Influence of cross-linker concentration on the cross-linking of PDMS and the network structures formed

A.C.C. Esteves [a,*], J. Brokken-Zijp [a], J. Laven [a], H.P. Huinink [b], N.J.W. Reuvers [b], M.P. Van [a], G. de With [a]

[a] Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
[b] Department of Applied Physics, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

ABSTRACT

The cross-linking of linear di-vinyl-terminated poly(dimethylsiloxanes) (PDMS) with tetrakis(dimethylsiloxane) was studied in the presence of different concentrations of the cross-linker (H/V = ratio of Si–H groups of the cross-linker and C=C bonds). The consumption of the Si–H and C=C bonds was monitored simultaneously by *in situ* Confocal Raman Microscopy (CRM) and ATR-FTIR spectroscopy. When formulations with H/V $\geq$ 1.0 are cross-linked at low temperature (25 °C) in air and atmospheric humidity conditions, hydrosilylation and secondary reactions occur simultaneously at early stages of the reaction. For H/V = 1.0 the C=C bonds are also consumed by side reactions.

Films cross-linked from formulations with different H/V ratios were studied by NMR imaging, swelling/extraction experiments and SEM. Films cross-linked with H/V = 1.0 showed a slower magnetization decay due to the presence of a large percentage of extractable material not connected to the cross-linked network. After extraction, all the films show faster relaxation behavior, explained by the presence of two types of chemical cross-links as well as one type of physical cross-links. These cross-links result from the occurrence of hydrosilylation and secondary reactions and counterbalance each other at different H/V ratios.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Poly(dimethylsiloxanes) (PDMS) have unique properties such as elastic behavior or resistance to high temperatures, light degradation and chemical attack [1]. These exceptional characteristics make cross-linked PDMS suitable for a wide range of applications such as in electrical and/or optical devices [2,3], anticorrosion [4] or anti-fouling materials [5], sealants and adhesives [6] and biomedical applications [7,8].

Cross-linked PDMS materials have also attracted particular interest in adhesion studies [9–11] and related applications due to their low surface energy and hydrophobic surfaces. The performance of these materials is determined to a large extent by the structure of the cross-linked network formed and the residual chemical groups in the bulk material and interfaces. Therefore it is of great interest to understand and control the reactions involved in the cross-linking processes, as well as to characterize the cross-linked networks being formed.

Typically, linear PDMS polymers containing two vinyl end groups react with a multifunctional cross-linker leading to a three-dimensional cross-linked network [1]. The hydrosilylation addition has been commonly used to prepare cross-linked PDMS materials [12]. The rate of the hydrosilylation reaction depends on the type and molecular structure of the catalytic complex, the vinyl groups of the PDMS and the number of Si–H groups on the cross-linker, as well as on their concentrations. It is well known that for vinyl-terminated PDMS, the most probable reaction is the β-addition of a silicon hydrogen to the vinyl bond [1,12,13]:

$$R-Si-H + CH_2=HC-Si-R' \xrightarrow{\text{catalyst, heat}} R-Si-CH_2-CH_2-Si-R' \tag{1}$$
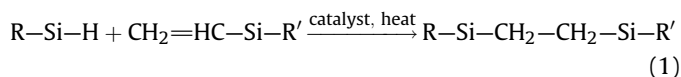
It has also been reported that this hydrosilylation reaction catalyzed by a platinum complex, proceeds in three stages [14]: I) first a slow reaction regime called the induction period, in which the active species of the catalyst are formed; II) a rapid exothermic regime, during which (most of) the products of the hydrosilylation reaction are formed and III) a regime in which the reaction proceeds very slowly or stops [14], frequently referred to in the related literature as post-curing stage.
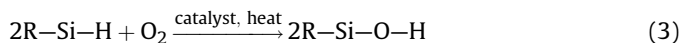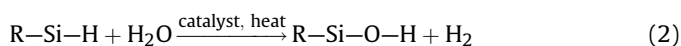
Since the early 70s model cross-linked PDMS networks have been prepared through hydrosilylation [15–17]. The relation between the rheological behavior and elastomeric properties of the

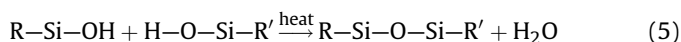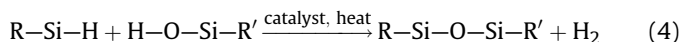* Corresponding author. Tel.: +31 40 247 3051; fax: +31 40 244 5619.
E-mail address: c.esteves@chem.tue.nl (A.C.C. Esteves).

final cross-linked material was intensively investigated [18–21]. However, many of these studies were made under the assumption that the cross-linking hydrosilylation reaction proceeds without any side reactions.

Gorshov et al. firstly proposed the occurrence of secondary reactions with the silane groups of the cross-linker [22]. They reported that the degree of cross-linking was strongly dependent on the amount of silane groups present. This effect was attributed to competitive oxidation/hydrolysis secondary reactions of the silane groups [22], leading to the formation of Si–OH groups, via reaction with other compounds such as moisture and O_2.

$$R-Si-H + H_2O \xrightarrow{\text{catalyst, heat}} R-Si-O-H + H_2 \qquad (2)$$

$$2R-Si-H + O_2 \xrightarrow{\text{catalyst, heat}} 2R-Si-O-H \qquad (3)$$

The silanol groups formed can react with Si–H groups (Eq. (4)) or with each other (Eq. (5)), producing silsesquioxane network structures, or forming additional Si–O–Si cross-links.

$$R-Si-H + H-O-Si-R' \xrightarrow{\text{catalyst, heat}} R-Si-O-Si-R' + H_2 \qquad (4)$$

$$R-Si-OH + H-O-Si-R' \xrightarrow{\text{heat}} R-Si-O-Si-R' + H_2O \qquad (5)$$

The same authors reported that these secondary reactions are slower than the hydrosilylation reaction and are only relevant when the Si–H groups are present in significant excess [22]. In a similar study Podoba et al. [23] confirmed that the rate of Si–H consumption increases significantly as the amount of Si–H groups increases with respect to the vinyl bonds. They also compared the rate of disappearance of the Si–H groups with the rate of cross-link formation, concluding that the cross-linking occurred both by hydrosilylation and by unspecified side reactions.

A further evaluation of the secondary reactions and their relevance in the cross-linking process was provided by Quan [24], who studied the properties of cross-linked siloxane networks submitted to an extensive thermal treatment at high temperature, the so-called "post-curing" procedure. This author showed that when a high temperature post-cure was carried after reaching the gel point the network formed did no longer behave as an ideal network. This was attributed to bimodal distributions of cross-links which are formed during post-curing.

The term *cross-linking reaction* is often used to refer to hydrosilylation while the term post-curing identifies secondary reactions. However, the secondary reactions may also contribute to the cross-linking of the PDMS material, although with different types of cross-links. Hence for clarity, we will refer to *hydrosilylation* (Eq. (1)) and *secondary reactions* (Eq. (2)–(5)) to distinguish the two contributions, and use the term *cross-linking process*, when all the contributions are considered.

In this work we studied linear PDMS polymers containing two vinyl end groups which are cross-linked through hydrosilylation with a four-functional silane-terminated cross-linker, in the presence of a Pt[II] catalyst (Scheme 1).

An approach based on ATR-FTIR and Confocal Raman Microscopy (CRM) was used to follow *in situ* the consumption of the silane groups of the cross-linker and the double bonds of PDMS, respectively. Nuclear Magnetic Resonance (NMR) imaging, swelling/extraction experiments, and SEM analyses were used to investigate the final cross-linked materials in more detail. This study focuses on the effect of the cross-linker concentration on the reactions occurring during the cross-linking process, as well as on the cross-linked structures formed. The cross-linking was studied in presence of air and moisture to approach the conditions frequently used in practical/industrial applications of such cross-linked materials.

2. Experimental

2.1. Materials

For the cross-linking experiments linear vinyl-terminated poly-(dimethylsiloxanes) (PDMS17 with $\overline{M}_w = 17,200$ g/mol; ABCR GmbH & Co) were cross-linked with the four-functional siloxane, tetrakis(dimethylsiloxane) (density 0.886 g/mL; ABCR GmbH & Co). The hydrosilylation reactions (Scheme 1) were catalyzed by *cis*-dichlorobis(diethylsulphide) platinum (II) catalyst (Strem Chemicals, Inc) previously dissolved in a toluene solution (0.0024 g/mol), and carried out under air and moisture at different temperatures (25 and 60 °C). For identifying the IR absorptions also poly-(dimethylsiloxanes) with $\overline{M}_w = 6000$ g/mol (PDMS6) was used (ABCR GmbH & Co).

2.2. ATR-FTIR spectroscopy

The infrared spectroscopy studies were carried out with a Bio-Rad Excalibur FTS3000MX infrared spectrometer, a temperature controlled single reflection accessory (Golden gate) and an MCT (Mercury Cadmium Tellurium) detector.

