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Contactless Raman Spectroscopy-Based Monitoring of Physical States of Silyl-Modified Polymers during Cross-Linking

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Abstract

Cross-linking of silyl-modified polymers occurs at the alkoxysilane groups attached to the ends of polymer chains by hydrolysis and polycondensation mechanisms in the presence of moisture. During these reactions, three different physical states can be identified (viscous, skin effect and cross-linked state). Knowledge of the evolution of these states at each reaction time is essential to determine the open time for the adhesive industry and is generally obtained by a manual method. Automation of this monitoring could avoid operator error and could be used for very long cross linking reactions or to screen a large number of catalysts. Thus, a contactless micro process technology was developed to correlate these physical states with an optical technology, Raman spectroscopy, by monitoring the decrease in intensity of the $Si-OCH_3$ groups during chemical reactions. This online characterization method can also be used to compare the efficiencies of several catalysts for the cross-linking of silyl-modified polymers, using a minimum amount of chemical materials.

1. Introduction

Silyl-modified polymers (SMPs) are key materials used as binders for elastic adhesives [1] [2], composites [3] [4] and electrolytes [5] and for coating [6] [7] applications.

These hybrid polymers are also becoming increasingly common in aeronautical and aerospace applications [8]. They can be used in several other applications because of their adjustable properties [9] such as Young's modulus, tensile strength, thermal properties, gas barrier and photonic properties. Cross-linking of SMPs occurs when alkoxysilane groups attach to the ends of polymer chains via hydrolysis and polycondensation mechanisms in the presence of moisture [10] [11]. There are several intermediate states during cross-linking. Real-time monitoring of these intermediate states is essential to determine the behavior of polymers in many applications. For instance, it is crucial to know the application time (viscous state), setting time (skin effect) and time to reach maximum properties (cross-linked state) for adhesive materials.

According to the literature, several analytical methods, including ^{29}Si NMR [12], FTIR [13] and Raman spectroscopy [14]-[16] have been used to characterize the intermediate products formed during the hydrolysis and condensation reactions of alkoxysilanes.

Herein, we report on a contactless method based on Raman spectroscopy to characterize the different physical states obtained during cross-linking of different SMP.

2. Experimental

2.1. Adhesive Materials

Silyl modified polymers are silane-based chemicals that contain inorganic and organic parts and form new high-performance sealant polymers. Two silyl-terminated prepolymers were used for this study, SMP1 and SMP2, which were obtained from BOSTIK. SMP1 is a dimethoxysilane-based polyether with a urethane moiety in **Figure 1(a)**, and SMP2 is a trimethoxysilane-based polyurethane in **Figure 1(b)**.

2.2. Chemical Products

Tertiary amine catalysts: 1, 8-Diazabicyclo [5.4.0] undec-7-ene (DBU, 98% wt), 1, 5 Diazabicyclo [4.3.0] non-5-ene (DBN, 98% wt) and triethylamine (TEA, ≥99% wt) were purchased from Sigma Aldrich and were used as received without further purification.
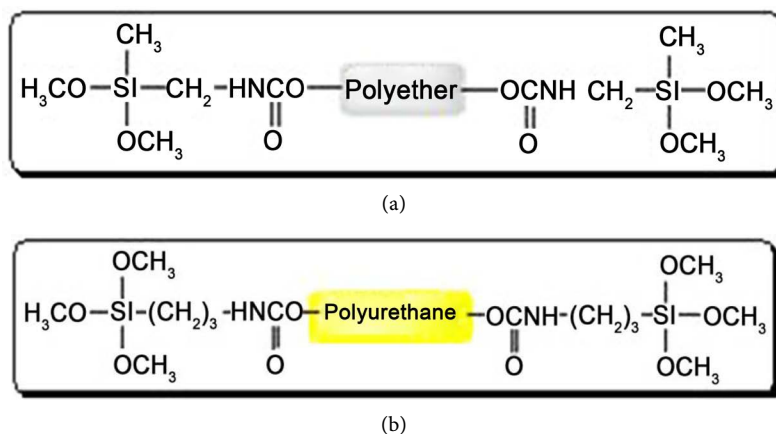
Figure 1. Scheme of silyl terminated polymers, SMP1 (a) and SMP2 (b).

General procedure for cross-linking of SMP1 in bulk: Various rates of tertiary amine catalysts (0.032 mmol to 0.32 mmol) were added to SMP1 (10 g) in a plastic cup (diameter 50 mm and height 30 mm). The mixture was stirred during 1 minute under argon. The reaction begins when mixture is in contact of moisture to allow the cross-linking.

Conditions in the room are 55% H_2O (+/− 5%) at 23°C (+/− 1°C), and cross-linking rate is followed by Raman spectroscopy.

General procedure for cross-linking of SMP2 in bulk: 1, 8-Diazabicyclo [5.4.0] undec-7-ene (DBU) (0.32 mmol) was added to SMP2 (10 g) in a plastic cup (diameter 50 mm and height 30 mm). The mixture is stirred during 1 minute under argon. The reaction begins when mixture is in contact of moisture to allow the cross-linking. Conditions in the room are 55% H_2O (+/− 5%) at 23°C (+/− 1°C), and cross-linking rate is followed by Raman spectroscopy.

