

Variable stiffness biological and bio-inspired materials

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Abstract

This article reviews the main mechanisms of stiffness variation typically found in nature. The temporal changes in stiffness may be fully or partially reversible, or completely irreversible, and can be very slow or fast in time depending on the strategy adopted to alter the mechanical properties. It is also possible to observe changes in the stiffness in order to recover the original mechanical properties in damaged natural materials by means of self-healing mechanisms. In addition to stiffness variations in time, natural materials can also exhibit stiffness changes in space. These variations can be represented by alterations in the spatial distribution of the microscopic constituents across multiple hierarchical scales, from very small physical scales to large macroscopic dimensions. In order to optimise the strength and multifunctionality of these materials, spatial changes can also occur over larger areas at one single scale. In addition, several examples are provided to illustrate how natural materials have been exploited further in order to develop new bio-inspired materials.

Keywords

Variable stiffness, natural materials, bio-inspired materials

Introduction

The natural or biological materials can be understood as the result of an optimisation process developed over hundreds of millions of years of evolution. By assembling very weak constituents, natural (solid) materials are able to display outstanding mechanical properties (Meyers et al., 2008). The large body of publications currently available in this field dates back to the very early fundamental work performed by D'Arcy W. Thompson (1968) at the beginning of the 20th century, with his famous treatise *On Growth and Form*. In this book, Thompson emphasises the relevance of mechanical and physical laws on the form and structure of living organisms, highlighting some examples of correlation between biological forms and mechanical phenomena.

From an engineering point of view, one of the most important consequences in fully understanding the mechanical behaviour of natural materials is the inspiration of new strategies to design more advanced materials. By mimicking morphological patterns and natural mechanisms of interaction among basic constituents, scientists have found promising guidelines in the next generation of engineering materials. This relatively new field of so-called bio-inspired materials has been the subject of increasing interest in scientific communities (Bonderer et al., 2008; Broedling et al., 2008; Buehler, 2010b; Fratzl and Barth, 2009; Gao, 2006; Luz

and Mano, 2009; Stanzl-Tschegg, 2011; Yao and Gao, 2007). Thus, several biological materials have been investigated in recent years in conjunction with their extraordinary mechanical properties in order to inspire new designs. For instance, spider silk and its unique combination of high tensile strength and extensibility (Yang et al., 2005), bone density and the lightweight skeletons of birds (Dumont, 2010), wood and its remodelling capabilities and nacre from mollusk shells, with its extraordinary toughness amplification (Barthelat, 2010; Barthelat and Rabiei, 2011; Luz and Mano, 2009; Smith et al., 1999), among many others.

As adaptation mechanisms, most of these natural materials show exceptional changes in their stiffness during loading conditions or under new external environments. It is also possible to observe changes in their stiffness in order to recover the original mechanical properties in damaged areas. These changes can be very slow or fast in time. For instance, a slow stiffness

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variation can be found typically in plants. Here, water swelling and shrinking are generally responsible for these relatively slow changes as a consequence of the long diffusion times (Fratzl and Barth, 2009). In some flowers, the change of stiffness in their petals due to reversible expansion and contraction of cells associated with their opening or closure may take few minutes (Van Doorn and Van Meeteren, 2003). A much faster stiffness variation can be found in some biological materials such as nacre, in order to recover its original stiffness when damaged and therefore to arrest fast-moving cracks (Jackson et al., 1988).

The alteration of the stiffness in natural materials can be dramatic and totally reversible, such as those temporal changes in the matrix of wood cells upon moisture fluctuations (Cousin, 1976). However, partially or fully irreversible processes are also common in nature, such as those mechanisms based on growth and adaptation (Mollica et al., 2007).

The variation of stiffness in biological materials can also be understood depending on the origin of the actuation mechanism that induces the corresponding alterations. The temperature and moisture changes are typically associated with a temporal and reversible transition of the mechanical properties in natural polymers (Vasile and Zaikov, 2006). The mechanical forces can also induce non-linear geometric variations in the microscopic composition and organisation of biological materials, resulting in stiffness changes that have been widely documented in the literature (Holzapfel, 2000; Leondes, 2003; Speirs et al., 2008). The chemical and electrical actuation mechanisms are typically found in living tissues belonging to more complex organisms, such as animals. They have the ability to change temporarily the stiffness of their muscles, converting electrical and chemical energy into mechanical energy that is necessary for their survival and function (Kim and Tadokoro, 2007; Neiman and Varghese, 2011; Sinkjaer et al., 1988). The light irradiation seems to affect some mechanical properties of plant tissues (Takagi et al., 1991).

In addition to stiffness variations in time, natural materials typically exhibit stiffness changes in space. These variations are represented by alterations in the spatial distribution of the microscopic constituents across multiple hierarchical scales, from very small physical dimensions to large macroscopic scales. In order to optimise the strength and multifunctionality of these materials, spatial changes can also occur over larger areas at one single scale. These features constitute examples of passive stiffness variation, requiring no actuation mechanisms to adapt to loading conditions and environmental scenarios that are constant over very long timescales.

