



Structural and Microstructural Evolution During Pyrolysis of Hybrid Polydimethylsiloxane-Titania Nanocomposites

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Abstract. The evolution during pyrolysis of hybrid polydimethylsiloxane-titania nanocomposites has been studied as a function of the ratio between polysiloxane and titania phases. The xerogels, prepared by the sol-gel process starting from diethoxydimethylsilane and titanium isopropoxide, have been heated under argon atmosphere and the evolution with temperature has been followed by infrared and ^{29}Si solid state nuclear magnetic resonance spectroscopies, thermal analyses, X-ray diffraction, N_2 sorption measurements and scanning electron microscopy. Below 800°C , the polymer-to-ceramic conversion takes place at different temperatures with changing the titania content. The stability of Si-C bonds in polydimethylsiloxane networks depends on the metal oxide amount. The high reactivity of titanium atoms towards the Si-C bonds produces Si-C bond cleavage with mild thermal treatments and in the case of 30 mol% TiO_2 , leads to the ceramization of the hybrid nanocomposite at 500°C . Decreasing the titania load, a shift towards higher temperatures to complete the polymer-to-ceramic conversion is observed. The structural rearrangement of the siloxane moiety produces mesoporous and microporous materials, depending on the composition; in the case of 10 and 20 mol% TiO_2 content, the samples present high specific surface area up to 1200°C .

The crystallization process begins at 1000°C and the phase evolution depends on the composition. The phase analysis obtained from XRD spectra shows that different crystalline oxide and oxycarbide phases develop during the thermal process, as a function of the amount of available carbon, ultimately leading to the preferential crystallization of titanium carbide. Between 1000 and 1600°C the amorphous silicon oxycarbide phase undergoes a continuous structural evolution caused by the decrease of carbon content in the phase, leading to almost pure silica at 1600°C .

Keywords: polydimethylsiloxane-oxide hybrids, nanocomposites, pyrolysis, silicon oxycarbide, TiC

Introduction

A variety of hybrid organic-inorganic composites have been produced using the sol-gel process [1]. The organic moiety present in such hybrid materials can derive either from organic polymers or monomeric pre-

cursors [2, 3]. Using methyl-substituted silanes and different metal alkoxides, a broad range of compositions based on polymethylsiloxanes and metal oxides have been produced and their features have been studied for different applications [4]. During the last decade, a variety of polydimethylsiloxane-oxide hybrid nanocomposites have been prepared starting from diethoxydimethylsilane (DEDMS) and silicon, titanium,

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zirconium, aluminum and vanadium alkoxides, and a great effort has been carried on in order to characterize the evolution of the hydrolysis-condensation process and the structural morphology of resulting hybrid xerogels [5–13]. In either case, the stability of heterometallic bonds affects the structural features of the resulting materials. As a matter of fact, the multinuclear NMR study of these hybrid materials pointed out the different lability of Si—O—Me (Me = metal) bonds in solution, depending on the nature of the metal alkoxide [8]. In general, polydimethylsiloxane-oxide gels have been described as nanocomposites based on long and mobile polydimethylsiloxane chains and oxide particles that are nanometric in size [7, 8, 13, 14]. However, in the case of zirconia-based hybrid materials, both the solid state NMR study of the xerogels [7] and the characterization of the pyrolysis process by TG-GC-MS [15] led to the proposal of different structural models as a function of the composition. The degree of interaction between polydimethylsiloxane and zirconia phases increases with increasing the zirconium content, leading to a higher number of heterometallic Si—O—Zr bonds and shorter and more constrained polydimethylsiloxane chains. These structural features strongly affect the physical properties of the hybrid xerogels and govern the pyrolytic conversion of these hybrid materials, with a different extent of Si—C bond cleavage as a function of the Zr content. At high temperature, these effects produce a phase evolution strictly related to the chemical ratio between the precursors, ultimately leading to the formation of ZrO₂-SiO₂-SiC composites [16].

The metal oxide influence on the extent of phase mixing of different hybrid polysiloxane-oxide nanocomposites has been recently studied by means of equilibrium swelling experiments and measurements of mechanical properties [17]. The polydimethylsiloxane chain length clearly depends not only on the metal loading but also on the nature of the metal oxide, which leads to different cross-linking densities of the xerogels as a function of the amount of residual heterometallic bonds.

The liquid-state NMR study of the hydrolysis-condensation process of polydimethylsiloxane-titania hybrids revealed that Si—O—Ti bonds undergo redistribution reactions leading to the formation of Si—O—Si and Ti—O—Ti bonds [8]. Recently, the ¹⁷O MAS NMR spectra recorded on different hybrid titania-based xerogels [18] allowed quantifying the number of Si—O—Ti linkages, which appears significant indicating small titania-based domains. Previous re-

sults on the pyrolysis of a sample with 30% TiO₂ showed the formation at high temperature of a TiC-silica composite [19]. By comparing the pyrolysis products of polydimethylsiloxane-zirconia hybrids [16], a substantial difference appears in the ceramization process of polysiloxane-oxide nanocomposites with changing the nature of the metal alkoxide employed as network former. These previous findings have prompted us to study the pyrolytic transformation of polydimethylsiloxane-titania hybrid xerogels prepared with different diethoxydimethylsilane/titanium isopropoxide ratios. Preliminary results concerning the crystallization process have been recently published [20]. The goals of this paper are to examine closely the whole pyrolytic process and discuss the microstructural evolution and the phase composition of the final ceramics, taking into account the influence of titanium during the ceramization process.

