



## Production of CaCO<sub>3</sub>/hyperbranched polyglycidol hybrid films using spray-coating technique

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### ABSTRACT

Biominingalizing organisms employ macromolecules and cellular processing strategies in order to produce highly complex composite materials such as nacre. Bionic approaches translating this knowledge into viable technical production schemes for a large-scale production of biomimetic hybrid materials have met with limited success so far. Investigations presented here thus focus on the production of CaCO<sub>3</sub>/polymer hybrid coatings that can be applied to huge surface areas via reactive spray-coating. Technical requirements for simplicity and cost efficiency include a straightforward one-pot synthesis of low molecular weight hyperbranched polyglycidols (polyethers of 2,3-epoxy-1-propanol) as a simple mimic of biological macromolecules. Polymers functionalized with phosphate monoester, sulfate or carboxylate groups provide a means of controlling CaCO<sub>3</sub> particle density and morphology in the final coatings. We employ reactive spray-coating technique to generate CaCO<sub>3</sub>/hybrid coatings among which vaterite composites can be prepared in the presence of sulfate-containing hyperbranched polyglycidol. These coatings show high stability and remained unchanged for periods longer than 9 months. By employing carboxylate-based hyperbranched polyglycidol, it is possible to deposit vaterite–calcite composites, whereas phosphate-monoester-based hyperbranched polyglycidol leads to calcite composites. Nanoindentation was used to study mechanical properties, showing that coatings thus obtained are slightly harder than pure calcite.

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### 1. Introduction

Biominingalizing organisms produce scales, shells or skeletons that are hybrid materials, composed of inorganic components such as calcium carbonate or phosphate and a (minor) organic part consisting of acidic macromolecules that display a high content of carboxylate, phosphate or sulfate groups [1,2]. These biominerals often possess unique crystal textures that give rise to unusual mechanical

and optical properties such as strongly increased toughness, impact resistance and characteristic luster [3,4]. By using nanoindentation, it was demonstrated that calcite semi-nacre ( $H \sim 3\text{--}6$  GPa;  $E = 60\text{--}120$  GPa) and pure calcite ( $H \sim 2\text{--}3$  GPa) are harder and stiffer than calcite fibers ( $H \sim 0\text{--}3$  GPa;  $E = 20\text{--}80$  GPa). Rhynchonelliform brachiopods, for instance, have a three-layered shell, where the secondary layer is composed of calcite fibers [5]. Many scientists were intrigued by the hierarchical order and structure of biominerals [6] leading to excellent mechanical properties [7], which provide a source of inspiration for the fabrication of novel organic–inorganic composites. From the perspective of producing materials reminiscent of biominerals (e.g., nacre) at large scale, two technological aspects deserve further attention: First, to implement biomimetic production strategies requires vast conceptual simplifications of the putative mechanism(s) by which biominerals are formed and thus the value of a production strategy has to be assessed by screening gross morphological features of the as-synthesized composite materials. This more or less descriptive (yet fast) step might then be augmented by more sophisticated analyses of

*Abbreviations:* SAM, self-assembled monolayer; ACC, amorphous calcium carbonate; LBL, layer-by-layer; LFS, liquid-feed solution;  $M_n$ , number average molecular weight; *hb*-PG, hyperbranched polyglycidol; *hb*, hyperbranched; COO-terminated *hb*-PG, hyperbranched polyglycidol carboxylates (carboxylate functionalized *hb*-PG); OPO<sub>3</sub>HPhOH-terminated *hb*-PG, hyperbranched polyglycidol phosphates (phosphate monoester functionalized *hb*-PG); SO<sub>4</sub>-terminated *hb*-PG, hyperbranched polyglycidol sulfates (sulfate functionalized *hb*-PG); DHBCs, double-hydrophilic block copolymers; CaCO<sub>3</sub>, calcium carbonate; at.%, atomic concentration;  $E_R$ , reduced Young's modulus; PAANa, poly(acrylic acid) sodium salt.

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mechanical properties, which constitutes a limiting factor in terms of time and equipment required to obtain meaningful results. Second, genetic control over biomineral production has to be replaced by simple self-assembly approaches. For the latter, it is anticipated that finding appropriate synthetic models of biomacromolecules occluded within biominerals might pave the way toward hierarchical materials that exhibit superior mechanical performance. It should be noted in this context, however, that even a seemingly simplistic task such as selective formation of artificial aragonite platelets that bear morphological features closely related to the brick-and-mortar arrangement of tabular aragonite crystals found in nacre has remained elusive so far, despite partial success reported by several groups [8–12].

