Synthesis and Characterization of Transparent PDMS−Metal-Oxo Based Organic−Inorganic Nanocomposites

Beatriz Julián,[†] Christel Gervais,[‡] 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, and Laboratoire de Chimie de la Matière Condensée, UMR-CNRS 7574, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, France

Poly(dimethylsiloxane)(PDMS)−metal-oxo nanocomposites have been prepared as transparent monoliths from dimethyldiethoxysilane (DMDES) and metal alkoxides, $M(OR)_n$, where M = Al(III), Ge(IV), Sn(IV), Ti(IV), Zr(IV), Nb(V), and Ta(V). An accurate structural analysis of these hybrid materials has been performed by FTIR, Raman, and multinuclear NMR (^{1}H, ^{13}C, and ^{29}Si) spectroscopies, SAXS, and DSC measurements. These techniques show that all the hybrid systems present a structure based on amorphous metal-oxo nanodomains embedded within the siloxane network. However, a strong influence of the cross-linking metal nature on the size of the metal-oxo nanoparticles and on the extent of the interface between inorganic domains and the siloxane component has been found. Spectroscopic measurements reveal a more important nanophase separation for the PDMS systems incorporating Al(III), Ti(IV), or Zr(IV) species as cross-linking agent than for the ones cross-linked with Nb(V), Ta(V), or Ge(IV) (in which 45% of the silicon atoms are spatially near a metal species).

Introduction

Hybrid materials have received special attention in recent years because of their versatility in composition, structure, and properties, leading to very promising materials for applications in many fields such as optics, electronics, mechanics, sensors, or catalysis.[1−4] These materials are currently prepared by the sol−gel technology because the mild reaction conditions and use of organic solvents permit organic and inorganic components to be combined at a molecular level in a unique composite material.

Among hybrid materials, poly(dimethylsiloxane)(PDMS)-based compounds have been widely studied.[5−17]

The interesting intrinsic properties of PDMS[18,19] (such as a high elasticity of the siloxane backbone, excellent relaxation properties, and hydrophobicity) and the possibility of their shaping as a transparent material allow this polymer to be used as a host matrix for optical devices.[7−9,20,21] The introduction of metallic species within the siloxane framework permits the improvement or conjugation of these properties with those of inorganic components, leading to oxide−siloxane systems with singular properties.

PDMS-based hybrids can be prepared in situ via hydrolysis and condensation reactions between dimethyldiethoxysilane, $(CH_3)_2Si(OC_2H_5)_2$ (DMDES), and metal alkoxides, $M(OR)_n$, with M = Si, Ti, Zr, or VO. They can

* To whom correspondence should be addressed. Tel: +33 144 27 55 34. Fax: +33 144 27 47 69. E-mail: clems@ccr.jussieu.fr.
† Universitat Jaume I.
‡ Université Pierre et Marie Curie.

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be described as a material in which PDMS chains are cross-linked by oxo-metallic species.[4,9−14]

Synthesis and structural studies of PDMS-based hybrids have been widely reported in the literature for systems with M = Si,[11,15] Ti,[11,16,17,22] Zr,[10,11,17] and V.[12,23] However, scarce structural information can be found about siloxane-based hybrid systems cross-linked with other metal species such as Al,[24] Ta,[25,26] or Nb because most of the literature reported about these last systems is focused on only mechanical or optical properties.[27−31] Furthermore, most of the studied systems introduce chemical modifiers in the synthesis (such as acetyl-acetone,[20,26] ethyl acetoacetate,[27−31] or *p*-toluenesulfonic acid[15]) to control and retard hydrolysis of nonsilicate alkoxides, which are highly reactive toward water.[32] The presence of these complexing agents strongly modifies the kinetics of hydrolysis and condensation reactions and introduces important variations in the final structure of the hybrid.

Few studies have been performed about siloxane−oxide materials without modifier agents with the aim of characterizing the structure of the hybrid (not only the nature and the extent of the siloxane−metal-oxo interface but also the size of the different domains).[10,23] This is basically controlled by the reaction mechanism that accounts for the formation of the material. In this sense, metal alkoxides have a special influence because they act not only as cross-linking reagents but also as a catalyst for the condensation reactions of the siloxanes. As an example, it is known that for difunctional alkoxysilanes, only short-chain polymers or cyclic species are generated, and the introduction of Ti or Zr alkoxides catalyzes the increase of the siloxane chain length and helps the ring opening of cyclic species.[3] This mechanism induces a nanophase separation between the two phases.[11,16,17,33] Moreover, the stability of the Si−O−M bond also seems to have a special influence on the degree of dispersion reached by the metal-oxo polymers in the siloxane matrix.

The nature of the cross-linking metal (coordination number, electronegativity, oxidation state, charge, acidity, and size) and the reactivity of the precursor alkoxide are directly involved in the chemical reaction between inorganic and organic components. Consequently, these parameters play an essential role in the efficiency of the catalytic process and in the structural arrangement of the hybrid material.

From our point of view, a better comprehension of the metal nature influence could allow the structure of the nanocomposite to be modulated and permit design of materials for specific application fields. However, no systematic investigation has been performed in this sense.

The present paper addresses, for the first time, the structural characterization of PDMS−oxide hybrid materials without chemical modifiers in which only the metal nature has been systematically modified in order to obtain a wide variety of oxidation states, coordination numbers, electronegativities, charges, etc. Cross-linking agents used in this study have been Al(III), Ge(IV), Sn(IV), Ti(IV), Zr(IV), Nb(V), and Ta(V). Reaction mechanisms and final structures derived from the change of metal alkoxide are discussed. Special attention is also given to the characterization of the interface between the poly(dimethylsiloxane) framework and the oxo-metallic components.

