

Spectroscopic and Thermal Studies of Polyalkoxysilanes and Silica-Chitosan Hybrid Materials

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Abstract

Polymers of organoalkoxysilanes (or polyalkoxysilanes) were synthesized through sol-gel process using different organosilanes: Tetraethylorthosilicate (TEOS), (3-Glycidioxypropyl) trimethoxysilane (GPTMS), Trimethoxy(propyl)silane (TMPS), and/or Triethoxy(octyl)silane (EOS). Different carboxylic acids (acetic, formic, and citric) were used to prepare polyalkoxysilanes, with citric acid acting as a reactant rather than a catalyst for the sol-gel reaction. Silica-chitosan hybrid materials were synthesized reacting polyalkoxysilanes and chitosan, one of the most important and most studied natural polymers, through sol-gel process. The synthesized materials were characterized using Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), differential Scanning Calorimetric (DSC) and solid-state Carbon-13 Nuclear Magnetic Resonance (solid-state ¹³C-NMR) spectroscopy, obtaining information on the structural properties of each modified materials. The results obtained by NMR indicate that the oxirane group of GPTMS remains in all reaction products to form different polyalkoxysilanes.

Keywords: sol-gel process, hybrid materials, polyalkoxysilanes, silica-chitosan

1. Introduction

Polyalkoxysilanes (alkoxysilanes or organofunctional alkoxysilanes) are inorganic/organic hybrid materials at a molecular level, which have been used on different materials in order to modify their surface (Chen & Yakovlev, 2010; Ebnesajjad, 2011) and act at the interface between organic polymers and inorganic substrates as adhesion promoters or coupling agents (Gelest, 2015). They provide a great level of adhesion with resistance to environmental and other destructive forces, such as heat and moisture, without affecting physical or chemical forces at the interface (Ebnesajjad, 2011). Chitosan is the deacetylated form of chitin *K*-glucosamine for utilization in chemical reactions, and it has three kind of reactive functional groups at the C-2, C-3, and C-6 positions. The chemical modification of C-2, C-3 and C-6 positions can provide numerous materials with different physical properties for applications in biomaterials, anti-bacterial textiles (Ivanova & Philipchenko, 2012), tissue reconstruction (Gingras, Paradis, & Berthod, 2003), artificial skin (Muzzarelli, 1993), drug delivery systems (Rui & San Román, 2005), food additives (Ruiz-Hitzky, Darder, & Aranda, 2008) supports for cells (Khor, 2004), enzymes, and catalysts (Khor, 2004).

1.1 Hybrid Materials

Silica-chitosan hybrid materials have been commonly synthesized by sol-gel process reacting chitosan and alkoxysilanes. For example, Smitha, Shajesh, Mukundan, and Warriar (2008) obtained highly transparent silica-chitosan hybrids through a sol-gel process by in situ hydrolysis–condensation reaction of methyltrimethoxysilane (MTMS) and vinyltrimethoxysilane (VTMS) with chitosan that may be used for optical applications. Similarly,

Budnyak, Pylypchuk, Tertykh, Yanovska, and Kolodynska (2015) synthesized a chitosan-silica material by the sol-gel method through hydrolysis of Tetraethoxysilane (TEOS) in a chitosan solution.

These materials have been synthesized for biomedical applications, such as for bone regeneration (Dorozhkin, 2009). For example, Eun-Jung et al. (2009), fabricated a silica-chitosan xerogel with Tetramethylorthosilane (TMOS) and medium molecular weight chitosan for guided bone regeneration (GBR) through sol-gel process. The osteoblastic cells adhered well and grew actively on the silica-chitosan material higher than on the chitosan material. Also, silica-chitosan hybrid materials have been applied in nanomedicine (Solansk et al., 2009). Moreover, Solanki et al. (2009), developed a cholesterol biosensor through multi-walled carbon nanotubes (MWNs) silica-chitosan nanobiomaterials by sol-gel process using Tetraethylorthosilicate (TEOS), 86% deacetylated chitosan, and acetic acid. Other applications have been developed in order to aid healing processes (Susuki, & Mizushima, 1997; Knapczyk, Macura, & Pawlik, 1992; Biagini et al., 1991), as well as for separation membranes (Liu, Su, & Lai, 2007).

The properties of hybrid materials do not simply result from the sum of the individual contributions of their components, but also from the strong synergy created by an extensive hybrid interface (Sanchez et al., 2001). For instance, the mineral/organic interface, including the types of interactions present, the surface energy, and the existence of labile bonds play a strong role in modulating a number of properties (optical, mechanical, separation capacity, catalysis, and chemical and thermal stability) (Nicole, Rozes, & Sanchez, 2010). The existence of covalent chemical bonds between organic and mineral components presents a number of advantages: (i) the potential of synthesizing entirely new materials from functionalized alkoxides, (ii) the minimization of phase separation, and (iii) a better definition of the organic-inorganic interface. Such defined control can lead to a better understanding of the material and the relationship between microstructure and properties, and an easier adjustment of the hydrophilic-hydrophobic balance (Nicole, Rozes, & Sanchez, 2010; Ciriminna et al., 2013).

