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Research paper

Robustness and optimal use of design principles of arthropod exoskeletons studied by ab initio-based multiscale simulations

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ABSTRACT

Recently, we proposed a hierarchical model for the elastic properties of mineralized lobster cuticle using (i) *ab initio* calculations for the chitin properties and (ii) hierarchical homogenization performed in a bottom-up order through all length scales. It has been found that the cuticle possesses nearly extremal, excellent mechanical properties in terms of stiffness that strongly depend on the overall mineral content and the specific microstructure of the mineral–protein matrix. In this study, we investigated how the overall cuticle properties changed when there are significant variations in the properties of the constituents (chitin, amorphous calcium carbonate (ACC), proteins), and the volume fractions of key structural elements such as chitin–protein fibers. It was found that the cuticle performance is very robust with respect to variations in the elastic properties of chitin and fiber proteins at a lower hierarchy level. At higher structural levels, variations of design parameters such as the volume fraction of the chitin–protein fibers have a significant influence on the cuticle performance. Furthermore, we observed that among the possible variations in the cuticle ingredients and volume fractions, the experimental data reflect an optimal use of the structural variations regarding the best possible performance for a given composition due to the smart hierarchical organization of the cuticle design.

1. Introduction and motivation

Most biological materials with structural functions in the animal kingdom consist of an organic matrix of structural biopolymers like collagen and chitin which is modified and reinforced with different proteins and in many cases also with biominerals. The most prominent examples of such materials, like the bones of vertebrates, the exoskeletons of arthropods, and mollusk shells, are known to possess excellent mechanical properties (e.g., in terms of stiffness-to-density ratio and fracture toughness). The origins of these properties have become the subject of intensive research in

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recent years (Vincent, 1990; Currey, 1996; Weiner and Addadi, 1997; Vincent and Wegst, 2004; Ashby and Wegst, 2004; Tai et al., 2007; Buehler and Wong, 2007; Ortiz and Boyce, 2008; Chen et al., 2008; Meyers et al., 2008; Al-Sawalmih et al., 2008; Fabritius et al., 2009). It has been observed that the specific design and properties at the nanoscale contribute significantly to their macroscopic properties (Nikolov et al., 2010). Evidently, the overall properties depend on the specific microstructure at all levels of hierarchy. However, in particular, the properties at small length scales are experimentally hard, if not impossible, to access due to methodological constraints. Hence, multiscale modeling that can systematically describe and investigate materials properties from the atomistic scale up to the macroscopic level has become a major approach to tackle the structure–property relations of biological organic/inorganic nanocomposites and has been applied to bone, mother of pearl, lobster cuticle, and related heterogeneous natural compounds (see, e.g., Vincent and Wegst, 2004; Ashby and Wegst, 2004; Raabe et al., 2005, 2006; Fratzl and Weinkamer, 2007; Nikolov and Raabe, 2008). In addition to modeling fully differentiated structural composites, the approach has been successfully applied to model the mechanical properties of individual constituents and to explain the structure–property relations on increasingly complex structural hierarchy levels. For non-mineralized soft tissues, important work on collagen fibril and tissue mechanics based on a multiscale approach linking molecular to continuum scales (Buehler, 2008; Tang et al., 2009) showed that there is a strong dependence of the fibril (tissue) response on nanoscopic structural features such as the density of crosslinks between neighboring collagen molecules.

Most multiscale models use fixed averaged values for the properties and volume fractions of the constituents (structural polymers, proteins, minerals) to predict the overall tissue properties. However, in reality, due to structural variations such as caused by different stages of growth, molt cycle, injuries, and synthesis heterogeneity, the properties and the volume fractions of the tissue constituents may vary considerably locally. Thus, an important question is how much the overall tissue properties change upon such structural variations of the building blocks on the small length scale. Tackling this question helps to better understand the robustness of biological tissue design. Experimentally validated physics-based multiscale models are an excellent vehicle to conduct such structure–property tolerance studies as the different ingredients and their behavior can be systematically varied. In a very recent work, a similar sensitivity analysis using multiscale modeling has been applied to bone (Reisinger et al., 2010).

The fact that the structure and mechanical properties of some constituents in biological hard tissues (e.g., proteins) are not well understood at present suggests an additional benefit of theory-assisted structural design analysis. It is therewith possible to identify at least the most probable order of magnitude of some of their properties by the comparison of corresponding multiscale predictions with experimental data.

A similar question arises with respect to biomimetic considerations. The aim of reproducing certain properties of biological matter in a synthetic material does not necessarily require copying the original biological structure but rather understanding the mechanical principle behind the material and replacing the underlying building blocks or their topological connectivity. A corresponding multiscale modeling approach can help to identify the relevant key ingredients with respect to a certain property and the tolerance of the overall material behavior against structural variations. We also address that current experimental observations suggest that among a set of possible structural variations real biological materials often reveal an optimal use of their ingredients regarding the best possible performance for a given composition.

In this work, we investigated these two questions of structural tolerance and optimal use taking mineralized load-bearing parts of the chitin-based exoskeleton of the crustacean *Homarus americanus* as a case study. The exoskeletons of all Arthropoda are formed by the cuticle which covers the entire animal and is locally modified in microstructure and chemical composition to perform all the functions required to meet the ecophysiological strains encountered by the organism. The cuticle represents a multilayered chitin–protein-based composite whose microstructure is hierarchically organized (Fig. 1). On the low levels of structural hierarchy, this general scheme appears to be valid for all arthropods. On the higher levels, significant differences can be found both in structural organization and in chemical composition between different taxa and even in closely related species (Neues et al., 2009; Hild et al., 2008, 2009). Crustaceans, for instance, reinforce the hard, load-bearing parts of their cuticle by incorporating various biominerals. The shell of the American lobster contains variable amounts of amorphous (ACC) and crystalline (calcite) calcium carbonate (Boßelmann et al., 2007).

The lowest level of hierarchy in the general arthropod model is represented by acetylglucosamine molecules (I) which polymerize to form chains of chitin (II). At the next hierarchy level (III), 18–25 chitin molecules arrange anti-parallel to form crystalline α-chitin nanofibrils with a diameter of about 3 nm. Each nanofibril is individually wrapped with proteins. Next, the chitin–protein nanofibrils cluster to form chitin–protein fibers (IV) with diameters $\sim$20 nm. In the plane of the cuticle, the mineralized chitin–protein fibers are arranged in planes with roughly parallel orientation of their long axes (V). In *H. americanus*, level V is formed directly by chitin nanofibrils arranged in horizontal planes. The arrangement is interrupted by voids originating from the pore canal system whose original function is to enable transport of minerals after molting, the process where arthropods replace their old exoskeleton with a new, larger one in order to grow. Hence, the resulting tissue appears as a honeycomb-like structure (V*). At this level, nanoscopic calcium carbonate particles become embedded in the protein matrix of the nanofibrils. The individual chitin–protein fiber planes (V) or nanofibril planes in case of our lobster (V*) are stacked over each other and gradually rotate around the normal direction of the cuticle, which results in a twisted plywood (Bouligand) structure (VI) pierced by pore canals in the form of twisted ribbons with elliptical cross section. At the macroscopic scale (VII), the cuticle consists of three layers: endocuticle, exocuticle, and an outer thin waxy layer, the epicuticle. The mechanically relevant exocuticle and endocuticle share the same