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Abstract. Some results of the influence of γ radiation on the mechanical properties of Polymethylmethacrylate are presented. Doses of 0, 50, 100, 150 and 200 kGy were employed. The internal friction (loss tangent) and storage shear modulus were measured at temperatures between 173 K and 300 K using a damped torsion pendulum. Compressive tests were made at room temperature with strain rates between 1.4×10^{-3} s^{-1} and 3.5×10^{-2} s^{-1}. The materials studied were previously characterized by means of their molecular weight with the GPC technique. Loss tangent versus frequency curves are given, showing the α, α' and β relaxations. A linear relationship between the glass transition temperature, calculated at a fixed frequency, and the irradiation dose is obtained. An anomalous behaviour of the shear storage modulus of the material when it was irradiated at doses lower than 100 kGy was noticed. A similar response was observed in measurements of the yield point in the same material.

1. INTRODUCTION

Previous works [1-4] have shown that the overall effect of gamma radiation on vinyl polymers with at least one quaternary carbon atom, e. g. polymethylmethacrylate (PMMA), is main-chain degradation. These studies indicated the absence of monomeric products and that the main-chain fracture occurs at random, at room temperature; this fact was demonstrated by the variation of the molecular weight with the irradiation dose [2,5]. Changes in the molecular structure produced by the γ radiation are reflected in modifications of mechanical and thermal properties [5-7]. Of special interest are the dynamic mechanical properties since they reflect most readily both strong and more subtle changes.

In the present work we show the dynamic mechanical behaviour of γ-irradiated PMMA over an extended frequency scale at temperature of 298 K, using the method of reduced variables. A comparison between the variation of the elastic storage modulus G' with the irradiation dose and results from compression tests on the same material is made. Finally, the results are discussed considering the changes in the molecular structure produced by γ radiation.

2. EXPERIMENTAL

For this study commercially-available polymethylmethacrylate (PMMA) was used. Probes of 25 mm of length were cut from cylindrical rods of 3 mm of diameter.
The samples were g-irradiated at room temperature using a 60Co cell of the Comisión Nacional de Energía Atómica (CNEA, Argentina). Doses of 50, 100, 150 and 200 kGy were employed.
In order to characterize the molecular weight distribution of the specimens, gel permeation chromatograms (GPC) of PMMA were obtained using a Shimadzu L-6A liquid chromatograph system. THF was used as

the elute. The measured values of the number average molecular weight M_n and polydispersity for both the unirradiated and irradiated samples are shown in table 1.

Table 1: Variation of the molecular weight and polydispersity with the γ irradiation dose

Dose [kGy]	Mn [g/mol]	polydispersity
0	$1.878 \ 10^6$	1.86
50	$1.417 \ 10^5$	1.87
100	$5.750 \ 10^4$	2.16
150	$4.303 \ 10^4$	1.98
200	$3.205 \ 10^4$	1.85

The internal friction IF and elastic storage modulus G' were measured using a torsion, free-decay pendulum in argon atmosphere at a pressure of 60 Torr and a temperature ramp of 0.4 K/min [8]. Mechanical compression tests were performed with strain rate between $1.4 \times 10^{-3} \ s^{-1}$ and $3.5 \times 10^{-2} \ s^{-1}$ at room temperature using an Instron machine.

3. RESULTS

The dynamic mechanical properties were measured at temperatures between 183 K and 423 K and frequency varying from 2 Hz to 0.2 Hz. In order to compare the experimental data to compression tests at room temperature, the method of reduced variables [9] was used to transform dynamic data to $T_0 = 293$ K. Following Ferry [9], the shift factor a_T used in this method is calculated according to

$$\log a_T = -c_1^0 \ (T-T_0)/(c_2^0 + T-T_0) \tag{1}$$

where $c_1 = -14.72$ and $c_2 = 175$ K. These constants were calculated for 293 K from reported values [9]. A recent work [10] suggests that these values do not depend on the irradiation dose, since measurements on γ-irradiated PMMA performed with both dynamic and dilatometric methods show, up to an additive constant, the same linear relationship between the temperature of the α transition and $1/M_n$.

