HYPERELASTICITY MODELING FOR THERMALLY AGED SILICONES

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ABSTRACT

Two families of Room Temperature Vulcanized PDMS with different hardness were thermally aged. Mechanical properties were monitored by tensile tests and macromolecular architecture was followed by differential scanning calorimetry (crystallization) and sol gel analysis (swelling degree). Data showed that PDMS display a loss of plasticity due to a crosslinking process. The main novelty was to describe mechanical behavior by a hyperelastic so called Ogden's model whose coefficients were correlated with macromolecular properties and then ageing degree. The model coefficients were also used to derive an embrittlement criterion.

KEYWORDS

Silicone Rubber, thermal ageing, mechanical properties, crosslinking

1. INTRODUCTION

Room temperature vulcanization (RTV) silicone rubbers are commonly used in the biomedical field. They are obtained by blending vinyl terminated PDMS linear polymers with a PDMS containing some hydrosilane groups. The reaction between hydrosilane and vinyl is catalyzed by organoplatinum molecules and forms an insoluble network.

The thermal stability of PDMS has been extensively studied in the literature. TGA studies were performed under nitrogen or oxygen atmosphere. Thanks to the coupling of TGA with analysis of volatiles compounds, the degradation mechanisms were betted understood [1,2]. Under inert atmosphere, an "unzipping" mechanism possibly by concerted rearrangement occurring in random position of the PDMS chains was proposed. Under air, the same kinds of volatiles species are observed [1], but the presence of oxygen seems to induce some increase in crosslink density The effect of aromatic comonomers [3], or fillers was also illustrated [4,5].

Only a few papers deal with isothermal degradation. Lacoste and coll [6] investigated the thermal degradation of PDMS based copolymers, in which a significant oxidation was observed

possibly due to the aliphatic nature of comonomers. Other illustrate the modeling of joint radio thermal aging [7]. It seems clear that ageing under air induces a crosslinking mechanism leading to increase in elastic moduli, and decrease in ultimate strain [8]. The effect of chemical changes on mechanical properties constitutes the missing link in predicting the lifetime of thermally aged PDMS. A recent paper [9] illustrated the link between mass loss and elastic modulus increase but this remains to be generalized. In particular, the identification of the critical state corresponding to the loss of mechanical properties and/or the existence of a causal chain allowing the embrittlement to be predicted remains an open question.

To answer to those questions, this paper aims at:

- Perform thermal ageing at various temperatures on PDMS differing by their initial crosslink densities, commonly described by their hardness.

- Perform a multiscale monitoring of ageing so as to identify the nature of macromolecular change.

- Propose the relationship between structure to link macromolecular changes and drop of mechanical properties.

2. EXPERIMENTAL

2.1. Samples Preparation

RTV silicones obtained by mixing part A ("base") and part B ("catalyst") i.e. PDMS chains functionalized by hydrosilane and PDMS functionalized by vinyles. Pt catalyst is present in only one of the parts so that reaction starts when part A and part B are mixed. Samples were manufactured in 2 mm thick samples according to ISO 527-2 5B standard by injecting parts A and B into acrylic 3D printed molds. Two PDMS grades differing by their hardnesses (15A and 30A) are investigated here. Some details are given in **Supplementary Information**. Dogbones samples were aged and analyzed by mechanical testing. Some other were used for DSC, gravimetry and sol gel analysis.

The heterogeneity due to diffusion-limited oxidation will not be considered in the following. One thing to note is that the oxygen diffusivity in PDMS is almost 10 to 100 times higher than any other rubber [10] meanwhile those rubbers degrade quite slowly compared to other polymers [11]. The original densities of both materials were measured to be 1.100 for PDMS 15A and 1.113 for PDMS 30A.

2.2. Ageing procedures

Samples were isothermally aged under air at various temperatures (180, 200, 220 and 250°C) in ventilated ovens (AP60, System Climatic France). Isothermal ageing durations ranged from 4h-30h (for ageing at 250°C) to about 1 year (for ageing at 180°C).

2.3. Characterization methods

2.2.1. Tensile tests

Samples were made in dog bone shape according to ISO 527-2 – 5B. The testings were performed by Instron 4301 tensile machine with a 100 N load cell. The testing speed was set at 10 mm.min^{-1} elongation rate. 3 samples were tested per condition.

2.2.2. Sol gel analysis

Samples (m_0 about 100 mg) were immerged in toluene. After 72 h, the swollen mass $m_{swollen}$ was estimated. NB: this duration was verified to correspond to the equilibrium for solvent ingress. Samples were thus left and the mass of dried samples m_{dried} corresponding to the insoluble network was measured after 24h drying. Data were used to estimate:

The swelling ratio:

$$SR = \frac{m_{swollen} - m_{dried}}{m_{swollen}} \quad (1)$$

The soluble fraction:

$$SF = \frac{m_0 - m_{dried}}{m_0} \quad (2)$$

2.2.3. Differential Scanning Calorimetry

Approximately 10 mg of sample was analyzed using a Q1000 DSC device (TA Instruments). The samples were placed in sealed aluminum pans, cooled from room temperature to -85°C, and then heated to -40°C. DSC cell was continuously purged by a nitrogen flow of 50 ml min^{-1}. Data were processed using TA Analysis software. The DSC was calibrated with an indium standard before the experiment.

2.2.4. Gravimetry

Samples (initial mass 0.5 – 1 g) were regularly weighted after ageing using an AT261 DeltaRange balance (Mettler Toledo) with an accuracy higher than 0.1 mg meaning that the uncertainty is lower than 0.01%.

2.2.5. Thermogravimetric analysis

TGA measurements were performed using a Q500 apparatus driven by QSeries Explorer (TA Instruments). Isothermal measurements were performed under 100% N_2 atmosphere supplied by a continuous 50 ml min^{-1} gas flow. Isothermal degradation was performed at a constant

temperature equal to 500°C. Papers dealing with anisothermal degradation monitored by TGA under nitrogen [1,2] suggest that (i) onset of mass loss curves is close to 500°C and (ii) cyclic oligomers are released, in line with an unzipping mechanim. This is the reason why this temperature was chosen. It is possible that the same mechanism occurs at lower temperature, but in a timescale unsuitable with simple lab tests.

3. RESULTS

3.1. Changes of mechanical properties during thermal ageing

Figure 1 displays stress-strain curves for virgin and degraded PDMS after ageing at 180°C under air (**Figures 1a** and **1c**) and after ageing at 250°C (**Figures 1b** and **1d**). At first, it is clear that ageing induced the same kind of consequences either for PDMS 15A and for PDMS 30A. Identically to literature [12,13,14,15,16], curves for unaged polymers display a hyperelastic behavior with two domains: one corresponding to low strains (typically < 200 %) and another associated to high strains (typically > 500%). The possibility of Stress Induced Crystallization was rejected for two reason: first, according to previous papers, this phenomenon occurs at very low temperature [17], and secondly, SIC is expected to disappear in the case where ageing induces crosslinking [18] (which is the case here, as it will be seen later). Basing on a previous work by Mark and coll [19], the « low strain domain » would correspond to the presence of long elastically active chains whereas the « high strain domain », would express the presence of shorter chains. In the « intermediate » domain, we guess that mechanical behaviour for instance at 300% is the same than at 100 or 200% since elastic modulus value are very close and linked to the stretching of long chains.