ATR (Attenuated Total Reflectance)-FTIR stands for multiple reflection mode reflectance-IR spectroscopy. The only difference between single and multiple reflection modes resides on the total attenuation of the multiple reflections (ATR), which results in an improvement of the signal/noise ratio. For easy recognition of the technique the ATR-FTIR nomenclature will be used here, although the single reflection accessory was used.

For the *in situ* studies, the cross-linker was added to the PDMS polymer according to three initial ratios of Si–H to vinyl groups (H/V = 1.0, 1.7 and 2.7). After stirring by hand for approximately 1 min the catalyst solution was added to the starting formulation (20 ppm of Pt[II] relative to PDMS polymer from a toluene solution of 0.0024 g/mL) which was stirred by hand for another minute. A typical starting formulation contains: PDMS (1.00 g), Pt[II] catalyst toluene solution (20 μL) and cross-linker (11 μL, for H/V = 1).

Typically, a droplet of the starting formulation was deposited on the diamond crystal of the golden gate, forming a layer of typically 500 μm, in the presence of air and the measurement was immediately started. The golden gate accessory had previously been stabilized at the temperature of the run. One background spectrum (averaged from 100 scans co-added) was collected just before starting each of the measurements.

All the spectra were recorded *in situ* during the cross-linking reaction between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}. A full spectrum (in average 20–50 scans co-added per spectrum) was taken every 2, 10 or 30 s (depending on conditions of the system). The total integrated area of the Si–H bending band of the cross-linker at 902 cm^{-1} was used to follow the cross-linking reaction. The band located at 864 cm^{-1} attributed to the Si–C stretching vibration of PDMS Si–CH$_3$ groups was used to normalize the spectra.

To confirm that the integrated area of the band at 902 cm^{-1} could be used to determine the actual Si–H concentration, the total integrated area of several formulations of PDMS and cross-linker with different H/V ratios (where H/V is the ratio between Si–H groups of the cross-linker and vinyl groups of PDMS in the starting formulations) was measured. It was observed that Beer's law is valid in the range of Si–H concentrations used for our formulations, which are directly proportional to the total integrated area of the band being used to follow the changes in the Si–H concentration.
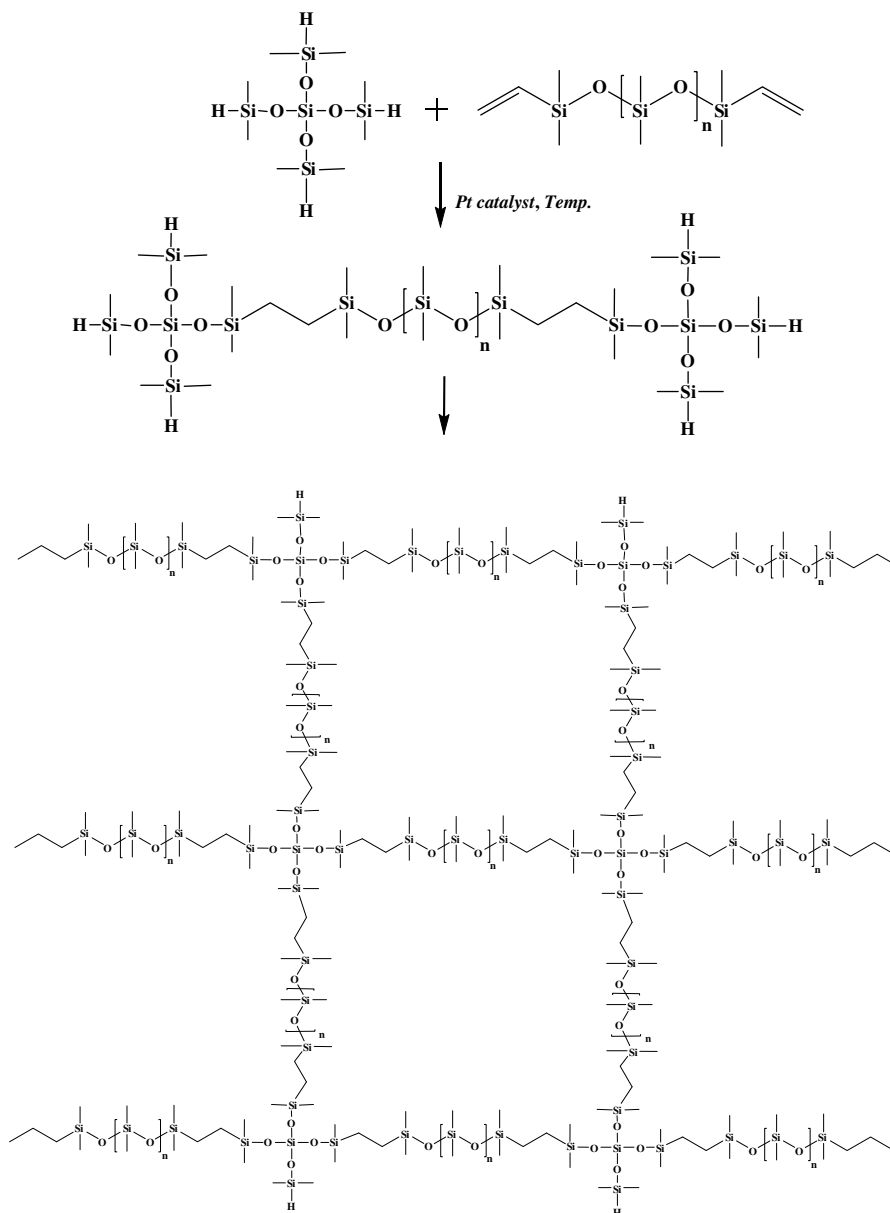
Scheme 1. Scheme of the formation of a (model) cross-linked network through hydrosilylation reaction in PDMS materials.

For all the reactions studied in this work, the concentration of Si–H groups at each time t of the measurement $[\text{Si–H}]_t$, was calculated from the total area of the band at 902 cm^{-1} at that time. The zero concentration of the Si–H groups was considered to be the spectrum for which the absorption of the band at 902 cm^{-1} was the minimum value for the formulation with H/V = 1.0, within the uncertainty of the measurement (t_f in Fig. 1).

2.3. Confocal Raman Microscopy (CRM)

A Confocal Raman microscope (Dilor Labram) was used with a HeNe laser at a wavelength of 632 nm. An ultra-long working distance objective with magnification 100× was used (Olympus) to focus inside the polymer films before, during and after cross-linking. By changing the focus of the Raman microscope to a specific depth, the Raman spectrum of the corresponding volume element can be obtained. All the spectra were collected between 400 and 3000 cm^{-1}, and each spectrum was averaged from 60 scans of 5 s accumulation.

All the spectra adjusted with the following functions available with the Raman Software: manual baseline correction, normalization and filtering (3×). In case of the *in situ* measurements the glass support was placed on a Linkam cell previously stabilized at 25 ± 1 °C.

To analyze the materials made in the ATR-FTIR with CRM, they were carefully removed with a razor blade from the golden gate and placed on a glass support in the Raman microscope.

For the *in situ* measurements three formulations of PDMS (1.00 g) with cross-linker (H/V ratios of 1.0, 1.7 and 2.7) were prepared. To each starting formulation the catalyst (10 μL of a toluene solution corresponding to 20 ppm of Pt^{II}) was added, and the starting formulation was stirred by hand for 1 min. Immediately after this homogenization period, a droplet of the starting formulation was placed on the top of a glass support at 25 ± 1 °C. The focus of the Raman microscope was adjusted in the droplet below its surface (typically 5–10 μm).

The cross-linking reactions were followed in air with a relative humidity of typically 50% for 120 min. After cross-linking the three
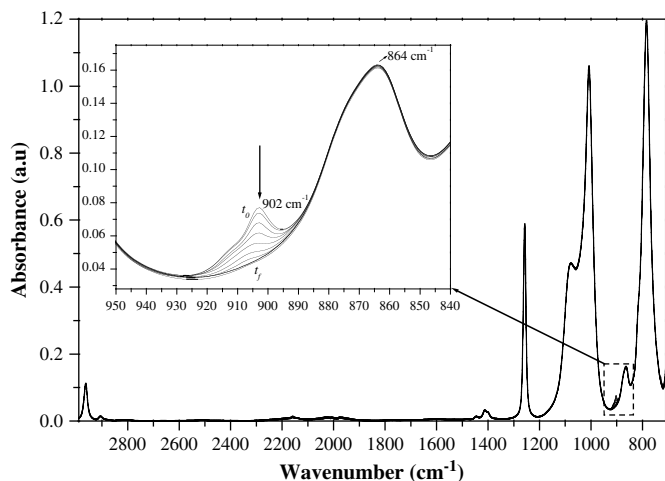
Fig. 1. Example of ATR-FTIR spectra of the cross-linking of PDMS17 at different times of measuring (t_0 = initial time; t_f = final time). *Inset*: expansion of the area from 950 to 840 cm^{-1}. The spectra at different times were normalized to the PDMS17 band at 864 cm^{-1}.

materials on the glass plate were stored under air and moisture at room temperature and after 1 month final spectra were collected again.