All these strategies employed by nature to develop these changes in the mechanical properties of biological materials have great potential in engineering. For instance, the proposal of novel morphing structures

(Barbarino et al., 2011) based on the study of fully reversible changes in the skin tissue of marine animals (Capadona et al., 2008), the design of new self-repairing man-made polymers inspired by bone (Trask et al., 2007) and new composite materials inspired by the mechanics and structure of plant cells (Saavedra Flores and Friswell, 2012) are some of the many examples of potential applications.

In the following, we will review the main strategies of stiffness variation found in nature and will examine some examples of how natural materials have been exploited further in order to synthesise new biologically inspired materials.

Stiffness variation due to moisture and temperature changes – glass transition

Upon minor fluctuations in their moisture and temperature conditions, natural materials are typically able to exhibit reversible alterations in their stiffness (Peleg, 1994). These changes are normally attributed to glass transition (Slade and Levine, 1991), a phenomenon generally found in polymers and amorphous materials, represented by a reversible transition from a stiff and relatively brittle state into a molten or rubber-like state (ISO11357-2, 1999).

Peleg (1994) proposed a very simple mathematical model to describe the mechanical properties of biological materials at and around their glass transition. Figure 1 shows the simulated changes in the stiffness normalised by its value at the glass state (which can be interpreted as a measure of Young's modulus) of a biological material around the glass transition. According to this model, T_c and M_c are the temperature and moisture content at the inflection points in the corresponding curves, respectively. The material parameters a and a' define the steepness of the curves within the transition region.

A notable example of this abrupt loss of stiffness can be found in hemicellulose, one of the basic constituents of plants. The high dependence of the hemicellulose Young's modulus on changes in the moisture content has been widely reported (Cave, 1978; Cousin, 1978; Salmén, 2004; Salmén and Back, 1977; Salmen and Back, 1980). Cousin (1978) reported a variation of almost three orders of magnitude, between 8 and 0.01 GPa, from the nearly dry state to nearly saturated conditions, respectively. Salmén (2004) reported that Young's modulus of hemicellulose varied from 2 GPa in a dry state to 0.02 GPa under moist conditions. In wood, the reduction of moisture content leads to dramatic changes in the overall material response, particularly by the reduction of ultimate strains at the instant of fracture. As the moisture content reduces, the type of fracture changes from ductile, associated with the development of large strains, to brittle, in which failure happens at very small strains, almost instantaneously.

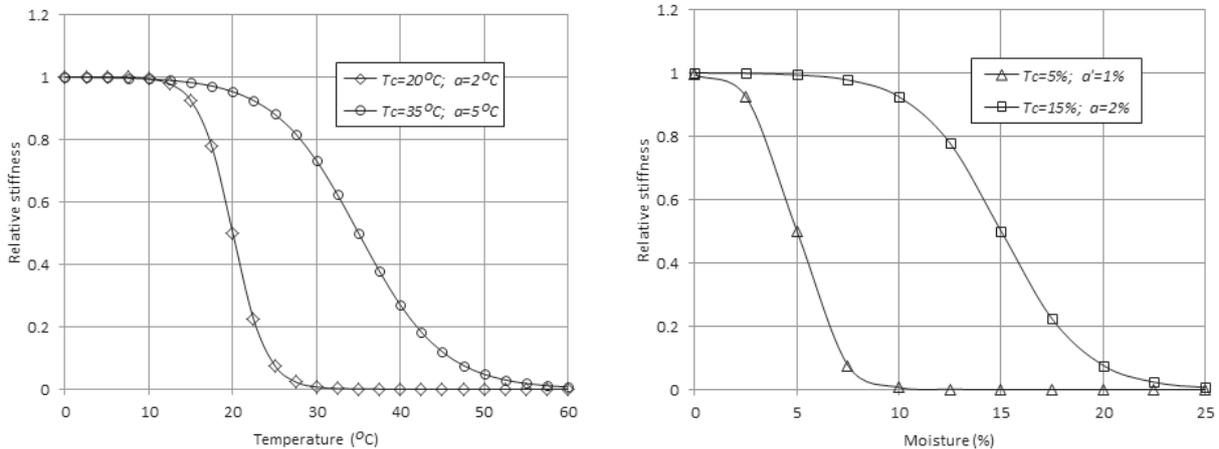


Figure 1. Simulated changes in the relative stiffness of a natural material around the glass transition. Adapted with permission from (Peleg, 1994).

For a re-increase of the humidity, wood is able to recover its original (and natural) compliant mechanism of deformation.

A transition of stiffness has also been reported by Aldred (2007), for byssal threads in mussels. Here, dynamic analyses revealed glass transition and an operational range of temperatures in which Young's modulus remains constant. A temperature lower than this operational range results in an abrupt increase in Young's modulus by almost one order of magnitude (when samples are kept at dry conditions). By reducing the moisture content of samples, Aldred (2007) also showed a reduction of failure strain up to about 40% with respect to the values in wet state.

