Characterization of polydimethylsiloxane rubber upon photochemical, thermal, salt-fog ageings and exposure to acid vapours

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Abstract: The changes in the chemical structure and the physical properties of a filled cross-linked polydimethylsiloxane rubber were monitored as a function of various ageing factors. The variables included photochemical, thermal, salt-fog ageings and exposure to acid vapours. Unaged and aged samples were studied by IR spectroscopy, hardness measurements, Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) coupled with IR spectroscopy. No significant oxidation was detected after all ageings, except for nitric acid treatment. The presence of aluminium trihydrate was clearly identified as responsible for the observed chemical changes. Then an important vulnerability of this filled silicone rubber towards the cross-linking reactions provoked by usual ageings was also detected. The DSC-thermoporosimetry measurements of the mesh size distribution gave a comparison of cross-linking densities for each ageing. The complementary analysis with TGA-IR allowed us to differenciate the thermal stability of the formulation after various ageings and to acquire new knowledge about thermal decomposition.

Introduction

Polysiloxanes are widely used as protective surface coatings for a variety of specialized applications. The long term behaviour of cross-linked polysiloxanes is often very satisfactory. Compared with usual dienic elastomers, silicone rubber has outstanding heat resistance and a low chemical reactivity. However, it is important to recognise and identify the principal factors involved in rubber ageing so that degradation prevention can be applied. Knowledge of the amount of change that can be tolerated over the life of a material helps towards the determination of the lifetime expectancy.

Literature about polydimethylsiloxane (PDMS) ageing essentially concerns the unfilled uncross-linked polymer. The photochemical behaviour of polydimethyl siloxane (PDMS) oil has been examined previously [1-4]. Y. Israeli *et al.* have focussed in particular on the photoreactivity of the main substituent groups used in the silicone field. The other studies deal with the thermal behaviour of polysiloxanes. N. Grassie *et al.* have reported on the thermal stability of PDMS to 300°C under vacuum [5]. Thermal degradation of PDMS has also been studied by G. Camino *et*

al.[6,7]. Thermal oxidative degradation in the presence of air gives results much different from the decomposition in nitrogen. Kinetic treatment shows that PDMS thermal volatilization as rate of heating increases becomes dominated by rate of diffusion and evaporation of oligomers produced on its decomposition [6]. The products of the thermal degradation are essentially determined by the temperature and the heating rate [7]. The evaluation of cross-linking after photo-ageing of silicone rubber has been proposed by using calorimetrical analysis (Differential Scanning Calorimetry–DSC) and densimetry. No significant oxidation was detected, but competitive routes such as cross-linking and chain scission were clearly identified [8]. Most studies on filled cross-linked silicone rubber gave results on hydrophobicity changes after corona discharge and plasma treatment [9-13]. One of the major drawbacks with siloxanes is hydrolysis, which leads to low molecular weight cyclic fragments in the rubber network for which a mechanism has been proposed by M. Zeldin *et al.* [9]. The hydrophobic character or the water repellancy of PDMS is due to the close packing of the methyl groups, which under usual conditions point outward from the surface. Reorientation of the main chain, a change in the surface roughness, the deposition of contaminants on the surface, or surface oxidation can play a major role in the change from a hydrophobic to a hydrophilic state on PDMS surface [10]. Owen *et al.* have summarized the plausible mechanisms for hydrophobicity recovery after exposure to corona or plasma [13]. Migration of low molar mass species is undoubtedly the process that most researchers in the field believe as the dominant mechanism for hydrophobicity recovery. Outdoor expositions of silicone rubber have also been carried out and analysed by X-ray photoelectron spectroscopy (XPS) to understand the water repellancy [14-16]. Another paper is a review about the recent performance experience of silicone composite insulators in outdoor service [17]. The ageing of silicone started with the loss of hydrophobicity, and then a depolymerisation was also reported using gas chromatography-mass spectrometry [18]. The degradation is indicated by permanent changes such as increase in depolymerisation and changes in the surface physical structure brought about by an increase in the degree of crystallization of the polymer and the conglomeration of small particles into larger ones. Recent papers concerned the effect of antioxidants on the surface oxidation of cross-linked PDMS after air-plasma treatment [19]. Degradation at 180-200°C in air of PDMS rubber was studied by chemiluminescence [20]. Ageing is due to small fragments and catalyst solvents rather than the main siloxane network. Storage of siloxane rubbers in a closed inert atmosphere results in softening of the material. Thermal ageing studies on room-temperature rubbers and compression set experiments were also proposed to give the lifetime prediction [21]. Kinetics of the thermal degradation and thermal stability of conductive silicone rubber (unfilled, filled with carbon black or silica) have been studied by J. Zhang *et al.* [22]. The thermal stability of carbon black rubber was the best, compared to unfilled or silica elastomer.