2.4. NMR imaging

NMR depth profiling has been used to study the network structure and the homogeneity of these networks over the thickness of the cross-linked PDMS films with a thickness of typically 60 μm. Making use of the so-called GARField concept [25], layers can be measured with a spatial resolution of about 5 μm depth. For details of the set-up we refer to a previous publication [26]. In these experiments the rate with which the signal of transversal magnetization decays is specially used to characterize the sample. The signal decay (S) of transversal magnetization is generally described by one or more exponential functions (Eq. (6)),

$$S(nt_e) = S_\infty + \sum_i S_i \exp\left(\frac{-nt_e}{T_{2,i}}\right) \tag{6}$$

where t_e is the inter-echo time of the used pulse sequence and the $T_{2,i}$s are the characteristic time scales for the relaxation of the signal. Furthermore n is the sequence number of the acquired echo. Since the transversal relaxation processes are very sensitive to the mobility of the protons, a way to observe heterogeneities is by measuring the relaxation times $T_{2,i}$ as function of depth. The more mobile the protons are, the slower is the magnetization decay and the larger are $T_{2,i}$ values.

In this study the Ostroff–Waugh [27] sequence ($90^\circ_x - \tau - [90^\circ_y - \tau - \text{echo} - \tau]_n$) was used to measure the transversal relaxation. To enable a full recovery of the magnetization a long delay of 7 s is added after each sequence. In the experiments the inter-echo time ($t_e = 2\tau$) has been set to 2000 μs. The amount of averages (5100) used, in combination with the aforementioned delay, results in a total time of about 20 h to measure one sample.

For the NMR experiments several PDMS cross-linked films were prepared from the formulations with different initial H/V ratio. The formulations made as described before were spin-coated on a microscope glass slide substrate ($\sim$1.8 cm $\times$ 1.8 cm) (first step: 300 rpm, 15 s; second step: 600 rpm, 30 s) to prepare a film with approximately 60 μm. The films were cross-linked in a vacuum

oven at 60 °C for 20 h and subsequently at 90 °C for 4 h in order to fully cross-link the films and reduce the amount of non-reacted species left in the bulk material.

2.5. Extractable fraction determination – swelling/extraction experiments

The cross-linked PDMS materials were extracted using swelling experiments. These cross-linked PDMS materials had been prepared from formulations containing 2.00 g of PDMS17 and different H/V ratios (1.0, 1.7 and 2.7), to which 40.00 μL of a platinum solution (20 ppm of Pt^{II} relative to PDMS17 polymer, from a toluene solution of 0.0024 g/mL) was added. The formulations were cast on a poly(carbonate) substrate, molded to form a sheet (1.0 cm $\times$ 1.0 cm), and left standing for 1 h, after which the cross-linking is carried out in a vacuum oven at 60 °C for $\sim$24 h. The cross-linked PDMS materials, typically 300 μm thick, were removed from the PC substrate and immersed in toluene (20.00 mL) for 24 h. The toluene was refreshed each 24 h for 6 days. To the last fraction of toluene, small parts of ethanol were sequentially added (up to 20% of the toluene volume) for 5 days. After this extraction procedure, the materials were left to dry overnight under air and finally placed in a vacuum oven at 60 °C for 24 h. The samples were cooled down inside an exsiccator containing drying silica gel.

The weights of the material before (m_0) and after extraction (m_{ext}), were accurately measured to calculate the extractable fraction (W_{ext}) according to (Eq. (7)) [28].

$$W_{ext}(\%) = m_0 - m_{ext}/m_0 \times 100 \tag{7}$$

2.6. Scanning Electron Microscopy (SEM)

The SEM images were recorded with a JEOL JSM-840A equipment, operating with an acceleration voltage of 15 kV and a probe current of 10^{-8} A. The pressure inside the chamber was kept constant below 10^{-5} mbar and the working distance was set to 39 nm. Small fragments from the center of the cross-linked materials were detached by hand from the poly(carbonate) substrate and placed vertically in a metallic support, with the middle part of the fragment facing upwards. A thin layer of gold was deposited over the samples with a current of 20 mA for 3 min. The cross-section of the materials was analyzed on the microscope with a tilting angle of approximately 30°.

3. Results and discussion

In this work cross-linked materials were prepared through hydrosilylation reaction between di-vinyl-terminated PDMS and a four-functional silane-terminated cross-linker in the presence of a Pt^{II} catalyst (Scheme 1). The reactions and products (networks) involved in the cross-linking of these systems are very sensitive to changes in several parameters such as: concentration and nature of the reactants (e.g. PDMS, cross-linker and catalyst), variations on external factors (e.g. O$_2$ or moisture) or even processing circumstances (temperature, film thickness or type of substrate used).

Hence, in this study only one type and concentration of platinum catalyst, one type of cross-linker and di-vinyl-terminated PDMS polymers were used.

The catalyst used in this work, *cis*-dichlorobis(diethylsulphide) platinum (II) was specifically chosen for several reasons. Previous studies in our group on the adhesion and elastic moduli of cross-linked PDMS films [28,29], have shown a good reproducibility for the cross-linked materials when this catalyst was used for the hydrosilylation reaction. Moreover in comparison with the typical catalysts used for hydrosilylation reactions, i.e. Karstedt's, the

ligands of the catalyst used here do not have reactive groups (e.g. double bonds) which can interfere with the main reaction. Finally, this catalyst can be obtained from the suppliers in a rather pure form (as a pure solid, and not a solution) and it's soluble in toluene, a good solvent for PDMS, which helped to mix the catalyst within the PDMS formulations used.

To study the effect of the cross-linker concentration, formulations with three H/V ratios (molar ratio between the Si–H groups of the cross-linker and the vinyl bonds of PDMS) were prepared: 1.0, 1.7 and 2.7. The concentration of PDMS and catalyst was kept constant and the reactions studied at 25 and 60 °C, in the presence of air and atmospheric humidity.

The effect of the cross-linker concentration on the cross-linking of these systems was investigated by monitoring the consumption of the silane groups of the cross-linker and the vinyl groups of the PDMS polymer for a certain period of time. The results obtained with *in situ* ATR-FTIR (Attenuated Total Reflectance-Fourier Transform Infrared) Spectroscopy and Confocal Raman Microscopy (CRM) will be discussed in the first two sub-sections.

To analyze the effect of the cross-linker concentration on the network structure and the morphology of the cross-linked materials, Nuclear Magnetic Resonance (NMR) imaging, swelling/extraction experiments and Scanning Electron Microscopy (SEM) experiments were also made. These results will be presented in the last two sub-sections.

3.1. Consumption of the silane groups (Si–H) of the cross-linker during the cross-linking reactions: in situ ATR-FTIR

In the present work we used *in situ* ATR-FTIR spectroscopy to follow the changes in the concentration of Si–H groups of the cross-linker during the preparation of cross-linked PDMS (Scheme 1). Transmittance Fourier Transform Infrared (FTIR) Spectroscopy has been used to monitor the cross-linking of PDMS following the evolution of the stretching band of the silane groups of the cross-linker at 2136 cm^{-1} [17,30]. However, for the materials studied here it was not possible to monitor the evolution of the cross-linking reaction through the stretching band of the Si–H groups of the cross-linker because it overlaps with a second band at 2160 cm^{-1}. This second band arises from the background (noise) of the highly sensitive MCT detector. We report for the first time the use of the band at 902 cm^{-1}, assigned to the bending vibration of the Si–H groups of the cross-linker [30], to follow the cross-linking reactions in PDMS-based formulations. As is shown in Fig. 1 this band is reasonably sharp, well-defined and can be normalized using the band at 864 cm^{-1}. This band decreases during the cross-linking reaction.

The bending band positioned at 902 cm^{-1} did not show any shift when different concentrations of cross-linker or catalyst and or PDMS polymer were present. This is a good indication that the coefficient of extinction of this band does not change during the cross-linking reactions and therefore can be used to follow the changes in the Si–H groups.

The Si–H bending vibration in pure liquid form occurs at 890 cm^{-1} (Fig. 2). This shift is likely caused by interactions of the cross-linker (in the pure liquid form) with itself because when the cross-linker is diluted with PDMS6, PDMS17, ethylene glycol or hydroxyl-terminated PDMS, this band is also shifted to 902 cm^{-1}.

Two vinyl-terminated PDMS polymers with $\overline{M}_w$ = 6000 and 17, 200 g/mol, named here as PDMS6 and PDMS17 respectively, were studied. Both have shown a similar behavior with respect to the decrease of the band at 902 cm^{-1} during the cross-linking over time. In order to simplify the analysis of these systems, the majority of the experiments were made with PDMS17 and these experiments are discussed in length here.
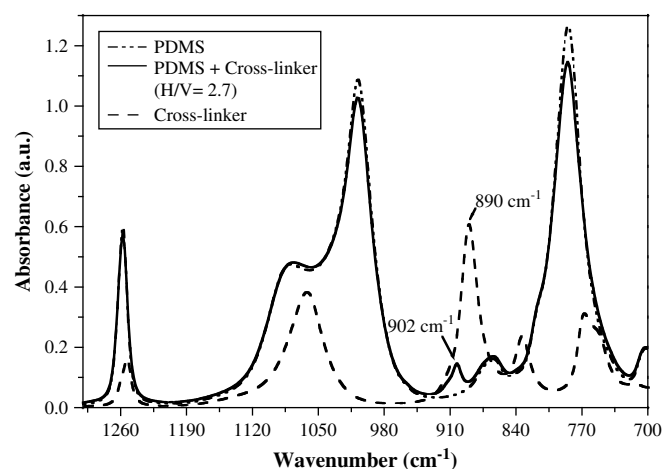

Fig. 2. ATR-FTIR spectra of: pure cross-linker, PDMS17 and a starting formulation with PDMS17 and H/V = 2.7. The spectra were normalized to the PDMS17 band at 864 cm^{-1}.