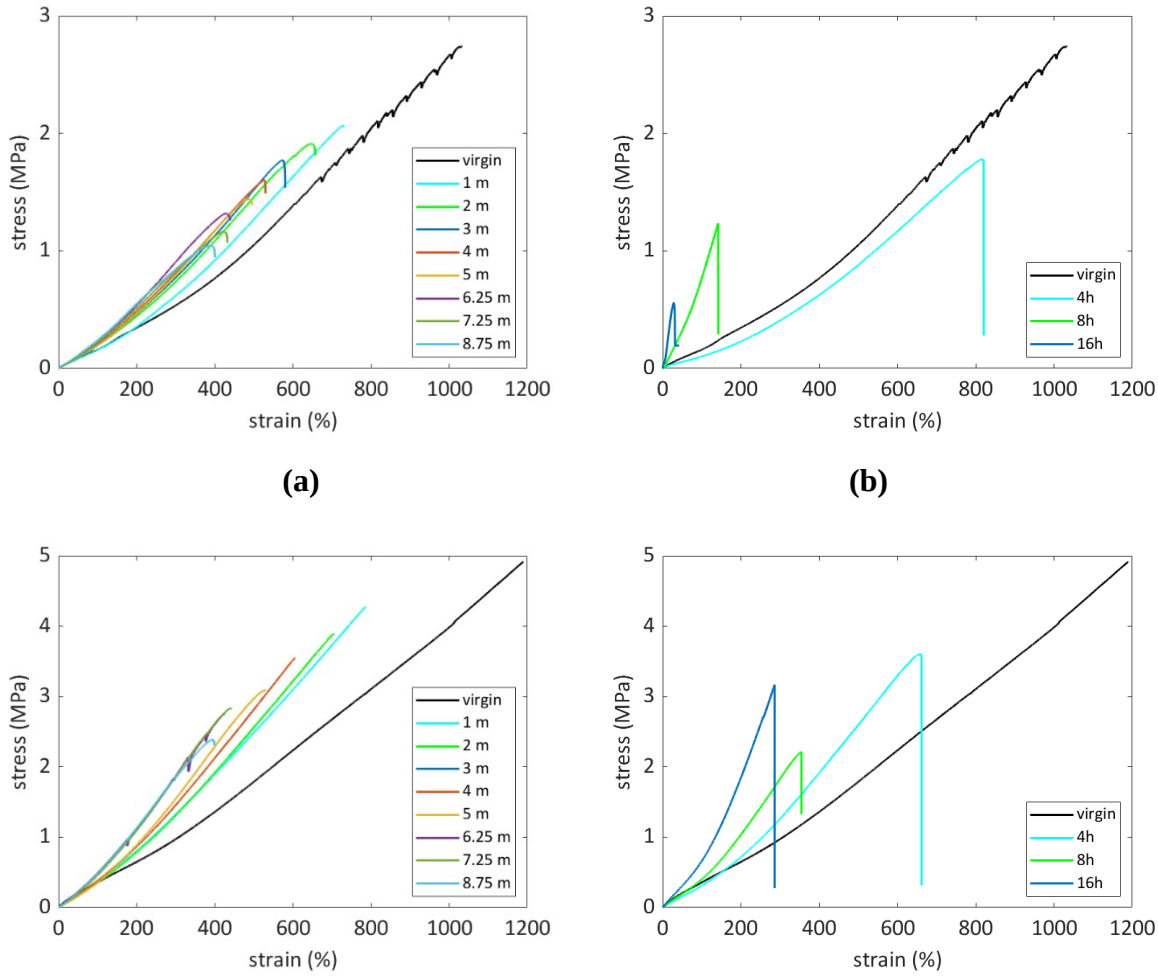


Figure 1. Stress strain curves of PDMS RTV 15A (a, b) and 30A (c, d) aged at 180°C (a, c) and 250°C (c, d) under air. NB: ageing durations are given in months.

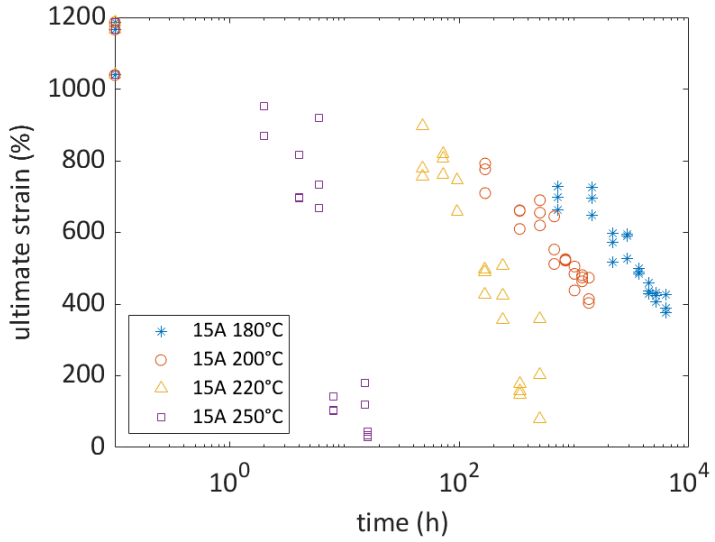
After thermal ageing, it is mainly observed that:

- ultimate elongation decreases but stays higher than 400% after almost 9 months at 180°C.

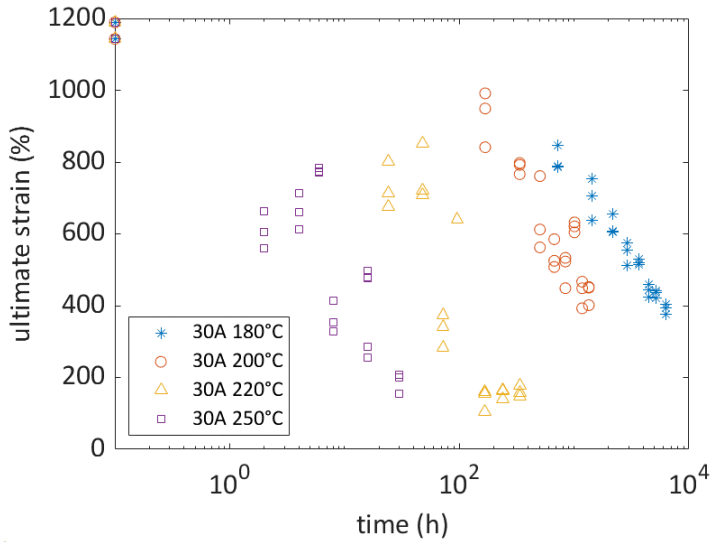
- the domain expressing the « shortest » chain seems to predominate over the domain corresponding to the long chains, which seems to indicate the conversion of « long » elastically active chains into « short » ones, i.e. a crosslinking mechanism. This will be confirmed by the modeling of stress strain curves using an hyperelastic model as explained in the "discussion section".

