Modelling molecular weight changes induced in polydimethylsiloxane by gamma and electron beam irradiation

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Abstract

A commercial linear polydimethylsiloxane (PDMS) was subject to gamma irradiation under vacuum and in air, as well as to accelerated electron beam radiolysis (EB). All irradiation treatments were done at room temperature. The molecular weight changes induced by the radiation processes have been investigated using size exclusion chromatography (SEC) with refraction index (RI) and multi angle laser light scattering (MALLS) detectors to obtain the number and weight average molecular weights of the irradiated samples.

The analysis of the data indicates that crosslinking reactions predominated over scission reactions in all cases. Gamma irradiation under vacuum was the most efficient process within the analyzed dose range, reaching the gel point earlier. Irradiation in the presence of oxygen induces oxidative effects, both in gamma and EB irradiations. A previously developed mathematical model of the irradiation process that accounts for simultaneous scission and crosslinking and allows for both H and Y crosslinks fitted well the measured molecular weight data.
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1. Introduction

The radiation chemistry of polymeric materials has been a field of extensive research, motivated in part by the useful modifications that ionizing radiation may induce in them. Radiation treatment of a polymeric material always produces crosslinking and scission reactions, which affect the molecular

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weight, the molecular weight distribution, and in turn the physical properties of the treated material [1–3].

In practical applications of this technology two sources are commonly available, namely gamma irradiation and electron beam irradiation. Both sources produce high energy ionizing radiation and are used to treat polymers for a variety of uses. It is known that the interaction of such sources of radiation with polymer molecules produces a great amount of ions and excited molecules along their path into the polymer. The distribution of these species throughout the polymer sample is determined by the type and energy of the ionizing radiation, and is related to the linear rate of radiation energy transfer to the polymer, denominated LET [4]. Gamma and electron beam radiations are typical examples of low LET radiations. They transfer energy predominantly in small isolated events through the polymer inducing the formation of macroradicals which in turn become involved in several chemical reactions that produce the cross-linking and scission. However one must consider that, besides the similar energy transfer, these ionizing radiations differ in several ways such as dose rate, sample temperature rise, oxygen availability and treatment duration.

From a practical point of view the study on radioinduced changes in PDMS is a suitable field of research. Polydimethylsiloxane has been widely used in medical applications. Medical devices and implants require sterilization using high energy radiation [5]. Also in controlled drug delivery from polydimethylsiloxane matrices, irradiation cross-linking has been found effective to produce useful elastomeric support without affecting the stability of the controlled drug delivery systems [6].

In the specific case of radiation modified PDMS, crosslinking predominates over chain scission reactions. Because of this, the net effect of an irradiation treatment on PDMS is an increase of the molecular weight. Molecular architecture also changes due to chain branching. After a certain radiation dose, denominated the gelation dose D_{gel}, an infusible and insoluble three-dimensional network results. Beyond this gelation dose, further irradiation transforms the originally liquid PDMS into a soft to rubberlike gel.

Fig. 1 shows the different radicals that could be radioinduced in PDMS under vacuum. The same radicals should appear in gamma in air or in electron beam irradiation, with the addition of oxidized species and macroradicals.
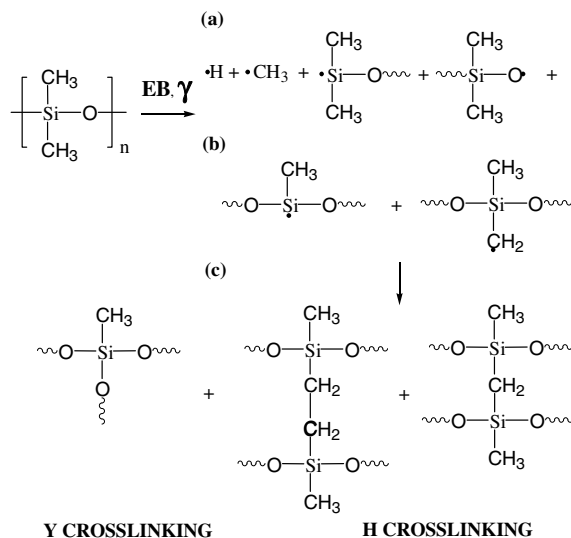

Fig. 1. (a) Radioinduced radicals due to chain scission; (b) radioinduced macroradicals due to methyl or hydrogen abstraction; (c) radioinduced H and Y crosslinks produced in PDMS irradiated with gamma rays under vacuum.

