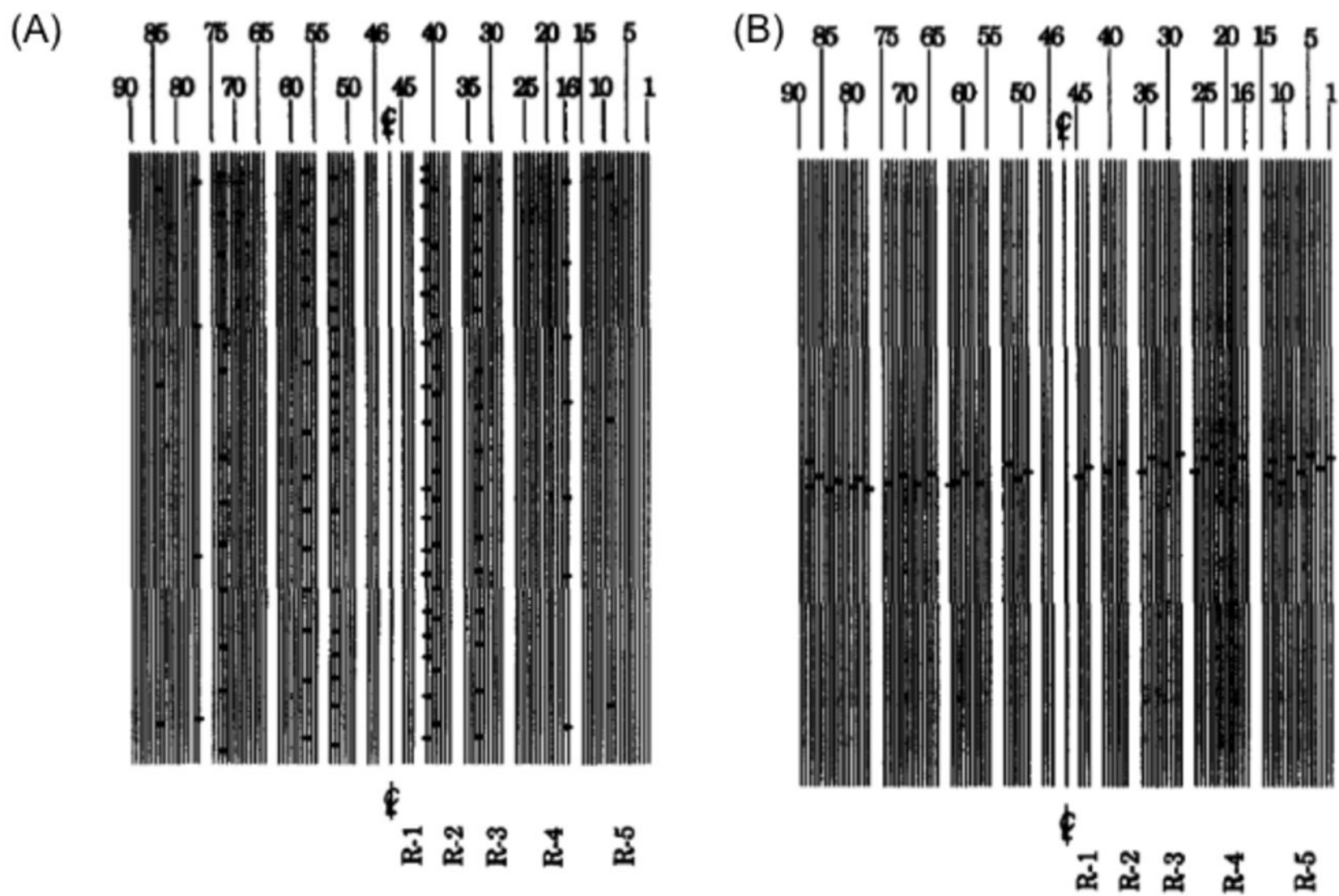
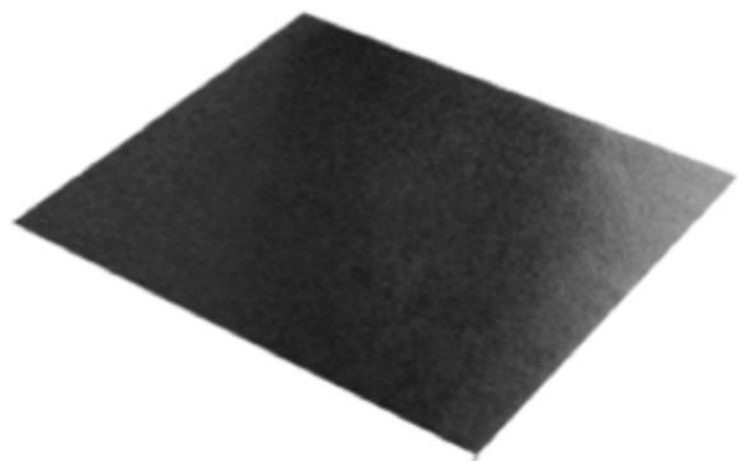