Those observations seem valid in the whole range of temperatures under investigation (Figures 1a vs 1b and 1c vs 1d).

Ageing at other temperatures ranging from 180°C to 250°C were also performed. Changes of ultimate strain and stress are given in **Figures 2** and **3**. Overall, the characteristic degradation times are relatively close for both rubbers, which will be commented in the "discussion" section.

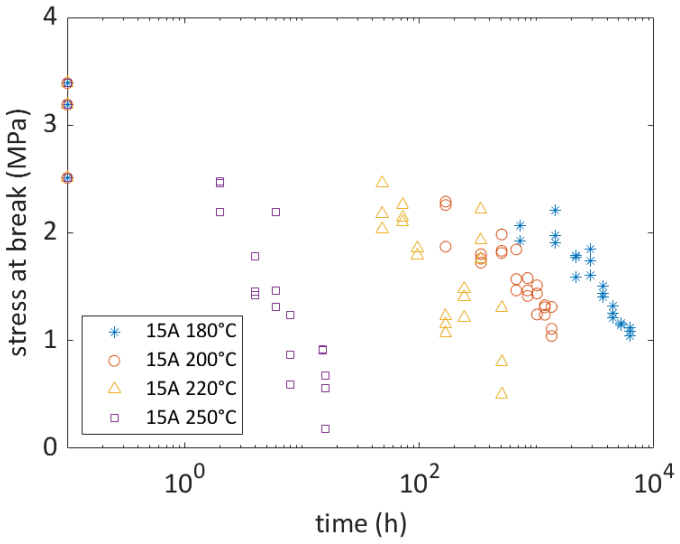


(a)

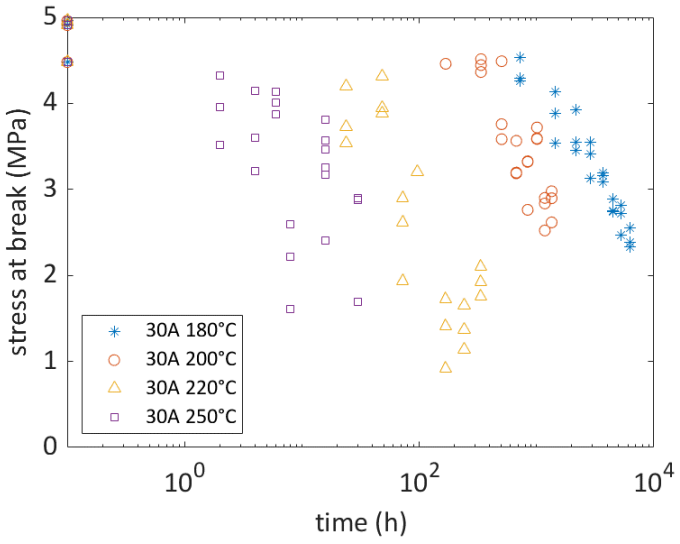


(b)

Figure 2. Changes of ultimate strain for PDMS 15A (a) and 30A (b) for thermal ageing under air.



(a)

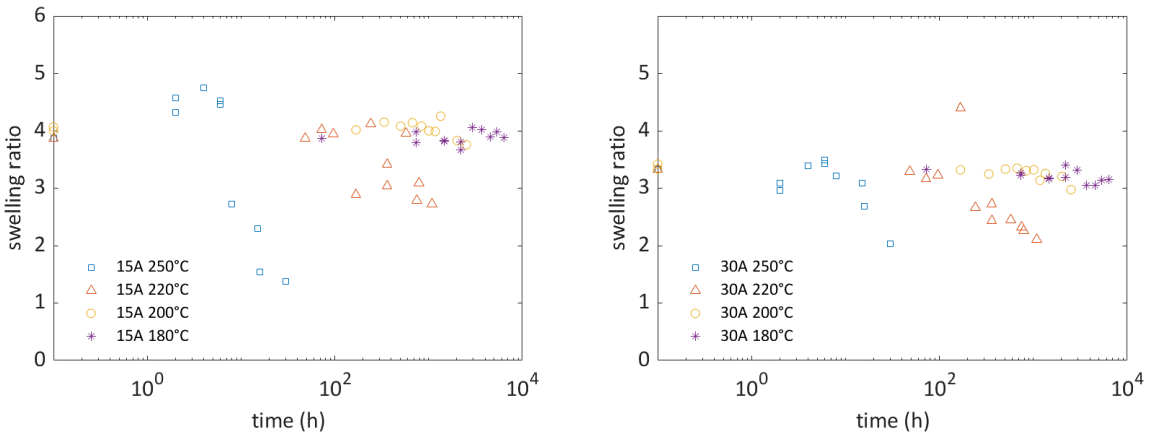


(b)

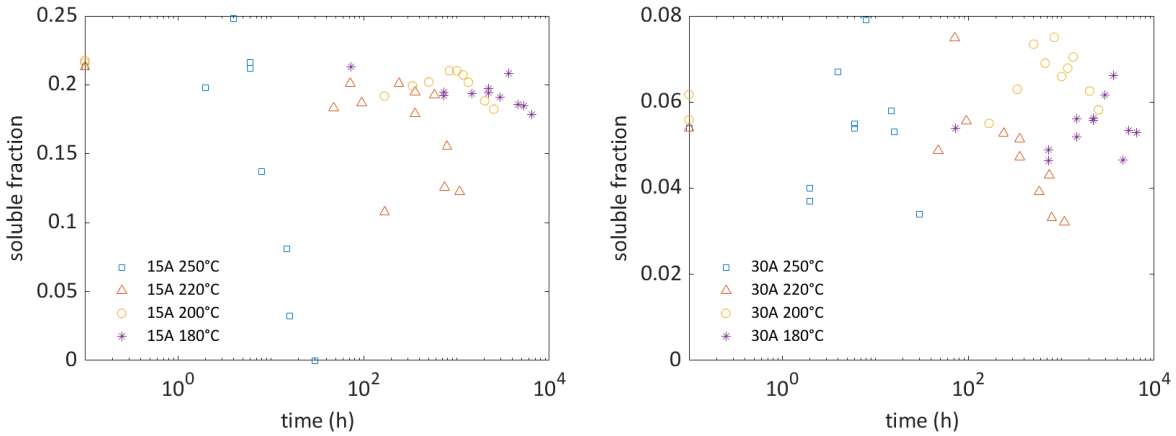
Figure 3. Changes of stress at break for PDMS 15A (a) and 30A (b) for thermal ageing under air.

3.2. Macromolecular changes

The effect of ageing on macromolecular architecture was first investigated by sol gel analysis. Toluene absorption is used here as a probe to estimate the crosslink density, which is expected to change with thermal aging due to oxidation-induced crosslinking and/or chain scission. The changes in swelling ratio and soluble fraction are shown in **Figure 4**.



(a)



(b)

Figure 4. Changes of swelling ratio (a) and soluble fraction (b).