An interesting aspect related to these radicals is that they can react producing four-armed H crosslinks, and also three-armed Y crosslinks [7]. The Y-type crosslinks have been generally ignored in favor of the H-type crosslinks [3,8]. However, both of them have been reported in the literature [9,10]. It has been shown that their presence may help to explain the behavior of the molecular weights in the postgel region [7].

In this work we irradiate a commercial PDMS at room temperature using three methods: gamma irradiation under vacuum, gamma irradiation in air, and accelerated electron beam (EB) radiolysis. Of the three processes, EB is the one that has been analyzed the least in the literature. To the best of our knowledge, this is the first time that this type of experimental data on electron beam irradiated PDMS are discussed. Particular care was taken to follow the molecular weight changes of the studied polymers as a function of the applied radiation dose using double detection – refractive index and light scattering – SEC system. The experimentally measured molecular weights were compared with the predictions of a mathematical model specially developed for the PDMS irradiation process.

2. Experimental part

A commercial linear methyl terminated PDMS (Mw = 141,000 Da, Mn = 76,600 Da) purchased

from Petrarch Systems Inc. was used as received. A portion of this polymer was treated with gamma radiation at the Centro Atómico Ezeiza (CAE), Argentina, using a ^{60}Co source at room temperature. Samples were enclosed in sealed glass vials, some of which were evacuated with high vacuum (10^{-3} atm) for 24 h, while the rest contained atmospheric air. All samples received identical doses. The gamma radiation doses applied to the polymers ranged from 10 kGy to 160 kGy, at a dose rate of 10 kGy/h. The applied doses were measured with a Red Perspex dosimeter.

Another group of samples was irradiated in closed LDPE bags using a 2.2 MeV electron beam accelerator (Model AS2000 from HVEC at CRITT AERIAL in Schiltigheim France). The liquid samples were approximately 1 mm thick. The doses ranged from 5 kGy to 160 kGy, with a dose rate of about 9000 kGy/h (2.5 kGy/s). Because of the high dose rate of the electron beam accelerator, a local temperature rise could be produced into the treated material. To minimize this problem, a split dose technique, consisting of 2.5 kGy step increments up to final dose, was applied to avoid excessive heating of samples during the irradiation process.

In order to ensure undetectable levels of long-lived radicals, all irradiated samples were annealed after the irradiation for 2 h at 140 °C.

For samples that received doses above the gel point, the soluble part was extracted to study the molecular weight evolution in the postgel region. The extraction was performed using toluene at ambient temperature for 72 h. After that, the soluble fraction and the gel fraction were vacuum dried up to a constant weight. Beyond the critical gelation dose, only the soluble fraction of the irradiated material may be studied by SEC chromatography. The equipment used for this purpose was a Waters 150 C ALC/GPC equipped with three PLgel Mixed-A 300 mm × 7.5 mm 20 μm columns (Polymer Laboratories) and a set of two detectors. These were a refractive index detector from Waters and a DAWN DSP Multi Angle Laser Light Scattering (MALLS) from Wyatt Technology Corporation. Measurements were carried out at room temperature with a flow rate of 1 mL/min of toluene. Universal calibration was carried out using polystyrene standards (Pressure Chemical).

Chemical changes in the PDMS structures were followed by FTIR, using a Micro-FTIR Thermo Nicolet equipment. Spectra were obtained from a drop of the treated materials taken without further

conditioning from the containers where they had been irradiated. They were registered using a NEXUS spectrometer attached to a continuum microscope working on reflection mode. The resolution used for the analysis was 4 cm^{-1}.