2.3. Raman Instrumentation

Raman spectra were collected with LabRAM HR 800 (Jobin-Yvon) with a 632.8 nm from an He-Ne laser and equipped with a confocal microscope. Detection was achieved with an air cooled CCD detector and a grating 600 grooves/mm, giving a spectral resolution of 4 cm^{-1}. Before recording the spectrum of a new sample, the calibration of the spectrometer is checked by using the peak at 521 cm^{-1} of the silicon sample. For our study, a 100 x objective was used to focus the surface of the mixture containing silyl modified polymers and catalyst in the 100 - 3600 cm^{-1} region and more preferably in 400 - 750 cm^{-1} region. The slit and hole parameters were respectively fixed at 125 μm and 1100 μm. The time required to measure one spectrum was 1 min decomposed with an acquisition time of 30 seconds and 2 accumulations. This acquisition was repeated during 1 hour for SMP1 and 2 hours for SMP2 in order to follow the evolution of Si-OCH$_3$ groups during the hydrolysis and polycondensation reactions. The measurements were performed at 23°C (+/− 1°C), and moisture ratio at 55% H2O (+/− 5%). Initial spectrums of each silyl modified prepolymer (SMP1 and SMP2) without catalyst were performed in order to determine the initial intensity of Si-OCH$_3$ before the cross-linking. In the same way, spectrums of each cross-linked silyl modified polymers (SMP1 and SMP2 aged of 3 month) were performed to determine the final intensity of Si-OCH$_3$ groups. All spectra were baseline corrected before the integration with the software LabSpec v4.04. The integration was performed with following parameters: w (FWHM = full-width half maximum) fixed at 15 and gaussien/lorentzien ratio equal to 0.5. After the automatical fitting procedure, the area or intensity of Si-OCH$_3$ peak can be used to follow the tendency of chemical reaction. Results with area and intensity give the same results due to high resolution of Raman spectra. However, fitting procedure based on intensity of peaks was faster than fitting procedure based on area of peaks (approximately 5 to 10 times in our case). Thus, in order to quickly compare and to evaluate in real time the physical states (viscous, skin effect or gum aspect) samples containing different mixture of catalysts to determine were analyzed.

3. Results and Discussion

SMPs typically cure in two reactions. In the first reaction, the end polymeric alkoxysilane groups hydrolyze in the presence of moisture, catalyzing their transformation into silanol groups. In the second reaction, the silanol groups condense with other silanols or alkoxy-silanes in the presence of a catalyst to form Si-O-Si bonds. The hydrolysis and conden-sation reactions occur almost simultaneously and compete with each other.

At the beginning, the silyl modified prepolymer is viscous and remains viscous during the hydrolysis process in **Figure 2**. This corresponds to the viscous state (state 1). The three-dimensional network is not formed, but the formation of dimeric structures increases the viscosity. When polymer chains continue to grow or form rings, a skin effect appears due to the formation of many Si-O-Si bonds during the polycondensation process (state 2). In the end, a three-dimensional structure is formed and corresponds to a cross-linked state (state 3), leading to gum-like properties.
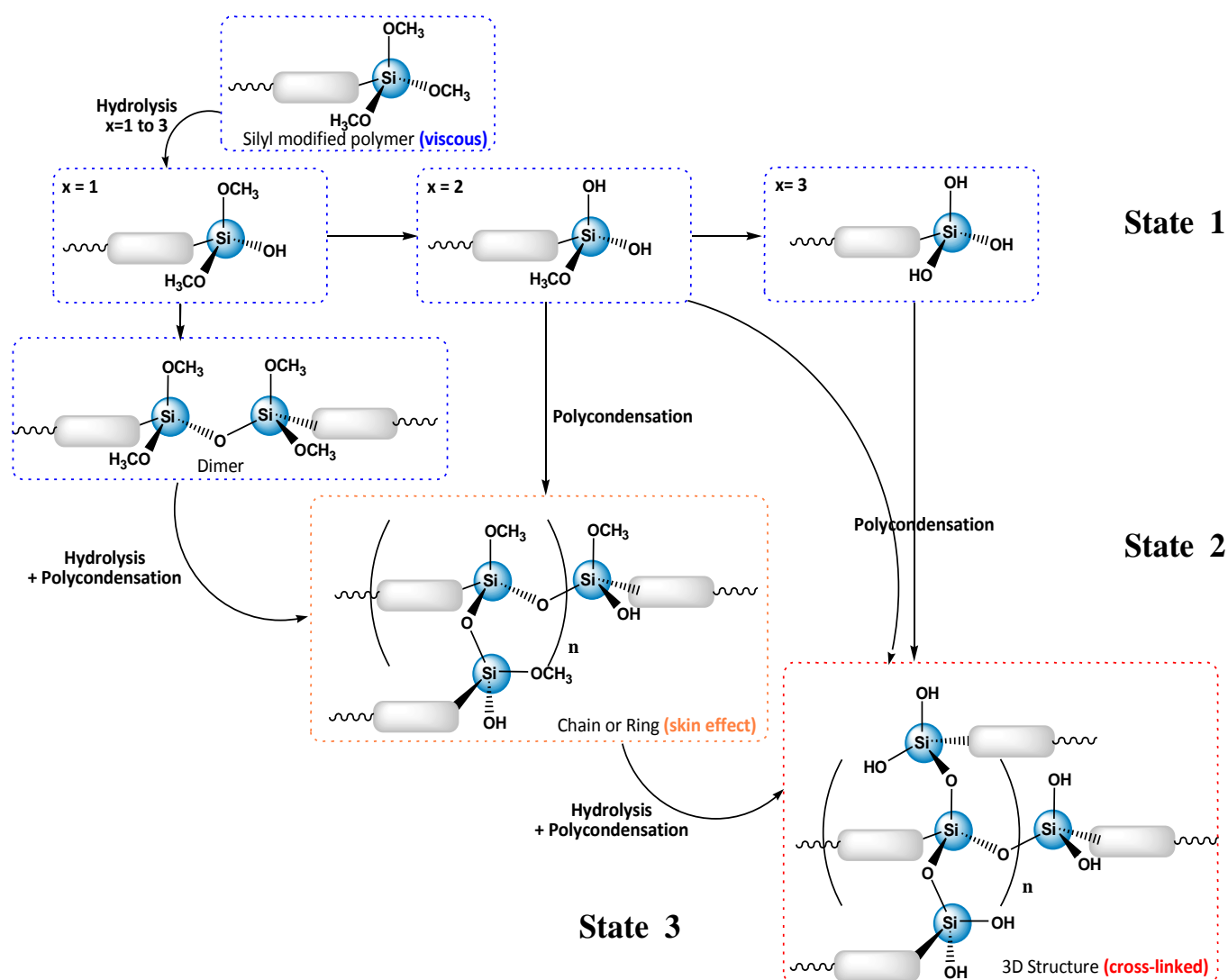
Figure 2. Scheme of different states between hydrolysis and condensation: viscous, skin effect and cross-linked state.