The concentration in elastically active chains n_A can be calculated from the Flory Rehner equation [20]:

$$-[\ln(1-\phi)+\phi+\chi.\phi^2]=V_{m\,toluene}.n_A.\left(\phi^{\frac{1}{3}}-\frac{2\phi}{f}\right) \quad (3)$$

In which:

- n_A is the concentration in elastically active chains (mol l^{-1}).
- ϕ is the volume fraction of PDMS in the PDMS-toluene swollen mixture
- $V_{m\,toluene}$ is the toluene molar volume (106.1 cm^3 mol^{-1}).
- f is the functionality of PDMS network
- χ is the Flory parameter describing the interaction between PDMS and toluene.

Using f = 3, $\chi \sim 0.54$, n_A values coming from **Eq. 3** can be found in good agreement with values coming from the classical rubber elasticity equation used here for the data obtained in the low deformation domain of **Figure 1**, typically at strains lower than 50% i.e. $\lambda < 1.5$ [21]:

$$\sigma_0 = n_A RT . \left(\lambda - \frac{1}{\lambda^2} \right) \quad (4)$$

where σ_0 is the nominal stress and λ is the draw ratio. Results are given in **Table 1**. It must be emphasized that χ was adjusted. Its value is found slightly higher than in literature, where there is certain discrepancy about χ values for the PDMS-toluene mixture in literature. For example, its value is given by $\chi = 0.459 + 0.134\phi + 0.59\phi^2$ [22] or $\chi = 0.452 + 0.265\phi$ [23].

	SR	SF	ϕ_P	χ	n_A (Eq. 3)	n_A (Eq. 4)	χ [22]	χ [23]
15A	3.873	0.213	0.215	0.54	42.4	42.8	0.52	0.51
30A	3.329	0.054	0.250	0.54	81.6	79.1	0.53	0.52

Table 1. Sol gel properties of PDMS where SR is the swelling ratio, SF the soluble fraction, ϕ_P is the volume fraction of polymer in the swollen network, n_A is adjusted from Eq. 3 and from Eq. 4 and comparison with χ values from literature.

In the following, to avoid the uncertainties linked to the χ value in aged network, the "raw" sol gel properties data will be discussed instead of their exploitation using Eq. 3. Despite the uncertainties due to sol gel measurements, at 250°C, a significant decrease seems to be observed in both swollen ratio and soluble fraction, which is evidence of a predominant crosslinking. The same occurs at lower temperature but in a lower extent. Interestingly, mechanical properties seem to drop meanwhile sol gel properties are hardly changed. This will be discussed in the following in terms of structure properties involved for predicting embrittlement.

The crystallization and melting of PDMS were also investigated by DSC (**Figure 5**). For unaged PDMS 15A and 30A samples, a crystallization peak is observed at -70°C, and is accompanied by a melting peak at about -45°C, consistently with literature [24]. Values for crystallization are given in Table 2. More in detail:

- Unaged PDMS 15A sample displays a higher crystallization temperature than PDMS 30A on both peak onset and the maximal temperature.

- The crystallization peak of PDMS 15A is obviously broader than PDMS 30A. A tentative explanation for the broadness of crystallization peak is due to the heterogeneity (bimodality) of crosslinking network. This will be confirmed by the value of constants expressing hyperelasticity, namely $c_{\alpha=3}$, $c_{\alpha=2}$, determined in the 'Discussion'section.

- During ageing, all the samples display a decrease of the crystallization temperature, together with the onset and the crystallization enthalpy which will be discussed later. Those observations are consistent with other polymers undergoing ageing induced crosslinking, since increase in molar mass implies reduced of macromolecular mobility [25].

	T_C (°C)	T_{onset} (°C)	ΔH_C (J g^{-1})
PDMS 15A	-72.3	-67.6	17.6
PDMS 30A	-74.3	-66.8	13.3

Table 2. Parameters of crystallization for unaged PDMS.

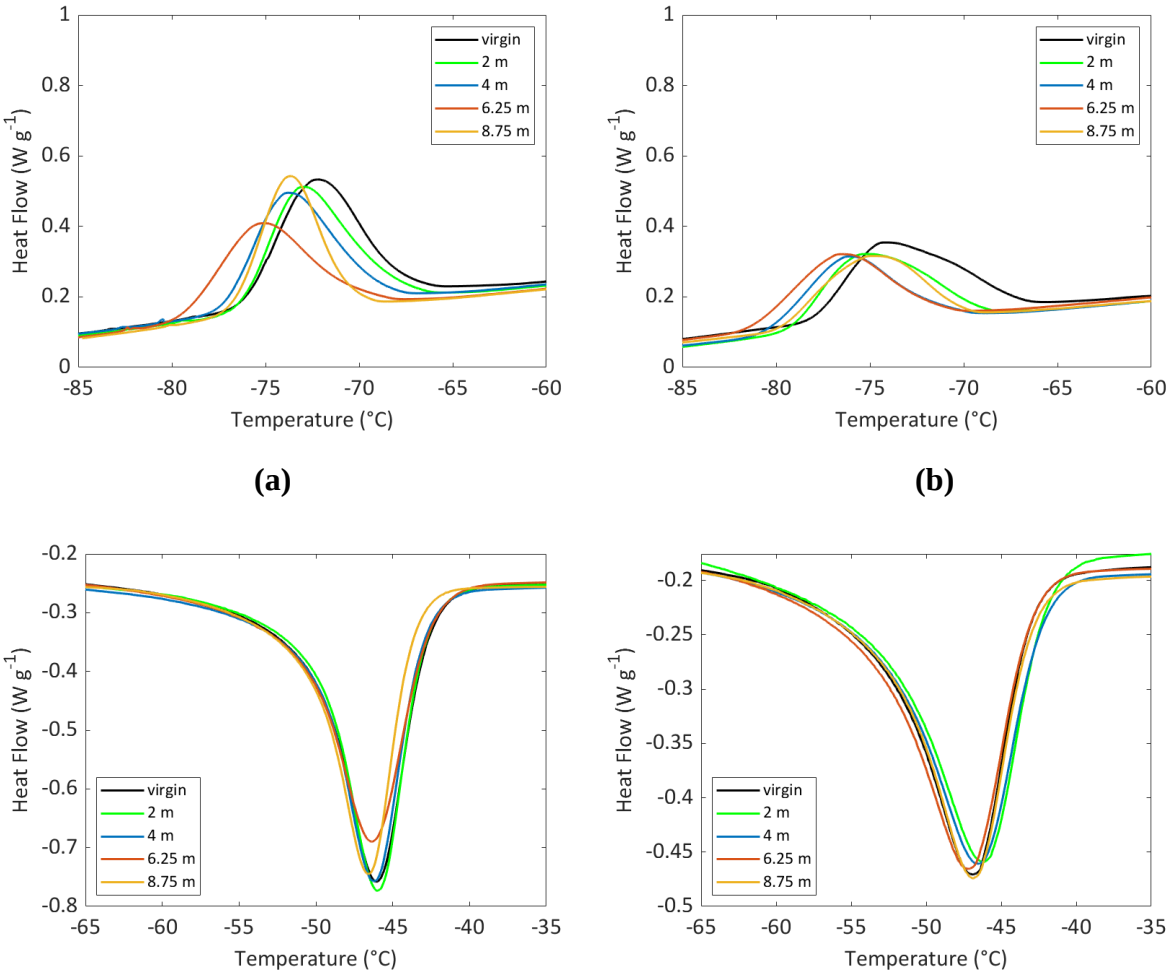


Figure 5. DSC thermograms of PDMS for crystallization (a, b) and melting (c, d) for PDMS 15A (a, c) and 30 A (b, d).

