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Study of the hydrolysis and condensation of γ-Aminopropyltriethoxysilane by FT-IR spectroscopy

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Abstract The hydrolysis and condensation reactions of γ-APS have been studied in different acid content aqueous solution by using Fourier Transform infrared (FT-IR) spectroscopy. The hydrolysis of γ-APS under the studied conditions can be followed by the increase of the ethanol band located at 882 cm^{-1} and the decrease of the band due to the $\rho(CH_3)$ of γ-APS molecules located at 959 cm^{-1}. Hydrolysis reaction is faster by increasing both H_2O and acid concentrations, and it is completed when 3 moles of H_2O per mole of γ-APS are used. The increase of the vibrational band located at 1146 cm^{-1} shows that condensation of the hydrolysed γ-APS molecules take place forming linear chains in poorly cross-linked structures. Besides, both 8-membered cyclic siloxane formations and poorly cross-linked structures are formed and increase as the water and acid content are increased. On the other hand, highly connected cross-linked structures do not appear due to the steric hindrance of the non-hydrolysable aminopropyl group. The silanol band shows that hydrolysis is faster than condensation except for samples with the lowest H_2O content.

Introduction

It is well known that, in the field of composite materials, organofuctional silane coupling agents such as alkyltrialkoxysilanes have been used for long time to improve the adhesion of glass fibres to plastics [1]. The reinforced mechanism has been already proposed by several authors [2–5]. Silanes are used for modifying the surface of the inorganic materials giving an organic character on them. One of the most studied silanes used as surface modifier is the γ-aminopropyltriethoxysilane (γ-APS). Ishida and co-workers [6–10] published numerous studies related to γ-APS. This silane has been applied to modify the surface of glass fibres [11], silica and silica gels [7, 12, 13], silicates [14–16], etc.

On the other hand, during the last decade, a high interest on organic–inorganic hybrid materials has grown [17–21]. These materials are prepared through the sol–gel process where completely hydrolysable metal alkoxides are mixed with organic molecules or with other metal alkoxides having at least one non-hydrolysable group. γ-APS has been very used for obtaining hybrid materials [22–24] whose function is acting as network former of the hybrid structure.

When γ-APS acts as surface modifier for glass fibres used in composite materials, it is not necessary to hydrolyze with water because the aminopropyl group acts as a catalyst by reacting with water molecules adsorbed on the surface of the glass fibre [12]. On the contrary when γ-APS acts as network former in organic–inorganic materials, water is usually needed for the hydrolysis of the alkoxy groups of γ-APS [1, 25]. After hydrolysis, condensation reactions take place where hydrolysed γ-APS molecules react with other γ-APS molecules through a self-condensation process, or with different molecules containing hydroxyl groups through a condensation reaction. When γ-APS is used as a network former in hybrid materials, the amount of

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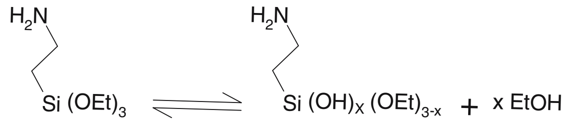
H_2O and the pH of the hydrolysis solution can provide an uncompleted hydrolysis. However, when a high amount of H_2O is used, a complete hydrolysis of γ-APS is obtained.

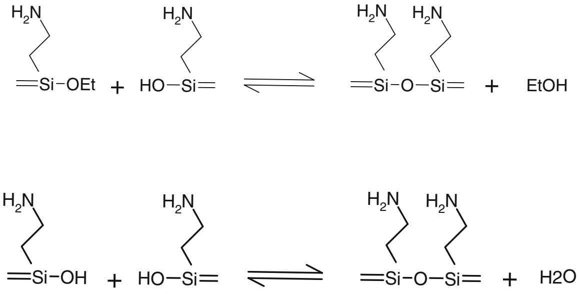
The following reactions show a general scheme of the hydrolysis and self-condensation reaction of γ-APS:

a) Hydrolysis:



(1)

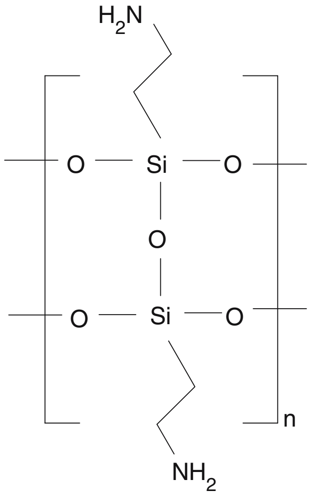
b) Condensation:



(2)

(3)

c) Final condensed product:



(4)

The first equilibrium (1) corresponds to the hydrolysis/esterification processes of the γ-APS molecules in an acidic medium [12, 26, 27]. Water molecules attack the ethoxy groups of γ-APS which produce one ethanol molecule for each hydrolysed radical. The second (2) and third (3) reactions correspond to condensation/alcoholysis step and are slower than the hydrolysis presented in reaction (1) as normally corresponds to silanes. Self-condensation can occur between one hydrolysed and one ethoxy radical of γ-APS, equilibrium (2), which results in a siloxane bond and an ethanol molecule, or between two hydrolysed radicals of γ-APS, equilibrium (3), which forms a water molecule. The final condensed product obtained is represented in [4].

There are a few works about the hydrolysis and condensation reactions of γ-APS [28] but most of them study these reactions when γ-APS is used as silanating agent on silica surfaces [12, 23]. Ishida and Suzuki [29] studied the hydrolysis of γ-APS at different water dilutions, between 0.5 and 13 mol H_2O per mole of silane and reaction times up to 2.5 h by infrared spectroscopy. They found that the molecular structure of γ-APS in aqueous solution was strongly influenced by both initial silane concentration and hydrolysis time. On the other hand, Beari et al. [28] studied the reaction process of several alkyltrialkoxysilanes by ^1H and ^{29}Si NMR spectroscopy. They also used different water/silane concentrations ranging from 12 to 296, which were inside general industrial uses. In this case, reaction times were higher than 180 h and they removed 2 mL of reacting solution to obtain each spectra. They determined the structural changes of these alkoxisylanes with their hydrolysis and condensation reaction and reported a semi-quantitative study of the different condensation products. They found that for such high water concentrations, the hydrolysis is completed in a few minutes and the rate of condensation increases as the initial silane concentration is increased. In such cases, oligomers are build-up through monomer crosslinking.

However, any of these works study the influence of the pH of the aqueous solution. The purpose of this work is to study the hydrolysis and condensation of γ-APS under several acidic water conditions (pH solutions) using ethanol as solvent. We have used FT-IR spectroscopy because this technique allows obtaining spectra with only 1 μL of the reacting solution.

Experimental

γ-aminopropyltriethoxysilane (γ-APS, from ABCR), hydrochloric acid (HCl Merck, 32% p.a.) and distilled H_2O were used as raw materials for the preparation of different reaction solutions. Nine different solutions were prepared as it is shown in Table 1.

The appropriate amount of γ-APS and half of the solvent volume, ethanol, were poured in a vessel with

Table 1 Composition of the samples: hydrolysis conditions

Sample	EtOH/γ-APS %(mol/mol)	H_2O/γ-APS %(mol/mol)	pH
ha11	4.5	1	1
ha13			3
ha17			7
ha21		2	1
ha23			3
ha27			7
ha31		3	1
ha33			3
ha37			7

magnetic stirring, and then placed into a water bath at 25 °C. The hydrolysis solution containing the H_2O, acid and the other half of the ethanol was stirred for 30 min at 25 °C and then added to the reaction vessel for allowing hydrolysis. The resulting solution was kept constant at 25 °C under continuous stirring until the end of the experiment. The study of the reaction was followed by FT-IR spectroscopy. The spectra were obtained from 4000 to 400 cm^{-1} by a Fourier Transform infrared (FT-IR) spectrometer Perkin-Elmer mod. 1760× using a 2 cm^{-1} resolution. Ten scans were recorded for each spectrum and background was subtracted in all cases for removing the bands not due to the samples. Solution samples were taken 30 s after the addition of the hydrolyzing solution, to allow the mixing of reagents, then each 3 min during the first hour of reaction and more spacing in time after this first hour depending on the spectral changes. FT-IR measurements were carried out adding a microdrop of the solution between two KRS-5 crystals, which are transparent to the infrared light. The 1 μL drop was taken with a Hamilton microsyringe. It is considered that the removal of 1 μL from the solution does not affect the reaction process because the total volume of the prepared solution is 300 mL.

Results and discussion

FT-IR spectroscopy

The studied reactions of the of γ-APS hydrolysis do not produce any transparent gel and remain in the sol state for periods of time longer than 1 month with only a few changes in the infrared spectra with time under the studied conditions [1, 28, 30].