The mechanical properties of spider silk are also severely influenced by humid environments that give rise to significant decreases in its length and Young's modulus (Elices et al., 2011; Plaza et al., 2006). Plaza et al. (2006) reported that the change from stiff to compliant tensile properties is associated with the transition from a glassy to a rubbery state. They found that the transition depends on both temperature and relative humidity. In all the cases, the reported Young's moduli decreased from 10 GPa at the lowest moisture content to almost 0.03 GPa at the highest humidity values (Plaza et al., 2006).

An example of a mechanically adaptive bio-inspired polymer that changes its mechanical properties upon exposure to water was investigated recently by Mendez et al. (2011). By introducing rigid cotton cellulose nanowhiskers into a rubbery polyurethane matrix, the authors developed a stimuli-responsive mechanically adaptive nanocomposite, able to display water-activated shape memory effects. For a 20% content of cellulose nanowhiskers, the new material

showed a decrease of Young's modulus from 1 GPa to 144 MPa upon exposure to water.

The above design has been inspired by the leathery skin of sea cucumbers. These marine animals have the ability to change reversibly the stiffness of their inner dermis. Capadona et al. (2008) suggested that Young's modulus of this tissue is controlled by regulating the interactions among collagen fibrils, which reinforce a low-modulus matrix. These authors reported a family of polymer nanocomposites that mimic this architecture and display similar chemo-responsive mechanic adaptability. It was found here a reversible reduction by a factor of 40 in Young's modulus of materials based on a rubbery host polymer and rigid cellulose nanofibres. This reduction was achieved upon exposure to a chemical regulator that mediates nanofibre interactions. By using a host polymer with a thermal transition in the regime of interest, they also showed a change in Young's modulus from 4200 to 1.6 MPa upon exposure to emulated physiological conditions. Similar works have been reported recently (Hess et al., 2011; Hsu et al., 2011; Rusli et al., 2010; Shanmuganathan et al., 2010a, 2010b, 2010c).

Cross-links and sacrificial bonds at the molecular level

Another way in which natural materials, and particularly biological polymers (such as proteins), reversibly change their stiffness is by means of sacrificial bonds. These are represented by molecular cross-links that connect one polymer chain to another. Normally, the toughness of the natural cross-linked polymers comes from the ability of the molecular chains to slip through entanglements at high stresses. Typically, highly

oriented fibrils are pulled out across a growing crack, with a large absorption of energy. These cross-links prevent this relative motion (McGrath and Kaplan, 1996) or make it difficult. Commonly, when the sacrificial bonds are broken and the stress is removed, they are able to reform and return again to their original position, resulting in an outstanding toughening mechanism.

For instance, bone is made of mineralised collagen fibrils that are bounded together by a cross-linked organic matrix to form a solid material (Fantner et al., 2006). Yeni and Fyhrie (2001) reported the exceptional fracture toughness in bone. Similarly, Nalla et al. (2003) reported uncracked ligament bridges in cortical human bone, where they show some evidence that these ligaments act as a toughening mechanism in bone. Fantner et al. (2005, 2006) suggested that these sacrificial bonds, which act as a glue that holds the mineralised collagen fibrils together, resist the separation of mineralised collagen fibrils. The function of the organic matrix as a glue has also been supported by Thompson et al. (2001), who reported that sacrificial bonds are present within the bone matrix.

These sacrificial bonds have also been reported in other biological materials such as nacre, in which the organic material glues aragonite plates together (Smith et al., 1999), contributing to the notable increase in fracture toughness of the natural composite when compared to the toughness of the basic mineral constituent. These sacrificial bonds are weak and reformable and

increase the energy required to stretch and break molecules (Fantner et al., 2006). When strain on the material is removed, these sacrificial bonds reform, representing a mechanism for repeatable energy dissipation (Fantner et al., 2006).

In wood, this toughening mechanism has also been reported. Keckés et al. (2003) showed how wood tissue and individual cells are able to undergo large deformations without apparent damage and also proposed a recovery mechanism after irreversible deformation, interpreted as a *stick-slip* mechanism at the molecular level. They showed that this *velcro-like* mechanism between cellulose fibres produces a plastic response similar to crystallographic sliding in polycrystalline metals.

Figure 2 shows a schematic relation between shear stress and strain in the hemicellulose and lignin matrix between two cellulose fibres. Beyond the elastic range (A–B), the deformation occurs at constant stress by an irreversible gliding of the matrix. When the deformation is interrupted (C), the bonds between cellulose fibres recover, as does the original stiffness. Keckés et al. (2003) suggested that this deformation mechanism does not result in damage if the matrix has the character of velcro.

