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# Full length article

# Discrete element models of tooth enamel, a complex three-dimensional biological composite

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## ABSTRACT

Enamel, the hard surface layer of teeth, is a three-dimensional biological composite made of crisscrossing mineral rods bonded by softer proteins. Structure-property relationships in this complex material have been difficult to capture and usually require computationally expensive models. Here we present more efficient discrete element models (DEM) of tooth enamel that can capture the effects of rod decussation and rod-to-interface stiffness contrast on modulus, hardness, and fracture resistance. Enamel-like microstructures were generated using an idealized biological growth model that captures rod decussation. The orthotropic elastic moduli were modeled with a unit cell, and surface hardness was captured with virtual indentation test. Macroscopic crack growth was also modeled directly through rupture of interfaces and rods in a virtual fracture specimen with an initial notch. We show that the resistance curves increase indefinitely when rod fracture is avoided, with the inelastic region, crack branching, and 3D tortuosity being the main sources of toughness. Increasing the decussation angle simultaneously increases the size of the inelastic region and the crack resistance while decreasing the enamel axial modulus, hardness, and rod stress. In addition, larger contrasts of stiffness between the rods and their interfaces promote high overall stiffness, hardness, and crack resistance. These insights provide better guidelines for reconstructive dental materials, and for development of bioinspired hard materials with unique combinations of mechanical properties.

#### Statement of Significance

Enamel is the hardest, most mineralized material in the human body with a complex 3D microarchitecture consisting of crisscrossing mineral rods bonded by softer proteins. Like many hard biological composites, enamel displays an attractive combination of toughness, hardness, and stiffness, owing to its unique microstructure. However few numerical models explore the enamel structure-property relations, as modeling large volumes of this complex microstructure presents computational bottlenecks. In this study, we present a computationally efficient Discrete-element method (DEM) based approach that captures the effect of rod crisscrossing and stiffness mismatch on the enamel hardness, stiffness, and toughness. The models offer new insight into the micromechanics of enamel that could improve design guidelines for reconstructive dental materials and bioinspired composites.

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# 1. Introduction

Enamel is the thin layer of material at the surface of teeth that is anisotropic and heterogeneous [1-9]. Like many natural materials such as fish scales and nacre, the architecture of enamel has evolved to generate micro-mechanisms and mechanical properties to fulfill specific functions (structural support, protection, mastica-

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https://doi.org/10.1016/j.actbio.2019.04.058 1742-7061/© 2019 Published by Elsevier Ltd on behalf of Acta Materialia Inc. tion) [10]. Contrary to hard biological materials such as bone, the enamel microarchitecture is highly dependent on species and ultimately linked to dietary requirements [11]. In humans, the enamel micro-architecture mainly consists of tightly packed (~96% vol.) hydroxyapatite rods, making it the most mineralized and hardest material in the body (a critical requirement for the cutting, crushing, and tearing of aliments). Individual hydroxyapatite rods are 4– 8 µm in diameter and run across the entire thickness of enamel (in the order of millimeters, Fig. 1a). The interfaces between the rods are thin (~0.1 µm) and consist mostly of water with possible remnant proteins from post-maturation [11]. In the deeper regions of









Fig. 1. (a) The microarchitecture of tooth enamel and (b) typical crack resistance for a crack propagating from the surface of enamel and into the decussation region. Crack resistance taken from [2] and converted to energetic terms using Irwin's relation [21].

enamel, the rods and interfaces are intertwined in a complex, 3D decussating arrangement (Fig. 1a). Decussation is evident in many other species [2,12,13] (although not all), and while it differs in basic structure and location within the enamel thickness, the underlying mechanical function of decussation is arguably straightforward: to promote crack resistance (Fig. 1b) by creating obstacles for the crack, which ultimately serves to prevent chipping and spallation from the underlying living tissue. The role of decussation on the enamel toughness, hardness, and stiffness is of critical importance in dental medicine and bioinspired materials design [1-6,8,14-19]. Nanoindentation experiments have shown that both the enamel axial modulus and hardness decrease by nearly 50% going from the free surface to the dentine-enamel junction (DEJ) [14–16], with imaging suggesting this drop is due to changes in chemical composition and the presence of rod misalignment (decussation) that occur in the deeper regions of enamel. Fracture toughness in enamel has been measured mostly from nanoindentation tests [18,19], but the results are difficult to interpret because of frictional effects, anisotropy and the inability to monitor subsurface cracks [20]. More recently, fracture tests in compact tension have revealed a direct correlation between rod decussation (inner enamel) and rising R-curve behavior (Fig. 1b) [1–6,8]. As the crack entered the decussating region, it interacted with the microstructure and a variety of toughening mechanisms were activated including microcracking, bridging, and deflection [1,2]. No steady state crack resistance was observed, although the specimen sizes were rather small (8x6x2 mm) and therefore restricted the range of measurable crack growth. Larger, mixedmode conventional fracture specimens were used in the work of Bechtle et al. [8] (albeit from bovine incisors), but no correlation was made with the presence of decussation and steady-state crack resistance was not observed.

It is clear from experiments that the enamel microstructure governs its toughness, hardness, and modulus, yet there are no models that quantify these structure-property relationships in a unified fashion. The numerical models of enamel proposed to date often rely on homogenization of the complex enamel microstructure. For example, XFEM (Extended Finite Element Modeling, a numerical approach that can capture crack growth without remeshing) enamel models homogenized the spatial distribution in toughness and modulus [22]; while useful in tracking crack growth, this approach overlooks the explicit effect of microstructure on crack resistance. Other non-homogenized approaches have been used in enamel that model its microstructure directly but did not consider non-parallel (decussating) rods [9] or capture only deformation [23]. More recent approaches such as phase field models have not been used in enamel but have captured fracture in nacre [24], another type of highly mineralized biological composite. However, the volume of microstructure that can be captured with phase field models is limited. The main challenge in modeling the micromechanics of tooth enamel is to capture the mechanical response of large volumes of its complex threedimensional microstructure. Model generation in itself can present challenges due to the complex shapes and arrangements of the enamel rods. This problem can be tackled using biological growth models proposed by Cox and co-workers [12] to capture the salient geometrical patterns observed in the enamel microstructure [2]. Modeling fracture in enamel presents additional obstacles as multiple toughening mechanisms often work together but at different length scales to resist crack growth [2] (similar to other natural composites [25]), and moreover large models are required to enforce small scale yielding conditions [21]. In this regard, the discrete element method (DEM) offers a powerful modeling alternative and is attractive for modeling enamel as it can handle large volumes of material efficiently [26] by only tracking center-tocenter interactions. DEM has proven particularly useful in large scale fracture models in other hard biological composites and recovers many known fracture mechanics based scaling laws [26-30].

The aim of this work is to quantify systematically the role of rod decussation and stiffness on the enamel toughness, hardness, and modulus, incorporating specific geometric details of enamel architecture from biological growth models [12,31] into large scale mechanics based DEM models in a unified approach. The orthotropic enamel moduli were first captured with a minimum unit-cell elastic model. Hardness and crack growth were then modeled with virtual tests that explicitly captured the rupture of nonlinear interfaces that connect the rod elements, providing new insights into the deformation and fracture of this complex biological composite.

#### 2. Material model

We adopted an idealization of the 3D enamel morphology that captures rod decussation using a simplified biological growth model inspired from Cox et al [12,32]. In our idealized approach we assumed that the ameloblasts follow straight but nonparallel trajectories that periodically alternate in direction from one row to the next which produces a periodic material in the *y*-direction (Fig. 2). While this assumption is not directly based on any biological growth mechanics considerations, it captures enamel rod



**Fig. 2.** Growth fields for (a)  $\theta_D = 0^\circ$  (no decussation) and (b)  $\theta_D = 10^\circ$ . The generated 3D microarchitectures are shown alongside cross section slices for the respective growth fields. The rod diameter is denoted as *d* for the general case, and  $d_0$  for the case when  $\theta_D = 0^\circ$ .

decussation (largely responsible for crack resistance) on a basic geometrical level. Therefore, this simplified approach serves as a shortcut to generate different enamel configurations without relying on complex growth models. In order to isolate the role of decussation, we neglected the effect of rod waviness, DEJ curvature, and morphology changes within the enamel layer [12,32]; these features are beyond the scope of this work but could be implemented by combining more complex and multi-scale models of organogenesis [12,31] with the DEM approach. The model generation starts with an array of equidistant triangular seeds on a base xy-plane. A standard 2D Voronoi tessellation contour is then computed using these seed points as inputs, which produces a regular tiling of hexagons. Each hexagon represents the initial ameloblast cell and surrounds the initial cross-section of each enamel rod. The initial seeds and their associated ameloblasts are then migrated along the general growth (+z) direction by an increment  $+\Delta z$  and moved transversally along the x-axis by an increment  $\Delta x = \pm \Delta z$  tan  $\theta_D$ , where  $\theta_D$  is the rod decussation angle. The updated positions of the seeds are then used as inputs to generate a new Voronoi contour in a translated base plane. This process is iterated for all successive increments in seed motion which produces a full 3D space filling architecture (shown in Fig. 2 for  $\theta_D = 0^\circ$  and  $\theta_D = 10^\circ$ ) that is fully characterized by the average rod diameter d and the decussation angle  $\theta_D$ . The decussation wavelength  $\lambda_D$  is defined as the vertical distance between the crossing points of the growth lines, expressed as  $\lambda_D = d/\sin(\theta_D)$ .