Experimental

Preparation of Samples

As previously reported [6], a mixture of DEDMS (D), absolute ethanol and acidified water (pH = 1; HCl) in 1:1:1 molar ratio was allowed to react for three minutes before addition of the appropriate amounts of Ti(OPrⁱ)₄ (TI). The reactions were performed in air at 25°C. Samples were labeled DTIx where D and TI stand for silicon and titanium precursors, respectively and x is the molar percentage of TI, ranging from 10 to 30%. The homogeneous sols were cast in polypropylene vessels and gave transparent gels which were dried in air at 25°C for two weeks before the thermal treatments. The DTIx xerogels were heated under flowing Ar at different temperatures up to 1600°C with a heating rate of 1°C/min.

Characterization Techniques

FTIR spectra were recorded in transmission mode on KBr pellets using a Nicolet 5DXC spectrometer, collecting 64 scans in the 4000–400 cm⁻¹ range, with 2 cm⁻¹ resolution. ²⁹Si MAS NMR spectra were recorded on a Bruker MSL 400 spectrometer with pulse width and delay between pulses of 2 μs and 60 s, respectively. Peaks are labeled according to the conventional notation: M, D, T and Q refer to SiC_{4-x}O_x units with x = 1, 2, 3 and 4 respectively. N₂ sorption

experiments were carried out at 77K on an ASAP 2010 Micromeritics instrument. Gel samples and pyrolyzed samples were degassed below 1.3 Pa at 25°C and 250°C, respectively. The specific surface area (SSA) was calculated by the BET equation in the interval $0.05 \leq p/p_0 \leq 0.33$ with a least-squares fit of 0.998. Single point total pore volume (TPV) was calculated at $p/p_0 = 0.995$.

Thermogravimetric and differential thermal analyses (TGA and DTA) were performed on a Netzsch STA 409 thermobalance under 100 cc/min Ar flow and with 10°C/min heating rate. XRD spectra were collected on a Rigaku DMax diffractometer in the Bragg-Brentano configuration, using Cu K α radiation and a monochromator in the diffracted beam. Quantitative XRD analyses were performed using a modified Rietveld method, developed for the amorphous phase determination in ceramic materials [21]. This method allows the determination of the whole phase fractions and the calculation of the crystallite sizes on the basis of the Warren-Averbach theory. According to the reported method, we assume that an amorphous phase could be computed as a nanocrystalline structure with crystallite size corresponding to about one unit cell. Accordingly, the amorphous silica is fitted with a simple cubic structure (P213), derived from the hexagonal α -Carnegieite structure [22]. SEM micrographs were obtained with a Jeol 5500 microscope working at 20 kV.

Results and Discussion

The Polymer-to-Ceramic Transformation

Polydimethylsiloxane-titania xerogels, prepared from $(\text{CH}_3)_2\text{Si}(\text{OEt})_2$ and $\text{Ti}(\text{OPr}^i)_4$, are transparent and homogeneous up to 30 mol% TI loads and change from compliant to brittle with increasing TI content [17]. The evolution of the FTIR spectra with temperature indicates that the thermal stability depends on the chemical composition. The FTIR spectra of DTI10 at different temperatures are shown in Fig. 1(a). The main signals due to Si—O—Si bonds in polydimethylsiloxane chains (1099 and 1018 cm^{-1}) [23] and Si—CH₃ absorption peaks ($\delta(\text{CH}_3) = 1266\text{ cm}^{-1}$, $\delta(\text{Si—C}) = 796\text{ cm}^{-1}$) [24] do not show any significant change after the thermal treatment at 500°C. A strong modification of the Si—O—Si signals appears only after heating at 800°C: a wide and broad Si—O band centered at 1051 cm^{-1} , and the disappearance of signals due to the Si—CH₃ groups characterize the spectrum, and the peaks due to the adsorbed water increase in intensity. At 1000°C, these spectral features are almost unchanged and the spectrum exhibits the relevant presence of Si—OH bonds, whose absorption is detected at 957 cm^{-1} . The intensity of signals due to adsorbed water (3300 and 1620 cm^{-1}) increases with increasing temperature, suggesting the increase of the surface

