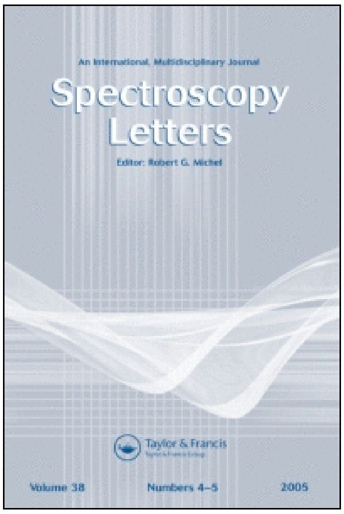

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FT-IR Study of the Hydrolysis and Polymerization of Tetraethyl Orthosilicate and Polydimethyl Siloxane in the Presence of Tetrabutyl Orthotitanate

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ABSTRACT

In this work, we have used FT-IR spectroscopy to study the hydrolysis and polymerization reactions of tetraethyl orthosilicate (TEOS) and polydimethyl-siloxane (PDMS) in the presence of tetrabutyl orthotitanate (TBOT). These reactions are used for obtaining SiO_2–PDMS–TiO_2 organically modified silicates (Ormosils). In order to obtain semi-quantitative information about such reactions, a deconvolution procedure

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of the FT-IR spectra has been done by use of a computer program. Hydrolysis reactions have been characterized by Me–O–C (Me = Si, Ti) bonds, and polymerization reactions by Me–O–Me bonds. Instantaneous hydrolysis of TEOS has been observed, together with condensation reactions between Si–OH groups, which give crosslinked and linear Si–O–Si structures. The TBOT is also hydrolyzed, but the high acid concentration inhibits condensation reactions between Ti–OH groups. The PDMS also condenses mainly with Si–OH groups and probably with Ti–OH, finally forming Me–O–PDMS bonds. The formation of Si–O–Si crosslinked structures and also Me–O–PDMS structures continues until the end of reaction. The gelling time is dependent on TBOT concentration in the reaction medium and, therefore, polycondensation reactions are dependent on TBOT concentration.

Key Words: Titanium alkoxide; Hydrolysis; FT-IR spectroscopy; Deconvolution; Ormosils.

INTRODUCTION

In the last two decades hybrid organic/inorganic materials have been successfully prepared by sol–gel processes.[1–4] These materials are synthesized by chemically incorporating organic polymers into inorganic networks. For SiO_2-related materials, alkoxysilanes have been used as starting materials.[5] Tetra-functional alkoxysilane such as Tetraethyl orthosilicate (TEOS) was used as the basic inorganic component. This was mainly due to its controllable hydrolysis reaction rate,[5] which could assist in the possibility of incorporating oligomeric species into the system.

Extensive studies have been focused on hybrid materials prepared from polydimethyl-siloxane (PDMS) and TEOS. These materials are known as "Ormosils" (organically modified silicates).[2,4,6] The introduction of other inorganic components, such as metal alkoxides, into the Ormosils structure, is done in order to improve their mechanical, thermal, and optical properties.[7–13] The alkoxides of titanium, zirconium, tantalium, etc., are some of the metal alkoxides with which PDMS can be copolymerized.[7–12]

Hg porosimetry, N_2 adsorption, He picnometry, SAXS, DSC, UV were some techniques that have been used to characterize mechanical, optical, and thermal properties of TEOS–PDMS–Ti Ormosils.[7–10] Reactions among TEOS–PDMS–Ti alkoxides and TEOS–dimethyldiethoxysilane(DMDES)–Ti alkoxides were investigated by liquid state ^{29}Si NMR spectroscopy.[14] The structural evolution and properties of other systems, such as diethoxydimethylsilane (DEDMS)–Ti, PDMS–Ti and TEOS–DMDES-Ti, have been characterized by ^{17}O and ^{29}Si solution NMR, ^{29}Si and ^{1}H MAS-NMR, x-ray absorption spectroscopy, and FT-IR spectroscopy.[11,14–17] However, the hydrolysis and polymerization mechanism of the TEOS–PDMS–Ti system has been scarcely studied.

In the present work, we have studied the influence of titanium alkoxide in the hydrolysis and polymerization reactions of the TEOS–PDMS system in order to obtain SiO_2–PDMS–TiO_2 Ormosils. This study has been done by means of FT-IR spectroscopy. The systems were followed all along the synthetic process, from the molecular precursors to the final gelled materials.

EXPERIMENTAL

Materials

The Ormosils were prepared using TEOS (Merck, analytical reagent grade), PDMS of 550 molecular weight (Gelest, Germany), tetrabutyl orthotitanate (TBOT) (Aldrich, analytical reagent grade), isopropyl alcohol (iPr-OH, Merck), hydrochloric acid (HCl, Merck), and deionized distilled H_2O. The inorganic part of these Ormosils is considered as the sum of TEOS and TBOT and the organic one is PDMS. In this work, the inorganic/organic mass ratio was 70/30 and the other molar ratios were HCl/inorganic = 0.5, H_2O/inorganic = 3, and iPr-OH/inorganic = 4.5. In order to know the influence of TBOT, we have prepared Ormosils with TEOS/TBOT mass ratios of 70/0, 69/1, 67/3, 65/5, 63/7 (i.e., %TBOT of 0, 1, 3, 5, and 7). Simultaneously, molar and mass ratios are used here as it is usually employed in published works related to Ormosil materials.

