The toughness of tooth enamel, a natural fibrous composite

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It is suggested on the basis of experiments carried out *in vitro* on whole caries-free human premolars that the energy absorbing capacity (mechanical toughness) of the enamel depends upon the explusion of liquid from between the mineral fibre of this natural composite material. Classical theory of flow through narrow channels with recent modifications to allow for the influence of the electrical double layers at the surface of the fibres has been applied to show how toughness can be influenced and controlled by wholly chemical methods. In particular the effect of replacing the hydroxyl groups with flouride ions is shown to result in an increase in toughness. Finally, it is suggested that the flow of liquids through fine capillaries may be responsible for toughness in other natural fibrous composites such as wood.

1. Introduction

The most widely sought properties of load bearing materials are high strength and toughness. These two qualities are usually mutually exclusive although reasonable compromises may be struck with metals because of their high elastic moduli and because, by making suitable alloying additions, the toughness can be manipulated by controlling the mobility of microscopic defects such as dislocations.

These possibilities are not available in natural materials since the range of substances is limited to a few relatively weak organic molecules such as collagen and cellulose and an even more restricted choice of inorganic compounds such as calcium hydroxyapatite found in hard tissue such as bone and teeth. None of these materials would form obvious choices in man-made structures and under these circumstances Nature resorts to designing in composite materials.

In this work the origin of toughness in human dental enamel is considered, which appears, in

structure, to be a particularly simple natural fibrous composite. It seems likely, however, that the ideas described may equally well apply to more complicated materials such as bone and wood.

2. The composition and structure of tooth enamel

Tooth enamel is the hard ceramic-like material which forms a protective shell on the surface of mammalian teeth. It consists, in mature human teeth, of about 96 wt% calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, the remainder being largely water with some organic material including proteins. The inorganic material is arranged as closely spaced fibres (prisms) of the order of micrometres in diameter, which run from the enamel/dentine interface to the outer surface of the tooth which they intersect at an angle of less than 90°. The fibres are not, themselves, monolithic, being made up of many smaller crystallites ~ 200 nm in diameter and up to 100 μm in length with their long axes approximately parallel to the axis of the fibre but with the crystallites nearest to the outer surfaces of the fibre tilted somewhat off axis. The whole is an efficient fibrous composite in which the water and organic materials form the matrix.

Because of the high volume-fraction of fibres, maximum benefit accrues from their high stiffness [1] while at the same time allowing greater toughness than a monolithic structure of this rather brittle material could be expected to possess. A discussion of the detailed microscopic structure of human and bovine enamel has been given by Poole and Brookes [2] and Glimcher, Daniel, Travis and Kamki [3].

The one additional feature of interest to the present study is that the enamel is porous with pore radii lying in the range 1 to 25 nm depending upon the method of measurement. For example, non-polar rare gas molecular adsorption gives a lower value for total pore volume than if the measurements are made with water as the adsorbate. The disparity in these measurements has led to differences in interpretation not only in pore-size distribution but also in the spatial distribution of pores within the enamel structure. Thus Poole [4] and Dibden [5] associated the large uptake of water with macropores filled with organic material capable of adsorbing water but inaccessible to krypton. These spaces are associated with growth features near the enamel/dentine junction. Intermediate size pores partially filled with organic

material and capable of taking up both krypton and water are believed to be located at the fibre boundaries while the smallest size pores are thought to lie between the crystallites of which the fibres are composed. Moreno and Zahradnik [6], on the other hand, interpret a bimodal distribution of pore size deduced from measurements of water adsorption hysteresis as representing necked or constricted pores, those of smaller radius being located within the fibres while the larger pores are found between the fibres. While the results of both groups of workers are ambiguous with respect to the location of pores within the enamel structure, the author of the present work is inclined towards the interpretation given by Moreno and Zahradnik for pore sizes because of the more detailed adsorption model used by them and because measurements of water uptake at 25° C relate more closely to the conditions used in the present investigation.