3.1. Development of the Raman Method

3.1.1. Selection of Peaks Corresponding to the Cross-Linking Reaction

The key point for any Raman approach is to ensure that the correct peak is monitored, which depends on the chemical groups involved in the reaction. The first step consists of determining which peaks are associated with the hydrolysis or condensation reactions during the cross-linking of SMPs.
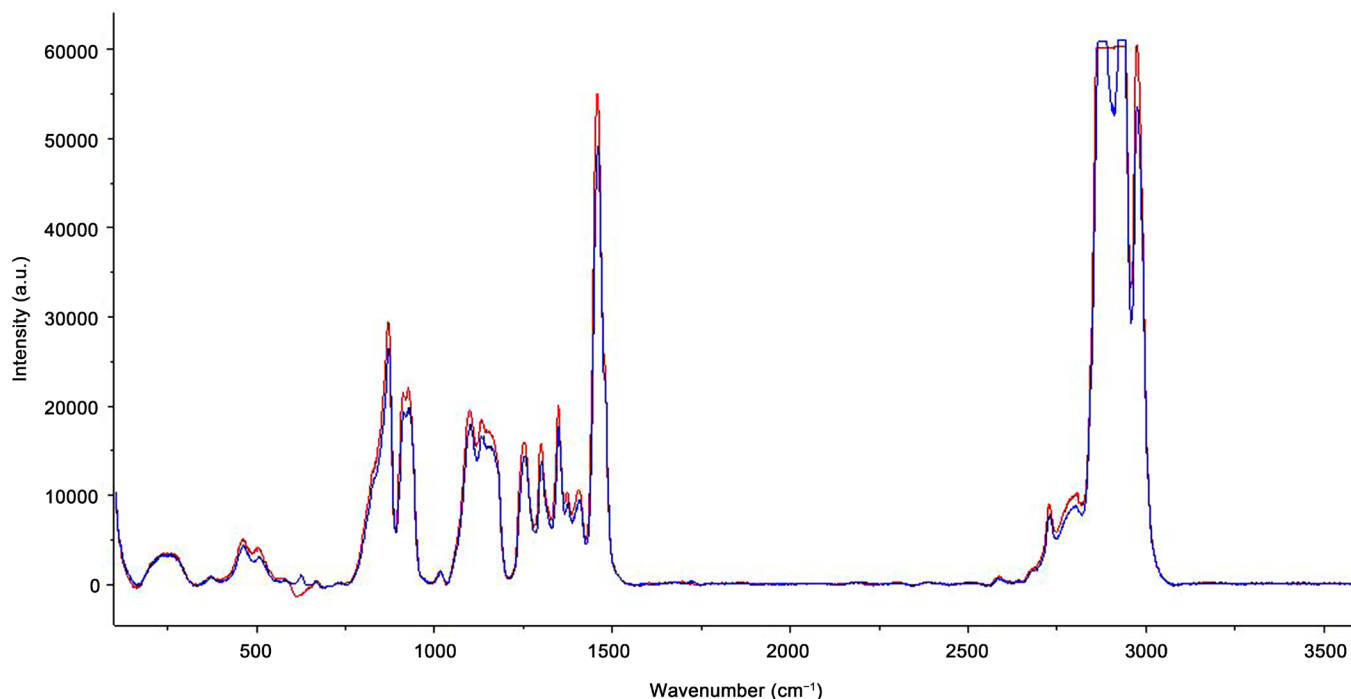
The Raman spectra of pure SMP1 without a catalyst in **Figure 3(a)** a cross-linked.

SMP1 with 0.5 wt% DBU in **Figure 3(b)** in the 100 - 3600 cm^{-1} region, and both materials in the 400 - 750 cm^{-1} region in **Figure 4** are shown. These Raman spectra demonstrate the differences between the initial state with no cross-linkage and the cross-linked end state.

Therefore, the frequencies, relative intensities and tentative assignments of the observed Raman bands for cross-linked SMP1 with 0.5 wt% DBU catalyst and the initial state of SMP1 are summarized in **Table 1**.

Both spectra have very similar features because they share the same polymer backbone. Most of the peaks from 800 to 3000 cm^{-1} were assigned based on several studies [17]-[20] and on the book by Socrates about Infrared and Raman Characteristic Group Frequencies [21]. As a reminder, SMP1 is a dimethoxysilane-based polyether with a urethane moiety. Several peaks correspond to C-O-C and N-C vibrations, respectively, at 1250 cm^{-1} and 1370 cm^{-1}.

The observation of alkoxysilane groups is difficult because SMP1 contains only a few percent of dimethoxysilane end groups (approximately 3 wt%). Thus, it is necessary to

