Durability of crosslinked polydimethylsyloxanes: the case of composite insulators

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Abstract

Most applications of silicones are linked to their hydrophobic properties and (or) their high resistance to ageing (e.g. thermal ageing and photoageing). However, when placed in extreme environments, these materials can fail as in the case of epoxy/fiber glass composite powerlines insulators, where crosslinked polydimethylsyloxanes (PDMSs) are used as the protective envelope (housing) of the insulator. We report on the behavior of both pure/noncrosslinked PDMSs and typical formulations used in industrial insulators, i.e. containing peroxide crosslinked PDMS, alumina trioxide hydrated (ATH) and silica. Special attention is paid on both (i) the sources of potential degradation and (ii) the best analytical methods that can be applied to the study of very complex formulations. (i) Aside from conventional types of ageing such as photo-ageing and thermal, hydrolytic, and service life ageings, treatments with acidic vapors, plasma and ozone possibly generating species from the reaction of a high electric field with air were also performed, which allowed to accelerate electrical and out-door ageings and to obtain differently aged materials. (ii) Aside from conventional analytical methods of polymer degradation such as FTIR/ATR spectroscopy and SEC, TG, hardness measurements, more specific methods like photo/DSC, TG/IR, thermoporosimetry, resistivity and density measurements were also performed to characterize the chemical and physical evolutions of polymer materials. In particular, it was found that treatment with nitric acid vapor has detrimental effects on the properties of both fire retardants (e.g. ATH) and PDMSs, affecting the hardness and resistivity of the formulated material.

Keywords: durability, composite insulators, PDMS, silicone, post-crosslinking

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The salient properties of dimethylsilicones include thermal and oxidative stabilities, resistance to weathering, low surface tension, high resistivity and chemical and biological inertness [1,2]. Heat-cured rubbers can be produced using peroxides and their tensile strength can be largely improved by adding silica as filler [3]. Thus, silicone elastomers have found increasing applications in the industry of electric insulators.

These composite insulators typically consist of a central rod made of epoxy and fiber glass enclosed in an envelope/housing made of elastomer, which is the part we are interested in studying. The housing material is subjected...
to multiple extreme environments during its service life. The extreme environments depend on the climate and installation site (proximity to the coast or petrochemical environment).

This research deals with the study of the long-term behavior of the above-mentioned insulators, and will help in improving the stability of the formulation and the choice of material for improving their service life. Aside from pure noncrosslinked polydimethylsiloxane (PDMS), three industrial formulations based on PDMS are studied. Because of the specific use of silicones, we focused on searching the best means of simulating/accelerating the degradation, particularly that observed in special areas (e.g. coastal and petrochemical environment).

In this paper, we will also describe a set of analytical techniques that can be used to monitor the degradation of both pure silicone and complex industrial formulations of composite insulator housings. Finally, on the basis of our salient results, we propose an approach to improving the service life of the materials studied.

2. Experimental

2.1. Materials

Five polydimethylsiloxanes (pure, unfilled and noncrosslinked) with different molecular weights (36 000 < Mw < 115 000) and terminal groups (e.g. dihydroxy, acetoxy and methyl acetoxy) were provided by SP2-USA (Scientific Polymer Products). The polysiloxanes used were mainly liquids and aged in small glass tubes.

Three industrial formulations of insulator housings were provided by Sediver Co., France. They contained 100 parts of peroxide-crosslinked PDMS, 80 parts of alumina trihydrate (ATH), 23 parts of silica and 0.4 parts of peroxide (2,5-dimethyl, 2,5-dibutylperoxihexane, DHBP). For the study, 2-mm-thick sheets were prepared by compression molding (12 min at 170°C). In one of the formulations, ATH was silane-surface-treated. The other formulations were finally prepared by adding several stabilizers.

2.2. Artificial and outdoor ageing

Owing to the multiple extreme environments to which the insulators were exposed, we considered various types of artificial ageing.

2.2.1. Accelerated photoageing. Accelerated photoageing was performed using a SEPAP 12/24/ATLAS device that was described previously [4]. The system is composed of a source, medium-pressure Hg lamps (filtered with borosilicate envelope, in this case, λ > 300 nm) and a thermocouple for the careful control of the temperature set in contact with one of the samples. The 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 400 W lamps. Under such conditions, the accelerated factor of pure polyethylene is approximately 12 (1 month in SEPAP corresponds to roughly 1 year in natural ageing; however, this factor is strongly dependent on both polymer type, formulation analysed and climatic conditions taken in reference). Few irradiations were also performed with a Hamamatsu light generator equipped with a ‘Lightningcure LC6’ source (Xe/Hg, ‘medium pressure’, changeable intensity) which was fixed to a DSC device (see the description of PhotoDSC instrument below).

