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# Synthesis of inorganic-organic hybrid materials from TEOS, TBT and PDMS

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Inorganic-organic hybrid materials have been synthesized by reaction of tetraethoxysilane (TEOS), titanium tetrabutoxide (TBT) and silanol-terminated polydimethylsiloxane (PDMS). The hydrolysis and polymerization reactions of TEOS and PDMS in presence of TBT have been followed by means of FT-IR spectroscopy. Hydrolysis reactions have been characterized by Si–O–C and Ti–O–C bonds and polymerization reactions by Si–O–Si, Si–O–Ti and Ti–O–Ti bonds. The instantaneous hydrolysis of TEOS, the condensation reactions between Si–OH groups forming crosslinked and linear Si–O–Si structures and the copolimerization reactions between Si–OH groups and PDMS molecules have been observed. The reaction between Ti–OH and Si–OH groups or PDMS gives Si–O–Ti bonds. Si–O–Ti bonds are formed during the addition step of TBT and they show a decrease along the reaction time up to gelling. By another hand, the concentration of crosslinked and linear Si–O–Si structures depend on the TBT concentration. High TBT concentration favors the formation of crosslinked chains. TBT influences the hydrolysis and copolymerization reactions between hydrolyzed TEOS and PDMS molecules. © *2003 Kluwer Academic Publishers*

## 1. Introduction

The synthesis of inorganic-organic hybrid materials via sol-gel process has been widely investigated [1, 2]. They are known as "ceramers" or "ormosils" and they are prepared through the combination of inorganic metal alkoxides and functionalized organics. An important characteristic or inorganic-organic hybrid materials is the homogeneous dispersion of the organic species at molecular level into the inorganic network. The development of the hybrid material is based on the incorporation of oligomers and polymers species into the inorganic matrix constituted primarily by Si–O–Si. Tetra-alkoxysilanes gives *in situ* the inorganic matrix from hydrolysis and polycondensation reactions into organic polymers [3, 4]. Many authors [5, 6] have demonstrated that silanol-terminated polymers or oligomers can be incorporated into an oxide network derived from tetra-ethoxysilane (TEOS). Other authors [7, 8] have incorporated titanium, aluminium, zirconium, etc., alkoxides instead of/with TEOS. The incorporation of silanol-terminated PDMS into an oxide network was studied by spectroscopy techniques and the reaction mechanisms and structure development have been reported [5, 9].

In this work inorganic-organic hybrid material have been prepared from TEOS and TBT alkoxides and silanol-terminated PDMS using a strong acid medium. FT-IR spectroscopy has been used in order to study the structural evolution of hydrolysis and polymerization reactions to form the hybrid material.

## 2. Experimental

Inorganic-organic hybrid materials were prepared using TEOS (Merck, for analysis), silanol-terminated polydimethylsiloxane (PDMS) of molecular weight of 550 (Gelest, Germany) and TBT (Aldrich, for analysis) as raw materials. Isopropyl alcohol (iPrOH) was used as solvent, hydrochloric acid (HCl) as catalyst and deionized water as the hydrolysis agent. The inorganic part of these hybrid materials is considered as the sum of TEOS and TBT and the organic one is PDMS. In this work the mass ratio of inorganic/organic was 70/30 and it has been kept constant. The concentrations of raw material used in this work are given in Table I.

The synthesis of hybrid materials is as follows. Three solutions were prepared containing 1/3 of the total volume of isopropyl alcohol. In the first solution were added the total volumes of TEOS and PDMS. The second solution contained the total volumes of HCl and $H_2O$, and the third one was added the total volume of TBT. The three solutions were independently stirred for 1 hour. After that a flask container was introduced into

TABLE I Composition of the studied samples

| | Precursor (%w) | | | Solvent and catalyst (mol/mol) | | |
|---|---|---|---|---|---|---|
| | Inorganic | | Organic | | | |
| Sample | TEOS | Ti $(OC_4H_9)_4$ | PDMS | $H_2O$/Inorganic | HCl/Inorganic | iPrOH/Inorganic |
| T0 | 70 | 0 | 30 | 3 | 0.2 | 4.5 |
| T1 | 69 | 1 | | | | |
| T3 | 67 | 3 | | | | |
| T5 | 65 | 5 | | | | |
| T7 | 63 | 7 | | | | |

a thermostatic bath at 80°C under refluxing and then the first and second solutions were added. Immediately the third solution was drop-wise added for 30 minutes and total solution was kept reacting for 30 minutes more. Stirring was maintained during the overall reaction time (1 hour). After this time, the solution was poured into a plastic container and sealed until gelling. The gelling times for T0, T1, T3, T5 and T7 samples were 420, 540, 620, 720 and 840 minutes, respectively.

FT-IR spectroscopy was used to study hydrolysis and polymerization reactions that take place between TEOS, TBT and PDMS. A FT-IR spectrophotometer (Perkin-Elmer model 1720X) with a resolution of 2 $cm^{-1}$ was used. Each spectrum was obtained by adding a drop (of 1 microlitre) of solution between two KRS-5 window crystals by using a microburete (KRS-5 crystals are transparent to IR light). In order to maintain constant the thickness of the IR path length, the KRS-5 windows were spaced by an aluminium foil of 0.01 mm thick with an aperture in which a microdrop was placed. Each spectrum was obtained every 5 minutes during the reaction time, and after that, every 30 or 60 minutes until gelling. In all cases background was subtracted.

