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Effects of asperities and organic-inorganic interactions on the strength of nacre-mimetic composites

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ABSTRACT

Nacre is a natural organic-inorganic hybrid composite, whose hierarchical structure has a complex influence on its high strength. Many structural features have been discovered, which influence the mechanical properties of nacre, and the authors have a particular interest in the role of the asperities and organic-inorganic interactions. In this study, a composite was prepared which mimics the asperity structure using clay minerals. Organic-inorganic bonding was induced with silane treatment. Both factors increased the yield strength of the composites; however, different deformation behavior was exhibited. It was found that asperities improved the strength of the composite, and that composition influences the stiffness of the composite. The organic-inorganic interaction between the resin and the other components of the composite reduced the deformation of the composite and consequently improved strength.

1. Introduction

Nacre is an attractive structure, because it possesses excellent mechanical properties, even though it consists of >95% polygonal aragonite [1–3]. Many articles have explained the high strength of nacre, associating this property with structural features. This has inspired some groups to develop lightweight, high strength composites based on nacre's structure. The structure of nacre resembles bricks and mortar - tablet-shaped aragonite stacked with bio-polymer [4–5]. This fundamental structural model, has led to various fabrication methods for nacre-mimetic composites being suggested, including layer-by-layer assembly, simple methods, hot pressing, and electrophoretic deposition [6–14]. Those methods aim to mimic the well-oriented laminate structure, using plate-like inorganic materials, such as alumina, silicate, clay, and graphene.

The structure of nacre, whilst initially appearing simple, is far more complex; it is a hierarchical structure. Several structural models haves been proposed to explain its high strength behavior, such as interlocked tablets, an organic matrix, and a mineral asperities on the tablet surface [15–21]. Some researchers have focused on mimicking the specific features mentioned above. For example, Kotov et al. studied the mechanical properties of composites made using different kinds of polymers [8, 22–23]. Tomsia et al. emulated the mineral bridge in nacre, to fabricate alumina-poly(methyl methacrylate) (PMMA) composites, using the ice templating method. These composites demonstrated high strength and toughness [24–26]. Xia et al. grew nanoasperities on silica platelets by bio-mineralization and fabricated a layered composite film with poly(-vinyl alcohol) (PVA) [27]. Niebel et al. built asperities on alumina platelets, using silica spheres, and subsequently showed improvement of the strength of epoxy resins, by using 15 vol% of the alumina platelets as reinforcement [28].

In this study, we focused on the role of the asperities, and the effect of organic-inorganic interactions on the fracture behavior of the composites. To fabricate a composite, flake-type alumina, with a thickness of 0.5 μm and particle diameters in the range 5–20 μm, was used. PMMA resin was employed as an organic material. The asperities were generated using clay minerals, with the method proposed in a previous work [29]. Clay is a good source for the formation of nano-sized mineral asperities, and it exhibits excellent adhesion with alumina. In addition, it demonstrated the possibility that artificial asperities could improve the strength of the composites. The organic-inorganic interaction was induced by silane treatment. The effect of the nacre-mimetic structure on the mechanical properties of the composites was evaluated using bending tests.

2. Experimental procedure

2.1. Preparation of mineral asperities

Mineral asperities were prepared using the procedures described in a previous study [29]. Commercial plate-like alumina (RonaFlair® White Sapphire, >99.0%, Merck Performance Materials) was used to replace the aragonite tablets of the nacre structure. A kaolinite suspension

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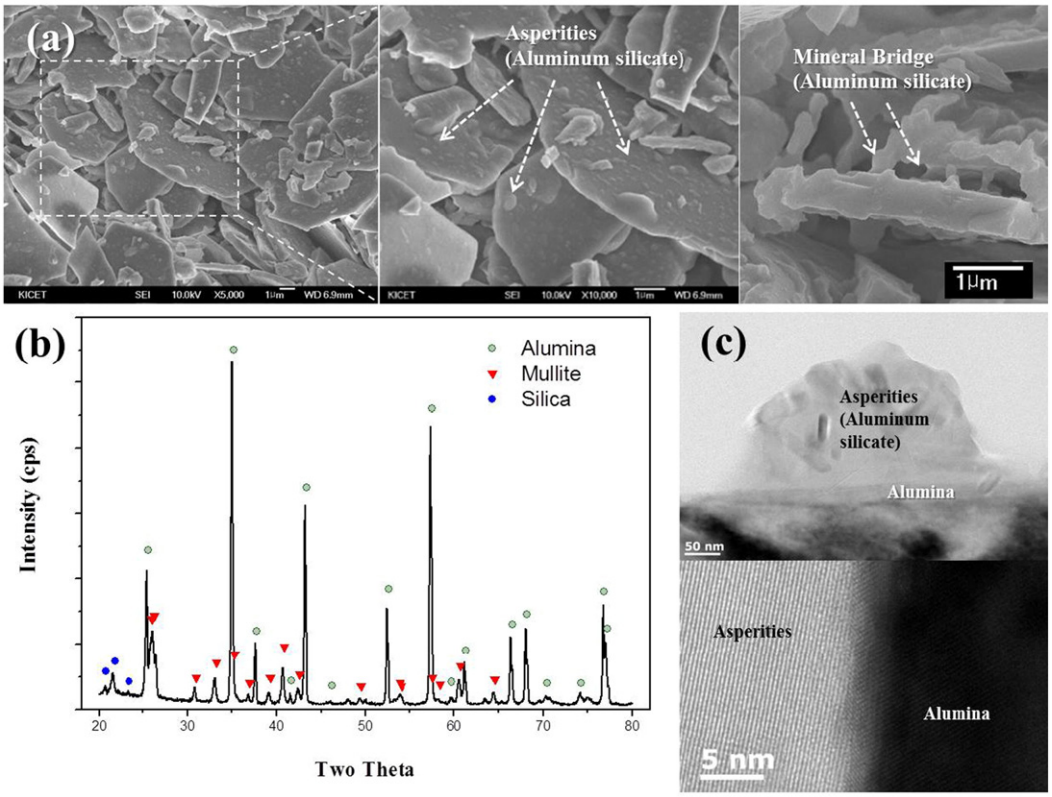

