Solid-State ^{17}O NMR Characterization of PDMS−M_xO_y (M = Ge(IV), Ti(IV), Zr(IV), Nb(V), and Ta(V)) Organic−Inorganic Nanocomposites

Beatriz Julián,[†,‡] Christel Gervais,[‡] Marie-Noëlle Rager,[§] Jocelyne Maquet,[‡]
Eloisa Cordoncillo,[†] Purificación Escribano,[†,||] Florence Babonneau,[‡] and
Clément Sanchez*[,‡]

Departamento de Química Inorgánica y Orgánica, Campus de Riu Sec, Universitat Jaume I, 12071, Castellón, Spain, Laboratoire de Chimie de la Matière Condensée, UMR−CNRS 7574, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France, and Service de RMN, UMR 7576, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

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PDMS−M_xO_y (where M = Ge(IV), Ti(IV), Zr(IV), Nb(V), and Ta(V)) hybrid materials have been studied from the solution to the solid state through ^{17}O NMR spectroscopy. Si−O−Si, Si−O−M, and M−O−M oxo bridges could be identified, giving a better picture of the structure of these hybrid materials based on amorphous metal−oxo nanodomains embedded within the siloxane network. The quantitative accuracy of the spectra is investigated and the relative nanoscale phase separation depending on the nature of the metal is discussed.

Introduction

Hybrid materials in which organic and inorganic components are combined in the nanometer range can be used in application fields such as electronics, photonics, biology, catalysis, sensors, and mechanics.[1−3] The interest of these hybrids is focused not only in their compositional and structural versatility but also in the special properties conferred by the coexistence of the different components in a unique material.[4,5] Furthermore, the double nature of these nanocomposites permits the material to be used as a host matrix for incorporating species with specific properties such as luminescent or photochromic organic dyes,[2,6] luminescent rare earth ions,[7−10] and species with NLO properties. The control of the organic−inorganic interactions is especially important in these kinds of multifunctional materials.

An interesting family of nanocomposites based on poly(dimethylsiloxane) (PDMS) incorporating metal−oxo species have been widely studied since the 1980s.[11−13] The introduction of metal−oxo nanoparticles within the siloxane network strongly modifies the structure of the polymeric material and allows the modulation of parameters such as the thermal expansion coefficient, chemical stability, refractive index, and mechanical properties.[14−17]

These hybrid nanocomposites can be easily synthesized in situ at room temperature from molecular precursors, through hydrolysis and condensation reactions. They have been described as materials in which linear PDMS chains, constituted by D_2 units ($(-O(CH_3)_2SiO-)_n$), are cross-linked by metal−oxo species through Si−O−M linkages.[18,19] Previous studies performed on PDMS−M_xO_y nanocomposites[18−21] have underlined the essential influence of the cross-linking metal nature in the final structure of the material. A nanophase separa-

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* To whom correspondence should be addressed. Fax: +33 144 27 47 69. Tel: +33 144 27 55 34. E-mail: clems@ccr.jussieu.fr.

[†] Universitat Jaume I.

[‡] Université Pierre et Marie Curie.

[§] ENSCP.

[||] Fax: +34 964 72 82 14. Tel: +34 964 72 82 47. E-mail: escriban@qio.uji.es.

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tion has been found in PDMS-based hybrid systems incorporating Al(III), Ti(IV), or Zr(IV) species, probably due to the differences in the chemical nature between the siloxane network and the oxo–metal species. The hybrids can be described as elastomeric materials in which segregated oxo–metal particles are immersed in PDMS chains through a poor siloxane–metal–oxo interface. In contrast, in PDMS–GeO_2 or PDMS–VO_{2-x} systems, the significant presence of Si–O–M linkages indicates the effectiveness of germanium and vanadium species to act as cross-linking agents, leading to well-dispersed metal–oxo species in the polymer structure, which are constituted by short (4–5 D_2 units length) PDMS chains. For other systems such as PDMS–Nb_2O_5 or PDMS–Ta_2O_5, the length of the PDMS chains and the effectiveness of the siloxane–M_xO_y interface has been found intermediate between the above-mentioned hybrid systems.[20]

Knowledge of the extent and the nature of the interface between the constituents in hybrid materials is of special interest because it usually controls the properties of the material. Nevertheless, whereas the siloxane component can be easily characterized through vibrational spectroscopy and ^{29}Si nuclear magnetic resonance (NMR), and the size or the average distance between metal–oxo nanodomains can be deduced from small-angle X-ray scattering (SAXS) analysis, characterization of the interface is not a direct task. Evidence of the Si–O–M linkages have been obtained for certain siloxane–oxide hybrid systems from FTIR measurements,[18,20,22,23] but the attribution of the vibrational bands to the asymmetric Si–O–M stretching mode is not trivial, and furthermore, they can be masked by other vibrational bands. Previous studies reporting liquid ^{17}O NMR spectra of $(CH_3)_2SiO$–SiO_2,[24] $(CH_3)_2SiO$–TiO_2,[25] $(CH_3)_2SiO$–ZrO_2,[25] and GPTS (glycidoxypropyltrimethoxysiloxane)–Ta_2O_5[26] have evidenced the sensitivity of this technique to differentiate the signals originated from oxygen atoms belonging to the siloxane chains, the metal–oxo nanodomains, and the interface between both components. The main drawback of this technique is its poor sensitivity due to the low natural abundance of the ^{17}O isotope, but this problem can be overcome using ^{17}O-enriched water for the hydrolysis step of the precursors.