We focussed our study on filled cross-linked PDMS and used different analytical technics such as IR spectroscopy, hardness measurements, DSC to evaluate the polymer long term behaviour upon usual ageings and specific acidic treatments. The new DSC-thermoporosimetry technique was first used upon photoageing of PDMS [8]. In this work we present new DSC-thermoporosimetry results for the estimation of the cross-linking level after various ageings. We will compare the competitive ways of degradation such as oxidation, post cross-linking and chain scission for each ageing.

Results and discussion

Study with FTIR spectroscopy

First we analyzed the ATR-IR spectrum of the unaged cross-linked filled polydimethylsiloxane (Table 1, Figure 1) [27]. The specific bands attributed to PDMS are localised at 2960, 1256, 1090, 1030 and 795 cm^{-1}. The main bands of the flame retardant are found at 3615, 3524, 3430 and 3375 cm^{-1} due to hydroxyl bonds. The presence of silica is not significative for this analysis; the Si-O band from inorganic filler will be overlayed with the Si-O band of PDMS. The presence of the crosslinks due to peroxide is not detected because of the small quantity of curing agent. The other spectra (Figure 1) were obtained after UV irradiation, thermal exposure, salt-fog test, nitric acid treatment and sulphuric acid treatment. The spectra obtained by photochemical, thermal, salt-fog or sulphuric acid ageings were identical with the initial spectrum of unaged material, for various times of exposure. These results confirmed the silicone stability towards oxidation. The evolution of any oxidation products (carbonyl and hydroxyl) was not significant, even after 10.000 hours of accelerated photo-ageing or thermal exposure. The repeted cycle in salt-fog test was not a degradative test for the silicone material. The polymer was not damaged by sulphuric acid vapour even after two weeks of exposure. On the other hand the exposure under nitric acid vapours was very aggressive for silicone rubber. The quick formation of three bands in the region 1700-1300 cm^{-1} was observed after a few hours of this acid ageing. These bands are the nitrate bands, resulting from the decomposition of Al(OH)$_3$. The intensity of the hydroxyl vibration (3600-3400 cm^{-1}) is decreasing after 24 or 64 hours under acid exposure.

Tab. 1. Main absorption observed for unaged filled uncross-linked PDMS then assignments of IR bands (ν = stretching vibration; δ = in-plane deformation).

| Wavenumber (cm^{-1})	Tentative assignment
3615, 3524, 3432, 3375	ν OH of Al(OH)$_3$
2960 (median intensity)	ν CH in CH$_3$
1646 (weak)	ν C=C
1408 (weak)	Not assigned
1256 (strong)	ν CH in Si-CH3
1090 (strong)	Si-O-Si
1030 (strong)	Si-O-Si
795 (strong)	Si-O-C
730 (weak)	Not assigned
665 (weak)	Not assigned
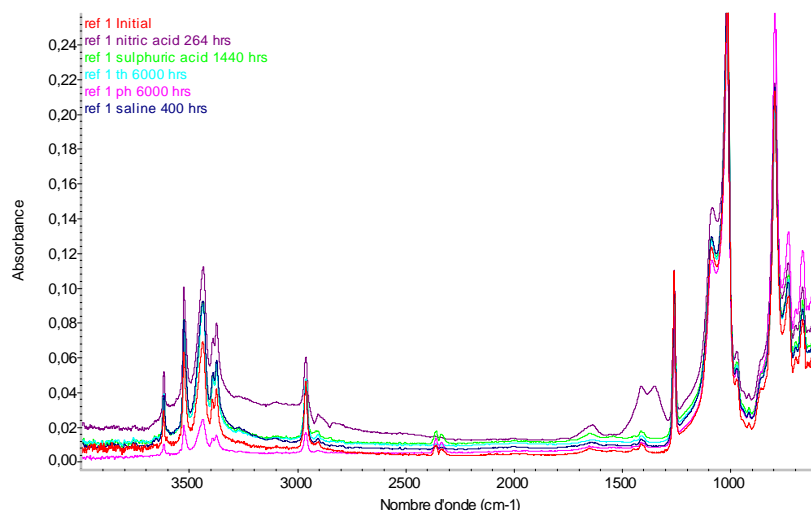
Fig. 1. FTIR-ATR spectra of silicone rubber before and after ageing. Curve a – Unaged sample; b – 6000 hours after photochemical ageing; c – 6000 hours after thermal ageing; d – 400 hours after salt-fog test; e – 264 hours under nitric acid vapours; f – 1400 hours under sulphuric acid vapours.