Figure 3. Raman spectra of (a in blue) pure SMP1 without catalyst and (b in red) cross-linked SMP1 with 0.5% of DBU, in the 100 - 3600 cm^{-1} region.
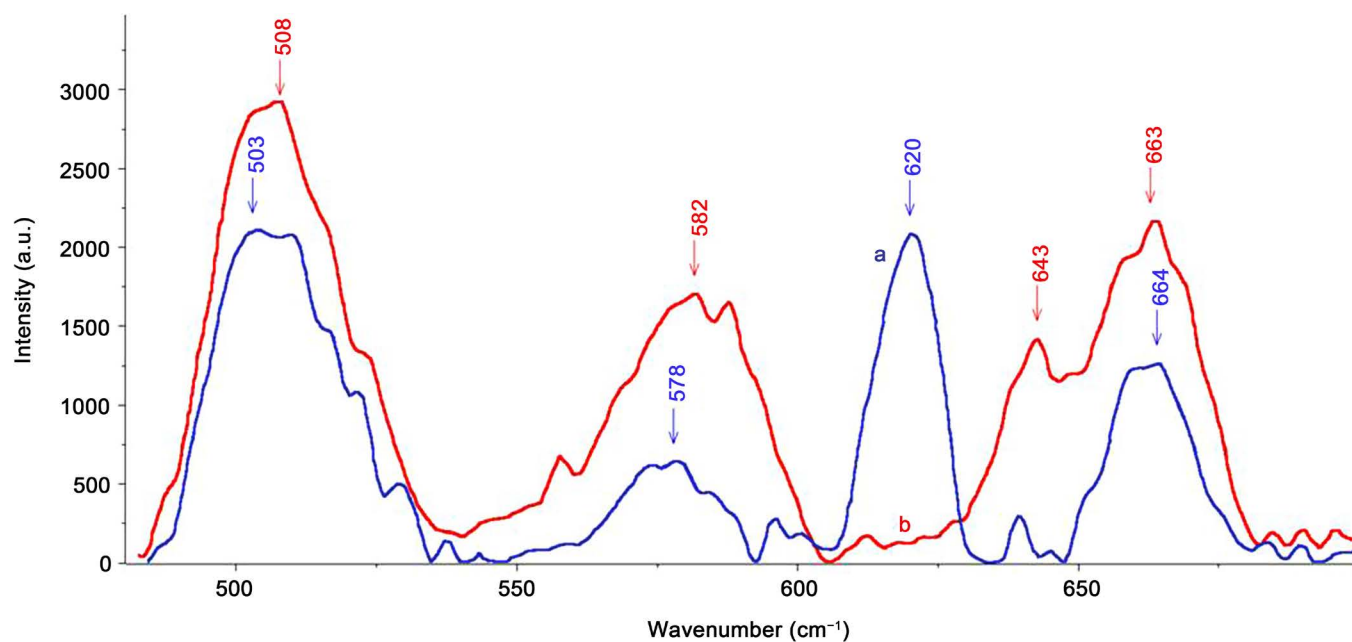
Figure 4. Raman spectra of (a in blue) pure SMP1 without catalyst and (b in red) cross-linked SMP1 with 0.5% of DBU, in the 400 - 750 cm^{-1} region.

Table 1. Raman spectral frequencies of initial and cross-linked SMP1 and suggested assignments (* = peaks of cross-linked SMP1 and + = initial SMP1). Abbreviations: s, strong; m, moderate; w, weak; vw, very weak, stretch; deformation, twist; subscript s, symmetric; subscript a, asymmetric.

Wavenumber (cm^{-1})	Suggested Assignments	References
503[+] m	δ(Si-O-C)	[17]
508* m	ν_s(Si-O-Si ring)	[22] [23]
582* m	ν_s(Si-O-Si chain)	[22] [23]
620[+] vw	ν_s(Si-(OCH$_3$)$_2$)	[22]-[25]
643* vw	ν_s(HO-Si(OCH$_3$))	[22] [23]
663* vw	ν_s(Si-(OH)$_2$)	[22] [23]
664[+] vw	ν_s(Si-C)	[22] [23]
838 m	ν(C-O)	
863 m	ν(C-O)	
910 m	ν(C-C)	[17]
1010 w	ν_a(Si-O-Si)	[21]
1090 m	ν_a(Si-O-C)	[17] [18]
1155 m	ν_s(C-O-C)	
1250 m	ν_a(C-O-C)	[21]
1297 m	τ(CH$_2$)	[18]
1370 m	ν(N-C)	[19] [21]
1403 m	δ_s(CH$_2$)	[17] [19]
1455 s	δ_a(CH$_2$)	[17] [19]
2808 m	ν_s(CH$_2$)	[17] [20] [21]
2875 s	ν_s(CH$_3$)	[17] [20] [21]
2932 s	ν_a(CH$_2$)	[17] [20] [21]
2973 s	ν_a(CH$_3$)	[17] [20] [21]

zoom in on the 400 - 750 cm^{-1} region to observe the differences between the two states (cross-linked and no cross-linked). We referred to vibrational spectroscopic studies of compounds containing alkoxysilane groups such as methylmethoxysilanes [22], tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) [23], glycidoxypropyltrimethoxysilane (GPTS)/amiopropyltriethoxysilane (APTS) systems [24] and silica aerogels [25]. As described in these studies, Si-O-Si vibrations could be assigned to the 500 - 600 cm^{-1} region.

In addition, different structures of Si-O-Si bonds can be formed in intermediate products by polycondensation reactions. Indeed, many condensed structures (chain, branched and ring) can be formed due to the large number of active sites available per silicon atom. However, the peak at 620 cm^{-1} is only present in the SMP1 without cross-linkage and gradually decreases during the cross-linking reaction. Thus, this peak is characteristic of the symmetric Si-(OCH$_3$)$_2$ vibration, corresponding to the first reactive groups susceptible to reaction during the hydrolysis step. Moreover, the peaks at 643 and 663 cm^{-1} are only found in the cross-linked product and directly shift to higher wave numbers compared to the peaks in Si-(OCH$_3$)$_2$. We suggest that the peaks at 643 and 663 cm^{-1} represent the intermediate products at different degrees of hydrolysis (x = 1 at 643 cm^{-1} and x = 2 at 663 cm^{-1}).

3.1.2. Monitoring of Si-(OR) Groups

The most adaptive peak should be used to follow the cross-linking reaction and characterize the three physical states (viscous, skin effect and cross-linked states). We expect to see a decrease in the peak at 620 cm^{-1} during the hydrolysis step and the increase in the peak of Si-O-Si groups at 500 - 600 cm^{-1} during the polycondensation reaction. A mixture of SMP1 and 0.5 wt% of DBU catalyst was monitored by Raman spectroscopy to determine the evolution of the alkoxysilane groups during the cross-linking reaction in Figure 5.