The presence of Si–O–Ti[27] and Si–O–Ta[28] bridges in SiO_2–oxide materials or Si–O–Zr[18] in PDMS–ZrO_2 hybrid xerogels has already been evidenced by solid ^{17}O NMR spectroscopy. Even in the solid state, this technique seems to be an efficient tool to characterize the structure of these functional hybrids because the signals appearing at different chemical shifts permit one to distinguish and quantify the different types of oxo bridges (M–O–M of the oxide network, Si–O–Si of siloxane chains, and Si–O–M siloxane–M_xO_y interface) of the nanocomposites.

This paper presents the structural study of PDMS–M_xO_y nanocomposites, with a large set of metallic species [M = Ge(IV), Ti(IV), Zr(IV), Nb(V), Ta(V)] using ^{17}O nuclear magnetic resonance (NMR) spectroscopy. The study includes the evolution of the hybrid systems, from the initial hydrolysis–condensation reaction steps to the formation of the dried xerogel. Special attention has been given to (a) the evolution of the different types of oxo species (M–O–M, Si–O–M, and Si–O–Si) along the formation of the xerogel and (b) the extent of Si–O–M, the interface in the final structure of the hybrid material.

Experimental Section

Sample Preparation. The hybrid samples were synthesized as follows: a solution of diethoxydimethylsilane, DEDMS (Strem, 97%), absolute ethanol, and acidified 20% ^{17}O-enriched water (with pH adjusted to 1 by addition of HCl) was allowed to react for 20 min. The appropriate amount of metal alkoxide was then added to the prehydrolyzed DEDMS solution under fast stirring. The Si:EtOH:H_2O and Si:M molar ratio were 1:1:1 and 80:20, respectively. Metal alkoxides used in the experiment were $Ge(OEt)_4$ (ABCR, 98%), $Ti(OBu^n)_4$ (ABCR), $Zr(OPr)_4$ (70 wt % in propanol, Fluka), $Nb(OEt)_5$ (Strem Chemicals, 99.9%), and $Ta(OEt)_5$ (ABCR, 99.99%). Different amounts of the sols (ranging from 0.5 to 2 mL) were poured into vessels and allowed to dry at a constant temperature of 35 °C in a desiccator under intermittent vacuuming to allow the drying process but minimizing the interchange of ^{17}O-enriched water by $H_2{}^{16}O$ from the atmosphere. Transparent and homogeneous monoliths were obtained after 2–3 weeks.

Amorphous pure metal oxides (GeO_2 and Nb_2O_5) were also synthesized to determine the ^{17}O chemical shift values of the OM_n bridges because of a lack of data in the literature. Fine white (for GeO_2) and yellow (for Nb_2O_5) powders were obtained by slowly adding acidified 20% ^{17}O-enriched water to an ethanolic solution of the respective metal alkoxides.

The hybrid samples are labeled as DM, where D refers to DEDMS and M (with M = Ge, Ti, Zr, Nb, Ta) refers to the cross-linking metal.

For solid ^{17}O NMR measurements, the monolithic samples were reduced to powder just before the experiment, to minimize the atmospheric water adsorption derived from the hygroscopic character of the hybrid materials.

Characterization Techniques. ^{17}O liquid-state NMR experiments were performed on a Bruker AVANCE 400 spectrometer operating at 54.22 MHz using the following parameters: 21 μs (90°) pulse width, 500 ms recycle delay, and 256 scans. ^{17}O-enriched water (10 atom %) was used in the liquid NMR experiments.

^{17}O solid-state NMR spectra were recorded on Bruker MSL 300 and 400 spectrometers operating respectively at 40.67 and 54.24 MHz. Samples were spun at 12.5 kHz using 4-mm ZrO_2 rotors. Spectra were recorded using a spin–echo θ–θ–2θ pulse sequence ($\theta = 90°$ corresponding to a pulse length of 1.5 μs, $\tau = 80$ μs determined by the spinning frequency), with recycle delays of 2 s. Between 25000 and 120000 FIDS were typically accumulated to obtain a reasonable signal-to-noise ratio. Chemical shifts were referenced to tap water ($\delta = 0$), and the resulting spectra were simulated with the DMFIT program.[29]

Results

In this section, the results obtained for the hybrid systems DTa, DNb, and DGe will be extensively presented due to the scarce information found in the

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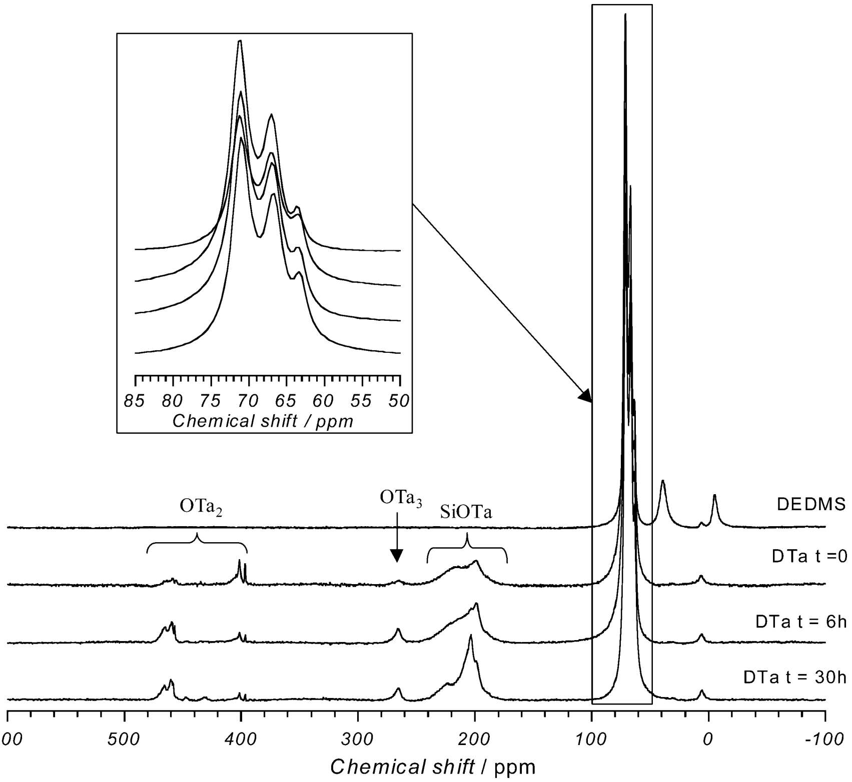

Figure 1. ^{17}O NMR spectra of a prehydrolyzed solution of DEDMS and DTa sol at different reaction times ($t = 0$ min, $t = 6$ h, and $t = 30$ h).

literature, whereas only some data about the hybrid matrixes cross-linked with Ti(IV) and Zr(IV) species will be eventually included to compare all the hybrid systems.