3. Mathematical model

The model proposed by Sarmoria and Vallés [7] was used to simulate the three irradiation processes. This model considers irradiation to produce both scission and crosslinking in the treated polymer. In this mean-field approach, all bonds are considered to be equally likely to be subject to crosslinking or scission. Crosslinking may occur in either of two ways. In the first one, two macroradical chains of the type shown in Fig. 1b may be joined together, forming a tetrafunctional or H crosslink. In the second one, a scissioned end of type 1(a) may attach itself to another macroradical chain of the type shown in Fig. 1b, producing a trifunctional or Y crosslink. Scissioned ends are the only possible sources of Y crosslinks. If two macroradicals of type 1(a) recombine, a linear chain is regenerated.

The model requires as input parameters the molecular weight distribution (MWD) of the untreated polymer, the doses of irradiation applied, the dose at which the gel point occurs (D_{gel}), the percentage of energy used to produce scission as opposed to crosslinking (Sc), and the proportion of energy used to produce trifunctional crosslinks (CY). The model calculates the average molecular weights (Mw, Mn) at different irradiation doses, as well as the proportion of energy used to produce tetrafunctional crosslinks (CH). For postgel doses, the molecular weights calculated are those of the soluble fraction. The model uses probability theory in order to calculate the quantities of interest, and employs the conversion of bonds to produce crosslinks, α, as the independent variable. There is also a conversion of bonds to produce scission, β, which is a constant fraction of α. Assuming that at any point in the irradiation treatment the same proportion of the applied energy results in either crosslinking or scission, it is possible to relate the conversion to a dose through the equation

$$\frac{D}{D_{gel}} = \frac{\alpha + \beta}{\alpha_{gel} + \beta_{gel}} = \frac{\alpha(1 + fs)}{\alpha_{gel}(1 + fs)} = \frac{\alpha}{\alpha_{gel}}$$

where D is the applied dose, and the subscript *gel* indicates the gel point. In this way, all quanti-

ties may be reported as functions of the applied dose.

The final model is too long to present here in complete form; 54 equations were needed to do so in Sarmoria and Vallés [7]. As an example, we show next how to calculate the different yields. For further details, see Sarmoria and Vallés [7].

Traditionally, the yields are indicated with the letter G and are defined as the number of events per 100 eV of applied radiation. If the event is the formation of a crosslink, the corresponding yield is G(X). Other possible events are scissions (S), formation of tetrafunctional crosslinks (XH) or formation of trifunctional crosslinks (XY), all of which have an associated yield. Yields should be the same regardless of the amount of applied energy, so in particular they may be calculated at the gel point. At that point, the number of crosslinks in one kilogram of polymer will be

$$\# \, X - \text{links} = \alpha_{\text{gel}} \cdot \# \, \text{bonds} = \alpha_{\text{gel}} \cdot \frac{1 \, \text{kg}}{M_0} \cdot N_A$$

where M_0 is the molecular weight of the repeat unit, 0.074 kg/mol, and N_A is Avogadro's number. In order to produce all these crosslinks, the applied dose was D_{gel}. Therefore, the yield G(X) is

$$G(X) = \frac{\alpha_{\text{gel}} N_A}{M_0 D_{\text{gel}}}$$

Since a fraction γ of all crosslinked sites forms trifunctional crosslinks, the yield of trifunctional crosslinks is

$$G(XY) = \frac{\alpha_{\text{gel}} \gamma \, N_A}{M_0 D_{\text{gel}}}$$

Similarly, the yield of tetrafunctional crosslinks is

$$G(XH) = \frac{\alpha_{\text{gel}}(1 - \gamma) \, N_A}{M_0 D_{\text{gel}}}$$

Finally, there is a scission yield that may be calculated as

$$G(S) = \frac{fs \alpha_{\text{gel}} \, N_A}{M_0 D_{\text{gel}}}$$

However, if a scissioned end reacts to form a Y-crosslink, there will be no apparent scission at all. Therefore, the yield of apparent scission should be calculated as

$$G(S) = \frac{(fs - \gamma)\alpha_{\text{gel}} \, N_A}{M_0 D_{\text{gel}}}$$

4. Results and discussion

Absolute measurements of weight average molecular weights were performed on a large number of pregel and postgel samples of the linear PDMS, using the SEC-MALLS apparatus under the conditions indicated in Section 2. The measured Mw values in Table 1 correspond to the three different irradiation treatments.

