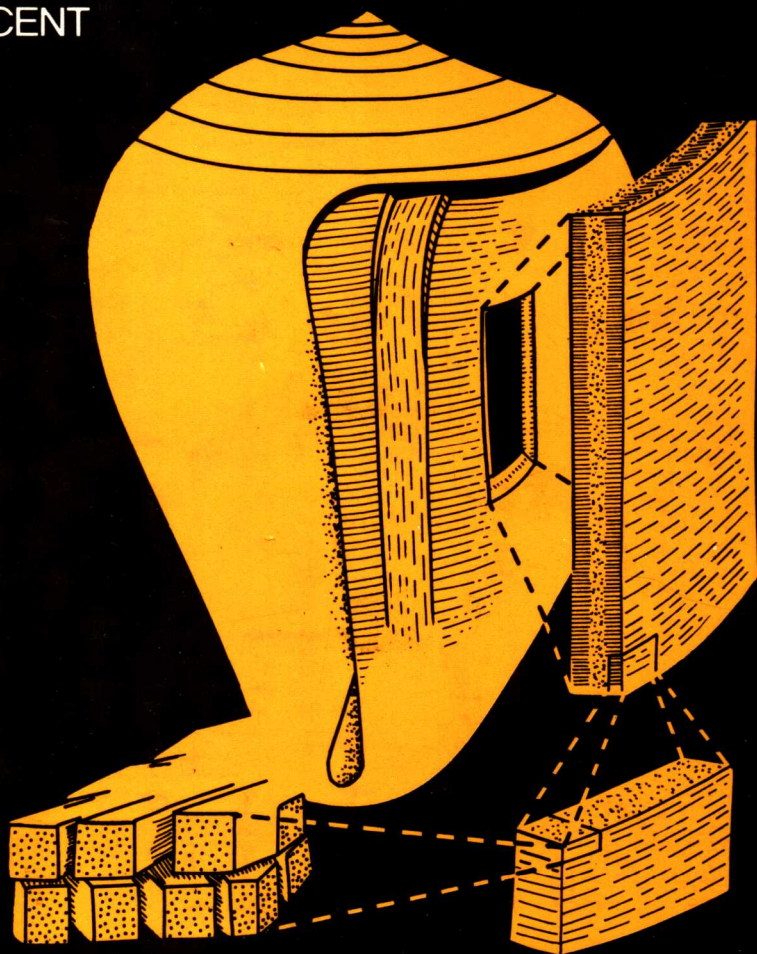


# Structural Biomaterials

JULIAN F. V. VINCENT



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Julian F. V. Vincent

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# Preface

This book, like so many others produced by lecturers and teachers, has its foundations in a lecture course. There were few books devoted, even in part, to biomaterials when this course was written, so it was conceived, *de novo*, as showing the increasing complexity of materials, starting from simple building blocks. This is the biologist's approach and probably that of the biochemist. The physicist or engineer much prefers to treat the material as a conceptual 'black box', describe what it does, then model it mathematically. This is probably difficult for the biologist, who tends to think pictorially. So the first chapter (which takes just this approach) is as much an appendix as an introduction. For the rest of it, this book is not intended to be a review of facts, more an illustrated discussion on ways of thinking about biomaterials. It is therefore somewhat bitty and unbalanced, but with odd thoughts and asides which I hope will stimulate.

My thanks are due to my colleagues Profs J. E. Gordon, W. D. Biggs and J. D. Currey, and to Drs C. R. Chaplin, G. Jeronimidis, P. P. Purslow and J. E. Smeathers. Sometimes it didn't seem like help, but I'm sure it was for my own good.

*Reading, 1981*

J.F.V.V.

