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# Garnet particles effect on the cross-linking of PDMS and the network structures formed

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ABSTRACT

Poly(dimethylsiloxane) (PDMS) cross-linked films with different concentrations of micrometer-sized garnet particles were prepared through hydrosilylation reaction between a di-vinyl-terminated PDMS and a four-functional silane cross-linker in the presence of a Platinum catalyst. The garnet particles, consisting of micrometer-sized Ce doped $Y_3Al_5O_{12}$ particles commonly used on light converters (for solid state light devices, e.g. Light emitting diodes LEDs), were homogeneously and individually dispersed through the bulk of the cross-linked films for a concentration up to 20% in volume.

The effect of the garnet on the cross-linking of the composite films was investigated by *in-situ* ATR-FTIR Spectroscopy. When formulations with an excess of cross-linker were used the overall consumption of Si–H groups of the cross-linker is slowdown in the presence of the garnet. The same effect was observed for an increasing concentration of the garnet. This effect is attributed to a strong interaction of the catalyst with the garnet during the cross-linking process. The possible origins of this interaction are discussed.

NMR Imaging was used to investigate the cross-linked networks formed in the composite films. All the networks are homogeneous through the depth of the cross-linked composite films (approx. 5 μm resolution). The films prepared in the presence of the garnet particles showed similar relaxation behavior, regardless of the cross-linker concentration used in the initial formulation, contrary to previous results with PDMS cross-linked films. This behaviour is explained based on the presence of different type of chemical cross-links, resulting from the occurrence of hydrosilylation and secondary reactions, which are influenced by the interaction between the garnet particles and the catalyst.

## 1. Introduction

In the last decades polymer based composites have been intensively investigated for the replacement of traditional materials such as ceramics, glass, wood or metal alloys. Due to their excellent properties, such as good resistance to high temperatures, light irradiation and chemical attack [1] silicon based polymers have been widely used as sealants and adhesives [2], in the biomedical field [3] and in electrical [4] or optical devices.

Creating new sources of white light to replace the conventional light sources available (e.g. incandescent bulbs) is the ultimate objective of solid state lighting technology. For this purpose materials which can withstand high temperatures and visible irradiation for long operation times are needed. In this work cross-linked Poly(dimethylsiloxanes) (PDMS) composite films containing garnet particles, with potential applications in high power white Light Emitting Diodes (LEDs), were prepared. The garnet used was Yttrium Aluminum Oxide doped with Cerium ($Y_3Al_5O_{12}$:Ce, abbreviated here as YAG:Ce), which is frequently used as a phosphor light-converter, in combination with a Galium Nitride (GaN)–based LED, to produce white light LEDs [5,6]. Part of the blue light emitted from the blue LED is converted by the phosphor particles, and the combined light emitted by the two solid materials is perceived by the human eye as white light [6]. The PDMS-based composite materials containing the garnet particles provide flexible polymer films for direct application on LEDs, with many advantages in relation to the current technologies [6–8], namely the easy processing and shaping of the phosphor layer with a lower financial and energy cost.

PDMS are amongst the most used silicone based polymers due to their unique chemical structure that combines an inorganic backbone and organic methyl groups attached to the silicon atoms [1]. However, to convert these amorphous polymers into commercially useful materials such as rubbers, resins or films

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a three-dimensional cross-linked structure is usually required [1,9]. This is typically achieved by reacting functional end groups on the PDMS chains with a multifunctional cross-linker in the presence of a catalyst [10,11]. Another strategy frequently used to improve PDMS properties is the insertion of fillers. Silica [12] and titanium dioxide particles [13] are the most common fillers in PDMS matrices. Many authors reported the improvement of the rheological [14], mechanical [15] or thermoelastic [16] properties of PDMS materials by the insertion of such fillers with nanometer dimensions. However, in practical applications PDMS materials are filled with many other inorganic compounds such as pigments, stabilizers, or thickeners which very frequently have larger sizes, i.e. in the micrometer range. Far less has been done to investigate the influence of the presence of such components on the cross-linking of PDMS materials. In particular, potential effects from micrometer-sized particles have been completely neglected so far. This was in fact a strong motivation to study cross-linked PDMS films with garnet particles.

When inorganic particles are present during the cross-linking reaction they can interact directly with the other components or influence the reaction indirectly by changing the properties of the system, such as viscosity and heat conductivity. These interactions can have different effects on the cross-linking such as: i) decrease of the cross-linking rate; ii) lower final conversion of PDMS reactive groups (i.e. vinyl bonds) and iii) un-reacted groups of the cross-linker (or PDMS) left in the composite material.

The non-reacted residues of cross-linker, catalyst and/or monomers remaining in the composite material after the cross-linking have typically very reactive groups. These chemical groups can trigger secondary reactions in time and cause undesired consequences, such as appearance of color, loss of gloss, brittleness or phase segregation. Moreover, these leftover residues can react further with air and humidity adding cross-links and defects to the initial cross-linked structure [17]. Most likely these reactions lead to changes in the mechanical and thermal properties of the materials. Hence, it is important to study the effect of the presence of inorganic particles on the cross-linking process and the networks formed thereafter.

In the current work, composite materials with different concentrations of the micrometer-sized garnet (YAG:Ce) homogeneously dispersed in a cross-linked PDMS matrix were prepared. The dispersion of the particles in the composites was investigated by Scanning Electron Microscopy (SEM). The influence of the presence of the garnet on the cross-linking of PDMS formulations was investigated by *in situ* ATR-FTIR Spectroscopy. The homogeneity of the cross-linked networks in the PDMS composite films and the effect of the presence of the particles on the networks formed was studied by Nuclear Magnetic Resonance (NMR) imaging.

## 2. Experimental

### 2.1. Preparation of the cross-linked composite films

A linear vinyl-terminated poly(dimethylsiloxane) (PDMS17 with $\overline{M}_w = 17200$ g/mol; ABCR-GmbH & Co) was cross-linked with the four-functional siloxane tetrakis(dimethylsiloxane) (density 0.886 g/mL; ABCR-GmbH & Co). The hydrosilylation reaction was catalyzed by cis-dichlorobis(diethylsulphide) Platinum (II) catalyst (Strem Chemicals, Inc) previously dissolved in a toluene solution and made under air and atmospheric humidity conditions, at 25 °C.

Dispersions of the garnet in the di-vinyl-terminated PDMS polymer with different concentrations of the garnet (YAG:Ce, $Y_3Al_5O_{12}$:Ce) were prepared. The garnet was supplied by Philips (Maarheze, The Netherlands) with average particle size of 3.5 μm and density ~4.55 g/cm$^{-3}$. The nomenclature chosen for the cross-linked films prepared according to the respective garnet, cross-linker and catalyst content is described in Table 1.

A typical procedure to prepare the cross-linked PDMS films (G20-HV2.7-Pt20 from Table 1) with 20% (v/v) of garnet, an H/V (ratio of Si–H groups of the cross-linker to vinyl bonds) 2.7, and 20 ppm catalyst was as follows: 2.612 g of garnet was added to 2.00 g of PDMS. The PDMS dispersions were stirred by hand for approximately 10 min until a homogeneous paste was obtained. The cross-linker was added to the mixture. After stirring the mixture by hand for approximately 5 min, 40 μL of a Pt$^{II}$ catalyst solution (with 0.0024 g catalyst/mL) were added to the mixture. This volume corresponds to 20 ppm of Pt$^{II}$ in relation to the PDMS polymer.