The Ormosils were obtained as follows. Firstly, three solutions were prepared. The first solution contains the total volume of TEOS, PDMS, and one-third of the total volume of iPr-OH. The second solution contains one-third of total volume of iPr-OH and the total volume of HCl and H_2O and the last one contained the remaining iPr-OH and the total volume of TBOT. The three solutions were mixed separately for 30 min in order to obtain homogeneous solutions. The first and the second solutions were mixed in a flask (introduced into a thermostatic bath at 80°C previously) and immediately the last solution was added dropwise for 15 min in order to avoid precipitation of $Ti(OH)_4$. The addition steps of the three solutions were done under reflux and stirring at 80°C. Such condition were maintained for 20 min. After that time, the solutions were poured into a plastic container and sealed until gelling occured. In this work, all samples were prepared following the same procedure. The gelling time for 0, 1, 3, 5, and 7 %TBOT samples were 37, 40, 45, 50, and 90 min, respectively. The total volume of solutions was always 300 mL. It must be taken into account that for the first solution, the PDMS used is perfectly soluble with TEOS and iPr-OH, and therefore does not have phase separation. When the second solution is added to the first solution, the presence of H_2O may give phase separation due to the nonsolubility of PDMS in H_2O. However, as it will be shown later, the very fast hydrolysis of TEOS gives ethanol, which maintains the solubility of PDMS in the whole solution, and no phase separation is observed.

The aim of this work is to study the hydrolysis and polycondensation reactions involved in the Ormosil obtained, from the mixing of raw materials to gelling of the final solution. The Ormosils were obtained after the gel was dried.

Methods

The FT-IR measurements were done by use of a Perkin–Elmer spectrophotometer mod. 1720X with a resolution of $2\,cm^{-1}$. Ten scans were recorded for each spectrum and the background was subtracted in all cases. The FT-IR measurements were done by adding one micro-drop of reacting solution between two KRS-5 crystals (KRS-5 is transparent to IR light) using a micro-burette. Each spectrum was recorded, by taking a new drop from the reacting solution at a given time. Spectra were stored in a computer and analyzed as will be shown in the next section.

RESULTS AND DISCUSSION

As noted above, gelling times of the final solutions increase as the TBOT concentration increases. This result shows that TBOT plays an important role in the reactions involved in the preparation of SiO_2–PDMS–TiO_2 Ormosils. In this work, we studied these reactions by means of FT-IR spectroscopy. The FT-IR spectra are taken from raw materials to gelled samples.

The assignments of absorption bands from TEOS,[18–20] PDMS,[21,22] and TBOT[23–25] are shown in Table 1.

In order to know the influence of TBOT in reactions above noted, a sample was prepared without TBOT, and analyzed by FT-IR spectroscopy. The FT-IR spectra of the reacting solutions, at a given time, are shown in Fig. 1. It must be taken into account that in all cases time $t = 0$ corresponds to TEOS–PDMS-1/3iPr-OH solution (see Experimental section).

In the $4000–2500\,cm^{-1}$ spectral region of spectrum 1(a), it can be observed that there are four bands located at 3335, 2975, 2930, and $2893\,cm^{-1}$. The wide band of high intensity, located at $3335\,cm^{-1}$ correspond to the O–H bond vibrations from to the iPr-OH, which was used as the solvent. From

Table 1. Absorption bands of raw materials.

PDMS		TEOS		TBT	
Absorption (cm^{-1})	Assignment	Absorption (cm^{-1})	Assignment	Absorption (cm^{-1})	Assignment
3306	νO–H	2976	$\nu_{a\ C-H}$ in CH_3	3330	νO–H
2964	$\nu_{a\ C-H}$ in CH_3	2930	$\nu_{a\ C-H}$ in CH_2	2960	$\nu_{a\ C-H}$ in CH_3
2905	$\nu_{s\ C-H}$ in CH_3	2891	$\nu_{s\ C-H}$ in CH_3	2930	$\nu_{a\ C-H}$ in CH_2
1413	δ_a CH_3	1484	$\delta_{a\ C-H}$ in CH_2	2870	$\nu_{a\ C-H}$ in CH_3
1262	δ_s CH_3 in $Si(CH_3)_2$	1444	$\delta_{s\ C-H}$ in CH_2–O	1465	$\delta_{a\ C-H}$ in CH_2
1088, 1034	$\nu_{a\ Si-O}$ in Si–O–Si	1391	$\delta_{s\ C-H}$ in CH_3	1375	$\delta_{s\ C-H}$ in CH_3
895	$\nu_{a\ Si-O}$ in Si–OH	1279	$\delta_{w\ C-H}$ in CH_3	1125	ν_{Ti-O-C} in CH_3–$(CH_2)_3$–O
860	CH_3 rocking	1170	CH_3 rocking	1085	ν_{Ti-O-C} in CH_3–$(CH_2)_3$–O
805	ν_a Si–C	1108	ν_a Si–O–C	1035	ν_{Ti-O-C} in CH_3–$(CH_2)_3$–O
698	ν_s Si–C	1080	ν_s Si–O–C	994	
658	Si–CH_3 rocking	968	CH_3 rocking	969	
		810	CH_2 rocking	901	
		795	SiO_4 a.	864	νC–O
		656	SiO_4 s.	606	νTi–O
		480	δO–C–C		
		464	δO–Si–O		

