Hydrolysis/Condensation Reactions at the Sol−Gel/Air Interface: Pure Titania Alkoxide Exposed to Air−Water Molecules

Germain Puccetti* and Roger M. Leblanc

Department of Chemistry, University of Miami, P.O. Box 249118, Coral Gables, Florida 33124-0431

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Sol−gel alkoxides are very often sensitive to the surrounding air humidity, especially when the chemical evolution of the sol is operating at time scales comparable to the water-molecule diffusion from the surrounding air inside the medium and their interaction with the alkoxide molecules. The present study reports the in situ observation and interpretation of hydrolysis/condensation reactions occurring within the surface layers of pure titanium(IV) butoxide exposed to air, which illustrates the interest of the methodology for studies of near-surface chemistry in sol gel evolutions and thin films.

Introduction

The fabrication of advanced materials for new technologies requires a high adaptability of material synthesis in order to develop custom-tailored solutions to application problems. Sol−gel compounds have been shown to possess numerous advantages, which explains the intensive study of these materials over the past decades.[1,2] The array of possibilities in their chemical synthesis allows for adjustments in the sol evolution, yielding the structure needed for an application, e.g., dominant 1D polymer formation necessary to draw fibers from a viscous sol.[3] However, the controlled elaboration of such materials requires a careful adjustment of the initial chemistry and monitoring of the evolution of the medium under environmental factors. Such a sensitive process can result in an extreme difference in the final state/properties of the material developed, e.g., the slow aging of an alkoxide sol under continuous agitation in order to process fibers from it when the optimal polymer state is reached.[4,5]

Sol−gel material processing can be strongly affected by environmental conditions through the surface exposed to air. A modification of the rates of hydrolysis/condensation reactions is typically observed near their surface, which often leads to additional physical constraints. This is mainly due to a rapid solvent evaporation leading to densification in these regions but can also be affected by the presence of water molecules from the surrounding air penetrating into the surface layers and their participation in the local chemistry. This surface effect is even more critical in the case of materials possessing a large surface exposed to air while having a small total volume, e.g., thin films, fibers.

This work presents the in situ study of the hydrolysis/condensation reactions near the surface of pure titanium tetrabutoxide (TBT) when exposed to air. A Fourier fingerprint is obtained from the time-resolved photoacoustic technique (pulsed photoacoustic spectroscopy, PPAS)[6] as both chemical reactions occur near the air-exposed surface of the sample. The results are discussed in light of previous measurements on bulk titania sol−gel evolutions obtained by the same technique. A correlation of these observations with data from FTIR and UV absorption spectroscopies is given, which shows the proposed methodology to be highly sensitive for noninvasive studies of localized chemical changes. Results are given which evidence

the potential of this technique to investigate changes in hydrolysis/condensation reactions under environmental constraints, e.g., the sol−gel chemistries of thin films and coatings.

Experimental Section

The principles of PPAS were outlined in a previous study showing its potential for evidencing the chemical changes within bulk sol−gel materials.[6] However, the present work is the first, to our knowledge, to demonstrate the potential of PPAS as a noninvasive technique for in situ monitoring of local, i.e., surface, reactions, namely chemical changes occurring in the first layers of TBT when exposed to air. A Fourier fingerprint, obtained at different points in time, is characteristic of the momentary chemical composition of the medium. TBT samples (Aldrich, 99%) were exposed to air with 65% humidity at room temperature (300 K).

FTIR spectra were obtained from a thin layer of alkoxide exposed to air for a controlled duration (averaging over 20 spectra, Perkin-Elmer 2000 FTIR). For each spectrum, we ensured a good transparency of the film during enclosure between two ZnSe windows by application of progressive pressure to enclose the film in a prism-shaped space with a progressively reducing angle, until the two windows were quasi parallel. This method also avoids enclosure of air bubbles within the layer. However, the amorphous nature of the surface crust forming on the titanium alkoxide prevented us from performing spectrum measurements after 6 min of air exposure.

Measurements in PPAS were conducted on a sample enclosed in a hermetically closed cell. Exposure of the TBT to air was made by opening the cavity. For measurement purposes (signal detection by a microphone in contact with an air buffer), the hermeticity can be simply restored without perturbing the sample. It was found that a very small volume of air buffer (0.2 mL) contains only enough water to supply chemical reactions within the sample for 25 s after the signal stabilizes. This time delay was accounted for in the delay between each measurement. After this time, no further change is observed on either the response pulse or the Fourier spectrum. The typical amount of sample used was of 0.22 mL in a cavity 6 mm thick and 9.6 mm in diameter.