Soft chemistry-based routes including sol-gel chemistry (hydrolytic or non-hydrolytic) may be performed from simple precursors or via the use of specific bridged and polyfunctional precursors. Conventional sol-gel pathways to hybrid networks are obtained through condensation of organically modified metal alkoxides. These materials, exhibiting infinity of microstructures, are amorphous, generally transparent, and easily shaped as films or bulks (Sanchez et al., 2014). The sol-gel process is very versatile as it allows the incorporation of inorganic component like metal alkoxides, namely Si (Ahmad, Sarwar, & Mark, 1997; Ahmad, Sarwar, & Mark, 1997), Ti (Ahmad, Sarwar, & Mark, 1998; Ahmad, & Sarwar, 1997), Zr (Rehma, Sarwar, Ahmad, Krug, & Schmidt, 1997), or even bioactive materials (Juhasz, & Best, 2011) in order to modify final chemical and physical properties of materials at low processing temperatures (Al-Sagheer, & Muslim, 2010).

In this work we prepared organoalkoxysilane $[RSi-(OR')_3]$ polymers (polyalkoxysilanes), and hybrids of polyalkoxysilanes with low molecular weight chitosan obtaining silica-chitosan hybrid materials, synthesized by sol-gel method. Spectroscopic and thermal characterization was done by solid-state Carbon-13 Nuclear Magnetic Resonance (^{13}C -NMR), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and differential Scanning Calorimetric (DSC) to obtain a better understanding of the structure and chemistry of the different reactions.

2. Experimental Section

2.1 Materials

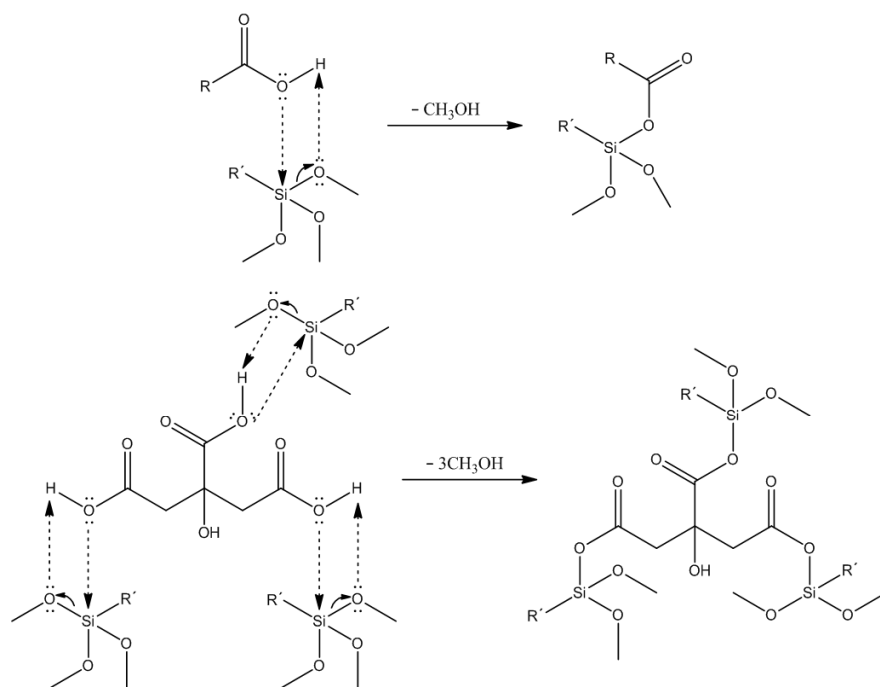
Tetraethylorthosilicate (TEOS), (3-Glycidyloxypropyl) trimethoxysilane (GPTMS), Trimethoxy(propyl)silane (TPMS), Triethoxy(octyl)silane (EOS), formic acid, acetic acid, and citric acid were obtained from Sigma-Aldrich and used without further purification. Low molecular weight chitosan with a degree of deacetylation of $\geq 75\%$, distilled water, and ethanol, were also purchased from Sigma-Aldrich.

2.2 Synthesis of Polyalkoxysilanes

In order to prepare polyalkoxysilanes 45 mL of ethanol, 50 mL of distilled water, and 12.5 mL of acetic acid, or formic acid were placed a glass container; and then the reagents TEOS, TMPS, GPTMS, and EOS were added in the concentrations shown in Table 1 (in mol). The reaction mixture was kept under constant stirring, and placed at 50 °C during 24 h; after evaporating the solvent, then the sample was aged for 24 h at room temperature. Polyalkoxysilanes prepared with citric acid were done in a 1 L reactor mixing 250 mL of distilled water, 20 mL of ethanol, and TMPS or GPTMS (Table 1). The temperature was kept at 50 °C, and the reaction time was 2 h. This was done in order to obtain esters of organoalkoxysilanes with the carboxylic groups of citric acid. Thus, if each of the carboxylic groups of the citric acid reacts with an organoalkoxysilane it may lead to a three-dimensional cross-linked polymer, as shown in Figure 1.

