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► **To cite this version:**

Emmanuel Richaud, Leticia Pires, Sébastien Roland, Laurianne Truffault, Lucien Laiarinandrasana, et al.. Thermal Degradation of Fluorosilicone Elastomers. *Macromolecular Symposia*, 2022, 405 (1), pp.2100220. 10.1002/masy.202100220 . hal-03825121v2

HAL Id: hal-03825121

<https://hal.science/hal-03825121v2>

Submitted on 21 Oct 2022

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Thermal Degradation of Fluorosilicone Elastomers

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Summary: This paper explores the structure-relationships involved in the degradation of fluorosilicones (FVMQs). For that purpose, FVMQs were 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.

Keywords: ageing; elastomers; crosslinking

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 ^[1,2] 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 ^[3]. Due to their relatively high cost compared to other rubbers ^[4], they are usually employed in industrial domains such as aeronautics or defense where high and long lasting performances are required 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 [5,6]. 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 [7] is poorly reliable. 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.

Experimental

FVMQ (Figure 1) was supplied as a crude rubber, which 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 was found close to 1.8% by ¹H NMR, corresponding to a double bond concentration about 0.12 mol kg⁻¹. DCP concentration was about half the concentration of double bond. Since each DCP decomposes into 2 radicals, it can be assumed that each double bond is reacted after curing. Number and weight average molar mass (in PS equivalent) were found close to Mn = 300 and Mw = 740 kg mol⁻¹.

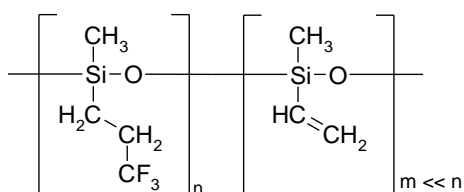


Figure 1. Possible structure of FVMQ under study.

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).

The samples with various ageing times were characterized by tensile tests to plot the stress strain curves and to derive the evolution of the initial Young's modulus with respect to the ageing time. Samples were punched as H4 dogbones samples prior to ageing. Tensile tests were conducted in standard conditions (20 °C, 50% HR) at a 20 mm min⁻¹ 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% O₂ or 100% N₂ supplied by a 50 ml min⁻¹ gas flow (samples being previously heated from room temperature to 280 °C under nitrogen at a 20 °C min⁻¹).

Characterization at molecular scale was performed by FTIR in transmission mode: spectra were obtained by averaging 16 spectra obtained at a 4 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).

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, ΔL 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.

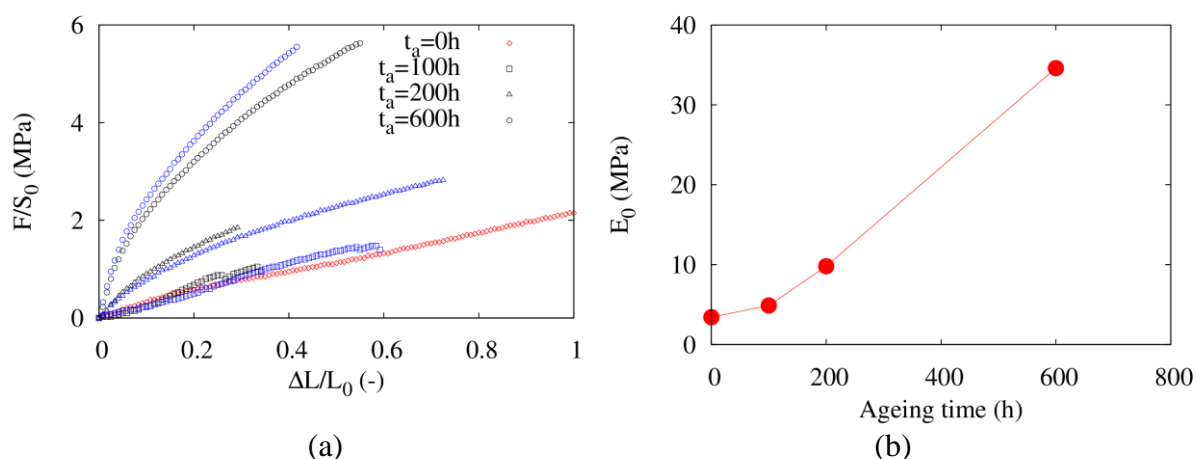


Figure 2. Experimental results for FVMQs aged at 280°C under air: Engineering stress-strain curves (a) and evolution of the initial Young's modulus E_0 with respect to the ageing time (b).

