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Influence of SiO_2 fillers on the irradiation ageing of silicone rubbers

I. Stevenson[a,*], L. David[b], C. Gauthier[b], L. Arambourg[a], J. Davenas[a], G. Vigier[b]

[a]*Laboratoire des Matériaux Polymères et des Biomatériaux, UMR CNRS 5627, Université Claude Bernard Lyon 1, Bât ISTIL,*
43, Boulevard du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France
[b]*Groupe d'Etudes de Métallurgie Physique et de Physique des Matériaux, UMR CNRS 5510, INSA de Lyon,*
20 Av. A. Einstein 69621 Villeurbanne Cedex, France

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Abstract

Effects of irradiation on the viscoelastic properties of peroxide-crosslinked PDMS elastomers (EVC) without filler (1), filled with 30% untreated nanoscopic SiO_2 (2) and with 30% surface modified silica (3) were investigated. Electron irradiation in air using a high dose rate allowing homogeneous irradiation at different doses ranging from 25 to 500 kGy have led to additional crosslinking of these three types of silicone rubbers making them become more rigid and brittle. The apparent crosslink density is higher for filled elastomers since links at the polymer–silica interfaces have been created as a result of irradiation. A further crosslink density enhancement is obtained for the surface-treated silica fillers. High resolution low frequency dynamic mechanical spectroscopy shows that the magnitude of the crystallisation peak located at approximately −40°C decreases with the irradiation dose. As a result, the amplitude of the relaxation process associated with the glass transition near −125°C increases, since a larger amount of amorphous phase is present due to the hindrance of the crystallisation behaviour. DSC measurements confirm that crystallisation is limited by the formation of a higher number of crosslinks, and that this effect is amplified for filled PDMS samples. A study of mechanical hysteresis at high strains (Mullins effect) shows an increase of the associated dissipative phenomena due to the induced polymer/silica bonds.

Keywords: Silicone rubbers; Elastomers; Poly(dimethylsiloxane)

1. Introduction

Silica fillers (colloidal silica or in situ generated silica by sol–gel routes) [1,2] are well known to improve the mechanical properties of elastomers, as indicated by the increase of modulus, hardness and wear resistance. Poly(dimethylsiloxane) (PDMS) chain molecules $-(Si(CH_3)_2-O)_n-$ in particular, can be bonded to the surface of SiO_2 particles by means of covalent bonds thus leading to the filler acting as a crosslinker of high functionality inducing significant changes in mechanical properties. These interactions between filler and polymer chains affect the mobility and crystallisation behaviour [3]. Concerning the influence of fillers on the ageing of polymers, no general trends can be concluded from the literature [4]. In some cases, a stabilising effect of fillers against oxidation is evidenced, whereas in other cases fillers induce undesirable catalytic effects as shown by TiO_2 upon UV exposure. Irradiation ageing in PDMS/silica systems is, in particular, poorly documented [5]. Silicone rubbers are known to exhibit a high resistance to various kinds of irradiation. For example, since the energy to break the Si–O bond is high, the silicone-based rubbers are resistant to UV irradiation. However, the formation of intermolecular crosslinks upon irradiation has been established for a long time, and has stimulated further studies in the vulcanisation of silicone rubbers [6]. Since crosslinking is generally considered to improve the mechanical properties of polymers, limited attention has been drawn on the radiation ageing of PDMS. For example, little information is available on the influence of the fillers on the irradiation ageing of silicone rubbers. Gamma irradiation is known to increase the crosslink density [7]. It has been reported that ZnO and carbon black fillers tend to increase the rate of crosslinking under X-rays irradiation [8] through the formation of chemical links between filler particles and polymer chains, but the consequences of the formation of the crosslinking network on the crystalline phase has not been investigated precisely. The ability to sustain high gamma irradiation dose is important for sterilisation purposes for medical applications [9], as well as for the use of silicone material in nuclear industry.

The aim of this work is to investigate the effects of electron irradiation on the mechanical behaviour of filled PDMS

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* Corresponding author. Tel.: +33-4-7244-6213; fax: +33-4-7243-1249.
E-mail address: steven@matplast.univ-lyon1.fr (I. Stevenson).