In all cases a significant increase in the molecular weight was observed up to the dose necessary to reach the gel point. The molecular weights at doses closest to the gel point are highlighted in boldface in Table 1 for each radiation condition. The gel doses estimated from the SEC measurements are reported in Table 2.

After the critical gelation dose, the gel grows at the expense of the sol by preferentially incorporating the largest molecules. Therefore the analyzed fraction is enriched in low molecular weight material. This is the reason for the decrease in molecular weights of postgel samples observed in Table 1.

Table 1
Weight average molecular weight (Mw) obtained at different doses

Dose (kGy)	Mw (Da)		
	γ-Vacuum	γ-Air	EB
0	141,000	141,000	141,000
5	–	–	143,000
10	267,000	194,000	215,000
15	–	–	227,000
20	**959,000**	481,000	284,000
25	–	–	461,000
30	951,000	**912,000**	506,000
35	–	–	**995,000**
40	372,000	772,000	987,000
50	–	–	–
60	281,000	326,000	–
80	256,000	151,000	171,200
100	–	–	–
120	–	–	81,800
124	71,700	–	–
160	–	–	60,700

Experimental error in doses and molecular weights is estimated to be about 10%.

Table 2
Gel dose estimated from SEC measurements

	D_{gel} (kGy)		
	γ-Vacuum	γ-Air	Electron beam
PDMS	23 ± 2.3	35 ± 3.5	39 ± 3.9

Comparing the evolution of the weight average molecular weights in Table 1 and the experimental gel points in Table 2, it is evident that vacuum gamma irradiation is the most efficient process since it needs the lowest dose to reach the gel point.

The gel doses found for air gamma irradiation and electron beam processes are very similar.

The SEC elution curves were very sensitive to changes in the polymer molecular weight distribution induced by each irradiation treatment, as may be seen in Fig. 2. Here we compare the cumulative weight distribution of the untreated PDMS with those of the samples that received 20 kGy with the three different irradiation processes that we study in this work. The ordinate in this figure indicates the cumulative mass percentage at a given molecular weight. At the 20 kGy dose all samples remain in the pregel region. We observe a gradual broadening on the high molecular weight zone of all cumulative molecular weight distribution curves relative to the untreated polymer. These distribution curves confirm the results from the critical gelation dose that indicate that the vacuum gamma irradiation is the most efficient crosslinking treatment for PDMS. This may be concluded from the observation that under these conditions the polymer reaches the highest molecular weights at 20 kGy. Also, according to Fig. 2, the gamma in air and electron beam irradiations have lower crosslinking efficiencies. Similar results are obtained at other irradiation doses. The higher crosslinking level in vacuum gamma irradiation could be explained by the absence of oxygen in that particular treatment. When irradiation processes are performed in air,

the oxygen diffusing into the polymer may react with some of the radioinduced free radicals, producing inactive species. This has a two-fold effect: the number of scission reactions increases, while fewer free radicals remain available for crosslinking [11].

If we search for indications of oxidation using FTIR in the region corresponding to oxidation of carbonyl groups we find similar responses for samples treated with gamma rays in air or with electron beam, in Fig. 3, where we show the FTIR traces between 1500 and 1800 cm^{-1} for all treatments. The response in the region where the characteristic oxidative bands appear [11] is different for the sample treated under vacuum, and similar for the samples subjected to the other two treatments.

