Tooth—A natural biocomposite

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Abstract. The inorganic content of human tooth is predominantly hydroxyapatite. The content varies in enamel and dentin. A reversible thermal transformation at 157 °C is observed and has correspondence in the dielectric measurements. The dental decay is related to the piezoelectric property of tooth, which is similar to a polar glassceramic. The toughness of tooth is higher than hotpressed hydroxyapatite and owes it to the microstructure signifying the importance of a weak, pliable interface. The hardness is graded, higher for enamel in the crown and very much lower for dentin, to suit their function and environment. The relevance of biomimics in designing materials for advanced performance is discussed.

Keywords. Tooth; biocomposite; caries; hydroxyapatite; biomimics.

1. Introduction

In recent years attention has turned on natural materials as they are light and tough. It has been noticed that no man-made material is able to achieve the toughness at such low densities as in shell, wood or tooth. Various approaches have been made to copy them, which encompasses a new subject called biomimics (Calvert 1990). Tooth is nature's cutting and grinding tool. It is a natural composite consisting of collagen, biopolymers and hydroxyapatite (HAp). Tooth has three major sections called the enamel, dentin and the core pulp, each having a different composition, property and function.

Synthetic HAp is a phosphate of calcium and is often used in restorative dental surgery and in implants. Tests have confirmed that it is bioactive and bonds to the biotissues (Hench 1991). HAp content is different in natural bone, dental enamel and dentin. The tooth enamel is wear-resistant. This paper presents the study of the physical and mechanical properties of teeth with a future aim for (i) designing better implants which can match with the properties of natural tissues, (ii) obtaining composites with higher values of toughness for multivariant applications and (iii) elucidating the problem of dental decay, which is said to relate to the piezoelectricity of tooth (Masi and Masi 1989). The investigation has shown the role of micro and macrostructure in achieving high toughness in tooth compared to synthetic HAp. The relevance of biomimics for enhancing toughness in light materials is discussed.

2. Material and experimental methods

Twelve samples in all of deciduous (MT), normal (NT) and diseased (DT) teeth were examined. They were cleaned and sterilized. X-ray diffraction and infrared (FTIR) measurements were carried out to identify phases and molecular groups.

An impedance bridge was used for measuring the capacitance in the frequency range 1 kHz to 1 MHz and at temperatures from ambient to 400 °C. The samples were coated with silver paint for good electrical contact. Dielectric constants were calculated from

a) MAIN SECTION OF TOOTH

b) SHADED SECTIONS ON WHICH HARDNESS WAS MEASURED

1. 2640 - 3400 MPa

2. 560 - 800 MPa

3. 440 - 740 MPa

Figure 1. a. Layers of tooth and b. sections for microstructure and hardness.

measured capacitances. Differential scanning calorimetry (DSC) methods identified the temperatures of transformation. Repeated reruns were taken while heating and cooling to confirm the reversibility of the transformations.

SEM and EDX analyses on carbon-coated fractured surfaces reveal the microstructures, fracture patterns and elemental content.

The Vickers hardness numbers were measured with a Leitz tester at a load of 100 g. The variations of hardness with load in the range 50 to 500 g were also studied to know the initiation of cracks. The toughness was calculated from the initiation of cracks and indentation at 2 kg load. Linear thermal expansion measurements were carried out in the range 20 to 400°C using a dilatometer.

3. Results and discussion

Tooth has three parts—the root, the neck and the enamel (figure 1a). The root is within the gum attached to the tooth-bearing bone. The crown projects into the mouth cavity. It has enamel and dentin. The neck is the in-between area. Forms of teeth reflect their functions—the incisor crowns have cutting edges and the molars have elevations and valleys suited for grinding. The enamel is the hardest of calcified tissues. Dentin grows at the expense of primary pulp as dentinal tubules. It has less mineral as compared to enamel and is more elastic. Cement is formed as layers on the surface of roots—similar in composition and structure to bone. Pulp occupies the central cavity and connects to the root canal. The pulp consists of cells, fibres, blood vessels, nerves etc. The tooth

grows from the pulp. The three sections of tooth can have different properties as their compositions are different.