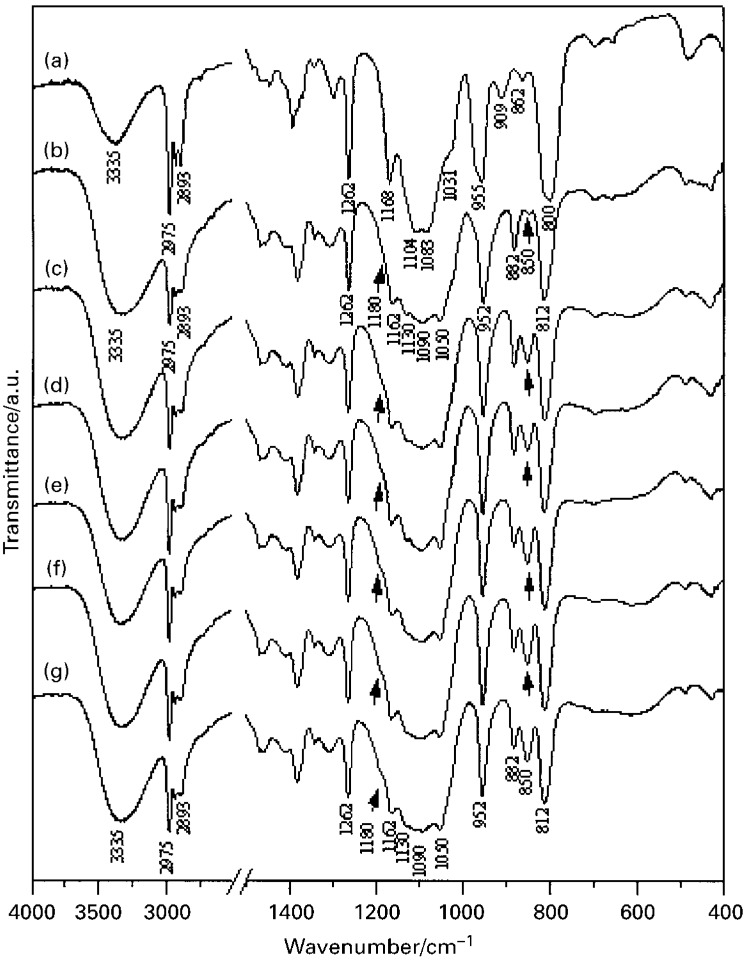

Figure 1. The FT-IR spectra of the reaction of sample without TBOT at (a) 0 min, (b) 0.5 min, (c) 3 min, (d) 9 min, (e) 15 min, (f) 20 min, and (g) 25 min.

Fig. 1(b)–(g), the intensity and width of this band increases. This result is due to the water and iPr-OH added, and to the ethanol (Et-OH) produced during the hydrolysis of TEOS. Three bands located at 2975, 2930, and 2893 cm^{-1} correspond to the overlapping bands of the C–H stretches of TEOS, PDMS, and iPr-OH (see Table 1) and they appear in spectra from 1(a)–(g).

In the 1300–700 cm^{-1} region (Fig. 1), the main bands of the studied reactions can be observed. At 1262 cm^{-1}, there appears the characteristic symmetric deformation of the CH_3 group in $Si(CH_3)_2$ from the PDMS chains. This band does not change along the reaction time. The high intensity bands located between 1200–1000 cm^{-1} are due to the Si–O (TEOS and PDMS) and C–O bonds (iPr-OH and Et-OH from hydrolyzed TEOS) [(spectra 1(b)–(g)]. An increase can be observed in the small shoulder located at 1180 cm^{-1} due to the self-condensation of Si–OH groups. The four bands located at 1168, 1104, 1083, and 1031 cm^{-1} [Fig. 1(a)] are assigned to TEOS and PDMS molecules (see Table 1). The band located at 1168 cm^{-1} (CH_3 rocking from TEOS) disappears in spectrum 1(b). The disappearance of this band is in accordance with the high hydrolysis rate of TEOS in a strong acid medium.[18,26] Such hydrolysis produces Et-OH that gives two new and intense bands [spectrum 1(b)] located at 1090 and 1050 cm^{-1}. However, the width of these bands is due to the contribution of Si–O bonds from both PDMS molecules and self-condensed Si–O–Si bonds from hydrolyzed TEOS.[18,19,26] The iPr-OH gives two more bands located at 1130 and 1162 cm^{-1}. Spectra 1(c)–(g) show a behavior very close to the spectrum of 1(b).

In the spectral region from 1000 to 700 cm^{-1} [Fig. 1(a)] two high intensity bands can be observed, which are located at 955 cm^{-1} (iPr-OH) and 800 cm^{-1} (TEOS and PDMS) both have a shoulder at 966 cm^{-1} (TEOS) and 817 cm^{-1} (iPr-OH), respectively. Also, two low intensity bands can be observed at 909 and 862 cm^{-1} (PDMS). The change of intensity of these bands from pure PDMS to mixed PDMS–TEOS–iPr-OH [Fig. 1(a)] is due to the dilution process, which causes the separation of PDMS molecules to break hydrogen bonds from such PDMS molecules.[27] In the spectrum 1(b), is observed a strong band at 952 cm^{-1} (iPr-OH), and the disappearance of the shoulder located at 966 cm^{-1} is due to the hydrolysis of TEOS. Such hydrolysis gives a new strong band located at 882 cm^{-1} (Et-OH). The bands located at 909 and 862 cm^{-1}, assigned to PDMS, are not readily observable because of the presence of Et-OH, which increases the dilution of the PDMS in the reaction medium. Copolymerization of PDMS molecules with the Si–OH groups formed from the hydrolysis of TEOS[21] gives a new small band located at 850 cm^{-1} [Fig. 1(b)]. Andrianov has shown that the synthesis of polymers having inorganic molecular chains, by means of mixed hydrolysis and condensation reactions, leads to the formation of linear or branched structures, and when monomers with functionality greater than two are used, primarily cyclo-linear and cyclo-branched structures are obtained. These cyclo-branched structures give an IR band located at 850 cm^{-1}.[21] The overlap of iPr-OH and PDMS bands at 817 and 800 cm^{-1}, respectively, gives a new strong band at 812 cm^{-1} [Fig. 1(b)]. The band attributable to PDMS molecules located at 800 cm^{-1} is very sensitive to the structure of PDMS so that when PDMS has a linear structure the band is located at 800 cm^{-1}, and when it has a cyclic structure the band shifts to high wavenumber (up to

805 cm^{-1}).[27] This latter band overlaps the band located at 817 cm^{-1} of iPr-OH. According to this, the increase in intensity of the band situated at 812 cm^{-1} [spectrum 1(b)] can be assigned to the increase in cyclic PDMS molecules, and this gives a decrease in the bands located at 909 and 862 cm^{-1}. Spectra from 1(c)–(f) show the same above-mentioned bands at 952, 882, 850, and 812 cm^{-1}. Also, a continuous increase in the intensity of the band located at 850 cm^{-1} can be observed, which reaches the intensity of the Et-OH band at 882 cm^{-1}.

