ESR Study on the Effect of Temperature on the Diffusion of Oxygen into PMMA and PVAc Polymers

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ABSTRACT: The free radicals produced by γ irradiation in the polymer network are formed with ionizing radiation. The decay rates of radicals in the temperature range were used to estimate the diffusion coefficient of oxygen into polymeric spheres by an electron spin resonance (ESR) technique. The ESR results showed that the activation energy of the diffusion of oxygen into poly(methyl methacrylate) (PMMA) in the temperature range 10–40°C is 29.6 kJ/mol. There are two activation energies of the diffusion of oxygen into poly(vinyl acetate) (PVAc) in the temperature range 25–50°C. The activation energies below and above 35°C, which is the glass transition temperature of PVAc, were found to be 16.8 and 82.5 kJ/mol, respectively. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1203–1207, 1999

Key words: oxygen diffusion; ESR; temperature effect; PMMA; PVAc

INTRODUCTION

When polymers are irradiated with ionizing radiation, free radicals are generated and an electron spin resonance (ESR) spectrometer detects these radicals. It is known that free radicals in a glassy polymeric network are so long-lived that no significant radical decay occurs at room temperature when the polymeric network is kept in vacuum-sealed glass ampules. When vacuum-irradiated polymers are exposed to air, however, the radicals trapped in the network are transformed into peroxide radicals by the addition of molecular oxygen to the free radicals. The decay kinetics of these radicals can be used as an indicator to find the diffusion coefficient D^{1-3} of oxygen or any other radical scavenger into polymers.

Recently, using poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) as model systems, the oxygen-diffusion mechanisms and kinetics were studied in considerable detail both theoretically and experimentally in our laboratories. In those studies, we determined the diffusion coefficients of oxygen for PMMA, PVAc, polymethacrylonitrile (PMAN) and polypropylene (PP) by ESR.[4–8]

In this ESR study, the effect of temperature for the oxygen diffusion into PMMA and PVAc were studied. Previously used and approaches given below were used to find a relationship between the diffusion coefficient (D), the activation energy of diffusion of oxygen (ΔE), and temperature (T).

THEORY

In our previous works with PMAN, PP, PMMA, and PVAc, we gave the theory of oxygen diffusion in spherical particles, cylinders, and thin sheets and the relationship between the radical concentration at any time t, (R_t) and D.[4–8] Since in the present work the samples used had spherical shapes, brief theoretical information is given below that relates R_t with D.

The solution of Fick's second law of diffusion in spherical systems gives[2,3]

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

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

where a is the radius of the sphere; D, the diffusion coefficient; and C_0 and C, the concentration of the diffusant at time zero and t, respectively, and 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):

$$M = \int_v C\, dV \quad (2)$$

When eq. (2) is considered for a spherical volume element and substituted in eq. (1), the following solution is obtained[4–6]:

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

where M_t and M_∞ represent the amounts of the diffusant entering the spheres at time t and infinity, respectively.

In the present technique, it is possible to obtain either decrease of ESR signal intensities of the radical or increase of 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[4–6]:

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

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

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

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

Figure 1 Radical concentration change versus oxygen permeation time at different temperatures for PMMA spheres.

Figure 2 Radical concentration change versus oxygen permeation time at different temperatures for PVAc spheres.

value with $6/\pi^2$ and considering the $n = 1$ case, eq. (5) can be rewritten as

$$R_t = R_0 \exp(-D\pi^2 t/a^2) \qquad (6)$$

In the present study, the determination of D is based theoretically on eq. (6). By inspecting the relative change in the radical concentration with time, that is, the R_t/R_0 of γ-irradiated polymer spheres with known radii, a, it is possible to fit the above equation to the experimental data and determine D, the diffusion coefficient of oxygen. The same quantity can also be determined from the slope of the $\ln(R_t/R_0)$ versus the time graph. Similar equations are also derived and used for other geometries, such as cylinders and thin sheets.[7,8]

EXPERIMENTAL

The PMMA and PVAc samples with 105 and 300 μm average diameters were used. These samples were placed in Pyrex glass ampules and 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. Total dose given to PMMA and PVAc were 0.375 and 15 kGy, respectively. These dose values were determined after some preliminary

tests confirming that the radical decay studies were easily conducted in the temperature interval mentioned below. The paramagnetic centers produced in the Pyrex glass of sample tubes were removed by heating carefully the inverted ends of the tubes. This heated ends of the sample tubes were later placed in the cavity of the ESR spectrometer. The ESR spectra of the PMMA and PVAc samples were taken at 10, 20, 30, and 40°C and 25, 30, 35, 40, 45, and 50°C, respectively. The microwave power was kept at 1 mW throughout the study.