3. Materials and experimental method
3.1. The teeth
The teeth used were whole caries-free human premolars which had been extracted for orthodontic reasons. After extraction they were stored in saline solution and tested as soon as possible and usually within a few days. In the event of a delay between extraction and testing, the teeth were refrigerated.

The teeth were taken from both male and female mouths ranging in age from 11 to 15 years and in those experiments in which a comparison of behaviour is made, teeth from the same mouth were used whenever possible. The results are based upon experiments on a total of about fifty teeth.

3.2. Mechanical testing
Tests were carried out on a Meyes servo-hydraulic machine. Because of the frequency of cyclic loading, the load—deformation curves were displayed on the screen of a storage oscilloscope and subsequently photographed.

Before the tests, the root of each tooth was ground flat to within 5 to 6 mm of the cervical margin such than when standing on a horizontal surface, the vertical bisected the angle between the occlusal surfaces as judged by eye. This ensures that the load which was applied via a 3 mm diameter steel ball lying in the cusp of the tooth was roughly evenly distributed. The tooth was then mounted at the centre of a Perspex tube
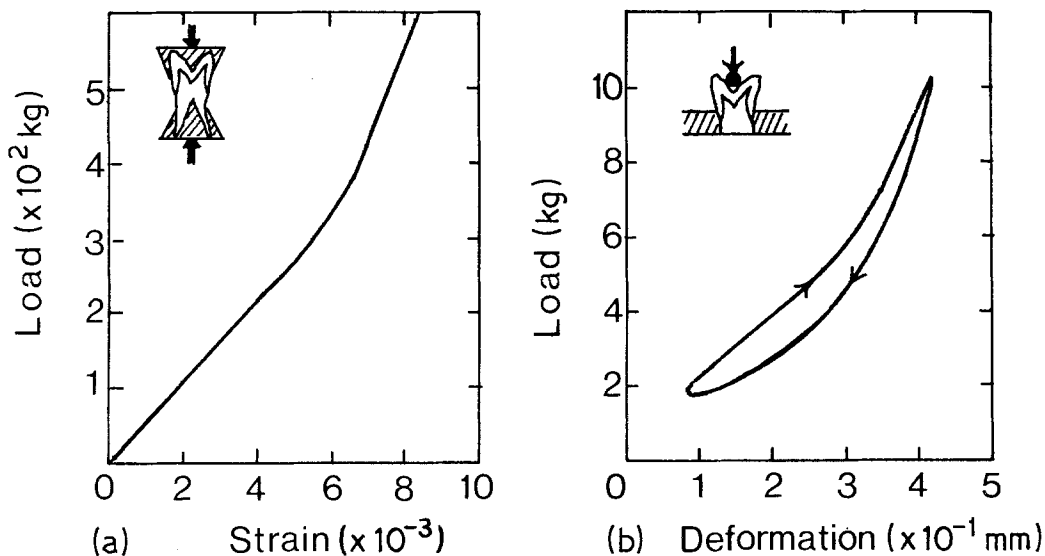
Figure 1 Load–deformation characteristics of human tooth enamel. (a) results of Haines *et al.* [7] obtained from static loading tests (b) typical hysteresis loop obtained in the present cyclic loading tests. The insets show the method of applying the load.

(which ultimately formed the container for the fluids in which the testing was carried out) by pouring cold setting resin around the remaining portion of the root and up to the enamel.

The advantage of this method of testing in which the load is applied by point contact of the ball, over that adopted by, for example, Haines, Berry and Poole [7], is that the stresses are confined to a relatively small region just below the ball while the rest of the tooth is lightly loaded (see for example the photoelastic and finite element stress analyses shown by Farah, Craig and Sikarskii [8]). This avoids ambiguities about whether the effects observed are largely the result of deformation of the less rigid dentine and mounting resin. The compressive displacement of the whole tooth (labelled deformation in Fig. 1b) was measured by using an LVDT transducer contacting the platten on which the tooth was mounted.