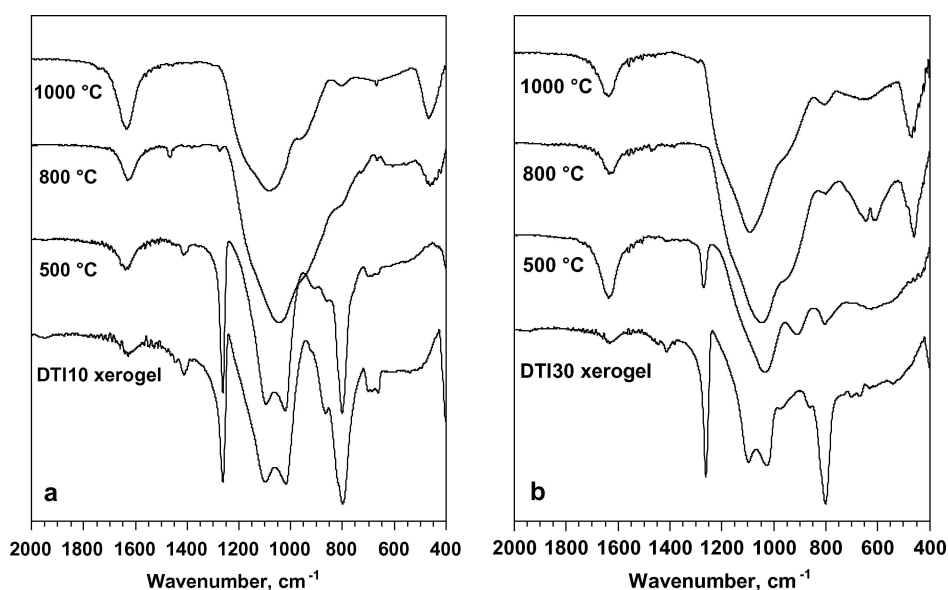


Figure 1. FTIR spectra evolution with temperature of: (a) DTI10 and (b) DTI30.

area during the pyrolysis process and favoring the formation of Si-OH terminal groups. The titanium percentage increase results in the decrease of thermal stability of hybrid gels, as revealed by the evolution of FTIR spectra of DTI30 (Fig. 1(b)). In the DTI30 xerogel, the polydimethylsiloxane chains are recognizable from two absorption peaks, due to Si-O-Si bonds, at 1099 and 1031 cm^{-1} . These signals turn to a single broad absorption band centered at 1038 cm^{-1} at 500°C. At this temperature, the decrease in intensity of the peaks related to Si-CH₃ bonds is also observed. DTI20 shows an intermediate behavior with a less pronounced Si-O-Si band evolution, which corresponds to a lower reduction of the Si-CH₃ signals. The transformation of the Si-O-Si peaks and the consumption of Si-CH₃ groups are related to the loss of the initial arrangement between siloxane units in the gel network as a consequence of Si-O-Si bond redistribution reactions. For all compositions, heating up to 1000°C (Fig. 1(a) and (b)) produces a shift of the Si-O-Si band towards higher frequencies, which is consistent with length and energy modification of Si-O-Si bonds.

The different thermal stability revealed by the FTIR study is confirmed by the thermogravimetric behavior of DTIx samples, studied by TG analyses. The TGA traces, reported in Fig. 2, show different thermal pathways for DTI10 and DTI30 with the exception of the first broad effect between 20 and 250°C, mainly due to the loss of condensation products like water and alcohols. The TG curve of DTI10 is characterized by two defined weight loss steps in the ranges 300–500°C and 500–1000°C, which correspond in the DTG curve to two peaks at 400 and 640°C, respectively. DTI30 shows a continuous weight loss between 250 and 650°C. The

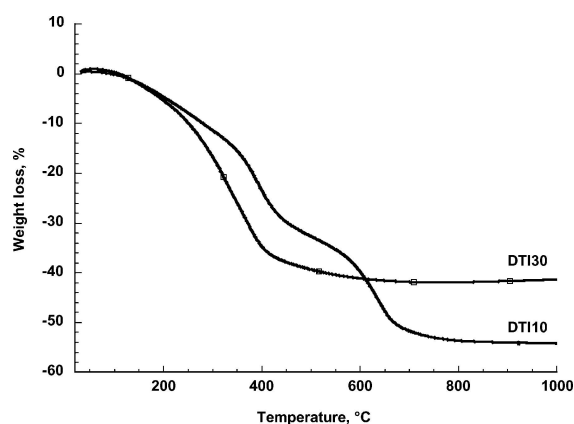


Figure 2. TGA curves of DTI10 and DTI30.

derivative of the TG trace presents a broad peak generated by the overlapping of two peaks at 310 and 370°C, respectively. The total weight loss increases with a decrease in the metal oxide content, as already reported for analogous nanocomposites [16], but in the case of DTI30 the end of the thermal evolution is reached at a temperature around 200°C lower than for DTI10. This confirms the influence of the metal oxide loading in decreasing the stability of polysiloxane-oxide networks and favoring the polymer-to-ceramic conversion, as observed for polysiloxane-zirconia gels [15]. Equilibrium swelling, mechanical and dynamic mechanical results [17] have revealed that the extent of phase interaction, due to co-condensation between siloxane and oxide counterparts, increases with increasing % of metal oxide. The higher Si-O-Ti bond number allows DTI30 to undergo redistribution and Si-C decomposition reactions at mild temperatures, with the evolution of methane and volatile Si-based species as was shown by the evolved gas analysis [25].