DTa Hybrid System. The ^{17}O solid-state MAS NMR spectrum of Ta_2O_5 has recently been reported by Pickup et al.[28] They attributed the signals appearing at ~270 and ~430 ppm to OTa_3 and OTa_2 configurations, respectively. Ta−O−Ta resonances spread over a quite different range than those of Si−O−Si belonging to D_2 units (appearing at 80−90 ppm). It could thus be possible to discriminate an intermediate peak associated with Si−O−Ta linkages characteristic of the siloxane−metal oxide interface in the DTa system.

The evolution of the hydrolysis and condensation reactions of this hybrid system was preliminary followed by ^{17}O liquid-state NMR (Figure 1). The spectrum of the DEDMS prehydrolyzed solution was first recorded to exactly know the species present in the sol (and their relative proportion) 20 min after water addition. Then, an accurate study of the ^{17}O liquid spectra evolution versus time was performed after addition of tantalum ethoxide to the prehydrolyzed DEDMS solution.

The spectrum of prehydrolyzed DEDMS solution shows a peak around −5 ppm, characteristic of residual water (probably shifted compared to pure water because of its acidity), a peak of ethanol in natural abundance at 6 ppm,[30] a signal of silanol groups[31] (Si−OH) at 40 ppm, and three signals corresponding to Si−O−Si oxo bridges between 60 and 75 ppm. The three components detected at 63.7, 66.7, and 71.1 ppm have been attributed to oxo bridges involving D_1 units, D_2 units in linear chains, and in cyclic species, respectively.[25] The signal at 71.1 ppm is the more intense, underlining the tendency of DEDMS to condense in cyclic species under our synthetic conditions.

After addition of the tantalum alkoxide, the signal due to silanol groups completely disappears while new peaks appear around 200−215, 265, and 400−460 ppm. According to the assignments of Pickup[28] (in a solid ^{17}O NMR study of the SiO_2−Ta_2O_5 system) and Nacken[26] (in a liquid ^{17}O NMR study of the GPTS−Ta_2O_5 system), these new signals can be attributed to Si−O−Ta, OTa_3, and OTa_2 oxo bridges, respectively. The presence of OTa_3 and OTa_2 species indicates the formation of metal−oxo oligomers from the beginning of the synthesis, but the appearance of the Si−^{17}O−Ta signal evidences an effective heterocondensation in the early stages of the synthesis that remains after 30 h of reaction. The signal of water (at $\delta = -5$ ppm) disappears, indicating a rapid hydrolysis rate of the $Ta(OEt)_5$, whereas the profile of the Si−O−Si signals remains almost identical. The global intensity of the ^{17}O signals has been maintained with time; however, a clear evolution of the signals involving tantalum species is denoted. The different components included in the chemical shift range between 190 and 225 ppm characteristic of Si−O−Ta species decrease in intensity in favor of the 203 ppm signal, more stable in time. The stability of the Si−O−Ta bonds is thus corroborated in the hybrid solution after 30 h, contrary to the PDMS−TiO_2 hybrid system, in which Si−O−Ti bonds almost disappear at this reaction time under similar synthetic conditions. In the case of the PDMS−ZrO_2 hybrid system, the signal

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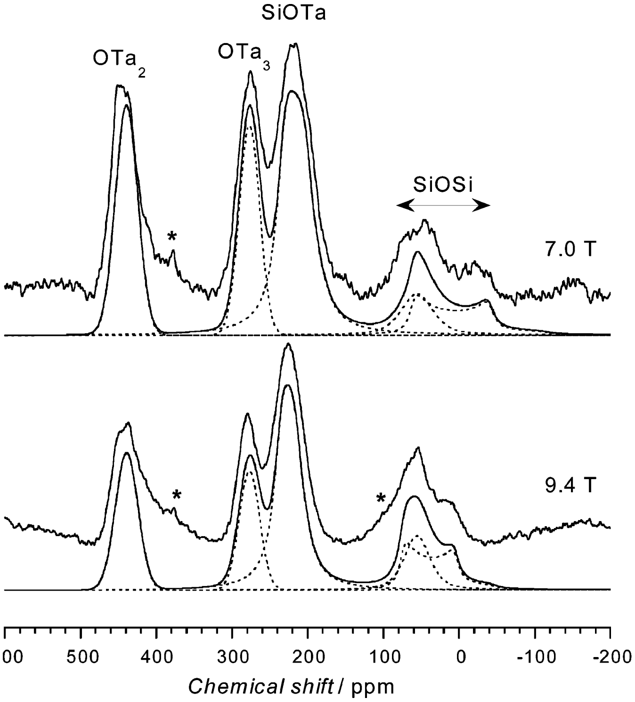

Figure 2. Experimental and simulated ^{17}O solid-state MAS NMR spectra of the DTa xerogel recorded at 7.0 and 9.4 T. The global simulation is indicated in the solid line while the individual components of the fits are depicted in the dotted lines. Spinning sidebands are indicated with an asterisk.