Experimental Section

Sample Preparation. The hybrid matrixes were prepared using a standard procedure for the synthesis of siloxane−oxide materials.[10] A solution of dimethyldiethoxysilane, DMDES (Strem, 97%), absolute ethanol, and acidified water (with pH adjusted to 1 by addition of HCl) was allowed to react for 20 min in 1:1:1 molar ratio. The appropriate amount of metal alkoxide was added to the prehydrolyzed DMDES solution under fast stirring to obtain the sols with a constant Si/M molar ratio of 80:20. Metal alkoxides used in the experiment were Al(OBu^s)$_3$ (Gelest, 98%), Ge(OEt)$_4$ (ABCR, 98%), Sn(OPr^i)$_4$·i-PrOH adduct (Gelest) previously dissolved in dry i-PrOH, 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. Transparent and homogeneous monoliths were obtained after 2−3 weeks.

In the present paper, the samples are labeled as DM, where D refers to DMDES and M (with M = Al, Ge, Sn, Ti, Zr, Nb, or Ta) is the metal introduced as cross-linking agent.

Characterization Techniques. Elemental chemical analyses were performed at Service Central d'Analyze (CNRS, Lyon).

The Fourier transform infrared (FTIR) spectra were recorded between 4000 and 400 cm^{-1} (resolution of 2 cm^{-1}) on a Nicolet Magna-IR 550 spectrometer. The spectra were obtained by measuring directly on bulk samples with an attenuated total reflection (ATR) instrument equipped with a ZnSe monocrystal. The great advantage of measuring directly on bulk samples is to avoid absorption of atmospheric water molecules during the grinding process necessary to prepare pellets with KBr, and this fact allows detection of the presence of hydroxyl groups inside PDMS network.

Raman analysis was carried out with a Perkin-Elmer FTIR−Raman spectrum 2000 system and the spectral window was 200−1200 cm^{-1} with a resolution of 8 cm^{-1}.

Differential scanning calorimetry (DSC) measurements were performed on hybrid xerogels using a Perkin-Elmer differential scanning calorimeter from −150 °C to room temperature at a heating rate of 20 °C min^{-1} under helium atmosphere.

The nuclear magnetic resonance (NMR) spectra were recorded on Bruker MSL 300 and 400 spectrometers operating at 75.47, 59.63, and 40.67 MHz for ^{13}C, ^{29}Si (both recorded on the 300 spectrometer), and ^{17}O (recorded on the 400 spectrometer), respectively. Samples were spun at 4 kHz for the ^{29}Si experiments and at 5 kHz for the ^{13}C using 7-mm ZrO$_2$ rotors, whereas the ^{17}O spectra were recorded in 4-mm ZrO$_2$ rotors

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Table 1. Elemental Chemical Analysis of DM Dried Bulk Hybrids

sample	Si/M molar ratio ($\pm$ 1)
DAl	72:28
DGe	75:25
DSn	70:30
DTi	64:36
DZr	74:26
DNb	74:26
DTa	77:23

spinning at 12.5 kHz. [13]C and [29]Si cross polarization—magic angle spinning (CP—MAS) NMR spectra were performed under the same Hartmann—Hahn match condition: both RF channel levels, $\omega_{1S/2\pi}$ and $\omega_{1I/2\pi}$ were set at about 42 kHz. [1]H high-power decoupling was always applied during acquisition. Chemical shifts were determined relative to TMS for [29]Si and ^{13}C and relative to tap water for [17]O.

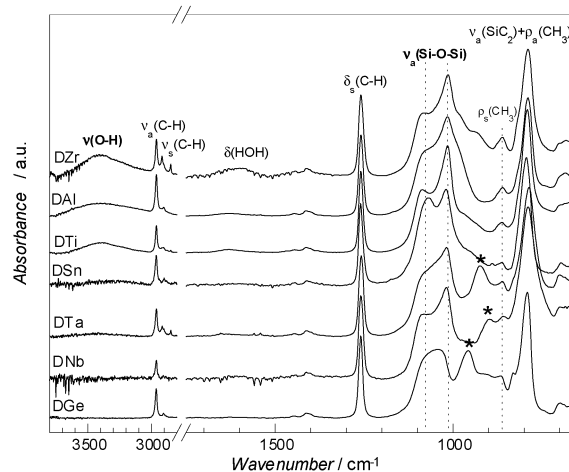The spectra were simulated with the DMFIT program.[34]

To confirm the existence of oxo-metal domains in DGe, DNb, and DTa samples, small-angle X-ray scattering experiments were carried out (SAXS profiles of DTi, DZr, and DAl systems have already been reported[10]). $I(q)$ was determined for q values ranging from 1.5 10^{-2} to 2 Å^{-1} using SAXS apparatus. Measurements in the q range 1.5 10^{-2} to 0.3 Å^{-1} were made on a Huxley—Holmes-type camera using a rotating anode Rigaku H3R X-ray source with a copper target (E = 8 keV, λ = 1.54 Å). The detector was a 2D position-sensitive gas chamber. The higher q range from 8 10^{-2} to 2 Å^{-1} was obtained on a Guinier—Méring-type camera using a molybdenum anode source (E = 17.4 keV, λ = 0.71 Å). The detector was an image plate. The samples were held in window-free sample holders. Intensities were corrected for transmission, background scattering, and smearing before being combined.[10]

Results

Experimental results of structural characterization of the oxo-metallic—poly(dimethylsiloxane) hybrid matrixes are described in this section.

Chemical Analysis of DM Gels. To confirm that the Si/M initial ratio was maintained during the synthesis and drying process, chemical analysis of the different dried bulk hybrids was done. The results shown in Table 1 indicate a slight variation in the Si/M molar ratios from initial composition of the sols (80:20). These values seem reproducible according to different synthesis conducted on a given system.

