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#### 1 HYPERELASTICITY MODELING FOR THERMALLY AGED SILICONES

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### 10 ABSTRACT

11 Two families of Room Temperature Vulcanized PDMS with different hardness were thermally

- 12 aged. Mechanical properties were monitored by tensile tests and macromolecular architecture
- 13 was followed by differential scanning calorimetry (crystallization) and sol gel analysis
- 14 (swelling degree). Data showed that PDMS display a loss of plasticity due to a crosslinking
- 15 process. The main novelty was to describe mechanical behavior by a hyperelastic so called
- 16 Ogden's model whose coefficients were correlated with macromolecular properties and then
- 17 ageing degree. The model coefficients were also used to derive an embrittlement criterion.
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### 19 KEYWORDS

- 20 Silicone Rubber, thermal ageing, mechanical properties, crosslinking
- 21

### 22 1. INTRODUCTION

- 23
- 24 Room temperature vulcanization (RTV) silicone rubbers are commonly used in the biomedical
- 25 field. They are obtained by blending vinyl terminated PDMS linear polymers with a PDMS
- 26 containing some hydrosilane groups. The reaction between hydrosilane and vinyl is catalyzed
- 27 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 [<sup>1</sup>,<sup>2</sup>]. 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 [<sup>3</sup>], or fillers was also illustrated [<sup>4</sup>,<sup>5</sup>].

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

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

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#### 55 2.1. Samples Preparation

RTV silicones obtained by mixing part A ("base") and part B ("catalyst") i.e. PDMS chains 56 functionalized by hydrosilane and PDMS functionalized by vinyles. Pt catalyst is present in 57 only one of the parts so that reaction starts when part A and part B are mixed. Samples were 58 manufactured in 2 mm thick samples according to ISO 527-2 5B standard by injecting parts A 59 and B into acrylic 3D printed molds. Two PDMS grades differing by their hardnesses (15A and 60 30A) are investigated here. Some details are given in Supplementary Information. Dogbones 61 samples were aged and analyzed by mechanical testing. Some other were used for DSC, 62 gravimetry and sol gel analysis. 63

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 [<sup>10</sup>] meanwhile those rubbers degrade quite slowly compared to other polymers [<sup>11</sup>]. The original densities of both materials were measured to be 1.100 for PDMS 15A and 1.113 for PDMS 30A.

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#### 70 **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

**73** 4h-30h (for ageing at 250°C) to about 1 year (for ageing at 180°C).

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#### 75 2.3. Characterization methods

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#### 77 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<sup>-1</sup> elongation rate. 3 samples were tested per condition.

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#### 82 2.2.2. Sol gel analysis

Samples (m<sub>0</sub> about 100 mg) were immerged in toluene. After 72 h, the swollen mass m<sub>swollen</sub> 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<sub>dried</sub> corresponding to the insoluble
network was measured after 24h drying. Data were used to estimate:

87 The swelling ratio:

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

89 The soluble fraction:

90

88

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

91

#### 92 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<sup>-1</sup>. Data
were processed using TA Analysis software. The DSC was calibrated with an indium standard
before the experiment.

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#### 99 **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%.

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#### 104 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<sub>2</sub> atmosphere supplied
 by a continuous 50 ml min<sup>-1</sup> gas flow. Isothermal degradation was performed at a constant

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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 [<sup>12</sup>, <sup>13</sup>, <sup>14</sup>, <sup>15</sup>, <sup>16</sup>], 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 [<sup>17</sup>], and secondly, SIC is expected to disappear in the case where ageing induces crosslinking [<sup>18</sup>] (which is the case here, as it will be seen later). Basing on a previous work by Mark and coll [<sup>19</sup>], 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.

144

152 After thermal ageing, it is mainly observed that:

153 - 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".

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<sup>159</sup> Those observations seem valid in the whole range of temperatures under investigation (Figures160 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

164 times are relatively close for both rubbers, which will be commented in the "discussion" section.

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





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 [<sup>20</sup>]: 

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

In which: 

- n<sub>A</sub> is the concentration in elastically active chains (mol l<sup>-1</sup>).