Previous work has shown that interpreting the PPAS response signals in the Fourier space provides more detailed information
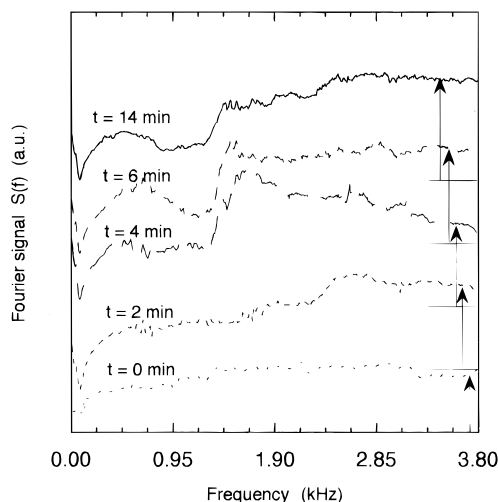
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Figure 1. Near-surface heat emission profile in PPAS (Excitation of the sample by 266 nm irradiation): Normalized spectra of a TBT sample at different times of exposure to free air. All spectra are represented at an identical *y* scale but shifted for a better view of the changes.

on the changes occurring in the sample.[6] Therefore, all response signals were interpreted in the Fourier space. Additional work was also performed to minimize the influence of external parameters (cavity geometry, change of composition of the gas buffer, surface tension between the sample and the air) on the signal and Fourier spectrum.[6,7] These external effects are negligible in the present measurements. Finally, all Fourier spectra were normalized by a reference signal obtained from a blackbody-like sample. Further details can be found in previous studies.[7]

Two configurations of excitation/detection were used for their complementary information: (i) direct light absorption by the sample (266 nm from a Nd^{3+}:YAG laser) and (ii) indirect light absorption (532 nm from a Nd^{3+}:YAG laser) by a black carbon layer (BCL) in contact with the sample followed by the diffusion of the thermal emission from the BCL through the alkoxide sample. The first configuration yields a depth-related heat emission, while the second case yields a heat transmission pattern. Due to the origin of the heat emission, the first configuration is expected to be more sensitive to changes in the properties of the surface layers of the alkoxide sample. The signal-to-noise ratio was dependent on the source of heat emission, i.e., the wavelength of irradiation. For surface excitation (266 nm), this ratio was about 35, while it was only about 22 in the case of backing excitation (532 nm) due to the weak perturbation regime of these measurements. This explains the noisier appearance of spectra obtained from the later configuration. A detailed explanation of the experimental procedure was given elsewhere.

Results and Discussion

"Depth profiles" are obtained from Fourier transforms of the heat response pulse under 266 nm irradiation (Figure 1). For clarity, spectra were only reported at time intervals of 2 min even though measurements were performed every minute. According to the principles of PPAS, higher Fourier frequencies correspond to near-surface heat emission while lower frequencies include deeper contributions to the response pulse.[8,9] Depending on the nature of the sample, the heat response pulse is characteristic of three material properties: the thermal diffusion length, μ_D, the optical penetration, $\mu_\beta = 1/\beta$ (where β

is the absorption coefficient at the excitation wavelength), and the sample thickness, *l*. In Fourier space, these parameters result in monotonically varying shapes of spectra in the case of a homogeneous sample. However, it has been shown that any physical discontinuity such as in multilayered structures appears as a perturbation on the Fourier spectrum, due to differences in thermal and/or light absorption properties.[9] This is exactly the case in Figure 1, at times greater than 2 min, in which case one observes irregularities from 2.4 ($t = 2$ min) up to 1.3 kHz ($t = 14$ min). These correspond to the interface between the bulk alkoxide and the surface layer which forms, due to the water present in the surrounding air. The shift toward lower frequencies corresponds to the growth of the film thickness. For an air exposure of 3 min, this irregularity was found at 2.21 kHz. It appears that the film formation stabilizes after 4 min. Approximating the sample to butanol allows one to use its thermal property values ($\rho = 0.992$ g/mL for TBT; $k = 1.48$ mW/cm K; $C = 2.39$ J/gK) for an estimate of the depth inside the sample corresponding to the above frequencies by using the expression $\mu = (k/\rho Cf)^{1/2}$ (ρ, density; k, thermal diffusivity; C, heat capacity; f, Fourier frequency).[8] The resulting μ values range from 5.3 (2.6 kHz) to 7.4 μm (1.3 kHz).