The influence of the titania loading on thermal behavior of polysiloxane-titania nanocomposites leads to different microstructural features of the DTIx samples during the pyrolysis process. The DTIx are non-porous solids at the xerogel state, with very low nitrogen adsorbed volume and specific surface area lower than 1 m^2/g . These features are maintained at 250°C for all compositions. According to the nitrogen adsorption isotherms shown in Fig. 3(a), at 500°C the thermal treatment transforms DTI30 in a microporous solid, whereas DTI10 remains non porous and DTI20 shows a modest adsorbed volume increase. Between 500 and 800°C, the pyrolytic transformation leads to the production of high porosity in DTI10 (Fig. 3(b)), which is characterized by the typical isotherm of mesoporous solids with hysteresis in the desorption branch (not reported). At 800°C (Fig. 3(b)), DTI20 is microporous and DTI30 displays very low porosity, and these features are maintained at 1000°C. Table 1 reports the evolution of SSA and TPV calculated from the adsorption isotherms at different temperatures. Starting from 800°C, the pyrolytic conversion of DTI10 leads to very high porosity (TPV) and SSA, which is retained even at high temperature (192 m^2/g at 1200°C). On the contrary, DTI30 presents the highest SSA value at 500°C, afterwards the porosity collapses leading to a non-porous material at 800°C. These differences in microstructure have been also recognized in the SEM micrographs. The DTIx xerogels are characterized by the typical flat and featureless surface of

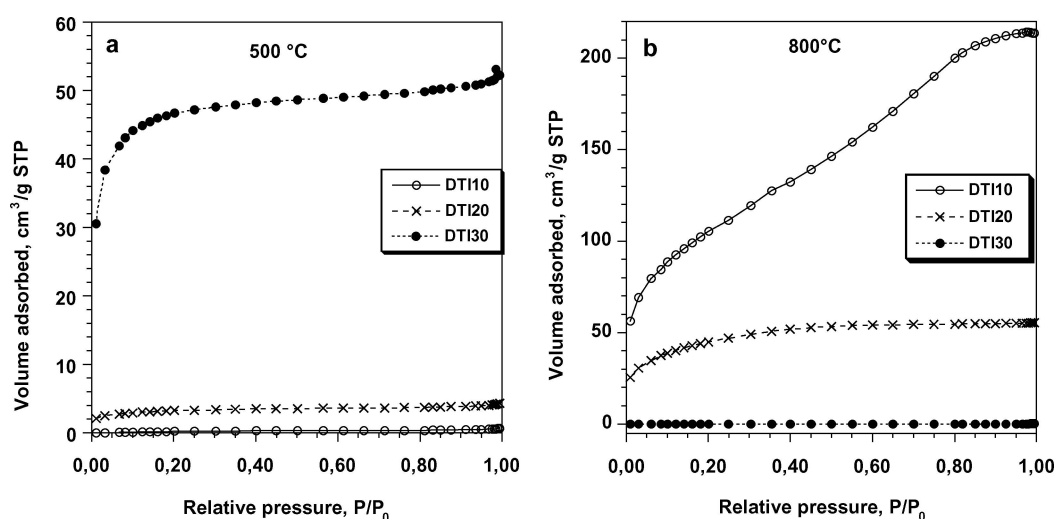


Figure 3. N_2 adsorption isotherms of DTIx at: (a) 500 °C and (b) 800 °C.

amorphous organic/inorganic hybrids, and this appearance is maintained up to 800 °C in DTI10 and DTI20. On the contrary, at 500 °C DTI30 shows a rough surface characterized by fine porosity typical of inorganic materials.

The Thermal Evolution Between 800 and 1600 °C

The modification of FTIR signals related to Si—O and Si—C bonds (Fig. 1(a) and (b)) during the first pyroly-

Table 1. Specific surface area (SSA) and total pore volume (TPV) calculated from N_2 sorption isotherms.

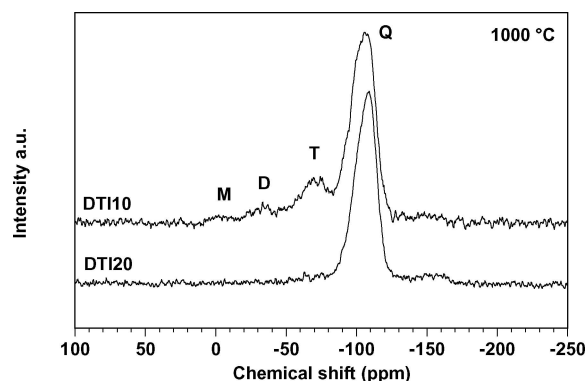
Sample	Temperature, °C	*SSA, m ² /g	*TPV, cm ³ /g (STP)
DTI10	500	2	0.001
	800	384	33
	1000	273	0.3
	1600	3	0.008
DTI20	500	11	0.007
	800	159	0.09
	1000	112	0.07
	1600	1	0.002
DTI30	500	175	0.08
	800	0.2	0.0003
	1000	0.8	0.001
	1600	0.8	0.001

*SSA calculated using BET equation; TPV calculated at $P/P_0 = 0.995$.