Table 1. Reagents and quantities in moles for polyalkoxysilanes and silica-chitosan hybrid materials

Polyalkoxysilanes	Acetic acid (mol)	Formic acid (mol)	Citric acid (mol)	TEOS (mol)	TMPS (mol)	GPTMS (mol)	EOS (mol)
S-T ₁	0.22				0.275		
S-T ₁ -f	-	0.33	-	-	0.275	-	-
S-T ₁ -c	-	-	0.092	-	0.275	-	-
S-G-c	-	-	0.074	-	-	0.222	-
S-GE	0.22	-	-	-	-	0.057	0.040
S-T ₁ G	0.22	-	-	-	0.049	0.057	-
S-T ₁ E	0.22	-	-	-	0.049	-	-
S-TT ₁	0.22	-	-	0.056	0.049	-	-
S-TT ₁ G	0.22	-	-	0.038	0.048	0.039	-
S-TGE	0.22	-	-	0.038	-	0.039	0.027
S-T ₁ GE	0.22	-	-	-	0.048	0.039	0.027
S-TT ₁ GE	0.22	-	-	0.006	0.005	0.006	0.004
Silica-chitosan hybrid	Chitosan (g)			TEOS (mol)	TMPS (mol)	GPTMS (mol)	EOS (mol)
SCh-TT ₁	6			0.11	0.14	-	-
SCh-T ₁	6			-	0.28	-	-
SCh-GE	6			-	-	0.11	0.08



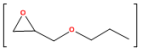
R = H, CH₃; R' = Alkyl group, or  functional group

Figure 1. Reaction mechanism of organoalkoxysilanes with carboxylic acids (acetic, formic, or citric)

2.3 Synthesis of Silica-Chitosan Hybrid Materials

Several studies have demonstrated the commercial importance of chitosan as a core component for different applications (Ivanova & Philipchenko, 2012; Gingras, Paradis, & Berthod, 2003; Muzzarelli, 1993; Rui & San Román, 2005; Lee et al., 2009; Solanski et al., 2009; Susuki & Mizushima, 1997; Knapczyk, Macura, & Pawlik, 1992; Biagini et al., 1991; Liu, Su, & Lai, 2007). Though chitosan offers a great alternative to other polysaccharides, it is imperative to understand the effect of the incorporation of suitable functional groups on its surface for higher-end applications

Selected polyalkoxysilanes were chosen to prepare silica-chitosan hybrid materials due to their thermal behavior by DSC, as shown in Table 4; thus, silica-chitosan hybrids SCh-T₁, SCh-TT₁, and SCh-GE were synthesized.

Low weight chitosan (6g) and acetic acid were placed in a glass container in a concentration of 5 % v/v to distilled water and stirred at 90 °C for 1 h. Afterwards 20 mL of ethanol was added to the solution and stirred at 90 °C. Finally, organoalkoxysilanes TEOS, TMPS, GPTMS, and EOS were added to the solution drop by drop using a funnel. The completed solution was aged at room temperature (25 °C) for 48 h. The reagents and concentrations for the preparation of silica-chitosan materials are shown in Table 1.

2.4 Characterization Methods

All samples were analyzed by solid-state ¹³C-NMR spectroscopy with an 11.7 Tesla Bruker Avance III equipment. Each sample was tested using cross-polarization (CP) and magic-angle-spinning (MAS) with a spinning rate of 125 MHz. A 4 mm inner diameter rotor with a spinning rate of 7 kHz was used. FT-IR characterization was carried out with a Thermo Nicolet 6700 spectrophotometer using the Attenuated Total Reflectance (ATR) technique. Each sample was scanned 42 times at a resolution of 4 cm⁻¹ from 4000 - 400 cm⁻¹. TGA was done with a SDT Q600 TA Instruments Thermogravimetric Analyzer with DSC, with a heating rate of 10 °C min⁻¹ from room temperature (25°C) to 800°C, and a flow rate of 100 ml/min of nitrogen gas.

3. Results and Discussion

Hybrid organic-inorganic solids represent an important class of engineering materials, usually prepared by sol-gel processes through cross reaction between organic and inorganic precursors. For the reaction under acid catalysis and nucleophilic attack of a silanol oxygen atom at the Si atom of a protonated silanol under displacement of water, the nucleophilic oxygen atom in such a reaction is not restricted to be a central oxygen atom in a siloxane chain, as a silanol or alcohol or water oxygen atom will act in a similar manner. Furthermore, it has long been known that polyalkoxysilanes can be formed by strong Bronsted or Lewis acids. Therefore, while the pK_a of formic acid (3.74) is smaller than that of acetic acid (4.76) the resulting product is similar in structure and their infrared spectrum has no appreciable differences for each material synthesized, except for the reaction of citric acid and GPTMS producing the corresponding ester. Thus, the pK_a of each of the carboxylic acids of the citric acid molecule does not affect the reaction. Polyalkoxysilane S-T₁-c formed a viscous gel, whereas S-G-c was a crystalline product most likely due to the opening of the epoxy group of GPTMS (Figure 3b) in S-G-c forming C-OH groups. This in turn may result in a further condensation reaction forming Si-OR from a hydroxyl group (where R is alkyl radical), as depicted in Figure 1.