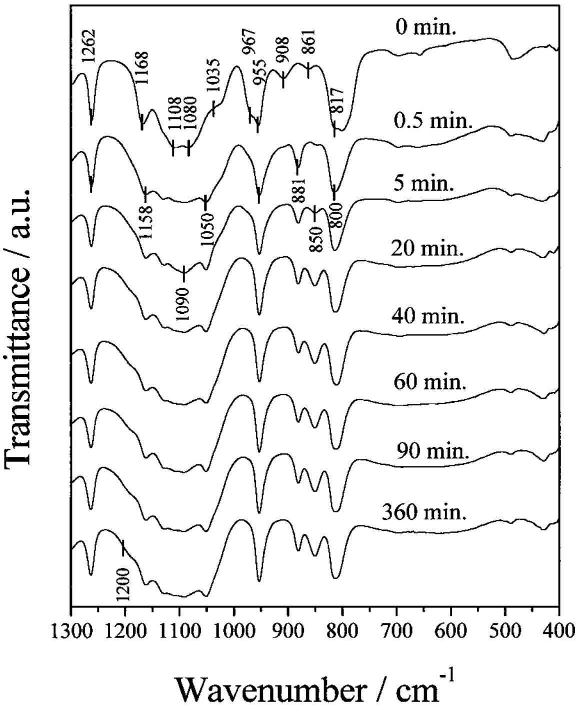


*Figure 1* FT-IR Spectra of evolution reaction of sample without TBT at different reaction times.

## 3. Results

FT-IR spectra of pure components (not shown here) were previously obtained and tested with those published in previous works [10–16]. These spectra were used as reference ones and will be commented below. Fig. 1 shows the FT-IR spectra in the 1300–400 $cm^{-1}$ spectral range for sample referred as T0 (see Table I). Spectrum at 0 minutes corresponds to the TEOS-PDMS-iPrOH solution. Here different high intensity bands can be observed and they can be assigned to the corresponding raw materials. The band located at 1262 $cm^{-1}$ is unambiguously assigned to PDMS [13]. The band lying at 1168 $cm^{-1}$ corresponds to TEOS, and those at 1108 and 1080 $cm^{-1}$ correspond to Si—O and C—O stretching modes of TEOS, PDMS and iPrOH molecules [11, 13]. The shoulder that it is observed at 1035 $cm^{-1}$ is due to cyclic structures of PDMS molecules. These structures contain eight-membered rings with a smaller number of six-membered rings [13]. Therefore, both 1108 and 1035 $cm^{-1}$ bands of PDMS permit to conclude that this polymer has cyclic and linear structures in the reaction medium. The high intensity band at 955 $cm^{-1}$ is unambiguously assigned to iPrOH. This band has a shoulder located at 967 $cm^{-1}$ that corresponds to the TEOS molecule. The two low intensity bands at 908 and 861 $cm^{-1}$ are assigned to PDMS molecules (Si—O stretching in Si—OH and $CH_3$ rocking, respectively [14]. Close to 800 $cm^{-1}$ appear two overlapped and high intensity bands, the contribution of TEOS ($CH_2$ rocking and $SiO_4$ a.) and PDMS ($\nu_a$ Si—C) gives the band located at 800 $cm^{-1}$, and the band at 817 $cm^{-1}$ is due to the iPrOH. In the 800–400 $cm^{-1}$ spectral region appear different low intensity bands, which correspond, to both deformation modes of C—H, O—H bonds and bending vibrations of Si—O bonds [10, 17].

The spectrum at 0.5 minutes of Fig. 1 corresponds to the mixture of the above-mentioned first and second solutions (i.e., TEOS-PDMS-iPrOH and $H_2O$-HCl-iPrOH). It is well known that acidic aqueous solutions promote the hydrolysis of TEOS molecules [10, 12] and this reaction produces the spectral changes observed in this spectrum. In this spectrum the bands located at 1168, 967 and 800 $cm^{-1}$ (TEOS) have disappeared, showing the very fast hydrolysis rate of this molecule in this acid medium. Four new bands are now observed in this spectrum lying at 1158, 1050, 881 and 850 $cm^{-1}$. The band at 1158 $cm^{-1}$ corresponds to iPrOH ($\nu_a$ C—O) used as solvent. Bands at 1050 and 881 $cm^{-1}$ correspond to the ethanol (EtOH) generated from hydrolyzed TEOS. And the band at 850 cm$^{-1}$ is assigned to the copolymerization reaction between Si—OH groups of hydrolyzed TEOS and Si—OH groups of PDMS molecules [13, 18].

The next spectra of Fig. 1 correspond to different reaction times. They are very similar to the spectrum of 0.5 minutes, showing almost the same IR bands although some remarks must be given. Firstly, it can be observed a wide shoulder at around 1200 cm$^{-1}$ which corresponds to Si—O—Si stretching of crosslinked silica structures produced by self-condensation of Si—OH groups of hydrolyzed TEOS [11, 19]. The intensity of this shoulder shows a little increase with reaction time. Secondly, the peak at 850 cm$^{-1}$ attributed to Si—OH-PDMS copolymerization, increases in intensity. And finally a smoothing of the 1130–1050 cm$^{-1}$ spectral region occurs as result of an increase in intensity and width of the Si—O—Si stretching close to 1090 cm$^{-1}$. These results confirm that self-condensation and copolymerization reactions take place simultaneously before gelling to obtain the hybrid material [20].