As it has been shown before, TEOS is hydrolyzed very rapidly (given Si–OH groups and Et-OH), Si–OH groups are self-condensed and copolymerization reactions (between Si–OH groups and PDMS molecules) occur up to gelling. The latter results give the main changes in spectra of Fig. 1. Such changes are located between 1300 and 700 cm^{-1}. According to that, since TBOT gives the main IR bands in this spectral range, and because the subject of this work is to know the influence of TBOT on the hydrolysis and polymerization reactions of the TEOS–PDMS system, Fig. 2 shows the spectra of the reacting solution of a sample with 7% of TBOT. The spectra of Fig. 2 may be described in the same way as the spectra of Fig. 1. It can be seen in Fig. 2, the fast hydrolysis of TEOS, copolymerization reaction, and self-condensation reaction noted above. Therefore, the bands from these reactions are situated at almost the same wavenumber. On the other hand, the main bands of TBOT are placed at 1125, 1085, and 1035 cm^{-1}[23,24] (see Table 1). The first band overlaps with that of iPr-OH and last two bands overlap with those of PDMS, Et-OH, and Si–O–Si bonds from self-condensed Si–OH groups. Such overlaps give both displacement of the bands (at 1127, 1087, and 1038 cm^{-1}) and broadening in the 1000–1250 spectral range of Fig. 2. The broadening of spectra as a function of time in Fig. 2, suggest that the Ti–O–C bonds are not hydrolyzed totally and then the formation of Si–O–Ti bonds is so small that the band of Si–O–Ti bonds located at 920–950 cm^{-1}[11,12,21,28–30] is not easy observable in the spectra. However, as it will be shown below, between 920 and 950 cm^{-1} there appears a very low intensity band that can be followed during the reaction time. Therefore, in the 1000–700 cm^{-1} spectral range, there appears only the same bands as those of Fig. 1 because there exists only contributions from Et-OH, iPr-OH, PDMS, and TEOS. On the other hand, the band located at 850 cm^{-1}, due to copolymerization reactions between PDMS and Si–OH groups, increases in intensity during the first minutes of reaction and remains with the same intensity until the end.

By comparing the 600–400 cm^{-1} spectral range of Figs. 1 and 2 an increase in intensity is observed in the spectra of Fig. 2. This result must be assigned to some formation of Ti–O–Ti bonds, after TBOT hydrolysis, because the high molar ratio HCl/TBOT used in this work avoids the formation of TiOH gels or precipitates.[31]

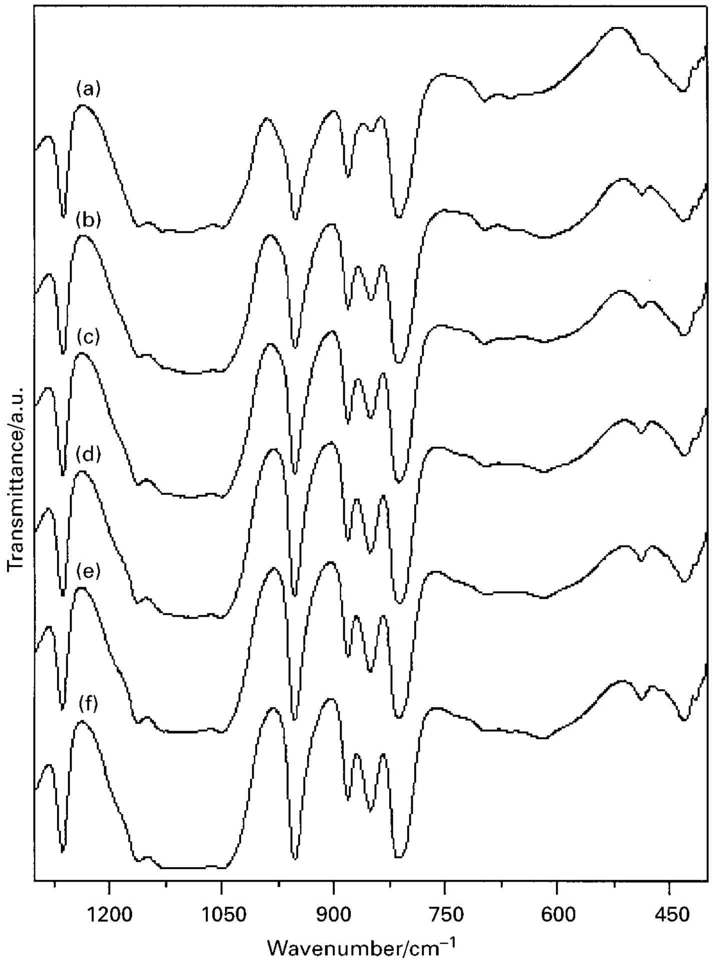

Figure 2. The FT-IR spectra of the reaction of sample with 7% TBOT at (a) 0.5 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, and (f) 25 min.

