NOTES

Permeability of Irradiated Silicone Rubber Membranes to Gases

INTRODUCTION

Permeability coefficients of gases and vapors in silicone rubber membranes have been reported by a number of investigators.[1–6] The results suggested that this material has very high permeability to gases and vapors. Some important applications of this material are based on its high permeability. However, the ratio of the permeability coefficient of a gas to that of another gas in this material is low as compared to that in the usual vinyl polymers. On the other hand, it has been reported that irradiation of silicone rubber causes crosslinking between its molecules.[7] Accordingly, it was assumed that the ratio of the permeability coefficient may be improved by irradiation of silicone rubber membrane.

It is the purpose of this paper to investigate the effect of irradiation on the permeability of silicone rubber membranes to gases. Commercial medical-grade silicone rubber membranes were used, and the irradiation was by ^{60}Co in air or under vacuum. A permeation apparatus equipped with a Pirani gauge was developed. The permeability, diffusion, and solubility coefficients for helium, krypton, nitrogen, oxygen, carbon dioxide, and propane were measured over the temperature range of 0°–70°C.

EXPERIMENTAL

Permeability Measurements

The general theory of gas transport in polymers and detailed discussions of the methods of measurement and calculation of the permeability, diffusion, and solubility coefficients have been published elsewhere.[8] The experimental method used in this study was an adaptation of the high-vacuum gas transmission technique described by Stannett and co-workers.[9] A time lag method was used for the calculation of diffusion coefficients. The apparatus was equipped with a Pirani gauge Model PG-3A (Wakaida Si. Co. Ltd., Japan) to monitor the pressure increase downstream of the membrane; this method was used to achieve accurate measurement of the diffusion coefficient for all gases studied, since the time lags for these gases were about 20 sec in some cases and manual pressure determination with a McLeod gauge could not provide meaningful data. The Pirani gauge was calibrated with the McLeod gauge before measurements, and calibration curves were drawn.

Materials

Commercial medical-grade silicone rubber membranes of Silastic sheeting 500-7 (nonreinforced) supplied by the Dow-Corning Corporation were used throughout this work. A nominal membrane thickness (1 mm) was used for both irradiated and unirradiated samples. The silicone rubber membranes were irradiated at a dose rate of 1 Mrad/hr from a ^{60}Co source at 23°C under vacuum or in air to a total dose of 37 Mrad.

The crosslinking densities for irradiated and unirradiated samples were calculated according to the following equation,[10] using the stress–strain curve of each sample at 25°C observed by Instron TMM type (Instron Engineering Co.):

$$f = nRT\left(\alpha - \frac{1}{\alpha^2}\right) \tag{1}$$

where f is stress, n is the crosslinking density, R is the gas constant, T is absolute temperature, and α is the ratio of length.

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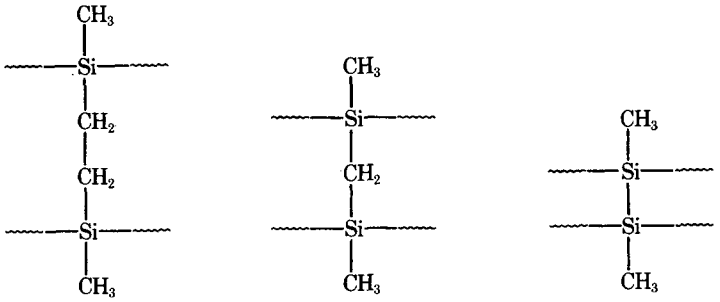
RESULTS AND DISCUSSION

It is reported that when silicone rubber is irradiated, the polymer chains become crosslinked.[7] The crosslinking densities for irradiated and unirradiated samples were calculated according to eq. (1). The crosslinking densities for the unirradiated samples, the samples irradiated in air, and those irradiated under vacuum were 4.0×10^{-4}, 9.0×10^{-4}, and 10.9×10^{-4} mole/cm^3, respectively. It is known that the crosslinking density of a polymer irradiated under vacuum is generally larger than that of a polymer irradiated in air. This conclusion was thus confirmed by our experimental results.