4. Mechanical properties of tooth enamel
4.1. The stress–strain behaviour of enamel and whole teeth
Neumann and Di Salvo [9] seem to have been the first to observe that whole teeth under compressive loading show two distinct linear regions in the load–compression curve. At low loads, the tooth appeared to have greater compressibility. Later work by Haines, Berry and Poole [7] and Haines [10] confirmed this observation, Fig. 1a, and the effect was attributed to the expulsion of liquid

from the matrix of the composite. In the present study, it was shown that when the load is released, the compressive displacement recovers elastically although the original shape is not achieved immediately and the load–compression curve shows hysteresis, Fig. 1b. The tooth enamel thus behaves like a stiff sponge from which liquid is expelled in compression and drawn in again when the load is released. The area under the hysteresis loop is a measure of the energy required to squeeze out the liquid and, as with other viscoelastic materials, provides the enamel with toughness in elastic deformation.

4.2. The effect of repeated loading
On cyclically loading the tooth, the area under the hysteresis loop was found to diminish with the number of cycles, Fig. 2. Moreover, on interrupting the loading cycle, the tooth rapidly "recovered". This recovery is fast enough that the tooth recovers its original energy absorbing capacity in the time taken to refill the mouth during eating.

In the present experiments, the rate of fall of energy absorption with number of cycles was insensitive to loading frequency over a four-fold range of frequency although little information is to be gained from this observation in view of the difficulty of making close comparisons of results because of differences in shape and possible variations in structure from one tooth to the next.
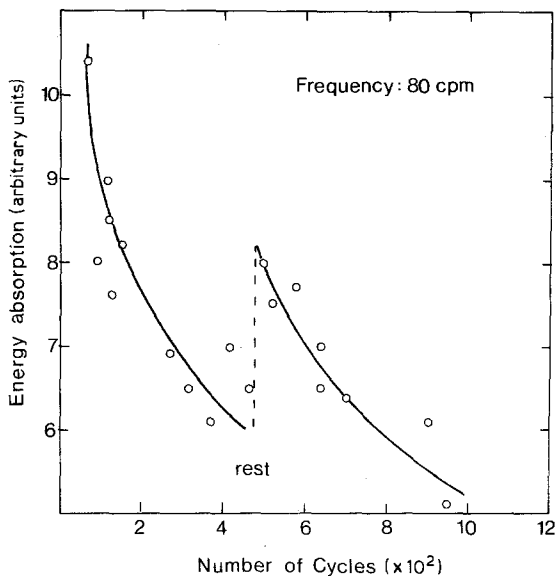
Figure 2 The effect of repeated loading on the energy absorption (area under the hysteresis loop) of tooth enamel. After a rest period lasting 1 sec, the enamel "recovers". Tests carried out in 1% w/v saline.

Figure 3 The effects of 75% lactic acid (■) on the energy absorption in cyclic loading of tooth enamel. The results are compared with a similar test carried out in 1% w/v saline, (○).

4.3. Effect of liquid environments on loading hysteresis

The effects of those liquid environments which are known to have an effect on the susceptibility of teeth to carious attack were also tested. Lactic acid, in which the fibre fraction of the enamel is extremely soluble, had no effect on the area under the hysteresis loop, Fig. 3, until breakdown of the tooth structure vitiated the test. Testing in 1% wt/vol stannous fluoride solution in which the tooth had been soaked for 24 h resulted in a over-all increase in the area under the hysteresis loop, Fig. 4. This signifies an increase in toughness of the tooth enamel after the fluoride treatment.