The mixture was placed in a sonication bath for 1 min to release the air bubbles, and immediately after it was poured on a substrate. The type of substrate, time and temperatures specifically chosen for each cross-linking reaction are described in the following subsections. The cross-linked PDMS films were opaque and dark yellow, due to the presence of the garnet particles.

### 2.2. Scanning Electron Microscopy (SEM)

SEM images were recorded with a JEOL JSM-840A, 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 mm.

The cross-linked films analyzed by SEM were casted on poly(carbonate) (PC) substrates by spin-coating. A range of cross-linked composite films with thicknesses varying from 20 to 200 μm was prepared. Films with typical thickness between 20 and 60 μm were chosen for the SEM analysis. To prepare the cross-linked films with approximately 60 μm a spin-coating two step program was used (first: 300 rpm, 15 s; second: 600 rpm, 30 s). The composite films were cross-linked in a vacuum oven at 60 °C for 20 h.

Small fragments of the center of the cross-linked films were detached by hand from the 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 film current of 20 mA for 3 min. The cross-section of the cross-linked composite materials was analyzed on the microscope with tilting angle of approximately 30°.

### 2.3. ATR-FTIR Spectroscopy

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

**Table 1**
Overview of the cross-linked materials prepared (typical thickness, 60 μm).

| Films nomenclature | Garnet % (v/v) | HV[a] | Pt$^{II}$ catalyst (ppm)[b] |
|---|---|---|---|
| G0–HV1.0–Pt20 | 0 | 1.0 | 20 |
| G5–HV1.0–Pt20 | 5 | 1.0 | 20 |
| G10–HV1.0–Pt5 | 10 | 1.0 | 5 |
| G10–HV1.0–Pt10 | 10 | 1.0 | 10 |
| G10–HV1.0–Pt20 | 10 | 1.0 | 20 |
| G10–HV1.7–Pt20 | 10 | 1.7 | 20 |
| G10–HV2.7–Pt20 | 10 | 2.7 | 20 |
| G20–HV1.0–Pt20 | 20 | 1.0 | 20 |
| G20–HV1.7–Pt20 | 20 | 1.7 | 20 |
| G20–HV2.7–Pt20 | 20 | 2.7 | 20 |

[a] HV = molar ratio between Si–H groups of the cross-linker and vinyl groups of PDMS17.

[b] Pt concentration, added from a toluene solution of cis-dichlorobis(diethylsulphide) Pt$^{II}$.

The procedure to make the *in situ* studies was according to previous studies with cross-linked PDMS films [17]. The silane cross-linker was added to the garnet/PDMS dispersions prepared as described in Section 3.1, 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 and stirred by hand for another minute. A typical starting formulation with 20% volume of garnet contains: PDMS (1.00 g), garnet (1.306 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 accessory, forming a layer of approximately 500 μm, 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 measurement.

All the spectra were collected *in situ* during the cross-linking reaction, between 4000 and 400 $cm^{-1}$ and a resolution of 2 $cm^{-1}$, under air and atmospheric humidity conditions. A full spectrum (in average 20 to 50 scans per spectrum) was taken every 30 s. The Golden Gate accessory was stabilized at the temperature of the run 25 °C, before starting the measurements. 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 total integrated area of the band at 902 $cm^{-1}$ could be used to determine the 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, as described in a previous work [17]. A linear calibration curve was obtained. Beer's law is valid in the range of Si–H concentrations used in the current formulations, which are directly proportional to the total integrated area of the band being used to follow the changes in the Si–H concentration.

For all the reactions studied the concentration of Si–H groups at each time $t$ of the reaction $[Si\text{–}H]_t$, 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. Calculation details are given in previous work with PDMS cross-linked films [17].

### 2.4. Interaction of the $Pt^{II}$ catalyst and cross-linker with the garnet

To investigate the interaction of the $Pt^{II}$ catalyst used with the garnet experimental tests were made using two dispersions with different formulations. *Dispersion* 1: 2.00 g of PDMS17, 10% volume of garnet and 40 μL of a toluene solution of the $Pt^{II}$ catalyst (see Section 2.1 for calculation details). *Dispersion* 2: 2.00 g of PDMS, 10% volume of garnet and 38 μL of cross-linker, corresponding to H/V = 1.7.

The two dispersions were left for 2 h on a roller mixer. After the mixing period the garnet fractions were isolated through ultra-centrifugation (30 min at 30,000 rpm). The garnet fractions collected were washed with toluene (approximately 6.00 mL) which is a good solvent for PDMS, the catalyst and cross-linker. The garnet fractions were separated again by ultra-centrifugation (30 min, 30,000 rpm), dried under a $N_2$ flow and left overnight inside an exsiccator. To the garnet fraction collected from *Dispersion* 1, 2.00 g of PDMS17 and 38 μL of cross-linker were added. Cross-linking of the mixture was observed through a viscosity increase after approximately 30 min. To the garnet fraction collected from *Dispersion* 2, 2.00 g of PDMS17 and 40 μL of a toluene solution of the Platinum catalyst were added. No cross-linking of the mixture was observed, as no change in the viscosity was detected for several days.

### 2.5. NMR imaging

NMR depth profiling was used in a previous work to study the network structure and the homogeneity of the networks over the thickness of cross-linked PDMS films with a thickness of typically 60 μm [17]. Making use of the so called GARField concept [18], layers can be measured with a spatial resolution of about 5 μm in depth. The details of the set-up used to detect the transversal magnetization of the $^1H$ hydrogen nuclei in the film were described in a previous publication [19]. The rate with which the signal $S$ of the transversal magnetization decays is used to characterize the homogeneity of the sample. The signal can be described by one or more exponential functions (Eq. (1)),

$$S(nt_e) = S_\infty + \sum_i S_i \exp\left(\frac{-nt_e}{T_{2,i}}\right) \tag{1}$$

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 transversal relaxation processes are very sensitive to the mobility of the hydrogen nuclei, a way to observe heterogeneities is by measuring the relaxation times $T_{2,i}$ as function of depth. The more mobile the hydrogen nuclei are, the slower is the magnetization decay and the larger are the $T_{2,i}$ values.

In this study the Ostroff-Waugh [20] sequence ($90o_x$-τ-[$90o_y$-τ-echo-τ]$_n$) 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, PDMS cross-linked materials containing garnet particles were prepared as described in Section 2.1. A typical starting formulation contained 20% volume of the garnet, 2.00 g of PDMS, H/V = 1.7 (38 μL of cross-linker) and 40 μL of the $Pt^{II}$ catalyst solution.

