Effect of γ-Irradiation Dose for the Oxygen Diffusion into Polymers

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ABSTRACT: Electron spin resonance (ESR) spectroscopy has been used for the measurement of the diffusion coefficient of oxygen into polymeric spheres. It has been shown that there is an inverse dependency between the irradiation dose and the oxygen diffusion coefficient (D). The free-radical concentration (R_0) produced in the polymer depends on the dose of the γ rays. In this study, we tried to find a relationship between the oxygen diffusion coefficient and the free-radical concentration produced in the polymer during the irradiation. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1291–1294, 1997

Key words: polymer; oxygen diffusion; ESR, γ-irradiation; PMMA; PVAc

INTRODUCTION

Pure poly(methyl methacrylate) (PMMA) is not a paramagnetic substance and therefore there is no paramagnetic centers in it. So, it cannot give an electron spin resonance (ESR) spectrum. But after γ irradiation, it gives an ESR signal.[1,2] When polymers are irradiated with ionizing radiation, free radicals are generated and the ESR spectrometer detects these radicals. If a polymer is irradiated in a vacuum, the radical concentration (R_0) produced in the polymer depends on the irradiation dose. When vacuum-irradiated polymers are exposed to air (postirradiation oxidation), the radicals trapped in the material are transformed into peroxide radicals by the addition of molecular oxygen to the free radicals. This effect can be used as a tool to measure the oxygen uptake of irradiated material. In previous works, the oxygen uptake of γ-irradiated spherical PMMA and poly-(vinyl acetate) (PVAc) was determined from changes in the intensity of the ESR signal. For low doses or small R_0, the diffusion coefficients of

oxygen are determined to be 3.7×10^{-8} and 5.1×10^{-8} cm^2/s for PMMA and PVAc, respectively.[3,4]

In our previous works with PMMA and PVAc, we gave the theory of the oxygen diffusion in spherical particles.[3,4] In the present work, we used the same method and tried to find a relationship between the primary radical concentration (R_0) and the diffusion coefficient (D).

THEORY

The solution of Fick's second law of diffusion in spherical systems gives[5]

$$\frac{C}{C_0} = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n}$$

$$\times \sin \frac{n\pi r}{a} \cdot \exp(-Dn^2\pi^2 t/a^2) \quad (1)$$

where a is the radius of the sphere; D, the diffusion coefficient; and C_0 and C, the concentration of the diffusant at time 0 and t, respectively. r corresponds to the radial distance at which C is measured. We can replace the concentration

terms directly with the amount of diffusant by using eq. (2):

$$M = \int_{\nu} C \, dV \qquad (2)$$

When eq. (2) is considered for a spherical volume element and substituted in eq. (1), the following solution is obtained[5,6]:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \qquad (3)$$

where M_t and M_∞ represent the amounts of diffusant entering the spheres at time t and infinity, respectively. In the present technique, it is possible to obtain either a decrease of the ESR signal intensities of the radical or an increase of the ESR signal intensities of the peroxide radical with time. It is therefore necessary to find a direct relation between the measured quantity (signal intensity) and the ratio M_t/M_∞. Before expressing the M_t/M_∞ ratio in terms of radical concentrations which are directly followed as intensities of the ESR signal, we assume that the generation of radicals within the polymeric spheres is completely uniform. We further assume that a single oxygen molecule is responsible for the scavenging of a radical and the diffusion of oxygen takes place radially from the surface into the center of spheres as concentric spherical segments. We can therefore write the following[3,4,6]:

$$\frac{M_t}{M_\infty} = 1 - \frac{R_t}{R_0} \qquad (4)$$

where R_0 and R_t are the primary radical concentrations initially at $t = 0$ and upon exposure to oxygen after a time t, respectively. Substitution of eq. (4) into eq. (3) gives

$$\frac{R_t}{R_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \qquad (5)$$

We already know that in the expansion of the exponential term under the summation sign in eq. (5) the contribution of higher values of n ($n > 1$) can be neglected. By combining the R_0 value with $6/\pi^2$ and considering the $n = 1$ case, eq. (5) can be rewritten as

$$R_t = R_0' \cdot \exp(-D\pi^2 t/a^2) \qquad (6)$$

The above equation forms the theoretical basis for
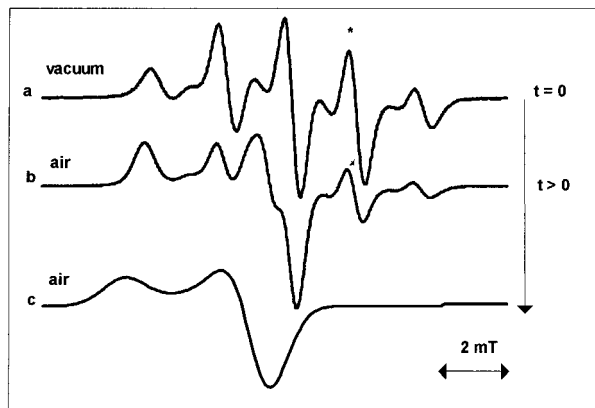

