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Thermal stability of octadecylsilane hybrid silicas prepared by grafting and sol–gel methods

Rodrigo Brambilla [a], João H.Z. dos Santos [a,*], Márcia S.L. Miranda [b], Ray L. Frost [c]

[a] *Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500, Porto Alegre 91501-970, Brazil*
[b] *Braskem S.A., III Pólo Petroquímico, Via Oeste, Lote 05, Triunfo 95853-000, Brazil*
[c] *Inorganic Materials Research Program, Queensland University of Technology, 2 George St. Brisbane, Queensland 4001, Australia*

Abstract

Hybrid silicas bearing octadecylsilane groups were prepared by grafting and sol–gel (SG) methods. The effect of the preparative route on the thermal stability was evaluated by means of thermal gravimetric analysis (TGA), infrared emission spectroscopy (IRES) and, complementary, by ^{13}C solid-state nuclear magnetic resonance (^{13}C NMR) and matrix assisted laser deionization time of flight mass spectroscopy (MALDI-TOF-MS). Silicas prepared by the grafting route seem to be slightly more stable than those produced by the sol–gel method. This behavior seems to be associated to the preparative route, since grafting affords a liquid-like conformation, while in the case of sol–gel a highly organized crystalline chain conformation was observed.
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Keywords: Hybrid silica; Octadecylsilane; Infrared emission spectroscopy; Thermal gravimetric analysis; Sol–gel

1. Introduction

The so-called hybrid inorganic–organic materials combine properties such as resistance, thermal and chemical stability, among others, typical of ceramic derivatives with the capacity of specific physical–chemical interactions of organic moieties in a single material [1].

Among inorganic–organic materials, hybrid silicas have been largely investigated. Several preparative routes are described in the literature, among them, grafting reactions and the sol–gel (SG) method. In the former, commercial silica is reacted by the modifying molecule in a slurry system. The grafting takes place by chemical reaction between silanol groups (Si−OH) from the silica with ligands (such as chloride or alkoxides) from the modifying molecule. In this method, the thermal treatment temperature of the support influences on the grafted amount and on the nature of the surface species. In the case of hybrid silica prepared by the sol–gel method, silicon alkoxides are combined, involving two fundamental reactions: hydrolysis and condensation. In the first step, the hydrolysis led to the formation of Si−OH bonding, with alcohol release. In the second step, condensation reactions, producing water or alcohol, lead to the generation of siloxane (Si−O−Si) bonds, which generate the bulk skeleton of silica. The final product bears organic ligands on the surface. In this method, experimental parameters such as pH, reagents concentration, reaction time, aging time, influence on the texture and morphology of the resulting hybrid materials, as well as on the content and nature of the generated species [3].

One of the applications of hybrid materials is the dispersion of inorganic fillers, such as silica, in polymeric matrices in order to modify the viscoelastic, mechanical and reological properties, or even to engender new ones in the resulting composites. For this application, the role of the organic moieties in the hybrid material resides in conciliating the inorganic filler (silica, for instance) with the polymeric matrix, avoiding phase separation. [4] Besides, the organic moieties must be thermal stable, not suffering degradation during composite processing in the final polymer. Therefore, many studies in the literature deal with thermal stability of hybrid silica or polymer-hybrid silica composites, by characterizing them by thermogravimetrical analysis (TGA) [5–10]. A few have used infrared emission spectroscopy (IRES) for the characterization of such materials [11,12].

* Corresponding author. Tel.: +55 51 3316 7238; fax: +55 51 3316 7304.
E-mail address: jhzds@iq.ufrgs.br (J.H.Z. dos Santos).

In previous studies, we investigated the effect of the preparative route (grafting or sol–gel) of hybrid octadecylsilane silicas on the organosilane content and nature of the surface species, as well as on the textural and morphological properties [13,14]. As an extension of these previous studies, we report here the effect of the preparative route on the thermal stability of the resulting hybrid silicas, bearing octadecylsilane. Hybrid materials were characterized by TGA and IRES in order to evaluate the potential use of such materials as polymer compatibilizers.