5. The origin of toughness in tooth enamel

The experimental observations described in Section 2 can be rationalized if it is assumed that energy absorption in a composite such as tooth enamel derives from the work done in forcing liquid through the narrow channels between the hydroxyapatite fibres. This method of energy absorption is often used in shock absorbers and dampers and has been suggested as a method of protecting large engineering structures during earthquake activity [11, 12]. It bears little direct relationship to the mode of energy absorption in conventional man-made fibrous composite materials which rely on a combination of plastic
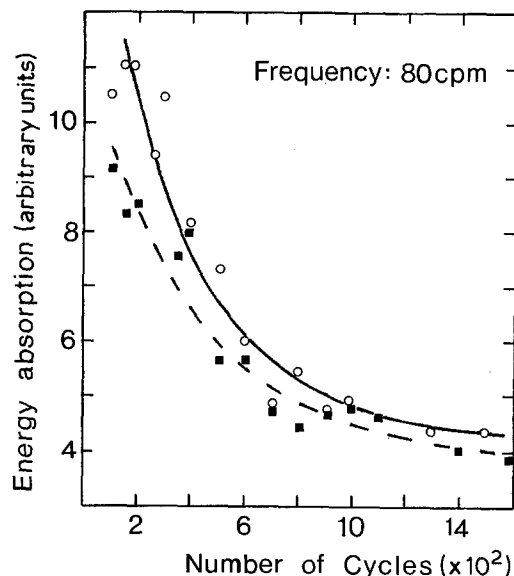
deformation in matrix or fibre and the work of fibre—matrix debonding and fibre pull-out [3].

5.1. The theory of flow through narrow channels

The classical theory of flow through wide channels describes the phenomenon in terms of the liquid

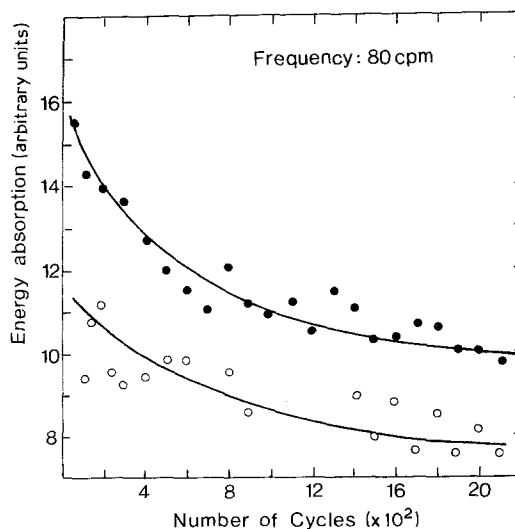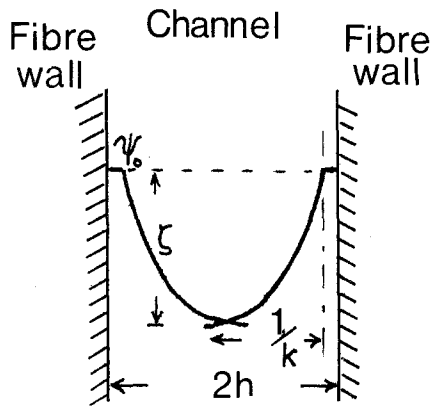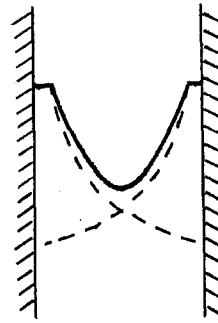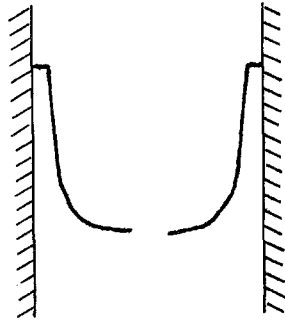

Figure 4 The influence of F⁻ ions on the energy absorption of tooth enamel. The teeth were tested after immersion in 1% w/v stannous fluoride solution for 24 h. The results (●) are compared with those for teeth tested in 1% w/v saline (○).

Fibre wall | Channel | Fibre wall

(a) Wide channel
$G = 0$; $H \to 0$

(b) Narrow channel
$$G \to 1 \; ; \; H = \cosh\left\{\frac{e\zeta}{kT} - 1\right\}$$
$$\approx 0 \text{ for small } \zeta$$

(c) Narrow channel
with $1/k$ small

Figure 5 Schematic representation of the effect of channel width and double layer thickness on flow through electrically charged pores. (a) Wide channel in which electrical double layers have no influence on each other. (b) Narrow channel in which considerable overlap of double layers impedes liquid flow. (c) Decreasing the electrical double layer thickness by increasing the concentration of electrolyte effectively increases channel size and flow of liquid.

viscosity, channel width and pressure gradient [14]. The implication of "wide" in this context is that effects due to the walls of the channel can be neglected. When the wall consists of an ionic material it is, under most circumstances, electrically charged and has associated with it an electrical double layer in which the charge distribution normal to the surface is described by Poisson's equation.