The Si/M ratio of the dried gels varies depending on the metal introduced: from 77:23 (for DTa) to 64:36 (for DTi). The increase of the M/Si ratio can be attributed to the volatilization of cyclic siloxane species during drying step. These differences found in the Si/M molar ratio of DM gels could indicate differences in the condensation process. These facts have been observed by other authors. For glycidoxypropylsiloxane-based materials,[26] during the hydrolysis—condensation process the formation of intermediates containing Si—O—M bonds (M = Ti, Zr ·and Ta) has been evidenced and structural rearrangements during the drying step lead to degradation of Si—O—M bonds in favor of Si—O—Si bonds formation. In the case of PDMS cross-linked with titanium species,[33] these rearrangements produce the disappearance of Si—O—Ti bonds and cyclic siloxane species are formed. These cyclic species volatilize lead-

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Figure 1. FTIR spectra of DM gels.

Table 2. Assignment of FTIR and Raman Band Positions of Siloxane Backbone Component

IR (ν/cm^{-1})	Raman (ν/cm^{-1})	assignment
2960s [a]	2964s	ν_a(C—H)
2905w	2904vs	ν_s(C—H)
1412m	1410m	δ_a(C—H)
1259vs	1256w	δ_s(C—H)
1000—1100vs	nonactive	ν_a(Si—O—Si)
860w	862vw	ρ_s(CH$_3$)
790s	790w	ν_a(C—Si—C) + ρ_a(CH$_3$)
700m	709s	ν_s(C—Si—C)
	490s	ν_s(Si—O—Si)

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak; ν = stretching, δ = bending, and ρ = rocking.

ing to very poor Si/M molar ratio from initial composition. This fact is in agreement with our results.

FTIR and Raman Spectroscopy. Infrared and Raman spectra of the samples were carried out, but only the most relevant results obtained by vibrational spectroscopies are discussed.

Infrared spectra of the hybrid matrixes are presented in Figure 1, in which all the spectra have been normalized by the δ_s(C—H) band located at 1259 cm^{-1}.

Significant differences can be observed depending on the metal introduced in the framework. The first one refers to the hydroxyl content. FTIR spectra of DZr, DTi, and DAl samples present a significant broad absorption band centered at around 3410 cm^{-1} assigned to OH stretching. This band can be originated by water molecules or X—OH groups (where X = Si or M) linked to water by hydrogen bonds. The presence of a second band located at 1630 cm^{-1}, specially intense for the DZr system, denoted the presence of molecular water. Only very weak bands characteristic of hydroxyl groups have been found for DTa (at 3420 cm^{-1}) and DSn (at 3325 cm^{-1}) and no OH vibrations have been detected for DGe and DNb samples. From these results, it can be deduced that the hydroxyl content in each system could be related with the existence of more or less hydrophilic regions (in which OH groups would be retained) and this hydrophilic character could be directly associated to the nature of the oxo-metallic domains.

On the other hand, the spectra exhibit the characteristic bands assigned to siloxane chains (see Table 2), but several differences have been found in the region between 1000 and 1100 cm^{-1} (assigned to antisymmetric stretching of Si—O—Si bonds).

It is known that open-chain PDMS show two maxima centered at around 1020 and 1098 cm^{-1}, but vibration energies of this stretching mode are very sensitive to the geometry and dimension of the siloxane species.[35,36] In our systems, several profiles have been detected. DGe presents a unique broad band centered at 1045 cm^{-1}, DSn shows two bands located at 1018 and 1069 cm^{-1}, DNb and DTa also present two bands but they are located at 1018 and 1081 cm^{-1}, and finally, for DTi, DZr, and DAl two maxima centered at 1015 and 1085 cm^{-1} have been detected. These results suggest variations in the shape and size of the siloxane condensed species depending on the metal introduced in the system.

Another relevant aspect is the detection of bands associated to Si−O−M bonds (where M is a metal different from silicon), that have been found in the literature between 800 and 1050 cm^{-1}. The energy of their vibrational stretching modes strongly depends on the M−O bond energy and the atomic mass of the metal. In our system's DGe, DTa, and DNb samples strong absorption bands have been detected at 957, 923, and 897 cm^{-1}, respectively, which can be assigned to Ge−O−Si,[37] Ta−O−Si,[25] and Nb−O−Si[38] antisymmetric stretching modes (they have been represented with an asterisk in Figure 1). Only a shoulder can be observed for Si−O−Zr[39] at 980 cm^{-1} (the shoulder found at 944 cm^{-1} could be attributed to Si−OH vibration) and no evident signals of Si−O−Sn[40] (at 945 cm^{-1}), Si−O−Ti[41,42] (at 950 cm^{-1}), and Si−O−Al[43] (at 1050 cm^{-1}) have been identified. The detection of these stretching modes is the unequivocal confirmation of the existence of a chemical interface between siloxane and inorganic-oxo polymer domains through M−O−Si bonds, which is specially important in DGe and DTa.