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Table 1
Values of the initial Young's modulus E determined from tensile tests with $d\epsilon/dt \sim 0.05\ s^{-1}$, true stress at break ($\sigma_v$) and true strain at break (ϵ_v) for the three different elastomers in the non-irradiated state

Sample	E (MPa)	σ_v (MPa)	ϵ_v
(1) Pure PDMS	0.72 ± 0.05	0.65 ± 0.05	0.8 ± 0.1
(2) PDMS + non treated silica	6.5 ± 0.5	42 ± 5	1.5 ± 0.1
(3) PDMS + treated silica	9 ± 0.5	60 ± 5	1.8 ± 0.1

systems, pointing out the specific effect of the different fillers. The mechanical behaviour is investigated in the low strain regime ($<10^{-4}$) by mechanical spectroscopy, and in the higher strain regime by the study of non-linear effects associated with the Mullins hysteresis.

2. Experimental

Electron irradiation at 2 MeV were performed in the CEA (Grenoble, France) at 35°C (i.e. above the melting temperature of the crystallites, in the rubbery state) in air, with different doses ranging from 25 to 500 kGy to allow homogeneous irradiation throughout the sample. The dose rate used was 500 kGy/h. The samples were provided by Rhodia Silicones (St Fons, France). System (1) was a PDMS rubber crosslinked at high temperature with organic peroxides. This PDMS had a $\langle M_w \rangle = 5,00,000$ g/mol and a polydispersity factor $I_p = 2$ approximately. The mean molar mass between two crosslinking sites was 20,000 g/mol. The filled rubbers contain 30% weight of silica (pyrogenated silica, 200 m^2/g from Degussa–Aerosil 200) aggregates of primary particles around 10 nm without (system 2) and with (system 3) a surface treatment (the silica was treated with $-Si(Me)_2-O-$ oligomers). Depending on the dispersion conditions, the aggregates are likely to form larger scale aggregates, i.e. regions of silica aggregates in the micron range without PDMS. The crosslinking agent used was dimethyl-2,5 bis(tertiobutylperoxy)-2,5 hexane (75%) peroxide. The preparation of the samples was carried out in the following two steps: the first one was anaerobic at 170°C using a pressure of 100 bars for 10 min, the second one was curing at 200°C for 4 h in aerobic conditions (under a flow of air).

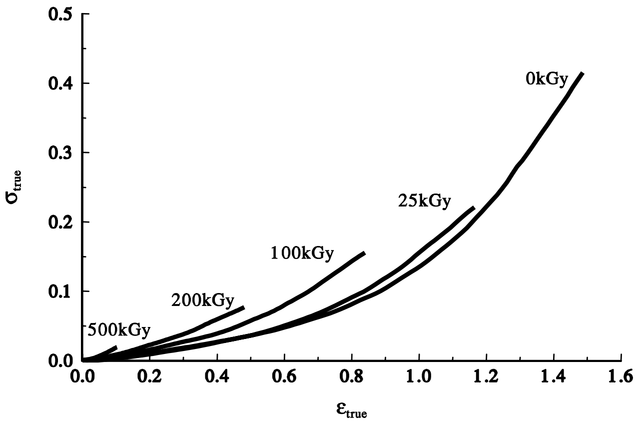

Fig. 1. Tensile tests on PDMS with untreated SiO_2 filler for non-irradiated and irradiated samples at different doses ($d\epsilon/dt \sim 0.05\ s^{-1}$). The end of each stress–strain curve is due to sample breaks.

Dynamic mechanical spectroscopy experiments were performed on a 'home-made' high resolution apparatus [10] working in forced torsion mode in the frequency range $1–10^{-4}$ Hz, and in the temperature range −180–+400°C. Such experimental conditions yield the complex shear modulus, $G^*(\omega\tau) = G' + iG''$. Tan($\varphi$) is defined as the ratio G''/G'. The experiments were carried out in air. Temperature scanning measurements were performed in swapping mode at three frequencies (alternatively 1, 0.316 and 0.1 Hz) at a constant heating rate of 1 K/min. Typical dimensions of the film sample were: $2 \times 6 \times 0.5\ mm^3$. Low frequency high resolution mechanical spectroscopy revealed to be a pertinent tool for the analysis of the effects of irradiation on the molecular mobility and crystallisation behaviour. Dielectric spectroscopy was used to extend the data to high frequencies. However, in all cases, the samples were not polar enough to give better or complementary results.