Table 1. Chemical Shifts (δ), Quadrupolar Coupling Constant (C_Q), Relative Percentage (M_0), and Assignments of Each Peak Detected in the ^{17}O Solid-State NMR Spectra for the Studied Hybrid Systems[a]

sample	δ/ppm ($\pm$4)	C_Q/MHz ($\pm$0.1)	assignment	M_0/% ($\pm$3)	
				7.0 T	9.4 T
DTa	440		OTa_2	22	20
	277		OTa_3	19	15
	243	3.0	Si−O−Ta	41	40
	90	5.0	Si−O−Si	11	14
	55		Si−O−Si	7	11
DNb	545		ONb_2	19	14
	361		ONb_3	22	20
	275		Si−O−Nb	32	37
	97	5.0	Si−O−Si	12	11
	70		Si−O−Si	15	17
DTi	719		OTi_2	9	
	523		OTi_3	26	
	360		OTi_4	11	
	332	3.0	Si−O−Ti	18	
	97	4.9	Si−O−Si	10	
	73		Si−O−Si	26	
DZr	402		OZr_3	14	
	338		OZr_4	2	
	291		OZr_4	15	
	219	3.4	Si−O−Zr	28	
	100	5.0	Si−O−Si	16	
	45		Si−O−Si	25	

[a] Asymmetry parameter is about zero for all determined quadrupolar coupling constants.

attributed to SiOZr linkages slightly decreases with reaction time and it is perfectly visible at this reaction time. In the region of autocondensed Ta−O−Ta species, a significant increase of the OTa_3 (at 265 ppm) and OTa_2 component (at 460 ppm) oxo bridges is observed after 6 h, while the OTa_2 signal located at 400 ppm progressively disappears. This evolution indicates that an important redistribution of the oxo−metal species within the siloxane network takes place in the first stages of the synthesis, during the hydrolysis and co-condensation steps.

Figure 2 shows the experimental and simulated ^{17}O MAS NMR spectra of the DTa xerogel recorded at two different magnetic fields (7.0 and 9.4 T) to improve confidence in the simulations by providing additional constraints.

They show two relatively sharp lines at 440 and 277 ppm that can be attributed to OTa_2 and OTa_3 species, respectively. The line widths in Hertz of these resonances scale directly with the applied magnetic field, indicating that they are determined almost completely by chemical shift dispersion. These Ta−O−Ta signals were therefore simulated using simple Gaussian shape peaks with the same line width (in ppm) at each field as already reported for Ti−O−Ti signals.[27] The signal in the siloxane region was simulated using two different components: a relatively narrow one simulated by a Gaussian line centered at 55 ppm, attributed to very mobile D_2 units (in the middle of the PDMS chains), and a second−order quadrupolar shape characteristic of such oxo bridges due to D_2 units in a more rigid environment[27,32] (as those located at the end of the PDMS chains and directly bonded to metal−oxo nanoparticles through Si−O−M linkages). ^{17}O signal of mobile PDMS chains has already been reported in PDMS−vanadate materials[33] showing a single Gaussian signal at 70 ppm while no quadrupolar shape is observed. It can be noticed that in the case of the less mobile tantalate system, the Gaussian signal appears at higher field, probably indicating a residual quadrupolar interaction, shifting the signal from the isotropic value. Moreover, this description is in good agreement with the results obtained by ^{29}Si NMR experiments.[20] The intense resonance appearing at 227 ppm can be clearly attributed to Si−O−Ta bonds, indicating an important extent of the siloxane−oxide interface in this hybrid material. It could be simulated at both fields with a quadrupolar line shape. The corresponding C_Q value of 3.0 MHz is well below the value in Si−O−Si and close to the ones in Si−O−Ti linkages.[27] The isotropic chemical shift (227 ppm) is in good agreement with the position of the Si−O−Ta bridges observed in the liquid state[26] and in another $SiO_2−Ta_2O_5$ system[28] prepared from TEOS and $Ta(OEt)_5$.

The simulation of the spectra leads to the determination of the peak position and ^{17}O NMR parameters (C_Q and η) of each resonance. These values together with the peak assignments for all the studied hybrid systems are summarized in Table 1.

DNb Hybrid System. A similar study was performed for the DNb hybrid system. The evolution of the hydrolysis and condensation reactions of the DNb sol performed by ^{17}O liquid-state NMR is presented in Figure 3.

The immediate consumption of the silanol groups (δ = 39 ppm) and water molecules (δ = −5 ppm) after

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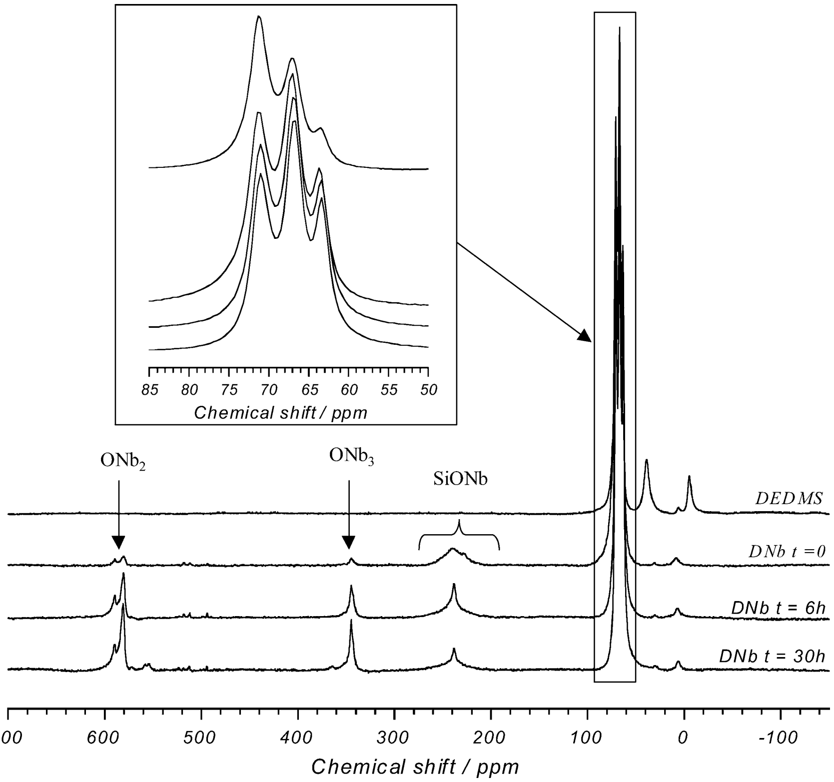