The generated 3D geometry was used to create a discrete element (DE) mesh consisting of nodes and element connectivity (Fig. 3). The nodes of the DE mesh were computed as the centroids of the polygonal cross sections of the individual rods, which were not necessarily aligned with the seed points. 3D Bernoulli-Euler beam elements (elastic, isotropic, and homogeneous; see Appendix B for detailed formulation) were placed between every pair of adjacent nodes within every rod, which captured the axial, torsional, and flexural deformation of the individual enamel rods. The enamel rods themselves follow a hierarchical structure and are composed of HAP-nanocrystallites and of a small amount of organic tissue at the crystalline level [9]. For simplicity we assume a homogenized elastic response and strength of the enamel rods. The nanostructure of the rods probably impacts their modulus and strength, but these effects were not explicitly captured the models presented here, which focus on micromechanisms. As such, all rod elements were assigned the same modulus  $E_r$ . The height of the rod elements is denoted as  $h_e$  (Fig. 3b) and controls the model resolution. The shape of the true rod cross section was computed by projecting the cross section in the *xy*-plane (shown in Fig. 3b) onto a plane whose normal is aligned with the rod neutral axis. The rod principal second area moments ( $I_{xx}$ ,  $I_{yy}$ , and  $I_{zz}$ ) were then computed from the true rod cross section shape. In our model the cross sections of the rods were assumed to be aligned exactly with the outer contour of the migrating ameloblast cells, which are represented here with the polygons generated from the Voronoi algo-



**Fig. 3.** Different views of a 3D enamel architecture generated with  $\theta_D = 10^\circ$ . (a) Shows the enamel rod architecture, the DEM beam and interface elements, as well as three cross sections with rod contours and DEM elements. (b) Shows the same architectures viewed from a different angle with different cross sections.

rithm, which greatly simplified the connectivity generation between adjacent rods. In reality the formed rods are roughly circular in cross section (even though the ameloblasts are hexagonal) with an interfacial boundary shape resembling a horseshoe [11]. A strength of the DEM method is that the geometrical details of the interfaces between the rods do not need to be considered. Using Voronoi contours as outlines for the rods overestimated the axial and bending stiffness of the beam elements by about 10 and 22%, (respectively) compared to that of a circular cross section.

The interfaces were modeled with a trapezoidal tractionseparation law shown in Fig. 4, which captured the interfacial deformation and rupture of the material between enamel adjacent rods. This is a highly idealized representation as the composition and mechanical behavior of enamel interfaces is much less understood. Historically, the interfaces have been regarded as continuous protein sheaths' [15], however recent microscopy of bovine enamel indicates that very little protein (if any at all) exists between the rods after maturation [33]; subsequent mechanical tests suggest that the rods may in fact be connected by hard mineral bridges instead [34,35]. While these complexities are not meant to be overlooked, for the practical purposes details of the interface composition are all homogenized into the interface law shown in Fig. 4 as a simplified approach to explore the parameter space. We note that our interface representation is the same one used in previous models of nacre [29] which follows a similar strategy to generate stiffness and toughness through architecture of hard phases with weak interfaces. While the composition of enamel interfaces is largely different from those found in nacre, both materials exhibit high fracture toughness relative to their respective hard phases [19,25], with the toughness enhancement in nacre owing largely to the



**Fig. 4.** (a) Schematic of deformation modes of a pair of adjacent rods in normal and tangential separation. The normal traction  $T_n$  vs. normal separation  $\Delta_n$  response of the interface is shown in (b) for various tangential separations. The response of the interface is assumed to be mode independent, therefore the tangential traction  $T_t$  vs. tangential separation  $\Delta_t$  curves (not shown) are identical in form to those for normal tractions.

ductility of the interfaces [36] combined with its intricate microstructure. It is therefore reasonable to infer that some ductility (albeit a possibly very small amount) is present in enamel interfaces and plays a similar role on fracture toughness as in nacre. We also note that there have been no direct measurements in either biocomposite of the interface bulk macroscopic stress-strain response via conventional testing standards due to size-scale complications; therefore an idealized approach is justified. The deformation modes of the interface are shown independently in Fig. 4a alongside the initial undeformed configuration. The full mathematical definitions of the interface law omitted for brevity but are given in [29].

The interface cohesive law (Fig. 4b) is defined by four independent parameters: the interface stiffness k, strength  $\sigma_0$ , work of separation  $\Gamma_i$ , and ultimate separation  $\Delta_U$ . The interface work of separation  $\Gamma_i$  is defined as the area under the tractiondisplacement response in pure normal separation. It is assumed that  $\Gamma_i$  is exactly the energy required to separate the interface completely to a traction-free state through bulk deformation only, which effectively combines all of the nonlinear failure mechanisms of the interface into one. Irreversibility in the interfaces was accounted for through an idealized triangular unloading law shown in Fig. 4b; our recent calculations in brick-and-mortar composites have shown that the shape of the unloading law has a numerically insignificant effect on the results so long as the mesh is resolved. We also assumed that the displacement jump vector was uniform along a given interface, which neglects the geometrical effect of rotations at the adjacent nodes on the deformation of the interface. This assumption greatly facilitated the numerical implementation, as the response of the interface only depends on its normal and tangential displacements (Fig. 4a). We verified by full 3D finite element calculations of a subset of the model microstructure shown in Fig. 2 (not shown here) that this approximation has a negligible effect on the calculation results provided that the mesh is sufficiently resolved ( $h_e << d$ ). We also assumed that the response of the interfaces was mode independent and therefore the interface properties were set equal in the normal and tangential separation. While many ductile and guasi-ductile interfaces exhibit mode dependent fracture toughness [37], this assumption greatly simplified the numerical implementation and isolated the role of microstructure. The effects of mixed-mode interface laws are beyond the scope of this work but have been studied in detail in [38] and one would expect similar scaling if implemented here. The interface traction-separation law was then converted to a multi-axial force-displacement relationship by scaling the interface stiffness k (N/m<sup>3</sup>) and strength  $\sigma_0$  (N/m<sup>2</sup>) by the interface area  $A_i = l_i h_e$  (Fig. 4a), which gives an effective spring stiffness  $k_e = kA_i$  and peak force  $F_0 = \sigma_0 A_i$ . This simplification is valid because the tractions have been assumed to be uniform across the interface, similar to the approach in [28]. More details on the interface formulation, including the stiffness matrix entries, can be found in Appendix B.

The system of governing equations in the DEM approach was formed by assembling the local elemental stiffness matrices for the beams and interfaces via the standard finite element assembly procedure [39]:

$$[K] = \sum_{i=1}^{n_e} [k]_e \tag{1}$$

where [K] is the unconstrained global stiffness matrix and  $[k]_e$  are the local elemental stiffness matrices for the beam and interface elements (shown in detail in Appendix B). Boundary conditions and linear constraints were applied using the method of Lagrange multipliers, resulting in augmented system of governing equations represented in block matrix form as follows:

$$\begin{bmatrix} K & A^T \\ A & 0 \end{bmatrix} \begin{Bmatrix} u \\ \lambda \end{Bmatrix} = \begin{Bmatrix} f \\ Q \end{Bmatrix}$$
(2)

where {*u*} is the vector of unknown nodal displacements and rotations, { $\lambda$ } is the vector of unknown Lagrange multipliers, {*f*} is the known vector of externally applied forces and moments, {*Q*} is the vector of known boundary conditions and linear constraint equation constants, and [*A*] is the matrix of boundary conditions and constraint equations. In more compact notation, Eq. (2) is expressed as:

$$[K]^{+}\{u\}^{+} = \{f\}^{+} \tag{3}$$

where  $[K]^+$  is the augmented stiffness matrix, and  $\{u\}^+$  and  $\{f\}^+$  are the vectors of generalized knowns (forces and boundary conditions) and unknowns (nodal displacements and Lagrange multipliers), respectively. Details on the solution of Eq. (3) will be discussed in the subsequent sections. Once solved, the structural reaction forces were computed directly from the Lagrange multipliers:  $\{R\} = [A]^T \{\lambda\}$ .

Using the DEM approach, we carried out virtual mechanical tests on the enamel architecture, with the main goal of the models to capture trends and identify microstructural parameters that govern the enamel mechanical properties. Three types of virtual tests were performed: Uniaxial tension (orthotropic elastic moduli) along three directions, indentation (point force), and crack propagation (fracture toughness). In all subsequent results we represented the input and output variables in dimensionless form, with the ranges of dimensionless inputs for the DEM models calculated from approximate ranges of properties and constants measured in experiments. This representation reduces the number of virtual experiments required to capture basic trends, and moreover represents the results in a more general form that could translate to similar bioinspired crossply composites manufactured at larger length scales.

#### 3. Orthotropic elastic moduli

We measured the orthotropic elastic moduli of a unit cell of the enamel architecture (Fig. 5) using virtual uniaxial tensile tests along the *x*, *y* and *z* directions. The dimensions of the minimum unit cell in the *x*, *y* and *z* directions were  $d_0$  by  $\sqrt{3}d_0$  by  $\lambda_D$ , respectively. Periodic boundary conditions were enforced in all three directions using multi-point constraint equations, as shown in Fig. 5b. Redundant elements within the unit cell were removed and reference nodes were placed along the neutral axis of the next would-be rod neighbor.

A uniform strain was applied to the unit cell by imposing a displacement gradient between the opposing faces of the model. For these elastic simulations, we set  $\sigma_0=\infty$  which guaranteed that Eq. (3) is linear. The deformed nodal displacements and rotations were therefore solved for with a single function call to a standard sparse linear solver:

$$\{u\}^{+} = [K]^{+} left\{f\}^{+}$$
(4)

The average stress along a face of the unit cell was computed by summing the constraint reaction forces along that face and dividing by its area. The enamel modulus in any direction was defined as the ratio of average stress to average strain at any level of deformation. It was verified that results were independent of the mesh size ( $h_e$ ) and specimen size by stacking several unit cells. We focused on the tensile moduli in three orthogonal pulling directions, which are subsequently referred to the transverse moduli  $E_{xx}$  and  $E_{yy}$ , and the axial modulus  $E_{zz}$ . All moduli were normalized by the Reuss modulus at  $\theta_D = 0^\circ$  ( $E_{Reuss} = kd$ ). The stiffness contrast was defined as  $E_t/kd$ , which can be expressed in terms of the inter-



**Fig. 5.** Schematic of (a) the enamel architecture for  $\theta_D = 10^\circ$  and (b) DEM model of the minimum unit cell corresponding to the periodic microstructure shown in (a). The multi-point constraints (MPC's) are shown separately for clarity in (b). An arbitrary node was clamped to prevent rigid body motion.

face modulus  $E_i$  and rod volume fraction  $\phi_r$  as  $E_r/kd = \frac{1}{2}(E_r/E_i)(1/\phi_r - 1)$ . To obtain ranges for stiffness contrast for the DEM simulation inputs, we assumed  $E_r$  to be in the range 93–113 GPa and  $\phi_r = 0.95$  [9]. For practical purposes we idealized the interface modulus  $E_i$  to be in the range of 50–500 MPa which is reasonable given that it consists mostly of water, protein remnants [40], and possible mineral nano-bridges [34,35]; it unlikely that  $E_i$  is in the GPa range. With these ranges of parameters, the dimensionless stiffness contrast can range from  $E_r/kd = 5-50$  at the approximate extrema of the property space, which were used in all subsequent parameter studies.