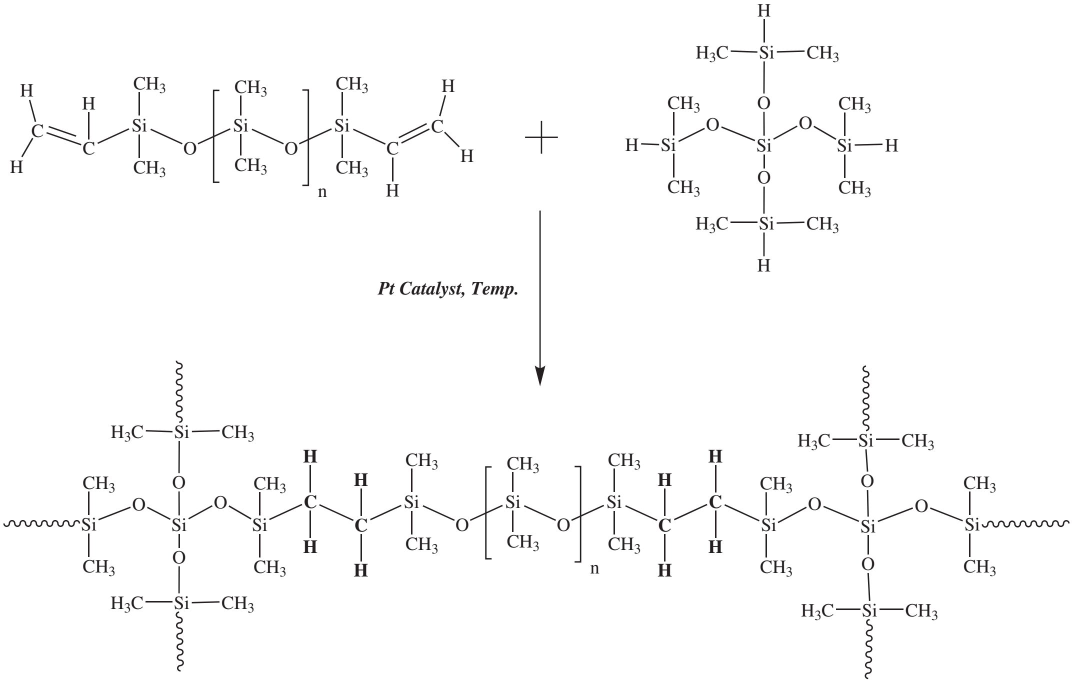
The formulations made as described above were spin-coated on a microscope glass slide substrate (~1.8 cm × 1.8 cm) (first step: 300 rpm, 15 s; second step: 600 rpm, 30 s) to prepare a film with approximately 60 μm. The composite films were cross-linked in a vacuum oven at 60 °C for 20 h and subsequently 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.

## 3. Results and discussion

To prepare cross-linked composite films, the garnet was initially dispersed in a di-functional vinyl-terminated Poly(dimethylsiloxane) (PDMS) polymer. The mixture was cross-linked via hydrosilylation reaction between the PDMS vinyl bonds and a four-functional cross-linker, tetrakis(dimethylsiloxane) (Scheme 1).

The cross-linking reaction was catalyzed by a Pt catalyst (cis-dichlorobis(diethylsulphide)) Platinum (II), under air and atmospheric humidity conditions, leading to a tri-dimensional network in which the particles are entrapped.

The PDMS formulations and the catalyst used in this work were chosen according to our previous studies on the cross-linking of PDMS films [17]. The specific choice of this catalyst was based on



**Scheme 1.** Scheme of the formation of a (model) cross-linked network through hydrosilylation reaction of PDMS materials.

the good reproducibility obtained in previous works [21,22], the fact that it can be obtained from the suppliers in a rather pure form (as solid and not in solution) and its solubility in the solvents which can be easily mixed with the PDMS formulations. It should also be noticed that the composite cross-linked films were prepared in air and atmospheric humidity conditions on purpose, to approach the real conditions which will be used in practical (industrial) applications for which these composite films will be used.

The cross-linked films were prepared varying separately three different parameters: the concentration of the garnet particles, the initial concentration of the cross-linker in the PDMS dispersion or the concentration of the Pt catalyst. Table 1 gives an overview of the cross-linked materials prepared and the corresponding nomenclature. For comparison, PDMS films without particles were also prepared using the same experimental conditions [17].

### 3.1. *Cross-linked composite films morphology: SEM characterization*

To investigate the homogeneity of the films in terms of particles dispersion, Scanning Electron Microscopy (SEM) analyses were performed. In Fig. 1 a representative example of the SEM images obtained for the cross-section of cross-linked composite films, prepared from starting formulations with H/V = 2.7 is shown. For comparison, one SEM image of the initial garnet particles is included.

The images collected for the cross-section of composite films showed that the garnet particles are homogeneously and individually dispersed in depth, independently of: 1) the thickness of the film, 2) the concentration of the garnet (up to 20% v/v in relation to PDMS) and 3) the concentration of the cross-linker in the starting formulation.

From Fig. 1 it can also be seen that no aggregates were identified through the depth of the films, neither at the air/film or film/substrate interfaces, even when the concentration of the garnet was increased to 20% v/v. This was further confirmed by FIB (Focused Ion Beam)-SEM analyses of slices cut-off from the film/substrate interface to a depth of approximately 10 μm (not shown). These results indicated that the formulations used were suitable to prepare homogeneous cross-linked composite garnet/PDMS films.

During the preparation of the composite films it was observed that a large excess of cross-linker was needed in the formulations (H/V = 1.0 formulations were sometimes remaining fairly viscous during many days) to obtain stable and flexible cross-linked materials, which could be easily handled as free films. This observation suggested an effect of the garnet on the cross-linking of the films and triggered further studies on composite cross-linked PDMS films. The results obtained will be discussed in the following sections.

### 13.2. *Garnet particles effect on the cross-linking reaction: ATR-FTIR Spectroscopy*

Previously we reported the use of ATR-FTIR Spectroscopy and Confocal Raman Microscopy (CRM) to follow *in situ* the cross-linking of PDMS17 films and monitor simultaneously, the consumption of the silane groups of the cross-linker and of the double bonds of PDMS [17]. We have shown that when PDMS films were cross-linked at 25 °C in air and atmospheric humidity conditions, from formulations of PDMS17 with $H/V \geq 1.0$, hydrosilylation (Eq. (4)) and secondary reactions (Eq. (5) and (6)) occur simultaneously at early stages of the cross-linking process. Secondary reactions have been previously reported for similar PDMS systems and were suggested to occur in the presence of water and oxygen [23]. In Eq. (2)–(6) only the relevant functional groups are shown and R, R′ represent generically the remaining composition of the reactant species.

$$R{-}Si{-}H + CH_2{=}HC{-}Si{-}R' \xrightarrow{\text{Catalyst,Heat}} R{-}Si{-}CH_2{-}CH_2{-}Si{-}R' \tag{2}$$

$$R{-}Si{-}H + H_2O \xrightarrow{\text{Catalyst,Heat}} R{-}Si{-}O{-}H + H_2 \tag{3}$$

$$2R{-}Si{-}H + O_2 \xrightarrow{\text{Catalyst,Heat}} 2\,R{-}Si{-}O{-}H \tag{4}$$