- $\phi$  is the volume fraction of PDMS in the PDMS-toluene swollen mixture
- V<sub>m toluene</sub> is the toluene molar volume (106.1 cm<sup>3</sup> mol<sup>-1</sup>).
- f is the functionality of PDMS network
- -  $\chi$  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

207 deformation domain of **Figure 1**, typically at strains lower than 50% i.e.  $\lambda < 1.5$  [<sup>21</sup>]:

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

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where  $\sigma_0$  is the nominal stress and  $\lambda$  is the draw ratio. Results are given in **Table 1**. It must be emphasized that  $\chi$  was adjusted. Its value is found slightly higher than in literature, where there is certain discrepancy about  $\chi$  values for the PDMS-toluene mixture in literature. For example,

213 its value is given by  $\chi = 0.459 + 0.134\phi + 0.59\phi^2$  [<sup>22</sup>] or  $\chi = 0.452 + 0.265\phi$  [<sup>23</sup>].

214

	SR	SF	фр	χ	n <sub>A</sub> (Eq. 3)	n <sub>A</sub> (Eq. 4)	χ[22]	<b>χ</b> [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<sub>P</sub> is the volume fraction of polymer in the swollen network, n<sub>A</sub> is adjusted from
 Eq. 3 and from Eq. 4 and comparison with χ values from literature.

218

In the following, to avoid the uncertainties linked to the  $\chi$  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.

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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 [<sup>24</sup>]. Values for crystallization are

230 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.

233 - 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 [<sup>25</sup>].



	Т <sub>с</sub> (°С)	T <sub>onset</sub> (°C)	$\Delta H_{\rm C} (J g^{-1})$
PDMS 15A	-72.3	-67.6	17.6
<b>PDMS 30A</b>	-74.3	-66.8	13.3
Table 2. Paran	neters of crys	stallization for	unaged PDMS.







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Dealing now with melting, a very slight decrease is observed in melting temperature. It is for example consistent with observation by Labouriau et al [<sup>17</sup>] 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 [<sup>26</sup>]:

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

256

257  $\Delta H_m$  being the melting enthalpy of crystallizable unit, p the probability of finding an 258 homopolymer crystallizable sequence and  $x_B$  the fraction of non-crystallizable defect B 259 (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.

263

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

- 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**).

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

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288 4. DISCUSSION
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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
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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.

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#### 298 4.1. Degradation mechanism

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

301 Under inert atmosphere, several mechanisms are documented [1,2,<sup>27</sup>,<sup>28</sup>,<sup>29</sup>]:

- end initiated scission (Scheme 1a): this reaction decreases the size of the dangling chains,

303 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

305 crosslink. i.e. increase the crosslink density.

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



14 Under

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

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Scheme 2. Possible mechanism of crosslinking [<sup>30</sup>].

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Some further mechanisms initiated by thermolysis of  $CH_2$ -H, Si-O or Si-CH<sub>3</sub> may lead to the formation of trifunctional nodes (**Figure 8**) [<sup>31</sup>].



#### 321

## 322

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.

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#### 328 4.2. Description of mechanical properties

329

There are two ways to describe the stress and strain curves and the changes during ageing time. 330 The first is based on the simple lecture of apparent elastic modulus at low and high deformation 331 [<sup>32</sup>]. A plot of modulus change versus time is given for several temperatures (Figure 9). An 332 increase was observed, which is evidence of the crosslinking process. The increase of the 333 maximal value observed at the highest strains E<sub>2</sub> seems to be higher than observed at low strains 334  $E_1$  consistently with previous reports showing a decrease of ultimate elongation and work to 335 break with minor change of hardness and modulus at 100% deformation for "naturally" aged 336 337 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 338 15A is interesting: **Figures 1-3** show the progressive embrittlement of the rubber family, but E<sub>1</sub> 339 340 and E<sub>2</sub> 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 341 domain" is progressively reduced and disappears. This fact cannot be fully depicted by the 342 343 simple measurement of E<sub>1</sub> and E<sub>2</sub>, which led us to find other descriptors of PDMS ageing.



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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 [<sup>33</sup>] at least for low deformations or the Ogden model [<sup>34</sup>] allowing the total description of the shape of the curve:

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$$\sigma_{0} = c_{1} \cdot \left( \lambda^{\alpha_{1}-1} - \frac{1}{\lambda^{\frac{\alpha_{1}}{2}+1}} \right) + c_{2} \cdot \left( \lambda^{\alpha_{2}-1} - \frac{1}{\lambda^{\frac{\alpha_{2}}{2}+1}} \right) + \dots (6)$$

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Formally, it is strictly equivalent to the Flory model of affine networks when  $c_2 = 0$  and  $\alpha_1 = 2$ [<sup>35</sup>]. 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 15 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<sup>2</sup> > 0.99) were obtained (see **Supplementary Information**).