It seemed to be interesting to investigate the mechanisms responsible for those architectural changes. For that purpose, TGA experiments were performed either under 100% O₂ or 100% N₂ 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: in the earlier times, residual mass under oxygen is higher than under nitrogen, suggesting that oxygenated species accumulate in the FVMQ matrix and display a certain stability even at 280 °C. At longer time, the sudden drop of mass suggests that those species decompose and generate volatile byproducts. Their nature remains to be determined.

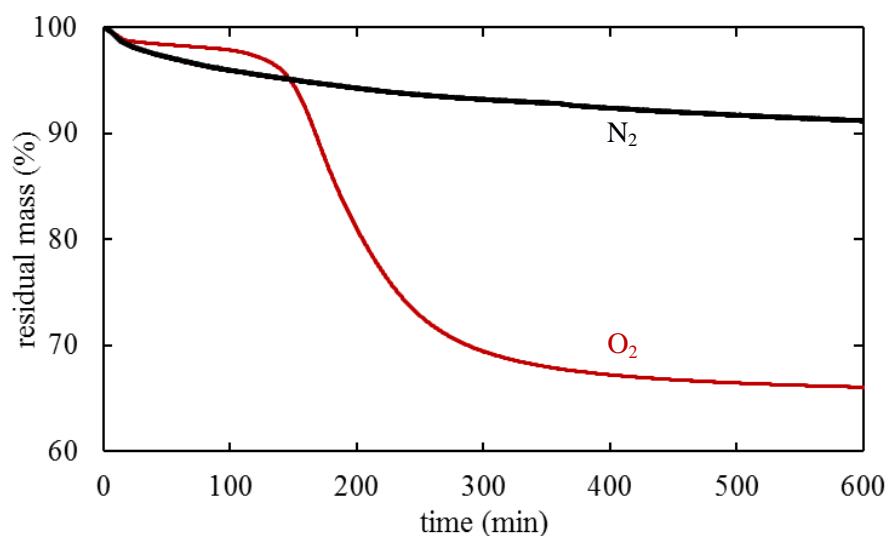


Figure 3. In situ ageing experiments monitored by TGA under N₂ or O₂.

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.

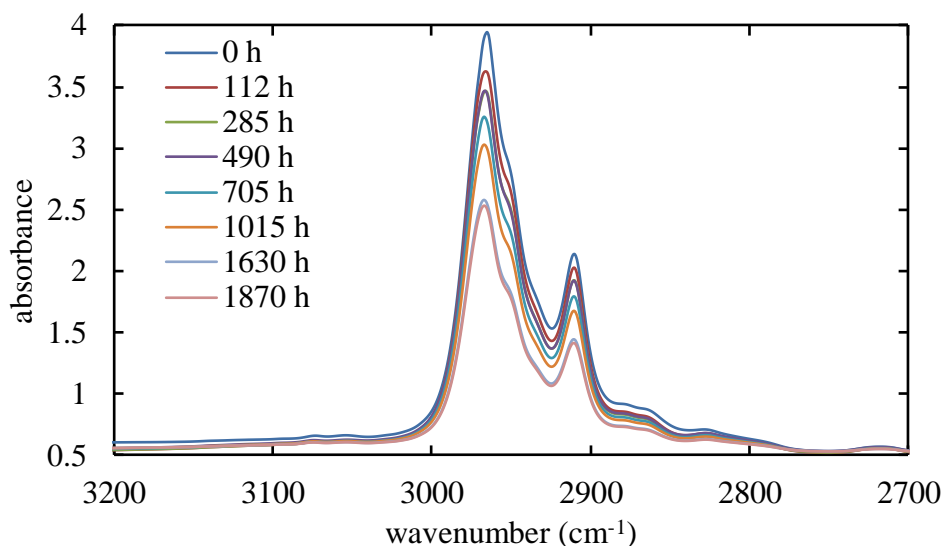


Figure 4. Changes in the C-H stretching region of FVMQs after ageing at 280 °C under air.