We also studied the crude PDMS (unfilled uncross-linked silicone, reference 870) and showed that no oxidation is detected after photochemical, thermal, sulfuric acid or nitric acid treatment (Figure 2). This proves that the silicone matrix is not affected by acid vapours in the absence of additives and fillers. The direct acidic treatment on aluminium trihydrate powder confirmed the results on filled polysiloxane (Figure 3). The formation of aluminium nitrate is clearly detected in this case.
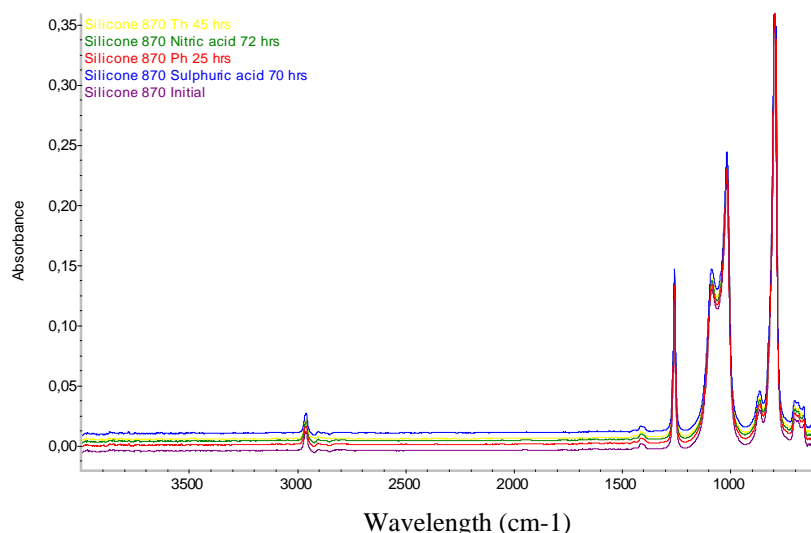

Fig.2. FTIR-ATR spectra of crude polysiloxane before and after ageing.
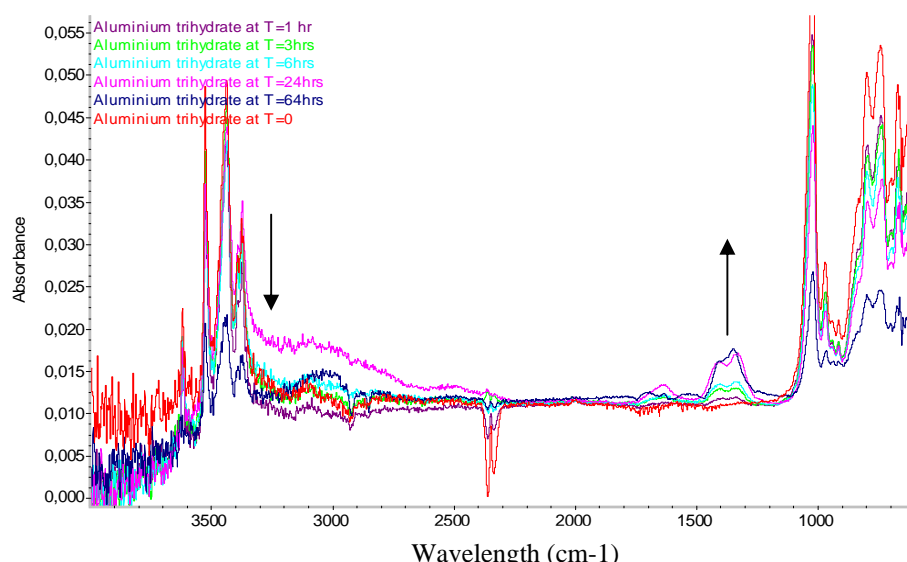
Fig. 3. Nitric acid treatment on aluminium trihydrate powder characterized by FTIR spectroscopy.

Hardness measurements

The hardness measurements are given in Figure 4. Hardness measurements on the initial material gave an average value of 70.0 (+/- 2.1) Shore A. During ageings the samples became harder on their surface layers. The surface is harder because the polymer chains cannot explore different configurations during constraint and are less flexible; hence the material is more cross-linked. The hardness values quickly increased after acidic treatments without induction period. After photo- or thermo-ageing an induction period of around 500 hours was detected, then the hardness increased till a stabilized value 87.1 (+/- 1.4) Shore A. The evolution towards hardness is accelerated after polluted ageings with acidic vapours. The evolution of the fire retardant with HNO_3 is supposed to enhance the hardness of the rubber. The evolution with H_2SO_4 is more surprising because we could not detect any change on IR spectra. The results also show that post cross-linking reactions occur upon usual ageings such as UV and thermal exposures.
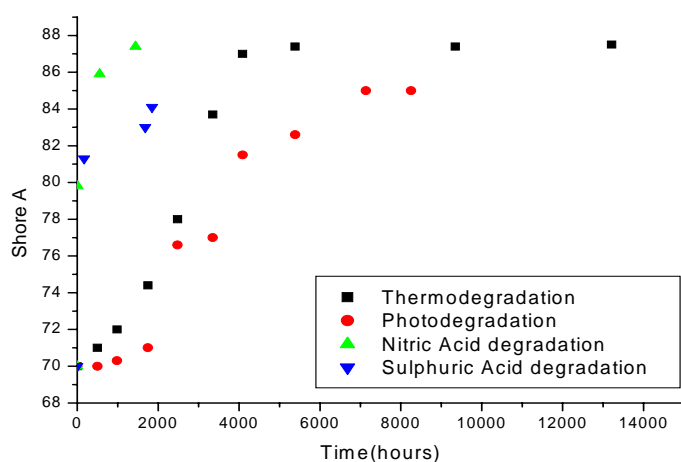
Fig. 4. Hardness measurements after different ageing.