For an air humidity of 65%, the first iridescence can be observed visually on the pure alkoxide after 3−4 min. However, one can already distinguish the beginning of the surface layer formation at a time of 2 min of exposure on Figure 1. In addition, one can notice an increase in the signal amplitude at higher frequencies: relative amplitudes of 47 ($t = 6$ min) and 50 ($t = 14$ min) compared to 30 ($t = 0$ min). This can be explained by an increase in the local heat emission resulting from increased light absorption. Such an increase in absorption can be explained by the formation of a polymer network, which induces a shift in the absorption band from 215 to 265 nm, leading to a higher absorption at the irradiation wavelength (266 nm).[10,11]

The shift in the maximum absorbance can be clearly observed in the absorption spectra of a bulk TBT-based sol−gel, as shown in Figure 2a during its evolution from sol to gel. In this case, a sol preparation was dip-coated onto a quartz slide and exposed to dry air. One can clearly observe the shift in the maximum wavelength with polymerization of the titanium oxo network, which confirms our previous assumption. The increase in absorption of 266 nm radiation is also observed on the transmittance of a thin film of pure TBT at air (Figure 2b). The measured transmittances were converted into absorbance coefficients using Beer's law. A very wide TBT film on a wide quartz support was used in this case to avoid meniscus deformations within the region of the optical measurement area. A thin surface film is observed starting from 4 min of air exposure. Over the first time intervals (0−9 min), this thin film remains very smooth in appearance and does not show any ridges or grooves, which would affect the light transmission by scattering. The results are very reproducible. An increase in absorbance at 266 nm is clearly observed during the first 6 min, indicating the formation of polymers similar to bulk gels. This observation supports the explanation of the signal increase observed in Figure 1. Finally, a strong increase in signal is observed in the middle of the spectrum (0.9−3.0 kHz) at a specific exposure time of 4 min. This sudden variation is ascribed to local changes in the thermal diffusion length of the sample, but further measurements are required to determine its exact origin.

Further information on the aging is obtained by inducing the heat emission inside a thin BCL layer forming the backing of
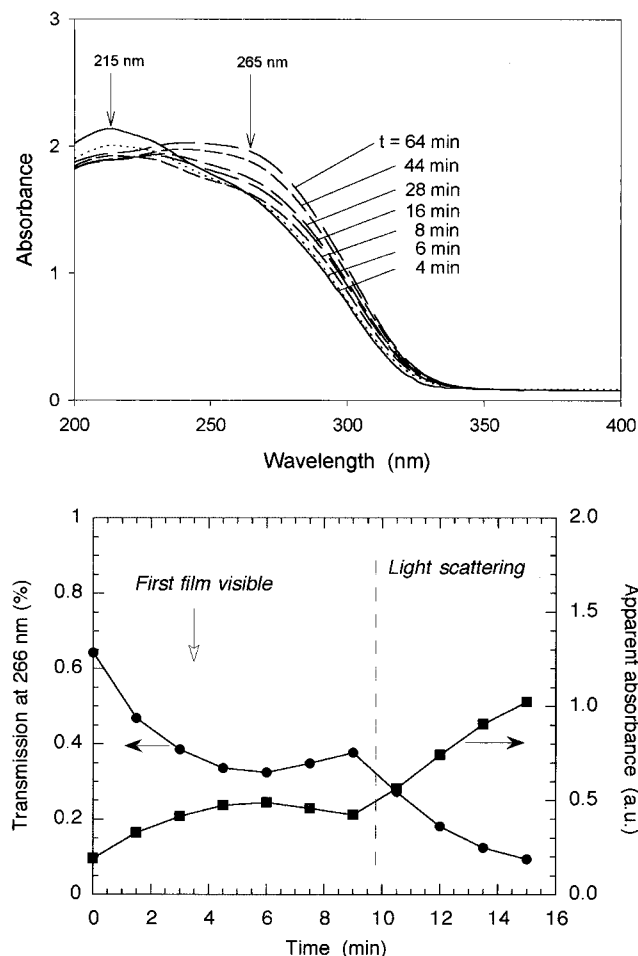
Figure 2. (a) UV−Visible absorption spectra of a bulk TBT-based gel dip-coated on a quartz slide. Volume ratios for TBT, butanol, and water are 0.4:0.5:0.1, in which water was acidified by HCl at 0.5 M. (b) Variations of the optical transmittance of a thin film of pure TBT exposed to air versus time. Absorbance coefficients are deduced from Beer's Law.

Figure 3. Thermal transmittance in PPAS (Excitation of the BCL backing by 532 nm irradiation): Normalized spectra of a TBT sample at different times of exposure to free air. All spectra are represented at an identical *y* scale but shifted for a better view of the changes.