3.1 Density

The densities of tooth samples were measured by the displacement method. They are in the range 1.67 to 2.0 g/cc. The tooth consists of enamel, dentin and pulp, which have different densities owing to different HAp content. The density of hydroxyapatite is 3.1 g/cc. The density of dental enamel with 95% HAp content is about 3 g/cc (Manabe *et al* 1987) whereas dentin with 48% HAp has lower density — 1.5 g/cc agreeing with the average density of whole tooth. The hardness in the sections shown in figure 1 relates to the variation in the HAp content.

3.2 Structure

XRD patterns showed broad peaks with the d spacings confirming to the HAp content (figure 2). The broadness could either be due to the fine grain size of crystallites or off-stoichiometry. Our experiences in the processing of HAp through different chemical routes show that initially (before calcination at 600°C) the peaks are broad and that several phosphate phases can coexist along with the carbonate (Saraswati 1995). The presence of vacancies when Ca/P is off-stoichiometric could account for some disorder and broadening.

The bone in animals and human beings contain some carbonate in the apatite, the carbonate replacing partially either the hydroxyl or the phosphate group such as $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$ or $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)_y(\text{OH})_{2-y}$ (Nordstrom and Karlsson 1990). The carbonate replaces hydroxyls when the reactions are at low temperatures and replaces phosphate ion at high temperatures (at fusion) (Stack and Feranhead 1965). The carbonate amount varies in bones and can occur as calcium carbonate and carbonate apatite. The calcium to phosphate ratio also varies from 1.4 to 2.1. Since XRD of our samples did not reveal a CaCO_3 phase we presume that the free calcium carbonate content is below 5 w%. The FTIR absorption patterns had vibration modes corresponding to carbonate groups at 1460, 1410, 872 cm^{-1} apart from the vibrations expected of PO_4 and OH groups of apatite. The patterns differ from those of synthetic

Figure 2. X-ray diffraction on normal tooth.

Figure 3. FTIR of synthesized HAp.

HAp. The characteristic modes for apatite hydroxyl groups at 3570 and 633 cm^{-1} were absent in the teeth samples (figure 3) confirming that hydroxyl ions were replaced by carbonates. The role of carbonate in the structure is to reduce ionic activity and to inhibit crystal growth and size.

3.3 Dielectric properties and caries

Dental decay, caries, is the most common of dental diseases and is frequently associated with the destruction of calcified tissues, enamel or dentin (Nikifuruk 1985). Several reasons associated with the electrical, mechanical and physical properties are suggested. It commonly arises from the biochemic action of acids produced by the bacterial fermentation of food debris, especially starch and sugar. Caries of dental enamel was attributed to the bulk diffusion of hydroxyl ions arising from the decomposition of HAp in the acidic environment (Young *et al* 1969). Incorporation of fluoride ions was found to reduce the incidence of caries as bulk diffusion was inhibited. However, self-diffusion experiments for Ca^{2+} and PO_4^{3-} in fluorapatite showed extremely low values for the diffusion coefficients for all ions in the apatite structure indicating that bulk diffusion processes are insignificant at biological temperatures (Den Hartog *et al* 1972). Hence diffusion could not be the cause for caries. The piezoelectric property of teeth is said to cause root caries (Masi and Masi 1989).

Figure 4. DSC measurements in normal and diseased tooth.

Figure 5. Temperature dependence of ϵ and $\tan \delta$.

The piezoelectric nature of tooth was confirmed through dielectric measurements. On varying the temperature the $\tan \delta$ values show a broad peak at about 150°C (figure 5), whereas the capacitance broadening was around 200°C. The shift is plausible because $\tan \delta$ losses are from ion migration whereas capacitance changes arise from electrical charges. The temperature dependence of capacitance (figure 5) and $\tan \delta$ bear a strong resemblance to those of polar glassceramics, which show piezo and pyroelectricity arising from the oriented microstructure. In these materials the orientation of poles is achieved through processing and not by applying an external electric field (Halliyal *et al* 1985). It needs to be mentioned that in some glassceramics no crystalline phase transformation was observed at these temperatures (Halliyal *et al* 1985). In

Figure 6. Thermal expansion coefficient—variation with temperature.

Figure 7. Frequency variation of capacitance.

thermal expansion measurements of tooth sample (figure 6) we observed an anomaly around the transformation temperature compared to HAp (dashed line).