Fig. 6a shows the effect of the decussation angle  $\theta_D$  on the normalized axial modulus  $E_{zz}/kd$  for various levels of stiffness contrast  $E_r/kd$ . For all values of stiffness contrast, the axial modulus  $E_{zz}$  is maximized at  $\theta_D = 0^\circ$  and is equal to the upper theoretical limit (Voigt modulus), as indicated by the dashed guidelines on Fig. 6a where  $E_{zz} = E_r$ . Fig. 6a shows that as decussation is introduced, the axial modulus decreases and approaches the lower theoretical limit (Reuss modulus) when  $\theta_D$  approaches 90°. This trend suggests that decussation may provide a gradual decrease of modulus from the surface and towards the underlying softer dentin layer, in order to reduce the elastic mismatch between these two materials. The effect of decussation on the axial modulus  $E_{zz}$  is amplified by the rod-to-interface stiffness contrast.

In the limit of straight rods ( $\theta_D = 0^\circ$ ), the transverse modulus  $E_{xx}$  approaches the theoretical Reuss lower bound for all values of stiffness contrast. In the regime where  $\theta_D$  is less than about 20°,  $E_{xx}$  is insensitive to decussation for all values of stiffness contrast and nearly equal to the Reuss bound. For larger decussation angles ( $\theta_D > 20^\circ$ ),  $E_{xx}$  increased more significantly with  $\theta_D$  as the stiff rods

carry an increasing amount of stress, and the effect of decussation was again amplified by the stiffness contrast. The normalized transverse modulus  $E_{yy}/kd$  (Fig. 6c) did not change with  $\theta_D$  and was equal to the Reuss modulus ( $E_{yy}/kd = 1$ ). The instantaneous transverse modulus  $E_{yy}$  is therefore the same at any 2D slice in the *xy*-plane shown in Fig. 2b. Fig. 6b and c also show that the enamel model is nearly transversely isotropic when  $\theta_D = 0^\circ$ ( $E_{xx} = E_{yy}$ ), as expected given the symmetry planes in a uniform hexagonal tiling.

#### 4. Hardness

Surface hardness is critical to the functionality of the teeth as a cutting, tearing and crushing tool. In this second set of virtual experiments we captured hardness as function of decussation angle and stiffness contrast. The setup of the hardness model is shown in Fig. 7a: A flat volume of material with thickness t was first generated and meshed using the procedure described in Section 2. The thickness was held constant for all  $\theta_D$ , and the input values of  $\theta_D = \{5.7^\circ, 11.5^\circ, 23.6^\circ, 53.1^\circ\}$  were chosen such that the specimen thickness was an integer multiple of the decussation wavelength; this ensured that the indenter boundary condition was always applied at the same relative z-position within the microstructure. The bottom face was clamped and a vertical indenter displacement was applied to the center node on the top face. This idealized procedure is not exactly the same of a true hardness test [41] but it provided a simple approach to explore the effect of different enamel architectures and properties on surface hardness. Moreover, contact forces in humans and many mammals are often



Fig. 6. Effect of rod decussation angle  $\theta_D$  and stiffness contrast  $E_{t/kd}$  on (a) the normalized axial modulus  $E_{zz/kd}$ , and (b and c) the normalized transverse moduli  $E_{xx/kd}$  and  $E_{yy/kd}$ , respectively.



**Fig. 7.** (a) Schematic of hardness test setup. A point displacement  $\Delta$  is applied to the center node on the top face while the bottom of the model is clamped. (b) Force displacement curves for various  $\theta_D$  and fixed stiffness contrast  $E_t/kd = 5$ . (c) Distribution of inelastic region at the peak indenter load  $F = F_c$  for  $\theta_D = 5.7^\circ$  and  $\theta_D = 23.6^\circ$ . Interface center-points are rendered and superposed onto the deformed rod cross section slices indicated (a). Vertical surface displacements shown at 75× amplification.

non-vertical and may have tangential components as well due to frictional loads. This scenario is not considered here but could be implemented with a basic scratch test within the DEM framework [42]. In these models, the cohesive zones representing the interfaces were set to have both finite strength  $\sigma_0$  and toughness  $\Gamma_i$ , which resulted in a nonlinear system of governing equations:

$$\{g(u)\} = [K(u)]^{+} \{u\}^{+} - \{f\}^{+}$$
(5)

where  $\{g(u)\}$  is the residual force vector. Eq. (5) was solved iteratively using the Newton-Raphson method:

$$\{u\}_{i+1}^{+} = \{u\}_{i}^{+} - [J(u)]^{+} left\{g(u)\}$$
(6)

where  $[J(u)]^+$  is the global augmented Jacobian and is assembled elementwise in the same manner as the global stiffness matrix in Eq. (3); the local element Jacobian matrices are shown in Appendix B. A small amount of artificial viscosity was added to the cohesive law to promote numerical convergence [43] of Eq. (6) and was verified to not influence the calculation results. The global force residual norm tolerance was set at 0.01% of the minimum model reaction force which ensured accurate results. Some efficiency improvements were made to the NR-scheme, including an adaptive loading scheme, parabolic extrapolation of the new displacement solution guess (based on the previous converged load increments), and use of sparse triplet form for all matrix manipulation operations including assembly and updating [27,44]. The indentation simulations were run on the McGill supercomputer Guillimin using Matlab R2016b and took about 3 h each. Each indentation simulation consisted of about 30,000 nodes which gives a global stiffness and Jacobian matrix size of about 180,000 by 180,000 (6 degrees of freedom per node).

Fig. 7b shows the effect of decussation on the indenter forcedisplacement curves for fixed stiffness contrast. In all cases, the force-displacement curves were nonlinear and approached a well-defined maximum followed by a region of post-peak softening. For comparative purposes, we defined the hardness H as the maximum of the normalized indenter force-displacement curve. The hardness is maximized for low decussation angles and decreases smoothly and monotonically as the decussation is increased. This trend is consistent with the mechanical function of enamel: At the outer surface, maximum hardness is needed for efficient biting and chewing of food Many nanoindentation tests on human enamel have confirmed that enamel hardness is functionally graded [15,16,45,46]. While the decrease in hardness away from the surface has shown some variation depending on the location and age of the extracted tooth (Cuy et al: 5–6 GPa to 2-3 GPa [15], Low: 4-1.5 GPa [45], Park et al: 5-3.5 GPa [16], He et al: 4.5–2.5 GPa [47]), the decrease of the hardness with depth is consistent in human enamel and in other species as well [40]. The decrease of hardness with depth has been attributed to many different factors, including rod orientation, chemical structure, as well as issues with demineralization that occur at greater depths during maturation [15,45,47]. While there appear to be no universal connections between the enamel structure and these hardness gradients, the results here support the notion that the relative orientation of the rods can greatly influence these spatial changes in hardness (Figs. 7 and 8). While our idealized model predicts a hardness which is roughly 30% higher than the experimental value (assuming experimental values of  $F_c = 6.5$  mN,  $\sigma_0 = 50$  MPa,  $\theta_D$  = 30°, and *d* = 4 µm [12,15,48]), the fraction of decrease of hardness with rod decussation in the experiments and in our DEM simulations are remarkably close. Fig. 7c shows the distribution of the



**Fig. 8.** Normalized enamel hardness as a function of decussation angle for various rod-to-interface stiffness contrasts  $E_{r/k}d$ .

inelastic region ahead of the indenter tip at the peak load superposed on the deformed rod configuration. For brevity, only two different decussation angles are shown in Fig. 7c ( $\theta_D = 5.7^\circ$  and  $\theta_D$  = 23.6°), but the trend was consistent along all decussation angles modeled: as the decussation angle was reduced towards  $\theta_D = 0^\circ$ , the inelastic region was larger in the thickness (-z) direction to maintain equilibrium of the larger indenter reaction forces associated with the harder material (Fig. 7b and c) but was still contained within 3-4 rod diameters. For all decussation angles, the inelastic region was highly localized and contained within one rod diameter in the xy-plane as shown in the representative contours for  $\theta_D = 5.7^\circ$  and  $\theta_D = 23.6^\circ$ . The distribution of vertical surface displacements was also highly localized (shown at  $75 \times$ amplification in Fig. 7c) at the indenter, with the indented rod displacement being about 20-30 times larger than its neighboring rods in both cases. This result confirms the simulations reproduce the rod 'sinking' mechanism observed in nanoindentation experiments of enamel [17], which promotes strain tolerance and prevents widespread damage via relative rod sliding within the segmented architecture.

Fig. 8 summarizes the hardness test results and shows the combined effect of stiffness contrast and decussation. As the stiffness contrast is increased, the hardness is amplified over all decussation angles and has the most pronounced effect when the rods are nearly aligned ( $\theta_D \approx 5^\circ$ ). This trend can be explained in part by considering the opposite limit of infinite interface stiffness ( $E_t/kd \rightarrow 0$ ). In this limit, the deformation state approaches the Boussinesq solution for a point force [49] which predicts infinite compliance at the point force. As the interfaces are made more compliant ( $E_t/kd > 0$ ), combined relative rod sliding and interface yielding and provide a mechanism for strain tolerance that decreases the local compliance and increases the hardness.