DSC (Differential Scanning Calorimetry) measurements have been carried out using a DSC 2920 from TA Instruments. Samples weighing approximately 10 mg have been analysed between −165 and 25°C (it was verified that no transition was to be observed above 25°C since vulcanisation is completed). An argon gas flow was circulating over the samples, the cooling fluid used was liquid nitrogen and the heating as well as the cooling rate chosen was 6 K/min. Glass transition temperatures were measured at the conventional onset point, and melting and crystallisation temperatures were measured at the position of the peak maximum. The enthalpies of melting or crystallisation were determined by measuring the area under the corresponding peaks, and are proportional to the polymer crystallinity.

The mechanical properties were measured using an INSTRON 1260 apparatus at a constant crosshead speed of 50 mm/min at room temperature. The samples were cut in the H2 form (AFNOR NF 51-034).

3. Results

3.1. Effect of silica filler on non irradiated material

The mechanical properties of non-irradiated and irradiated PDMS/silica samples were studied by conventional tensile tests leading to classic stress–strain curves. Table 1 shows the reinforcement effect of the silica filler on the values of the initial Young's moduli for non-irradiated samples. The filler acts in two ways: as a composite effect giving rise to a higher modulus and as a crosslinking agent (it is difficult to separate the two phenomena). A higher crosslink density can be obtained with the surface-treated silica fillers, which further develops the crosslinking

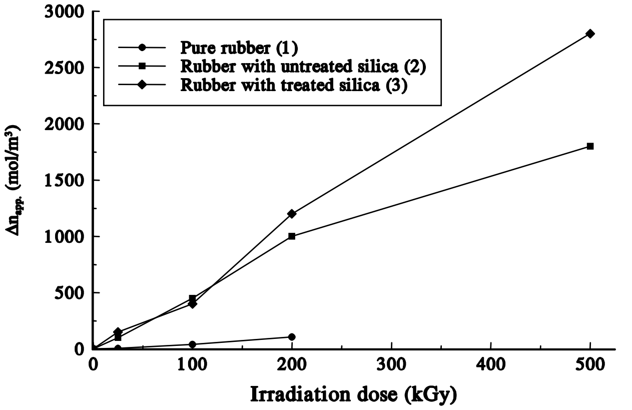

Fig. 2. Variation of apparent crosslink density with irradiation dose for pure PDMS rubber (1), rubber with untreated silica (2), rubber with treated silica (3).

functionality of the silica particles. The same trend is observed on the true stress and strain at break (σ_v and ϵ_v see Table 1). A further reinforcement effect is noticeable with surface-treated silica particles.

The effect of electron irradiation was also evidenced by tensile tests. Typical results for PDMS/silica systems (2) is shown in Fig. 1. Irradiation induces an increase in the elastic modulus and decrease in the elongation at break. In order to see the effect of irradiation alone, the values of the initial Young's moduli E can be converted to an apparent crosslink density n according to:

$$n = E/3\mathrm{RT}$$

If n_0 is the obtained value for non-irradiated samples, the net increase of crosslink density due to irradiation Δn, is given by $\Delta n = n - n_0$.

Fig. 2 shows the increase in Δn with irradiation dose. The apparent crosslink density increases with irradiation dose, but this sensitivity to irradiation is much stronger in the presence of the silica filler. This effect is even larger for the surface-treated silica, which shows that the free radicals created by irradiation increase the apparent crosslink density by their recombination at the surface of the filler. To summarise, the irradiation has a significant effect on the macromolecular networks and enhances the interactions between nanoparticles and the polymer matrix. These interactions are likely to modify the macromolecular mobility which, therefore, influences the crystallisation behaviour as studied in the next section.

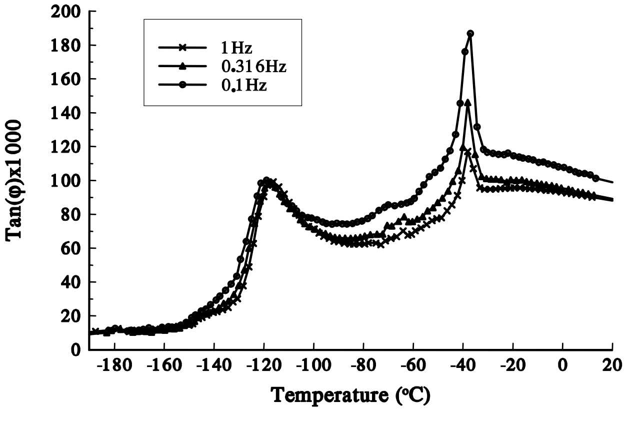

Fig. 3. Tan (φ) as a function of temperature during a heating rate of $\mathrm{d}T/\mathrm{d}t =$ 1 K/min at three different frequencies (1, 0.316 and 0.1 Hz) for the non-irradiated, surface treated filler PDMS rubber (3). The sample was previously cooled at 6 K/min down to −180°C.