In order to follow the consumption of the silane groups during the cross-linking process and to evaluate the effect of its concentration in the cross-linking reaction, formulations of PDMS17 with three different initial concentrations of the cross-linker were prepared (H/V = 1.0, 1.7 and 2.7). Fig. 3 shows the evolution of the concentration of the Si–H groups of the cross-linker, as a function of time of the cross-linking reaction at 25 °C.

As discussed in the literature [31] the hydrosilylation reaction can be separated into three stages: an induction period, a reaction period between Si–H and C=C bonds and a post-cure slow reaction of the remaining Si–H groups. As can be seen in Fig. 3 the occurrence of an induction period was observed for all the three H/V formulations. However, the slow reaction period seems to occur only for formulations with H/V = 1.7 and 2.7. Moreover, the results indicate that this slow period starts before the point at which the C=C bonds should have been theoretically completely consumed by hydrosilylation reaction (see horizontal lines in Fig. 3). This suggests that a considerable amount of Si–H is consumed through
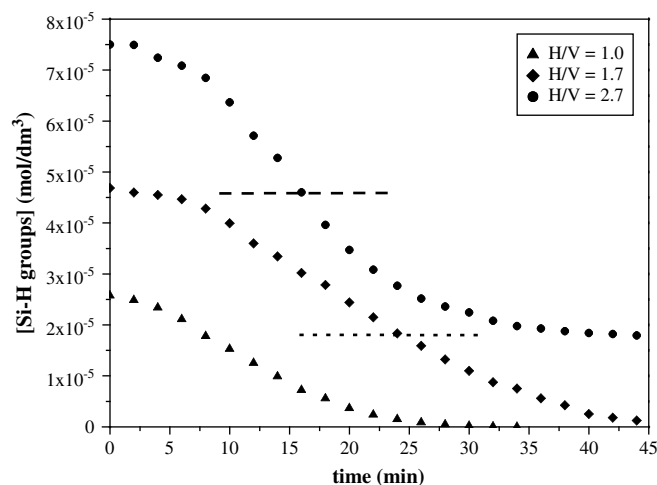

Fig. 3. Evolution of the concentration of Si–H groups (mol/dm^3) of the cross-linker during the cross-linking reaction at 25 °C, obtained by ATR-FTIR spectroscopy. The curves show the results obtained for formulations of PDMS17 with three different initial concentrations of cross-linker: H/V = 1.0, 1.7 and 2.7. *Horizontal lines*: Si–H group concentration at which the C=C bonds were expected to be completely consumed by hydrosilylation reaction with the Si–H group, assuming that no secondary reactions occur: (*dot*) H/V = 1.7; (*dash*) H/V = 2.7.

secondary reactions with groups other than C=C. Nevertheless, in the case of H/V = 1.0 the results suggest that a complete consumption of the Si–H is achieved by reacting with the C=C.

From the comparison of the data shown in Fig. 3, it can also be seen that for the formulation with H/V = 1.0 all the silane groups are consumed in approximately 32 min. Moreover, when the same amount of PDMS17 is present and a considerable excess of cross-linker is used in the starting formulation, the consumption of the Si–H groups proceeds faster. The same experiments were repeated for three different formulations at 60 °C and the results obtained are shown in Fig. 4.

As expected, the consumption of Si–H groups is accelerated for all the studied materials; note that the time scale of the reactions at 60 °C is in the order of seconds. For all three formulations an induction period was found and the overall rate of the initial Si–H conversion after this induction period is faster than the corresponding rate at 25 °C. A three-step reaction is suggested for all the H/V formulations cross-linked at 60 °C. At least for H/V = 1.7 and 2.7 the slow step seems to occur when a considerable amount of Si–H has been consumed through secondary reactions with groups other than C=C, although the effect seems to be less pronounced than at 25 °C.

Although a quantitative analysis of the IR data was possible, the interpretation of the results in terms of Si–H consumption over time was inconclusive for the formulations used here. The clear attribution of three main regimes, as suggested in the literature [31–33], was unfeasible. Similar results were obtained when PDMS6 was used in our formulations instead of PDMS17. Our data suggest that after the induction period, the Si–H consumption has to be explained by a mutual occurrence of both, the hydrosilylation and the secondary reactions of Si–H. These secondary reactions continue over a long period after our ATR-FTIR measurements were stopped, and most probably involve O_2 and moisture (Eqs. (2)–(5)), as reported before by many authors [22–24]. Nevertheless, we should point that with the data provided we cannot exclude completely other possible secondary reactions, which do not involve O_2 and moisture. However it should be noticed that O_2 can be consumed during the cross-linking process by the excess of silane groups of the cross-linker (Eq. (3)), but is also required in the

reaction medium as it plays a role in the catalytic cycle of Pt catalyst [34,35].

Many studies on PDMS materials, namely on model networks [16,18,20], have been made under the assumption that the hydro-silylation reaction between the Si–H groups and the vinyl groups of PDMS forms –Si–CH_2–CH_2–Si– cross-links without any side reactions. However, as discussed in Section 1, this situation does not hold true for all the hydrosilylation systems, particularly in real applications when the cross-linking is carried out under air atmosphere and an excess of cross-linker. Moreover, most of the studies described in the literature were made on PDMS materials cross-linked at very high temperatures (>150 °C) [22–24]. Until now, it has been generally accepted in the literature that the effect of the secondary reactions is not relevant at lower temperatures (<60 °C), particularly on the earlier stages of the cross-linking process.

Our ATR-FTIR measurements strongly suggested that this is no longer true for our formulations. This may be caused by the Pt catalyst used, for which quantitative reaction rates at different H/V ratios were not determined so far and/or by other factors, such as the presence of air, which could not be precisely determined at the current time. Furthermore, our results indicate that the excess of Si–H and the related secondary reactions have an important effect on the overall cross-linking process, even at earlier stages of the cross-linking process and low temperatures.

Because the cross-linking process can have a strong effect on the final material properties, we decided to study the cross-linking of our formulations in more detail using CRM. In our case using CRM allowed to understand how the silane groups are consumed through the cross-linking process because we could investigate at the same time the C=C bonds and Si–H consumption. This gives us the possibility to directly relate the consumption of the cross-linker with the consumption of the double bonds, an approach which was to our knowledge never used before.

3.2. Study of the consumption of the C=C groups of PDMS17 and Si–H groups of the cross-linker with Confocal Raman Microscopy (CRM)

Although the intensities of the Si–CH=CH_2 and Si–H stretching vibrations are weak, both can be observed with CRM at 1595 cm^{-1} and 2132 cm^{-1}, respectively (see Fig. 5a) [30].

Fig. 5b shows the Raman spectra of the formulations of PDMS17 cross-linked at 25 °C on the golden gate of our IR equipment (H/V = 1.0 and 2.7). The spectrum of the di-vinyl-terminated starting polymer PDMS17 is also shown in Fig. 5b.

These spectra show that after 30 min of ATR-FTIR measuring time, the double bonds of PDMS17 are fully consumed for both the materials. Also the Si–H groups of the cross-linker in the H/V = 1.0 samples are completely consumed. Only in the sample with H/V = 2.7, the band corresponding to the emission of the Si–H groups is still present. This confirms the results obtained with the ATR-FTIR measurements which showed the presence of un-reacted Si–H groups after ~32 min of reaction, for materials cross-linked at 25 °C with an excess of cross-linker in the initial formulation. Moreover, they show that at this point of the cross-linking process no more hydrosilylation reactions are occurring, as the double bonds are fully consumed. This means that if the Si–H groups are consumed after this point in time, it has to be via secondary reactions. Very similar behavior was observed for the consumption of the Si–H groups, for materials cross-linked on the ATR-FTIR facility at 60 °C, for 5 min.

