

SELF-ASSEMBLED SILANE MONOLAYER ON THE SURFACE OF NANOMETRIC PARTICLES OBTAINED USING A SUPERCRITICAL TREATMENT

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The problem of the lack of interfacial interaction between inorganic fillers and organic matrixes has been extensively reported and it requires to be solved in order to obtain stable hybrid composites. The interfacial interaction can be improved by modifying the surface of inorganic fillers with organic bifunctional molecules. Surface modification is addressed in this work through silanization. High quality siloxane monolayers are not easy to synthesize using the traditional solution-phase methodology, mainly because of the difficulty in controlling the amount of water in the liquid medium. This article reports an anhydrous and generic SCCO₂ method for coating the surface of particulate materials through the deposition of self-assembled silane monolayers. The reaction of a trifunctional alkoxy silane with the surface of nanometric hydroxyapatite substrates is reported.

INTRODUCTION

The increasing demand for smarter and smaller products call for the development of multifunctional materials. Nanostructured multiphase materials are ideally suited to achieve multifunctionality. It has been proved that the addition of a small amount of nanometric (inorganic) particles to (organic) polymers dramatically modify a wide variety of polymer properties. Composites, used in diverse applications, ranging from the development of lightweight structural materials to the advancement of medical devices [1], are thus obtained. In this research field, considerable attention has been focused in the study of surface modification of nanoparticles with organic bifunctional molecules [2]. The organic coating facilitates filler dispersability and manipulation behavior and, in this way provides a method to construct nanomaterials from nanocomponents. Bifunctional silanes are widely used to form spontaneous self-assembled monolayers [3]. Depositions of self-assembled monolayers of a large variety of silane molecules on flat or micrometric particle surfaces have been extensively studied using either gaseous or liquid phase reactions [4] or even supercritical methods [5,6]. However, few publications have described efficient solution silanization methods for nanometric powders due to the intrinsic necessity of having the particles in a completely dispersed state [7,8]. This paper reports an alternative and generic supercritical method to modify the surface of nanoparticulate materials through the deposition of self-assembled silane monolayers in conditions where it is difficult to achieve due to nanoparticles agglomeration. Nanometric hydroxyapatite (HA) powders were selected as substrates. HA powder is a biocompatible filler used for the reinforcement of biopolymers, producing biocomposites suitable for repairing the skeletal system. The use of nanometric acicular HA particles is based on the biomimetic concept, since these particles are of the same size and shape than the HA conforming human bond.

MATERIALS AND METHODS

Nanometric particles of HA were synthesized in our laboratories following a reported procedure [9]. The obtained HA powder was composed of acicular particles of 50-100 nm length and with an aspect ratio of ~ 6 to 8. HA particles were hydrophilic and had ~ 3 wt% of adsorbed moisture. The organosilane γ -methacryloxypropyltrimethoxysilane (MPTMS, Fluka), with molecular formula $C_{10}H_{20}O_5Si$, was used as a coating agent. The general formula of trialkoxysilanes is $R'Si(OR)_3$. In the chosen MPTMS, R' corresponded to $H_2C=C(CH_3)-CO-O-(CH_2)_3-$ and R to $-CH_3$.

Surface silanization of inorganic particles was performed either *via* an anhydrous supercritical method (SC-method) or *via* a wet conventional method (cv-method).

Anhydrous supercritical method: high pressure deposition experiments were carried out in a stainless steel apparatus (Fig. 1). Liquefied CO_2 was compressed to the operating pressure using a membrane pump (Lewa EK-M-210). A CO_2 preheating spiral, a saturator (S) and impregnator (I) tubular reactors (10 mL) were placed into an air oven heated to the required working temperature. The system pressure was controlled with a back pressure regulator (Tescom 26-1761). The saturator was filled with glass wool previously impregnated with drops of liquid silane. A small portion of this impregnated glass wool was also placed at the bottom of the impregnator. Substrate fine particles (~ 0.5 g) were enclosed in small cylinders made of $0.45 \mu m$ pore filter paper and added to the top of the impregnator together with 1 mm glass beads. The silanization procedure was initiated by raising the temperature and pressure to 353 K and 25 MPa, respectively. After system stabilization, the experimental conditions were maintained for the required period of time (between 15 min and 24 h) at a very low flow rate of $SCCO_2$. Successive cycles of approximately 10-min static process and 5-min dynamic purge, were followed during this period of time. In the 24-h run process, the system was maintained in the static mode overnight. At the end of the deposition period, the samples were washed with a 2-h dynamic CO_2 purge (~ 2 sLmin $^{-1}$).