3.2. *Effects of irradiation on molecular mobility and crystallinity*

The viscoelastic response of PDMS rubbers filled with treated silica (3) in the non-irradiated state is shown in Fig. 3 at three different frequencies. The glass transition relaxation, with an apparent activation energy higher than 100 kJ/mol, is present at 1 Hz at approximately −120°C and is in agreement with DSC measurements (T_g is of the order of −126 to −130°C). At higher temperatures, close to −40°C, a peak of a different nature can also be observed. The frequency dependence of this peak yields infinite activation energy and the amplitude is lower at high frequencies, as expected for a phase or structural transition. In this study, this microstructure change is associated with the melting of the crystalline phase as confirmed by calorimetry. The viscoelastic behaviour of irradiated samples at several dose levels ranging from 0 to 0.5 MGy is shown in Fig. 4. The melting peaks are affected by irradiation, and nearly vanish for doses exceeding 0.5 MGy i.e. crystallinity decreases and an amorphous state is obtained (after cooling at 6 K/min before the experiment). This decrease of crystallinity is related to the evolution of the apparent crosslink density that can limit segmental diffusion and crystallisation. The amplitude of the glass transition mechanical relaxation appears to be correlated with the amplitude of the melting peak: if a well defined melting peak is present, i.e. if a crystalline phase is present, then the amplitude of the glass transition relaxation decreases. Consequently, the glass transition relaxation is governed by the presence of the crystalline phase, acting as an additional crosslink or skeleton of physical and morphological nature. Thus, it is not possible to evaluate the direct effect of irradiation in terms of chain scission or crosslinking on the glass transition relaxation. Nevertheless, the indirect effect of irradiation on the crystallisation behaviour is more apparent.

The decrease of the crystallisation behaviour with irradiation can also be confirmed by calorimetric analysis. An example of a DSC thermogram obtained for PDMS (2) irradiated with different doses is given in Fig. 5 for cooling rates at −6 K/min, and in Fig. 6 during subsequent heating at 6 K/min. Both crystallisation and melting of the crystalline phase appear to be affected by irradiation. The results for all types of samples are summarised in Table 2. The value of the melting enthalpy ΔH_m depends on the irradiation dose and on the presence and type of silica filler. The same trends are also observed for ΔH_c (crystallisation enthalpy).

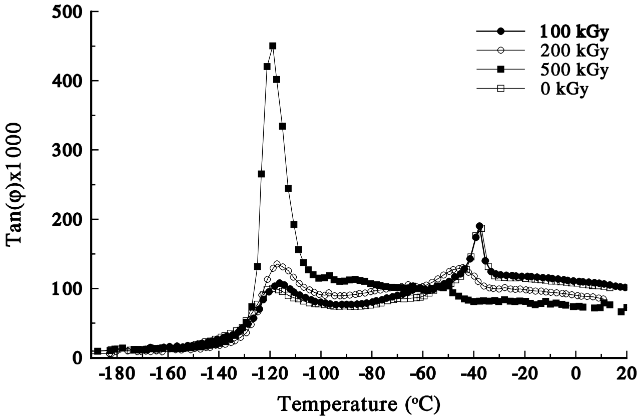

Fig. 4. Evolution of Tan (φ) measured at 0.1 Hz for a surface treated filler PDMS rubber (3) at different irradiation doses. $dT/dt = 1$ K/min. The samples are previously cooled at 6 K/min down to -180°C.