ysis steps highlights the structural modification of the silicon local environment as a consequence of the Si—C bond cleavage and redistribution reactions with formation of new Si—O bonds. The structural evolution of DTIx during the further pyrolysis has been studied using ^{29}Si MAS NMR spectroscopy. The ^{29}Si MAS NMR spectra of DTIx xerogels are characterized by a main sharp peak at -22 ppm due to D units in flexible polydimethylsiloxane chains and a broad peak centered at -16 ppm, which corresponds to more constrained D units close to titania-based particles [8]. The evolution of the ^{29}Si MAS NMR spectra during the pyrolysis of DTI30 was reported in a previous paper [19], which pointed out the rearrangement reactions involving the silicon atoms during pyrolysis. The results obtained on DTIx at different temperatures are collected in Table 2. At 800 °C, the DTI10 spectrum shows three main signals corresponding to the presence of *D*, *T* and *Q* units in a $\text{SiC}_x\text{O}_{4-x}$ oxycarbide phase (SiOC). Increasing the Ti% leads to an increase in *Q* units with the almost complete disappearance of *D* and *T* units in DTI30. This is due to the extent of Si—C bond cleavage observed during the pyrolysis at lower temperature, which depends on the Ti content and determines the amount of bonded carbon present in the network at high temperature. At 1000 °C (Fig. 4), the DTI10 spectrum presents signals at -3 , -32 , -72 and -105 ppm attributed to different Si units of the SiOC phase, whereas DTI20 shows the main peak due to *Q* units, which accounts for 95 mol% of total silicon. The spectrum of DTI10 at 1400 °C (Fig. 5) is characterized by broad signals at

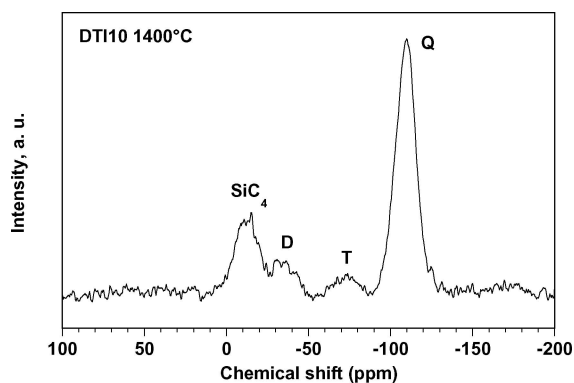
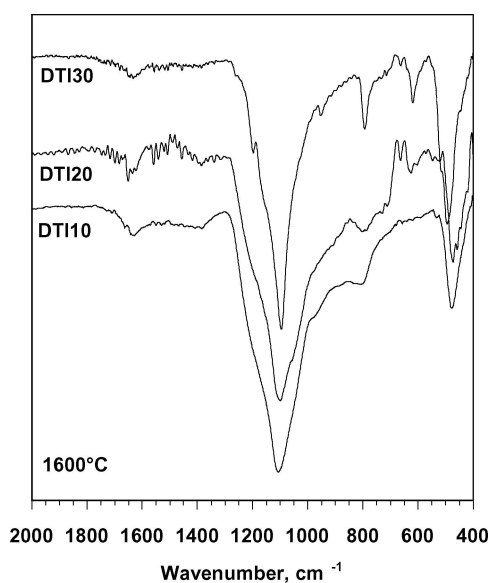
Table 2. Results calculated from the fitting of ^{29}Si MAS NMR spectra.

Sample	Temperature, °C	Chemical shift, ppm	Mol%
DTI10	800	-22.6	17
		-62.5	32
		-101.1	51
		-3.3	2
	1000	-31.9	6
		-72.2	25
		-105.2	67
	1400	-12.4	22
		-34.9	8
		-73.2	4
DTI20	800	-109.3	66
		-60.7	20
	1000	-106.5	80
DTI30	800	-72.6	5
		-106.7	95
	800	-107.6	≈ 100

Figure 4. ^{29}Si MAS NMR spectra of DTI10 and DTI20 at 1000°C.

-12, -35, -73 and -109 ppm, assigned to the presence of SiC and $\text{SiC}_x\text{O}_{4-x}$ phases.

Particularly noteworthy are the high chemical shift shown by the Q units at 800°C in DTI10 and the dependence of the Q signal position on the titanium loading and the pyrolysis temperature. In fact, at 800°C the Q signal shifts to lower fields from DTI10 (-101 ppm) to DTI20 (-106 ppm) and DTI30 (-108 ppm). Moreover, the chemical shift of the Q units in DTI10 changes from -101 ppm at 800°C to -105 ppm at 1000°C, finally reaching the usual value shown by SiO_4 units in silicon oxycarbide glasses (-109 ppm) at 1400°C. This behav-

Figure 5. ^{29}Si MAS NMR spectrum of DTI10 at 1400°C.Figure 6. FTIR spectra of DTI x at 1600°C.

ior has been observed in the case of nanocomposites obtained by pyrolysis of polydimethylsiloxane-zirconia xerogels, and has been attributed to a contribution of Si—O—metal bonds to the Q unit peak [16].

