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Solvothermal synthesis of hydrophobic chitin–polyhedral oligomeric silsesquioxane (POSS) nanocomposites

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ABSTRACT

Chitinous scaffolds isolated from the skeleton of marine sponge *Aplysina cauliformis* were used as a template for the deposition of polyhedral oligomeric silsesquioxanes (POSS). These chitin–POSS based composites with hydrophobic properties were prepared for the first time using solvothermal synthesis (pH 3, temp 80 °C), and were thoroughly characterized. The resulting material was studied using scanning electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and thermogravimetry. A mechanism for the chitin-POSS interaction after exposure to these solvothermal conditions is proposed and discussed.

1. Introduction

Chitin is a linear polysaccharide composed of N-acetyl-D-glucosamine and D-glucosamine units, linked together by β-1,4-glycosidic bonds. From a biological point of view this aminopolysaccharide plays a crucial role in the formation of various skeletal structures within diatoms [1,2], protists [3] and other invertebrates including marine sponges [4–6] as well as freshwater sponges [7,8], corals [9], and many arthropods [10]. From a practical point of view, this polysaccharide is a biopolymer with very attractive properties; such as biodegradability, non-toxicity, affinity to peptides, biocompatibility etc. [11] Consequently, these properties contribute to their use in chitin-based materials for a wide range of applications including drug delivery systems [12], tissue engineering [11], enzyme immobilizations [13], waste water treatment [14,15]. The presence of hydroxyl groups in the chitin molecule enables efficient surface modification [16–18]. There are many well described methods for chitin modification, including: acetylation [17,19], tosylation [20], phthaloylation [16], phosphorylation [21], and graft polymerization [16,22]. Moreover, a number of reports have been published on the modification of chitin properties by incorporation of inorganic compounds into a polymer matrix [23,24].

Chitin is high in crystallinity in its natural form and does not dissolve in hot water; which often leads to decomposition reactions such as hydrolysis, deacetylation, and dehydration of numerous polysaccharides when hydrothermally processed [25]. Recently, we firmly demonstrated that the thermal stability of chitin is key for using chitinous matrices, for example those of poriferan origin, as a nanoporous and nanostructured biological material in a broad variety of both non-metal and metal oxide hydrothermal synthesis in vitro; according to our extreme biomimetics approach [26–28]. From the definition, solvothermal synthesis is a process that utilizes homogenous or heterogeneous phase reactions in aqueous media at elevated temperatures ($T > 25$ °C) and pressures

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(~100 kPa) to crystallize inorganic materials directly from solution [29]. The term solvothermal is general and may refer to reactions carried out in organic solvents as well in aqueous solution. However, processes carried with use of aqueous solutions are preferentially called hydrothermal reactions. Solvothermal technology has recently evolved as a powerful tool in materials processing which can generate everything from bulk single crystals to fine and ultrafine crystals, down to nanocrystals or nanoparticles. Moreover, solvothermal technology allows for the synthesis of crystalline phases under "mild" conditions; which is preferable from both economic and environmental standpoints [29].

Hydrophobization of biopolymers is among one of the modern, applied needs that can be addressed via functionalization [30]. To make a hydrophobic surface from selected poriferan chitin scaffolds, we decided to utilize polyhedral oligomeric silsesquioxanes (POSS). It is known [31,32] that POSS compounds can react with chitin. Ifuku et al. reported a unique preparation of silsesquioxane-urethaneacrylate films reinforced with alpha-chitin nanofibers of crustacean origin at ambient temperature. Their study strongly confirms that not only cage-like, but also ladder-like [31], and double-decker [32] silsesquixanes improve the mechanical properties and thermal stability of chitin-based biopolymers. Unfortunately, these authors did not investigate the hydrophobic properties of their products.

Polyhedral oligomeric silsesquioxanes are a class of discrete, 3-dimensional polycyclic compounds with the basic chemical formula of $(RSiO_{1.5})_n$, where "n" is an integer and R can be a range of organic substituents [33]. The main task of the organic functional groups is to improve the affinity of the inorganic core to the polymer matrix. POSS, as hybrid organic/inorganic molecules, represent versatile 3-dimensional polycyclic compounds, which continue to be of interest in a wide range of scientific and technological areas [33]. Nowadays, there has been a large volume of research published on the modification of a range of synthetic [34,35] as well as biological [36,37] polymeric systems by these interesting molecules.