In tooth the piezoelectricity makes it function like a sensor. When the acidic attack on tooth erodes the root or enamel the possibilities are that the orientation is lost.

which disturbs the sensor (or immune) action and the disease progresses without any check. Piezoelectricity cannot be the primary cause for caries. In many natural materials e.g. mollusc shells, the damages arising from attacks are repaired through such immune actions.

Figure 8. a–b. For caption, see p. 839.

Figure 8. c–d. For caption, see p. 839.

DSC measurements showed reversible, endothermic peaks for both normal (NT) and diseased (DT) tooth. The peaks differed in shape and heat energies—13.5 J/g for NT and 11.7 J/g for DT. The microstructure showed disturbed orientation in DT. At this point it is difficult to comment more on this difference.

Figure 8. Scanning electron micrographs of (a) section perpendicular to long axis, (b) section parallel to long axis, (c) oblique section, (d), (e) and (f) crack paths at different tilt.

The variation of C and $\tan \delta$ with frequency in the kilo to megahertz region were similar for normal, diseased tooth and synthetic HAp (figure 7). Different factors contribute to the frequency dependence of dielectric constant. Below 1 kHz contributions come from the space charge effects due to mobile or trapped charges at the surface

Table 1. Elemental analysis of tooth samples (EDX) in atomic %.

Element	MT	NT	DT
Mg	3.76	1.16	1.63
Al	3.47	1.45	2.04
Si	10.33	5.62	5.97
P	30.31	31.62	33
S	9.71	1.26	1.45
Cl	5.13	0.9	1.04
Ca	36.28	57.79	54.75
Fe	1.02	0.19	0.11
Ca/P	1.2	1.83	1.66

MT, deciduous tooth; NT, normal tooth; DT, diseased tooth.

or interface. In the intermediate kHz to MHz frequency regions the dipole effects contribute significantly to the dielectric constant. The charge imbalances due to off-stoichiometry or partial carbonate replacements for OH or PO_4 can give rise to a net dipole moment.

3.4 Microstructure

The microstructure shows orientation (figure 8). In dental enamel the microstructure consists of units called prisms or rods, which are not exactly cylindrical but with round heads and narrower tails (Stack and Fearnhead 1965). These form a close-packed structure by interlocking heads with tails from adjacent prisms. The long axis of apatite crystallites appear to be oriented parallel to the long axis of the prism in the front half of the head end of the prism cross section. As one moves towards the tail, the crystallites change in direction till they are nearly perpendicular to the axis at the tail end of the prism. The apatite crystallites within, change in orientation at the junction of prisms and from top towards the tail by almost 90° . Strictly there is no demarkation like a prism or rod. Apparent shapes arise from crystallite orientation changes. Depending on the sections cut—perpendicular, parallel or oblique to the long axis of tooth, one sees the microstructure as depicted, as depressions or bands.

Apart from the oriented microstructure we note the presence of silicon and magnesium from the EDX analysis (table 1). Silica gel is known to promote the formation of apatite and magnesia keeps the grain sizes small. The deciduous teeth had higher silicon content. The Ca/P ratios are low for the deciduous (MT) and high for normal teeth. This has implications in their functions and durability.

4. Hardness and toughness

The hardness of samples varied at different sections. The pulp area is so soft that it peels off while polishing. We have not been able to measure the hardness of pulp. It is hard at the enamel and soft at dentin. The values show gradation rather than abrupt changes. Tooth enamel, dentin and pulp have different HAp content. Hence the hardness values

are different. In figure 1b we have indicated the sections and the range in values. There is gradient with low hardness values at the core and at the sides in contact with gums, which gives excellent stress compatibility with soft tissues. The higher values for enamel are in tune with its function.

Synthetic HAp, hot-pressed at 1150°C for 2 h (Takagi *et al* 1992) had hardness of 6 GPa and toughness $K_{Ic} = 1 \text{ MPa.m}^{1/2}$ at theoretical density. Measured through indentation techniques at 2 kg load the toughness of enamel is 2.68 MPa.m^{1/2} and hardness, 2.6 to 3.4 GPa. The dentin is tougher (4.2 MPa.m^{1/2}) with hardness lower than enamel. The toughness of tooth is due to the microstructure consisting of long tubes of HAp in a soft biopolymer matrix (figure 8). All natural composites use a pliable, weaker interface, which is able to bear and dissuade stresses. One of the micrographs show crack propagating through the fine particles. The crack propagation is intergranular. The mechanisms for increase in toughness are, crack branching, blunting and pull-outs arising from the complex microstructure.