Solid-state NMR is an extraordinarily powerful physical method widely applied in different fields of chemistry. It is particularly valuable at probing complex molecular systems, representing an ideal tool for characterizations of materials with dimensions on a nanoscale. Solid-state NMR experiments at MAS, performed for nuclei ¹H, ¹³C, ¹⁵N, ³¹P, ²⁹Si, and ²⁹Xe, play a central role in various investigations of structures and dynamics in catalysts, polymers, glasses, zeolites, batteries, liquid crystals, natural products, pharmaceutical compounds, membrane proteins, and amyloid fibrils (Lesage, 2009). Figure 2 shows the ¹³C NMR spectra from samples S-GE, and S-T1G, indicating the obtained signals in ppm.

Table 2. Signals obtained from silica-chitosan materials using ¹³C-NMR spectroscopy

Sample	Signal (ppm)							
	C1	C2	C3	C4	C5	C6		
SCh-TT ₁	103.6	61.1	76.8	84.4	62.5	64.5	-----	17.7
SCh-T ₁	105.1	61.1	77.4	86.5	64.5	66.3	18.9	17.9
SCh-GE	102.9	61.0	76.9	84.0	61.0	64.0	18.4	18.0

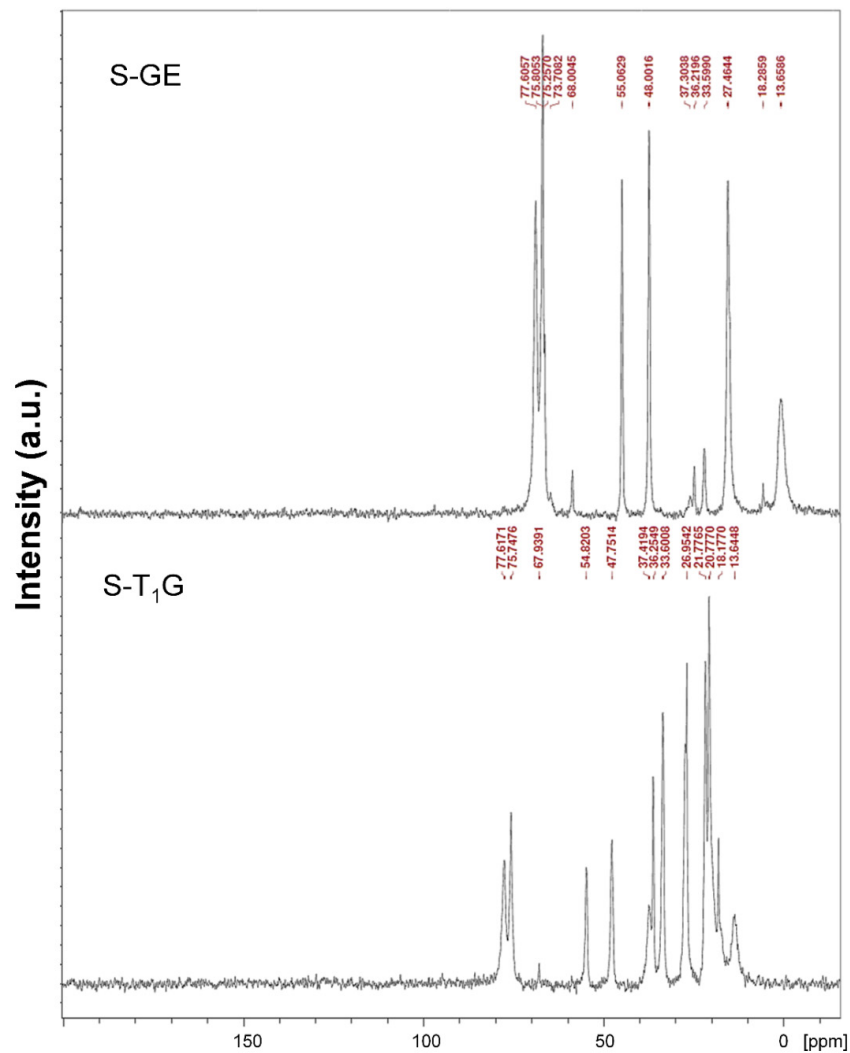


Figure 2. ^{13}C NMR spectra from samples S-GE and S-T₁G

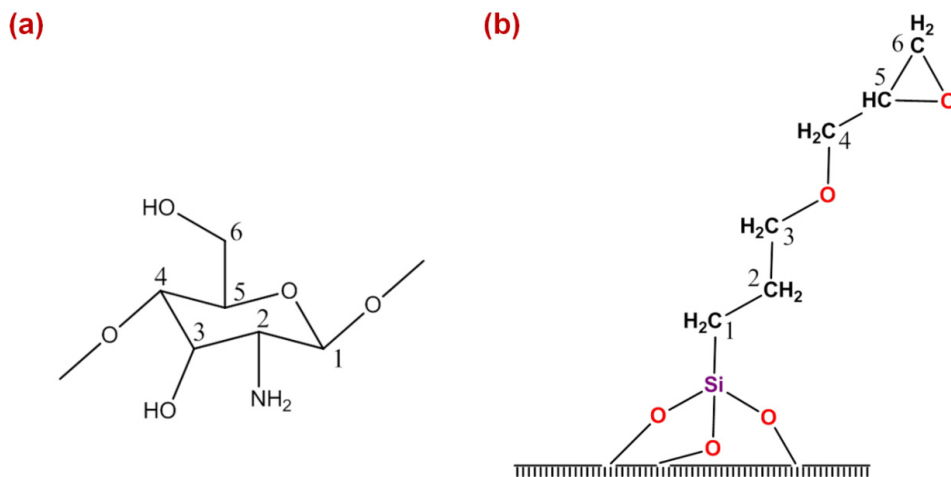


Figure 3. a) Structural unit of chitosan biopolymer indicating carbon numbers to establish the spectroscopic assignments in ^{13}C NMR. b) Schematic representation of a GPTMs unit grafted onto the surface of a polyalkoxysilane showing the spectroscopic designations of each C

Spectral assignments in solid-state ^{13}C NMR of SCh-TT₁, SCh-T₁, and SCh-GE are shown in Table 2. The carbon numbers are indicated in structure of the Figure 3b. The signals at 18.9 ppm and 17.7 and 17.9 ppm indicate the presence of the corresponding organoalkoxysilanes.