On the other hand, the FT-IR spectra corresponding to the reaction for obtaining the T5 hybrid material is shown in Fig. 2. This material contains 5% of TBT (see Table I). Spectrum at 0 minutes corresponds to the TEOS-PDMS-iPrOH solution and the IR bands are the same as those commented for spectrum of 0 minutes of Fig. 1. Spectrum at 5 minutes of this Fig. 2 corresponds to the reaction containing TEOS-PDMS-iPrOH-HCl-$H_2O$ and 0.15% of TBT. Here it is observed that TEOS is completely hydrolyzed because the 1168 cm$^{-1}$ band is not present and the EtOH band at 881 cm$^{-1}$ has high intensity. In this spectrum it is also observed that the TEOS-PDMS copolymerization reaction (850 cm$^{-1}$ band) has yet started. The presence of TBT is not detected due to the low concentration added. TBT gives three characteristic IR bands located at 1130, 1087 and 1038 cm$^{-1}$ [15, 16]. These bands produce the smoothing of the 1130–1050 cm$^{-1}$ spectral region that is mainly observed for spectrum of 40 minutes and following. However, as it has been commented in Fig. 1, the formation of Si—O—Si bonds also give a smoothing of such spectral region. In order to check if Si—O—Si bonds or TBT produces such effect, the spectra samples containing different concentration of TBT at 40 minutes of reaction time are represented in Fig. 3. In such spectra the smoothing of the 1130–1050 cm$^{-1}$ spectral region increases as the TBT concentration in the reaction is increased and therefore such smoothness can be mainly assigned to TBT.

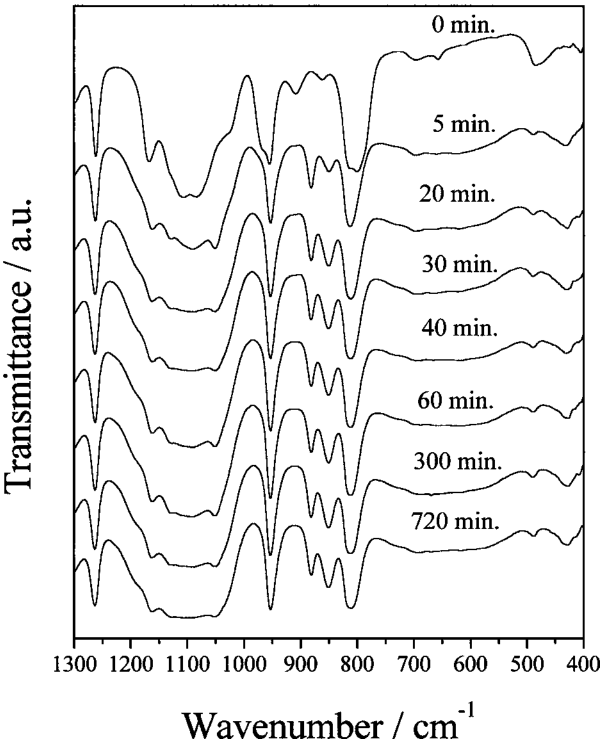


*Figure 2* FT-IR Spectra of evolution reaction of sample with 5% of TBT at different reaction times.

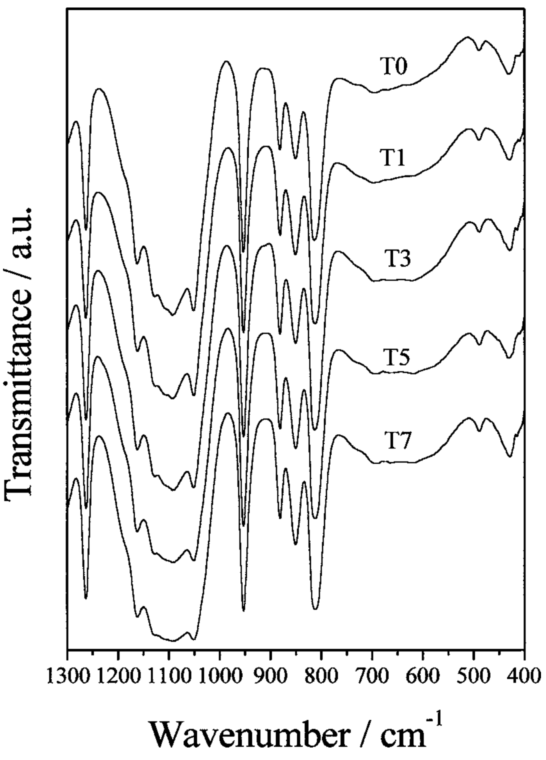


*Figure 3* FT-IR Spectra of samples with different TBT concentration at 40 minutes of reaction time.