Figure 1 presents the evolution of the IR spectra for the sample of molar ratio $[H_2O]/[\gamma\text{-APS}] = 3$ and pH = 1 (sample ha31). The spectrum at 0 min shows a broad band between 3030 and 3630 cm^{-1} due to O–H asymmetric stretching of ethanol [32]. This band shows two small peaks located at 3368 and 3295 cm^{-1} due to the N–H asymmetric and symmetric stretching of γ-APS, respectively [6, 31]. Bands at 2974, 2928 and 2885 cm^{-1} corresponds to $\nu_A(C\text{–}H)_{CH3}$, $\nu_A(C\text{–}H)_{CH2}$ and $\nu_S(C\text{-}H)_{CH3}$ [6, 12, 31, 32] from both, the γ-APS and EtOH. There is a small band at 1602 cm^{-1} due to NH_2 bending [6, 12, 31] of γ-APS.

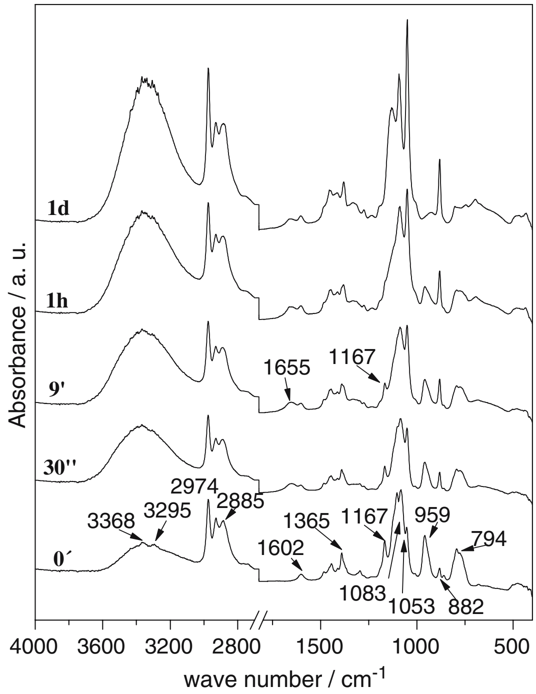


Fig. 1 Sequence of spectra for the reaction of the sample ha33

The spectral region between 1500 and 1250 cm^{-1} shows several bands whose intensity is mainly due to γ-APS, although there is some contribution of ethanol which slightly change the shape and relative intensity of the γ-APS bands: δ (NH_2) at 1483 cm^{-1}, $\delta_A(CH_3)$ at 1444 cm^{-1}, $\delta(Si\text{-}CH_2)$ as a small peak at 1410 cm^{-1}, the highest intensity band at 1391 cm^{-1} due to $\delta(CH_3)$, a small shoulder at 1365 cm^{-1} due to $t(CH_2)$ and the peak at 1296 cm^{-1} due to $w(CH_2)$ [6, 7, 11, 12, 14].

The most intense spectral region is found between 1200 and 1000 cm^{-1}. Located at 1167 cm^{-1} the C–H rocking in CH_3 of the γ-APS ethoxy groups [6, 7, 31] is observed, lying at 1103 cm^{-1} the Si–O–C asymmetric stretching, at 1083 cm^{-1} the C–O symmetric stretching of γ-APS [6, 7, 12, 31]and at 1053 cm^{-1} the C–O asymmetric stretching of ethanol [32].

Below 1000 cm^{-1}, the spectrum shows several peaks: at 959 cm^{-1} the CH_3 rocking of γ-APS [6, 7, 31], at 882 cm^{-1} the ethanol skeletal vibration [32] and at 794 cm^{-1} the ethoxy groups of γ-APS.

The start of the hydrolysis reaction produces spectral changes from the initial spectrum at 0 min up to 1 day of reaction as it can be seen in Fig. 1. First of all, an increase and broadening of the band above 3000 cm^{-1} is observed. This is mainly due to the addition of water and ethanol from the hydrolysing solution and the ethanol generated by the hydrolysis of the γ-APS molecules. Bands between 3000 and 2880 cm^{-1} show small changes due to the addition of more ethanol with the hydrolysing solution. A new band located at 1655 cm^{-1} appears due to the presence of H_2O. This band has the highest intensity in the spectrum 30 s after mixing reactants and decreases with time because water is consumed as the hydrolysis proceeds. This fact indicates that water is being consumed gradually during hydrolysis reaction and hydrolysis does not occur instantaneously. The band lying at 1601 cm^{-1} due to NH_2 bending of γ-APS is close to that of water located at 1650 cm^{-1} but both of them are very well defined and differentiated. According to Naviroj et al. [7] the little shift towards a higher wavenumber of the band at 1601 cm^{-1} could be due to the formation of $NH_3^+Cl^-$ species whose NH_3^+ bending is located around 1613 cm^{-1} whose corresponding vibration band is observed at 2768 cm^{-1}. Moreover, the broadening of the 1601 cm^{-1} band towards lower wavenumber is due to NH_2 hydrogen bonding whose stretching is located at 1575 cm^{-1} as it was described by Chiang et al. [31]. The spectral region between 1500 and 1250 cm^{-1} shows small changes and they are due to the presence of a higher amount of ethanol added with the hydrolysing solution and produced during the hydrolysis reaction of γ-APS.