In the case of DTI30, the silicon atoms appear involved in an amorphous silica-based structure starting from 800°C and no relevant changes to silicon local environment take place on increasing the temperature. At 1600°C, the DTI30 FTIR spectrum (Fig. 6) shows the presence of cristobalite, with signals at 1200, 1098, 798 and 622 cm^{-1} [23]. On the contrary, the broad signal ($\approx 1100 \text{ cm}^{-1}$) assigned to Si—O vibrational modes is consistent with the presence of amorphous silica in DTI10 and DTI20 at 1600°C.

Table 3. XRD quantitative analyses on DTI samples.

Sample	T , °C	Amorphous phase (wt.%) cell parameter a^a , Å	TiOC ^b (wt.%) cell parameter a^c , Å	Crystalline phases ^d , (crystallite sizes, nm)
DTI10	1000	(72.3 ± 0.4) 6.82 ± 0.03	(17 ± 2) 4.280 ± 0.003	TiO ₂ (b)
	1200	(67.5 ± 0.3), 6.94 ± 0.03	(32 ± 3) 4.3139 ± 0.0009	–
	1400	(56 ± 1) 7.16 ± 0.02		SiC, TiC, SiO ₂ (c)
	1600	(63 ± 1) 7.20 ± 0.01		TiC (15), β -SiC (2), SiO ₂ (c) (32)
DTI20	1000	(68.7 ± 0.5), 7.10 ± 0.04	(23 ± 3) 4.264 ± 0.002	TiO ₂ (b + r)
	1200	(62.8 ± 0.4), 7.10 ± 0.02	(37 ± 3) 4.3080 ± 0.0008	–
	1400	(70 ± 2) 7.15 ± 0.02		TiC, SiO ₂ (c), Ti ₃ O ₅ (d)
	1600	(70 ± 5) 7.23 ± 0.01		TiC (10), TiO (6), Ti ₂ O ₃ (37), SiO ₂ (c) (13)
DTI30	1000	(76 ± 3), 7.12 ± 0.03	(18.0 ± 0.4) 4.218 ± 0.001	TiO ₂ (r)
	1200	(53.4 ± 0.7), 7.18 ± 0.02	(33 ± 2) 4.2827 ± 0.0003	Ti ₃ O ₅ (g)
	1400	(22.8 ± 0.8) 7.13 ± 0.01	(29 ± 2) 4.3110 ± 0.0002	SiO ₂ (c), Ti ₃ O ₅ (g + d)
	1600	–		SiO ₂ (c) (65), TiC (33), Ti ₃ O ₅ (d) (78), Ti ₂ O ₃ (39), TiO (13)

^a a (SiO₂ glass) = 7.2100 Å [11].^bTiOC = TiO_xC_{1-x} [20].^c a (TiO) = 4.177 Å, a (TiC) = 4.3274 Å.^db = brookite; r = rutile; c = cristobalite; g = γ -Ti₃O₅ (PDF card n. 40-806); d = D-Ti₃O₅ (PDF card n. 23-606).

The phase evolution with temperature has been studied by X-ray diffraction analysis [20]. XRD spectra have been collected for all samples from 800 to 1600°C; as an example, the spectra evolution of DTI10 is reported in Fig. 7. The results of qualitative and quantitative phase analysis calculated from the profile fitting procedure are collected in Table 3. In spite of the chemical composition, at 800°C the samples are amorphous. Further heating gives rise to the onset of crystallization processes, with phase evolution dependent on the titanium content. For all compositions, the first assignable signals are present at 1000°C. Two main phases are recognizable, an amorphous silica-based phase (broad band centered at $2\theta = 22^\circ$) and a titanium-based phase (main signals at $2\theta = 35^\circ$ and 43°).

During the pyrolysis process, the silicon atoms are involved in the formation of a silicon oxycarbide phase SiC_xO_{4-x}, and the amount of carbon retained in the

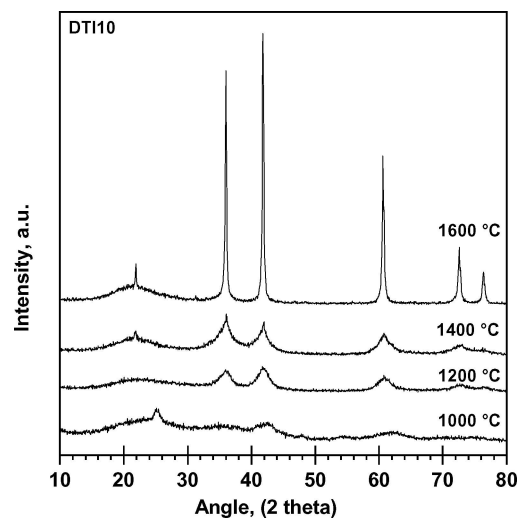


Figure 7. Evolution with temperature of DTI10 XRD patterns.