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

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372 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.

380

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**).



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**.

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	15A				30A			
	t <sub>50%</sub>	SR	SF	mass loss	t <sub>50%</sub>	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" (herecorresponding to 50% of initial elongation at break).

402

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

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406

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

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<sup>410</sup> Initially,  $c_{\alpha = 3} \ll c_{\alpha = 2}$  which corresponds to highly stretchable samples. Samples display an 411 ultimate strain lower than half its initial value when  $c_{\alpha = 3} \sim c_{\alpha = 2}$ . At this stage, it is noteworthy 412 that in general, swelling ratio stays close to it is initial value, and mass loss level is moderate 413 keeping in mind that a great part of mass loss occurs at early exposure time.

- 414 Samples become fully brittle when  $c_{\alpha=3}/c_{\alpha=2}$  becomes much higher than 5 but at this degradation
- 415 level, the determination of  $c_{\alpha = 3}$  and  $c_{\alpha = 2}$  by the Matlab® routine becomes quite unreliable.
- 416 According to the sol gel measurements, it seems to correspond to a very lowered capability of
- 417 network to swell into toluene, because of a higher crosslinking extent. It brings an explanation
- 418 to the fact that both PDMS degrade almost at the same rate: PDMS 15A is initially less 419 crosslinked than PDMS 30A. Mass loss (presumably of cyclic oligomers) is thus faster and
- 420 leads to a faster increase of crosslink density.
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### 422 5. CONCLUSIONS

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This paper presents the thermal ageing at temperatures ranging from 180 to 250°C of two grades 424 of Room Temperature Vulcanized silicone rubbers differing in the initially crosslinking 425 426 densities. Ageing result in the depletion of ultimate elongation. The stress and strain curves 427 remain almost unchanged in the low strain domain whereas the high strain domain displays the 428 most significant changes: the apparent elastic modulus increases, and the « transition » between 429 the « low » and « high » strain domains occurs earlier and earlier. Those results were interpreted 430 by an overall crosslinking process due to the two possible chemical mechanisms: thermal unzipping and thermal oxidation. 431

In the ageing conditions under investigation, the ultimate properties are lost at « low » 432 433 conversion degrees since sol-gel properties or mass loss display only slight changes. The 434 concavity of the stress and strain curve expressed by the coefficient of the Ogden model of 435 hyperelastic solids were used as an embrittlement criterion. It appears that sample became « 436 brittle » when the contribution linked to short chains became higher than the contribution linked 437 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 [<sup>36</sup>] and exploring the case of 438 ageing modes leading to chain scissions such as aminolysis <sup>37</sup> for a better scrutiny of the 439 440 proposed end of life criteria.

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### 442 6. REFERENCES

39

42

45

- 49
- 50

 <sup>&</sup>lt;sup>1</sup> Camino G, Lomakin SM, Lazzari M (2001) Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects.
 Polymer 42(6):2395-2402. https://doi.org/10.1016/S0032-3861(00)00652-2

Camino G, Lomakin SM, Lageard M (2002) Thermal polydimethylsiloxane degradation. Part 2. The degradation
 mechanisms. Polymer 43(7):2011-2015. https://doi.org/10.1016/S0032-3861(01)00785-6

N. Grassie, K.F. Francey. The thermal degradation of polysiloxanes—Part 3: Poly(dimethyl/methyl phenyl siloxane). Polymer Degradation and Stability 2(1), 1980, 53-66.

Lewicki JP, Worsley MA, Albo RLF, Finnie JA, Ashmore M, Mason HE, Baumann TF, Maxwell RS (2014) The effects of highly structured low density carbon nanotube networks on the thermal degradation behaviour of polysiloxanes. Polym Degrad Stab 102:25-32. https://doi.org/10.1016/j.polymdegradstab.2014.02.013