2. Experimental part

2.1. Materials

Silica Wacker (HDK N20) was activated under vacuum ($P < 10^{-5}$ bar) for 16 h at different temperatures in the 100–450 °C range. Octadecyltrimethoxysilane (ODS) (Acros), octylsilane (Acros) and tetraethylorthosilicate (TEOS) (Merck) were used without further purification. Pure grade toluene (Nuclear) and ethanol (Merck) were deoxygenated and dried by standard techniques before use. Ammonium hydroxide (Merck) was purchased as a 25% solution. Sinapic acid (Aldrich, >99.0%) was used as matrix for MALDI-TOF-MS measurements.

2.2. Synthesis of xerogel by hydrolitic alkaline route

Xerogels were synthesized in accordance with Stöber synthesis [15]. In a typical preparation, 20 mL of ammonia solution was diluted in 100 mL of ethanol in a two-neck flask equipped with a mechanical stirrer. 5 mL of a TEOS ethanol solution (1:4; v/v) was added to that solution. The mixture was kept under stirring for 2 h. Then, the organosilane (ODS), 2.10 mmol diluted in ethanol (4 mL) were dropwisely added to the solution. The addition time last ca. 1 h 45 min. After the addition, the mixture was kept under stirring for more 2 h. The silica was then dried under vacuum and washed with 5 mL × 10 mL of ethanol and finally dried under vacuum for 16 h.

2.3. Synthesis of grafted silica

All the chemicals were manipulated under inert atmosphere using the Schlenk technique. ODS (1.57 mmol diluted in 10 mL of toluene) was added to thermally activated silica (ca. 2.0 g) and kept stirring for 1 h. The slurry was then heated to 80 °C, under reflux, for 2 h. The slurry was then filtered, and washed with 12 mL × 2 mL of toluene. The solid was finally dried under vacuum for 16 h.

2.4. Characterization of silicas

2.4.1. Elemental analysis (CHN)

Carbon content was determined in a PerkinElmer M-CHNSO/2400 analyzer.

2.4.2. ^{13}C Magic angle spin nuclear magnetic resonance (^{13}C MAS-NMR)

Solid-state NMR measurements of ^{13}C were performed on a Chemagnetics CMX-300 (Varian, USA). Samples were transferred to zirconia rotors. Measurements were performed at 75.3 MHz for ^{13}C. The number of scans was 5000 for ^{13}C. NMR parameters for ^{13}C were a contact time of 2 ms and a recycle time of 1 s.

2.4.3. Fourier transform infrared spectroscopy (FT-IR)

Transmission FT-IR spectra were recorded on a Bomem MB-102 Spectrometer, (32 scans at a 2 cm^{-1} resolution). The study was restricted to the mid-infrared region (4000–1300 cm^{-1}) due to strong bulk absorption of silica at lower wavenumbers. The samples analyzed by this technique consisted of 50–60 mg of silica pressed under 12 MPa into a self-supporting tablet (Ø = 17 mm) which was introduced into a Pyrex cell with CaF$_2$ windows. The unit was attached to a greaseless glass gas/vacuum handling system and the silica tablet was activated *in situ* under vacuum (<10^{-4} mbar) at temperatures between 100 and 400 °C for 16 h. Octadecylsilane impregnation was then conducted from a toluene solution containing an amount of organosilane calculated to produce the same carbon content as determined by elemental analysis, when silica was pretreated at the same temperature.

Infrared emission spectra were obtained using a Nicolet Nexus 870 FT-IR spectrometer equipped with a liquid N$_2$-cooled TGS detector. The spectrometer had been modified by replacing the infrared source with a home-built emission cell. A small amount of the sample was placed on a 6-mm diameter Pt surface and held in an inert atmosphere within a N$_2$-purged cell during heating process. The spectra were recorded at 50 °C intervals in the 100–1000 °C range and different numbers of scans were collected depending on the temperature actually being investigated. All spectral manipulations, including baseline correction, smoothing and normalization, were performed using the software package GRAMS®(Galactic Industries Corporation, Salem, NH, USA). The band component analysis was achieved using PeakFit software (Jandel Scientific, CA, USA).

2.4.4. Thermogravimetric analysis (TGA)

TGA experiments were carried on a Universal V2.6D (Ta Instruments). Samples were heated from 0 to 1000 °C in a 20 °C min^{-1} rate under nitrogen or air atmosphere.