Figure 3 shows the FT-IR spectra at 15 min of reaction for samples with different TBOT amounts. There appear the same IR bands as those already noted in Figs. 1 and 2. Both the 1200–1000 cm^{-1} and 600–400 cm^{-1} spectral regions show differences as the TBOT concentration is increased. The bands situated at 1127, 1087, and 1038 cm^{-1} are observed to increase with the TBOT concentration as it does in the 600–400 cm^{-1} spectral region, due to the high contribution of TBOT bands.[23,24]

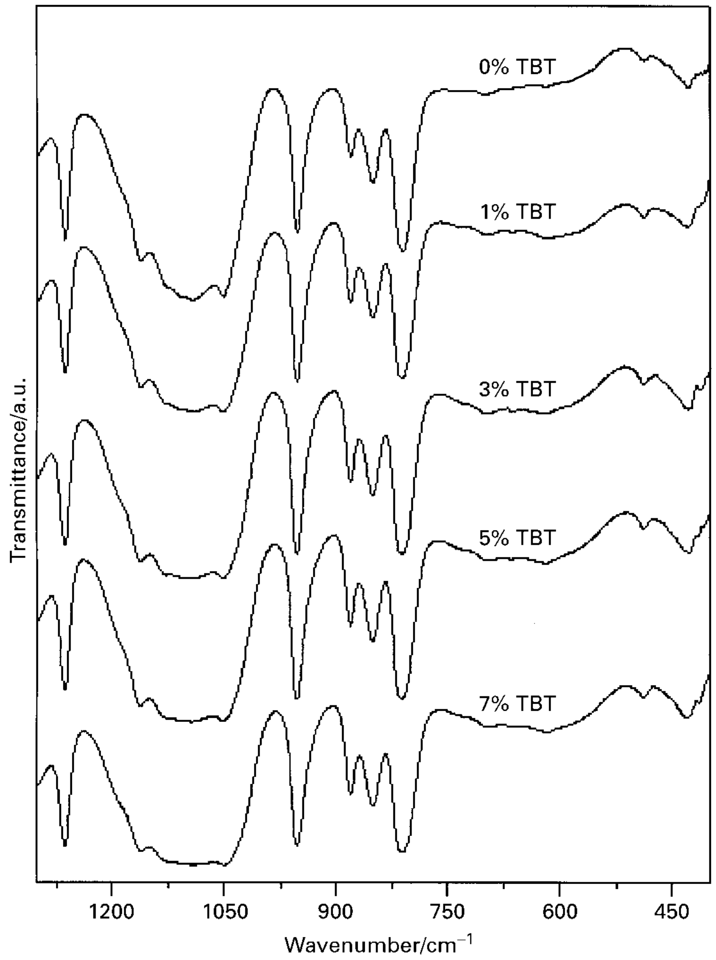

Figure 3. The FT-IR spectra of the reaction of samples at 15 min of reaction time with (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 7% TBOT concentration.

In order to obtain semi-quantitative information about the effect of TBOT on the reaction between TEOS and PDMS, we have done a semi-quantitative analysis by deconvolution of the IR spectra using a computer program. In this program each IR band is determined by three parameters: intensity, half width, and wave number, and it has been assumed that the IR bands have a gaussian profile. Figure 4(a)–(c) shows the deconvoluted FT-IR spectra from 1260 to 1000 cm^{-1} and Fig. 5(a)–(c) shows the deconvolution procedure for the

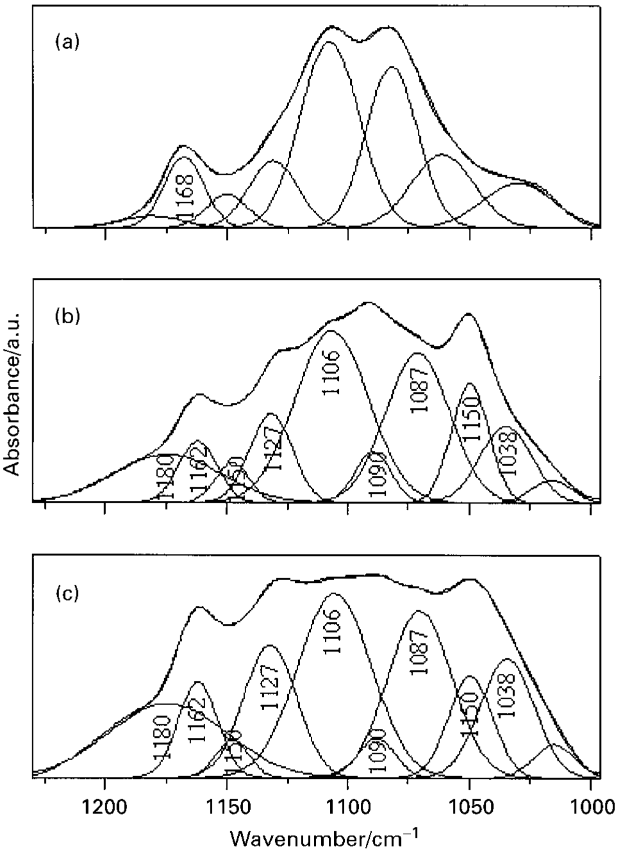

Figure 4. Spectral deconvolution of the sample with 7% of TBOT in the spectral range 1260–1000 cm^{-1}: (a) 0 min, (b) after 1 min of reaction, and (c) after 27 min of reaction.

900 to 760 cm^{-1} spectral ranges. Both figures correspond to the sample with 7% of TBOT. In such spectra can be observed the changes in the main bands, noted above, at each given time.