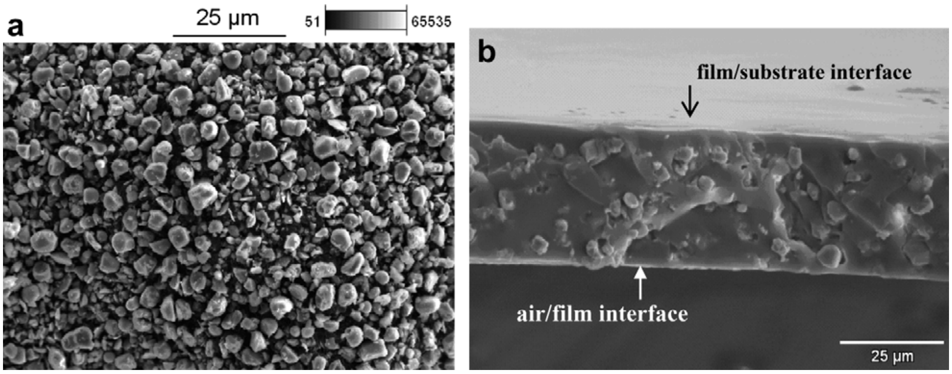


**Fig. 1.** Typical SEM images of: a) $Y_3Al_5O_{12}$ garnet doped with Cerium (as supplied by Philips) and b) cross-section of a PDMS films (free films detached from PC substrates) with 20% volume of garnet (G20-HV2.7-Pt20).

The Si–OH groups formed by the secondary reactions can react further with each other (Eq. (5)) or with silane groups of the cross-linker (Eq. (6)) adding *–Si–O–Si–* cross-links to the cross-linked network [23].

$$\mathrm{R{-}Si{-}OH} + \mathrm{H{-}O{-}Si{-}}R' \xrightarrow{\mathrm{Heat}} R\mathrm{{-}Si{-}O{-}Si{-}}R' + \mathrm{H_2O} \tag{5}$$

$$\mathrm{R{-}Si{-}OH} + R'\mathrm{{-}Si{-}H} \xrightarrow{\mathrm{Catalyst,Heat}} R\mathrm{{-}Si{-}O{-}Si{-}}R' + \mathrm{H_2} \tag{6}$$

In the present work, we use the same ATR-FTIR Spectroscopy approach to follow the consumption of the silane groups of the cross-linker during the cross-linking of PDMS17 films under air and humidity conditions in the presence of the garnet particles. For this purpose, two main parameters were varied for the initial formulations: the concentration of the cross-linker and the concentration of the garnet. The results obtained for the *in situ* studies will be discussed in the following sub-sections.

### 3.2.1. Garnet effect on formulations with an excess of cross-linker

Fig. 2 shows the concentration of the Si–H groups of the cross-linker during the cross-linking of formulations with 10% (v/v) of garnet and different H/V ratio.

A first observation from Fig. 2 is that a considerable amount of silane groups is leftover in the cross-linked films with garnet, after the point where the C=C bonds should have been completely consumed (horizontal lines from Fig. 3). The films used for the cross-linking *in situ* ATR-FTIR studies, with 10% (v/v) of garnet and H/V ≥ 1.7, were carefully detached from the Infrared crystal of the Golden Gate accessory, and kept at room temperature for one month. After this period the Si–H concentration for the films with garnet particles was measured. The remaining Si–H concentration decreased considerably after 1 month (see Fig. 2). These results indicate that in the PDMS17 formulations with garnet particles the Si–H groups are being consumed by hydrosilylation and secondary reactions, which most likely occur simultaneously and at very early stages of the cross-linking process. In fact, this was shown before for PDMS17 formulations, without garnet [17]. It was also shown that the Si–H groups remaining in the material after all the double bonds are consumed, react further through secondary reactions, most probably with water and oxygen [17], adding –Si–O–Si– cross-links to the cross-linked network (Eq. (3)–(6)).

Another important observation from Fig. 2 is that for all the formulations with garnet, the overall consumption of the silane groups occurs slower. The decrease is extremely accentuated when formulations with H/V ≥ 1.7 were used. These results suggested an interaction of the garnet with one or more components of the cross-linking formulation which slows down both, the hydrosilylation and the secondary reactions occurring during the cross-linking process. This possible interaction is further supported by the absence of an initial induction period (Fig. 3), which suggests a two step reaction for the cross-linking process in the presence of the garnet, whereas for PDMS formulations without garnet a three step process was previously reported [17]. These observations strongly suggest an interaction between the garnet and the catalyst and/or cross-linker. The nature of this interaction and its effect on the cross-linking process are discussed in the next sub-section.

In order to investigate further a possible interaction of the garnet with the cross-linker and/or the catalyst some experiments were made (Scheme 2). A mixture of PDMS, garnet and cross-linker was prepared. The mixture was left under stirring for a long period. After this mixing period, the particles were thoroughly washed with toluene, which is a good solvent for PDMS and the cross-linker. The garnet was collected by high-speed centrifugation and dried. The washed garnet was finally re-dispersed in PDMS. Upon addition of a Pt catalyst solution to this dispersion no cross-linking was observed (*route* 1). The mixture remained a viscous liquid after weeks at room temperature, even after an extra addition of catalyst. The supernatant collected did however cross-link after addition of a catalyst solution (*route* 1′). This clearly indicates that no cross-linker was available in the washed garnet fraction to cross-link the PDMS added.

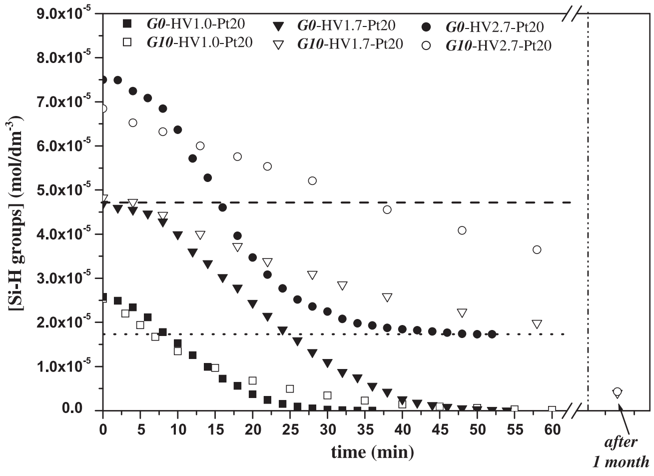


**Fig. 2.** Concentration of the Si–H groups of the cross-linker as a function of measuring time, for films with 0 and 10% (v/v) of garnet, prepared with different H/V ratio. See samples nomenclature in Table 1. The cross-linking reaction was done at 25 °C, in air and atmospheric conditions. (*Horizontal lines*: Si–H groups 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: *dots*) H/V = 1.7; *dashes*) H/V = 2.7).