Raman spectra of DM samples[44] also show the characteristic bands of siloxane chains (Table 2) and some interesting information can be extracted about the structure of the siloxane network. All the spectra present a narrow band at 490 cm^{-1}, characteristic of symmetric stretching Si−O−Si groups mode from siloxane units located in the middle of PDMS chains,[45] whereas for DGe, DTa, and DNb matrixes a broad band has been also detected at lower wavenumbers (between 440 and 460 cm^{-1}). This latter band has been found in other hybrid systems[46] and it has been attributed to the same symmetric stretching mode, but originated by Si−O−Si groups in a more rigid environment than that of
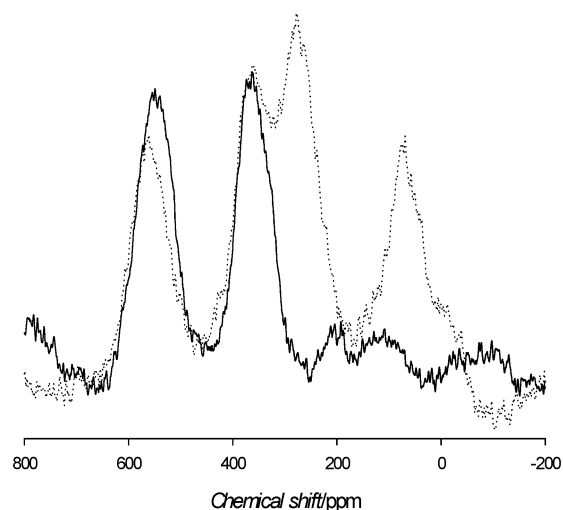

Figure 2. ^{17}O MAS NMR spectra of (a) Nb$_2$O$_5$ (solid line) prepared by hydrolysis of Nb(OEt)$_5$ showing two Nb−O−Nb signals at 550 and 360 ppm, and (b) DNb sample (dotted line) showing two supplementary signals at 275 and 69 ppm corresponding to Si−O−Nb and Si−O−Si bonds, respectively.

mobile siloxane units in PDMS chains. The rigidity of the siloxane units probably could be explained by the presence of metallic atoms near them, in agreement with the extended interface between siloxane and oxo-metallic species in DGe, DTa, and DNb matrixes evidenced through FTIR measurements and confirmed by ^{17}O MAS NMR experiments. These measurements are currently under progress but preliminary results on the DNb matrix clearly evidence the presence of Nb−O−Si mixed oxo-bridges (Figure 2).

^{1}H and ^{13}C NMR Experiments of DM Gels. The ^{1}H MAS NMR spectra of the gels dried at 35 °C are characterized by a sharp peak at around 0.1 ppm due to the methyl groups in D units (as labeled with the conventional notation[47]). For DGe and DNb samples, this is the only peak detected, whereas for the other systems an additional peak assigned to hydroxyl groups has been detected at 4.5 ppm (for DAl, DZr, DTi, and DTa) or 6 ppm (for DSn). The assignment of the nature of the hydroxyl groups (Si−OH, M−OH, or adsorbed H$_2$O) present in the dried xerogel is not trivial. However, after a thermal treatment at moderate temperatures (T < 250 °C) the vibration bands located at 3400 cm^{-1} strongly decrease in intensity, or even disappear, indicating that they are mainly due to adsorbed water.

A peak at 0.5 ppm associated with the carbon atoms in methyl groups of siloxane units was the only one detected in ^{13}C MAS NMR experiments for all the hybrid systems. No signals attributed to other organic groups have been detected, indicating that hydrolysis and condensation of the precursor alkoxides have been completed and the alcohol generated has been evaporated.

^{29}Si MAS NMR Experiments. Figure 3 (left) shows the ^{29}Si MAS NMR spectra of each DM sample. All of them present a sharp signal at a chemical shift (δ) of −22 ppm, characteristic of D$_2$ units bonded to D units.[48] For DZr, DTi, and DAl this signal is the only one

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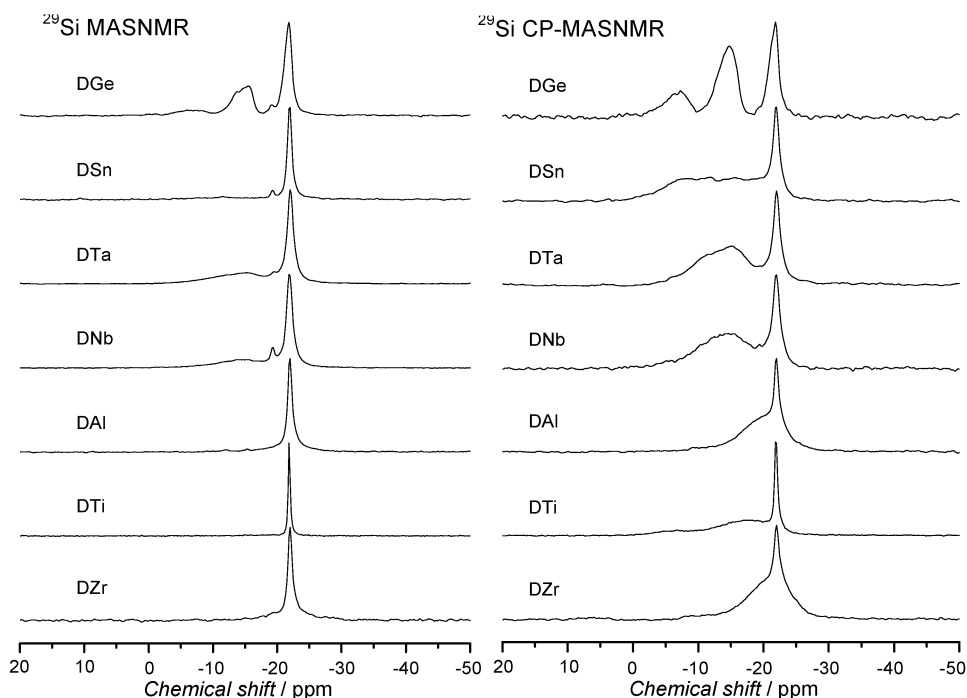(48) Harris, R. K.; Robbins, M. L. *Polymer* **1978**, *19*, 1123.