However, the results above do not reveal what happens with the double bonds or the Si–H groups at earlier stages of the cross-linking process. To investigate the double bond consumption during the cross-linking reaction in these PDMS systems, *in situ*
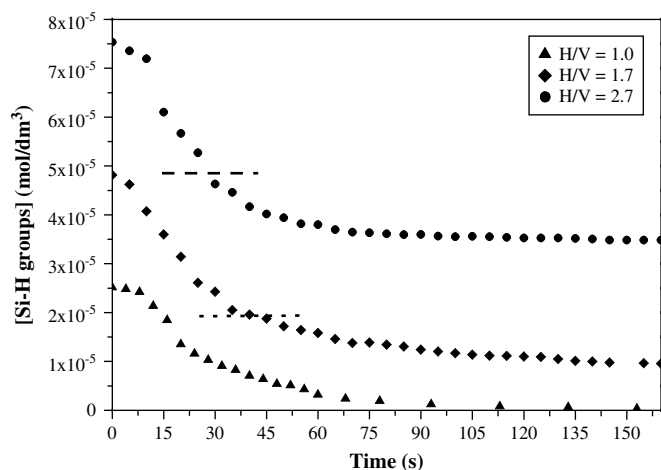

Fig. 4. Evolution of the concentration of Si–H groups (mol/dm^3) of the cross-linker during the cross-linking reaction at 60 °C, obtained by ATR-FTIR spectroscopy. The curves show the results obtained for formulations of PDMS17 with three different concentrations of cross-linker: H/V = 1.0, 1.7 and 2.7. *Horizontal lines*: Si–H group concentration at which the C=C bonds were expected to be completely consumed by hydrosilylation reaction with the Si–H group, assuming that no secondary reactions occur: (*dot*) H/V = 1.7; (*dash*) H/V = 2.7.
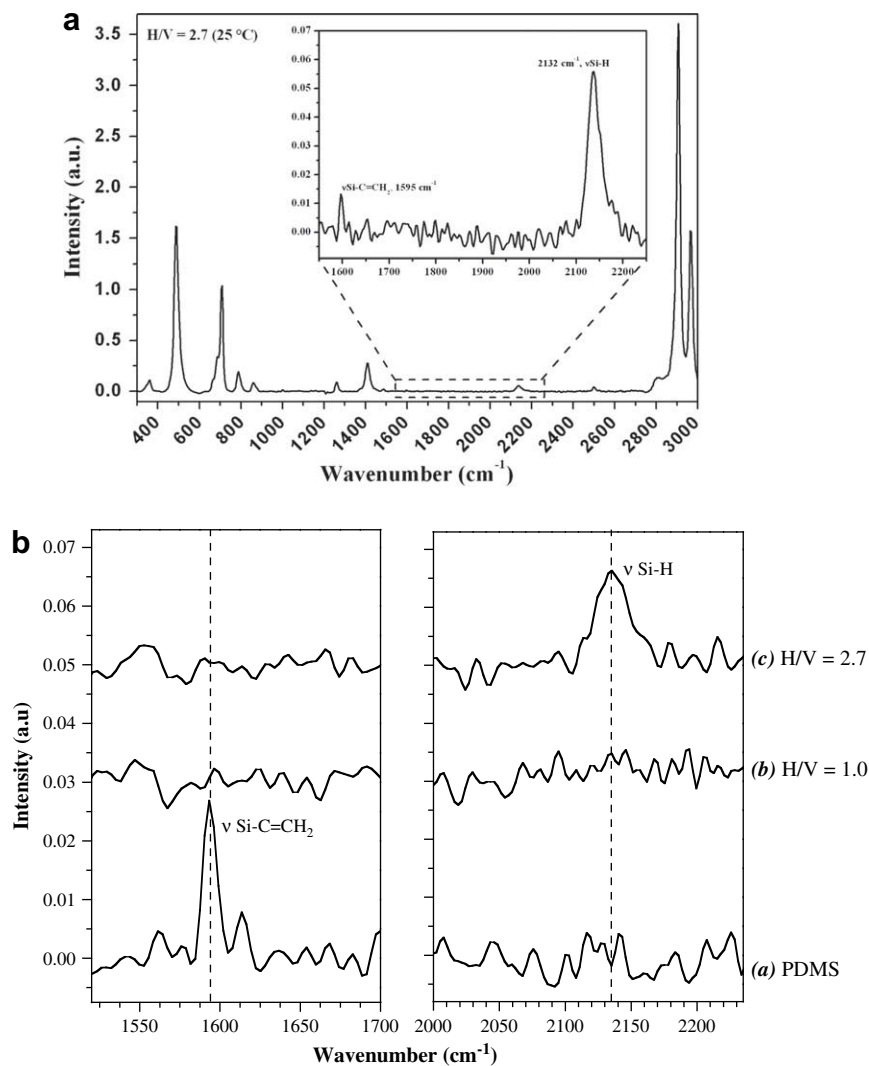
Fig. 5. a: Example of Confocal Raman Microscopy (CRM) spectrum of a starting formulation with PDMS17 cross-linker (H/V = 2.7) and Pt catalyst. *Inset*: expansion of the area between 1550 and 2250 cm^{-1}. b: Confocal Raman Microscopy (CRM) spectra of: PDMS17 *(a)* and samples cross-linked on the ATR-FTIR crystal at 25 °C after 30 min of reaction with; *(b)* H/V = 1.0 and *(c)* H/V = 2.7.

Confocal Raman Microscopy was used also. The Raman spectra collected at different times of the cross-linking reaction at 25 °C for a starting formulation with initial H/V = 1.0 are shown in Fig. 6. For clarity only the relevant part of the CRM spectra are shown.

From Fig. 6 it can be seen that the intensity of the emission bands of the vinyl and silane groups (at 1595 and 2132 cm^{-1}, respectively) decreases during the cross-linking reaction. After 30 min of measuring time, the band corresponding to the silane groups of the cross-linker is no longer observed, which is in good agreement with the *in situ* ATR-FTIR measurements (Fig. 3) when the errors in reaction time of both measurements are taken into account. A small amount of C=C is still observed after 30 min which suggests that part of the Si–H groups is converted by secondary reactions (Eqs. (2)–(5)). Moreover, part of the double bond still reacts further by side reactions different from the cross-linking reactions (see spectrum after one month, Fig. 6). Evidence for the occurrence of these side reactions with the double bonds was to our knowledge never reported before.

The same *in situ* CRM experiments were made for formulations with H/V = 2.7 cross-linked at 25 °C, and the results are shown in Fig. 7.

For this case it was also observed that both emission bands (corresponding to the double bonds and silane groups) decrease progressively in time. However, contrary to the starting formulation with H/V = 1.0, these spectra show that a considerable amount of cross-linker remains in the material after the double bonds have been completely consumed. It should also be noticed that when the H/V ratio increases above 1.0 the double bonds are more rapidly consumed and the amount of Si–H left behind after complete consumption of the vinyl bonds is larger.

Finally, it can be seen from the spectra collected for the samples with H/V = 2.7 after one month of storage in air (and atmospheric humidity) (Fig. 7), that the Si–H band intensity decreased further, probably by the secondary reactions mentioned before.

According to the *in situ* ATR-FTIR measurements for a sample with H/V = 1 formulation (Fig. 3) the amount of Si–H groups left behind is negligible after 30 min, which is confirmed by the CRM measurements (Fig. 6). Next to the hydrosilylation reaction between Si–H and C=C bonds, secondary reactions of Si–H always occur simultaneously when the H/V ≥ 1. Therefore for these formulations the IR measurements cannot be used to calculate accurately the rate of the hydrosilylation reaction. Moreover, these
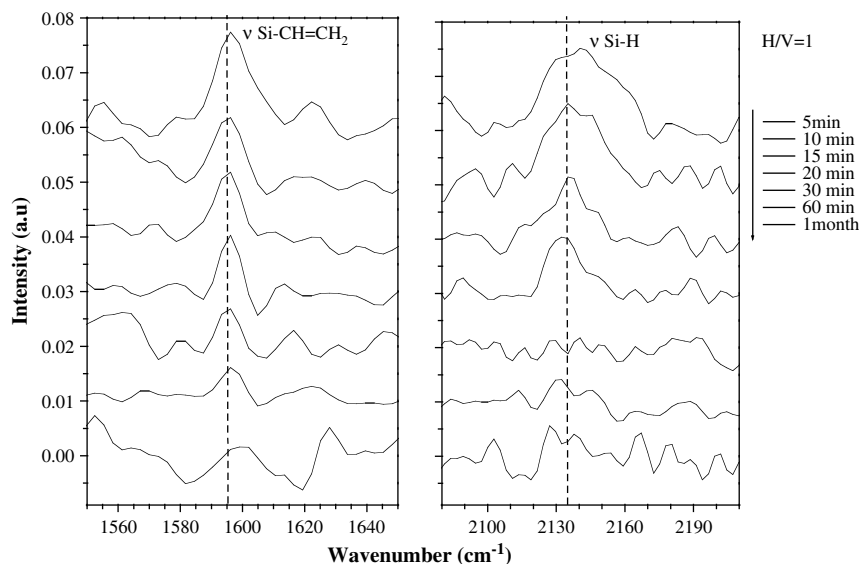
Fig. 6. Confocal Raman Microscopy (CRM) spectra taken at different measuring times of the cross-linking reaction at 25 °C, in a formulation of PDMS17 with H/V = 1.0.

secondary reactions continue to occur for a long time after the C=C has been completely consumed. Also, the results suggest that for H/V = 1.0 side reactions occur with the C=C double bonds. To the best of our knowledge these findings have not been demonstrated in practice before for linear di-vinyl-terminated PDMS polymers.