The light-activated shape memory polymers are some of the examples in which molecular cross-links are altered in order to change temporarily the mechanical properties (Lendlein et al., 2005). In this case, light changes the cross-linking density within the polymer,

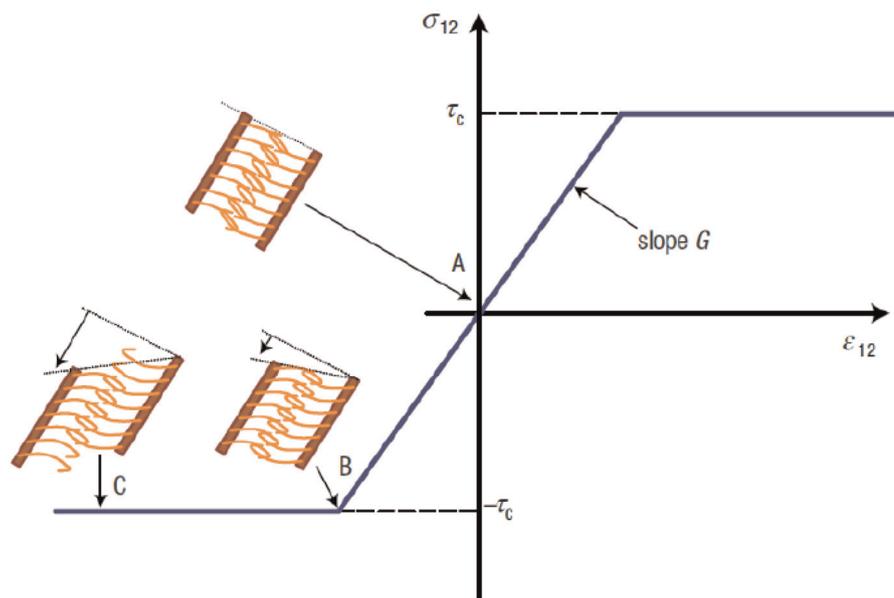


Figure 2. Schematic representation of sacrificial bonds at the molecular level in the wood cell-wall and relation between shear stress and strain between two cellulose fibres. It was suggested that this deformation mechanism does not result in damage if the matrix has the character of velcro, resulting in an outstanding toughening mechanism. Reprinted with permission from Keckés et al. (2003).

resulting in a material that may be reversibly switched between an elastomer and a rigid polymer (Havens et al., 2005). The relevance of cross-linker content, for instance, in the context of electro- and light-responsive hydrogels, has been studied by Kulawardana (2010).

Several additional examples can be found in the literature about bio-materials, which change temporarily their mechanical properties by altering their molecular cross-links. Kumpfer and Rowan (2011) investigated films with multi-responsive shape memory capabilities by means of covalently cross-linked metallo-supramolecular polymers. Ware et al. (2012) proposed a triple shape memory polymer capable of changing shape and stiffness based on the temporal modification of glass transition temperature and cross-link density. Cross-linked elastomers containing reversibly binding side groups, capable of storing elastic energy on multiple timescales and giving rise to shape memory properties, have also been studied (Li et al., 2011).

Synthetic rubber used in many engineering applications is made by cross-linking rubber through the process of vulcanisation. This process consists of adding sulphur or other equivalent substances to rubber, forming cross-links between individual polymer chains, which results in a more durable material (Mark and Erman, 2005) ideal for applications in which high extensibility and fatigue are essential requirements. For instance, Griffin (2007) investigated the use of vulcanised rubber materials, a thermoplastic elastomer, polyurethane and a woven material as candidate materials for a morphing wing. He found that rubber materials along with the combination of rubber and woven materials were the best candidates, providing an optimal balance between flexibility and strength in a flexible wing skin. Magalhães da Costa Aleixo (2007) also included the use of vulcanised rubber in his study of flexible skins for morphing wings. Synthetically cross-linked polymers have many other uses, including those in the biological sciences, such as applications in forming polyacrylamide gels (Tuncaboylu et al., 2011).

Stiffness recovery by self-healing mechanisms

Most natural materials have the ability to repair themselves (Zwaag, 2007) and to recover completely their original stiffness after moderate damage or steady microscopic cracks in repeated events. A remarkable example is a bone that is not only able to return to its full functionality but also to restore completely its initial structure (Fratzl and Weinkamer, 2007). The healing process consists of bone deposition, resorption and remodelling. This natural process involves blood clotting, the formation of collagen fibres, the subsequent mineralisation and the transformation of collagen

matrix into bone (Trask et al., 2007). After the healing process, the bone is restored to its original shape, structure and mechanical strength (Kalfas, 2001).

Inspired by these natural self-healing characteristics, several strategies have been proposed in order to restore the mechanical properties of damaged engineering materials. One of these strategies consists of the fusion of fractured surfaces. Chen et al. (2002) developed a transparent organic polymeric material that can repeatedly mend or re-mend itself under mild conditions. The material is a tough solid at room temperature and below with mechanical properties equalling those of commercial epoxy resins. At temperatures above 120°C, some of its inter-monomer linkages disconnect but then reconnect upon cooling. The process was demonstrated to be fully reversible with potential applications to restore a fractured portion of the polymer at multiple times. To determine the fracture-mending efficiency of this polymer, Chen et al. (2002) performed experimental tests on tension test specimens. Similar approaches have been investigated in thermoplastic elastomers (Raghavan and Wool, 1999), glass (Inagaki et al., 1985; Stavrinidis and Holloway, 1983) and structural polymers (Jud et al., 1982; Wang et al., 2003; Wool and O'Conner, 1982).

