Dynamic glass transition of filled polysiloxane upon electron irradiation

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ABSTRACT

The influence of radiation-induced crosslinking on the molecular mobility of a filled silicone elastomer near the glass transition (α-relaxation) was analyzed using broadband dielectric spectroscopy. Samples of the isolated polysiloxane matrix (neat) were also studied so as to assess the filler influence on the evolution of the α-relaxation.

A slowing-down of the segmental dynamics was observed with increasing ionizing dose. It was ascribed to the relaxing dipoles losing degrees of freedom as a result of network stiffening. An enhancement of intermolecular coupling, associated with the cooperativity of the α-relaxation, was deduced from the dielectric analysis. Similar observations were made in the past with chemically crosslinked polysiloxanes. This study evidenced that even though the crosslinks formed upon chemical crosslinking (mainly Si—CH_2—CH_2—Si) differ in nature from those formed upon irradiation (mainly SiO_3 and SiO_4), they affect the dynamic glass transition in a very similar way.

The filler influence on the dynamic glass transition was also studied upon irradiation. One of the main outcomes of this study is the fading of the filler-related effect in the most irradiated samples: both the shape and dynamics of the α-relaxation were identical in the most highly irradiated neat and filled samples.

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1. Introduction

This study is encompassed within the field of materials ageing in space environment. It is focused on a silicone elastomer used as an adhesive in solar panels bonded assemblies for communication satellites.

In a previous study [1], the structural evolution of a space-used filled silicone elastomer exposed to high energy electrons was investigated. A preferential crosslinking process of the polysiloxane matrix was observed, involving the formation of SiO_3 bonds in the network. Moreover, the inorganic fillers (silica and iron oxide) were shown to cause further radiation-induced crosslinking through the formation of SiO_4 bonds at the filler-matrix interfaces. This additional crosslinking process resulted in an increase in mechanical modulus upon irradiation that was more pronounced in the filled samples than in the isolated matrix (neat samples). On another hand, scanning calorimetry measurements showed no significant filler influence on the evolution of the glass transition temperature.

The α-relaxation of model linear PolyDiMethylSiloxane (PDMS) [2–4] and PolyMethylPhenylSiloxane (PMPS) [5,6] has been studied thoroughly, partly because neither secondary relaxations (they occur at much lower temperatures) nor electrical conductivity (observed at higher temperatures) interfere with it. Broadband Dielectric Spectroscopy proved to be a particularly adequate tool for that purpose. Regarding three-dimensional polymer networks, multiple studies involving a variety of polymers [7–10] – including silicone networks [11,12] – led to the general conclusion that an increasing degree of crosslinking results in a slowing-down of the α-relaxation dynamics, as well as a more pronounced deviation from Arrhenius behavior: crosslinked polymers tend to be more fragile than linear ones with the same backbone. In such studies, the degree of crosslinking is generally controlled chemically (i.e. by varying hardener proportion). Polyadditive crosslinking of the two components-RTV silicone rubbers mainly proceeds through the formation of silethylene links (Si—CH_2—CH_2—Si) [13], while radiation-induced crosslinking primarily involves the formation of SiO_3 crosslinks [1,14].

Silicone elastomers for space applications are filled with inorganic particles. Silica fillers are undoubtedly the most used as they enhance their mechanical properties [15]. Fillers incorporated in a polysiloxane matrix affect the α-relaxation: it is generally accepted that a polymer layer of reduced mobility (~a few nm) is formed at the surface of the fillers [16]. The filler influence on the α-relaxation mainly depends on their geometry, relative quantity, and on their interactions with the matrix.

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The present study aims at assessing the influence of the crosslinks nature (chemical or radiation-induced) on the α-relaxation of a silicone elastomer. It will also bring insight in the filler influence on the dynamic glass transition throughout chemical ageing, which has not been studied yet.

2. Materials and methods

2.1. Materials

The studied material is a commercial (Wacker) two components silicone elastomer which crosslinks at room temperature (RTV, *Room Temperature Vulcanization*). Part A mainly consists of a poly(dimethylsiloxane-*co*-methylphenylsiloxane) resin (approx. 35 wt%) mixed with crystalline silica (α-quartz particles of the glass splinter type, the size of which is comprised in the range [0.2–20 μm]) and iron(III) oxide (spherical particle size in the range [0.1–1 μm]) fillers. Part B is a hardener containing a Pt catalyst responsible for polymerization. A filtering process performed on part A allowed separation and removal of the fillers from the resin. Consecutive polymerization with unmodified part B allowed the elaboration of *neat* samples (no fillers), as opposed to *filled* unmodified samples (with fillers).

The two components are manually mixed (weight ratio 9:1, according to data sheet) and poured into a mold consisting of a 50×50 mm^2 aluminum substrate the borders of which had been covered with aluminum tape. Even though this material is able to crosslink at room temperature, a curing process of 6 h at 100 °C was performed after mixing in order to enhance sample reproducibility.