#### 5. Fracture mechanics and crack propagation

Finally, we used our DEM approach to explore crack propagation in enamel and to assess how variations in the enamel architecture govern fracture toughness. The models in this section are based on fracture mechanics and therefore only consider cases where a dominant crack has already formed. The nucleation of a dominant crack in enamel is complex; for example cracks can nucleate at the DEJ from local stresses in radial arrays [50] or from cyclically induced microwear events at the surface [51]. For the DEM models these events are not modeled explicitly and it is assumed that the crack has already initiated well into the microstructure, with lengths larger than any characteristic length present in the microstructure. The specimen geometry and boundary conditions used to capture crack resistance are shown in Fig. 9. The coordinate system for these models uses the fracture mechanics convention where the x-axis is aligned with the crack. The specimen width, height, and initial crack length are noted as  $w_s$ ,  $h_s$ , and  $a_0$  respectively. The specimen was assumed to be infinitely deep and periodic along the z-axis (plane strain conditions) and therefore periodic boundary conditions were enforced the z-direction using tie constraints between the first and third layer of rods, with only reference nodes in the third layer (Fig. 9c). This reduces the scaling of the computational time from  $n^3$  to  $n^2$  and is permitted because the microstructure was assumed to be periodic (Fig. 2). The strength and the toughness of the interfaces were set to be finite to capture crack propagation directly. The initial crack was inserted at the mid-height of the specimen along the *xz*-plane by deleting any DEM elements that intersected the crack plane. Displacement boundary conditions were applied at the top and bottom of the specimen and followed a linearly decaying spatial distribution (Fig. 9c), which promotes stable crack growth [21]. The nonlinear governing equations were solved via the full Newton-Raphson method discussed in Section 4.

The crack driving force was computed at each load increment using the 3D *J*-integral [52]:

$$J_{k}(\eta) = \int_{\Gamma} \left[ Wn_{k} - t_{i} \frac{\partial u_{i}}{\partial x_{k}} \right] ds + \int_{A} \frac{\partial}{\partial x_{3}} \left[ W\delta_{k3} - \sigma_{i3} \frac{\partial u_{i}}{\partial x_{k}} \right] dA$$
(7)

where W is the elastic strain energy density,  $n_k$  is the kth component of the normal vector to the integration contour (where k is the direction coordinate aligned with the crack),  $t_i$  is the traction vector,  $u_i$  is the displacement vector,  $x_k$  is the spatial coordinate,  $\sigma_{i3}$  is the 3rd row of the Cauchy stress tensor, and  $\delta_{k3}$  is the Kronecker delta. The term  $\eta$  represents the position of the intersection of the area contained within the line integral contour with the crack front [52]. The terms  $\Gamma$  and A represent the integration lines and surfaces, respectively. The J-integral has been shown to be accurate and path independent for discrete systems [26]. The 3D *J*-integral surface contour was taken to be the outermost faces of the specimen in Fig. 9c. and the line contour was taken along the outer edges of the front face of the cube. The *I*-integral simplifies with this contour choice and can be expressed entirely in terms of the nodal reactions and interface separations. The crack resistance curves were constructed by evaluating the *I*-integral at each unique increment in crack advance, where the crack tip position was defined as the average position of the first pair of adjacent interfaces where one interface is broken but the other is intact.

The cohesive law in Fig. 4 introduces a nonlinear fracture length when a crack is present that scales directly with the cohesive stiffness and toughness, and inversely cohesive strength squared [38,53]. However, the fracture length does not influence the calculation results provided it is large relative to the mesh size (resolution) but small compared to the specimen, where the latter corresponds to the condition required for linear elastic fracture mechanics (LEFM) to be valid. [29,38,53–55]. Therefore, for all models we checked model size independence by running a small and large specimen and checked mesh size independence by running a fine and coarse mesh. The largest fracture models contained about 200,000 DEM nodes (1,200,000 degrees of freedom) and took about 4 days wall time to compute on the McGill supercomputer Guillimin.

We first examined the effects of decussation angle on toughness while holding the stiffness contrast constant at  $E_r/kd = 5$ . Fig. 10 shows the effects of decussation on the volumetric process zone evolution and on crack growth (columns 1–3), on the enamel *R*-curves (column 4), and on the maximum tensile stress in the rods over the entire model (column 5). The models were sufficiently large, and fracture was stable enough to capture crack propagation over distances of about 10–20 rod diameters. In the limiting case of



**Fig. 9.** Schematic of (a) generated enamel fracture specimen and (b) cross section slices at various depths along the *x*-axis in the enamel fracture model. (c) Shows the specimen dimensions, crack length, applied boundary conditions ( $\Delta_{app}$ ), and periodic boundary conditions.

uniformly straight rods ( $\theta_D = 0^\circ$ ), relatively little inelastic deformation occurred as the crack propagated between the parallel rods. For this case, the toughness remained unchanged as the crack propagated past initiation, with a value corresponding to the theoretical delamination toughness  $(R/\Gamma_i = 4/3)$ , inferred from the geometry of the surface area shown in Fig. 9b). For cases where  $\theta_D > 0^\circ$  (Fig. 10, rows 2–4), the crack was forced into a non-planar configuration due to the decussating rod architecture, which promoted the development of a large inelastic region ahead of the crack through progressive yielding of interfaces and contributed to the initiation toughness and crack resistance. The initiation toughness increased monotonically with both decussation angle and process zone size, and reached about five times the interface toughness in the case for  $\theta_D = 30^\circ$ . As the crack advanced past initiation, the toughness increased significantly with no apparent steady state reached for all cases where  $\theta_D > 0^\circ$ . For the case with the largest decussation ( $\theta_D = 30^\circ$ ), the crack resistance reached up to five times the initiation toughness (twenty-five times the interface toughness). The simulations were stopped when the *R*-curves from the small and large specimen diverged (Fig. 10), at which point the crack interacted with the specimen boundary.

For smaller non-zero decussation angles ( $\theta_D = 10^\circ$ ), we observed that the crack advanced by bursts and between crack pinning points spaced by a distance of about 6 rod diameters. Interestingly, this distance matches the decussation wavelength  $\lambda_D$  discussed above. This finding suggests that the crossing points of the rods act as obstacles for the cracks, and that for low decussation angles the 3D crack tortuosity is the primary toughening mechanism. At higher decussation angles, this effect is obscured by more powerful toughening mechanisms: crack branching and energy dissipation in the process zone (Fig. 10). We also monitored the maximum tensile stress carried by individual rods during the simulation. For the case with no decussation ( $\theta_D = 0^\circ$ ), we found a maximum stress of  $\sigma_r = 15\sigma_0$ , generated by flexural stresses in the rods that form the crack tip opening displacements. For higher decussation the maximum stress in the rods initially increased as the crack advanced (Fig. 10, column 5) but appeared to reach a steady state maximum value of  $40\sigma_0$  to  $60\sigma_0$  for  $\theta_D > 0^\circ$ . This observation is rationalized by the finite strength of the cohesive interfaces, which has been shown by previous analyses of cohesive zone models to eliminate the LEFM singularity ahead of the crack tip and provide an upper bound for the model stresses [38]. Interestingly, the toughness kept increasing with crack advance for  $\theta_D > 0^\circ$  even though the rod stresses reached a steady state value. As the decussation angle increased from  $\theta_D = 0^\circ$  to  $\theta_D = 10^\circ$ , the maximum stress in the rods increased by a factor or 4–5. In going from  $\theta_D = 10^\circ$  to  $\theta_D = 30^\circ$ , the steady state rod stresses decreased. This observation can be explained by considering the physical limit of  $\theta_D = 90^\circ$ , where the stress state along the cross sections of the individual rod elements tends to be uniform in mode I loading. For a given state of stored elastic energy in a vertical slice within a single rod element (which directly scales the elastic energy release rate to drive cracking), a state of uniform tensile stress has a lower peak stress than one with a linear stress distribution.

Fig. 11 shows the 3D structure of the crack path and process zone in more detail for  $\theta_D = 30^\circ$  and  $E_r/kd = 5$  at  $\Delta a/d \approx 5$ . In ply 1, the pre-crack kinks into an interface between the rods at +30°, while in ply 2 it kinks into an interface at  $-30^\circ$ . In the interlayer,



**Fig. 10.** Effect of decussation angle ( $0^{\circ} \le \theta_D \le 30^{\circ}$ , rows 1–4) on the volumetric process zone (columns 1–3), the crack resistance (column 4), and maximum stress over all rods (column 5) as a function of crack length. For all calculations shown, the stiffness contrast was set at  $E_t/kd = 5$  and the relative cohesive separations were set at  $\Delta_S/\Delta_Y = 10$  and  $\Delta_U/\Delta_S = 1.8$ . For the case with the largest process zone ( $\theta_D = 30^{\circ}$ ), *R*-curves are shown for both a small and larger (2x) specimen. The volumetric process zone was defined as the region of interfaces whose maximum displacement (over the entire loading history) has exceeded its elastic limit ( $\Delta_{max} > \Delta_Y$ ).

the crack follows a branched trajectory with a symmetry about the x-axis. Within each ply, a dense process zone is generated from "intralayer" shearing between the plies. These parts of the process zone are close to symmetric about the x-axis (even though crack propagation is not). The results also show interlayer shearing between the plies which is symmetric about the x-axis and identical in the interlayer 1–2 and 2–3. This interlayer process zone is more sparse and heterogeneous, with a substantial volume fraction of interfaces remaining in the elastic region.