Measurements of the infrared spectra of the irradiated and unirradiated samples were carried out to elucidate the changes in chemical structure of the samples when irradiated in air or under vacuum. No remarkable difference in spectra among these samples could be seen. Charlesby reported that the following crosslinked molecular structures were formed in silicone resin by 200-Mrad irradiation[7]:



Therefore, we may conclude that the difference between the sample irradiated in air and that irradiated under vacuum is not one of chemical composition changes such as oxidation and unsaturation but is one of crosslinking densities. Moreover, it is thought that similar crosslinked molecular structures were formed in our samples, though our total dose of irradiation was about 1/5 that of Charlesby's samples.

The permeability coefficient P [(cm^3 (S.T.P.)·cm/cm^2·sec·cm Hg)], the diffusion coefficient D_θ (cm^2/sec), and solubility coefficient S [(cm^3 (S.T.P.)/cm^3·cm Hg)] of the irradiated and unirradiated silicone rubber membranes are plotted against the inverse temperature in Figures 1–3, respectively; P, D_θ, and S of the irradiated membranes are of about the same magnitude as those of the unirrad-

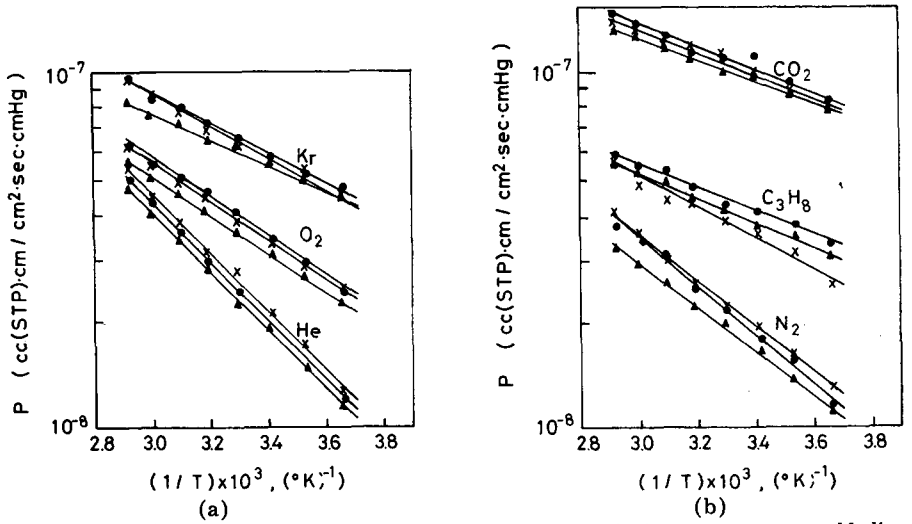


Fig. 1. Dependence of permeability coefficient on temperature for krypton, oxygen, and helium (○) and carbon dioxide, propane, and nitrogen: (●) unirradiated membrane; (▲) membrane irradiated in air; (X) membrane irradiated under vacuum.

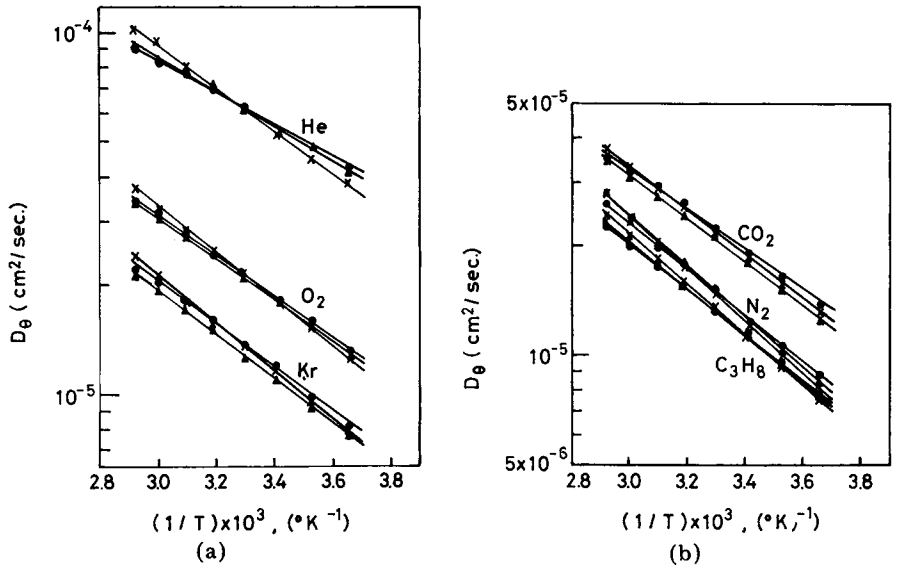


Fig. 2. Dependence of diffusion coefficient on temperature. For key, see Fig. 1.

