FAST AND SCALABLE SELF-ASSEMBLY APPROACHES TO BIOINSPIRED NANOCOMPOSITE FILMS AND COATINGS

A. Walther*

1 DWI at RWTH Aachen University - Interactive Materials Research, Forckenbeckstr 50, 52056 Aachen, Germany

* walther@dwi.rwth-aachen.de

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1 General Introduction

Nature’s load-bearing materials are paradigms for lightweight engineering as they uniquely combine stiffness, strength and toughness with low density. Spider silk, wood, mother of pearl (nacre), crustacean cuticles and bone are prime examples that have spurred the quest for bioinspired materials engineering. Such biocomposites are characterized by ordered structures combining large fractions of hard, reinforcing segments with a minor amount of soft, energy-adsorbing and lubricating biopolymer. The interface between hard and soft is durable and well controlled, and, moreover, the materials are capable of self-repair and exhibit high resilience and fatigue resistance. Nacre exhibits a brick-and-mortar architecture in which 95 vol% of CaCO3 microtablets are arranged in a minority phase of biopolymer (Figure 1).

Fig. 1. Natural Nacre with its intrinsic brick and mortar architecture.

Nature very slowly grows such hierarchically structured materials into complex shapes in water at ambient temperature – a technique inapplicable for man-made structural materials manufacturing. Importantly, classical polymer processing techniques (extrusion, injection molding etc.) fail for bioinspired materials as they prevent order formation or are simply not feasible due to large fractions of reinforcements. At present sequential deposition methods and tedious multistep pathways, using excessive time and energy, dominate preparations of biomimetic model materials; thinnest films (1-50 μm) are typically prepared. Future generations of synthetic bioinspired materials (at best ordered on several length scales, imparted with molecular energy dissipation mechanisms and with high fractions of reinforcements) will inevitably require the development of new processing strategies to allow the fabrication of complex shapes and bulk materials. This will require to master self-assembly of nanoscale hard and soft components into hierarchically structured complex macroscale materials. This contribution discusses how to make nacre-inspired films with fast self-assembly methods in water and at room temperature. High mechanical properties (E = 45 GPa, UTS > 300 MPa) are combined with attractive functional properties such as high transparency, gas barrier properties and remarkable fire shielding.

2 Results and Discussion

2.1 Self-Assembled Artificial Nacre

The general strategy is based on preparing hard/soft core/shell nanoplatelets via coating of nanoclay (montmorillonite, MTM) with suitable polymers in solution. Subsequently these core-shell platelets undergo concentration-induced self-assembly during water removal [1,2]. The process is both rapid and scalable (Figure 2).

Fig. 2. General approach to self-assembled nacre-inspired films based on core/shell nanoplatelets with intrinsic hard/soft character.
A recent extension of this work to using biobased carboxymethyl cellulose (CMC) instead of previously used petro-chemically based polyvinylalcohol (PVA) has also opened the way towards increased sustainability of these layered composite materials [3]. The final materials are composed of a majority fraction of nanoclay (up to 70 wt%), which are arranged in a highly layered arrangement as can be seen in scanning and transmission electron microscopy images and further quantified by wide angle x-ray scattering (Figure 3). The materials can be prepared as self-standing, thick films either with rapid filtration/paper-making or they can be coated/doctor-bladed from concentrated slurries.

Fig. 3. (Left) Large-area film prepared from CMC and MTM (6/4 w/w) with ca. 50 µm thickness. (Right) Scanning electron micrograph of a PVA/MTM nacre-inspired film demonstrating the highly layered architecture.

2.2 Mechanical Properties

Owing to the highly organized, layered internal structure of the materials, we find properties exceeding classical polymer/clay nanocomposite materials by one order of magnitude. Typical values for stiffness and strength range between 10-45 GPa and 100-350 MPa, respectively, depending on the choice of polymer and the applied covalent or supramolecular crosslinking.

In comparison to the natural role model, nacre, these values are in range with respect to stiffness and exceed it in terms of strength up to 4 times.

2.3 Functional properties

Due to the presence of a majority fraction of nanoclay and its organization into a layered structure, we find excellent gas barrier properties. The extension of the self-assembly concept to synthetic clays also allows to combine these gas barrier properties with essentially full transparency as needed for future flexible barrier materials (Figure 4). These properties are combined with a remarkable fire and heat-shielding ability. On exposure to fire, the nacre-inspired films hardly burn and self-extinguish immediately once the flame is removed. Moreover, the materials self-expand into a porous ceramic structure and the condensation of the silanol groups contributes an auto-cooling due to release of water. A permanent barrier against fire can be formed.

Fig. 4. (Left) Fully transparent nacre mimetic based on synthetic nanoclay and PVA (thickness ca. 30 µm). Fire-Shielding properties of a ca. 50 µm thick film of CMC/MTM (6/4 w/w)

In summary the strategy provides a facile approach to bioinspired nanocomposites marrying both excellent mechanical and functional properties. The bioinspired design manifests in the structural control achieved by self-assembly, realizing a majority fraction of activated reinforcements, and the well-ordered hard-soft layers and excellent global alignment of them (brick and mortar architecture). Further biomimetic design in future should aim at developing molecular energy-dissipation mechanisms for the soft phase and enlarging the platelets thickness to be closer to the real natural dimensions of the platelets in nacre.

3 References