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Research Paper

Nacre-like hybrid films: Structure, properties, and the effect of relative humidity

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ABSTRACT

Functional materials often are hybrids composed of biopolymers and mineral constituents. The arrangement and interactions of the constituents frequently lead to hierarchical structures with exceptional mechanical properties and multifunctionality. In this study, hybrid thin films with a nacre-like brick-and-mortar microstructure were fabricated in a straightforward and reproducible manner through manual shear casting using the biopolymer chitosan as the matrix material (mortar) and alumina platelets as the reinforcing particles (bricks). The ratio of inorganic to organic content was varied from 0% to 15% and the relative humidities from 36% to 75% to determine their effects on the mechanical properties. It was found that increasing the volume fraction of alumina from 0% to 15% results in a twofold increase in the modulus of the film, but decreases the tensile strength by up to 30%, when the volume fraction of alumina is higher than 5%. Additionally, this study quantifies and illustrates the critical role of the relative humidity on the mechanical properties of the hybrid film. Increasing the relative humidity from 36% to 75% decreases the modulus and strength by about 45% and triples the strain at failure. These results suggest that complex hybrid materials can be manufactured and tailor made for specific applications or environmental conditions.

1. Introduction

A considerable research effort is currently focused on the synthesis of stronger, tougher, and "greener" materials based on the principles of function and optimization found in natural materials such as bone, teeth, lobster cuticle, mollusk shells and beaks (Munch et al., 2008; Bonderer et al., 2008; Bonderer et al., 2009; Walther et al., 2010; Dunlop and Fratzl, 2010). This is because natural materials often exhibit a superior mechanical performance in comparison to their synthetic, monolithic counterparts due to their hierarchical structural arrangements (Zhang et al., 2011; Launey and Ritchie, 2009). One example of such a natural material, that has attracted particular interest in recent years, is nacre. Also termed "mother of pearl", it forms

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the inner layer of the shells of a large number of mollusks (e.g., abalone), and has demonstrated impressive performance under tensile loading (Studart, 2012). Nacre is essentially a two-phase composite material with an intricate, interlocked brick-and-mortar structure comprised of about 95 vol%, of hexagonal aragonite platelets "glued" together by a thin polymer film (~10–50 nm thick) composed of proteins and polysaccharides (Kakisawa and Sumitomo, 2011; Jackson et al., 1988; Barthelat, 2010). The tensile strength of nacre is about 78–130 MPa (wet) and 90–167 MPa (dry), and the Young's modulus is about 58–70 GPa (wet) and 68–90 GPa (dry) (Kakisawa and Sumitomo, 2011). With a high volume fraction of ceramic, one would expect the material to be brittle. However, nacre has a work of fracture as high as 1240 J m^{-2}, in a three-point bending test, which is about 3000 times greater than that of monolithic $CaCO_3$ (Jackson et al., 1988; Meyers et al., 2008). The work of fracture, in this case, is defined as the critical strain energy release rate or the energy necessary to drive a crack through a sample. This intriguing observation and the relative simplicity of the structure of nacre were the motivation for this study of fundamental structure–property relationships, including the often neglected effect of moisture, in a nacre-like model material system.

The bio-inspired research presented here aims to identify the principles of function and optimization in biological materials and to mimic the same in engineered material systems. Numerous studies have described materials that match or even exceed the properties of nacre (Bonderer et al., 2008; Bonderer et al., 2009; Podsiadlo et al., 2007; Wegst et al., 2010; Malwitz et al., 2004; Deville et al., 2006). For example, using a layer-by-layer (LBL) assembly yields nanocomposites that can have tensile strengths up to 400 MPa (Bonderer et al., 2008; Bonderer et al., 2009; Podsiadlo et al., 2007; Malwitz et al., 2004). Freeze casting yields, when infiltrated by a second phase, layered structures that are up to 300 times tougher than its constituents (Munch et al., 2008; Wegst et al., 2010; Deville et al., 2006). Toughness, in this case, is defined as the plane-strain fracture toughness, K_{Ic}. Casting methods, such as slip-casting (Walther et al., 2010), evaporation (Yao et al., 2010), and combined gel-casting and hot-pressing (Bonderer et al., 2010a, 2010b), all yielding a brick and mortar structure, have been reported to produce materials with tensile strengths up to 250 MPa, thus exceeding that of nacre. Samples with a nacre-like structure that can be produced using some of the techniques described in prior literature are usually extremely small in volume and require time-consuming processes and specialized equipment. The scaling-up both of sample volumes and production rates for real-life applications continues to pose considerable difficulties and usually leads to a considerable loss in mechanical properties.

The use of self-assembly mechanisms is increasingly being explored to overcome these problems. Taking advantage of particle self-assembly that occurs during freeze casting, for example, the manufacture of large sample sizes with a nacre-like structure could recently be demonstrated (Hunger et al., 2013a). The resulting cellular materials, composed of alumina platelets in a chitosan–gelatin matrix, had a honeycomb-like structure, whose cell walls exhibited nacre-like structures and resulted in considerably improved mechanical properties both parallel and perpendicular to the long pore axis (Hunger et al., 2013a, 2013b). In an effort to better understand the mechanisms that determine the mechanical properties of the wall material of the freeze-cast scaffolds and to mimic the structure of biological materials in a well-controlled model system, we fabricated alumina–platelet reinforced chitosan films. Alumina platelets were chosen as the inorganic ceramic phase because of their close resemblance, in shape and aspect ratio, to the aragonite platelets in nacre (Gao et al., 2003). Chitosan, a linear biopolymer derived by N-deacetylation of chitin was chosen for the matrix material, because it is ideally suited for a study of property dependence on relative humidity (Dutta et al., 2004).

One critical factor that is frequently not addressed and reported is the effect of moisture content on the mechanical properties of the films produced. Since chitosan readily absorbs water, its mechanical properties will greatly vary depending on the relative humidity of the environment at the time of the test (Domard and Domard, 2002). Chitosan films have been reported to have as much as a 99% loss in Young's modulus and 88% loss in stress at break when immersed in deionized water for one night and an 80% loss in tensile strength when the conditioning relative humidity was increased from 15.6% to 93% (Domard and Domard, 2002; Rachtanapun and Wongchaiya, 2012). To investigate the effect of moisture content, this study focused on controlled relative humidities of 36%, 56%, and 75%.

A relatively simple and reproducible processing method to fabricate thin hybrid films is utilized in this study. The goals are to show that the films produced using this technique result in highly aligned microstructures, to investigate the mechanical properties of these films in tension, and to show that relative humidity of the environment can have a significant effect on the measured mechanical properties.

2. Materials and methods

2.1. Materials

Low molecular weight chitosan (75–85% deacetylated) was purchased from Sigma Aldrich, St. Louis, MO, USA. Glacial acetic acid, deionized water, and tissue culture dishes were purchased from VWR International, Radnor, PA, USA. Alumina platelets with a diameter and a thickness of 5–10 μm and 300–500 nm, respectively, were obtained from Alusion™, Antaria Limited, Bentley, Western Australia. Deionized water was used for all experiments and all chemicals were used without further modifications.

2.2. Film preparation

To prepare the nacre-inspired alumina–chitosan hybrid films, first 3.6% (w/v) of low molecular weight chitosan was dissolved in 1% (v/v) glacial acetic acid in de-ionized water. The chitosan solution was homogenized on a bottle roller for 48 h at room temperature (25 °C). To prepare the ceramic slurry, alumina platelets were added to the chitosan solution to achieve the required volume fraction of alumina in the dry film once the solution was cast. For example, to prepare a 5%