Wet conventional method: Conventional coating procedure was initiated by adding the required amount of water to a suspension of inorganic particles in alcohol, in order to obtain a 95:5 %v/v methanol:water mixture. The mixture was stirred and the coating was accomplished by adding the alkoxy silane. Excess of silane had to be added (*ca.* 1.5 equivalents) because the silane hydrolysis reaction is a slow process and it is not completed when alcohol is used as a solvent. The suspension was stirred at room temperature under low pressure for *ca.* 24 h. The remaining slurry was heated at 393 K for the required period of time (between 15 min and 8 h). Finally, the recovered sediment was washed several times with dichloromethane and then dried for successive research.

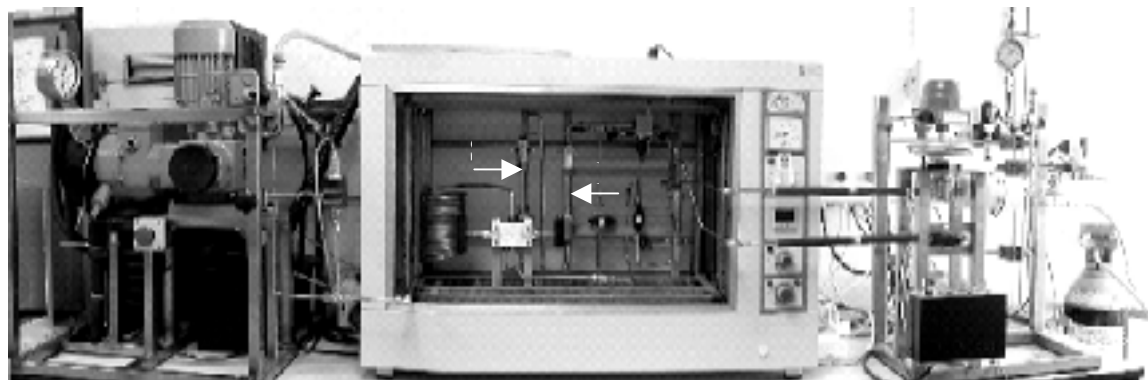


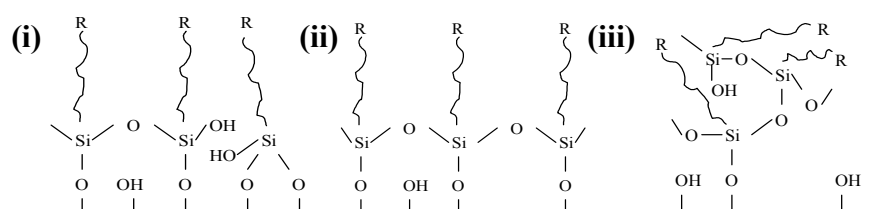
Figure 1. Continuous flow equipment with tubular reactors

The specific surface area (S_a), pore volume (P_v) and mean pore size (P_s) of raw and prepared samples were determined by low-temperature N_2 adsorption, using an ASAP 2000 Micromeritics INC. Micrographs of the samples were recorded in both scanning (SEM, Hitachi S-570) and transmission (TEM, JEOL JEM-1210) electron microscopes. Particle size distribution was determined by a light scattering method, using a Coulter LS 130 instrument, after dispersing the samples in hydrophobic petroleum (Fluka, purum). Thermal stability of obtained samples was measured using thermogravimetric analysis (TGA, Perkin Elmer 7) under Ar atmosphere.