Another self-healing strategy has been proposed by Zako and Takano (1999). In their developed system, a cold-setting epoxy resin was used as the matrix, unidirectionally arranged glass fibres were used as the reinforcement and a thermosetting epoxy particle was used as a repairing actuator. The strategy consists of embedding small grain particles in the glass/epoxy composite laminate. Then, by applying heat, the embedded particles melt and flow to repair the crack. If, on the one hand, this strategy offers a self-healing mechanism suitable for repairing cracks, on the other hand, this strategy requires a damage detection system that is likely to be impractical in a real application (Trask et al., 2007). Lee et al. (2004) showed that nanoparticles embedded in polymers become localised at nanoscale cracks and effectively form patches to repair the damaged regions. This strategy seems to be inspired by the mechanism of blood clotting (Trask et al., 2007). The results revealed cases where the mechanical properties of the repaired composites can potentially be restored up to 100% of the undamaged material. Similarly, Gupta et al. (2006) developed a self-healing system with potential applications in multilayer composites that combine ductile polymers with brittle films. It consists of nanoparticles dispersed in a polymer matrix. The authors showed that the particles migrate to cracks at the interface between the polymer and a glassy layer.

A third type of strategy consists of incorporating a microencapsulated healing agent in the material, with the ability to heal cracks autonomically. White et al. (2001) reported a structural polymeric material with embedded microcapsules containing the healing agent

that is released into the crack plane through capillary action. Polymerisation of the healing agent is then triggered by contact with an embedded catalyst, bonding the crack faces. The authors found a recovery of about 75% of the virgin fracture load and emphasised that the system could be used in multiple healing events. Other similar approaches have been adopted recently in the literature (Bai et al., 2012; Dehoux et al., 2012; Singh et al., 2012; Wang et al., 2012). Probably, the main drawback of this microencapsulation strategy is the need to fracture some microcapsule and to mix the catalyst and resin prior to any repair occurs (Trask et al., 2007).

Inspired by arteries in natural systems, the use of hollow fibres is another strategy investigated in this context. This involves the filling of hollow fibres with a resin, which is released into the damaged area when the fibre is fractured in a polymer matrix composite (Bleay et al., 2001). This approach has also been investigated by Dry (1996) and Motuku et al. (1999). In order to quickly and easily observe the internal damage in composite materials, a damage visual enhancement method has been designed by Pang and Bond (2005a, 2005b). In addition, Trask and Bond (2010) studied a Plantae-inspired vascular network within a fibre-reinforced polymer composite laminate and illustrated the potential of this vasculature concept in terms of providing a self-healing function with minimum mass penalty, without initiating premature failure within a composite structure. Williams et al. (2008) derived an expression for the optimum vessel diameter for the design of minimum mass branching or vascular networks in engineering applications.

Stiffness variation across multiple spatial scales – hierarchical microstructures

One of the most important features present in natural materials, with potential applications in engineering, is their hierarchical nature (Lakes, 1993) distributed across multiple spatial scales, from sub-micrometer dimensions to macroscopic levels. The transition from one to another scale represents a stiffness variation in space. Each of these scales is defined by a *microstructure* or arrangement of microscopic structural elements with physical dimensions of the same order of magnitude. Probably, the earliest studies date back to 1665, with Robert Hooke (1665) and his monumental work called *Micrographia*. Hooke was the first scientist to observe for the first time the elementary microstructures encountered in plants and insects. Apart from structural support, microstructures may display other functionalities, such as transport of nutrients, protection against bacterial attacks and self-healing mechanisms, among many others. They can also exhibit periodic patterns and symmetries.

The generally large number of material scales found in nature constitutes a fundamental difference with what normally happens in man-made materials, in which no more than one or two scales can be typically found in their internal structure. In particular, one remarkable example is wood, in which five different levels of organisation can be distinguished clearly through its entire composition (Hofstetter et al., 2005). Figure 3 shows a schematic representation of the hierarchical structure of wood. At the nanoscopic scale, wood is composed of three fundamental constituents – cellulose, with its crystalline and amorphous periodic fractions; hemicellulose and lignin. For instance, the sketch labelled ① in Figure 3 illustrates the molecular arrangement of the crystalline cellulose portion (Fratzl, 2003) at that scale. These three fundamental constituents form a spatial arrangement called microfibril that represents the unit building block of the wood cell-wall microstructure at the scale of tens or hundreds of nanometres (refer to ② in Figure 3). At the next scale, the above microstructure gives rise to the elementary wood cell, which is depicted in this figure by ③. It can be represented by a long and slender cylinder with a wall made of several layers (such as S_1 , S_2 and S_3 layers) depending on the orientation of the microfibrils with respect to the longitudinal axis depending on the microfibril angle (MFA) or orientation of the cellulose fibres with respect to the longitudinal cell axis. The generation of new cells across the transversal plane forms a new microstructure at the scale of hundreds of micrometres, called wood tissue, which is represented in Figure 3 by ④. Finally, periodic variations in the wood tissue microstructure due to seasonal changes form concentric growth rings that are typically found in the trunks of trees. This corresponds to the macroscopic scale and is illustrated in Figure 3 by ⑤.