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).

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

	virgin	100 h air	200 h air	300 h air	100 h N ₂
% 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

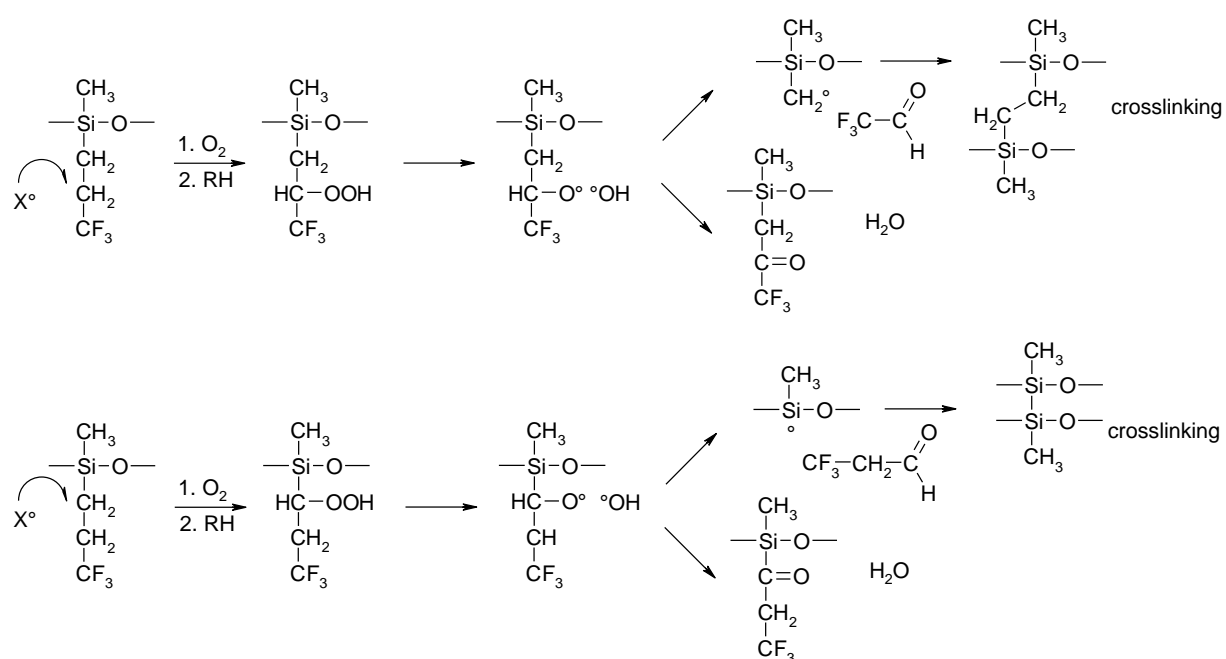
Those results call for the following comments:

- 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 content decrease under air whereas the value 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 content remains about 6 for all ageing under air, suggesting that the mechanisms responsible for their loss must be strongly linked.

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, but it remains now to validate this one by further experimental approach, in particular by evaluating the stability of peroxide species (formed in α or β position of Si atom) and the nature of crosslink bridges (Si-Si, Si-CH₂-CH₂-Si or Si-CH₂-Si).



- under nitrogen, an “unzipping” (depolymerization) mechanism would be plausible. The analysis of volatiles evolved under N₂ must be helpful to check its existence.

This preliminary mechanism remains to be fully validated basing for example on the analysis of evolved molecules by TGA-GC-MS or TGA-FTIR having in mind that the nature of some gaseous compounds (trifluoroethanal or trifluoropropanal) generated from the decomposition of alkoxy radicals by a β -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.

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.

Acknowledgements

ITC Elastomères is gratefully acknowledged for having supplied the FVMQs samples. Agence Nationale de la Recherche is gratefully acknowledged for having granted the FLuorosilicones Ageing Mechanisms and Synthesis (FLAMS ANR-20-CE06-0024) project.

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