# Introduction

Bone and wood are familiar supportive materials and provide part of the framework upon which the cells of many organisms are arrayed. Without some such framework the cells would not be able to arrange themselves relative to each other and so form tissues and organs, nor would those tissues and organs be able to be organised into a whole organism. The importance of this framework is obvious – without it multicellular life as we know it would be impossible. A framework of such basic importance will obviously have many important attributes since it will dictate or restrict the means by which the cells can communicate and integrate their activities. These latter functions are not the concern of this book – it is the mechanical aspect of the framework which is to be examined. But in all that follows it is important that the mechanical properties and functions should be considered in context. The roots of a plant serve several functions; the mechanical anchorage of the plant is only one of these functions and cannot be said to be either more or less important than any other function. Much the same can be said of the extracellular material which glues cells together and of the long bones of the body, to name but two examples.

For the modern biologist, familiar with the emphasis which molecular biology places on the building blocks of protoplasm and its products, it is probably easier to gain entry into, and understand the mechanical functioning of, the extracellular framework if the properties of the units of the framework are considered first, with the emphasis on the molecular aspects. This is the approach taken in this book.

# List of Symbols

|                |   |
|----------------|---|
| $A_0$          | initial cross-sectional area                                      |
| $A_s$          | area of shearing  |
| $b$            | $l/r$   |
| $C_1, C_2$     | Mooney constants  |
| $c$            | (as subscript) composite  |
| $d$            | diameter  |
| $E$            | stiffness; the Young modulus                                      |
| $e$            | strain (one-dimensional)  |
| $f; f$         | force; (as subscript) fibre                                       |
| $G; G$         | shear modulus; giga- ( $10^9$ )                                   |
| $G^*, G', G''$ | complex, storage and loss moduli                                  |
| $G(t)$         | relaxation modulus  |
| $g$            | acceleration due to gravity                                       |
| $H(\tau)$      | relaxation spectrum function                                      |
| $h$            | elastic loss factor   |
| $J; J$         | compliance; joule   |
| $J(t)$         | creep compliance  |
| $k; k$         | kilo- ( $10^3$ ); Boltzmann's constant                            |
| $L_0$          | initial length  |
| $dl, l$        | change in length  |
| $M$            | mega- ( $10^6$ )  |
| $M_c$          | molecular weight between cross-links                              |
| $m; m$         | metre, milli- ( $10^{-3}$ ), (as subscript) matrix, Maxwell; mass |
| $N$            | newton  |
| $n$            | nano- ( $10^{-9}$ )   |
| $R$            | resilience, the gas constant                                      |
| $r$            | end-to-end distance of a randomly orientated chain                |
| $S$            | entropy   |
| $T$            | temperature   |
| $t$            | time  |
| $U$            | internal energy   |
| $V$            | volume fraction   |
| $v$            | velocity  |
| $W_f$          | work of fracture  |

|           |                                    |
|-----------|------------------------------------|
| $x, y, z$ | (subscripts) three orthogonal axes |
| $\gamma$  | shear strain                       |
| $\Delta$  | small change, decrement            |
| $\delta$  | phase angle                        |
| $\eta$    | viscosity                          |
| $\theta$  | angle                              |
| $\lambda$ | extension ratio ( $= e + 1$ )      |
| $\mu$     | micro- ( $10^{-6}$ )               |
| $\nu$     | Poisson ratio                      |
| $\rho$    | density                            |
| $\sigma$  | stress, strength                   |
| $\tau$    | shear stress, relaxation time      |
| $\omega$  | frequency                          |

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# 1 Basic Theory of Elasticity and Viscoelasticity

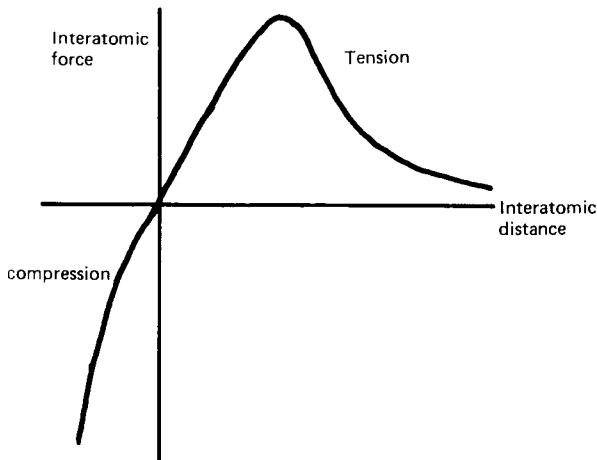
In the physically stressful environment there are three major ways in which a material can respond to external forces. It can add the load directly on to the forces which hold the constituent atoms or molecules together. This occurs in simple crystalline (including polymeric crystalline) and ceramic materials, and such materials are typically very rigid. Or it can feed the energy into large changes in shape (the main mechanism in rubber and other non-crystalline polymers). And finally it can flow away from the force and deform either semi-permanently (as with viscoelastic materials) or permanently (as with plastic materials).