Fig. 1 shows the curves of IF as a function of ωa_T for the different doses at T_0, where ω is the angular frequency. It is interesting to note that, when measuring at room temperature, frequencies as low as $10^{-5} \ s^{-1}$ must be reached in order to obtain the α relaxation. On the other hand, a broad peak is observed for frequencies around $5 \ s^{-1}$, corresponding to the β relaxation. Besides, the smaller peak at around $3 \times 10^{-3} \ s^{-1}$ can be associated to the α' relaxation [11].

In Fig. 2 the storage shear modulus reduced to $T = T_0$, $G_r'(\omega)$ [9], is plotted against $\log(\omega a_T)$ for the different irradiation doses. In this figure it can be seen that the effect of γ-irradiation on the modulus is slight for doses of 50, 100 and 150 kGy, a significative decrement of the modulus being produced only for the dose of 200 kGy.

4. DISCUSSION

The rupture of the main chain in PMMA causes a decrement in the number average molecular weight M_n [4]. According to Bueche [12], the α relaxation temperature T_α decreases linearly with $1/M_n$, and consequently, with the irradiation dose [3]. The values of T_α at a fixed frequency for each dose can be calculated from the α peak maximum of the IF curves of Fig. 1 using eq. (1), since $\log a_T = \log (\omega_0/\omega)$ where ω_0 is the frequency measured at T_0. These values were estimated from the fitting of the curves given

in Fig. 1 to the composition of three Gaussians. Each Gaussian corresponds to one of the three relaxations observed.
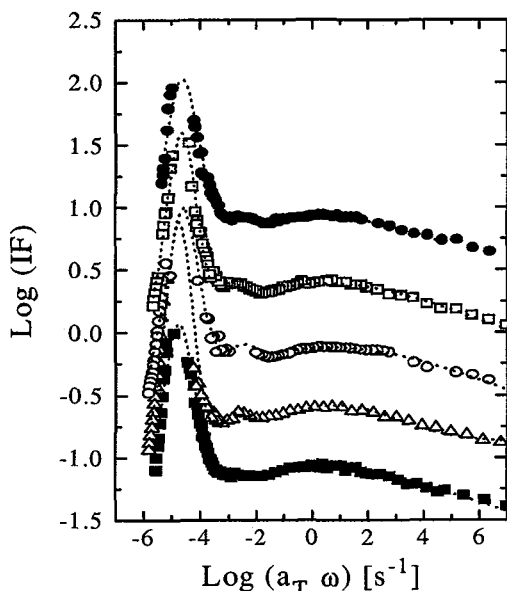

Fig. 1: Internal Friction as a function of reduced frequency for: ■ 0 kGy, △ 50 kGy, ○ 100 kGy, □ 150 kGy and ● 200 kGy. Curves are shifted along the y-axis 0.5 per dose, beginning at 0 kGy.
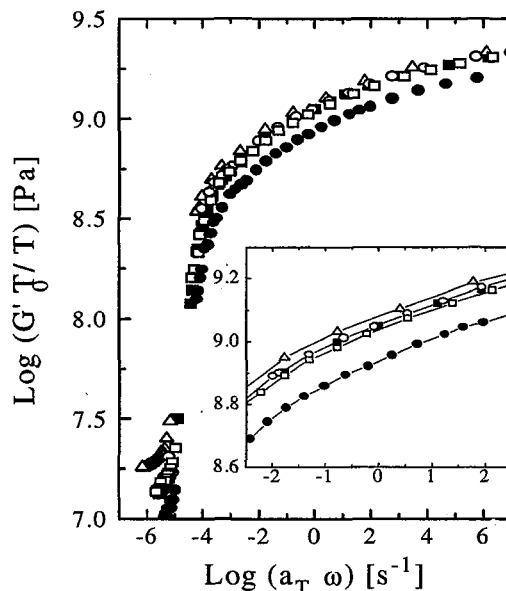
Fig 2: Reduced shear modulus as a function of reduced frequency for all studied irradiation doses. Same symbols as before.