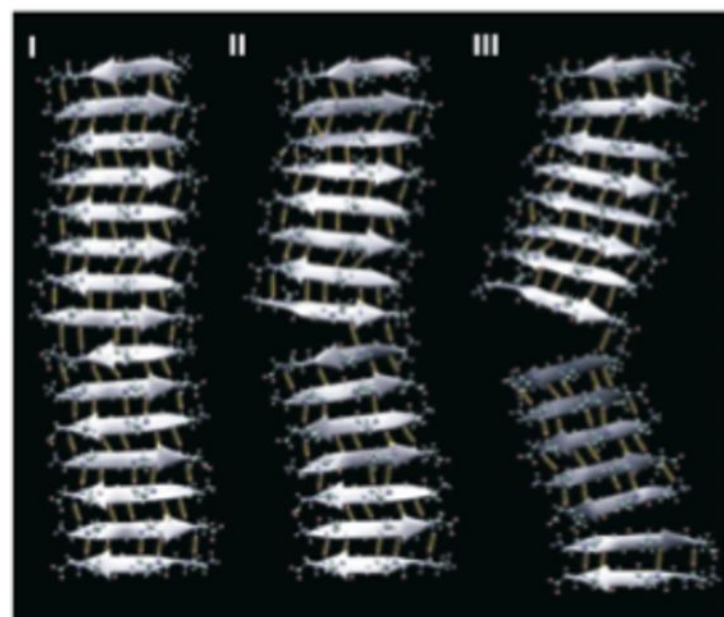
Figure 9



(A)



(B)



(C)

Fig. 10.