As expected, we noted a decrease in the intensity of the Si-(OCH$_3$)$_2$ groups at 620 cm^{-1}, the formation of Si-O-Si bonds at 583 cm^{-1} and an increase in the intensity of the peaks at 643 and 663 cm^{-1}. Thus, there are still Si-(OH) groups after 1 hour of reaction, indicating that the polymer is not fully cured after 1 hour. Moreover, some silyl-modified polymers require several days to achieve complete cross-linking because of the slow diffusion of water into a three-dimensional structure.

As mentioned previously, hydrolysis and condensation reactions occur simultaneously and depend on experimental conditions such as the nature and concentration of the hydrolyzable groups, temperature and pH values. Indeed, for a sol-gel process of alkoxysilane in aqueous solution [26] [27], the kinetics of the hydrolysis and condensation reactions are generally controlled by the pH of the solution. Under acidcatalyzed conditions, the hydrolysis kinetics are favored over condensation, which starts when hydrolysis is completed. For instance, if the pH value changes from 7 (the rate is minimal) to 6, the rate constant is multiplied by 10. In base-catalyzed conditions, condensation is faster than hydrolysis, resulting in a highly 3 D condensed structure. In our case, with DBU as a catalyst, the decrease in Si-(OCH$_3$)$_2$ groups is a direct characteristic
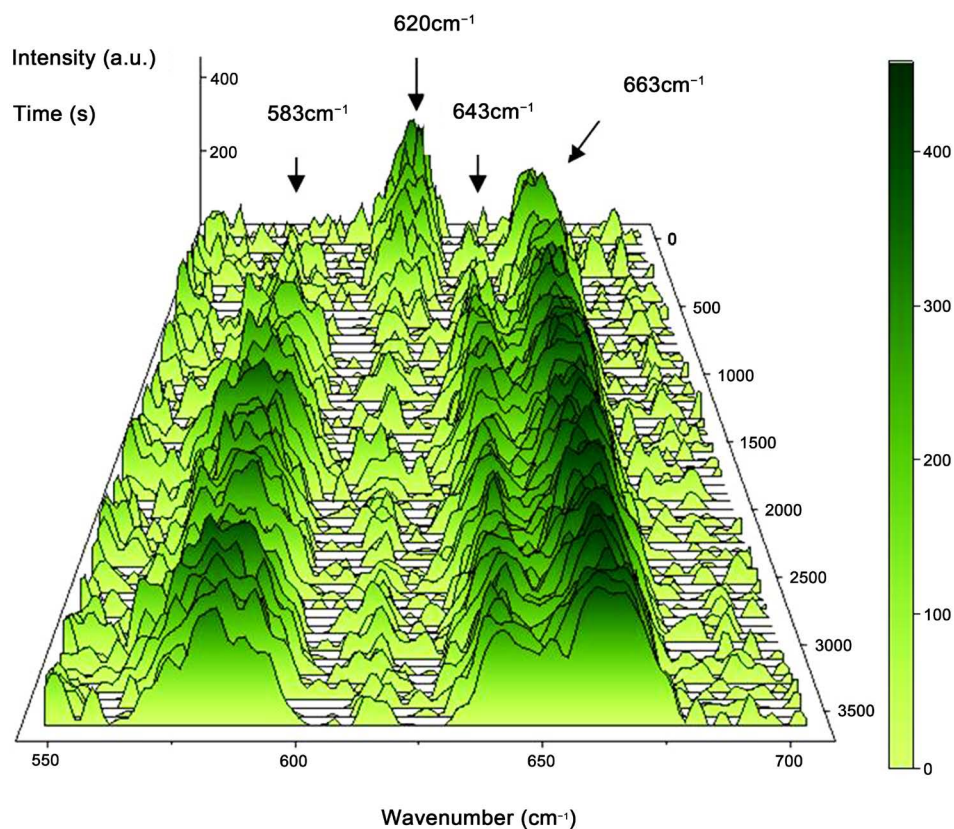
Figure 5. Series of Raman spectra of SMP1 during hydrolysis and condensation reactions (0 to1 h) in 550 - 700 cm^{-1} region.

of the cross-linking reaction. Thus, this peak seems to be the best spectroscopic probe to follow the cross-linking reaction.

3.1.3. Quantification of Si-(OCH$_3$) Groups

Cross-linking of SMP1 catalyzed with different ratios of DBU (0.05, 0.1, 0.3 and 0.5 wt%) was monitored, and the Raman intensities of the Si-(OCH$_3$)$_2$ groups at 620 cm^{-1} were plotted against time in **Figure 6**.

The analysis was repeated three times for each catalyst ratio in order to determine the reproducibility of the results.

The reaction time decreases when the rate of catalysis increases. Indeed, by using 0.5 wt% DBU, a cross-linked structure (corresponding to the complete disappearance of Si-(OCH$_3$)$_2$ groups) is obtained after only 15 to 20 minutes; whereas, with 0.05 wt% catalyst more than 30 minutes is necessary to observe the total disappearance of the Si-(OCH$_3$)$_2$ groups. These results are reproducible as the deviation between the two experiments was lower than 10% for each value. The monitoring of the Si-(OCH$_3$) intensity allowed for fast and online monitoring of the cross-linking reaction.

