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Understanding the influence of structural hierarchy and its coupling with chemical environment on the strength of idealized tropocollagen–hydroxyapatite biomaterials

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ABSTRACT

Hard biomaterials such as bone, dentin, and nacre have primarily an organic phase (e.g. tropocollagen (TC)) and a mineral phase (e.g. hydroxyapatite (HAP) or aragonite) arranged in a staggered arrangement at the nanoscopic length scale. Interfacial interactions between the organic phase and the mineral phase as well as the structural effects arising due to the staggered arrangement significantly affect the strength of such biomaterials. The effect of such factors is intricately intertwined with the chemical environment of such materials. In the present investigation, an idealized TC–HAP composite system under tensile loading is analyzed using explicit three-dimensional (3-D) molecular dynamics (MD) simulations to develop an understanding of these factors. The material system is analyzed in three different environments: (1) in the absence of water molecules (non-hydrated), (2) in the presence of water molecules (hydrated), and (3) in the presence of water molecules with calcium ions (ionized water). The analyses focus on understanding the correlations among factors such as the structural arrangement, the peak stress during deformation, Young's modulus, the peak interfacial strength, and the length scale of the localization of peak stress during deformation. Analyses show that maximizing the contact area between the TC and HAP phases results in higher interfacial strength as well as higher fracture strength. Due to the staggered arrangement, the orientation of HAP crystals has insignificant effect on the biomaterial strength. Analyses based on strength scaling as a function of structural hierarchy level reveal that while peak strength follows a multiscaling relation, the fracture strength does not. The peak strain for failure was found to be independent of the changes in levels of structural hierarchy. Overall, the analyses, being limited in size due to the computational time constraint, point out important correlations between the mechanical strength and chemically influenced structural hierarchy of biomaterials.

1. Introduction

Hard biological materials such as bone, dentin, nacre, etc., are a class of hierarchical nanocomposite material systems primarily consisting of a mineral phase (e.g. calcium hydroxyapatite (HAP with chemical formula: $Ca_5(PO_4)_3OH$), aragonite) and an organic phase (e.g. tropocollagen (TC), chitin) in a staggered arrangement at the nanoscopic length scale. In the structural studies of such materials, it is observed that the mineral crystals are preferentially aligned along the length of the

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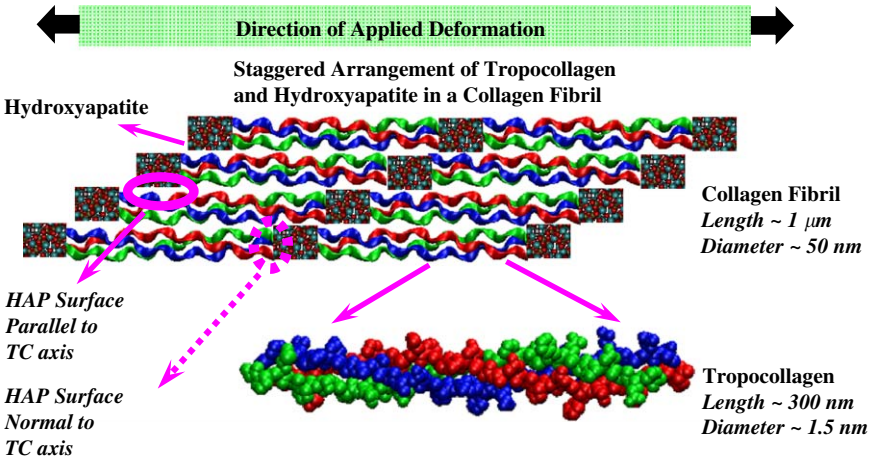

Fig. 1. A schematic of staggered and layered assembly of TC molecules and HAP blocks to form a fibril. For the shown loading direction, solid ellipse shown illustrates a possible tension–shear type of load transfer between the HAP crystal and the TC molecules. Dotted ellipse shows a possible tension–tension type of load transfer.

polypeptide molecules permitting maximum contact area in a staggered arrangement (Weiner et al., 1983; Fratzl et al., 1991; Landis et al., 1996a, b) (Fig. 1).

As shown using dotted and solid ellipses in Fig. 1, a staggered arrangement is responsible for possible tension–shear or tension–tension types of load transfer between the TC molecules and the HAP crystals (Ji, 2008). Interfacial interactions between the organic phase and the mineral phase as well as the structural effects arising due to the staggered arrangement significantly affect the strength of such biomaterials (Gao, 2006; Fratzl and Weinkamer, 2007; Chen et al., 2008; Meyers et al., 2008). The effects of the structural factors and the extent of interfacial interactions are intricately intertwined with the chemical environment of such materials. For example, earlier studies have shown that aqueous and ionic media has considerable effect on the mechanical properties of biomaterials (Bembey et al., 2006; Lucksanasombool et al., 2001; Thompson et al., 2001; Fantner et al., 2005). In the present investigation, an idealized TC–HAP composite biomaterial system under tensile loading is analyzed using explicit three-dimensional (3-D) molecular dynamics (MD) simulations to develop an understanding of these factors. The material system is analyzed in three different environments: (1) in the absence of water molecules (non-hydrated), (2) in the presence of water molecules (hydrated), and (3) in the presence of water molecules with calcium ions (ionized water).

The mechanical behavior of biological materials with a view to understand the role of TC molecules and HAP mineral has been earlier analyzed using experiments, modeling, and simulations. Experimental approaches have focused on analyzing tensile failure of single collagen fibers and fibrils (Sasaki and Odajima, 1996a, b; Eppell et al., 2005; Gupta et al., 2005), and on analyzing structural features at the nanoscale and its relation with the bone tissue failure (Hodge and Petruska, 1963; Fantner et al., 2005; Thurner et al., 2007). Modeling using the continuum approaches has focused on understanding the role played by the shear strength of TC molecules and the tensile strength of HAP mineral in fault tolerant hierarchical structural design of biomaterials (Jager and Fratzl, 2000; Ji and Gao, 2004; Gao, 2006; Ji, 2008). Explicit simulations using MD schemes have focused on understanding mechanical behavior and properties of TC molecules in different structural configurations (Lorenzo and Caffarena, 2005; Buehler, 2006a, b, 2007) on understanding hierarchical organization of TC molecules into collagen fibrils and its effect on mechanical properties (Israelowitz et al., 2005; Buehler, 2008), on understanding properties of hydrated TC molecules (Handgraaf and Zerbetto, 2006; Zhang et al., 2007), and on understanding TC molecule stability with respect to changes in residue sequences (Radmer and Klein, 2006). This work examines the effect of nanoscale interfacial interactions between the TC and HAP phases and the effect of structural hierarchy on mechanical strength of TC–HAP biomaterials in different chemical environments. Such analyses could bring forth important evidence on the role of interfacial arrangement, structural hierarchy, and chemical environment in biomaterial failure. The results of the MD simulation in the present investigation are compared with experimental results as well as analyzed using a well established tension shear chain (TSC) model for biomaterial failure characterization (Gao, 2006; Ji, 2008).

2. Method and framework

For analyses four different kinds of simulation cells are generated (Fig. 2): two *p*rimary *c*ells (PC) corresponding to the lowest structural level (level 1: PC1 and PC2) of TC–HAP interactions and two *s*econdary *c*ells (SC) with HAP crystals arranged in a staggered manner (level 2: SC1 and SC2) in a TC matrix. All cells are analyzed for quasi-static uniaxial deformation using a well-established method (Tomar and Zhou, 2007), in three different chemical environments: (1) non-hydrated, (2) hydrated, and (3) ionized water. The PC1 and PC2 cells are generated based on two distinct types of load