## 1.1 Hookean materials and short-range forces

The first class of materials is exemplified amongst biological materials by bone and shell (chapter 6), by the cellulose of plant cell walls (chapter 3), by the cell walls of diatoms, by the crystalline parts of a silk thread (chapter 2), and by the chitin of arthropod skeletons (chapter 5). All these materials have a well-ordered and tightly bonded structure and fall into the same class of material as metals and glasses. What happens when such materials are loaded, as when a muscle pulls on a bone, or when a shark crunches its way through its victim's leg?

At equilibrium, in the unloaded state, the distance between the constituent atoms is 0.1 to 0.2 nm. At this interatomic distance the repulsion forces between the two atoms balance the attraction forces. When the material is stretched or compressed the atoms are forced out of their equilibrium positions and are either parted or brought together until the forces generated between them, either of attraction or repulsion respectively, balance the external force. This is shown schematically in figure 1.1. Note that the line is nearly straight for a fair distance on either side of the origin and that it curves eventually on the compression side (the repulsion forces obey an inverse square law) and on the extension side. With most stiff materials the extension or compression is limited by other factors (see section 1.6) to a matter of a fraction of the bond length so that the relationship between force and distance is, to all intents and purposes, linear. When the load is removed, the interatomic forces take the atoms back to their original equilibrium positions.

It is a fairly simple exercise to extend this relationship to a material such as a



**Figure 1.1** Stress–strain curve at the atomic level for a rigid material – the idealised curve for a ‘perfect’ material. The origin represents the equilibrium interatomic distance. On either side of the origin the curve is nearly straight

crystal of hydroxyapatite in a bone. This crystal consists of a large number of atoms held together by bonds. Then the behaviour of the entire crystal in response to the force is the summed responses of the individual bonds. Thus one arrives at the phenomenon known as Hooke’s law, originally stated (anagrammatically) as *ut tensio, sic vis* – as the extension, so the force. In other words extension and force are directly and simply proportional to one another and this is a direct outcome of the behaviour of the interatomic bond. But when dealing with a material it is obvious that measurements cannot conveniently be made of the interatomic distance (though they have been made using X-ray diffraction, which confirms the following). What is actually measured is the increase in length of the whole sample or a part of the sample (making the verifiable assumption that in a homogeneous material one part will deform as much as the next). This is then expressed as a ratio which is called the *strain*:

$$e = \Delta l / L_0 \quad (1.1)$$

This ratio is expressed either as a number (e.g. 0.005) or as a percentage (e.g. 0.5%). The force acting on each bond is a function of the number of bonds available to share the load. So if the area over which the force acts is doubled, then the load carried by each bond will be halved. Thus it is important, if one is to bring the data to the (notionally) irreducible level of the atomic bond, to express the force as a function of the number of bonds which are responding to it. In practice this means expressing the force as force per unit area, which is called the *stress*:

$$\sigma = f / A_0 \quad (1.2)$$

The force is nowadays expressed in newtons (a function of mass and the acceleration due to gravity – one newton is approximately the force due to 100 g, the weight of an average apple), the area in square metres. The slope of the straight, or Hookean, part of the curve in figure 1.1 is characteristic of the bond type and is a function of the energy of the bond. For the same reason it is found that the ratio of stress to strain is more or less characteristic of a material. The ratio of stress to strain is the stiffness or *Young modulus*:

$$E = \sigma/e \quad (1.3)$$

The units of  $E$  are the same as for stress, since strain is a pure number. Graphs showing the relationship between stress and strain are conventionally plotted with the strain axis horizontal and the stress axis vertical, irrespective of whether the relationship was determined by stretching the test piece in a machine and recording the developed forces or by hanging masses onto the test piece and recording the extension. Do not be surprised if it takes a long time for the mental distinctions between stress and strain to become totally clear. Not only are the concepts surprisingly difficult to disentangle, but the confusion is compounded by the usage of stress and strain in everyday speech.