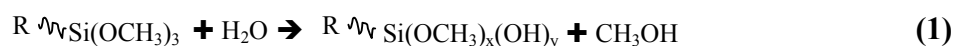
RESULTS AND DISCUSSION

It has been reported in the literature that the deposition of trialkoxysilane from solutions can give rise to a number of possible surface structures [10] schematized in Fig. 2: covalent, self-assembled and polycondensated. The final configuration mainly depends on the curing temperature and water concentration in the bulk and adsorbed on the surface.

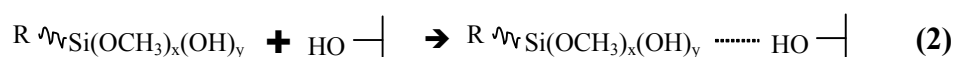
Figure 2. (i) Covalent, (ii) self-assembled and (iii) polycondensated structures.



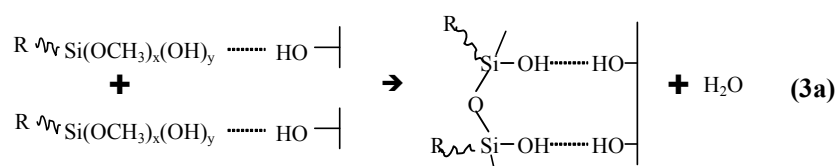
Initiation of the silanization reaction occurs by the hydrolysis of one or more alkoxy groups (eq. 1):



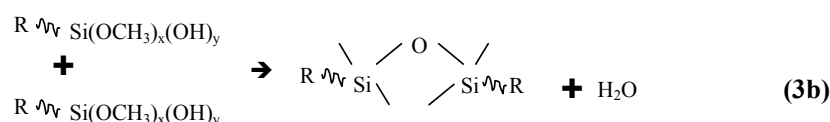
the hydrolyzed groups then form hydrogen bonds with hydroxyl groups of the substrate (eq. 2):



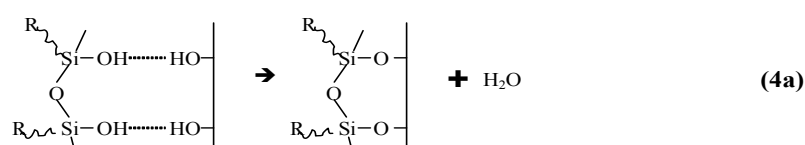
favoring siloxane bonds between adjacent molecules placed on the surface (eq. 3a):



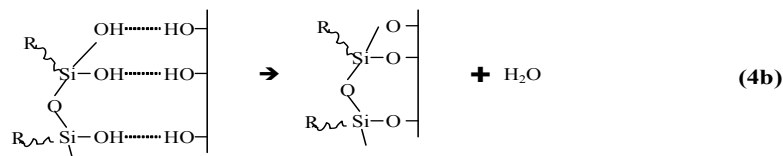
Both, polycondensation of hydrolyzed bonds prior to deposition onto the surface (eq. 3b) and vertical polymerization are therefore possible reactions.



Finally, during curing, monodentated (eq. 4a):



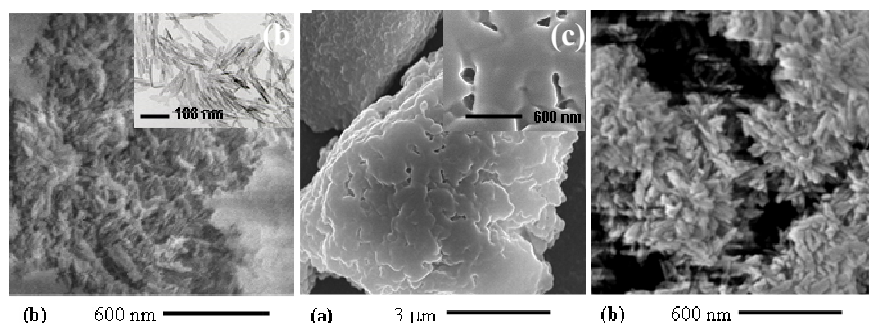
and bidentated (eq. 4b) covalent links were formed with the substrate:



The favored formation of a monolayer through horizontal polymerization leading to two-dimensional nanometric coverage (configuration ii in Fig. 2) could be qualitatively rationalized in the supercritical procedure based on the preferred occurrence of the model reactions depicted in eqs. 1, 2, 3a and 4a. The supercritical procedure is an anhydrous method in which only moisture adsorbed to the powder surface was added to the medium [6,8]. Since the solubility of water in SCCO₂ is low, water molecules were expected to remain mainly associated on the surface and not free in solution. In this way, the hydrolysis reaction (eq. 1) could only be initiated near the particles surface and not in the bulk solution. In this approach, the ultrathin interfacial film of adsorbed water on the substrate, allowed the formation of a highly organized film of hydrolyzed MPTMS molecules, which consequently formed hydrogen bonds with the substrate and the final polymerized film by compliant cross-linking of the siloxane network (eq. 3a was favored with respect to eq. 3b). On the other hand, in the used wet conventional procedure, the water molecules were present not only adsorbed on the particles surface, but also dissolved in the alcoholic solution. Therefore, alkoxy silanes can undergo hydrolysis and condensation into polysiloxanes in the bulk prior to deposition onto the surface (eq. 3b). Both bulk-formed polysiloxanes deposition and vertical polymerization led to polycondensed structures (configuration iii in Fig. 2). Furthermore, covalent attachment (configuration i in Fig. 2) has been described to be promoted by high temperature [10]. Thermal curing of silanes in the conventional method was carried out at 393 K whereas the complete supercritical process described herein was carried out at 353 K. Consequently, silane bidentated bindings formed through the reaction depicted in eq. 4b were expected to be favored in the conventional method rather than in the supercritical process.

SEM pictures and BET analysis of the raw inorganic materials showed that the nanometric powder formed aggregates with a disordered mesoporous structure (Fig. 3a and 4a, respectively). The estimated BJH mesopore diameter was ~ 20 Å.

Figure 3. Electronic micrographs of (a) raw HA; (b) cv-silanized during 8 h; and (c) SC-treated during 24 h



A significant disadvantage in using the traditional solution-phase silanization process for the coating of nanometric particles was that the solution containing the dispersed inorganic powder and the reactive silane occurred to be very viscous during reaction and solvent evaporation step. Therefore, kinetics became restricted by the mass transport of the silane to the inner mesopore surface of the agglomerates and, eventually, transport was hindered by channels blockage. As a result, the outer surface of the agglomerates was coated

with the organic molecules instead of the primary particles. For longer processing times, no more surface was available for deposition and polycondensation of the excess silane was the predominant reaction (eq. 3b). This effect was observed for conventionally treated HA powders, where agglomerates of $\sim 50 \mu$ were mainly observed by SEM (Fig. 3b) and the nanometric needles were no longer distinguished. Additionally, the HA aggregates lost their mesoporous character as shown by BET curves (Fig. 4b). Using the conventional method, the negative effect could be diminished by shortening the curing time to 15 min, however, the obtained silane coating showed low thermal stability (Fig. 5a). On the other hand, SEM micrographs of HA silanized powders (Fig. 3c) using the supercritical method revealed the formation of aggregates similar to those corresponding to non-treated powders, in which the primary particles were still evident. The mesoporous character was also maintained although the mesopore volume and total surface area diminished as shown by the N_2 adsorption/desorption measurements (Fig. 4c). The superior kinetics of mass transfer from the supercritical fluid to the interior of the mesopores with respect to liquid solvents caused organosilanes to coat preferentially primary particles.