The occurrence of secondary reactions of Si–H after complete consumption of the C=C was reported before [22–24] as discussed in Section 1. In these secondary reactions O_2 and moisture (Eqs. (2) and (3)) as well as additional cross-linking (Eqs. (4) and (5)) are involved. Hence it is likely that the secondary reactions of the Si–H groups in our formulations are comparable to these reactions and therefore, next to the cross-linking between the vinyl bonds and Si–H, Si–O–Si cross-links are also formed at the same time, after the vinyl bonds have disappeared. As mentioned before, the contribution of other minor secondary reactions not possible to identify with the data available, cannot be completely excluded.

In conclusion, in contrary to what has been reported before, we demonstrated that when concentration of Si–H is equal to or larger than the C=C concentration in our formulations, two types of

cross-links can be formed at the same time, namely Si–CH₂–CH₂–Si and Si–O–Si cross-links. The latter ones also continue to be formed especially at high H/V ratios, when all the vinyl bonds are consumed, and when the cross-linking is done at low temperature (25 °C) in the presence of air (and atmospheric humidity). This implies that the cross-linking of the PDMS6 and PDMS17 formulations cannot be analyzed in three independent stages and questions about the usefulness of this approach for other PDMS formulations can be raised. The occurrence of secondary (cross-linking) reactions at early stages of the reaction should be taken into account even when the cross-linking is performed in air and moisture at low temperatures, because they will have a direct impact on the products formed through the cross-linking process, and the material properties of these cured formulations. The impact of these findings on modulus properties will be discussed later on in this article.

To characterize our network structures in more detail further studies were made using NMR spectroscopy, SEM and extraction experiments. The results are discussed below.
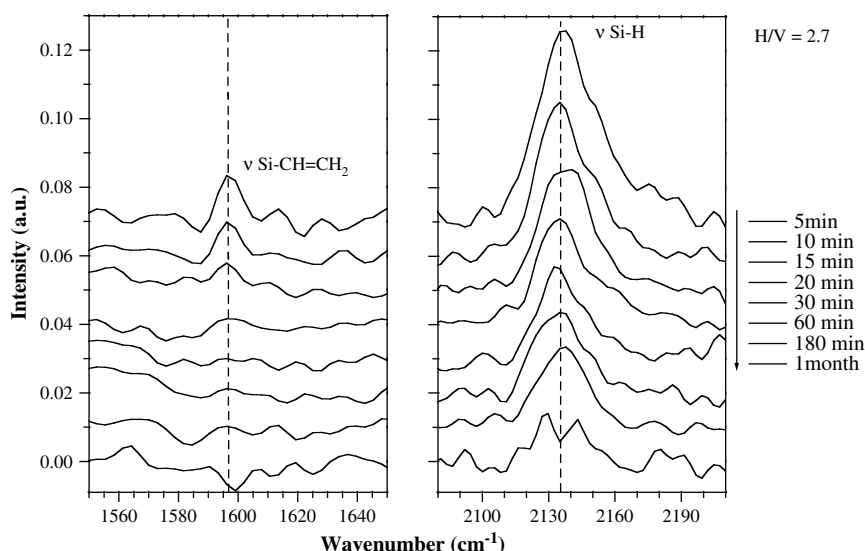

Fig. 7. Confocal Raman Microscopy (CRM) spectra taken at different measuring times of the cross-linking reaction at 25 °C, in a formulation of PDMS17 with H/V = 2.7.

3.3. NMR imaging and extraction experiments for materials with different initial H/V ratios

To study the influence of the cross-linker concentration on the networks formed during the cross-linking reaction, three cross-linked films were prepared with different initial H/V: 1.0, 1.7 and 2.7. Using NMR spectroscopy, the relaxation of the transversal magnetization in the cross-linked materials was studied as a function of the depth of the cross-linked films. As the signal decay is not a simple exponential, the relaxation process it has to be characterized with more than one relaxation time ($T_{2,i}$ in Eq. (8)). Therefore to analyze the data in more detail, the signal decay data were measured throughout the film thickness and fitted with a bi-exponential function (Eq. (8)), where $T_{2,s}$ and $T_{2,f}$ are time constants for the slow and fast components of the relaxation process and the parameters S_s and S_f are the slow and fast contributions to the signal of these components. The parameter S_∞ represents the noise level in the experiment.

$$S \approx S_\infty + S_f \exp(-t/T_{2,f}) + S_s \exp(-t/T_{2,s}) \qquad (8)$$

In principle, these different time scales can be assigned to groups of protons having a different local environment. The fast moving protons will contribute to the slow decaying part of the signal, while groups of slow moving protons contribute to the fast decaying part of the signal.

Fig. 8 shows the relaxation times plotted as a function of the film depth using Eq. (8). The vertical dotted lines refer to the material interfaces: the air/material interface (left) and the material/glass interface (right). The first important observation is that the T_2 values are nearly constant throughout the cross-linked films for all the materials made with different H/V ratios in the formulations. This indicates that the cross-linking of these PDMS17 materials is rather homogeneous and that the network structure does not vary in depth. To be more precise the cross-linked PDMS materials can be regarded as homogeneous materials throughout the thickness of the films, on length scales bigger than 5 μm (NMR resolution).

The second important observation from Fig. 8 is that the T_2 values measured for the material prepared with H/V = 1.0 are considerably higher as compared to the other materials. It should be noticed that these results are reproducible as several films prepared at different locations and times were tested. This difference was also observed while measuring with other inter-pulse times.

The decay curves represented for samples cross-linked with different H/V ratios are shown in Fig. 9. These results indicate that the relaxation in the material cross-linked with H/V = 1.0 is much slower, meaning that the motions of the major part of the hydrogen atoms in these films, are much faster. This can be explained by the presence of a high amount of species such as linear polymer chains or small network fragments not connected to the network.

To verify the presence of non-bonded species the cross-linked materials were submitted to a swelling/extraction procedure. The amounts of extractable species removed from the PDMS17 materials cross-linked with different initial H/V ratios are shown in Table 1.

As can be seen in Table 1, a high percentage (~25%) of non-bonded material was removed from the films cross-linked with an initial H/V ratio of 1.0. When the initial Si–H concentration in relation to the concentration of the C=C bonds was increased, the sol fraction decreases considerably, for H/V = 2.7 only approximately 1% of non-bonded species was extracted. Several samples cross-linked from formulations with H/V = 1 and H/V = 2.7 were submitted to extraction, and similar results were obtained, indicating that these results are reproducible for our systems, and that the extraction procedure was correctly carried out.
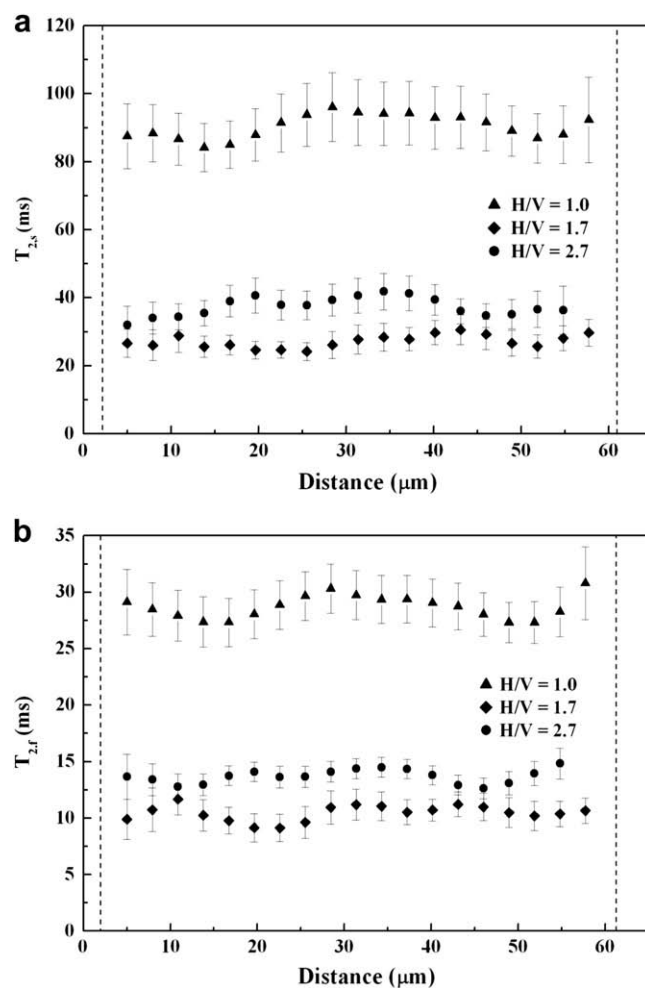

Fig. 8. The fast and slow relaxation rates $T_{2,f}$ and $T_{2,s}$ are plotted as a function of the position in the material. Measurements are shown for materials cross-linked from formulations with H/V = 1.0, 1.7 and 2.7. The vertical dotted lines refer to the material interfaces: the air/material interface (left) $x = 0$ and the material/glass interface (right).

