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AFM PeakForce QNM mode: Evidencing nanometre-scale mechanical properties of chitin-silica hybrid nanocomposites

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ABSTRACT

PeakForce Quantitative Nanomechanical Mapping (QNM) AFM mode was used to explore the mechanical properties of textured chitin-silica hybrid films at the nanoscale. The influence of the force applied by the tip on the sample surface was studied for standard homogeneous samples, for chitin nanorods and for chitin-silica hybrid nanocomposites. Thick films of superimposed chitin nanorods showed a monotonous increase of DMT modulus (based on the Derjaguin-Muller-Toporov model) owing to an increase in modulus at the interface between nanorods due to geometrical constraints of the AFM acquisition. A similar variation of DMT modulus was obtained for chitin-silica hybrid thick films related to mechanical strengthening induced by the presence of silica. This work revealed the role of the organic-inorganic interface, at the nanoscale, in the mechanical behaviour of textured materials using PeakForce QNM mode, with optimized analysis conditions.

1. Introduction

Chitin nanorods (Belamie, Davidson, & Giraud-Guille, 2004) are the main matrix component for a number of biocomposites, in particular found in arthropods carapaces like crustacean and insect shells (Bouligand, 1972). The mechanical properties of these composites are enhanced by an anisotropic organisation of the chitin nanorods, as well as by the presence of a mineral component like nanoscopic calcite or amorphous calcium carbonate (Fabritius, Sachs, Triguero, & Raabe, 2009; Peterlik, Roschger, Klaushofer, & Fratzl, 2006; Weiner, Traub, & Wagner, 1999), or even silica (Brunner et al., 2009). The synthesis of nanocomposites of similar properties through biomimetic approaches is still a challenging task for materials scientist (Mann, 1995; Sanchez, Arribart, & Guille, 2005; Spinde et al., 2011). Chitin-silica hybrids were recently obtained by a new method via sol-gel processes (Alonso & Belamie, 2010; Belamie, Boltoeva, Yang, Cacciaguerra, & Alonso, 2011; Boltoeva et al., 2013). To this purpose, ethanolic homogeneous isotropic suspensions of chitin nanorods and siloxane oligomers were prepared. The sol-gel transition, and further material solidification, may be promoted by solvent evaporation, allowing chitin nanorods organisation and siloxane condensation. The procedure is developed here for the formation of films using spin coating. Because of the organic nature and nanometric dimensions of chitin nanorods, their removal by calcination at high temperature left nanometre-size porous imprints (Belamie, Boltoeva, Yang, Cacciaguerra, & Alonso, 2011) suited for applications in supported catalysis (Sachse, Hulea, Kostov, Belamie, & Alonso, 2015; Sachse et al., 2012) with textures reminiscent of the initial nanocomposites structure. It was shown that, notably because of the liquid-crystal properties of the polysaccharide nanorods suspensions and their susceptibility to external fields (shear, electric, magnetic) (Boltoeva et al., 2013), ordered and aligned chitin-silica nanocomposites could be obtained. In all cases, chitin nanorods were homogenously dispersed in the silica matrix, suggesting interactions between the two colloids at the nanometre scale. The interface between the organic (chitin) and inorganic (silica) components was probed with spectroscopic (NMR, XPS) and scattering (SAXS, DLS) techniques giving useful and consistent evidences of intimate interactions between the two phases.

PeakForce Quantitative Nanomechanical Mapping (PeakForce QNM) is a new AFM mode, which allows mapping of the mechanical properties simultaneously with topography, at the same spatial resolution (Fisher, Stadler, & Erina, 2013; Pakzad, Simonsen, & Yassar, 2012; Sweers, Werf, Bennink, & Subramaniam, 2011; Trtik,

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Kaufmann, & Volz, 2012; Wang, Russell, Nishi, & Nakajima, 2013; Young et al., 2011). Several studies have been carried out by PeakForce QNM with composite materials containing biopolymer nanorods, namely cellulose and collagen (Frone, Berlioz, Chailan, & Panaitescu, 2013; Khelifa, Habibi, Leclere, & Dubois, 2013; Liu et al., 2013). In particular, Liu et al. were able to assess the intrafibrilar mineralization of collagen fibrils. However, up to now, the effect of the applied force on the value of the mechanical modulus at the nanoscale and the determination of the optimal scanning conditions were not studied in details. In this respect, chitin-silica hybrid materials comprised of stiff chitin nanorods and hard silica phase, with a strong modulus contrast at the nanoscale, offered an interesting model system. The effect of the applied force was considered in previous studies on polyurethane and polystyrene samples (Dokukin & Sokolov, 2012a, 2012b). It was shown that, for small deformations $d < 2$ nm (low applied force), the measured modulus increased. This observation was termed the "skin effect" (Dokukin & Sokolov, 2012b) and explained by the stress, which is too high and does not correspond to a linear stress-strain regime. Another reason for the skin effect might be the adhesion contribution, but the latter is taken into account by the appropriate choice of the model for the modulus estimation from AFM force curves. Nevertheless, in the case of a sharp tip, the modulus can be overestimated even for a sufficient deformation, if the nonlinear regime is reached. However, for textured materials, a sharp tip is required to achieve a high resolution and to distinguish different nanometre-sized domains.