2.4.5. Matrix assisted laser dionization time of flight mass spectroscopy (MALDI-TOF-MS)

Measurements were performed in Applied Biossystem Tof/Tof spectrometer, bearing a deionization MALDI source of Nd:YAG laser operating at 200 Hz. Samples were prepared as a slurry, mixed with sinapic acid as matrix and deposited on a spotter in triplicate.

2.4.6. Small angle X-ray scattering (SAXS)

The SAXS experiments were carried out using synchrotron radiation at LNLS (Campinas, Brazil) with a wavelength

$\lambda = 1.488$ nm. The beam was monochromatized by a silicon monochromator and collimated by a set of slits defining a pin-hole geometry. A solid-stated CCD detector (MAR 160) was used to collect two-dimensional (2D) images with 2048×2048 pixels located at 6752.5 mm of the sample. The angular range of the scattering curves was 0.02 nm$^{-1} \leq q \leq 0.49$ nm^{-1}, where q is the scattering vector ($q = (4\pi/\lambda)\sin(\theta/2)$). The data were corrected for sample transmission and background scattering using an empty cell as reference. Samples were placed in stainless steel sample holders closed by two mica windows.

3. Results and discussion

In the present work, TGA was employed in the evaluation of the thermal stability of the ODS groups present on the surface of the chemically modified silicas produced by both grafting and sol–gel methods.

Fig. 1 shows a typical thermogram (nitrogen atmosphere) of silica GR100 produced by grafting (GR), which was previously activated at 100 °C.

The thermogram shown in Fig. 1 presents a small mass loss (0.7%) in the range of 100–250 °C, probably due to water and toluene release. However, a higher mass loss amount (7.7%) was observed in the range of 250–550 °C, which can be assigned to the octadecylsilane loss. Similar results have been reported in the literature [16,17].

Fig. 2 shows the transmission FT-IR spectra of GR100 at room temperature and after thermal treatment in the range of 100–400 °C. In each step, the system was kept under isothermal condition for 1 h under vacuum.

According to Fig. 2, after heating the system at 100 °C, the large band centered at ca. 3400 cm^{-1} is reduced probably due the removal of adsorbed water or methanol, which were inter-acting with surface silanol groups by hydrogen bonding. An increase in intensity in the band associated to the isolated silanols (3747 cm^{-1}) can be observed. This increase up to 300 °C can be attributed to condensation reactions between vicinal silanol groups, generating isolated silanol ones and siloxane bondings [2].
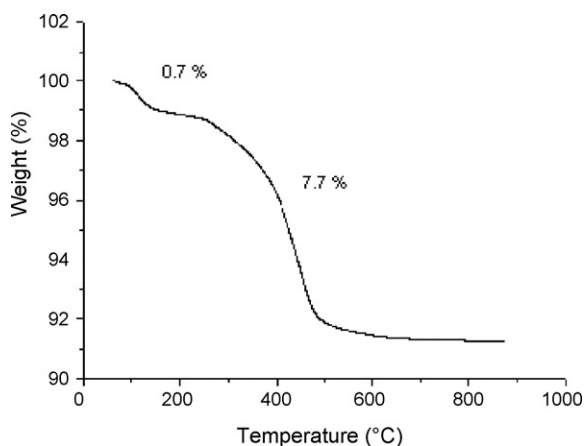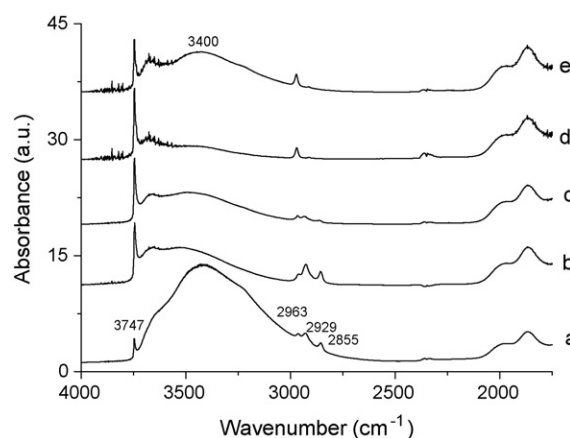

Fig. 2. FT-IR spectra of GR100 system: (a) 25 °C and after thermal treatment under vacuum for 1 h at: (b) 100 °C; (c) 200 °C; (d) 300 °C and (e) 400 °C.