Dealing now with melting, a very slight decrease is observed in melting temperature. It is for example consistent with observation by Labouriau et al [17] where crystallization temperature decreases faster than melting temperature for gamma irradiated PDMS. The latter can be

commented as follows: according to Flory, the melting temperature T_m of a copolymer is depressed compared to the value of homopolymer T_{m0}, as described by the general formula [26]:

$$\frac{1}{T_m} - \frac{1}{T_{m0}} = \frac{-R}{\Delta H_m} \ln(p) \quad \frac{R}{\Delta H_m} x_B \quad (5)$$

ΔH_m being the melting enthalpy of crystallizable unit, p the probability of finding an homopolymer crystallizable sequence and x_B the fraction of non-crystallizable defect B (comonomers in the Flory's paper, crosslink sites in this work).

Here, the depletion of melting temperature is consistent with the existence of a crosslinking, under the assumption that crosslinking nodes behave as molecular defects inhibiting the crystallization.

Last, residual mass was monitored for thermally aged samples. Two kinds of experiments were conducted:

- measurement of mass loss for thermal oxidation under air as monitored by gravimetry (**Figure 6**),

- in situ degradation in TGA cell of samples before and after thermal ageing (**Figure 7**).

According to **Figure 6**, PDMS aged under air showed a continuous mass loss. It means that despite a predominant crosslinking phenomenon as seen above, some chain scission phenomena occur and lead to the release of small volatile units as already described in [1-3]. It seems also that PDMS 30A is more stable in terms of mass loss than PDMS 15A. According to our interpretation, it suggests that crosslinking nodes exert a "stabilizing" effect regarding the mechanism responsible of mass loss.

This last result seems confirmed by TGA under the inert atmosphere (**Figure 7**). The comparison of virgin PDMS 15A and 30A highlights that crosslinking slows down the mechanisms responsible for mass loss. For each type of PDMS, the mass loss of the degraded samples was slower than the unaged material, suggesting that aging in air induces additional crosslinking.

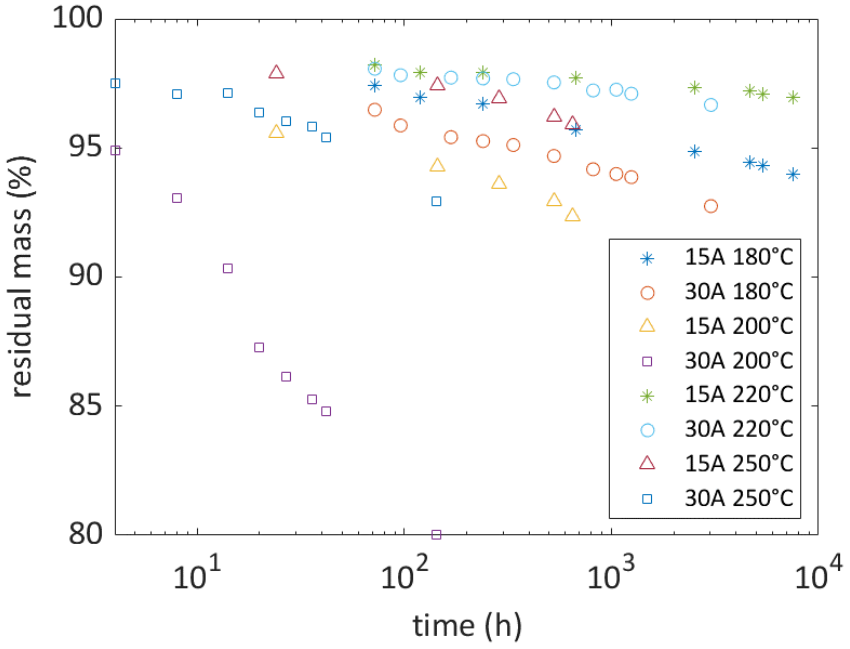


Figure 6. Mass loss of PDMS aged under air.

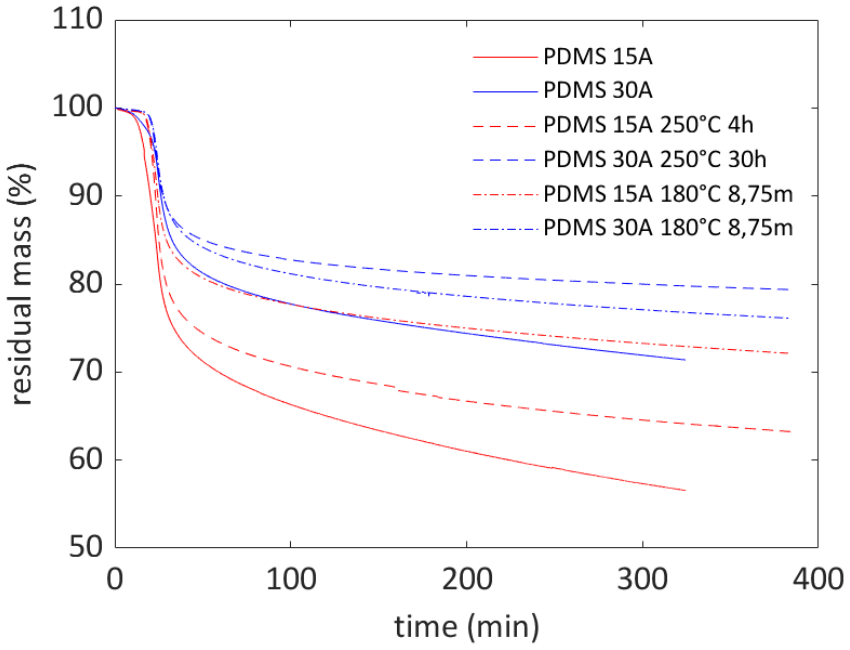


Figure 7. TGA runs at 500°C under inert atmosphere for virgin and degraded PDMS samples.

4. DISCUSSION

The main purpose of this discussion section is to explain, describe and model the changes in mechanical properties. To this end, possible mechanisms that occur at molecular and

macromolecular scales will be recalled together with their expected effects on mechanical properties. In a second time, we will identify an adequate model for describing the hyperelastic behavior of PDMS and its coefficient will be linked with macromolecular trackers describing the occurrence of ageing. Finally, we will propose a possible embrittlement criterion for PDMS under investigation.

