

## Chitosan–silane sol–gel hybrid thin films with controllable layer thickness and morphology

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### ABSTRACT

The preparation of thin films of chitosan–silane hybrid materials by combining sol–gel processing and spin coating is reported. A variety of silanes can be used as starting materials for the preparation of such thin films, namely tetraethoxysilane, tri-*tert*-butoxysilanol, trimethylethoxysilane, *p*-trifluoromethyltetra-fluorophenyltriethoxysilane, trivinylmethoxysilane, (methoxymethyl)trimethylsilane, and hexamethoxydisilane. These silanes are subjected to a sol–gel process before they are added to acidic chitosan solutions. The chitosan:silane ratio is kept constant at 6:1 (w/w) and dilutions with ethanol are prepared and spin coated. Depending on the degree of dilution, film thickness can be controlled in a range between 5 and 70 nm. For the determination of additional surface properties, static water contact angle measurements and atomic force microscopy have been employed.

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### 1. Introduction

Hybrid materials (HM) are able to combine the advantages of organic polymers (e.g. photoluminescence) with those of inorganic compounds, e.g. enhanced stability (Gómez-Romero & Sanchez, 2004; Kickelbick, 2006). The most convenient way to synthesize such HM is based on sol–gel chemistry. This approach enables a simple control of the materials' properties by varying easily accessible experimental parameters including temperature, pH, etc. (Avnir, Klein, Levy, Schubert, & Wojcik, 2001; Corriu & Boury, 2001). Sol–gel processes are widely used to combine synthetic polymers with inorganic parts. In recent years, several approaches for the preparation of hybrid materials using polysaccharides as matrix for inorganic compounds have been described (Chen, Liu, Zhang, & Zhang, 2007; Jun et al., 2010; Rangelova et al., 2008; Samuneva et al., 2008; Schaub, Wenz, Wegner, Stein, & Klemm, 1993; Shchipunov & Karpenko, 2004; Shchipunov, Karpenko, & Krekoten, 2005; Shchipunov, Kojima, & Imae, 2005; Shirosaki et al., 2009; Smitha, Shajesh, Mukundan, & Warriar, 2008).

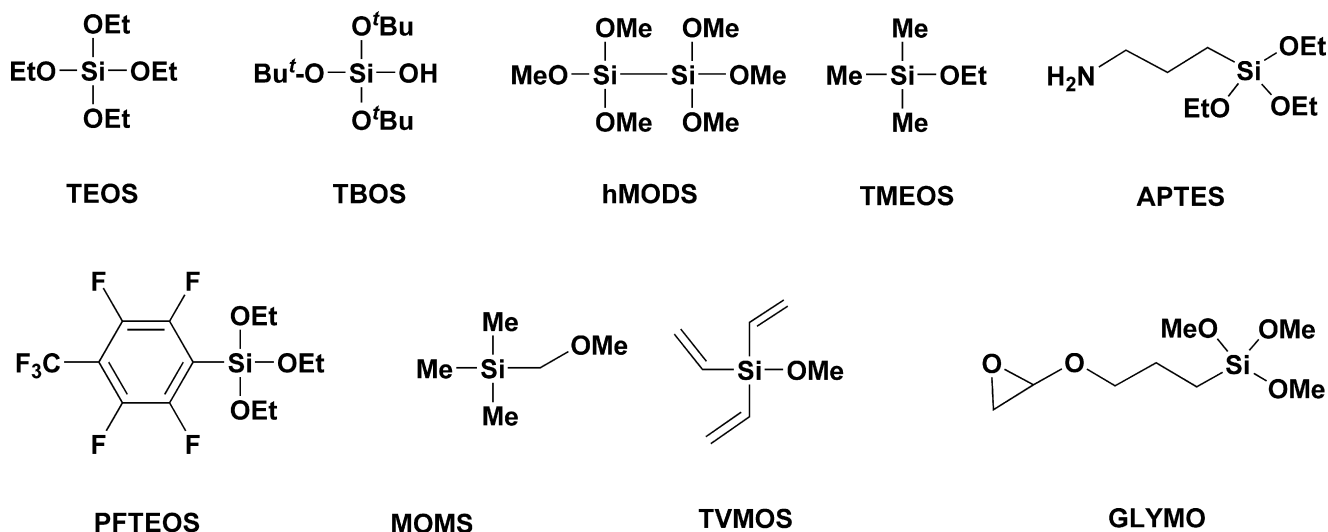
One major problem of performing sol–gel processes with polysaccharides is the compatibility in terms of solubility, pH-value, hydrophilicity and charge between the sol–gel system and the polysaccharide of interest. If any of the compatibility parameters is not fulfilled, homogenous materials usually cannot be obtained as partial phase separation takes place. Following the criteria of compatibility, some polysaccharides can be incorporated into sol–gel processes easier than others. Among all naturally occurring polysaccharides, chitosan is one of the few which is soluble in aqueous acidic medium due to protonation of the primary amine functionalities. This property makes this poly- $\beta$ -1-4 glucosamine an interesting candidate for the preparation of HM. Moreover, chitosan features biocompatibility, biodegradability, low toxicity, low cost, enhancement of wound-healing and antibacterial effects; properties which are of great importance in respect to the development of new materials in medical applications (Pavinatto, Caseli, & Oliveira, 2010).