Moreover, the presence of the silicate particles results once again in a greater sensitivity to irradiation, in terms of crystallisation behaviour. Specifically, the value of ΔH_m for the pure PDMS resin varies from 26 J/g (at 0 kGy-non-irradiated) to 20 J/g (500 kGy), whereas in the presence of silica, the melting enthalpy decreases down to 3 J/g (for surface modified silica). This effect is even more pronounced in the case of treated silica where the system becomes practically amorphous. The surface of the silica fillers thus plays an important role in the increase of crosslinks after irradiation, which in turn decreases the chain mobility and thus the crystallinity ratio. The values of melting temperatures (T_m) are related to the crystallite thickness [11]. A decrease of T_m with irradiation should thus reflect in a decrease in the crystallite thickness as a result of irradiation crosslinking. The crystallisation temperatures (T_c) are also affected by irradiation, and mostly reflect the nucleation and growth rates of the crystallites. A decrease of T_c with irradiation, hence with crosslinking is observed. Here again, the results are interpreted as crosslinking which slows down the overall kinetics of crystallisation.

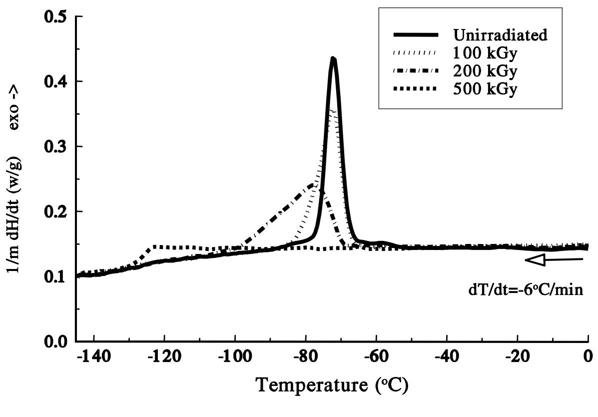

Fig. 5. Cooling thermograms (at $dT/dt = 6$ K/min) of non-irradiated and irradiated PDMS (2) at 100, 200 and 500 kGy.

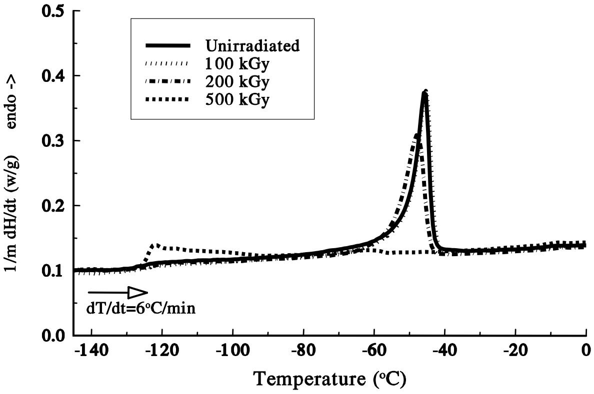

Fig. 6. Heating thermograms of non-irradiated and irradiated PDMS (2) at 100, 200 and 500 kGy after cooling at 6 K/min (see Fig. 5).

3.3. Effects of irradiation on high strain mechanical properties

The non linear mechanical behaviour of the PDMS systems was analysed during stress–strain load/unload cycles. The results for the PDMS system (3) is shown in Fig. 7. The loading stress/strain is always at higher stress than the unloading pattern, implying an energy dissipative phenomenon. This so-called Mullins effect is well known in carbon-black reinforced rubbery polymers [12–15], and was discussed in relation to energy dissipation mechanisms at the level of the macromolecules in contact with the particles with irreversible [16] or reversible [17,18] chain debonding at the surface of the filler. Other mechanisms were also invoked at the level of the branched or bushy structure of the aggregates [19–21]. The effect of deformation on the morphological changes at the level of aggregates of fillers were also studied [22]. In addition, the formation of voids in the vicinity of the primary particle/rubber interface or in the agglomerate structures is believed to be responsible for the observed changes of volume with deformation. Although all these phenomena contribute to the Mullins effect, the surface of the filler plays an important role in some cases, governing either the PDMS/filler interactions, or filler/filler

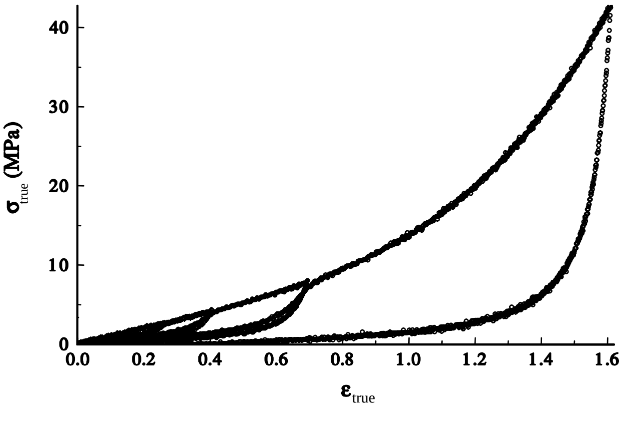

Fig. 7. Stress–strain cycles showing the hysteresis of the Mullins effect in PDMS (3) surface-treated silica samples.