4.1. Degradation mechanism

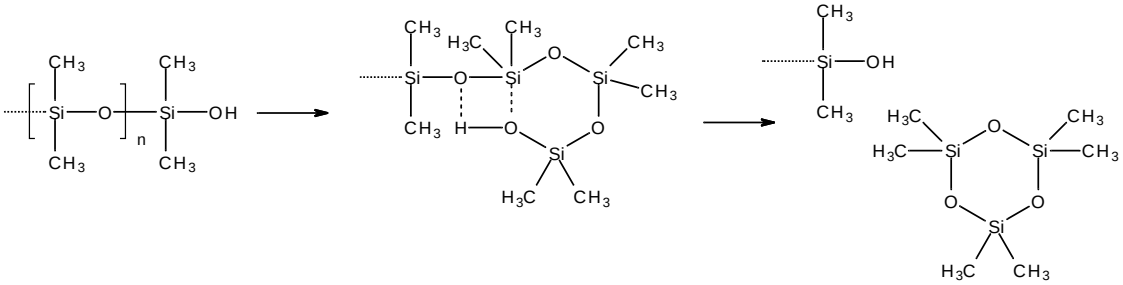
The main mechanisms for thermal degradation are described in the following.

Under inert atmosphere, several mechanisms are documented [1,2,[27],[28],[29]]:

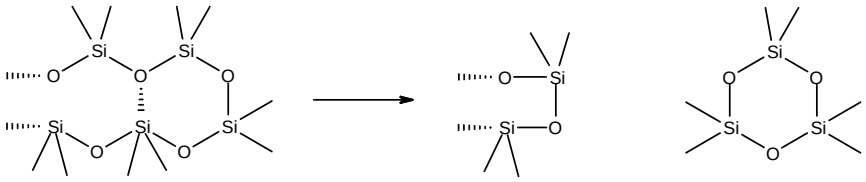
- end initiated scission (**Scheme 1a**): this reaction decreases the size of the dangling chains, which do not participate to the elastic network and might thus increase the crosslink density.

- random main chain scission (**Scheme 1b**): this reaction decreases the chain length between crosslink. i.e. increase the crosslink density.

- externally catalyzed mechanisms for polymer containing impurities and residual catalyst.



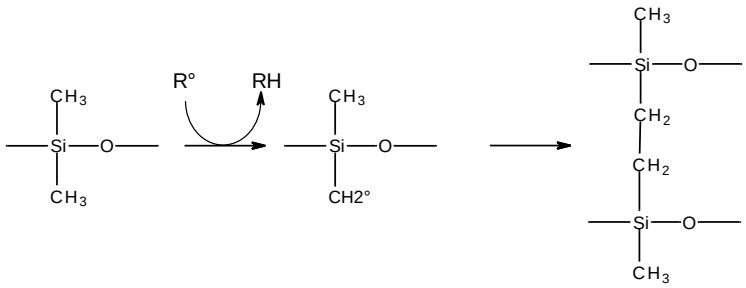
(a)



(b)

Scheme 1. Unzipping mechanisms initiated by chain ends (a) and by random chain scission (b) [24].

Under oxygen condition, other reactions may occur. They involve the in-chain radical oxidation of methyl groups as depicted in **Scheme 2**.



Scheme 2. Possible mechanism of crosslinking [30].

Some further mechanisms initiated by thermolysis of CH_2-H, Si-O or Si-CH_3 may lead to the formation of trifunctional nodes (**Figure 8**) [31].

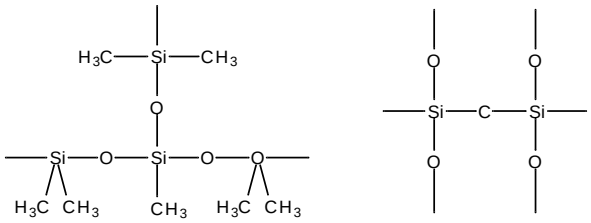


Figure 8. Nature of crosslink nodes formed by radical mechanisms [28].

In any case, the balance of "thermolysis" mechanisms associated to unzipping and oxidation processes, with two distinct activation energies explain that changes of mechanisms can be observed with the ageing temperature. It is clear that the thermal aging mechanism may produce some mass loss phenomena, but eventually lead to the observed increase in crosslink density.

4.2. Description of mechanical properties

There are two ways to describe the stress and strain curves and the changes during ageing time. The first is based on the simple lecture of apparent elastic modulus at low and high deformation [32]. A plot of modulus change versus time is given for several temperatures (**Figure 9**). An increase was observed, which is evidence of the crosslinking process. The increase of the maximal value observed at the highest strains E_2 seems to be higher than observed at low strains E_1 consistently with previous reports showing a decrease of ultimate elongation and work to break with minor change of hardness and modulus at 100% deformation for "naturally" aged silicones rubbers [8]. The effect at high temperature is higher than at low temperature possibly because a crossover of the various mechanism recalled in the last section. The case of PDMS 15A is interesting: **Figures 1-3** show the progressive embrittlement of the rubber family, but E_1 and E_2 changes are hard to detect. In fact, the embrittlement is associated to the "faster" upturn of stress and strain curves i.e. the "high strain domain" occurs earlier, and the "low strain domain" is progressively reduced and disappears. This fact cannot be fully depicted by the simple measurement of E_1 and E_2, which led us to find other descriptors of PDMS ageing.