To the best of our knowledge, all chitosan–silane hybrid materials prepared up to now have been synthesized either by reaction of a reactive silane species with the amine functionality (e.g. isocyanate or epoxy substituted alkoxy silanes; Liu, Su, & Lai, 2004; Shirosaki et al., 2009; Silva et al., 2005) thus forming a covalent bond or by crosslinking at the OH groups with hydroxy rich silane compounds such as oligomeric  $\text{Si}(\text{OH})_4$  yielding a mixture of covalently and hydrogen bonded hybrid materials (Chen et al., 2007; Enescu et al., 2009; Fuentes, Retuert, Ubilla, Fernandez, &

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**Fig. 1.** Silane precursors used for thin hybrid film preparation. TEOS: tetraethoxysilane, TBOS: tri-*tert*-butylsilanol, hMODS: hexamethoxydisilane, TMEOS: trimethylethoxysilane, APTES: aminopropyltriethoxysilane, PFTEOS: 2,3,5,6-tetrafluoro-4-(trifluoromethyl)-triethoxysilane, MOMS: (methoxymethyl)trimethylsilane, TVMOS: trivinylmethoxysilane, GLYMO:  $\omega$ -glycidylpropoxytrimethoxysilane.

Gonzalez, 2000; Uragami et al., 2004). The thickness of the resulting films is in the  $\mu\text{m}$  to mm range. Several very interesting applications for these materials, e.g. as membranes (Uragami et al., 2004), for tissues (Shirosaki et al., 2009), as scaffolds (Braga et al., 2009; Molvinger, Quignard, Brunel, Boissiere, & Devoisselle, 2004; Shirosaki et al., 2009; Witoon, Chareonpanich, & Limtrakul, 2009; Yan et al., 2009; Yeh, Chen, & Huang, 2007), for better cell proliferation (Shchipunov & Karpenko, 2004), and for enhanced nerve regeneration (Amado et al., 2008) have been described. For a deeper understanding of structure–property relationships in such materials, it would be desirable to produce materials with defined surface morphology and wettability. Therefore, the fabrication of model films is of significant interest (Mohan et al., 2011). The demands on these films vary depending on the intended application. Besides chemical, morphological equivalence is the most important point because surface interactions such as adsorption (e.g. of proteins) or wetting strongly depend on the surface morphology and composition (Kulterer et al., 2012). In this paper, an easy, fast and highly reproducible method to prepare chitosan–silane hybrids on the nanometer range ( $\sim 5$ – $70$  nm thickness) by sol–gel chemistry is demonstrated.

## 2. Experimental

### 2.1. Materials

Chitosan (degree of deacetylation: 85%,  $M_w \sim 400,000$  Da, practical grade, from crab shells) is obtained from Sigma–Aldrich (Steinheim, Germany) and used without further treatment. Alkoxysilanes (reagent grade) are obtained from ABCR (Karlsruhe, Germany) and used without further purification. Acetic acid (reagent grade) and ethanol (reagent grade) are obtained from Roth (Karlsruhe, Germany).

### 2.2. Preparation of the hybrid thin films

For the synthesis of prehydrolyzed/precondensed sol–gel solutions, 1.0 g of the alkoxysilane is dissolved in 98.5 g EtOH and 0.5 g acidic water (pH = 1.5, adjusted with HCl) is added. These solutions are stirred for two days in a closed vessel, before they are used for hybrid material preparation. Chitosan solutions are prepared by slowly adding chitosan (1.5 g) to 7 M acetic acid (98.5 g) at  $60^\circ\text{C}$ .

This solution is stirred overnight at this temperature, cooled to room temperature and filtered prior to use.

For spin-coating experiments, 1.0 g of the silane solution is added to 4.0 g of the chitosan solution and mixed vigorously for 1 min. Then  $100 \mu\text{l}$  of the resulting solution are deposited onto surfs and subjected to spin coating ( $\alpha = 2500$  rpm/s,  $\nu = 4000$  rpm,  $t = 60$  s). For the dilution experiments, the stock solution is prepared as mentioned above, diluted with the corresponding amount of EtOH and allowed to crosslink for 1 min. For each dilution, two surfs with a total surface of  $1 \text{ cm}^2$  each are coated. After spin coating, the resulting materials are dried for one week at room temperature (relative humidity in our labs on average is 50–70%). Alternatively, drying can be performed for 4 h in a drying oven with adjusted humidity (50%) at  $40^\circ\text{C}$  without changing surface morphology and contact angles.

### 2.3. Layer thickness determination – Sarfus

Optical microscopy (Sarfus) is done on a polarization light microscope from Leica (Wetzlar, Germany). Surfs are obtained from Nano Lane (Montfort-le-Gesnois, France) and analyzed using the Sarfusoftware program. A more detailed description of this method can be found elsewhere (Ausserre & Valignat, 2006). For layer thickness determination, two surfs of each dilution are used. The films are scratched using a stainless steel cannula to obtain a small area which is uncoated. Consequently, the height difference between this uncoated area and the coated part is measured at different positions and height profiles are created using the Sarfusoftware. For layer thickness determination, at least three height profiles have been used on each surf.

### 2.4. Atomic force microscopy

AFM measurements were performed in tapping mode with an Agilent 5500 AFM multimode scanning probe microscope (Digital Instruments, Santa Barbara, CA). The images were scanned using silicon cantilevers (ATEC-NC-20, Nanosensors, Germany) with a resonance frequency of 210–490 kHz and a force constant of 12–110 N/m. Image processing, analysis and root mean square roughness calculation are performed with WSxM freeware (Horcas et al., 2007).

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