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# Thermal Degradation of Fluorosilicone Elastomers

Emmanuel Richaud,\* Leticia Pires, Sébastien Roland, Laurianne Truffault, Lucien Laiarinandrasana, Alice Corfa, Julien Pinaud, Sylvain Caillol, Vincent Ladmiral, and Christophe Beauvais

This paper explores the structure-relationships involved in the degradation of fluorosilicones (FVMQs). For that purpose, FVMQs are thermally aged at 280 °C under various atmospheres (nitrogen, atmospheric air, pure oxygen). It seems that FVMQs undergo a strong mass loss irrespectively of the atmosphere. Under nitrogen, a chain scission (unzipping) mechanism is suspected whereas under air, a crosslinking mechanisms leads to an increase in tensile modulus. A degradation mechanism is proposed as a basis for lifetime prediction.

as aeronautics or defense where high and long lasting performances are required (i.e., in fluid sealing, compression resistance, or stability to chemicals). Scientific literature mainly deals with their synthesis and the (relatively) wide range of structures and properties which can be improved by using comonomers.<sup>[5,6]</sup> Their mechanisms of degradation have been much less studied than that of other elastomers and assessment of their lifetime from predictive approaches such as Arrhenius extrapolations<sup>[7]</sup> is poorly reliable.

## 1. Introduction

Fluorosilicone rubbers (FVMQs) are known for their high performances in harsh environment, because of their high resistance to non-polar solvents, mineral oils, fuels compared to non-fluorinated silicones,<sup>[1,2]</sup> and good level of gas permeability. However, they present a lower resistance to moderately polar solvents (esters, ketones...) and a lower thermal stability compared to silicones.<sup>[3]</sup> Due to their relatively high cost compared to other rubbers,<sup>[4]</sup> they are usually employed in industrial domains such

The aim of the present work is thus to address a multiscale study of FVMQs thermal degradation as a preliminary step in order to identify some trackers of ageing and, in a close future, to establish the structure relationships involved in their ageing-induced failure.

## 2. Experimental Section

FVMQ (Figure 1) supplied as a crude rubber, was cured using a dicumyl peroxide in a Gibitre press (170 °C—4 min) so as to get 150 μm thin films. Vinyl group content of the crude rubber was found close to 1.8% by <sup>1</sup>H NMR corresponding to a double bond concentration of about 0.12 mol kg<sup>-1</sup>. DCP concentration was about half the concentration of double bond. Since each DCP decomposes into two radicals, it can be assumed that each double bond was reacted after curing. Number and weight average molar mass (in PS equivalent) of the crude rubber were found close to 300 and 740 kg mol<sup>-1</sup> respectively.

Films were thermally aged in oven at 280 °C. Complementary experiments of ageing under pure oxygen or pure nitrogen were performed in a TGA cell (Q50 apparatus—TA Instruments).

Samples with various ageing times were characterized by tensile tests to plot the engineering stress–strain curves and to derive the evolution of the initial Young's modulus with respect to the ageing time. H4 dogbones samples were punched from plates prior to ageing. Tensile tests were conducted in standard conditions (20 °C, 50% HR) at a 20 mm min<sup>-1</sup> elongation rate using an Instron 5966 tensile machine. Elastic modulus was determined in the 0–5% deformation region.

In situ isothermal ageing experiments at 280 °C were performed using TGA (Q500—TA Instruments) under 100% O<sub>2</sub> or 100% N<sub>2</sub> supplied by a 50 mL min<sup>-1</sup> gas flow (samples being previously heated from room temperature to 280 °C under nitrogen at a 20 °C min<sup>-1</sup>).

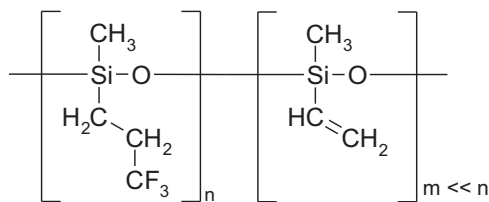
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**Figure 1.** Possible structure of FVMQ under study (NB: a dimethyl siloxane comonomers is also present with a low concentration—around 10%—and its effect will be neglected in the following in a first approach).

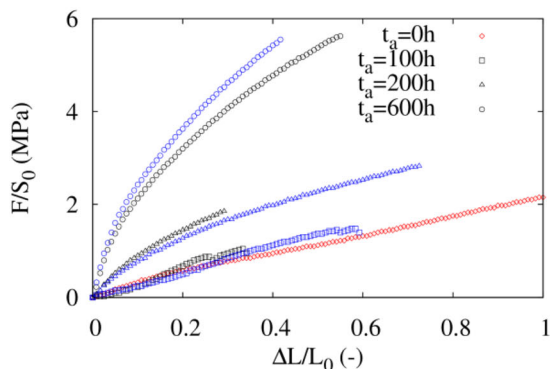
Characterization at the molecular scale was performed by FTIR in transmission mode: spectra were obtained by averaging 16 spectra obtained at a  $4\text{ cm}^{-1}$  minimal resolution using a Frontier 100 apparatus (Perkin Elmer). Elemental analyses were subcontracted at Institut des Sciences Analytiques (Lyon, France) and Crealins (Lyon, France).