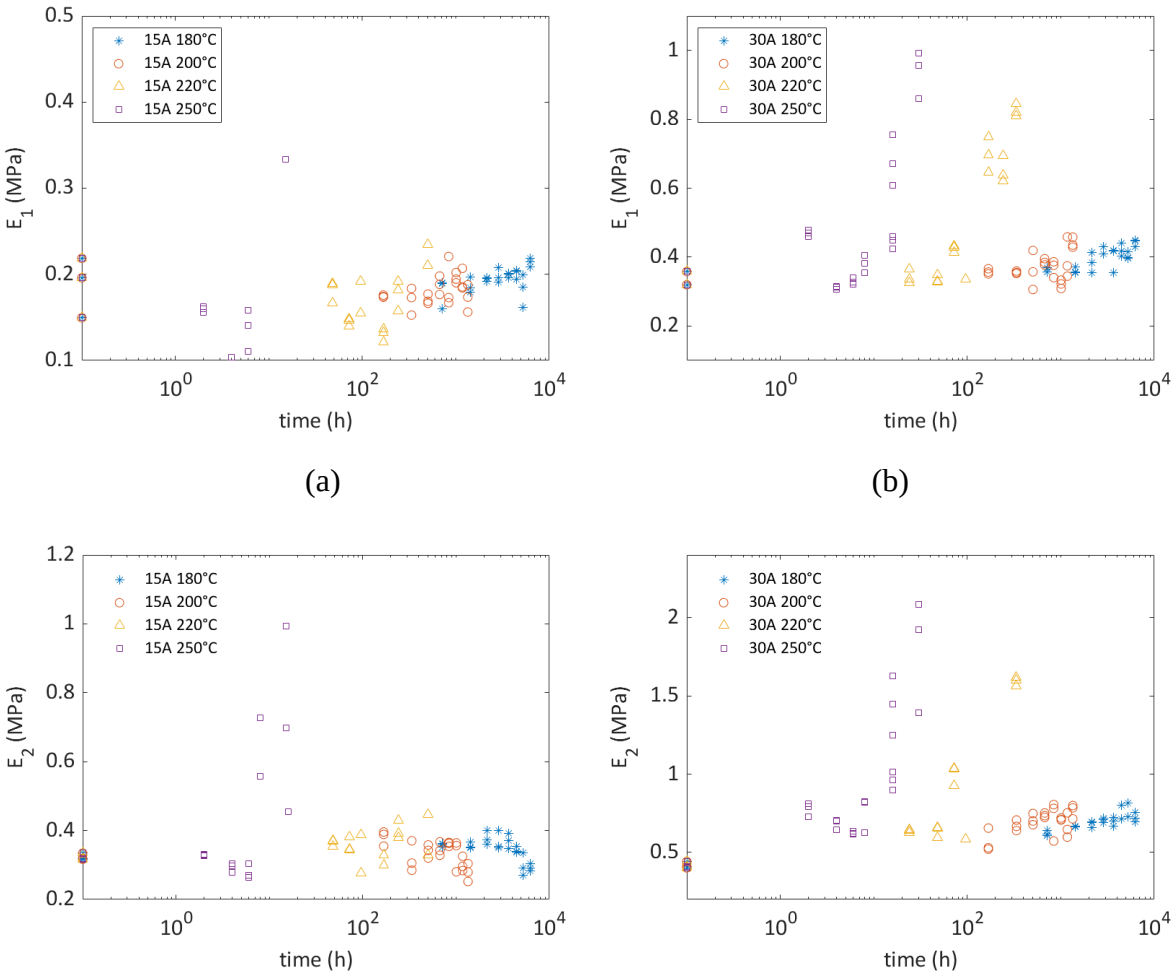


Figure 9. Changes of elastic moduli at low (a, b) and high strains (c, d).

Meanwhile E_1 and E_2 give a "local" description of the curve, the hyperelastic behaviour of virgin and aged PDMS can also be represented through Mooney and Rivlin model [33] at least for low deformations or the Ogden model [34] allowing the total description of the shape of the curve:

$$\sigma_0 = c_1 \cdot \left(\lambda^{\alpha_1 - 1} - \frac{1}{\lambda^{\frac{\alpha_1}{2}+1}} \right) + c_2 \cdot \left(\lambda^{\alpha_2 - 1} - \frac{1}{\lambda^{\frac{\alpha_2}{2}+1}} \right) + \ldots (6)$$

Formally, it is strictly equivalent to the Flory model of affine networks when $c_2 = 0$ and $\alpha_1 = 2$ [35]. In this last case, c_1 directly expresses the entropic elasticity of Gaussian chains connected to two crosslink nodes. Bernardi et al [14] have for example described the stress and strain curves of unaged PDMS with an Ogden model made of three terms. Basing on [19], the hyperelastic behavior will be justified as the sum of only two components: one given with $\alpha_1 = 2$ for long elastic chains and the second is characterized by an arbitrary fixed $\alpha_2 = 3$ parameter expressing

the presence of shorter chains. Its increase would express the occurrence of crosslinking process as explained in the previous paragraph. In this approach, $c_{\alpha=3}$ and $c_{\alpha=2}$ represent the relative contribution of each chain family. Those coefficients were extracted from a Matlab® routine (see **Supplementary Information)**. In general, very good fits ($R^2 > 0.99$) were obtained (see **Supplementary Information).**

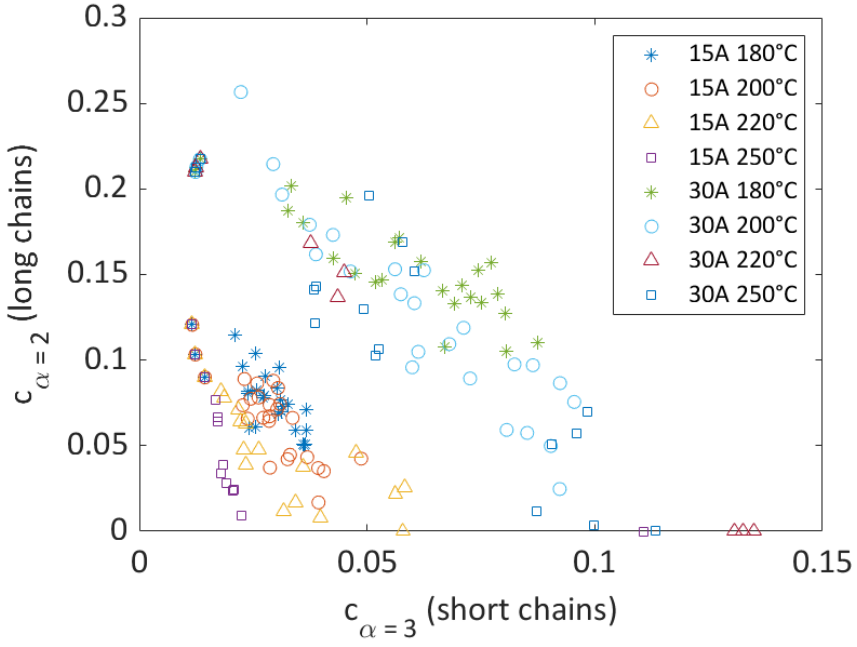


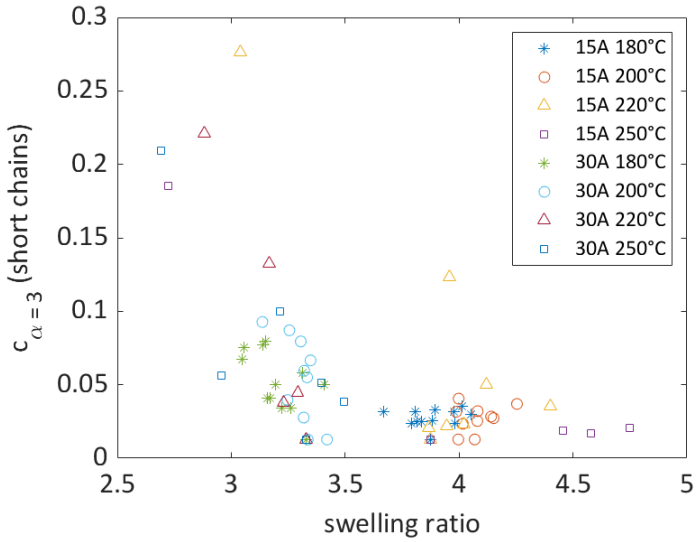
Figure 10. Changes of Ogden's coefficients for PDMS 15A and 30A aged at various temperatures.

The values are given in **Figure 10** calling for the following comments:

- overall, the contribution of « long » elastically active chains decreases because of the appearance of « shorter » elastically active chains.

- interestingly, it seems that there is a slight effect of temperature: at higher temperatures e.g. 250°C, the ratio of short chains over long chains seems higher than at low temperatures e.g. 180°C. It means that the chemical mechanisms at the origin of the crosslinking are not exactly the same, which can be discussed in terms of the relative contribution of reactions given in **Schemes 1** and **2**.