5. Tough materials through biomimics

Compared with HAp, densified under most ideal conditions (Takagi *et al* 1992), tooth shows higher toughness for a lower density and varying levels of hardness. The investigations show that it is due to the microstructure (Currey 1977). Hence, mimicing them may lead, in general, to tougher materials and composites. Biomimics is an upcoming process idea to copy the efficiency of natural materials (Calvert 1990).

Microstructure plays a significant role in enhancing the strength and toughness of natural materials e.g. wood and shells. Mollusc shells are mostly aragonite and/or calcite with little amount of organic, 0.1 to 5 w%. The binding protein is chitin. The strength and toughness are enormous compared to those of crystalline calcium carbonate. In shells the microstructural arrangements could be as staggered layers, crossed-lamellar, foliated or prismatic arrangements. The rat incisor and sea urchin tooth also show crossed layer arrangements (Calvert and Mann 1988). The toughness arises from the tortuous crack path given by the microstructure, which gives rise to

Table 2. Strength of natural and synthesized materials.

	Min(%)	Stiff	Mor	J/m ²
enamel	95	45	76	13–200
dentin	48	12	250	270–550
bone	51	16	247	1700
antler	40	7.7	240	13000
nacre	95	64	130	600–1240
alumina	100	500	300–1000	50
pmma	0	4	140	200
pmma + alumina	47	10	65	238
pmma + silica	56	13	110	287
PE + HAp40%		5	22	1800
PE + HAp50%		9	26	1000
PE		1	30	8000
Ti alloy		106	900	104

Stiff, stiffness; Mor, modulus of rupture; J/m², critical strain intensity

Table 3. Comparison of natural and synthetic reinforcements.

	YM (GPa)	Tensile strength (MPa)	Tensile strain (%)
chitin	80	4000	4.2
collagen	2	100	8–10
cellulose	100	1000	10
keratin	1–4	200	25
E-glass	70	1500–2000	2–3
carbon	200–400	1900–2600	0.5–1.5
boron	400	3400	0.5–1
kevlar-49	130	2700	2.0–3.5

crack branching, blunting, bridging and pull-outs. In biomaterials the toughness with low densities is achieved through planned architecture. There are various levels of structure in scale—ultra, micro and macrostructural. The organization has levels differing in density, composition and unit arrangements. Reinforcement phases or fibres are low in stiffness and can bear higher tensile strain (table 3) compared to the fibres in common use. Bonfield *et al* (1981) succeeded in making artificial bone material of light polyethylene-HAp composites, which had reasonable toughness with low elasticity. For stress-compatibility density and stiffness matching are important criteria for bioimplants.

Polymer–ceramic composites come close to the bone in density but when the stiffness is matched by adjusting the ceramic volume (table 2) strength and toughness decrease. Comparing man-made material with the natural composite it becomes obvious that the natural one does not have a uniform density or composition in bulk e.g. tooth. Nature has processed it from the pulp through nucleation and growth mechanism. The area near the gum matches the soft tissues in hardness and stiffness whereas at the crown the enamel is the hardest of tissues as the function is cutting and grinding. This is efficiency as several functions are managed with no wastage in material or effort. It is done by controlling the macrostructure through natural process. Shells and wood are similarly designed, in layers, while growth through controlled process.

By mimicing nature through modified process techniques, which results in oriented microstructures with weak interfaces one can hope to get light and tough materials. This is especially important for armours, which require light, tough and impact-resistant materials. Biomimics can also give us good bio-implant materials with specific, stress-matched behaviour (Saraswati 1993) with graded strengths and density and even functional if one is able to incorporate a sensor or intelligence to the material.

6. Conclusions

The inorganic content of tooth is HAp with some carbonate. The density is graded and so is the hardness. The enamel is hard and the pulp is soft. The microstructure consists of long rods of HAp arranged almost parallel to the long axis. Interfacing with soft organic collagen and proteins makes the tooth tough. A transformation temperature near 157°C in NT and DT finds correspondence in dielectric measurements. It could be

related to piezoelectric transition. Nature's materials like teeth and shell could lead the way for light and tough materials.

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