Such smoothness of the 1130–1050 cm$^{-1}$ spectral range may suggest that TBT is not fully hydrolysed. However, the increase of the intensity and width of the 750–500 cm$^{-1}$ spectral range with the increase of TBT concentration is also observed. This result is due to the formation of Ti—O—Ti bonds from Ti—OH groups formed after TBT hydrolysis [21]. Therefore it may be concluded that some TBT molecules are also hydrolyzed. It must be taken into account that in accordance with Kallala *et al.* the high molar ratio HCl/TBT used in this work avoids the formation of TiOH gels or precipitates [22].

## 4. Discussion

In order to obtain information about of effect of TBT on the reaction between TEOS and PDMS for obtaining hybrid materials, a semi-quantitative approach by a careful deconvolution of the IR spectra was carried out. In order to carry out such spectral deconvolution, firstly all spectra were transformed from transmittances

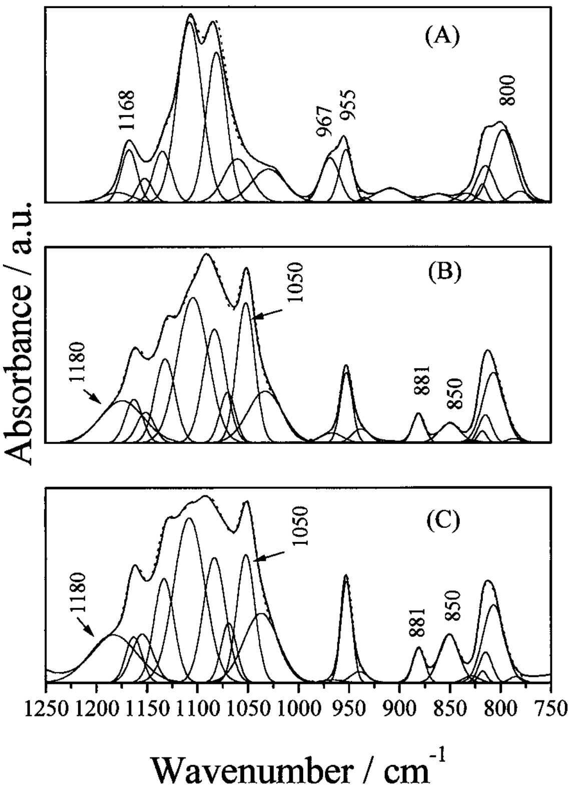


*Figure 4* Spectral deconvolution of sample with 7% of TBT in the spectral range 1250–750 cm$^{-1}$ at (A) 0 minutes, (B) after 5 minutes of reaction, and (C) after 60 minutes of reaction.

to absorbances because the concentration of any chemical bond is proportional to their corresponding IR absorbance. Fig. 4 (A, B and C) shows the deconvolution procedure for different FT-IR spectra in the 1250–750 cm$^{-1}$ spectral region.

Spectral deconvolution was carried out assuming gaussian profile for the different IR bands. Firstly, the raw materials (TEOS, TBT, etc.) were deconvoluted and three parameters of each band: intensity, half width and frequency (wavenumber) were determined. These parameters were used as starting point in the deconvolution procedure for the next spectra. After that, any spectrum was deconvoluted mainly determining the parameters of new bands formed and then changing the intensities of the different IR bands. This procedure was repeated until obtaining the best fit between experimental and deconvoluted spectra. In all cases the difference between deconvoluted and experimental spectra was less than 1%. After that, the area of each deconvoluted IR band was obtained by normal integration. This area is then related to the concentration of the corresponding chemical bond. Obtained results are only a semiquantitative because absorption coefficients are unknown. It is well known [17] that for any chemical bond the IR absorption coefficients are dependent on both experimental temperature and vibration wave number. Because of the experimental temperature was the same for all samples, the absorption coefficients are only dependent on wave number. For Si—O—Si, Ti—O—Ti and Si—O—Ti bonds the vibration wave numbers generally show variations in a given quantity depending on the strengthened of the oxide network. This gives a little change in the absorption coefficients of such bonds, which makes impossible to obtain a quantitative analysis. On the other hand, for Si—O—C, Si—C and Ti—O—C bonds of organic molecules, vibration wave numbers appear approximately in the same position during the whole reaction, however the preparation of standards with well-known concentrations of such bonds is difficult because of the reactions take place instantaneously when such compounds are mixed. Therefore, the analysis carried out in this work must be considered only as semi-quantitative. Taking into account that firstly the IR transmission of the KRS-5 windows was the same for all spectra and, secondly, that for obtaining the corresponding IR spectra we have used 1 microlitre of sample in all cases, then for a given IR spectral region their area (in absorbance units) is proportional to the concentration of chemical bonds which give IR vibrations in such region. Then, is possible to normalize any IR deconvoluted band to the whole deconvoluted spectral area. Therefore by analysing the IR deconvoluted bands, which appear in any spectral region it is possible to follow the chemical reactions which take place in the synthesis process of the hybrid materials studied in this work.