Table 2
Values of T_c (crystallization temperature), T_m (melting temperature) and ΔH_m (variation of melting enthalpy) for the different elastomers studied at different irradiation doses — : corresponds to not measurable values

Sample	Dose (kGy)	T_c (°C) ±1°C	T_m (°C) ±1°C	ΔH_m (J/g of polymer)
(1)	0	−71	−43	26 ± 1
	25	−72	−45	25 ± 1
	100	−73	−46	23 ± 1
	200	−73	−46	22 ± 1
	500	−76	−47	20 ± 1
(2)	0	−72	−45	32 ± 1
	25	−75	−45	31 ± 1
	100	−77	−48	30 ± 1
	200	−78	−49	21 ± 1
	500	—	—	—
(3)	0	−75	−45	24 ± 1
	25	−76	−46	23 ± 1
	100	−77	−47	19 ± 1
	200	−78	−50	17 ± 1
	500	—	−53	3 ± 2

interactions. In this work, the hysteresis associated with the Mullins effect was characterised as the ratio of the dissipated mechanical energy (area of the hysteresis) over the energy of first loading (area below the first loading curve) as explained in Fig. 8 as the ratio $R_M = A/(A + B)$ where A is the area between the loading and the unloading curves and B is the area under the unloading curve. Fig. 9 shows an example of the evolution of the Mullins ratio R_M as a function of applied strain, at different irradiation doses for system (2). The main figure shows the corrected data using the method described in the Appendix A of this paper. The insert shows the raw data obtained from Mullins ratio deducted from successive cycles. A significant difference can be observed, but it is relatively small. Hence, the method described does not change the results drastically, and corrected results are very close to results obtained on 'fresh' samples. A stronger effect concerning the evolution of Mullins ratio as a function of applied strain, at different irradiation doses, can be observed on the surface treated silica samples (3). This evolution cannot be directly obtained from successive stress–strain cycles, because a given loading curve is influenced by previous loading, as shown in Fig. 7. The methodology to estimate the true value of R_M from successive loads of the same sample is given in the Appendix A (see the end of this paper).

Irradiation yields an increase in the Mullins Ratio, indicating that for the same applied strain, an increase in the dissipative phenomena associated with the Mullins effect can develop. Again, these results are consistent with an increase in the number of crosslinks between silica particles and PDMS rubber. For example, 'chain debonding' increases with irradiation due to the higher fraction of chains that are fully extended for a given strain, and are thus extracted sooner from the surface of the particles. The same argument is also valid for the formation of PDMS/filler interface decohesion. The deformation of

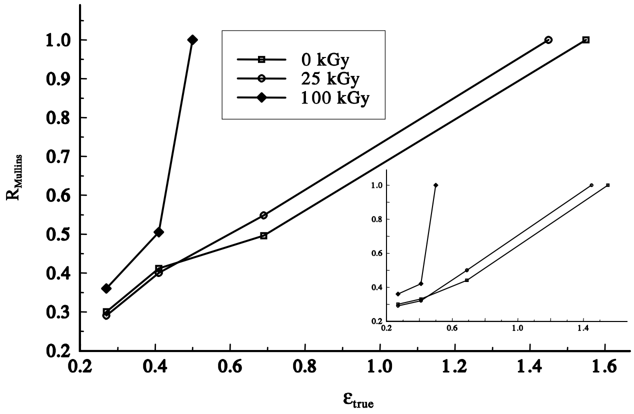

Fig. 8. Evolution of Mullins ratio with irradiation for the PDMS system (2). $R_M = 1$ is obtained at sample break. The data shown have been corrected using the method described in the Appendix A. The insert shows the raw data corresponding to Mullins ratio deducted from successive cycles to compare with corrected data.