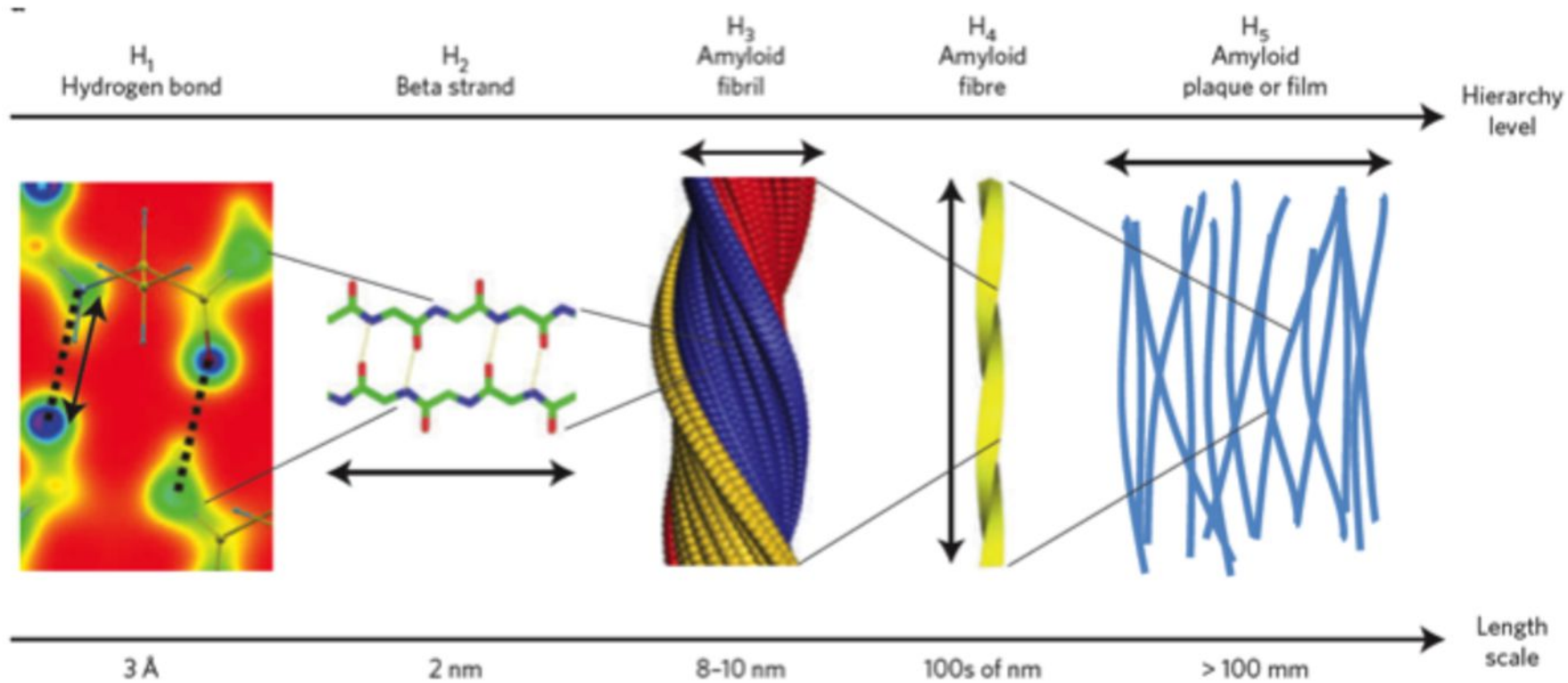


Figure 11

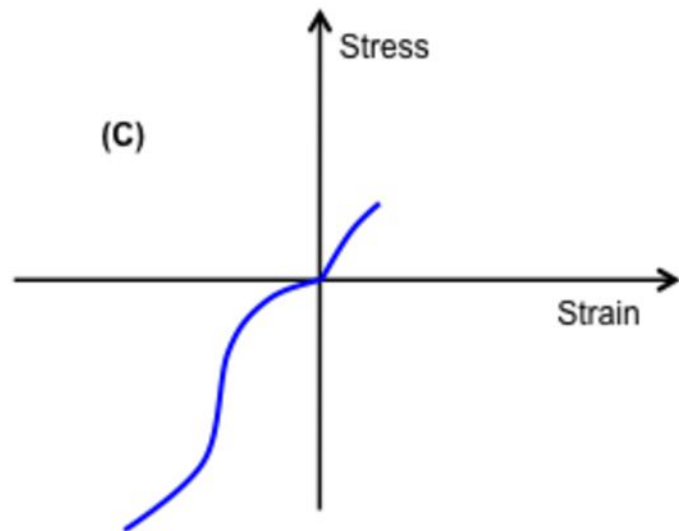