The theory of electro-kinetic flow through two-dimensional channels is often restricted to those cases in which there is no overlap of the double layers on opposite faces and in this case the velocity of flow U under zero external pressure is given [15] by

$$U = -\frac{\chi \epsilon \epsilon_0 \zeta}{\eta}, \tag{1}$$

where χ is the electric field parallel to the channel wall, ζ is the zeta-potential, η is the liquid viscosity,

ϵ is the dielectric constant of the liquid and ϵ_0 is the permittivity of free space.

Burgreen and Nakache [16] and, more recently, Levine, Mariott and Robinson [17] have extended the theory to include the case of very narrow channels in which there is overlap of the electrical double layers. In these treatments U is reduced to u where

$$u = V(1 - G), \tag{2}$$

in which $G = \psi_0/\zeta$. ψ_0 is the mean electrical potential across the channel and $\psi_0 = \zeta$ at the channel wall, Fig. 5. The nature of G is such that as the channel width $h \to 0$, $G \to 1$ and all flow ceases.

For narrow channels of fixed size, the degree of overlap of the electrical double layers depends also on the thickness of the double layer $1/\kappa$ which is controlled by the concentration of ions in the liquid filling the channel. The parameter κ is given by

$$\kappa^2 = \frac{2e^2 n}{\epsilon \epsilon_0 kT}, \tag{3}$$

in which e is the electronic charge and n is the concentrations of ions for a uni–univalent electrolyte.

The volume of liquid transported in unit time, V, can now be written

$$V = 2 h u = -\frac{2 \chi \epsilon \epsilon_0 h \zeta}{\eta} (1 - G). \qquad (4)$$

Alternatively, in the absence of an applied electric field, the volume flow for a pressure gradient P induces a streaming potention χ' and is given by

$$V' = \frac{2}{3} \frac{P h^3}{\eta} - \frac{2 \chi' \epsilon \epsilon_0 h \zeta}{\eta} (1 - G), \qquad (5)$$

in which the first term on the right hand side is the two-dimensional Poiseuille flow. The effect of narrowing the channel width to the point where the double layers overlap is to increase the apparent viscosity to η_a for which

$$V' = \frac{2}{3} \frac{P h^3}{\eta_a}. \qquad (6)$$

In reducing Equation 5 to Equation 6, the relationship between χ' and P [17] has been used

$$\frac{\chi'}{P} = \frac{\epsilon \epsilon_0}{\eta \lambda} \zeta \frac{(1 - G)}{(1 + H)} \qquad (7)$$

for zero current flow. $\lambda = 2 n e^2 / f$ is the specific conductivity of the fluid in the pores and f is the friction coefficient of ions transported. H, like G, depends upon the value of the ζ-potential and the thickness of the electrical double layer relative to the channel width. It approaches zero for large channels. Its precise form has been evaluated by Levine et al. [17]. Finally the ratio of viscosities in the presence of surface charge to that without is given by

$$\frac{\eta_a}{\eta} = \left\{ 1 - \frac{1.5}{(1 + H)} \left[\frac{e \zeta}{kT} \cdot \frac{(1 - G)^2}{\kappa h} \right] \right\}^{-1}. \qquad (8)$$

5.2. Application of the theory to tooth enamel

In tooth enamel, the crystallites are closely spaced and ideally provide a system of interconnecting lamellar channels. Measurements of water vapour adsorption give a pore size distribution with a double maximum, Fig. 6, [6]. At these pore sizes, the sides of the channel are close enough for interaction of the electric double layers to occur. For example, solution of Equation 3 shows that the thickness of the diffuse double layer $1/\kappa$ is 1 nm for a solution concentration of 0.1 M.