Regarding the alkyl stretching region, after heating up to 200 °C, the bands at 2963, 2929 and 2855 cm^{-1}, assigned to symmetrical and asymmetrical $\nu_{(C-H)}$ of CH$_2$ and CH$_3$ groups from ODS, [18] are reduced. Heating as high as 400 °C engenders a reduction in the isolated silanol band (3747 cm^{-1}), suggesting that probably the hydrogen from the silanol group is participating in the cleavage of the alkyl ligands from ODS at these higher temperatures. It is worth noting that the dissociation energy of C–C (alkanes), Si–C, Si–O and C–H (alkanes) bonds are, respectively, 331, 306, 444 and 413 kJ mol^{-1} [19]. Therefore, Si–C and C–C bonds are relatively weak. Probably, the decomposition products are hydrocarbon derivatives (C$_x$H$_y$), as observed in the case of analogous alkyl silicon hydrides and alkylphosphonic acids immobilized on silica, alumina and zir-conia [20].

Fig. 3 shows the thermogram of a hybrid silica (SG10) produced by the sol–gel method, in a ODS to TEOS ratio 1:10.

The thermogram in Fig. 3 shows little mass loss (6%) in the range of 70–250 °C, probably due to removal of ethanol and water generated during the synthesis and encapsulated within the silica matrix [21]. Nevertheless, a significant loss (24%) was observed in the range of 250–550 °C due to ODS degradation [16,17].

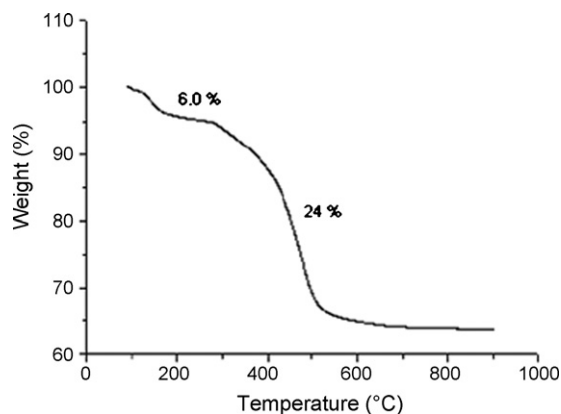Fig. 1. Thermogram of GR100 system in N$_2$ atmosphere. Rate: 20 °C min^{-1}.

Fig. 3. Thermogram of SG10 system in N$_2$ atmosphere. Rate: 20 °C min^{-1}.

Table 1
Maximum temperatures and weight loss of octadecylsilane groups for hybrid silicas produced by grafting and sol–gel routes

Silica	T_{max} (°C)[a]	Mass loss (%)[a]	Carbon (%)[b]
GR100	518	7.6	3.5
GR200	540	2.4	1.9
GR450	477	2.1	1.2
SG2	501	51.1	53.4
SG10	474	24.5	19.9
SG10[c]	352	19.9	19.9

[a] Obtained by TGA/DTG.
[b] Obtained by elemental analysis.
[c] Analyzed under air atmosphere.

Table 1 shows the maximum temperature determined by TGA, the mass loss percentage associated to ODS groups and carbon content measured by elemental analysis for the hybrid materials produced by grafting and sol–gel methods.

The maximum temperature of ODS mass loss shown in Table 1 were determined by derivative thermogravimetric (DTG) analysis. According to these data, the T_{max} laid between 350 and 550 °C, i.e., an enough high temperature higher than that usually employed in polymer processing. Silicas prepared by the grafting route seem to be a little more stable than those produced by the sol–gel method. Taking into account those prepared by the grafting route, the more stable hybrid silica was that, which support was previously treated at 200 °C (GR200). In the case of the sol–gel route, SG2A (produced by ODS to TEOS ratio 1:2) was that with higher thermal stability. Kulkarni et al. observed that in octadecylsilane self-assembled monolayers on a flat surface (Si (1 1 0) substrate), the alkyl chains were highly organized and packed, bearing lower thermal stability (252 °C) in comparison to those disposed on spherical silicas (352 °C), in which the alkyl chains were twisted [16]. It is worth mentioning that in our systems, in our hybrid silicas, the chain conformation depends on the preparative route: grafting affords a liquid-like conformation, while in the case of sol–gel, a highly organized crystalline chain conformation was observed [13,14]. Therefore, a similar trend as that observed by Kulkarni et al. [16] is found in the present systems in terms of thermal stability.