Solid-state ^{13}C -NMR showed that there was no cleavage of Si-C bonds. Likewise, the oxirane functional group remained at the experimental reaction conditions. In solids, because of the absence of high-amplitude molecular motions, resonance shapes detected in static samples, will strongly depend on the symmetry of tensors σ (or δ) and chemical shift anisotropies. Significantly smaller anisotropies can be observed for nuclei ^1H , ^{13}C , ^{27}Al , and ^{29}Si , which are also used as target nuclei in studies of different materials. The oxirane groups in GPTMS may undergo epoxy opening when reacted with carboxylic acid, thus leading to the formation of primary and/or secondary alcohols. At the same time GPTMS may crosslink via hydrolysis and condensation of alkoxy silane fragments forming species containing Si-O-Si moieties under the acid conditions provided by carboxylic acid. However, the ^{13}C CP efficiencies are generally different among different carbons depending on their spatial vicinity to protons in the system. As a result, the observed signal intensities of ^{13}C -NMR may not relate directly to the number of ^{13}C nuclei present to the different functional groups. However, in this case, the signals (δ_{C}) of Si-C at about 10.8 ppm and 13.6 ppm in all polyalkoxysilanes, and about 19.0 ppm and 21.8 ppm when TMPS was in the compounds (Fig 2, bottom), confirmed that cleavage of Si-C bond had not occurred. Additionally, the signals between 73.1 to 75.8 ppm, and 74.9 to 77.6 ppm correspond to C4 and C3, respectively, and Si-O-C. Similarly, the signals at 47.8 ppm (C6) and 54.9 ppm (C5) indicate that the opening of the oxirane function did not occur during the synthesis of polyalkoxysilanes, as shown in Figure 2 and Figure 3b.

The FT-IR spectra shown in Figure 4 and Figure 5 depict differences and similarities between the structure of the obtained polyalkoxysilanes and their respective chitosan hybrids. The absorption IR spectra of chitosan and its hybrids are complex due to complicate and specific network of H-bonds, in which the -OH, C=O and, NH groups are involved, and to typical broadness of the IR bands of natural polymers (Duarte, Ferreira, Marvao, & Rocha, 2002).