The snapshot shown in Fig. 11 represents a crack propagated in the decussated region. The crack has propagated over a distance of about five rods and the toughness has increased from  $G_c/\Gamma_i = 4.4$ (initiation toughness) to  $R/\Gamma_i$  = 10.8. At initiation, there was no observed crack branching or bridging, and tortuosity contributes only 30% to the toughness (4/3 $\Gamma_i$  at maximum). The remaining 70% is therefore accounted for by the inelastic work expended in the yielded interfaces ahead of the crack tip that form the initiation process zone. As the crack propagates, the process zone grows substantially in volume while the inelastic region unloads behind the crack tip, which consumes a large amount of energy and contributes to the crack resistance [56]. We computed the contribution of the process zone to toughness  $(R_{pz})$  using numerical differentiation as rate of change of total interface inelastic energy with respect to crack area ( $\partial W_i/\partial A$ ). The contributions from crack branching and tortuosity were grouped as surface area toughness effects  $(R_{sa})$  and were computed as the total crack surface area normalized by the projected crack area [57]. From the snapshot shown in Fig. 11b, we determined that 82.6% of the crack resistance is generated by process zone toughening, with 22.1% from interlayer shearing and 60.5% from intralayer rod shearing. The remaining 17.4% is accounted for from surface area effects (3D tortuosity and crack branching). Summing these individual contributions in raw form provides an overall toughness which is very close to the measured *J*-integral (within 1.7%), which shows that all the important toughening mechanisms (branching/tortuosity and process zone) where taken into account in this fracture model. These relative contributions are illustrated on Fig. 11c. The process zone within the plies (intraply shearing between rods) is the largest contributor to toughness, followed by interply shearing. Branching and tortuosity have a more modest but non-negligible effect. Parsing the relative contributions to the toughness in this manner helps establish strategies for designing tougher composites. For example, the interfaces in the interlayer could be made artificially weaker to provide greater homogeneity between the ply and interlayer process zones; while this would impact the material strength, the fracture resistance would likely increase.

We also explored the effect of stiffness contrast for a fixed decussation angle  $\theta_D = 20^\circ$  (Fig. 12). Fig. 12 shows that larger stiffness contrasts tend to simultaneously amplify the process zone size, which is consistent with the scaling expected from



**Fig. 11.** (a) Schematic showing the nomenclature for the plies and interlayers. (b) Distribution of the volumetric process zone in the thickness (-z) direction (c) Sources of crack resistance in the interlayers and the plies. Results in (b and c) are shown for a single load increment  $\Delta a/d \approx 5$  for  $\theta_D = 30^\circ$  and  $E_r/kd = 5$ .



**Fig. 12.** Effect of stiffness contrast on the enamel process zone distribution, *R*-curves, and maximum rod stresses. Rows 1–3 represent stiffness contrasts of  $E_{t/kd}$  = 5, 10, and 20, respectively, with  $\theta_D$  fixed at 20°.

LEFM [21]. Accordingly, fracture toughness also increased with the size of the process zone. The maximum steady state stress in the rods was also amplified for higher stiffness contrasts, which can be explained by Voigt composite theory: as the modulus of one of the constituents increases, the effective composite modulus also increases (as in Fig. 6), amplifying the stress state in both constituents for fixed strain. Interestingly, the rate at which rod stresses reach steady state also increased as the stiffness contrast was increased. Considering the case for  $E_r/kd = 5$ , the maximum rod stress appears to reach steady state in the later stages of the simulation ( $\Delta a/d \approx 20-25$ ), whereas when  $E_r/kd = 20$  it is reached very early on ( $\Delta a/d \approx 3$ ). This is consistent with LEFM scaling for the process zone size: the effective modulus dictates the rate of growth of the process zone  $(r_p = EG_q/\sigma_0^2)$  [21]. For larger effective moduli, the rods within the process zone become surrounded by larger volumes of fully vielded interfaces so that these models approach a constant stress state earlier in the simulation.

To further illustrate the capabilities of the DEM approach and explore the interaction of longitudinal cracks with the heterogeneous enamel microstructure, a hybrid bimaterial virtual specimen was also generated. In this model, half of the specimen had no decussation, and the other half had substantial decussation ( $\theta_D = 30^\circ$ ), analogous to the spatial distribution of decussation observed in natural enamel [1,4,5]. The pre-crack was inserted in the non-decussating region parallel to the rods with the crack tip located about 13 rod diameters from the boundary of the decussating region. The boundary conditions were identical to those shown in Fig. 9c.

Fig. 13 shows the process zone growth, crack propagation, and crack resistance curves for the bimaterial enamel model. Initially, the crack grows parallel to the straight rods with a localized process zone but is quickly arrested as the crack tip 'hits' the decussating region (Fig. 13a). As the load is ramped, the crack remains trapped at the decussation boundary while a large process zone spreads well across the boundary into the decussating region. This crack pinning mechanism is accompanied by a rapid rise in crack resistance (Fig. 13b) which is qualitatively identical to the experimental results shown in Fig. 1b [2].

For the last set of virtual fracture experiments, we allowed for the possibility of brittle rod fracture (in addition to interface fracture). We used a simple brittle fracture criterion where the rod element is removed from the simulation if its maximum stress  $\sigma_r$ exceeds the rod strength  $\sigma_{rs}$ . For these calculations, we chose the strength ratio based on the elastic rod stresses in Fig. 12 such that the first rod would fracture after an interface crack has initiated ( $\sigma_r \approx 30\sigma_0$  for  $\theta_D = 30^\circ$  when  $\Delta a > 0$ ).

Fig. 14 shows the effect of finite rod strength on the process zone and *R*-curves for the case where  $\theta_D = 30^\circ$ ,  $E_r/kd = 5$ , and  $\sigma_{rs}/kd = 5$  $\sigma_0$  = 30, alongside the case with infinite rod strength, with the relative toughness contributions shown in Fig. 14c. Initially, the process zone size and shape are identical in both cases as well as the initiation toughness. As the crack advances, both rods and interfaces fracture just ahead of the crack tip along a line which is symmetric to the delamination crack forming a full branch rather than just a kink. The crack from rod fracture in ply 1 follows the delamination crack in ply 2 and vice versa. A branch of broken interfaces was also formed in the interlayer for  $\sigma_{rs}/\sigma_0$  = 30 nearly identical to Fig. 11b. The fracture of the rods therefore does not completely suppress the fracture of interfaces between the rods, and the trajectory of the cracks is still largely affected by the architecture of the material. However, since the fracture of rods releases stresses ahead of the crack tip, the process zone size and ultimately toughness are diminished compared to the case of infinite rod strength (Fig. 14) and both reach steady state concurrently when  $\Delta a/\Delta a$  $d \approx 5$ . Rod fracture also alters the relative contributions to the toughness which are shown in Fig. 14c for  $\sigma_r \sqrt{\sigma_0} = 30$  at steady state ( $\Delta a/d \approx 5$ ). The process zone now contributes to 57.4% (compared to 82.6% when  $\sigma_{rs}/\sigma_0 = \infty$ ) of the toughness, which raises the relative contribution from surface area effects to 42.6% (compared to 17.4% when  $\sigma_{rs}/\sigma_0 = \infty$ ).

The predicted *R*-curves in Fig. 14 can be compared with fracture experiments on human enamel [1,2]. Evaluating the experimental crack resistance at the largest crack extension involved in [2]  $(\Delta a \approx 1.5 \text{ mm})$  gives  $K_R = 2.3 \text{ MPa} \cdot \text{m}^{1/2}$  Assuming an interface fracture energy  $\Gamma_i = 10 \text{ J/m}^2$  [48] and an enamel modulus E = 100 GPa[15], the experimental values of  $R/\Gamma_i$  for human enamel can be roughly estimated through Irwin's relation  $(R/\Gamma_i = K_R^2/E\Gamma_i)$  [21] and gives a value around  $R/\Gamma_i \approx 5.3$ . As with many mammalian species, the decussation patterns in human enamel are far more complex than the idealized cross-ply structure shown in Fig. 2, with no single well-defined decussation angle  $\theta_D$ . Mouse incisor enamel appears to be the exception, with a simple cross-ply structure with relative ply angles ranging from 30 to 55° [12]. Therefore  $\theta_D$  = 30° is reasonable for the sake of comparison. Unfortunately there are no published *R*curves for mouse incisor enamel so direct comparisons could not be made. To compare with the DEM simulations, we assumed a stiffness contrast  $E_r/kd$  = 5, which corresponds to  $E_r \sim 100$  GPa and  $\phi_r \sim 0.95$ , and an interface modulus  $E_i$  of about 500 MPa which is on the upper end of what would be realistic. Examining the DEM data for  $E_r/kd = 5$ and  $\theta_D = 30^\circ$  predicts a steady state fracture resistance of  $R/\Gamma_i \approx 7$ (Fig. 14), by comparison the estimated experimental value was about  $R/\Gamma_i \approx 5.3$ . This is in fact quite reasonable given that many of the experimental constants, especially those of the interface, had to be



**Fig. 13.** Results from the heterogeneous bimaterial enamel model where the rods are straight on the left side of the boundary ( $\theta_D = 0^\circ$ ) and decussating on the right side of the boundary ( $\theta_D = 30^\circ$ ). (a) Shows the process zone evolution as the crack approaches the decussation boundary and (b) shows the corresponding *R*-curve. Contours are clipped at 50% of the specimen size.



**Fig. 14.** Effect of finite rod strength for  $\theta_D = 30^\circ$  and  $E_{t/k}d = 5$ . (a) Shows the growth of the volumetric process zone as a function of crack propagation for  $\sigma_{rs}/\sigma_0 = \infty$  (top row) and  $\sigma_{rs}/\sigma_0 = 30$  (bottom row). The broken rods are rendered as black dots. (b) Shows the respective *R*-curves for both  $\sigma_{rs}/\sigma_0 = 30$  and  $\sigma_{rs}/\sigma_0 = \infty$ . The relative contributions to the toughness are shown in (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

roughly estimated given that they are much less understood. Moreover, we emphasize that our objective was not to model the full 3D structure of enamel, but to capture the effect of decussation and rod/ interface properties on the enamel mechanical properties with an idealized geometry. Still, the DEM model predicts properties that are relatively close to experimental trends even with its many idealizations and simplifying assumptions.