Figure 3. ^{29}Si MAS NMR and ^{29}Si CP-MAS NMR (at t_c = 1ms) spectra of DM dried gels.

detected, whereas for matrixes with M = Ge, Sn, Ta, and Nb a small sharp resonance at around −19 ppm and other broad resonances at lower fields can be observed. The signal at −19 ppm can be assigned to Si atoms in tetrameric cycles,[48] and the broad resonances, which appear at different chemical shifts depending on the hybrid system, can be associated to dimethylsiloxane units in a constrained environment. These broad signals have already been reported for polysiloxane/transition metal oxide hybrids[10,11,14,17,49] and their broadness is derived from the rigidity of the Si atom, probably due to the presence of oxo-metal species near the silicon atom.

^{29}Si CP-MAS NMR Experiments. With the aim of investigating the nature of the rigid siloxane species ^{29}Si CP-MAS NMR experiments were carried out. This NMR technique allows the enhancement of the signal of the constrained siloxane species above that of the mobile siloxane units because the high mobility induces the rapid relaxation of the protons and consequently reduces the efficiency of the cross-polarization process (CP). It should thus be possible to distinguish D units in very mobile chains and D units bonded to oxide-based particles as already observed in $(CH_3)_2SiO/TiO_2$ gels.[17]

Figure 3 (right) shows ^{29}Si CP-MAS NMR spectra of DM samples registered at a short contact time (1 ms). In this figure, the enhancement of the signals located at chemical shifts higher than −22 ppm is clearly evidenced, confirming that these signals are associated to less mobile siloxane species. Even for DZr, DTi, and DAl the existence of constrained siloxane units located at the end of the PDMS chains can be noticed at short contact times.

For a given system, all the spectra (recorded at different contact times) were simulated with a single set of peaks (Table 3) by keeping the chemical shifts,

Table 3. Characteristic Parameters of DM Gels Obtained from ^{29}Si NMR Experiments: Chemical Shift (δ), Relative Percentage (P, obtained by fitting the MAS NMR spectra), line width (LW), Cross-Relaxation Time (T_{SiH}) and Spin−Lattice Relaxation Time ($T_{1\rho}$)

sample	δ/ppm ($\pm$ 0.5)	P/% ($\pm$ 1)	LW/ppm ($\pm$ 0.2)	T_{SiH}/ms ($\pm$ 0.5)	$T_{1\rho}$/ms ($\pm$ 1)
DGe	−4.4	3	3.8	1.1	27.0
	−7.3	6	3.2	2.5	37.3
	−13.6	16	2.5	3.4	45.0
	−15.3	20	2.5	5.8	74.8
	−19.0	2	0.8		
	−21.6	53	1.5	12.5	45.2
DSn	−7.3	7	5.5	0.5	10.4
	−11.8	6	4.9	0.6	10.2
	−15.4	4	4.0	0.4	13.9
	−19.0	4	5.1	0.8	7.2
	−19.4	4	0.9		
	−22.0	75	0.8	11.1	
DTa	−6.8	5	4.0	0.9	17.2
	−11.0	12	4.9	1.3	34.9
	−15.5	17	4.6	1.6	34.5
	−19.5	4	1.1	0.9	19
	−22.0	62	1.1	9.0	34.9
DNb	−6.8	3	4.0	0.6	23.4
	−11.0	8	4.9	1.0	22.4
	−15.2	15	5.0	1.2	24.6
	−19.4	7	1.1	1.9	36.0
	−22.0	66	1.1	4.5	62.5
DAl	−19.2	9	5.4	0.9	16.1
	−22.0	91	1.0	3.9	29.6
DTi	−6.3	5	5.5	0.9	14.2
	−17.5	17	9.0	1.3	15.4
	−22.0	78	0.4	5.8	
DZr	−12.9	2	6.2	1.1	10.5
	−21.0	20	7.3	1.5	14.3
	−22.0	78	1.0	10.6	30.8

line widths, and shapes constant and by fitting only the amplitudes for each spectra.

As an example, the simulation performed for DGe spectrum at 1 ms is represented in Figure 4.

In this case, the spectrum has been simulated with six peaks (located at −21.6, −19.0, −15.3, −13.6, −7.3,
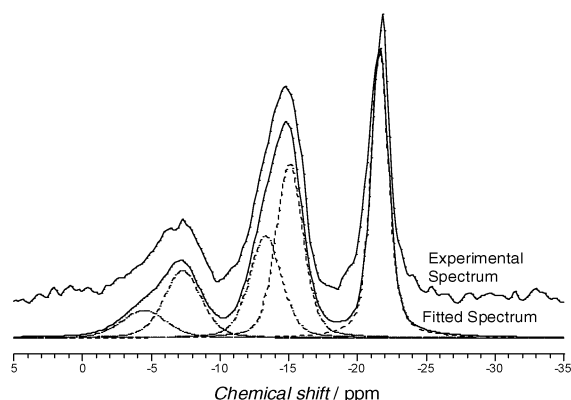
(49) Babonneau, F. *New J. Chem.* **1994**, *18*, 1065.

Figure 4. Experimental and simulated ²⁹Si CP-MAS NMR spectrum of DGe at t_c = 1 ms. The global simulation is indicated in solid line and the individual components of the fit are depicted in dotted lines.
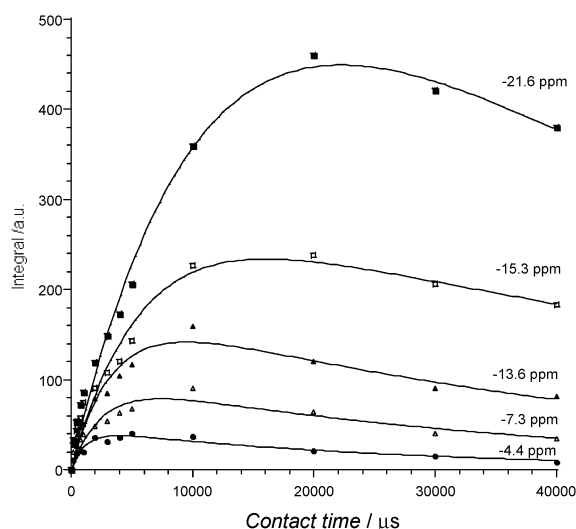

Figure 5. Integrated ²⁹Si CP-MAS intensities as a function of contact time for DGe system.

and −4.4 ppm) and a good agreement between the fitted and experimental spectra has been obtained regardless of contact time. It must be remarked that the signal at −19.0 ppm is visible only at very short contact times.