52 53 54	M. Englert, F. Minister, A. Moussaoui, W. Pisula. Mechanical properties of thermo-oxidative aged silicone rubber thermally stabilized by titanium oxide based fillers. Polymer Testing 115, 2022, 107726
55 56	N.S. Tomer, F. Delor-Jestin, L. Frezet, J. Lacoste. Oxidation, Chain Scission and Cross-Linking Studies of Polysiloxanes upon Ageings. Open Journal of Organic Polymer Materials 2(2), 2012, 13-22
57	
58	<sup>7</sup> Gillen KT, Kudoh H (2020) Synergism of radiation and temperature in the degradation of a silicone elastomer.
59	Polym Degrad Stab 181:109334. https://doi.org/10.1016/j.polymdegradstab.2020.109334
60	8
61	D. Oldfield, T. Symes. Long term natural ageing of silicone elastomers. Polymer Testing 15(2), 1996, 115-128.
62	
03 64	P. Banet, L. Chikh, T. Fouet, O. Fichet. Phenyl effect on properties evolution of silicone network sunder
65	isothermal and dynamic high temperature aging. Journal of Applied Polymer Science 137, 2022, 32420.
66	<sup>10</sup> D.W. Van Krevelen, K. Te Nijenhuis – Chap. 18. Properties Determining Mass Transfer In Polymeric Systems. In
67	"Properties of Polymers – Their correlation with chemical structure: Their numerical estimation and estimation
68	from additive group contribution. Fourth, completely revised edition 2009. Elsevier.
69	11
70	Han R, Li Y, Zhu Q, Niu K (2022) Research on the preparation and thermal stability of silicone rubber composites:
71	A review. Comp C 8:100249. https://doi.org/10.1016/j.jcomc.2022.100249
72	12
73	Panou AI, Papadokostaki KG, Tarantili PA, Sanopoulou M (2013) Effect of hydrophilic inclusions on PDMS
74	crosslinking reaction and its interrelation with mechanical and water sorption properties of cured films. Eur Pol J
75	49(7):1803-1810. https://doi.org/10.1016/j.eurpolymj.2013.04.004
76	13
77	Bernardi L, Hopf R, Sibilio D, Ferrari A, Ehret AE, Mazza E (2013) On the cyclic deformation behavior, fracture
/8 70	properties and cytotoxicity of silicone-based elastomers for biomedical applications. Polym Test 60:117-123.
/9	nttps://doi.org/10.1016/j.polymertesting.2017.03.018
00 81	Bernardi L. Honf P. Ferrari A. Ebret AF. Mazza F. (2017) On the large strain deformation behavior of silicone-based
82	elastomers for biomedical applications Polym Test 58:189-198
83	https://doi.org/10.1016/i.polymertesting.2016.12.029
84	15
85	Kong J, Tong Y, Sun J, Wei Y, Thitsartarn W, Jayven CCY, Kinyanjui Muiruri J, Wong SY, He C (2018) Electrically
86	conductive PDMS-grafted CNTs-reinforced silicone elastomer. Comp Sci Tech 159:208-215.
87	https://doi.org/10.1016/j.compscitech.2018.02.018
88	16
89	Stricher AM, Rinaldi RG, Barrès C, Ganachaud F, Chazeau L (2015) How I met your elastomers: from network
90	topology to mechanical behaviours of conventional silicone materials. RSC Adv 5:53713-53725.
91	https://doi.org/10.1039/C5RA06965C
92	17
93	Zhao J, Chen P, Lin Y, Chang J, Lu A, Chen W, Meng L, Wang D, Li L (2018) Stretch-Induced Crystallization and
94 05	Phase Transitions of Poly(dimethylsiloxane) at Low Temperatures: An in Situ Synchrotron Radiation Wide-Angle
95 07	X-ray Scattering Study. Macromolecules 51(21):8424-8434. https://doi.org/10.1021/acs.macromol.8b01872
90 97	Le Gac PV, Broudin M, Boux G, Verdu L, Davies P, Eavolle B (2014). Pole of strain induced crystallization and
98	oxidative crosslinking in fracture properties of rubbers Polymer 55(10) 2535-2542
99	https://doi.org/10.1016/j.polymer.2014.03.023
100	19
101	Llorente MA., Andrady AL, Mark JE (1981) Model networks of end-linked polydimethylsiloxane chains. XI. Use of
102	very short network chains to improve ultimate properties. J Polym Sci Polym Phys 19(4):621-630.
103	https://doi.org/10.1002/pol.1981.180190406
104	20