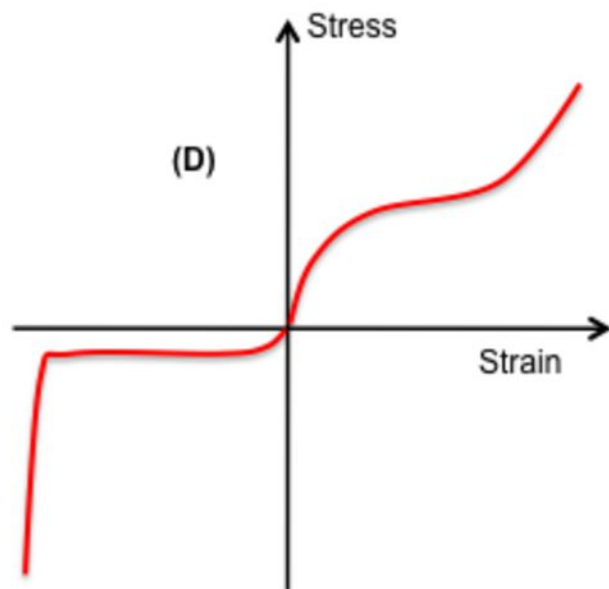
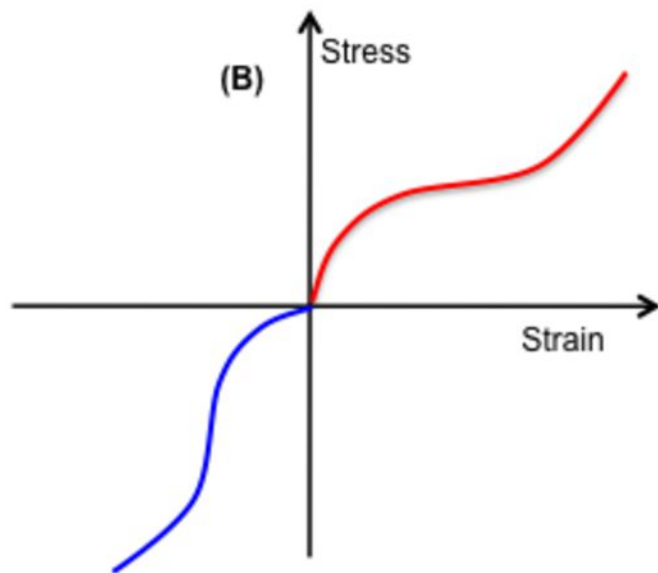
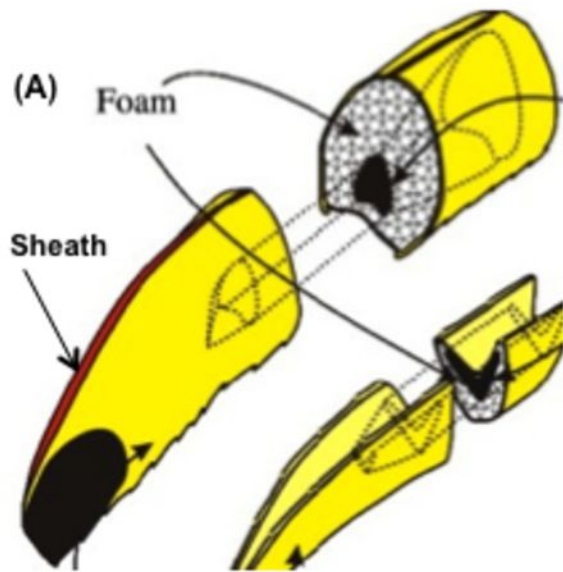


Fig. 12.

