



Rheological behavior of hybrid suspensions of chitin nanorods and siloxane oligomers



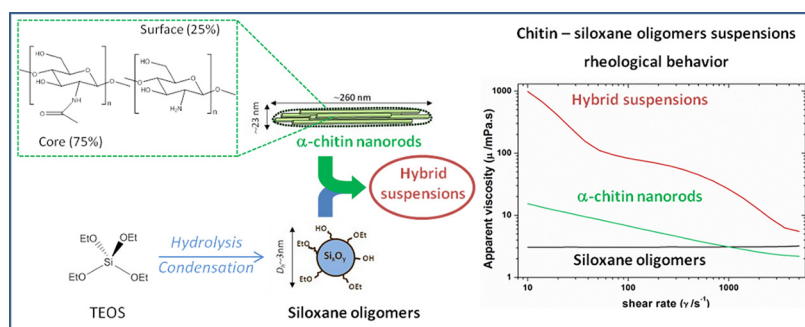
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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Chitin nanorods
Sol-gel chemistry
Hybrid materials
Nanoparticles suspensions
Rheology
Colloidal interactions

ABSTRACT

Polysaccharide nanocrystals (chitin, cellulose) extracted from biomass are increasingly considered as templates to produce hierarchical anisotropic features in inorganic phases. The organization of nanostructured solids obtained after sol-gel processing results from the complex combination of van der Waals and electrostatic interactions as well as excluded volume effects. Here, we investigate the rheological behavior of colloidal suspensions of chitin nanorods and siloxane oligomers in ethanol. The effects of solvothermal treatments and hydrophobized oligomers were also studied to decipher the respective role of inter-particle colloidal interactions. We demonstrate that interactions between chitin nanorods are strongly affected by the presence of siloxane oligomers. In agreement with previous works, the rheological data confirm the association of the small colloidal siloxane oligomers with the chitin surface. This knowledge is key information to further control the localization of functions in the resulting materials (nanocomposites, catalysts).

1. Introduction

Colloidal rodlike chitin nanoparticles can be extracted from the cuticle of arthropods, crustacean and insect shells for instance, by acid

hydrolysis and stably suspended in aqueous media [1–4] in a similar manner as cellulose whiskers from plants [1,5,6]. In their biological tissue of origin, the linear polysaccharide chains are arranged into regularly spaced thin elongated crystals (monocrystals with lateral

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<https://doi.org/10.1016/j.colsurfa.2018.09.021>

Received 26 July 2018; Received in revised form 7 September 2018; Accepted 7 September 2018

Available online 10 September 2018

0927-7757/ © 2018 Published by Elsevier B.V.

dimensions of a few nanometers). Throughout the cuticle, the long-range organization of the polysaccharide rodlike crystals often exhibits long-range uniaxial or chiral ordering [7–10]. Acidic extraction of chitin and cellulose nanorods produces bundles of a few monocrystals which remain bound together by amorphous polysaccharide chains [2,4,11,12]. As for other biological macromolecules or supramolecular entities [13–17], the internal structure of these nanoparticles, their morphology and colloidal properties have been exploited to template nano-structured materials [18–21]. In particular, inorganic species can be associated to organic rodlike colloids to elaborate hybrid nanocomposites using sol-gel processes in conditions defined by the “Chimie douce” approach. Because the organic precursors are extracted from readily available biomass, produced notably in considerable amounts as a waste by industrial fisheries [22,23], they are interesting renewable starting agents for materials synthesis. The elaboration of nanocomposites from such bio-based precursors also takes inspiration from biomineralization processes [24–34] occurring at moderate temperature and pressure. Most interestingly, colloidal suspensions of polysaccharide nanocrystals exhibit lyotropic liquid crystal properties, forming cholesteric mesophases in acidic water with a long-range chiral organization [1–4]. The resulting self-ordering and strong susceptibility to the application of external fields can be exploited to impart long-range order to hybrid materials [18,35]. After removal of the organic template, the porous replicas exhibit textural properties reminiscent of the structure and 3D organization of the initial nanorods [36–39]. The porous materials thus obtained have properties amenable to a variety of applications in the fields of biotechnologies, heterogeneous catalysis, photonics... [39–46]

Within this field, we proposed a new synthesis route for hybrid nanocomposites based on the colloidal association of polysaccharide nanorods with siloxane oligomers obtained by hydrolysis and condensation of an alkoxide monomer [18]. Hybrid suspensions containing chitin nanorods and siloxane oligomers in ethanol are found to be stable over weeks and can be processed to elaborate materials after complete solvent evaporation, where the nanorods are homogeneously dispersed in the silica matrix. To tailor the properties and texture of the dry chitin-silica nanocomposites, it is crucial to control: intermolecular

interactions at the organic-inorganic interface, inter-colloidal interactions in the liquid suspensions and finally self-assembly properties. The composition of the resulting hybrid solids can be characterized by the chitin volume fraction ϕ_{chi} , representing the volume occupied by chitin nanorods in the dry nanocomposite (obtained after sol-gel processing of the suspensions and complete solvent evaporation) divided by the total solid volume of this nanocomposite:

$$\phi_{chi} = \frac{V_{chi}^{solid}}{(V_{chi}^{solid} + V_{SiO_2}^{solid})} \quad (1)$$