## 6. Summary: Ashby plots

The effects of decussation and stiffness contrast can be conveniently summarized in Ashby plots (Fig. 15). As the decussation angle is increased, both the axial modulus and hardness decrease simultaneously. Higher stiffness contrast between the rods and the interfaces ( $E_t/kd$ ) decreases the rate that hardness decreases with modulus. Fig. 15b shows the initiation toughness vs. axial

modulus for different architectures and stiffness contrast. Toughness and stiffness are mutually exclusive properties, which is consistent with other biological and engineering materials [58]. Low decussation angles produce stiff materials in the axial direction with low toughness in the transverse direction. Conversely, higher decussation angles produce more compliant materials in the axial direction that are much tougher transversally to the crack plane. The implication is that natural enamel transitions from a very hard and stiff (but brittle) material on the surface where the rods are parallel, to a tougher but more compliant material in the deeper regions where decussation increases. The decussation region serves as a smooth transition of modulus from the outer enamel to dentin, and as demonstrated by experiments and the models presented here, can arrest cracks and prevent them from propagating into the more infection prone dentin and pulp. Interestingly, our models show that higher stiffness and toughness



Fig. 15. Various properties plotted parametrically as a function of decussation angle. (a) and (b) show hardness and initiation toughness vs. axial modulus, respectively. (c) Shows the maximum steady state rod stress vs. initiation toughness. In all plots, an arrow is shown along the direction of increasing decussation.

can both be achieved by increasing the contrast of stiffness between rods and interfaces. This finding is consistent with guidelines for nacre [59], and can be generalized to hard biological materials that rely on hard building blocks bonded by softer interfaces [48]. Fig. 15c however illustrates the limitations of increasing the stiffness contrast: the stresses within the rods are amplified and therefore presents a higher likelihood of brittle rod fracture, which we showed substantially limit the crack resistance (Fig. 14). For example, considering the case where  $E_r/kd = 5$ , the maximum rod stress reaches about 40 times the interface strength for the case modeled with the largest toughness ( $\theta_D = 30^\circ$ ), indicating that the rod strength would have to be about 40 times that of the interface to avoid brittle rod fracture. This strength contrast is substantial, and consistent with mechanical tests on bovine enamel where individual rods were shown to have high strengths (1.5-1.7 GPa [34,35]), at least in compression. These simulation results reinforce the conclusions here that high strength contrast is needed to generate toughness. In bioinspired materials, this high contrast of strength could be achieved by combining a relatively low strength polymer (~25 MPa) for the interfaces with a higher strength metallic or ceramic material for the rods ( $\sim 1$  GPa) [60].

#### 7. Conclusions

While it has been understood for some time [1,2,5,6,8,14,15] that decussation influences the properties in enamel (particularly its ability to arrest through-thickness longitudinal cracks emanating from the surface to prevent them from reaching the DEI), detailed numerical models that explicitly quantify effect of decussation and stiffness contrast had not been performed. This study shows that DEM offers a powerful, computationally efficient approach for simulations of complex architectures that would otherwise not be tractable with conventional 3D finite elements. By combining the efficiency of the DEM approach with the raw processing power of modern supercomputers, we conducted parameter studies with very large 3D models of enamel (over 10<sup>6</sup> degrees of freedom). While the DEM models are highly idealized and make many simplifying assumptions, the results are remarkably close to experiments and capture the toughening mechanisms observed in natural enamel [2] as well as bioinspired crossplies [61]. The DEM models quantitatively elucidate the role of specific micromechanics, which are summarized below:

- 1. Parallel rod alignment generates high stiffness. The axial modulus ( $E_{xx}$ ) is maximized at  $\theta_D = 0^\circ$  and recovers the theoretical upper bound constant-strain (Voigt) model. As decussation is introduced the material becomes more compliant and approaches the lower bound constant-stress (Reuss) model. This trend is consistent with experiments [14–16] and suggests decussation functionally grades enamel and alleviates DEJ stresses due to modulus mismatch.
- 2. Hardness is governed by inelastic shearing between rods, which spreads primarily in the depth direction (-z). The spread in the depth direction was largest (3–4 rod diameters) for near straight rods ( $\theta_D = 5.7^\circ$ ) and decreased as more decussation was introduced which accounts for the drop in hardness (Fig. 8), consistent with many experiments [14–16]. In all indentation simulations the inelastic region and rod displacements were highly contained (within 2 rod diameters) inplane, thus reproducing the 'sinking' mechanism [17] that prevents widespread damage.
- 3. Toughness and rising crack resistance are generated by a confluence of mechanisms that are activated with increasing decussation, including crack branching, 3D tortuosity, and spreading of the volumetric process zone. For straight rods ( $\theta_D = 0^\circ$ ), only 3D tortuosity was activated but for higher

decussation angles, a nonlinear process zone developed along with a 3D partially-branched partially-kinked crack configuration which both amplified the crack resistance. For  $\theta_D = 30^\circ$ , the process zone contributed the most to crack resistance at 82.6% (for  $\Delta a/d = 5$ ), with about 60.5% from intralayer deformation and 22.1% from interlayer deformation. Crack branching and 3D tortuosity accounted for the remaining 17.4%.

- 4. Crack resistance is substantially limited when rod fracture is allowed ( $\sigma_{rs} \neq \infty$ ) and approaches a steady state value of  $R/\Gamma_i \approx 7$  (for  $\theta_D = 30^\circ$ ,  $E_r/kd = 5$ , and  $\sigma_{rs} = 30$ ), close to experimental values [2]. In this case full crack branching and process zone toughening are activated but the fracture of rods releases elastic stresses ahead of the crack that would otherwise process zone energy dissipation. Hence, the process zone size is reduced relative to the infinite rod strength model and quickly reaches steady concurrently with the crack resistance.
- 5. For all decussation angles  $\theta_D > 0^\circ$  (and  $\sigma_{rs} = \infty$ ), the crack resistance increased indefinitely with crack advance while the maximum stresses in the rods approached steady state due to fully yielded interfaces. This finding is consistent models for process zone toughening in [25] with elastic-plastic interfaces: the stresses in the interfaces surrounding the hard phase remain constant but energy is continually dissipated which raises the overall crack resistance.

The results from the DEM analyses may be incorporated into existing dental practices to offer improvements in many regards. For example the DEM models could help assess the stability of surface cracks and sub-surface defects (largely dictated by the spatial distribution in fracture toughness) to decide whether conservative treatment options are realistic [62]. The DEM models also offer insight on how to make better tooth replacements with unique combinations of properties (e.g., hardness and toughness) that incorporate architecture and expand the material selection space [10]. This is particularly advantageous as modern tooth replacements are rather limited in material selection [63] due to strict requirements in terms of reliability and function. Many microfabrication techniques have been recently proposed [64.65] that could reproduce similar geometries to those represented by the DEM models (Fig. 2), although attaining high concentrations of the hard phase remains a substantial challenge [66]. Interestingly, many of the 'design' concepts in natural enamel shown in this work are mirrored in the design of modern engineering coatings. For example, both experiments and the DEM models indicate that enamel is a functionally graded system [14–16], which is a technique used in synthetic coatings to mitigate stress concentrations at interfaces by gradually reducing the elastic mismatch [67]. Thermal barrier coatings (TBC's), which serve as a protective layer against heat and environmental attack in modern turbine engines, are also similar in microstructure to enamel. The deposited TBC microstructure is typically arranged in micron-sized feathery 'columns' [68] that are analogous to the 'rods' found in enamel. The classic columnar microstructure provides protection against contact forces (e.g., foreign object damage) via localization and provides a mechanism for thermal strain tolerance due to CTE mismatch over larger length scales. While there are many similarities between modern and natural systems, modern coating systems still exhibit reliability concerns due to their inherently brittle composition [68]. The DEM simulations can help in the exploration of mechanics-based bioinspired strategies for increasing the crack resistance and reliability of such systems.

The DEM models could be improved in many regards to capture the effects of geometric complexities such as defects (e.g., 'intruder cells' [32]) and Hunter-Schreger bands [69] on stiffness, hardness and toughness. As shown in many mammals, the rods are in fact not straight as assumed here but are arranged in wavy bands with near sinusoidal profiles [70]. The rods are offset in phase from adjacent layers which creates a periodically varying distribution of decussation and could be studied under mechanical loading with the current DEM simulation tools. The assumption of a semiinfinite periodic structure (Fig. 2, y-direction) could also be relaxed as many species show nonperiodic microstructure with rod entanglement in 3D [12,70], although this would require further optimization of the DEM approach to manage the  $n^3$  computational complexity of modeling a full nonperiodic 3D microstructure. Strain-hardening could also be implemented into the interfaces. Although strain-hardening has not been directly observed in natural enamel, it was shown in our previous DEM models for staggered composites [26] that even a small amount of hardening (5%) amplifies the crack resistance nearly 50% and therefore presents a plausible hypothesis in enamel. Lastly, the approach could be combined with genetic algorithms [71] to generate optimized architectures that serve as future guidelines for engineered composites, as well as offer an evolutionary explanation for many morphological features observed in natural enamel.