Of greater importance from the point of view of increased toughness is the value of ζ. It is
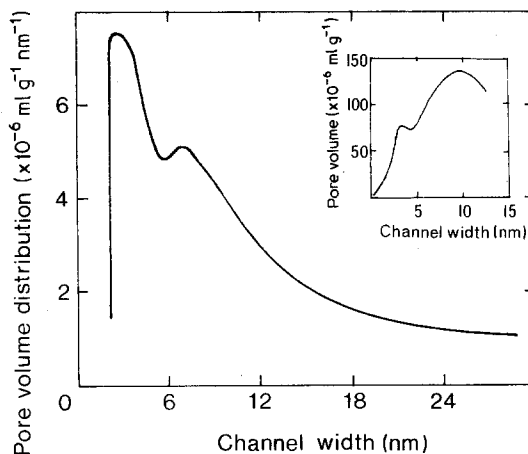

Figure 6 Distribution of channel sizes in human tooth enamel (after Moreno and Zahradnik [6]). Idealized model assumes the channels to be parallel sided. The cumulative pore volume is shown in the inset.

known from the work of Bell, Posner and Quirk [18] that the point of zero charge i.e. the pH at which equal numbers of positively and negatively charged ions are present on the surface of hydroxyapatite crystals is at pH 7.6 with the crystals immersed in saline solution as in the present experiments. It is assumed that the pH in the oral environment is about 7, which implies an electrical double layer potential of about 36 mV. This value used in Equation 7 gives the variation of η_a/η with κh shown in Fig. 7. For fixed pore

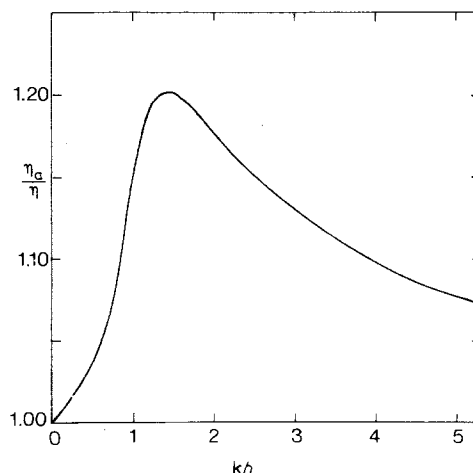

Figure 7 The influence of channel width and double layer thickness on the relative viscosity of liquid in the channel. The curve is evaluated assuming the value of $\zeta = 36$ mV which is the potential ideally generated at the surface of pure hydroxyapatite at the pH of the oral environment. The effect of decreasing the pH would be to increase the value of η_a/η at the maximum.

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sizes, the maximum in the curve will occur at a particular double layer thickness.

The effect of repeated loading on the energy absorbing capacity of the enamel can now be seen as the result of disruption of the diffuse double layer on squeezing the liquid from the pores. The rest period enables the double layer to re-establish. The energy absorption does not fall to zero, however, since the finite viscosity of the liquid η will set the minimum value irrespective of the influence of double layer effects.

5.3. Influence of system variables on toughness

It is clear that the major factors controlling η_a/η are ζ and κ for a given pore size. κ can be varied by changing the ionic concentration of the liquid flowing through the pores, the double layer thickness decreasing with increasing concentration. It seems likely that under normal circumstances this would not be an easily changed variable. ζ is controlled by the pH of the oral environment and also by the composition of the fibre surfaces and it is this last factor which can most readily influence the value of η_a/η.

The hydroxyl groups in hydroxyapatite can be easily replaced by fluoride ions which have the same electrical charge and about the same size. Waters [19, 20] has demonstrated that tooth enamel acts as an ion exchange membrane and that replacement of hydroxyl with fluoride ions results in an increase in the negative fixed charge density at the surface. This is consistent with the observations of Bell et al. [18] that the point of zero charge of fluorapatite crystals is at pH 6.8 which implies that, at the pH of the oral environment, the surface of the fibres would change from being positively to negatively charged.