Basing on **Figure 11**, the "physical" meaning of $c_{\alpha=3}$ as an expression of the crosslinking induced by thermal ageing can be tentatively justified: its increase results in a decrease of the swelling degree, and in several parameters expressing the crystallization: onset temperature, maximal crystallization temperature and crystallization enthalpy (see **Supplementary Information**).



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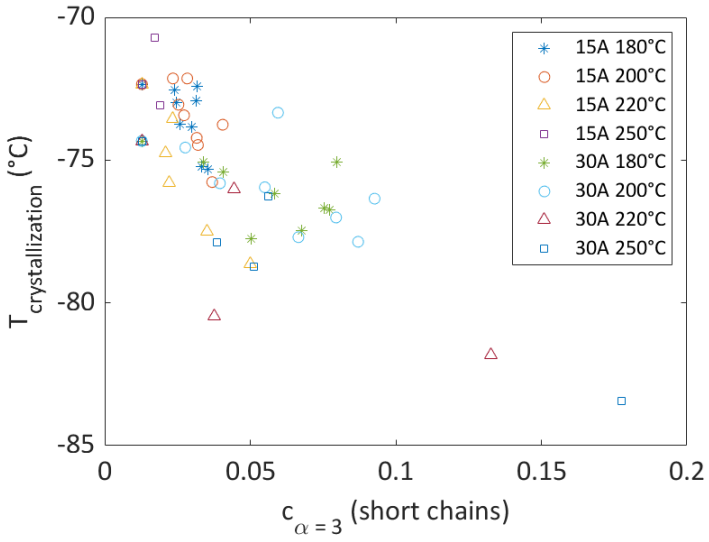

(b)

Figure 11. Plot of swelling degree (a) and onset crystallization temperature (b) vs the $c_{\alpha = 3}$ component (see Eq. 6).

4.3. Proposal of an embrittlement criteria

The last aim of this discussion is to link the changes of descriptors of the mechanical behavior and in particular ultimate properties with Ogden coefficients. At first, it is noteworthy that sample have lost most than 50% of their initial elongation at break whereas both swollen ratio and mass loss display only very limited change (**Table 3**). Interestingly, mass loss is higher for PDMS 15A samples than PDMS 30A, which is in line with results given in **Figure 7**.

	15A				30A			
	$t_{50\%}$	SR	SF	mass loss	$t_{50\%}$	SR	SF	mass loss
virgin		3.9	0.21			3.3	0.05	
250°C	8 hours	2,7	0.13	6,50%	8 hours	3.2	0.08	3%
220°C	7 days	2,9	0.11	6%	3 days	3,2	0.07	3%
200°C	5 weeks	4.1	0.2	6%	5 weeks	3,3	0.07	3%
180°C	5 months	4	0.21	5%	5 months	3,3	0.07	3%

Table 3. Changes of sol-gel properties and mass loss at "embrittlement" (here corresponding to 50% of initial elongation at break).

The coefficients can be proposed as another criterion for describing the stress and strain curves given in previous paragraph.

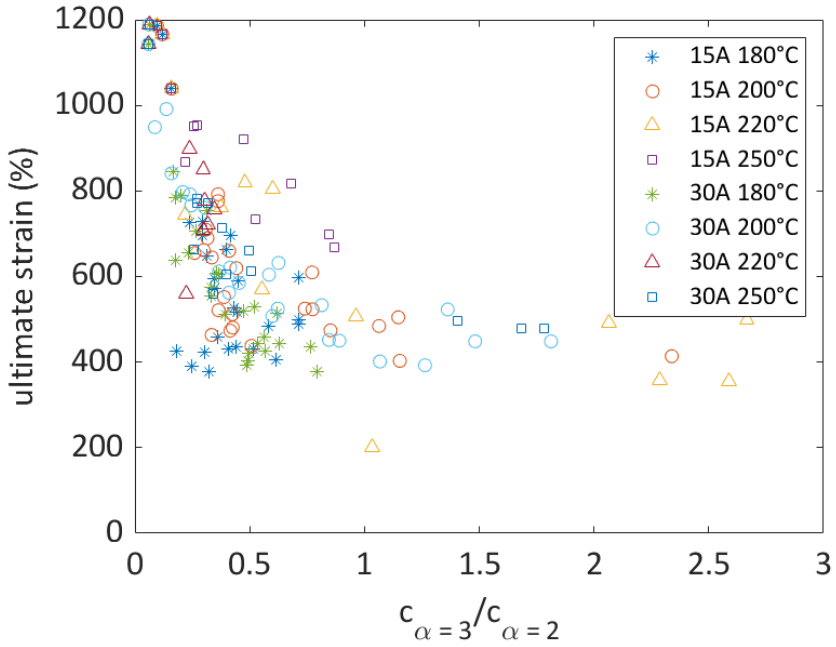

Figure 12. Changes of ultimate strain vs the ratio expressing the contribution of short/long chains.

Initially, $c_{\alpha=3} << c_{\alpha=2}$ which corresponds to highly stretchable samples. Samples display an ultimate strain lower than half its initial value when $c_{\alpha=3} \sim c_{\alpha=2}$. At this stage, it is noteworthy that in general, swelling ratio stays close to it is initial value, and mass loss level is moderate keeping in mind that a great part of mass loss occurs at early exposure time.

Samples become fully brittle when $c_{\alpha=3}/c_{\alpha=2}$ becomes much higher than 5 but at this degradation level, the determination of $c_{\alpha=3}$ and $c_{\alpha=2}$ by the Matlab® routine becomes quite unreliable. According to the sol gel measurements, it seems to correspond to a very lowered capability of network to swell into toluene, because of a higher crosslinking extent. It brings an explanation to the fact that both PDMS degrade almost at the same rate: PDMS 15A is initially less crosslinked than PDMS 30A. Mass loss (presumably of cyclic oligomers) is thus faster and leads to a faster increase of crosslink density.

5. CONCLUSIONS

This paper presents the thermal ageing at temperatures ranging from 180 to 250°C of two grades of Room Temperature Vulcanized silicone rubbers differing in the initially crosslinking densities. Ageing result in the depletion of ultimate elongation. The stress and strain curves remain almost unchanged in the low strain domain whereas the high strain domain displays the most significant changes: the apparent elastic modulus increases, and the « transition » between the « low » and « high » strain domains occurs earlier and earlier. Those results were interpreted by an overall crosslinking process due to the two possible chemical mechanisms: thermal unzipping and thermal oxidation.

In the ageing conditions under investigation, the ultimate properties are lost at « low » conversion degrees since sol-gel properties or mass loss display only slight changes. The concavity of the stress and strain curve expressed by the coefficient of the Ogden model of hyperelastic solids were used as an embrittlement criterion. It appears that sample became « brittle » when the contribution linked to short chains became higher than the contribution linked to long chains. It remains to pursue those investigations by a better understanding of the mobility and the relaxation of chains during the ageing process [36] and exploring the case of ageing modes leading to chain scissions such as aminolysis [37] for a better scrutiny of the proposed end of life criteria.

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