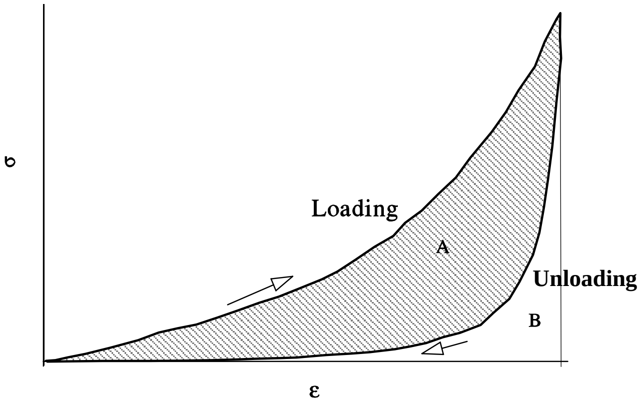

Fig. 9. Definition of the Mullins ratio. $R_M = A/A + B$ and represents the energy fraction that is dissipated during one stress–strain cycle. A represents the area between the loading curve and the unloading curve. B represents the area under the unloading curve.

micronic aggregates of silica is also possible, since the stress transferred by the PDMS matrix increases with increasing crosslinking. To go a step further, small angle X-ray scattering was used to study the presence of nanoscopic voids, in situ during the stress–strain tests on system (2) and (3). Although the samples become whiter as a result of micronic cavitation at large strains, the scattering of X-rays at low angle did not show any significant change during and after loading. This indicates that the SAXS patterns are mostly due to the presence of nanoscopic silica particles and aggregates, and if they exist, the voids initiated at the polymer/filler interface rapidly grow, becoming too large for detection by this technique. Damage in these filled rubbers can thus be described as individual chain debonding at the polymer/filler interface followed by a rapid growth of voids to the micron range and/or the deformation of aggregates, but without the simultaneous formation of nanoscopic voids at the level of the surface of silicate particles.

4. Conclusion

The interface between particles and polymer matrix plays a dominant role in the irradiation ageing of filled silicone rubbers. Irradiation is shown to induce further crosslinking at the surface of the nanoparticles. This yields a modification of (i) the crystallisation behaviour and (ii) the high strain mechanical properties (Mullins effect) which are known to be partly determined by the characteristics of the filler and PDMS/silica interfaces.

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Appendix A. Appendix

Let us consider a succession of load/unload cycles as displayed by Figs. 7 and 8. Cycle i is obtained by loading at ϵ_i and unloading, the hysteresis area is A'_i and the area under the unloading curve is B'_i, knowing that (i-1) cycles were performed before cycle (i). In the absence of previous cycles, the corresponding areas of a cycle at maximum strain ϵ_i would be A_i and B_i. The problem is to find a relation between the true and approximated Mullins ratios, respectively, defined as:

$$R_{\mathrm{M},i} = A_i/(A_i + B_i)$$

and

$$R'_{\mathrm{M},i} = A'_i/(A'_i + B'_i) \qquad \text{with } R_{\mathrm{M},i} > R'_{\mathrm{M},i}.$$

Simple approximations, such as:

$$B'_i \sim B_i$$

$$A_i \sim A'_i + A_{i-1}$$

lead to

$$R_{\mathrm{M},i} = R'_{\mathrm{M},i} + R_{\mathrm{M},i-1}(C_{i-1}/C_i)(1 - R'_{\mathrm{M},i})$$

where $C_i = A_i + B_i$ is the area under the loading curve.

In uniaxial loading, the ratio (C_{i-1}/C_i) can be related to the extension ratios λ_i using the rubber elasticity theory, as:

$$\begin{aligned}(C_{i-1}/C_i) &= (\lambda_{i-1}^2 + 2/\lambda_{i-1} - 3)/(\lambda_i^2 + 2/\lambda_i - 3)\\ &= (\exp(2\epsilon_{i-1}) + 2\exp(-\epsilon_{i-1}) - 3)/(\exp(2\epsilon_i)\\ &\quad + 2\exp(-\epsilon_i) - 3)\end{aligned}$$

The value of $R_{\mathrm{M},i}$ is thus calculated using the known values of ϵ_i, $R'_{\mathrm{M},i}$, and the true corrected value of the preceding cycle, $R_{\mathrm{M},i-1}$.

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