It must be taken into account that first of all the FT-IR spectra of pure components were deconvoluted and the obtained IR bands were used as starting point for the deconvolution of the reaction spectra. In the deconvolution example of Fig. 4 the different bands, above commented, can be observed. TEOS bands located at 1168, 967 and 800 cm$^{-1}$ disappear from spectrum 4(A) to spectrum 4(B) and at the same time appearing the EtOH bands lying at 1050 and 881 cm$^{-1}$. In the deconvoluted spectra 4(B) and 4(C) can also be observed the wide band at 1180 cm$^{-1}$ assigned to Si—O—Si bonds due to the crosslinked structure [11, 19] and the 850 cm$^{-1}$ band due to the copolymerization of Si—OH-PDMS groups [13, 18]. The evolution of integrated areas for the most representative bands is shown in the next Figures.

Fig. 5 shows the evolution of the 881 cm$^{-1}$ band due to the EtOH generated after TEOS hydrolysis. In this Figure can be observed that the hydrolysis of TEOS molecules is instantaneously completed after the addition of the HCl-$H_2O$-iPrOH solution. A similar result has been obtained by Iwamoto *et al.* using liquid state $^{29}$Si NMR (nuclear magnetic resonance) spectroscopy [20]. In accordance with this Fig. 5, hydrolysis of TEOS occurs before TBT addition. The hydrolysis of TEOS

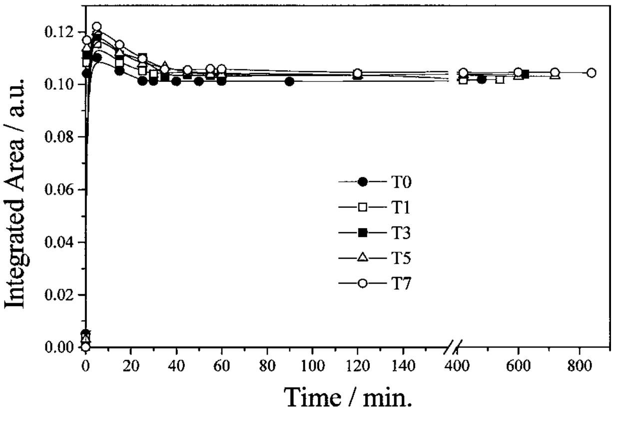


*Figure 5* Time evolution of integrated areas corresponding to 881 cm$^{-1}$ band for studied samples with different TBT concentration.

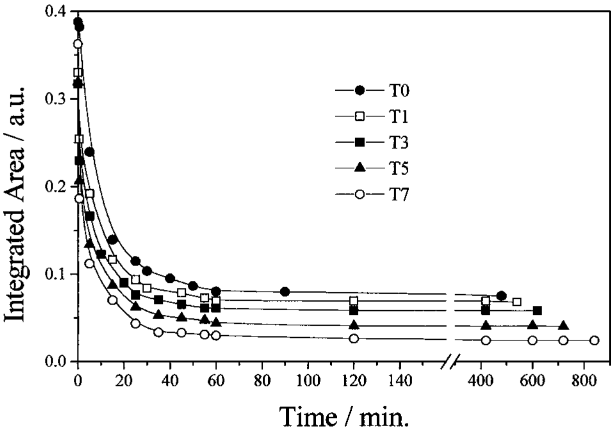


*Figure 6* Time evolution of integrated areas corresponding to 967 cm$^{-1}$ band for studied samples with different TBT concentration.

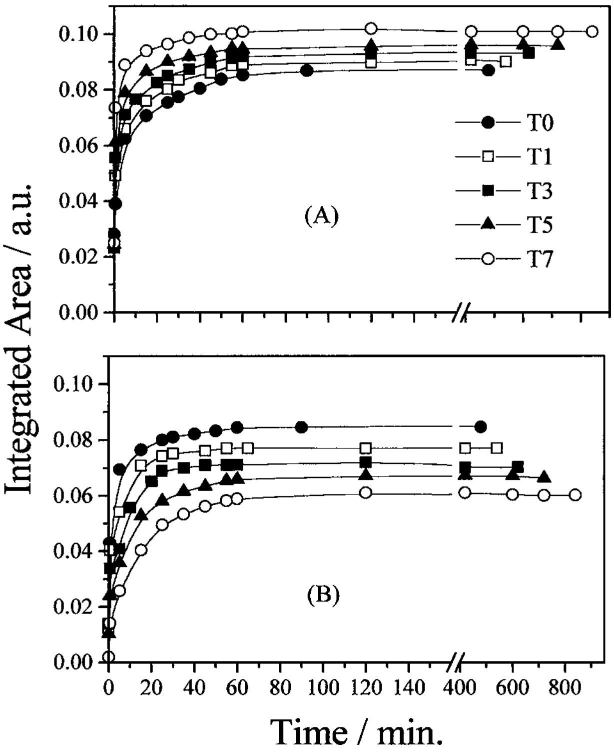


*Figure 7* Time evolution of integrated areas corresponding to (A) 1180 cm$^{-1}$ and (B) 1158 cm$^{-1}$ bands for studied samples with different TBT concentration.

produces Si—OH groups that gives a band at 967 cm$^{-1}$. This band has a very low intensity appearing in the deconvoluted spectra close to the 955 cm$^{-1}$ band of iPrOH (Fig. 4). Fig. 6 shows the evolution of the 967 cm$^{-1}$ band and can be observed that Si—OH groups are immediately formed in accordance with TEOS hydrolysis. These silanol groups also have a very fast decrease up to 1 hour of reaction, and after this time the decrease is very low. In Fig. 6 can also be observed that increasing the TBT concentration in the solution decrease the amount of silanol groups. These silanol groups decrease by self-condensation and copolymerization reactions.