Fig. 1. (a) SEM images showing the microstructure of the alumina particles on which asperities were formed. (b) XRD pattern of the particles after formation of the asperities, and (c) TEM image of the interface between the asperities and the alumina surface.

in ethanol was prepared, and the alumina was added into the suspension. The weight ratio of kaolinite and alumina was 1:0.1. The mixture was stirred for 24 h, dried, and then heated at 1200 °C for 1 h.

For the silane treatment, 3-(trimethoxysilyl)propyl methacrylate (98%, Aldrich) was used. The silane solution was prepared as a 10% solution in ethanol. The alumina, on which the asperities were formed, was suspended in the solution. The pH of the suspension was adjusted to 4.2 using acetic acid, and the suspension was stirred for 5 h. When the silane treatment was complete, the alumina powder was filtered, washed, and dried in 80 °C oven.

2.2. Fabrication of alumina-PMMA composites

Methyl methacrylate (MMA) monomer (99%, Aldrich) was selected to fabricate the alumina-PMMA composites, and benzoyl peroxide BPO (99%, Aldrich) was used as a polymerization catalyst. Three types of alumina particles were used to fabricate the composites: as purchased, with asperities, and particles with silane treatment. The composites were labeled Al-PMMA, ASP-PMMA, and SUR-PMMA, respectively.

Nacre-mimetic alumina-PMMA composites were assembled using the simple method described in a previous work [29,30]. The composites were prepared in a three-stage process: packing of alumina, infiltration of MMA, and hot-pressing. The green compact of alumina was molded under a pressure of 1 ton using a hand press. The compact was soaked in MMA/BPO mixture and placed in an oven at 45 °C for 1 day. This allowed the solution to penetrate into the compact and degassing to take place. During this step, MMA was slowly polymerized, and an alumina-PMMA composite block was prepared. Finally, in the hot-pressing step, the PMMA was cured, using a two-step process: 10 MPa at 100 °C and 20 MPa at 200 °C.

2.3. Characterization

The asperities were characterized using field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F); X-ray diffraction (XRD, P/MAX 2200 V/PC, Rigaku Corp., Cu target, Kα = 1.54 Å); and transmission electron microscopy (TEM, TEM-4010, JEOL). The crystal phases of the asperities and their shapes were determined using the as-obtained powder. To examine the microstructure of the interface between the asperities and alumina, TEM analysis was performed using focused ion beam milling, after the particles were mounted with epoxy resin.

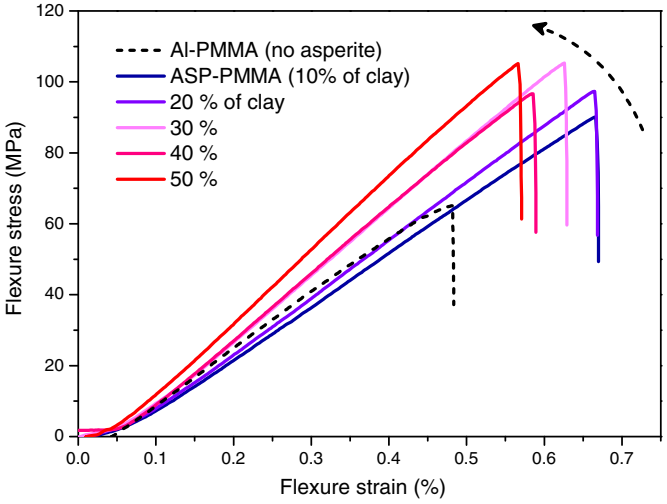

Fig. 2. Stress–strain curves of the composites containing various amounts of clay.