The differences in the three irradiation treatments that result in different responses of the irradiated material must have a molecular basis. Some treatments probably produce more scission than others, or the functionality of the crosslinks may vary with the type of treatment. The density of radicals that are produced may also differ, and with it the possibility of recombination of radicals. Such recombination would appear as a diminished efficiency when observing the macroscopic result of a given irradiation dose. We are in no position to measure such fine differences, but we can model them mathematically and see which characteristics are able to produce the observed behavior. For this purpose the model already described above was applied, comparing its predictions with the measured weight average molecular weight values shown in Table 1. This required finding the model parameters. Of the five parameters mentioned above (MWD of the untreated polymer, irradiation doses used, D_{gel}, Sc
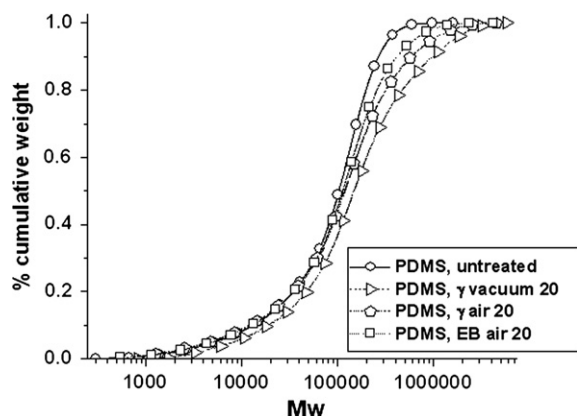

Fig. 2. Cumulative SEC distribution curves for treated and untreated PDMS samples. Untreated; gamma under vacuum; gamma in air; electron beam. All treated samples received a 20 kGy dose.
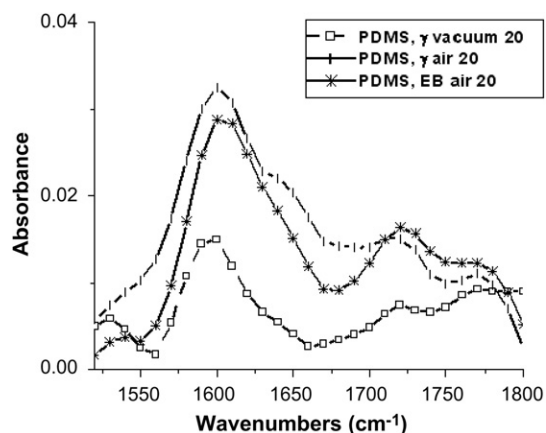

Fig. 3. FTIR spectra for gamma and electron beam irradiated PDMS at 20 kGy.

and CY), only the first two are easily obtained. The gel point may only rarely be pinpointed with accuracy, since the irradiation doses are discrete. As for the proportion of energy that produces scission Sc and the fraction of trifunctional crosslinks CY, we do not have a way of measuring them directly. Therefore we performed a multivariable optimization using Marquardt's method and the experimental values obtained for the weight average molecular weights of our samples. The problem consisted in finding the values of D_{gel}, Sc and CY that would minimize the objective function shown in Eq. (1).

$$Fg = \sum_{j=1}^{N_{exp}} (\log(Mw_{exp})_j - \log(Mw_{calc})_j)^2 \qquad (1)$$

In Eq. (1) the subscript exp refers to a measured value, and the subscript calc to a calculated value. This work was performed for the three irradiation treatments considered in this work: gamma under vacuum, gamma in air, and electron beam. As a strategy for finding the global optima for the parameters, we used many different starting points for the optimization processes. For each type of irradiation we used at least 65 different initial points, covering all the permissible range of the parameters D_{gel}, Sc and CY.

In a first stage, we forced CY to be zero, indicating that trifunctional crosslinks were not allowed; tetrafunctional crosslinks were the only ones present. We obtained a poor fit of the experimental data, particularly in the postgel region. Fig. 4 shows a representative example.