Self-condensation reactions of Si—OH groups give Si—O—Si bonds that are responsible for the two bands located at 1180 and 1158 cm$^{-1}$ being assigned to more crosslinked or to more linear structures respectively [11, 19]. Fig. 7A and B show the evolution of the Si—O—Si bonds in both crosslinked and linear structures respectively, formed by self-condensation of Si—OH groups. It is clearly observed that both types of structures increase during the first 60 minutes of reaction time and after that the increase is very slow. The high concentration of such crosslinked structures appears for the high concentration in TBT (Fig. 7A), but on the other hand, the high concentration of linear structures corresponds to the material without TBT. This result shows that TBT plays an important role in the final structure of the hybrid material. The crosslinked and linear structures can be seen in Fig. 8. In such Figure have been included PDMS molecules which react with Si—OH groups of TEOS and Ti—OH groups of TBT, as is discussed below.

Si—OH groups can also react with end-chain OH groups of PDMS molecules through a copolymerization reaction. The band assigned to such reactions is that appearing at 850 cm$^{-1}$ [13, 18]. Fig. 9 shows the evolution of the copolymerization band and can be observed that such reaction increase during the first 60–80 minutes of reaction, and after that the increase is very slow. The higher copolymerization rate is for the higher concentration in TBT. A similar result has been above commented for the Si—O—Si crosslinked structures. Therefore the TBT increase in the reaction medium increases the formation of crosslinked structures. This result is in accordance with those obtained

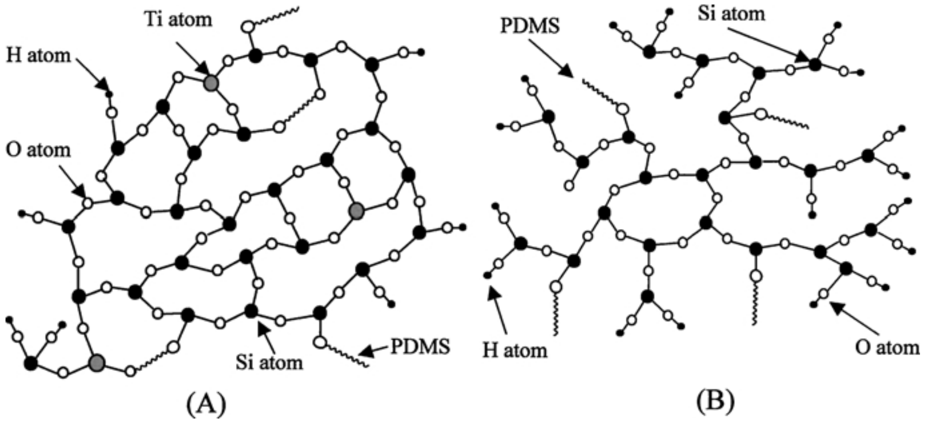


*Figure 8* (A) Crosslinked structure for sample with 7% of TBT and (B) Linear structure for sample without TBT.

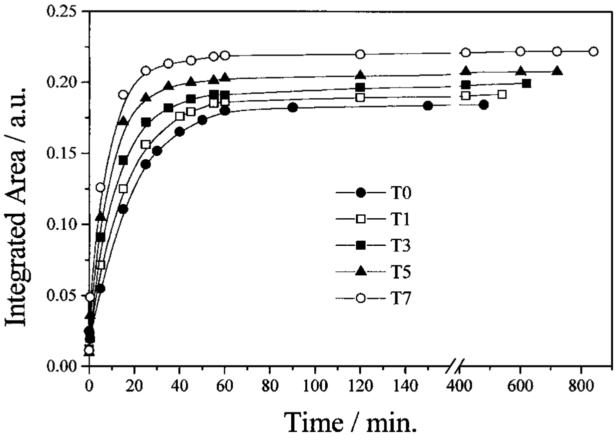
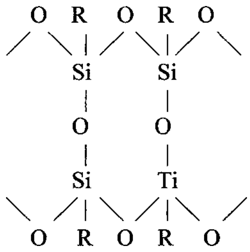


*Figure 9* Time evolution of integrated areas corresponding to 850 cm$^{-1}$ band for studied samples with different TBT concentration.

by Babonneau *et al.* [9, 23], which showed that titanium alkoxides act as both crosslinking agents and catalyse condensation reaction. This permits to assume a hybrid material structure as given below:



Therefore TBT influences the hydrolysis and copolymerization reactions between hydrolyzed TEOS and PDMS molecules, however it must be considered the high hydrolysis rate of TBT in presence of $H_2O$ [16, 22, 24]. The hydrolysis of TBT molecules can be followed by the high intensity IR band appearing at 1130 cm$^{-1}$ [16]. Fig. 10 shows the evolution of this band. Integrated area values increase as the TBT concentration increases. The integrated area increases during the first 30 minutes of reaction as it corresponds with addition of TBT to the solution. After this addition time, the integrated area values decrease with the reaction time showing that the hydrolysis of TBT is occurring.