2.2.2. Thermal ageing. Thermal-ageing was performed in an aerated oven (Memmert) in the temperature range of 60–100°C. Some experiments were also performed in a TG instrument using oxygen flow (see below).

2.2.3. Ageings under acid vapors. Ageing in different acid vapors (i.e. nitric and sulfuric acids) was performed in laboratory desiccators (concentrated aqueous solutions were poured to the bottom of the desiccators and polymer samples were placed on the upper ceramic grid). A few tests were also performed in salt fog chambers (H. Kohler-HK320) with 5 wt% NaCl aqueous solution. All types of ageing were performed at room temperature.

2.2.4. Ozone ageing. Ozone ageing was performed in ‘Laboratoire de Recherches et de Contrôle du Caoutchouc et des Plastiques’, LRCCP in Vitry sur Seine, France. The formulations were aged for 8 weeks at 200 ppm and 23 ± 2°C without stress.

2.2.5. Plasma treatment. Plasma treatment was carried out in an Alcatel SCM 450 unit equipped with a 13.56 MHz radio-frequency generator. The treatment was performed at pressures of 1.33 × 10⁻² mbar and 2.56 × 10⁻² mbar with a mixture of argon, nitrogen and oxygen and in the power range of 400–550 W. The disk on which the samples were exposed to the plasma in the unit was rotated in order to obtain uniform exposure of the specimens.

2.2.6. Laboratory electrical ageing. Laboratory electrical ageing (of the housings) was performed at 20 kV for 5 years at Sediver test lab in France.

2.2.7. Natural ageings. Natural ageing (of the housings) was performed near petrochemical sites in Texas and Saudi Arabia for 6 years.

The combination of high electric fields with air, water, UV light (λ > 300 nm) and heat (60°C) could result in a large variety of reactive species of oxygen (O, O₂, HO, …) or nitrogen (NO, NO₂, NOx, HNO₃, …) [5, 6] that can attack most components of the housing formulation. This is why ozone, oxygen plasma and nitric acid treatments were also performed aside from conventional photo/thermal ageing exposures. Complementary sulfuric acid and sodium chloride treatments were also performed in polluted and coastal areas.
2.3. Analysis

The degradation of a material usually involves chemical modifications, which are often (but not always) detrimental to the performance of the materials during its service life. Thus, to study the ageing of PDMS and insulators housings, the following two analyses were performed.

2.3.1. Chemical modifications. The main chemical changes expected concern both chain scission/branching-crosslinking and oxidation, which are not necessarily measured using the same analytical tool.

(a) FTIR spectroscopy. FTIR spectroscopy is a basic tool for polymer oxidation analysis as oxidation products (hydroxy and carbonyl functional groups) are easily detected, some of which (e.g. carboxylic acids and aldehydes) are signs of scission reactions. We used a FTIR spectroscope (Nicolet Impact 400) equipped with a reflectance accessory (ThermoDome with germanium crystal). The analysis dealt with only the first 2–3 $\mu$m of the surface of the PDMS and housing samples.

(b) Size exclusion chromatography. Size exclusion chromatography is also a conventional tool for determining changes in molecular weights, especially those due to chain scission upon ageing. The instrument, we used was a Vissectok with universal calibration. The detectors used were a refractive index detector (Vissectok VE 3580) and a viscosimeter detector (Viscottok TriSec Model 270). The column was made of cross-linked PMMA with a flow rate of 1 mL min$^{-1}$. The solvent used was HPLC-grade toluene.

For the identification of crosslinking reactions, other techniques were used:

Density measurement: The initial noncrosslinked polymer (PDMS) was dissolved in an appropriate solvent (cyclohexane) and the eventual crosslinking appearing during degradation could be monitored from the decrease in density resulting from the precipitation of insoluble/crosslinked degraded polymers. Density measurement was carried out with an accurate vibrating densimeter tube (Anton Paar DMA 58). The accuracy of the instrument was $\pm 0.00001$ g cm$^{-3}$. Air and water were used for its calibration.

Differential scanning calorimetry (DSC)-thermoporosimetry: The initial noncrosslinked or crosslinked polymer (PDMS) was dissolved in an appropriate solvent (cyclohexane for the PDMS and housings) and for the in situ measurement of the solvent trapped in eventual meshes (resulting from crosslinkings) was measured by DSC (in the case of cyclohexane, a solid/solid transition at $-90 \, ^\circ \text{C}$ was shown to be more sensitive than the freezing point). The thermodynamic treatment of the phenomena allowed the conversion of temperature shifts into porous size distribution (thermoporosimetry). We developed this approach in a few studies [7–10]. DSC was carried out using two calorimeters.

(i) Mettler Toledo DSC30 equipped with two systems of cooling: this calorimeter had an intracooler that permits cooling up to $-65 \, ^\circ \text{C}$ or another system using liquid nitrogen cooling up to $-150 \, ^\circ \text{C}$.