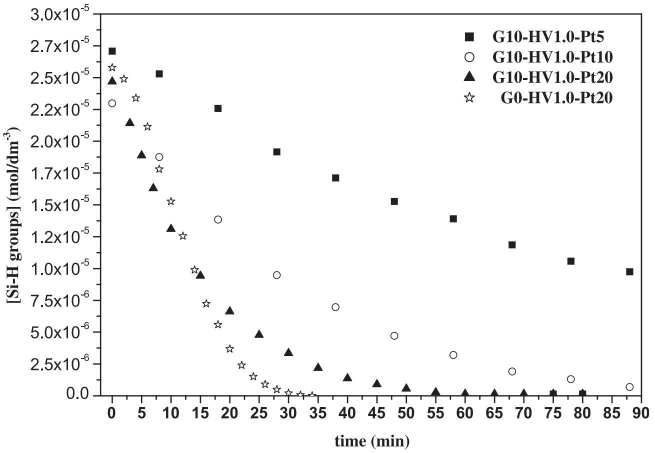


**Fig. 3.** Concentration of the Si–H groups of the cross-linker as a function of measuring time for films with 10% (v/v) of garnet, prepared with different initial concentrations of catalyst, and H/V = 1.0. The cross-linking reaction was carried at 25 °C and in air and atmospheric humidity conditions. The nomenclature of the films is described in Table 1.

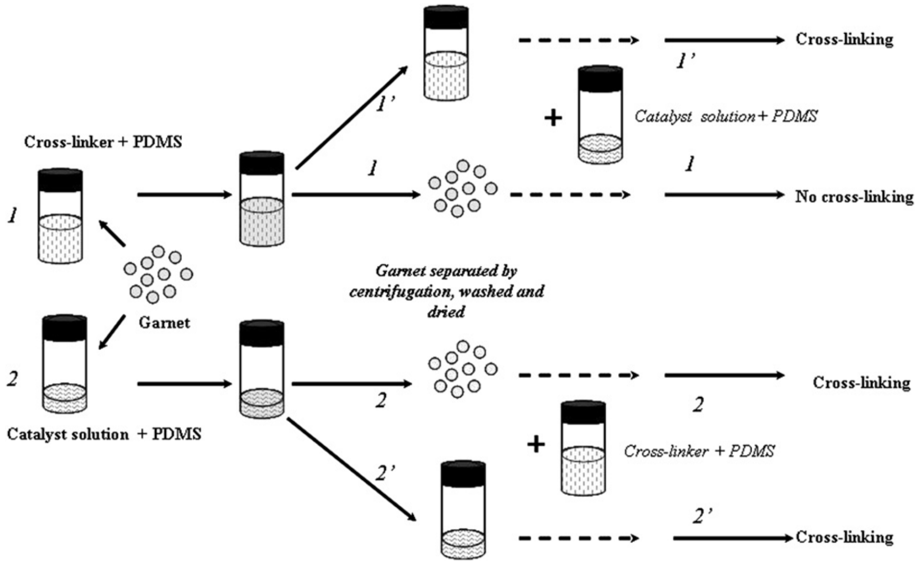
A similar experiment was made to test the interaction of the cross-linker with the Pt catalyst (Scheme 2, *route* 2). The garnet particles dispersed in PDMS were in contact with the Pt catalyst for a long period and the same washing and drying procedure described above was followed. It should be noticed that toluene is a good solvent to the Pt catalyst as well. Upon final addition of cross-linker to a dispersion of the washed garnet in PDMS, the mixture was completely cross-linked after approx. 30 min, indicating the presence of catalyst in the washed garnet, even after the extensive washing and drying procedure (*route* 2). The supernatant collected was also cross-linked upon addition of cross-linker (*route* 2′).

Due to the very small amount of catalyst used in the initial mixture, it was not possible to quantify the amount of Pt remaining at the particles surface. Nevertheless, these tests are a clear indication that there is a strong interaction between the Pt catalyst used in these formulations and the garnet. A sufficient amount of active catalyst was present in the washed garnet to cross-link the final dispersion (to which no extra catalyst was added). This interaction is probably responsible for the decrease of the overall consumption rate of the silane groups observed with the ATR-FTIR measurements. The rates of the cross-linking reactions are strongly dependent on the type and concentration of the catalyst. Moreover the active form of the catalyst and a possible formation of a complex with the cross-linker has been actively discussed in the literature. The interaction of the garnet with the catalyst could have an effect either on the concentration of the catalyst or on the formation of active/inactive forms of the catalytic species [24–27], as will be discussed later.

From this experiment we cannot exclude the possibility of interaction between the cross-linker and the particles. However, if this is the case, the remaining cross-linker was not in an active form or not enough concentrated, to cross-link the final mixture with the garnet. In fact, it has been previously reported that when a low concentration of reactive groups (either silane or vinyl groups) is reached (approx. $8 \times 10^{-3}$ mol reactive groups/dm$^3$) the hydrosilylation reaction becomes inactive [28,29]. Nevertheless, this experiment suggested that the interaction of the garnet with the cross-linker is weak, and therefore it is unlikely to be responsible for the decrease of the overall rate of Si–H consumption observed in the ATR-IR measurements.

To investigate further the interaction of the garnet with the catalyst, the cross-linking of formulations with 10% v/v of garnet and different initial concentration of catalyst was followed by *in situ* ATR-FTIR. To avoid the influence of the cross-linker concentration [17] a constant H/V = 1.0 was chosen for all formulations. From Fig. 3 it can be seen that decreasing the initial concentration of the catalyst in the formulations containing the garnet, slows down the overall consumption of the Si–H groups. By decreasing the Pt concentration in the bulk, a lower amount of catalyst is available to the overall cross-linking process, (hydrosilylation and secondary reactions). Moreover, it should also be noticed that an initial induction period was also not observed for any of these formulations, and a two step cross-linking process is suggested.

Although these experiments give further support to an interaction of the garnet with the catalyst, the results can only be interpreted quantitatively if the same study would be made on PDMS samples without garnet and different amounts of catalyst. However, the interpretation of the quantitative data and the comparison with the composite films would be impaired by



**Scheme 2.** Scheme of the experiments made to test the interaction of the garnet particles with: *route* 1) cross-linker and *route* 2) catalyst used in the current formulations.

simultaneous occurrence of secondary reactions, as reported before [17]. Moreover in this particular case the presence of the garnet may introduce additional side reactions which could not be accounted for. Instead, we decided to study the cross-linking process in similar PDMS formulations, in the presence of different concentrations of the garnet.

### 3.2.2. *Garnet concentration effect*

The variation in time of the concentration of the Si–H groups of the cross-linker in formulations with different concentrations of the garnet and a constant concentration of the Pt catalyst is shown in Fig. 4. For comparison the result obtained with a similar formulation without garnet is included [17].

From Fig. 4 it can be seen that, in the presence of the garnet, the overall consumption of the cross-linker proceeds slower as compared to the similar PDMS17 formulation cross-linked in the absence of particles, as described above. Moreover, as the amount of the garnet increases, for the same formulation conditions, the overall Si–H consumption rate decreases. This slowdown effect is more evident for the films with a higher amount of garnet in the initial formulation (20% v/v). Considering the possibility discussed above, of interaction between the garnet particles and Pt catalyst, as the garnet concentration increases (in formulations with constant amount of catalyst) a higher amount of catalyst will be interacting with the particles surface and therefore a slowdown of the overall cross-linking process was expected.

From the experiments made within this work it is not possible to conclude about the nature of the interaction between the catalyst and the particles. Detailed experiments on the determination of the Pt concentration and catalytic complex forms would be needed, which we consider to be out of the scope of this study. We can, however, discuss possibilities.