3.2. Correlation with the Standard Method

The second step of this study was to correlate the results obtained by Raman spectro-
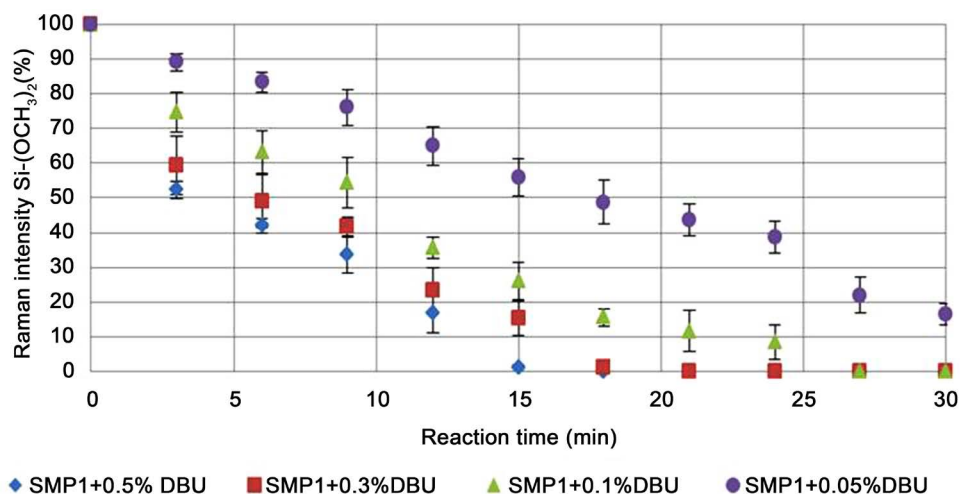
Figure 6. Raman intensity of Si-(OCH₃)₂ groups during cross-linking of SMP1 catalyzed with different rate of DBU (0.05; 0.1; 0.3 and 0.5% wt).

scopy with the physical states observed by an iterative and manual method already described by BOSTIK [28]. This method requires an operator to touch the surface of the mixture (SMP + catalyst) with a needle during the cross-linking reaction to determine the physical states: viscous, skin effect or cross-linked in Figure 7. Characteristic times for the appearance of these states were measured using this standard method at different ratios of DBU (Table 2).

This classical method is efficient but time-consuming and does not allow for an accurate comparison of a large number of mixtures. In addition, this method is based on a visual aspect and is operator dependent. Thus, it was interesting to determine the physical states directly from Raman analysis by monitoring the chemical evolution of the alkoxysilane groups. Indeed, the levels of Raman intensity at 620 cm⁻¹ were determined for each state during the curing process of SMP1. An intensity of 100% corresponds to the initial intensity at 620 cm⁻¹ for the Si-(OCH₃)₂ groups at the beginning of the reaction, and 0% Raman intensity at 620 cm⁻¹ corresponds to an SMP sample aged for 3 months. We observed that for Raman intensities between 100% and 60%, the physical state of the mixture is viscous; for Raman intensities between 60% and 25%, the skin effect occurs; and below 25%, a cross-linked product is obtained. For a fast and easy correlation between the Raman intensity and the physical state of the sample, we attributed blue color to the intensity level between 100% and 60%, corresponding to the viscous state; orange color to the intensity level between 60% and 25%, corresponding to the skin effect; and red color to the intensity level below 25%, corresponding to a cross-linked gum state in Figure 8.

This spectroscopic method allows for fast detection of the physical states of SMP1 at any time. In addition, the color assigned to each state could be key for easily establishing the open time for this adhesive. For example, when the polymer is viscous (blue, Raman intensity higher than 60%) and until the appearance of the skin effect (orange, Raman intensity between 60% and 25%), an adhesive can be easily repositioned on a
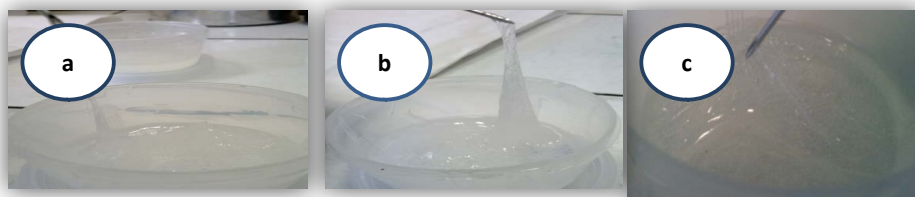
Figure 7. Pictures representing the interaction between the surface of polymer and a needle during cross-linking reaction, (a) viscous to skin effect, (b) skin effect and (c) skin effect to cross-linked gum aspect.

Table 2. Measurements of characteristic times for each physical state were taken using the operator standard method for four mixtures containing different ratios of DBU catalyst. State a) corresponds to the transition from viscous to skin effect, state b) is the skin effect state, and state c) is the transition from skin effect to cross-linked structure, and, finally, the time to reach a gum-like state.

DBU% wt	State a (min)	State b (min)	State c (min)	Cross-linked (min)
0.05	8'	11'	14'	29'
0.1	5'45	7'45	10'30	19'
0.3	3'30	5'	6'30	11'
0.5	2'30	3'45	4'45	8'
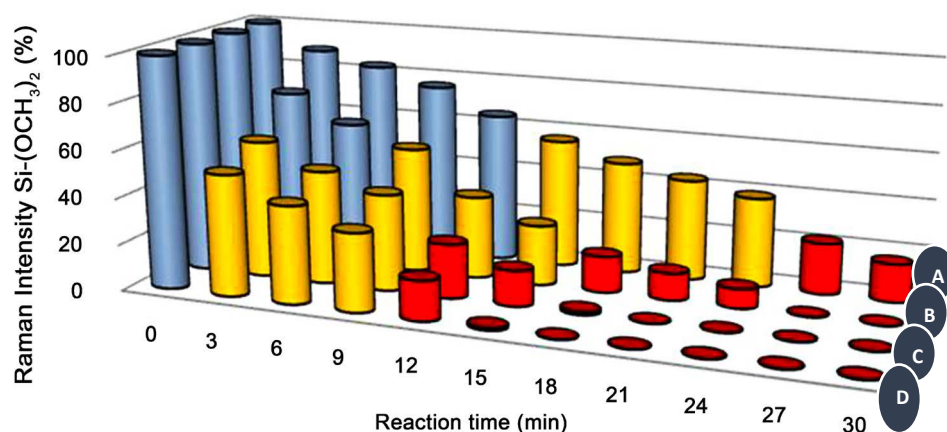
Figure 8. Raman intensity of $Si-(OCH_3)_2$ from SMP1 catalyzed with 0.05 to 0.5% wt DBU (A to D) and correlation with physical states, blue = viscous, orange = skin effect and red = cross-linked.

support. Then, when the polymer is cross-linked (red, Raman intensity lower than 25%), the support containing the adhesive can be manipulated without any risk of disbonding.