Here, it can be observed that the band at 1168 cm^{-1} [Fig. 4(a)], corresponding to TEOS, disappears and, at the same time, the formation of a new band at 1050 cm^{-1} is observed, corresponding to Et-OH [Fig. 4(b)]. This result shows that TEOS is fully hydrolyzed. Also, two new bands can be observed at 1180 and 1150 cm^{-1} corresponding to Si–O–Si bonds in more cross-linked or more linear structures, respectively.[18,19,26,32] In Fig. 4(c) appears the bands of Et-OH at 1050 cm^{-1}, those of Si–O–Si bonds at 1180

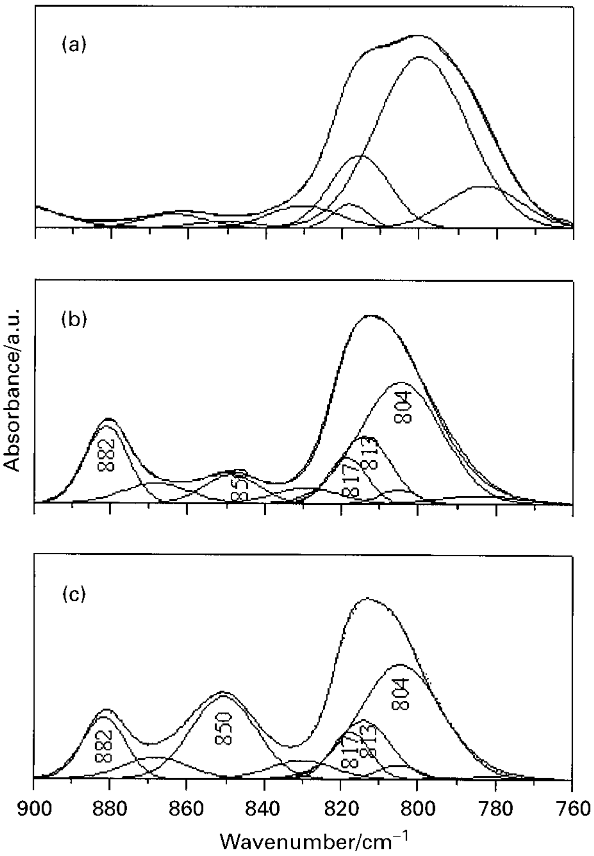

Figure 5. Spectral deconvolution of the sample with 7% of TBOT in the spectral range 900–760 cm^{-1}: (a) 0 min, (b) after 1 min of reaction, and (c) after 27 min of reaction.

and 1150 cm^{-1}, and three TBOT characteristic bands at 1127, 1087, and 1038 cm^{-1}.[23,24] The presence of these TBOT bands at this reaction time leads to the conclusion that in this strong acid medium some TBOT molecules remains unhydrolyzed.

Figure 5(a)–(c) shows the spectral deconvolution in the 900–760 cm^{-1} range. It must be taken into account that TBOT does not gives IR bands in this range. Figure 5(a) shows the bands of TEOS, PDMS, and iPr-OH specified in Table 1. Figure 5(b) corresponds to 1 min of reaction, and here appears two bands located at 882 and 850 cm^{-1} corresponding to Et-OH and Si–O–PDMS copolymerization, respectively.[21] The TEOS band at 783 cm^{-1}

also disappears and it is observed as a new low intensity band at 795 cm^{-1} corresponding to the asymmetric stretching of the SiO_4 tetrahedron.[18,32] Also, the iPr-OH band at 817 cm^{-1}, and those of linear and cyclic PDMS chains at 804 and 812 cm^{-1}, respectively, can be observed. The ratio linear/cyclic PDMS chains changes rapidly as we have said before.[27] In Fig. 5(c), the increase of the 850 cm^{-1} band can be observed showing that copolymerization reaction between Si–OH groups and probably Ti–OH groups with PDMS molecules continues. Also, a decrease of the intensity bands corresponding to cyclic and linear PDMS chains can be observed, showing that they are incorporated into the Ormosil network. On the other hand, the Et-OH band at 882 cm^{-1} shows the same intensity, according to the faster hydrolysis of TEOS.

It must be taken into account that by the spectral deconvolution procedure it is possible to obtain several sets of bands for a given experimental spectrum. However, three steps have been taken in order to obtain the best fit. Firstly, a bibliography on all organic molecules used in this work and their hydrolysis behavior has been collected. Secondly, an FT-IR spectrum has been obtained for all organic molecules used in this work, where the exact values of wave number, half width, and intensity have been obtained. Thirdly, the hydrolysis of TEOS and TBOT have been done independently by using only acidic water, and from these results it has been possible to know the evolution of their respective IR bands. And finally, the minimum difference between second derivatives between experimental and deconvoluted spectra has been used as a criteria for the exactness of both spectra. In all cases the standards deviations were less than 0.01. Besides, the IR deconvoluted bands that will be used to study the hydrolysis and polycondensation reactions of the TEOS–TBOT–PDMS system will be those with the least overlap possible, and then the influence of any side bands will have little effect on the measured integrated area.

In this work, we have analyzed the integrated area of the most representative IR bands from the deconvoluted spectra, and the evolution of each band has been studied in order to know its contribution to the reaction from the raw materials to the final Ormosils products.

The polycondensation of Si–OH groups gives new Si–O–Si bonds that show two bands at 1180 and 1150 cm^{-1} assigned to cross-linked and linear structures, respectively.[30] The evolution of these bands is shown in Figs. 6 and 7, respectively. Both bands correspond to the self-condensation reaction.

Figure 6 shows a rapid increase in the integrated area of the 1180 cm^{-1} band during the firsts 5 min of reaction and then such increase slows until gelling. The highest concentration of cross-linked Si–O–Si structures occurs for the sample with a high amount of TBOT. This result shows that TBOT aids the cross-linking self-condensation reaction. On the other hand, the behavior

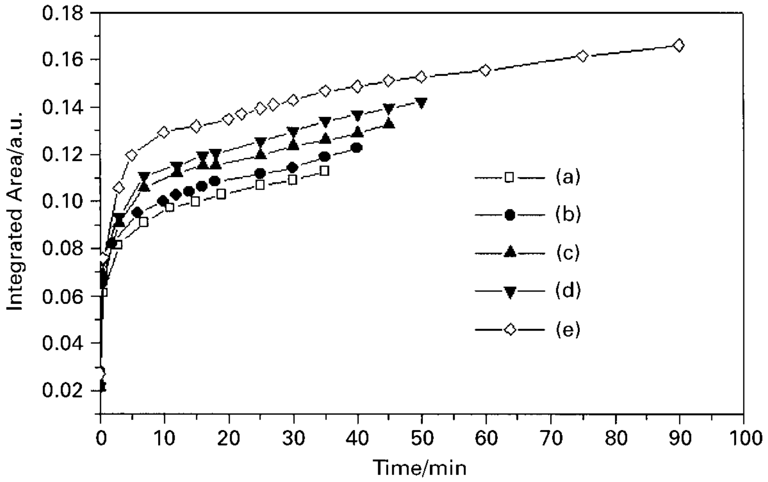

Figure 6. Time evolution of the integrated areas corresponding to the 1180 cm^{-1} band. Amount of TBOT: (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 7%.