Figure 3. ^{17}O NMR spectra of a prehydrolyzed solution of DEDMS and DNb sol at different reaction times ($t = 0$ min, $t = 6$ h, and $t = 30$ h).

$Nb(OEt)_5$ addition and the appearance of new signals at 344 and 550−590 ppm (probably due to Nb−O species) denotes the fast hydrolysis of this precursor.

Little information about Nb−O−Nb characteristic ^{17}O NMR parameters has been reported until now in the literature. A reference compound (labeled as Nb_2O_5 in this paper) was therefore prepared by precipitation with 20% ^{17}O-enriched water of niobium(V) ethoxide to determine the position of the Nb−O−Nb oxo-bridge resonance peaks. The ^{17}O solid-state NMR spectrum of this compound (Figure 4) shows two peaks at 360 and 545 ppm that can be respectively assigned to ONb_3 and ONb_2 environments.[34] As in the DTa system, the presence of niobium oxo oligomers in the DNb sol (Figure 3) is observed at the first stages of the hydrolysis of the metal alkoxide (ONb_3 at 344 ppm and ONb_2 at 550−590 ppm).

At $t \approx 0$, a broad signal is observed at 220−240 ppm in the DNb sol. The position of this signal spreads between the niobium oxo species and siloxane regions, and therefore, it could be attributed to Si−O−Nb oxo bridges. This fact underlines an effective co-condensation between siloxane and niobium precursors. The evolution of peak intensities versus time shows a significant increase in the Nb−O−Nb bonds content to the detriment of Nb−O−Si species. This evolution indicates that redistribution reactions occur, with the cleavage of the Si−O bonds. Moreover, the different broad components of the Si−O−Nb and ONb_2 signals observed at $t \approx 0$ min, probably due to the presence of slightly different species in terms of coordination and mobility, become narrower and more defined with time. As for the DTa system, after 30 h, the most significant signals for ONb_2 and SiONb are detected at 580 and 344 ppm, respectively.

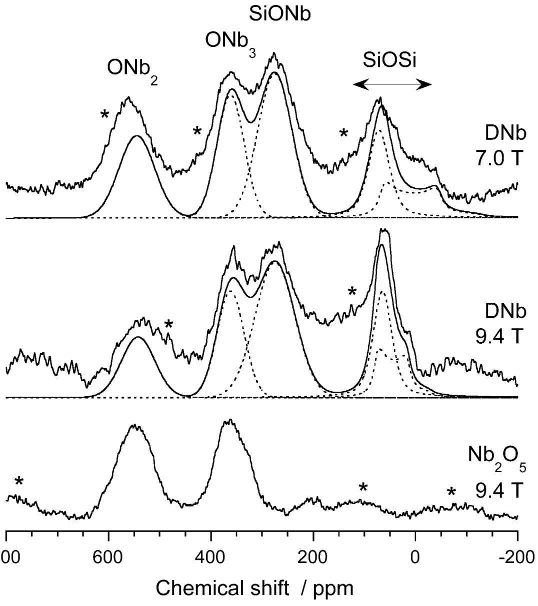

Figure 4. Experimental and simulated ^{17}O solid-state MAS NMR spectra of the DNb xerogel recorded at 7.0 and 9.4 T and Nb_2O_5 reference compound recorded at 9.4 T. The global simulation of the spectra is indicated in the solid line while the individual components of the fits are depicted in the dotted lines. Spinning sidebands are indicated with an asterisk.

In the siloxane region, a drastic change takes place after niobium addition: the signal at 66.7 ppm, characteristic of linear D_2 units, strongly increases in

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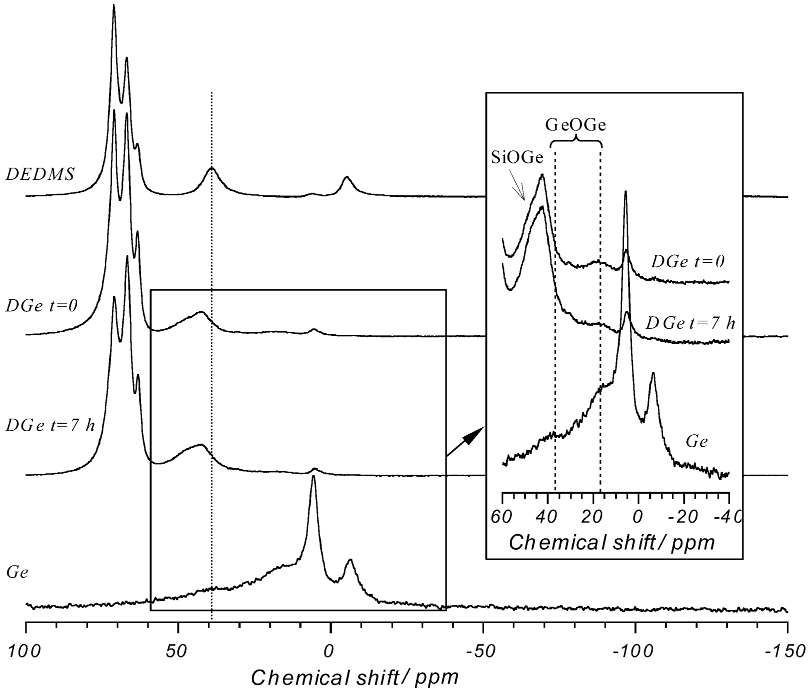