The glass transition temperature of both filled and neat materials were measured at -117 ± 1 °C, suggesting a low phenyl side groups content (the phenylmethylsiloxane mass fraction was estimated to be approximately 10% [17]).

2.2. Electron irradiations

Electron irradiations were performed under secondary vacuum in the SIRENE facility at ONERA [18]. The procedure and dose calculations are detailed elsewhere [1] and summarized here. 150 μm-thick elastomer films were irradiated using a 400 keV-Van de Graaff electron accelerator along with a scattering foil in order to uniformly expose the sample surface. Ionizing doses up to 1.4×10^6 Gy were achieved in <12 h thanks to high beam currents in the order of 10 nA.cm^{-2}. Ionizing dose D expressed in Grays (1 Gy = 1 J·kg^{-1}) is defined by Eq. (1).

$$D = \Phi \frac{1}{d}\left(\frac{dE}{dx}\right) \tag{1}$$

where Φ is the particle fluence, d the material density and dE/dx the energy lost by an incident particle by unit length travelled in the material.

The samples irradiated in this way are uniformly aged and the indicated doses are mean values in the middle of the films.

2.3. Broadband dielectric spectroscopy

Broadband Dielectric Spectroscopy (BDS) measurements were performed isothermally in the frequency range [10^{-2}–10^6 Hz] on 150 μm-thick films placed between gold-plated stainless steel electrodes (30 mm diameter), using a Novocontrol BDS 4000 impedance analyzer.

Complex dielectric permittivities (Eq. (2)) were calculated from the experimental values of impedance.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \frac{1}{i\omega C_0 Z^*(\omega)} \tag{2}$$

where ε' is the real component of the complex dielectric permittivity, ε'' its imaginary component, C_0 the capacitance in air and Z^* the complex impedance.

The Havriliak-Negami parametric equation (see Eq. (3)) and the Schönhals-Schlosser model (see Eqs. (7a) and (7b)) were used to perform the fits of the experimental data.

3. Results and discussion

First of all, in the ionizing dose range performed in this study, the crosslink densities of the materials were previously shown to be linearly increasing functions of absorbed ionizing dose [1], in agreement with Delides and Shepherd [19] who observed a linear increase of crosslink density up to 1.6×10^6 Gy of γ-rays in PDMS. In this section, the 'ionizing dose' abscissae in most of the figures are therefore proportionally linked to the 'crosslink density' of the samples.

3.1. Crosslinking-induced constraints on the α-relaxation

In Fig. 1 are represented the Broadband Dielectric Spectroscopy (BDS) loss spectra obtained at -105 °C from pristine and irradiated filled samples. The glass transition manifests as a well-defined dielectric loss peak. This is mainly due to the absence of crystallization peak – hindered by both the crosslinks of the network and the phenyl side groups [20] – and local segmental β-relaxation in the vicinity of the α-relaxation. With increasing ionizing dose, the maximum of the peak is shifted to lower frequencies, its intensity decreases, and its breadth increases.

The spectra in Fig. 1 were individually normalized to the coordinates of their respective maxima (f_{max}, ε''_{max}). They are represented in the inset of Fig. 1. The increase in the breadth of the peak is highlighted in the normalized spectra: the half-height width of the most irradiated sample is approximately 7 times larger than the pristine one. This broadening will be discussed in the subsection entitled "*shape of the α-relaxation loss peak*".

In order to analyze the α-relaxation segmental dynamics, the BDS isothermal dielectric loss comprising the relaxation (such as those in Fig. 1) were fitted using the Havriliak-Negami parametric equation [21]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\left(1 + (i\omega\tau_{H-N})^{\alpha_{H-N}}\right)^{\beta_{H-N}}} \tag{3}$$

where ε_s and ε_∞ are respectively the low and high frequency limits of the real relative permittivity, ω the angular frequency of the applied voltage, τ_{H-N} the mean relaxation time for the distribution of dipoles and α_{H-N} and β_{H-N} adjustment parameters in the range [0–1] respectively controlling the breadth and the symmetry of the relaxation function.

Thus obtained τ_{H-N} are represented in the Arrhenius plot in Fig. 2 for the pristine and irradiated filled samples. The mean relaxation times
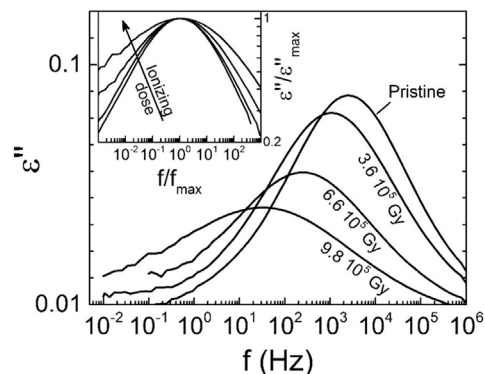

Fig. 1. BDS loss spectra at -105 °C of filled samples exposed to various ionizing doses. Inset: same spectra normalized to their respective maxima.