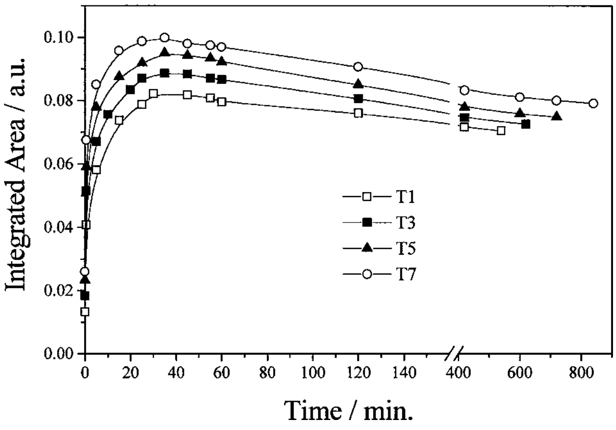


*Figure 10* Time evolution of integrated areas corresponding to 1130 cm$^{-1}$ band for studied samples with different TBT concentration.

It is observed that at the end of the reaction some Ti—OR from TBT remains in the material. Different works [15, 16, 22, 24, 25] have studied the hydrolysis of TBT as a function of water and acid (HCl) concentration. They have found that the removal of the four butoxy groups is difficult and that titanium oxopolymers are formed through reaction of Ti—OH groups.

The hydrolysis reaction of TBT gives Ti—OH groups, which can react by self-condensation or copolymerization reactions. Self-condensation reaction gives Ti—O—Ti bonds, however copolymerization reaction gives Ti—O—Si bonds. In accordance with Sanchez *et al.* [22, 24] the ratio $H^+$/TBT influences the final form of the obtained material. Babonneau have shown that Ti-O-Ti bonds can grow up forming hydrous titanium oxide nanoparticles responsible for the transparency of the samples [9]. In accordance with Babonneau the presence of such nanoparticles can be seen through the broad bands about 500 cm$^{-1}$ assigned to Ti—O—Ti bonds [9, 21]. Fig. 11 shows the evolution of the 750–500 cm$^{-1}$ spectral region. It must be taken into account that in this spectral region also appears out of plane IR bands of OH groups from $H_2O$ and alcohols. These bands are of high width and mainly overlap most part of this spectral region. If it is assumed that: first, the reactions consume the same $H_2O$ amount, second, that the amount of $H_2O$ generated from Si—O—Si condensation is similar in all cases, and third, taken into account that the amount of iPrOH is the same in all reactions, then the increase observed in Fig. 11 must be associated to two factors: the EtOH formed from TEOS hydrolysis and the Ti—O—Ti formation. The amount of EtOH depends on the TEOS concentration, being higher for that reaction without TBT, therefore the difference between integrated areas of reactions with a given amount of TBT with respect to that of 0% TBT must be associated with the Ti—O—Ti formation. Fig. 11 shows that Ti—O—Ti bond formation increases with the amount of TBT, and that such formation mainly occurs during the TBT addition (30 minutes). After this time the amount of Ti—O—Ti bonds shows a very little increase with time. This result is in accordance with the above

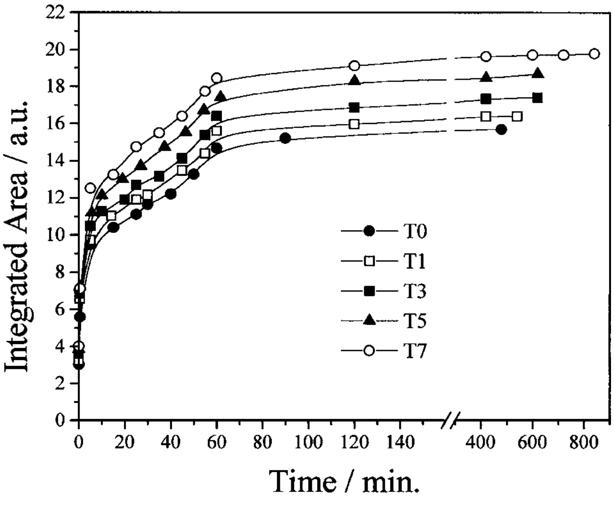


*Figure 11* Time evolution of integrated areas corresponding to 750–500 cm$^{-1}$ spectral range for studied samples with different TBT concentration.

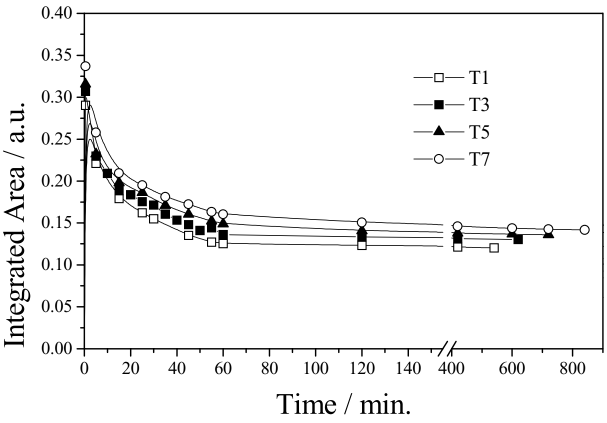


*Figure 12* Time evolution of integrated areas corresponding to 937 cm$^{-1}$ band for studied samples with different TBT concentration.

commented of Sanchez *et al.* [22, 24]. The formation of Ti—O—Ti bonds leads to growing of titanium hydroxide based particles nanometric in size as must be expected from the transparency of the obtained materials.