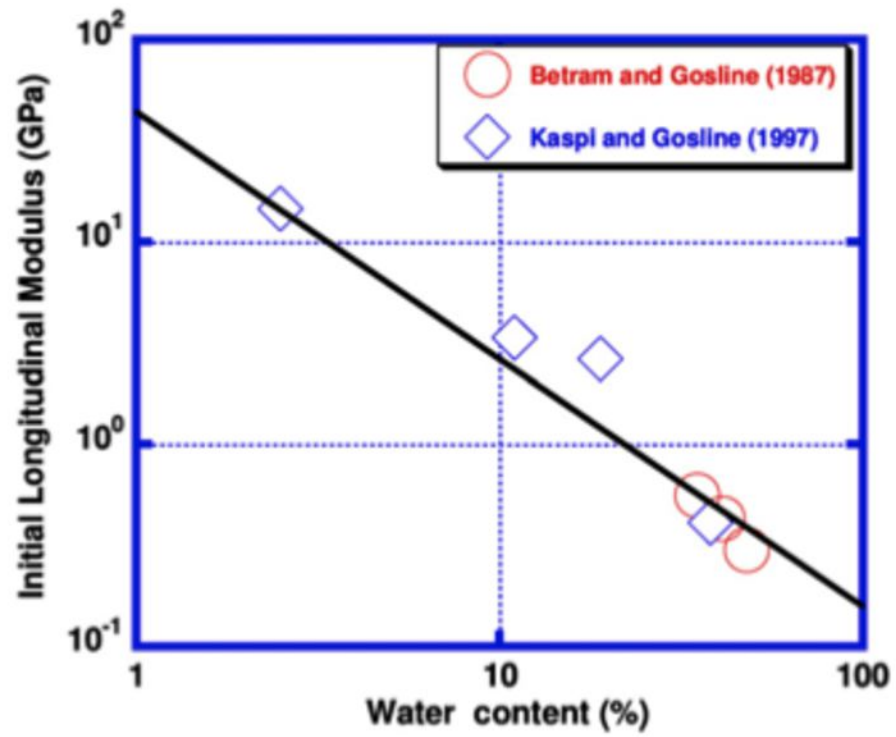
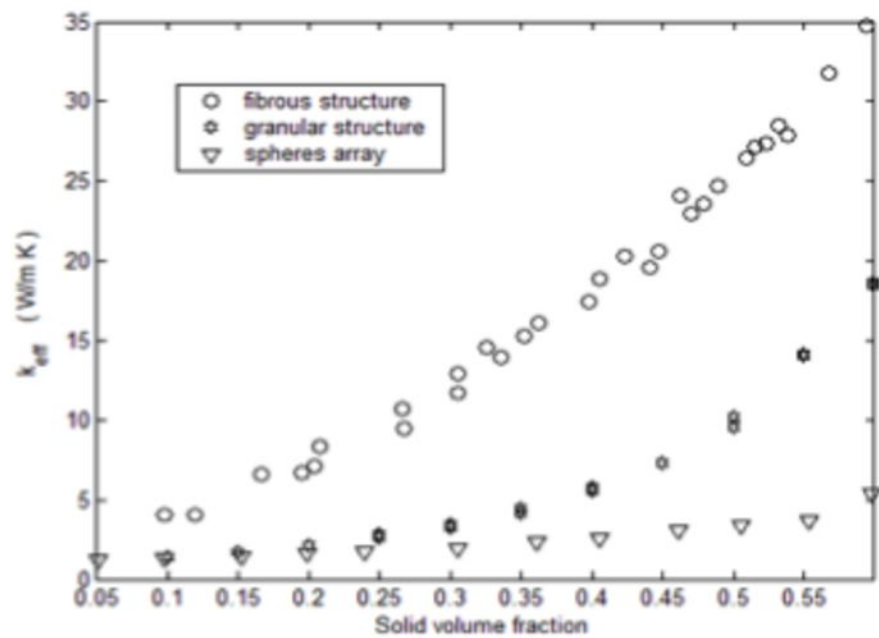
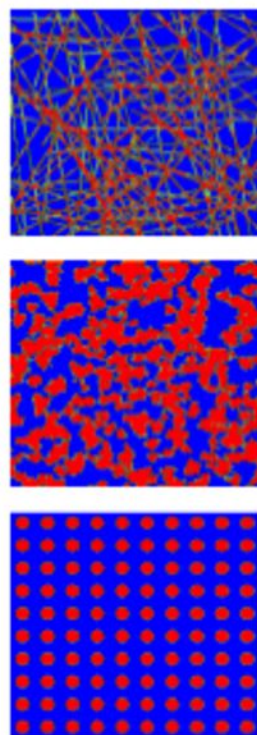
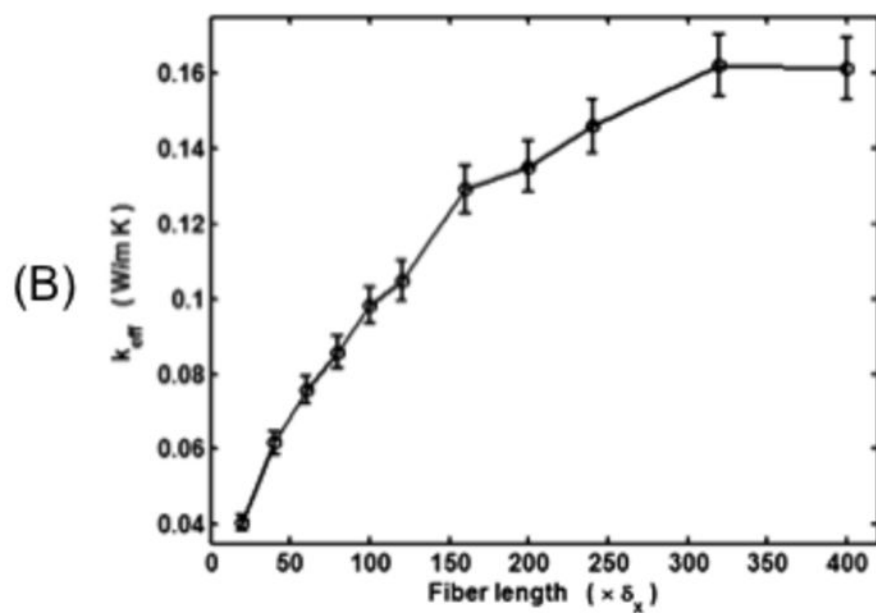