### 3. Results

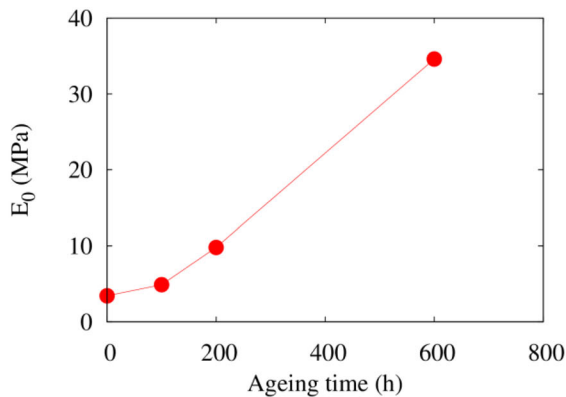
The engineering stress–strain curves of thin films after several ageing durations is given in **Figure 2**, where  $F$  is the load,  $S_0$  is the initial cross section area,  $\Delta L$  is the applied displacement and  $L_0$  is the gauge length. Nonlinear profile typically encountered for elastomers is observed (Figure 2a.) The initial Young's moduli ( $E_0$ ) were then determined and plotted with respect to the ageing duration (Figure 2b). Young's modulus is increasing with the duration of ageing time. The ageing continuously stiffens the FVMQ material.

It seemed to be interesting to investigate the mechanisms responsible for those architectural changes. For that purpose, TGA experiments were performed either under 100%  $\text{O}_2$  or 100%  $\text{N}_2$  atmosphere, in order to enhance the specific effects of each associated mechanism (either thermal ageing with possibly unzipping, or pure oxidation) (**Figure 3**):

- The existence of a mass loss even under nitrogen suggests the existence of an unzipping process.
- Under oxygen, kinetics of mass loss are relatively different: at shorter times, residual mass under oxygen is higher than un-

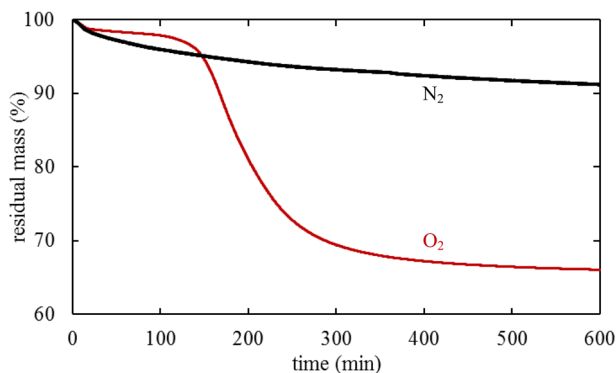


(a)



(b)

**Figure 2.** Experimental results for FVMQs aged at  $280\text{ }^\circ\text{C}$  under air: Engineering stress–strain curves a) and evolution of the initial Young's modulus  $E_0$  with respect to the ageing time b).



**Figure 3.** In situ ageing experiments monitored by TGA under  $\text{N}_2$  or  $\text{O}_2$ .

der nitrogen, suggesting that oxygenated species accumulate in the FVMQ matrix and display a certain stability even at  $280\text{ }^\circ\text{C}$ . At longer time, the sudden drop of mass suggests that those species decompose and generate volatile byproducts. Their nature remains to be determined.

FTIR spectroscopy was used to highlight the structural changes. Spectra were recorded after several ageing durations under air (**Figure 4**). Contrarily to the case of many other polymers, there is no evidence of carbonyl species remaining in the polymer matrix after ageing, possibly because they evaporate as seen above. Interestingly, the decrease of C–H absorbance is observed and occurs simultaneously with mass loss.

To better understand the chemical mechanisms involved in the thermal degradation of FVMQs, elemental analyses were carried out for samples aged either under air or under nitrogen (**Table 1**).

Those results call for the following comments:

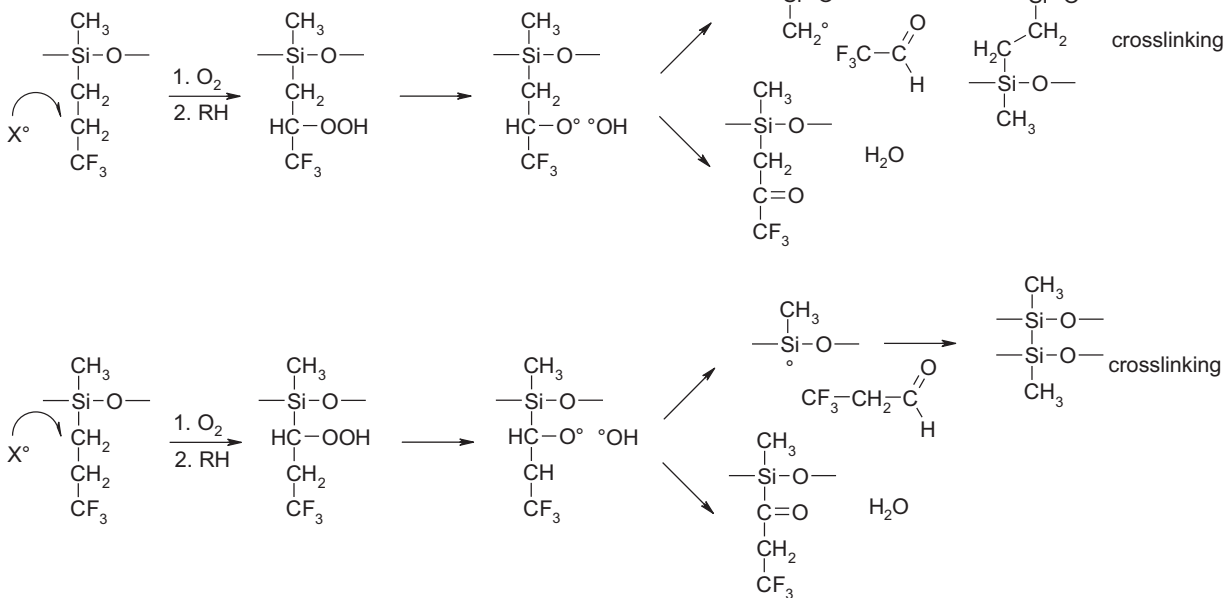
- at first, for unaged samples, H and Si contents are in good agreement with the theoretical structure given in Figure 1. C content is lower than expected (ca. 30–31%).
- Under air, the content in Silicon increases whereas it stays closer to initial value for ageing under nitrogen.

- Reversely, C and H contents decrease under air whereas the values would remain closer to the value observed for unaged sample. Despite the uncertainty on carbon content (see above), it can be noted that the ratio between C and H contents remains about six for all ageing under air, suggesting that the mechanisms responsible for the loss of these elements must be strongly linked.

#### 4. Discussion

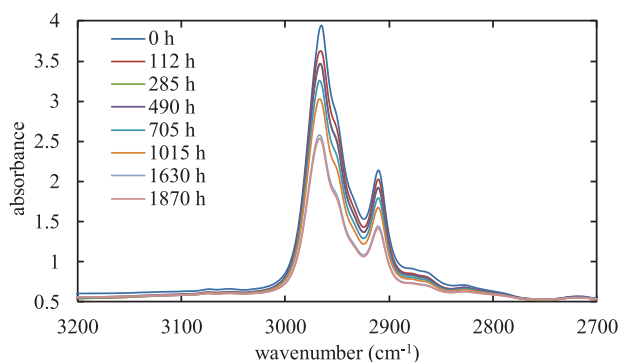
According to experimental results, it seems that:

- under air, samples undergo a degradation mechanism leading to volatile release together with crosslinking. According to Table 1, the volatiles would be constituted of hydrocarbonated groups, consistently with the observed correlation between mass loss and depletion of absorbance relative to C–H groups. A proposal of degradation mechanism is given below. This hypothesis would need to be validated experimentally, in particular by evaluating the stability of the peroxide species (formed in  $\alpha$  or  $\beta$  position of Si atom) and the nature of the crosslink bridges (Si–Si, Si–CH<sub>2</sub>–CH<sub>2</sub>–Si or Si–CH<sub>2</sub>–Si).



- Under nitrogen, an “unzipping” (depolymerization) mechanism would be plausible. The analysis of volatiles evolved under N<sub>2</sub> must be helpful to check its existence.

This preliminary mechanism remains to be fully validated from, for example, the analysis of evolved molecules by TGA-GC-MS or TGA-FTIR keeping in mind that the nature of some gaseous compounds (trifluoroethanal or trifluoropropanal) generated from the decomposition of alkoxy radi-



**Figure 4.** Changes in the C–H stretching region of FVMQs after ageing at 280 °C under air.

cals by a  $\beta$ -scission process would allow to identify the “parent” hydroperoxide. The analysis of residual aged polymer in a wider range of temperatures would also be helpful in particular to investigate the possible presence of carbonyl products.

**Table 1.** Elemental analysis of aged FVMQs (percentage values in mass).

	Virgin	100 h air	200 h air	300 h air	100 h N <sub>2</sub>
% Si	23.57	28.02	30.24	29.47	26.39
% C	24	15.85	13.52	12.99	23.74
% H	4	2.38	2.25	2.01	3.11



## 5. Conclusions

This preliminary work reports a study on the thermal degradation of FVMQs. According to a multiscale study, ageing under nitrogen induces a non-negligible mass loss meanwhile elemental analysis suggests the overall composition remains the same. Reversely, under air, a strong mass loss is accompanied by the release of hydrocarbon segments and crosslinking. This results in an increase of the Young's modulus of the material. A tentative mechanism is proposed and will be used to derive a kinetic model in a future step.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Data available on request due to privacy/ethical restrictions

## Keywords

ageing, crosslinking, elastomers

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