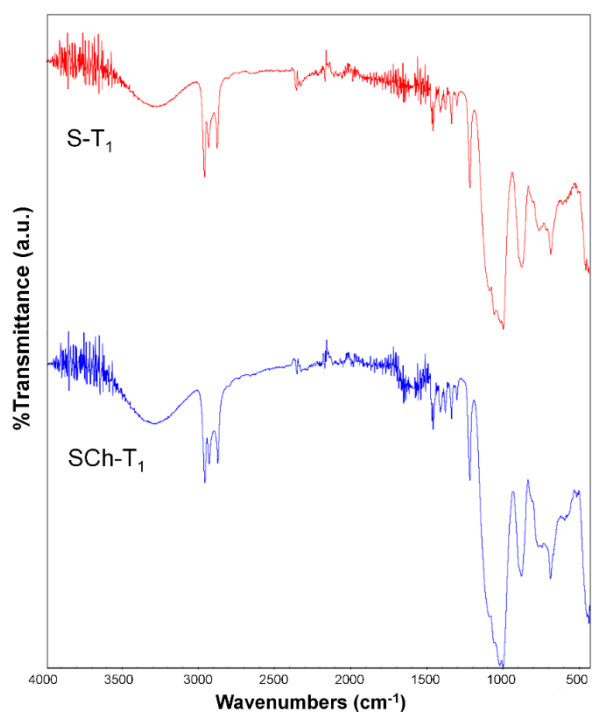


Figure 4. Infrared spectroscopy of samples S-T₁ and SCh-T₁

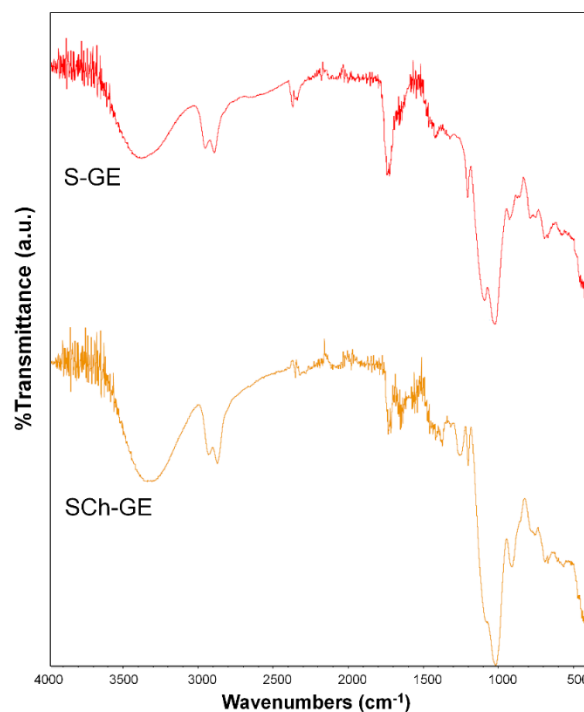


Figure 5. Infrared spectroscopy of samples S-GE and SCh-GE

FT-IR spectroscopy results of silica-chitosan samples depicted in Figure 4 and Figure 5 showed absorption in the domain of -OH, -NH₂, and Si-O functional groups as a result of the reaction of carboxylic groups in citric acid with organoalkoxysilanes. This reaction allowed chitosan to react with the free -OH from citric acid. The peaks

centered at 2850 and 2920 $\bar{\nu}$ (cm^{-1}) are due to C–H_{str} (C–H stretching) and 1450 cm^{-1} for C–H_{bend} (C–H bending). The bands at 1100 and 1000 cm^{-1} can be assigned due to Si–O–Si_{str} from cage-structured, and incompletely condensed linear/network siloxanes, respectively. The characteristic Si–O–Si band at 1100 cm^{-1} for a cage is due to its highly symmetric structure. The peak centered at 905 cm^{-1} confirmed the presence of Si–OH from incompletely condensed cage-structured and incompletely condensed linear/network siloxanes. Moreover, the peak at 3400 cm^{-1} suggests the presence of adsorbed water/alcohol. However, the spectroscopic band at 3400 cm^{-1} in samples of chitosan hybrid is more pronounced due to the free hydroxyl groups present in that molecule, as evident in Figure 4 and Figure 5. For example, the hydroxyl group of the SCh-T₁ hybrid (Figure 4, bottom) is more pronounced than in the S-T₁ polyalkoxysilane (Figure 4, top). The absorption peak at 1730 cm^{-1} in S-GE is characteristic of the ester obtained by reacting citric acid with GPTMS, confirming that the esterification reaction was performed successfully (Figure 5, top), whereas in SCh-GE hybrid (Figure 5, bottom) this peak is not present. This is possibly the result of the reaction of the hydroxyl group in C6 of the chitosan (Figure 3) with the silicon in GPTMS and not with the oxirane group; that can be confirmed by the disappearance of oxirane group in ¹³C-NMR (Figure 2, top) and the appearance of the signal of a carbonyl group observed in the infrared spectra that does not appear in the silica-chitosan hybrid, as evidenced in Figure 5.

Table 3 shows the weight loss obtained by TGA for polyalkoxysilanes and silica-chitosan hybrids. In general, the main-weight loss of the samples were located in two ranges of temperature.

Table 3. TGA results showing a main-weight loss between 375 °C and 700 °C

Sample	375-475 °C (%)	475-700 °C (%)
S-T ₁		31*
S-T ₁ -f		35*
S-T ₁ -c		31*
S-G-c		41*
S-GE	30	20
S-T ₁ G	25	20
S-T ₁ E	5	45
S-TT ₁		18*
S-TT ₁ G	20	15
S-TGE	30	20
S-T ₁ GE	30	25
S-TT ₁ GE	15	25
SCh-TT ₁		15*
SCh-T ₁	10	30
SCh-GE	30	10

* Samples have a single transition between 375 and 700 °C.

Thermograms of prepared materials showed a gradual loss of about 4% up to 200 °C, a significant loss above 375 °C, leading to an approximately 40% thermally stable residue at 700 °C. The weight loss taking place above 375 °C is attributed to the degradation of the alkyl chain with production of volatiles, which end up with a thermally stable Si–O–Si residue at 700 °C.

The thermograms of selected polyalkoxysilanes and silica-chitosan materials are shown in Figure 6 and 7. As previously mentioned, due to their DSC behavior some polyalkoxysilanes, such as S-T₁, S-T₁-f, S-T₁-c, were chosen to synthesize the hybrid SCh-T₁, as shown in Figure 6. In the same way, S-TT₁ was used to prepare SCh-TT₁ in order to determine the presence of a similar endotherm (Figure 7c). Also, due to the presence of an exotherm in the polyalkoxysilane S-GE the hybrid SCh-GE was synthesized (Figure 7c).