Complementary measurements were carried on by small angle X-ray scattering, which allowed determining the characteristic distance (d) assigned to the aggregated silica primary particle, separated by the octadecyl chains. Table 2 shows the characteristic distances for hybrid silicas prepared by both methods. For comparative reasons, data obtained with the hybrid silica, chemically modified with a shorter alkylchain, i.e., octadecylsilane (OCS), is also included.

Table 2
Characteristic distances for the hybrid silicas determined by SAXS

Hybrid system	d (nm)[a]
SG10	151
GR100	72
SG (OCS)	80

[a] $d = 2\pi/q_{max}$.
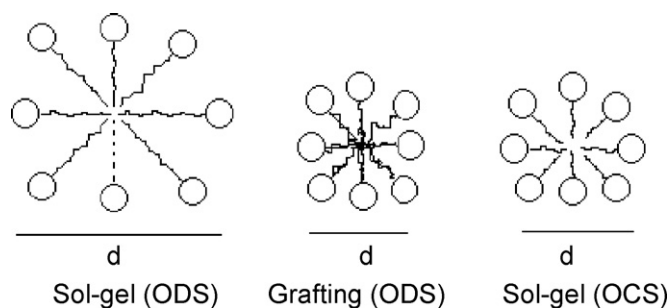
Scheme 1. Particle aggregation in hybrid silicas prepared by the sol–gel and grafting methods (d = characteristic distance).

As shown in Table 1, the hybrid silica prepared by the sol–gel method presented a longer characteristic distance (151 nm) in comparison to that produced by the grafting reaction (72 nm). These results suggest that the primary silica particles are displayed in a more separated configuration, probably due to a lower interaction among alkyl chains from ODS, which in turn engender a more crystalline (all-trans) conformation. On the other hand, the lower distance observed in the case of GR100 indicates that the primary particles are closer and the alkyl chains might be twisted, affording a liquid-like conformation (see Scheme 1). It is worth noting that the hybrid silica produced with a shorter alkyl chain (OCS), depleted of the capacity of entangling, present a much lower characteristic distance (80 nm), if compared to SG10 (151 nm). These results suggest that the organic group attached to the silica surface might influence on the textural characteristics of the resulting hybrid material.

According to Table 1, TGA under air atmosphere affords a reduction on the maximum temperature loss from 474 to 352 °C, due to combustion of ODS chains by oxygen. This data is important since in the case of polymer processing, the procedures are carried out in the air.

Concerning carbon percentage determined by elemental analysis and TGA, both values are proportional, i.e., the higher carbon content, the higher the mass loss percentage due to ODS release.

The thermal stability of such hybrid silicas was further evaluated by infrared emission spectroscopy (IRES). Fig. 4 shows a series of infrared spectra of GR100 in the temperature range of 100–900 °C between 4000 and 500 cm^{-1}.