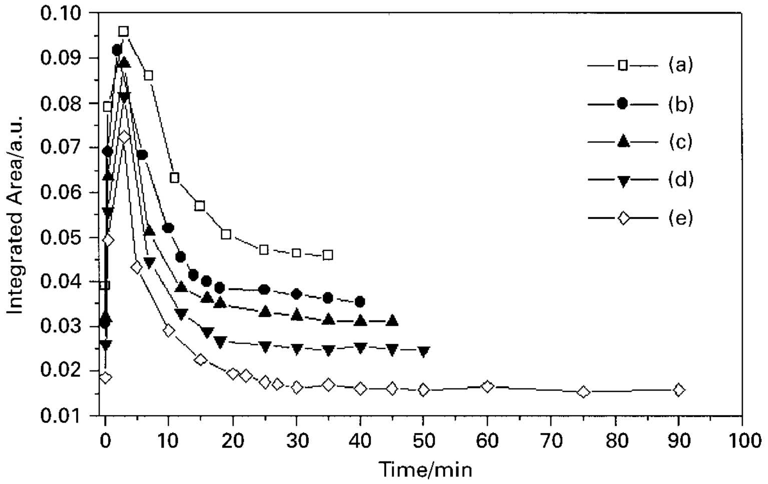

Figure 7. Time evolution of integrated areas corresponding to the 1150 cm^{-1} band. Amount of TBOT: (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 7%.

of linear Si–O–Si structures (Fig. 7) as a function of TBOT concentration shows a rapid increase during the first moments of reaction and after that a rapid decrease during the following 20 min. This result shows that linear structures are formed and removed during reaction and finally maintains a certain concentration in the resultant Ormosil. The concentration of cross-linked and linear Si–O–Si structures is dependent on the TBOT concentration. Also, these results can be compared with those obtained when no PDMS had been added to the reaction.[26] The evolution with reaction time of both bands is similar: cross-linked Si–O–Si structures increase with time, and linear Si–O–Si structures show a rapid increase, after that they decrease and finally a stabilization appears. However, the main difference that occurs when the reaction has PDMS molecules is that such behaviors are more rapid than when no PDMS is used. This result is due to the hydrophobicity of the CH_3 groups of PDMS molecules, which makes the Si–OH groups be closer, thus increasing the velocity of the self-condensation reactions.

The evolution of Ti–O–C bonds may be followed by the intense band of TBOT located at 1127 cm^{-1}. Figure 8 shows the evolution of this band. An increase in this band is observed during the first 10–15 min of reaction, which correspond to the addition of TBOT. After that, it shows only a little decrease during the reaction suggesting that not all alkoxide groups of TBOT molecules are hydrolyzed in the strong acid medium used in this work. Also, it was observed that the integrated area of Ti–O–C bonds is highest when an

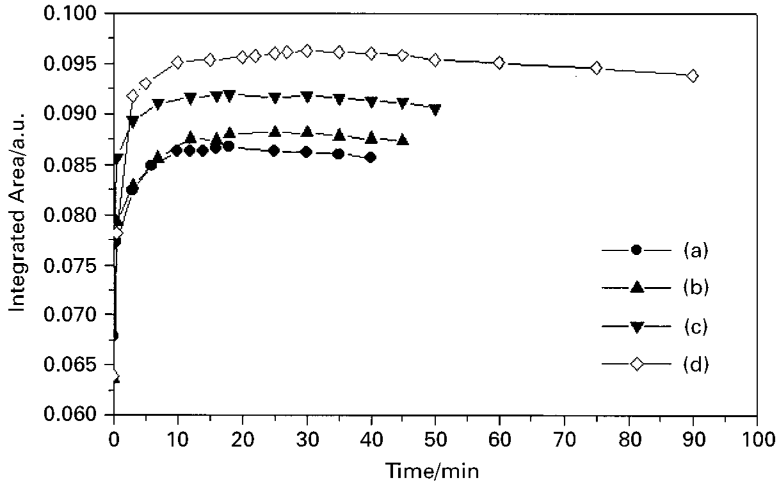

Figure 8. Time evolution of integrated areas corresponding to the 1127 cm^{-1} band. Amount of TBOT: (a) 1%, (b) 3%, (c) 5%, and (d) 7%.

increased amount of TBOT is added. A similar behavior has been observed when no PDMS and TEOS are used for studying the hydrolysis of TBOT,[24] although the effect of the acid medium must be considered. Here it must be taken into account the work of Sanchez et al.[31,33] They have shown that in strong acid media, H^+ ions catalyze the hydrolysis of $Ti(OR)_4$ into Ti–OH through protonation of the leaving groups; however, H^+ ions also act as inhibitors of Ti–O–Ti reactions by protonation of Ti–OH groups and inhibiting the nucleophilic attack of Ti by Ti–OH. This result shows that condensation reactions are hindered in strong acid media. However, in their work they did not show if in such media, TBOT hydrolysis is completed. On the other hand, Yoldas[34] and Rubio et al.[35] have shown the difficulty of hydrolysis of all the alkoxide groups. The results of Fig. 8 show that TBOT is not completely hydrolyzed.