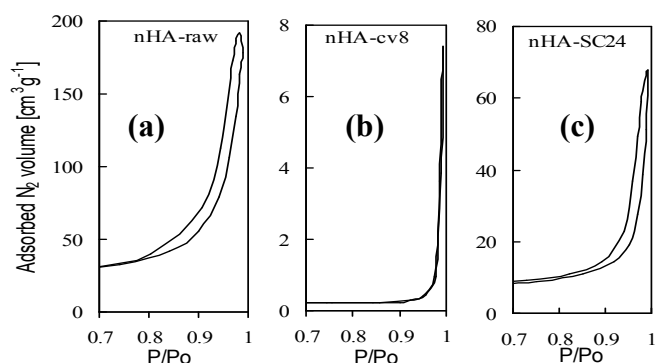
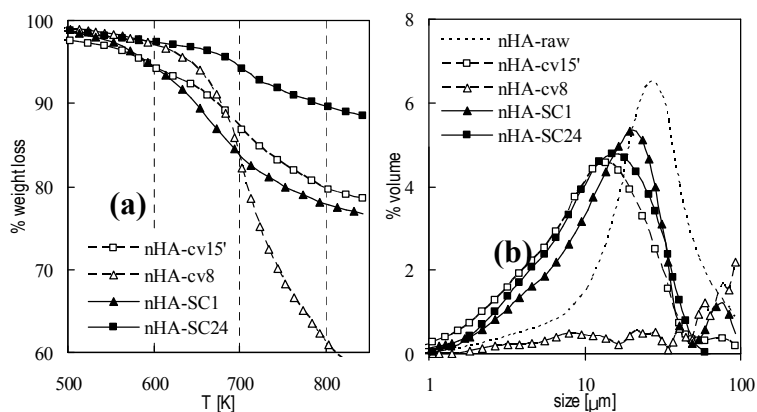


Figure 4. BET analysis: (a) raw HA; (b) cv-cured during 8 h; and (c) SC-treated during 24 h

Thermal analysis (TGA) measurements showed that minimum processing times of 8 h and 1 h in the conventional and supercritical methods, respectively, were needed to obtain surfaces with durably attached silane molecules. Using these processing times, the highest thermal stability was obtained for the sample processed with the conventional mode (Fig. 5a). However, the 8-h conventionally treated sample could not be dispersed in the used hydrophobic liquid (Fig. 5b), since it was composed of very large agglomerates ($> 100 \mu\text{m}$). In order to improve the dispersion capacity of the conventionally prepared sample, and the thermal stability of the supercritical processed sample, the processing time was decreased to 15 min in the former and increased up to 24 h in the latter. In the conventional process, the dispersion capacity achieved for the obtained particles increased (Fig. 5b), despite the thermal stability of the coating diminished considerably (Fig. 5a). On the other hand, the thermal stability of the supercritical processed sample increased significantly by increasing the processing time (Fig. 5a), while the particle size distribution was almost not modified with respect to the 1-h run (Fig. 5b).

Figure 5. (a) TGA and (b) Coulter analysis of samples obtained using either the cv or SC methods and applying different curing periods.



The low viscosity and the absence of surface tension in supercritical fluids allow the complete wetting of substrates with intricate geometries, including the internal mesopore surface of agglomerates. SCCO₂ solutions can permeate and penetrate small orifices rapidly because the enhanced diffusivity of the functional molecules in the interparticle voids. Kinetics of mass transfer from the supercritical silane solution to the internal mesoporous surface were enhanced with respect to liquid solvents even at the used low working temperature.

CONCLUSION

Surface modification of inorganic nanoparticles was addressed in this work through silanization. High quality monolayers are not easy to form using the traditional solution-phase methodology, mainly because of the difficulty in controlling the amount of water in the liquid medium. This article reports an anhydrous and generic SCCO₂ method for coating the surface of nanoparticulate materials through the deposition of self-assembled silane monolayers, where multilayer formation can be avoided by controlling the processing time. While the wet alcoholic conventional method is considered a relatively effective coating strategy for micrometric particles and even isometric nanoparticles, it is a rather time and energy-consuming process, particularly in the final cleaning and drying steps. On the contrary and because CO₂ is a gas at room temperature, the coated materials were isolated from the medium by simple depressurization, resulting in a dry product. Using the supercritical method, coating efficiency was considerably improved for elongated HA nanoparticles in comparison with the conventional method, plausible because of the geometry of the mesopore structure of formed aggregates. Surface modification of inorganic nanoparticles by trialkoxysilanes involves a significant organophilization, which is the prerequisite for embedding high filler content into organic polymers.

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