(ii) Mettler Toledo DSC822 equipped with liquid nitrogen for cooling: this calorimeter was controlled using STARe software and calibrated with indium (156 $^\circ \text{C}$), zinc (420 $^\circ \text{C}$) and heptane ($-92 \, ^\circ \text{C}$). The DSC programme method used was $-88$ to $-106 \, ^\circ \text{C}$ at $0.7 \, ^\circ \text{C} \text{min}^{-1}$ to observe crystalline solid–solid transition. In a few cases, a cryogenic microtome LEICA Jung Supercut LN20 was used at $-50 \, ^\circ \text{C}$ to cut the 2 mm sheets into thin slices 180 $\mu$m thick (to see the crosslinking profile).

Differential scanning calorimetry-polymer crystallinity: DSC is conventionally used to observe the crystallinity of polymers. Crosslinking reduces the ability of the polymer to crystallize, that the evolution of DSC curves upon ageing can be an indirect method of monitoring crosslinking [11]. Recently [12], a device allowing us to perform in situ photoageing in DSC capsules was installed in our DSC instrument. Thus, the change in crystallinity (linked to crosslinking) could be monitored during the time of irradiation. The DSC instrument used was a Mettler Toledo DSC822e apparatus equipped with an Intracooler and liquid nitrogen cooling. A Hamamatsu light generator equipped with a ‘Lightningcure LC6’ source (Xe/Hg, ‘medium pressure’) was fixed to the DSC device. The light generator was servocontrolled by DSC software (STARe) which permitted a choice of light intensity from 0 to 324 mW cm$^{-2}$ and the duration of irradiation. Two identical fiber bundles supplied the irradiation light to both the sample and reference DSC pans. The source was filtered using sapphire disks to deliver radiations of wavelengths longer than 300 nm. In this technique, we could also control the atmosphere used for ageing. We carried out all the PhotoDSC experiments in air atmosphere.

2.3.2. Changes in physical properties. We were interested in properties directly associated with the use of insulators.

(a) Thermogravimetric analysis (TGA) coupled with FTIR spectroscopy. This versatile analytical technique can be used for (i) the simulation/acceleration of thermal ageing when conducted in the presence of oxygen, (ii) the evaluation of the thermal resistance of a material or (iii) the identification of decomposition products. This last application generally derived from the weight loss can be improved by connecting an FTIR spectroscope for the analysis of effluents. We used a Mettler Toledo TGA/SDTA851—Nicolet Nexus TGA/FTIR instrument. The gases coming from TGA were transferred to a heating tube in a gas cell and characterized by FTIR spectroscopy. The temperature method used a dynamic segment from 25 to 800 $^\circ \text{C}$ at 10 $^\circ \text{C} \text{min}^{-1}$ in oxygen or nitrogen atmosphere (40 mL min$^{-1}$). IR spectra were recorded every minute throughout the thermogravimetric program using the series option of OMNIC software.

(b) Dielectric properties (resistivity and conductivity). Surface resistivity measurement was performed on a Keithley 6517 Hi-R Test model that can measure surface resistivity from $10^3$ to $10^{17}$ $\Omega$ and volume resistivity from $10^3$ to $10^{18}$ $\Omega$ cm. Conductivity measurement was
performed with a Schering bridge (scheme 1) on the basis of capacity measurement and capacitor dielectric loss. We modify $R_4$, $C_4$ and $R_3$ until the galvanometer reading is 0 in the Schering bridge. Finally, $\tan\delta$ has been calculated using $\tan\delta = \frac{\Pi \times R_4 \times C_4}{1}$. For this purpose, 2-mm-thick samples were cut in circles of 8 cm diameter.

(c) Permeability to water vapor. The instrument used to characterize the samples is a Mocon Permatran W3-33 with an IR detection system. The coefficients for the transmission of water vapor for the films are determined according to ASTM F 1249 at 38°C and 90% relative humidity. The results are expressed in g m$^{-2}$ 24 h$^{-1}$. The surface area analyzed was 50 cm$^2$.

(d) Contact angle measurement. We used a CAM unit (KSV instruments, France) with a firewire camera with telecentric optics and 55 mm focus length. Distilled water was used as the liquid.

(e) Hardness test. The hardness test measures the depth of an indentation in the material created by a given force. The depth is dependent on the hardness and viscoelastic properties of the material and on the duration of the test. We performed the test with a Zwick Werk (NR 83195) – Shore A (weight 1 kg) system on 6-mm-thick polymer sheets before and after ageing. The average of ten measurements of each sample was calculated.