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DSC-thermoporosimetry results

To estimate the cross-linking densities and to explain other structural changes upon degradation, DSC-thermoporosimetry measurements were carried out. This application of DSC has already been validated for dienic elastomers and silicone rubber [9]. The initial material (unaged sample) shows a distribution of mesh sizes with two peaks (figure 5). Different cuts (180 μm thick slices) from the surface of the rubber sheet have been characterized. We can underline that most meshes have a radius (distance between cross-links) around 200 Å, the other mesh size is around 700Å.

After photochemical or thermal ageings (Figure 6) we obtain different distributions. After short exposures (< 1000 hours, Figure 6A) we always get two peaks. The first one gives a radius around 200 Å, the second peak is shifted to 400 Å. This means that post cross-linking reactions are first detected. The cross-linking density is therefore affected by usual ageing. For longer time (1,000-5,000 hours) we can notice with figure 6B that only one peak is observed at 550 Å after thermal ageing. Chain scissions largely occured and gave such repetitive results. The same behaviour is confirmed after 10,000 hours.
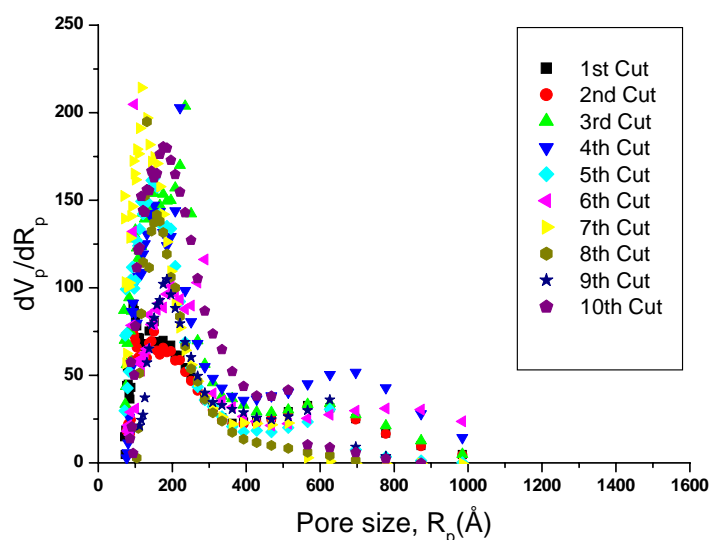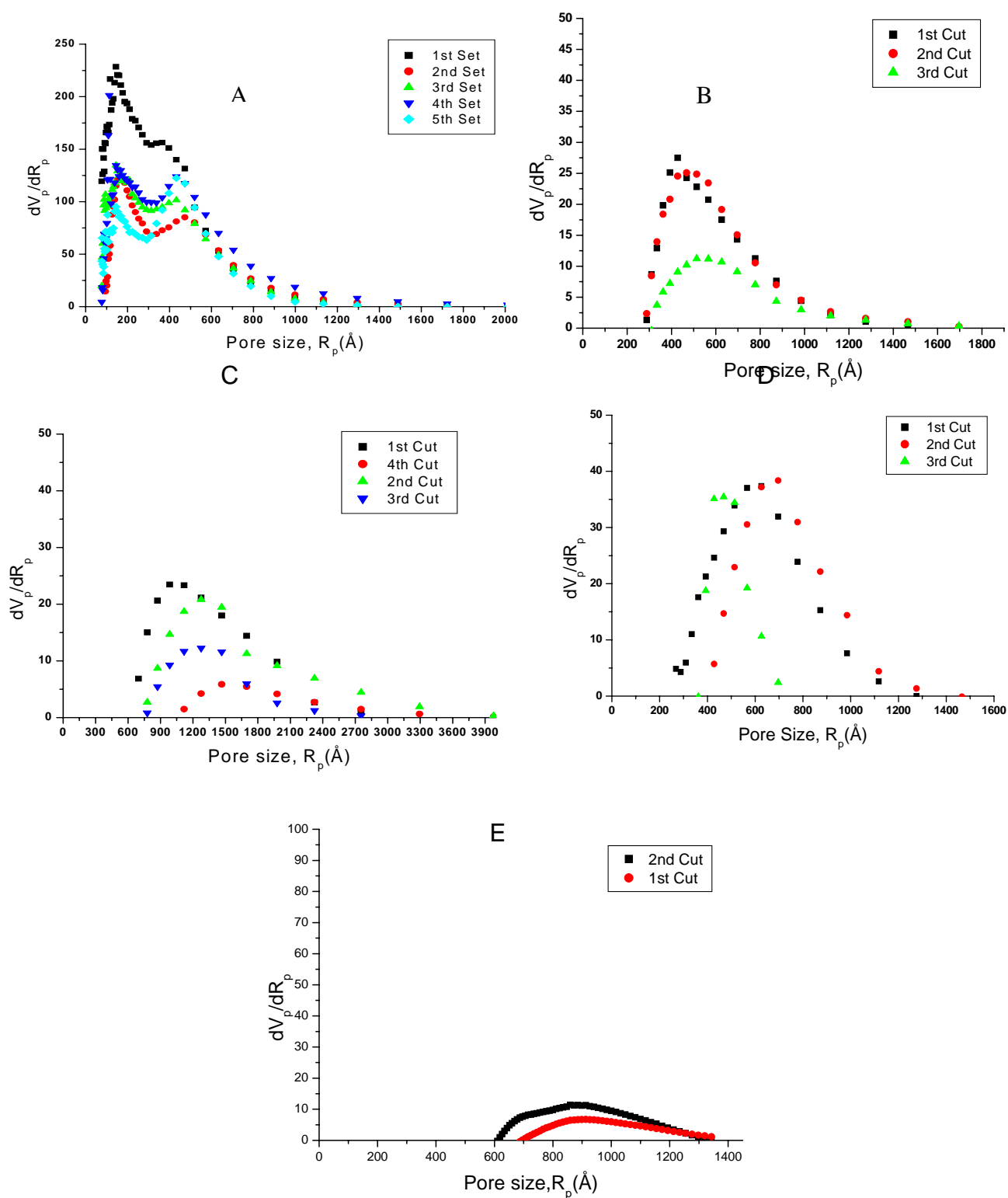