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#### Appendix A:. Glossary of symbols

[A]	Boundary condition matrix
[J(u)]	Augmented Jacobian matrix
[K]	Unconstrained global stiffness matrix
[K] <sup>+</sup>	Augmented global stiffness matrix
[k] <sub>e</sub>	Elemental stiffness matrix
{f}	Global fodal force vector
{f} <sup>+</sup>	Augmented generalized force vector
{f}e	Elemental nodal force vector
$\{g(u)\}$	Nonlinear augmented force residual
{Q}	Prescribed boundary condition vector
{R}	Nodal reaction force and moment vector
{u}	Global nodal solution vector
${u}^{+}$	Augmented generalized solution vector
{u} <sub>e</sub>	Elemental nodal solution vector
Α	3D J-integral area contour
$a_0$	length of initial pre-crack
$A_i$	interface area
$A_r$	Rod cross sectional area
d	average rod diameter
$d_0$	initial tile spacing
Ei	Interface modulus
Er	elastic modulus of rods
E <sub>Reuss</sub>	Reuss modulus of enamel model ( $\theta_D = 0^\circ$ )
$E_{xx}$	modulus of enamel model (x-direction)
$E_{yy}$	modulus of enamel model (y-direction)
E <sub>zz</sub>	modulus of enamel model (z-direction)
Fo	effective peak force of interface
F <sub>c</sub>	Peak force in virtual indentation test

$f_{i,x-z}$	Element <i>i</i> local nodal forces
G <sub>c</sub>	fracture initiation toughness
Н	Enamel model hardness, $F_c/\sigma_0 d^2$
h <sub>e</sub>	height of beam elements (mesh size)
hs	height of fracture specimen
Ixx	Rod polar moment of inertia
Ivv	Rod 2nd area moment about local v-axis
уу I <sub>22</sub>	Rod 2nd area moment about local z-axis
k	interface stiffness
k.	effective interface spring stiffness
Kp	Experimental crack resistance
I.	interface length
L <sub>1</sub>	Length of rod element
L <sub>r</sub> M	Element i local nodal moments
IVI <sub>1,X-Z</sub>	integration contour normal vector
n <sub>k</sub>	
ĸ	
r <sub>p</sub>	size of process zone (maximum radius)
R <sub>pz</sub>	process zone contribution to crack resistance
<i>R</i> <sub>sa</sub>	surface area contribution to crack resistance
t	thickness of virtual indentation specimen
t <sub>i</sub>	traction vector
$u_{i,x-z}$	Element <i>i</i> local nodal displacements
W	elastic strain energy density
$W_i$	inelastic work expended in process zone
Ws	width of fracture specimen
Γ	3D J-integral line contour
$\Gamma_i$	interface toughness (area under Fig. 4b)
$\Delta$	applied indentor displacement (hardness)
$\Delta$	Indenter displacement in hardness models
$\Delta a$	crack length
$\Delta_{app}$	peak applied displacement in fracture test
$\delta_{kj}$	Kronecker delta
$\Delta_n$	interface normal separation
$\Delta_S$	interface softening displacement
$\Delta_{t1}$	interface tangential separation (direction 1)
$\Delta_{t2}$	interface tangential separation (direction 2)
$\Delta_U$	interface ultimate displacement
$\Delta_Y$	interface yielding displacement
η	3D J-integral crack front coordinate
$\theta_D$	decussation angle
$\theta_{i,x-z}$	Element <i>i</i> local nodal rotations
λη	decussation wavelength
$\sigma_0$	interface strength
$\sigma_{ii}$	Cauchy stress tensor
$\sigma_r$	maximum elastic stress within rods
$\sigma_{rss}$	steady state maximum rod stress
$\sigma_{rc}$	brittle fracture strength of rods
ф.,	Rod volume fraction
Ψſ	Roa volume nuction

## Appendix B:. Elemental stiffness and Jacobian matrices

The stiffness and Jacobian matrices are shown in this appendix section for completeness. The elemental governing equation for a single beam or interface element is given as:

$$[K(u)]_e \{u\}_e = \{f\}_e \tag{B.1}$$

where  $[K]_e$  is the local element stiffness matrix,  $\{u\}_e$  is the vector of local nodal degrees of freedom, and  $\{f\}_e$  is the vector of local nodal forces and moments. For the beam elements used to model the rods, Eq. (B.1) is linear and is expressed in expanded form as [39]:

The beam element Jacobian is simply equal to its stiffness matrix ( $[J]_{beam} = [K]_{beam}$ ) as it is a linear element. For the interfaces, Eq. (B.1) is nonlinear and the stiffness matrix depends on the nodal degrees of freedoms. For a mode independent, isotropic interface, the local stiffness equation is given as:

where  $u_{1-12}$  are now the generalized displacements ( $u_1 = u_{1x}$ ,  $u_2 = u_{1y}$ ...). The individual entries of the interface Jacobian matrix ( $J_{ij}$ ) were computed and simplified symbolically with Mathematica [72] and inserted into the main routine of the DEM code; the full expressions are omitted here for brevity.

$k_e(\Delta)$	0	0	0	0	0	$-k_e(\Delta)$	0	0	0	0	0		$\int u_{1x}$	)	$\int f_{1x}$
0	$k_e(\Delta)$	0	0	0	0	0	$-k_e(\Delta)$	0	0	0	0		$u_{1y}$		$f_{1y}$
0	0	$k_e(\Delta)$	0	0	0	0	0	$-k_e(\Delta)$	0	0	0		$u_{1z}$		$f_{1z}$
0	0	0	0	0	0	0	0	0	0	0	0		$\theta_{1x}$		$M_{1x}$
0	0	0	0	0	0	0	0	0	0	0	0		$\theta_{1y}$	l	$M_{1y}$
0	0	0	0	0	0	0	0	0	0	0	0		$\theta_{1z}$		$M_{1z}$
$-k_e(\Delta)$	0	0	0	0	0	$k_e(\Delta)$	0	0	0	0	0	Ì	$u_{2x}$	$\int_{0}^{\infty}$	$\int f_{2x}$
0	$-k_e(\Delta)$	0	0	0	0	0	$k_e(\Delta)$	0	0	0	0		<i>u</i> <sub>2y</sub>		$f_{2y}$
0	0	$-k_e(\Delta)$	0	0	0	0	0	$k_e(\Delta)$	0	0	0		$u_{2z}$	l	$f_{2z}$
0	0	0	0	0	0	0	0	0	0	0	0		$\theta_{2x}$		$M_{2x}$
0	0	0	0	0	0	0	0	0	0	0	0		$\theta_{2y}$		$M_{2y}$
0	0	0	0	0	0	0	0	0	0	0	0		$\theta_{2z}$	J	$M_{2z}$

Where the displacement jump  $\Delta$  is given directly in terms of the local nodal displacements:

$$\Delta = \sqrt{\left(u_{2x} - u_{1x}\right)^2 + \left(u_{2y} - u_{1y}\right)^2 + \left(u_{2z} - u_{1z}\right)^2}$$
(B.4)

The is the effective stiffness  $k_e$  is computed from the cohesive traction displacement relationship  $T(\Delta)$  in Fig. 4:

$$k_e(\Delta) = \frac{T(\Delta)}{\Delta} A_i \tag{B.5}$$

For an element with nonlinear stiffness, the elemental Jacobian is represented in index notation as:

$$J_{ij} = K_{ij} + \frac{\partial K_{ik}}{\partial u_j} (u_1, u_2, ..., u_{12}) u_k$$
(B.6)

~ \* \*

#### References

- D. Bajaj, D. Arola, Role of prism decussation on fatigue crack growth and fracture of human enamel, Acta Biomater. 5 (8) (2009) 3045–3056.
- [2] D. Bajaj, D.D. Arola, On the R-curve behavior of human tooth enamel, Biomaterials 30 (23-24) (2009) 4037-4046.
- [3] D. Bajaj, A. Nazari, N. Eidelman, D.D. Arola, A comparison of fatigue crack growth in human enamel and hydroxyapatite, Biomaterials 29 (36) (2008) 4847–4854.
- [4] D. Bajaj, S. Park, G.D. Quinn, D. Arola, Fracture processes and mechanisms of crack growth resistance in human enamel, Jom 62 (7) (2010) 76–82.
- [5] M. Yahyazadehfar, D. Bajaj, D.D. Arola, Hidden contributions of the enamel rods on the fracture resistance of human teeth, Acta Biomater. 9 (1) (2013) 4806–4814.
- [6] M. Vahyazadehfar, J. Ivancik, H. Majd, B. An, D. Zhang, D. Arola, On the mechanics of fatigue and fracture in teeth, Appl. Mech. Rev. 66 (3) (2014) 030803.
- [7] S. Habelitz, S. Marshall, G. Marshall Jr, M. Balooch, Mechanical properties of human dental enamel on the nanometre scale, Arch. Oral Biol. 46 (2) (2001) 173–183.