In a second stage, we set CY as one of the parameters to be found in the optimization. We found that several sets of parameters could fit the data, with varying degrees of cut ends finding their way into trifunctional crosslinks. For each scissioned bond, two new ends appear, of which one is active and may either crosslink or deactivate. If scissioned ends remain scissioned, one would expect to see more low molecular weight material in the MWD plots. However, no such increase is apparent in the cumulative molecular weight distributions. We were then led to the conclusion that the majority of active cut ends must be producing trifunctional crosslinks. Therefore, we performed a third optimization where we forced Sc and CY to be equal. The best results are shown in Table 3. Note that the columns for Sc and CY have identical values, since we forced the model to do that. The level of scission is the proportion of the energy used along the reaction that produced scission, although the observed level of scission would be zero because every active split end has reacted to form a Y-crosslink. The sum of squared differences between predicted and measured values dropped by an average factor of three with respect to the best fit without allowing for Y crosslinks. The values of the radiation chemical yields $G(\cdot)$ are also reported in Table 3. They are calculated from the optimal parameters of the model reported in the same table. The values reported are the apparent scission yield G(S), which is zero for all cases, the yield of Y crosslinks G(XY), and the yield of H crosslinks G(XH). A composite G(X) yield for all crosslinks is obtained as the sum of the yields for Y and H crosslinks. The values reported in Table 3 are consistent with yield values reported in the literature for PDMS [3,10,12,13].
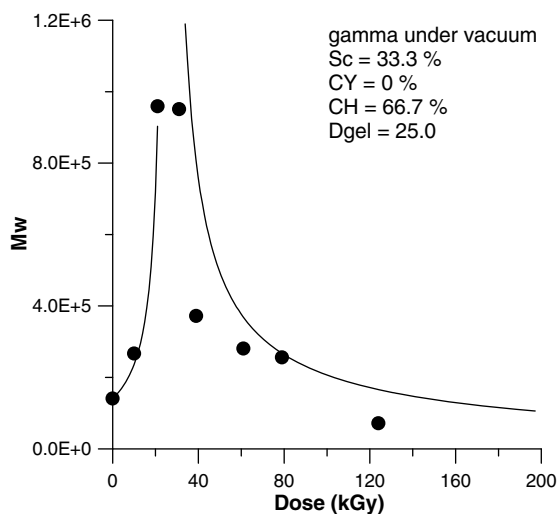

Fig. 4. An optimal fit without allowing Y-crosslinks.

Table 3
Optimal values of optimization parameters for the three different irradiation processes