Fig. 5. Cross-linking profile obtained by DSC-thermoporosimetry on unaged sample surface (radius or pore size Rp, distribution dV/dR).

In the case of photo-ageing (Figure 6C) we also get one peak around 1,200 Å after 2,000 hours. The photo-degradation process leads to a number of chain scissions. After 5,000 hours, new cross-linking reactions on the rubber surface can be detected (Figure 6D). The observed distribution curve gives one peak at 700 Å. With hardness measurements, we do not observe such differences between photochemical and thermal ageings. DSC-thermoporosimetry is a more sensitive technique.

After acidic treatment such as HNO_3 the estimation of post cross-linking is done for short time of exposure (Figure 6E). It was not possible to do the measurements for very hard samples (aged more than 3 hours). The distribution is narrower and the average radius value is 900 Å. Chain scission reactions are the main path for material degradation, simultaneously with the decomposition of the fire retardant at the polymer surface.

Fig. 6. Cross-linking profile obtained by DSC-thermoporosimetry on aged sample surface; A- 907 hours in oven; B- 4000 hours in oven; C- 2000 hrs in photochemical device; D- 7000 hours in photochemical device; E- Nitric acid treatment 1 hour.
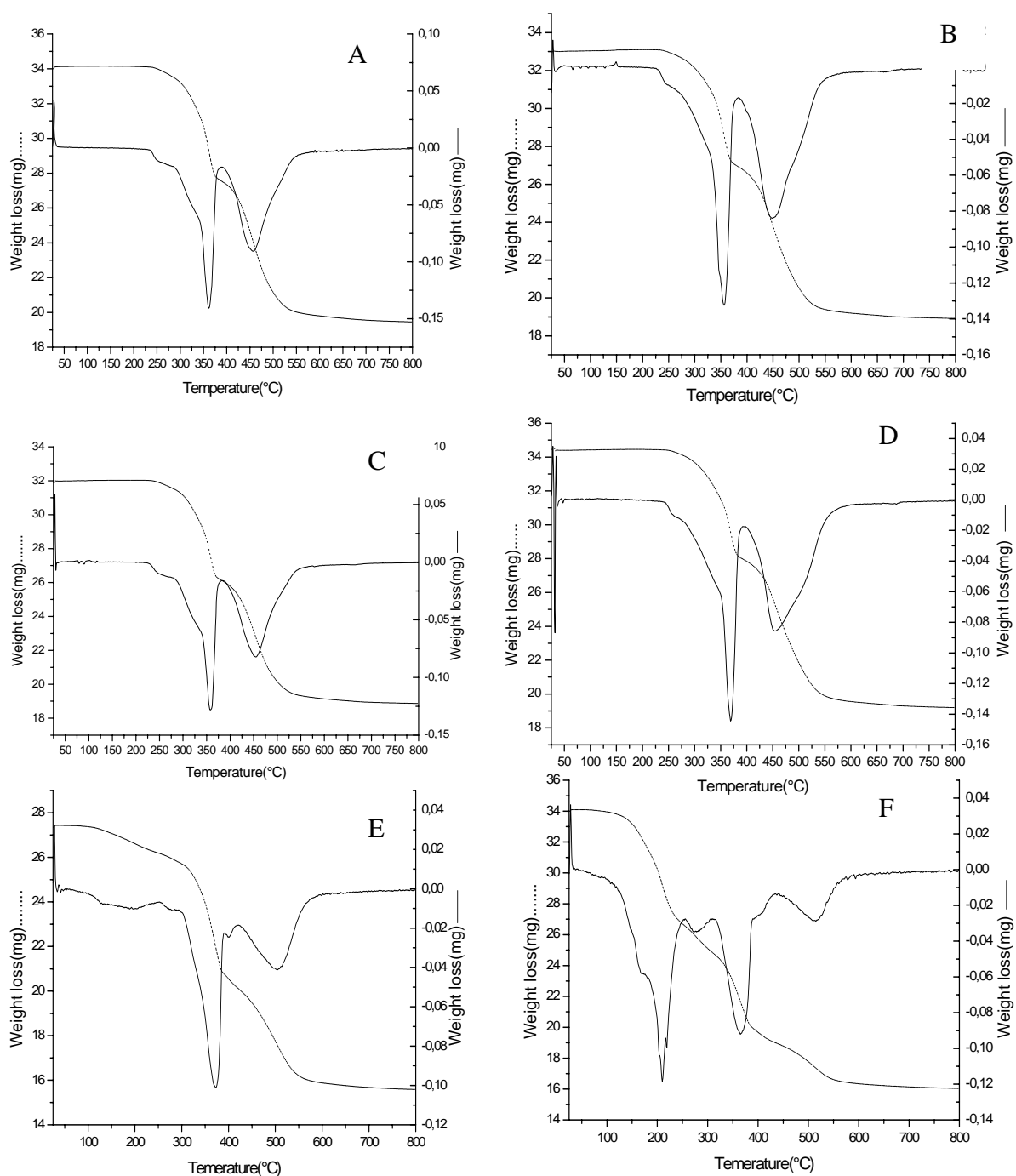
Fig. 7. TGA of silicone rubber before and after ageing (weight loss and derivate curves); A– Unaged sample; B– 10 000 hours in photochemical device; C- 10 000 hours in oven; D-260 hours under sulfuric acid treatment; E– 48 hours under nitric acid treatment; F– 2 months under nitric acid treatment.