The influence of this replacement on the energy absorption of the enamel measured experimentally is shown in Fig. 4 in which the effect of soaking the teeth in a 1% wt/vol solution of stannous fluoride (pH 4.1) for 24 h before testing in this solution is shown. The area under the viscoelastic hysteresis curve increased relative to that measured in saline solution and also falls with increasing number of loading cycles.

Fig. 7 shows that the maximum value of η_a/η is achieved for $\kappa h \sim 2$. Using the value of $h = 1.4$ nm measured by Moreno and Zahradnik [6], $\kappa \simeq 1.4 \times 10^9$ m^{-1}. Moreover the concentration of electrolyte needed to achieve this value of κ can be evalu-
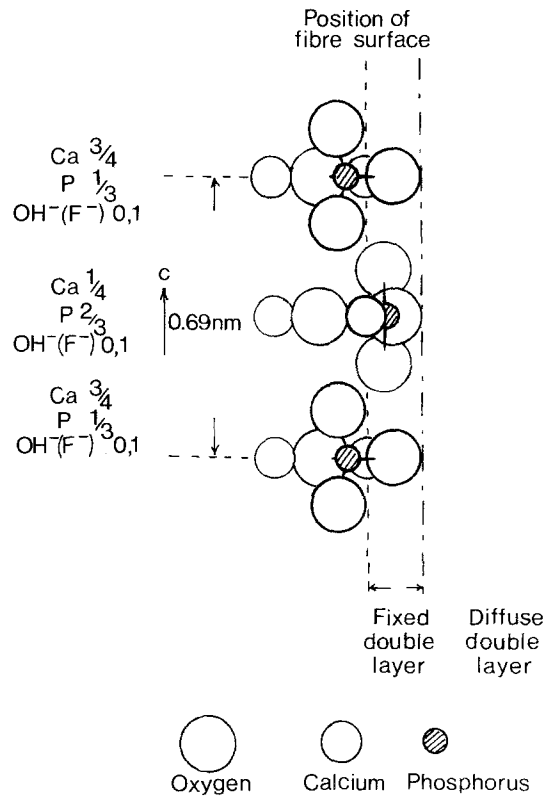

Figure 8 Projection onto (1 0 0 0) plane of the surface region of the hydroxyapatite. In fluorapatite, the F$^-$ ions occupy positions at the corners and mid points of the side of the unit cell. In fluoride solutions, F$^-$ ions first replace OH$^-$ groups attached to hydrated surface Ca^{2+} ions. At higher concentrations, the structural OH$^-$ groups at the positions mentioned are replaced.

ated from Equation 3, and is 0.2 M. Bell et al. [18] have suggested that the fluoride concentration required to replace all the hydroxyl groups which form the hydration sheath of the calcium ions on the surface of hydroxyapatite crystals is about 2.5×10^{-4} M. Higher concentrations of fluoride are believed to replace the structural OH groups attached to Ca^{2+} ions (Fig. 8) thus lowering the pH of the point-of-zero charge and increasing the negative charge on the fibre surfaces at the pH of the oral environment. It appears, therefore that replacement of OH$^-$ by F$^-$ on the surface of the fibres provides the best possibility for influencing the toughness of the enamel without substantially altering the structure or the biological function of the tooth.

5.4. Absolute value of energy absorption

The absolute value of the energy absorption is difficult to calculate from the areas under the

loading curves. This is largely because of the complex stress distribution in the irregularly shaped tooth. However, an order of magnitude calculation can be made of the energy required to squeeze liquid through pores of the same diameter as those found in tooth enamel. Starting with the classical Poiseuille formula for the rate of flow of liquid through a capillary and assuming a viscosity of $1 \, kN \, m^{-1} \, sec^{-1}$ for the liquid in the pores, the energy absorbed in capillary flow is calculated to be about $10^4 \, J$. The increase in energy due to the influence of the interacting diffuse double layers at the fibre surfaces is linearly dependent upon the change in viscosity as predicted by Equation 7.