The simulation of the CP spectra allows the dynamics of the magnetization transfer for each silicon species to be determined. The variation of the peak area versus contact time for every sample is shown in Figure 5 and the corresponding curves were fitted according to equation[50] 1):

$$M(t_c) = \frac{M_0}{1 - \lambda}(e^{-t_c/T_{1\rho}{}^I} - e^{-t_c/T_{IS}}) \qquad (1)$$

Table 3 summarizes the peak position (δ), the line width (LW), and the parameters T_{SiH} and $T_{1\rho}$ extracted from the curves for each silicon species of every sample.

Some general trends can be extracted from this table. For a given sample, the peak located at around −22 ppm presents a longer cross-relaxation time T_{SiH} (which varies from 3.9 to 12.5 ms depending on the hybrid system) than the other peaks. Moreover, it presents a narrow line width (LW = 0.4−1.5 ppm). The values of

(50) Mehring, M. *Principles of High-Resolution NMR in Solids*; Springer-Verlag: Berlin, 1983.

these two parameters are characteristic of highly mobile siloxane species (D₂ units located in the middle of PDMS chains). On the contrary, the signals at higher chemical shifts present short T_{SiH} values (between 0.5 and 5.8 ms) and high line width values (LW = 2.5−7.3 ppm). These values could correspond to poly(dimethylsiloxane) units with a low mobility, for example at the end of the PDMS chains or close to metal-oxo nanoparticles. Note that similar LW and T_{SiH} values have been previously reported for PDMS/TEOS and PDMS/TiO₂ gels.[17]

Tetrameric cyclic siloxane species have been detected at around −19 ppm in DGe, DSn, DTa, and DNb samples. Their signals are characterized by a narrow line width (1 ppm), but the low amount of these species in the samples (2−7%) does not allow the simulation of their evolution with contact time.

A quantitative analysis of the ratio between rigid and mobile siloxane units in DM samples has been obtained by fitting the MAS NMR spectra, using the set of signals extracted from CP experiments. The relative percentage (*P*) has been calculated from the area of each fitted signal and the results are also specified in Table 3. For DZr, DTi, and DAl samples, practically no broad signals can be observed, indicating that almost all the siloxane units (80−90%) belong to long PDMS chains. This fact evidences a nanophase separation between siloxane and oxo-metal regions. Nevertheless, a high percentage of rigid siloxane species has been found for DGe, DTa, DNb, and DSn matrixes, showing 45, 34, 27, and 21% of constrained Si atoms, respectively. These values reveal a larger extent of the siloxane−metal-oxo interface and a higher degree of dispersion of the metal within the PDMS backbone, especially in DGe.

²⁹Si MAS NMR Experiments of PDMS Reference Materials. To confirm the origin of the broad signals detected in the ²⁹Si NMR spectra for DGe, DTa, DNb, and DSn gels, several reference materials have been prepared from commercial OH-terminated PDMS (M_w ≈ 550) and each metal alkoxide. In these samples, the metal-cross-linked PDMS chains are constituted of at least 5−9 siloxane units, thus, the ²⁹Si MAS NMR study of these reference materials will permit the determination of the position of the peaks associated with the terminal silicon atom of a "relatively long" PDMS chain linked to the metal-oxo domains. Therefore, signals appearing at higher chemical shift only in the DM gels could indicate the presence of "short" siloxane chains isolated between two metal-oxo species, M−[O−(CH₃)₂Si−O]ₙ−M (where 1 < n <4).

The synthesis of these materials has been realized by a slow addition of the metal alkoxide to the PDMS precursor (without solvent) until gelation occurs. In this protocol, water has not been directly introduced in order to prevent the formation of metal-oxo precipitates. Finally, the samples are allowed to dry, first at room temperature and then at 60 °C.

As a general remark, the ²⁹Si MAS NMR spectra of all the reference materials show a narrower line width for the signal located at −22 ppm, denoting a higher mobility of the PDMS network compared to that of DM gels.

The ²⁹Si MAS NMR spectrum of the PDMS reference material cross-linked with Ge(IV) (see Figure 6 (a)) shows obvious differences in the region associated with
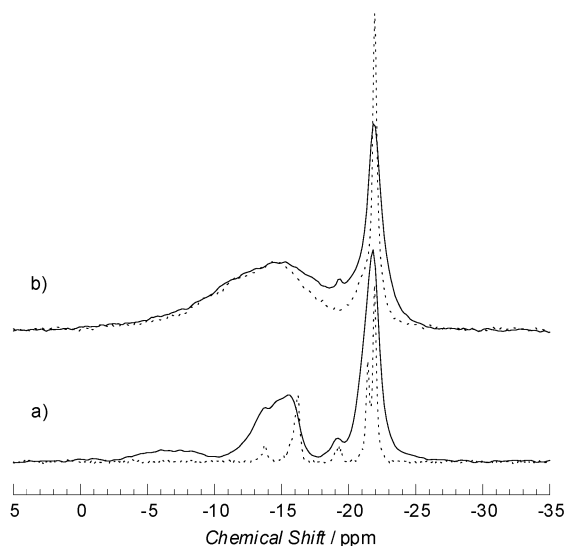
Figure 6. (a) ^{29}Si MAS NMR spectra of DGe (solid line) and PDMS−Ge reference sample (dotted line), and (b) ^{29}Si CP-MAS NMR spectra recorded at $t_c = 1$ ms of DNb (solid line) and PDMS−Nb reference sample (dotted line).