The most important changes as a function of reaction time are observed in the highest intensity spectral region: 1200–1000 cm^{-1}. It can be seen how the band located at 1167 cm^{-1}, which was due to CH_3 rocking of the γ-APS ethoxy groups, decreases with hydrolysis time. Moreover, it can be seen a broadening of the region between this band at 1167 cm^{-1} and the next band located at 1085 cm^{-1} due to the presence of a new band vibration, which shows a high intensity band between 1131 and 1150 cm^{-1} in the last spectrum. This new band is due to long linear chains in poorly cross-linked structures formed by self-condensation of the hydrolysed γ-APS molecules, which gives the asymmetric Si–O–Si stretching at 1146 cm^{-1} [6, 8, 9]. The absence of the band at 1185 cm^{-1} is due to the absence of highly connected cross-linked structures because of the steric hindrance of the non-hydrolysable aminopropyl group. The band at 1083 cm^{-1} due to the C–O symmetric stretching of γ-APS shifts towards higher wavenumber because of the gradual decrease of this band and the increase of the band at 1092 cm^{-1} due to ethanol added with the hydrolysing solution and produced by the hydrolysis reaction. Related to this, the ethanol band at 1053 cm^{-1} increases with hydrolysis time.

The band lying at 959 cm^{-1} from the γ-APS ethoxy groups decreases as a function of time and at the same time the shoulder located at 930 cm^{-1} increases. Finally, it can also be seen an increase of the ethanol band lying 882 cm^{-1} with reaction time due to the hydrolysis process.

Figure 2 shows the spectral region 1250–840 cm^{-1} for all prepared samples after 30 min of reaction. These spectra show different shape depending on the H_2O and acid content as an indication of different degrees of hydrolysis. Band located at 1167 cm^{-1}, ρ (C–H)$_{CH3}$, decreases with H_2O as the extent of the hydrolysis increases. Moreover, when the pH of the hydrolysing solution decreases the extent of hydrolysis increases and therefore, the intensity of the 1167 cm^{-1} band decreases.

The spectra exhibit a broadening of the spectral region between 1200 and 1000 cm^{-1} with the hydrolysis time due to the presence of the already mentioned new band located at 1146 cm^{-1}. This new band corresponds to the Si–O–Si asymmetric stretching. As it can be seen in Fig. 2, sample ha31 shows the lowest intensity of the

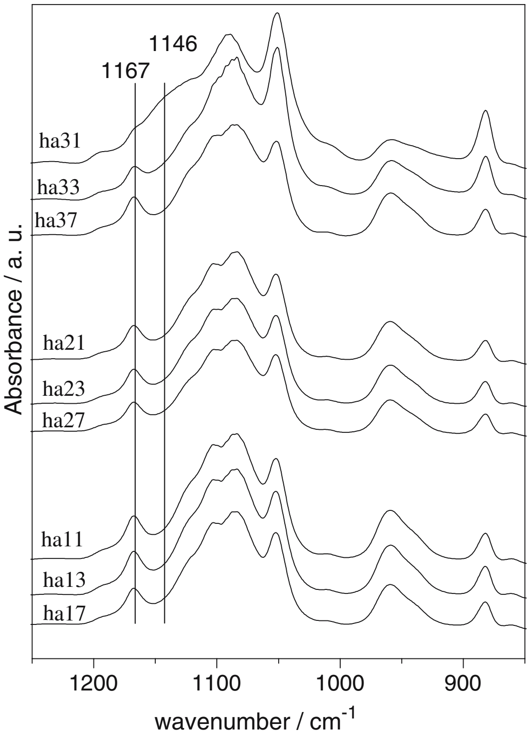


Fig. 2 Spectra for all the samples at 30 min of reaction time

1167 cm^{-1} band and therefore, this is the highest hydrolysed sample after 30 min of reaction. This sample also presents the higher increase of the 1146 cm^{-1} band (Si–O–Si lineal self-condensation asymmetric stretching band) [6, 8, 31], which indicate the higher degree of condensation. The greater intensity of the 1146 cm^{-1} band together with the decrease of the 1167 cm^{-1} one reveals a general smooth of the spectral region 1185–1105 cm^{-1}.