One other characteristic of Hookean materials is that they are usually *elastic*. That is to say, they can be deformed (within limits) and will return to their original shape almost immediately the force is removed (almost immediately because the stress wave travels through the material at the speed of sound in that material. So when you pull on the brake lever on your bicycle the brake blocks begin to move a short time later, the time dependent partly on the speed of sound in the steel cable and on the length of the cable). This use of the word 'elastic' must not be confused with the usage of the term as in 'elastic band' where elastic is taken to mean highly extensible.

The Young modulus is a measure of stiffness in simple extension or compression. There are other ways of deforming a material which have different effects on the interatomic forces and therefore different effects on the material. Such a mode of deformation, frequently met, is shear. (Another mode of deformation – volume change from which is derived the bulk modulus – is ignored here.) As with the Young modulus, the shear modulus is defined as the ratio of stress to strain. The shear stress ( $\tau$ ) is defined as (see figure 1.2):

$$\tau = f/A_s \quad (1.4)$$

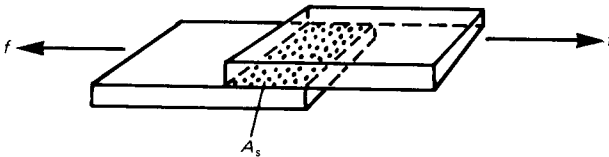
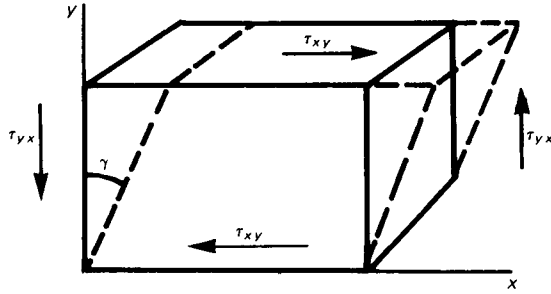


Figure 1.2 Conditions for the definition of shear stress (equation 1.4)



**Figure 1.3** Conditions for the definition of shear strain (equation 1.5)

The shear strain is defined somewhat differently (figure 1.3). The strain,  $\gamma$ , is measured in radians and the shear modulus ( $G$ ) is given by:

$$G = \tau / \gamma \quad (1.5)$$

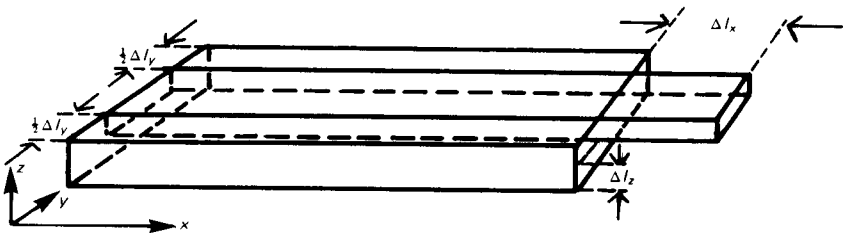
The simple picture given here is for isotropic materials whose structure and mechanical response are the same in all directions. The Young modulus and the shear modulus in an isotropic material can be related to each other by the expression:

$$G = \frac{E}{2(1 + \nu)} \quad (1.5a)$$

where  $\nu$  is the Poisson ratio. This is simply the ratio between the elongation and the lateral contraction (in either width or thickness) of the specimen (figure 1.4) as formalised in equation (1.5b):

$$\nu = -e_y / e_x = -e_z / e_x \quad (1.5b)$$

The Poisson ratio is often neglected: it usually appears as a small, constant number in many equations concerning biological materials and, as often as not, its value is assumed to be 0.5, which is the value for rubbers at small extensions (figure 1.5) and which assumes that the material retains a constant volume. This problem is returned to in section 4.4.2 where some results are given for soft tissues of various sorts. The problem occurs partly because soft tissues are extended by relatively large amounts (50% and more) and because they contain