An active debate concerning the hydrosilylation mechanism, namely the possibility of homogeneous or heterogeneous catalysis, is still ongoing in the related literature [24]. The Chalk–Harrod mechanism reported for catalytic species of transition metal complexes [25] has been accepted for this reaction for a long time. However, this mechanism could not explain some facts observed during the reaction, such as the induction period, the requirement of oxygen or the appearance of color (brown). In the late 80′s, Lewis et al. [26] proposed a heterogeneous catalytic process in which the induction period was attributed to the formation of an active form of platinum colloids $Pt^0$. Later on, Lewis [27] proposed several roles for the requirement of oxygen in the reaction: 1) prevent colloid agglomeration and formation of larger particles, which have reduced activity and are responsible for the appearance of color, 2) make the Pt–Si–H complex more electrophilic and therefore more prone to the nucleophilic attack of the double bond and 3) to act as a weak ligand, holding a coordination site between the hydrosilylation cycles.

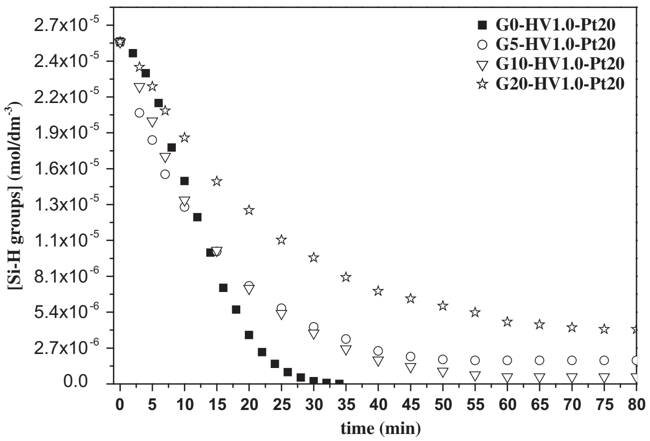


**Fig. 4.** Concentration of the Si–H groups of the cross-linker as a function of the measuring time, for films prepared with initial H/V = 1.0 and with different concentration (v/v) of garnet. The cross-linking was carried at 25 °C in air and atmospheric humidity conditions. The nomenclature of the films is explained in Table 1.

For the catalyst used in the current work, there are no studies available in the literature to support either a heterogeneous or homogeneous catalysis. Nevertheless, for $Pt^{II}$ based catalysts the heterogeneous route has been frequently reported. In this case the formation of a catalytic complex with the cross-linker or of Pt colloids would be strongly affected by an interaction of the catalyst with the garnet particles, and this could be a possible explanation for the decrease observed in the rate of the cross-linking process and absence of an induction period. Firstly, if the active form of Pt catalyst would interact with the garnet surface it would not be readily available to the cross-linking reactions. Secondly, if the $Pt^0$ colloids are formed at the surface of the particles they would also be less accessible to the bulk reactants. Finally, it should be mentioned that several authors [11,27] reported that nucleophiles such as R′-OH, can interact with the catalyst/cross-linker complex, regenerating the active form of the catalyst ($Pt^0$) [27]. This secondary reaction could be another possible explanation for the interaction observed in the current work between the catalyst and the garnet, which is an inorganic oxide and therefore very likely to have hydroxyl groups at the surface.

Although the data from the ATR-FTIR studies strongly suggest an interaction of the catalyst with the garnet particles, it should also be noticed that the viscosity of the initial formulations is different for each formulation due to the presence of the particles. Moreover the progressive build-up of the cross-linked network might have a different effect in each case, because the diffusion of the reactants is also affected. The reactive groups of the cross-linker and PDMS will be hindered by the presence of the particles which are entrapped in the cross-linked structure formed in the bulk of the film. In fact, the higher the concentration of the particles, the slower the reaction proceeds. Hence, this additional effect should not be disregarded, but it should be pointed out that for all the formulations with garnet (and initial H/V = 1.0), the silane groups were almost fully consumed within the time of the measurement. This is an indication that the effect of viscosity is not strongly affecting the cross-linking reactions.

In industrial applications PDMS-based films are frequently cross-linked at high temperatures, with high concentration of catalyst and cross-linker, in order to achieve a certain cross-linking density, or accelerate the films preparation procedures. The experiments described above, were repeated at higher temperature (60 °C, not shown in this paper). The effects observed at 25 °C were extremely accentuated. The cross-linked networks are formed very rapidly and the slow reaction stage [17] is achieved very early in the cross-linking process (in a few minutes).

The results reported herein are extremely relevant considering that these cross-linked composite films might be used in applications which will require some flexibility and long time stability under high temperatures and humidity conditions, i.e. for high power LEDs. Light conversion experiments were made on these materials and its thermal behavior was studied. All the prepared films emitted white light upon irradiation with a commercial blue LED, see example in graphical contents image. Detailed studies on the optical and thermal properties of these cross-linked films are reported elsewhere [30]. The changes in the network structure, caused by the additional cross-links or by the further reaction of the reactive groups leftovers, can result in increasing brittleness, coloring, phase segregation or other defects, which leads to failure of the product/device and low performance in long operation times. For this reason we also investigated the effect of the garnet on cross-linked networks formed on the composite films. The results obtained will be discussed in the following section.

### *13.3. Effect of the garnet on the cross-linked composite films network structure: NMR imaging*

In previous work [17] we used NMR imaging to study the networks formed on PDMS films cross-linked from formulations with different concentrations of cross-linker. In the current work, NMR Imaging was used to study composite PDMS materials, cross-linked from similar formulations, but containing different concentrations of garnet. The relaxation of the transversal magnetization in the composite cross-linked films was studied as a function of the depth of the films. To investigate the effect of the garnet on the network structure formed, cross-linked films were prepared from PDMS17 formulations with 10 and 20% v/v of garnet; and three initial H/V ratios = 1.0, 1.7 and 2.7.

In Fig. 5 typical decay curves for the transversal magnetization observed for films cross-linked from formulations containing 10% v/v of garnet and with H/V = 1.0, 1.7 and 2 are shown. The magnetization decays were taken from an average middle position in the depth of the composite cross-linked films.

The relaxation process was characterized with more than one relaxation time ($T_{2,i}$ in Eq. (7)), and the data were fitted with a bi-exponential function (Eq. (7)) where $T_{2,s}$ and $T_{2,f}$ are the time constants for the slow and fast components of the relaxation process,

$$S \approx S_\infty + S_f \exp\left(-t/T_{2,f}\right) + S_s \exp\left(-t/T_{2,s}\right) \quad (7)$$

and $S_s$ and $S_f$ parameters are the slow and fast contributions to the signal of these components. The parameter $S_\infty$ represents the noise level in the experiment.

In Fig. 6 the relaxation times are plotted as a function of the film depth using Eq. (7). The vertical dotted lines refer to the material interfaces: the air/film interface (left) and the film/glass interface (right).

The first observation from Fig. 6, is that the $T_2$ values are nearly constant throughout the cross-linked films for all the materials made from formulations with different H/V ratios and the same garnet concentration. This indicates that the cross-linking of these PDMS17 materials in the presence of the garnet is homogeneous through the bulk of the film and that the network structure does not vary in depth. This means that the cross-linked composite PDMS materials can be regarded as homogeneous throughout the thickness of the composite films, on length scales larger than 5 μm (NMR resolution).