-	
2	0
1	Flory PJ, Rehner Jr J (1943). Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling . J Chem Phys L1:521. https://doi.org/10.1063/1.1723792
ł	Mark JE (1981). Rubber Elasticity. Journal of Chemical Education. 58(11):898-903 https://doi.org/10.1021/ed058p898 2
2	<sup>2</sup> Chassé W. Lang M. Sommer IU. Saalwächter K (2012) Cross-Link Density Estimation of PDMS Networks with
F 2	Precise Consideration of Networks Defects. Macromolecules 45:899-912. https://doi.org/10.1021/ma202030z
F 2	Patel SK, Malone S, Cohen C, Gillmor JR, Colby RH (1992) Elastic Modulus and Equilibrium Swelling of Poly(dimethylsiloxane) Networks. Macromolecules 25(20):5241–5251. https://doi.org/10.1021/ma00046a021
2	Rey T, Chagnon G, Le Cam JB, Favier D (2013) Influence of the temperature on the mechanical behaviour of filled and unfilled silicone rubbers. Polym Test 32(3):492-501. https://doi.org/10.1016/j.polymertesting.2013.01.008 <sup>5</sup>
i ł	Labouriau A, Cady C, Gill J, Stull J, Ortiz-Acosta D, Henderson K, Hartung V, Quintana A, Celina M (2015) Gamma rradiation and oxidative degradation of a silica-filled silicone elastomer. Polym Degrad Stab 116:62-74. https://doi.org/10.1016/j.polymdegradstab.2015.03.009
2	<sup>6</sup> Flory PJ (1955) Theory of crystallization in copolymers. Trans. Farad Soc 51:848-857.
	Tasic A, Pergal MV, Antić M, Antic VV (2017) Synthesis, structure and thermogravimetric analysis of a,w- relechelic polydimethylsiloxanes of low molecular weight. J Serb Chem Soc 82(12):1395-1416. https://doi.org/10.2298/JSC170427082T
۲ ۲ ۲	Lewicki JP, Liggat JJ, Patel M (2009) The thermal degradation behaviour of polydimethylsiloxane/montmorillonite nanocomposites. Polym Degrad Stab 94(9):1548-1557. https://doi.org/10.1016/j.polymdegradstab.2009.04.030
3	Thomas TH, Kendrick TC (1969) Thermal analysis of polydimethylsiloxanes. I. Thermal degradation in controlled atmospheres. J Polym Sci A-2 Polym Phys 7(3):537-549. https://doi.org/10.1002/pol.1969.160070308 º
F	Tomer NS, Delor-Jestin F, Frezet L, Lacoste J (2012) Oxidation, Chain Scission and Cross-Linking Studies of Polysiloxanes upon Ageings. Op J Org Polym Mat 2:13-22. DOI: 10.4236/ojopm.2012.22003
<b>۱</b> 3	Hill DJT, Preston CML, Whittaker AK (2002) NMR study of the gamma radiolysis of poly(dimethyl siloxane) under vacuum at 303 K. Polymer 43(4):1051-1059. https://doi.org/10.1016/S0032-3861(01)00711-X ²
3	Aguilar-Bolados H, Contreras-Cid A, Neira-Carrillo A, Lopez-Manchado M, Yazdani-Pedram M (2019) Removal of Surfactant from Nanocomposites Films Based on Thermally Reduced Graphene Oxide and Natural Rubber. J Comp Sci 3:31. https://doi.org/10.3390/jcs3020031 3
ł ł 3	Rivlin RS (1948) Large elastic deformations of isotropic materials. II. Some uniqueness theorems for pure, nomogeneous deformation. Phil Trans Royal Soc London A 240 A:491-508. https://doi.org/10.1098/rsta.1948.0003
i 3	Ogden RW (1972) Large deformation isotropic elasticity – on the correlation of theory and experiment for ncompressible rubberlike solids. Proc Roy Soc A 326:565–584. https://doi.org/10.1098/rspa.1972.0026
3	Flory PJ (1985) Molecular Theory of Rubber Elasticity. Polym J 17(1):1-12.
	21

- Somers AE, Bastow TJ, Burgar MI, Forsyth M, Hill AJ (2000) Quantifying rubber degradation using NMR. Polym
   Degrad Stab 70(1) :31-37. <u>https://doi.org/10.1016/S0141-3910(00)00076-8</u>

163 <sup>37</sup> Chang CL, Don TM, Shih-Jen Lee H, Sha YO (2004) Studies on the aminolysis of RTV silicone rubber and