Figure 5. ^{17}O NMR spectra of a prehydrolyzed solution of DEDMS and DGe sol at different reaction times ($t = 0$ min and $t = 7$ h). The spectrum of an ethanolic solution of $Ge(OEt)_4$ prehydrolyzed with ^{17}O-enriched water is also represented.

intensity while the intensity of the signal at 71.1 ppm, attributed to cycles, decreases. This could be explained by a catalytic effect of the niobium alkoxide, as observed for other transition metal alkoxides (such as $Ti(OR)_4$[35,36]), inducing the co-condensation of the siloxane polymer by a ring-opening process, leading to longer PDMS linear chains.[3]

The ^{17}O solid-state NMR spectra of the DNb xerogel were also recorded at two different magnetic fields (Figure 4).

In these spectra, the resonances at 545, 361, and 70–90 ppm can be directly attributed to ONb_2, ONb_3, and SiOSi oxo bridges, respectively. The profiles of the ONb_2 and ONb_3 signals have approximately the same shape and relative ratio as those in the Nb_2O_5 reference compound, indicating the existence of niobium oxo nanoparticles within the siloxane material. As for Ta–O–Ta, Nb–O–Nb signals were simulated using simple Gaussians with the same line width at each field, and the siloxane signal was simulated with a Gaussian peak centered at 70 ppm for mobile D_2 units and a quadrupolar shape at $\delta_{iso} = 97$ ppm for rigid D_2 units. The peak located at 275 ppm can be assigned to SiONb linkages. Contrary to the Ta–O–Si signal, this peak exhibits the same line width at both fields, indicating a negligible quadrupolar interaction. The Nb–O–Si signal was therefore simulated at both fields with a simple Gaussian. In the siloxane region, the narrow signal is highly enhanced (as denoted in the spectrum recorded at 9.4 T) and appears at a lower field compared to the DTa system. This suggests a smaller quadrupolar interaction probably due to a higher mobility of the system and indicates a longer siloxane chain length in the DNb system.

DGe Hybrid System. The evolution of the hydrolysis and condensation reactions of the DGe sol has been followed by ^{17}O liquid-state NMR. Figure 5 shows the spectra of the DEDMS prehydrolyzed before and after addition of $Ge(OEt)_4$, at $t \approx 0$ and 7 h of reaction.

These spectra spread over a short chemical shift range, complicating the assignments compared to those of DTa and DNb sols. The DGe spectra show the peaks characteristic of SiOSi bonds (at 63.7, 66.7, and 71.1 ppm), ethanol (at 6 ppm), and a broad signal located at 42.5 ppm that does not correspond to SiOH groups ($\delta = 39$ ppm). The rapid hydrolysis of the germanium ethoxide can be deduced from the disappearance of the water peak, and thus, this broad signal at 42.5 ppm could be associated with species containing germanium, although its assignment is not clear. To clarify this attribution, two experiments were realized. First, the ^{17}O solid-state NMR spectrum of a reference compound (labeled as GeO_2) prepared by precipitation of germanium ethoxide with ^{17}O-enriched water was recorded (Figure 6). A broad signal that could be simulated with a pure quadrupolar line shape at different fields ($\delta_{iso} = 51$ ppm, $C_Q = 6.9$ MHz, $\eta = 0.5$) was detected for germanium oxo species, in good agreement with previously reported results on GeO_2.[37] From this information, the interpretation of the DGe liquid NMR spectra is still ambiguous. Considering that the peak position can be shifted from solid to liquid systems, the oligomerization of the germanium ethoxide was therefore followed by ^{17}O liquid-state NMR. ^{17}O-enriched water at pH = 1 (obtained by addition of HCl) was added to an ethanolic solution of $Ge(OEt)_4$ and the evolution versus time of the ^{17}O liquid NMR spectra was recorded. The spectrum of the hydrolyzed germanium solution after 40 min of reaction is presented in Figure 5. Sharp signals of EtOH

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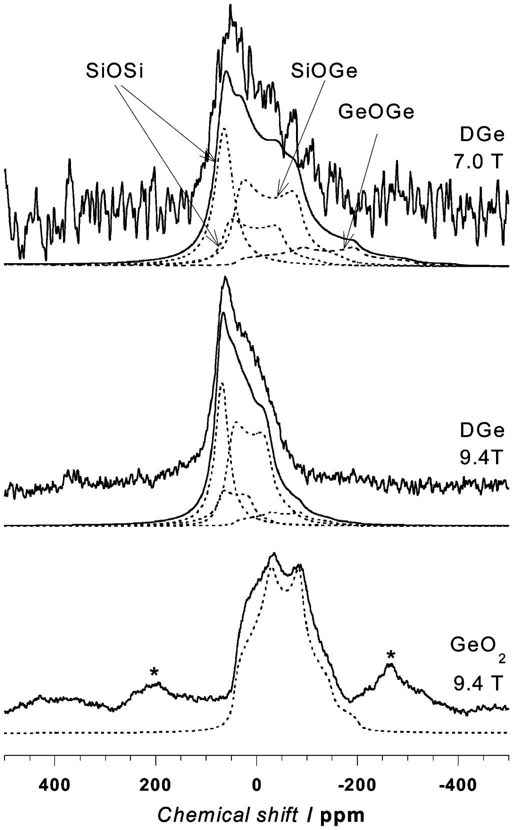

Figure 6. Experimental and simulated ^{17}O solid-state MAS NMR spectra of the DGe xerogel recorded at 7.0 and 9.4 T and GeO_2 reference compound recorded at 9.4 T. The global simulation of the spectra is indicated in the solid line while the individual components of the fits are depicted in dotted lines. Spinning sidebands are indicated with an asterisk.