If a given quantity of alkoxide TBOT groups is hydrolyzed, they give Ti–OH groups, which can react with other Ti–OH, Si–OH groups, or PDMS molecules. The reaction of Ti–OH groups with Si–OH ones or with PDMS molecules forms new Ti–O–Si bonds, which gives a new absorption band at 936 cm^{-1}.[11,12,21,28–30] The evolution of this Ti–O–Si band is shown in Fig. 9. Here it is not possible to distinguish if Ti–OH groups are bonded to Si–OH groups from TEOS or PDMS. It is observed that this band increases in

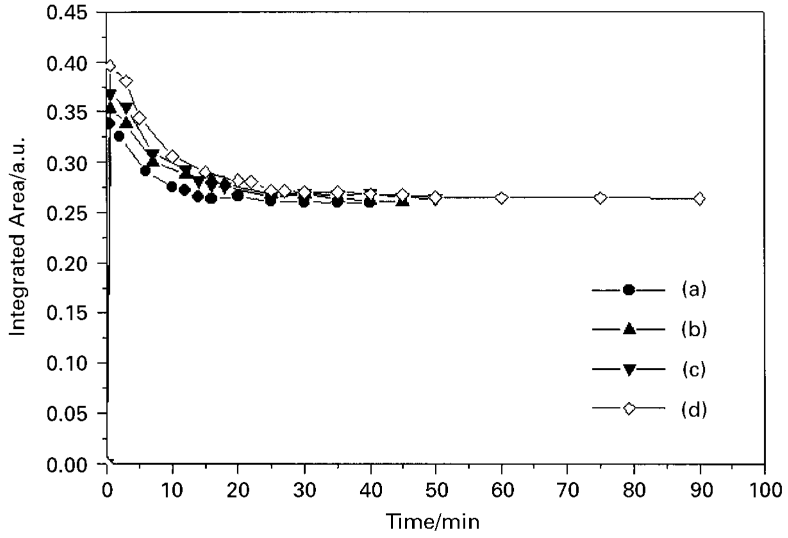

Figure 9. Time evolution of integrated areas corresponding to the 936 cm^{-1} band. Amount of TBOT: (a) 1%, (b) 3%, (c) 5%, and (d) 7%.

the first minutes of reaction and after that it decreases until about 30 minutes of reaction. From this time to the end it remains constant. The integrated area of this band is higher for the reaction of higher amount of TBOT, and at the end of the reaction this band does not disappear, which shows that a given quantity of Ti–O–Si bonds remains in the final Ormosil. This result is in accordance with those of Babonneau[15,16] and Kotani et al.,[30] which showed that Ti–O–Si bonds are of little stability being formed during the hydrolysis step but decrease in the reaction medium and then finally they can disappear during aging.

The copolymerization reaction between both Si–OH and/or Ti–OH groups from isolated molecules or from condensed structures, and OH groups of silanol terminated PDMS molecules can be studied from the evolution of the 850 cm^{-1} band showed in Fig. 10. It is observed that the integrated intensity of this band increases with the reaction time for all concentrations of TBOT added. The higher slope occurs for the firsts 20 min of reaction, and then shows a slow increase with time until gelling. It is observed that the higher integrated intensity corresponds to the sample with the higher amount of TBOT, showing that TBOT increases the Si–O–PDMS and Ti–O–PDMS polycondensation reactions. This result is in accordance with that of Andrianov[21] and Babonneau et al.,[36] which showed that TBOT could also catalyze the condensation reactions of PDMS units into cyclo-branched structures and long PDMS chains.

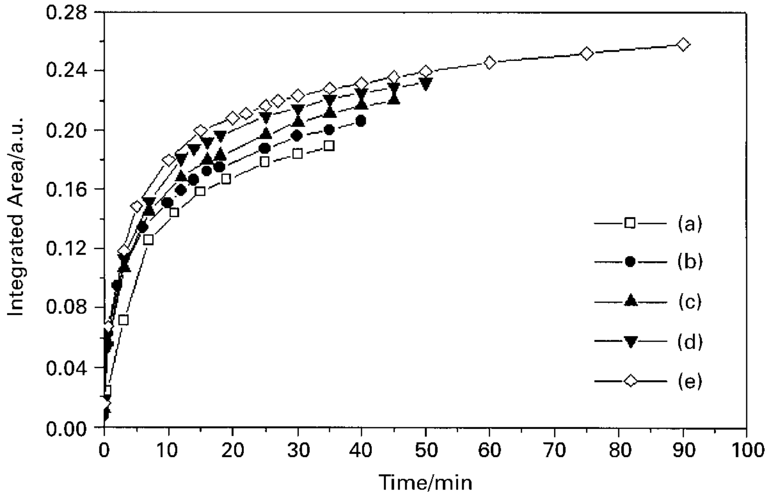

Figure 10. Time evolution of integrated areas corresponding to the 850 cm^{-1} band. Amount of TBOT: (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 7%.

CONCLUSIONS

In summary, TEOS and TBOT are rapidly hydrolyzed (although not all alkoxy groups of TBOT do) and forms Si–OH and Ti–OH groups in the reaction medium. Both groups react through condensation reactions (self-condensation and poly-condensation) although Ti–OH self-condensation is highly inhibited by the strong acid medium. Such condensation reactions give structures with Si–O–Si, Si–O–PDMS bonds where Ti–O–Ti, Ti–O–Si, and probably Ti–O–PDMS bonds are found. Si–OH self-condensation reactions give cross-linked and linear structures. Linear structures are mainly formed during the first minutes of reaction, and then decrease with time. On the other hand, cross-linked structures increase during the whole reaction time. A similar behavior is observed for polycondensation reactions, which increase with time. The gelling time is dependent on the relative concentration of cross-linked, linear, and poly-condensed structures, all of them being dependent on the TBOT concentration in the reaction medium.

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