RESULTS AND DISCUSSION

The changes of the radical concentration of PMMA and PVAc with time at different temperatures are shown in Figures 1 and 2. These data points are corrected for the self-decay of the rad-

Table I Diffusion Coefficients of Oxygen for PMMA at Different Temperatures

T (°C)	D (cm^2/s)
10	9.80×10^{-9}
20	1.93×10^{-8}
30	2.75×10^{-8}
40	3.29×10^{-8}

Table II   Diffusion Coefficients of Oxygen for PVAc at Different Temperatures

T (°C)	D (cm^2/s)
25	1.50×10^{-8}
30	1.65×10^{-8}
35	1.87×10^{-8}
40	2.94×10^{-8}
45	6.47×10^{-8}
50	7.84×10^{-8}

icals on polymer spheres kept at the same temperatures for the indicated periods.

From these figures, it can be clearly seen that the decay rates of radicals with oxygen permeation increase with increasing temperatures. This is an expected behavior for the decay of radicals. From these decay curves, it is possible to find D by using eq. (6). By fitting the data points in Figures 1 and 2 into eq. (6) (with correlation coefficients better than 0.99), the D values were determined for PMMA and PVAc for the indicated temperatures. The D values obtained for the PMMA and PVAc agree very well with the literature values of MacCallum and Rudkin,[9] Higashide et al.,[10] and Crank and Park.[2] This study has also shown that by using the ESR technique it is possible to determine the diffusion coefficient of oxygen into polymers easily. These D values are collected in Tables I and II.

The diffusion coefficients thus determined are later plotted against the inverse temperature on a semilogaritmic scale in Figures 3 and 4. Both the tables and Figures 3 and 4 clearly show that the diffusion coefficient of oxygen into these two poly-

mers increase with increasing temperature. The linear relation observed in these two figures implies that the Arrhenius-type relation is valid for the temperature dependence of D in these systems.

Due to the rapid decay of radicals at relatively high temperatures and an increasing noise-to-signal ratio, it was not possible to follow decay kinetics at temperatures higher than 40°C for PMMA irradiated to a 0.375 kGy dose. The maximum temperature where the reliable measurements were carried out was 50°C for PVAc irradiated to a 15-kGy dose.[11]

The ln D versus inverse temperature plot is represented by a single line for PMMA. The same plot, however, shows a break at 35°C for PVAc. This break point is very clear and this temperature is the glass transition temperature (T_g) of the PVAc used in this study. The coincidence of the break point in Figure 4 and the corresponding glass transition temperature is not unique for PVAc. A quite similar effect was observed by Li et al. in their ESR study on the permeation of oxygen in crosslinked poly(ethylene glycol dimethacrylate) [poly(EGDMA)].[12] A similar break point would have been observed if it could be possible to work at temperatures around 100°C for PMMA in this work. The significant change in chain mobility around the T_g values in polymers will directly affect the diffusion of small molecules into polymeric spheres or networks, which explains the difference in the slope values as seen in Figure 4.

From the slope of the lines given in Figures 3 and 4, the activation energies for the diffusion of oxygen into PMMA and PVAc are determined. The activation energy of oxygen diffusion for

Figure 3   Arrhenius relationship for the diffusion of oxygen in PMMA spheres.

Figure 4 Arrhenius relationship for the diffusion of oxygen in PVAc spheres.

PMMA was found to be 29.6 kJ/mol in the 10–40°C temperature range. Since there are two linear regions in Figure 4, two activation energy values were determined for PVAc. The activation energies of oxygen diffusion for PVAc below and above T_g = 35°C (308 K) were found to be 16.8 and 82.5 kJ/mol, respectively. These activation energy values and their respective change on the crossing T_g value are in good accordance with the results reported in the literature.[2,3,12–15]

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