The second conclusion that can be drawn from Fig. 6 (and Fig. 5), is that the $T_2$ values measured for films cross-linked from formulations with different concentrations of garnet and H/V ratios do not differ significantly from each other. This suggests that for a constant concentration of garnet, similar cross-linked networks are formed, regardless of the cross-linker amount in the initial formulations. It should be noticed that, several composite cross-linked films were prepared at different locations and times, and the same behavior was always observed attesting the reproducibility of these results.

From our previous results with PDMS cross-linked films [17], it was expected that the presence of the garnet would influence mainly the films cross-linked from formulations with H/V = 1.0. This is confirmed by the data shown in Fig. 6. Whereas adding the garnet does not influence the signal relaxation in the case of H/V > 1.0, adding garnet dramatically reduces the relaxation times in the case of H/V = 1.0. Interestingly, when the films are cross-linked from a formulation with H/V = 1.0 in the presence of garnet, the

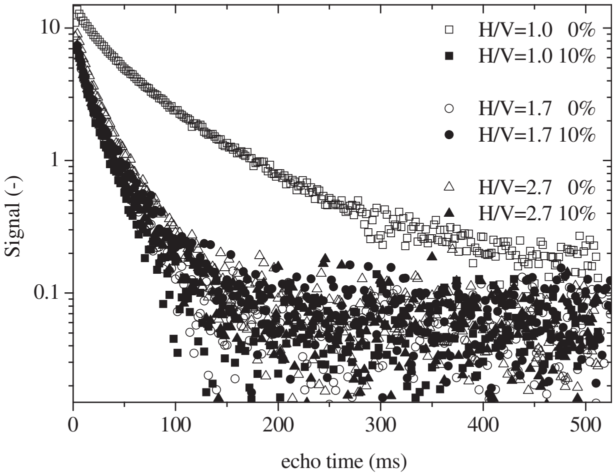


**Fig. 5.** Decay curves of the transversal magnetizations on PDMS17 materials cross-linked from formulation with H/V = 1.0, 1.7 and 2.7 and 10% v/v of garnet.

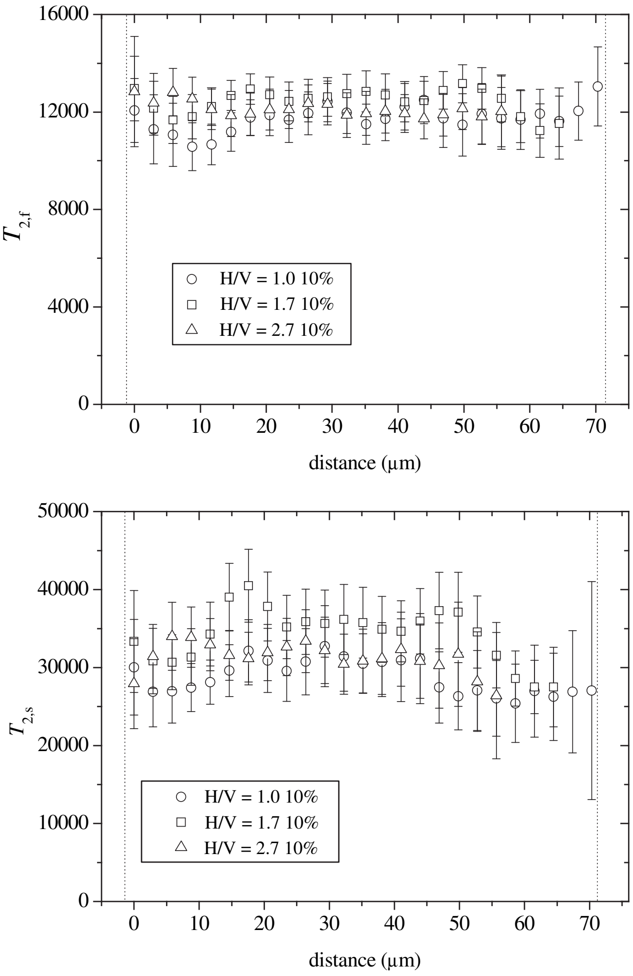


**Fig. 6.** Fast and slow relaxation rates $T_{2,f}$ and $T_{2,s}$ plotted as a function of the position in the material. Measurements are shown for materials cross-linked from formulations with 10 v/v of garnet, and H/V = 1.0, 1.7 and 2.7. The vertical dotted lines refer to the material interfaces: the air/material interface (left) $x = 0$ and the material/glass interface (right) (see SEM image on Fig. 1).

relaxation of the protons is much faster, indicating that the overall motion of the protons is slowdown.

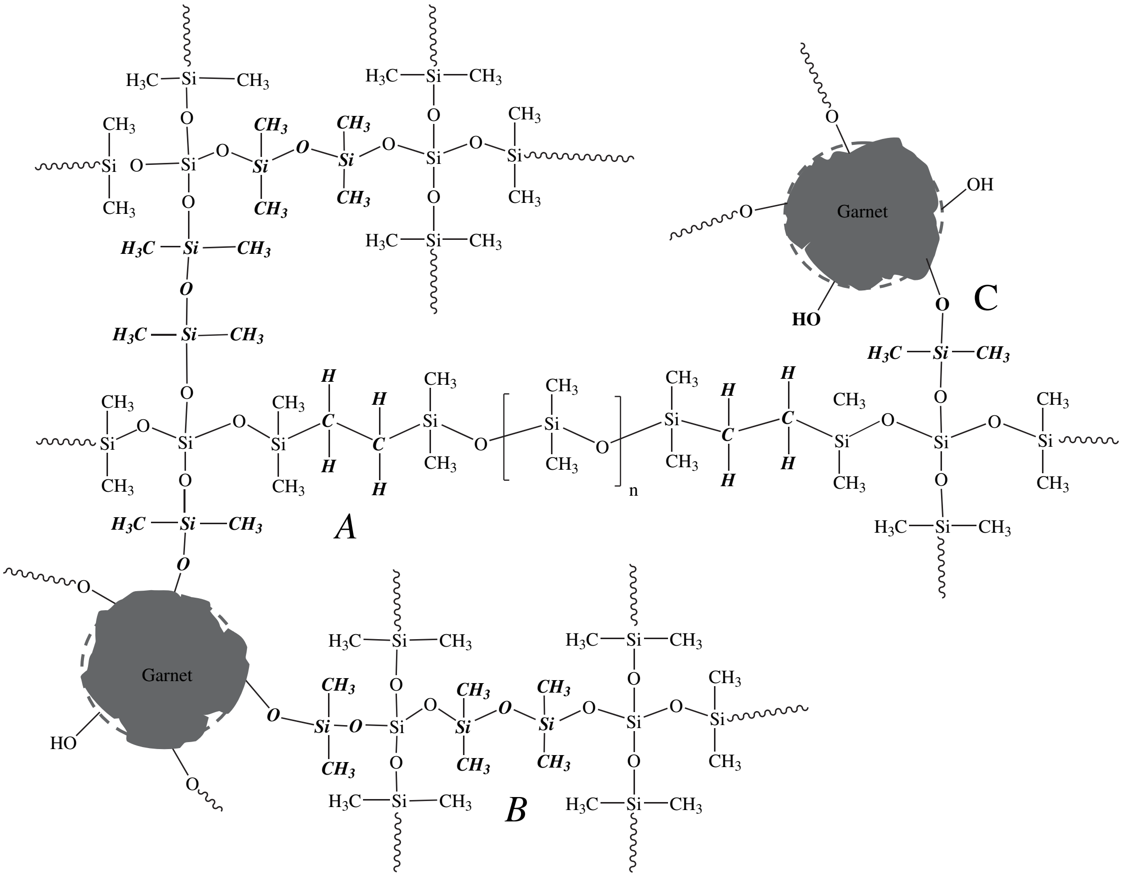
In previous work a large percentage of the material not connected to the main network was reported in PDMS films cross-linked from a starting formulation with H/V = 1.0. For the films cross-linked from formulations with H/V = 1.7 and 2.7, before and after being submitted to extraction, as well as from H/V = 1.0 after extraction, very similar decay curves were found. This was 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 seem to counterbalance each other at different H/V ratios, in the network structure [17] (Scheme 3).