Fig. 13.





(A)



(B)

Fig. 14.

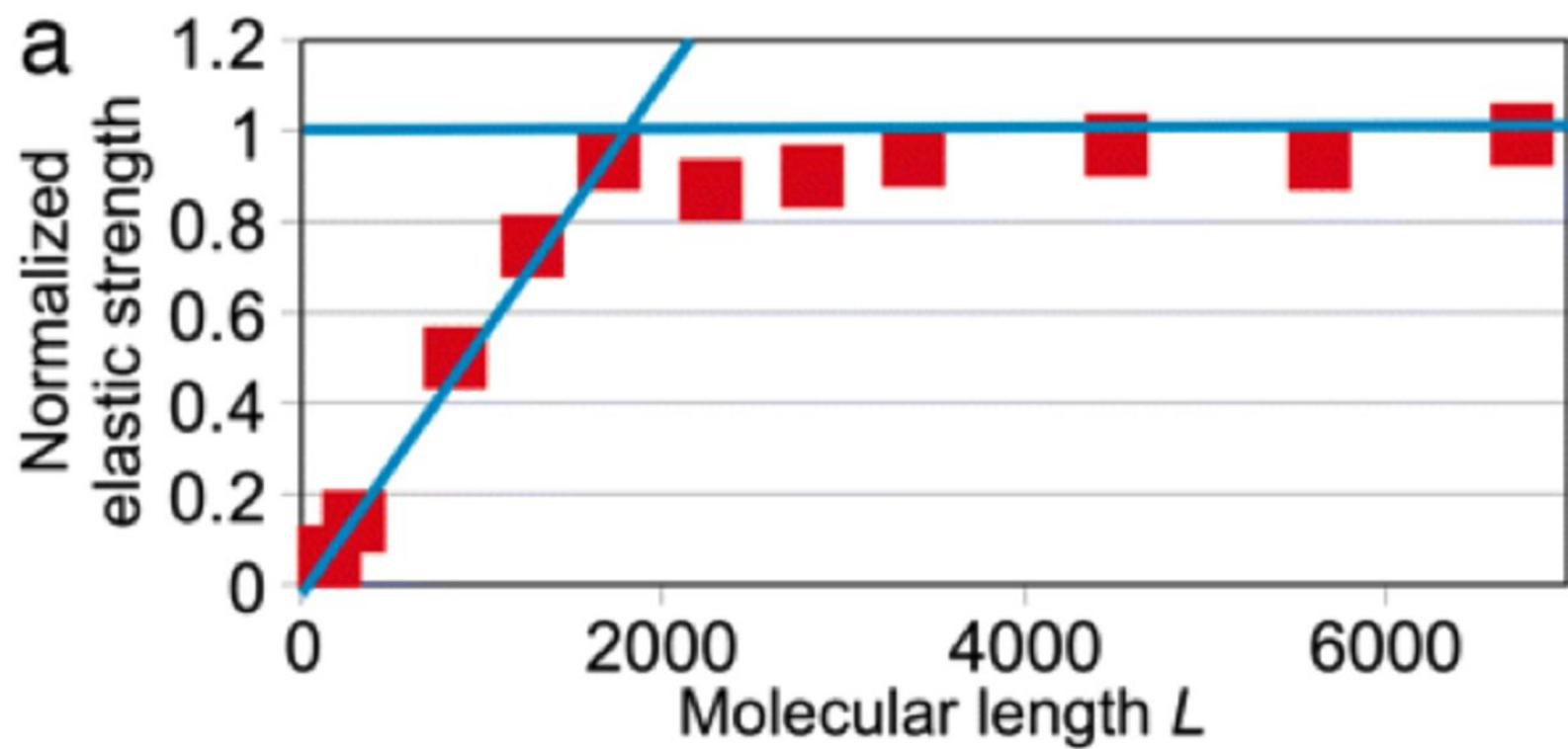
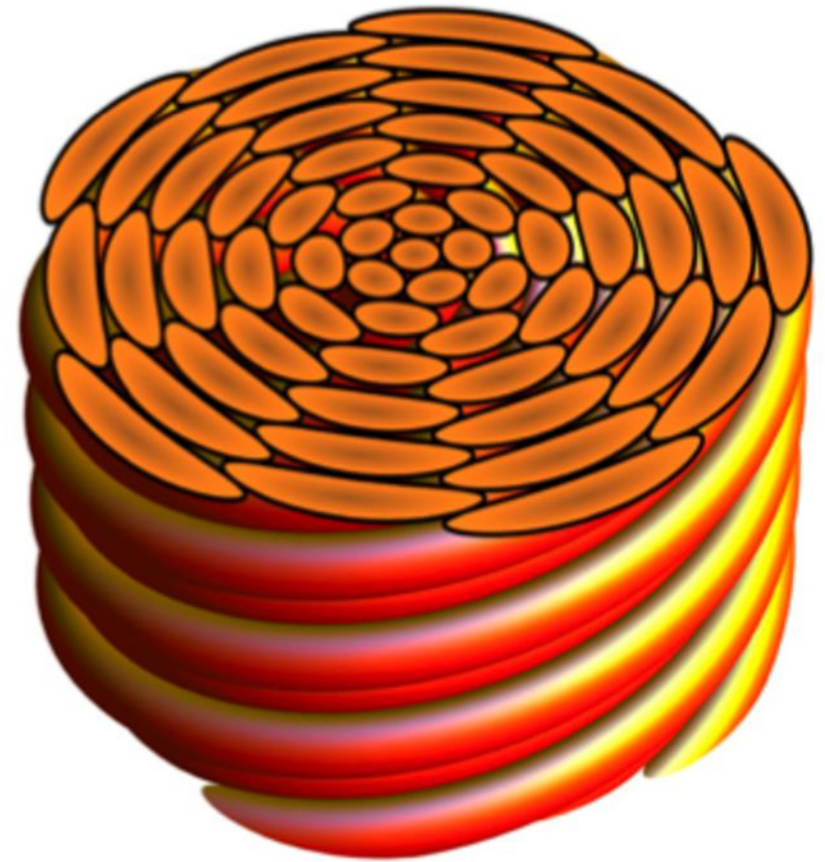


Fig. 15



(A)



(B)