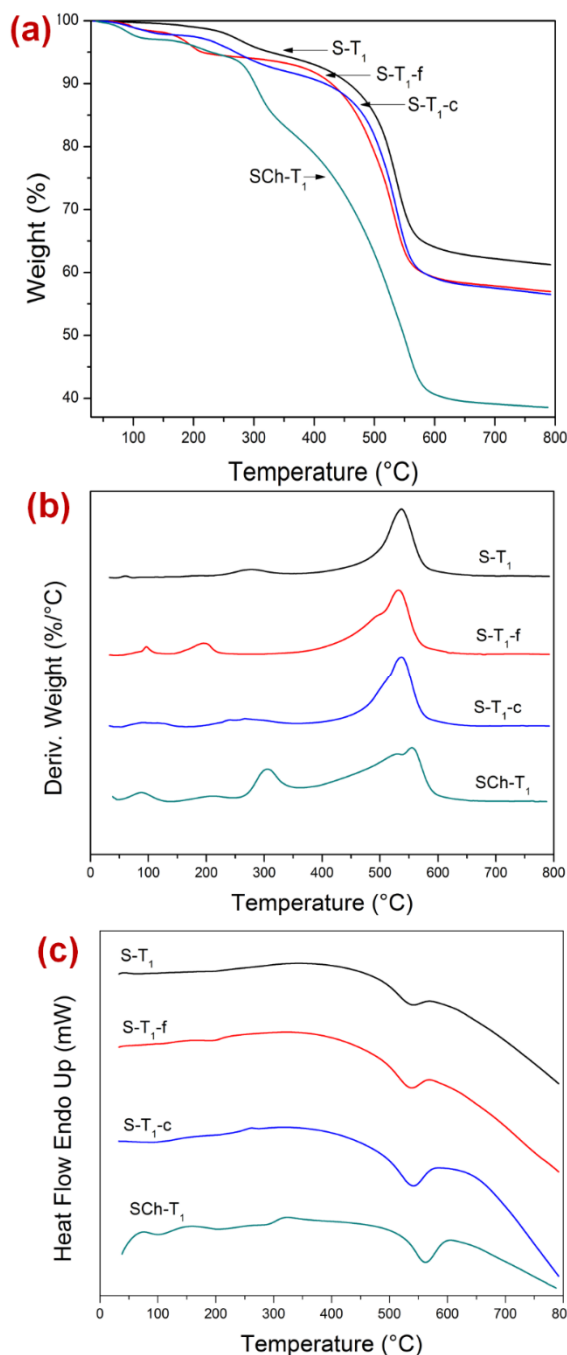


Figure 6. (a) TGA and (b, c) DSC thermograms of S-T₁, S-T₁-f, S-T₁-c, and SCh-T₁

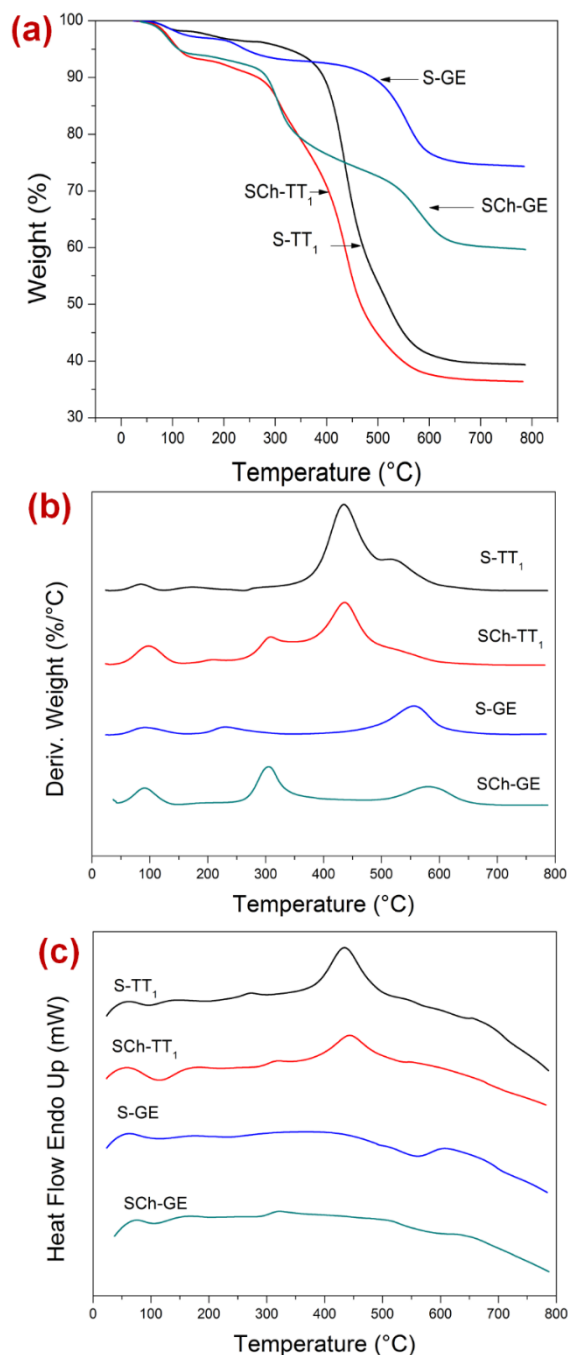


Figure 7. (a) TGA and (b, c) DSC thermograms of S-GE, S-TT₁, SCh-GE, and SCh-TT₁

As shown in Figure 6, differences in thermal behaviour of polyalkoxysilanes are evident according to the media: acetic (S-T₁), formic (S-T₁-f), or citric acid (S-T₁-c), compared to the hybrid SCh-T₁. While S-T₁ and S-T₁-f show only endothermic transitions, S-T₁-c and SCh-T₁ exhibit endothermic, as well as exothermic transitions (Figure 6c). In S-Ch-T₁ a shift of 68°C and 27°C was found in the exotherm and endotherm, respectively, compared to S-T₁-c. More importantly, chitosan formulated materials transitions showed a wider DTGA area (Figure 6b).

TGA results of silica-chitosan hybrids SCh-T₁ (Figure 6a) and SCh-TT₁ (Figure 7a), show that their weight loss is slower, indicating that the degree of polymerization is probably lower than the samples without chitosan. The gradual mass loss below 150 °C shown in Figure 6a and Figure 7a may be due to the evaporation of adsorbed water molecules formed through the condensation of silanol (Si-OH) groups, the vaporization of trapped solvent

in the compound, as well as decomposition of low molecule weight polyalkoxysilanes, and other trapped impurities. Also, at 800 °C the hybrid of SCh-T₁ had lost more than 60 % of its weight, indicating that after adding chitosan, the heat-resistant property decreased, compared to S-T₁, S-T₁-f, S-T₁-c (Figure 6a). Nevertheless, this did not occur in SCh-GE (Figure 7a), where after adding chitosan, the sample slightly increased its heat-resistant property, compared to S-GE. Furthermore, the molecular weight distribution for SCh-GE was broader, and the degree of polymerization was probably lower, due to the polymer converting at lower temperatures.

Table 4 shows the maximum transition temperature (T_{peak}) found by DSC of polyalkoxysilanes and silica-chitosan hybrids materials.

Table 4. DSC transitions of polyalkoxysilanes and silica-chitosan hybrids materials. Values in parentheses correspond to the maxima of the derivative weight loss obtained by TGA.

Sample	Exotherm (°C)	Endotherm (°C)
S-T ₁	-	541 (534)
S-T ₁ -f	-	192, 536 (197, 529)
S-T ₁ -c	256 (261)	535 (530)
S-G-c	418 (417)	-
S-GE	434 (435)	-
S-T ₁ G	431 (426)	567 (548)
S-T ₁ E	-	557 (511)
S-TT ₁	-	233, 557 (232, 558)
S-TT ₁ G	435 (435)	576 (546)
S-TGE	433 (433)	-