Figure 4. (a−d) FTIR spectra of a TBT sample at different times of exposure to free air. (e) FTIR spectrum of pure butanol.

the TBT sample. The BCL plays the role of the source of the heat pulse, which must then diffuse through the sample in order to be detected by the microphone. The resulting signal is again analyzed in Fourier space, after normalizing by a reference (Figure 3). This spectrum is dominantly subject to changes in the thermal properties of the sample, due to various chemical species with distinctive properties. For comparison, the Fourier spectrum of pure butanol, obtained under identical conditions, is also shown in Figure 3. Here, only some spectra could be reported for clarity. One can see that the spectrum for $t = 3$ min does not show any significant changes with respect to the one at $t = 2$ min. The bands appearing for $t = 4$ min are sudden and very reproducible between samples. Spectra at times higher than 4 min show a progressive evolution, e.g., the band observed around 2 kHz for $t = 4$ min shifts toward 1.3 kHz. On the high-frequency side of the spectrum, a signal increase is observed in the form of a high-amplitude band (3.6 kHz) which progressively dampens toward long exposure times but is still clearly visible at 10 min. While no important changes are evidenced for times from 0 to 3 min, a very sudden and strong change becomes apparent after 4 min of sample exposure to air. This change appears at the same moment than a thin film on the surface of the alkoxide sample is visually observed. The similarity in spectral profiles for $t = 4$ min with that of pure butanol (also possessing two bands around 1.8 and 3.4 kHz) tends to indicate an important butanol release. Both hydrolysis
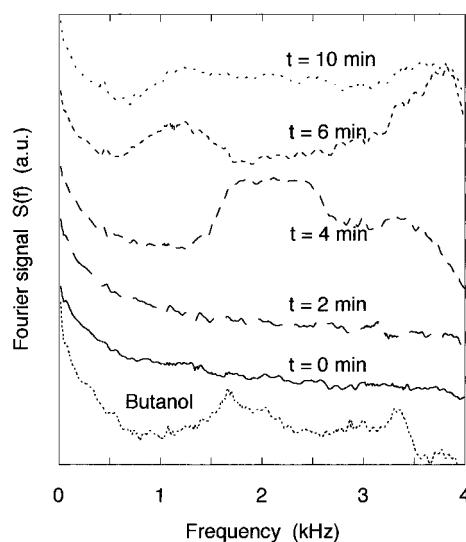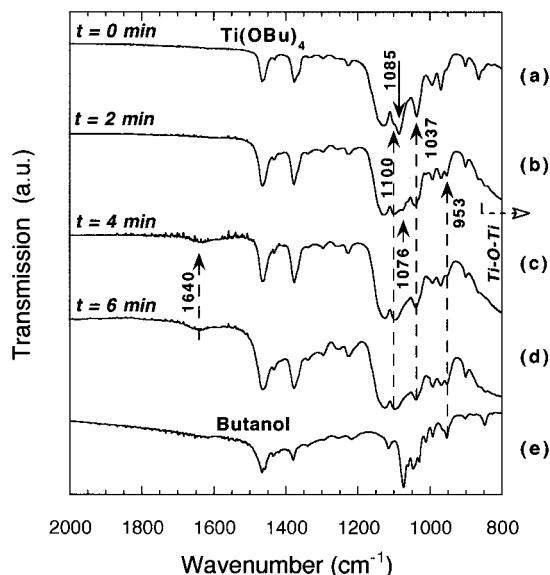
and condensation reactions could be responsible for butanol emission. However, due to the very small amount of water present, this effect is believed to be the result of condensation reactions.

One will notice that FTIR measurements (Figure 4) do not evidence any significant change around $t = 4$ min. The presence of butanol, at this moment, is reinforced by the similarity of these bands on Figure 3 with previously reported data of a bulk TBT-based sol−gel, i.e., the short time spectrum in which butanol has a dominant contribution in the initial sol during hydrolysis.[6] Finally, the spectrum at 6 min has a band around 1.2 kHz which lies in the same region as the one observed for a bulk gel at times shortly after gelation.[6] This could indicate the presence of a larger polymer network. No butanol band appears for these times because the titania oxide network tends to homogenize the spectral features of the response signal by lateral diffusion of the heat signal. This was previously observed for bulk gels and occurs here at faster times. No measurements were performed for times longer than 15 min

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because of the inhomogeneity of the surface structure of the sample. It has been observed that, at this stage, samples tend to break up in the surface due to surface-tension strains.