Table 4. T_g Values of DM Xerogels

sample	T_g (°C) ($\pm$ 1)
DAl	−123
DGe	−119, −111
DSn	not detected
DTi	−117
DZr	−115
DTa	−120, −109
DNb	−109

the rigid silicon atoms compared to that of the DGe gel. It does not present signals at chemical shift values between −3 and −10 ppm, evidencing the existence of "short" PDMS chains (M−[O−(CH$_3$)$_2$Si−O]$_n$−M, with 1 < n <4) in the material. In contrast, the spectra of the PDMS reference material cross-linked with Sn(IV), Nb(V), and Ta(V) are very similar to those of the corresponding DM gels (as illustrated in Figure 6(b) for the niobium system), except for the absence of the peak associated with cyclic tetramers (narrow peak at around −19 ppm). This suggests that the DSn, DNb, and DTa gels contain chains of at least 5 siloxane units.

DSC Experiments. DSC measurements of DM hybrids were performed to confirm the elastomeric character of the nanocomposites and to determine their glass transition temperatures (T_g). The high mobility of the siloxane chains in pure poly(dimethylsiloxane) polymer confers them an anomalously low T_g value (−123 °C), but the introduction of inorganic components as cross-linking agents restricts the micro-Brownian motion of the siloxane chains and a higher energy is required to induce the backbone movements, leading to higher T_g values. Table 4 shows the glass transition temperatures obtained for DM gels, which vary from −123 °C (for DAl) to −109 °C (for DTa or DNb). The error limit in the T_g measurements is ±1 °C.

These values effectively evidence the influence of the cross-linking metal on the degree of rigidity of the material. In samples DGe and DTa two vitreous transitions have been detected, which could correspond to the existence of two siloxane domains with different mobilities.
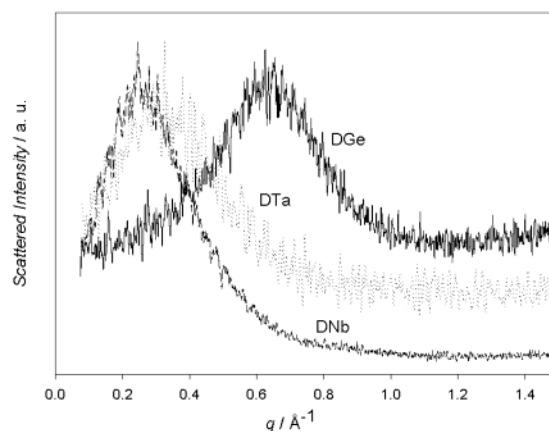

Figure 7. SAXS diffusion profiles ($\lambda = 1.54$Å) of DGe, DNb, and DTa.

SAXS Experiments. SAXS studies of hybrid materials made from PDMS polymers cross-linked with silica, titania, or zirconia based nanoparticles have been reported[10,51−54] and they show small heterogeneities corresponding to the oxo-metal nanodomains embedded in the siloxane network. To corroborate the presence of metal-oxo nanoparticles in the systems not reported till now, SAXS experiments have been carried out for DGe, DNb, and DTa hybrid samples.

Figure 7 shows the scattered intensity versus the scattering vector q(Å^{-1}) ($q = [(4\pi/\lambda)\sin\theta/2]$) for these samples.

The maxima of these profiles give an estimation of the distance (d) between these metal-oxo domains: $d = 2\pi/q_{max}$. From this expression, the distances calculated for DGe, DNb, and DTa are 0.97, 2.24, and 1.79 nm, respectively. The inter-domain distances increase in the sense DGe < DTa < DNb. Considering that the metal molar content for these systems is similar (Si/M $\approx$ 75:25), a major distance between these domains implies a major size of these aggregates and a worse dispersion of the cross-linking agent.

Discussion

As mentioned in the Introduction, this exhaustive study has been realized for determining the structure of PDMS-based hybrid nanocomposites in which the cross-linking metal has been systematically modified.

Considering the results from all the techniques employed, important structural differences have been evidenced depending on the hybrid system. First, the presence of hydroxyl groups in the samples which contain titanium, zirconium, and aluminum as cross-linking agents suggests the existence of hydrophilic domains. Taking into account the formation of PDMS chains evidenced by NMR experiments and the hydrophobic nature of the siloxane structure, this result can be explained supposing the existence of localized hydrophilic regions. On the other hand, if we consider the high degree of unsaturation (difference between oxida-

(51) Ulibarri, T. A.; Beaucage, G.; Schaefer, D. W.; Oliver, B. J.; Assink, R. A. *Mater. Res. Soc. Symp. Proc.* **1992**, *274*, 85.
(52) Glaser, R. H.; Wilkes, G. L. *Polym. Bull.* **1988**, *19*, 51.
(53) Huang, H. H.; Wilkes, G. L.; Carlson, J. G. *Polymer* **1989**, *30*, 2001.
(54) McCarthy, W.; Mark, J. E.; Schaefer, D. W. *J. Polym. Sci. B* **1998**, *36*, 1167.

tion state and coordination number) of Ti(IV), Zr(IV), or Al(III) species, and the tendency of the hydroxo nucleophilic groups to complete the unsaturated coordination sphere of these metals, it is reasonable to suppose that the OH groups detected by FTIR measurements could be situated inside oxo-metallic regions or in the interface between the siloxane network and the inorganic nanodomains. From this approach, the absence of OH groups in the other hybrids is in relation with a better dispersion of the cross-linking agent within the PDMS network.