- [8] S. Bechtle, S. Habelitz, A. Klocke, T. Fett, G.A. Schneider, The fracture behaviour of dental enamel, Biomaterials 31 (2) (2010) 375–384.
- [9] I. Spears, A three-dimensional finite element model of prismatic enamel: a reappraisal of the data on the Young's modulus of enamel, J. Dental Res. 76 (10) (1997) 1690–1697.
- [10] F. Barthelat, Architectured materials in engineering and biology: fabrication, structure, mechanics and performance, Int. Mater. Rev. 60 (8) (2015) 413–430.
- [11] M.C. Maas, E.R. Dumont, Built to last: the structure, function, and evolution of primate dental enamel, Evolutionary Anthropol.: Issues, News, and Reviews 8 (4) (1999) 133–152.
- [12] B.N. Cox, How the tooth got its stripes: patterning via strain-cued motility, J. R Soc. Interface 10 (84) (2013) 20130266.
- [13] J.M. Rensberger, W.v. Koenigswald, Functional and phylogenetic interpretation of enamel microstructure in rhinoceroses, Paleobiology 6 (4) (1980) 477–495.
- [14] H. Jiang, X.-Y. Liu, C.T. Lim, C.Y. Hsu, Ordering of self-assembled nanobiominerals in correlation to mechanical properties of hard tissues, Appl. Phys. Lett. 86 (16) (2005) 163901.
- [15] J.L. Cuy, A.B. Mann, K.J. Livi, M.F. Teaford, T.P. Weihs, Nanoindentation mapping of the mechanical properties of human molar tooth enamel, Arch. Oral Biol. 47 (4) (2002) 281–291.
- [16] S. Park, D.H. Wang, D. Zhang, E. Romberg, D. Arola, Mechanical properties of human enamel as a function of age and location in the tooth, J. Mater. Sci. – Mater. Med. 19 (6) (2008) 2317–2324.
- [17] L.H. He, M.V. Swain, Contact induced deformation of enamel, Appl. Phys. Lett. 90 (17) (2007) 171916.
- [18] H. Xu, D. Smith, S. Jahanmir, E. Romberg, J. Kelly, V. Thompson, E. Rekow, Indentation damage and mechanical properties of human enamel and dentin, J. Dent. Res. 77 (3) (1998) 472–480.
- [19] S. White, W. Luo, M. Paine, H. Fong, M. Sarikaya, M. Snead, Biological organization of hydroxyapatite crystallites into a fibrous continuum toughens and controls anisotropy in human enamel, J. Dent. Res. 80 (1) (2001) 321–326.
- [20] G.D. Quinn, R.C. Bradt, On the Vickers indentation fracture toughness test, J. Am. Ceram. Soc. 90 (3) (2007) 673–680.
- [21] H. Tada, P.C. Paris, G.R. Irwin, The stress analysis of cracks, Del Research Corporation, Handbook, 1973.
- [22] A. Barani, M.B. Bush, B.R. Lawn, Effect of property gradients on enamel fracture in human molar teeth, J. Mech. Behav. Biomed. Mater. 15 (2012) 121–130.
- [23] D. Shimizu, G.A. Macho, Functional significance of the microstructural detail of the primate dentino-enamel junction: a possible example of exaptation, J. Hum. Evol. 52 (1) (2007) 103–111.
- [24] A. Khandelwal, A. Kumar, R. Ahluwalia, P. Murali, Crack propagation in staggered structures of biological and biomimetic composites, Comput. Mater. Sci. 126 (2017) 238–243.
- [25] F. Barthelat, R. Rabiei, Toughness amplification in natural composites, J. Mech. Phys. Solids 59 (4) (2011) 829–840.
- [26] N. Abid, J.W. Pro, F. Barthelat, Fracture mechanics of nacre-like materials using discrete-element models: effects of microstructure, interfaces and randomness, J. Mech. Phys. Solids (2018).
- [27] R.K. Lim, J.W. Pro, M.R. Begley, M. Utz, L.R. Petzold, High-performance simulation of fracture in idealized 'brick and mortar'composites using adaptive Monte Carlo minimization on the GPU, Int. J. High Perf. Comput. Appl. 30 (2) (2016) 186–199.
- [28] N. Abid, M. Mirkhalaf, F. Barthelat, Discrete-element modeling of nacre-like materials: effects of random microstructures on strain localization and mechanical performance, J. Mech. Phys. Solids 112 (2018) 385–402.
- [29] J.W. Pro, R.K. Lim, L.R. Petzold, M. Utz, M.R. Begley, GPU-based simulations of fracture in idealized brick and mortar composites, J. Mech. Phys. Solids 80 (2015) 68–85.
- [30] J.W. Pro, R.K. Lim, L.R. Petzold, M. Utz, M.R. Begley, The impact of stochastic microstructures on the macroscopic fracture properties of brick and mortar composites, Extreme Mech. Lett. 5 (2015) 1–9.
- [31] B. Cox, A multi-scale, discrete-cell simulation of organogenesis: application to the effects of strain stimulus on collective cell behavior during ameloblast migration, J. Theor. Biol. 262 (1) (2010) 58–72.
- [32] B.N. Cox, M.L. Snead, Cells as strain-cued automata, J. Mech. Phys. Solids 87 (2016) 177–226.
- [33] E.D. Yilmaz, J. Koldehoff, G.A. Schneider, On the systematic documentation of the structural characteristics of bovine enamel: a critic to the protein sheath concept, Dent. Mater. 34 (10) (2018) 1518–1530.
- [34] E.D. Yilmaz, H. Jelitto, G.A. Schneider, Uniaxial compressive behavior of micropillars of dental enamel characterized in multiple directions, Acta Biomater. 16 (2015) 187–195.
- [35] E.D. Yilmaz, G.A. Schneider, Mechanical behavior of enamel rods under microcompression, J. Mech. Behav. Biomed. Mater. 63 (2016) 183–194.
- [36] A.K. Dastjerdi, R. Rabiei, F. Barthelat, The weak interfaces within tough natural composites: experiments on three types of nacre, J. Mech. Behav. Biomed. Mater. 19 (2013) 50–60.

- [37] M.R. Begley, J.W. Hutchinson, The Mechanics and Reliability of Films, Multilayers and Coatings, Cambridge University Press, 2017.
- [38] J. Parmigiani, M. Thouless, The effects of cohesive strength and toughness on mixed-mode delamination of beam-like geometries, Eng. Fract. Mech. 74 (17) (2007) 2675–2699.
- [39] R.D. Cook, D.S. Malkus, M.E. Plesha, Concepts and applications of finite element analysis, Wiley, New York, 1974.
- [40] A. Nanci, Ten Cate's Oral Histology-E-Book: Development, Structure, and Function, Elsevier Health Sciences, 2017.
- [41] D. Tabor, The hardness of solids, Rev. Phys. Technol. 1 (3) (1970) 145.
- [42] V. Jardret, H. Zahouani, J.-L. Loubet, T. Mathia, Understanding and quantification of elastic and plastic deformation during a scratch test, Wear 218 (1) (1998) 8–14.
- [43] Y. Gao, A. Bower, A simple technique for avoiding convergence problems in finite element simulations of crack nucleation and growth on cohesive interfaces, Modell. Simul. Mater. Sci. Eng. 12 (3) (2004) 453.
- [44] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical recipes 3rd edition: The art of scientific computing, Cambridge University Press, 2007.
- [45] I.M. Low, Depth-profiling of crystal structure, texture, and microhardness in a functionally graded tooth enamel, J. Am. Ceram. Soc. 87 (11) (2004) 2125–2131.
- [46] N. Meredith, M. Sherriff, D. Setchell, S. Swanson, Measurement of the microhardness and Young's modulus of human enamel and dentine using an indentation technique, Arch. Oral Biol. 41 (6) (1996) 539–545.
- [47] L.-H. He, M.V. Swain, Enamel a functionally graded natural coating, J. Dent. 37 (8) (2009) 596–603.
- [48] F. Barthelat, Z. Yin, M.J. Buehler, Structure and mechanics of interfaces in biological materials, Nat. Rev. Mater. 1 (4) (2016) 16007.
- [49] J.R. Barber, Elasticity, Springer, 2002.
- [50] H. Chai, J.J.-W. Lee, P.J. Constantino, P.W. Lucas, B.R. Lawn, Remarkable resilience of teeth, Proc. Natl. Acad. Sci. 106 (18) (2009) 7289–7293.
- [51] O. Borrero-Lopez, A. Pajares, P.J. Constantino, B.R. Lawn, Mechanics of microwear traces in tooth enamel, Acta Biomater. 14 (2015) 146–153.
- [52] M. Chiarelli, A. Frediani, A computation of the three-dimensional J-integral for elastic materials with a view to applications in fracture mechanics, Eng. Fract. Mech. 44 (5) (1993) 763–788.
- [53] J. Parmigiani, M. Thouless, The roles of toughness and cohesive strength on crack deflection at interfaces, J. Mech. Phys. Solids 54 (2) (2006) 266–287.
- [54] G.T. Camacho, M. Ortiz, Computational modelling of impact damage in brittle materials, Int. J. Solids Struct. 33 (20–22) (1996) 2899–2938.
- [55] A. Turon, C.G. Davila, P.P. Camanho, J. Costa, An engineering solution for mesh size effects in the simulation of delamination using cohesive zone models, Eng. Fract. Mech. 74 (10) (2007) 1665–1682.
- [56] A.G. Evans, Z. Ahmad, D. Gilbert, P. Beaumont, Mechanisms of toughening in rubber toughened polymers, Acta Metall. 34 (1) (1986) 79–87.
- [57] T.L. Anderson, Fracture mechanics: fundamentals and applications, CRC Press, 2017.
- [58] R.O. Ritchie, The conflicts between strength and toughness, Nat. Mater. 10 (11) (2011) 817.
- [59] F. Barthelat, Designing nacre-like materials for simultaneous stiffness, strength and toughness: optimum materials, composition, microstructure and size, J. Mech. Phys. Solids 73 (2014) 22–37.
- [60] M.F. Ashby, D. Cebon, Materials selection in mechanical design, Le Journal de Physique IV 3 (C7) (1993) C7-1-C7-9.
- [61] Z. Yin, A. Dastjerdi, F. Barthelat, Tough and deformable glasses with bioinspired cross-ply architectures, Acta Biomater. 75 (2018) 439–450.
- [62] B.U. Zachrisson, Ö. Skogan, S. Höymyhr, Enamel cracks in debonded, debanded, and orthodontically untreated teeth, Am J. Orthodont. 77 (3) (1980) 307–319.
   [63] R. Osman, M. Swain, A critical review of dental implant materials with an
- emphasis on titanium versus zirconia, Materials 8 (3) (2015) 932–958.
- [64] S. Deville, E. Saiz, R.K. Nalla, A.P. Tomsia, Freezing as a path to build complex composites, Science 311 (5760) (2006) 515–518.
- [65] R.M. Erb, R. Libanori, N. Rothfuchs, A.R. Studart, Composites reinforced in three dimensions by using low magnetic fields, Science 335 (6065) (2012) 199–204.
- [66] E. Munch, M.E. Launey, D.H. Alsem, E. Saiz, A.P. Tomsia, R.O. Ritchie, Tough, bio-inspired hybrid materials, Science 322 (5907) (2008) 1516–1520.
  [67] J. Kim, W.-J. Kim, D. Choi, J. Park, W.-S. Ryu, Design of a C/SiC functionally
- graded coating for the oxidation protection of C/C composites, Carbon 43 (8) (2005) 1749–1757.
- [68] D. Clarke, C. Levi, Materials design for the next generation thermal barrier coatings, Annu. Rev. Mater. Res. 33 (1) (2003) 383–417.
- [69] F. Hirota, Prism arrangement in human cusp enamel deduced by X-ray diffraction, Arch. Oral Biol. 27 (11) (1982) 931–937.
- [70] G.A. Macho, Y. Jiang, I.R. Spears, Enamel microstructure a truly threedimensional structure, J. Hum. Evol. 45 (1) (2003) 81–90.
- [71] D.E. Goldberg, M.P. Samtani, Engineering optimization via genetic algorithm, ASCE, Electronic computation, 1986, pp. 471–482.
- [72] I. Wolfram, Res. Mathematica Version 11 (2018) 3.