Figure 1   (a) ESR spectrum of PMMA irradiated in a vacuum; (b) the change of the spectrum after exposure to air; (c) spectrum of the peroxide radical.

determining D in this study. By inspecting the relative change in the radical concentration with time, i.e., R_t/R_0 of γ-irradiated PMMA spheres with known radii, a, it is possible to fit the above equation to experimental data and determine D, the diffusion coefficient of oxygen. The same quantity can also be determined from the slope of the $\ln(R_t/R_0)$ vs. time graph.

EXPERIMENTAL

The PMMA samples with a 70 μm average diameter and 23,000 viscosity-average molecular weight were placed in Pyrex glass ampules, then connected to a vacuum line of 10^{-4} Torr and flame-sealed. The samples kept in a vacuum were irradiated with a Gammacell 220-type ^{60}Co gamma source at room temperature at a dose rate of 1.5 kGy/h. The paramagnetic centers produced in the Pyrex glass of sample tubes were removed by heating carefully the inverted ends of the tubes. These heated ends of the sample tubes were later placed in the cavity of the ESR spectrometer. The ESR spectra of the samples were taken with a Varian E-9 type X-band spectrometer at room temperature. The microwave power was kept at 1 mW throughout the study.

RESULTS AND DISCUSSION

The radicals trapped in vacuum-irradiated PMMA gave rise to a characteristic nine-line ESR spectrum. This spectrum observed in this study is shown in Figure 1. The change in the shape and intensity of the spectrum was followed for a period
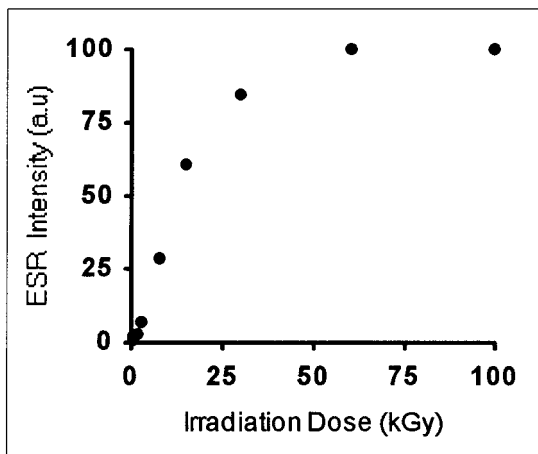
Figure 2 The change of R_0 with the irradiation dose.

Figure 4 The change of $\ln(R_t/R_0)$ with time.

of 5 min after irradiation. During this time interval, no change was observed in the intensity and in the shape of the spectra of samples kept in a vacuum. When the samples were exposed to air, however, the intensity of the spectrum begins to decrease; after a short time, its line shape changes into the asymmetric peroxide radical line. These observations show that there is no appreciable self-decay of radicals that would interfere with the decay due to the interaction of diffused oxygen molecules with the macroradicals. In Figure 1, the ESR spectrum of the final product peroxide is given together with the spectrum of freshly irradiated PMMA. As can be seen from this figure, some of the lines of the PMMA spectrum overlap with those belonging to peroxide. Therefore, in the selection of a noneffected suitable line, one has to
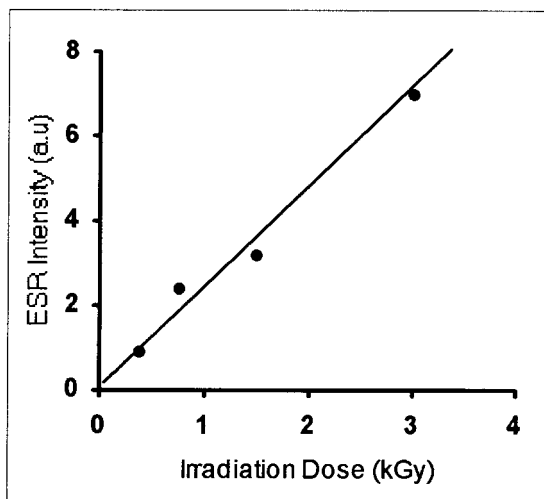
consider those that are not interfering. The line represented by an asterisk (*) in Figure 1 does not overlap with the lines of peroxide radicals; that is why in the present study the rate of changes of the intensity of this line is followed upon exposure to air.