The band at 959 cm^{-1} due to γ-APS ethoxy groups decreases with both H_2O and acid contents. However, the shoulder of this band, which is located at 930 cm^{-1}, increases with both the H_2O and acid content (decreasing the pH), as it can be expected because such band corresponds to Si–OH groups from the hydrolysed γ-APS [8, 9].

Curve fitting of FT-IR spectra

The analysis of the infrared spectra provide general information about hydrolysis and condensation of the γ-APS molecules in different water and acid conditions but more information about these reactions can be known by a deeper analysis of such FT-IR spectra. In this sense, all the collected spectra have been analysed by a curve fitting program which makes use of gaussian distribution functions. Such curve fitting of the FT-IR profiles gives an approach of the spectra by fitting the experimental profiles, which corresponds to the different vibrational modes of the chemical bonds present in the reaction. The position of the bands corresponding the different vibrational modes is based on literature data. The second derivative of the spectra was also taken into account for curve fitting as it provides a better known of the band's location, width and relative intensity. Figures 3 to 7 present the evolution of the normalized area of the most important bands as a function of time obtained from the curve fitting process.

The hydrolysis reaction of γ-APS molecules has been followed by both the removal of hydrolysable ethoxy groups and the formation of ethanol by such hydrolysed groups that corresponds to the 882 cm^{-1} band. The condensation processes have been followed by the increasing of the siloxane stretching band, located at 1146 cm^{-1}.

The evolution of the band located at 882 cm^{-1} due to ethanol is represented in Fig. 3. The increase of this band shows that the hydrolysis of γ-APS occurs for all samples because all plots present an increasing trend of the ethanol band as a function of time. It can be seen that the hydrolysis is faster for those samples with higher content of both H_2O and acid.

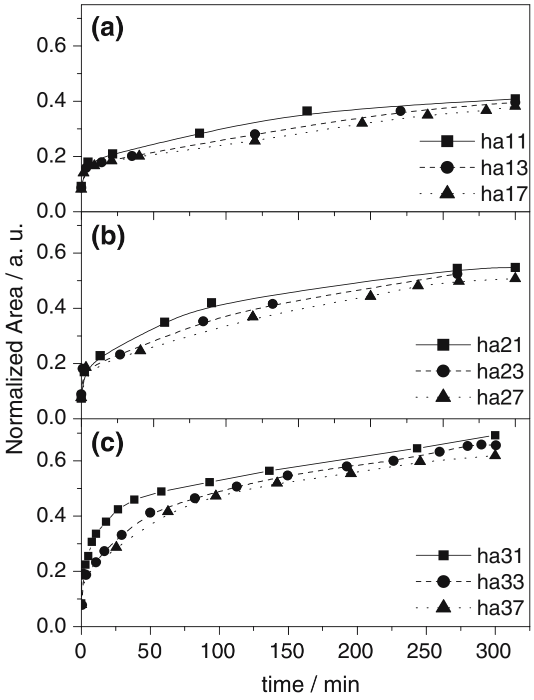


Fig. 3 Evolution of the ethanol band located at 882 cm^{-1}

Time evolution of the CH_3 rocking at 959 cm^{-1} assigned to the ethoxy groups of the γ-APS molecules is shown in Fig. 4. All samples exhibit a decreasing trend of the normalized area of the 959 cm^{-1} band as a