From this equation it is easy to obtain the values of the glass transition temperature (T_g) at a fixed frequency. Typical measurements of non irradiated PMMA are usually given at 1 s^{-1}. The variation with the dose of T_g calculated at this frequency is shown in Fig. 3, in good agreement with the relationship expected according to the precedent paragraph.

According to Fig. 1, the β peak at 298 K is obtained at ω = 5 s^{-1} (f = 0.79 Hz). Muzeau et al. [11] report, for unirradiated PMMA, a value of 0.1 Hz at 285 K and 1 Hz at 300 K.

Considering a compression test up to the yield point as 1/4 of cycle of a cyclic test, we can define an equivalent frequency for the compression tests as $\omega_{eq} = 2\pi\dot{\epsilon}/4\epsilon_y$ where $\dot{\epsilon}$ is the strain rate and ϵ_y is the deformation at yield. In the compression tests ϵ_y was found at around 0.07; with this value, for $\dot{\epsilon} = 1\times10^{-2}$ s^{-1} ω_{eq} results 0.22 s^{-1}.

In Figure 4 we compare the values of the compressive yield stress σ_y for each dose at $\dot{\epsilon} = 1\times10^{-2}$ s^{-1} with the value of the reduced tensile modulus, calculated as $E_r' = 2(1+\nu)G_r'$ with G'_r taken at ω_{eq} and Poisson's ratio $\nu = 0.36$ [13]. The functional form that σ_y presents is similar to that of G_r'. The material seems to harden for an irradiation dose of 50 kGy and softens at higher doses. Finally, it is interesting to note that the ratio of the yield strength to the tensile modulus, obtained through different techniques, is approximately constant for the studied doses, and its value is of the order of that reported by Seitz [13] for unirradiated PMMA, with both σ_y and E obtained from tensile tests.
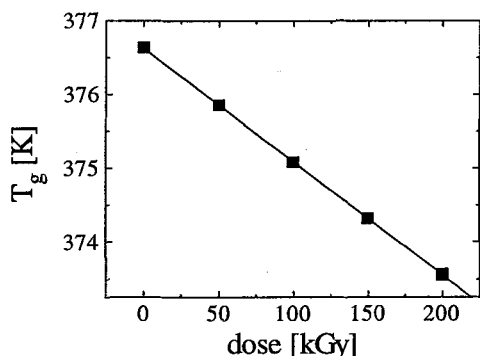
Fig. 3: Change of the glass transition temperature calculated at 1 s^{-1} with irradiation dose.
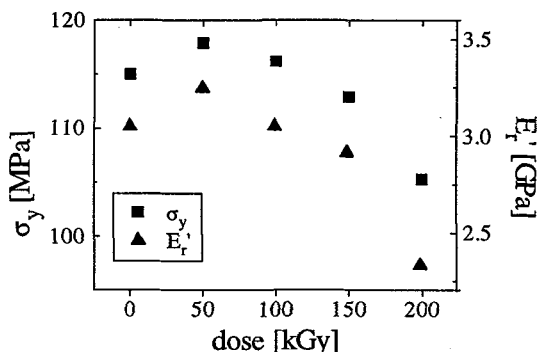
Fig. 4: Variation of the yield stress and reduced Young's modulus with irradiation dose.

5. CONCLUSIONS

The mechanical behaviour of γ-irradiated PMMA was studied. Glass transition temperature of the polymer shifts to lower values at higher irradiation dose with a corresponding decrease in the molecular weight. According to our experience, the dependence of the yield stress of PMMA with the γ-irradiation dose seems to be linked to the storage elastic modulus.

Acknowledgments

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