3.3. Extension of the Contactless Raman Method

Different intermediate products can be obtained depending on the type of catalyst used and whether the conditions are basic or acidic, allowing cross-linking of silyl modified

polymers. Indeed, strong acids such as CF_3SO_3H [29] or HCl [30] efficiently accelerate the process of hydrolysis. Under basic conditions, hydroxyl (OH^-) ions attack the most positively charged atom by nucleophilic reaction [31]. Super-bases such as DBU or TBD are very efficient at accelerating the reaction and increasing the density of cross-linking [32]. Thus, Raman spectroscopy seems to be an ideal technique for screening different catalysts to determine their catalytic effect on the hydrolysis [33] [34] and polycon-densation steps because the analysis is rapid and can be performed in situ for different SMPs.

### 3.3.1. Study with Different Catalysts for SMP1 Cross-Linking

This method was applied to compare the cross-linking activity of several basic catalysts (DBU, DBN and NEt₃) on SMP1 in **Figure 9**. The Raman intensity levels and their colors which were previously determined were directly applied to observe the different physical states of SMP1.

The physical states measured with DBU and DBN seem identical because of the relatively identical structure of these two catalysts. We noted that NEt₃ was not efficient for cross-linking of SMP1 after 30 minutes of reaction with moisture. The different efficiencies of these catalysts can be explained by their pKa values. In fact, only super bases such as DBU or DBN are really active. The very high basicities of DBU and DBN (pKa at 12) [35] compared to NEt₃ (pKa at 10, 75) [36] are induced by the amidinium stabilization and seem to be a key point for high catalytic activity.

Furthermore, the application of this method can be an efficient way to quickly screen catalytic systems on SMP1 and obtain the corresponding open times (time window for repositioning of the sample or time before the sample can be used), which are key parameters for the adhesive industry.

### 3.3.2. Study of SMP2 Cross-Linking

This method was also applied to another SMP called SMP2, which is a trimethoxysilane-based polyurethane as described in **Figure 1** Cross-linking reactions between SMP1 and SMP2 are very different because of the molecular structure of the terminal
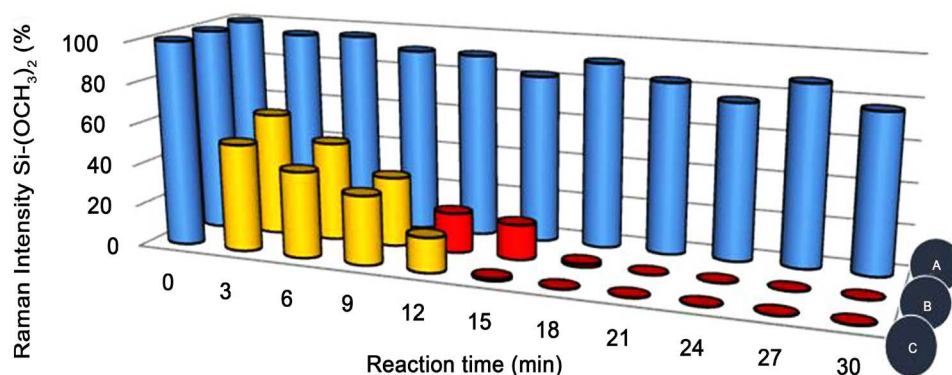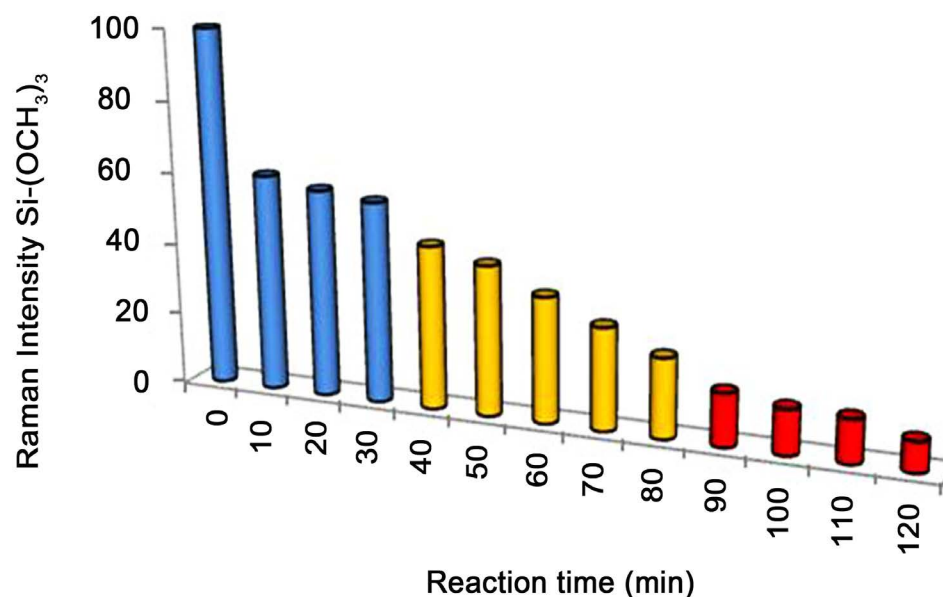

Figure 9. Raman intensity of $Si\text{-}(OCH_3)_2$ from SMP1 catalyzed with 0.32mmol of NEt₃ (A), DBN (B), and DBU (C) and correlation with physical states, blue = viscous, orange = skin effect and red = cross-linked.

silyl groups. In the case of urethane-dimethoxysilane (SMP1), the electron donor (nitrogen atom with a free electron pair) is attached to a silicon atom via one methylene group as a spacer. Additionally, the methyl group attached to the silicon atom can play an important role through an inductive effect. Indeed, the electron density is shifted to the silicon atom, and the Si-(OCH₃) bond is weakened. In this case, the cross-linking reaction time decreases because of the activation of the alkoxide group. Therefore, the alkoxide groups split off more easily, and hydrolysis is accelerated. However, the cross-linking time of SMP2, which is terminated with trimethoxysilane, is slower than that of SMP1 because there is no alkoxide group activation (nitrogen atom attached to silicon via a propylene group as a spacer). It is well known that the Raman shift may depend on the environment of a group of atoms and their position in a prepolymer or polymer network. That is why it is necessary to determine the peak characteristics of the Si-(OCH₃) groups in SMP2 in Figure 10.