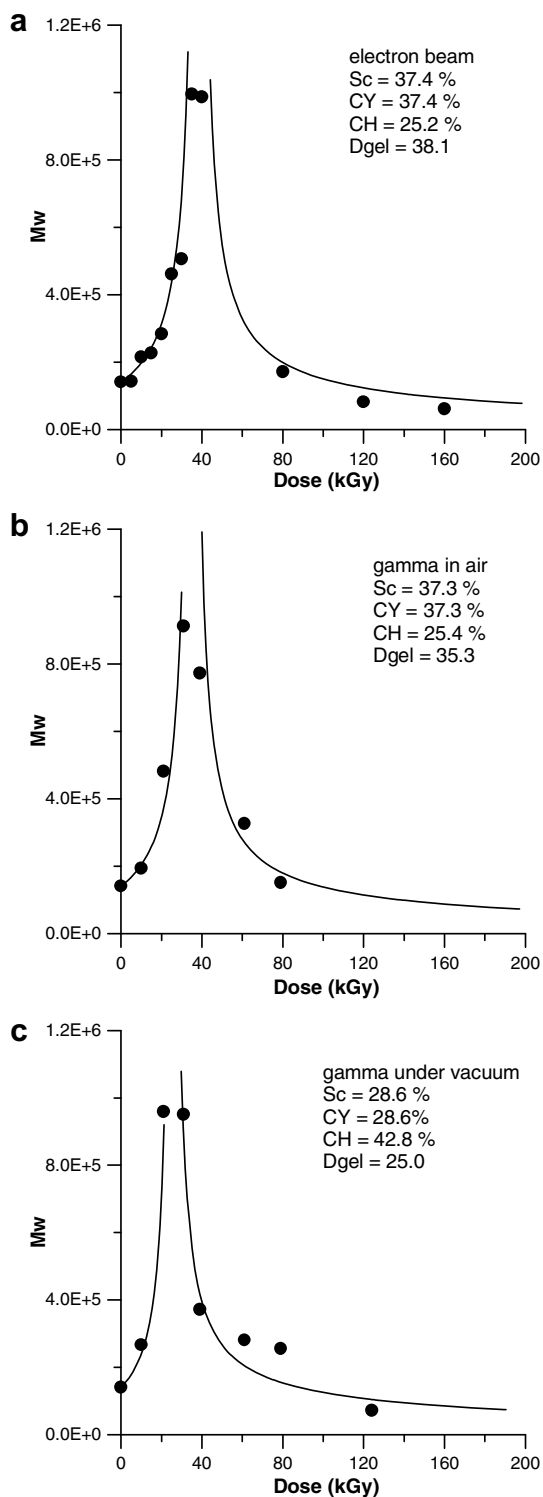| Irradiation method	D_{gel} (kGy)	Sc (%)	CY (%)	CH (%)	G(S)	G(XH)	G(XY)
EB	38.1	37.4	37.4	25.2	0	0.80	1.19
γ-Vacuum	25.0	28.6	28.6	42.8	0	1.71	1.14
γ-Air	35.3	37.3	37.3	25.4	0	0.88	1.28

Fig. 5. Experimental values (points) of Mw vs. dose, compared with the theoretical predictions (solid line). PDMS irradiated with (a) electron beam, (b) gamma rays in air and (c) gamma rays under vacuum.

The results in Table 3 indicate that there is a non-negligible amount of trifunctional Y crosslinks. This is consistent with observations published in the literature [10]. We may also observe that according to this model treating PDMS with electron beam or with gamma rays in air produces very similar results. This is evidenced by the very close gel doses, and the almost identical proportions of energy used to produce Y-crosslinks or H-crosslinks. The treatment with gamma rays under vacuum, on the other hand, needs a lower gel dose and a higher proportion of energy used to produce H crosslinks. Both these characteristics are consistent with a more efficient use of the energy to produce high molecular weight material, as discussed previously.

Experimental values of the evolution of Mw as a function of the applied dose are shown in Fig. 5, and compared with the theoretical predictions for PDMS irradiated with electron beam, gamma rays in air and gamma rays under vacuum, always at room temperature. The parameters used are indicated in the figure, and are the global optima from Table 3.

Aside from some scattering in the experimental results, the agreement between the calculated and measured molecular weights is good for the three irradiation conditions analyzed in these figures. The data are then consistent with the model assumptions that every scissioned bond gives rise to one trifunctional crosslink.

5. Conclusions

The atmosphere of treatment can influence the radiation chemistry of PDMS. The lower D_{gel} and the larger high molecular weight tail in SEC cumulative curves showed that the vacuum gamma irradiation is the most efficient of the three processes studied. The presence of oxygen during irradiation treatment could lead to the capture of some free radicals producing inactive species that do not contribute to the final crosslinking efficiency.

A previously published model that allows scission and two types of crosslinking was applied with success. Neglecting Y crosslinks resulted in poor predictions of average molecular weights. The best agreement between experimental data and model predictions were found if every scissioned bond was considered to produce one dead end and one Y crosslink. According to the results of the optimization, gamma under vacuum irradiation produces a higher proportion of H crosslinks on PDMS than

the other treatments. EB radiolysis and gamma irradiation in air produce very similar results.

Since we used a commercial polymer with a polydispersity index close to two, it was not possible to measure fine differences in low molecular weight tails induced by radiation. In order to do that, monodisperse material would have to be irradiated. Work in this direction is under way.

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