**Figure 1.4** Conditions for the definition of Poisson ratio (equation 1.5b)

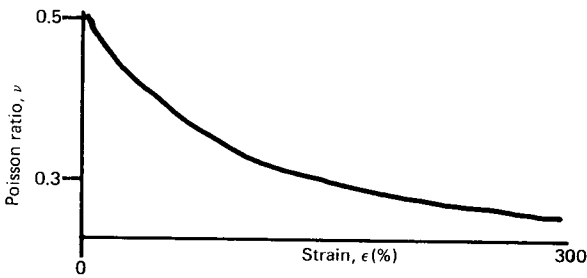


Figure 1.5 Variation of Poisson ratio with strain in a rubber

fibres. For instance a Poisson ratio of 1.0 can be obtained from a network or trelliswork such as an orthogonally woven cloth (e.g. a handkerchief) but only in directions at  $45^\circ$  to the warp and weft. A high Poisson ratio in all directions is characteristic, if not diagnostic, of an open feltwork rather like a haystack. Nonetheless it is quite feasible to have an open feltwork which is embedded in a soggy jelly which will flow in and out of the mesh, whose Poisson ratio is 1.0 or greater, yet whose volume is constant or nearly so. Thus the assumption that because biological materials contain water and are therefore incompressible it therefore follows that their Poisson ratio is 0.5 is not tenable. Not only is it possible to have voids in a material filled with 'alien' fluids but it is also possible to have a high Poisson ratio *and* constant volume (or a vanishingly low Poisson ratio, section 4.4.2) with a feltwork of fibres embedded in a viscous matrix. And once you start thinking of different ways of putting a material together it soon appears possible (using strut frameworks resembling the fibres in a feltwork, figure 1.6) to generate Poisson ratios of all magnitudes, even negative ones (material *expands* in one of the directions orthogonal to the extension). But until such studies are made – until a proper study is made of the Poisson ratios of soft tissues under varying states of initial strain –  $\nu$  will remain not merely neglected but inscrutable. Worse still,  $E$  and  $G$  cannot be related with any certainty using equation (1.5a) so that much of biomechanics theory (many equations concerning the mechanics of skin and artery) is wrong since the assumption ' $\nu = 0.5$ ' has been made.

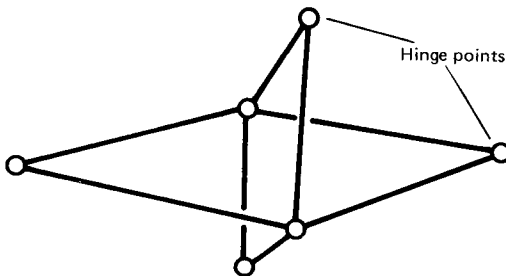


Figure 1.6 A strut framework which will give strange Poisson ratios

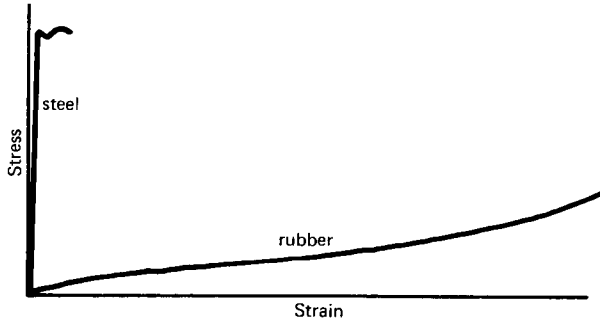
## 1.2 Rubbers and long-range forces

The second type of material to be considered is the rubbers or 'elastomers'. Very few rubbers exist in Nature in a pure and simple form. Obviously there is the latex of *Hevea brasiliensis*, but this is neither cross-linked (as is required if the rubber is to bear loads) nor are its rubbery properties used within the plant. There are two animal rubbers which have been investigated — resilin (found in wing-hinges, hair bases and so on in insects) and abductin (found in the inner hinge ligament of bivalve molluscs). Both these have the properties which one would expect of a rubber.