The peak at 644 cm⁻¹ represents the Si-(OCH₃)₃ groups in the trifunctionnal prepolymer (SMP2). The shift of these bands is different from that seen in SMP1 (620 to 644 cm⁻¹) and is probably due to the difference in the chemical environment of each polymer backbone: polyether (SMP1) and polyurethane (SMP2). A correlation between the cross-linking reaction and physical properties was also established for SMP2 by monitoring the decrease in the intensity of the Si-(OCH₃)₃ peaks at 644 cm⁻¹. New Raman intensity levels were determined and correlated with each physical state. The levels are characteristic of each prepolymer because of their different structures. For SMP2, the Raman intensities between 100% and 50% indicate that the mixture is viscous, those between 50% and 20% indicate that the skin effect occurs, and those below 20% indicate that a cross-linked product is obtained (Figure 11).
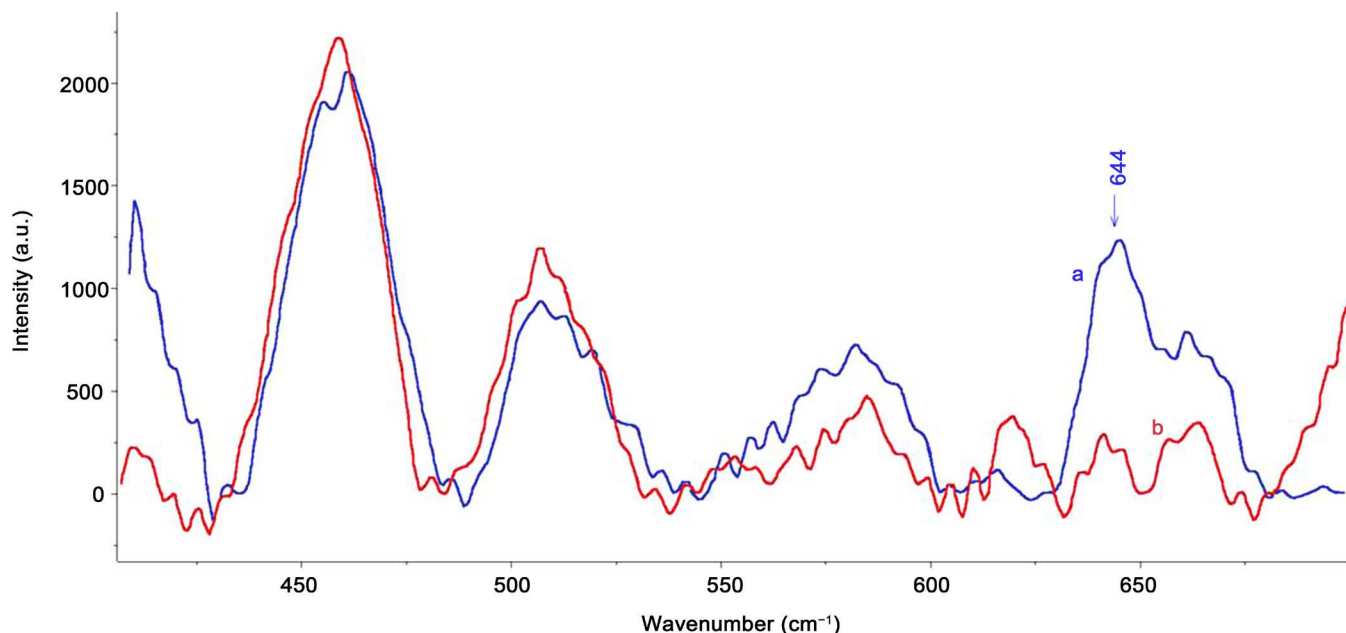
Figure 10. Raman spectra of (a in blue) pure SMP2 without catalyst and (b in red) cross-linked SMP2 with 0.5% of DBU, in the 400 - 700 cm⁻¹ region.

Figure 11. Raman intensity of Si-(OCH$_3$)$_3$ from SMP2 catalyzed with 0.5% wt DBU catalyst and correlation with physical states, blue = viscous, orange = skin effect and red = cross-linked.

This result indicates that our method can be applied to different SMPs by determining the peak that corresponds to the alkoxysilane end groups and allows for fast detection of physical states at any time without the manual intervention of an operator. Based on this, this method could be useful for analyzing SMPs that have higher cross-linking times (several hours or several days).

4. Conclusions

An original spectroscopic method was developed to characterize the physical states of SPM prepolymers during moisture curing. The Raman intensity of the alkoxysilane groups allows for quick determination of the physical states, viscous, skin effect and cross-linked, with good reproducibility. This method is an attractive and efficient way to characterize the physical state and determine the open time for the adhesive industry.

Thanks to commercially available miniaturized Raman spectrometer, one can envision to apply this non-contact optical method for on line or on site applications for adhesives. Furthermore, an approach that combines micro-reactor technology with fiber-optic Raman spectroscopy was already described for the performance of real-time measurements [37]. Based on our recent study on the development of a semi-quantitative high-throughput screening (HTS) method to compare and detect efficient catalysts for adhesive materials [38], we can envisage coupling the HTS approach with the Raman method developed in this study to create a powerful quantitative method. This method could be used to detect new catalysts for adhesive materials with specific time windows for applications such as repositionable samples or samples that are ready to use after a specific time for irreversible adhesion.

Acknowledgements

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