R_0 values were directly determined from the height of the peak with an asterisk at time $t = 0$ for all doses. Figure 2 shows the change of the R_0 with the irradiation doses. Figure 3 shows the change of the R_0 in the low irradiation dose region.

It can be seen from Figures 2 and 3 that in the low irradiation dose region the radical concentration R_0 changes in a linear way, while in the high-dose region, the change of the concentration is not linear and reaches a saturation value. When the vacuum-irradiated samples are exposed to air, the intensity of the signal begins to decrease with time. Figure 4 shows the change of $\ln(R_t/R_0)$ with time. By using the curves given in Figure 4, one can determine the D values from the slopes. The diffusion coefficient calculated from the slopes of those curves are listed in Table I.

Figure 3 The change of R_0 with the dose in the low-dose region.

Table I Dependence of Radical Concentration and Oxygen Diffusion Coefficient on the Irradiation Dose

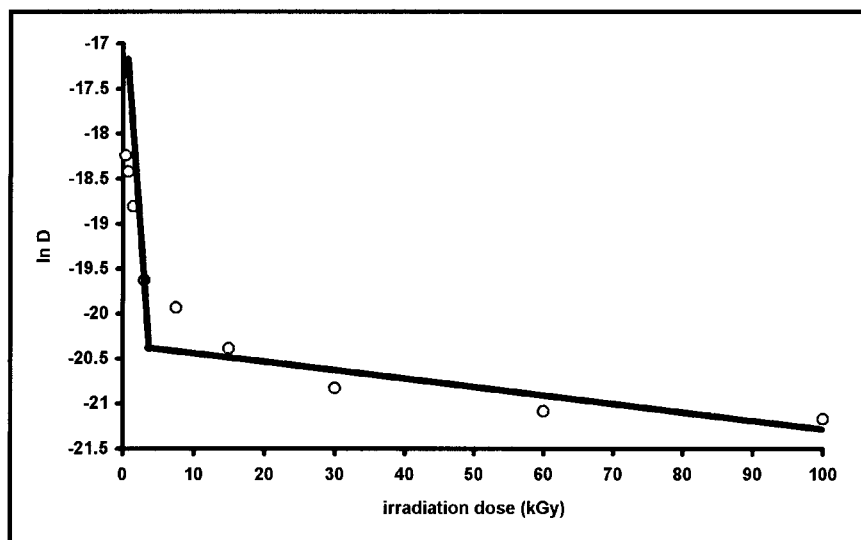| Dose (kGy)	R_0	D (cm^2/s $\times 10^8$)
0.37	0.9	1.2
0.75	2.4	1.0
1.50	3.2	0.68
3.00	7.0	0.30
7.50	28.7	0.22
15	61	0.14
30	84.4	0.09
60	100	0.07
100	100	0.07

Figure 5 The change of ln D with dose.

The D values decrease with the dose. This may be due to the peroxide radicals formed at the outside shell of the spherical particles, which further behave as a barrier hindering the penetration of new oxygen molecules further into the center of the polymer sphere, making the diffusion of oxygen more and more difficult in the deeper parts of the particles. So, the diffusion coefficient determined from the high doses is smaller than the diffusion coefficient determined from the low doses.

Figure 5 is obtained by using the data in Table I. As can be seen from this figure, the variation of ln D with dose can be divided into two regions: low- and high-dose regions which correspond to low and high R_0 regions. The linear dependence of ln D vs. dose from Figure 5 suggests that there is an exponential relation between these two quantities in the form

$$D = D_0 \cdot \exp(-\alpha \cdot \text{dose}) \qquad (7)$$

Similar relations are also reported in the literature.[5,7]

Figure 5 clearly shows that the dose dependency of the diffusion coefficient of oxygen changes significantly at a certain critical dose value for PMMA. Below this value (~ 5 kGy), D is strongly dependent on dose, whereas for higher doses, this dependency becomes less significant. The occurrence of a critical dose value can be due to the accumulation of the destructive effect of radiation on PMMA with dose.

Considering the low-dose region and by doing a fit, D_0 is determined as 3.70×10^{-8} cm^2/s. The D value obtained for the PMMA irradiated to low doses agrees very well with the literature values of 3.3×10^{-8} and 3.8×10^{-8} cm^2/s.[8,9] This study has also shown that by using the ESR technique it is possible to determine the diffusion coefficient of oxygen into polymers easily. Also, this technique can be applied to any polymeric system in which ESR signal lines do not completely overlap the peroxide radical signal.

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