According to Fig. 4, heating up to 200 °C affords a reduction in the large band centered at 3400 cm^{-1}. This reduction can be attributed to physically adsorbed water desorption (dehydration). In the range of 200–450 °C, the band at 3200 cm^{-1} assigned to surface silanol interactions is reduced, leading to an increasing in the band at 3747 cm^{-1}, attributed to isolated silanol groups. As observed in the case of transmittance FT-IR (Fig. 2), the condensation of vicinal and germinal silanol groups engenders the formation of isolated silanol ones (accompanied with the formation of siloxane bonds) [2]. For temperature higher than 450 °C up to 900 °C, the band assigned to isolated silanol groups (3747 cm^{-1}) is reduced due to condensation reactions and structural reorganization with generation of siloxane groups. According to the literature, after 800 °C, the formation of siloxane rings in the silica structure is irreversible [22]. One cannot
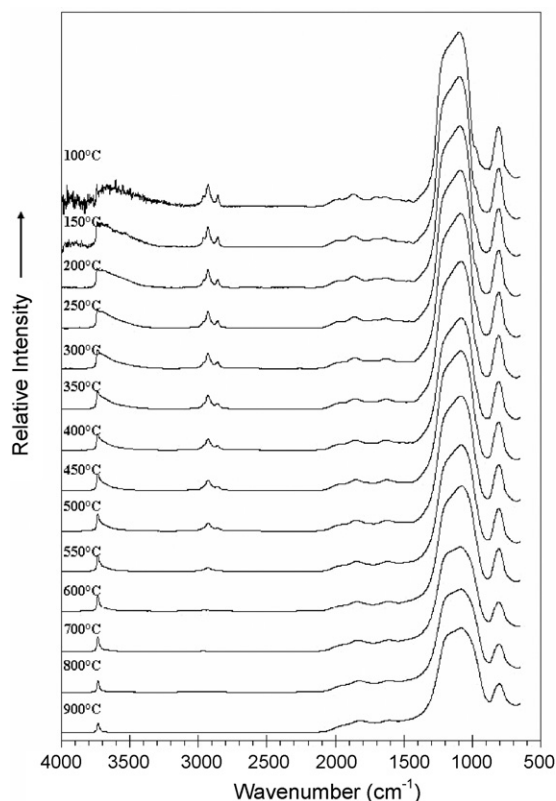
Fig. 4. IRES spectra of GR100 system. Heating in the range of 100–900 °C.

Fig. 5. IRES spectra of SG10 system. Heating in the range of 100–900 °C.

neglect, as already mentioned, that the reduction in intensity of such band can be associated to the cleavage of Si–C and C–C bonds in the ODS groups.

Concerning the $\nu_{(C–H)}$ stretching region, the bands at 2963, 2929 and 2855 cm^{-1} are reduced in the range of 250–550 °C. This reduction in intensity can be attributed to the thermal degradation of ODS chains, being in accordance with the results observed by TGA.

Fig. 5 presents the IRES spectra of the system produced by the sol–gel method: SG10.

According to Fig. 5, the bands at the $\nu_{(O–H)}$ stretching region present a similar behavior as that already commented in the case of hybrid silica produced by grafting (Fig. 4). Concerning the bands attributed to the $\nu_{(C–H)}$ stretching, they are much more intense, due to the higher ODS content achieved by the sol–gel method. The temperature range of ODS loss is roughly the same (250–550 °C) observed in the case of GR100.

In order to better evaluate the thermal stability of such systems, the relative band area in the $\nu_{(C–H)}$ region in the IRES spectra was monitored along the temperature treatment. Fig. 6 shows these values along the temperature heating for GR100 and SG10.

According to Fig. 6, both hybrid silicas showed reduction in band area along the heating treatment. Comparing both systems, in the GR100 the reduction is monotonous up to 500 °C. Then, a sharp decreasing is observed up to 600 °C. In the case of SG10, up to 500 °C the band area is reduced one third of the initial value, and then sharply reduced up to 600 °C. Such results confirm the higher thermal stability of the hybrid silica prepared by the
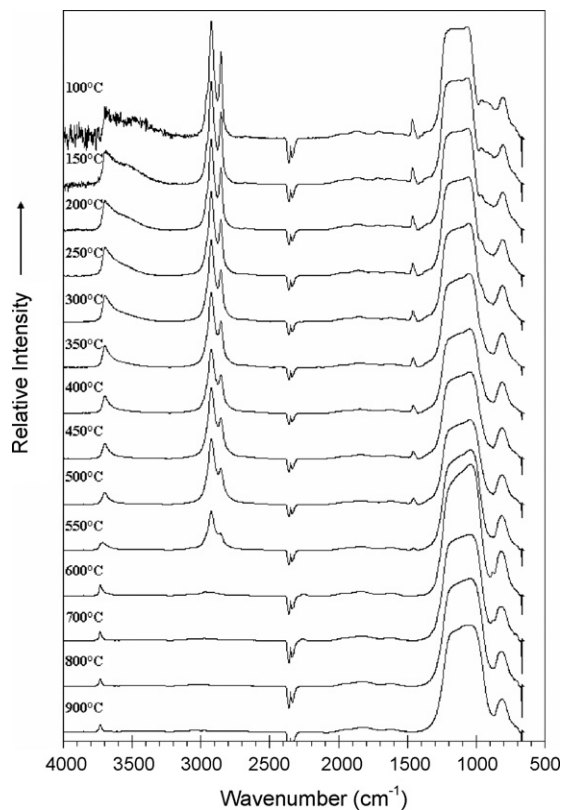
grafting method in comparison to that prepared by the sol–gel method.