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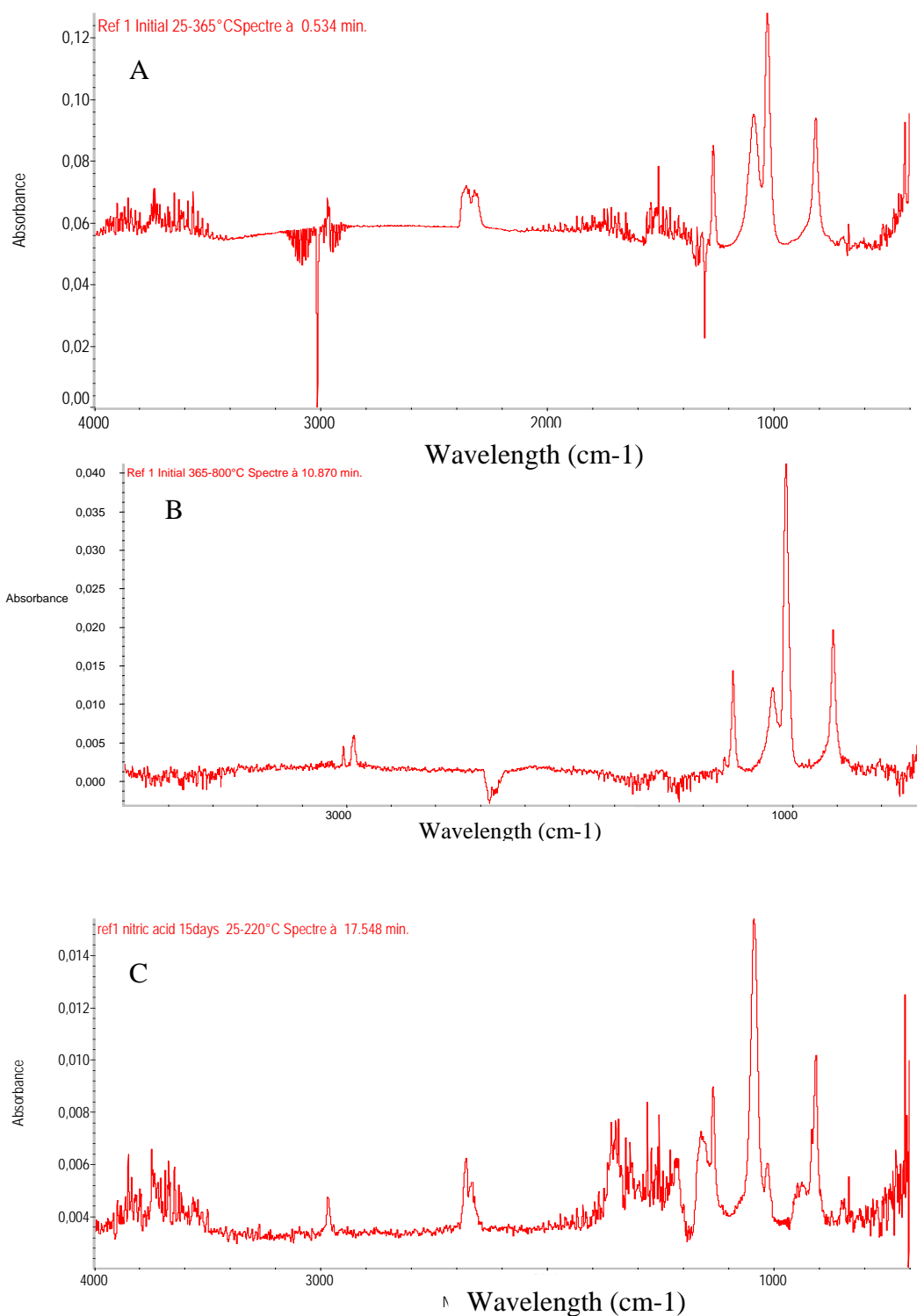
Fig. 8. FTIR results on gaz coming from TGA. A– First part (360°C) for unaged sample; B– Second part (450°C) for unaged material; C– New bands for the sample under nitric acid treatment (15 days).