SiOC network depends on the Ti load, as shown by the ^{29}Si MAS NMR results. In order to perform the phase fraction analysis by the computing procedure, the amorphous halo at $2\theta = 22^\circ$ has been attributed to the $\text{SiC}_x\text{O}_{4-x}$ phase, and it has been assumed that the carbon retained in the silica-based network could affect the cell parameter a , the only adjustable parameter for a cubic structure. The signals due to the titanium-based phase have been assigned to a mixed $\text{TiO}_x\text{C}_{1-x}$ phase (TiOC) [26], which can be considered from a pure computational point of view as a solid solution of two cubic structures, TiC (PDF card n. 32-1383, a parameter = 4.3274 Å) and TiO (PDF card n. 8-117, a parameter = 4.177). Like in the case of SiOC, the analogous modification of the TiOC a parameter with changing carbon content has been considered. At 1000°C, minor crystalline TiO_2 phases are present in all compositions, attributed to TiO_2 primary separation as brookite for DTI10 and rutile for DTI30 (both phases are present for DTI20). Further heating at 1200°C leads to the evolution of the oxycarbide phases with the disappearance of TiO_2 , and the appearance of titanium suboxide, $\gamma\text{-Ti}_3\text{O}_5$, in DTI30. The most important differences among the samples are found at 1400°C. The amorphous silica-based phase is the main phase in DTI10 and DTI20 whereas DTI30 shows an extensive crystallization of cristobalite SiO_2 . Peaks due to crystalline TiC overlapped to those of crystalline SiC appear in DTI10 and can be recognized because TiC and SiC cubic phases have quite similar a values but opposite relative intensity for the first two peaks [27]. At 1400°C, DTI30 still presents the $\text{TiO}_x\text{C}_{1-x}$ phase together with the polymorphic mixture of γ - and D- Ti_3O_5 . Final heating to 1600°C produces nanocomposites made of amorphous silica and TiC, with TiC crystallite sizes smaller than 40 nm. Minor phases as SiC and cristobalite are found in DTI10, whereas pure TiO, Ti_2O_3 and cristobalite are present in the case of DTI20. At 1600°C, DTI30 is fully crystallized, with the presence of cristobalite, TiC and a minor content of titanium oxides (TiO, Ti_2O_3 , Ti_3O_5).

The quantitative phase analyses describe the thermal evolution of the amorphous silica-based phase and TiOC phase as a function of Ti content, which also determines the amount of carbon retained into the network. In DTI10, the cell parameter calculated for the Si-based amorphous phase shows an increase on increasing the temperature (Table 3) from 1000 to 1600°C. At 1000°C, the DTI10 SiOC phase is characterized by $a = 6.825$ Å, a value far from that found for pure silica

glass ($a = 7.21$ Å) [21]. Taking into account the distribution of Si units obtained by NMR (Table 2), this result can be justified on the basis of the structure proposed for silicon oxycarbide glasses [28], where the carbon atom, bonded to four different silicon atoms, increases the bond density of the structure leading to a denser system, characterized by smaller a value in the case of a cubic crystal structure. In DTI10, the parameter a progressively increases during the pyrolysis and reaches the reference value of pure silica glass at 1600°C as a consequence of the decrease of carbon content in the silicon oxycarbide phase. With increasing the titanium content, at 1000°C very few carbon atoms remain bonded to silicon in the silica network and the parameter a is close to that of silica, as in the case of DTI20.

Above 1200°C the crystallization of SiC is detected in the case of DTI10, due to the SiOC phase separation into SiO_2 and SiC. A similar behavior was observed for samples obtained by co-hydrolysis of DEDMS and tetraethoxysilane in 1/1 molar ratio; in the 1000–1300°C temperature range, redistribution reactions between Si–O and Si–C bonds occurred, leading to an enrichment of SiO_4 and SiC_4 units [29]. As long as the Ti load increases, the extent of Si–C bond cleavage during the ceramization process increases, reducing the carbon available in the network at high temperature. According to the greater affinity of titanium towards carbon in comparison to silicon, in the samples with higher Ti load the SiC crystallization is not detected and the formation of TiC could account for the disappearance of the remaining Si–C bonds in the amorphous oxycarbide phase. The preferential formation of Ti–C bonds was already observed in other polymer-derived ceramics cross-linked using titanium alkoxides [30]. The change in TiOC cell parameter as a function of composition and temperature supports the change in Ti local environment. The increase of a value indicates the replacement of oxygen with carbon as titanium nearest neighbors. The evolution of TiOC cell parameter in DTI30 perfectly agrees with the structural evolution determined using X-ray absorption and showing the progressive transformation of Ti–O into Ti–C environment from 1000 to 1600°C [19]. The TiC formation could consequently derive from TiOC decomposition. Different titanium oxides are formed during the thermal process, depending on the reduction ability of the matrix that determines the extent of redox reactions involving titanium atoms ($\text{Ti}^{4+} \rightarrow \text{Ti}^{3+} \rightarrow \text{Ti}^{2+}$). Again, this fact could be related to the carbon presence