Other authors [18,20,28,29,36] used similar PDMS formulations (same cross-linker and catalyst type and amount) and reported extractable fractions similar to ours for materials cross-linked with H/V > 1.0. This also validates our extraction procedure. However
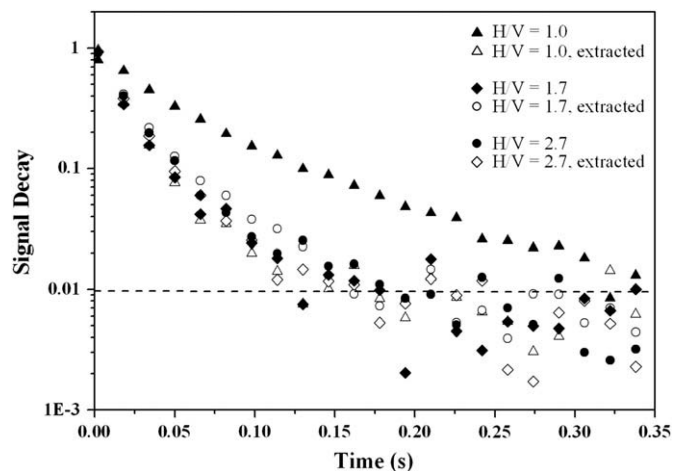

Fig. 9. Decay curves of the transversal magnetization on materials cross-linked from formulation with H/V = 1.0, 1.7 and 2.7, before and after the extraction procedure.

Table 1
Percentage of extractable species (extractable fraction, W_{ext}) removed from PDMS17 materials cross-linked with different initial H/V ratios, obtained from the swelling/extraction.

Sample	W_{ext} (%)	$[Si-H]_0$ (mol/dm^3)
H/V 1.0	25.2	2.9×10^{-05}
H/V 1.7	3.6	5.0×10^{-05}
H/V 2.7	1.2	7.0×10^{-05}

Scheme 2. Scheme representing the behavior of physical cross-links after the swelling/extraction procedure: a) loose chains and b) unfolded chains due to cross-over.

the extractable amount observed for the samples cross-linked from formulations with H/V = 1.0 is rather high, as compared to the values available in the literature for similar systems [28].

It was shown by the CRM results that for materials cross-linked at 25 °C using a formulation with H/V = 1.0, part of the C=C and Si–H groups react through side reactions, which may result in extractable small network fragments and loose ends not connected to the network. Hence, our results indicate the presence of imperfect networks with loose ends for the films cross-linked from formulations with H/V = 1.0, which can be easily extracted. For a stoichiometric ratio of C=C bonds and Si–H groups, the steric hindrance will probably result in an unequal reactivity of the Si–H sites [20]. Patel et al. [20] studied model and imperfect networks, prepared from formulations very similar to ours, and reported that the imperfect networks with many pendant chains were less effective at permanently trapping entanglements than the model networks.

It should be also pointed out that the films studied here were cross-linked in air and moisture conditions, and are much thinner as compared to the ones usually reported in the literature (60 μm as compared to ∼1.25 mm [37]). These conditions can contribute to a larger extent of secondary reactions of the Si–H groups available, as they are more exposed to side reactants, resulting in smaller network fragments and such high extractable fraction, never reported before. Moreover, the extensive slow and lengthy swelling/extraction procedure reported in the literature to extract very thick cross-linked films, has been used here to extract much thinner films, which provides the solvents a better access to the bulk of the films, resulting in a very efficient extraction.

To verify if this large amount of extractable material is responsible for the much higher T_2 values in the H/V = 1.0 materials, NMR imaging experiments were carried out on the extracted (dried) films. The results are also presented in Fig. 9 and show two interesting features. Firstly, the extraction procedure seems to influence the NMR signal only in the case of the materials cross-linked with initial H/V = 1.0. Secondly, after extraction the NMR signal decay of material cross-linked with H/V = 1.0, is faster and becomes comparable to that of the films cross-linked with higher H/V values.

The first observation shows that for H/V = 1.0 the relaxation behavior is strongly influenced by the extractable fraction present in this material, see Table 1. Hardly any extractable fraction was found for the materials made from H/V = 1.7 and 2.7 formulations. The decay curves before and after extraction, are identical for these materials within the uncertainty of the measurement. This is also an indication that physical cross-links, which can be removed by swelling/extraction (Scheme 2a), are hardly present in the materials made with H/V = 1.7 and 2.7. These observations confirm that the extractable fraction is responsible for the different behavior observed for T_2 values of the film cross-linked with H/V = 1.0.

The second observation can be interpreted as follows. In the extracted films prepared from H/V = 1.0 formulations and all other films before and after extraction, the mobility of the protons does not depend on the H/V value of the starting formulation, which indicates that the topology of the molecular network does not limit the motions of the protons. This suggests that in these cases,
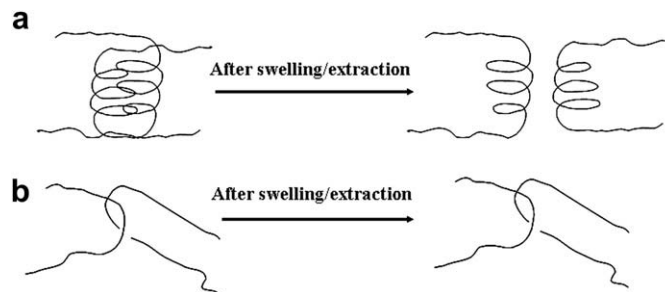
physical constraints dominate the mobility of the protons and that the distribution of these constraints throughout the system is hardly sensitive for the H/V value of the starting formulation.

Taking into account the results of the IR and CRM measurements we propose a possible explanation for this effect. From the in situ studies it was shown that a large part of the network structure is formed by hydrosilylation (Eq. (1)). However, other cross-linking reactions are likely to occur forming Si–O–Si cross-links (Eqs. (4) and (5)). The occurrence of these additional reactions is expected to shorten the distances between the cross-links and lower the relaxation time of the hydrogen atoms. Moreover, physical cross-links which cannot unfold during swelling because of the cross-over of the chains can also occur (Scheme 2b).

When the amount of cross-linker used in the starting formulation was higher than H/V = 1.0, the average distance between the Si–CH$_2$–CH$_2$–Si cross-links is expected to become larger. In principle this would increase the mobility of part of the hydrogen atoms. However, the Si–O–Si amount of cross-links increases, as well as the amount of physical cross-links, limiting the mobility of the protons. From the NMR data these two effects seem to counterbalance each other with increasing H/V ratio, resulting in very similar decay curves for the films prepared with starting formulation of H/V = 1.0 after extraction, as well as for all the other extracted and non-extracted cross-linked films made from formulations with H/V = 1.7 and 2.7.

This hypothesis is further supported by previous work [28] in which the contribution of both cross-links to the network structure formation was reported. JKR (Johnson–Kendall–Roberts) measurements [28] were made on materials cross-linked from formulations of vinyl-terminated PDMS with varied molecular weights, H/V = 1.6, and the same four-functional cross-linker and catalyst reported here. The moduli (E_l^{eff}) measured by these authors [28] before and after extraction, on cross-linked films of PDMS with different molecular weight, are compiled in Table 2. The extractable fractions (W_{ext}) determined from extraction measurements made with a procedure very similar to what is reported in the present experiments, are also shown in Table 2.

Table 2
Values of the modulus E_l^{eff}, average molar mass between cross-links (M_c) and extractable fraction (W_{ext}) for PDMS samples cross-linked from a formulation with H/V = 1.6, before and after being submitted to swelling/extraction procedures. Data compiled from Ref. [28].

Cross-linked films	M_n,[a] (g/mol)	E_l^{eff} (MPa), before extraction	$W_{ext.}$ (%)	E_l^{eff} (MPa), after extraction	M_c (g/mol)
PDMS6	6000	1.18	2.52	1.21	5700
PDMS9	9400	1.01	2.84	1.03	6800
PDMS17	17,200	0.92	2.93	0.92	7800
PDMS28	28,000	0.80	2.68	0.83	8600

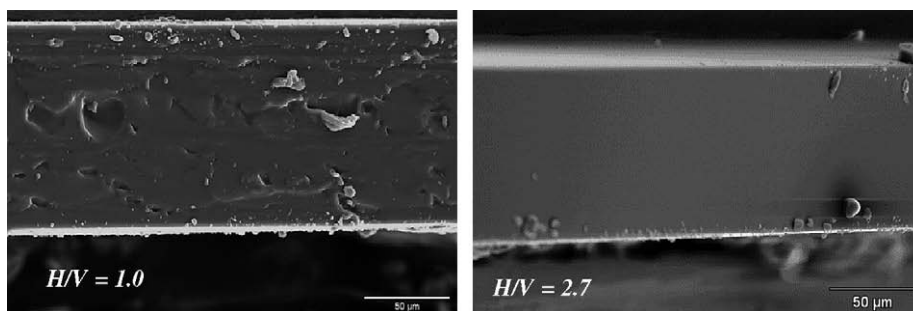[a] Provided by the suppliers (ABCR GmH & Co, Germany).