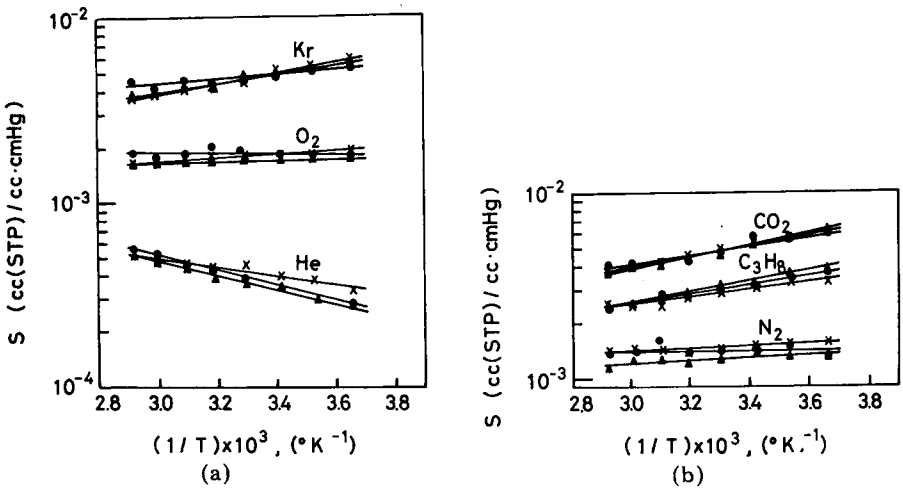


Fig. 3. Dependence of solubility coefficient on temperature. For key, see Fig. 1.

iated membranes. The effect of crosslinking on the activation process for diffusion may be to alter the size of the activation zone and thus the entropy of activation, or it may increase the activation energy by chain restriction. In Figure 2, the linear relationships for all membranes can be seen in the range of the temperature studied. Accordingly, the preexponential factor D_θ^0 and apparent activation energy E_d for diffusion were calculated using the following equation by the least-squares method:

$$D_\theta = D_\theta^0 \exp(-E_d/RT) \quad (2)$$

These data are summarized in Table I. The apparent activation energies for diffusion in the unirradiated membranes are low. These low activation energies have been attributed to the ease of segmental motion about the Si–O linkage. The apparent activation energies E_d for diffusion in the membranes irradiated in air or under vacuum are also low in spite of the formation of crosslinking by irradiation. The D_θ^0 values increase slightly with increase in crosslinking density. Thus, D_θ^0 and E_d show no remarkable change upon irradiation, though the diffusion behavior of gases with various molecular diameters, from helium to propane, were studied.

TABLE I
Preexponential Factors and Apparent Activation Energies for Diffusion

Gas	Unirradiated membrane		Membrane irradiated in air		Membrane irradiated under vacuum	
	$D_\theta^0 \times 10^3$[a]	E_d[b]	$D_\theta^0 \times 10^3$	E_d	$D_\theta^0 \times 10^3$	E_d
He	1.61	1.95	2.15	2.13	4.82	2.61
Kr	1.03	2.60	1.20	2.72	2.05	3.01
O_2	1.37	2.49	1.62	2.61	2.54	2.87
N_2	1.81	2.88	2.80	3.15	3.13	3.21
CO_2	1.49	2.53	2.05	2.75	2.31	2.80
C_3H_8	1.32	2.71	1.42	2.81	1.75	2.94

[a] D_θ^0 in cm^2/sec.
[b] E_d in kcal/mole.

According to Bixler's paper relating to the transmission of gases in irradiated polyethylene membranes,[11] decreases in diffusion coefficients and increases in solubility coefficients were observed in irradiated membranes as compared to the respective values in unirradiated membranes. The decrease in diffusion coefficients was due to the tortuosity of the penetrant and the restriction of segmental motion of polymer chain based on the crosslinking. The decrease in diffusion coefficient for helium and propane was 30% and 54%, respectively. The increase in the solubility coefficients was due to chemical composition changes such as oxidation and unsaturation, and was 40%. However, the apparent activation energies for diffusion showed no significant change upon irradiation.

Therefore, it is concluded that the effects of irradiation on transport of gases through silicone rubber membranes are negligibly small in comparison with those of polyethylene.

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