(5 ppm) and water (−5 ppm) are clearly observed, but broader signals are also detected at 37 and 16 ppm. The poor signal/noise ratio and broadness of these signals are due to the high reactivity of the germanium alkoxide, forming rapidly oligomers of large size precipitating in the NMR tube. Therefore, only small remaining oligomers can be detected in the liquid state. Although it is difficult to determine the specific species responsible for these signals, they are most probably due to germanium oxo species (GeOGe, GeOH).

In the DGe spectra, a quite weak signal at 17 ppm can be detected (see Figure 5), revealing the existence of these kind of germanium−oxo species. Thus, the main signal at 42.5 ppm of the hybrid sol can possibly be deconvoluted in a mixture of germanium−oxo species (at around 37 ppm) and Si−O−Ge oxo bridges at lower fields. The corresponding chemical shift is indeed intermediate between SiOSi and GeOGe resonances. The small relative percentage of GeOGe in the sol does not permit evaluation of any evolution versus time. In the case of the SiOGe resonance, no significant evolution has been detected with reaction time, even 3 weeks after the start of the reaction, indicating the important stability of the bonds formed in the initial co-condensation. In the siloxane region (60−70 ppm), an interesting increase of the D_2 linear chains can be observed with the reaction advance. It reveals a certain catalytic effect of the germanium species on the condensation of PDMS polymer, but less important than niobium species.

The ^{17}O solid-state NMR spectrum of the dried xerogel DGe recorded at 7 and 9.4 T is shown in Figure 6.

They show overlapping broad peaks ranging over 200 ppm at 9.4 T, making difficult the deconvolution of the DGe spectra. A simulation can be nonetheless proposed (Figure 6), assuming NMR parameters comparable to those determined on the DTa and DNb systems for Si−O−Si environments and with the GeO_2 reference compound for Ge−O−Ge bridges: two components for siloxane oxo bridges at 90 ppm ($C_Q = 4.9$ MHz, $\eta = 0$ corresponding to rigid D_2 units) and 69 ppm (mobile D_2 unit) and a quadrupolar shape at 51 ppm ($C_Q = 6.9$ MHz, $\eta = 0.5$) for Ge−O−Ge oxo bridges. A last signal at an intermediate chemical shift (72 ppm) can be assigned to Si−O−Ge oxo bridges. A quadrupolar shape with a C_Q of 5.4 MHz, intermediate value between Si−O−Si ($C_Q = 4.9$ MHz) and Ge−O−Ge (6.9 MHz), was reasonably assumed.

Discussion

The ^{17}O liquid NMR experiments performed on the DGe, DNb, DTa, DTi (not explicitly shown), and DZr (not explicitly shown) sols have underlined the high reactivity toward water of the metal alkoxides. For all the hybrid systems, the products of the auto- and co-condensation between the prehydrolyzed siloxane moieties and metal−oxide precursors can be detected at the early stages of the reaction (Si−O−Si, M−O−M, and Si−O−M). However, a different evolution of the ^{17}O-containing species versus time reveals differences in the stability of the oxo-bridging linkages. In the DGe system, the assumed Si−O−Ge species formed in the first stage seem to remain stable with reaction time, whereas in the DNb and DTa sols further redistributions of the tantalum and niobium oxo species (including Si−O−M and M−O−M linkages) have been detected. Despite these redistributions, some Si−O−Ta linkages remain stable with time, whereas a decrease in intensity of the Si−O−Nb signal has been noticed, which could indicate a higher tendency to phase separation for this hybrid system. In the DZr and DTi, a diminution of the Si−O−M signal has been detected after several hours of reaction, and in the latter system the complete disappearance of this resonance takes place at ~30 h.

From these results, it can be deduced that the stability of the Si−O−M linkages in the liquid state increases in the order DTi < DZr ≤ DNb < DTa. In our previous work based on the ^{29}Si solid NMR characterization of PDMS−M_xO_y (where M were more particularly Ge(IV), Ti(IV), Zr(IV), Nb(V), and Ta(IV)) xerogels,[20] it was demonstrated that the dispersion of the cross-linking metal within the siloxane matrix and the extent of the interface increased in this order: DTi < DZr < DNb < DTa < DGe. This fact could be in agreement with the results obtained about the SiOM bonds stability performed by ^{17}O liquid NMR.

The homogeneity of the enrichment in the solid state is not easy to control because it depends on the chemical nature of the elements involved in the sol−gel reactions. An experiment was therefore carried out to shed more light on this phenomenon. The samples were dried in a desiccator in which a vessel containing ^{17}O-enriched water was introduced, and a moderate vacuum was applied for minimizing the initial atmospheric humidity.

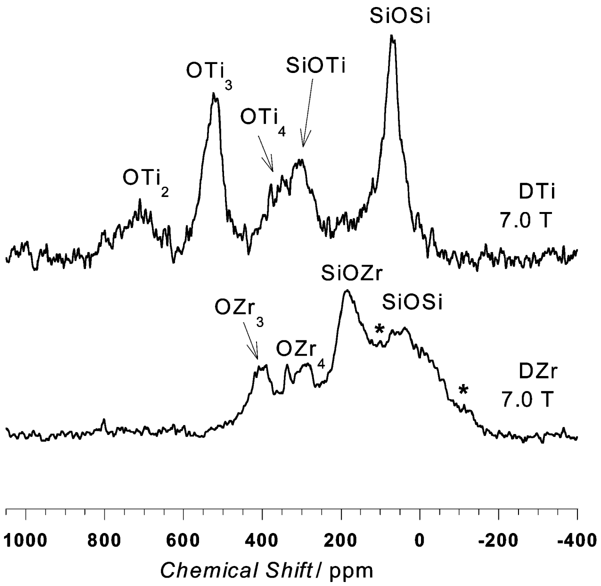

Figure 7. Experimental ^{17}O solid-state MAS NMR spectra of the DTi and DZr xerogel recorded at 7.0 T. Spinning sidebands are indicated with an asterisk.