Whether fluoride ions penetrate the enamel to a substantial depth (which in this case would imply a distance of about 0.5 mm below the enamel surface such as to influence the deformation produced by the ball) is a matter for conjecture. Hecules and Craig [21, 22] have examined the surface of fluoridated enamel using the sensitive technique of X-ray photoelectron spectroscopy. Used in conjunction with argon ion etching to remove the outermost surface layers, they were able to obtain some idea of the variation in composition with depth. Although they were able to show marked compositional changes involving fluorapatite, the method gives no indication of the location of the fluoride ions relative to the fibre or crystallite surfaces of the pores. For the present mechanism, to be effective, requires a low bulk concentration of fluoride in the structures provided it is concentrated at the surfaces of the pores.

6. Other natural fibrous composites

Both hard- and softwoods consist of bundles of hollow fibres, the tracheids, parallel to the long axis of the tree trunk or branch. These fibres are normally filled with sap which flows from roots to crown through circular orifices in the radial walls of the tracheids. Flow is normally restricted by a porous membrane which can be degraded by bacterial activity, thus increasing the permeability of the tracheids to the flow of liquid [23]. It is matter of common experience that the toughness of wood as judged by its resistance to fracture across the longitudinal axes of the tracheids is very dependent upon the water content of the material, decreasing with water content. As with tooth enamel, therefore, toughness is depen-
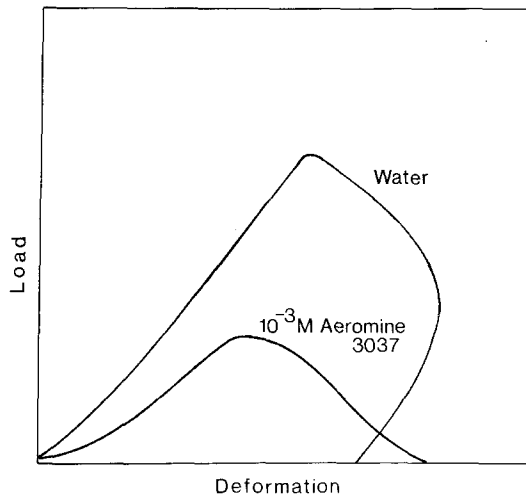

Figure 9 The influence of surface charge on the deformation of wet sand. The experiment in which a punch loads and unloads the surface of the compacted sand in a time interval of about 0.5 sec is purely qualitative and illustrates the effect of reducing the negative charge on the silicate grains by the addition of a cationic surfactant.

dent upon the flow of liquid through the hollow fibres and is dependent upon the porosity of the membranes separating the tracheids. To date no work seems to have been carried out to test this hypothesis.

7. Relationship between natural and "man-made" composites

The question inevitably arises as to what can be learned from Nature about toughness mechanisms in composite materials which could be applied to the design of man-made materials. It is clear that in tooth enamel the key factor in controlling toughness is that the surfaces of the fibres should be in close proximity. The hexagonal section of the hydroxyapatite crystals ensures that such close packing can be achieved. Man-made fibres are usually circular in section and so make contact at three points only, when closely packed. This would not be expected to enable sufficient interaction of the electrical double layers at the surface to occur. Nevertheless, that the deformation of a compact of spherical particles can be influenced by control of the charge on the surface of the particles is demonstrated by the behaviour of wet sand with different amounts of surfactant adsorbed at the interface between the grains. The effect is shown qualitatively in Fig. 9 for sand in solutions of a commercial flotation agent (Aeromine 3037,

Cyanamid). Silica sand in water would be expected to be negatively charged at the surface of the grains due to the formation of silicate anions. Increasing concentrations of the surfactant reduce the net electrical charge at the surface and this can be seen from the figure to result in reduced area under the load–deformation curves.

The possibility of simulating composites with controllable toughness based on the structure of wood seems to be more realistic, however, since the concept of utilizing the increased energy needed to squeeze a liquid through a porous structure is already well established.

Acknowledgements

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