S-T ₁ GE	430 (442)	554 (517)
S-TT ₁ GE	439 (450)	538 (521)
SCh-TT ₁	345 (305)	negligible (580)
SCh-T ₁	324 (306)	562 (555)
SCh-GE	325, 450 (313, 440)	-

Also shown is a comparison of DSC transitions and the maximum values of the derivative weight loss obtained by TGA. For example, the difference in the exothermic and endothermic transitions found in S-T₁, S-T₁-f, and S-T₁-c are due to the different media used for preparing each polyalkoxysilane. While the exotherms can be easily attributed to the cleavage of Si—Si and Si—C, resulting in a weight loss at the indicated temperature, the endotherm can be attributed to the melting point of polyalkoxysilanes.

4. Conclusions

Polymerization of polyalkoxysilanes of TEOS, TMPS, GPTMS, and EOS with acetic, formic, and citric acid was done through sol-gel process. Through characterization by FT-IR, TGA, DSC, and solid-state NMR it was possible to confirm the successful polymerization of alkoxy silanes and obtain detailed quantitative information on the different kinds of silicon sites. Solid-state ¹³C-NMR showed that there had been no cleavage of Si—C bonds. Likewise, the oxirane functional group remained at the experimental reaction conditions. However, when reacted to carboxylic acid it lead to epoxy opening forming primary and/or secondary alcohols. The exotherms obtained by TGA, can be easily attributed to the cleavage of Si—Si and Si—C, where the presence of Si—C in polyalkoxysilanes was confirmed by ¹³C NMR. The endotherms in DSC are attributed to the melting point of polyalkoxysilanes.

FT-IR spectra showed differences and similarities between the structure of the obtained polymers using citric acid and chitosan. Silica-chitosan materials obtained by TMPS, TEOS/TMPS, and GPTMS/EOS presented similar infrared spectroscopic results; this suggests no significant changes regarding chemical composition. On the contrary, for the citric acid and GPTMS reaction, the infrared spectrum indicated the formation of an ester by opening the oxirane functionalization. It was also found that citric acid was too weak to react itself with the

organoalkoxysilanes. Therefore, if a polymerization of organoalkoxysilanes with carboxylic groups is intended, a higher concentration of carboxylic acid in water should be used. Since citric acid is solid and has to be dissolved in water first, it is adequate as a reactant but rather as a catalyst for the sol-gel reaction.

Acknowledgments

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