As it has been commented, copolymerization reaction by Ti—OH and Si—OH groups can give Ti—O—Si bonds that give an IR band close to 930 cm$^{-1}$ [13, 26]. Babonneau has shown that such bonds are formed during the polymerization reactions between titanium and silicon alkoxides and PDMS molecules, but such bonds are very unstable when they are formed and then they disappear during the aging process [9]. Fig. 12 shows the evolution of the 937 cm$^{-1}$ band assigned to Ti—O—Si bonds. It is clearly observed that such bonds are formed during the adding step of TBT and then it decreases along the reaction time. In accordance with Babonneau [9], a given amount of Ti—O—Si bonds remains when the final material is obtained. Fig. 12 also shows that the concentration of Ti—O—Si bonds increase with the TBT concentration in the reaction medium.

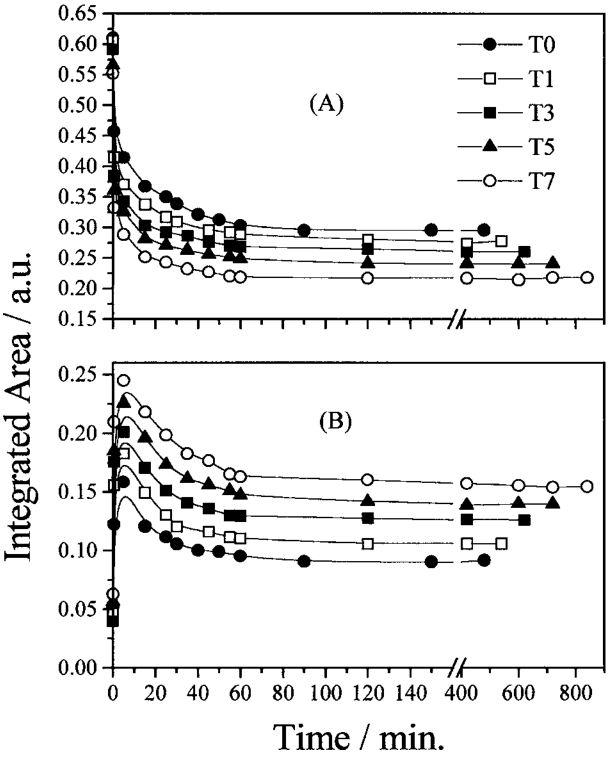


*Figure 13* Time evolution of integrated areas corresponding to (A) 813 cm$^{-1}$ and (B) 800 cm$^{-1}$ bands for studied samples with different TBT concentration.

As said before, PDMS is a polymer that has cyclic ($D_{4c}$ units) and linear (D units) structures in the reaction medium [13]. FT-IR spectroscopy can be used to follow the evolution of such structures because they give two bands at 813 and 800 cm$^{-1}$ [27], which can be well defined by spectral deconvolution. Fig. 13A and B show the evolution of cyclic and linear PDMS chains respectively, as a function of the reaction time and TBT concentration. It is clearly observed that during the first moments of reaction linear PDMS chains are cycled and after that both chains decrease due to the incorporation to the material structure through copolymerization reactions. In this figure it is also observed that increasing the TBT concentration the crosslinked process of PDMS molecules are increased. Iwamoto *et al.* [20] have shown that both the copolymerization and condensation reactions help the gelling of the solution and then cyclic and non-bonded PDMS chains are released from the gel.

## 5. Conclusions

In this work, the hydrolysis and polymerization reactions of TEOS, PDMS and TBT system to obtain hybrid materials were studied by means of FT-IR spectroscopy. The obtained conclusions may be summarized as follows:

1. The fast hydrolysis of TEOS gives Si—OH groups, which also show fast self-condensation and copolymerization reactions. Self-condensation of Si—OH groups gives crosslinked and linear Si—O—Si chains which are responsible for the inorganic structure of the hybrid material. The concentration of crosslinked chains increases with TBT and the high concentration of linear chains corresponds to the material without TBT. This result shows that TBT plays an important role in the final structure of the hybrid material. On the other hand, copolymerization reactions between Si—OH groups and PDMS molecules give the organic structure of the hybrid material and this reaction is simultaneous with the self-condensation one. The higher copolymerization rate occurs for the higher concentration in TBT.

2. The hydrolysis of TBT is not complete and some butoxy groups remains in the hydrolyzed TBT molecules where Ti—OH groups are also present. These later groups are involved in both self-condensation reactions to give Ti—O—Ti bonds and copolymerization reactions to give Ti—O—Si bonds. It has been observed that Ti—O—Ti bonds increase with both the TBT concentration and with reaction time. On the other hand Ti—O—Si bonds are rapidly formed but decrease with time. A very low concentration of Ti—O—Si bonds remains in the final hybrid material.

3. In summary, the presence of Ti—OH groups increases the formation of both crosslinked inorganic and organic-inorganic structures making more rigid the final hybrid material.

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