Fig. 10. SEM images of the cross-section of cross-linked PDMS17 materials prepared with initial H/V = 1.0 and 2.7.

From these moduli the average distance between the cross-links was calculated [38] from:

$$E = \frac{3\rho RT}{M_c} \qquad (9)$$

In Eq. (9) ρ is the density of the PDMS chain ($\sim$0.96 g/mL) and M_c is the average molar mass between cross-links including physical cross-links (Scheme 2b) and chemical cross-links. These data previously obtained by other researchers [28], strongly suggest that the average distance between the cross-links is much shorter than expected based on the distances between the vinyl end groups of the PDMS, for all the cross-linked PDMS studied. Therefore the authors suggest that additional cross-linking has to be taken into account.

Hence, these moduli data support the simultaneous occurrence of two different cross-links and the absence of physical cross-links which can be removed by extraction (Scheme 2a) for the formulations (H/V = 1.7 and 2.7) studied here. The occurrence of different cross-links was also observed earlier by Quan [24] who reported that this fact leads to bimodal distributions of chain lengths between cross-links during the post-curing. Formulations very similar to ours were used in a broad range of adhesion measurements [11,39,40]. In these studies ideal networks with one type of cross-links are usually assumed. The impact of our findings on adhesion properties will be published elsewhere.

3.4. SEM characterization of materials made with different initial H/V ratios

Finally, in order to investigate the morphology of the materials cross-linked with different initial H/V ratios, the cross-linked films were analyzed by SEM (Fig. 10).

In Fig. 10, representative cross-section SEM images of the cross-linked films prepared with H/V ratios of 1.0 and 2.7 are shown. The film prepared with H/V = 1.0 shows some different characteristics indicating a softer and more flexible material. This observation is in agreement with the results described above, obtained from the extraction and NMR experiments, which suggest a higher amount of extractable material for the materials cross-linked from a starting formulation with H/V = 1.0, which can have a plasticizer effect. This observation can be of interest from the material properties point of view, e.g. softer or more rigid cross-linked materials will behave differently in what concerns their mechanical and adhesion properties.

4. Conclusions

For the PDMS formulations studied in this work it was shown that although the data provided from *in situ* infrared spectroscopy (ATR-FTIR) suggest a three-step approach, the quantitative data obtained cannot be used to accurately interpret the hydrosilylation reaction progress.

The use of additional characterization techniques to follow the cross-linking process *in situ* can provide more information about the cross-linking process. Using Confocal Raman Microscopy (CRM) we were able to follow the consumption of Si–H groups and C=C bonds simultaneously. To our knowledge this was the first time that CRM was used to study hydrosilylation reactions for such PDMS systems. Combined results from IR and Raman experiments show that contrary to what was expected, when the cross-linking is made at low temperatures ($\leq$60 °C) under air and moisture for formulations with H/V $\geq$ 1.0, the consumption of the Si–H has to be explained by the mutual occurrence of the hydrosilylation (Eq. (1)) and secondary reactions, possibly with oxygen and moisture (Eqs. (2)–(5)). The results also indicate that part of the C=C bonds are consumed by side reactions at H/V = 1.0.

The use of NMR imaging, reported here for the first time to study hydrosilylation reactions, showed that the cross-linked films are homogeneous (across the whole film thickness) on a length scale of 5 μm, for all the H/V ratios studied. Moreover, NMR imaging and swelling/extraction experiments confirmed that for materials cross-linked with a starting formulation with H/V = 1.0, a large percentage of the material is not connected to the network. Such high amount of extractables has not been reported before, and suggests the presence of small network fragments with many pendant chains [20]. For the films made with starting formulation of H/V = 1.7 and 2.7 before and after extraction, as well as with H/V = 1.0 after extraction, very similar decay curves were found. This can be explained by the presence of two different chemical cross-links (Si–CH$_2$–CH$_2$–Si and Si–O–Si) as well as physical cross-links, which could not be unfolded after swelling/extraction. In the network structure these cross-links counterbalance each other at different H/V ratios.

The moduli measured for materials cross-linked with very similar formulations and variable PDMS molecular weights suggest a much higher cross-link density than expected, on the basis of the distance between the vinyl groups of the PDMS polymers. Our results provide an explanation for this observation showing the mutual occurrence of both cross-links at the same time. Contrary to what is generally assumed in the literature, cross-linked PDMS materials made by hydrosilylation may not lead to ideal network structures, even when the reactions are carried out at very low temperature.

It is expected that particles present in the formulations discussed here may also influence the network formation. This was studied in more detail by us using micro-sized garnet particles. The results will be published in a separate article.

References

[1] Owen MJ. Siloxane polymers, 1st ed. Englewood Cliffs, NJ: Prentice Hall; 1993.
[2] Morent R, De Geyter N, Axisa F, De Smet N, Gengembre L, De Leersnyder E, et al. Phys D Appl Phys 2007;40:7392–401.
[3] Andersson LHU, Hjertberg T. J Appl Polym Sci 2003;88:2073–81.
[4] Wu KH, Chao CM, Yeh TF, Chang TC. Surf Coat Technol 2006;201:5782–8.
[5] Pike JK, HoKenneth T, Wynne K. Chem Matter 1996;8:856–60.
[6] Buyl F. Int J Adhes Adhes 2001;21:411–22.
[7] Ikada Y. Biomaterials 1994;15:725–36.
[8] Abbasi F, Mirzadeh H, Katbab A. Polym Int 2002;51:882–8.
[9] Amouroux N, Léger L. Langmuir 2003;19:1396–401.
[10] Chaudhury MK, Whitesides GM. Langmuir 1991;7:1013–25.
[11] Perutz S, Kramer EJ, Baney J, Hui CY. Macromolecules 1997;30:7964–9.
[12] Marciniec B, Gulinskí J, Urbaniak W, Kornetka ZW. Comprehensive handbook on hydrosilylation. Pergamon Press; 1992.
[13] Mark HF. Encyclopedia of polymer science and technology. Wiley & Sons, Inc; 2001.
[14] Stein J, Lewis LN, Smith KA, Lettko KX. J Inorg Organomet 1991;1:325–34.
[15] Llorente M, Andrady AL, Mark JE. Colloid Polym Sci 1981;259:1056–61.
[16] Llorente M, Mark JE. Macromolecules 1980;13:681–5.
[17] Venkataraman S, Coyne L, Chambon F, Moshe G, Winter H. Polymer 1989;30:2222–6.
[18] Valles EM, Macosko CW. Macromolecules 1979;12:521–6.
[19] Mark JE. J Am Chem Soc 1970;92:7252–7.
[20] Patel SK, Malone S, Cohen C, Gilmore JR, Colby RH. Macromolecules 1992;25:5241–51.
[21] Sivasailam K, Cohen C. J Rheol 2000;55:897–915.
[22] Gorshov A, Kopylov Y, Dontsov A, Khazen L. Int Polym Sci Technol 1986; 13:T/26.
[23] Podoba AM, Goldovski EA, Dontsov AA. Int Polym Sci Technol 1987;14:T/42.
[24] Quan X. Polym Eng Sci 1989;29:1419–25.
[25] Glover PM, Aptaker P, Bowler C, McDonald PJ. J Magn Reson 1999;139:90–7.
[26] Erich SJF, Laven J, Pel L, Huinink HP, Kopinga K. Prog Org Coat 2005;52: 210–6.
[27] Ostroff ED, Waugh JS. Phys Rev Lett 1966;16:1097–8.
[28] Li Z. Mesoscopic adhesion of poly(dimethylsiloxane): self-adhesion, effects of fillers, surface modfication and thin top layers. Eindoven: Eindhoven University of Technology; 2007.
[29] Li Z, Brokken-Zijp JCM, De With G. Polymer 2004;45:5403–6.
[30] Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. The handbook of infrared and Raman characteristic frequencies of organic molecules. San Diego, California: Academic Press; 1991.
[31] Stein J, Lewis LN, Gao Y, Scott RA. J Am Chem Soc 1999;121:3693–703.
[32] Simpson TRE, Tabatabaia Z, Jeynes C, Parbhoo B, Keddie JL. J Polym Sci A Polym Chem 2004;42:1421–31.
[33] Simpson TRE, Parbhoo B, Keddie JL. Polymer 2003;44:4829–38.
[34] Lewis LN, Lewis N. Chem Matter 1989;1:106–14.
[35] Lewis LN. J Am Chem Soc 1990;112:5998–6004.
[36] Valles EM, Macosko CW. Macromolecules 1979;12:673–9.
[37] Hedden RC, Wong C, Cohen C. Macromolecules 1999:5154–8.
[38] Carré A, Shanahan MR. J Colloid Interface Sci 1997;191:141–5.
[39] Kim S, Choi GY, Ulman A, Fleischer C. Langmuir 1997:6850–6.
[40] Silberzan P, Perutz S, Kramer EJ, Chaudhury MK. Langmuir 1994;10:2466–70.