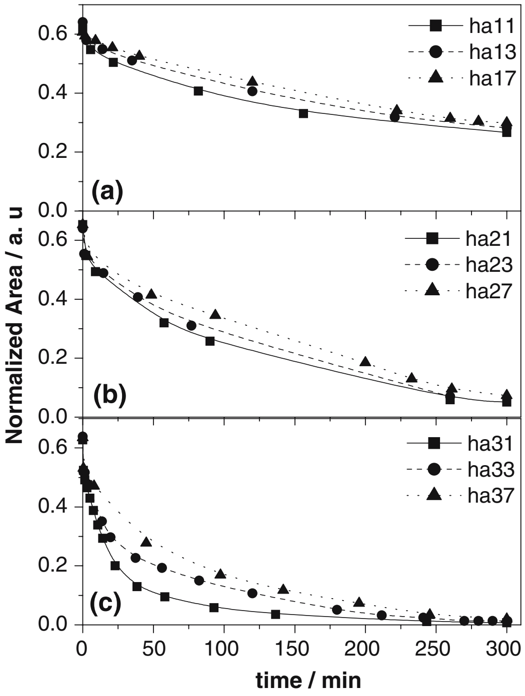


Fig. 4 Evolution of the CH_3 rocking of γ-APS lying at 959 cm^{-1}

function of time. The higher decrease occurs in samples with the highest amount of H_2O and, when the same amount of H_2O is used for those samples with the higher acid content. As it can be seen, sample ha31 shows a fast decrease during the first minutes of reaction and then stabilization. On the other hand, samples ha33 and ha37 show first a less pronounced decrease and then a slow stabilization. After 200 min of reaction samples ha31 and ha33 reached the same value of the normalized area and therefore, a similar degree of hydrolysis. Moreover, after 200 min of reaction, the normalized area for the samples hydrolysed with 3 moles of H_2O are close to zero. This shows that, as may be expected, 3 moles of H_2O are necessary and sufficient to hydrolyse completely the γ-APS molecules. Samples with a molar ratio H_2O/γ-APS = 3 (Fig. 4c) present the highest differences in the decreasing behaviour during the first hour of reaction in comparison with samples of molar ratio water to γ-APS 1 and 2 (Fig. 4a and b). On the other hand, samples with 1 and 2 moles of H_2O per mole of γ-APS show a more gradual decrease of the 959 cm^{-1} band and stabilization occurs at higher reaction times because the hydrolysis of those samples is slow due to the less amount of H_2O used in such reactions. The evolution of the 1167 cm^{-1} band, corresponding to the CH_3 rocking of γ-APS, showed the same behaviour that this band at 959 cm^{-1}.

Self-condensation reactions between hydrolysed γ-APS molecules were followed by the IR bands located at 1146 (Fig. 5) and 1030 cm^{-1} (Fig. 6). The first one corresponds to siloxane asymmetric stretching, ν_A (Si–O–Si) corresponding to long linear chains in poorly cross-linked Si–O–Si structures [6]. The second one has been assigned to 8-membered cyclic siloxane structures and has been identified in some siloxane polymers [10, 34]. As said before, it is interesting to note that the band lying at 1185 cm^{-1} assigned to Si–O–Si bonds in highly connected cross-linked structures does not appear in any spectrum [33] (See Figs. 1 and 2). This result shows that hydrolysed γ-APS does not form such structures due to steric hindrance of the non-hydrolysable aminopropyl groups.

Linear condensation in poorly cross-linked structures takes place from the first moments of the reaction and tend to increase as reaction time increases as it can be seen in Fig. 5. During the first hour of reaction the increase of the linear structures is faster for all studied samples and after such time tend to stabilize. The increase of the band located at 1146 cm^{-1} is different depending on the hydrolysis conditions. Samples with the higher amount of H_2O increase faster and the normalized area values are higher than those of samples with low amount of H_2O. Therefore, it can be observed that when 3 moles of H_2O per mole of γ-APS are used the normalized area reaches higher values than samples with 2 moles of H_2O per mole of γ-APS and these values are higher than those for samples with molar ratio H_2O/γ-APS = 1. Higher observed values for sample of molar ratio H_2O/γ-APS = 3 are due to major presence of the long linear condensation band (1146 cm^{-1}). Moreover, samples with molar ratio H_2O/γ-APS = 1 and 2 do not show a stabilization of the condensation process with time. On the other hand, samples with the same H_2O/γ-APS molar ratio show different trend of such curves depending on the acid content. It can be observed that decreasing the pH the normalized area of the band located at 1146 cm^{-1} increases indicating an increase of self-condensation process. For example, sample ha11 reaches higher values than sample ha13, and this is higher than the value for sample ha17. Therefore, from pH 1 to pH 7 there is a decrease in the self-condensation process. Samples with 2 and 3 moles of H_2O per mole of γ-APS show the same behaviour, increasing the condensation process by decreasing the pH.