A second example of a natural hierarchical material is nacre from mollusk shells, in which at least four spatial scales can be typically observed, as shown in Figure 4. At the scale of tens or hundreds of nanometres, the microstructure is composed of an assembly of nanoscopic grains delimited by a network of organic material (Li et al., 2004; Luz and Mano, 2009). This base material is called aragonite and is shown in Figure 4 by ①. In a higher hierarchical scale, a new microstructure emerges. It consists of polygonal aragonite platelets distributed in columnar arrangements (Espinosa et al., 2009) as indicated by ②. This three-dimensional brick and mortar wall-type architecture presents densely packed layers of aragonite platelets (95%) held together by a very small amount (5%) of a thin organic layer (Espinosa et al., 2009; Munch et al., 2008; Wang et al., 2011). This microstructure extends over hundreds of micrometres, giving an inner nacreous aragonite layer (indicated by letter N in ③ of Figure 4), which together with an external prismatic calcite layer (denoted by letter P in the same figure), constitute the whole mollusk shell at the macroscopic scale (indicated by ④, Figure 4).

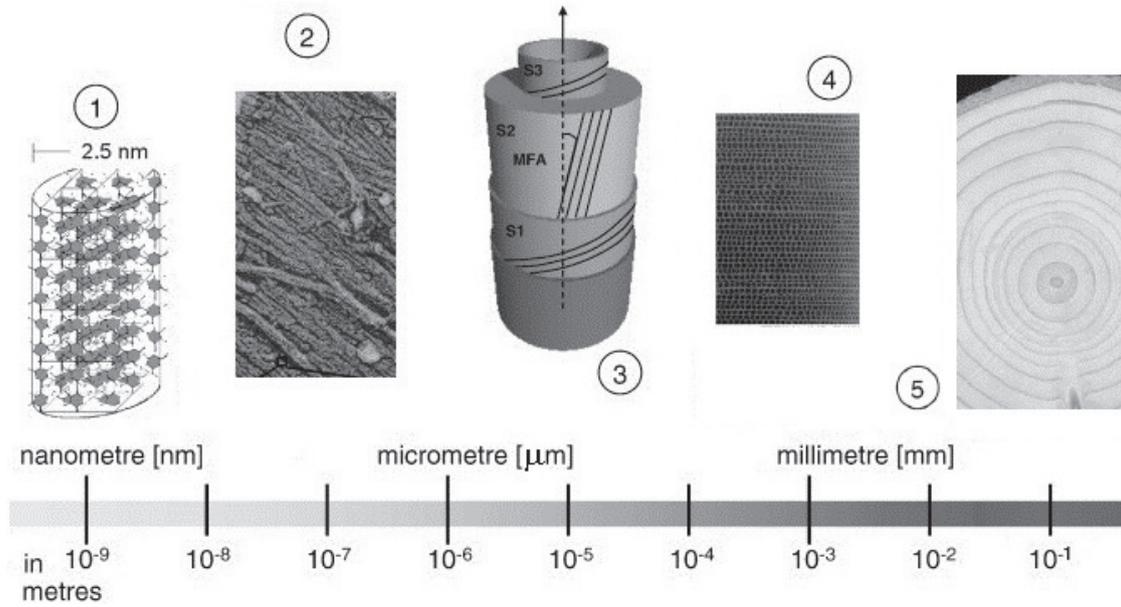


Figure 3. Schematic representation of several scales found in wood. Adapted with permission from Fablet et al. (2008), Fratzl (2003), Fratzl and Weinkamer (2007), Weinkamer and Fratzl (2011).