Figure 16

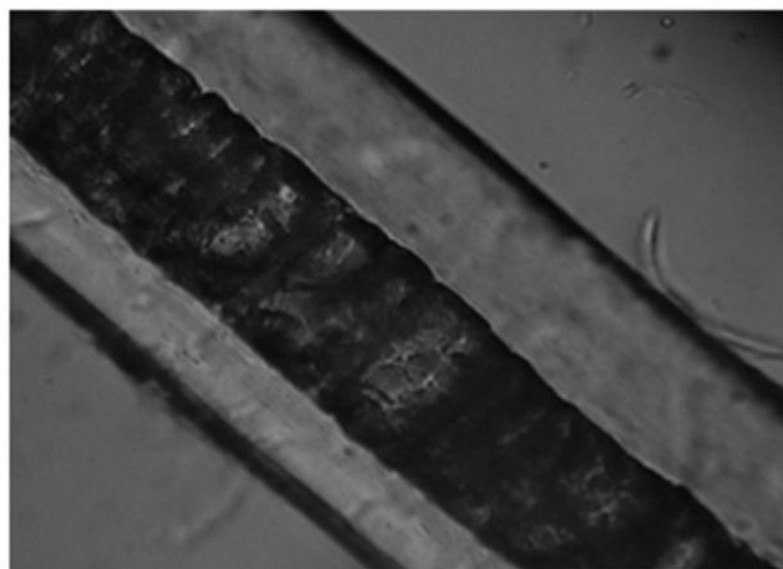
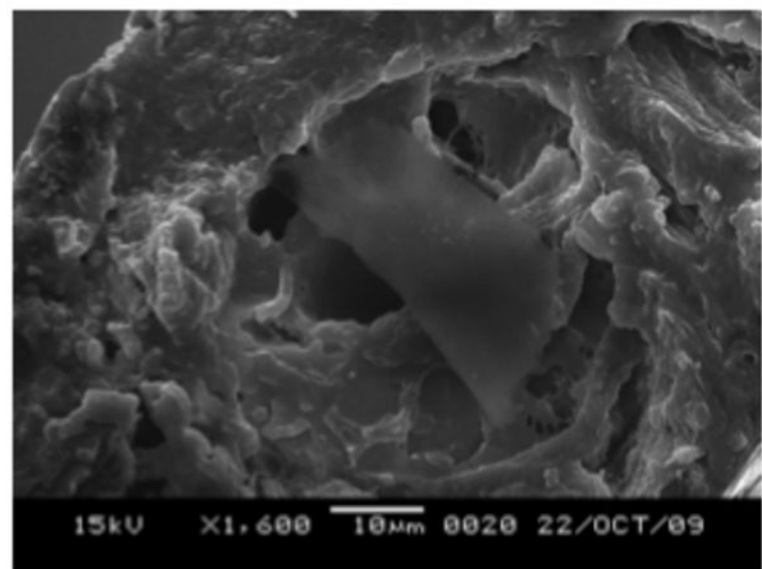