This drying process was performed to provide to the sample additional ^{17}O-enriched water for the condensation process and to minimize the exchange of ^{17}O-enriched water by atmospheric moisture during the gelation process. Despite these precautions, no significant differences in the spectra profiles were observed in the different systems. This suggests that, under our synthetic conditions, a relatively homogeneous enrichment of the samples is obtained even if the enriched water initially added for prehydrolysis is not sufficient for total condensation of the system. It can indeed be noticed from Table 1 that the M−O−M/Si−O−X (X = Si, M) ratio for all systems is close to 1/2, in good agreement with the initial Si/H_2O and Si/M molar ratio being 1/1 and 80/20, respectively (2 mol of H_2O are necessary to hydrolyze the $(Me)_2Si(OEt)_2$ alkoxides versus 4 (or 5) mol for metal alkoxides). This relatively homogeneous enrichment can possibly be explained by the following reactions: the nucleophilic water molecules coming from the air moisture attack the more electrophilic centers M and the enriched O* is selectively removed, the siloxane moieties being a good leaving group:

$$\mathrm{Si{-}O^{*}{-}M + H_2O \rightarrow Si{-}O^{*}H + M{-}OH} \qquad (1)$$

Upon drying and ethanol evaporation, further condensation reactions occur between silanol groups and nanoparticles surface M−OR groups:

$$\mathrm{M{-}OR + Si{-}O^{*}H \rightarrow Si{-}O^{*}{-}M + ROH} \qquad (2)$$

However, this picture, which takes into account the experimental data, is rather simplistic and some concurrent redistribution reactions also occur.[3] Nonetheless, they do not modify the enriched O* repartition regarding the accuracy of quantitative evaluation.

The Si−O−M/Si−O−Si ratio value should increase according to the extent of the siloxane−oxide interface and the dispersion degree of the metal species within the PDMS network. The ratio values found for DTa, DNb, DZr, and DTi xerogels from the simulation of the ^{17}O solid-state NMR spectra are about 40/22, 35/27, 28/41, and 18/36 values, which slightly vary according to the simulation with the magnetic field. It is necessary to point out that these values must be taken with a margin error of about 5% because of the presence of spinning sidebands overlapping and making difficult a precise evaluation. The DGe results are not further discussed because of the very low accuracy of the simulation due to overlapping Ge−O−Ge, Ge−O−Si, and Si−O−Si signals. The results obtained for the DTi and DZr hybrid systems have been included for discussion and the corresponding ^{17}O solid-state NMR spectra recorded at 7.0 T (Figure 7).

Comparing the relative ratio values obtained for all hybrid systems cross-linked with transition metal oxides, it appears that the extent of the siloxane−M_xO_y interface increases as follows: DTi < DZr < DNb < DTa. This tendency is in good agreement with the results obtained from ^{29}Si NMR experiments,[20] underlining the ability of the ^{17}O NMR technique to be used for identifications and estimations of the oxygen resonances in a family of nanocomposites.

Conclusion

PDMS−M_xO_y (where M = Ge(IV), Ti(IV), Zr(IV), Nb(V), and Ta(V)) hybrid materials have been studied from the solution to the solid state through ^{17}O NMR spectroscopy. The utility of this technique for characterizing both liquids (sols) and amorphous solid materials (xerogels) has been underlined.

The evolution of the DM sols followed by ^{17}O liquid-state NMR showed that the hydrolysis of the metal precursor takes place immediately after addition of the metal alkoxide to the prehydrolyzed DEDMS solution, as indicated by the disappearance of the residual water signal. The presence of species generated from self- and cross-condensation between the siloxane and metal precursors can also be detected in the first stages of the reaction, as indicated in the appearance of new peaks associated with Si−O−Si, M−O−M, and Si−O−M linkages. Differences in the stability of Si−O−M and M−O−M oxo bridges have been observed depending on the hybrid system. The one cross-linked with Ge(IV) seems to initially generate species containing Si−O−Ge oxo bridges, which remain stable with the reaction time, contrary to DTi, DZr, DNb, and DTa for which redistributions of the new species take place several hours after the start of the reaction. Despite these redistributions, a stable Si−O−Ta signal is maintained with time, whereas a decrease in intensity of the Si−O−Nb, Si−O−Zr, and Si−O−Ti resonances is detected with time. The stability of the cross-condensated species in the DM sols seems to increase as follows: DTi < DZr ≤ DNb < DTa < DGe.

The ^{17}O solid-state NMR spectra of the DTi, DZr, DNb, and DTa hybrid xerogels present the resonances characteristic of Si−O−Si and M−O−M oxo bridges and evidence the existence of a real siloxane−oxide interface, through Si−O−M linkages. In the DGe xerogel, as the ^{17}O solid NMR spectrum spreads on a short range, it is more difficult to make the assignments, but a simulation has been nonetheless proposed. From this simulation, the existence of Si−O−Ge and Ge−O−Ge can be detected. Therefore, all the studied hybrid xerogels present a certain degree of homocondensation, deduced from the presence of M−O−M and Si−O−Si oxo bridges, but also an effective siloxane−oxide interface (detection of SiOM resonances). An estimation of the extent of the interface in the hybrid was obtained from ^{17}O solid NMR experiences, which is in agreement with previous ^{29}Si solid NMR studies.

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