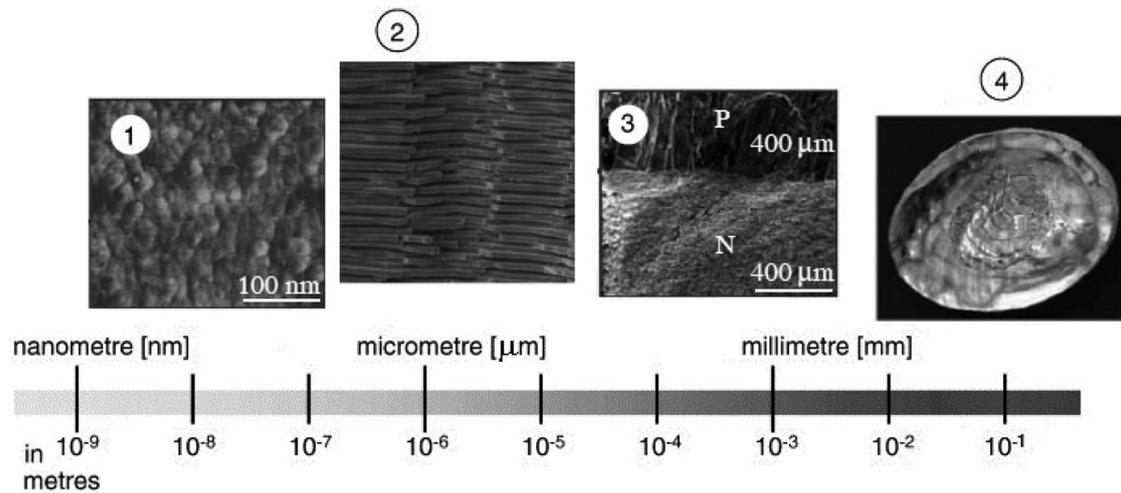


Figure 4. Schematic representation of four scales found typically in nacre from mollusk shells. Reprinted with permission from Espinosa et al. (2009), Luz and Mano (2009) and Li et al. (2004). Copyright 2004 American Chemical Society.

Further investigation on multi-scale natural hierarchical materials has been carried out, for instance, in the context of spider silk (Keten and Buehler, 2010), revealing at least four scales; turtle shells and their carapaces (Rhee et al., 2009), with at least four scales; bone, with seven levels of hierarchy (Launey et al., 2010); and other collagen-based materials (Buehler, 2010a; Gautieri et al., 2011), such as tendon, ligament, skin, cartilage, hair, with at least five levels of organisation, among many others.

In spite of the considerable effort devoted to the understanding of natural designs in biological materials, there are still many unsolved issues that remain

open at present and that require further research. One of these unsolved issues is the factor (or factors) that determines the number and size of each scale. In order to understand the principle of structural hierarchy, Zhang et al. (2010) developed a quasi-self-similar model and suggested that depending on the mineral content, there exists an optimal number of scales that maximises the toughness of the hierarchical material. Figure 5 shows the variation of toughness in a hierarchical material with N scales (Zhang et al., 2010). The material is idealised as a quasi-self-similar composite with hard mineral inclusions embedded in a soft protein matrix. Here, Γ_N is the fracture energy of the material at the

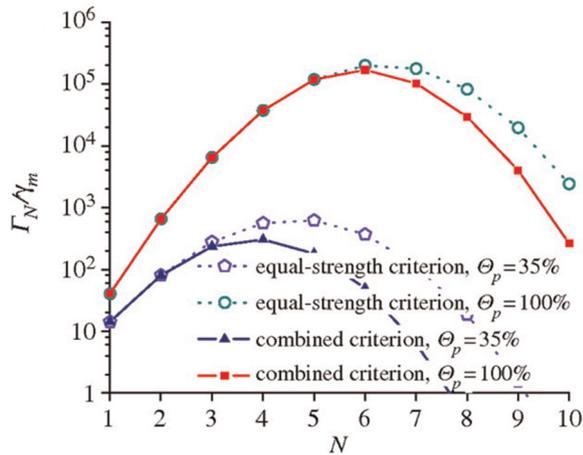


Figure 5. Variation of toughness in a quasi-self-similar hierarchical material with N scales Reprinted with permission from Zhang et al. (2010).

N level, γ_m is the surface energy of the mineral content and Θ_p is the failure shear strain of the soft matrix. In this work, Zhang et al. assumed two different criteria for their calculations: (1) in which matrix and inclusions reach failure at the same time (equal-strength criterion) and (2) which combines the previous criterion plus efficiency in the transfer of stresses in the matrix (combined criterion). These authors reported an optimal number of scales of 4 for $\Theta_p = 0.35$ and 6 for $\Theta_p = 1.0$, finding good agreement with experimental observations.

Thus, by adding an optimal number of scales, nature seems to maximise the toughness of the material at the macroscopic level. This amplification mechanism constitutes a clear example of how natural materials change their stiffness through the different spatial scales and adapt themselves to loading conditions and environmental scenarios that are constant over time.

Stiffness variation at one single spatial scale

Over larger areas, and at one single scale, natural materials normally show considerable variation in the distribution of their mechanical properties and microstructure. For instance, Tai et al. (2007) reported significant scatter in the mechanical properties of bone at the nanoscopic scale for different anatomical locations, as well as for different regions within a particular anatomical location. These authors quantified the spatial distribution of nanomechanical properties of bone at the length scale of individual collagen fibrils, the most abundant protein in mammals' bones, and showed elaborate patterns of stiffness ranging from 2 to 30 GPa. This nanomechanical heterogeneity was considered as a means for ductility enhancement, damage evolution and toughening (Tai et al., 2007). These authors also predicted that non-uniform inelastic deformation over

larger areas and increased energy dissipation arising from nanoscale heterogeneity lead to markedly different biomechanical properties compared with a uniform material.

Minary-Jolandan and Yu (2009) suggested that the mechanical heterogeneity found in bone at the nanoscopic scale has an important connection with multifunctional properties. A similar example is the chitinous cuticle of the exoskeleton in arthropods. It shows chemical and structural modifications in its fibrous matrix, which results in a wide variety of mechanical properties to perform multiple functions (Gupta, 2011).