From the current NMR studies the relaxation behavior of composite cross-linked films seems to be independent of the cross-linker amount used in the starting formulation. This indicates that in the film cross-linked with H/V = 1.0 a very small percentage of material non-connected to the main network is expected. This can be due to the following explanations.

From the IR experiments it was suggested that an interaction of the garnet with the Pt catalyst has a strong effect either on the concentration or on the active form of the catalytic species available in the formulation. Hence the consumption of the Si–H groups of the cross-linker proceeds slower and the Si–H groups are available in the bulk for a longer period, promoting secondary reactions [17] and the formation of additional –Si–O–Si– cross-links (Scheme 3).

Therefore for films cross-linked with H/V = 1.0 in the presence of particles, the hydrosilylation reaction proceeds slower, the secondary reactions became more relevant and cross-linked networks similar to the ones obtained from formulations with H/V ≥ 1.7 are formed. Furthermore, the presence of particles might introduce additional humidity in the system as well as hydroxyl groups, which can react with the Si–H groups of the cross-linker (Eq. (4) and (5)) forming additional cross-links (Scheme 3 A and B). Many other authors reported composite films made from cross-linked PDMS and oxide fillers, e.g silica [15,31] and clays [16], in which chemical bonds are established between the polymer and hydroxyl groups at the fillers surface. In the current case this would result in chemical bonds between the cross-linked network and the garnet particles and therefore, less non-bonded material in the overall cross-linked film.

In order to confirm this explanation, extraction experiments were made to try to remove the material non-bonded to the cross-linked networks. Unfortunately, it was observed that for the extraction procedure used the data obtained were not reproducible. One fact that may contribute to this irreproducibility is the random access of the solvent to the bulk of the composite cross-linked films, due to the presence of the micrometer-sized particles and differences in the swelling degree of the films, resulting in variable extractable fractions and solvent leftover in the bulk of the film. A very small solid residue was observed on the extracted fractions (solvent), indicating the presence of garnet particles (easily recognized by the yellow color). It should be noticed however, that after an extensive extraction procedure to which the cross-linked composite films were submitted, the residual amount of colored solids was negligible and the majority of the garnet particles remain in the film. This constitutes another good indication of the presence of chemical bonds between the garnet particles and the polymeric chains cross-linked in the polymer network. However,



**Scheme 3.** Schematic representation of the possible "network fragments" on the cross-linked networks formed in the presence of the garnet, showing the different chemical cross-links formed: A) $-CH_2-CH_2-$ polymer chain; B) –Si–O–Si– cross-linker/polymer and C) –Si–O–Si– cross-linker/particle. Physical cross-links and are not considered in this scheme.

for a quantitative analysis of the extracted fractions an adequate extraction procedure would have to be optimized for the composite materials. This would require extended extraction experiments which we consider to be outside of the scope of the current paper.

## 4. Conclusions

PDMS cross-linked films containing different concentrations of garnet particles were prepared from starting formulations with different concentrations of cross-linker. SEM analyses of the composite cross-linked films have shown that regardless of different starting formulations or thickness of the composite film, the particles are homogeneously and individually distributed through the depth of the film up to 20% v/v of the garnet particles. Hence, the cross-linked materials prepared show a great potential to be used in solid state light devices, i.e. high power LEDs. Further studies on the performance of these cross-linked materials in terms of optical and thermal properties are reported somewhere else [30].

From the IR experiments on composite films, cross-linked at 25 °C under air and atmospheric humidity conditions, from starting formulations with different concentration of particles, cross-linker and catalyst amount, it was observed that the presence of the particles slowdown the overall cross-linking process. This effect was attributed to an interaction between the garnet particles and the Pt catalyst used, which has an effect either on the concentration or on the nature of the active catalytic species available in the bulk during the cross-linking process. The presence of the garnet particles strongly influences the hydrosilylation reaction in the earlier stages of the cross-linking process but also the secondary reactions occurring in the system, possibly with oxygen and water.

Several authors studied the influence of the presence of fillers with different sizes, within the nano and micrometer range, in the networks formed as well as on the final cross-linked PDMS materials physical properties [14,16,32,33]. However, only a few indirect studies have reported potential effects on the cross-linking behaviour, based on the physical characterization of the final cross-linked networks [34]. To the best of our knowledge, the effect of the fillers on the chemistry of the cross-linking reactions has not been addressed before in the open literature, using our current *in situ* methodologies.

NMR imaging studies on films cross-linked at higher temperature (60 °C) showed that the cross-linked films are homogeneous (across the whole film thickness) on a length scale of 5 µm, for different H/V ratios and concentrations of particles. Moreover, the NMR imaging experiments confirmed an influence of the presence of the garnet on the cross-linked networks formed. The relaxation behavior of the films cross-linked from different starting formulations is similar. For the film made from a formulation with $H/V = 1.0$, a large amount of non-bonded material was expected, and therefore a different behavior on the proton relaxation should have been observed. The fact that all the films show the same relaxation behavior suggests that in the presence of the garnet the secondary reactions became more relevant and at least two different chemical cross-links ($Si{-}CH_2{-}CH_2{-}Si$ and *Si–O–Si*) are present in all the cross-linked films. This is a further indication of the interaction of the catalyst with the garnet. As the consumption of the Si–H groups proceeds slower they are available to the secondary reactions for a longer period. Moreover, the Si–H groups can react with O–H groups at the surface of the garnet, or with water introduced through the particles presence and the fillers will promote additional polymer-particles cross-links and interactions, as reported by other authors [32], which can result in lower amount of non-bonded material.

The current work clearly shows an influence of the presence of micrometer-sized garnet particles on the cross-linking of PDMS materials and on the networks formed thereafter, by an interaction of the particles with other components of the formulation, i.e. catalyst. This work provides useful data for the optimization of PDMS formulations with inorganic particles, namely garnet, to be used on the preparation of cross-linked materials for optical applications, in order to obtain stable materials which will perform better on long time operation, under high temperature, air and atmospheric humidity conditions.

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