Surprisingly, with accordance to our best knowledge, the solvothermal growth of POSS nanostructures within a chitin matrix has not been reported. We strongly believe that this study will open new possibilities for synthesis of advanced inorganic–organic materials and will result in the prompt development of chitin-based composites with hydrophobic properties.

2. Experimental

2.1. Chitin isolation

The *Aplysina cauliformis* sponge fragments (Fig. 1A) were provided by INTIB GmbH (Germany). The α-chitin standard from *A. cauliformis* (Fig. 1B) was prepared according to method previously described by Ehrlich et al. [38]. In brief, isolation was performed in three steps, as follows: (i) removal of water-soluble salts and impurities by washing with distilled water; (ii) deproteinization and removal of residual pigments by treatment with a 2.5 M NaOH solution; (iii) demineralization (removal of calcium and magnesium carbonates) by treatment with 20% acetic acid. The isolation procedure was repeated several times to obtain colorless three-dimensional chitin scaffolds. These scaffolds were stored in glass bottles with ultra-pure water at 4 °C.

2.2. Solvothermal modification of chitin with POSS

Fragments of chitinous template obtained as described above were introduced into a 1 M solution (25 cm^3) of epoxycyclohexylisobutyl-POSS® (Hybrid Plastics, USA). Tetrahydrofuran (THF)

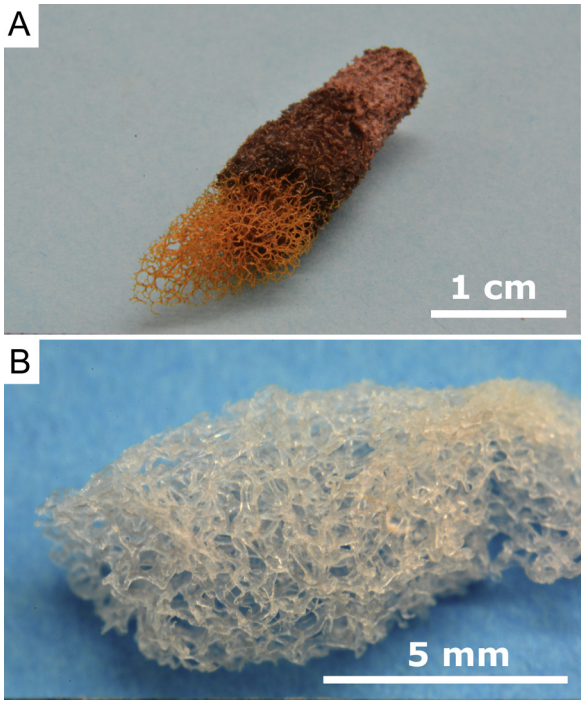

Fig. 1. Dried fragments of marine sponge *A. cauliformis* with the fingerlike bodies (A), are a renewable source for isolation of the 3D skeletal chitinous scaffolds (B).

(Sigma–Aldrich, Germany) was used as a POSS solvent and reaction medium. After that, the pH was adjusted to ~3 by adding 1 M HCl. Following this, the whole volume was transferred into a Teflon-lined vessel (100 cm^3) of a hydrothermal reactor (Amar, India), and heated to 80 °C for 24 h. After this time, the chitinous template was carefully isolated and washed with THF. To remove all unbound particles, the sample was washed with THF in an ultrasound bath (Elmasonic GmbH, Germany) for 15 min. Finally, samples were dried at 90 °C for 48 h.

2.3. Scanning electron microscopy

SEM images were recorded using an EVO40 scanning electron microscope (Zeiss, Germany). Prior to testing, the samples were coated with Au for a time of 15 s, using a Balzers PV205P coater.

2.4. Raman spectroscopy

The Raman scattering spectra were investigated within the spectral range of 3500–50 cm^{-1} on a Bruker IFS 66V/S (Germany) with the use of FRA 106/S Raman module. The spectral resolution was 4 cm^{-1}, as an excitation light a laser operating at 520 nm was used.

2.5. X-ray photoelectron spectroscopy

XPS analyses were performed using an ESCALAB 250Xi from Thermo Scientific, with a monochromatic Al Ka X-ray source (1486.6 eV). The X-ray source has a spot size of 650 mm and operates at a power of 14.8 kV and 19.2 mA. The spectra were taken with a pass energy of 20 eV and an energy step width of 0.1 eV. The base pressure was 2×10^{-10} mbar. During the measurement the pressure increased to 3×10^{-7} mbar due to the ion gas flow from the flood gun, which was used for charge compensation.