The TGA curves obtained after a thermal decomposition from 20°C to 800°C by 10°C/min under oxygen allowed us to compare the thermal stability of silicone rubber after various ageing (figure 7). The curve 7A with the weight loss shows the

decomposition of unaged filled cross-linked sample, which starts at 250°C, due to $Al(OH)_3$ deshydratation. We can mainly notice two peaks (derivative curve) with two stages of decomposition (end-set temperatures 360 and 450°C). We get the same results after different times under photochemical, thermal ageing and exposure to sulphuric acid vapours (curves B, C and D)It means that post cross-linking or chain scission occurred upon ageing and detected with other techniques, does not affect the thermal stability of silicone material. The first IR spectra of the gas coming from the degradation show main bands attributed to H_2O and CO_2. Then new bands of siloxane oligomers at 1260, 1090, 1030, and 790 cm^{-1} are detected (figures 8A and B). The two peaks at 360°C and 450°C show the presence of several siloxane oligomers. The presence of H_2O and CO_2 decreases upon the degradation after 360°C is also noticed for the last part of decomposition. Its assignment was not successful. The thermal oxidative decomposition after nitric acid treatment is quite different and depends on the time of exposure. After 48 hours in HNO_3 vapours the weight loss starts at 150°C (figure 7E). This means that the thermal stability of the formulation is weaker compared to other ageing. The main peak on derivative curve gives an end-set temperature at 360°C. We underline also the presence of a peak around 500°C. After 7 days the weight loss for the first peak at 150-200°C increases (figure 7F). The second peak intensity at 360°C decreases. We can always observe the peak at 500°C. The IR spectra allow detecting of the presence of H_2O and CO_2 and new siloxane oligomers bands (figure 8C). A new band at 1380 cm^{-1} of strong intensity is also noticed for the last part of decomposition. Its assignment was not successful.

Conclusion

This work confirms the stability towards oxidation upon accelerated ageings of filled cross-linked silicone rubber. Changes in the IR spectra could not be detected even after 10000 hours in UV device or oven. The presence of aluminium trihydate in the formulation is clearly identified to be a problem in terms of long term behaviour after nitric acid treatment. Post cross-linking and chain scission reactions are revealed by hardness mesurements and DSC-thermoporosimetry after usual ageings (photochemical, thermal) and exposures to acidic vapours. The main path of degradation (chain scission or cross-linking) depends on the ageing. To avoid this degradation process stabilizers should be tested in such formulation. TGA-FTIR results allow us to compare the thermal stability of silicone rubber after various ageings. The thermal decomposition of samples after nitric acid treatment is quite different from the degradation obtained for unaged material or other aged rubbers.

The studied formulation gives satisfactory results towards usual ageings (an induction period is identified). In the case of polluted ageing (with HNO_3) we need to do some improvements by adding specific stabilizer or removing the actual fire retardant. In this paper we have also tried to highlight the choice of techniques and the complementary nature of each.

Experimental part

Materials

Silicone rubber (HTV – High Temperature Vulcanized) is polydimethylsiloxane kindly provided by SEDIVER, France. The composition of the filled cross-linked PDMS is

given in Table 2. The presence of silica can be noticed. The curing agent is 2, 5 dimethyl 2,5 di(t-butylperoxy) hexane (DHBP).

$$(CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}(CH_3)_2C\text{-}O\text{-}O\text{-}C(CH_3)_3$$
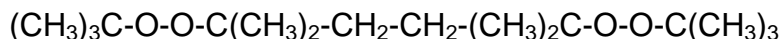
The formulation contains a flame retardant which is aluminium trihydrate. Thick 2 mm sheets were prepared for the ageing and the characterization. The curing time by compression moulding at 170°C was 12 minutes; this time corresponds to the usual optimal curing conditions. Sulphuric acid (95%), nitric acid (68%) and sodium chloride were products coming from Prolabo (VWR). We also used a crude hydroxy terminated PDMS coming from Scientific Polymer Products (Sp^2). This sample is reference 870 with a molecular weight of 90,000 g/mol (GPC).