In the realm of  $\text{CaCO}_3$ /polymer composites, many studies have shown that numerous experimental parameters, including pH [13], temperature [14], foreign ions [15], chemical nature of the organic additives [9,15] and templates (matrices such as chitin, cellulose or chitosan) [9] affect the  $\text{CaCO}_3$  crystal phase and the resulting crystal morphology. DHBCs polymers demonstrated remarkable effects in crystallization for a wide range of inorganic and inorganic–organic hybrids [13,15,16]. Other classes of polymers such as dendrimers were also discovered as active additives for controlled  $\text{CaCO}_3$  precipitation [17]. Hyperbranched polymers belong to these synthetic tree-like macromolecules class and furthermore, they are also accepted to be polysaccharide and polyethylene glycol analogues due to their good water-solubility and biocompatibility [18–20]. Due to their unique properties, easy one-pot synthesis, low cost production and well-defined architecture with the possibility to attach different reactive terminal groups in a straight-forward manner, hyperbranched polymers have a wide range of industrial and biomedical applications [21]. Hyperbranched materials also have outstanding mechanical properties such as tensile strength and compressive modulus which reflect the compact highly branched structures [22]. The application of hyperbranched polymers is largely unexplored in  $\text{CaCO}_3$  mineralization processes. Only few reports [20,23–25] as yet appeared in the literature where functionalized hyperbranched polymers possessing carboxylate or sulfate groups were employed as additives for the growth of isolated  $\text{CaCO}_3$  crystals. To the best of our knowledge, hyperbranched polyglycidols bearing phosphate monoester end groups as well as their influence on  $\text{CaCO}_3$  crystallization are unknown until now. As outlined above, the appropriate selection of both the synthetic polymers and a scalable production method is of major importance for producing hybrid thin films. Numerous established laboratory (i.e., small scale) techniques exist for the fabrication of  $\text{CaCO}_3$  thin films (carbonate diffusion in different variants [26], self-assembled monolayers (SAMs) [23], layer-by-layer (LBL) [10], Langmuir monolayer [27], electrophoretic deposition [11], are known, as well as continuous flow deposition techniques [12]. Each of these techniques suffers from specific disadvantages: Most of them are time consuming, pH dependent, and none of them can be applied using high concentrations, thus resulting in low deposition rates [28]. Therefore, there is a demand for improved methods in order to cover large surface areas with dense composite thin films in a production efficient and economically viable fashion.

We here present a novel strategy to obtain nanostructured composites of  $\text{CaCO}_3$  by using spray-coating technique in a combination with functionalized hyperbranched low molecular weight polyglycidols. For the preparation of calcium carbonate composites, the spray-coating technique offers many advantages as compared to conventional deposition techniques, such as (1) simple, fast and easy to handle spraying process; (2) no need to apply pre-coatings; (3) easy scale-up due to the usage of simple and industrially established equipment; (4) the possibility to cover large areas and (5) to apply highly concentrated solutions,

resulting in deposition rates superior to that of all other methods. In this work, we focus on the preparation of low molecular weight hyperbranched polyglycidols bearing different functional groups and effects of these on the formation of calcium carbonate composites prepared via spray coating. Attractive targets for these  $\text{CaCO}_3$ /polymer composites might include traditional wall paintings, coatings of transportation systems such as ships or off-shore buildings, coatings of medical devices (i.e., tubings, syringes or pumps), ceramics, as well as biocompatible biomaterials such as bone or dental implants [29].

## 2. Materials and methods

$\text{CaCl}_2 \times 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  were purchased from Merck. These chemicals were used as received without further purification. High-purity 18.2 M $\Omega$  cm double-demineralized water was used as solvent for all solutions. Microscopy glass slides (ca. 76 × 26 mm; Menzel-Gläser) were used as test substrates in spray coating procedures leading to calcium carbonate composites.

The deposited calcium carbonate composites were characterized with the following techniques: Thermogravimetric analysis (TGA) was performed with a TGA/SDTA851 Mettler Toledo analyzer in a temperature range of 25–1100 °C in flowing nitrogen at a heating rate of 5 °C min<sup>-1</sup>. Scanning electron microscope (SEM) images were recorded using a Zeiss DSM 962 scanning electron microscope. Energy dispersive X-ray analysis (EDX) was performed on an EDAX (Phönix) X-ray detection system with 30 mm<sup>2</sup> SUTW window. Fourier transform infrared (FTIR) spectra were recorded from KBr pellets in the range 4000–400 cm<sup>-1</sup> on a Bruker IFS FT-IR spectrometer. X-ray powder diffraction (XRPD) patterns were measured using Philips PANalytical X'Pert PRO diffractometer with Cu K $\alpha$ -radiation (Philips PW 3373, 45 kV, 40 mA) between 5° and 80° (2 $\theta$ ) with a step-size of 0.0334° (2 $\theta$ ) and a sample time of 10 s/step. The refinement process was performed by using the Jana2000 Program. Raman spectroscopy was performed with a Jobin Yvon Horiba Raman spectrometer equipped with a He–Ne-laser at a wavelength of 633 nm. Thickness profile measurements were performed with a Dektak 150 profilometer from Veeco (stylus diamond tip with radii 2.5  $\mu\text{m}$ ). X-ray photoelectron spectroscopy (XPS) measurements were performed by a Physical Electronics 5800 Multitechnique ESCA System using monochromatic Al K $\alpha$  radiation (1486.6 eV) X-ray source operated at 250 W (13 kV and 19 mA). The photoelectrons were analyzed using a spherical capacitor analyzer (Phi Model 10-360). The pressure in the sample analysis chamber was 4 × 10<sup>-9</sup> Torr. Survey scans (187.85 eV pass energy, 0.4 eV step size), and high-resolution XPS spectra (23.35 eV pass energy, 0.125 eV step size) were acquired to determine surface compositions. The spot size was 800 × 800  $\mu\text{m}$  at normal incidence to the sample. Physical Electronics MULTIPAK V6.1A software was applied to deconvolute XPS spectra. XPS analysis was taken at a take-off angle of 45°, and the binding energy was calibrated by setting the C(1s) peak of hydrocarbons to 284.8 eV. For all cases studied, XPS analysis indicated the presence of S(2p), Ca(2p), O(1s) and C(1s) peaks. An Olympus IX70 inverted stage microscope was used to capture optical micrographs and polarization optical micrographs of polycrystalline thin films mounted between crossed polarizers. Mechanical properties were measured by using a Nanotest™ 600 by Micro Materials Ltd., Wrexham (UK), which is a pendulum-based nanoindenter (i.e., samples are mounted vertically). A Berkovich pyramidal diamond tip was used for all indentation measurements, penetrating into the specimen surface at a controlled loading rate of 7.5 mN. The load–displacement curves for each sample were performed at a depth until 500 nm. The nanoindentation instrument uses NanoTest Platform software, which employs Oliver–Pharr data analysis

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