For comparison, FTIR spectra of films at different times of exposure to air are presented in Figure 4. Our spectrum of pure TBT was verified to be in agreement with literature results, excluding any product degradation prior to its use (despite its freshness). Previous work[12−14] has reported the presence of dimers and trimers of TBT in a pure state, so that the C−O vibration shows the classical peaks at 1037 and 1085 cm^{-1}, respectively, due to butanol in the bridging and terminal positions. In addition, one can distinguish the presence of Ti−O−C stretching at 1100 cm^{-1}. As the time of exposure to air increases, several changes can be noticed. While the peak of bridging butanol (1037 cm^{-1}) stays present in time, that of the terminal butanol is replaced by one around 1076 cm^{-1} at 2 min and vanishes for $t > 2$ min. The water molecules of the surrounding air induce hydrolysis of mainly the terminal butoxy groups, while bridging butoxy groups appear to be stabilized by the presence of several neighboring titanium atoms. Due to their unsatisfied coordination, the titanium atoms have the possibility to increase their initial coordination through the partially hydrolyzed oligomers and form an olated polymer.[12,15] This weak polymer appears on the FTIR spectra at 2 min of exposure, as indicated by the presence of a featureless band below 850 cm^{-1} (broad band extending between 850 and 300 cm^{-1}),[13] attributable to the Ti−O−Ti vibrations of a polymeric network. Limitations due to the optics of the spectrometer prevented us from showing this entire band. The presence of this band after a short time confirms the presence of polymers and is in agreement with the small increase in amplitude observed in Figure 1.

At times longer than 1 min, free butanol molecules are released, as evidenced by the peak at 953 cm^{-1}. The more sudden butanol release around 4 min in Figure 3 tends to indicate that only a small fraction of butanol substituents were removed at early times while the remaining butanol endgroups were released at the moment of film formation. Condensation immediately begins (thanks to the absence of protons which would slow this reaction), including the olated bridges, and leads to covalent oxo bridges between titanium atoms. The beginning of condensation is confirmed by the appearance of a small water band, around 1640 cm^{-1}, in Figure 4 at $t = 4$ min. The absence of this band at $t = 2$ min confirms that the observed polymer is predominantly due to olation and butanol bridges. The band at 1640 cm^{-1} increases in intensity with time, with respect to the other bands. At a time of 4 min, the beginning of massive condensation also corresponds to the moment of formation of the surface film (iridescence) responsible for the thermal discontinuity observed in Figure 1.

One will notice that no drastic change in butanol bands is observed at ca. 4 min. Such a sudden butanol release could be observed by FTIR in a thin film but would require a physical contact between the sample surface and an IR crystal (such as that used in attenuated total reflection) and is, therefore, destructive for the film. Finally, iridescence cannot be correlated with the very beginning of condensation because of the optical index contrast necessary for a good visual effect (contrast of an asymmetric Fabry−Perot). Thus, the film is probably much thicker than $\lambda/2n$, where λ is the wavelength of light in the visible range and n is the corresponding optical index.

The remaining peak due to C−O vibration of butanol at longer times ($t = 6$ min) is simply due to the contribution of bulk TBT to the FTIR spectra. The observed changes, reported above, are only occurring nearby the surface of the sample. While FTIR was limited to short times because of a degradation of the optical quality of the sample surface, PPAS could be applied to times much longer (20 min), limited by structural instabilities of the surface. The PPAS fingerprint at this time shows a homogenization of the medium, due to the progressive penetration of water molecules into the deeper layers. It can be expected that the slight discontinuity, still apparent around 1.4 kHz for $t = 14$ min, will be eliminated as condensation proceeds throughout the medium.

Conclusion

It has been shown that photoacoustic spectroscopy is well-suited for the noninvasive study of chemical surface reactions occurring in sols and gels when exposed to outside factors such as air humidity or massive solvent evaporation. This is very important in all applications of sol−gels involving a large surface exposure to air with respect to a small total volume, i.e., coatings or fibers, because such sol to gel evolutions occur very differently from those in bulk. The present work has shown the potential of the pulsed photoacoustic technique to study interface and surface phenomena by (i) providing depth- and time-resolved information on reactions in an amorphous material, (ii) delineating an important aspect of the hydrolysis/condensation evolution, namely the sudden occurrence of the second step in hydrolysis followed by rapid condensation at 4 min of air exposure, and (iii) providing sensitive measurements on localized reactions which would be difficult to assess by conventional techniques. A direct field of potential application of this technique lies in the study of modified sol−gel preparations for coatings and fibers to account for surface effects such as exposure to air−water molecules and massive solvent evaporation.

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