The different profiles of the Si−O−Si stretching vibrations region in the FTIR spectra of DM gels reveals variations in siloxane chains arrangement. Several studies have been reported in order to understand the influence of the siloxane chain length on the position and intensity of the bands located between 1000 and 1100 cm^{-1}. Mauritz et al. proposed the first correlation between the band positions and the chain length.[55] From this study, a first interpretation of the nature of the siloxane component in the DM hybrid nanocomposites could be proposed. According to Mauritz's assignments, the DGe hybrid system, whose spectrum shows only a wide band centered at 1045 cm^{-1}, could be described as a material constituted by PDMS chains that contain about 4−5 siloxane units. Contrarily, the positions of the two stretching bands for the systems with M = Ti, Zr, and Al correspond to long PDMS chains. The matrixes with M = Ta, Nb, and Sn could present an intermediate structure, with an average number of siloxane segments between that observed for Ge and Ti, Zr and Al. Nevertheless, from this approach, only the general trends can be taken into account because the presence of metallic atoms near siloxane species can modify the energy of the asymmetric Si−O−Si stretching vibrations.

A more quantitative result has been obtained from the simulation of the ^{29}Si MAS NMR spectra of the DM samples, in which the percentage of the rigid/mobile silicon ratio can give some information about the length of the siloxane chains. For DGe gel the corresponding ratio is almost 1, which could be in agreement with a chain length of 4 siloxane units. This value underlines the high cross-linking character of the germanium species, probably due to an effective co-condensation between DMDES and Ge(OEt)$_4$ precursors. On the contrary, only 10−20% of the silicon species of the DZr, DTi, and DAl samples indicate the presence of a metal atom in their environment. This fact can be explained in terms of a much longer siloxane chain length than that for DGe gel, being in agreement with the results reported in the literature. Finally, the hybrid systems cross-linked with pentavalent elements showed an intermediate behavior, presenting siloxane chain lengths that oscillate between 6 (for DTa) and 10 units (for DSn). These results are completely in agreement with the trends analyzed from FTIR spectroscopy and the results of the ^{29}Si MAS NMR spectra of the PDMS reference materials.

The high extent of the interface between the inorganic and organic components of the hybrid material has been clearly evidenced by FTIR spectroscopy for DGe, DTa, and DNb systems. The detection of the M−O−Si stretching vibrations in their corresponding spectra corroborates an effective interaction between the two phases that takes place through ionocovalent Si−O−M bonds indicating a better molecular dispersion than in the other systems showing a smaller extent of the interface. Moreover, the presence of Si−O−M bonds produces severe constraints in the movements of the dimethylsiloxane units near the end of the chains. This effect is basically due to the high coordination number of the metal atom, especially in transition metals, that must be satisfied through a large number of M−O bonds. The rigidity of siloxane units has been evidenced by Raman and ^{29}Si MAS NMR spectroscopies and DSC measurements. Moreover, differences in the degree of structural constraints have been found for the distinct matrixes. Thus, the broad signals located at chemical shifts between −4 and −20 ppm appearing in ^{29}Si CP-MAS NMR spectra can be attributed to these constrained silicon species, and the nearer the metallic atom is, the higher the chemical shift. From DSC measurements, the low T_g value presented for DAl sample (−123 °C) could correspond to pure PDMS polymer, probably due to a more significant nanophase separation between siloxane and aluminum-oxo species. DTi and DZr gels show T_g values of −117 and −115 °C, respectively. The small increase in the glass transition temperature could indicate that the material presents relatively long siloxane chains which are weakly cross-linked by Ti and Zr species (due to a phase separation). The most important increase in T_g has been detected in DTa and DNb systems, at −109 °C, indicating a more effective cross-linking of the siloxane chains. The detection of two vitreous transitions in DTa and DGe can be attributed to the existence of regions with different rigidity. The relatively low T_g values, −119 and −111 °C, found in the DGe system, despite its being the most cross-linked system, could be explained by the low coordination of the germanium ion compared to that of the transition metals. This tendency was already observed for PDMS−vanadium-oxo hybrids inside which all V−O species are dispersed at molecular level.[12,23]

Conclusion

The PDMS−metal-oxopolymer nanocomposites presented in this work are hybrid materials constituted by metal-oxo nanodomains embedded in a PDMS framework. Nevertheless, a different arrangement of the constituents of the hybrid composite has been developed depending on the nature of the cross-linking agent. For hybrid systems incorporating Ti(IV), Zr(IV), or Al(III) in the polymer a nanophase separation was observed. In the hybrid system cross-linked with Sn(IV), despite Sn(IV) belonging to the same group as Si(IV), a poor dispersion degree of the metal is achieved, probably due to the 6-fold coordination of Sn(IV). In the case of DNb and DTa gels, a better dispersion of the metal-oxo domains is achieved, especially in the latter hybrid system. This fact has been deduced from the clear detection of Si−O−Ta bonds through FTIR and the high proportion of "rigid" silicon atoms detected by ^{29}Si NMR. Finally, the PDMS−germanium-oxo polymer presents a highly cross-linked structure in which germanium-

(55) Deng, Q.; Mauritz, K. A.; Moore, R. B. In *Hybrid Organic−Inorganic Composites*; Mark, J. E., Lee, C. Y. C., Bianconi, P., Ed. ACS Symposium Series 585; American Chemical Society: Washington, DC, 1994; p 66.

oxo domains are well-dispersed between short-length siloxane chains.^{17}O MAS NMR experiments are currently in progress to demonstrate the existence of M−O−Si in DNb, DTa, and DGe hybrid systems.

Supporting Information Available: Raman spectra of the DM dried gels (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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