In a previous work, we investigated the effect of the preparative route on the conformation of the octadecylsilane chains. As already mentioned, silicas prepared by sol–gel were characterized by a crystalline conformation [13]. Thus, in order to investigate the effect of the temperature on this system, a hybrid silica prepared by sol–gel was analyzed by solid-state ^{13}C NMR spectroscopy at room temperature and after heating. Fig. 7 shows the ^{13}C NMR spectra of SG10, before and after heating at 120 °C for 4 h.
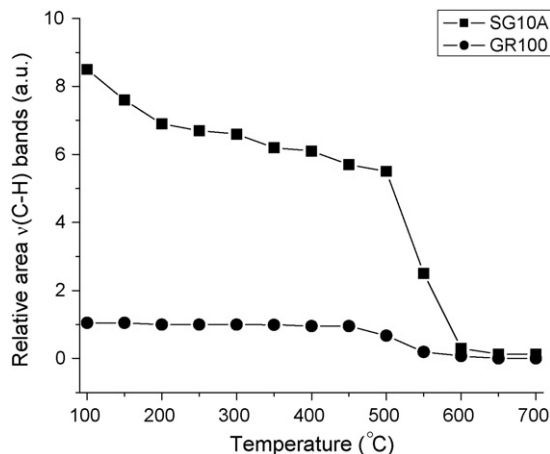

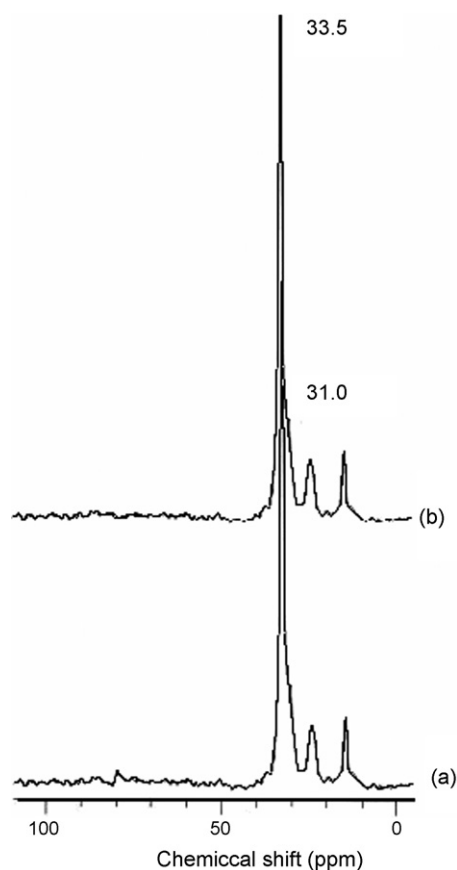Fig. 6. Relative area of $\nu_{(C–H)}$ bands *versus* temperature for GR100 and SG10 hybrid silicas.

Fig. 7. Solid-state ^{13}C NMR spectra of octadecylsilane hybrid silica SG10, in which ODS was added two hours later: (a) before and (b) after heating at 120 °C for 4 h.

the low intensity of the signal placed at 31.0 ppm. In the literature, the effect of temperature on the alkyl chain conformation was already investigated in the cases of systems resulting of the chemically modification of commercial silicas. In such systems, the loss in the chain organization was already reported even for temperature lower than 120 °C [23–25]. However, in the present study, this behavior was not observed, which suggests that hybrid silicas produced by the sol–gel method, in which ODS was added two hours after the addition of TEOS, present highly organized ODS chains, which conformation was stable up to 120 °C.