Fig. 17

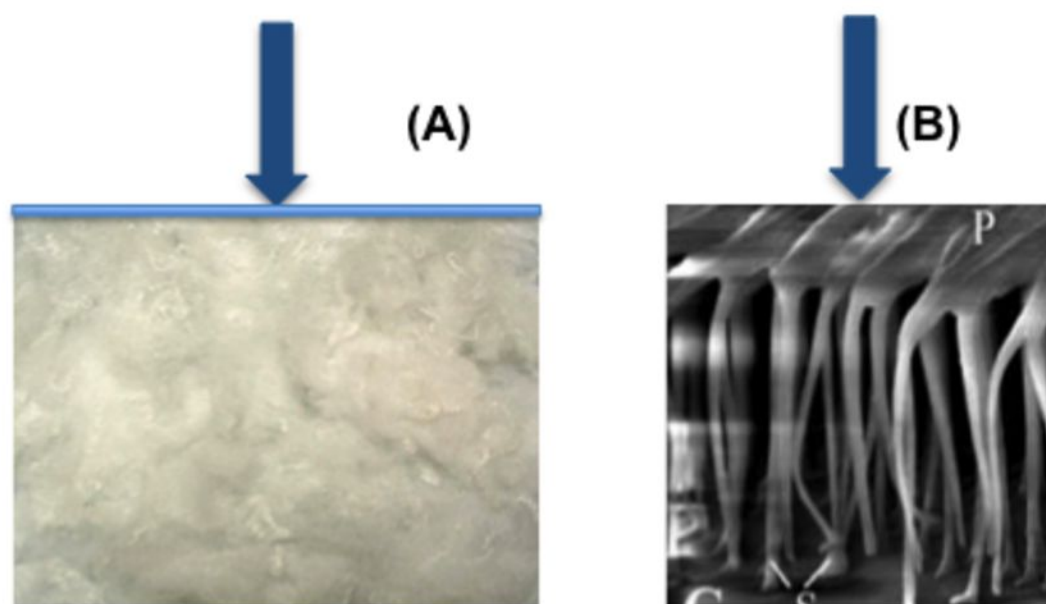


Fig. 18

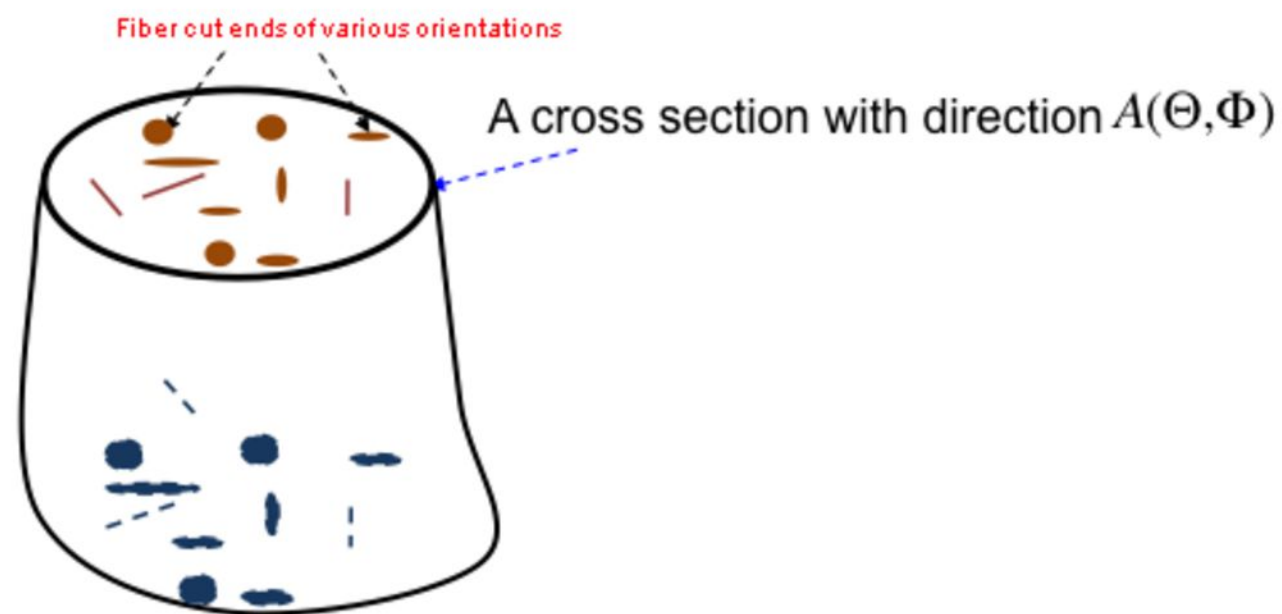
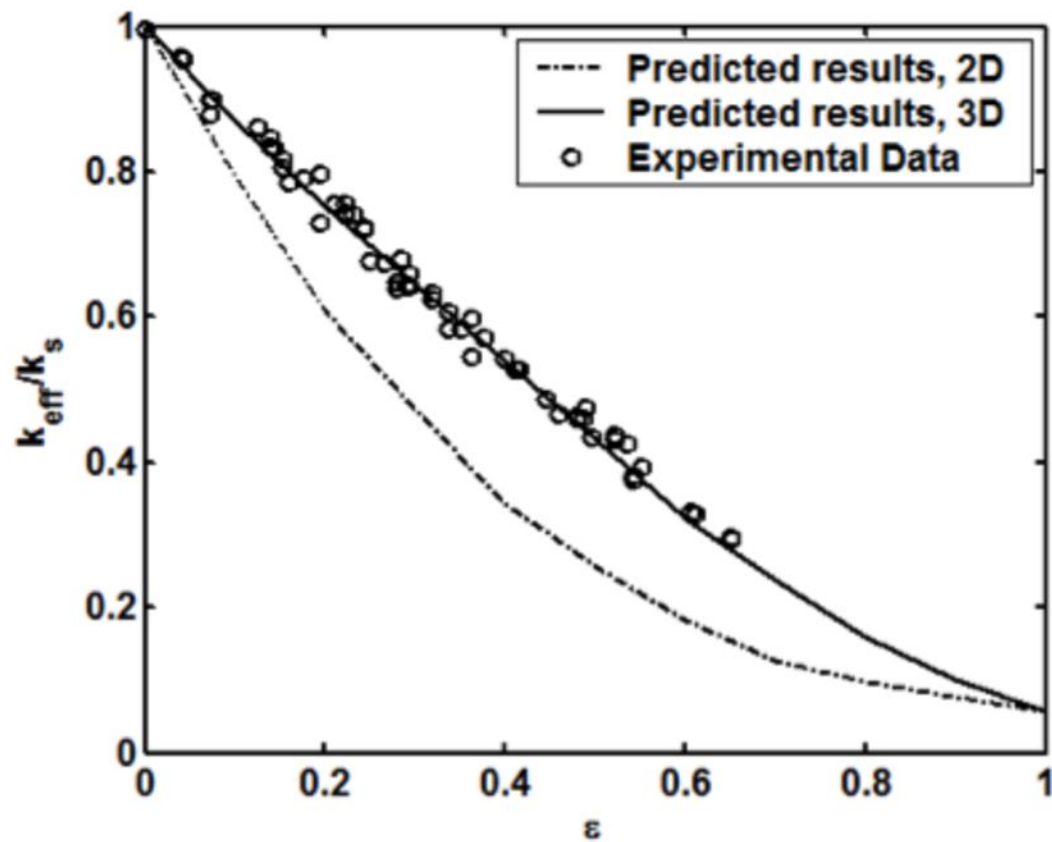


Figure 19



**Experimental data by hot plate technique**

Figure 20

Fig. 21