Assembly and organization of the colloids from the hybrid suspensions into the hybrid solid were shown to be strongly dependent on ϕ_{chi} , which can be varied from 0 (pure siloxane oligomers suspensions) to 1 (pure chitin nanorods suspensions). In fact, ϕ_{chi} can also be used to characterize the initial suspensions and reflects the relative proportions of both precursors. Rough calculations, based on geometrical considerations and on preliminary experimental data [18], strongly suggested that, for a critical value ϕ_{chi}^* in the 0.2-0.4 range, the chitin monocrystals (elemental units of the nanorods, Fig. 1a) are completely covered by siloxane oligomers. Below this estimated critical value ϕ_{chi}^* , siloxane oligomers would be in excess, resulting either in free siloxane oligomers in the medium (i.e. not involved in the chitin nanorod coverage) or additional siloxane oligomers bound at the nanorods' surface. Further, it was also noticed that transitions in the characteristics of the materials obtained from the hybrid suspensions occur when ϕ_{chi} approach $\phi_{chi}^* \sim 0.3$. For instance, the diameter of hybrid chitin-silica rods deposited as thin films increased with the siloxane content for $\phi_{chi} < 0.3$ while it remained constant for $\phi_{chi} \geq 0.4$ [47]. Also, the pore texture of mesoporous materials, obtained by calcination of chitin-silica composites, evolved from mostly isolated elongated pores ($\phi_{chi} < 0.35$) to a more interconnected porosity ($\phi_{chi} > 0.40$) [36]. Therefore, we can hypothesize the existence of various kinds of colloids in the suspension that we want to investigate here. These colloids would depend on ϕ_{chi} (Fig. 1c): bare chitin nanorods ($\phi_{chi} = 1$), chitin nanorods partially covered by siloxane oligomers ($\phi_{chi}^* < \phi_{chi} < 1$) or fully coated chitin nanorods ($\phi_{chi} \leq \phi_{chi}^*$) that can be surrounded by an excess of siloxane oligomers at low ϕ_{chi} .

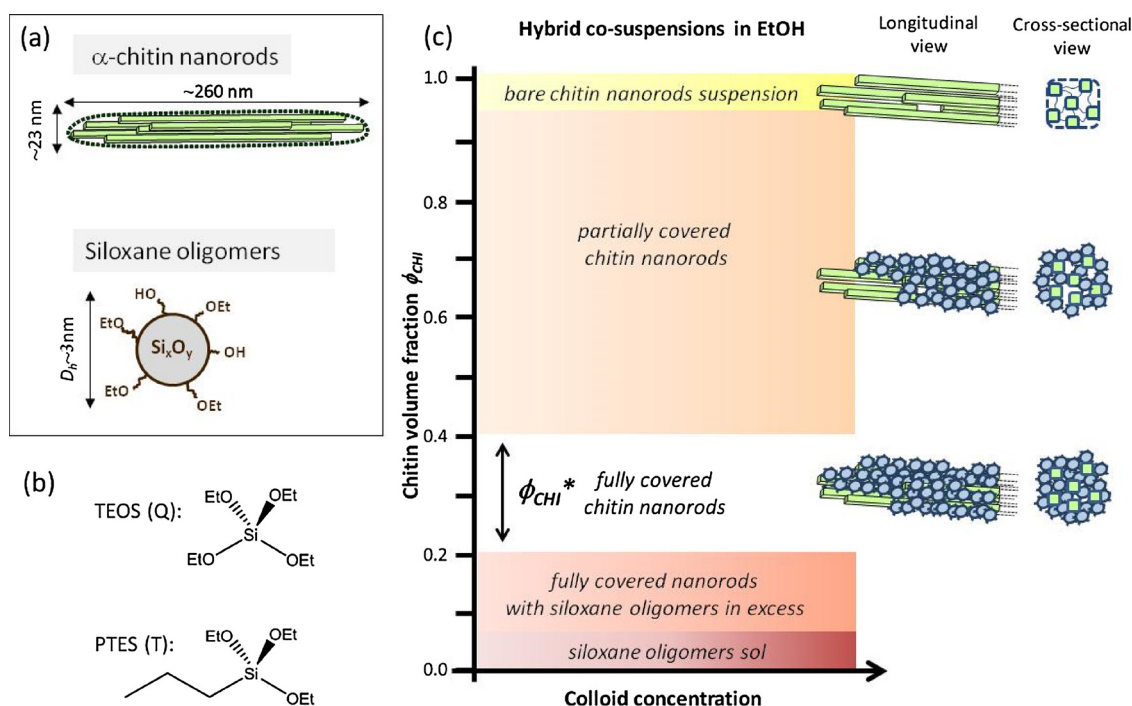


Fig. 1. (a) Colloidal precursors, chitin nanorods and siloxane oligomers, (b) Q (TEOS : tetraethoxysilane) and T (PTES : propyltriethoxysilane) siloxane precursors employed and (c) solid particles suspected to occur in suspension as a function of ϕ_{chi} .

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