The objective of the reported work is to study the nanocomposite films structure and mechanical properties at the nanoscale using the PeakForce QNM mode in atomic force microscopy (AFM). In particular, the effect of the applied force on the measured mechanical properties (modulus, deformation, adhesion and dissipation) is described. After optimization with homogeneous reference materials, polystyrene (PS) film and silica surface, pure chitin samples (individual nanorods and films) and chitin-silica hybrid films were analysed.

2. Materials and methods

2.1. Preparation of the chitin-siloxane hybrid suspension

The hybrid suspension is obtained by mixing the chitin nanorods and siloxane oligomers, dispersed in pure ethanol (Boltoeva et al., 2013). The chitin nanorods (260 nm long; 23 nm in diameter by TEM) are formed by hydrolysis of raw chitin flakes (France Chitin) in boiling 4 M HCl during 90 min (Belamie, Davidson, & Giraud-Guille, 2004). Their stable dispersion is obtained after ultrasound treatment and exchanging in pure ethanol. These nanorods are composed of chitin monocrystals with diameter of 2–3 nm.

The siloxane oligomers suspension is prepared by mixing and refluxing (4 h) tetraethoxysilane (TEOS) (ABCR, pur. > 99.9%), 10^{-1} M aqueous HCl and absolute ethanol (Sigma-Aldrich, pur. > 99.8%) in the molar proportions 1TEOS:2H_2O:2EtOH. The resulting siloxane oligomers have a hydrodynamic diameter 2.9 ± 0.2 nm (measured by dynamic light scattering) and an average degree of siloxane condensation of 0.72 ± 0.01 (from ^{29}Si liquid-state NMR, see Fig. S1 of the Supporting information for details).

The suspensions used in the present study were chitin – siloxane mixtures prepared with a composition set to yield, after complete evaporation of the solvent and siloxane condensation, a solid material with a chitin volume fraction of 0.2 ($\phi_{CHI} = 0.2$). For details about the suspensions preparation see for instance (Belamie, Boltoeva, Yang, Cacciaguerra, & Alonso, 2011).

2.2. Formation of the films

The solid chitin-silica hybrid nanocomposites were obtained by solvent evaporation, which induced further siloxane condensation, while the α-chitin internal structure was preserved (shown by X-ray diffraction and ^{13}C solid-state NMR (Alonso & Belamie, 2010)). In the present work, all the films were prepared by spin-coating. Spin-coating was carried out at a spin rate of 4000 rpm for 30 s, by depositing one drop of suspension onto a glass slide. The suspension was used at a concentration of 2 wt.% for the formation of thick films, diluted to 0.4 wt.% to obtain thin films and to 0.1 wt.% for the deposition of individual nanoparticles.

In the case of chitin-silica hybrid materials, a thermal post-treatment was further realized at 60 °C during 24 h to consolidate the silica network.

The standard polystyrene PS thin film was obtained in the same way, except for the solvent used (toluene for PS solubilisation).

2.3. AFM measurements in tapping and PeakForce QNM modes

The AFM study is performed on a MultiMode 8 Bruker's microscope with the Nanoscope V controller. The measurements were carried out under ambient conditions at room temperature in order to characterize the morphology and the mechanical properties of the film at the nanometric scale.

The probe Tap525 was used for most of the measurements, possessing a nominal spring constant $k = 200$ N/m and a nominal tip radius $R = 8$ nm, suitable for a studied modulus range from 1 GPa up to tens of GPa. For the nanorods diameter determination, a ScanAsyst-Air probe has been applied, with $k = 0.4$ N/m and $R = 2$ nm. The deflection sensitivity was measured with a sapphire surface. k was calibrated by thermal tuning method, and R was evaluated by the relative method on Bruker's polystyrene test sample.

A scanning size was $3 \times 3\ \mu m^2$ for all measurements, except for the determination of films thickness ($4 \times 4\ \mu m^2$). A digital resolution of 256 px × 256 px and a scanning rate of 0.977 Hz were used. The maximum force in PeakForce QNM mode ranged from 50 to 250 nN. For every experiment, three measurements on three different samples were done, and a representative one is illustrated in this article. Importantly, for all the samples in this work, successive surface scans have not revealed any modification of the surface, hence no plastic deformation took place during the measurements.

2.4. Theoretical background for PeakForce QNM mode

In PeakForce QNM mode, the tip oscillates at a frequency $f \approx 2$ kHz well below the resonance frequency of cantilever f_0, at which a classical Tapping Mode (TM) operates (Hansma et al., 1994; Zhong, Inniss, Kjoller, & Elings, 1993). In addition, the maximum applied force, called the peak force, is precisely controlled, being the feedback signal. These factors allow extracting the force curves for each tap. The analysis of these force curves brings the information about the mechanical properties of a material, in particular about deformation, modulus, adhesion and dissipation (Fig. 1 of the application note AN128(Pittenger, Erina, & Su, 2010)). The Derjaguin-Muller-Toporov (DMT) model is used to calculate the modulus (Derjaguin, Muller, & Toporov, 1975). This model is appropriate in the case of deformation lower compared to the tip radius, and takes adhesion into account. The DMT model can be applied for hard polar samples, which is the case presented here. The DMT model assumes a spherical contact between the sample and the tip. Although the shape of the tip used in this experiment does not fulfil this hypothesis, the calibration step on the sapphire makes the tip smoothed approaching the required conditions of the DMT model. Another alternative model is the Johnson-Kendall-Roberts (JKR) one (Johnson, Kendall, & Roberts, 1971), although it requires