Tab. 2. Composition of filled cross-linked PDMS

Composition	Quantity
PDMS	100 parts
Silica	23 parts
Alumina Trihydrate	80 parts
DHBP	0.4 part

Ageing

Five types of ageing were tested for comparison. An accelerated classical photoageing was performed directly on the silicone rubber sheets. The irradiation device (SEPAP 12-24) has been described previously [23]. The system is characterised by the source, medium pressure Hg lamps filtered with borosilicate envelope (λ>300 nm) and by careful control of the temperature with a thermocouple in close contact with one of the samples. Samples are rotated at a constant distance (20 cm) from the sources. The samples were irradiated at 60°C in a SEPAP chamber equipped with four lamps.

We used an aerated oven (MEMMERT) for thermal exposure at 100°C. The other ageing was salt-fog test usually used for metallic materials (H. KOHLER – HK 320). The conditions of this test were the concentration of NaCl (5% weight) and the temperature at 35°C. We finally used dessicators to carry out polluted ageings, such as nitric acid vapours or sulphuric acid vapours at room temperature.

Analytical tools

The chemical changes upon irradiation were followed by FTIR-ATR spectroscopy (Attenuated Total Reflectance - Nicolet Impact 400 and Thunderdome accessory with germanium crystal). With this reflection analysis we can operate on thick sheets (for example cross-linked and coloured polymers). We analyse the material surface upto a few micrometers.
Hardness measurements were done with a Zwick Werk (NR 83195) – Shore A (weight 1 kg) system on polymer sheets before and after ageings. Ten measurements were made and an average value was then given.
The evolution of cross-linking is followed by DSC-thermoporosimetry. It is a calorimetrical technique used for the visualization of the material texture by studying the phase transition (crystallization, melting or other change of state) undergone by

the swelling solvent (cyclohexane) trapped in the polymeric network. The transition temperature of this confined solvent depends on the characterisation of the surrounding polymeric swollen network. The thermoporosimetry has essentially been applied to rigid porous substrates [24, 25]. The theoretical basis was established by Brun *et al.* [24]. It is assumed that a polymeric gel is equivalent to a three dimensional network of adjacent cells that is called mesh. The solvent swells the crosslinked polymer until equilibrium state is reached. It yields to a swollen gel where the solvent is present under two environments : the confined solvent which is trapped inside the gel and the part of solvent which remains out and represents the excess (free solvent). The free solvent behaves like a pure solvent in term of phase transitions. On the other hand the confined solvent undergoes the phase transitions at different temperatures depending on the characteristics of surrounding polymeric network and especially depending on the size of the network mesh. The difference in the transition temperature ΔT between free and confined solvent can be related to the size of the mesh for elastomers. Differential Scanning Calorimetry can be used to measure ΔT precisely. Calibrations have been done for obtaining useful thermodynamical data from the solid to solid cyclohexane transition [26]. The following empirical relationships have been established :

$$R(A) = 16.93 + 125.43 * \exp(-\frac{\frac{1}{\Delta T} + 0.0756}{0.0205}) \quad with \quad -55 \le \Delta T \le 0°C \quad for \quad cyclohexane \quad (1)$$

$$\frac{dV}{dR} = K \frac{y*(\Delta T)^2}{Wa*\exp(-\frac{\frac{1}{\Delta T} + 0.0756}{0.0205})} \quad (2)$$

$$Wa(J/g) = 0.0203*(\Delta T)^2 + 2.6034*\Delta T + 82.199 \quad with \quad 0 > \Delta T > -55°C \quad (3)$$

where *R(Å)* is the distance between cross-links in the swollen gel, expressed in *Angstrom* and $\Delta T = T - T_0$, the temperature depression of the swelling solvent determined from the thermal DCS curve with T_0 = -88.63°C for cyclohexane, V is the volume of the solvent concerned by the thermal transition and contained in network cells, R is the distance between cross-links, *K* is a proportionality coefficient that depends on both the DSC instrument and the swelling solvent, *y* is the DSC thermal curve ordinate and *Wa* the apparent energy of the solid-solid transition. DSC instrument is a METTLER TOLEDO DSC 30 used from −88°C to −106°C at 0.7°C/min to see the crystalline solid-solid transition. A cryogenic microtome LEICA Jung Supercut LN20 was used at −50°C to cut the 2 mm sheets into small slices of 180 μm thick.

Other results were obtained with a coupled equipment TGA-FTIR (METTLER TOLEDO TGA/SDTA851 – NICOLET Nexus). Gas coming from TGA is transfered with a heating tube in a gas cell and characterized by FTIR. The temperature method was a dynamic segment from 20 to 800°C by 10°C/minute under oxygen (40ml/min). The IR experiments were done every minute during the entire thermogravimetric program.

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