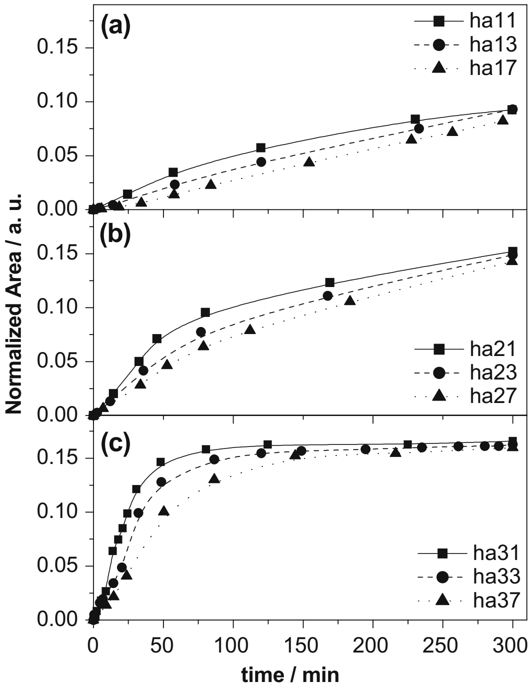


Fig. 5 Evolution of the Si–O–Si asymmetric stretching of linear self-condensation process of g-APS at 1146 cm^{-1}

Figure 6 represents the evolution of the band located at 1030 cm^{-1} as a function of reaction time. This band corresponds to the formation of 8-membered cyclic structures of siloxanes [10, 34]. For the highest H_2O content samples cyclic formations occur

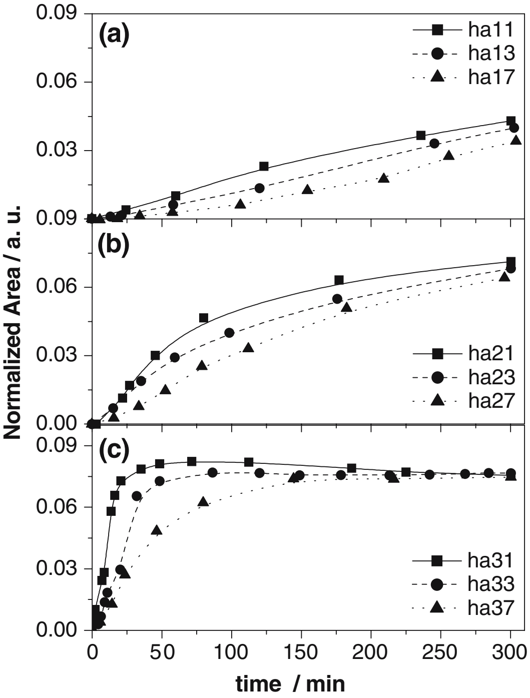


Fig. 6 Evolution of siloxane cyclic structures band of γ-APS at 1030 cm^{-1}

faster during the first minutes of reaction. These structures are formed more gradually for samples of molar ratio H_2O/γ-APS = 2 and 1, respectively. Samples ha31 and ha33 show a small decrease of the 8-membered cyclic structures after 50 min of reaction, once they have reached the maximum value. This decrease is higher for the sample with the higher acid content. On the other hand, the sample at pH 7, ha37, does not show same decreasing trend as the previous ones. Samples ha21 and ha23 show a predictable stabilization with time, whereas the sample ha27 shows a more gradual increasing behaviour and a less clear trend to stabilization. Finally, samples ha11, ha13 and ha17, tend to increase continuously the 8-membrered cyclic formations as a function of time. This increase is higher as the amount of acid increases and there is no stabilization after 300 min.

Finally, it must be taken into account that hydrolysis and condensation reactions occur simultaneously for all the studied reaction conditions. The rate of such reactions may be followed by the formation and consumption or elimination of silanol groups, which give a band lying at 930 cm^{-1}. If the hydrolysis reaction is faster than the self-condensation reaction, then such band must increase and, on the other hand it must decrease. Figure 7 shows the region between 1000 and 840 cm^{-1} for one of the studied spectra. Such figure reveals that the integrated area of the band located at 930 cm^{-1} is high enough to perform the curve fitting analysis and to correlate the mentioned hydrolysis-condensation process described in next paragraphs.

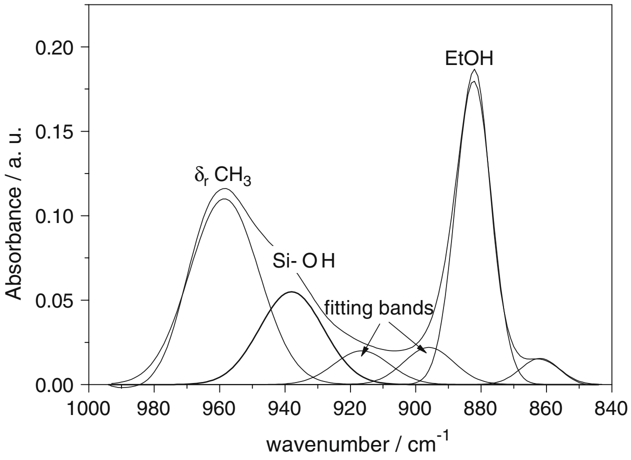


Fig. 7 Example of the curve fitting of one of the studied IR spectra in the region between 1000 and 840 cm^{-1}