The distribution of porosity in bone changes in such a manner that strength is provided only where it is needed (Meyers et al., 2008). For instance, the metacarpal bone in vulture wings seems to be optimised for weight. Here, most of the mass is displaced away from the neutral plane where little stiffness is required (Meyers et al., 2008).

In wood, substantial variations of stiffness at the microscopic scale can be found over large areas. Figure 6(a) illustrates the orientation of the cellulose fibres in a coniferous tree branch (Fratzl and Barth, 2009). This orientation is defined by the MFA (refer to the 'Stiffness variation across multiple spatial scales – hierarchical microstructures' section), which changes from large angles, greater than 45° on the lower side of the branch, to much smaller angles, close to 0° on the upper side. It has been shown that this stiffness spatial variation has important implications on the generation of actuation mechanisms based on differential cell-wall swelling (Fratzl and Barth, 2009), facilitating seed dispersal (Hart, 1990) and growth reorientation due to changes in the environmental conditions.

The basis for this differential swelling is the complex microstructure of the wood cell-wall composite. It consists of hydrophobic cellulose fibres embedded in a hygroscopic hemicellulose–lignin matrix. As a consequence of the opposite hygroscopic properties between the cellulose fibres and the matrix, the cells expand in the axial direction for large MFAs, whereas for smaller MFAs, they contract. This implies that on swelling, the cells on the lower side of the branch expand in the axial direction, whereas the cells on the upper side contract, resulting in an upward movement (Fratzl and Barth, 2009) as shown in Figure 6(b). One of the most remarkable features present in this type of actuation system is that it functions without the need of an active metabolism to perform such movements (Burgert and Fratzl, 2009).

The smooth stiffness variation given by the gradual change of the cellulose microfibril angle in the above case, and in the transition of porosity between trabecular bone and cortical bone Martin (1984), or in the gradual variation of cell diameter and cell-wall thickness in the fibrous tissue of some palms has been interpreted as a model system for avoiding stress discontinuities in

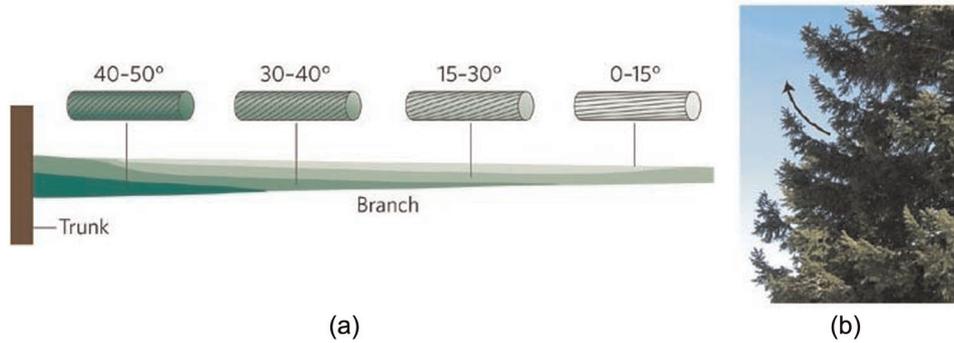


Figure 6. Actuation mechanism in trees branches resulting from the stiffness spatial variation over large areas of microstructure. Reprinted with permission from Fratzl and Barth (2009).

inhomogeneous and anisotropic fibre-reinforced composite materials (Rüggeberg et al., 2008).

The above transition of stiffness contrasts with a much more abrupt change found typically in the anchoring of fibres into a substrate material (Dunlop et al., 2011), as for instance, the insertion of tendons and ligaments into bone (Benjamin et al., 2002) or the human tooth fixated into the alveolar bone (Ho et al., 2010). In the particular case of teeth, the abrupt change of stiffness also occurs through its internal microstructure, passing by several tissues with very different levels of stiffness, from hard enamel to a much softer dentin (Dunlop et al., 2011). A key parameter in controlling the stiffness is the amount of mineral incorporated in these materials, ranging from more than 95% of the volume in enamel to roughly 50% in dentin (Dunlop et al., 2011; Lawn et al., 2010; Tesch et al., 2001; Zaslansky et al., 2006). This abrupt variation of stiffness seems to be related to a natural mechanism to deflect cracks and increase toughness.

Conclusion

This article has reviewed the main strategies adopted by nature to change the stiffness in biological materials. Several examples of variable stiffness natural materials are examined in conjunction with some examples of biologically inspired materials. Glass transition, sacrificial bonds at the molecular level and self-healing mechanisms are some of the natural strategies of stiffness variation reviewed in this article. In addition to stiffness variations in time, stiffness changes in space can also be displayed by natural materials. These spatial changes can be represented by several microscopic scales distributed hierarchically or by microstructural changes distributed over larger areas at one single scale.

The exceptional changes in stiffness of biological materials may be interpreted as the result of an adaptation mechanism to temporal alterations in the loading conditions or in the external environment and as the

consequence of an optimisation process to withstand scenarios that are constant over very long periods of time.

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