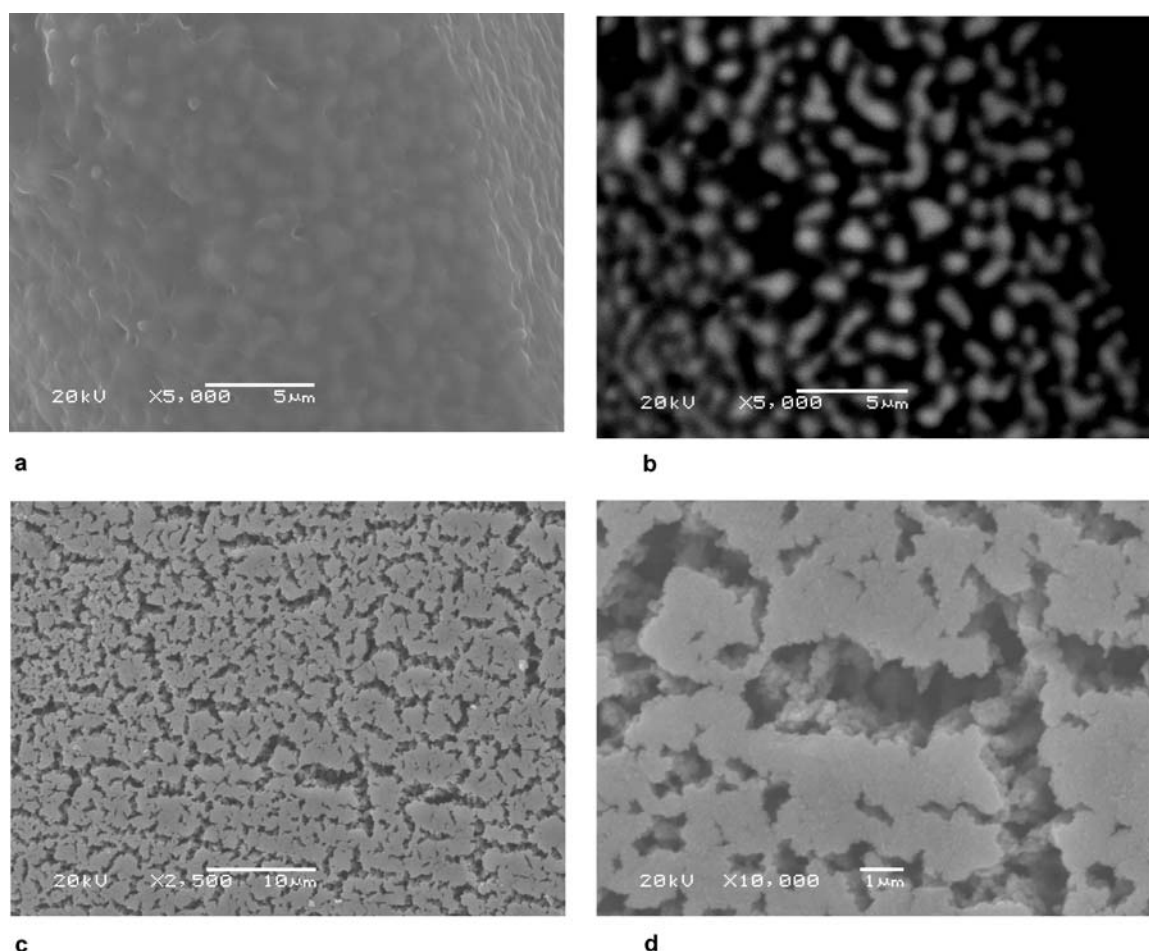


Figure 8. SEM micrographs of DTI30 [(a) and (b) (backscattered electrons)] and DTI10 [(c) and (d)] at 1600°C.

in the network depending on the Ti load. Between 1000 and 1200°C, another process involves the TiO_2 crystalline phase, which disappears leading to an increase of TiOC phase. Since a concomitant decrease of SiOC phase takes place, the reaction between SiOC and TiO_2 could account for the formation of TiOC . This process can be brought to an end only when enough carbon is available. In fact, in DTI30 the reaction leads also to the formation of Ti_3O_5 . We have to stress the fact that the TiO_2 decomposition pathway proposed here (for networks containing bonded carbon) is quite different from the commonly accepted process involving titania and free carbon, which produces TiC [26].

More details on the microstructure have been obtained from the SEM study. The SEM micrographs of DTI10 and DTI30 at 1600°C are presented in Fig. 8. DTI30 appears fully dense and shows the separation in two phases, one of which rich in titanium (Fig. 8(a)), as

confirmed by the image obtained by backscattered electrons (Fig. 8(b)). On the contrary, a residual macroporosity is present in DTI10, and is probably determined by the decomposition reactions of the silicon oxycarbide phase (Fig. 8(c) and (d)).

Conclusions

The structural and microstructural evolution of polydimethylsiloxane-titania nanocomposites has been studied as a function of the composition. During the ceramization process, the titanium loading determines the amount of carbon retained in the network as a consequence of Si-C bond cleavage and leads to a different evolution of porosity of DTIx samples. The different evolution below 800°C affects the crystallization process at high temperature. Carbon availability, titanium

affinity towards carbon, and titanium redox properties lead to the formation of silicon and titanium oxycarbide phases and different phase crystallization depending on titanium load. The evolution of SiOC and TiOC cell parameters can be related to the amount of carbon bonded in the silicon oxycarbide phase and the changes of titanium local environment, respectively.

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