The evolution of the band located at 930 cm^{-1} corresponding to silanol groups is shown in Fig. 8. The normalized area of this band increases for all studied samples during the first minutes of reaction but depending on the H_2O and acid content such band present a different trend. Samples with the

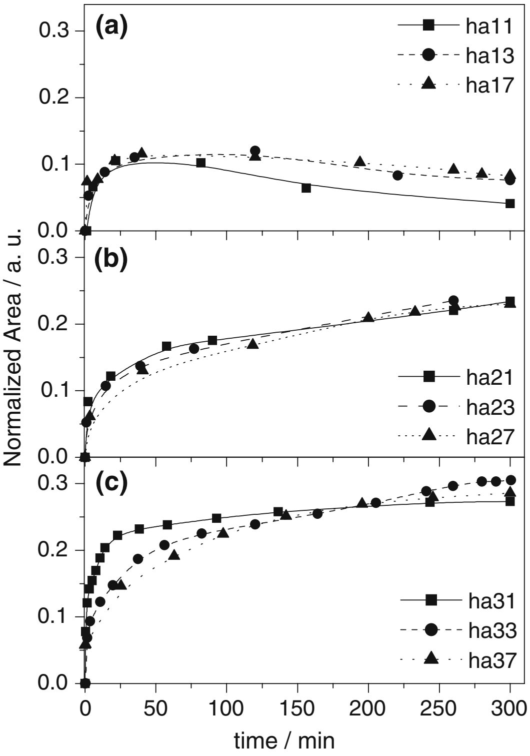


Fig. 8 Evolution of the Si–OH stretching at 930 cm^{-1}

highest H_2O content show a trend to stabilization after 200 min of reaction time approximately. For the highest acid content sample, ha31, this stabilization is faster occurring at shorter time. The three samples with a molar ratio H_2O/γ-APS = 2 show a similar trend. On the contrary, samples with 1 mole of H_2O per mole of γ-APS show an increase of the silanol groups during the first 40 min of hydrolysis and after that a decreasing. This decrease is higher for the sample with the higher acid content. All these results indicate that there exits condensation between the hydrolysed γ-APS molecules and this condensation increases as the acid concentration is increased. The decrease of the Si–OH groups is only observed in the less hydrolysed samples. These results show that the hydrolysis reaction is faster than condensation when 2 and 3 moles of H_2O per mole of γ-APS are used. In contrast, those samples with 1 mole of H_2O per mole of γ-APS show that until about 50 min the hydrolysis reaction is faster than the condensation one and, after this time, the condensation is faster that is observed by the decrease of the normalized area of the 930 cm^{-1} band.

Conclusions

Hydrolysis and condensation of γ-APS take place under different conditions of acidic H_2O. The hydrolysis reaction has been followed by the CH_3 symmetric rocking located at 959 cm^{-1}. Condensation of the hydrolysed γ-APS molecules has been followed by the 1146 cm^{-1} (ν_A (Si–O–Si)) and 1030 cm^{-1} (cyclic Si–O–Si) bands.

The decrease of the 959 cm^{-1} band as a function of reaction time together with the gradual increase of the ethanol band confirms that hydrolysis takes place during the first minutes of reaction and after that presents stabilization. Moreover, the extension of the hydrolysis increases with both H_2O and acid content and it is complete for those samples of molar ratio H_2O to γ-APS equal to 3.

Under the studied conditions, γ-APS shows linear condensation forming long linear chains in poorly cross-linked structures. This linear condensation increases by increasing H_2O and acid content. Such structures are mainly formed during the first hour of reaction for the highest water content samples and occur more gradually for the samples with lower water content. 8-membered cyclic siloxane formations present similar behaviour than linear condensation except those with the highest water and acid content, which shows a small decrease of the 8-membred cyclic structures after 50 min of reaction. The results do not show the formation of a highly connected structure due to the steric hindrance of the non-hydrolysable aminopropyl group.

The silanol band lying at 930 cm^{-1} shows that hydrolysis is faster than condensation when the molar ratio H_2O to γ-APS is higher than 2. On the other hand, samples with a molar ratio H_2O/γ-APS = 1 shows that hydrolysis is faster than condensation during the first 50 min of reaction and after such time condensation is the main reaction.

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