The hybrid silicas were further characterized by MALDI-TOF-MS in order to investigate the nature of the surface species produced according to each preparative route. Laser-induced desorption techniques have been employed for the characterization of the chemical nature of organic-modified silicas [26,27]. Fig. 8 shows MALDI-TOF-MS spectra of the hybrid silicas GR100 and SG10, using sinapic acid as matrix.

According to Fig. 8, the spectra of both hybrid silicas present a sign in $m/z = 458$, possibly assigned to a cyclic tetramer formed by siloxane and vicinal silanol groups. Peaks at $m/z = 453$, 472, 496, 523, 524, 551 and 552 can be attributed to matrix (sinapic acid) fragmentation. The mass spectrum of the hybrid silica produced by the sol–gel method (SG10) showed a sign at $m/z = 579$, which could be assigned to cyclic structure containing a ODS group. This peak is not observed in the case of silica chemically modified by grafting (GR100). The presence of such structure in SG10 could be one of the factors which lead to a lower stability found in the hybrid silicas prepared by the sol–gel method, as observed by TGA. As shown in the fragment ($m/z = 579$) proposed in Fig. 8, the presence of silanol and ethoxide groups in the neighborhood of the ODS chains might promote the Si–C and C–C scission, affording in turn lower thermal stability for such systems. One cannot neglect the presence of residual alkoxy and silanol groups in the hybrid silica prepared by the sol–gel method, which could suffer condensation reactions, contributing, therefore, also to the lower
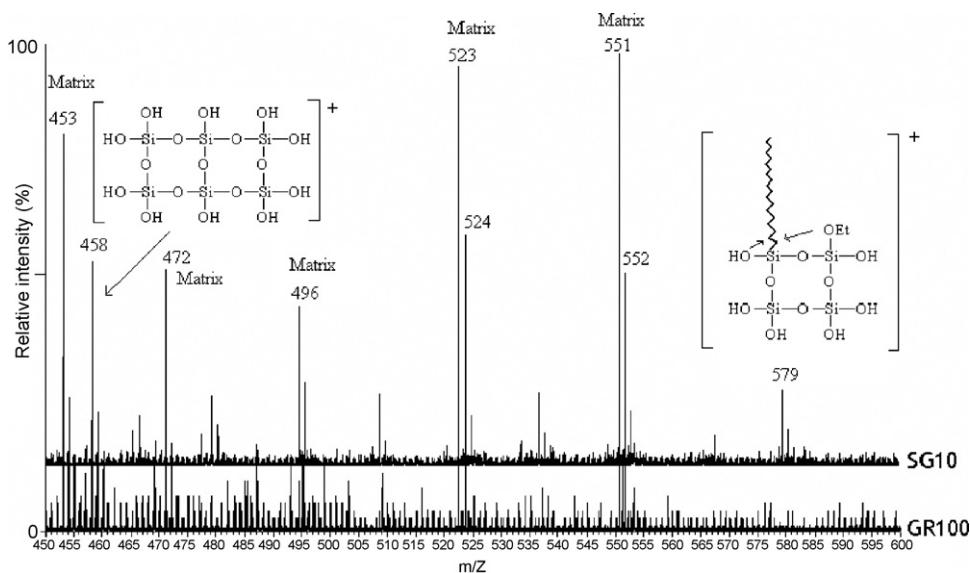
According to Fig. 7, no change in the ODS alkyl chain conformations was observed after heating the hybrid silica up to 120 °C, i.e., the chains remained highly organized (*trans*), which is evident by the high intensity of the signal at 33.5 ppm and

Fig. 8. MALDI-TOF-MS spectra of GR100 and SG10. Matrix: sinapic acid.

thermal stability exhibited by the hybrid materials prepared by this route.

4. Conclusions

The conformation achieved according to the preparative route of octadecyl-modified silicas influences on the thermal stability of such hybrid materials. According to MALDI-TOF-MS, some patterns are absent or present depending on the material if it was prepared by the sol–gel or grafting method. The materials are stable at least up to 250 °C, which guarantees a potential use of such materials as polymer fillers. The conformation of the alkyl chains seems to determine the thermal stability of these hybrid silicas. A liquid-like conformation, in which the alkyl chains are twisted, affords a higher thermal stability than the crystalline conformation. The behavior of such hybrid materials incorporated in polymer matrixes is under investigation.

Acknowledgements

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