3. Results and discussion

3.1. Pure PDMS (unfilled, noncrosslinked)

No change in OH or carbonyl regions of IR spectra was observed after 500 h of phototreatment ($\lambda > 300$ nm) and thermal (60–100°C) and vapor acidic treatments, confirming the high stability of PDMS independently of molecular weight and type of chain end (hydroxy or acetoxy). An opposite behavior was observed by crosslinking analysis.
As shown in figure 1, both density (of cyclohexane solution of PDMS) and SEC measurements show marked changes upon exposure, consistent with fast crosslinking reactions. In addition, when PDMS has a significant crystallinity (55%), photo/DSC shows a fast decrease of crystallinity also proving crosslinking reaction. However, an opposite change was observed for low-crystallinity samples (15–20%) probably because of a stronger effect of scission reactions that may facilitate crystallization. More details can be found in some of our recent papers [13, 14], including the effect of pendant alkyl groups, and in the TG/FTIR measurements.

3.2. Housing formulations (crosslinked PDMS + ATH + SiO₂)

A strong detrimental effect was observed with nitric acid vapor treatment. After HNO₃ ageing, the IR spectra of both housing formulation and pure ATH showed a distinct (aluminum) nitrate band at 1400 cm⁻¹, indicating that ATH is involved in degradation. The behavior of housing formulation using silica-surface-treated ATH was slightly better. Very sharp changes in dielectric properties, hardness, thermal properties (TG/IR) and post-crosslinking behavior were also observed, proving that PDMS is also affected by the degradation. As can be seen in figure 2, photoageing and thermal ageing also affect hardness and thermoporosimetry value, confirming the ability of PDMS to post-crosslink under such conditions. By thermoporosimetry, we observed an initial bimodal curve showing the heterogeneity of the initial crosslinking; after thermal ageing part of the material that is weakly crosslinked (porous size, 500 Å) was converted into fully crosslinked PDMS (porous size, 180 Å). The same phenomenon was also observed occurring in the core of the sample by analysing microtomed slices (180 µm each) [15]. A similar post-crosslinking upon thermal degradation was also observed in the case of EPDM-based formulations [16].

Many results show that the housing formulation based on PDMS can be degraded by different types of environmental ageing, particularly nitric acid, photoageing and thermal treatments (plasma, ozone, sulfuric acid and sodium chloride treatments showed minor effects). ATH, particularly when used without surface protection is very
sensitive to the presence of nitric acid, and the PDMS part (peroxide crosslinked) is also modified probably by scission/crosslinking. Unfortunately, such degradation markedly modifies the essential properties of insulator housings, such as hardness and dielectric properties.

3.3. Improvement in housing formulation

The sensitive parts of the housing (PDMS and ATH) were modified with the aim to improve housing durability. An ATH modified by surface treatment with silane was added to the formulation in place of normal ATH. The reactivity with nitric acid markedly decreased compared with ATH. The protection of PDMS was tentatively realized by adding stabilizers (phenolic (BHT, Irganox 1076, Silanox), HALS (Tinuvin 770) and phosphate (Irgafos PEPO) compounds). Among these compounds, Silanox, a phenolic antioxidant with a PDMS squeletum, gave slightly better protection probably because of its better compatibility with the PDMS part of the material. The improvement achieved with the use of both surface-treated ATH and Silanox was observed by infrared spectroscopy and photoDSC.

4. Conclusions

PDMSs show a relatively poor stability upon photoaging, thermal ageing and nitric acid ageing when the analysis used focuses on the changes induced by scission/crosslinking reactions instead of the conventional carbonyl index method. Photoaging and thermal ageing in oxygen proceed generally by a radical-based mechanism and, based on the model of the conventional peroxide curing of silicones, the main steps are probably hydrogen abstraction from the methyl group and the subsequent crosslinking reactions [3]. Note that the substitution of methyl groups by longer alkyl chains results in the oxidation of the alkyl pendant chain instead of crosslinking reactions [17–19]. Nitric acid reacts on the Si–O bond, which is sensitive to basic and acidic hydrolyses [20], and both scissions and crosslinking reactions possibly occur in this case.

Peroxide-crosslinked PDMS also show significant post-crosslinking upon the same ageing and, when an ATH fire retardant is added (case of insulator housings), an additional acid/base reaction with nitric acid is observed. The combination of both reactions results in a marked change in the properties of the housing such as hardness and dielectric properties. The presence of high electric fields close to the housings could result in the formation of oxidized forms of nitrogen (e.g. nitric acid and acidic rain). The efficiency of this species is probably reinforced by the high permeability of silicones to gases [1, 2]. Both the surface treatment of the filler and the addition of phenolic stabilizers to the housing formulation resulted in an improvement in housing durability. However, such improvement should still be checked under outdoor conditions, particularly under climatic conditions where the material has been observed to fail. The prediction of the long-term behavior of such complex materials using accelerated conditions is always a difficult task, particularly with regards to the identification of the main factor affecting the properties of the material.

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