The important point about a rubber is that it is a long-chain polymer of random conformation. That is to say it is composed of very long chains (molecular weight  $\approx 10^5$ ) of one or more monomer units, and that each unit is more or less freely jointed into the chain so that each joint allows a wide range of movement. This is called 'free rotation' about the bonds of the backbone and is what distinguishes a rubbery polymer from a crystalline one: in a crystalline polymer (or in areas of crystallinity) the free rotation of the units is severely restricted by close packing, and rubbery behaviour is impossible. In actual fact it takes more than one monomer unit or residue to make a freely rotating unit or 'random link'. This is because the monomer units are of a finite size and shape and so cannot move with absolute freedom without hitting their neighbours ('steric hindrance'). With paraffin chains with a tetrahedral valence angle it takes three C—C links to make up a freely rotating or equivalent random link; with *cis*-polyisoprene units, as in *Hevea* rubber, the number of monomer units per random link is 0.77, since there are four bonds to each isoprene unit. With proteins the equivalent random link is 4 to 6 amino acids. Under the influence of Brownian motion the free rotation of the equivalent random links about the backbone of the polymer allows the chain to assume a random conformation. In other words there is no pattern to the angles which each link makes with its neighbour other than a statistical one. The fact that the molecules are in Brownian motion also leads to the concept of kinetic freedom, which is a way of saying that the chains are free to thresh around in any direction. Brownian motion is temperature dependent — as the temperature increases so the movement of the molecules and their subunits becomes more and more frenetic. In a similar manner, reduction in temperature causes the kinetic activity to be reduced until finally, at a temperature dependent on the particular rubber in question, it ceases altogether and any force which is exerted on the rubber meets the resistance of the covalent bonds linking the atoms, probably bending rather than stretching them. A rubber at the temperature of liquid nitrogen has similar properties to the ceramic phase of bone, although it has a lower modulus, is Hookean and is said to be glassy. The temperature at which this occurs is called the glass transition temperature.

However, the response of rubber to stress at normal temperatures is very different (figure 1.7 compares the shape of curve for a rubber and a mild steel). Rather than going deeply into the thermodynamics, suffice it to say that it is





**Figure 1.7** Comparison of the stress–strain curves of steel and rubber (the slopes have not been accurately calculated but give some idea of the differences – probably greater than shown here)

possible to divide the internal reaction of a material to an external force into two components: one is due to the bonds holding the components together (as in metals and glasses) and is loosely called the internal energy term. The other is due to the mobility of the components and is called the entropy term. Now entropy is a measure of the disorder of a system (life itself has been characterised as a continual battle against entropy) and the significance of this term can be appreciated as follows. When a piece of rubber is stretched the chains are pulled out of their random configuration and come to be arranged rather more parallel to the direction in which they are being extended. This partial orientation represents an increase in order and thus a decrease in entropy. Now consider the system as a kinetic one, with the rubber chains writhing in Brownian motion. It is this writhing which produces the tension. Imagine that you hold one of these writhing molecules by the ends and try to pull it straight. You are trying, by doing work on the molecule, to decrease its entropy. If the temperature increases and the molecule writhes more violently it opposes your efforts with greater force.

These ideas can be enshrined in the following mathematical expressions whose derivations are not considered here but which are described in Wainwright *et al.* (1976) and Treloar (1975). First the thermodynamic equation of state:

$$f = \left( \frac{dU}{dl} \right)_T - T \left( \frac{dS}{dl} \right)_T \quad (1.6)$$

This states that the force is distributed between a change in internal energy ( $dU/dl$ ) and a (temperature dependent) change in entropy ( $dS/dl$ ). In addition it can be shown that:

$$\left( \frac{dS}{dl} \right)_T = - \left( \frac{df}{dT} \right)_l \quad (1.7)$$

and therefore that:

$$\left( \frac{dU}{dl} \right)_T = f - T \left( \frac{df}{dl} \right) \quad (1.8)$$